Altinok, E.; Frausto, F.; Thomas, S. W. III "Water-Soluble Fluorescent Polymers that Respond to Singlet Oxygen" *J. Polym. Sci. A Polym. Chem.* **2016**, *54*, 2526–2535. doi: 10.1002/pola.28130.

Water-Soluble Fluorescent Polymers that Respond to Singlet Oxygen

Esra Altinok, Fanny Frausto and Samuel W. Thomas III*

Department of Chemistry, Tufts University, 62 Talbot Avenue, Medford, MA 02155 USA

Correspondence to: sam.thomas@tufts.edu

(Additional Supporting Information may be found in the online version of this article.)

ABSTRACT

Although acenes with more than three fused rings can both fluoresce efficiently and react with singlet oxygen ($^1O_2$) rapidly, their hydrophobic nature presents a challenge to their use in aqueous environments. Herein we report a series of fluorescent, water-soluble random copolymers that each comprise (oligoethylene glycol) methacrylate (OEGMA) and one of several diarylacene methacrylates, including a tetracene methacrylate and a tetraceneothiophene methacrylate. Exposure to $^1O_2$ in water oxidizes the pendant acenes, resulting in diminution of their fluorescence intensities. The observed rate of oxidation of the tetracene-containing polymers compares favorably with a commercial $^1O_2$-sensitive dye. Polymers that also include energy-donating coumarin side chains show ratiometric fluorescence changes in response to $^1O_2$.

KEYWORDS: Singlet Oxygen, Fluorescence, Ratiometric, POEGMA, Acene

INTRODUCTION

Due to the large driving forces and rapid rates for its formation from excited triplet states, many different chromophores can generate the lowest energy electronic excited state of O_2, singlet oxygen ($^1O_2$), upon irradiation with light under oxygenated conditions.[1,2] $^1O_2$ is a key reactive oxygen species (ROS) for a number of reasons.[3,4] When generated upon irradiating a photosensitizer *in vivo*, its cytotoxic nature makes it is the key ROS in Type II photodynamic therapy.[5,6] $^1O_2$ is an important ROS when human cells are exposed to oxidative stress,[7,8] and when photosynthetic organisms are exposed to excess light.[9,10] Its readily amplified nature—one sensitizer molecule can yield many $^1O_2$ molecules—also makes it a key secondary analyte used for transmitting information regarding the binding of proteins to surfaces of beads in luminescent oxygen channeling assays.[11,12]

In terms of specificity, the phosphorescence of $^1O_2$ in the infrared region of the spectrum is a particularly useful analytical tool in a variety of studies.[13-16] Alternatively, a number of luminescent probes for $^1O_2$ are reported in the literature;[3,17] these reactive dyes often rely upon [4+2] cycloaddition reactions between $^1O_2$ and a diene (such as an anthracene derivative) to slow the rate of photoinduced electron transfer quenching between an excited state of a coupled chromophore and the anthracene.[18-21] The resulting 'unquenching' yields increased quantum yield of luminescence of the fluorophore. This class of $^1O_2$-reactive dyes includes a commercially available probe, Singlet Oxygen Sensor Green.[22]

Our group has used acenes other than anthracene as dienes in luminescent materials that respond to $^1O_2$.[23] The broad palette of available acenes offers highly tunable emission wavelengths as well as a wide range of reactivity with $^1O_2$, including some with

bimolecular rate constants of cycloaddition that approach ~ 10^9 $M^{-1}s^{-1}$.[24,25] We have used in several instances tetracene derivatives as $^1O_2$-reactive energy acceptors, together with energy donating conjugated polymers, to show ratiometric fluorescent responses to $^1O_2$.[26-28] Other examples of ratiometric luminescent responses to $^1O_2$ are also reported in the literature.[29] The hydrophobic nature of acenes, however, presents a challenge for our approach of using large acenes in aqueous environments. We therefore present herein oligo(ethylene glycol) (OEG) side-chain acrylic polymers as an alternative construct for rendering acenes soluble in water for $^1O_2$-responsive fluorophores.

EXPERIMENTAL SECTION

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 for $CHCl_3$. 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 using either UV or 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. All reactants and solvents were purchased from commercial suppliers and used without further purification, unless otherwise noted.

Optical Experiments

All solution optical spectra were acquired of samples in quartz cuvettes (NSG Precision Cells). 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 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 OD, corresponding to concentrations of acene moieites between 2-10 μM. Fluorescence quantum yields were determined relative to either quinine sulfate in 0.1 N H_2SO_4 or Coumarin 6 in ethanol. Irradiation of the photosensitizer to generate $^1O_2$ was performed with 200W Hg/Xe lamp (Newport-Oriel) equipped with a condensing lens, water filter, shutter, and 635 nm high-pass filter.

Fluorescence Response to Singlet Oxygen

A cuvette containing the test sample solution was irradiated for numerous timed intervals. Both absorbance and fluorescence spectra were taken after each interval of irradiation. The excitation wavelengths used for emission measurements are: 285 nm (P1), 300 nm (P2), 350 nm (P3), 340 nm (P4), 340 nm (P5). The absorbance for both methylene blue and acene chromophores were approximately 0.1 OD. A typical 120 minute irradiation resulted in an approximate ~15% decrease in absorbance at 663 nm.

Protein Labeling with Eosin

Neutravidin Biotin Binding Protein (10 mg, Thermo Scientific) was dissolved in 1.0 mL of 0.10 M carbonate buffer at pH 9.4 in an Eppendorf tube. In another Eppendorf tube, eosin-5-isothiocyanate (5 mg) was dissolved in 0.5 mL of DMF and 100 uL of it immediately added to the protein solution, with continuous stirring for an hour at room temperature. A Sephadex column was prepared to separate the Neutravidin-Eosin conjugate from any excess Eosin. Approximately 5 g of Sephadex G-50 was allowed to swell overnight in excess distilled water. The Sephadex gel filtration column was

