ELECTRONIC SUPPLEMENTARY INFORMATION FOR:

UV-Induced Fluorescence Recovery and Solubility Modulation of Photocaged Conjugated Oligomers

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General Considerations

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 $CHCl_3$). 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. All reactants and solvents were purchased from commercial suppliers and used without further purification, unless otherwise noted.

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 OD. Fluorescence quantum yields were determined relative to Coumarin 6 in ethanol. Fluorescence lifetime of **3** was measured using frequency modulation using a Horiba-Jobin-Yvon MF2 lifetime spectrometer equipped with a 365 nm laser diode and using the modulation of POPOP as a calibration for reference. Irradiations of samples to cleave nitrobenzyl ester groups were performed with a 200W Hg/Xe lamp (Newport-Oriel) equipped with a condensing lens, recirculating water filter, manual shutter, either a 365 nm interference filter (Semrock) or 295 nm long-pass filter (Newport), and a focusing lens in the light path.

Synthesis and Characterization

General procedure for diiodides (6a, 6b): A reaction vessel was charged with 1.0 equivalents 2,5-bis(chloromethyl)1,4-dimethoxybenzene or 2,5-bis(chloromethyl)1,4-dioctyloxybenzene. The vessel was evacuated and refilled with argon gas three times. Under argon flow, 2.7 equivalents triethylphosphite were added. The mixture was heated to 150 °C and stirred overnight, cooled to room temperature and re-dissolved in dichloromethane and washed with brine. The brine was extracted with dichloromethane, the organic layers were combined, and washed again with brine. The organic layer was dried with magnesium sulfate and the solvent was removed *in vacuo* and purified as detailed below, yielding the diphosphonates, each as a white solid. The product (2,5-bis(diethylphosphonate) 1,4-dimethoxybenzene or 2,5-bis(diethylphosphonate) 1,4-dioctyloxybenzene) was added to a round bottom flask with 2 equivalents 4-iodobenzaldehyde. The flask was evacuated and refilled with argon three times. Dry THF was added to the vessel via cannula transfer, yielding a 0.13 M solution. 2 equivalents KOH (as a 1.0 M solution in THF) were added dropwise as the reaction mixture stirred. The reaction stirred at room temperature overnight, the mixture was filtered through a medium glass frit and the supernatant was dried *in vacuo*. The crude product was purified as detailed below yielding **6a** or **6b** as a yellow powder.

General DCC-mediated esterification procedure (9, 11, 18): A round bottom flask was flame-dried and charged with 1.0 equivalents **6**, 4-iodobenzoic acid, or **17**, 1.0 mol equivalents *o*-nitrobenzyl alcohol (NBA) or 2-nitro 4,5-dimethoxy benzyl alcohol (OMeNBA), and 0.1 mol equivalents *N,N*-dimethylaminopyridine (DMAP) and evacuated and refilled with argon three times. Anhydrous dichloromethane was added via cannula transfer yielding a 0.04 M solution of the acid. 1.5 equivalents dicyclohexylcarbodiimide (DCC) were added to the reaction mixture under argon flow with stirring. The reaction mixture was refluxed at 40 °C overnight with stirring, the mixture was cooled to room temperature, filtered through a medium glass frit, and washed successively with 10% aqueous HCl, 10% aqueous $NaHCO_3$, and brine. Drying over with $MgSO_4$ and removal of solvent *in vacuo* gave the crude products **9, 11** or **18**, which were purified by flash chromatography.

General Sonogashira coupling procedure with TMSA (methyl 4-(trimethylsilyl)ethynyl benzoate, 10, 15): A round bottom flask was charged with 1.0 equivalents methyl 4-iodobenzoate, **9**, or **14**, 0.01 equivalents $Pd(PPh_3)_2Cl_2$, 0.01 equivalents PPh_3 and 0.02 equivalents CuI. The flask was evacuated and refilled with argon three times. Triethylamine, deoxygenated by sparging with argon at least 15 minutes prior to use, was added via cannula transfer to the flask. While stirring, 1.1 equivalents of trimethylsilylacetylene (TMSA) were added dropwise to the flask. The reaction was stirred at least 3 hours at room temperature. The solvent was removed *in vacuo*, and the crude product, methyl 4-(trimethylsilyl)ethynyl benzoate, **10**, or **15**, was purified by flash chromatography.

General Sonogashira procedure for PEPV analogs (1, 1Q, 1OMeQ, 3, 3Q, 4, 5): A round bottom flask was charged with 2.2 equivalents alkyne **8**, **9**, **12**, **16**, **18**, 4-ethynyl benzonitrile or 2-ethynyl thiophene, 1.0 equivalent diiodide **6a** or **6b**, 0.03 equivalents $Pd(PPh_3)_4$, and 0.09 equivalents CuI. 1:1 THF:NEt_3 (v/v, deoxygenated with at least 15 minutes of argon sparging) was added via cannula transfer, yielding a 0.005 M solution of diiodide **6a** or **6b**. The reaction was stirred overnight at 55 °C. The crude products were isolated and purified by flash chromatography followed by recrystallization, yielding product **1**, **1Q**, **1OMeQ**, **3**, **3Q**, **4**, or **5**.

***para*-dimethoxyphenylene diiodide (6a)**: A 25 mL Schlenk tube was charged with 0.50 g (2.2 mmol) 2,5-bis(chloromethyl)1,4-dimethoxybenzene and reacted with 1.0 mL (5.8 mmol) triethylphosphite according to the general procedure and washed three times with hexanes and dried *in vacuo* yielding 0.58 g (62%) of **2,5-bis(diethylphosphonate) 1,4-dimethoxybenzene**. ^{1}HNMR ($CDCl_3$, 500 MHz): 6.93 (s, 2H), 4.05-4.03 (t, J=7.5 Hz, 8H), 3.81 (s, 6H), 3.26-3.22 (d, J=20 Hz, 4H), 1.27-1.24 (t, J=7.0 Hz, 12H). ^{13}CNMR ($CDCl_3$, 125 MHz): 151.0, 119.5, 114.1, 61.9, 56.1, 27.0, 25.9, 16.3. NMR spectra agreed with the same compound reported by Eldo *et al.*[1] Then, a 100 mL round bottom flask was charged with 220 mg (0.5 mmol) of the diphosphonate and 230 mg of 4-iodobenzaldehyde. 40 mL of THF was added, and the mixture was reacted with 1.0 mL of 1.0 M (1.0 mmol) potassium *tert*-butoxide in THF according to the general procedure. The crude product was purified by recrystallization from $CHCl_3$/hexanes, yielding 200 mg **6a** (77%) as a yellow powder. ^{1}HNMR ($CDCl_3$, 300 MHz): 7.70-7.67 (d, J=8.5 Hz, 4H), 7.51-7.46 (d, J= 16.5, 2H), 7.31-7.28 (d, J=8.5 Hz, 4H), 7.12 (s, 2H) 7.07-7.02 (d, J=16.5 Hz, 2H) 3.93 (s, 6H). ^{13}CNMR ($CDCl_3$, 125 MHz): 151.6, 137.7, 137.4, 128.3, 128.0, 126.5, 124.0, 109.2, 92.6, 56.3. HRMS calcd for $C_{24}H_{20}I_2O_2$ $(M+H)^+$, 594.9625, found, 594.9606.

