SYNTHESIS AND CHARACTERIZATION OF NOVEL MATERIALS FOR THE DETECTION AND REMOVAL OF TOXICANTS

Daniel R. Jones
University of Rhode Island, derg28@gmail.com

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SYNTHESIS AND CHARACTERIZATION OF NOVEL MATERIALS FOR THE
DETECTION AND REMOVAL OF TOXICANTS.

BY

DANIEL R. JONES

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DANIEL R. JONES

APPROVED:

Dissertation Committee

Major Professor: Mindy Levine

Matthew Kiesewetter

Michael Greenfield

URI: Nasser H. Zawia

Dean, The Graduate School – URI

UNIVERSITY OF RHODE ISLAND
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ABSTRACT

The goal of this graduate research has been to develop novel materials for the detection and removal of small molecule toxicants that have been introduced into natural water sources as a result of human industries. Traditional methods for detection of small molecule toxicants rely on laboratory grade equipment, such as gas chromatography (GC), mass spectroscopy (MS), GC-MS, and high-performance liquid chromatography (HPLC). These traditional methods have high sensitivity; however, they suffer from a lack of portability, a high degree of training needed to use them, expensive instrumentation, and extended times for data processing and analysis. To address this problem, several novel conjugated fluorescent polymers have been developed for the rapid detection of multiple small molecule toxicants.

Fluorescence as a means of detection was chosen due to the high sensitivity, ease of use, and the existence of inexpensive portable instrumentation. This research has focused on conjugated fluorescent polymers for their typically high quantum yields, low toxicity, and their burgeoning use as components of hydrophobic nanoparticles. Conjugated fluorescent polymers can form colloidal nanoparticles in water which provide a large surface area and a loose structure in which small molecules can interact or agglomerate. As the nanoparticle is held together through hydrophobic association, the hydrophobic nature of the toxicants will favor interacting with the nanoparticle, leading to a highly sensitive detection system.

The first manuscript “Turn-on Detection of Pesticides via Reversible Fluorescence Enhancement of Conjugated Polymer Nanoparticles and Thin Films” describes the detection of organochloride pesticides by monitoring the fluorescence modulation of
conjugated polymer nanoparticles. This nanoparticle system was able to detect DDT, its metabolites DDD and DDE, and notably its structural isomer o, p'-DDT with high degrees of differentiation among the analytes. This system has a limit of detection (LOD) within the literature-reported levels of concern for these analytes, with an LOD of 1.6 ppm for DDT. In addition to high sensitivity, this system was proven to be reversible with the introduction of molecular iodine, increasing the reusability of the detection system. Finally, polymer thin films were made and used for the detection of DDT vapor, showing the robustness of this detection scheme across multiple polymer platforms.

The second manuscript “Novel Fluorescent Fluorene-Containing Conjugated Polymers: Synthesis, Photophysical Properties, and Application for the Detection of Common Bisphenols” describes the synthesis of eight novel polymers, their photophysical properties, and their application for the detection of bisphenol A (BPA), bisphenol F (BPF), and bisphenol S (BPS). The experiment begins with an optimization of the general Suzuki polycondensation typically used to synthesize conjugated fluorescent polymers. Through experimental optimization, the chain length of synthesized polymers was doubled compared to the general Suzuki polycondensation. This optimization is of particular importance as these polymers have few solubilizing side chains leading to the polymers having a low solubility which severely limits the chain length of these polymers during synthesis. Through this optimized Suzuki polycondensation, eight novel polymers were synthesized, five of which had Stokes shifts of over 100 nm. Such large Stokes shifts better separate the excitation signal from the emission signal, allowing the fluorescence emission to be more accurately measured without interference.
from the excitation signal. Finally, all eight polymers were used as solutions of nanoparticles for the detection of BPA, BPF, and BPS. Using linear discriminant analysis, the changes in fluorescence of the polymers can be used to differentiate 100% among all three analytes, demonstrating the potential of these polymers for use in practical bisphenol detection.

The third manuscript “Effects of Structural Variation in Conjugated Side Chains on the Photophysics of Conjugated Polymers in Nanoparticles” investigates how the structural identity of aromatic side chains affects the photophysics of conjugated fluorescent polymers, in a manner that is highly dependent on the polymer’s state of aggregation. Three novel polymers were synthesized, each having an aromatic side chain attached to the polymer backbone either with an alkene or alkyne linker. Nanoparticles made from these polymers were then swollen using tetrahydrofuran (THF) so that the change of aggregation could be measured by dynamic light scattering (DLS) and the change in photophysical properties could be judged by measuring the fluorescence of the polymer nanoparticles. This study revealed that the aromatic entity on the side chain had a large impact on the fluorescence of the nanoparticle and the linker has a very modest effect on the interaction between the polymer chains.

The fourth manuscript “Hydrophobically coated cyclodextrin metal-organic frameworks for the rapid removal of small molecule toxicants from contaminated aqueous environments” describes four novel metal-organic frameworks (MOFs) and their use for the removal of nonpolar toxicants from water. MOFs have been the focus of a lot of research recently as they are highly porous and versatile materials. In this work a MOF was made using potassium cations and gamma-cyclodextrin, then after
fabrication the MOF was covalently functionalized with four different nonpolar entities yielding four novel MOF materials. The highly porous MOF structure and the use of cyclodextrin, which has a cavity suitable for small molecule encapsulation, creates a material with an exceedingly high internal volume optimal for small molecule storage. However, cyclodextrin MOFs (CD-MOFs) degrade into their component parts in water making them ill-suited for use in aqueous environments. In this work the CD-MOFs were covalently functionalized with nonpolar molecules which increased the CD-MOFs bulk hydrophobicity allowing them to remove selected small molecule toxicants from water while retaining their structure. This work is not yet published and the properties and abilities of these novel CD-MOFs are still being elucidated, but so far they have demonstrated a high potential for the removal of various small molecule toxicants from water.
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PREFACE

The dissertation of my research has been presented in manuscript format according to guidelines of the Graduate School of the University of Rhode Island. The complete dissertation is divided into four manuscripts. The first manuscript (chapter 1) was published in the *New Journal of Chemistry* in 2016 with authors W. Talbert, D. Jones, J. Morimoto, and M. Levine. The second manuscript (chapter 2) was published in *Synlett* in 2018 with authors D. Jones, R. Vallee, and M. Levine. The third manuscript (chapter 3) was submitted for publication to *The Journal of Physical Chemistry* in 2019 with the authors D. Jones, B. Point, and M. Levine. The fourth manuscript (chapter 4) has not been submitted. We plan to submit it to *Nanoscale* in 2019 with the authors D. Jones, A. Yonchak, and M. Levine.
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CHAPTER 1


Turn-on Detection of Pesticides via Reversible Fluorescence Enhancement of Conjugated Polymer Nanoparticles and Thin Films.

William Talbert, Daniel Jones, Josh Morimoto, Mindy Levine

Department of Chemistry, University of Rhode Island, Kingston, RI, USA

Corresponding Author:

Mindy Levine, Ph.D.

Department of Chemistry

University of Rhode Island Kingston,

Rhode Island 02881, USA

mlevine@chm.uri.edu
Manuscript 1

Turn-on Detection of Pesticides via Reversible Fluorescence Enhancement of Conjugated Polymer Nanoparticles and Thin Films.

Abstract: Reported herein is the significant fluorescence enhancement of conjugated polymer nanoparticles in the presence of aromatic organochlorine pesticides. This pesticide-mediated fluorescence enhancement leads to reversible pesticide detection systems with high sensitivity (as low as 5 µM), as well as significant generality and straightforward reversibility.

The widespread use of pesticides has been highly effective in increasing the harvested yields of many crops worldwide through eliminating the threat of common pests, but their use has also been of concern due to their known and suspected toxicity to humans and other species, as well as their long term environmental persistence.¹ One class of pesticides that is of continuing concern is organochlorine pesticides (OCPs), the most common of which is dichlorodiphenyltrichloroethane (DDT), sold commercially as a mixture of the para, para- (compound 1, Figure 1) and ortho, para- (compound 4) isomers.² Dichlorodiphenyldichloroethane (DDD, compound 2) and dichlorodiphenyldichloroethylene (DDE, compound 3) are some of the primary metabolites of DDT, also with known toxicities.³ Techniques for the detection of organic pesticides generally rely on chromatography followed by mass spectrometry.⁴ These methods offer good sensitivity and resolving power, but suffer from the high cost of operation and
tedious and time-consuming sample preparations,\textsuperscript{5} which limits the ability to conduct high throughput assays. Newer techniques for pesticide detection include molecularly imprinted polymer systems,\textsuperscript{6} nanoparticle-based immunoassays,\textsuperscript{7} and gold nanoparticle-based Raman spectroscopy.\textsuperscript{8} A variety of fluorescence-based methods for pesticide detection have also been reported,\textsuperscript{9} although in many cases these methods require derivatization steps,\textsuperscript{10} chromatographic purification,\textsuperscript{11} and/or are substantially limited in terms of the range of pesticides that can be detected.\textsuperscript{12}

One method of detection that has shown a lot of promise in the detection of multiple classes of analytes with extremely high sensitivity and selectivity is the use of conjugated fluorescent polymer sensors.\textsuperscript{13} Typically, detection efficiencies are optimal in polymer aggregates such as thin films\textsuperscript{14} or conjugated nanoparticles,\textsuperscript{15} which enable inter-polymer as well as intra-polymer exciton migration.\textsuperscript{16} Formation of conjugated polymer-derived nanoparticles can occur through a variety of methods,\textsuperscript{17} including reprecipitation,\textsuperscript{18} in which the hydrophobic polymer collapses upon its introduction into aqueous solution, resulting in the formation of well-defined spherical nanoparticles.
Figure 1: Pesticides (1-4), control analytes 5-6, and conjugated polymer 7.

Reported herein is the detection of DDT and its metabolites (compounds 1-4) in aqueous solutions via the fluorescence enhancement of nanoparticles derived from conjugated organic polymers. These particles were fabricated via the reprecipitation of 2,1,3-benzoxadiazole-alt-fluorene (PFBO, polymer 7), synthesized following literature-reported procedures. This polymer was fully characterized by spectroscopic techniques, with a $M_n = 3.8 \times 10^3$ g/mol and $M_w = 7.3 \times 10^3$ g/mol. The polymer-derived nanoparticles were characterized by dynamic light scattering experiments, with an average particle diameter of 139 nm (see ESI for details on the polymer and nanoparticle characterizations).

The degree of fluorescence changes observed with the introduction of aromatic pesticides to the aqueous nanoparticle (or free polymer) solution was calculated according to Equation 1:

$$\text{Fluorescence Modulation} = \frac{\text{PFBO}_{70\mu M}}{\text{PFBO}_{0\mu M}}$$

where PFBO$_{70\mu M}$ is the integrated polymer fluorescence in the presence of 70 $\mu$M analyte in acetonitrile, and PFBO$_{0\mu M}$ is the integrated polymer fluorescence
in the presence of 0 µM analyte in acetonitrile. Little to no fluorescence interference from the pesticides themselves is expected due to the fact that these analytes show absorption and emission maxima primarily in the ultraviolet region of the UV-Vis spectra, well removed from the absorption and emission of the donor-acceptor polymer (\(\lambda_{\text{max}}\) absorption: polymer = 413 nm; nanoparticles = 411 nm; \(\lambda_{\text{max}}\) emission: polymer = 507 nm; particles = 534 nm).21

The concentration of 7 was varied (see ESI for more details), and optimal fluorescence responses were obtained with a 1.25 x 10^{-3} mg/mL polymer solution.

Results of the fluorescence modification experiments are shown in Table 1 and Figure 2, and key trends are discussed in further detail below.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Fluorescence Modulation Party(\text{cle}^a)</th>
<th>Fluorescence Modulation Polymer(a)</th>
<th>Particle Size(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.47</td>
<td>1.02</td>
<td>220 nm</td>
</tr>
<tr>
<td>2</td>
<td>1.17</td>
<td>1.03</td>
<td>164 nm</td>
</tr>
<tr>
<td>3</td>
<td>3.48</td>
<td>0.96</td>
<td>190 nm</td>
</tr>
<tr>
<td>4</td>
<td>3.08</td>
<td>1.01</td>
<td>205 nm</td>
</tr>
<tr>
<td>5</td>
<td>1.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.99</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(a\) Fluorescence modulation calculated according to Equation 1; [PFBO] = 1.25 E-3 mg/mL

\(b\) Particle size with 70 µM analyte in acetonitrile as measured by dynamic light scattering experiments
Figure 2: Fluorescence changes of PFBO nanoparticles in the presence of pesticides: Compound 1; Compound 2; Compound 3; and Compound 4. The red line represents the fluorescence of PFBO particles in the presence of 70 µM pesticide and the black line represents the fluorescence of PFBO in the presence of 0 µM pesticide. [PFBO] = 1.25 E-3 mg/mL.

Figure 3: Fluorescence changes of PFBO polymer in the presence of pesticides: (A) Compound 1; and (B) Compound 2. The red line represents the fluorescence of PFBO in the presence of 70 µM pesticide and the black line represents the fluorescence of PFBO in the presence of 0 µM pesticide. [PFBO] = 1.25 E-3 mg/mL.

Fluorescence enhancements of the PFBO nanoparticles were observed in the presence of DDT, o,p-DDT, DDD, and DDE (compounds 1-4). In contrast to the strong fluorescence responses observed in the case of the conjugated polymer-derived nanoparticles, the conjugated polymer itself displayed a marked insensitivity to the presence of any of the pesticides investigated (Table 1, Figure 3). The strong dependence of the PFBO fluorescence responses on its aggregation state indicates the necessity of inter-chain polymer communication.
to enable efficient fluorescence enhancement behaviors, a result that has been demonstrated previously in the literature for the detection of other analytes, although not for the detection of pesticides to date.\textsuperscript{22} Additionally, the differential responses of compound 1 and compound 4 are particularly noteworthy as these compounds are structural isomers (with identical masses) and would be difficult to differentiate using standard mass-spectral techniques. This phenomenon was shown to be specific for organochlorine pesticides by measuring the fluorescence responses of the nanoparticles to aromatic compounds 5 and 6, which have been found in a variety of food products.\textsuperscript{23} Neither analyte was found to effect significant fluorescence changes (a fluorescence modulation value of 1.02 with 70 µM of analyte 5 in acetonitrile; a value of 0.99 with 70 µM of analyte 6 in acetonitrile). Substantially higher concentrations of the control analytes led to limited fluorescence decreases of the nanoparticle solution (Figure 4), highlighting the selectivity of the fluorescence-based detection system.

![Figure 4](image-url)

**Figure 4**: Fluorescence changes of PFBO nanoparticle solutions in the presence of (A) analyte 5 and (B) analyte 6. The black line represents emission in the presence of 0 µM analyte, the red line represents emission in the presence of 70 µM analyte, and the blue line represents emission in the presence of 1 mM analyte.

The sensitivity of the fluorescence enhancement-based detection for analytes 1-
is shown through the low limits of detection (Table 2),8 which approach current levels of concern for these pesticides24 and highlight the practicality of this fluorescence-based detection system. Other literature-reported detection systems for these compounds have also been reported, with somewhat more sensitive detection limits (8 µg/L for a custom-made C18 column;20 50 ppt for a molecularly imprinted polymer),25 although many of these systems may have other operational disadvantages.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>LOD</th>
<th>Literature-Reported Levels of Concern</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.6 ppm</td>
<td>0.05-5 ppm26</td>
</tr>
<tr>
<td>2</td>
<td>33.8 ppm</td>
<td>0.05-5 ppm26</td>
</tr>
<tr>
<td>3</td>
<td>27.9 ppm</td>
<td>0.05-5 ppm26</td>
</tr>
<tr>
<td>4</td>
<td>26.2 ppm</td>
<td>0.05-5 ppm26</td>
</tr>
</tbody>
</table>

Literature precedent by Swager and co-workers demonstrated that fluorescent polymer systems underwent reversible fluorescence enhancements as a result of analyte-mediated reduction of the polymer chain,27 an effect that was easily reversed by introduction of iodine vapor.28 Although similar reversibility was observed in this system, with the fluorescence increases demonstrated by solutions of polymer 7-derived nanoparticles in the presence of analyte 1 nearly completely reversed with the addition of iodine (Figure 5A), the analyte DDT compound 1 is highly unlikely to act as an effective reductant of the polymer.
chain. Rather, the reversibility in our system is likely a result of the formation of reversible charge-transfer complexes between the conjugated polymer chain and iodine vapor, which is disrupted with the addition of aromatic organochlorine pesticides that are able to pi-stack efficiently with the conjugated polymer chain. Selectivity for compounds 1-4 compared to control analytes 5 and 6, in turn, is likely due to the electron deficient nature of analytes 1-4 and the resultant electronic complementarity with the conjugated polymer. Other examples of iodine doping of conjugated polymer systems have also been reported, although to the best of our knowledge, this phenomenon has not been used for reversible fluorescence-based detection to date. The fact that this fluorescence switching was reversible over several cycles (Figure 5B) is highly significant for the development of practical fluorescence detection systems.

Figure 5: (A) Illustration of reversibility of fluorescence changes of polymer 7-derived nanoparticles (polymer treated with I$_2$ prior to addition of compound 1). (B) Switching behavior of polymer 7-derived nanoparticles with alternating additions of I$_2$ and compound 1 DDT over 11 cycles.

Oftentimes fluorescence enhancements of conjugated polymer-derived nanoparticles involve macroscopic changes in the particle architecture that translate into measurable fluorescence response changes, however, in this case the addition of pesticides 1-4 effected little to no change in the average particle size and size distribution (Figure 6).
An extension of this fluorescence-based detection to polymer 7-derived thin films was conducted by fabricating fluorescent thin films from the spin casting of a polymer 7 solution in chloroform onto glass slides. These films were briefly exposed to the vapor from a solution of compound DDT 1 in tetrahydrofuran. The measurable response of these films to compound 1 DDT vapor (Figure 7A) is remarkable considering the low vapor pressure of compound 1 DDT, and indicates high levels of sensitivity in these fluorescent polymer-derived detection systems. Moreover, control experiments indicated that the tetrahydrofuran itself had negligible effects on the photophysical properties of polymer 7–derived thin films. These fluorescence changes were also reversible with exposure of the thin film to iodine vapor, leading to a nearly complete return to the initial thin film fluorescence state (1.27-fold increase followed by 1.20-fold decrease, Figure 7).

**Figure 6:** Dynamic light scattering experiments of polymer 7-derived nanoparticles with (A) pesticide 1 and (B) pesticide 2, indicating no significant changes in particle size in the presence of the pesticides.
Finally, the fluorescence responses of other conjugated polymers (Figure 8) in the presence of 70 µM of compound DDT 1 were measured, and the results are summarized in Table 3 and Figure 9. These polymers were either commercially available (compounds 8, 10, and 11) or easily synthesized using a synthetic procedure developed for the undergraduate teaching laboratory (compound 9).  

For most of the polymers, analogous fluorescence enhancements in the presence of compound 1 DDT were observed, highlighting the general applicability of the pesticide-mediated fluorescence enhancements. In all cases, the fluorescence enhancements of the nanoparticle solution were markedly higher than the enhancements observed in the presence of the free polymer, which confirms the importance of inter-polymer communication in enabling the highly sensitive fluorescence changes to occur.

**Figure 8**: Structures of other fluorescent conjugated polymers investigated.
Table 3: Average % change fluorescence of polymers 8-11 with 70 µM analyte 1a.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Fluorescence Modulation Particle&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Fluorescence Modulation Polymer&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>1.81</td>
<td>0.96</td>
</tr>
<tr>
<td>9</td>
<td>2.34</td>
<td>1.03</td>
</tr>
<tr>
<td>10</td>
<td>1.67</td>
<td>1.28</td>
</tr>
<tr>
<td>11</td>
<td>1.23</td>
<td>0.94</td>
</tr>
</tbody>
</table>

<sup>a</sup>Fluorescence modulation calculated according to Equation 1; [Particles] = 1.25 E-3 mg/mL; [Polymers] = 1.25 E-3 mg/mL
Figure 9: Illustration of fluorescence emission of conjugated polymers in the presence of 70 µM of analyte 1 with: (A) Polymer 8 in nanoparticles; (B) Polymer 9 in nanoparticles; and (C) Polymer 8 in free solution. The black line represents the fluorescence emission of the polymer in the presence of 0 µM analyte 1 and the red line represents the emission of the polymer in the presence of 70 µM analyte 1.

In summary, reported herein is the substantial fluorescence enhancement of PFBO-derived nanoparticles and thin films in the presence of aromatic organochlorine pesticides, and marked class-specific fluorescence changes of PFBO-derived nanoparticles in the presence of a variety of other small molecule pesticides. These fluorescence responses have a number of notable features, including: (a) a requirement for polymer chain aggregation to enable efficient inter-polymer exciton migration; (b) high levels of reversibility through the introduction of iodine vapor; (c) a ‘turn-on’ rather than ‘turn-off’ fluorescence signal, which has the potential to lead to improved sensitivity in practical detection schemes; (d) low limits of detection, which approach practical levels of concern; and (e) general applicability for other fluorescent organic polymers, including both commercially available and easily synthesized polymers. Efforts towards developing practical turn-on detection systems for aromatic pesticides based on this research are currently in progress in our research laboratory, and results of these and other investigations will be reported in due course.
Acknowledgements: Funding for this research was provided by the University of Rhode Island Chemistry Department start-up funds.

References

11. E. Watanabe and K. Baba, *J. Chromatography A*, 2015, **1385**, 35.


Supporting Information

Turn-On Detection of Pesticides via Reversible Fluorescence Enhancement of Conjugated Polymer Nanoparticles and Thin Films

MATERIALS AND METHODS

All the starting materials, reagents, and solvents were purchased from Sigma Aldrich, Acros Organics, TCI chemicals, Alfa Aesar, or Fisher Scientific and were used as received. All reactions were carried out under an inert atmosphere. Solvents were dried using an MBraun dual solvent purification system prior to use. Reactions were all monitored via analytical thin layer chromatography (TLC) using polyester backed TLC plates. Visualization was accomplished with UV light at 254 nm and/or with a KMnO₄ TLC stain. Product isolation was performed by using preparative TLC plates or silica gel chromatography. Both TLC plates and preparative TLC plates were purchased from Sorbent Technologies, GA. Column chromatography was performed with SiliaFlash F60 (230-400 mesh) silica gel, obtained from Silicycle Inc. Canada.

¹H NMR and ¹³C NMR spectra were taken on a Bruker 300 MHz spectrometer and were recorded in CDCl₃ at ambient temperature. Fluorescence experiments were recorded on a Shimadzu RF 5301 spectrophotometer with 1.5 nm excitation and 3.0 nm emission slit widths for solution measurements and 1.5 nm excitation and 1.5 nm emission slit widths for thin films. Absorbance measurements were recorded on an Agilent 8453 UV-visible spectrophotometer at a concentration of 0.02 mg/mL.

Thin films were spin-cast onto 22 x 22 cm glass cover slips using a 1.0 mg/mL
PFBO solution in chloroform at 1000 rpm for 20 seconds. For fluorescence experiments, slides were placed on top of a 20 mL vial containing iodine powder or a 1 mg/mL solution of DDTin THF for 10 seconds. The emission spectrum was recorded with the slides at a 45 degree angle relative to the beam.

Dynamic light scattering experiments were run on a Malvern Zetasizer Nano ZS90, measuring particle size at 25°C and a 90° measurement angle, using Mark-Houwink parameters for the calculation of molecular weight.

Gel permeation chromatography (GPC) data were obtained using an Agilent Infinity GPC system equipped with three Agilent PLGel columns 7.5mm x 300mm (5 μm, pore sizes: 103, 104 and 105 Å). Molecular weight and Mw/Mn ratios were determined versus PS standards (500g/mol – 3150kg/mol; Polymer Laboratories).

SYNTHESIS OF FLUORESCENT POLYMERS

Fluorescent polymer 7 was synthesized following procedures described in Scheme S1. All chemical intermediates and products were fully characterized using 1H and 13C NMR spectroscopy.

Scheme S1: Synthesis of polymer 7.
Fluorescent polymer 9 was synthesized following procedures described in the reference below. All chemical intermediates and products were fully characterized using 1H and 13C NMR spectroscopy.