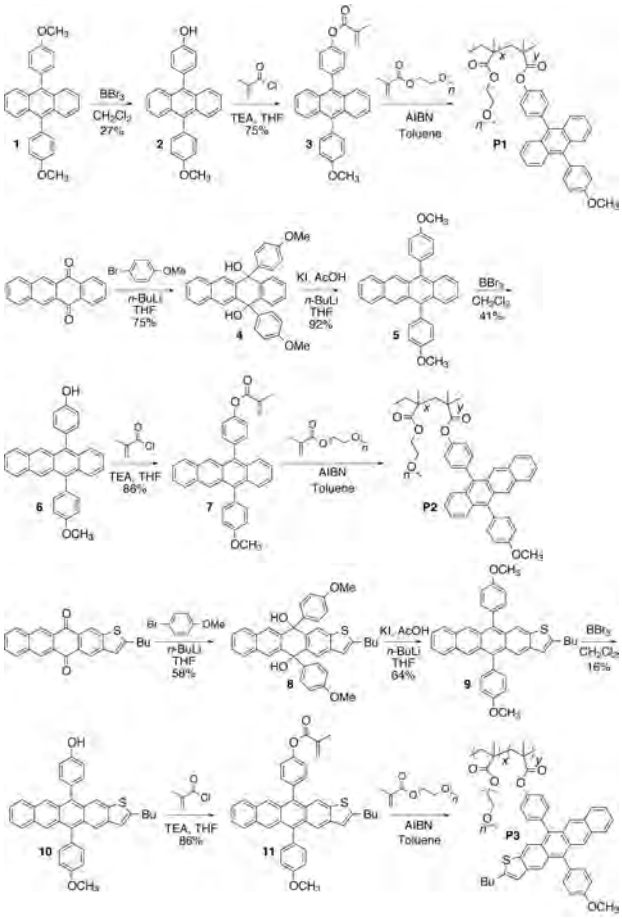
then prepared using 0.10 M pH 9.4 carbonate of the fraction containing the conjugate was acquired. The concentration of the labeled protein was determined as 0.6 µM at 280 nm by taking into account for additional absorbance at 280 nm from the methylene blue.

9,10-Bis-(4-methoxyphenyl)-anthracene (1)

4-methoxyphenylboronic acid (525 mg, 3.45 mmol, 2.2 eq) and 9,10-dibromoanthracene (525 mg, 1.56 mmol, 1 eq) was placed in a 100 mL two neck flask and evacuated and refilled with argon three times. Na_2CO_3 (415 mg, 3.92 mmol, 2.5 eq) was dissolved in 5 mL of DI H_2O and then added to reaction mixture followed by the addition of 30 mL of a THF/toluene (1:1) mixture. The suspension was then deoxygenated by sparging with argon for 30 minutes followed by the addition of $Pd(PPh_3)_4$ (53 mg, 0.045 mmol, 0.03 eq) under an argon atmosphere. The mixture was heated to 85 °C and stirred overnight. The mixture was then cooled to room temperature water was added. Organics were extracted twice with Et_2O, and combined organic phases were washed with brine and dried over $MgSO_4$, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (3:1, v/v) to yield **1**. Yield: 235 mg (60%). ^{1}H and ^{13}C NMR of this compound is in good agreement with the same compound reported in the literature.[30]

4-(10-(4-methoxyphenyl)anthracen-9-yl)phenol (2)

Compound **1** (215 mg, 0.55 mmol, 1.0 eq) was suspended in 35 mL of dry CH_2Cl_2, followed by the addition of BBr_3 (0.55 mL, 1.0 M in CH_2Cl_2, 0.55 mmol, 1 eq) at -78 °C under argon and stirred overnight at room temperature. The reaction was stopped by adding 10% $HCl_{(aq)}$. Organics were extracted twice with CH_2Cl_2, and combined organic phases were washed with water and brine, dried over $MgSO_4$, and filtered. The crude product was purified *via* flash chromatography using pure dichloromethane to yield **2**. Yield: 55 mg (27%). ^{1}H NMR (500 MHz, buffer as the eluent. An absorbance spectrum $CDCl_3$): δ 7.77-7.76 (m, 4H), 7.43-7.41 (m, 2H), 7.38-7.35 (m, 6H), 7.18-7.16 (m, 2H), 7.11-7.09 (m, 2H), 4.89 (s, 1H), 3.99 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159, 154.9, 132.6, 132.4, 131.4, 131.1, 130.3, 127.1, 126.9, 124.9, 124.8, 115.4, 113.9, 55.4.



Scheme 1. Synthesis of diarylacene-linked **P1-P3**, with *x* ~ 99*y*.

4-(10-(4-methoxyphenyl)anthracen-9-yl)phenyl methacrylate (3)

Compound **2** (55 mg, 0.15 mmol, 1.0 eq) and DMAP (catalytic amount) was placed in a 25 mL two neck flask and evacuated and refilled with argon three times. Then, 0.1 mL of dry Et_3N and 3.6 mL of dry THF was added to the flask, followed by the addition of freshly distilled methacryloyl chloride (14 uL, 0.15 mmol, 1 eq) at 0 °C under argon and stirred overnight at

room temperature. The reaction was stopped by adding 5% aqueous $NaHCO_3$. Organics were extracted twice with CH_2Cl_2, and combined organic phases were washed with water and brine, dried over $MgSO_4$, and filtered. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (1:1, v/v) to yield **3**. Yield: 50 mg (75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79-7.74 (m, 4H), 7.53 (d, J=8.5 Hz, 2H), 7.43-7.40 (m, 4H), 7.38-7.36 (m, 4H), 7.18 (d, J=8.5 Hz, 2H), 6.49 (s, 1H), 5.86 (s, 1H), 3.99 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.9, 159.1, 150.4, 137.2, 136.6, 136, 135.9, 132.37, 132.36, 131.1, 130.2, 130, 127.4, 127.1, 126.9, 125.1, 124.9, 121.7, 113.9, 55.4, 18.4. HRMS calcd for $C_{31}H_{24}O_3$ $(M+H)^+$, 445.1798, found, 445.1787.

5,12-bis(4-methoxyphenyl)-5,12-dihydrotetracene-5,12-diol (4)

30 mL dry THF was added to 1-bromo-4-methoxybenzene (6.8 mL, 54 mmol, 7 eq), followed by dropwise addition of *n*-butyllithium (29 mL, 47 mmol, 6 eq, 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 (2.0 g, 7.8 mmol, 1 eq), which was dissolved in 100 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 CH_2Cl_2. The organic layer was washed with brine and dried over $MgSO_4$. The crude product was purified *via* flash chromatography using hexanes and EtOAc (1.5:1, v/v) to yield **4**. Yield: 2.8 g (75%). ^{1}H and ^{13}C NMR of this compound is in good agreement with the same compound reported in the literature.[28]

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

Compound **4** (2.77 g, 5.8 mmol, 1.0 eq) and potassium iodide (4.62 g, 28 mmol, 4.8 eq) was dissolved in 115 mL of acetic acid at room temperature. The reaction mixture was then heated to 115 °C for 2 hours. After cooling to room temperature, 300 mL deionized H_2O was added to the reaction mixture, and the resulting orange solid was collected *via* vacuum filtration and washed with deionized H_2O. The crude product was used without further purification. Yield 2.3 g (92%). ^{1}H and ^{13}C NMR of this compound is in good agreement with the same compound reported in the literature.[28]

4-(12-(4-methoxyphenyl)tetracen-5-yl)phenol (6)

