Supporting Information for

Dynamic anti-counterfeiting security features using multicolor dianthryl sulfoxides

Jennifer Yuan, Peter R. Christensen, and Michael O. Wolf*

Department of Chemistry, 2036 Main Mall, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1

Corresponding author: mwolf@chem.ubc.ca

Table of Contents

Experimental Details

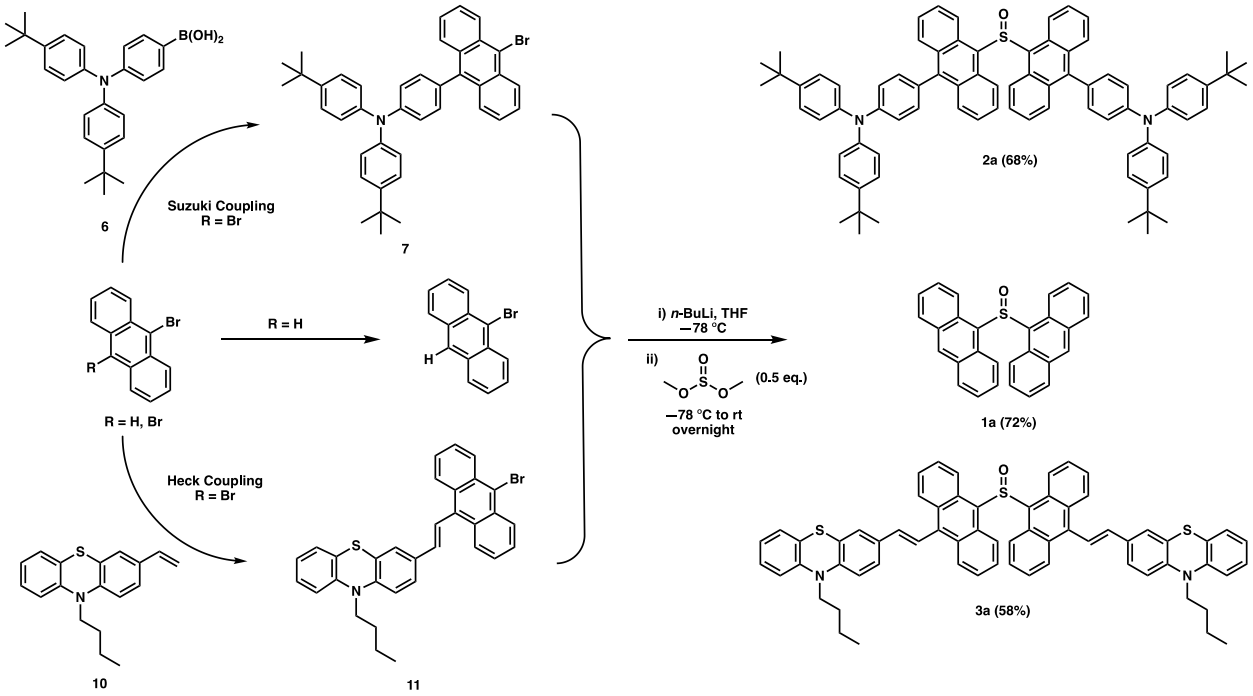
General Considerations

All reactions and manipulations were conducted using standard Schlenk techniques. Dry and degassed solvents were obtained from an Innovative Technology Inc. solvent purification system, collected under vacuum in an oven-dried flask and stored under a nitrogen atmosphere. All reagents (Alfa Aesar, Sigma-Aldrich, Tokyo Chemical Industry) were used as received without further purification unless otherwise indicated. Bis(4-tert-butylphenyl)amine (TCI) was purified by recrystallization from MeOH. *N*-bromosuccinimide (Sigma-Aldrich) was purified by recrystallization from H_2O. The following compounds were prepared according to literature procedures: 4-(*tert*-butyl)-*N*-(4-(*tert*-butyl)phenyl)-*N*-phenylaniline (**4**),[1] 4-bromo-*N*,*N*-bis(4-(*tert*-butyl)phenyl)aniline (**5**),[2] (4-(bis(4-(*tert*-butyl)phenyl)amino)phenyl)boronic acid (**6**).[3] Compounds **8** to **10** were prepared using a modified literature procedure.[4]

NMR solvents were purchased from Cambridge Isotope Laboratories ($CDCl_3$) or Sigma-Aldrich (CD_2Cl_2). Solution-phase NMR spectroscopy was conducted on a Bruker AV III HD 400 MHz spectrometer at 298 K. Multiplicities are described as s (singlet), d (doublet), t (triplet), or m (multiplet). Fourier transform infrared (FTIR) spectroscopy was conducted on a PerkinElmer FT-IR spectrometer with a universal attenuated total reflectance (ATR) attachment using a diamond crystal. High-resolution mass spectrometry (HRMS) was performed by Marshall Lapawa (UBC Mass Spectrometry/Microanalysis Facility).

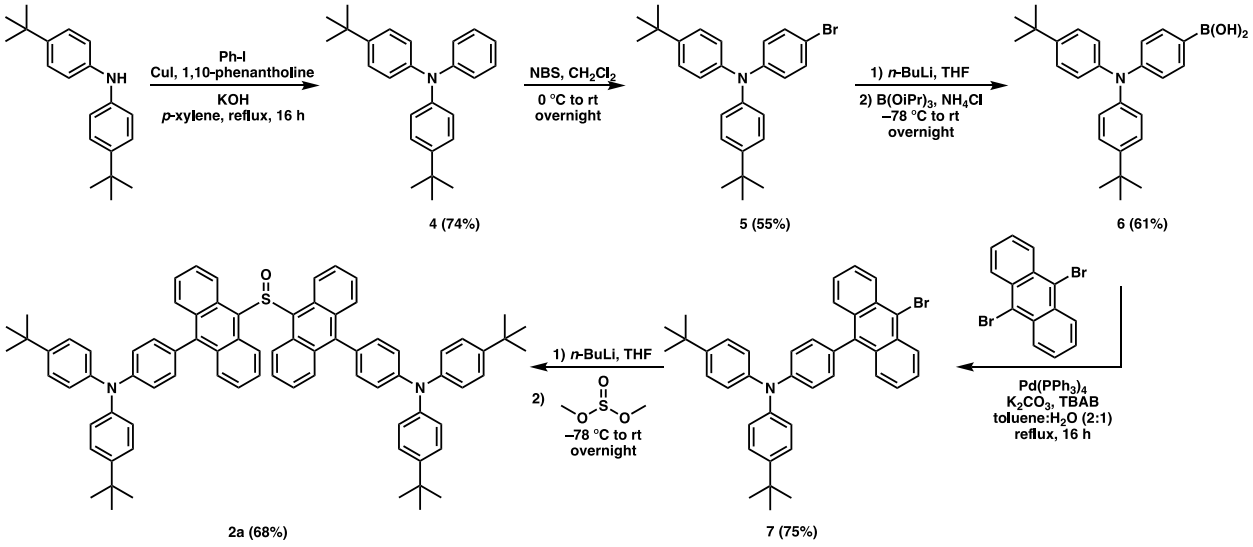
For photophysical characterization, solution samples in a quartz cell with a 1 cm path length were prepared in the dark to minimize photoconversion. UV-vis spectroscopy was conducted on a Cary Varian 5000 UV-vis-NIR spectrophotometer. Photoluminescence (PL) spectroscopy was conducted on an Edinburgh Instruments FS5 spectrofluorometer. The excitation wavelength was 365 nm. For solution samples, the slit width for excitation was 1.5 mm and the slit width for emission was 1.5 mm. The integration time was 0.1 s. For solid state samples, the slit width for excitation was 8 mm and the slit width for the emission was 1.25 mm. The integration time was 0.1 s. Absolute quantum yields were measured using a SC-30 integrating sphere module on the FS5 spectrofluorometer. Irradiation experiments were performed using a handheld lamp (365 nm, Entela) or a custom-built UV-LED photoreactor with a peak output wavelength of 400 nm. The design of the photoreactor has been previously reported.[5]

Synthetic Procedures



Scheme S1. General reaction conditions for the synthesis of dianthryl sulfoxides.

