

ELECTRONIC SUPPLEMENTARY INFORMATION FOR:
Acene-Linked Conjugated Polymers with Ratiometric
Fluorescent Response to $^1\text{O}_2$

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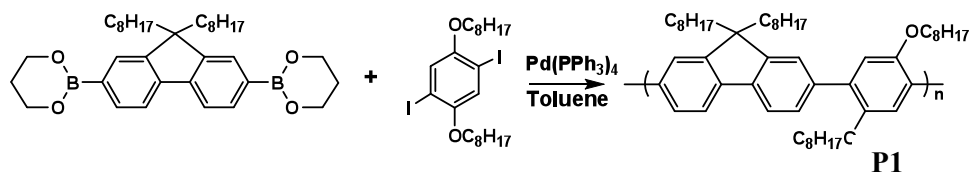
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1. Synthesis and Characterization

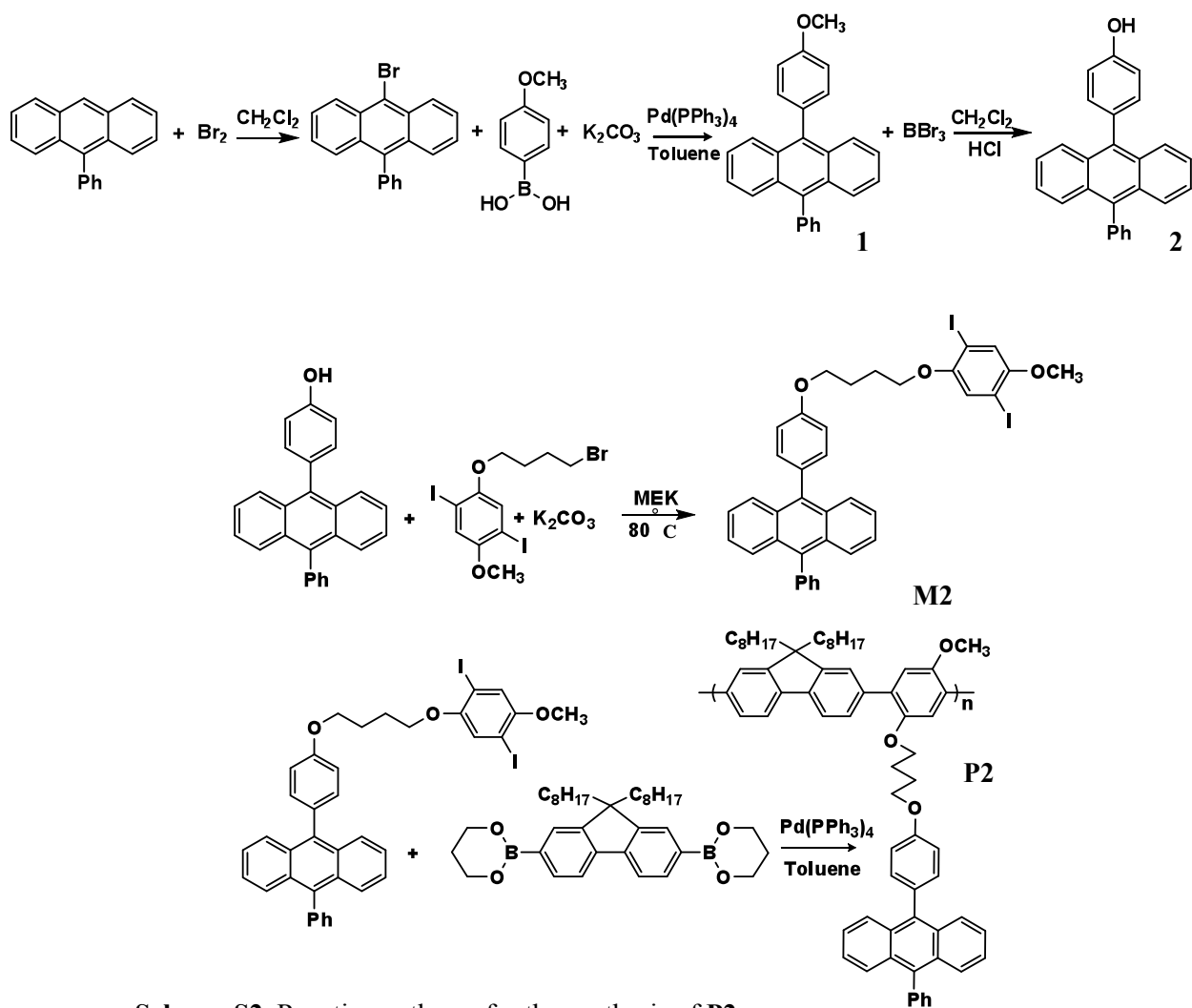
General considerations

The following chemicals were purchased from commercial sources and used as received: 9-phenylanthracene (Aldrich), 4-methoxyphenylboronic acid (Aldrich), bromine (Aldrich), 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (Aldrich), 5,12-naphthacenequinone (Aldrich), 4-bromoanisole (Alfa Aesar), *n*-butyllithium (Acros), methyl iodide (Aldrich), Pd(PPh₃)₄ (Strem), and Aliquat 336 (Aldrich). Dry tetrahydrofuran (THF), dichloromethane (DCM), and toluene were obtained using a column purification system. 1-(4-bromobutoxy)-2,5-diiodo-4-methoxybenzene,¹ 2,5-diiodo-1,4-dioctyloxybenzene,² and **P1**³ were prepared using previously reported procedures.