Compound **5** (500 mg, 1.13 mmol, 1.0 eq) was dissolved in 56 mL of dry CH_2Cl_2, followed by the addition of BBr_3 (1.13 mL, 1.0 M in CH_2Cl_2, 1.13 mmol, 1 eq) at -78 °C under argon and stirred overnight at room temperature. The reaction was stopped by adding 10% $HCl_{(aq)}$. Organics were extracted twice with CH_2Cl_2, and combined organic phases were washed with water and brine, dried over $MgSO_4$, and filtered. The crude product was purified *via* flash chromatography using pure dichloromethane to yield **6**. Yield: 200 mg (41%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.38 (s, 1H), 8.37 (s, 1H), 7.84-7.82 (m, 2H), 7.77-7.74 (m, 2H), 7.51-7.49 (m, 2H), 7.46-7.44 (m, 2H), 7.34-7.32 (m, 2H), 7.31-7.28 (m, 2H), 7.24-7.22 (m, 2H), 7.17-7.15 (m, 2H), 4.95 (s, 1H), 4.04 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1, 155, 136.7, 136.5, 132.8, 132.6, 131.7, 131.4, 130.94, 130.93, 129.7, 129.51, 129.49, 128.44, 128.41, 127.1, 127, 125.8, 125.7, 125.14, 125.11, 124.7, 124.6, 115.5, 114, 55.4.

4-(12-(4-methoxyphenyl)tetracen-5-yl)phenyl methacrylate (7)

Compound **6** (160 mg, 0.38 mmol, 1.0 eq) and DMAP (4.8 mg, 0.04 mmol, 0.1 eq) was placed in a 25 mL two neck flask and evacuated and refilled with argon three times. Then, 0.25 mL of dry Et_3N and 6 mL of dry THF was added to the flask, followed by the addition of freshly distilled methacryloyl chloride (38 uL, 0.38 mmol, 1 eq) at 0 °C under argon and stirred overnight at room temperature. The reaction was stopped by adding 5% aqueous $NaHCO_3$. Organics were extracted twice with CH_2Cl_2, and combined organic phases were washed with water and brine, dried over $MgSO_4$, and filtered. The crude product was purified *via* flash

chromatography using hexanes and ethyl acetate (4:1, v/v) to yield **7**. Yield: 162 mg (86%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.39 (s, 1H), 8.36 (s, 1H), 7.86-7.83 (m, 2H), 7.77-7.75 (m, 1H), 7.73-7.71 (m, 1H), 7.61-7.59 (m, 2H), 7.51-7.46 (m, 4H), 7.35-7.33 (m, 2H), 7.31-7.28 (m, 2H), 7.24-7.23 (m, 2H), 6.51 (s, 1H), 5.89 (t, 1H), 4.04 (s, 3H), 2.2 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166, 159.2, 150.5, 137.1, 136.8, 136, 135.8, 132.6, 131.3, 131.1, 130.9, 129.6, 129.5, 129.4, 129.2, 128.43, 128.4, 127.5, 127.1, 126.9, 125.9, 125.5, 125.3, 125.2, 125.1, 124.9, 124.7, 121.8, 114, 55.4, 18.5. HRMS calcd for $C_{35}H_{28}O_3$ $(M+H)^+$, 495.1955, found, 495.1944.

2,3-Bis(1,3-dioxolan-2-yl)thiophene (S1)

2,3-Thiophenedicarboxaldehyde (2.0 g, 14 mmol, 1.0 eq), *p*-toluenesulfonic acid monohydrate (6 mg, 0.03 mmol, 0.002 eq), and ethylene glycol (3.9 ml, 70 mmol, 5 eq) were dissolved in 25 mL of benzene. The mixture was refluxed and water was collected in a Dean-Stark trap. After cooling, the reaction mixture was washed with 10% NaOH, then H_2O and dried over $MgSO_4$. The crude product was used directly in the next step without further purification. ^{1}H and ^{13}C NMR of this compound is in good agreement with the same compound reported in the literature.[31]

5-butyl-2,3-thiophenedicarboxaldehyde (S2)

2,3-Bis(1,3-dioxolan-2-yl)thiophene (3.0 g, 13 mmol, 1 eq) was dissolved in 27 mL of dry THF under argon and cooled to -78°C. *n*-BuLi (10.8 mL, 17 mmol, 1.3 eq, 1.6 M in hexane) was then added dropwisely. After 75 minutes of stirring, 1-bromobutane (2.1 mL, 18 mmol, 1.4 eq) was added. The solution was left to warm to room temperature and stirred overnight. Organics were extracted twice with diethylether, and combined organic phases were washed with water and brine, dried over $MgSO_4$, and filtered. The crude product was purified *via* flash chromatography using hexanes and ethyl acetate (2:1, v/v) to yield 2,3-bis(1,3-dioxolan-2-yl)-5-butylthiophene. Yield: 2.0 g (54%). The crude product was used directly in the next step without further purification.

A solution of 1.4 g of 2,3-bis(1,3-dioxolan-2-yl)-5-butylthiophene in 50 mL of THF:3M HCl (1:1) was stirred at room temperature for 4 hours. The mixture was extracted with diethylether. The combined organic phases was washed with water and brine, and dried over $MgSO_4$. The crude product was used directly in the next step without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.4 (s, 1H), 10.3 (s, 1H), 7.35 (s, 1H), 2.91 (t, 2H), 1.76-1.7 (m, 2H), 1.47-1.39 (m, 2H), 0.99 (t, 3H) ^{13}C NMR (125 MHz, $CDCl_3$): δ 184.8, 182.2, 156.3, 145, 143.9, 126.9, 33.2, 30.2, 22.1, 13.7.

1,4-Dihydroxyanthracene (S3).

1,4-anthraquinone (850 mg, 4.1 mmol, 1.0 eq) and $Na_2S_2O_4$ (2.3 g, 15.5 mmol, 3.8 eq) was placed in a 100 mL round bottom flask and evacuated and refilled with argon three times. A solution of 40 ml of 1,4-dioxane:H_2O (1:1) was then added to the flask and stirred overnight at room temperature. The precipitate was collected by filtration and filtrate was diluted with EtOAc. Organic phase were washed twice with water and brine, dried over $MgSO_4$, and filtered. The crude product was used directly in the next step without further purification. ^{1}H and ^{13}C NMR of this compound is in good agreement with the same compound reported in the literature.[32]

2-butyltetraceno[2,3-b]thiophene-5,12-dione (TMT quinone) (S4)

5-butyl-2,3-thiophenedicarboxaldehyde (142 mg, 0.72 mmol, 1 eq) and 1,4-dihydroxyanthracene (152 mg, 0.72 mmol, 1 eq) were dissolved in 6 mL of ethanol, and the mixture was vigorously stirred for 1 h at room temperature followed by the addition of 1 mL of 10% aqueous NaOH. After stirring at room temperature for 1 hour, the precipitate was collected via vacuum filtration. The crude product was used directly in the next step without further purification. Yield: 225 mg (85%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.91 (s, 2H), 8.83 (s, 1H), 8.69 (s, 1H), 8.14-8.12 (m, 2H),

7.72-7.7 (m, 2H), 7.27 (s, 1H), 3.01 (t, 2H), 1.85-1.79 (m, 2H), 1.53-1.47 (m, 2H), 1.01 (t, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 183.3, 182.9, 154.1, 144.7, 144.3, 135.24, 135.19, 130.8, 130.3, 130.1, 129.5, 129.3, 122.4, 122.3, 121.7, 32.9, 30.9, 22.3, 13.8.