Synthesis of 4,4'-(sulfinylbis(anthracene-10,9-diyl))bis(*N*,*N*-bis(4-(*tert*-butyl)phenyl)aniline) (2a)

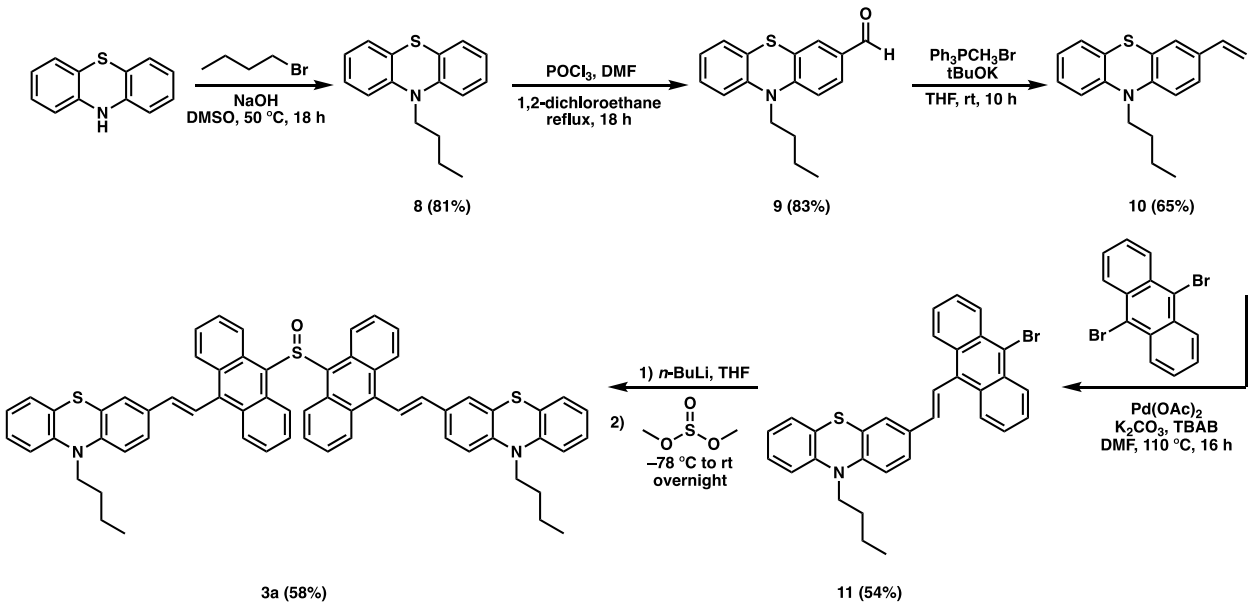


Scheme S2. Reaction conditions for the synthesis of 4,4'-(sulfinylbis(anthracene-10,9-diyl))bis(*N*,*N*-bis(4-(*tert*-butyl)phenyl)aniline) (**2a**).

4-(10-bromoanthracen-9-yl)-*N*,*N*-bis(4-(*tert*-butyl)phenyl)aniline (7). In a Schlenk flask, toluene (50 mL) and water (15 mL) were sparged with N_2 for 1 h before **6** (0.500 g, 1.24 mmol, 1.0 equiv.), 9,10′-dibromoanthracene (0.440 g, 1.30 mmol, 1.05 equiv.), tetrabutylammonium bromide (TBAB) (0.400 g, 1.24 mmol, 1.0 equiv.) and K_2CO_3 (0.860 g, 6.20 mmol, 5.0 equiv.) were added. The reaction mixture was sparged with N_2 for another 10 mins. $Pd(PPh_3)_4$ (0.0014 g, 0.01 mmol, 0.1 equiv.) was added to the reaction mixture and the reaction heated to 110 °C and left overnight with stirring. The reaction was quenched with water (100 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The organic layers were combined, washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was dry loaded onto silica and purified by flash column chromatography on silica gel using a solvent gradient, starting with hexanes and ending with CH_2Cl_2 /hexanes (1:1) to afford **7** as a yellow solid. Yield: 0.375 g (75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (dt, *J* = 8.9, 0.9 Hz, 2H), 7.85 (dt, *J* = 8.8, 0.9 Hz, 2H), 7.62 (ddd, *J* = 8.9, 6.5, 1.2 Hz, 2H), 7.45 (ddd, *J* = 8.8, 6.5, 1.2 Hz, 2H), 7.40 – 7.33 (m, 4H), 7.27 – 7.19 (m, 8H), 1.37 (s, 18H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 147.75, 146.02, 144.98, 138.00, 131.78, 131.31, 130.86, 130.28, 127.82, 127.63, 126.93, 126.19, 125.41, 124.37, 122.42, 122.09, 34.36, 31.48. HR-ESI-MS: *m/z* calcd for $C_{40}H_{38}NBr$ 611.2188, found 611.2192.

4,4'-(sulfinylbis(anthracene-10,9-diyl))bis(*N*,*N*-bis(4-(*tert*-butyl)phenyl)aniline) (2a). In an oven-dried Schlenk flask, **7** (0.875 g, 1.43 mmol, 1.0 equiv.) was dissolved in dry THF (30 mL) and the flask was cooled to –78 °C. *n*-BuLi (1.6 M in hexanes, 1.06 mL, 1.71 mmol, 1.2 equiv.) was added dropwise at –78 °C and stirred for 1 h. The reaction was kept in the dark and wrapped with foil before proceeding. Dimethyl sulfite (0.060 mL, 0.715 mmol, 0.5 equiv) was added in one portion and the reaction was warmed to room temperature and allowed to stir overnight. The solvent was removed *in vacuo.* With minimal light exposure, the crude product was dry loaded onto silica and purified by flash column chromatography in the dark, on silica gel using a solvent gradient, starting with hexanes/CH_2Cl_2 (1:1) and ending with CH_2Cl_2 to afford **2a** as a yellow solid. Yield: 0.686 g (68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.45 (d, *J* = 9.0 Hz, 4H), 7.81 (dt, *J* = 8.8, 1.1 Hz, 4H), 7.44 (ddd, *J* = 9.1, 6.5, 1.4 Hz, 4H), 7.40 – 7.32 (m, 12H), 7.25 – 7.13 (m, 16H), 1.35 (s, 36H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 147.85, 146.09, 144.86, 131.52, 130.56, 130.34, 128.42, 127.14, 126.18, 126.14, 124.99, 124.39, 123.25, 121.82, 34.35, 31.46. HR-ESI-MS: *m/z* calcd for $C_{80}H_{77}N_2OS$ 1113.5757, found 1113.5757. IR (neat): $\tilde{\nu}$ (σ(SO)) 1062 cm^{-1}.

Synthesis of 3,3'-((1*E*,1'*E*)-(sulfinylbis(anthracene-10,9-diyl))bis(ethene-2,1-diyl))bis(10-butyl-10*H*-phenothiazine) (3a).



Scheme S3. Reaction conditions for the synthesis of 3,3'-((1*E*,1'*E*)-(sulfinylbis(anthracene-10,9-diyl))bis(ethene-2,1-diyl))bis(10-butyl-10*H*-phenothiazine) (**3a**).

10-Butyl-10H-phenothiazine (8). In a round bottom flask, phenothiazine (5.00 g, 25.0 mmol, 1.0 equiv.) and NaOH (ground up pellets) (1.10 g, 27.0 mmol, 1.1 equiv.) were dissolved in DMSO (65 mL) and stirred for 30 mins at room temperature. 1-Bromobutane (2.70 mL, 25.0 mmol, 1.0 equiv.) was added dropwise, and the reaction mixture was heated to 50 °C and left to stir overnight. The reaction was quenched with water (100 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The organic layers were combined, washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification was carried out by flash column chromatography on silica gel using hexanes as the eluent to afford **8** as a pale-yellow oil. Yield: 4.92 g (81%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.23 – 7.12 (m, 4H), 6.98 – 6.90 (m, 4H), 3.94 – 3.84 (m, 2H), 1.86 – 1.75 (m, 2H), 1.49 (h, *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ 145.36, 127.21, 127.19, 124.75, 122.24, 115.45, 46.98, 28.95, 20.12, 13.57. HR-ESI-MS: *m/z* calcd for $C_{16}H_{17}NS$ 255.1082, found 255.1078.

10-Butyl-10H-phenothiazine-3-carbaldehyde (9). In a three-neck round bottom flask, **8** (0.800 g, 3.13 mmol, equiv.) and DMF (1.94 mL, 25.0 mmol, 8 equiv.) were dissolved in 1,2-dichloroethane (15 mL) and cooled to 0 °C. $POCl_3$ (1.64 mL, 15.7 mmol, 5.0 equiv.) was added dropwise, then the reaction mixture heated to reflux and stirred overnight. The reaction mixture was poured over a saturated solution of $NaHCO_3$ (aq) (100 mL) on ice and extracted with CH_2Cl_2 (3 × 50 mL). The organic layers were combined, washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification was by flash column chromatography on silica gel using hexanes/CH_2Cl_2 (1:1) as the eluent to afford **9** as an orange oil. Yield: 0.731 g (83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.66 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.61 (d, *J* = 1.9 Hz, 1H), 7.24 – 7.09 (m, 2H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.92 (t, *J* = 7.7 Hz, 2H), 3.93 (t, *J* = 7.3 Hz, 2H), 1.88 – 1.78 (m, 2H), 1.50 (h, *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 190.04, 150.77, 143.46, 131.04, 130.07, 128.42, 127.58, 127.55, 125.05, 123.83, 123.57, 115.96, 114.80, 47.70, 28.84, 20.08, 13.77. HR-EI-MS: *m/z* calcd for $C_{17}H_{17}NOS$ 283.1031, found 283.1029.