***para*-dioctyloxyphenylene diiodide (6b):** A 25 mL round bottom flask was charged with 1.06 g (2.32 mmol) 2,5-bis(chloromethyl)-1,4-dioctyloxybenzene and reacted with 3.0 mL (17 mmol) triethylphosphite according to the general procedure, yielding a colorless oil. The oil was dissolved in hexanes and immediately cooled to -78 °C, precipitating a white solid which was filtered, washed with cold hexanes and dried *in vacuo* yielding 1.27 g (86%) of **2,5-bis(diethylphosphonate) 1,4-dioctyloxybenzene**. ^{1}HNMR ($CDCl_3$, 500 MHz): 6.91(s, 2H) 4.03-4.02 (t, J=7 Hz, 8H) 3.93-3.90 (t, J=6 Hz, 4H) 3.24-3.00 (d, J=20 Hz, 4H), 1.77-1.74 (q, J=7 Hz, 4H), 1.44-1.22 (m, 32H), 0.89-0.87 (m, 6H).

^{13}CNMR ($CDCl_3$, 125 MHz): 150.4, 119.5, 115.0, 69.1, 61.8, 31.8, 29.5, 29.4, 29.2, 26.8-25.7 (d, J=140 Hz), 26.1, 22.6, 16.4, 14.1. NMR spectra showed good agreement with the same compound reported by Detert *et al.*[2] Next, a 250 mL three neck round bottom flask was charged with 635 mg (1.5 mmol) of the octyloxy-diphosphonate and 700 mg (3.0 mmol) 4-iodobenzaldehyde. 50 mL of THF was added, and the mixture was reacted with 3.0 mL of 1.0 M (3.0 mmol) potassium *tert*-butoxide in THF according to the general procedure. The crude product was purified by recrystallization from CH_2Cl_2/hexanes, yielding 950 mg **6b** (79%) as a yellow powder. ^{1}HNMR ($CDCl_3$, 300 MHz): 7.70-7.67 (d, J=8 Hz, 4H) 7.50-7.44 (d, J=16.5 Hz, 2H), 7.28-7.26 (d, J=8 Hz, 4H) 7.10 (s, 2H), 7.09-7.03 (d, J=16.5 Hz, 2H) 4.07-4.03 (t, J=6.5 Hz, 4H), 1.92-1.83 (q, J=7.0 Hz, 4 H), 1.59-1.31 (m, 20H), 0.90-0.87 (m, 6H). ^{13}CNMR ($CDCl_3$, 125 MHz): 151.2, 137.7, 137.5, 128.2, 127.8, 126.8, 124.4, 110.8, 92.5, 69.6, 31.8, 29.5, 29.4, 29.3, 26.3, 22.7, 14.1. HRMS calcd for $C_{38}H_{48}I_2O_2$ $(M+H)^+$, 791.1816, found, 791.1796.

4-ethynylbenzoic acid (7): A 100 mL round bottom flask was charged with 1.57 g (6.0 mmol) methyl 4-iodobenzoate, 40 mg (0.06 mmol) $Pd(PPh_3)_4$, 20 mg (0.12 mmol PPh_3) and 16 mg (0.06 mmol) CuI in 45 mL triethylamine and reacted according to the general procedure. Flash chromatography was carried out on silica gel with 1:1 hexanes:dichloromethane eluent, yielding 1.14 g of **methyl 4-(trimethylsilylethynyl)benzoate** (82%) as an orange powder. ^{1}HNMR ($CDCl_3$, 500 MHz): 7.98-7.96 (d, J=8 Hz, 2H), 7.53-7.51 (d, J=8.5 Hz, 2H), 3.91 (s, 3H), 0.27 (s, 9H). ^{13}CNMR ($CDCl_3$, 125 MHz): 166.5, 131.9, 129.7, 129.4, 127.8, 104.1, 97.7, 52.2, -0.18. NMR spectra showed good agreement with the same compound reported by Li *et al.*[3] Next, a 50 mL round bottom flask was charged with 1.10 g (4.75 mmol) of methyl 4-(trimethylsilylethynyl)benzoate, evacuated and refilled with argon three times, and dissolved in 20 mL of THF. 10 mL of 2M KOH in methanol was added to the solution, and the solution was stirred overnight at room temperature, forming a white precipitate. Water was added until the precipitate was dissolved. The mixture was washed with ether, then 5% aqueous HCl was added until a white precipitate formed. The precipitate was extracted with ether (3x30 mL). The ether extract was washed with deionized water (2x25 mL) and brine (1x25 mL), dried with magnesium sulfate, and the solvent was removed *in vacuo*, producing 570 mg of **7** (82%) as a white solid (turns orange upon standing under ambient conditions). ^{1}HNMR ($CDCl_3$, 500 MHz): 8.08-8.07 (d, J=8.5 Hz, 2H), 7.61-7.60 (d, J=8 Hz, 2H), 3.27 (s, 1H). ^{13}CNMR (CD_3COOD, 75 MHz): 170.2, 132.0, 129.9, 129.4, 127.6, 82.4, 80.7. NMR spectra showed good agreement with the same compound reported by Louzao *et al.*[4]

Butyl 4-ethynylbenzoate (8): A 25 mL round bottom flask was charged with 50 mg (0.34 mmol) **7** and 7 mg (0.09 mmol) *para*-toluene sulfonic acid monohydrate (PTSA). The flask was evacuated and refilled with argon three times. 10 mL 1-butanol was added to the flask, and the reaction stirred at 50 °C for 16.5 hours. At that time, an additional 0.08 mmol PTSA was added and the temperature was increased to 80 °C, and the reaction was stirred an additional 24 hours. The mixture was cooled to room temperature, dissolved in dichloromethane (20 mL), washed with aqueous sodium bicarbonate (1x50 mL), washed with deionized water (2x50 mL), and washed with brine (1x50 mL), dried with magnesium sulfate, and the solvent was removed *in vacuo*. The resulting dark red oil was purified by flash chromatography on silica using 3:1 hexanes:dichloromethane as eluent, yielding 45 mg of **8** (74%) a dark yellow oil. ^{1}HNMR ($CDCl_3$, 500 MHz): 8.01-8.00 (d, J=8 Hz. 2H) 7.56-7.55 (d, J=8 Hz, 2H), 4.35-4.32 (t, J=6.5 Hz, 2 H), 3.23 (s, 1H), 1.78-1.75 (q, J=7.0 Hz, 2H) 1.51-1.46 (q, J=7.5 Hz, 2H) 1.01-0.98 (t, J=7.5 Hz, 3H). ^{13}CNMR ($CDCl_3$, 125 MHz): 166.0, 132.0, 130.6, 129.4, 126.6, 82.9, 79.9, 65.1, 30.8, 19.3, 13.7. HRMS calcd for $C_{13}H_{14}O_2$ $(M-H)^-$, 201.0921, found, 201.0926.