Scheme S2: Synthesis of polymer 9.
Synthesis: 200 mg of 2,5-bis(bromomethyl)-1-methoxy-4-(2-ethylhexyloxy)benzene S8 (0.47 mmol, 1.0 equivalents) was dissolved in 5.0 mL of oxygen- and moisture-free tetrahydrofuran (THF), and cooled to 0 °C. 210 mg of potassium tert-butoxide (1.9 mmol, 4.0 equivalents) were dissolved in 2.0 mL of anhydrous THF and added via syringe to the solution of 1 in THF. After 2 hours of vigorous stirring at 0 °C, the reaction mixture was quenched via the addition of a five-fold volume of methanol (approximately 35 mL), and
polymer 2 was isolated by vacuum filtration. The polymer was dissolved in deuterated chloroform for $^1$H NMR analysis.


EXPERIMENTAL DETAILS

DETAILS OF NANOPARTICLE FABRICATION

PFBO nanoparticles were formed following a modified literature-reported procedure. 2 mL of polymer solution (2 mg/mL) in THF was added to 8 mL of deionized sonicating water. The solution was allowed to sonicate for 30 minutes, at which point the THF was removed by bubbling nitrogen through the solution for 1 hour. An additional 2 mL of deionized water was added to the solution to make a 0.2 mg/mL stock nanoparticle solution.

DETAILS OF THIN FILM FABRICATION

Thin films were spin-cast onto 22 x 22 cm glass cover slips using a 1 mg/mL PFBO solution in chloroform at 1000 rpm for 20 seconds. For fluorescence experiments, slides were placed on top of a 20 mL vial containing iodine powder or a 1 mg/mL solution of DDT for 10 seconds. The emission spectrum was recorded after 10 seconds had passed. The thin film was mounted at a 45 degree angle relative to the beam.

DETAILS FOR RELATIVE QUANTUM YIELD DETERMINATION

To determine quantum yield, 5-6 solutions of each nanoparticle solution were made, with absorbances ranging from 0.01 to 0.1 (arbitrary absorption units).
The fluorescence emission of each solution was recorded. The integrated fluorescence signal was then plotted against the absorbances and a trendline was determined. The quantum yield (Q) was determined through comparison to standards using the equation: 
\[ Q = Q_R \times \frac{M}{M_R} \times \frac{n^2}{n^2_R}, \]
where \( M \) is the slope of the absorbance versus fluorescence trace and \( n \) is the refractive index of the media. Rhodamine B, Rhodamine 6G, and Fluorescein were the standards used to determine quantum yield. The solutions were excited at the following wavelengths: Rhodamine B: 545 nm; Rhodamine 6G: 530 nm.

**FLUORESCENCE EXPERIMENTAL DETAILS**

For fluorescence experiments, two solutions were prepared: one containing dilute PFBO nanoparticles in water (Solution A), and one containing dilute pesticide (1-10) in acetonitrile (Solution B). For each run, 2 mL of solution A (1.25 E-3 mg/mL) were added to the cuvette and mixed with 0.5 mL of solution B (0 – 70 μM small molecule). The optimal concentration for these solution-state fluorescence experiments was determined through testing a variety of polymer concentrations and looking for the one that gave reproducible data over several trials and with several different polymer-pesticide combinations. The polymers were excited at the following wavelengths: polymer 7: 420 nm; polymer 8: 490 nm; polymer 9: 500 nm; polymer 10: 480 nm; polymer 11: 480 nm.

**DYNAMIC LIGHT SCATTERING DETAILS**

To study the size of the nanoparticles, dynamic light scattering (DLS) was used. DLS data were obtained using a Malvern Zetasizer Nano S. A 0.0125 mg/mL
solution of PFBO nanoparticles in H2O was used to determine the Z-average (particle diameter) and polydispersity indices (PDI) of the nanoparticles.

DETAILS FOR LIMIT OF DETECTION EXPERIMENTS

The limit of detection (LOD) is defined as the lowest concentration of analyte at which a signal can be detected. The limit of quantification is defined at the lowest concentration of analyte that can be accurately quantified. These experiments were conducted following literature-reported procedures:


To determine the limit of detection (LOD) and limit of quantification (LOQ), each fluorophore-analyte combination was examined in the following manner: 2 mL of PFBO nanoparticles in H2O (1.25 e-3 mg/mL) was added to a cuvette, then 100 μL of analyte solution (1 mg/mL) in acetonitrile was added in 20 μL portions. All solutions were excited at 420 nm, and fluorescence emission spectra were recorded 6 times for each addition of analyte.

All fluorescence emission spectra were integrated versus wavenumber. Calibration curves were created with analyte concentration (in μM) on the X-axis and the integrated fluorophore emission of the Y-axis. The curve was fitted with a trend line and a corresponding equation for the line was determined.

For the LOD, the limit of the blank was defined by the following equation:

$\text{LOB}_{\text{LOD}} = m_{\text{blank}} + 3(SD_{\text{blank}})$
where \( m \) is the mean of the blank integrations and \( SD \) is the standard deviation.

The LOB value was then inserted into the line equation as the Y-value, and the X-value was solved for, giving the LOD in \( \mu M \).

For the LOQ, the limit of the blank was defined by the following equation:

\[
\text{LOB}_{\text{LOQ}} = m_{\text{blank}} + 10(SD_{\text{blank}})
\]

The LOB value was then inserted into the line equation as the Y-value, and the X-value was solved for, giving the LOQ in \( \mu M \).

SUMMARY TABLES

SUMMARY TABLES FOR THIN FILM EXPERIMENTS

Ratio of fluorescence in thin films with DDT and I2 additions: Ratio is defined as the integrated fluorescence of the film under a given set of experimental conditions to the integrated fluorescence of the film before treatment with any analyte or reagent.

**Table S1**: Fluorescence modulation of thin films of polymer 7.

<table>
<thead>
<tr>
<th></th>
<th>ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td>1.00</td>
</tr>
<tr>
<td>with DDT</td>
<td>1.27</td>
</tr>
<tr>
<td>with I2</td>
<td>1.06</td>
</tr>
</tbody>
</table>

**Table S2**: Fluorescence modulation of thin films of polymer 9.

<table>
<thead>
<tr>
<th></th>
<th>ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td>1.00</td>
</tr>
<tr>
<td>with I2</td>
<td>0.91</td>
</tr>
<tr>
<td>with DDT</td>
<td>1.04</td>
</tr>
</tbody>
</table>
SUMMARY TABLE FOR LOD EXPERIMENTS:

**Table S3**: Summary of LOD experiments.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Equation</th>
<th>( R^2 )</th>
<th>LOD (µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( y = 210.09x + 38261 )</td>
<td>0.9777</td>
<td>4.6</td>
</tr>
<tr>
<td>2</td>
<td>( y = 1929.2x + 453988 )</td>
<td>0.8212</td>
<td>83.1</td>
</tr>
<tr>
<td>3</td>
<td>( y = 1895.3x + 434915 )</td>
<td>0.9463</td>
<td>69.3</td>
</tr>
<tr>
<td>4</td>
<td>( y = 2454.3x + 292818 )</td>
<td>0.9789</td>
<td>58.2</td>
</tr>
</tbody>
</table>

SUMMARY TABLES FOR CONTROL ANALYTE EXPERIMENTS

**Table S4**: Fluorescence Modulation with 70 µM of Analyte

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Modulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bisphenol A (BPA)</td>
<td>0.68 ± 0.01</td>
</tr>
<tr>
<td>( o )-dichlorobenzene</td>
<td>0.68 ± 0.01</td>
</tr>
<tr>
<td>Diphenylmethane</td>
<td>0.75 ± 0.01</td>
</tr>
<tr>
<td>1,1-Diphenylpropane</td>
<td>0.77 ± 0.00</td>
</tr>
<tr>
<td>( m )-Xylene</td>
<td>0.63 ± 0.00</td>
</tr>
<tr>
<td>( o )-Xylene</td>
<td>0.65 ± 0.01</td>
</tr>
<tr>
<td>( p )-Xylene</td>
<td>0.63 ± 0.00</td>
</tr>
</tbody>
</table>

SUMMARY TABLE FOR QUANTUM YIELD EXPERIMENTS

**Table S5**: Quantum yield for polymer nanoparticles.

<table>
<thead>
<tr>
<th>Fluorophore</th>
<th>Lit Value(^{34})</th>
<th>Calculated Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhodamine 6G</td>
<td>0.95</td>
<td>0.98</td>
</tr>
<tr>
<td>Rhodamine B</td>
<td>0.50</td>
<td>0.56</td>
</tr>
<tr>
<td>Fluorescein</td>
<td>0.95</td>
<td>0.93</td>
</tr>
<tr>
<td>Polymer 8</td>
<td>-</td>
<td>0.69</td>
</tr>
<tr>
<td>Polymer 9</td>
<td>-</td>
<td>0.34</td>
</tr>
<tr>
<td>Polymer 10</td>
<td>-</td>
<td>0.25</td>
</tr>
<tr>
<td>Polymer 11</td>
<td>-</td>
<td>0.91</td>
</tr>
</tbody>
</table>
SUMMARY FIGURES OF ALL EXPERIMENTAL DATA

SUMMARY FIGURES FOR DYNAMIC LIGHT SCATTERING EXPERIMENTS

**Figure S1:** DLS of Analyte 1.

**Figure S2:** DLS of Analyte 2.
Figure S3: DLS of Analyte 3.

Figure S4: DLS of Analyte 4.
SUMMARY FIGURES FOR LIMIT OF DETECTION EXPERIMENTS

**Figure S5:** LOD of Analyte 1.

**Figure S6:** LOD of Analyte 2.
Figure S7: LOD of Analyte 3.

Figure S8: LOD of Analyte 4.
SUMMARY FIGURES FOR ABSORBANCE EXPERIMENTS

Figure S9: UV-Vis absorbance of polymer 8.

Figure S10: UV-Vis absorbance of polymer 9.
**Figure S11**: UV-Vis absorbance of polymer 10.

**Figure S12**: UV-Vis absorbance of polymer 11.
SUMMARY FIGURES FOR FLUORESCENCE EXPERIMENTS

[Polymer] = 1.25 E-3 M; NANOPARTICLE SOLUTIONS

Figure S13: Fluorescence emission of polymer 7 nanoparticle solution with analyte 1.

Figure S14: Fluorescence emission of polymer 7 nanoparticle solution with analyte 2.

Figure S15: Fluorescence emission of polymer 7 nanoparticle solution with analyte 3.
**Figure S16:** Fluorescence emission of polymer 7 nanoparticle solution with analyte 4.

**Figure S17:** Fluorescence emission of polymer 7 nanoparticle solution with analyte 5.

**Figure S18:** Fluorescence emission of polymer 7 nanoparticle solution with analyte 6.
**Figure S19:** Fluorescence emission of polymer 8 nanoparticle solution with analyte 1.

**Figure S20:** Fluorescence emission of polymer 9 nanoparticle solution with analyte 1.

**Figure S21:** Fluorescence emission of polymer 10 nanoparticle solution with analyte 1.
Figure S22: Fluorescence emission of polymer 11 nanoparticle solution with analyte 1.

[Polymer] = 1.25 E-3 M; FREE POLYMER SOLUTIONS

Figure S23: Fluorescence emission of polymer 7 free solution with analyte 1.

Figure S24: Fluorescence emission of polymer 7 free solution with analyte 2.
Figure S25: Fluorescence emission of polymer 7 free solution with analyte 3.

Figure S26: Fluorescence emission of polymer 7 free solution with analyte 4.

Figure S27: Fluorescence emission of polymer 8 free solution with analyte 1.
**Figure S28:** Fluorescence emission of polymer 10 free solution with analyte 1.

**SUMMARY FIGURES FOR CONTROL ANALYTES**

**Figure S29:** Fluorescence emission of Bisphenol A (BPA).
Figure S30: Fluorescence emission of o-Dichlorobenzene.

Figure S31: Fluorescence emission of Diphenylmethane.

Figure S32: Fluorescence emission of 1,1-Diphenylpropane.
Figure S33: Fluorescence emission of \( m \)-Xylene.

Figure S34: Fluorescence emission of \( o \)-Xylene.

Figure S35: Fluorescence emission of \( p \)-Xylene.
Figure S36: Fluorescence emission of o-dichlorobenzene, m-Xylene, o-Xylene, and p-Xylene.

Figure S37: Fluorescence emission of BPA, diphenylmethane, and diphenylpropane.

References

CHAPTER 2

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Novel Fluorescent Fluorene-Containing Conjugated Polymers: Synthesis, Photophysical Properties, and Application for the Detection of Common Bisphenols

Daniel Jones, Ryan Vallee, Mindy Levine

Department of Chemistry, University of Rhode Island, Kingston, RI, USA

Corresponding Author:

Mindy Levine, Ph.D.

Department of Chemistry

University of Rhode Island Kingston,

Rhode Island 02881, USA

mlevine@chm.uri.edu
Manuscript 2

Novel Fluorescent Fluorene-Containing Conjugated Polymers: Synthesis, Photophysical Properties, and Application for the Detection of Common Bisphenols

Abstract: Eight novel fluorescent conjugated polymers were synthesized by the Suzuki polycondensation reaction of 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester and a conjugated dihalogenated monomer. The photophysical properties of these polymers were investigated as well-dissolved solutions in chloroform and as nanoparticle suspensions in water. Several of the polymers had large Stokes shifts (greater than 100 nm) and others demonstrated unique changes in the fluorescence properties in aggregated verse non-aggregated forms. Preliminary applications of these polymers in the detection of common bisphenols are also reported.

Introduction:
The synthesis of conjugated fluorescent polymers with extremely large (greater than 100 nm) Stokes shifts is of interest for a broad variety of applications, including gas sensing and biological imaging. Examples of fluorophores with large Stokes shifts have been reported in the literature, and usually have charge-separated states or strong donor-acceptor coupling that are responsible for such large Stokes shifts. The practical advantage to large Stokes shifts is that such shifts generally lead to high signal-to-noise ratios as a result of the large separation between the emission signal and the excitation wavelength. Less research has focused on the synthesis and applications of conjugated polymers with analogously large Stokes shifts, with one reported example relying on the aggregation of a conjugated polymer to enable such shifts. Nonetheless,
conjugated polymers are well-known for their high sensitivity in fluorescence-based detection applications,\textsuperscript{39} and so the ability to combine extremely large Stokes shifts with the notable advantages of conjugated polymer chemistry is expected to provide architectures with the combined advantages of high signal-to-noise ratios and increased fluorescence sensitivity.\textsuperscript{40}

Previous work in our group has focused on the use of conjugated fluorescent polymers for the turn-on fluorescence detection of pesticides,\textsuperscript{41} for the turn-off (i.e. quenching-based) fluorescence detection of nitroaromatics,\textsuperscript{42} and for the highly sensitive detection of hydrogen peroxide via a non-covalent, electrostatically-driven anionic polymer-cationic titanium detection complex.\textsuperscript{43} All previously reported studies in the Levine group used polymers that were either commercially available or had been reported in the literature.\textsuperscript{44} None of these polymers had notable Stokes shifts, and methods to achieve such large shifts via synthetic modification of the polymer architectures were relatively limited.

Many of the notable benefits of conjugated polymer-based sensors are enhanced when the polymer is in an aggregated state, such as nanoparticles. This enhancement is due to the increased availability of interpolymer exciton migration in addition to intra-polymer migration, resulting in markedly more sampling of the analyte binding sites by the generated excitons. Researchers have used the increased sensitivity of conjugated polymer nanoparticles (CPNs) for the detection of numerous analytes, including pesticides,\textsuperscript{41} nitroaromatics,\textsuperscript{42} and cations\textsuperscript{45} at parts per billion (i.e. ppb) concentrations.\textsuperscript{46} This interest is driven by the typically high fluorescence quantum yield of CPNs (\textasciitilde80\%),\textsuperscript{37} low toxicity to biological systems,\textsuperscript{38} and ability to achieve
aggregation-induced emission of conjugated fluorescent polymers when localized as nanoparticles. Additionally, the modular design of conjugated fluorescent polymers and the ability to control the size of CPNs via straightforward experimental manipulation provides a system that is highly tunable and can be easily optimized.

One family of analytes of particular interest as detection targets is bisphenols. The most commonly used bisphenol is Bisphenol A (BPA, compound 1), with over 5 million tons of compound 1 manufactured worldwide per year. This prevalence has led to a chronic detectable level of BPA in biological fluids (i.e. urine, blood, saliva) from the majority of people living in developed nations. Such ubiquitous BPA exposure is concerning, as BPA is a known estrogen mimic and endocrine disruptor. Numerous studies have linked chronic low dose exposure to BPA to numerous negative health effects including prostate and breast cancer, obesity, early onset puberty, and Type II diabetes. Regulatory changes and consumer-driven pressure over the health effects of BPA have caused companies to replace BPA with other bisphenols (BPs), such as bisphenol S (BPS, compound 2) and bisphenol F (BPF, compound 3). The structural similarity and initial research on these BPs suggest that they have similar or more severe negative health effects compared to BPA, 1. Current methods for detecting BPs include gas chromatography coupled with mass spectrometry (GC-MS), liquid chromatography coupled with mass spectrometry (LC-MS), and electrochemical techniques. GC-MS and LC-MS techniques are costly and time-consuming, while electrochemical techniques for the detection of bisphenols require large overpotentials that damage electrodes and reduce the system sensitivity and selectivity. Newer BPA detection methods, including chemiluminescent sensors, have also been reported.
Reported herein is the synthesis and photophysical characterization of eight novel fluorescent polymers and their application for the fluorescence detection of common BPs. The use of Suzuki coupling to synthesize conjugated fluorescent polymers is well-precedented in the literature to access a number of polymeric architectures,\textsuperscript{57} and has significant advantages compared to other synthetic methods, including relative insensitivity to air and moisture, high functional group tolerance, and generally high yields.\textsuperscript{58} Of the eight new architectures, four demonstrated Stokes shifts greater than 100 nm, and three of the new polymers had significantly different fluorescence responses based on their level of aggregation. All polymers displayed some degree of fluorescence changes with the addition of BPA, BPF, or BPS (compounds 1-3, Figure 1), as both aggregated polymer nanoparticles and well-dissolved polymer solutions. Notably, 100\% differentiation between the bisphenols was observed using linear discriminant analysis of the resulting fluorescence response signals.

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{structures}
\caption{Structures of bisphenol analytes.}
\end{figure}

Results and Discussion:

Optimization of polycondensation: The solubility of conjugated polymers can pose problems in post-synthesis processing, as the propensity of the conjugated chains to \(\pi\)-stack and aggregate leads to low solubility in most solvents. Options to enhance polymer solubility include the incorporation of sterically bulky side chains,\textsuperscript{59} which reduces aggregation, and the inclusion of highly polar functional groups,\textsuperscript{60} which increases the
polymer solubility in polar solvents. Undesired effects of incorporating sterically bulky or polar substituents include added synthetic challenges\textsuperscript{61} to access more functionalized monomers, as well as difficulties in forming conjugated polymer nanoparticles via hydrophobic collapse of the polymer chain, as a result of the lower hydrophobicity of the highly polar groups.\textsuperscript{62}

Our fluorene containing polymers include only the two solubilizing hydrocarbon side chains found on 9,9-dioctyl-fluorene-2,7-diboronic acid bis(pinacol) ester (compound 4, Scheme 1) and no solubilizing polar groups. A range of optimized conditions from literature-reported studies\textsuperscript{63} were employed in an attempt to increase polymer weight (\(M_n\)) without increasing the number of solubilizing side chains. Scheme 1 illustrates the general reaction used for the optimization experiments, with the results of these experiments summarized in Table 1. The use of palladium zero complexes and tri(o-tolyl) phosphine ligands successfully increased the weights (\(M_n\)) of the polymers, with the combination of the two resulting in the highest polymer weights (\(M_n = 5000 \text{ g/mol}\)). For P1, this molecular weight corresponds to approximately 10 monomer units, and is comparable to the molecular weights of some other conjugated polymers reported in the literature.\textsuperscript{44} Moreover, literature precedent indicates that the photophysical properties of longer-chain conjugated polymers are comparable to those of shorter-chain oligomers, with an oligomer of five repeat units often displaying photophysical properties that are indistinguishable from that of the full-length polymer.\textsuperscript{64} However, removing ethanol and lowering the monomer concentration resulted in decreased polymer weights. The highest polymer weight was achieved with experiment number 8 (table 1),\textsuperscript{65} using
tris(dibenzylideneacetone)dipalladium(0) and tri(o-tolyl) phosphine as the ligand, and these optimized conditions were subsequently used for the synthesis of P2 – P9.

Scheme 1: Synthesis of P1.

Spectroscopic studies: The photophysical and structural properties of all synthesized polymers (Figure 2) were characterized as well-dissolved solutions and as aggregated nanoparticles. Of note, all polymers demonstrated measurable fluorescence emission from excitation at or near the maximum absorption wavelength, with key results summarized in Table 2.

Figure 2: Structure of newly synthesized polymers.
**P1** has a large Stokes shift of over 200 nm and is characterized by a relatively low molecular weight, likely due to limitations on the solubility of the monomers and polymer. Polymer **P2** was designed to increase the polymeric molecular weight while maintaining a large Stokes shift, similar to that of **P1**. This goal was achieved successfully by increasing the number of alkyl-branched monomer units to a 3:1 ratio of dioctylfluorene:fluorenone (Figure 2, **P2**) in a random copolymer structure. This increased the polymer weight ($M_n$) by a factor of approximately 5 (taking into account the larger molecular weight of the monomer repeat units) while still retaining the large Stokes shift observed in **P1** (Stokes shifts: $\textbf{P1} = 236$ nm, $\textbf{P2} = 230$ nm). Interestingly, the random copolymer displayed an additional fluorescence emission peak with a smaller Stokes shift of 34 nm. This peak (at 414 nm) matches the fluorescence emission of poly-9,9-dioctylfluorene$^{66}$ and the second peak (at 610 nm) matches the fluorescence emission of 9-fluorenone.$^{67}$ When **P2** is aggregated as nanoparticles, the emission peak at 414 nm disappears and the peak at 610 nm undergoes a hypsochromic shift to 550 nm, (Figure 3), indicating energy transfer from 9,9-dioctylfluorene monomer units (with emission at 414 nm) to 9-fluorenone (with lower energy emission). This energy transfer is facilitated in the aggregated state due to facile interchain exciton migration that is enabled in such architectures.
Table 1: Summary of reaction optimization experiments using P1 as the polymer target.