10-Butyl-3-vinyl-10H-phenothiazine (10). In an oven-dried Schlenk flask, **9** (1.00 g, 3.53 mmol, 1 equiv.) and methyltriphenyl phosphonium bromide (1.51 g, 4.23 mmol, 1.2 equiv.) were dissolved in dry THF (30 mL). To the reaction mixture, a suspension of *t*-BuOK (0.792 g, 7.06 mmol, 2.0 equiv.) in dry THF (10 mL) was added dropwise and left to stir overnight at room temperature. The reaction mixture was poured over water (30 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The organic layers were combined, washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification was by flash column chromatography on silica gel using hexanes/CH_2Cl_2 (1:1) as the eluent afford **10** as a yellow oil. Yield: 0.710 g (65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 – 7.12 (m, 4H), 6.95 – 6.85 (m, 2H), 6.82 (d, *J* = 8.3 Hz, 1H), 6.61 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.62 (dd, *J* = 17.5, 0.9 Hz, 1H), 5.15 (dd, *J* = 10.8, 0.9 Hz, 1H), 3.90 – 3.83 (m, 2H), 1.86 – 1.75 (m, 2H), 1.47 (dt, *J* = 14.8, 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 145.04, 144.80, 135.57, 132.12, 127.43, 127.22, 125.41, 124.93, 124.84, 124.42, 122.37, 115.32, 115.17, 112.13, 47.17, 28.98, 20.18, 13.84. HR-EI-MS: *m/z* calcd for $C_{18}H_{19}NS$ 281.1238, found 281.1236.

(*E*)-3-(2-(10-bromoanthracen-9-yl)vinyl)-10-butyl-10*H*-phenothiazine (11). 10 (2.11 g, 7.44 mmol, 1.0 equiv), 9,10-dibromoanthracene (2.75 g, 8.19 mmol, 1.1 equiv.), K_2CO_3 (4.11 g, 29.8 mmol, 4.0 equiv.) and TBAB (9.59 mmol, 29.8 mmol, 4.0 equiv.) were dissolved in DMF (150 mL) and sparged with N_2 for 1 h. $Pd(OAc)_2$ (0.0167 g, 0.07 mmol, 0.01 equiv) was added in one portion and reaction mixture was heated to 110 °C. The reaction mixture was stirred overnight under N_2. The reaction mixture was poured over water (100 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The organic layers were combined, washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was dry loaded onto silica and purified by flash column chromatography using a solvent gradient, starting with hexanes and ending with CH_2Cl_2 to afford **11** as a yellow solid. Yield: 1.48 g (54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 – 8.58 (m, 2H), 8.41 – 8.34 (m, 2H), 7.73 (d, *J* = 16.5 Hz, 1H), 7.63 (m, 2H), 7.51 (m, 3H), 7.43 (m, 1H), 7.24 – 7.16 (m, 2H), 6.95 (m, 3H), 6.80 (d, *J* = 16.5 Hz, 1H), 3.94 (t, *J* = 7.1 Hz, 2H), 1.87 (m, 2H), 1.56 – 1.45 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 145.19, 144.92, 136.75, 133.81, 131.52, 130.54, 130.37, 128.14, 127.51, 127.34, 127.01, 126.59, 126.05, 125.59, 125.45, 125.01, 124.29, 122.66, 122.57, 122.41, 115.44, 77.23, 47.28, 29.01, 20.20, 13.86. HR-ESI-MS: *m/z* calcd for $C_{32}H_{26}NSBr$ 535.0969, found 535.0965.

3,3'-((1*E*,1'*E*)-(sulfinylbis(anthracene-10,9-diyl))bis(ethene-2,1-diyl))bis(10-butyl-10*H*-phenothiazine) (3a). 11 (0.300 g, 0.559 mmol, 1.0 equiv.) was dissolved in dry THF (30 mL) and cooled to –78 °C. *n*-BuLi (1.6 M in hexanes, 0.41 mL, 1.12 mmol, 1.2 equiv.) was added at –78 °C and stirred for 1 h. The reaction was kept in the dark and wrapped with foil before proceeding. Dimethyl sulfite (0.02 mL, 0.280 mmol, 0.5 equiv.) was added in one portion and the reaction was warmed to room temperature and allowed to stir overnight. With minimal light exposure, the crude product was dry loaded onto silica and purified by flash column chromatography in the dark, using a solvent gradient starting with CH_2Cl_2/hexanes (1:1) to CH_2Cl_2 to afford **3a**, a red solid. Yield: 0.174 g (58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.44 – 9.35 (m, 4H), 8.39 – 8.27 (m, 4H), 7.67 (d, *J* = 16.5 Hz, 2H), 7.48 – 7.33 (m, 12H), 7.22 – 7.13 (m, 4H), 6.98 – 6.87 (m, 6H), 6.70 (d, *J* = 16.5 Hz, 2H), 3.91 (t, *J* = 7.2 Hz, 4H), 1.84 (m, 4H), 1.50 (dt, *J* = 14.8, 7.5 Hz, 4H), 0.98 (t, *J* = 7.3 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, Benzene-d_6) δ 145.21, 145.10, 138.74, 136.91, 134.80, 131.48, 130.96, 129.61, 128.30, 127.80, 127.56, 127.28, 127.11, 127.01, 126.91, 126.07, 125.86, 125.16,

125.00, 124.90, 123.91, 122.57, 122.42, 115.48, 115.31, 46.80, 28.78, 19.88, 19.75, 13.50. HR-ESI-MS: *m/z* calcd for $C_{64}H_{53}N_2S_3O$ 961.3320, found 961.3298. IR (neat): $\tilde{\nu}$ (σ(SO)) 1052 cm^{-1}.

General procedure for photoconversion

In an open 20 mL screw-top scintillation vial equipped with a magnetic stir bar, ~10 mg of **1a, 2a** or **3a** was dissolved in 0.5 mL of deuterated solvent. The solution was irradiated with a hand lamp (365 nm) or custom-built photoreactor (400 nm)[5] from above with stirring until completion (approximately 30 min) to obtain **1b**, **2b**, or **3b**. The photoreaction was monitored using ^{1}H NMR spectroscopy. The ^{1}H NMR shifts of **2b** and **3b** are in good agreement with reported related compounds.[4,6]

4,4'-([9,9'-bianthracene]-10,10'-diyl)bis(*N*,*N*-bis(4-(*tert*-butyl)phenyl)aniline) (2b). Yield: quantitative. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (m, 4H), 7.49 – 7.46 (m, 4H), 7.42 – 7.34 (m, 18H), 7.26 (m, 10H), 7.20 – 7.16 (m, 4H), 1.39 (s, 36H). HR-ESI-MS: *m/z* calcd for $C_{80}H_{76}N_2$ 1064.6009, found 1064.6013.

10,10'-bis((*E*)-2-(10-butyl-10*H*-phenothiazin-3-yl)vinyl)-9,9'-bianthracene (3b).

Yield: quantitative. ^{1}H NMR (400 MHz, Benzene-d_6) δ 8.60 (d, *J* = 8.8 Hz, 4H), 7.88 (d, *J* = 16.5 Hz, 2H), 7.56 – 7.43 (m, 6H), 7.29 – 7.20 (m, 6H), 7.05 – 6.85 (m, 10H), 6.76 (t, *J* = 7.5 Hz, 2H), 6.65 (dd, *J* = 8.3, 5.7 Hz, 4H), 3.52 (t, *J* = 7.0 Hz, 4H), 1.60 (p, *J* = 7.2 Hz, 4H), 1.29 (q, *J* = 7.5 Hz, 4H), 0.80 (t, *J* = 7.4 Hz, 6H). HR-ESI-MS: *m/z* calcd for $C_{64}H_{52}N_2S_2$ 912.3572, found 912.3567.

Additional Figures

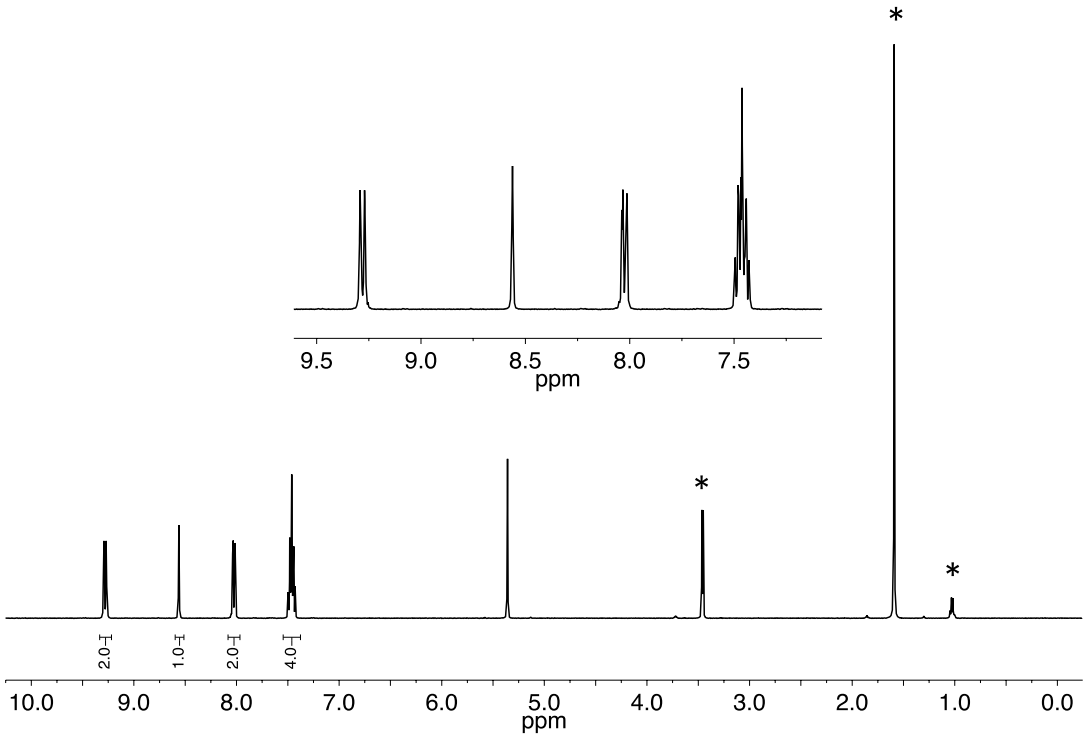


Figure S1. ^{1}H NMR spectrum of **1a** (400 MHz, CD_2Cl_2). * = MeOH, water, grease