2'-nitrobenzyl 4-ethynylbenzoate (9): 350 mg **6**, 29 mg DMAP, 404 mg NBA, and 742 mg DCC in 5 mL dichloromethane were reacted in a 25 mL round bottom flask according to the general procedure. The aqueous workup was 1x50 mL 10% HCl, 1x50 mL saturated $NaHCO_3$, 2x50 mL DI water and 1x25 mL brine. Flash chromatography was carried out on silica with 1:2 hexanes:dichloromethane as eluent, yielding 314 mg **9** (47%) as a white powder. ^{1}HNMR ($CDCl_3$, 500 MHz): 8.16-8.15 (d, J=8.5 Hz, 1H), 8.06-8.05 (d, J=8.5 Hz, 2H), 7.68-7.67 (m, 2H), 7.60-7.58 (d, J=8.5 Hz, 2H), 7.53 (m, 1H) 5.79 (s, 2H), 3.26 (s, 1H). ^{13}CNMR ($CDCl_3$, 75 MHz): 165.3, 147.7, 133.8, 132.2, 132.1, 129.6, 129.5, 129.0, 128.9, 127.3, 125.2, 82.7, 80.4, 63.6. HRMS calcd for $C_{16}H_{11}NO_4$ $(M+NH_4)^+$, 299.1026, found, 299.1031.

4',5'-dimethoxy 2'-nitrobenzyl 4-iodobenzoate (10): 838 mg (3.4 mmol) 4-iodobenzoic acid, 793 mg (3.7 mmol) OMeNBA, 41 mg (0.34 mmol) DMAP, and 1.04 g DCC were dissolved in 45 mL dichloromethane in a 250 mL round bottom flask and reacted according to the general procedure. The aqueous workup was 1x50 mL 10% HCl, extracted from aqueous layer with dichloromethane (2x50 mL), followed by washing the combined organic layers with 1x50 mL 5% $NaHCO_3$, 2x50 mL DI water and 1x50 mL brine. Flash chromatography was carried out on silica gel with dichloromethane as eluent, yielding 940 mg **10** (63%) as a pale yellow powder. ^{1}HNMR ($CDCl_3$, 500 MHz): 7.85-7.78 (m, 4H), 7.75 (s, 1H), 7.05 (s, 1H), 5.75 (s, 2H), 3.97 (s, 3H), 3.94 (s, 3H). ^{13}CNMR ($CDCl_3$, 125 MHz): 165.5, 153.5, 148.5, 140.3, 138, 131.1, 129.2, 126.7, 110.8, 108.4, 101.2, 63.9, 56.5, 56.4. HRMS calcd for $C_{16}H_{14}INO_6$ $(M+NH_4)^+$, 461.0204, found, 461.0208.

4',5'-dimethoxy 2'-nitrobenzyl 4-trimethylsilylethynylbenzoate (11): 536 mg (1.2 mmol) **10**, 184 µL (1.3 mmol) TMSA, 8 mg (0.01 mmol) $Pd(PPh_3)_2Cl_2$, 3 mg (0.01 mmol) CuI and 5 mg (0.02 mmol) PPh_3 were dissolved in 50 mL NEt_3 in a 100 mL round bottom flask and reacted according to the general procedure, with the following exception: at 3 hours reaction time, crude ^{1}HNMR showed an incomplete reaction, so TMSA, $Pd(PPh_3)_2Cl_2$,PPh_3 and CuI were added to the reaction vessel in their initial amounts and the reaction was heated to 35 °C for an additional 4.5 hours, at which point the solvent was removed i*n vacuo* and the crude product purified by flash chromatography on silica with dichloromethane as eluent yielding 456 mg **11** (91%) as a white powder. ^{1}HNMR ($CDCl_3$, 500 MHz): 8.04-8.02 (d, J=8 Hz, 2H), 7.76 (s, 1H), 7.56-7.54 (d, J=8 Hz, 2H), 7.07 (s, 1H), 5.77 (s, 2H), 3.98 (s, 3H), 3.93 (s, 3H) 0.27 (s, 9H). ^{13}CNMR ($CDCl_3$, 125 MHz): 165.4, 153.5, 148.4, 140.2, 132.1, 129.5, 129.2, 128.3, 127.0, 110.6, 108.4, 103.9, 98.3, 63.8, 56.5, 56.4, -0.18. HRMS calcd for $C_{21}H_{23}NO_6Si$ $(M+H)^+$, 414.1367, found, 414.1367.

4',5'-dimethoxy 2'-nitrobenzyl 4-ethynylbenzoate (12): A 100 mL round bottom flask was flame-dried and charged with 250 mg (0.6 mmol) **10** and evacuated and refilled with argon three times. 8 mL anhydrous THF was added via cannula transfer and the reaction was cooled to -15 °C. 620 µL 1.0 M (0.62 mmol) tetrabutylammonium fluoride (TBAF) in THF was added to the solution dropwise, resulting in an immediate solution color change from orange to dark purple. The reaction was stirred at -15 °C for 0.5 hours and then quenched with 30 mL DI water, turning the solution color from purple to orange. An additional 50 mL DI water was added and the mixture was extracted with dichloromethane (3x75 mL), washed with brine (2x50 mL), and dried with $MgSO_4$. The solvent was removed *in vacuo* yielding 170 mg **12** (83%) as a pale yellow solid, without further purification. ^{1}HNMR ($CDCl_3$, 300 MHz): 8.07-8.04 (d, J=8.5 Hz, 2H), 7.76 (s, 1H), 7.60-7.57 (d, J=8.5 Hz, 2H), 7.07 (s, 1H), 5.78 (s, 2H), 3.98 (s, 3H), 3.95 (s, 3H), 3.27 (s, 1H). ^{13}CNMR ($CDCl_3$, 125 MHz): 165.3, 153.5, 148.5, 140.3, 132.2, 129.7, 129.5, 127.3, 126.8, 110.7, 108.4, 82.6, 80.4, 63.9, 56.5, 56.4. HRMS calcd for $C_{18}H_{15}NO_6$ $(M+H)^+$, 342.0972, found, 342.0990.