<table>
<thead>
<tr>
<th>Exp #</th>
<th>Conditions</th>
<th>Monomer conc. (mol/L)</th>
<th>Solvent</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w$ (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1c</td>
<td>Pd(OAc)$_2$: 0.15 mol Eq PPh$_3$: 0.45 mol Eq</td>
<td>0.033</td>
<td>1:1:1 ethanol/toluene/water</td>
<td>2700</td>
<td>3800</td>
<td>1.41</td>
</tr>
<tr>
<td>2</td>
<td>Pd(OAc)$_2$: 0.15 mol Eq PPh$_3$: 0.45 mol Eq</td>
<td>0.033</td>
<td>1:1:1 ethanol/toluene/water</td>
<td>2600</td>
<td>4200</td>
<td>1.58</td>
</tr>
<tr>
<td>3</td>
<td>Pd(OAc)$_2$: 0.15 mol Eq PPh$_3$: 0.45 mol Eq</td>
<td>0.022</td>
<td>1:1 chloroform/water</td>
<td>2300</td>
<td>4200</td>
<td>1.52</td>
</tr>
<tr>
<td>4</td>
<td>Pd(OAc)$_2$: 0.15 mol Eq PPh$_3$: 0.45 mol Eq</td>
<td>0.033</td>
<td>1:2 chloroform/water</td>
<td>1800</td>
<td>2100</td>
<td>1.20</td>
</tr>
<tr>
<td>5</td>
<td>Pd(PPh$_3$)$_4$: 0.15 mol Eq</td>
<td>0.033</td>
<td>1:1:1 ethanol/toluene/water</td>
<td>4700</td>
<td>5600</td>
<td>1.19</td>
</tr>
<tr>
<td>6</td>
<td>Pd(OAc)$_2$: 0.15 mol Eq P(o-Tol)$_3$: 0.30 mol Eq</td>
<td>0.033</td>
<td>1:1:1 ethanol/toluene/water</td>
<td>3200</td>
<td>5400</td>
<td>1.66</td>
</tr>
<tr>
<td>7</td>
<td>Pd$_2$(dba)$_3$: 0.15 mol Eq PPh$_3$: 0.45 mol Eq</td>
<td>0.033</td>
<td>1:1:1 ethanol/toluene/water</td>
<td>2800</td>
<td>3900</td>
<td>1.38</td>
</tr>
<tr>
<td>8</td>
<td>Pd$_2$(dba)$_3$: 0.15 mol Eq P(o-Tol)$_3$: 0.30 mol Eq</td>
<td>0.033</td>
<td>1:1:1 ethanol/toluene/water</td>
<td>5000</td>
<td>6500</td>
<td>1.30</td>
</tr>
<tr>
<td>9</td>
<td>Pd(PPh$_3$)$_4$: 0.15 mol Eq</td>
<td>0.010</td>
<td>1:1:1 ethanol/toluene/water</td>
<td>3200</td>
<td>4200</td>
<td>1.29</td>
</tr>
<tr>
<td>10</td>
<td>Pd(PPh$_3$)$_4$: 0.15 mol Eq</td>
<td>0.005</td>
<td>1:1:1 ethanol/toluene/water</td>
<td>3100</td>
<td>4400</td>
<td>1.43</td>
</tr>
</tbody>
</table>

*a All reactions were heated at 50°C for 72 hours and used K$_2$CO$_3$ (3 molar equivalents) as the base

*b All results were obtained on an Agilent 1260 Infinity II Multi-Detector GPC/SEC System with a polystyrene internal standard

*c Experiment 1 was heated at 111°C for 72 hours

P3’s UV absorbance and fluorescence emission were visually similar to the spectra of polymers with significant amounts of dioctylfluorene units (P2 and P8). However, P3 has a much higher quantum yield (0.7650) than P2 (0.0058) and P8 (0.0025), which is qualitatively similar to the quantum yields of all fluorene conjugated polymers, and has the smallest Stokes shift (33 nm) of all the investigated polymers. The UV absorbance and fluorescence emission characteristics of P3 are of particular interest when compared to polymer P4, as both P3 and P4 include fused aromatic backbone segments in addition to their dioctylfluorene segments, however, their fused aromatic backbone segments result in vastly different photophysical properties. P4 incorporates an unsubstituted anthracene moiety into its polymer backbone, resulting in P4’s UV absorbance being
similar to anthracene’s,\textsuperscript{68} which indicates that the anthracene segment of \textbf{P4} is absorbing more than the dioctylfluorene segment. This is in contrast to \textbf{P3}, which contains an unsubstituted naphthalene backbone segment, but does not absorb at wavelengths typical of naphthalene (311 nm).\textsuperscript{69} Furthermore, \textbf{P4}’s fluorescence emission maximum is close to \textbf{P3}’s, resulting in a very large Stokes shift (178 nm) for \textbf{P4}. These small structural changes which result in large differences in the photophysical properties of the polymers demonstrate excellent tunability for tailoring the polymer products for specific applications.

Polymers \textbf{P5} and \textbf{P6} have similar photophysical properties, with UV absorbance maxima at 345 nm and 341 nm, respectively. Both polymers have two fluorescence emission maxima (\textbf{P5} = 424 nm, 447 nm; \textbf{P6} = 414 nm, 436 nm) and large Stokes shifts (\textbf{P5} = 79 nm, 102 nm; \textbf{P6} = 72 nm, 95 nm). The differences in wavelength between the photophysical properties of \textbf{P5} and \textbf{P6} are expectedly small as the structural difference between the two polymers is an alkoxy verses an alkane functional group, neither of which is on the polymer backbone.
Table 2: Properties of fluorescent polymers P1-P9 synthesized using the optimized reaction conditions

<table>
<thead>
<tr>
<th>Polymer</th>
<th>M_n (g/mol)</th>
<th>M_w (g/mol)</th>
<th>PDI</th>
<th>UV $\lambda_{\text{max}}$ (nm)</th>
<th>Stokes Shift (nm)</th>
<th>Fluorescence emission (nm)</th>
<th>Quantum Yield $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>F1 $\lambda_{\text{max}}$</td>
<td>F1 $\lambda_{\text{max}}$</td>
<td>$\lambda_{\text{max}}$ 1</td>
</tr>
<tr>
<td>P1</td>
<td>5000</td>
<td>6500</td>
<td>1.30</td>
<td>374</td>
<td>236</td>
<td>-</td>
<td>610</td>
</tr>
<tr>
<td>P2</td>
<td>26400</td>
<td>49300</td>
<td>1.87</td>
<td>380</td>
<td>34</td>
<td>230</td>
<td>414</td>
</tr>
<tr>
<td>P3</td>
<td>5300</td>
<td>14300</td>
<td>2.69</td>
<td>378</td>
<td>33</td>
<td>-</td>
<td>411</td>
</tr>
<tr>
<td>P4</td>
<td>300</td>
<td>4200</td>
<td>1.45</td>
<td>262</td>
<td>178</td>
<td>-</td>
<td>440</td>
</tr>
<tr>
<td>P5</td>
<td>4800</td>
<td>8000</td>
<td>1.64</td>
<td>345</td>
<td>79</td>
<td>102</td>
<td>424</td>
</tr>
<tr>
<td>P6</td>
<td>6000</td>
<td>12400</td>
<td>2.07</td>
<td>341</td>
<td>72</td>
<td>95</td>
<td>413</td>
</tr>
<tr>
<td>P7</td>
<td>3200</td>
<td>5700</td>
<td>1.79</td>
<td>374</td>
<td>53</td>
<td>75</td>
<td>427</td>
</tr>
<tr>
<td>P8</td>
<td>21500</td>
<td>59200</td>
<td>2.74</td>
<td>377</td>
<td>38</td>
<td>287</td>
<td>415</td>
</tr>
<tr>
<td>P9</td>
<td>6700</td>
<td>9800</td>
<td>1.46</td>
<td>353</td>
<td>223</td>
<td>-</td>
<td>576</td>
</tr>
</tbody>
</table>

$^a$ All reactions were heated at 50°C for 72 hours and used K$_2$CO$_3$ (3 mol Eq), Pd$_2$(dba)$_3$ (0.15 mol Eq), P(o-Tol)$_3$ (0.30 mol Eq), and 2 monomers (1 mol Eq each) at 0.033 mol/L in equal amounts ethanol, toluene, and water.

$^b$ Quantum yields were measured using an integration sphere with the following references: 9,10-diphenylanthracene, quinine bisulfate, and 2-aminopyridine.

Figure 3: Normalized fluorescence emission of P2 as a well-dissolved solution in chloroform (0.01 mg/mL) (black line) and as a nanoparticle suspension in water (red line) ($\lambda_{ex} = 380$ nm).

Interestingly, P7’s fluorescence emission changed from a spectrum with two emission maxima when dissolved in chloroform to a spectrum with much greater fine structure upon aggregation in nanoparticles, with four distinct maxima observed (Figure 4). The emission spectra with four maxima shows the same fine structure as the fluorescence emission of naphthalene$^{70}$ and has a bathochromic shift of 42 nm compared to the non-aggregated state, which suggests J-aggregate formation.$^{71}$ These spectral features strongly suggest a geometric arrangement in which the polymer chains stack in a
staggered arrangement with the pendant naphthalene moieties of P7 directly above and below the fluorene backbone segments from neighboring polymer chains.

Figure 4: Normalized fluorescence emission of P7 as a well-dissolved solution in chloroform (0.01 mg/mL) (black line) and a nanoparticle suspension in water (red line), ($\lambda_{\text{ex}} = 375$ nm).

P8 and P9 are comprised of the same monomer units, albeit with different ratios of monomer in the polymer product (P9: 1:1 monomer ratio; P8: 3:1 ratio of 9,9-dioctylfluorene to anthraquinone monomer, Figure 2). Interestingly, P8 displays two emission maxima at 414 nm and at 664 nm, while P9 has only one emission peak at 576 nm. In a well-solubilized polymer solution, the fluorescence emission peak of P8 at 664 nm accounts for less than 10% of the total fluorescence emission. However, similar to P2, the aggregated forms of P8 only displays one emission peak, at 570 nm, which is a significant hypsochromatic shift (94 nm) compared to the non-aggregated form. The large Stokes shift of P9 (223 nm) contrasts with the double Stokes shifts for polymer P8 (due to the dual emission) of 38 nm and 287 nm. Additionally, P8’s larger ratio of 9,9-dioctylfluorene monomer 4 compared to P9’s 1:1 monomer ratio results in P8 having a polymer weight approximately 2.5 greater than that of P9, while still displaying fluorescence properties that are comparable to P9 in the aggregated state.
In addition to characterizing the polymer’s photophysical properties, all polymers were screened for their ability to detect BPA, BPF, and BPS (compounds 1 - 3). The fluorescence modulation of the polymers in the presence of these analytes were measured as both well-dissolved chloroform solutions and as nanoparticles suspended in water. All polymers demonstrated some degree of fluorescence modulation in the presence of at least two bisphenols (Tables 3 and 4). The fluorescence response of P1, a previously reported polymer, to all bisphenol analytes is included in the ESI for this manuscript.

All polymers demonstrated some degree of fluorescence modulation when they were dissolved in chloroform; however, high analyte concentrations (1 mM) were required to achieve measurable fluorescence responses. Moreover, poor selectivity between structurally similar analytes was observed, with half of the polymers, when dissolved in chloroform, displaying nearly identical modulation values with all analytes investigated. P2 had one of the largest fluorescence modulations as a chloroform solution with the addition of BPS, with a modulation value of 1.48 obtained (Figure 5A), whereas P6 was one of the most selective as a chloroform solution, with noticeably different fluorescence spectra obtained for all bisphenol analytes (Figure 5B). Additionally, P4 showed similar selectivity to that of P6 and a similarly large fluorescence modulation to that of P2, with modulation values for P4 chloroform solution varying between 0.39 and 0.49. These fluorescence responses are promising as the intermolecular forces that drive the bisphenols to interact with the polymers are less prevalent in chloroform solution than in aggregated states. Impressively, linear discriminant analyses of the
relatively minor changes in spectral signals of the analyte-polymer complexes resulted in 100% successful differentiation of highly structurally similar analytes (Figure 6).

**Table 3:** Fluorescence modulation of polymers dissolved in chloroform with 1000 μM bisphenol

<table>
<thead>
<tr>
<th>Polymer</th>
<th>BPA</th>
<th>BPF</th>
<th>BPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2</td>
<td>0.99</td>
<td>0.98</td>
<td>1.48</td>
</tr>
<tr>
<td>P3</td>
<td>0.98</td>
<td>1.02</td>
<td>1.06</td>
</tr>
<tr>
<td>P4</td>
<td>0.44</td>
<td>0.49</td>
<td>0.39</td>
</tr>
<tr>
<td>P5</td>
<td>0.82</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>P6</td>
<td>0.83</td>
<td>0.78</td>
<td>0.76</td>
</tr>
<tr>
<td>P7</td>
<td>0.98</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>P8</td>
<td>0.98</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>P9</td>
<td>0.98</td>
<td>0.96</td>
<td>0.98</td>
</tr>
</tbody>
</table>

*0.5 mL of 1000 μM bisphenol in chloroform added to 2.0 mL 0.01 mg/ml polymer solution in chloroform. All modulation values were calculated according to Fluorescence Modulation = \( \frac{F_{\text{analyte}}}{F_{\text{blank}}} \).*

**Table 4:** Fluorescence modulation of polymer nanoparticles suspended in water with 50 μM bisphenol

<table>
<thead>
<tr>
<th>Polymer</th>
<th>BPA</th>
<th>BPF</th>
<th>BPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2</td>
<td>1.03</td>
<td>1.05</td>
<td>1.04</td>
</tr>
<tr>
<td>P3</td>
<td>2.90</td>
<td>2.94</td>
<td>0.74</td>
</tr>
<tr>
<td>P4</td>
<td>0.92</td>
<td>1.06</td>
<td>1.00</td>
</tr>
<tr>
<td>P5</td>
<td>0.87</td>
<td>1.03</td>
<td>0.84</td>
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<tr>
<td>P6</td>
<td>0.46</td>
<td>0.54</td>
<td>1.00</td>
</tr>
<tr>
<td>P7</td>
<td>0.98</td>
<td>1.07</td>
<td>0.96</td>
</tr>
<tr>
<td>P8</td>
<td>0.81</td>
<td>0.79</td>
<td>0.80</td>
</tr>
<tr>
<td>P9</td>
<td>0.96</td>
<td>0.97</td>
<td>0.97</td>
</tr>
</tbody>
</table>

*0.5 mL of 50 μM bisphenol in water added to 2.0 mL nanoparticle solution in water. All modulation values were calculated according to Fluorescence Modulation = \( \frac{F_{\text{analyte}}}{F_{\text{blank}}} \).*

**Figure 5:** Normalized fluorescence emission of (A) P2 and (B) P6 as well-dissolved chloroform solutions (0.01 mg/mL) with: no analyte (black line), 1000 μM BPA (red line), 1000 μM BPF (green line), and 1000 μM BPS (blue line), (P2 \( \lambda_{\text{ex}} = 380 \text{ nm} \), P6 \( \lambda_{\text{ex}} = 340 \text{ nm} \)).
While the chloroform solutions demonstrated sufficient fluorescence modulation to differentiate between the bisphenols at high concentrations, the polymer nanoparticles had markedly enhanced selectivity to the bisphenol analytes at far lower analyte concentrations. This greater selectivity is driven by hydrophobic aggregation of the bisphenols with the polymer nanoparticles and the higher propensity for interpolymer exciton migration in aggregated states, which increases the number of analyte binding sites that the exciton samples prior to relaxation to the ground state. The enhanced fluorescence modulation is seen with nearly all polymer nanoparticles-analyte combinations, except P4 and P6 with BPS, and current efforts in our laboratory are focused on elucidating reasons for the aberrant behavior of these particular combinations. Particularly notable fluorescence modulation is seen with polymer P3 and P5 nanoparticles (Figure 7). P3 demonstrates the most pronounced fluorescence modulation of all nanoparticles, whereas P5 has the greatest selectivity of all nanoparticle solutions between the less bulky BPF and the bulkier BPS and BPA. The difference in the selectivity of these polymers suggests that the electron rich P3 is interacting with the BPs primarily through electronic complementarity, whereas the
fluorescence responses of **P5** are likely due to sterically-driven interference between **P5**’s side chains and the BP analytes that disrupts the polymer aggregation. Furthermore, when the fluorescence emission of the nanoparticles in the presence of the analytes was analyzed using linear discriminant analysis (Figure 8), 100% differentiation between the three bisphenols at low concentrations (50 μM) was obtained. Finally, the stability of the nanoparticles in water was observed over 72 hours by DLS and no significant degradation or precipitation of the nanoparticles was observed. This is consistent with literature reported longevity studies of conjugated polymer nanoparticles generally remaining stable for weeks in aqueous solution.

**Figure 7:** Normalized fluorescence emission of (A) **P3** and (B) **P5** as nanoparticles suspended in water with: no analyte (black line), 50 μM BPA (red line), 50 μM BPF (green line), and 50 μM BPS (blue line) (**P3** λ<sub>ex</sub> = 378 nm, **P5** λ<sub>ex</sub> = 345 nm).

**Figure 8:** Statistical array of polymer nanoparticles in water with 50 μM bisphenols
Conclusions:

In summary, eight novel fluorescent polymers were synthesized using Suzuki polycondensation. All eight polymers were spectroscopically characterized and their potential use as fluorescent sensors was investigated. P2, P4, P5, and P9 had Stokes shifts that were greater than 100 nm, with a range of UV-Vis absorbance maxima. P2, P7, and P8 demonstrated significantly different fluorescence emission in aggregated states (i.e in nanoparticles) compared to their fluorescence emission profiles as well-dissolved solutions in chloroform. The fluorescence responses of the polymers to the addition of BPA, BPF, and BPS was investigated, both for well-dissolved polymer solutions and as aggregated polymer nanoparticles. The polymers demonstrated some degree of fluorescence modulation in the vast majority of polymer-analyte parings with isolated analyte-polymer pairs demonstrating little to no observed modulation. Using linear discriminant analysis, these distinctive fluorescence responses could differentiate between the three bisphenols with 100% selectivity, even among highly structurally similar analytes. Efforts towards extending this fluorescence-based detection system to other common environmental toxicants as well as evaluating the use of polymeric thin films for such sensing applications are currently underway in our laboratory. Further efforts towards determining the selectivity and robustness of this system by evaluating the system in complex aqueous media and expanding the analyte scope to other aromatic compounds both with and without bisphenols as competitive analyte studies will be performed, and the results of these and other investigations will be reported in due course.
Funding Information:

The authors acknowledge the University of Rhode Island chemistry department for funding of this work.

Acknowledgment:

The authors thank Dr. Matthew Kiesewetter and Mr. Kurt Fastnacht at the University of Rhode Island for the use of Dr. Kiesewetter’s Agilent 1260 Infinity II Multi-Detector GPC/SEC System. We would like to thank Dr. William Euler for the use of his Malvern Zetasizer Nano ZS.

yield (59.4 mg). M
product was precipitated in methano
over sodium sulfate, filtered, and concentrated on a rotary evaporator. The crude
palladium byproducts. The organic layer

C04

o

H

9,9

55.8 mg, 0.1 mmol, 1.0 eq.)

2,7

potassium carbonate
65

64

Wildeman, J.; Peteanu, L. A. 
2012

63

Park, T. J.; Yoo, P. J.; Kim, S.; Park, J. 
Mater .

61

Su, S. J.; Chen, J. W.; Cao, Y. 
2015

59

Prudnov, F. A.; Novikov, D. V.; Babenko, S. D.; Troshin, P. A. 
PMM. A: PM. Chem.

2001

57

X

Anal. Methods

53

(a) Ling, L. J.; Xu, J. P.; Deng, Y. H.; Peng, Q.; Chen, J. H.; Ya, S. H.; Nie, Y. J. 
Anal. Methods 2018, 10, 2722. (b) Tan, F.; Cong, L.; Li, X.; Zhao, Q.; Zhao, H.; Quan, 

54

200, 111.

55


56


57

(a) Babudri, F.; Farinola, G. M.; Naso, F. Synlett 2009, 2740. (b) Schlüter, A. D. J. 

58

Maluenda, I.; Navarro, O. Molecules 2015, 20, 7528.

59

Akkuratov, A. V.; Susarova, D. K.; Moskvin, Y. L.; Anokhin, D. V.; Chernyak, A. V.; 
2015, 3, 1497.

60


61

Mater. 2012, 22, 1711.

62


63

(a) Hohl, B.; Bertschi, L.; Zhang, X.; Schlüter, A. D.; Sakamoto, J. Macromolecules 
2012, 45, 5418; (b) Moscatelli, A.; Livingston, K.; So, W. Y.; Lee, S. J.; Scherf, U.; 

64


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Tris(dibenzylideneacetone)dipalladium(0) (13.7 mg, 0.015 mmol, 0.15 eq.), 
potassium carbonate (41.46 mg, 0.3 mmol, 3 eq.), 
T(0-tolyl)phosphine (9.1 mg, 0.03 mmol, 0.3 eq.), 
2,7-dibromofluorenone (compound 5, 33.8 mg, 0.1 mmol, 1.0 eq.), and 
9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (compound 4, 
55.8 mg, 0.3 mmol, 3 eq.) were added to a round-bottomed flask under an inert 
nitrogen atmosphere. Toluene (3 mL), 95% ethanol (3 mL), and water (3 mL) were 
each degassed and added to the flask via syringe, and the reaction mixture was heated 
at 50 °C for 72 hours under an inert nitrogen atmosphere. The reaction mixture was 
cooled to room temperature and excess chloroform (approximately 20 mL) was added 
to the flask. The resulting suspension was filtered using gravity filtration to remove all 
palladium byproducts. The organic layer was separated from the aqueous layer, dried 
over sodium sulfate, filtered, and concentrated on a rotary evaporator. The crude 
product was precipitated in methanol from chloroform affording a green solid in 96% 
yield (59.4 mg). Mn = 5000, Mw = 6500, PDI = 1.30. UV absorbance λmax = 374 nm;
Fluorescence emission $\lambda_{\text{max}} = 427$ nm, 449 nm; Quantum yield = 0.908.

72 0.5 mL of a bisphenol solution (100, 500, 1000 $\mu$M in chloroform or 50, 100 $\mu$M in water) was added to a quartz cuvette. 2 mL of a polymer solution (0.01 mg/mL in chloroform or as a nanoparticle solution suspended in water) was added to the cuvette. This sample was then measured on the fluorimeter four times and the average of the four runs was reported. The samples were excited at the polymer’s UV-Vis absorbance maximum with an excitation slit width of 1.5 nm and emission slit width of 3.0 nm.
73 Fluorescence Modulation = $F_{\text{analyte}} / F_{\text{blank}}$
Where $F_{\text{analyte}}$ is the integrated fluorescence emission of the polymer in the presence of the analyte and $F_{\text{blank}}$ is the integrated fluorescence emission of the polymer in the absence of analyte.
MATERIALS AND METHODS:
All chemicals were obtained from Sigma-Aldrich Chemical Company or Fisher Scientific, and used as received. Fluorescence spectra were acquired on a Shimadzu RF-6000 Spectrofluorophotometer, with a 1.5 nm excitation slit width and 3.0 nm emission slit width. Absorbance spectra were acquired on a Shimadzu UV-3600 Plus UV-Vis-NIR Spectrophotometer. All NMR spectra were acquired using a Bruker Ultrashield 300 MHz NMR Spectrometer. Polydispersities were calculated using size exclusion chromatography performed at 40 °C using dichloromethane eluent on an Agilent Infinity GPC system equipped with three Agilent PLGel columns 7.5 mm × 300 mm (5 μm, pore sizes: 50, 10^3, 10^4 Å). M_n and M_w/M_n were determined versus polystyrene standards (162 g/mol-526 kg/mol, Polymer Laboratories). The average nanoparticle diameters were measured using a Malvern Zetasizer Nano ZS. Fluorescence spectra were integrated vs. wavenumber on the X-axis using OriginPro. Arrays were generated in SYSTAT Version 13 using the following settings: linear discriminant analysis, analytes as grouping variables, P2-P9 as predictors, and Mahal long range statistics.

GENERAL PROCEDURES:

General procedure for fabrication of nanoparticles:
Nanoparticle solutions were prepared by adding 25 mL of 0.05 mg/mL polymer solution in tetrahydrofuran (THF) to 100 mL of sonicating water. This solution was sonicated for
one hour. The remaining THF was removed by bubbling nitrogen through the solution for 12 hours.

**General procedure for DLS measurements:**

0.5 mL of a nanoparticle solution was added to a quartz cuvette. The Zetasizer probe was inserted into the cuvette and the cuvette was placed in the sample holder. The following parameters were used for the measurements: material was set as polymer (RI: 1.700, absorption: 1.000), dispersant was set as water (temperature 25.0 °C, viscosity: 0.8872 cP, RI: 1.330), temperature was set as 25 °C (equilibration time: 120 sec), the measurement angle was set as 90°, and 5 measurements of 100 runs were performed on each sample.

**General procedure for fluorescence measurements:**

0.5 mL of a bisphenol solution (100, 500, 1000 μM in chloroform or 50, 100 μM in water) was added to a quartz cuvette. 2 mL of a polymer solution (0.01 mg/mL in chloroform or as a nanoparticle solution suspended in water) was added to the cuvette. This sample was then measured on the fluorimeter four times. The samples were excited at the polymer’s UV-Vis absorbance maximum with an excitation slit width of 1.5 nm and emission slit width of 3.0 nm. Fluorescence emission spectra are compared using Equation 1:

\[
\text{Fluorescence Modulation} = \frac{F_{\text{analyte}}}{F_{\text{blank}}} \tag{1}
\]

Where \(F_{\text{analyte}}\) is the integrated fluorescence emission of the polymer in the presence of the analyte and \(F_{\text{blank}}\) is the integrated fluorescence emission of the polymer in the absence of analyte.
**General procedure for UV-Vis measurements:**

3 mL of the solvent (water for nanoparticles and chloroform for polymers dissolved in chloroform) was added to a quartz cuvette, which was then placed in the reference holder. 3 mL of the solvent (water for nanoparticles and chloroform for polymers dissolved in chloroform) was added to a quartz cuvette which was then placed in the sample holder. A baseline measurement was taken from 800 nm to 250 nm. The cuvette in the sample holder was removed. 3 mL of polymer solution was added to a quartz cuvette which was then placed in the sample holder. The UV-Vis absorbance was then measured from 800 nm to 250 nm.