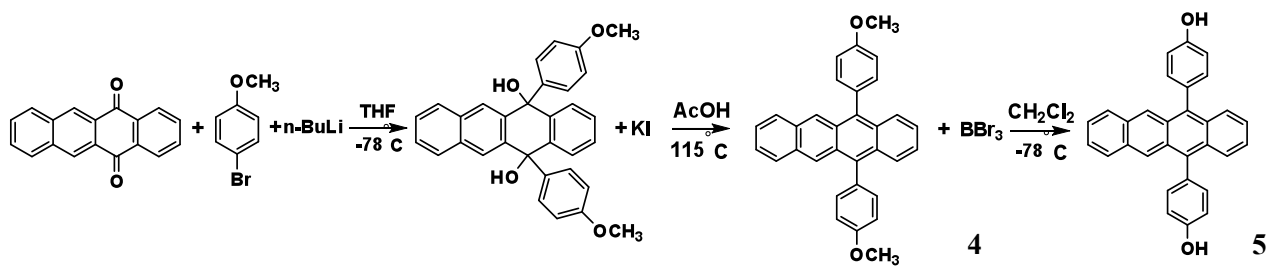
All synthetic manipulations were performed under standard air-free conditions under an atmosphere of argon gas with magnetic stirring unless otherwise mentioned. Flash chromatography was performed using silica gel (230-400 mesh) as the stationary phase. NMR spectra were acquired on a Bruker Avance III 500 or Bruker DPX-300 spectrometer. Chemical shifts are reported relative to residual protonated solvent (7.27 ppm for CHCl₃). High-resolution mass spectra (HRMS) were obtained at the MIT Department of Chemistry Instrumentation Facility using a peak-matching protocol to determine the mass and error range of the molecular ion. Molecular weight distribution measurements of the polymers were conducted with a Shimadzu Gel Permeation Chromatography (GPC) system equipped with a TOSOH TSKgel GMHhr-M mixed-bed column and guard column (5 μm), in addition to both UV and refractive index detectors. The column was calibrated with low polydispersity poly(styrene) standards (TOSOH, PSt Quick Kit) with THF as the mobile phase eluting at 0.75 mL/min. Schematic overviews of the reaction sequences followed are shown in Schemes S1~S3.