Bu-OctPEPV (1): 71 mg (0.40 mmol) **8**, 144 mg **6b**, 6 mg (0.005 mmol) $Pd(PPh_3)_4$ and 3 mg (0.016 mmol) CuI were dissolved in 10 mL 1:1 THF:NEt_3 and reacted according to the general procedure (**8** was dissolved in THF and added dropwise to the solution after the other reactants had dissolved). The crude product was isolated by solvent removal *in vacuo*, and purified by flash chromatography on silica with gradient elution, 1:1 hexanes:dichloromethane to 1:2 hexanes dichloromethane, followed by recrystallization from chloroform/hexanes, yielding 116 mg **1** (68%) as a fluffy, waxy bright red solid. ^{1}HNMR ($CDCl_3$, 300 MHz): 8.06-8.03 (d, J=8.5 Hz, 4 H), 7.62-7.651 (m, 14 H), 7.18-7.13 (d, J=16.5 Hz, 2H), 7.14 (s, 2H), 4.37-4.33 (t, J=6.5 Hz, 4H) 4.10-4.06 (t, J=6.5 Hz, 4H) 1.95-1.85 (q, J=6.5 Hz, 4H), 1.83- 1.73 (q, J=6.5 Hz, 4H) 1.58-1.32 (m, 26H) 1.03-0.98 (t, J=7.5 Hz, 6H), 0.93-0.88 (t, J=7 Hz, 6H) ^{13}CNMR ($CDCl_3$, 125 MHz): 166.1, 151.3, 138.5, 132.1, 131.4, 129.8, 129.5, 128.2, 128.0, 126.9,126.5, 124.8, 121.4, 110.7, 92.7, 89.6, 69.6, 65.0, 31.9, 30.8, 29.5, 29.4, 29.3, 26.3, 22.7, 19.3, 14.1, 13.8. HRMS calcd for $C_{64}H_{74}O_6$ $(M+Na)^+$, 961.5378, found, 961.5358. UV/Vis (dichloromethane) λ_{max}, nm (log ε): 422 (4.91), 349 nm (sh, 4.66).

NBA-OctPEPV (1Q), mono-NBAOctPEPV (13): 100 mg (0.36 mmol) **9**, 157 mg (0.20 mmol) **6b**, 7 mg (0.005 mmol) $Pd(PPh_3)_4$ and 3 mg (0.016 mmol) CuI were dissolved in 70 mL 1:1 THF:NEt_3 and reacted according to the general procedure. The crude product was isolated by solvent removal *in vacuo*. Two products were isolated by flash chromatography with gradient elution: 1:1 hexanes:dichloromethane yielded **13**, then dichloromethane yielded **1Q**. Both products were purified by recrystallization from chloroform/hexanes, yielding 28 mg **13** (74% of predicted based on stoichiometry) as a fluffy, waxy orange solid and 120 mg **1Q** (69% of predicted based on stoichiometry) as a waxy orange solid. **1Q:** ^{1}HNMR ($CDCl_3$, 500 MHz): 8.17-8.15 (d, J=8.5 Hz. 2H) 8.10-8.08 (d, J=8 Hz, 4 H), 7.70-7.69 (m, 4 H), 7.64-7.62 (d, J=8.5 Hz, 4H), 7.55-7.52 (m, 12H) 7.17-7.14 (d, J=16.5 Hz, 2H) 7.14 (s, 2H) 5.81 (s, 4H), 4.09-4.07 (t, J=7 Hz, 4H) 1.93-1.87 (q, J=7 Hz, 4H), 1.60-1.54 (q, J=7 Hz, 4H) 1.43-1.33 (m, 16H), 0.92-0.89 (t, J=7 Hz, 6H) ^{13}CNMR ($CDCl_3$, 125 MHz): 165.4, 151.3, 147.8, 138.6, 133.8, 132.2, 132.1, 131.6, 129.7, 129.1, 128.9, 128.8, 128.7, 128.2, 127.0, 126.5, 125.1, 124.8, 121.3, 110.8, 93.1, 89.5, 69.6, 63.5, 31.8, 29.5, 29.4, 29.3, 26.3, 22.7, 14.1. HRMS calcd for $C_{70}H_{68}N_2O_{10}$ $(M+Na)^+$, 1119.4766, found, 1119.4771. UV/Vis (dichloromethane) λ_{max}, nm (log ε): 424 (4.92), 350 nm (sh, 4.68).
13: ^{1}HNMR ($CDCl_3$, 500 MHz): 8.17-8.15 (d, J=8 Hz. 1H) 8.10-8.08 (d, J=8 Hz, 2 H), 7.69-7.68 (m, 4 H), 7.64-7.62 (d, J=8 Hz, 2H), 7.54-7.46 (m, 7H) 7.17-7.05 (m, Hz, 4H) 5.80 (s, 2H), 4.08-4.05 (t, J=7 Hz, 4H) 1.90-1.88 (q, J=7 Hz, 4H), 1.58-1.43 (q, J=7 Hz, 4H) 1.42-1.32 (m, 16H), 0.91-0.90 (t, J=7 Hz, 6H). ^{13}CNMR ($CDCl_3$, 125 MHz): 165.4, 151.3, 151.2, 147.7, 138.6, 137.7, 137.5, 133.8, 132.2, 132.1, 131.6, 129.7, 129.1, 128.9, 128.8, 128.7, 128.2, 128.1, 127.9, 126.9, 126.8, 126.5, 125.1, 124.8, 124.3, 121.3, 110.8, 93.2, 92.5, 89.5, 69.6, 63.5, 31.8, 29.5, 29.4, 29.3, 26.3, 22.7, 14.1. HRMS calcd for $C_{54}H_{58}INO_6$ $(M+H)^+$, 944.3382, found, 944.3368.

OMeNBA-OctPEPV (1OMeQ): 80 mg (0.23 mmol) **12**, 84 mg (0.11 mmol) **6b**, 4 mg (0.003 mmol) $Pd(PPh_3)_4$ and 2 mg (0.01 mmol) CuI were dissolved in 35 mL 1:1 THF:NEt_3 and reacted according to the general procedure. The crude product was isolated by solvent removal *in vacuo* and purified by flash chromatography with gradient elution, dichloromethane to ethyl acetate, followed by recrystallization from chloroform/hexanes, yielding 52 mg **1OMeQ** (40%) as an orange powder. ^{1}HNMR ($CDCl_3$, 500 MHz): 8.09-8.08 (d, J=8 Hz, 4 H), 7.77 (s, 2H) 7.64-7.62 (d, J=7.5 Hz, 4H), 7.54-7.51 (m, 8H), 7.17-7.09 (m, 6H) 5.79 (s, 4H), 4.09-4.06 (t, J=6.5 Hz, 4H) 3.98 (s, 6H), 3.96 (s, 6H), 1.91-1.88 (q, J=7 Hz, 4H), 1.60-1.52 (m, 4H) 1.43-1.32 (m, 16H), 0.91-0.89 (t, J=7 Hz, 6H). ^{13}CNMR ($CDCl_3$, 125 MHz): 165.5, 153.5, 151.3, 148.5, 140.3, 138.6, 132.1, 131.6, 129.6, 128.9, 128.7, 128.2, 127.0, 126.5, 124.9, 121.3, 110.8, 110.7, 1108.4, 93.2, 89.4, 69.6, 63.8, 56.5, 56.4, 31.8, 29.5, 29.4, 29.3, 26.3, 22.7, 14.1. UV/Vis (dichloromethane) λ_{max}, nm (log ε): 424 (4.90), 349 nm (sh, 4.76).