**General procedure for quantum yield measurements:**

3.0 ml of polymer solution in chloroform was added to a quartz cuvette. The cuvette was placed in the fluorimeter integration sphere sample holder and the fluorescence was measured. The fluorescence signal was compared to one of the following reference fluorophores: quinine bisulfate (0.01 mg/ml) in 1 N H$_2$SO$_4$ ($\phi_f = 0.55$, Ex$_\lambda$ = 345 nm), 2-aminopyridine (0.01 mg/ml) in 1 N H$_2$SO$_4$ ($\phi_f = 0.65$, Ex$_\lambda$ = 300 nm), or 9,10-diphenylanthracene (0.01 mg/ml) in degassed cyclohexane ($\phi_f = 0.91$, Ex$_\lambda$ = 373 nm). Each polymer used the reference fluorophore with the closest excitation wavelength to the UV-Vis $\lambda_{max}$ of the polymer to determine quantum yield.$^{77}$
**SUMMARY OF SYNTHESIZED POLYMERS:**

![Figure S1](image.png)

*Figure S1*: Structures of all synthesized polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w$ (g/mol)</th>
<th>PDI</th>
<th>UV $\lambda_{\text{max}}$ (nm)</th>
<th>Stokes Shift (nm)</th>
<th>Fluorescence Emission (nm)</th>
<th>Quantum Yield</th>
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<tbody>
<tr>
<td>P1</td>
<td>4100</td>
<td>7100</td>
<td>1.72</td>
<td>374</td>
<td>236</td>
<td>610</td>
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<tr>
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<td>26400</td>
<td>49300</td>
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<td>380</td>
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<td>230</td>
<td>0.0068</td>
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<tr>
<td>P3</td>
<td>5300</td>
<td>14300</td>
<td>2.69</td>
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<td>33</td>
<td>411</td>
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<tr>
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<td>178</td>
<td>440</td>
<td>0.1403</td>
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<tr>
<td>P5</td>
<td>4800</td>
<td>8000</td>
<td>1.64</td>
<td>345</td>
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<td>424</td>
<td>0.8278</td>
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<tr>
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<td>341</td>
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<td>6700</td>
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<td>353</td>
<td>223</td>
<td>576</td>
<td>0.3087</td>
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</table>
POLYMER SYNTHESIS PROCEDURES:

**Synthesis of P1:**

**Figure S2:** Synthesis of P1.

Procedure: Toluene (5 mL), 95% ethanol (5 mL), and deionized water (5 mL) were each degassed separately by bubbling nitrogen through each solvent for 30 minutes. Palladium acetate (11.2 mg, 0.05 mmol, 0.05 eq.), triphenylphosphine (39.3 mg, 0.15 mmol, 0.15 eq.), potassium carbonate (304.0 mg, 2.2 mmol, 2.2 eq.), 2,7-dibromofluorenone (compound 13, 338.4 mg, 1.0 mmol, 1.0 eq.), and 9,9-dioctyfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (compound 12, 558.4 mg, 1.0 mmol, 1.0 eq.) were added to a round-bottomed flask. This flask was evacuated using three nitrogen-vacuum purge cycles. The degassed solvents were added to the flask via syringe, and the reaction mixture was refluxed at 111 °C for 12 hours under an inert nitrogen atmosphere. The reaction mixture was cooled to room temperature and excess chloroform (approximately 50 mL) was added to the flask. The resulting suspension was filtered using gravity filtration to remove all palladium byproducts. The organic layer was separated from the aqueous layer, dried over sodium sulfate, filtered, and concentrated on a rotary evaporator. The crude product was precipitated in methanol.
from chloroform, yielding an orange solid in 43% yield (245 mg). $M_n = 4100$, $M_w = 7100$, PDI = 1.72. $^1$H NMR (300 MHz, CDCl$_3$, δ, ppm) 8.06 (m, 2 H), 7.84 (m, 4 H), 7.65 (m, 6 H), 2.10 (m, 4 H), 1.10 (m, 24 H), 0.79 (m, 8 H). UV absorbance $\lambda_{\text{max}}$ = 374 nm; Fluorescence emission $\lambda_{\text{max}}$ = 610 nm; Quantum yield = 0.006.

**Synthesis of P2:**

![Synthesis of P2](image)

**Figure S3:** Synthesis of P2.

**Procedure:** Toluene (5 mL), 95% ethanol (5 mL), and deionized water (5 mL) were each degassed separately by bubbling nitrogen through each solvent for 30 minutes. Palladium acetate (6.4 mg, 0.03 mmol, 0.1 eq.), triphenylphosphine (24.0 mg, 0.91 mmol, 0.32 eq.), potassium carbonate (174.0 mg, 1.26 mmol, 4.4 eq.), 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (compound 12, 335.0 mg, 0.60 mmol, 2.1 eq.), 2,7-dibromofluorenone (compound 13, 96.7 mg, 0.29 mmol, 1 eq.), and 9,9-dioctyl-2,7-dibromofluorene (compound S1, 156.9 mg, 0.29 mmol, 1 eq.) were added to a round-bottomed flask. This flask was evacuated using three nitrogen-vacuum purge cycles. The degassed solvents were added to the flask via syringe, and the reaction mixture was refluxed at 111 °C for 12 hours under an inert nitrogen atmosphere. The reaction mixture was cooled to room temperature and excess chloroform (approximately
50 mL) was added to the flask. The resulting suspension was filtered using gravity filtration to remove all palladium byproducts. The organic layer was separated from the aqueous layer, dried over sodium sulfate, filtered, and concentrated on a rotary evaporator. The crude product was precipitated in methanol from chloroform affording a yellow-orange solid in 68% yield (260 mg). $M_n = 26400$, $M_w = 49300$, PDI = 1.87. $^1$H NMR (300 MHz, CDCl$_3$, δ, ppm) 8.07 (S, 2 H), 7.84 (m, 8 H), 7.67 (m, 14 H), 2.10 (m, 8 H), 1.14 (m, 74 H), 0.81 (m, 26 H). UV absorbance $\lambda_{max} = 380$ nm; Fluorescence emission $\lambda_{max} = 414$ nm, 610 nm; Quantum yield = 0.007.

**Synthesis of P3:**

![Synthesis of P3](image)

**Figure S4:** Synthesis of P3.

**Procedure:** Toluene (5 mL), 95% ethanol (5 mL), and deionized water (5 mL) were each degassed separately by bubbling nitrogen through each solvent for 30 minutes. Palladium acetate (11.2 mg, 0.05 mmol, 0.05 eq.), triphenylphosphine (39.3 mg, 0.15 mmol, 0.15 eq.), potassium carbonate (304.0 mg, 2.2 mmol, 2.2 eq.), 9,9-diocytlfuorene-2,7-diboronic acid bis(1,3-propanediol) ester (compound 12, 558.4 mg, 1 mmol, 1 eq.), and 2,6-dibromonaphthelene (compound S2, 286.2 mg, 1 mmol, 1 eq.) were added to a round-bottomed flask. This flask was evacuated using three nitrogen-vacuum purge cycles. The degassed solvents were added to the flask via syringe, and
the reaction mixture was refluxed at 111 °C for 12 hours under an inert nitrogen atmosphere. The reaction mixture was cooled to room temperature and excess chloroform (approximately 50 mL) was added to the flask. The resulting suspension was filtered using gravity filtration to remove all palladium byproducts. The organic layer was separated from the aqueous layer, dried over sodium sulfate, filtered, and concentrated on a rotary evaporator. The crude product was precipitated in methanol from chloroform affording an orange solid in 71% yield (330 mg). $M_n = 5300$, $M_w = 14300$, PDI = 2.69. $^1$H NMR (300 MHz, CDCl$_3$, $\delta$, ppm) 8.19 (s, 2 H), 8.06 (m, 2 H), 7.90 (m, 4 H), 7.77 (m, 4 H), 2.14 (m, 4 H), 1.13 (m, 24 H), 0.80 (m, 8 H). UV absorbance $\lambda_{\text{max}} = 378$ nm; Fluorescence emission $\lambda_{\text{max}} = 411$ nm; Quantum yield = 0.765.

**Synthesis of P4:**

![Synthesis of P4](image)

**Figure S5:** Synthesis of P4.

**Procedure:** Toluene (4 mL), 95% ethanol (4 mL), and water (4 mL) were each degassed separately by bubbling nitrogen through each solvent for 30 minutes. Palladium acetate (5.6 mg, 0.025 mmol, 0.05 eq.), triphenylphosphine (19.7 mg, 0.025 mmol, 0.15 eq.), potassium carbonate (152.0 mg, 1.1 mmol, 2.2 eq.), 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (compound 12, 307.1 mg, 0.55 mmol, 1 eq.), and 9,10-
dibromoanthracene (compound S3, 168.0 mg, 0.5 mmol, 1.1 eq.) were added to a round bottom flask. This flask was evacuated using three nitrogen-vacuum purge cycles. The degassed solvents were added to the flask via syringe, and the reaction mixture was refluxed at 111 °C for 12 hours under an inert nitrogen atmosphere. The reaction mixture was cooled to room temperature and excess chloroform (approximately 40 mL) was added to the flask. The resulting suspension was filtered using gravity filtration to remove all palladium byproducts. The organic layer was separated from the aqueous layer, dried over sodium sulfate, filtered, and concentrated on a rotary evaporator. The crude product was precipitated in methanol from chloroform affording an orange solid in 69% yield (196 mg). M_n = 3000, M_w = 4200, PDI = 1.45. \(^1\)H NMR (300 MHz, CD_2Cl_2, \(\delta\), ppm) 8.04 (m, 2 H), 7.81 (m, 2 H), 7.50 (m, 4 H), 7.44 (m, 2 H), 7.35 (m, 4 H), 2.02 (m, 4 H), 1.11 (m, 24 H), 0.75 (m, 8 H). UV absorbance \(\lambda_{\text{max}} = 262\) nm; Fluorescence emission \(\lambda_{\text{max}} = 440\) nm; Quantum yield = 0.140.

**Synthesis of P5:**

![Figure S6: Synthesis of P5](image)

**Procedure:** Toluene (3 mL), 95% ethanol (3 mL), and water (3 mL) were each degassed separately by bubbling nitrogen through each solvent for 30 minutes. Tetrakis(triphenylphosphine)palladium(0) (9.5 mg, 0.0825 mmol, 0.15 eq.), potassium
carbonate (22.8 mg, 0.165 mmol, 3 eq.), 2,5-dibromo-1,4-bis[ethene-bis(octoxy)styryl]benzene (compound 9, 42.0 mg, 0.06 mmol, 1.1 eq.), and 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (compound 12, 30.7 mg, 0.055 mmol, 1 eq.) were added to a round-bottomed flask. This flask was evacuated using three nitrogen-vacuum purge cycles. The degassed solvents were added to the flask via syringe, and the reaction mixture was heated at 50 °C for 72 hours under an inert nitrogen atmosphere. The reaction mixture was cooled to room temperature and excess chloroform (approximately 20 mL) was added to the flask. The resulting suspension was filtered using gravity filtration to remove all palladium byproducts. The organic layer was separated from the aqueous layer, dried over sodium sulfate, filtered, and concentrated on a rotary evaporator. The crude product was precipitated in methanol from chloroform affording a dark green solid in 80% yield (41 mg). $M_n = 4800, M_w = 8000, PDI = 1.64$. $^1$H NMR (300 MHz, CDCl$_3$, $\delta$, ppm) 7.90-7.83 (m, 2 H), 7.52-7.46 (m, 4 H), 7.18-7.04 (m, 6 H), 6.79 (m, 4 H), 3.92 (m, 4 H), 1.98 (m, 4 H), 1.75 (m, 8 H), 1.26 (m, 12 H), 1.06 (m, 24 H), 0.86 (m, 16 H). UV absorbance $\lambda_{max} = 345$ nm; Fluorescence emission $\lambda_{max} = 424$ nm, 447 nm; Quantum yield = 0.828.
Synthesis of P6:

**Procedure:** Toluene (1 mL), 95% ethanol (1 mL), and water (1 mL) were each degassed separately by bubbling nitrogen through each solvent for 30 minutes. Tris(dibenzylideneacetone)dipalladium(0) (7.55 mg, 0.00825 mmol, 0.15 eq.), potassium carbonate (22.8 mg, 0.165 mmol, 3 eq.), Tri(o-tolyl)phosphine (5 mg, 0.0165 mmol, 0.3 eq.), 2,5-dibromo-1,4-bis[ethene-bis(methyl)styryl]benzene (compound 10, 28 mg, 0.06 mmol, 1.1 eq.), and 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (compound 12, 30.7 mg, 0.055 mmol, 1 eq.) were added to a round-bottomed flask. This flask was evacuated using three nitrogen-vacuum purge cycles. The degassed solvents were added to the flask via syringe, and the reaction mixture was heated at 50 °C for 72 hours under an inert nitrogen atmosphere. The reaction mixture was cooled to room temperature and excess chloroform (approximately 10 mL) and excess water (5 mL) were added to the flask. The resulting suspension was filtered using gravity filtration to remove all palladium byproducts. The organic layer was separated from the aqueous layer, dried over sodium sulfate, filtered, and concentrated on a rotary evaporator. The crude product was precipitated in methanol from chloroform affording

**Figure S7:** Synthesis of P6.
a dark solid in 87% yield (33 mg). \( M_n = 6000, M_w = 12400 \), PDI = 2.07. \(^1\)H NMR (300 MHz, CDCl\(_2\), \( \delta \text{ ppm} \)) 7.95 (m, 2 H), 7.89 (s, 2 H), 7.55 (m, 4 H), 7.30 (t, \( J = 8.4 \) Hz, 4 H), 7.23 (t, \( J = 6.0 \) Hz, 4 H), 7.11 (d, \( J = 8.0 \) Hz, 4 H), 2.32 (s, 6 H), 2.04 (m, 4 H), 1.05 (m, 24 H), 0.79 (m, 12 H). UV absorbance \( \lambda_{\text{max}} = 341 \) nm; Fluorescence emission \( \lambda_{\text{max}} = 413 \) nm, 426 nm; Quantum yield = 0.592.

SYNTHESIS OF P7:

![Synthesis of P7](image)

**Figure S8:** Synthesis of P7.
**Procedure:** Toluene (3 mL), 95% ethanol (3 mL), and water (3 mL) were each degassed separately by bubbling nitrogen through each solvent for 30 minutes. Tris(dibenzylideneacetone)dipalladium(0) (24.7 mg, 0.027 mmol, 0.15 eq.), potassium carbonate (73.4 mg, 0.531 mmol, 3 eq.), Tri(o-tolyl)phosphine (16.2 mg, 0.0531 mmol, 0.3 eq.), 2,5-dibromo-1,4-bis[2naphthyl-ethene]benzene (compound 11, 105 mg, 0.194 mmol, 1.1 eq.), and 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (compound 12, 98.8 mg, 0.177 mmol, 1 eq.) were added to a round-bottomed flask. This flask was evacuated using three nitrogen-vacuum purge cycles. The degassed solvents were added to the flask via syringe, and the reaction mixture was heated at 50 \( ^\circ \)C for 72 hours under an inert nitrogen atmosphere. The reaction mixture was cooled to room temperature and excess chloroform (approximately 20 mL) was added to the flask. The
resulting suspension was filtered using gravity filtration to remove all palladium byproducts. The organic layer was separated from the aqueous layer, dried over sodium sulfate, filtered, and concentrated on a rotary evaporator. The crude product was precipitated in methanol from chloroform affording a green solid in 45% yield (61 mg). 

\( M_n = 3200, M_w = 5700, \text{PDI} = 1.79 \). 

\(^1\text{H NMR (300 MHz, CD}_2\text{Cl}_2, \delta, \text{ppm)}\) 8.02 (s, 2 H), 7.95 (s, 3 H), 7.87 (t, J = 8.6 Hz, 6 H), 7.81 (t, J = 8.7 Hz, 4 H), 7.60 (d, J = 13.1 Hz, 2 H), 7.50 (m, 6 H), 7.33 (m, 3 H), 2.04 (m, 4 H), 1.11 (m, 24 H), 0.86 (m, 12 H). UV absorbance \( \lambda_{\text{max}} = 374 \text{ nm} \); Fluorescence emission \( \lambda_{\text{max}} = 427 \text{ nm, 449 nm} \); Quantum yield = 0.908.

**SYNTHESIS OF P8:**

![Synthesis of P8](image)

**Figure S9:** Synthesis of P8.

**Procedure:** Toluene (5 mL), 95% ethanol (5 mL), and water (5 mL) were each degassed separately by bubbling nitrogen through each solvent for 30 minutes. Tris(dibenzylideneacetone)dipalladium(0) (69.0 mg, 0.075 mmol, 0.15 eq.), potassium carbonate (207 mg, 1.5 mmol, 3 eq.), Tri(o-tolyl)phosphine (46 mg, 0.15 mmol, 0.3 eq.), 2,6-dibromo-9,10-anthraquinone (compound S4, 84 mg, 0.25 mmol, 1 eq.), 9,9-dioctyl-2,7-dibromofluorene (compound S1, 137 mg, 0.25 mmol, 1 eq.), and 9,9-
dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (compound 12, 293 mg, 0.525 mmol, 2.1 eq.) were added to a round-bottomed flask. This flask was evacuated using three nitrogen-vacuum purge cycles. The degassed solvents were added to the flask via syringe, and the reaction mixture was heated at 50°C for 72 hours under an inert nitrogen atmosphere. The reaction mixture was cooled to room temperature and excess chloroform (approximately 20 mL) was added to the flask. The resulting suspension was filtered using gravity filtration to remove all palladium byproducts. The organic layer was separated from the aqueous layer, dried over sodium sulfate, filtered, and concentrated on a rotary evaporator. The crude product was precipitated in methanol from chloroform affording a dark solid in 71% yield (245 mg). $M_n = 21500$, $M_w = 59200$, PDI = 2.74. $^1$H NMR (300 MHz, CDCl$_3$, $\delta$, ppm) 8.70 (s, 2 H), 8.48 (m, 2 H), 8.15 (m, 2 H), 7.83 (m, 4 H), 7.68 (m, 8 H), 2.12 (m, 8 H), 1.14 (m, 48 H), 0.82 (m, 24 H). UV absorbance $\lambda_{max} = 377$ nm; Fluorescence emission $\lambda_{max} = 415$ nm, 439 nm; Quantum yield = 0.003.
**SYNTHESIS OF P9:**

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**Figure S10:** Synthesis of P9.

**Procedure:** Toluene (6 mL), 95% ethanol (6 mL), and water (6 mL) were each degassed separately by bubbling nitrogen through each solvent for 30 minutes. Tris(dibenzylideneacetone)dipalladium(0) (49.0 mg, 0.054 mmol, 0.15 eq.), potassium carbonate (148 mg, 1.074 mmol, 3 eq.), Tri(o-tolyl)phosphine (33 mg, 0.1074 mmol, 0.3 eq.), 2,6-dibromo-9,10-anthraquinone (compound S4, 132 mg, 0.394 mmol, 1.1 eq.), and 9,9-diocetylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (compound 12, 200 mg, 0.358 mmol, 1 eq.) were added to a round-bottomed flask. This flask was evacuated using three nitrogen-vacuum purge cycles. The degassed solvents were added to the flask via syringe, and the reaction mixture was heated at 50° C for 72 hours under an inert nitrogen atmosphere. The reaction mixture was cooled to room temperature and excess chloroform (approximately 20 mL) was added to the flask. The resulting suspension was filtered using gravity filtration to remove all palladium byproducts. The organic layer was separated from the aqueous layer, dried over sodium sulfate, filtered, and concentrated on a rotary evaporator. The crude product was precipitated in methanol from chloroform affording a dark solid in 37% yield (79 mg). $M_n = 6700$, $M_w = 8800$, $n =$...
PDI = 1.46. $^1$H NMR (300 MHz, CDCl$_3$, $\delta$, ppm) 8.70 (s, 2 H), 8.48 (m, 2 H), 8.16 (m, 2 H), 7.92 (m, 2 H), 7.78 (m, 4 H), 2.16 (m, 4 H), 1.11 (m, 24 H), 0.79 (m, 12 H). UV absorbance $\lambda_{\text{max}}$ = 353 nm; Fluorescence emission $\lambda_{\text{max}}$ = 576 nm; Quantum yield = 0.309.

**MONOMER SYNTHESIS PROCEDURES:**

*Synthesis of Compound 5:*

![Synthesis of Compound 5](image)

**Figure S11:** Synthesis of compound 5.

**Procedure:** 1,4-dibromo-2,5-bis(bromomethyl)benzene (compound 4, 500 mg, 1.19 mmol, 1 eq.) and triphenylphosphine (937.9 mg, 3.57 mmol, 3 eq.) were added to an oven-dried round-bottomed flask. This flask was evacuated using three nitrogen-vacuum purge cycles. Dry dimethylformamide (DMF) (20 mL) was added via syringe and the reaction was heated at 100$^\circ$ C for 18 hours under an inert nitrogen atmosphere. After 18 hours, the reaction mixture was cooled to room temperature, and the solid was isolated using vacuum filtration and washed with methanol to yield a white solid in yield $> 99\%$ (814 mg). $^1$H NMR (300 MHz, CDCl$_3$, $\delta$, ppm) 7.81 (m, 6 H), 7.70 (m, 24 H), 7.39 (d, $J = 1.9$ Hz, 2 H), 5.72 (d, $J = 10.3$ Hz, 4 H).
Synthesis of Compound 6:

Figure S12: Synthesis of compound 6.
Procedure: Potassium carbonate (340 mg, 2.46 mmol, 1.5 eq.) and 4-hydroxybenzaldehyde (compound S5, 200 mg, 1.64 mmol, 1 eq.) were added to an oven-dried round-bottomed flask. This flask was evacuated using three nitrogen-vacuum purge cycles. Dry DMF (50 mL) was added via syringe and the reaction mixture stirred for 10 minutes at room temperature. 1-bromo-2-octane (compound S6, 348 mg, 0.311 mL, 1.80 mmol, 1.1 eq.) was added via syringe and the reaction mixture stirred at room temperature for 14 hours under an inert nitrogen atmosphere. The reaction mixture was then diluted with water (100 mL) and extracted with diethyl ether three times (40 mL each). The combined organic layer was dried over sodium sulfate, filtered, and concentrated on a rotary evaporator. The crude product was purified on a silica plug (eluent: 10% ethyl acetate in n-hexanes) giving a yellow solid in 86% yield (332 mg).

$^1$H NMR (300 MHz, CDCl$_3$, δ, ppm) 9.88 (s, 1 H), 7.82 (dt, J = 8.8 Hz, J = 2.7 Hz, 2 H), 6.99 (dt, J = 8.8 Hz, J = 2.7 Hz, 2 H), 4.04 (t, J = 6.5 Hz, 2 H), 1.79 (m, 2 H), 1.29 (m, 10 H), 0.89 (t, J = 7.0 Hz, 3 H).

Synthesis of Compound 9:

Figure S13: Synthesis of compound 9.
Procedure: 2,5-dibromo-1,4-bis[methylene(triphenylphosphonium bromide)]benzene (compound 5, 136.9 mg, 0.20 mmol, 1 eq.) and 4-octoxybenzaldehyde (compound 6, 104.0 mg, 0.44 mmol, 2.2 eq.) were added to an oven-dried round-bottomed flask. This flask was evacuated using three nitrogen-vacuum purge cycles. Absolute (200 proof) ethanol (10 mL) was added via syringe forming a suspension. Sodium ethoxide (0.25 mL, 0.60 mmol, 3 eq.) was then added slowly via syringe while the reaction mixture stirred at room temperature. The reaction mixture stirred at room temperature under an inert nitrogen atmosphere for 16 hours, after which time it was diluted with distilled water (20 mL) and extracted three times with dichloromethane (DCM) (20 mL each). The combined organic layer was dried over sodium sulfate, filtered, and concentrated using rotary evaporation. The crude product was eluted on a silica gel column (eluent: 5% ethyl acetate in n-hexanes) yielding a mixture of cis and trans alkenes. The isomeric alkene mixture was then dissolved in hexanes (230 mL) and refluxed in the presence of I\(_2\) for two hours to isomerize the product. After cooling to room temperature, the solution was washed with 3 M HCl twice (20 mL each) and vacuum filtered, giving a yellow solid in 30% yield (42 mg). \(^1\)H NMR (300 MHz, CDCl\(_3\), \(\delta\), ppm) 7.85 (s, 2 H), 7.48 (d, \(J = 8.7 \text{ Hz}, 4 \text{ H}\)), 7.22 (d, \(J = 16.3 \text{ Hz}, 2 \text{ H}\)), 7.00 (d, \(J = 16.1 \text{ Hz}, 2 \text{ H}\)), 6.91 (d, \(J = 8.7 \text{ Hz}, 4 \text{ H}\)), 3.99 (t, \(J = 6.6 \text{ Hz}, 4 \text{ H}\)), 1.80 (m, 4 H), 1.30 (m, 20 H), 0.89 (t, \(J = 7.1 \text{ Hz}, 6 \text{ H}\)).

