Supporting Information for:

Reduced Photobleaching of Conjugated Polymer Films Through Small Molecule Additives

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Experimental:

Materials: Synthetic manipulations that required an inert atmosphere (where noted) were carried out under argon using standard Schlenk techniques. All solvents were of ACS reagent grade or better unless otherwise noted. Anhydrous tetrahydrofuran, toluene and dichloromethane were obtained from J. T. Baker and dried on a solvent column purification system. Silica gel (40-63 µm) was obtained from SiliCycle Inc. Dioctyl phthalate, BHT, DABCO, (3,4-Dihydro-1-naphthyloxy)trimethylsilane, COT, cycloheptatriene and 1,4-dihydro-*o*-toluic acid were purchased from Aldrich and used without further purification. *trans*-Stilbene was purchased from TCI America and used without further purification. **P2** was purchased from H. W. Sands Co. and used without further purification. The pentiptycene-containing poly(*p*-phenylethynylene), **P1**, was donated by ICx Technologies, Inc. (Cambridge, MA, USA, Lot # ED04-2-238, M_n 88400 g/mol) and was prepared according to literature[1] and purified by extensive reprecipitation from methanol and washed free of palladium and copper residues using commercial metal scavengers.

NMR Spectroscopy: ^{1}H and ^{13}C NMR spectra for all compounds were acquired in $CHCl_3$ on a Bruker Avance Spectrometer operating at 400 and 100 MHz, respectively. The chemical shift data are reported in units of δ (ppm) relative to tetramethylsilane (TMS) and referenced with residual $CHCl_3$.

Mass Spectrometry: 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, employing either electron impact or electrospray as the ionization technique.

Gas Chromatography/Mass Spectrometry: GC-MS data were recorded on an Agilent 5973N Gas Chromatograph/Mass Spectrometer equipped with a unit mass electron impact mass spectrometer. The GC was operated in the temperature range of 100-350^{o}C under a vacuum of at least 10^{-5} torr. GC retention times are reported in minutes.

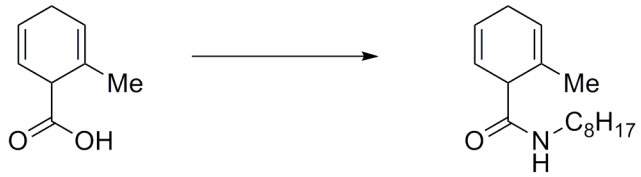
Infrared (IR) spectroscopy: IR spectra were recorded on a Perkin-Elmer Model 2000 FT-IR spectrophotometer at the MIT Department of Chemistry Instrumentation Facility and are reported as strong (s), medium (m) or weak (w).

Polymer Thin Films: Polymer thin films were spun cast on 22×22 mm^2 glass substrates using a WS-400 Spin Processor (Laurell Technologies Corp.) at a spinrate of 800 rpm for 1 min. To prepare the spin-coating solutions: in each case, stock solutions of individual additives were prepared in $CHCl_3$ (ca. 50-70 mg/mL) and an appropriate volume of these stock solutions added to 1.0 mL of a 0.5 mg/mL $CHCl_3$ solution of the polymers such that there was 25 or 50 wt% of the additive relative to the polymer. Typically 800µL of the spin-coating solution was used during the spin coating process. The uniformity of each thin film was confirmed by equivalent UV-vis absorption intensities from three different regions of the film. The optical densities at the exciting wavelength of all the thin films used were 0.1 ± 0.01.

[1] Yang, J.-S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 5321-5322.

Absorption and Emission Spectroscopy: Ultraviolet-visible absorption spectra were measured with an Agilent 8453 diode array spectrophotometer and corrected for background signal with either a solvent-filled cuvette (solutions) or a blank microscope slide (films). Fluorescence spectra were measured on a SPEX Fluorolog-τ3 fluorimeter (model FL-321, 450 W Xenon lamp) using front-face (22.5°) detection.