2-butyl-5,12-bis(4-methoxyphenyl)-5,12-dihydrotetraceno[2,3-*b*]thiophene-5,12-diol (8)

16 mL dry THF was added to 1-bromo-4-methoxybenzene (0.73 mL, 5.8 mmol, 4.6 eq), followed by dropwise addition of *n*-butyllithium (3.5 mL, 46.5 mmol, 5.7 eq, 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 **S4** (470 mg, 1.26 mmol, 1 eq), which was dissolved in 16 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. After removal of solvent, organics were dissolved in CH_2Cl_2 and then washed with 10% aqueous HCl. The combined organic layer was washed with brine and dried over $MgSO_4$. The crude product was purified *via* flash chromatography using hexanes and EtOAc (2:1, v/v) to yield **8**. Yield: 430 mg (58%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.91 (s, 2H), 8.34 (s, 3H), 8.23 (s, 1H), 7.91-7.89 (m, 2H), 7.57-7.54 (m, 2H), 7.06 (s, 1H), 6.51 (m, 4H), 6.17-6.15 (m, 4H), 3.57 (s, 6H), 2.98 (t, 3H), 1.84-1.78 (m, 2H), 1.53-1.45 (m, 2H), 1.01 (t, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158, 148, 140, 139.9, 139.7, 138.9, 138.1, 137.4, 135, 134.9, 132.6, 129, 128.9, 128.1, 126.2, 124.78, 124.77, 120.6, 119.9, 119.3, 112.6, 75.99, 75.97, 54.9, 33.2, 30.7, 22.3, 13.9.

2-butyl-5,12-bis(4-methoxyphenyl)tetraceno[2,3-*b*]thiophene (9)

Compound **8** (430 mg, 0.7 mmol) was dissolved in 15 mL of THF. Then, 20 mL of 10% HCl aqueous solution saturated with tin(II) chloride dihydrate was added to the reaction mixture. The solution stirred for 3 hours at room temperature. Organics were diluted with CH_2Cl_2, washed with water and brine, dried over $MgSO_4$, and filtered. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (2:1, v/v). Recrystallization from hexanes and dichloromethane yielded 260 mg (64%) of pure **9**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.37 (s, 2H), 8.13 (s, 1H), 8.02 (s, 1H), 7.82-7.80 (m, 2H), 7.54-7.52 (m, 4H), 7.30-7.27 (m, 6H), 6.89 (s, 1H), 4.06 (s, 3H), 4.05 (s, 3H), 2.87 (t, 2H), 1.76-1.72 (m, 2H), 1.47-1.42 (m, 2H), 0.98 (t, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.2, 159.1, 149.5, 139.8, 138.2, 136.4, 135.2, 132.8, 132.7, 131.9, 131.7, 130.72, 130.7, 128.9, 128.8, 128.5, 128.1, 125.6, 125.5, 124.91, 124.9, 119.8, 119.2, 118.8, 114.1, 114, 55.5, 32.3, 31.1, 22.2, 13.8.

4-(2-butyl-12-(4-methoxyphenyl)tetraceno[2,3-*b*]thiophen-5-yl)phenol (10)

Compound **9** (227 mg, 0.41 mmol, 1.0 eq) was dissolved in 21 mL of dry CH_2Cl_2, followed by the addition of BBr_3 (0.41 mL, 1.0 M in CH_2Cl_2, 0.41 mmol, 1 eq) at -78 °C under argon and stirred overnight at room temperature. The reaction was stopped by adding 10% $HCl_{(aq)}$. Organics were extracted twice with CH_2Cl_2, and combined organic phases were washed with water and brine, dried over $MgSO_4$, and filtered. The crude product was purified *via* flash chromatography using pure dichloromethane to yield **10**. Yield: 35 mg (16%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.36 (s, 2H), 8.12 (s, 1H), 8.00 (s, 1H), 7.81-7.80 (m, 2H), 7.53-7.52 (m, 2H), 7.49-7.47 (m, 2H), 7.30-7.25 (m, 4H), 7.20-7.18 (m, 2H), 6.89 (s, 1H), 5.09 (s, 1H), 4.06 (m, 3H), 2.86 (t, 2H), 1.77-1.71 (m, 2H), 1.48-1.40 (m, 2H), 0.97 (t, 3H).

4-(2-butyl-12-(4-methoxyphenyl)tetraceno[2,3-*b*]thiophen-5-yl)phenyl methacrylate (11)

Compound **10** (33 mg, 0.06 mmol, 1.0 eq) and DMAP (~ 1 mg) were placed in a 25 mL two neck flask and evacuated and refilled with argon three times. Then, 45 uL of dry Et_3N and 1.5 mL of dry THF was added to the flask, followed by the addition of freshly distilled methacryloyl chloride (6 uL, 0.06 mmol, 1 eq) at 0 °C under argon and stirred overnight at room temperature. The reaction was stopped by adding 5% aqueous $NaHCO_3$. Organics were

extracted twice with CH_2Cl_2, and combined organic phases were washed with water and brine, dried over $MgSO_4$, and filtered. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (1:1, v/v) to yield **11**. Yield: 21 mg (56%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.33 (s, 1H), 8.29 (s, 1H), 8.09-8.05 (m, 1H), 7.97-7.93 (m, 1H), 7.79-7.77 (m, 2H), 7.62-7.59 (m, 2H), 7.52-7.45 (m, 4H), 7.28-7.21 (m, 3H), 6.87-6.85 (m, 1H), 6.5 (s, 1H), 5.86 (s, 1H), 4.03 (s, 3H), 2.83 (t, 2H), 2.18 (s, 3H), 1.73-1.67 (m, 2H), 1.44-1.37 (m, 2H), 0.93 (t, 3H). HRMS calcd for $C_{41}H_{34}O_3S$ $(M+H)^+$, 607.2301, found, 607.2310.

General Polymerization Procedure

3, **7** or **11** (0.8 mol %), oligo(ethylene glycol) methyl ether methacrylate comonomer, and 1% (w/w) azobisisobutyronitrile (AIBN) were dissolved in toluene and sparged with argon for 30 minutes. The reaction was then heated to 65 °C and stirred overnight. The reaction mixture was precipitated into diethyl ether. The collected polymer was dissolved in THF and precipitated into diethyl ether twice.

P1: ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.11 (2H, broad), 3.69-3.67 (16H, broad), 3.57 (2H, broad), 3.41 (3H, broad), 1.8 (2H, broad), 1.05-0.89 (3H, broad). M_n [g/mol]: 36k, M_w [g/mol]: 55k (GPC).