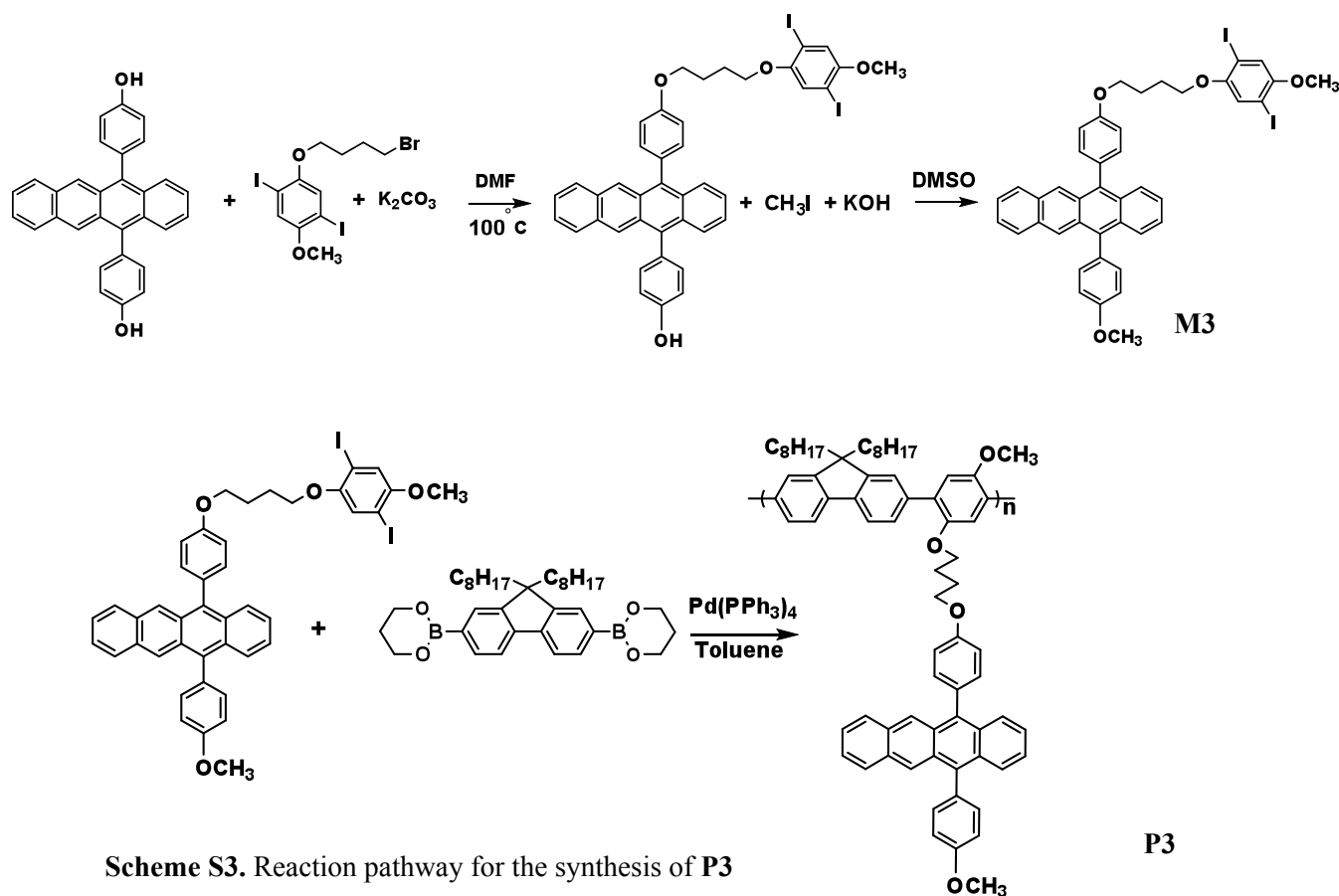


Scheme S1. Synthesis of **P1**



Scheme S2. Reaction pathway for the synthesis of **P2**





P1

P1 was prepared using standard Suzuki cross-coupling polymerization conditions. Equimolar amounts of the two monomers (9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester, 57 mg, 0.1 mmol; 1,4-diiodo-2,5-bis(octyloxy)benzene, 60 mg, 0.1 mmol) were weighed into a Schlenk tube equipped with a small magnetic stir bar. To the reaction tube was added a small amount of $\text{Pd}(\text{PPh}_3)_4$, as well as 2 mL of deoxygenated toluene, 2 mL of deoxygenated 2M aqueous potassium carbonate solution, and several drops of Aliquat 336 were added under a heavy argon flow. The mixture in the sealed tube was then stirred vigorously at 90 °C for 3 days. After cooling to room temperature, the aqueous layer was removed by pipette, and the organic layer was washed with several mL of water. The polymer was then precipitated from the toluene solution into 30 mL methanol, and collected by centrifugation and decanting. The polymer was then dissolved in 3 mL of diethyl ether and passed through a 0.45 μm PTFE syringe filter to remove insoluble catalyst residues, reprecipitated into 30 mL methanol and isolated by centrifugation and decanting. M_n [g/mol]: 28,137, M_w [g/mol]: 60,275.

9-(4-methoxyphenyl)-10-phenylanthracene (1)

9-phenylanthracene (2.0 g, 7.9 mmol) was dissolved in 25 mL CH₂Cl₂. Br₂ (0.44 mL, 8.67 mmol) was added dropwise into the 9-phenylanthracene solution at room temperature. The reaction mixture was stirred overnight at room temperature. The reaction was quenched with 40 mL 15% (w/v) Na₂S₂O₃ (aq), washed with 40 mL deionized H₂O and extracted with 40 mL CH₂Cl₂. The organic layers were washed with 20 mL H₂O, 30 mL brine, and dried with MgSO₄. Crude product was recrystallized from ethanol to give 9-bromo-10-phenylanthracene as yellow crystals. Yield 1.31 g (50%). ¹H NMR (500MHz, CDCl₃): δ 8.62-8.60 (d, 2H), 7.66-7.64 (d, 2H), 7.60-7.53 (m, 5H), 7.41-7.35 (m, 4H). ¹³C NMR (125MHz, CDCl₃): δ 138.4, 137.8, 131.1, 131.0, 130.2, 128.4, 127.8, 127.7, 127.4, 126.9, 125.5, 122.7.

9-bromo-10-phenylanthracene (0.42 g, 1.2 mmol), 4-methoxyphenylboronic acid (0.23 g, 1.5 mmol), potassium carbonate (0.34 g, 2.5 mmol) and a small amount of Pd(PPh₃)₄ were dissolved in 8 mL toluene and 3 mL deionized H₂O at room temperature, both of which were deoxygenated by sparging with Ar for 20 minutes. Then, three drops of Aliquat 336 were added into the solution under heavy argon flow and the reaction mixture was heated to 90 °C under an atmosphere of argon overnight. After cooling to room temperature, 20% (w/v) Na₂CO₃ solution (aq, 10 mL) and hexanes (15 mL) were added into the reaction mixture and the resulting precipitate was collected *via* vacuum filtration and washed with hexanes and methanol. The crude product was purified *via* flash chromatography using hexanes/CH₂Cl₂ (2.5:1, v/v) to yield **1**. Yield: 0.28 g (62%). ¹H NMR (500MHz, CDCl₃): δ 7.77-7.75 (m, 2H), 7.71-7.69 (m, 2H), 7.62-7.59 (t, 2H), 7.56-7.54 (t, 1H), 7.49-7.48 (d, 2H), 7.42-7.40 (d, 2H), 7.35-7.31 (m, 4H), 7.16-7.14 (d, 2H), 3.96 (s, 3H). ¹³C NMR (125MHz, CDCl₃): δ 158.0, 139.1, 137.0, 136.9, 132.4, 131.3, 131.1, 130.2, 129.9, 128.4, 127.4, 127.0, 126.9, 125.0, 124.9, 113.9, 55.4. HRMS calcd for C₂₇H₂₀O (M+H)⁺, 361.1587; found, 361.1592.