Synthesis of Compound 10:

Figure S14: Synthesis of compound 10.
Procedure: 2,5-dibromo-1,4-bis[methylene(triphenylphosphonium bromide)]benzene (compound 5, 250.3 mg, 0.365 mmol, 1 eq.) was added to an oven-dried round-bottomed flask. This flask was evacuated using three nitrogen-vacuum purge cycles. Absolute (200 proof) ethanol (20 mL) was added forming a suspension. 4-methylbenzaldehyde (compound 7, 0.095 mL, 0.803 mmol, 2.2 eq.) was added via syringe. Sodium ethoxide (0.45 mL, 1.095 mmol, 3 eq.) was then added slowly via syringe while the reaction mixture stirred at room temperature. The reaction mixture stirred at room temperature under an inert nitrogen atmosphere for 16 hours, after which time it was diluted with distilled water (20 mL) and vacuum filtered giving a mixture of cis and trans alkenes. The isomeric alkene mixture was then dissolved in hexanes (80 mL) and refluxed in the presence of I\textsubscript{2} for two hours to isomerize the product. After cooling to room temperature, the solution was washed with 3 M HCl twice (20 mL each) and vacuum filtered, giving a yellow solid in 28% yield (47.9 mg). \textsuperscript{1}H NMR (300 MHz, CD\textsubscript{2}Cl\textsubscript{2}, \(\delta\), ppm) 7.83 (s, 2 H), 7.39 (d, \(J = 8.1\) Hz, 4 H), 7.26 (d, \(J = 16.2\) Hz, 2 H), 7.13 (d, \(J = 7.8\) Hz, 4 H), 7.99 (d, \(J = 16.2\) Hz, 2 H), 2.29 (s, 6 H).

Synthesis of Compound 11:

![Chemical structure](image)

Figure S15: Synthesis of compound 11.

Procedure: 2,5-dibromo-1,4-bis[methylene(triphenylphosphonium bromide)]benzene (compound 5, 250.7 mg, 0.365 mmol, 1 eq.) and 2-naphthaldehyde (compound 8, 130.0 mg, 0.803 mmol, 2.2 eq.) were added to an oven-dried round-bottomed flask. This flask was evacuated using three nitrogen-vacuum purge cycles. Absolute (200 proof) ethanol
(20 ml) was added forming a suspension. Sodium ethoxide (0.45 mL, 1.095 mmol, 3 eq.) was then added slowly via syringe while the reaction mixture stirred at room temperature. The reaction mixture stirred at room temperature under an inert nitrogen atmosphere for 16 hours, after which time it was diluted with distilled water (20 ml) and vacuum filtered giving a mixture of cis and trans alkenes. The isomeric alkene mixture was then dissolved in hexanes (130 mL) and refluxed in the presence of I$_2$ for two hours to isomerize the product. After cooling to room temperature, the solution was washed with 3 M HCl twice (20 ml each) and vacuum filtered, giving a yellow solid in 88% yield (173 mg). $^1$H NMR (300 MHz, CD$_2$Cl$_2$, δ, ppm) 8.04 (d, J = 6.1 Hz, 2 H), 7.94 (s, 2 H), 7.88 (m, 4 H), 7.50 (m, 6 H), 7.31 (m, 2 H), 6.92 (d, J = 11.7 Hz, 2 H), 6.66 (d, J = 11.8 Hz, 2 H).

**Synthesis of Compound S4:**

**Figure S16:** Synthesis of compound S4.
**Procedure:** 2,6-diaminoanthraquinone (compound S7, 2.35 g, 10 mmol, 1 eq.) and copper(II)bromide (5.02 g, 22.5 mmol, 2.25 eq.) were added to an oven-dried round-bottomed flask. Acetonitrile (50 ml) was added forming a black suspension. Tert-butyl nitrite (90%, 2.94 ml, 22.5 mmol, 2.25 eq.) was then added slowly via syringe while the reaction mixture stirred at room temperature. The reaction mixture was then heated at 65$^\circ$ C for 2.5 hours, after which time it was cooled to room temperature and 3M HCl (25 ml) was added, followed by distilled water (25 ml). The reaction stirred for 20
minutes and then was vacuum filtered giving a brown solid. The brown solid was washed twice with distilled water and once with ethanol, before being recrystallized in chloroform, giving a tan solid in 43% yield (1.43 g). $^1$H NMR (300 MHz, CDCl$_3$, $\delta$, ppm) 8.44 (d, J = 2 Hz, 2 H), 8.17 (d, J = 8.32 Hz, 2 H), 7.94 (dd, J = 8.32 Hz, J = 2.01, 2 H).

COPIES OF $^1$H NMR SPECTRA:

![Figure S17: $^1$H-NMR Spectrum of P1 in CDCl$_3$ (300 MHz).](image-url)
Figure S18: $^1$H-NMR Spectrum of P2 in CDCl₃ (300 MHz).
Figure S19: $^1$H-NMR Spectrum of P3 in CDCl$_3$ (300 MHz).

Figure S20: $^1$H-NMR Spectrum of P4 in CD$_2$Cl$_2$ (300 MHz).
Figure S21: $^1$H-NMR Spectrum of P5 in CDCl₃ (300 MHz).

Figure S22: $^1$H-NMR Spectrum of P6 in CD₂Cl₂ (300 MHz).
Figure S23: $^1$H-NMR Spectrum of P7 in CD$_2$Cl$_2$ (300 MHz).

Figure S24: $^1$H-NMR Spectrum of P8 in CDCl$_3$ (300 MHz).
Figure S25: $^1$H-NMR Spectrum of P9 in CDCl$_3$ (300 MHz).

Figure S26: $^1$H-NMR Spectrum of 5 in CDCl$_3$ (300 MHz).
Figure S27: $^1$H-NMR Spectrum of 6 in CDCl$_3$ (300 MHz).

Figure S28: $^1$H-NMR Spectrum of 9 in CDCl$_3$ (300 MHz).
Figure S29: $^1$H-NMR Spectrum of 10 in CD$_2$Cl$_2$ (300 MHz).

Figure S30: $^1$H-NMR Spectrum of 11 in CD$_2$Cl$_2$ (300 MHz).
Figure S31: $^1$H-NMR Spectrum of S4 in CDCl$_3$ (300 MHz).
UV-VISIBLE AND FLUORESCENCE EMISSION SPECTRA OF ALL POLYMERS IN CHLOROFORM:
Due to some of the polymers’ large Stokes shift the double harmonic artifact peak overlaps with the tail end of the polymer’s emission peak. Where this has occurred, the double harmonic peak has been removed to accurately evaluate the fluorescence emission of the polymer. Figure S32 includes the spectra with and without the double harmonic peak.

**Figure S32:** The UV-Visible absorbance (black) and fluorescence emission (red) spectra of P1 in chloroform: (A) with the double harmonic peak; and (B) without the double harmonic peak.

**Figure S33:** Normalized UV-Visible absorbance (black line) and fluorescence emission (red line) spectra of P2 in chloroform.
**Figure S34:** Normalized UV-Visible absorbance (black line) and fluorescence emission (red line) spectra of P3 in chloroform.

**Figure S35:** Normalized UV-Visible absorbance (black line) and fluorescence emission (red line) spectra of P4 in chloroform.

**Figure S36:** Normalized UV-Visible absorbance (black line) and fluorescence emission (red) spectra of P5 in chloroform.
Figure S37: Normalized UV-Visible absorbance (black line) and fluorescence emission (red line) spectra of P6 in chloroform.

Figure S38: Normalized UV-Visible absorbance (black) and fluorescence emission (red) spectra of P7 in chloroform.
Figure S39: Normalized UV-Visible absorbance (black line) and fluorescence emission (red line) spectra of P8 in chloroform.

Figure S40: Normalized UV-Visible absorbance (black line) and fluorescence emission (red line) spectra of P9 in chloroform.
FLUORESCENCE EMISSION SPECTRA OF ALL POLYMERS IN VARIOUS STATES OF AGGREGATION:

**Figure S41:** Fluorescence emission of P1 as a well dissolved chloroform solution (black line) and as a solution of nanoparticles suspended in water (red line).

**Figure S42:** Fluorescence emission of P2 as a well dissolved chloroform solution (black line) and as a solution of nanoparticles suspended in water (red line).
**Figure S43:** Fluorescence emission of P3 as a well dissolved chloroform solution (black line) and as a solution of nanoparticles suspended in water (red line).

**Figure S44:** Fluorescence emission of P4 as a well dissolved chloroform solution (black line) and as a solution of nanoparticles suspended in water (red line).
Figure S45: Fluorescence emission of P5 as a well dissolved chloroform solution (black line) and as a solution of nanoparticles suspended in water (red line).

Figure S46: Fluorescence emission of P6 as a well dissolved chloroform solution (black line) and as a solution of nanoparticles suspended in water (red line).
**Figure S47:** Fluorescence emission of P7 as a well dissolved chloroform solution (black line) and as a solution of nanoparticles suspended in water (red line).

**Figure S48:** Fluorescence emission of P8 as a well dissolved chloroform solution (black line) and as a solution of nanoparticles suspended in water (red line).
Figure S49: Fluorescence emission of P9 as a well dissolved chloroform solution (black line) and as a solution of nanoparticles suspended in water (red line).
### SUMMARY OF FLUORESCENCE EMISSION OF ALL POLYMERS IN CHLOROFORM WITH BISPHENOLS:

#### Table S2: Fluorescence modulation of polymers in chloroform with bisphenols.

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<th>Concentration</th>
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</tr>
<tr>
<td></td>
<td></td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<td>0.00</td>
<td>0.00</td>
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</tr>
<tr>
<td></td>
<td>1000 μM</td>
<td>1.48±</td>
<td>1.03±</td>
<td>0.39±</td>
<td>0.80±</td>
<td>0.76±</td>
<td>0.98±</td>
<td>0.97±</td>
<td>0.98±</td>
</tr>
<tr>
<td>BPS</td>
<td>500 μM</td>
<td>1.25±</td>
<td>0.01</td>
<td>0.51±</td>
<td>0.80±</td>
<td>0.77±</td>
<td>0.98±</td>
<td>0.94±</td>
<td>1.00±</td>
</tr>
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<td></td>
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</tr>
<tr>
<td></td>
<td>100 μM</td>
<td>1.10±</td>
<td>1.06±</td>
<td>0.89±</td>
<td>0.79±</td>
<td>0.79±</td>
<td>0.94±</td>
<td>1.01±</td>
<td>0.99±</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.08</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.02</td>
<td>0.00</td>
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<td>0.00</td>
</tr>
</tbody>
</table>
Figure S50: Fluorescence emission of P2 – P9 in chloroform with: no analyte (black line), 100 μM BPA (blue line), 500 μM BPA (green line), and 1000 μM BPA (red line).
Figure S51: Fluorescence emission of P2 – P9 in chloroform with: no analyte (black line), 100 μM BPF (blue line), 500 μM BPF (green line), and 1000 μM BPF (red line).
Figure S52: Fluorescence emission of P2 – P9 in chloroform with: no analyte (black line), 100 μM BPS (blue line), 500 μM BPS (green line), and 1000 μM BPS (red line).
SUMMARY OF FLUORESCENCE EMISSION OF ALL POLYMER NANOPARTICLES WITH BISPHENOLS:

Table S3: Fluorescence modulation of polymers nanoparticles with bisphenols.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Concentration</th>
<th>P2</th>
<th>P3</th>
<th>P4</th>
<th>P5</th>
<th>P6</th>
<th>P7</th>
<th>P8</th>
<th>P9</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 (\mu M)</td>
<td>1.00 ± 0.01</td>
<td>2.87 ± 0.03</td>
<td>1.00 ± 0.04</td>
<td>1.02 ± 0.01</td>
<td>0.98 ± 0.01</td>
<td>1.03 ± 0.04</td>
<td>0.84 ± 0.01</td>
<td>0.98 ± 0.00</td>
</tr>
<tr>
<td></td>
<td>50 (\mu M)</td>
<td>1.03 ± 0.01</td>
<td>2.90 ± 0.01</td>
<td>0.92 ± 0.01</td>
<td>0.87 ± 0.02</td>
<td>0.46 ± 0.01</td>
<td>0.98 ± 0.01</td>
<td>0.81 ± 0.01</td>
<td>0.96 ± 0.00</td>
</tr>
<tr>
<td>BPA</td>
<td>100 (\mu M)</td>
<td>1.04 ± 0.00</td>
<td>2.85 ± 0.05</td>
<td>1.06 ± 0.07</td>
<td>1.02 ± 0.00</td>
<td>0.99 ± 0.02</td>
<td>1.03 ± 0.03</td>
<td>0.82 ± 0.01</td>
<td>0.99 ± 0.00</td>
</tr>
<tr>
<td></td>
<td>50 (\mu M)</td>
<td>1.05 ± 0.00</td>
<td>2.94 ± 0.01</td>
<td>1.06 ± 0.04</td>
<td>1.03 ± 0.01</td>
<td>0.54 ± 0.02</td>
<td>1.07 ± 0.01</td>
<td>0.79 ± 0.01</td>
<td>0.97 ± 0.00</td>
</tr>
<tr>
<td>BPF</td>
<td>100 (\mu M)</td>
<td>1.02 ± 0.00</td>
<td>2.87 ± 0.01</td>
<td>0.85 ± 0.05</td>
<td>1.02 ± 0.00</td>
<td>0.71 ± 0.05</td>
<td>0.95 ± 0.01</td>
<td>0.83 ± 0.01</td>
<td>0.99 ± 0.00</td>
</tr>
<tr>
<td></td>
<td>50 (\mu M)</td>
<td>1.04 ± 0.01</td>
<td>0.74 ± 0.01</td>
<td>1.00 ± 0.02</td>
<td>0.84 ± 0.06</td>
<td>1.00 ± 0.04</td>
<td>0.96 ± 0.00</td>
<td>0.80 ± 0.02</td>
<td>0.97 ± 0.00</td>
</tr>
<tr>
<td>BPS</td>
<td>100 (\mu M)</td>
<td>1.00 ± 0.01</td>
<td>2.87 ± 0.01</td>
<td>1.00 ± 0.02</td>
<td>0.84 ± 0.06</td>
<td>1.00 ± 0.04</td>
<td>0.96 ± 0.00</td>
<td>0.80 ± 0.02</td>
<td>0.97 ± 0.00</td>
</tr>
<tr>
<td></td>
<td>50 (\mu M)</td>
<td>1.04 ± 0.01</td>
<td>0.74 ± 0.01</td>
<td>1.00 ± 0.02</td>
<td>0.84 ± 0.06</td>
<td>1.00 ± 0.04</td>
<td>0.96 ± 0.00</td>
<td>0.80 ± 0.02</td>
<td>0.97 ± 0.00</td>
</tr>
</tbody>
</table>
Figure S53: Fluorescence emission of P2 – P9 nanoparticles in water with: no analyte (black line), 50 μM BPA (green line) and 100 μM BPA (red line).
**Figure S54:** Fluorescence emission of P2 – P9 nanoparticles in water with: no analyte (black line), 50 μM BPF (green line) and 100 μM BPF (red line).
Figure S55: Fluorescence emission of P2 – P9 nanoparticles in water with: no analyte (black line), 50 μM BPS (green line) and 100 μM BPS (red line).
SUMMARY TABLES FOR ARRAY GENERATION:

Table S4: Results of array generation for linear discriminate analysis of fluorescence responses of P2 – P9 in chloroform with 1000 μM analyte.

**Jackknifed Classification Matrix**

<table>
<thead>
<tr>
<th></th>
<th>BPA</th>
<th>BPF</th>
<th>BPS</th>
<th>%correct</th>
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</thead>
<tbody>
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<td>BPA</td>
<td>4</td>
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<td>0</td>
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</tr>
<tr>
<td>BPF</td>
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<td>BPS</td>
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</tr>
<tr>
<td>Total</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>100</td>
</tr>
</tbody>
</table>

**Cumulative Proportion of Total Dispersion**

| 0.999 | 1.000 |

Table S5: Results of array generation for linear discriminate analysis of fluorescence responses of P2 – P9 in chloroform with 500 μM analyte.

**Jackknifed Classification Matrix**

<table>
<thead>
<tr>
<th></th>
<th>BPA</th>
<th>BPF</th>
<th>BPS</th>
<th>%correct</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPA</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>BPF</td>
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<td>BPS</td>
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</tr>
<tr>
<td>Total</td>
<td>4</td>
<td>4</td>
<td>4</td>
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</table>

**Cumulative Proportion of Total Dispersion**

| 0.903 | 1.000 |

Table S6: Results of array generation for linear discriminate analysis of fluorescence responses of P2 – P9 in chloroform with 100 μM analyte.

**Jackknifed Classification Matrix**

<table>
<thead>
<tr>
<th></th>
<th>BPA</th>
<th>BPF</th>
<th>BPS</th>
<th>%correct</th>
</tr>
</thead>
<tbody>
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<td>BPA</td>
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<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>BPF</td>
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<td>BPS</td>
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<td>100</td>
</tr>
<tr>
<td>Total</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>100</td>
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</table>

**Cumulative Proportion of Total Dispersion**

| 0.962 | 1.000 |
Table S7: Results of array generation for linear discriminate analysis of fluorescence responses of P2 – P9 nanoparticles in water with 100 μM analyte.

<table>
<thead>
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<th>BPA</th>
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<th>BPS</th>
<th>%correct</th>
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<td>0</td>
<td>100</td>
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<tr>
<td>BPF</td>
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<td>BPS</td>
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</tr>
<tr>
<td>Total</td>
<td>4</td>
<td>4</td>
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<td>100</td>
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</tbody>
</table>

Cumulative Proportion of Total Dispersion

|       | 0.914 | 1.000 |

Table S8: Results of array generation for linear discriminate analysis of fluorescence responses of P2 – P9 nanoparticles in water with 50 μM analyte.

<table>
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<th>BPA</th>
<th>BPF</th>
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<tr>
<td>BPF</td>
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<td>BPS</td>
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<tr>
<td>Total</td>
<td>4</td>
<td>4</td>
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<td>100</td>
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</table>

Cumulative Proportion of Total Dispersion

|       | 0.999 | 1.000 |
Figure S56: Linear discriminate analysis of fluorescence responses of P2 – P9 in chloroform with 1000 μM analyte.

Figure S57: Linear discriminate analysis of fluorescence responses of P2 – P9 in chloroform with 500 μM analyte.
Figure S58: Linear discriminate analysis of fluorescence responses of P2 – P9 in chloroform with 100 μM analyte.

Figure S59: Linear discriminate analysis of fluorescence responses of P2 – P9 nanoparticles in water with 100 μM analyte.
Figure S60: Linear discriminate analysis of fluorescence responses of P2 – P9 nanoparticles in water with 50 μM analyte.
DLS SUMMARY OF ALL POLYMER NANOPARTICLES:

Table S9: Average nanoparticle sizes.

<table>
<thead>
<tr>
<th>Diameter (nm)</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>P4</th>
<th>P5</th>
<th>P6</th>
<th>P7</th>
<th>P8</th>
<th>P9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (nm)</td>
<td>4.19</td>
<td>7.53</td>
<td>4.95</td>
<td>4.05</td>
<td>6.63</td>
<td>4.67</td>
<td>4.97</td>
<td>9.37</td>
<td>5.56</td>
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</table>

DLS graphs of P1 nanoparticles

Figure S61: DLS size distribution measurements by intensity of P1 nanoparticles in water.
Figure S62: DLS size distribution measurements by volume of P1 nanoparticles in water.
DLS graphs of P2 nanoparticles

**Figure S63:** DLS size distribution measurements by intensity of P2 nanoparticles in water.

**Figure S64:** DLS size distribution measurements by volume of P2 nanoparticles in water.
DLS graphs of P3 nanoparticles

Figure S65: DLS size distribution measurements by intensity of P3 nanoparticles in water.

Figure S66: DLS size distribution measurements by volume of P3 nanoparticles in water.
DLS graphs of P4 nanoparticles

**Figure S67:** DLS size distribution measurements by intensity of P4 nanoparticles in water.

**Figure S68:** DLS size distribution measurements by volume of P4 nanoparticles in water.
DLS graphs of P5 nanoparticles

Figure S69: DLS size distribution measurements by intensity of P5 nanoparticles in water.

Figure S70: DLS size distribution measurements by volume of P5 nanoparticles in water.
DLS graphs of P6 nanoparticles

Figure S71: DLS size distribution measurements by intensity of P6 nanoparticles in water.

Figure S72: DLS size distribution measurements by volume of P6 nanoparticles in water.
DLS graphs of P7 nanoparticles

Figure S73: DLS size distribution measurements by intensity of P7 nanoparticles in water.

Figure S74: DLS size distribution measurements by volume of P7 nanoparticles in water.
DLS graphs of P8 nanoparticles

Figure S75: DLS size distribution measurements by intensity of P8 nanoparticles in water.

Figure S76: DLS size distribution measurements by volume of P8 nanoparticles in water.
DLS graphs of P9 nanoparticles

Figure S77: DLS size distribution measurements by intensity of P9 nanoparticles in water.

Figure S78: DLS size distribution measurements by volume of P9 nanoparticles in water.
DLS SUMMARY OF POLYMER NANOPARTICLE STABILITY OVER TIME:

DLS graphs of P1 nanoparticles after 24 hours

**Figure S79:** DLS size distribution measurements by intensity of P1 nanoparticles in water after 24 hours.

**Figure S80:** DLS size distribution measurements by volume of P1 nanoparticles in water after 24 hours.
DLS graphs of P1 nanoparticles after 48 hours

Figure S81: DLS size distribution measurements by intensity of P1 nanoparticles in water after 48 hours.

Figure S82: DLS size distribution measurements by volume of P1 nanoparticles in water after 48 hours.
DLS graphs of P1 nanoparticles after 72 hours

Figure S83: DLS size distribution measurements by intensity of P1 nanoparticles in water after 72 hours.

Figure S84: DLS size distribution measurements by volume of P1 nanoparticles in water after 72 hours.
DLS graphs of P2 nanoparticles after 24 hours

**Figure S85:** DLS size distribution measurements by intensity of P2 nanoparticles in water after 24 hours.

**Figure S86:** DLS size distribution measurements by volume of P2 nanoparticles in water after 24 hours.
DLS graphs of P2 nanoparticles after 48 hours

**Figure S87:** DLS size distribution measurements by intensity of P2 nanoparticles in water after 48 hours.

**Figure S88:** DLS size distribution measurements by volume of P2 nanoparticles in water after 48 hours.
DLS graphs of P2 nanoparticles after 72 hours

Figure S89: DLS size distribution measurements by intensity of P2 nanoparticles in water after 72 hours.

Figure S90: DLS size distribution measurements by volume of P2 nanoparticles in water after 72 hours.
DLS graphs of P5 nanoparticles after 24 hours

Figure S91: DLS size distribution measurements by intensity of P5 nanoparticles in water after 24 hours.

Figure S92: DLS size distribution measurements by volume of P5 nanoparticles in water after 24 hours.
DLS graphs of P5 nanoparticles after 48 hours

Figure S93: DLS size distribution measurements by intensity of P5 nanoparticles in water after 48 hours.