P2: ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.1 (2H, broad), 3.67 (16H, broad), 3.57 (2H, broad), 3.40 (3H, broad), 1.81 (2H, 3H, broad), 1.03-0.89 (broad). M_n [g/mol]: 47k, M_w [g/mol]: 92k (GPC).

P3: ^{1}H NMR (300 MHz, Tetrahydrofuran-d_8): δ 4.06 (2H, broad), 3.58 (16H, broad), 3.45 (2H, broad), 3.28 (3H, broad), 1.77 (2H, broad), 1.05-0.91(3H, broad). M_n [g/mol]: 41k, M_w [g/mol]: 58k (GPC).

7-(2-Hydroxyethoxy)-4-methylcoumarin (12)

A mixture of 17-hydroxy-4-methylcoumarin (1.0 g, 5.7 mmol, 1 eq), 2-bromoethanol (0.44 mL, 6.3 mmol, 1.1 eq) and potassium carbonate (2 g, 14.3 mmol, 2.5 eq) in 15 mL of ethanol was heated under reflux for overnight. Organics were diluted with diethylether and washed with water and brine, dried over $MgSO_4$, and filtered. The crude product was sufficiently pure to use in the next step without further purification. Yield: 1.1 g (88%)

7-(2-Methacryloyloxyethoxy)-4-methylcoumarin (13)

Compound **12** (500 mg, 2.27 mmol, 1.0 eq) and DMAP (28 mg, 0.2 mmol, 0.1 eq) was placed in a 100 mL two neck flask and evacuated and refilled with argon three times. Then, 2.5 mL of dry Et_3N and 37 mL of dry THF was added to the flask, followed by the addition of freshly distilled methacryloyl chloride (220 uL, 2.3 mmol, 1 eq) at 0 °C under argon and stirred overnight at room temperature. The reaction was stopped by adding 5% aqueous $NaHCO_3$. Organics were extracted twice with CH_2Cl_2, and combined organic phases were washed with water and brine, dried over $MgSO_4$, and filtered. The crude product was purified by recrystallization from ethanol. Yield: 520 mg (79%). ^{1}H NMR of this compound agrees with the literature.[33]

15%D-2%TET Polymer (P4)

Monomer **13** (43.7 mg, 0.15 mmol, 15 eq), monomer **7** (10 mg, 0.02 mmol, 2 eq), oligo(ethylene glycol) methyl ether methacrylate comonomer (251.7 mg, 0.84 mmol, 83 eq), and azobisisobutyronitrile (AIBN) (3 mg, 1% (w/w)) were dissolved in 2 mL of toluene and sparged with argon for 30 minutes. The reaction was then heated to 65 °C and stirred overnight. The reaction mixture was precipitated into hexanes. The collected polymer was dissolved in THF and precipitated into diethyl ether twice. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.5 (broad), 6.98 (broad), 6.15 (broad), 4.35-4.22 (broad), 4.1 (2H, broad), 3.67 (16H, broad), 3.57 (2H, broad), 3.4 (3H, broad), 2.4 (broad), 1.8 (2H, broad), 1.04-0.9 (3H, broad). M_n [g/mol]: 34k, M_w [g/mol]: 50k (GPC).

15%D-2%TMT Polymer (P5)

Monomer **13** (32 mg, 0.11 mmol, 15 eq), monomer **11** (9 mg, 0.015 mmol, 2 eq), poly(ethylene glycol) methyl ether methacrylate comonomer (185 mg, 0.62 mmol, 83 eq), and

azobisisobutyronitrile (AIBN) (2.3 mg, 1% (w/w)) were dissolved in 1.5 mL of toluene and sparged with argon for 30 minutes. The reaction was then heated to 65 °C and stirred overnight. The reaction mixture was precipitated into hexanes. The collected polymer was dissolved in THF and precipitated into diethyl ether twice. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.5 (broad), 6.9 (broad), 6.15 (broad), 4.35-4.27 (broad), 4.11 (2H, broad), 3.67 (16H, broad), 3.57 (2H, broad), 3.4 (3H, broad), 2.43 (broad), 1.91-1.82 (2H, broad), 1.05-0.90 (3H, broad). M_n [g/mol]: 37k, M_w [g/mol]: 55k (GPC).

RESULTS AND DISCUSSION

Our overall approach for incorporating acenes as side chains into hydrophilic acrylic polymers required the synthesis of methacrylate monomers with acene functionality. Based on our previous work examining how acene structural cores and substituents influence their reactivity with $^1O_2$ we chose three different diarylacenes as side-chains for our polymers—anthracene, tetracene, and tetraceneothiophene (TMT). The monomers were available through the syntheses summarized in Scheme 1.[24] Suzuki coupling of 4-methoxyphenylboronic acid and 9,10-dibromoanthracene gave dianisylanthracene **1**, which we were able to singly deprotect with BBr_3 to give phenol **2**. Esterification of **2** with methacryloyl chloride yielded the desired anthracene-substituted monomer **3.**

Analogous strategies gave the tetracene and TMT methacrylates: addition of a slight excess of the 4-methoxyphenyllithium, to either 5,12-tetracenequinone or 2-butyltetraceno[2,3-b]thiophene-5,12-dione[27] followed by either potassium iodide or tin(II)-mediated reduction of the resulting diols gave the dianisyltetracene **5** and dianisyl-TMT **9**. Single deprotection of each of these compounds with BBr_3, followed by esterification with methacryloyl chloride, yielded the corresponding acene methacrylates, **7** and **11**. For the synthesis of TMT quinone, we followed a strategy similar to that previously published, through a condensation 5-butylthiophene-2,3-dicarbaldehyde and anthracene-1,4-diol under basic conditions.[34] Finally, AIBN-initiated free radical polymerizations of monomers **3**, **7**, and **11** with oligo(ethylene glycol) methyl ether methacrylate (OEGMA) comonomer gave polymers **P1**, **P2**, and **P3**, respectively, after precipitation into diethyl ether multiple times. In all three polymerization reactions, the hydrophobic acene monomer was included at 0.8 mole-percent. All polymers had similar molecular weight distributions as determined by gel permeation chromatography, with number-average molecular weights of 36–47 kDa and polydispersity indices between 1.4 and 2.0 (Table 1). Polymers **P1**-**P3** were soluble in water at concentrations of at least 25 mg/mL, even without dissolution in polar organic solvents before dilution into water.

TABLE 1 Molecular weight distributions and optical properties of polymers **P1**-**P3** in water.