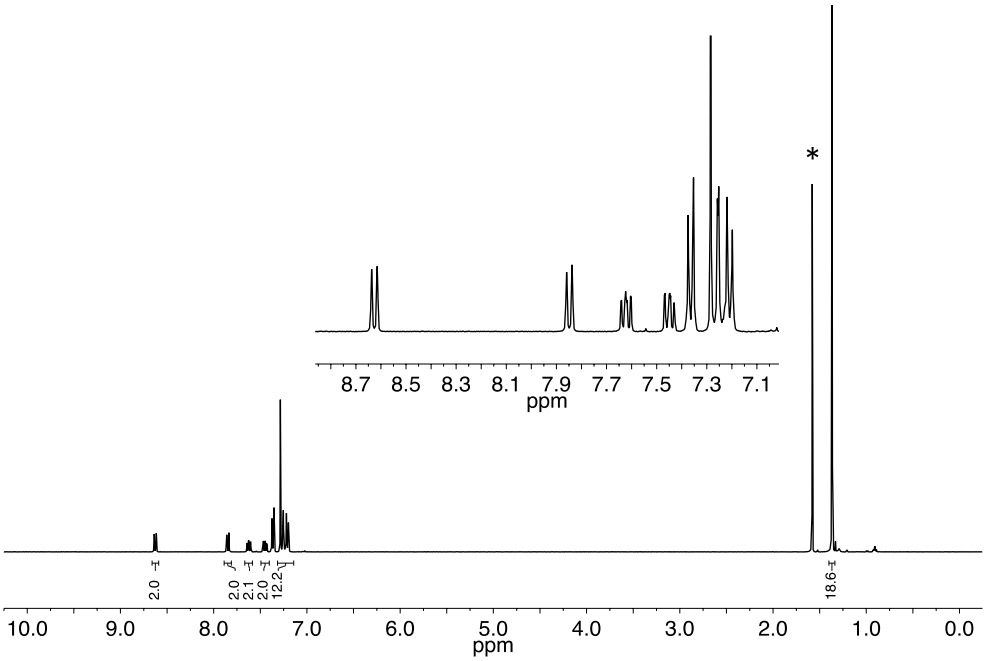


Figure S2. ^{1}H NMR spectrum of 4-(10-bromoanthracen-9-yl)-*N*,*N*-bis(4-(*tert*-butyl)phenyl)aniline (**7**) (400 MHz, $CDCl_3$). * = water

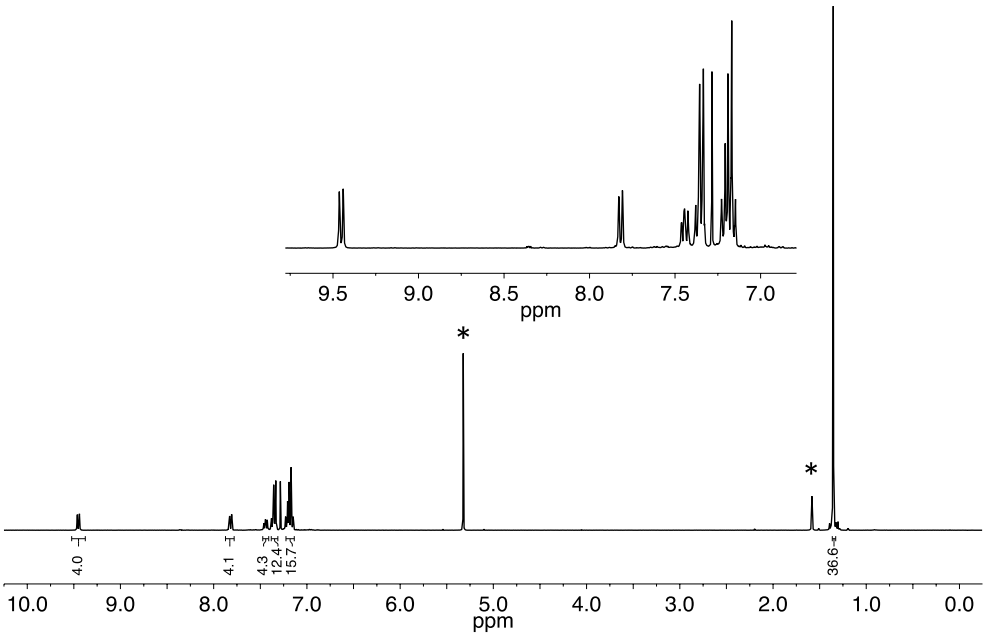


Figure S3. ^{1}H NMR spectrum of 4,4'-(sulfinylbis(anthracene-10,9-diyl))bis(*N*,*N*-bis(4-(*tert*-butyl)phenyl)aniline) (**2a**) (400 MHz, $CDCl_3$). * = CH_2Cl_2, water

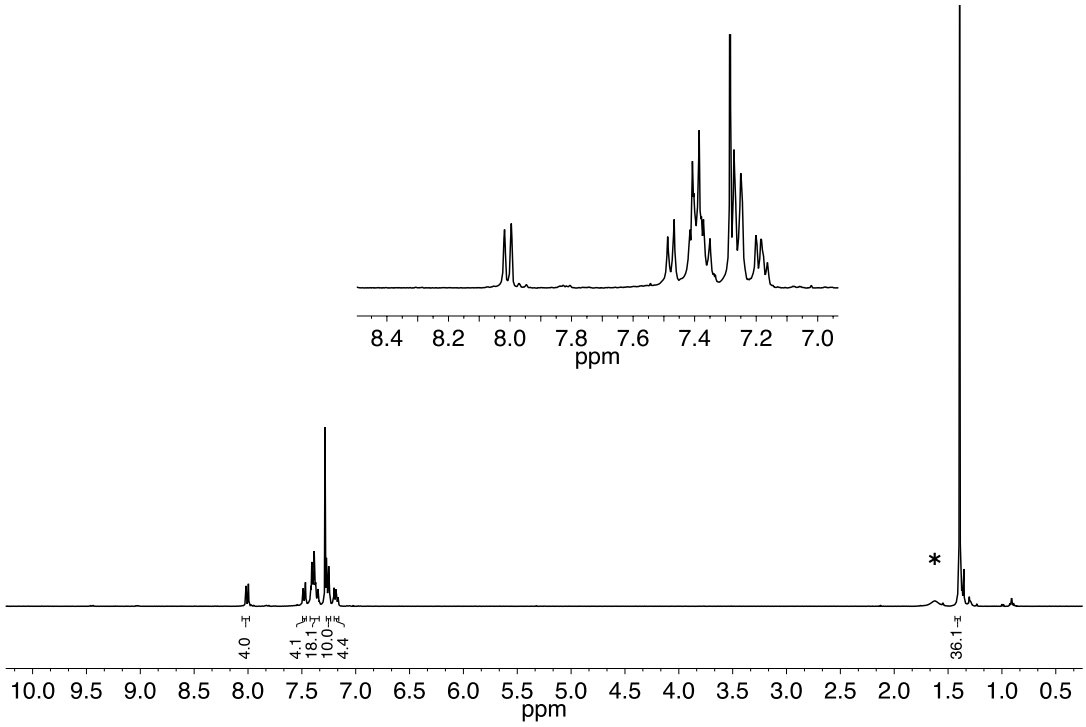


Figure S4. ^{1}H NMR spectrum of 4,4'-([9,9'-bianthracene]-10,10'-diyl)bis(*N*,*N*-bis(4-(*tert*-butyl)phenyl)aniline) (**2b**) synthesized by irradiation with 365 nm light (400 MHz, $CDCl_3$). * = water

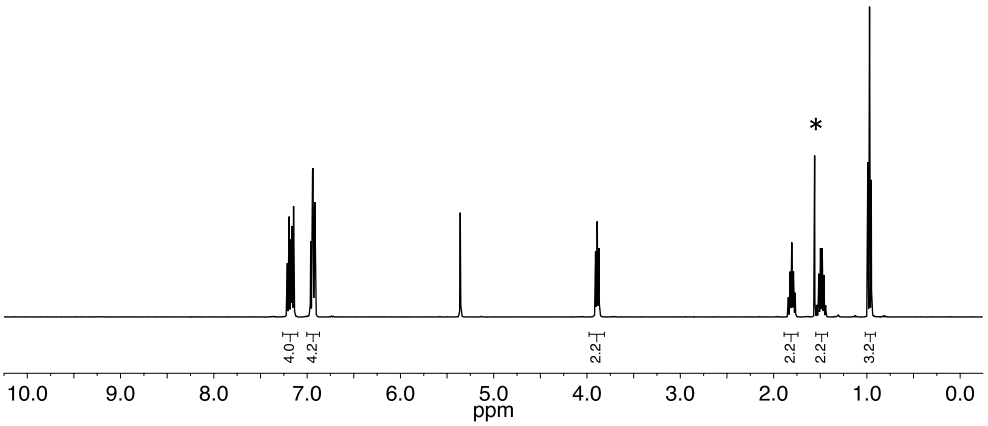


Figure S5. ^{1}H NMR spectrum of 10-Butyl-10H-phenothiazine (**8**) (400 MHz, CD_2Cl_2). * = water