Photobleaching: Emission intensity vs. time curves were obtained by continuous irradiation (λ = 440 nm for **P1**, 400 nm for **P2**) of a certain area of the microscope slide with the fluorimeter's Xe lamp and monitoring the emission intensity at λ = 460 nm (**P1**) or 440 nm (**P2**) every 60 s for a total of 30 min (**P1**) or 60 min (**P2**). Data was recorded under two conditions: high light intensity and low light intensity. For the high intensity conditions a 0.25 cm^2 area of the slide was irradiated at a power density of 6.3 mW/cm^2. For the low intensity conditions a 0.05 cm^2 area of the slide was irradiated at a power density of 6.3 mW/cm^2. Each emission vs. intensity curve was reproduced three times by irradiating a different region of the same thin film, and each polymer/additive combination was tested three times by spin-coating and bleaching three different thin films.



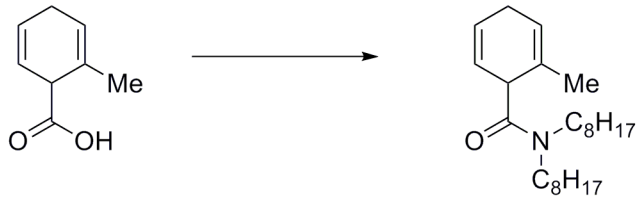
***N*-octyl-1,4-dihydro-*o*-toluamide.** A flame-dried 100mL two-neck round-bottom flask equipped with a condenser was charged with 1,4-dihydro-*o*-toluic acid (0.5g, 3.62mmol), oxalyl chloride (10ml, 15g, 118.1mmol) and 50mL dry dichloromethane under argon. DMF (0.1mL) was added via syringe and the reaction stirred overnight at room temperature then refluxed at 60^{o}C for 2 h under argon. After cooling, the condenser was replaced with a short-path distillation head and the excess oxalyl chloride was distilled off from the reaction mixture under argon. 80 mL dry dichloromethane was added under argon and the reaction mixture cooled to 0^{o}C in an ice bath. 2 mL triethylamine was added dropwise via syringe followed by octylamine (0.67mL, 0.53g, 4.1mmol). The reaction was stirred at 0^{o}C for 1 hour, allowed to warm up to room temperature and stirred overnight under argon. After quenching with saturated sodium bicarbonate, the organic layer was separated, dried over anhydrous potassium carbonate and the solvent evaporated under reduced pressure. The residue was purified by flash column chromatography with gradient elution, starting from 50% dichloromethane in hexanes (v/v) and progressing to 100% dichloromethane to yield 0.75g of a white solid (83%).

^{1}H NMR (400 MHz, $CHCl_3$) δ 0.087 (t, *J* = 6.8 Hz, 3H), 1.27 (m, 10H), 1.47 (t, *J* = 6.8 Hz, 2H), 1.73 (s, 3H), 2.76 (m, 2H), 3.21 (m, 2H), 3.46 (m, 1H), 5.64 (s, 1H), 5.77 (dd, *J* = 12 Hz, 1.6 Hz, 1H), 5.88 (s, 2H).

^{13}C NMR (100 MHz, $CHCl_3$) δ 14.2, 22.0, 22.7, 26.9, 29.3, 29.3, 29.7, 31.9, 39.7, 50.1, 121.9, 124.4, 126.1, 130.5, 172.3.

HRMS (ESI) calc for $C_{16}H_{27}NO$ $[M+Na]^+$ 272.1985, found 272.1990.

IR (KBr plate) cm^{-1} 3445 (s), 2957 (s), 2922 (s), 2853 (s), 1643 (s), 1550 (s), 1467 (m), 1378 (m), 1343 (m), 1227 (m), 979 (w), 951 (m), 908 (m), 893 (m).