Polymer	Mn (PDI)	λ_{max} (0,0)	Φ_F
P1	36 kDa (1.5)	397 nm	0.75
P2	47 kDa (2.0)	496 nm	0.52
P3	41 kDa (1.4)	554 nm	0.44

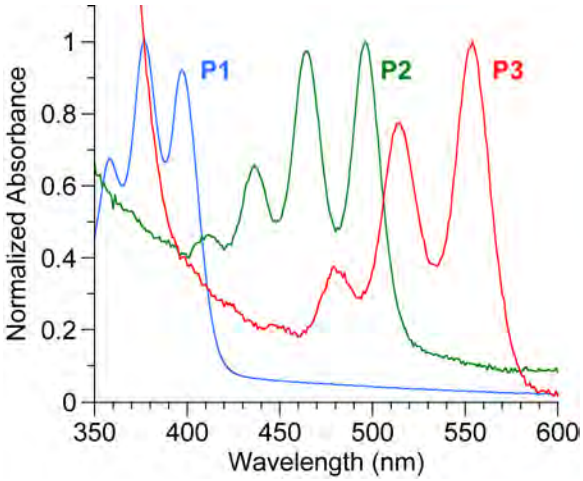


Figure 1. Height-normalized absorbance spectra of acene-substituted POEGMA polymers **P1**-**P3** in water.

We characterized each acene-containing polymer by electronic absorbance spectrophotometry and fluorescence spectroscopy in H_2O (Figures 1 and 2). These spectra are consistent with those known for linear acenes, having intense absorbance in the ultraviolet and a lower energy band with vibronic resolution. The TMT-based long wavelength absorbance band between 475 and 575 nm is the furthest red-shifted of the three. The emission spectra of all molecules follows a similar pattern to that found in absorbance, with **P3** red-shifted by 62 nm from **P2,** and **P2** red-shifted by 85 nm from **P1**. The spectral positions of absorbance and fluorescence bands in the visible portion of the spectrum for all three of these polymers in water are nearly identical to those reported for similarly substituted, small molecule acenes in organic solvent.[24] In addition, polymers **P1**-**P3** are fluorescent with quantum yields of greater than 0.4 (Table 1). These observations indicate that attachment of these hydrophobic acenes to the POEGMA backbone minimizes their aggregation in water.

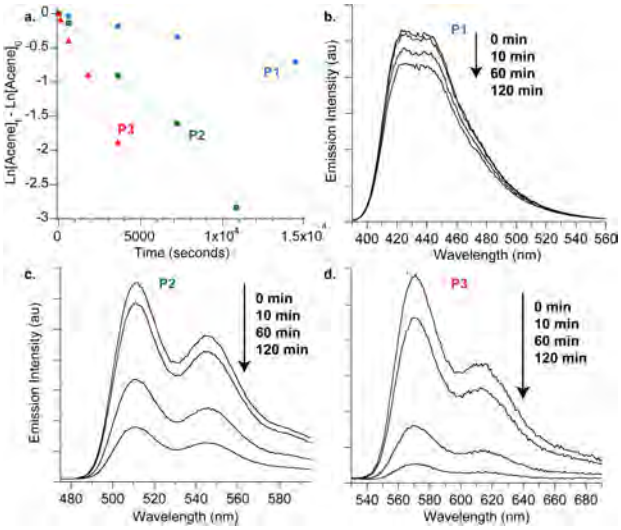


Figure 2. Demonstrations of the relative reactivity of acene pendants of **P1**, **P2**, and **P3**: a) Comparison of pseudo first-order rates of disappearance of acenes bound to **P1**-**P3** upon exposure to $^1O_2$ in water. b-d) Diminution of fluorescence intensity of **P1**-**P3** under identical conditions.

We next determined the relative rates of reaction of these polymers with $^1O_2$ by monitoring the absorbance and fluorescence of each acene chromophore as a function of irradiation time of the $^1O_2$ sensitizer methylene blue (MB). Figure 2 shows both the comparison in relative rates of reactivity determined by UV/vis spectrophotometry, as well as the diminution of fluorescence intensity of each of these three polymers during exposure to $^1O_2$ under identical irradiation conditions, using a Hg/Xe lamp and a 630 nm long-pass filter. Overall, these polymers reacted with $^1O_2$ more slowly in water than analogous small molecules in organic solvent, which we ascribe to two factors: i) the low solubility of O_2 in water, and ii) the short lifetime (~ 3 μs) of $^1O_2$ in water.[35] Nevertheless, although the differences in observed rates were compressed relative to those observed in organic solvent, the order of reactivities of these polymers was consistent with our previous study of analogous acenes in CH_2Cl_2: the diaryltetracenothiophene polymer **P3** reacted the fastest and the diarylanthracenene polymer **P1** reacted the slowest, with a difference of approximately 10x in their observed rates.

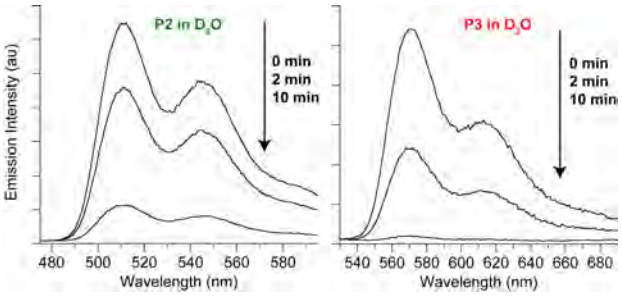


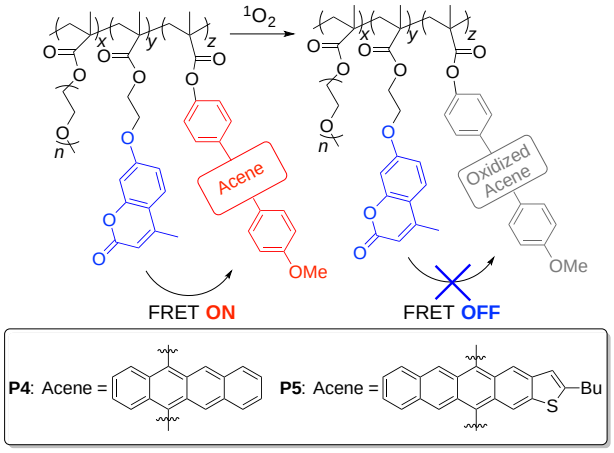
Figure 3. Faster diminution of acene emission intensity of **P2** and **P3** upon exposure to $^1O_2$ in D_2O when compared identical irradiation conditions as used in Figure 2.

A unique characteristic of $^1O_2$ is that its lifetime is approximately ten-fold longer in D_2O than in H_2O, because vibrations of the excited-state O_2 couple more efficiently to O-H bonds than to O-D bonds.[35] To support the role of $^1O_2$ in these observed spectroscopic changes, we compared the rates of acene disappearance upon

irradiation of **MB** in H_2O, as described above, to rates in D_2O. The acene pendants of both **P2** and **P3** (we did not further investigate **P1** in this context because its slow oxidation) oxidized more rapidly in D_2O than in H_2O, as shown in Figure 3. For example, after 10 minutes of irradiation of sensitizer in H_2O, I_0/I for **P2** and **P3** were 1.1 and 1.3, respectively, while identical exposure in D_2O for ten minutes gave I_0/I values of 5.8 and 25.