Figure S94: DLS size distribution measurements by volume of P5 nanoparticles in water after 48 hours.
DLS graphs of **P5** nanoparticles after 72 hours

![DLS size distribution measurements by intensity of P5 nanoparticles in water after 72 hours.](image1)

**Figure S95:** DLS size distribution measurements by intensity of **P5** nanoparticles in water after 72 hours.

![DLS size distribution measurements by volume of P5 nanoparticles in water after 72 hours.](image2)

**Figure S96:** DLS size distribution measurements by volume of **P5** nanoparticles in water after 72 hours.
DLS graphs of P9 nanoparticles after 24 hours

Figure S97: DLS size distribution measurements by intensity of P9 nanoparticles in water after 24 hours.

Figure S98: DLS size distribution measurements by volume of P9 nanoparticles in water after 24 hours.
DLS graphs of P9 nanoparticles after 48 hours

Figure S99: DLS size distribution measurements by intensity of P9 nanoparticles in water after 48 hours.

Figure S100: DLS size distribution measurements by volume of P9 nanoparticles in water after 48 hours.
DLS graphs of **P9** nanoparticles after 72 hours

**Figure S101:** DLS size distribution measurements by intensity of **P9** nanoparticles in water after 72 hours.

**Figure S102:** DLS size distribution measurements by volume of **P9** nanoparticles in water after 72 hours.

References:

CHAPTER 3

Submitted to the *Journal of Physical Chemistry*

Effects of Structural Variation in Conjugated Side Chains on the Photophysics of Conjugated Polymers in Nanoparticles.

Daniel Jones, Bryant Point, Mindy Levine

Department of Chemistry, University of Rhode Island, Kingston, RI, USA

Corresponding Author:

Mindy Levine, Ph.D.

Department of Chemistry

University of Rhode Island Kingston,

Rhode Island 02881, USA

mlevine@chm.uri.edu
Effects of Structural Variation in Conjugated Side Chains on the Photophysics of Conjugated Polymers in Nanoparticles.

Abstract: Conjugated Polymers (CPs) are widely used for a variety of applications as a result of their high quantum yields, strong extinction coefficients, and good stability to a variety of experimental conditions. In many cases the use of conjugated polymer nanoparticles (CPNs) provides additional practical advantages. The ability to understand how the structure of the CP affects its photophysical properties has the potential to significantly accelerate research in this area. In this work we examine 3 CPs, including two novel polymer architectures, and evaluate how the structures of the conjugated side chains affect the photophysical properties of the free polymer chains as well as the properties of aggregated CPNs. Both the linker identity and the terminal aromatic rings of the side chains were found to affect the photophysical properties of the CPs, with the terminal groups leading to the most substantial changes in photophysical properties in all of the polymeric forms (well-solubilized in organic solvent and aggregated in nanoparticles).

Introduction: The design, synthesis, and applications of conjugated polymers (CPs) have been the focus of many research groups due to the growing uses for these polymers as biomarkers, fluorescent sensors, and semiconductors. One class of CPs, termed donor-acceptor polymers, are comprised of two monomers, one of which acts as an energy donor and the other as an energy acceptor. Such donor-acceptor polymers have unique photophysical properties that can be targeted for solar cells, LEDs, and deep tissue imaging applications, with the photophysical properties tunable via
judicious choice of starting monomers.\textsuperscript{92,93} Moreover, the morphology of donor-acceptor polymers has significant additional effects on the emission profile, with polymers that are aggregated in thin films or nanoparticles generally having both decreased fluorescence emission and shifts in the emission maxima compared to the non-aggregated, well-solubilized polymer in solution.\textsuperscript{94,95,96,97}

Other morphology changes that affect the emission profile of CPs include solvent swelling on polymer resins\textsuperscript{98} and polymer incorporation in hydro- and aero-gels.\textsuperscript{99} For example, the group of Jason McNeill and co-workers has looked at the effects of solvent swelling on CP nanoparticles’ (CPNs) photophysical properties.\textsuperscript{100,101} In the absence of organic solvents, CPNs act as a disordered glassy phase, whereas upon the addition of organic solvent, some segments of polymer order into a crystalline planar $\beta$-phase. The effects of polymer side chain structure on such solvent-induced phase transitions have not been reported to date, despite the fact that side chain structural variations have been shown to have a number of other significant effects.\textsuperscript{102,103}

Here, we build on the initial work of McNeill and co-workers regarding the effects of solvent variation on the photophysical properties of CPNs, by investigating the effects of side chain structural variation on solvent-induced fluorescence changes. In particular, the polymers selected have photophysically active side chains with strong fluorescence emission from the side chain occurring only in the aggregated state. We use a previously reported CP (P1)\textsuperscript{104} as well as two novel polymeric architectures (P2 and P3) (Figure 1). By varying the structures of both the aromatic termini as well as that of the linkers between the main chain and termini, we found that the linker had minimal effect on the photophysics of the polymer in well dissolved solution, except when the side chain
termini was significantly bulky. However, in aggregated state the linker had a significant effect on how the polymer aggregated and thus significantly affected the photophysical properties in aggregation. The side chain termini had a more ubiquitous effect on the polymer in all states, though the side chain termini had a greater effect on the photophysical properties of the polymer in aggregation. The ability to use this nuanced understanding for the streamlined design of CPs and CPNs provides strong rationale for this research.

![Structures of all synthesized polymers](image)

**Figure 1**: Structures of all synthesized polymers

**Experimental:**

Materials and Methods: All chemicals were obtained from Millipore-Sigma chemical company or Fisher Scientific, and used without further purification. Fluorescence spectra were acquired on a Shimadzu RF-6000 spectrofluorophotometer, with a 1.5 nm or 3.0 nm excitation slit width, depending on the polymer identity, and 3.0 nm emission slit width. Quantum yields were taken on a Shimadzu RF-6000 spectrofluorophotometer using a RF-6000 series integrating sphere unit. Absorbance spectra were acquired on a Shimadzu UV-3600 Plus UV-Vis-NIR spectrophotometer. All NMR spectra were
acquired using a Bruker Ultrashield 300 MHz NMR Spectrometer and measured in deuterated chloroform (CDCl₃) or deuterated dimethylsulfoxide (d₆-DMSO). Polydispersities of the polymeric products were calculated using size exclusion chromatography performed at 40 °C with dichloromethane eluent on an Agilent Infinity GPC system equipped with three Agilent PLGel columns 7.5 mm × 300 mm (5 μm, pore sizes: 50, 10³, 10⁴ Å). Mₙ and Mₘ/Mₙ were determined versus polystyrene standards (162 g/mol-526 kg/mol, Polymer Laboratories). The average nanoparticle diameters were measured using a Malvern Zetasizer Nano ZS.

General Suzuki Polycondensation Procedure: All monomers were added to an oven-dried, round-bottomed flask that had been cooled to room temperature under an inert atmosphere, followed by addition of bis(dibenzylideneacetone)palladium(0) (0.15 eq.), tri(o-tolyl)phosphine (0.30 eq.), tetrabutylammonium bromide (1.0 eq.), and potassium carbonate (3.0 Eq). The flask was evacuated using three nitrogen-vacuum purge cycles. Equal volumes of toluene and water were degassed by bubbling nitrogen through them for 30 minutes, and were then added to the round-bottomed flask via syringe. The reaction mixture was heated under an inert atmosphere to 50° C for 72 hours, after which time the reaction mixture was cooled to room temperature and excess chloroform was added. The aqueous and organic layers were separated, and the organic layer was concentrated using rotary evaporation to yield a crude product. The product was then poured into methanol, the solids were centrifuged, and the supernatant was removed yielding the desired polymer product as a solid precipitate.

General Procedure for Fabrication of Nanoparticles: Nanoparticle solutions were prepared by adding 20 mL of 0.05 mg/mL polymer solution in tetrahydrofuran (THF).
to 80 mL of sonicating water. This solution was sonicated for one hour. The remaining THF was removed by bubbling nitrogen through the solution for 8 hours. After the THF was removed, 20 mL of water was added to the mixture to give a nanoparticle solution with a final concentration of 0.01 mg/mL.

General Procedure for DLS Measurements: 0.5 mL of a nanoparticle solution was added to a quartz cuvette. The Zetasizer probe was inserted into the cuvette and the cuvette was placed in the sample holder. The following parameters were used for the measurements: the material was set as polymer (RI: 1.700, absorption: 1.000), the dispersant was set as water (temperature 25.0 °C, viscosity: 0.8872 cP, RI: 1.330), the temperature was set as 25 °C (equilibration time: 120 sec), the measurement angle was set as 90°, and 5 measurements of 100 runs were performed on each sample.

General Procedure for Fluorescence Measurements of Nanoparticle Swelling: 1.5 mL of a 0.01 mg/mL nanoparticle solution was added to a quartz cuvette. A mixture of water and THF was then added to the cuvette to make a solution of 3 mL with varying ratios between 0 and 50 percent THF. Each sample was sonicated for 20 seconds, then measured on the fluorimeter four times and the average of the four spectra was reported. The samples were excited at the polymer’s UV-Vis absorbance maximum with an excitation slit width of 1.5 nm for P1 solutions and 3.0 nm for P2 and P3 solutions, and an emission slit width of 3.0 nm for all nanoparticle solutions.

General Procedure for Quantum Yield Measurements: 3.0 mL of a polymer solution in chloroform was added to a quartz cuvette. The cuvette was placed in the fluorimeter integration sphere sample holder and the fluorescence was measured. The fluorescence signal was compared to one of the following reference fluorophores: quinine bisulfate
(0.01 mg/ml) in 1 N H₂SO₄ (φᵣ = 0.55, λₑₓ = 345 nm), 2-aminopyridine (0.01 mg/ml) in 1 N H₂SO₄ (φᵣ = 0.65, λₑₓ = 300 nm), or 9,10-diphenylanthracene (0.01 mg/ml) in degassed cyclohexane (φᵣ = 0.91, λₑₓ = 373 nm). Each polymer used the reference fluorophore with the closest excitation wavelength to the UV-Vis λᵥᵥᵥ max of the polymer to determine quantum yield.⁹⁰⁵

Results and Discussion: The photophysical properties of the three polymers synthesized in this study are summarized in Table 1, with selected results highlighted in Figures 2 and 3. Interestingly, the effects of the solvent selected on the UV-visible absorption spectra varied substantially depending on the polymer structure (Figure 2). Polymer P₁ showed remarkable insensitivity in the absorption spectra to solvent choice for well-dissolved solutions, with essentially identical spectra observed in chloroform and tetrahydrofuran. As aggregated nanoparticles in water a blue shift of 50 nm is observed, though the absorption peak is broad and extends over a range greater than 100 nm. This blue shift in aggregation is attributed to the decreased in conjugation length caused by the bending and disorder of the system in aggregation. Furthermore, the broadness of the peak supports this argument as the arrangement of the polymers in aggregation will not be identical across all nanoparticles causing a broadening of the peak from the different amounts of bending and disorder over the nanoparticles in the sample.¹⁰⁶,¹⁰⁷ In contrast, the UV-visible spectra of P₂ in THF displays a peak that is red-shifted by 29 nm compared to the peak maxima observed in chloroform suggesting that the more polar THF results in a different local environment for the photophysically active moieties. This is further observed in the P₂ nanoparticles which have an absorption maximum between the chloroform and THF solutions. Furthermore, the less prominent peak of the
nanoparticle absorption suggests the more polar environment at the edge of the nanoparticles and the less polar environment of the interior of the nanoparticles yield a composite absorption peak with a maximum between the two well dissolved solutions. This absorption differs from P1 as the solvent has the greatest effect on the absorption of P2 rather than the interaction of the pendent groups with the backbone of the polymer due to the already close proximity of the large anthracene pendants to the backbone, even in well dissolved solution, due to the steric bulk of the anthracenes. Nanoparticles derived from P2 show an additional unique absorption signal in the near-infrared region (at 975 nm), which is likely due to a charge transfer band that forms, which involves the anthracene components and is induced by nanoparticle aggregation.\textsuperscript{108,109} Finally, P3 displays a 20 nm red shift in the absorption maxima of the nanoparticle solution compared to the THF and chloroform solutions of the same structure, which is consistent with nanoparticle-induced aggregation resulting in the formation of lower energy polymeric aggregates.\textsuperscript{110,111} As P3 has much stiffer alkyne linkers between the polymer backbone and the aromatic pendant groups, the pendants do not participate significantly in the absorption of well dissolved polymers (as seen with P2) and they create minimal disorder in aggregate state due to the limited rotational conformations of the linked pendants which caused the blue shift observed in P1.
Table 1: UV absorbance and fluorescence emission maxima for all polymers dissolved in chloroform, THF, and as nanoparticles.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>UV-Vis λ&lt;sub&gt;max&lt;/sub&gt; 1 (nm)</th>
<th>UV-Vis λ&lt;sub&gt;max&lt;/sub&gt; 2 (nm)</th>
<th>UV-Vis λ&lt;sub&gt;max&lt;/sub&gt; 3 (nm)</th>
<th>Fluorescence λ&lt;sub&gt;max&lt;/sub&gt; 1 (nm)</th>
<th>Fluorescence λ&lt;sub&gt;max&lt;/sub&gt; 2 (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1&lt;sup&gt;a&lt;/sup&gt; in chloroform&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-</td>
<td>401</td>
<td>-</td>
<td>438</td>
<td>464</td>
</tr>
<tr>
<td>P1 in THF&lt;sup&gt;d&lt;/sup&gt;</td>
<td>-</td>
<td>403</td>
<td>-</td>
<td>425</td>
<td>450</td>
</tr>
<tr>
<td>P1 nanoparticles&lt;sup&gt;d&lt;/sup&gt;</td>
<td>-</td>
<td>349</td>
<td>-</td>
<td>432</td>
<td>462</td>
</tr>
<tr>
<td>P2&lt;sup&gt;b&lt;/sup&gt; in chloroform&lt;sup&gt;e&lt;/sup&gt;</td>
<td>-</td>
<td>324</td>
<td>-</td>
<td>516</td>
<td>-</td>
</tr>
<tr>
<td>P2 in THF&lt;sup&gt;e&lt;/sup&gt;</td>
<td>-</td>
<td>353</td>
<td>-</td>
<td>507</td>
<td>-</td>
</tr>
<tr>
<td>P2 nanoparticles&lt;sup&gt;e&lt;/sup&gt;</td>
<td>261</td>
<td>337</td>
<td>975</td>
<td>509</td>
<td>-</td>
</tr>
<tr>
<td>P3 in chloroform&lt;sup&gt;f&lt;/sup&gt;</td>
<td>-</td>
<td>319</td>
<td>-</td>
<td>428</td>
<td>-</td>
</tr>
<tr>
<td>P3 in THF&lt;sup&gt;f&lt;/sup&gt;</td>
<td>-</td>
<td>334</td>
<td>-</td>
<td>435</td>
<td>-</td>
</tr>
<tr>
<td>P3 nanoparticles&lt;sup&gt;f&lt;/sup&gt;</td>
<td>228</td>
<td>356</td>
<td>-</td>
<td>353</td>
<td>780</td>
</tr>
</tbody>
</table>

<sup>a</sup>All P1 samples used excitation slit widths of 1.5 nm and emission slit widths of 3.0 nm. <sup>b</sup>All P2 and P3 samples used excitation and emission slit widths of 3.0 nm. <sup>c</sup>λ<sub>ex</sub> = 260 nm. <sup>d</sup>λ<sub>ex</sub> = 293 nm. <sup>e</sup>λ<sub>ex</sub> = 277 nm. <sup>f</sup>λ<sub>ex</sub> = 375 nm. The polymers dissolved in chloroform where also excited at wavelength above 300 nm and displayed the same fluorescence emission (spectra in ESI) verifying that the fluorescence is attributed to the entire polymer and not a subsection of the polymer.

![Figure 2](image-url)  
**Figure 2:** Normalized UV-Visible spectra of: (A) P1; (B) P2; and (C) P3 dissolved in chloroform (red line), THF (blue line), and as nanoparticles in water (black line).

The fluorescence emission spectra of P1 (Figure 3A) includes some degree of fine structure, which is reminiscent of fused aromatic ring systems, such as the naphthalene termini of the P1 side chains. The fluorescence emission of P1 nanoparticles has the same number of emission peaks at similar inter-peak intensity ratios as the fluorescence emission of naphthalene. This result suggests that the naphthalene termini act as exciton traps for P1 excited states, with the efficiency of such trapping from the dioctylfluorene moieties to the styryl-naphthalene acceptors enhanced in the aggregated
nanoparticle state as a result of more facile interpolymer exciton migration. Such migration, in turn, results in enhanced emission from the distyrylnaphthalene acceptors\textsuperscript{113} and decreased emission from the dioctylfluorene donors.\textsuperscript{114}

Of note, neither P\textsubscript{2} nor P\textsubscript{3} display analogous spectral fine structure (Figure 3), despite the fact that they both have terminal aromatic ring substituents. For P\textsubscript{3}, which also contains a naphthalene pendant attached via an alkyne linker, the fluorescence emission maxima of the well-solubilized solutions are close to the maxima of the P\textsubscript{1} samples. However, the lack of fine structure that is characteristic of naphthalene, is likely due to the rigidity of the alkyne linker that restricts conformational freedom between the termini and the polymer main chain.\textsuperscript{115,116} As a result of such restrictions, limited interactions between the distyrylnaphthalene acceptors and dioctylfluorene donors will occur, resulting in only limited exciton migration.

To further understand the photophysical interactions of these systems, electrostatic potential maps were generated using the minimized energy structures of one repeat unit of each polymer as a structural representative (Figure 4). The electrostatic potential map of the monomeric unit of P\textsubscript{3} (Figure 4C) displays a significant difference in charge between the dioctylfluorene of the polymer main chain and the distyrylnaphthalene of the side chain. Furthermore, the fluorescence emission of P\textsubscript{3} nanoparticles are blue shifted compared to the THF and chloroform solutions, suggesting the existence of H-aggregates. H-aggregation is a side by side stacking caused by the attractive force a difference in charge between two entities causes. In this case the Coulombic effects caused by the weakly electron withdrawing alkyne linker creates a great enough difference in charge between the main chain and terminal naphthalene to cause H-
aggregation in P3. In contrast, the P1 nanoparticles have no strong coulombic interactions between the main chain and alkene linked naphthalene (Figure 4A). CPs, which are composed of numerous dyes linked head-to-tail, are predisposed to act as J-aggregates, in which molecules are stacked head-to-tail. Without another driving force, such as strong coulombic interactions, P1 acts as a J-aggregate causing a red-shift upon aggregation. Lastly, all conformations of P2 have near identical fluorescence profiles. This is due to the steric bulk of the terminal side chain anthracenes which are bulky enough that the anthracenes remain close to the main polymer chain even when the polymer is not aggregated (Figure 4B).

Figure 3: Normalized fluorescence emission of (A) P1; (B) P2; and (C) P3 dissolved in chloroform (red line), THF (blue line), and as nanoparticles in water (black line).

Figure 4: Electrostatic potential maps of (A) P1, (B) P2, and (C) P3. Electrostatic potential map images where generated using Spartan'18 with a Semi-Empirical PM3 method. The energies were calculated in KJ/mol.
The CPN solutions were doped with THF and their diameters and fluorescence emission were measured to examine the effects of the conjugated side chains on the physical properties of the CPNs as they experienced solvent-induced swelling (Table 2, Figure 5). Because nanoparticle-induced aggregation generally leads to fluorescence quenching, the CPNs without any THF had the lowest fluorescence emission observed. All CPNs increased in fluorescence emission as the percentage of THF was increased from 0% to 25%, as a result of decreased polymer aggregation. Interestingly, increasing the percentage of THF further up to 50%, resulted in decreased emission intensities. The reason for this decrease is elucidated through the measured diameter of the nanoparticles (Table 2). As THF is added to the CPN solution, two distinct populations of nanoparticle are detected. At THF concentrations higher than 25%, a significant portion of the measured diameters are below 1 nm, corresponding to single polymer chains. The remainder of the sample, by contrast, is still composed of 5-10 nm diameter particles. Considering that there are CPN sizes both below 1 nm and between 5-10 nm, at the same time that the fluorescence intensity decreases, we posit that the nanoparticles are still aggregated but with a number of CP chains partially extending beyond the core of the nanoparticle, leading to the measured small diameters. This system which displays characteristics of both a well dissolved polymer solution and a CPN solution suggests that the system is approaching an organic solvent content in which CPNs will no longer exist. This is in good agreement with previously reported CPN swelling studies which found that around 40% organic solvent content, polymers in water are no longer structured as nanoparticles.101
Figure 5: Fluorescence emission of: (A) P1, (B) P2, and (C) P3 nanoparticles in various mixtures of THF in water, by starting with 0% THF in the aqueous nanoparticle solution and systematically increasing the percentage of THF included. The observed emission intensity reached a maximum around 25-30% THF and lower emissions observed at lower and higher percentages of THF.

Table 2: Measured diameters of P1 nanoparticles in various mixtures of THF in water

<table>
<thead>
<tr>
<th>THF (%)</th>
<th>Diameter 1 (nm)</th>
<th>Percent of sample</th>
<th>Diameter 2 (nm)</th>
<th>Percent of sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.685</td>
<td>84%</td>
<td>160.4</td>
<td>16%</td>
</tr>
<tr>
<td>5</td>
<td>6.592</td>
<td>100%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>5.166</td>
<td>86%</td>
<td>167.3</td>
<td>14%</td>
</tr>
<tr>
<td>15</td>
<td>7.314</td>
<td>78%</td>
<td>872.9</td>
<td>22%</td>
</tr>
<tr>
<td>20</td>
<td>0.7666</td>
<td>26%</td>
<td>7.707</td>
<td>74%</td>
</tr>
<tr>
<td>25</td>
<td>0.7233</td>
<td>36%</td>
<td>5.032</td>
<td>64%</td>
</tr>
<tr>
<td>30</td>
<td>0.9042</td>
<td>44%</td>
<td>8.381</td>
<td>56%</td>
</tr>
</tbody>
</table>

*DLS data for P2 and P3 can be found in the ESI, page S22. Data is an average of 5 intensity measurements.

Conclusions:

Three conjugated polymers, including two novel polymer architectures, were investigated and evaluated for how the structures of the conjugated side chains affect the photophysical properties of the free polymer chains as well as the properties of aggregated CPNs. The choice of linker for the side chain was found to have modest effect on the photophysical properties, primarily on the change from free polymer chain to aggregated CPN, with aggregated CPNs able to participate in interpolymer exciton migration from donor main chain moieties to acceptor side chain termini for distyrylnaphthalene acceptors. In cases where the linker was a weakly electron-withdrawing alkyne, by contrast, the charge differences between the main chain and the side chain terminal group caused significantly different photophysical properties based
off the level of aggregation. More influential in the design of the polymer was the choice
of the side chain terminal group. In non-aggregated states the side chain terminal group
played a role in the photophysical properties, whereas the linker only effected the CP in
aggregated state. Notably the side chain with the largest most bulky terminal group was
unchanged between non-aggregated and aggregated systems as the size of the terminal
group was so large as to always be close enough to the main chain to affect the polymers
photophysical properties. These results are expected to be of significant interest for
researchers seeking to develop rational design principles in CPs and CPN-based sensors.

References

78 Wei, L.; Zhou, P.; Yang, Q.; Yang, Q.; Ma, M.; Chen, B.; Xiao, L. Fabrication of
Bright and Small Size Semiconducting Polymer Nanoparticles for Cellular Labelling
and Single Particle Tracking. Nanoscale 2014, 6, 11351-11358.
79 De-La-Cuesta, J.; Gonzalez, E.; Pomposo, J. A. Advances in Fluorescent Single-
Reversible Fluorescence Enhancement of Conjugated Polymer Nanoparticles and Thin
81 Thomas, S. W.; Joly, G. D; Swager, T. M. Chemical Sensors Based on Amplifying
83 Shi, K.; Zhang, W.; Wei, C.; Lin, Z.; Liu, X.; Yu, G. Dithienylmethane-Based
Cross-Conjugated Polymer Semiconductors: Synthesis, Characterization, and
84 Luzio, A.; Canesi, E. V.; Bertarelli, C.; Caironi, M. Electrospun Polymer Fibers for
85 Tadesse, T. Application of Conjugated Organic Polymers for Photovoltaic’s: Review.
86 Gao, X.; Li, Y.; Yu, L.; Hou, F.; Zhu, T.; Bao, X.; Li, F.; Sun, M.; Yang, R. The
Regulation of \( \pi \)-Bridge of Indacenodithiophene-Based Donor-\( \pi \)-Acceptor Conjugated


D’Olieslaeger, L.; Braeken, Y.; Cheruku, S.; Smits, J.; Ameloot, M.; Vanderzande, D.; Maes, W.; Ethirajan, A. Tuning the Optical Propertied of Poly(p-Phenylene


Supporting Information
Effects of Structural Variation in Conjugated Side Chains on the Photophysics of Conjugated Polymers in Nanoparticles.