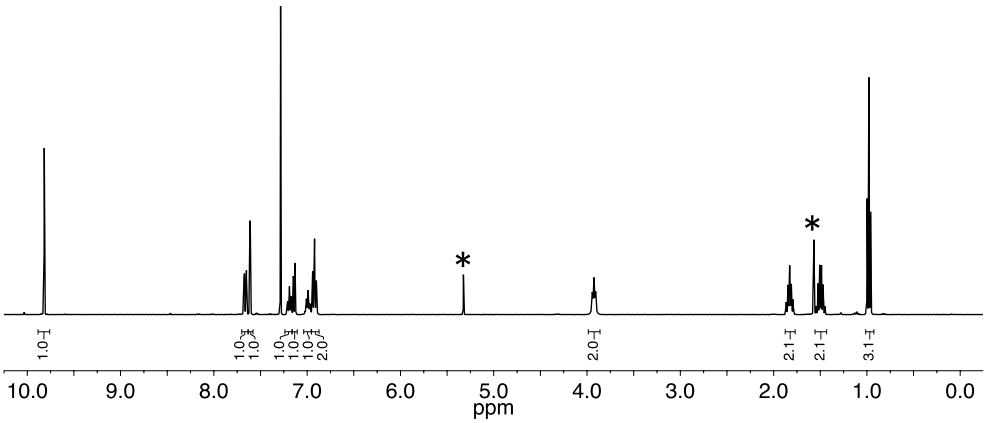


Figure S6. ^{1}H NMR spectrum of 10-Butyl-10H-phenothiazine-3-carbaldehyde (**9**) (400 MHz, $CDCl_3$). * = CH_2Cl_2, water

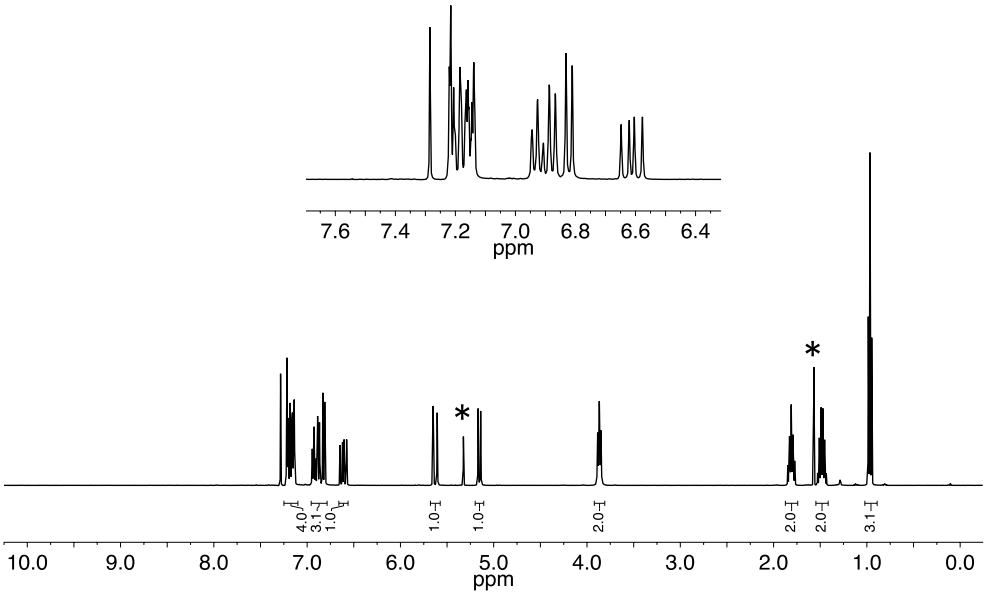


Figure S7. ^{1}H NMR spectrum of 10-Butyl-3-vinyl-10H-phenothiazine (**10**) (400 MHz, $CDCl_3$). * = CH_2Cl_2, water

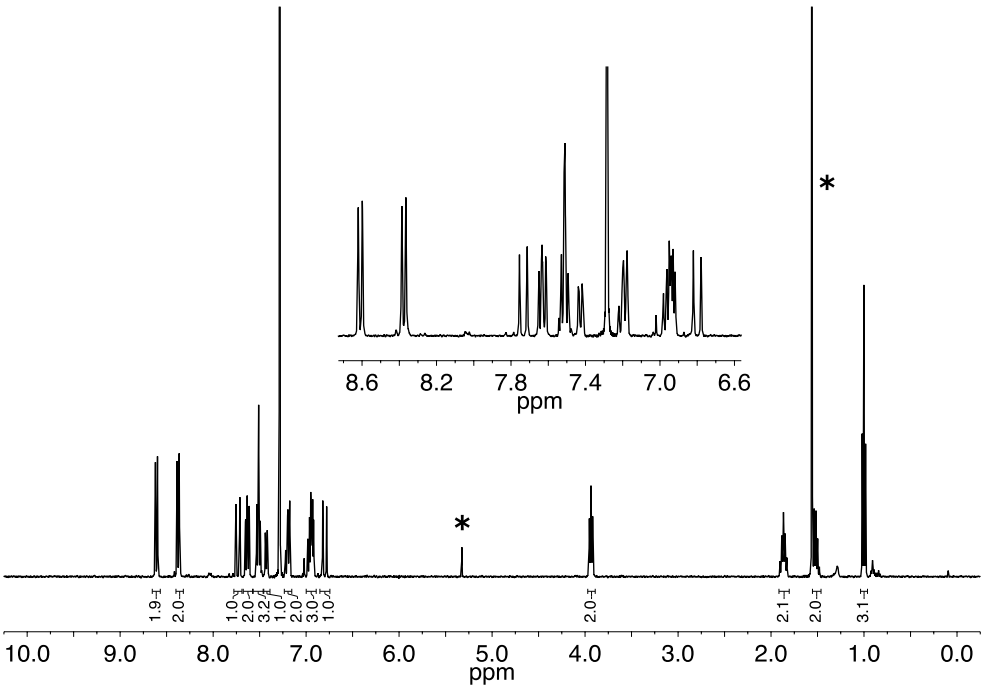


Figure S8. ^{1}H NMR spectrum of (E)-3-(2-(10-bromoanthracen-9-yl)vinyl)-10-butyl-10H-phenothiazine (**11**) (400 MHz, $CDCl_3$). * = CH_2Cl_2, water

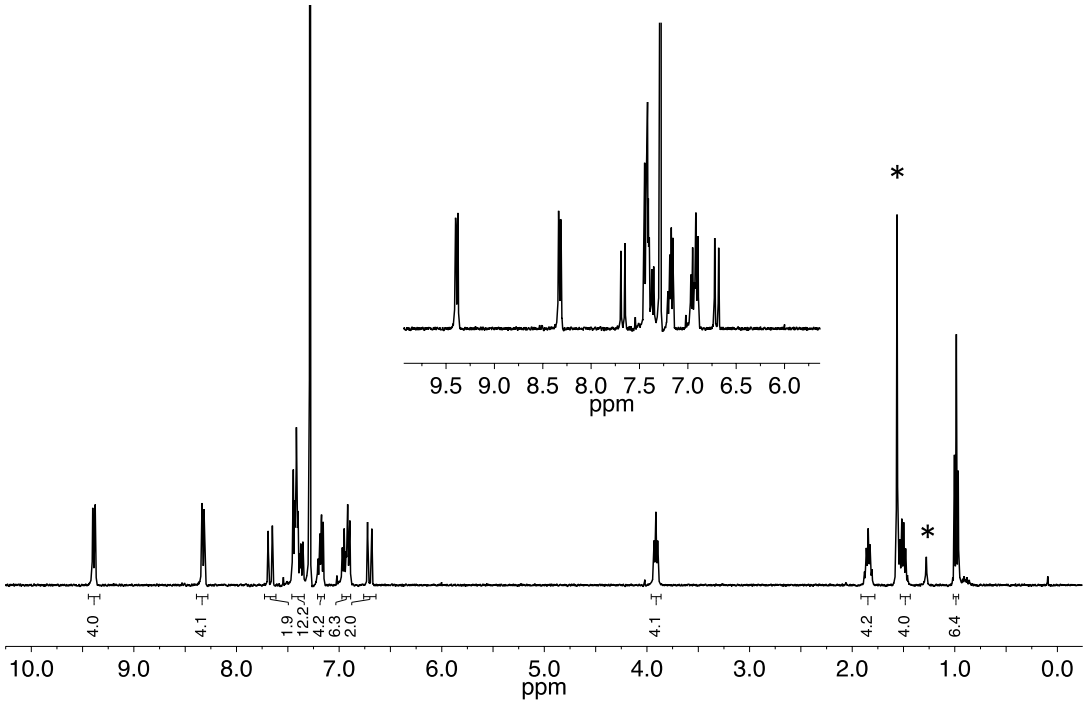


Figure S9. ^{1}H NMR spectrum of 3,3'-((1*E*,1'*E*)-(sulfinylbis(anthracene-10,9-diyl))bis(ethene-2,1-diyl))bis(10-butyl-10*H*-phenothiazine) (**3a**) (400 MHz, $CDCl_3$). * = water, hexanes