9-(4-hydroxyphenyl)-10-phenylanthracene (2)

9-(4-methoxyphenyl)-10-phenylanthracene (**1**) (81 mg, 0.23 mmol) was dissolved in 10 mL CH₂Cl₂ at room temperature. 0.6 mL BBr₃ solution (1.0 M in CH₂Cl₂) was then added dropwise at -78 °C. The reaction mixture was allowed to warm to room temperature overnight. It was then washed with 10% aqueous HCl and extracted with CH₂Cl₂. The organic layer was washed with brine and dried over MgSO₄. The crude product was purified *via* flash chromatography using hexanes/CH₂Cl₂ (1:6, v/v) to yield **2**. Yield: 71 mg (91%). ¹H NMR (500MHz, CDCl₃): δ 7.74-7.72 (m, 2H), 7.68-7.66 (m, 2H), 7.60-7.57 (m, 2H), 7.54-7.51 (m, 1H), 7.46-7.45 (d, 2H), 7.34-7.30 (m, 6H), 7.06-7.05 (m, 2H), 4.86 (s, 1H). ¹³C NMR (75MHz, CDCl₃): δ 155.2, 139.3, 137.2, 137.0, 132.8, 131.6, 131.5, 130.4, 130.1, 128.6, 127.6, 127.2, 125.2, 125.1, 115.6. HRMS calcd for C₂₆H₁₈O (M+H)⁺, 347.1430; found, 347.1433.

9-(4-(4-(2, 5-diiodo-4-methoxyphenoxy)butoxy)phenyl)-10-phenylanthracene (**M2**)

9-(4-hydroxyphenyl)-10-phenylanthracene (**2**) (78 mg, 0.22 mmol), 1-(4-bromobutoxy)-2,5-diiodo-4-methoxybenzene (95 mg, 0.18 mmol) and potassium carbonate (37 mg, 0.27 mmol) were dissolved in 10 mL 2-butanone at room temperature. The reaction mixture was heated to 80 °C under an atmosphere of argon overnight. After cooling to room temperature, the reaction mixture was partitioned between 10% aqueous HCl and CH₂Cl₂. The organic layer was washed with brine and dried over MgSO₄. The crude product was purified *via* flash chromatography using hexanes and CH₂Cl₂ (1:1, v/v) to yield **M2**. Yield: 68 mg (47%). ¹H NMR (500MHz, CDCl₃): δ 7.79-7.77 (m, 2H), 7.72-7.70 (m, 2H), 7.64-7.61 (t, 2H), 7.59-7.56 (d, 1H), 7.51-7.50 (d, 2H), 7.42-7.40 (d, 2H), 7.37-7.33 (m, 4H), 7.28 (s, 2H), 7.18-7.16 (d, 2H), 4.26-4.24 (t, 2H), 4.14-4.11 (t, 2H), 3.86 (s, 3H), 2.19-2.12 (m, 4H). ¹³C NMR (125MHz, CDCl₃): δ 158.7, 153.7, 153.1, 139.4, 137.2, 137.1, 132.6, 131.5, 131.3, 130.5, 130.2, 128.6, 127.6, 127.3, 127.2, 125.2, 125.1, 123.2, 121.8, 114.7, 86.6, 85.7, 70.2, 67.8, 57.4, 26.4, 26.3. HRMS calcd for C₃₇H₃₀I₂O₃ (M+H)⁺, 777.0357; found, 777.0377.

P2

P2 was prepared using standard Suzuki cross-coupling polymerization conditions. Equimolar amounts of the two monomers (9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester, 31 mg, 56 μmol; 9-(4-(4-(2,5-diiodo-4-methoxyphenoxy)butoxy)phenyl)-10-phenylanthracene (**4**), 44 mg, 56 μmol) were weighed into a Schlenk tube equipped with a small magnetic stir bar. To the reaction tube was added a small amount of Pd(PPh₃)₄. 2 mL of deoxygenated toluene, 2 mL of deoxygenated 2M aqueous potassium carbonate solution, and several drops of Aliquat 336 were added under a heavy argon flow. The reaction mixture in the sealed tube was then stirred vigorously at 90 °C for 3 days. After cooling to room temperature, the aqueous layer was removed by pipette, and the organic layer was washed with several mL deionized water. The polymer was then precipitated from the toluene solution into 30 mL methanol and collected by centrifugation and decanting. The polymer was then dissolved in 3 mL of diethyl ether and passed through a syringe filter to remove insoluble catalyst residues, reprecipitated into 30 mL methanol and isolated by centrifuging and decanting. ¹H NMR (500 MHz, CDCl₃): δ 7.78, 7.71-7.65, 7.55-7.51, 7.44-7.43, 7.33-7.27, 7.15-7.10, 7.03-7.02, 4.04, 3.83-3.76, 2.07-1.97. M_n [g/mol]: 10,339, M_w [g/mol]: 18,124.