Materials and Methods:

All chemicals were obtained from Millipore-Sigma chemical company or Fisher Scientific, and used without further purification. Fluorescence spectra were acquired on a Shimadzu RF-6000 spectrofluorophotometer, with a 1.5 nm or 3.0 nm excitation slit width, depending on the polymer identity, and 3.0 nm emission slit width. Quantum yields were taken on a Shimadzu RF-6000 spectrofluorophotometer using a RF-6000 series integrating sphere unit. Absorbance spectra were acquired on a Shimadzu UV-3600 Plus UV-Vis-NIR spectrophotometer. All NMR spectra were acquired using a Bruker Ultrashield 300 MHz NMR Spectrometer and measured in deuterated chloroform (CDCl$_3$) or deuterated dimethylsulfoxide (d$_6$-DMSO). Polydispersities of the polymeric products were calculated using size exclusion chromatography performed at 40 °C with dichloromethane eluent on an Agilent Infinity GPC system equipped with three Agilent PLGel columns 7.5 mm × 300 mm (5 μm, pore sizes: 50, 10$^3$, 10$^4$ Å). M$_n$ and M$_w$/M$_n$ were determined versus polystyrene standards (162 g/mol-526 kg/mol, Polymer Laboratories). The average nanoparticle diameters were measured using a Malvern Zetasizer Nano ZS.

General Procedures:

General procedure for fabrication of nanoparticles:

Nanoparticle solutions were prepared by adding 20 mL of 0.05 mg/mL polymer solution in tetrahydrofuran (THF) to 80 mL of sonicating water. This solution was sonicated for
one hour. The remaining THF was removed by bubbling nitrogen through the solution for 8 hours. After the THF was removed 20 ml of water was added to give a nanoparticle solution with a concentration of 0.01 mg/ml.

**General procedure for DLS measurements:**

0.5 mL of a nanoparticle solution was added to a quartz cuvette. The Zetasizer probe was inserted into the cuvette and the cuvette was placed in the sample holder. The following parameters were used for the measurements: material was set as polymer (RI: 1.700, absorption: 1.000), dispersant was set as water (temperature 25.0 °C, viscosity: 0.8872 cP, RI: 1.330), temperature was set as 25 °C (equilibration time: 120 sec), the measurement angle was set as 90°, and 5 measurements of 100 runs were performed on each sample.

**General procedure for fluorescence measurements of nanoparticle swelling:**

1.5 ml of 0.01 mg/ml nanoparticle solution was added to a quartz cuvette. A mixture of water and THF was then added to the cuvette to make a solution of 3 ml with a ratio of between 0 and 50 percent THF. Each sample was sonicated for 20 seconds, then measured on the fluorimeter four times and the average of the spectra was reported. The samples were excited at the polymer’s UV-Vis absorbance maximum with an excitation slit width of 1.5 nm for P1 and 3.0 nm for P2 and P3 and an emission slit width of 3.0 nm for all nanoparticle solutions.

**General Procedure for Quantum Yield Measurements:**

3.0 mL of a polymer solution in chloroform was added to a quartz cuvette. The cuvette was placed in the fluorimeter integration sphere sample holder and the fluorescence was measured. The fluorescence signal was compared to one of the following reference
fluorophores: quinine bisulfate (0.01 mg/ml) in 1 N H$_2$SO$_4$ ($\varphi_f = 0.55$, $\lambda_{ex} = 345$ nm), 2-aminopyridine (0.01 mg/ml) in 1 N H$_2$SO$_4$ ($\varphi_f = 0.65$, $\lambda_{ex} = 300$ nm), or 9,10-diphenylanthracene (0.01 mg/ml) in degassed cyclohexane ($\varphi_f = 0.91$, $\lambda_{ex} = 373$ nm).

Each polymer used the reference fluorophore with the closest excitation wavelength to the UV-Vis $\lambda_{max}$ of the polymer to determine quantum yield.$^{117}$

Summary of Synthesized Polymers:

**Figure S1:** Structures of all synthesized polymers.

**Table S1:** Summarized properties of synthesized polymers in chloroform

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w$ (g/mol)</th>
<th>PDI</th>
<th>UV-Vis $\lambda_{max}$ (nm)</th>
<th>Fluorescence Emission Max (nm)</th>
<th>Quantum Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>6670</td>
<td>9930</td>
<td>1.488</td>
<td>401</td>
<td>438</td>
<td>0.1022</td>
</tr>
<tr>
<td>P2</td>
<td>5590</td>
<td>12780</td>
<td>2.285</td>
<td>324</td>
<td>516</td>
<td>0.0481</td>
</tr>
<tr>
<td>P3</td>
<td>5180</td>
<td>15110</td>
<td>2.917</td>
<td>319</td>
<td>428</td>
<td>0.0300</td>
</tr>
</tbody>
</table>
Synthetic Procedures:

**Synthesis of P1:**

![Figure S2: Synthesis of P1.](image)

Procedure: Toluene (15 mL) and deionized water (15 mL) were each degassed separately by bubbling nitrogen through each solvent for 30 minutes. Bis(dibenzylideneacetone)palladium(0) (57.7 mg, 0.0630 mmol, 0.15 eq.), tris(o-tolyl)phosphine (38.4 mg, 0.1264 mmol, 0.30 eq.), potassium carbonate (174.5 mg, 1.264 mmol, 3.0 eq.), 2,5-dibromo-1,4-bis[2-naphthyl-ethene]benzene (compound 2, 250 mg, 0.4630 mmol, 1.1 eq.), and 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (compound 1, 235 mg, 0.4210 mmol, 1.0 eq.) were added to a round-bottomed flask. This flask was evacuated using three nitrogen-vacuum purge cycles. The degassed solvents were added to the flask via syringe, and the reaction mixture was heated at 50 °C for 72 hours under an inert nitrogen atmosphere. The reaction mixture was cooled to room temperature and excess chloroform and excess water (approximately 60 mL each) was added to the flask. The organic layer was separated from the aqueous layer, washed with brine (30 ml), dried over sodium sulfate, filtered, and concentrated on a rotary evaporator. The crude product was precipitated in methanol from chloroform, yielding a yellow-green solid in 90% yield (290 mg). Mn = 6670, Mw = 9930, PDI = 1.488. 1H NMR (400 MHz, CD2Cl2, δ, ppm) 7.99 (m, 8 H), 7.79 (m, 10
H), 7.43 (m, 8 H), 7.07 (d, 2 H), 6.71 (d, 2 H), 4.20 (t, 2H), 3.19 (t, 2H), 2.04 (m, 8 H), 1.03 (m, 16 H), 0.77 (m, 6 H). UV absorbance $\lambda_{\text{max}} = 241$ nm, 388 nm; Fluorescence emission $\lambda_{\text{max}} = 438$ nm; Quantum yield = 0.1022.

Synthesis of P2:

![Synthesis of P2](image)

Figure S3: Synthesis of P2.

Procedure: Toluene (5 mL) and deionized water (5 mL) were each degassed separately by bubbling nitrogen through each solvent for 30 minutes. Bis(dibenzylideneacetone)palladium(0) (20 mg, 0.0213 mmol, 0.15 eq.), tris(o-tolyl)phosphine (13 mg, 0.0426 mmol, 0.30 eq.), potassium carbonate (59 mg, 0.4260 mmol, 3.0 eq.), 2,5-dibromo-1,4-bis[9-anthryl-ethene]benzene (compound 3, 100 mg, 0.1560 mmol, 1.1 eq.), and 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (compound 1, 79 mg, 0.1420 mmol, 1.0 eq.) were added to a round-bottomed flask. This flask was evacuated using three nitrogen-vacuum purge cycles. The degassed solvents were added to the flask via syringe, and the reaction mixture was heated at 50 °C for 72 hours under an inert nitrogen atmosphere. The reaction mixture was cooled to room temperature and excess chloroform and excess water (approximately 20 mL each) was added to the flask. The organic layer was separated from the aqueous layer, washed with brine (20 ml), dried over sodium sulfate, filtered, and concentrated on a rotary evaporator. The crude product was precipitated in methanol from chloroform, yielding
a yellow-brown solid in 97% yield (120 mg). Mn = 5590, Mw = 12780, PDI = 2.285.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$, δ, ppm) 8.35 (m, 10 H), 7.99 (m, 10 H), 7.45 (m, 16 H),
2.04 (m, 8 H), 1.03 (m, 20 H), 0.77 (m, 6 H). UV absorbance $\lambda_{\text{max}} = 260$ nm, 353 nm;
Fluorescence emission $\lambda_{\text{max}} = 516$ nm; Quantum yield = 0.0481.

**Synthesis of P3:**

![Synthesis of P3](image.png)

**Figure S4:** Synthesis of P3.

Procedure: Toluene (2 mL) and deionized water (2 mL) were each degassed separately
by bubbling nitrogen through each solvent for 30 minutes.

Bis(dibenzylideneacetone)palladium(0) (4.0 mg, 0.0043 mmol, 0.15 eq.), tris(o-
tolyl)phosphine (2.6 mg, 0.0085 mmol, 0.30 eq.), potassium carbonate (12 mg, 0.085
mmol, 3.0 eq.), 2,5-dibromo-1,4-bis[2-naphthyl-ethyne]benzene (compound 4, 17 mg,
0.031 mmol, 1.1 eq.), and 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol)
ester (compound 1, 16 mg, 0.028 mmol, 1.0 eq.) were added to a round-bottomed flask.
This flask was evacuated using three nitrogen-vacuum purge cycles. The degassed
solvents were added to the flask via syringe, and the reaction mixture was heated at 50
°C for 72 hours under an inert nitrogen atmosphere. The reaction mixture was cooled to
room temperature and excess chloroform and excess water (approximately 10 mL each)
was added to the flask. The organic layer was separated from the aqueous layer, washed
with brine (10 ml), dried over sodium sulfate, filtered, and concentrated on a rotary evaporator. The crude product was precipitated in methanol from chloroform, yielding an amber solid in 86% yield (19 mg). Mn = 5180, Mw = 15110, PDI = 2.917. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, δ, ppm) 7.73 (m, 10 H), 7.43 (m, 12 H), 2.04 (m, 8 H), 1.03 (m, 20 H), 0.77 (m, 6 H). UV absorbance $\lambda_{\text{max}}$ = 241 nm, 285 nm, 335 nm; Fluorescence emission $\lambda_{\text{max}}$ = 428 nm; Quantum yield = 0.0300.

**Synthesis of Compound 6:**

![Synthesis of Compound 6](image)

**Figure S5: Synthesis of compound 6.**

**Procedure:** 1,4-dibromo-2,5-bis(bromomethyl)benzene (compound 5, 500 mg, 1.19 mmol, 1 eq.) and triphenylphosphine (937.9 mg, 3.57 mmol, 3 eq.) were added to an oven-dried round-bottomed flask. This flask was evacuated using three nitrogen-vacuum purge cycles. Dry dimethylformamide (DMF) (20 mL) was added via syringe and the reaction was heated at 100°C for 18 hours under an inert nitrogen atmosphere. After 18 hours, the reaction mixture was cooled to room temperature, and the solid was isolated using vacuum filtration and washed with methanol to yield a white solid in yield > 99% (814 mg). $^1$H NMR (300 MHz, CDCl$_3$, δ, ppm) 7.81 (m, 6 H), 7.70 (m, 24 H), 7.39 (d, $J = 1.9$ Hz, 2 H), 5.72 (d, $J = 10.3$ Hz, 4 H).
Synthesis of Compound 2:

Figure S6: Synthesis of compound 2.

Procedure: 2,5-dibromo-1,4-bis[methylene(triphenylphosphonium bromide)]benzene (compound 6, 250.7 mg, 0.365 mmol, 1 eq.) and 2-naphthaldehyde (compound 7, 130.0 mg, 0.803 mmol, 2.2 eq.) were added to an oven-dried round-bottomed flask. This flask was evacuated using three nitrogen-vacuum purge cycles. Absolute (200 proof) ethanol (20 ml) was added forming a suspension. Sodium ethoxide (0.45 mL, 1.095 mmol, 3 eq.) was then added slowly via syringe while the reaction mixture stirred at room temperature. The reaction mixture stirred at room temperature under an inert nitrogen atmosphere for 16 hours, after which time it was diluted with distilled water (20 ml) and vacuum filtered giving a mixture of cis and trans alkenes. The isomeric alkene mixture was then dissolved in hexanes (130 mL) and refluxed in the presence of I₂ for two hours to isomerize the product. After cooling to room temperature, the solution was washed with 3 M HCl twice (20 ml each) and vacuum filtered, giving a yellow solid in 88% yield (173 mg). ¹H NMR (300 MHz, CD₂Cl₂, δ, ppm) 8.04 (d, J = 6.1 Hz, 2 H), 7.94 (s, 2 H), 7.88 (m, 4 H), 7.50 (m, 6 H), 7.31 (m, 2 H), 6.92 (d, J = 11.7 Hz, 2 H), 6.66 (d, J = 11.8 Hz, 2 H).
Synthesis of compound 3:

Figure S7: Synthesis of compound 3.

Procedure: 2,5-dibromo-1,4-bis[methylene(triphenylphosphonium bromide)]benzene (compound 6, 500 mg, 0.73 mmol, 1 eq.) and 9-anthraldehyde (compound 8, 330 mg, 1.6 mmol, 2.2 eq.) were added to an oven-dried round-bottomed flask. This flask was evacuated using three nitrogen-vacuum purge cycles. Absolute (200 proof) ethanol (40 ml) was added forming a suspension. Sodium ethoxide (1.0 mL, 2.2 mmol, 3 eq.) was then added slowly via syringe while the reaction mixture stirred at room temperature. The reaction mixture stirred at room temperature under an inert nitrogen atmosphere for 16 hours, after which time it was diluted with distilled water (40 ml) and vacuum filtered giving a mixture of cis and trans alkenes. The isomeric alkene mixture was then dissolved in hexanes (130 mL) and refluxed in the presence of I₂ for 72 hours to isomerize the product. After cooling to room temperature, the solution was washed with 3 M HCl twice (20 ml each) and vacuum filtered, giving a yellow solid in 26% yield (120 mg). ¹H NMR (400 MHz, DMSO, δ, ppm) 8.65 (s, 2 H), 8.47 (d, 2 H), 8.37 (d, J = 16.3 Hz, 2 H), 8.16 (2, 6 H), 7.61 (m, 10 H), 7.23 (d, J = 16.5 Hz, 2 H).
Synthesis of compound 4:

Figure S8: Synthesis of compound 4.

Procedure: 2,5-dibromo-1,2-diiodobenzene (compound 8, 500 mg, 1.025 mmol, 1 eq.), palladium (II) chloride (3.6 mg, 0.0205 mmol, 0.02 eq.), and pyrrolidine (0.84 ml, 10.25 mmol, 10 eq.) were added to an oven-dried round-bottomed flask. This flask was evacuated using three nitrogen-vacuum purge cycles. Deionized water (4 mL) was degassed by bubbling nitrogen through it for 30 minutes. The degassed water was added to the flask via syringe, and the reaction mixture was heated at 50 °C for 5 minutes. 2-ethynylnaphthalene (compound 9, 374 mg, 2.46 mmol, 2.4 eq.) was added and the reaction stirred at 50 °C for 24 hours under an inert nitrogen atmosphere. The reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 x 10). The organic layer was washed with brine (10 ml), dried over sodium sulfate, filtered, and dried on a rotary evaporator. The crude product was purified by recrystallization in chloroform giving a golden-brown powder in 4% yield (20 mg). $^1$H NMR (400 MHz, CD$_2$Cl$_2$, $\delta$, ppm) 8.14 (s, 2 H), 7.94 (q, 8 H), 7.63 (d, 2 H), 7.55 (q, 4 H).
Copies of $^1$H NMR Spectra:

**Figure S9**: $^1$H-NMR Spectrum of P1 in CD$_2$Cl$_2$ (400 MHz).
Figure S10: $^1$H-NMR Spectrum of P2 in CD$_2$Cl$_2$ (400 MHz).

Figure S11: $^1$H-NMR Spectrum of P3 in CD$_2$Cl$_2$ (400 MHz).
Figure S12: $^1$H-NMR Spectrum of compound 6 in CDCl$_3$ (300 MHz).

Figure S13: $^1$H-NMR Spectrum of compound 2 in CD$_2$Cl$_2$ (300 MHz).
Figure S14: $^1$H-NMR Spectrum of compound 3 in DMSO (400 MHz).

Figure S15: $^1$H-NMR Spectrum of compound 4 in CD$_2$Cl$_2$ (400 MHz).
UV-Visible and Fluorescence Emission Spectra of all Polymers:

**Table S2**: UV-Visible absorbance and fluorescence emission maxima for all polymers dissolved in chloroform, THF, and as nanoparticles.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>UV max 1 (nm)</th>
<th>UV max 2 (nm)</th>
<th>UV max 3 (nm)</th>
<th>Fluorescence max 1 (nm)</th>
<th>Fluorescence max 2 (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1 in chloroform</td>
<td>-</td>
<td>401</td>
<td>-</td>
<td>438</td>
<td>464</td>
</tr>
<tr>
<td>P1 in THF</td>
<td>-</td>
<td>403</td>
<td>-</td>
<td>425</td>
<td>450</td>
</tr>
<tr>
<td>P1 nanoparticles</td>
<td>-</td>
<td>349</td>
<td>-</td>
<td>432</td>
<td>462</td>
</tr>
<tr>
<td>P2 in chloroform</td>
<td>-</td>
<td>324</td>
<td>-</td>
<td>516</td>
<td>-</td>
</tr>
<tr>
<td>P2 in THF</td>
<td>-</td>
<td>353</td>
<td>-</td>
<td>507</td>
<td>-</td>
</tr>
<tr>
<td>P2 nanoparticles</td>
<td>261</td>
<td>337</td>
<td>975</td>
<td>509</td>
<td>-</td>
</tr>
<tr>
<td>P3 in chloroform</td>
<td>-</td>
<td>319</td>
<td>335</td>
<td>428</td>
<td>-</td>
</tr>
<tr>
<td>P3 in THF</td>
<td>-</td>
<td>334</td>
<td>-</td>
<td>435</td>
<td>-</td>
</tr>
<tr>
<td>P3 nanoparticles</td>
<td>228</td>
<td>356</td>
<td>-</td>
<td>353</td>
<td>780</td>
</tr>
</tbody>
</table>
**Figure S16**: Normalized UV-Visible and fluorescence emission of P1 dissolved in chloroform.

**Figure S16B**: Normalized fluorescence emission of P1 dissolved in chloroform excited at 401 nm.
Figure S17: Normalized UV-Visible and fluorescence emission of P1 dissolved in THF.

Figure S18: Normalized UV-Visible and fluorescence emission of P1 nanoparticles suspended in water.
**Figure S19:** Normalized UV-Visible and fluorescence emission of P2 dissolved in chloroform.

**Figure S20B:** Normalized fluorescence emission of P2 dissolved in chloroform excited at 353 nm.
**Figure S20:** Normalized UV-Visible and fluorescence emission of P2 dissolved in THF.

**Figure S21:** Normalized UV-Visible and fluorescence emission of P2 nanoparticles suspended in water.
**Figure S22**: Normalized UV-Visible and fluorescence emission of P3 dissolved in chloroform.

**Figure S22B**: Normalized fluorescence emission of P3 dissolved in chloroform excited at 320 nm.
**Figure S23:** Normalized UV-Visible and fluorescence emission of P3 dissolved in THF.

**Figure S24:** Normalized UV-Visible and fluorescence emission of P3 nanoparticles suspended in water.
Fluorescence Emission Spectra of Nanoparticle Swelling Study:

**Figure S25:** Normalized fluorescence emission of P1 nanoparticles with various ratios of THF in water.

**Figure S26:** Normalized fluorescence emission of P2 nanoparticles with various ratios of THF in water.
Figure S27: Normalized fluorescence emission of P3 nanoparticles with various ratios of THF in water.

DLS Summary of all Polymer Nanoparticles:

Table S3: DLS measured diameters of P1 nanoparticles in various mixtures of THF in water.

<table>
<thead>
<tr>
<th>Percent THF (%)</th>
<th>Diameter 1 (nm)</th>
<th>Percent of sample</th>
<th>Diameter 2 (nm)</th>
<th>Percent of sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.685</td>
<td>84%</td>
<td>160.4</td>
<td>16%</td>
</tr>
<tr>
<td>5</td>
<td>6.592</td>
<td>100%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>5.166</td>
<td>86%</td>
<td>167.3</td>
<td>14%</td>
</tr>
<tr>
<td>15</td>
<td>7.314</td>
<td>78%</td>
<td>872.9</td>
<td>22%</td>
</tr>
<tr>
<td>20</td>
<td>0.7666</td>
<td>26%</td>
<td>7.707</td>
<td>74%</td>
</tr>
<tr>
<td>25</td>
<td>0.7233</td>
<td>36%</td>
<td>5.032</td>
<td>64%</td>
</tr>
<tr>
<td>30</td>
<td>0.9042</td>
<td>44%</td>
<td>8.381</td>
<td>56%</td>
</tr>
</tbody>
</table>

Table S4: DLS measured diameters of P2 nanoparticles in various mixtures of THF in water.

<table>
<thead>
<tr>
<th>Percent THF (%)</th>
<th>Diameter 1 (nm)</th>
<th>Percent of sample</th>
<th>Diameter 2 (nm)</th>
<th>Percent of sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.867</td>
<td>89%</td>
<td>329.7</td>
<td>11%</td>
</tr>
<tr>
<td>5</td>
<td>6.189</td>
<td>86%</td>
<td>151.9</td>
<td>14%</td>
</tr>
<tr>
<td>10</td>
<td>5.766</td>
<td>75%</td>
<td>331.5</td>
<td>25%</td>
</tr>
<tr>
<td>15</td>
<td>5.957</td>
<td>73%</td>
<td>632.7</td>
<td>27%</td>
</tr>
<tr>
<td>20</td>
<td>0.9178</td>
<td>51%</td>
<td>5.936</td>
<td>49%</td>
</tr>
<tr>
<td>25</td>
<td>2.570</td>
<td>69%</td>
<td>11.05</td>
<td>31%</td>
</tr>
<tr>
<td>30</td>
<td>0.6492</td>
<td>23%</td>
<td>6.521</td>
<td>77%</td>
</tr>
</tbody>
</table>
Table S5: DLS measured diameters of P3 nanoparticles in various mixtures of THF in water.

<table>
<thead>
<tr>
<th>Percent THF (%)</th>
<th>Diameter 1 (nm)</th>
<th>Percent of sample</th>
<th>Diameter 2 (nm)</th>
<th>Percent of sample</th>
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<tbody>
<tr>
<td>0</td>
<td>0.664</td>
<td>30%</td>
<td>7.098</td>
<td>70%</td>
</tr>
<tr>
<td>5</td>
<td>4.809</td>
<td>85%</td>
<td>77.47</td>
<td>15%</td>
</tr>
<tr>
<td>10</td>
<td>6.324</td>
<td>93%</td>
<td>70.54</td>
<td>7%</td>
</tr>
<tr>
<td>15</td>
<td>3.596</td>
<td>52%</td>
<td>856.1</td>
<td>48%</td>
</tr>
<tr>
<td>20</td>
<td>6.460</td>
<td>100%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>25</td>
<td>0.7768</td>
<td>45%</td>
<td>5.082</td>
<td>55%</td>
</tr>
<tr>
<td>30</td>
<td>3.54</td>
<td>87%</td>
<td>16.67</td>
<td>13%</td>
</tr>
</tbody>
</table>

Figure S28: DLS intensity measurement of P1 nanoparticles with 0% THF in water.
Figure S29: DLS intensity measurement of P1 nanoparticles with 5% THF in water.

Figure S30: DLS intensity measurement of P1 nanoparticles with 10% THF in water.
Figure S31: DLS intensity measurement of P1 nanoparticles with 15% THF in water.

Figure S32: DLS intensity measurement of P1 nanoparticles with 20% THF in water.
Figure S33: DLS intensity measurement of P1 nanoparticles with 25% THF in water.