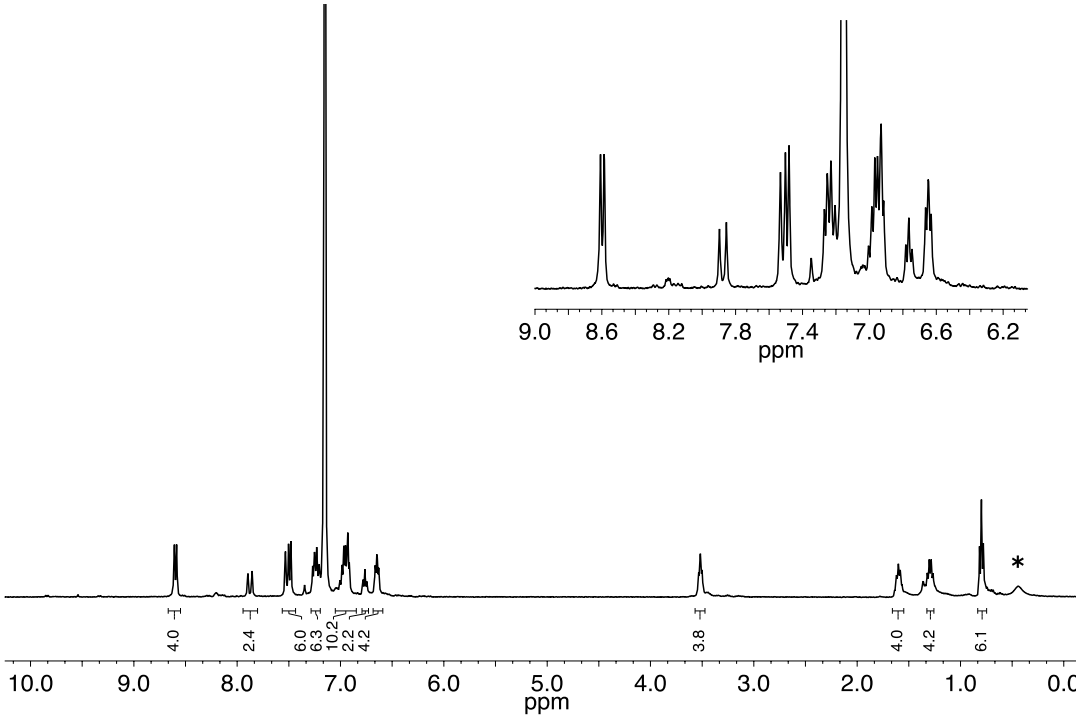


Figure S10. ^{1}H NMR spectrum of 10,10'-bis((*E*)-2-(10-butyl-10*H*-phenothiazin-3-yl)vinyl)-9,9'-bianthracene (**3b**) synthesized by irradiation with 400 nm light (400 MHz, C_6D_6). * = water

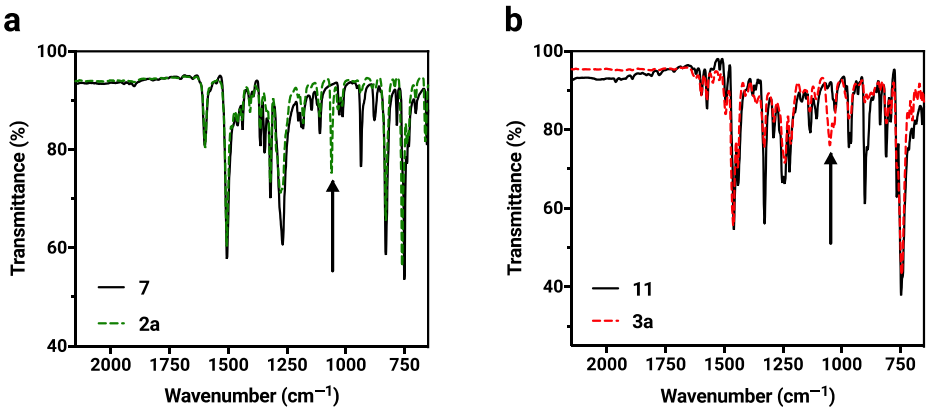


Figure S11. IR spectra of a) **2a** (green) and b) **3a** (red) compared to **7** and **11** respectively, with the SO stretch (~1050 cm^{-1}) highlighted by the arrow.

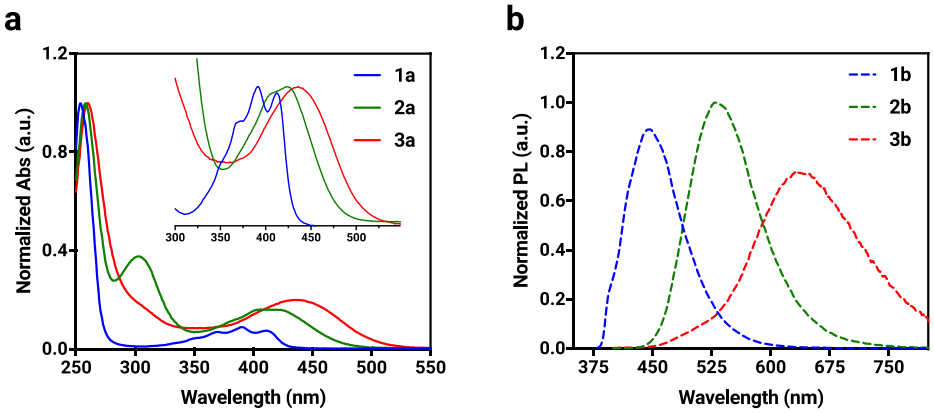


Figure S12. a) Normalized UV-vis absorption spectra of **1a** (blue), **2a** (green), **3a** (red) in CH_2Cl_2. Inset: expanded visible region. b) Relative PL spectra of **1b** (blue), **2b** (green), **3b** (red) in CH_2Cl_2. Concentration of solution samples was 4×10^{-6} M. λ_{exc} = 365 nm.

Table S1. Photophysical data for dianthryl sulfoxides in CH_2Cl_2 (4×10^{-6} M)

Compound	$\lambda_{max,\ abs}$ (nm)	ε (L mol^{-1} cm^{-1})[a]	$\lambda_{max,\ em}$ (nm)[b]	Φ_{PL}[c]
1a	391	19700	445	0.17
1b	392	29200	445	0.51
2a	424	37500	619	0.54
2b	405	37600	528	0.99
3a	436	32600	612	0.12
3b	424	36700	631	0.58

[a]Molar extinction coefficient determined at λ_{max} in the visible region; [b]Excitation wavelength was 365 nm; [c]Absolute quantum yield measurements were made in triplicate and reported as an average of the three measurements.