Methyl 4'-iodo-5-phenoxypentanoate (14): A 250 mL round bottom flask was flame-dried and charged with 2.2 g (10 mmol) 4-iodophenol, 1.66 g (12 mmol) potassium carbonate, 500 mg (3 mmol) potassium iodide and evacuated and refilled with argon three times. 40 mL 2-butanone was added to the flask, and then 2.5 g (12.8 mmol) methyl 5-bromopentanoate, dissolved in 5 mL 2-butanone, was added dropwise. The mixture was stirred overnight at reflux (85 °C), cooled to room temperature, and diluted with 40 mL diethyl ether. The solution was washed with 10% aqueous HCl (1x40 mL), extracted with diethyl ether (3x40 mL), washed with 10% aqueous $NaHCO_3$ (1x40 mL), washed with brine (1x40 mL), dried with $MgSO_4$, filtered, and the diethyl ether was removed *in vacuo*. The crude product **14** was recrystallized from hexanes and washed with cold hexanes yielding 1.61 g (48%) of **14**, a colorless solid. ^{1}HNMR ($CDCl_3$, 300 MHz): 7.56-7.53 (d, J=9 Hz, 2H), 6.68-6.65 (d, J=9 Hz, 2H), 3.95-3.93 (t, J=4 Hz, 2H), 3.68 (s, 3H), 2.42-2.39 (t, J=7 Hz, 2H), 1.85-1.79 (q, J=4 Hz 4H). ^{13}CNMR ($CDCl_3$, 75 MHz): 174.0, 159.0, 138.4, 117.1, 82.8, 67.7, 51.8, 33.9, 28.8, 21.8. Previously synthesized by Hajduk *et al*.[5] (NMR data not reported)

Methyl 5-(4'-(trimethylsilyl)ethynylphenoxy)pentanoate (15): 668 mg (2.0 mmol) **14**, 14 mg (0.02 mmol) $Pd(PPh_3)_2Cl_2$, 8 mg (0.04 mmol) CuI and 6 mg (0.02 mmol) PPh_3 were combined in a 50 mL round bottom flask, dissolved in NEt_3, and reacted with 310 µL (2.2 mmol) TMSA according to the general procedure. The crude product was isolated by solvent removal *in vacuo*, redissolved in dichloromethane and flushed through a pad of silica gel. The dichloromethane product solution was washed with 5% HCl (1x20 mL), deionized water (1x20 mL), 10% $NaHCO_3$ (1x20 mL) and brine (1x20 mL), dried with $MgSO_4$, and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography on silica, 1:1 hexanes:dichloromethane, yielding 360 mg of **15** (59%) as a white solid. ^{1}HNMR ($CDCl_3$, 300 MHz): 7.40-7.38 (d, J=9 Hz, 2H), 6.82-6.79 (d, J=9 Hz, 2H), 3.97 (m, 2H), 3.68 (s, 3H), 2.41 (m, 2H), 1.83 (m, 4H) 0.24 (s, 9H). ^{13}CNMR ($CDCl_3$, 125 MHz): 173.7, 159.1, 133.4, 115.2, 114.3, 105.3, 92.3, 67.4, 51.5, 33.6, 28.6, 21.6, 0.1. HRMS calcd for $C_{17}H_{24}O_3Si$ $(M+H)^+$, 305.1567, found, 305.1555.

Methyl 5-(4'-ethynylphenoxy)pentanoate (16): A 25 mL round bottom flask was charged with 150 mg (0.49 mmol) **15** and evacuated and refilled with argon three times. The reactant was dissolved in 1.5 mL THF. 0.75 mL (1.47 mmol) 2.0 M KOH in methanol was added to the reaction mixture dropwise with stirring. The mixture was stirred for 0.5 hours at room temperature followed by addition of 20 mL deionized water, turning the mixture cloudy. The crude product was extracted with dichloromethane (3x15 mL). Brine (1x15 mL) was added to separate the emulsion formed in the extraction steps. The extract solution was washed with deionized water (2x20 mL) and saturated aqueous NH_4Cl (1x20 mL), dried with MgSO4, and the solvent was removed *in vacuo* yielding 65 mg **16** (56%), as a white solid, without further purification. ^{1}HNMR ($CDCl_3$, 300 MHz): 7.44-7.41 (d, J=9 Hz, 2H), 6.84-6.81 (d, J=9 Hz, 2H), 3.98 (m, 2H), 3.68 (s, 3H), 3.00 (s, 1H), 2.41 (m, 2H), 1.83 (m, 4H). ^{13}CNMR ($CDCl_3$, 125 MHz): 173.8, 159.3, 133.6, 114.4, 114.1, 83.7, 75.7, 67.4, 51.6, 33.6, 28.6, 21.6. HRMS calcd for $C_{14}H_{16}O_3$ $(M+H)^+$, 233.1172, found, 233.1171.

AlkoxPEPV (3): 35 mg (0.06 mmol) **6a**, 30 mg (0.13 mmol) **16**, 2 mg (2 µmol) $Pd(PPh_3)_4$, 1 mg (5 µmol) CuI were dissolved in 5 mL 1:1 NEt_3:THF in a 50 mL Schlenk tube according to the general procedure. The crude product was isolated by centrifugation and purified by flash chromatography on silica with 4:1 dichloromethane:hexanes eluent followed by recrystallization from chloroform/methanol yielding 18 mg **3** (39%) as a yellow solid. ^{1}HNMR ($CDCl_3$, 300 MHz): 7.53-7.46 (m, 14H), 7.15 (s, 2H), 7.15-7.10 (d, J=15Hz, 2H) 6.89-6.86 (d, J=9 Hz, 4H), 4.01 (m, 4H), 3.95 (s, 6H), 3.69 (s, 6H), 2.42 (m, 4H), 1.85 (m, 8H). ^{13}CNMR ($CDCl_3$, 125 MHz): 173.8, 159.0, 151.6, 137.5, 133.0, 131.7, 128.4, 126.7, 126.5, 123.9, 122.5, 115.4, 114.6, 109.2, 90.4, 88.4, 67.5, 56.4, 51.2, 33.7, 28.6, 21.6. HRMS calcd for $C_{52}H_{50}O_8$ $(M+H)^+$, 803.3578, found, 803.3556. UV/Vis (dichloromethane) λ_{max}, nm (log ε): 418 (4.90), 345 nm (sh, 4.64).

5-(4’-ethynylphenoxy)pentanoic acid (17): A 50 mL three-neck round bottom flask was charged with 100 mg (0.33 mmol) **15** and evacuated and refilled with argon three times. 20 mL (60 mmol) 3M NaOH in 1:1 (v/v) methanol:water was added to the reaction flask and the mixture was refluxed (63 °C) overnight. The mixture was cooled and the crude product was precipitated with 10% aqueous HCl (1x20 mL). The crude product was extracted with diethyl ether, washed with deionized water (2x25 mL), washed with brine (1x25 mL), dried with $MgSO_4$, and the solvent was removed *in vacuo* yielding 68 mg **17** (95%) as a white solid, without further purification. ^{1}HNMR ($CDCl_3$, 300 MHz): 12.2-11.0 (br s, 1H), 7.44-7.41 (d, J=9 Hz, 2H) 6.85-6.82 (d, J=9 Hz, 2H), 3.99 (t, 2H), 2.46 (t, 2H) 1.87-1.84 (m, 4H). ^{13}CNMR ($CDCl_3$, 125 MHz): 179.9, 159.3, 133.6, 114.5, 114.2, 83.7, 75.8, 67.4, 33.6, 28.5, 21.4. HRMS calcd for $C_{13}H_{14}O_3$ $(M+H)^+$, 219.1016, found, 219.1014.