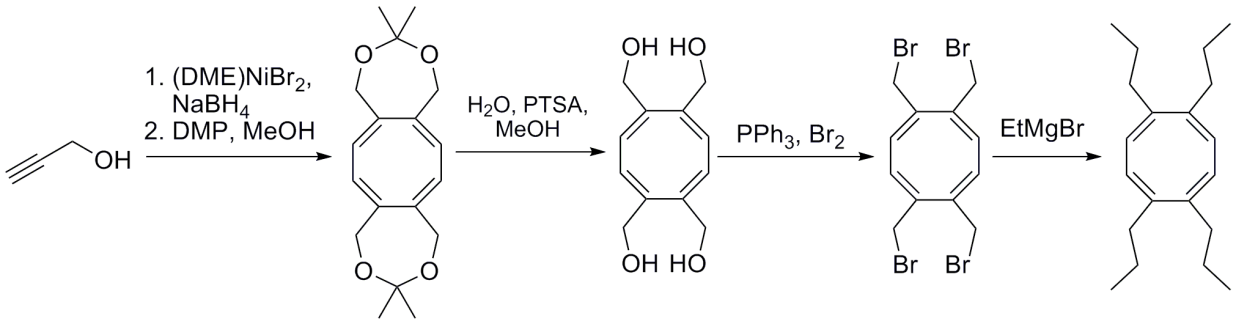
***N,N*-dioctyl-1,4-dihydro-*o*-toluamide.** A flame-dried 100mL two-neck round-bottom flask equipped with a condenser was charged with 1,4-dihydro-*o*-toluic acid (0.5g, 3.62mmol), oxalyl chloride (10ml, 15g, 118.1mmol) and 50mL dry dichloromethane under argon. DMF (0.1mL) was added via syringe and the reaction stirred overnight at room temperature then refluxed at 60°C for 2 h under argon. After cooling, the condenser was replaced with a short-path distillation head and the excess oxalyl chloride was distilled off from the reaction mixture under argon. 80 mL dry dichloromethane was added under argon and the reaction mixture cooled to 0°C in an ice bath. 2 mL triethylamine was added dropwise via syringe followed by dioctylamine (1.21g, 5mmol). The reaction was stirred at 0°C for 1 hour, allowed to warm up to room temperature and stirred overnight under argon. After quenching with saturated sodium bicarbonate, the organic layer was separated, dried over anhydrous potassium carbonate and the solvent evaporated under reduced pressure. The residue was purified by flash column chromatography using 10% ethyl acetate in hexanes as the eluent to yield 0.95g of a clear oil (73%). The sample was stored at -4°C but was still observed to oxidize slightly over time to the *o*-toluamide.

^{1}H NMR (400 MHz, $CHCl_3$) δ 0.087 (t, *J* = 6.8 Hz, 6H), 1.27 (m, 20H), 1.47 (t, *J* = 6.8 Hz, 4H), 1.73 (s, 3H), 2.76 (m, 4H), 3.21 (m, 2H), 3.46 (m, 1H), 5.77 (dd, *J* = 12 Hz, 1.6 Hz, 1H), 5.88 (s, 2H).

^{13}C NMR (100 MHz, $CHCl_3$) δ 14.2, 22.0, 22.7, 26.9, 29.3, 29.3, 29.7, 31.9, 39.7, 50.1, 121.9, 124.4, 126.1, 130.5, 172.3.

HRMS (ESI) calc for $C_{16}H_{27}NO$ $[M+Na]^+$ 384.3237, found 384.3242.

IR (KBr plate) cm^{-1} 2942 (s), 2920 (s), 2843 (s), 1639 (s), 1552 (s), 1467 (m), 1378 (m), 1343 (m), 1227 (m), 951 (m), 889 (m).



1,2,5,6-tetrakis(hydroxymethyl)COT diacetonide, 1,2,5,6-tetrakis(hydroxymethyl)COT, and 1,2,5,6-tetrakis(bromomethyl)COT were synthesized according to a literature procedure.[2]

1,2,5,6-tetrapropylCOT. A flame-dried Schlenk flask was charged with 1.2g 1,2,5,6-tetrakis(bromomethyl)COT (2.64 mmol) and 40 mL dry Et_2O under argon. The solution was cooled to 0°C in an ice bath and 5mL of a 3.0M solution of EtMgBr in diethyl ether (15mmol) was added dropwise. The reaction was allowed to warm to room temperature and stirred for 2 d under argon. After quenching with saturated NH_4Cl, the organic layer was separated, dried over $MgSO_4$ and the solvent evaporated under reduced pressure. The residue was purified by flash column chromatography using hexanes as the eluent to yield 0.5g (42%) of a yellow oil.