Photoreactivity Experiments

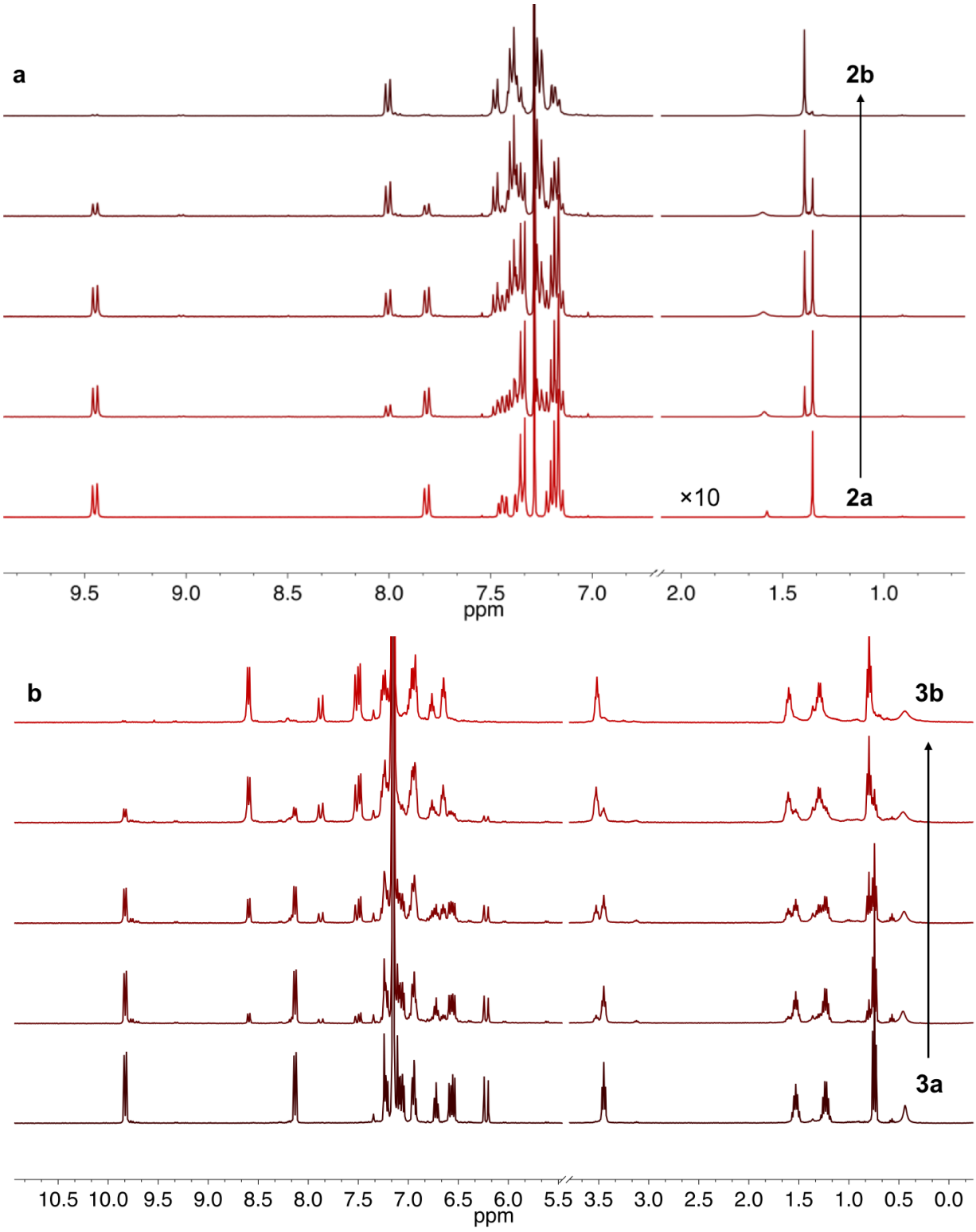


Figure S13. ^{1}H NMR spectra showing the conversion of (a) **2a** to **2b** using 365 nm light (400 MHz, $CDCl_3$) and (b) **3a** to **3b** using 400 nm light (400 MHz, C_6D_6).

General procedure for molar absorptivity measurements

For each compound, four solutions of **1a, 2a, 3a** of specific concentration were prepared in CH_2Cl_2. The molar absorptivity was determined at the wavelength of maximum absorbance (λ_{max}) using a calibration curve. Immediately following the absorbance measurement, the solutions were irradiated with 365 nm light (hand lamp) in the cuvette until no further change in the absorption spectra was observed. It is assumed that full conversion of the sulfoxide species (**1a**, **2a**, **3a**) to the respective bianthracene photoproducts (**1b**, **2b**, **3b**) occurred.

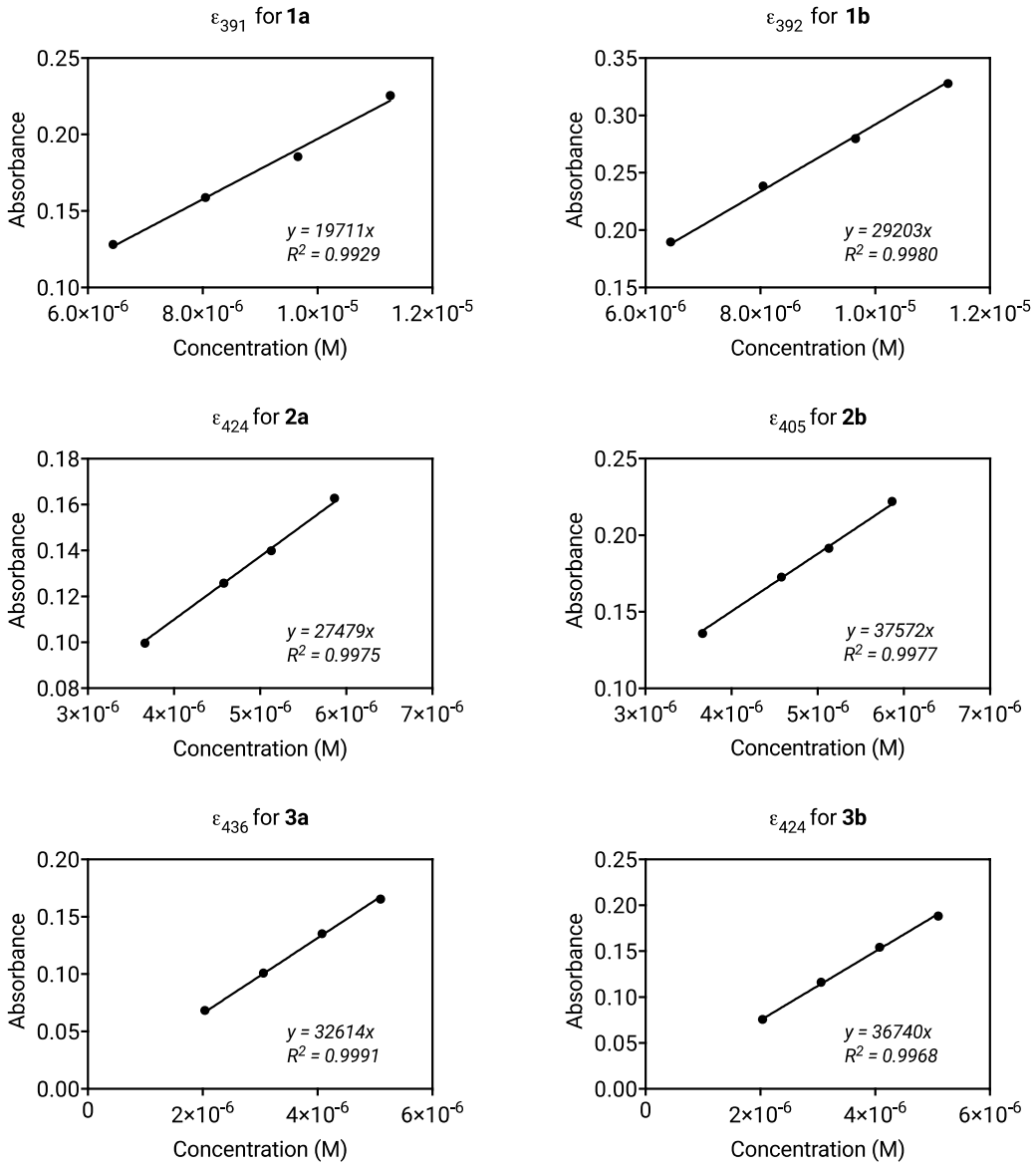


Figure S14. Calibration curves used to determine the molar absorptivity at λ_{max}.

Kinetics experiments

Dilute solutions of **1a**, **2a**, **3a** were prepared in CH_2Cl_2 with an absorption of 0.1 at the monitoring wavelength (approximately 3×10^{-6} to 6×10^{-6} M) (Figure S15, Table S2). A custom-made computer-controlled LED setup was used to irradiate dilute solutions at room temperature while simultaneously measuring the change in absorbance. An Arduino micro-controller enables control over LED exposure with microsecond precision. LEDs with peak wavelength outputs of 405 nm (BIVAR), 470 nm (Kingbright) and 500 nm (Lumex) operating at 120 mW and 20 mA were used for irradiation experiments. The intensity of the LEDs are ~160 mcd. In a typical experiment, the LED was turned on for the entire duration of the measurement until no further change in absorbance was observed. Pseudo first-order rate conditions are assumed (ie. the concentration of photons is in excess compared to the concentration of the compounds).

Table S2. Molar absorptivities for used to determine the % conversion

Conversion	Monitor at λ (nm)	ε_{SM} (L mol^{-1} cm^{-1})	ε_P (L mol^{-1} cm^{-1})
1a → **1b**	410	18397	1000[a]
2a → **2b**	410, 450[b]	25980, 16721[b]	37572, 3154[b]
3a → **3b**	470	21069	8982

[a]Beer's Law was not obeyed for **1b** at 410 nm as the absorbance was too low at this wavelength. A low molar absorptivity (1000 L mol^{-1} cm^{-1}) was used for ε_P in the calculations.
[b]When 470 and 500 nm LEDs were used for irradiation, the change in absorbance at 410 nm was monitored. When a 405 nm LED was used for irradiation, the change in absorbance at 450 nm was monitored for **2a** and the molar absorptivity was adjusted for accordingly.

Table S3. Calculated percent conversion for **1a**, **2a**, **3a** when irradiated with LEDs after 60 s at room temperature

λ_{irr} [nm][a]	1a → 1b	2a → 2b	3a → 3b
405	98%	99%	63%
470	4%	97%	60%
500	> 1%	42%	18%

[a]Purple (405 nm) BIVAR, blue (470 nm) Kingbright and green (500 nm) Lumex LEDs operating at 120 mW and 20 mA.