5,12-bis(4-methoxyphenyl)tetracene (**4**)

15 mL dry THF was added to 1-bromo-4-methoxybenzene (19.9 mmol, 2.5 mL), followed by dropwise addition of *n*-butyllithium (17.1 mmol, 10.7 mL, 1.6 M in hexanes) at -78 °C. The reaction mixture was stirred at -78 °C for 1 hour and then transferred *via* cannula to 5,12-naphthacenequinone (0.73 g, 2.8 mmol), which was dissolved in 15 mL dry THF and cooled to -78 °C. Upon completion of transfer, the reaction mixture was allowed to warm to room temperature and stirred overnight under argon. It was then washed with 10% aqueous HCl and

extracted with CH₂Cl₂. The organic layer was washed with brine and dried over MgSO₄. The crude product was purified *via* flash chromatography using hexanes and EtOAc (1.5:1, v/v) to yield 5,12-bis(4-methoxyphenyl)-5,12-dihydrotetracene-5,12-diol. Yield: 945 mg (70%). ¹H NMR (500 MHz, CDCl₃): δ 8.12 (s, 2H), 8.02-8.00 (m, 2H), 7.78-7.76 (m, 2H), 7.52-7.48 (m, 4H), 6.43-6.41 (d, 4H), 6.12-6.10 (d, 4H), 3.52 (s, 6H), 3.18 (s, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 158.0, 141.4, 139.6, 134.9, 132.5, 128.8, 128.1, 127.7, 126.0, 125.8, 124.6, 112.5, 75.4, 55.0. HRMS calcd for C₃₂H₂₆O₄ (M-H)⁻, 473.1758; found, 473.1764.

Acetic acid (69 mL) was added to a mixture of 5,12-bis(4-methoxyphenyl)-5,12-dihydrotetracene-5,12-diol (1.64 g, 3.4 mmol) and potassium iodide (2.45 g, 15 mmol) at room temperature. The reaction mixture was then heated to 115 °C for 1 hour. After cooling to room temperature, 300 mL deionized H₂O was added to the reaction mixture, and the resulting orange solid was collected *via* vacuum filtration and washed with deionized H₂O. The crude product was purified by recrystallization from CHCl₃/hexanes to yield **4**. Yield 1.4 g (92%). ¹H NMR (500 MHz, CDCl₃): δ 8.33 (s, 2H), 7.79-7.77 (m, 2H), 7.71-7.69 (m, 2H), 7.46-7.44 (d, 4H), 7.28-7.22 (m, 4H), 7.19-7.17 (d, 4H), 3.99 (s, 6H). ¹³C NMR (125 MHz, CDCl₃): δ 159.4, 136.9, 132.8, 131.6, 131.2, 130.0, 129.8, 128.7, 127.3, 126.0, 125.3, 124.8, 114.2, 55.7. HRMS calcd for C₃₂H₂₄O₂ (M+H)⁺, 441.1849; found, 441.1847.

5,12-bis(4-hydroxyphenyl)tetracene (**5**)

5,12-bis(4-methoxyphenyl)tetracene (**4**) (0.85 g, 1.9 mmol) was dissolved in 100 mL CH₂Cl₂ at room temperature. 53.5 mL BBr₃ solution (0.1 M in CH₂Cl₂) was then added dropwise at -78 °C. The reaction mixture was allowed to warm slowly by removal of the dry ice/acetone bath and vigorously stirred for 5 hours. It was then washed with 10% aqueous HCl and extracted with CH₂Cl₂. The organic layer was washed with brine and dried over MgSO₄. The crude product was purified *via* flash chromatography using hexanes and EtOAc (3:1, v/v) to yield **5**. Yield: 0.26 g (33%). ¹H NMR (300 MHz, CDCl₃): δ 8.33 (s, 2H), 7.80-7.77 (m, 2H), 7.72-7.69 (m, 2H), 7.42-7.39 (d, 4H), 7.30-7.20 (m, 4H), 7.13-7.11 (m, 4H), 4.94 (s, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 155.3, 136.5, 132.8, 131.7, 130.9, 129.7, 129.5, 128.4, 127.0, 125.7, 125.1, 124.6, 115.7. HRMS calcd for C₃₀H₂₀O₂ (M+H)⁺, 413.1536; found, 413.1532.