Chemical probes that show ratiometric responses to target analytes are generally preferable to those that show changes of intensity at only one wavelength.[36] Our previously reported design, using acene-linked conjugated polymers, naturally fits this design, as the conjugated polymer backbones are light-harvesting energy donors while the acene pendants are $^1O_2$-reactive energy acceptors.[28] The methacrylic polymers **P1**-**P3** presented above do not have distinct energy donors and acceptors. We therefore chose to integrate $^1O_2$-inert energy-donating chromophores as additional pendant groups in random copolymers of OEGMA and acene substituted methacrylates (Scheme 2). We prepared these polymers in analogous fashion to polymers **P1**-**P3**, using AIBN as initiator, 15 mole-percent coumarin methacrylate, and 2 mole-percent of monomer **7** (tetracene methacrylate) or **11** (tetracenothiophene methacrylate). The balance of monomer in each polymerization was OEGMA. The resulting isolated polymers **P4** (M_N = 34 kDa, PDI = 1.5) and **P5** (M_N = 37 kDa, PDI = 1.5) had molecular weight distributions similar to **P1**-**P3**. Although both **P4** and **P5** were somewhat soluble in water, the solubility of **P5** was limited to less than 1 mg/mL.

Regardless of their limited solubility in water, these polymers still showed optical spectra that responded to $^1O_2$ as expected. Although both polymers **P4** and **P5** showed evidence of energy transfer from the coumarin pendants to the acenes, the recovery of donor emission upon extended exposure times to $^1O_2$ was smaller (~ 30% of the original intensity) for **P5** (see supporting information) than for **P4** (100-150% of the original intensity). We attribute this observation to better spectral overlap of the fluorescence of coumarin donors (λ_{em} =394 nm) with the absorbance of tetracenes in **P4** than with the tetraceneothiophenes in **P5**. We therefore focused on the performance of **P4** due to its more robust ratiometric fluorescent response to $^1O_2$. Polymers prepared using smaller feed ratios of acene-based monomers (z = 0.01) showed insufficient energy energy transfer for a robust ratiometric response, while higher concentration of acene (where z = 0.05) showed self-quenching of acene fluorescence. Therefore, we performed $^1O_2$ exposure experiments with z=0.02.



Scheme 2. Design of donor-acceptor copolymers **P4** and **P5** for ratiometric fluorescent response to $^1O_2$ in water. In all cases, *x* = 0.83, *y* = 0.15, *z* = 0.02, based on feed ratios of monomers.

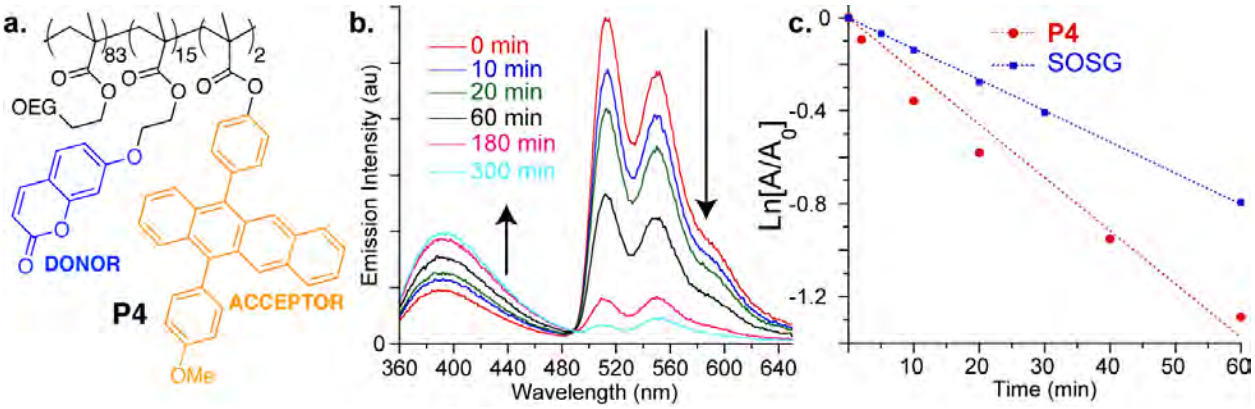


Figure 4. a. Chemical structure of **P4** used in these experiments. b. Ratiometric response of **P4** to selective irradiation of eosin-labeled Neutravidin in water. c. Comparison of rates of oxidation of the acenes in **P4** and Singlet Oxygen Sensor Green (SOSG) under identical conditions.

A number of important applications of photogenerated $^1O_2$ require that sensitizers are bound and kept in close proximity to proteins, including targeted delivery systems for photodynamic therapy and luminescent oxygen channeling assays.[5,11] That proteins can physically and chemically quench $^1O_2$ can present challenges for its productive use in these types of applications.[37] We therefore prepared a conjugate of the biotin-binding protein Neutravidin, which is useful in a variety of *in vitro* bioassay applications due to its reduced non-specific binding and near-neutral isoelectric point, with the brominated xanthene dye eosin, a sensitizer of $^1O_2$ for which an isothiocyanate derivative is commercially available. Selective irradiation of this protein-eosin conjugate in the presence of **P4** gave a ratiometric response of fluorescence, analogous to that observed for **P4** upon irradiation of methylene blue (Figures 4 and S2). The protein-bound eosin yielded oxidation of acenes in these polymers that was 3-10 fold slower than irradiation of solvated methylene blue, which we attribute at least in part to a combination of quenching of both sensitizer excited states and $^1O_2$ by readily oxidized amino acid residues. Interestingly, attempts to oxidize **P4** using a similar methylene blue-Neutravidin conjugate failed to yield significant oxidation, which we suspect may be due to efficient quenching of the methylene blue excited state by the covalently bound protein.

In addition to this fluorescence response, we also monitored tetracene oxidation as a function of irradiation time of this eosin-labelled protein using absorbance spectrophotometery. The rate of acene oxidation of **P4** compared favorably to that observed for the commercially available Singlet Oxygen Sensor Green (SOSG), in which an alkylated anthracene moiety reacts with $^1O_2$, under identical irradiation conditions (Figure 4c). This comparison highlights the potential utility of endoperoxidation of acenes with more than three fused aromatic rings in $^1O_2$-responsive luminescent materials.

CONCLUSIONS

The use of long, hydrophobic acenes for fluorophores that respond to $^1O_2$ holds promise due to the rapid rates of oxidation and the potential for ratiometric fluorescent responses. This work demonstrates the potential for harnessing these features in aqueous environments as pendants of water-soluble OEGMA-based polymers. Our overall synthetic approach is applicable for preparing water-soluble counterparts of highly hydrophobic fluorescent molecules. A key disadvantage of our approach is the low density of chromophores, which slows energy transfer and limits the range of ratiometric responses available using this design. Current work in our

laboratory is focusing on maintaining a high chromophore density in water for maximally sensitive $^1O_2$-responsive aqueous materials.