2’’-nitrobenzyl-5-(4’ethynylphenoxy)pentanoate (18): 48 mg (0.22 mmol) **17**, 2.7 mg (0.022 mmol) DMAP, 34 mg (0.22 mmol) 2-nitrobenzyl alcohol and 68 mg (0.33 mmol) DCC were dissolved in dichloromethane in a 25 mL 3-neck round bottom flask and reacted according to the general procedure. After filtration, the crude product was washed with 10% aqueous HCl (1x20 mL), 10% aqueous $NaHCO_3$ (1x20 mL) and brine (1x20 mL). The solution was dried with $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified with flash chromatography on silica with dichloromethane as eluent yielding 36 mg **18** (46%) as a pale yellow solid. ^{1}HNMR ($CDCl_3$, 500 MHz): 8.11-8.10 (d, J=8 Hz, 1H), 7.67-7.63 (t, J=9 Hz, 1H), 7.59-7.58 (d, J=8 Hz, 1H), 7.52-7.49 (t, J=7 Hz, 1H), 7.43-7.41 (d, J=7.5 Hz, 2H), 6.83-6.82 (d, J=8.5 Hz, 2H), 5.52 (s, 2H), 3.99 (m, 2H), 3.00 (s, 1H), 2.51 (m, 2H), 1.86 (m, 4H). ^{13}CNMR ($CDCl_3$, 125 MHz): 172.6, 159.3, 147.8, 133.6, 133.6, 132.0, 129.3, 128.9, 125.1, 114.5, 114.2, 83.7, 75.7, 67.4, 62.9, 33.7, 28.5, 21.6. HRMS calcd for $C_{20}H_{19}NO_5$ $(M+H)^+$, 354.1336, found, 354.1353.

NBA-AlkoxyPEPV (3Q): 40 mg (0.11 mmol) **18**, 30 mg (0.05 mmol) **6a**, 2 mg (0.002 mol) $Pd(PPh_3)_4$, and 1 mg (0.005 mmol) CuI were dissolved in 10 mL 1:1 NEt_3:THF in a 50 mL three neck round bottom flask according to the general procedure. The crude product was isolated by centrifugation and purified by flash chromatography on silica with gradient elution, 1:1 dichloromethane:hexanes to dichloromethane to 3:1 dichloromethane:ethyl acetate, followed by recrystallization from dichloromethane/hexanes, yielding 46 mg **3Q** (86%) as a yellow solid. ^{1}HNMR ($CDCl_3$, 500 MHz): 8.12-8.108 (d, J=8 Hz, 2H), 7.67-7.65 (t, J=7 Hz, 2H), 7.61-7.59 (d, J=8 Hz, 2H), 7.53-7.46 (m, 14H), 7.15 (s, 2H), 715-7.11 (d, 18 Hz, 2H), 6.88-6.86 (d, J=9Hz, 4H), 5.54 (s, 4H), 4.02 (m, 4H), 3.95 (s, 6H), 2.53 (m, 4H), 1.88 (m, 8H). HRMS calcd for $C_{64}H_{56}N_2O_{12}$ $(M+Na)^+$, 1067.3725, found, 1067.3707.

NBA-Bu-OctPEPV (2): 25 mg (0.03 mmol) **13**, 5 mg (0.03 mmol) **8**, 1 mg (0.001 mmol) $Pd(PPh_3)_4$ and <1 mg (<0.002 mmol) CuI were dissolved in 10 mL 1:1 THF:NEt_3 and reacted according to the general procedure (**13** and **8** were dissolved in 1:1 THF:NEt_3 (2x5 mL) and added to Schlenk tube containing $Pd(PPh_3)_4$ and CuI under argon flow). The crude product was isolated by solvent removal *in vacuo* and purified by flash chromatography on silica with 1:2 hexanes: dichloromethane as eluent followed by recrystallization from chloroform/hexanes yielding 23 mg **2** (83%) as an orange solid. ^{1}HNMR ($CDCl_3$, 500 MHz): 8.17-8.16 (d, J=8.5 Hz, 1H) 8.10-8.08 (d, J=8.5 Hz, 2 H), 8.05-8.03 (d, J=8 Hz, 2H), 7.70-7.52 (m, 17 H), 7.17-7.14 (m, 4H) 5.81 (s, 2H), 4.36-4.34 (t, J=7 Hz, 2H) 4.09-4.07 (t, J=6 Hz, 4H) 1.93-1.87 (q, J=7 Hz, 4H), 1.81-1.75 (q, J=7 Hz, 2 H) 1.56-1.32 (m, J=7 Hz, 22H) 1.02-0.99 (t, J=7.5 Hz, 3H), 1.01-0.92 (t, J=7 Hz, 6H) ^{13}CNMR($CDCl_3$, 125 MHz): 166.2, 165.4, 151.3, 147.8, 138.6, 138.4, 133.8, 132.2, 132.1, 131.6, 129.9, 129.7, 129.5, 129.1, 128.9, 128.8, 128.7, 128.2, 128.1, 128.0, 127.0, 126.5, 125.1, 124.9, 124.8, 121.5, 121.3 110.8, 93.1, 92.6, 89.6, 89.5, 69.6, 65.03, 63.5, 31.8, 30.8, 29.5, 29.4, 29.3, 26.3, 22.7, 19.3, 14.1, 13.76. HRMS calcd for $C_{67}H_{71}NO_8$ $(M+Na)^+$, 1040.5072, found, 1040.5068.

Acid-OctPEPV (1Q-hν): 20 mg (0.022 mmol) **1** was added to a 20 mL glass scintillation vial and dispersed into 2 mL MeOH. 10 mL 3M NaOH in 1:1 (v/v) MeOH:H_2O (0.033 mol) was added and the mixture stirred 16 hours. At this point, no reaction had occurred. The mixture was transferred to a 100 mL single neck round bottom flask and 50 mL of THF was added to dissolve the reactants. The mixture was stirred at 40 °C for 3 hours, and the solvent was removed *in vacuo*. The product was sparingly soluble in dichloromethane, so the resulting dispersion was washed with 5% aqueous $NaHCO_3$ (1x40 mL) and the organic layer was removed. The aqueous layer was brought to pH 3 with 10% aqueous HCl and the solid was collected and recrystallized in THF/hexanes yielding 17 mg **1Q-hν** (95%) as a bright yellow solid. ^{1}HNMR (THF-d8, 500 MHz): 8.03-8.01 (d, J=8 Hz, 4H), 7.61-7.52 (m, 14H), 7.29-7.27 (d, J=13.5 Hz, 2H), 7.27 (s, 2H), 4.12-4.09 (t, J=6.0 Hz, 4H), 1.93-1.87 (q, J=7Hz, 4H), 1.60-1.56 (q, J=7 Hz, 4H) 1.47-1.29 (m, 14H), 0.91-0.89 (t, J=6 Hz, 6H) ^{13}CNMR (THF-d8, 125 MHz): 167.2, 152.5, 139.9, 133.0, 132.2, 131.6, 130.7, 129.0, 128.7, 128.0, 127.4, 125.8, 122.6, 111.7, 93.2, 90.5, 70.2, 33.0, 30.6, 30.6, 30.5, 27.4, 23.7, 14.6. HRMS calcd for $C_{56}H_{58}O_6$ $(M-H)^-$, 825.4161, found, 825.4173. UV/Vis (tetrahydrofuran) λ_{max}, nm (log ε): 422 (4.91), 348 nm (sh, 4.65).