5-(4-(4-(2, 5-diiodo-4-methoxyphenoxy)butoxy)phenyl)-12-(4-methoxyphenyl)tetracene (**M3**)

5,12-bis(4-hydroxyphenyl)tetracene (**5**) (0.25 g, 0.6 mmol), 1-(4-bromobutoxy)-2,5-diiodo-4-methoxybenzene (0.38 g, 0.7 mmol) and potassium carbonate (0.33, 2.4 mmol) were dissolved in 2.6 mL DMF at room temperature. The reaction mixture was heated to 100 °C under an atmosphere of argon overnight. After cooling to the room temperature, it was extracted with CH₂Cl₂ from 10% aqueous HCl. The organic layer was washed with brine and dried over MgSO₄. The crude product was purified *via* flash chromatography using hexanes and CH₂Cl₂ (1:1, v/v) to yield 4-(12-(4-(4-(2, 5-diiodo-4-methoxyphenoxy)butoxy)phenyl)tetracene-5-

yl)phenol. Yield: 0.23 g (45%). ^1H NMR (300 MHz, CDCl_3): δ 8.34-8.32 (2s, 2H), 7.80-7.77 (m, 2H), 7.72-7.68 (m, 2H), 7.45 (m, 1H), 7.42-7.41 (m, 2H), 7.38 (m, 1H) 7.29-7.22 (m, 4H), 7.19 (s, 2H), 7.16 (s, 1H), 7.12-7.09 (s, 3H), 4.26-4.22 (t, 2H), 4.11-4.07 (t, 2H), 3.81 (s, 4H), 2.13(m, br, 4H). ^{13}C NMR (125 MHz, CDCl_3): δ 158.4, 155.0, 153.3, 152.8, 136.7, 136.4, 132.7, 132.5, 131.6, 131.4, 130.8, 129.6, 129.4, 128.3, 127.0, 126.9, 125.7, 125.6, 125.0, 124.6, 122.9, 121.5, 115.4, 114.5, 86.2, 85.4, 69.8, 67.5, 57.1, 26.2, 26.0. HRMS calcd for $\text{C}_{41}\text{H}_{32}\text{I}_2\text{O}_4$ ($\text{M}+\text{H}$) $^+$, 843.0463; found, 843.0458.

4-(12-(4-(4-(2,5-diiodo-4-methoxyphenoxy)butoxy)phenyl)tetracen-5-yl)phenol (0.2 g, 0.23 mmol), methyl iodide (25 μL , 0.36 mmol) and potassium hydroxide (42 mg, 0.75 mmol) were dissolved in 6.5 mL DMSO at room temperature. The reaction mixture was vigorously stirred at room temperature overnight. It was then extracted with Et_2O from 10% aqueous HCl. The organic layer was washed with brine and dried over MgSO_4 . The crude product was purified *via* flash chromatography using hexanes and CH_2Cl_2 (1:2.2, v/v) under argon. The purified product was further purified by recrystallization from CHCl_3 /hexanes to yield **M3**. Yield: 0.19 g (92%). ^1H NMR (500 MHz, $\text{DMSO}-d_6$): 8.33 (s, 1H), 8.32 (s, 1H) 7.91-7.89 (m, 2H), 7.61 (m, 2H), 7.48-7.44 (t, 4H), 7.42-7.33 (m, 6H), 7.29-7.27 (m, 4H), 4.27-4.24 (t, 2H), 4.17-4.12 (t, 2H), 3.95 (s, 3H), 3.78 (s, 3H), 2.06-2.03 (m, 2H), 1.99-1.96 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 159.0, 158.4, 153.3, 152.7, 136.6, 136.5, 132.5, 131.4, 131.3, 131.2, 130.8, 129.6, 129.4, 128.3, 127.0, 126.9, 125.7, 125.6, 124.9, 124.5, 122.6, 121.4, 114.4, 113.9, 86.2, 85.4, 69.8, 67.4, 57.1, 55.3, 26.1, 26.0. HRMS calcd for $\text{C}_{42}\text{H}_{34}\text{I}_2\text{O}_4$ ($\text{M}+\text{H}$) $^+$, 857.0619; found, 857.0597.

P3

P3 was prepared using standard Suzuki cross-coupling polymerization reaction conditions. Equimolar amounts of the two monomers (15 μmol) were weighed into a Schlenk tube equipped with a small magnetic stir bar. To the reaction tube was added a small amount of $\text{Pd}(\text{PPh}_3)_4$, 0.3 mL of deoxygenated toluene, 0.35 mL of deoxygenated 2M aqueous potassium carbonate solution, and several drops of Aliquat 336 were added under a heavy argon flow. The sealed tube was then wrapped with aluminum foil and stirred vigorously at 90°C for 3 days. After cooling to room temperature, the aqueous layer was removed by pipette, and the organic layer was washed with several mL of deionized water. The polymer was then precipitated from the toluene solution into 10 mL methanol, and collected by centrifugation and decanting. The polymer was then dissolved in 0.3 mL CH_2Cl_2 and passed through a syringe filter to remove insoluble catalyst residues, reprecipitated into 10 mL methanol, isolated by centrifugation and decanting, followed by Soxhlet extraction with methanol and hexanes. ^1H NMR (500 MHz, CDCl_3): δ 8.30, 7.74-7.73, 7.67, 7.58-7.56, 7.44-7.37, 7.23-7.18, 7.06-7.03, 4.12-4.09, 3.98, 3.83-3.77, 2.00-1.95. M_n [g/mol]: 13,656, M_w [g/mol]: 21,873.