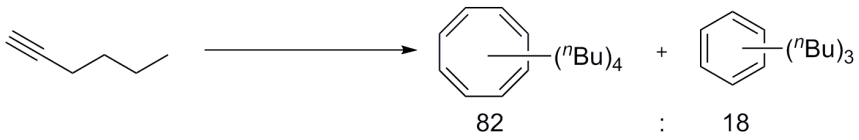
^{1}H NMR (400 MHz, $CHCl_3$) δ 0.87 (t, J = 6.5 Hz, 12H), 1.43 (m, 8H), 2.32 (t, J = 6.5 Hz, 8H), 5.55 (s, 4H).

^{13}C NMR (100 MHz, $CHCl_3$) δ 14.3, 22.3, 35.9, 126.0, 144.0.

HRMS (EI) calc for $C_{20}H_{32}$ $[M+H]^+$ 272.2504, found 272.2509.

IR (KBr plate) cm^{-1} 2962 (s), 2857 (s), 1465 (m), 1458 (m), 1290 (m).

[2] Boussie, T. R.; Streitwieser, A. *J. Org. Chem.* **1993**, *58*, 2377-2380.



TetrabutylCOT isomers. A two-neck round-bottom flaks equipped with a condenser was charged with 30mL 1-hexyne (21.45g, 261.1mmol), 0.02 g (DME)$NiBr_2$ (0.06mmol), 50mL dry THF, 5mL dry methanol and 0.025g $NaBH_4$ (0.67mmol). After refluxing for 20 h, the reaction mixture was cooled to room temperature and passed through a short silica plug and the solvent and unreacted hexyne were evaporated under reduced pressure. The residue was purified by flash column chromatography using hexanes as the eluent to yield 2.5g of a light yellow oil. GC-MS analysis of the oil revealed the composition to be 82% COT isomers and 18% tributylbenzenes. Due to the high boiling points of the compounds, the COT isomers could not be isolated by vacuum distillation as the sample was observed to decompose before boiling occured.

GC-MS t_R (min) 13.1 (m/z 246), 13.7 (m/z 246), 13.9 (m/z 246), 16.5 (m/z 328), 17.2 (m/z 328), 17.5 (m/z 328), 17.9 (m/z 328).

^{1}H NMR (400 MHz, $CHCl_3$) δ 0.90 (t), 1.37 (m) 1.55 (m), 1.97 (t), 2.16 (m), 2.58 (t), 5.43 (s), 5.49 (s), 5.53 (s), 5.5 (s), 6.81 (s).

^{13}C NMR (100 MHz, $CHCl_3$) δ 14.2, 14.3, 22.2, 22.3 (2), 22.5, 22.7 (2), 22.8, 23.0, 23.1, 30.8 (2), 30.9 (2), 31.0, 31.1, 33.8, 34.0, 35.0, 35.3, 35.4, 35.5, 35.6, 35.9, 37.5, 37.8 (2), 125.2, 125.4, 126.0, 126.3, 126.5, 126.9, 127.5, 128.1, 128.5, 142.8, 143.3, 143.6, 143.7, 143.8, 144.0, 144.7, 145.0, 145.1.

HRMS (EI) calc for $C_{24}H_{40}$ $[M]^+$ 328.3125, found 328.3128 (COTs); calc for $C_{18}H_{30}$ $[M]^+$ 246.2342, found 246.2346 (benzenes).

IR (KBr plate) cm^{-1} 2956 (s), 2847 (s), 1646 (w), 1462 (m), 1458 (m), 1377 (m).