Cyano-PEPV (4): A 100 mL round bottom flask was charged with 1.82 g (10 mmol) 4-bromobenzonitrile, 250 mg (0.36 mmol) $PdCl_2(PPh_3)_2$ and 10 mg (0.05 mmol) CuI and evacuated and refilled with Ar three times. The mixture was dissolved in 45 mL NEt_3 and 1.18 g (12 mmol) TMSA was added dropwise and the reaction mixture stirred 18 hours at room temperature. The solution was filtered through a Celite pad and the collected filtrate was concentrated *in vacuo* to produce brown crystals. The crude product was purified by flash chromatography (4:1 hexanes:dichloromethane) yielding 1.19g (60%) **4-[(trimethylsilyl)ethynyl]-benzonitrile** as iridescent white crystals. ^{1}HNMR (300 MHz, $CDCl_3$): δ (ppm) 7.61-7.53 (m, 4 H), 0.30 (s, 9 H). NMR spectrum showed good agreement with the same compound reported by Zhou *et al.*[6] Next, a 50 mL round bottom flask was charged with 700 mg (3.5 mmol) 4-[(trimethylsilyl)ethynyl]-benzonitrile and evacuated and refilled with argon three times. The reactant was dissolved in 10 mL 56 mM (0.56 mmol) Na_2CO_3 in methanol and stirred at room temperature for 16 hours. The solvent was removed *in vacuo* and the subsequent solid was redissolved in dichloromethane and washed with 5% $NaHCO_3$. The aqueous layer was extracted with dichloromethane (3x20mL). The combined organic layers were washed with brine (1x30 mL) and dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude product was purified by recrystallization from dichloromethane/hexanes yielding 306 mg (68%) **4-ethynyl-benzonitrile** as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.65-7.57 (m, 4 H), 3.31 (s, 1 H). NMR spectrum showed good agreement with the same compound reported by Zhou *et al.*[6] Finally, a 50 mL round bottom flask was charged with 18 mg (0.14 mmol) 4-ethynyl benzonitrile, 50 mg (0.06 mmol) **6b,** 2 mg (0.002 mmol) $Pd(PPh_3)_4$ and 1 mg (0.006 mmol) CuI and reacted according to the general procedure, with N,N-diisopropylamine (DIPA) used in place of NEt_3. The solvent was removed *in vacuo* and the crude product redissolved in dichloromethane and washed with 5% aqueous $NaHCO_3$ (1x50 mL). The aqueous layer was extracted with dichloromethane (3x50 mL) and the organic layers were combined and washed with brine (1x50 mL), dried with $MgSO_4$, and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography (1:1 hexanes:dichloromethane) to yield 37 mg **4** (73%) as a yellow/orange solid. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.67-7.61 (m, 8 H), 7.57-7.52 (m, 10 H), 7.16 (d, 4 H, J=14.7 Hz), 4.10-4.06 (t, 4 H, J=6.5 Hz), 1.95-1.86 (m, 4 H), 1.40-1.23 (m, 18 H), 0.90-0.88 (m, 8 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm)= 151.5, 139.1, 132.4, 132.3, 132.2, 128.6, 128.3, 127.2, 126.8, 125.3, 121.1, 118.8, 111.7, 111.0, 94.4, 88.8, 69.8, 32.1, 29.7, 29.6, 29.5, 26.5, 22.9, 14.3. HRMS calcd for $C_{56}H_{56}N_2O_2$ $(M+H)^+$, 789.4415, found, 789.4404. UV/Vis (dichloromethane) λ_{max}, nm (log ε): 425 (4.84), 349 nm (sh, 4.59).

Thiophene-PEPV (5): A 25 mL round bottom flask was charged with 110 mg (0.16 mmol) $PdCl_2[P(C_6H_5)_3]_2$ and 61 mg (0.32 mmol) CuI, evacuated and refilled with Ar three times, and the reactants dissolved in 10 mL 1:1 THF:NEt_3 (v/v, sparged with Ar 30 min). 1.30 g (8 mmol) 2-bromothiophene was added dropwise with stirring, followed by dropwise addition of 1.57 g (16 mmol) TMSA. The solution was heated to 70 °C and stirred 16 hours. Upon cooling to room temperature, diethyl ether was added and the solution was filtered through a Celite pad. The solvent was removed *in vacuo* to produce a dark oil. Flash chromatography on silica gel (hexanes) yielded **2-[(trimethylsilyl)ethynyl]thiophene** as a brown oil. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.25-7.22 (m, 2 H), 6.96-6.93 (m, 1 H), 0.27 (s, 9 H). NMR spectrum showed good agreement with the same compound reported by Sakai *et al.*[7] Then, a 50 mL round bottom flask was charged with 1.00 g (5.5 mmol) 2-[(trimethylsilyl)ethynyl]thiophene), evacuated and refilled with Ar three times, and the reactant dissolved in 10 mL 1.1 M KOH in methanol (11 mmol) and stirred for 18 hours. The reaction mixture was poured into water and extracted with diethyl ether (3x15mL). The combined organic layers were washed with brine (1x30 mL), dried over $MgSO_4$, and concentrated *in vacuo* yielding 170 mg (29%) **2-ethynyl thiophene** as a yellow oil**.** ^1HNMR (300 MHz, $CDCl_3$): δ (ppm) 7.30-7.25 (m, 2 H), 6.99-6.96 (m, 1 H), 3.36 (s, 1 H). NMR spectrum showed good agreement with the same compound reported by Patrick *et al.*[8] Finally, a 50 mL round bottom flask was charged with 75 mg (0.095 mmol) **6b**, 23 mg (0.2 mmol) 2-ethynyl thiophene, 1.6 mg (0.009 mmol) $Pd(PPh_3)_4$, and 3 mg (0.003 mmol) CuI and reacted according to the general procedure, except that NEt_3 was replaced with DIPA, the solvent was sparged with **6b**, $Pd(PPh_3)_4$ and CuI already dissolved, and 2-ethynyl thiophene was added dropwise after sparging. The solvent was removed *in vacuo* and the product was purified by flash chromatography with gradient elution (hexanes to 1:1 dichloromethane:hexanes) yielding 52 mg **5** (73%) as an orange solid. ^1HNMR (300 NMR, $CDCl_3$): δ (ppm) 7.55-7.49 (m, 10 H), 7.32-7.30 (m, 4 H), 7.17-7.12 (m, 4 H), 7.05-7.02 (dd, 2 H, J=4 Hz, J=5 Hz), 4.10-4.05 (t, 4 H, J=6.6 Hz), 1.94-1.85 (m, 4 H), 1.40-1.26 (m, 18 H), 0.93-0.88 (m, 8 H). ^{13}CNMR ($CDCl_3$, 125 MHz): 151.3, 138.1, 131.8, 131.7, 128.2, 127.3, 127.1, 126.4, 124.6, 121.7, 114.7, 110.8, 93.4, 83.5, 69.6, 31.8, 29.5, 29.4, 29.3, 26.3, 22.7, 14.1. HRMS calcd for $C_{50}H_{54}O_2S_2$ $(M+H)^+$, 751.3638, found, 751.3646. UV/Vis (dichloromethane) λ_{max}, nm (log ε): 421 (4.88), 350 nm (sh, 4.63).