2. Optical Experiments

Electronic absorbance spectra were acquired with a Varian Cary-100 instrument in double-beam mode using a solvent-containing cuvette for background subtraction spectra. Fluorescence emission spectra were obtained by using a PTI Quantum Master 4 equipped with a 75 W Xe lamp. All fluorescence spectra are corrected for the output of the lamp and the dependence of detector response to the wavelength of emitted light. Fluorescence spectra were acquired using sample absorbances less than 0.1. Fluorescence quantum yields were determined relative to either quinine sulfate in 0.1 N H₂SO₄ or Coumarin 6 in ethanol. Irradiation of the methylene blue photosensitizer to generate ¹O₂ was performed with a 200W Hg/Xe lamp (Newport-Oriel) equipped with a condensing lens, recirculating water filter, manual shutter, a 590nm high-pass filter, and a focusing lens in the light path.

a. Fluorescence response to singlet oxygen

A cuvette containing the test sample solution was irradiated in increments of 1 min. Both the absorbance and fluorescence spectra were taken after each interval of irradiation. The absorbances of methylene blue and **P3** were approximately 0.1. A focusing lens was attached to Hg/Xe lamp. The cuvette was placed at the focal point. UV/vis and fluorescence spectra were acquired between periods of irradiation.

In order to confirm that the acenes underwent a [4+2] cycloaddition with ¹O₂ to form endoperoxides, ¹H NMR of 5,12-bis(4-methoxyphenyl)tetracene (**4**) was taken after being exposed to ¹O₂. The singlet at δ 8.33 disappeared and a singlet was observed upfield at δ 6.06 corresponding to the bridgehead protons of one regioisomer of the endoperoxide. Similar changes in chemical shift were also observed in **P3** after exposure to ¹O₂.

b. Kinetics

A stock solution of methylene blue was prepared in CDCl₃ to give an absorbance of 1.0 at its peak. 5,12-bis(4-methoxyphenyl)tetracene (**4**) was dissolved in CDCl₃ at a concentration of 0.01 M. When the 0.01 M solution was diluted 100-fold with the methylene blue stock solution, the final concentration of the compound in the sample was 0.1 mM. For the irradiation of the solution, a Cary UV-Vis spectrophotometer was used along with the Hg/Xe Lamp. An initial absorbance, which was consistently ~1.0 for the peak of the characteristic vibronic pattern at λ > 300 nm, of the sample was recorded. With the sample placed 30 cm from the light source, the solution was irradiated using a 590 nm high-pass filter and convex lens. The solution was irradiated continuously with the time intervals recorded prior to the acquisition of each absorbance spectrum until the absorbance of the sample was around .01. This method was repeated several times for (**4**) and 9-(4-methoxyphenyl)-10-phenylanthracene (**1**) in CDCl₃. For the kinetics of **P2** and **P3**, a solution of the polymer in the CDCl₃ was prepared. The absorbance was directly measured after each addition of polymer stock solution in the 3.0 mL methylene blue. The initial concentration of the polymer was adjusted to give an absorbance of 1.0 in the

region of distinctive vibronic signals of the fused aromatic. The wavelengths used for **4**, **1**, and **P3** for analysis of kinetics were the peak of the highest absorbance in the characteristic vibronic pattern at $\lambda > 300$ nm. For **P2**, the absorbance at the 263 nm was analyzed.

3. Supplemental Figures:

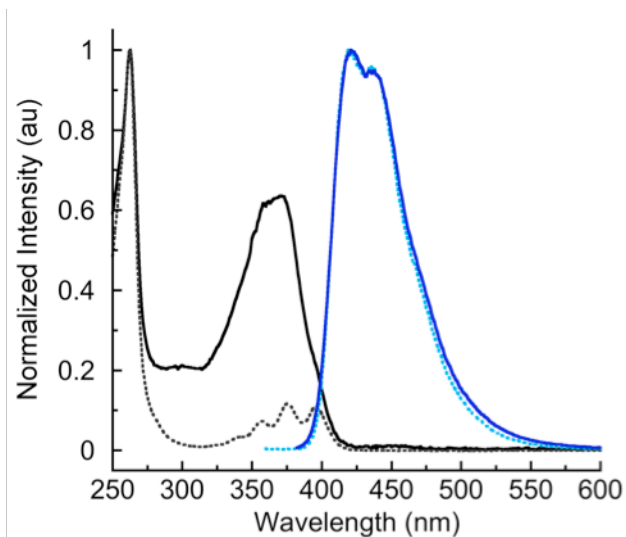


Figure S1. Normalized absorbance (black) and emission (blue) spectra of anthracene-containing CP **P2** (solid lines) and anthracene **1** (dotted lines) in CH_2Cl_2 .

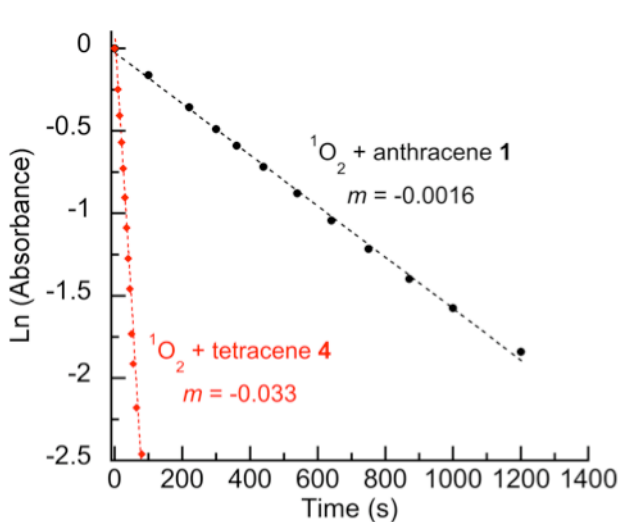


Figure S2. First order kinetics of reaction of model acenes **1** and **4** during irradiation of methylene blue in CDCl_3 .