ACKNOWLEDGEMENTS

The authors thank the National Science Foundation (CHE-1305832) for generous funding of this work.

REFERENCES AND NOTES

1. R. Schmidt. *Photochem. Photobiol.* **2006**, *82*, 1161-1177.
2. F. Wilkinson, W. P. Helman, A. B. Ross. *J. Phys. Chem. Ref. Data* **1993**, *22*, 113-262.
3. P. R. Ogilby. *Chem. Soc. Rev.* **2010**, *39*, 3181-3209.
4. P. R. Ogilby. *Photochem. Photobiol. Sci.* **2010**, *9*, 1543-1560.
5. D. E. J. G. J. Dolmans, D. Fukumura, R. K. Jain. *Nat. Rev. Cancer* **2003**, *3*, 380-387.
6. S. S. Lucky, K. C. Soo, Y. Zhang. *Chem. Rev.* **2015**, *115*, 1990-2042.
7. M. Rac, M. Krupka, S. Binder, M. Sedlarova, Z. Matuskova, M. Raska, P. Pospisil. *PLOS One* **2015**, *10*.
8. J. Terao, Y. Minami, N. Bando. *J. Clin. Biochem. Nutrition* **2011**, *48*, 57-62.
9. C. Triantaphylides, M. Havaux. *Trends Plant Sci.* **2009**, *14*, 219-228.
10. B. B. Fischer, E. Hideg, A. Krieger-Liszkay. *Antioxid. Redox Signal* **2013**, *18*, 2145-2162.
11. F. Poulsen, K. B. Jensen. *J. Biomolec. Screen.* **2007**, *12*, 240-247.
12. E. F. Ullman, H. Kirakossian, S. Singh, Z. P. Wu, B. R. Irvin, J. S. Pease, A. C. Switchenko, J. D. Irvine, A. Dafforn, C. N. Skold, D. B. Wagner. *Proc. Nat. Acad. Sci. USA* **1994**, *91*, 5426-5430.
13. J. W. Snyder, E. Skovsen, J. D. C. Lambert, L. Poulsen, P. R. Ogilby. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4280-4293.
14. J. W. Snyder, I. Zebger, Z. Gao, L. Poulsen, P. K. Frederiksen, E. Skovsen, S. P. McIlroy, M. Klinger, L. K. Andersen, P. R. Ogilby. *Acc. Chem. Res.* **2004**, *37*, 894-901.
15. M. K. Kuimova, G. Yahioglu, P. R. Ogilby. *J. Am. Chem. Soc.* **2009**, *131*, 332-340.
16. M. T. Jarvi, M. J. Niedre, M. S. Patterson, B. C. Wilson. *Photochem. Photobiol.* **2006**, *82*, 1198-1210.
17. Y. You, W. Nam. *Chem. Sci.* **2014**, *5*, 4123-4135.
18. K. Tanaka, T. Miura, N. Umezawa, Y. Urano, K. Kikuchi, T. Higuchi, T. Nagano. *J. Am. Chem. Soc.* **2001**, *123*, 2530-2536.
19. N. Umezawa, K. Tanaka, Y. Urano, K. Kikuchi, T. Higuchi, T. Nagano. *Angew. Chem. Int. Ed.* **1999**, *38*, 2899-2901.
20. S. K. Pedersen, J. Holmehave, F. H. Blaikie, A. Gollmer, T. Breitenbach, H. H. Jensen, P. R. Ogilby. *J. Org. Chem.* **2014**, *79*, 3079-3087.
21. S. Kim, T. Tachikawa, M. Fujitsuka, T. Majima. *J. Am. Chem. Soc.* **2014**, *136*, 11707-11715.
22. S. Kim, M. Fujitsuka, T. Majima. *J. Phys. Chem. B* **2013**, *117*, 13985-13992.
23. S. W. Thomas, E. Altinok, J. Zhang. *Synlett* **2016**, *27*, 355-368.
24. J. J. Zhang, Z. C. Smith, S. W. Thomas. *J. Org. Chem.* **2014**, *79*, 10081-10093.
25. W. Fudickar, T. Linker. *J. Am. Chem. Soc.* **2012**, *134*, 15071-15082.
26. E. Altinok, Z. C. Smith, S. W. Thomas. *Macromolecules* **2015**, *48*, 6825-6831.
27. D. Koylu, S. Sarrafpour, J. Zhang, S. Ramjattan, M. J. Panzer, S. W. Thomas. *Chem. Commun.* **2012**, *48*, 9489-9491.
28. J. J. Zhang, S. Sarrafpour, R. H. Pawle, S. W. Thomas. *Chem. Commun.* **2011**, *47*, 3445-3447.
29. D. Song, S. Cho, Y. Han, Y. You, W. Nam. *Org. Lett.* **2013**, *15*, 3582-3585.
30. W. Fudickar, T. Linker. *Chem. Commun.* **2008**, 1771-1773.
31. J. G. Laquindanum, H. E. Katz, A. J. Lovinger. *J. Am. Chem. Soc.* **1998**, *120*, 664-672.
32. Z. H. Chen, J. P. Amara, S. W. Thomas, T. M. Swager. *Macromolecules* **2006**, *39*, 3202-3209.
33. J. Q. Jiang, B. Qi, M. Lepage, Y. Zhao. *Macromolecules* **2007**, *40*, 790-792.
34. F. Valiyev, W. S. Hu, H. Y. Chen, M. Y. Kuo, I. Chao, Y. T. Tao. *Chem. Mater.* **2007**, *19*, 3018-3026.
35. N. J. Turro, V. Ramamurthy, J. C. Scaiano. Modern Molecular Photochemistry of Organic

Molecules; University Science Books: Sausalito, CA, **2010**.
36. M. H. Lee, J. S. Kim, J. L. Sessler. *Chem. Soc. Rev.* **2015**, *44*, 4185-4191.
37. M. J. Davies. *Biochem. Biophys. Res. Commun.* **2003**, *305*, 761-770.

GRAPHICAL ABSTRACT

Esra Altinok, Fanny Frausto and Samuel W. Thomas III

WATER-SOLUBLE FLUORESCENT POLYMERS THAT RESPOND TO SINGLET OXYGEN

Hydrophobic acenes of 3-5 fused aromatic rings, made water soluble by grafting onto POEGMA polymers, retain strong photoluminescence and reactivity with singlet oxygen ($^1O_2$). Combining these acenes with light harvesting, energy-donating coumarin methacrylate comonomers yields ratiometric responses to $^1O_2$ in water with reaction rates that compare favorably to a commercial $^1O_2$-responsive dye.