Figure S34: DLS intensity measurement of P1 nanoparticles with 30% THF in water.
Figure S35: DLS intensity measurement of P2 nanoparticles with 0% THF in water.

Figure S36: DLS intensity measurement of P2 nanoparticles with 5% THF in water.
Figure S37: DLS intensity measurement of P2 nanoparticles with 10% THF in water.

Figure S38: DLS intensity measurement of P2 nanoparticles with 15% THF in water.
Figure S39: DLS intensity measurement of P2 nanoparticles with 20% THF in water.

Figure S40: DLS intensity measurement of P2 nanoparticles with 25% THF in water.
**Figure S41**: DLS intensity measurement of P2 nanoparticles with 30% THF in water.

**Figure S42**: DLS intensity measurement of P3 nanoparticles with 0% THF in water.
**Figure S43:** DLS intensity measurement of P3 nanoparticles with 5% THF in water.

**Figure S44:** DLS intensity measurement of P3 nanoparticles with 10% THF in water.
Figure S45: DLS intensity measurement of P3 nanoparticles with 15% THF in water.

Figure S46: DLS intensity measurement of P3 nanoparticles with 20% THF in water.
Figure S47: DLS intensity measurement of P3 nanoparticles with 25% THF in water.

Figure S48: DLS intensity measurement of P3 nanoparticles with 30% THF in water.
Spartan Generated Images:

Electrostatic potential map images were generated using Spartan’18 with a Semi-Empirical PM3 method. Energies were calculated in KJ/mol.

**Figure S49:** Electrostatic potential map of P1 monomer segment.

**Figure S50:** Electrostatic potential map of P2 monomer segment.
Figure S51: Electrostatic potential map of P3 monomer segment.

Reference

CHAPTER 4

To be submitted to *Nanoscale*

Hydrophobically coated cyclodextrin metal-organic frameworks for the rapid removal of small molecule toxicants from contaminated aqueous environments.

Daniel Jones, Aditi Patel, Alexander Yonchak, Benjamin Cromwell, Mindy Levine

Department of Chemistry, University of Rhode Island, Kingston, RI, USA

Corresponding Author:

Mindy Levine, Ph.D.

Department of Chemistry

University of Rhode Island Kingston,

Rhode Island 02881, USA

mlevine@chm.uri.edu
Manuscript 4

Hydrophobically coated cyclodextrin metal-organic frameworks for the rapid removal of small molecule toxicants from contaminated aqueous environments.

Abstract: Industrial wastewater discharged into aqueous environments has been found to contain endocrine-disrupting toxicants, such as 2-phenylphenol. Long term exposure to such pollutants has been linked to developmental abnormalities, feminization, and decreased fecundity in aquatic organisms. Metal-organic frameworks (MOFs) were made using gamma cyclodextrin and potassium hydroxide. These MOFs were further functionalized by covalently binding naphthalene, coumarin, and m-xylene to the cyclodextrins on the exterior edges of the MOFs. This yields a highly porous structure that includes the hydrophobic cyclodextrin cavities, which favor non-covalent binding of aromatic compounds. Furthermore, the moieties on the exterior of the MOF create a hydrophobic shell that prevents the MOF from degrading in aqueous media. These functionalized MOFs were used for the effective removal of 2-phenylphenol and similar analytes from aqueous solution.

Introduction:

For decades, the impact of industrialization on the environment has been a growing concern for scientists, legislators, and the general public. One of the reasons for this concern is the large number of environmentally persistent toxicants that have been introduced by human activity. Some examples of such toxicants include polycyclic aromatic hydrocarbons (PAHs) and substituted biphenyls, which are byproducts of combustion reactions from both organic sources, such as wood fires, and fossil fuel sources, such as car exhaust and industrial waste streams. The widespread use of these
fuel sources has made the presence of these toxicants ubiquitous in the environment,\textsuperscript{118,16} which is concerning because these toxicants are known carcinogens, mutagens, and genotoxins,\textsuperscript{119} and the fact that they do not breakdown in the environment means that they can persist for decades.\textsuperscript{120} For the health and well-being of humans and the environment, the removal of these toxicants is of utmost importance. There has been a concerted effort by researchers to develop effective means for removing PAHs and substituted biphenyls from contaminated aqueous environments,\textsuperscript{121} including precipitation,\textsuperscript{122} filtration,\textsuperscript{123} coagulation,\textsuperscript{124} and biologically catalyzed degradation\textsuperscript{125} of the small molecule toxicants. Of these methods, filtration, especially using activated carbon and absorbent clay, is the most popular due to the fact that it is generally inexpensive and simple to execute.\textsuperscript{126} More recently, cyclodextrin (CD) based materials have received a lot of attention for the absorbance of toxicants from water due to their known high adsorption capacity.\textsuperscript{127} However, because unmodified CDs are water-soluble, they are of limited utility as filters for aqueous solutions. This has led researchers to develop CD-containing polymers, which are insoluble in water and demonstrate toxicant adsorption properties similar to activated carbon.\textsuperscript{128} In general, CD-based materials, including the CD-polymers mentioned above, are attractive due to the cheap, renewable, and non-toxic nature of CDs. Recently, CD-based metal-organic frameworks (CD-MOFs) have been investigated for their ability to separate,\textsuperscript{129} absorb,\textsuperscript{130} and store small molecules.\textsuperscript{131} CD-MOFs provide additional advantages over the CD-containing polymers, because the combined adsorptive properties of CDs and the highly porous structures of MOFs yield a material with an exceptionally high storage capacity. However, because CD-MOFs are not stable in
water, their ability to absorb molecules from aqueous solution is limited. Isolated reports of slightly more water-stable CD-MOFs include CD-MOFs with hydrophobic fullerenes bound in the cyclodextrin cavities and CD-MOFs with cholesterol moieties covalently linked to the cyclodextrin exterior. By loading a molecule into the CD cavities to achieve the desired solubility profile, the ability of the MOF to capture other small molecules is severely hampered. The cholesterol-appended cyclodextrin MOFs, by contrast, demonstrated high levels of biological safety as well as aqueous stability over a 24-hour time period, suggesting the covalent modification of CD-MOFs is a more practical way to create a water stable material.

Reported herein is the fabrication of four novel CD-MOFs that were covalently modified with small, hydrophobic moieties to increase the water stability of CD-MOFs while maintaining their high storage capacity and good absorptive properties. Three of these four CD-MOFs demonstrate excellent water stability over the course of two weeks as well as a high capacity for the absorption of eight different aromatic toxicants from water (Figure 1), including high priority toxicants such as PAHs, biphenyls, and biphenols. Overall, these novel CD-MOFs demonstrated high performance and have significant potential to be extremely effective filter materials for the removal of small molecule toxicants from water in a variety of real-world decontamination and environmental remediation scenarios.
Experimental section:

Fabrication of CD-MOFs.\textsuperscript{134} CD-MOFs were formed by adding 8 equivalents of potassium hydroxide to a solution of 0.05 M $\gamma$-cyclodextrin in distilled water, followed by 5\% methanol (vol/vol with water). The resulting solution was placed in an uncovered vial that was put into a larger, methanol-filled beaker. Of note, the height of the methanol solution in the larger beaker needed to be higher than the height of the solution in the smaller container, without having the methanol height exceed the height of the smaller container. The larger container was sealed and left undisturbed for 5 days. After 5 days, the smaller container was removed and the solution inside that container was removed via pipette, taking care not to disturb the solid MOFs. These MOFs were rinsed three times. For each rinsing cycle, dichloromethane (DCM) was added to the container so that all of the MOFs were submerged, the MOFs were allowed to remain submerged for
20 minutes, and then the dichloromethane was removed via pipette. The MOFs were then placed in an oven at 60 °C for 60 minutes to remove any remaining DCM.

General Procedure for the Modification of CD-MOFs: 4-dimethylaminopyridine (DMAP) (3.1 equivalents), dicyclohexylcarbodiimide (DCC) (3.1 equivalents), and the appropriate carboxylic acid (Scheme 1), (3.1 equivalents) were added to a round-bottomed flask and dissolved in DCM. CD-MOF was added (1 equivalent) to the round-bottomed flask (note: the MOF does not dissolve). The reaction mixture was stirred at 45 °C for 24 hours. After 24 hours, the reaction mixture was cooled to room temperature, and the solid was collected via vacuum filtration and washed with DCM. The resulting off-white solid was then placed in an oven at 60 °C for 60 minutes to remove any remaining DCM.

Thermogravimetric analysis (TGA): 3-6 mg of CD-MOFs were placed on an aluminum TGA pan and placed in the TGA, with the following experimental settings: (a) Counterbalance of 200 mg; (b) Oven atmosphere of nitrogen; (c) Flow rate of 10 mL/min; (d) Sample heating from room temperature to 60 °C at a rate of 10 °C/min; (e) Temperature held at 60 °C for 1 minute and then increased to 400 °C at a rate of 10 °C/min; (f) Final temperature held at 400 °C for 5 minutes.

X-Ray Diffraction (XRD): Between 40 and 80 mg of CD-MOF was placed on a 10 mm sample holder and placed in the XRD, with the following experimental settings: (a) Scan mode is 2θ / θ; (b) Scan speed of 0.15 degrees per minute; (c) Scan range of 3 – 90 degrees; (d) Step size of 0.02 degrees.

Fluorescence Spectroscopy: All fluorescence measurements were performed four times and the results reported represent the average spectrum of these four trials. 3 mL of
analyte solution (concentration = 0.01 mg/mL analyte in deionized water), was added to a quartz cuvette and excited at the UV-Vis max absorbance of the analyte (see ESI for a table of analyte excitation wavelengths, Table S1). 3 mg of MOF were added and the fluorescence was measured again. If the sample was still measurably fluorescent, another 3 mg of MOF were added and the fluorescence measurement was repeated. This process was repeated until the fluorescence signal reached zero (i.e. no observable spectrum from fluorescence excitation at the designated wavelength).
Results and Discussion:

Unmodified cyclodextrin based MOFs (CD-MOFs) have been fabricated by several different groups for various research applications, and have predominantly been characterized using solid-state techniques (due to aqueous instability). The unmodified CD-MOFs synthesized in this study had TGA and XRD datum that were comparable to the literature-reported data and were notably different from amorphous cyclodextrin powder used as the starting material for these experiments (see ESI for detailed spectroscopic comparison with amorphous cyclodextrin powder). The CD-MOFs synthesized in this study had TGA and XRD datum that were comparable to the literature-reported data and were notably different from amorphous cyclodextrin powder used as the starting material for these experiments (see ESI for detailed spectroscopic comparison with amorphous cyclodextrin powder). The CD-MOFs were modified with naphthalene, coumarin, m-xylene, and tert-butyl substituents (Scheme 1), with all of the modified CD-MOFs displaying notably different XRD patterns (Figure 2) compared to the unmodified CD-MOF. The XRD patterns were distinctive for each

**Scheme 1:** Synthesis of the hydrophobically modified cyclodextrin-MOFs
novel CD-MOF, with the bulky naphthalene and coumarin moieties in MOF 1 and MOF 2 giving characteristic peaks at 7, 20, and 22 degrees, while the less sterically large m-xylene and tert-butyl moieties in MOF 3 and MOF 4 display peaks at 7 and 28 degrees. In addition to these variations, all XRDs include the same large structural features at 17 and 24 degrees, indicating the main structure is the same throughout. Likewise, the TGA datum for all modified CD-MOFs (Figure 3) were distinctive from each other and from the cyclodextrin starting material, verifying that the CD-MOFs were successfully modified. All MOFs have a distinct mass loss between 225 °C and 275 °C characteristic of the breaking of the coordination bonds in the MOFs. Furthermore, all MOFs have a mass loss event starting at 275 °C which is indicative of the degradation of cyclodextrin, though the end of this mass loss event is different for each MOF dependent on what molecule is covalently bonded to the cyclodextrin.

**Figure 2:** XRD of all MOFs. Unmodified CD-MOF (black, bottom), MOF 1 (red), MOF 2 (blue), MOF 3 (orange), MOF 4 (cyan, top).
Figure 3: TGA of all MOFs. Unmodified CD-MOF (black), MOF 1 (red), MOF 2 (blue), MOF 3 (orange), MOF 4 (cyan).

The characterized modified CD-MOFs were tested for their stability in water. Of note, MOF 4 disintegrated immediately upon contact with water, and was therefore not used for the toxicant removal studies. MOF 1, MOF 2, and MOF 3 all maintained their structure for greater than three days when submerged in water, as shown through the XRD spectra of the submerged samples after removal from the aqueous environment (Figure 4).

Figure 4: XRD of MOF 1: before submersion in water (red, bottom), after 1 day in water (orange), after
3 days in water (green, top).

To test the ability of the modified CD-MOFs to absorb small molecule toxicants, the fluorescence of the toxicants in water was measured before and after the addition of MOFs 1-3. 15 mg or less of each MOF was required to fully absorb the toxicants from 3 mL of water (concentration of 10 ppm) (based on the complete disappearance of the analyte’s fluorescence signal), with the exact quantities of CD-MOFs required variable based on both the MOF and toxicant identity (Table 1). Overall, the MOFs demonstrated an extremely high capacity for small molecule absorbance, with the highest performing MOF 2 requiring only 3 mg of MOF 2 to fully absorb each analyte. MOF 3, by contrast, was the worst performing at toxicant removal, requiring 9-15 mg of MOF to fully remove most analytes. These performance differences between the MOFs can be related to their chemical structure, with the smallest m-xylene hydrophobic attachment of MOF 3 providing only modest hydrophobic association with the hydrophobic analytes. The coumarin appendages of the highly successful MOF 2, by contrast, have substantially larger hydrophobic surface area compared to m-xylene, and their flat, aromatic surfaces are better able to support the binding of aromatic analytes.

More information about differences in performance among the MOFs can be evaluated using Spartan and Molecular Operating Environment (MOE) computational software, with a particular focus on the extent to which the covalently attached hydrophobic moieties on the exterior of the CD-MOF hinders analyte access to the cyclodextrin cavities. The calculated lowest energy conformations of model cyclodextrin with the covalently appended moieties (naphthalene, coumarin, and m-xylene) are shown in Figure 5 and display visibly clear differences in the access provided to the cyclodextrin
cavity. MOF 3, modified with m-xylene, was the worst performing MOF, and demonstrates almost complete blocking of the cyclodextrin cavity by the inclusion of the xylene appendage. By contrast, the best performer, coumarin modified MOF 2, does not inhabit the cyclodextrin cavity, and instead the coumarin rests on top of the cavity like a lid. This is in part due to the size of the coumarin and the hydrogen bonding between the cyclodextrin rim and the coumarin’s cyclic ester. This results in the aromatic portion of the coumarin being on average 5.86 Å from the edge of the cyclodextrin cavity, and provides sufficient space for aromatic toxicant analytes to be included. MOF 1 has the naphthalene appendage bound in the cavity, with the naphthalene being an average of 5.447 Å away from the edge of the cyclodextrin cavity on one side and the other side being an average of 4.465 Å from the edge of the cyclodextrin cavity. Finally, the m-xylene appendage is bound most tightly in the cyclodextrin cavity with an average of 4.788 Å between the m-xylene and the edge of the cyclodextrin cavity on all sides.

Figure 5: Calculated lowest energy conformations of model functionalized cyclodextrins with the covalently attached moiety in the cavity.

Table 1: Amount of MOF required to remove analyte from 3 mL of water (concentration is 10 ppm).
The promising absorbance capabilities that MOFs 1-3 demonstrated (effective removal of most toxicants from a solution within seconds) were further investigated by direct comparison to monomeric cyclodextrin analogs. Amorphous cyclodextrin was functionalized with the same hydrophobic moieties that the CD-MOFs were, following analogous synthetic procedures. These functionalized cyclodextrins required 3 or 4 times more host material than the CD-MOFs in order to fully absorb the analyte. For example, analyte 3 (10 ppm in 3 ml water) was fully absorbed with 3 mg of MOF 2, whereas 12 mg of the monomeric coumarin-functionalized cyclodextrin was required to obtain the same benefit (Figure 6). Furthermore, the functionalized cyclodextrins rapidly dissolved in water while the MOFs remained solid, allowing the MOFs and the bound analytes in the MOFs to be removed from water and effective remediation to be accomplished.

<table>
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<tr>
<th>analyte</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
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<tr>
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<td>3 mg</td>
<td>9 mg</td>
<td>9 mg</td>
<td>6 mg</td>
<td>6 mg</td>
<td>6 mg</td>
<td>9 mg</td>
<td></td>
</tr>
<tr>
<td>MOF 2</td>
<td>3 mg</td>
<td>3 mg</td>
<td>3 mg</td>
<td>3 mg</td>
<td>3 mg</td>
<td>3 mg</td>
<td>3 mg</td>
<td></td>
</tr>
<tr>
<td>MOF 3</td>
<td>3 mg</td>
<td>6 mg</td>
<td>9 mg</td>
<td>12 mg</td>
<td>3 mg</td>
<td>12 mg</td>
<td>15 mg</td>
<td>12 mg</td>
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</table>

**Figure 6:** Fluorescence emission of analyte 3 with various amounts of: coumarin functionalized cyclodextrin (left) and MOF 2 (right). Amounts of materials as follows: 0 mg (black), 3 mg (red), 6 mg (blue), 9 mg (orange), 12 mg (cyan), 15 mg (dark red).
Conclusions:

Four novel CD-MOF were fabricated using straightforward, high-yielding methods and tested for their stability in water and their ability to absorb toxicants from water. Of the four CD-MOFs, three were water stable for significant amounts of time. The three water stable MOFs all demonstrated a high capacity to absorb toxicants from water, requiring as little as 3 mg to fully remove all small molecule toxicants from 3 mL of water (concentration of 10 ppm). Currently we are investigating the effectiveness of the CD-MOFs as compared to carbon black and absorbent ceramics. In the future these functionalized CD-MOFs will be tested with other filtration materials as a compulsory filtration material and the number of analytes that the CD-MOFs can absorb will be expanded upon.

References:


Conditions Via the Incorporation of C$_{60}$ in Their Matrices. Chem. Commun. 2016, 52, 5973-5976.


Supporting Information

Hydrophobically coated cyclodextrin metal-organic frameworks for the rapid removal of small molecule toxicants from contaminated aqueous environments.

MATERIALS AND METHODS

All chemicals were obtained from Sigma-Aldrich Chemical Company or Fisher Scientific, and used as received. Fluorescence spectra were acquired on a Shimadzu RF-6000 Spectrofluorophotometer, with a 1.5 nm excitation slit width and 3.0 nm emission slit width. Thermogravimetric analysis was performed on a Shimadzu TGA-50. X-Ray diffraction was performed on a Rigaku Miniflex 300/600 plus X-ray diffractometer. Modified cyclodextrin ground state energies were calculated using Spartan ’16 Semi-Empirical program with Parametric Method 3 (PM3) method and water as the solvent.

GENERAL PROCEDURES

Fabrication of CD-MOFs:

CD-MOFs were formed by adding 8 equivalents of potassium hydroxide to a solution of 0.05 M γ-cyclodextrin in water, followed by 5% methanol (vol/vol with water). The resulting solution was placed in an uncovered vial that was put into a larger, methanol-filled beaker. Of note, the height of the methanol solution in the larger beaker needed to be higher than the height of the solution in the smaller container, without having the methanol height exceed the height of the smaller container. The larger container was sealed and left undisturbed for 5 days. After 5 days, the smaller container was removed and the solution inside the smaller container was removed via pipette, taking care not to disturb the solid MOFs. These MOFs were rinsed three times. For each rinsing cycle, dichloromethane (DCM) was added to the container so that all of the MOFs were
submerged, the MOFs stayed submerged in the DCM for 20 minutes, and then the dichloromethane was removed via pipette. The MOFs were then placed in an oven at 60 °C for 60 minutes to remove any remaining DCM.

**General Procedure for the Modification of CD-MOFs:**

4-dimethylaminopyridine (DMAP) (3.1 equivalents), dicyclohexylcarbodiimide (DCC) (3.1 equivalents), and the appropriate carboxylic acid (3.1 equivalents) were added to a round-bottomed flask and dissolved in DCM. CD-MOF was added (1 equivalent) to the round-bottomed flask (note: the CD-MOF did not dissolve). The reaction mixture was stirred at 45 °C for 24 hours. After 24 hours, the reaction mixture was cooled to room temperature, and the solid was collected via vacuum filtration and washed with DCM. The resulting off-white solid was then placed in an oven at 60°C for 60 minutes to remove any remaining DCM.

**Thermogravimetric analysis (TGA):**

Between 3 and 6 mg of CD-MOF was placed on an aluminum TGA pan and placed in the TGA, with the following experimental settings: (a) Counterbalance of 200 mg; (b) Oven atmosphere of nitrogen; (c) Flow rate of 10 mL/min; (d) Sample heating from room temperature to 60 °C at a rate of 10 °C/min; (e) Temperature held at 60 °C for 1 minute and then increased to 400 °C at a rate of 10 °C/min; (f) Final temperature held at 400 °C for 5 minutes.

**X-Ray Diffraction (XRD):**

Between 40 and 80 mg of CD-MOF was placed on a 10 mm sample holder and placed in the XRD, with the following experimental settings: (a) Scan mode is 2θ/θ; (b) Scan
speed of 0.15 degrees per minute; (c) Scan range of 3 – 90 degrees; (d) Step size of 0.02 degrees.

**Fluorescence Spectroscopy:**

All fluorescence measurements were performed four times and the average spectrum was reported. 3 mL of analyte solution (concentration = 0.01 mg/mL analyte in deionized water) were added to a quartz cuvette and excited at the UV-Vis max absorbance of the analyte (see Table S1). 3 mg of MOF were added and the fluorescence was measured again. If the sample was still measurably fluorescent, another 3 mg of MOF were added and the fluorescence measurement was repeated. This was repeated until the fluorescence signal reached zero (i.e. no observable spectrum from fluorescence excitation).

**SUMMARY OF ANALYTES**

![Analytes of interest](Image)

*Figure S1: Analytes of interest.*
Table S1: Analyte excitation wavelengths.

<table>
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<tr>
<th>Analyte</th>
<th>1</th>
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<td>Excitation λ (nm)</td>
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<td>200</td>
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<td>275</td>
<td>200</td>
<td>290</td>
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TGA DATA FOR ALL MOFS

Figure S2: Normalized TGA of unmodified potassium γ-cyclodextrin MOF (black) and amorphous γ-cyclodextrin powder (red).

Figure S3: Normalized TGA of MOF 1.
**Figure S4:** Normalized TGA of MOF 2.

**Figure S5:** Normalized TGA of MOF 3.

**Figure S6:** Normalized TGA of MOF 4.
XRD DATA FOR ALL MOFS

Figure S7: XRD of unmodified potassium γ-cyclodextrin MOF (black) and amorphous γ-cyclodextrin powder (red).

Figure S8: XRD of MOF 1.
Figure S9: XRD of MOF 2.

Figure S10: XRD of MOF 3.
Figure S11: XRD of MOF 4.
Figure S12: Fluorescence emission of analytes with: 0 mg MOF 1 (black), 3 mg MOF 1 (red), 6 mg MOF 1 (blue), 9 mg MOF 1 (orange), 12 mg MOF 1 (cyan).
Figure S13: Fluorescence emission of analytes with: 0 mg MOF 2 (black), 3 mg MOF 2 (red), 6 mg MOF 2 (blue).
Figure S14: Fluorescence emission of analytes with: 0 mg MOF 3 (black), 3 mg MOF 3 (red), 6 mg MOF 3 (blue), 9 mg MOF 3 (orange), 12 mg MOF 3 (cyan).
**Figure S15:** Fluorescence emission of analyte 3 with various amounts of functionalized cyclodextrin: 0 mg (black), 3 mg (red), 6 mg (blue), 9 mg (orange), 12 (cyan), 15 mg (dark red).

**SUMMARY OF COMPUTATIONAL WORK**

**Table S2:** Distances calculated in Spartan 16’ from selected carbon atoms on the covalently linked moieties from model functionalized cyclodextrins to the nearest cyclodextrin carbons.

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<th>Naphthalene</th>
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Figure S16: Spartan generated images of naphthalene functionalized cyclodextrin.

Figure S17: Spartan generated images of coumarin functionalized cyclodextrin.

Figure S18: Spartan generated images of m-xylene functionalized cyclodextrin.
REFERENCES