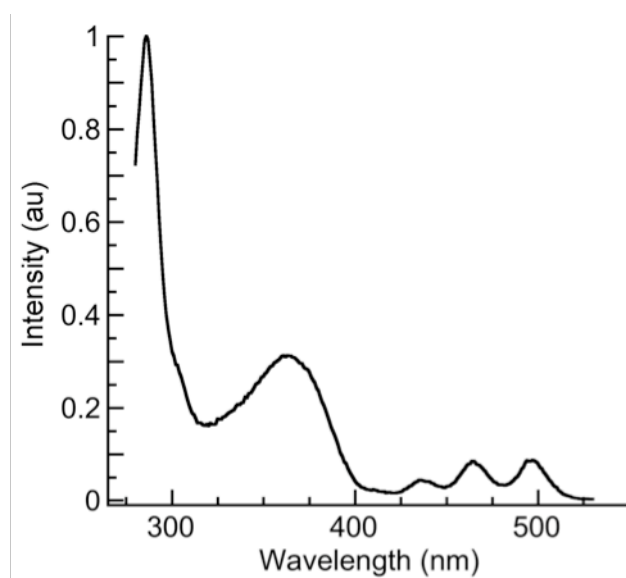


Figure S3. Excitation spectrum of **P3** in CH_2Cl_2 . $\lambda_{\text{em}} = 540 \text{ nm}$.

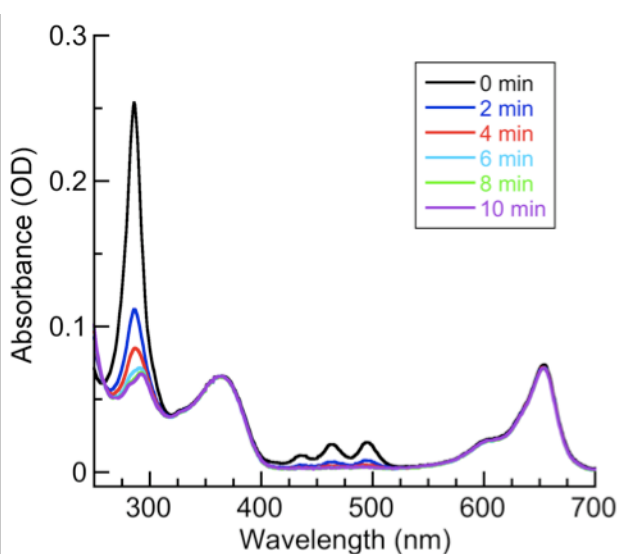


Figure S4. UV/vis response of polymer **P3** to $^1\text{O}_2$ photosensitization with methylene blue ($\lambda_{\text{max}} = 654 \text{ nm}$) in CH_2Cl_2 . Absorbance spectra correspond to the emission spectra in Figure 2 in the main text of the paper.

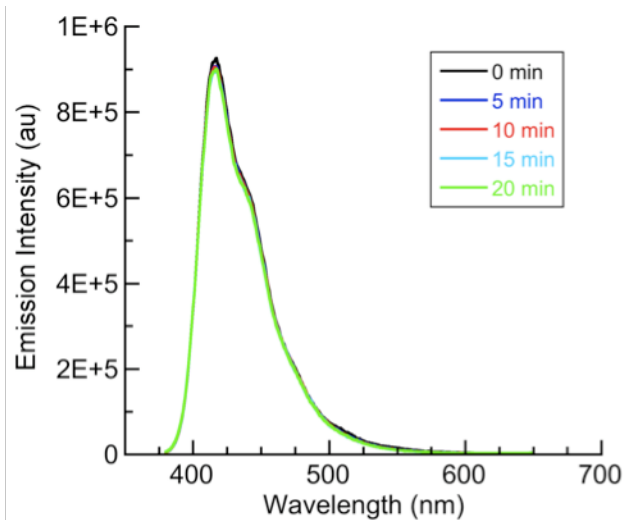


Figure S5. Lack of fluorescent response when an equimolar mixture of **P1** and tetracene **4** were exposed to $^1\text{O}_2$ via sensitization with MB in CH_2Cl_2 . In this experiment **P1** was selectively excited ($\lambda_{\text{ex}} = 373 \text{ nm}$).

4. References:

1. Y. Li, G. Li, X. Wang, C. Lin, Y. Zhang and Y. Ju, *Chem. Eur. J.*, 2008, **14**, 10331-10339.
2. T. M. Swager, C. J. Gil and M. S. Wrighton, *J. Phys. Chem.*, 1995, **99**, 4886-4893.
3. S. Thomas and T. Swager, *Macromolecules*, 2005, **38**, 2716-2721.