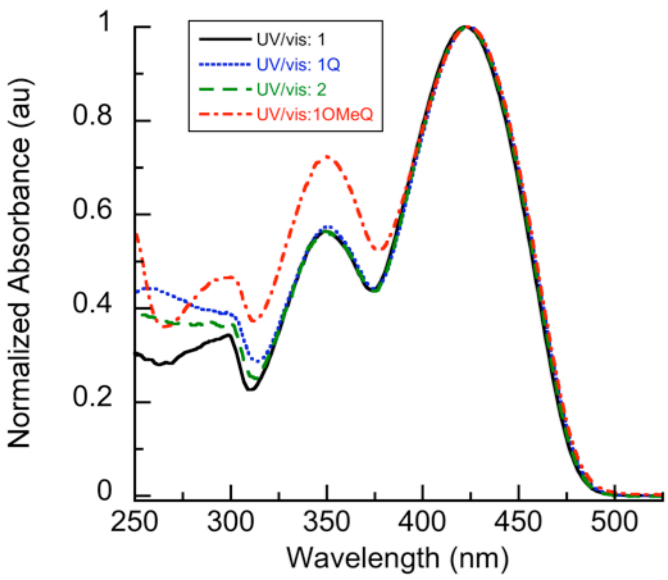

Figure S1. Normalized absorbance spectra of **1**, **1Q**, **1OMeQ**, and **2**, highlighting the increased absorbance of the dimethoxynitrobenzyl esters up to 390 nm.

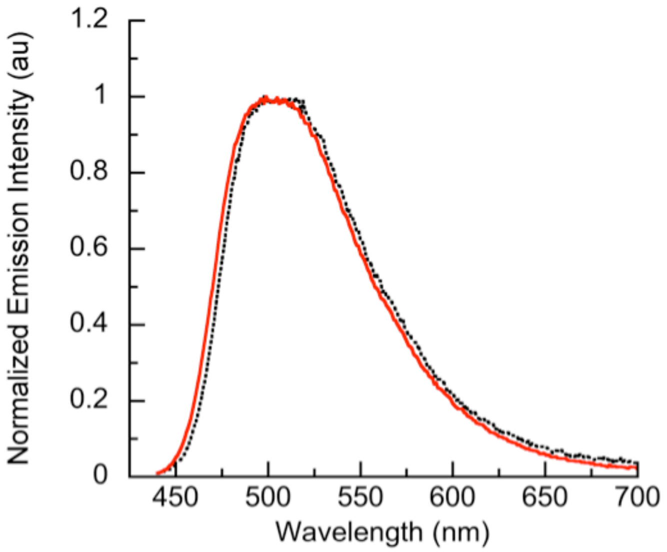

Figure S2. Normalized emission spectra of **2** before and after UV irradiation ($\lambda > 295$ nm) in acetonitrile.

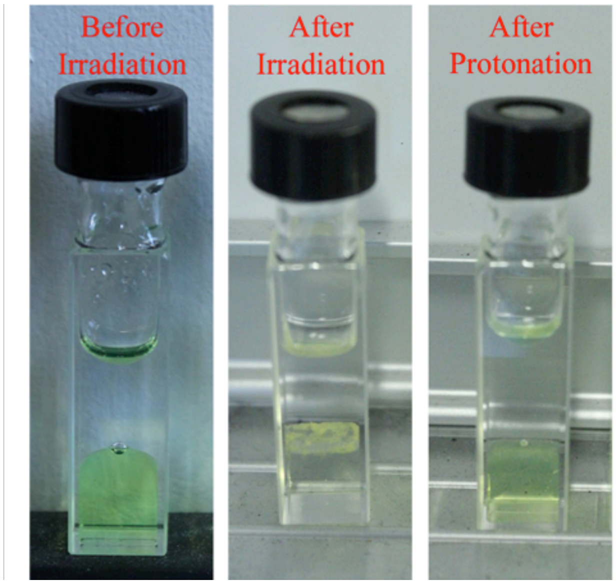

Figure S3. Solubility change of **1Q** upon UV irradiation ($\lambda > 295$ nm). *Left:* Diester is soluble in CH_2Cl_2 before irradiation; top layer is 0.1 M NaOH (aq). *Middle*: Upon 11 min. of irradiation, the resulting dicarboxylate is insoluble in both layers, and precipitates at the interface. *Right:* The diacid dissolves in CH_2Cl_2 upon acidification of the aqueous layer.

References:

(1) Eldo, J.; Ajayaghosh, A. *Chemistry of Materials* **2001**, *14*, 410.
(2) Detert, H.; Schollmeyer, D.; Sugiono, E. *European Journal of Organic Chemistry* **2001**, *2001*, 2927.
(3) Li, Q.; Rukavishnikov, A. V.; Petukhov, P. A.; Zaikova, T. O.; Jin, C.; Keana, J. F. W. *The Journal of Organic Chemistry* **2003**, *68*, 4862.
(4) Louzao, I.; Seco, J. M.; Quiñoá, E.; Riguera, R. *Angewandte Chemie International Edition* **2010**, *49*, 1430.
(5) Hajduk, P. J.; Sheppard, G.; Nettesheim, D. G.; Olejniczak, E. T.; Shuker, S. B.; Meadows, R. P.; Steinman, D. H.; Carrera, G. M.; Marcotte, P. A.; Severin, J.; Walter, K.; Smith, H.; Gubbins, E.; Simmer, R.; Holzman, T. F.; Morgan, D. W.; Davidsen, S. K.; Summers, J. B.; Fesik, S. W. *Journal of the American Chemical Society* **1997**, *119*, 5818.
(6) Zhou, N.; Wang, L.; Thompson, D. W.; Zhao, Y. *Tetrahedron* **2011**, *67*, 125.
(7) Sakai, N.; Komatsu, R.; Uchida, N.; Ikeda, R.; Konakahara, T. *Organic Letters* **2010**, *12*, 1300.
(8) Patrick, T. B.; Disher, J. M.; Probst, W. J. *The Journal of Organic Chemistry* **1972**, *37*, 4467.
(9) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, *1980*, 627.