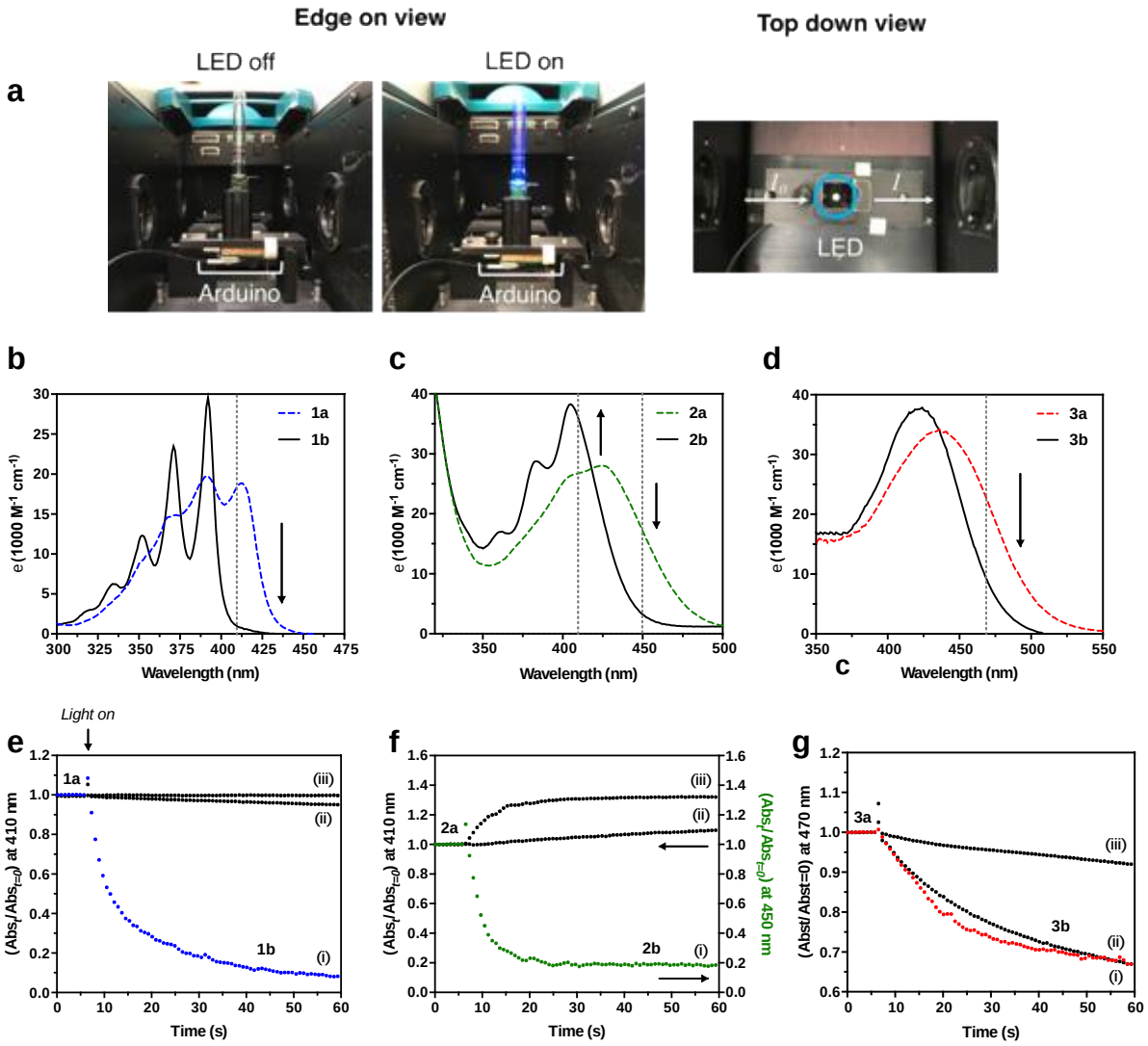


Figure S15. a) Experimental set up in the Cary Varian 5000 UV-vis-NIR spectrophotometer. b-d) UV-vis absorption spectra of dianthryl sulfoxide species (colored dashed line) and bianthryl photoproduct (black solid line) showing the change in absorbance at selected wavelengths (grey dotted line). e-g) The change in absorbance as a function of time when the dianthryl sulfoxide species is converted into the bianthryl photoproduct. The irradiation wavelengths used were 405 (i), 470 (ii) and 500 nm (iii).

Mathematical manipulation of kinetics data

The absorption spectra of the dianthryl sulfoxide species (A_{SM}) and its respective bianthracene photoproduct (A_P) overlap at the wavelength monitored during the photochemical conversion. In order to determine the change in concentration and % conversion accurately, the following equations were used to account for the overlapping regions of the spectrum:

Since,

$A_{SM} = \varepsilon_{SM} c_{SM}$ and $A_P = \varepsilon_P c_P$ (Eq. S1 and Eq. S2)

The total absorption in the overlapping regions of the spectrum is given by:

$A_{tot} = \varepsilon_{SM} c_{SM} + \varepsilon_P c_P$ (Eq. S3)

At t = 0 s, the initial concentration of the starting material ($c_{SM,0}$) is given by:

$c_{SM,0} = c_{SM} + c_P$ (Eq. S4)

Rearranging Eq. S4 and inserting into Eq. S3 gives

$A_{tot} = \varepsilon_{SM} c_{SM} + \varepsilon_P (c_{SM,0} - c_{SM})$

Solving for the concentration of the sulfoxide species at a given time:

$c_{SM} = -\frac{A_{tot} - (\varepsilon_P c_{SM,0})}{(\varepsilon_{SM} - \varepsilon_P)}$ (Eq. S5)

Where A_{tot} is the measured absorbance, ε_{SM} and ε_P are the molar absorptivities of the starting material (SM, dianthryl sulfoxide) and the product (P, bianthracene photoproduct) determined using a calibration curve at the wavelength monitored (Table S2). Therefore, the change in concentration as a function of time can be monitored using UV-vis absorption spectroscopy to determine the % conversion for **1a**, **2a** and **3a**.

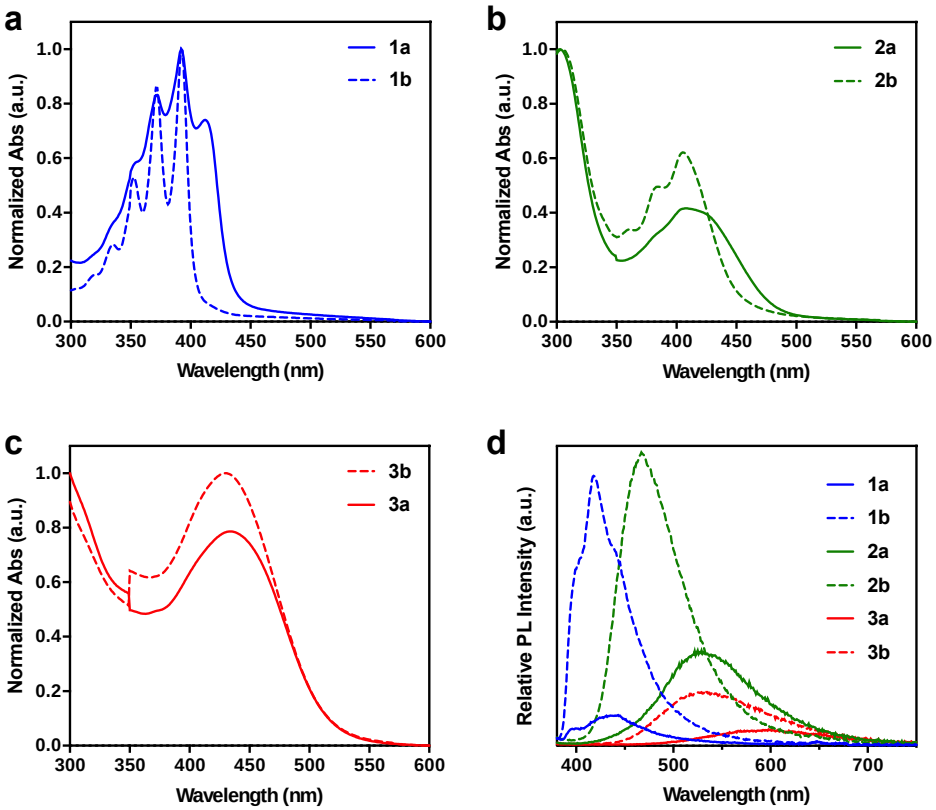


Figure S16. Change in absorbance of a) **1a**, b) **2a** and c) **3a** thin films before (—) and after (- - -) UV exposure in PMMA host matrix. d) Change in photoluminescence intensity of compounds thin films in PMMA before and after irradiation. Films were dried under vacuum before measurement.

Procedure for solid state measurements of thin films

Poly(methyl methacrylate) (PMMA) (Sigma-Aldrich, Mw ~ 120,000 by GPC) was dissolved in a mixture of chloroform and chlorobenzene (4:1 v/v) (25 mg/mL). In separate vials, **1a**, **2a**, and **3a** were dissolved using the same solvent mixture, and then added to the polymer host (1 wt%) to formulate the fluorescent "ink". Glass microscope slides (~3 cm^2 for absorbance measurements, ~6 cm^2 for fluorescence measurements) were used as substrates for thin films. For absorbance measurements, films were prepared by drop-casting the ink (50 μL) onto the substrate and allowed to dry under air at room temperature prior to the measurement. The absorbance measurement was taken of the dried drop cast films. For fluorescence measurements, thin films were prepared by spin-coating the ink (200 μL) onto the substrate at 1000 rpm for 5 s, followed by 2000 rpm for 5 s. Immediately following preparation, the initial fluorescence measurement was taken and then the wet film was subjected to 400 nm irradiation (photoreactor) for 2 s and the change in fluorescence intensity and chromaticity was monitored over 8 s on an Edinburgh Instruments FS5 Spectrofluorometer using a SC-10 front face holder module (λ_{exc} = 365 nm). The flashlight on an iPhone 7 and a commercial UV flashlight (Vansky, Amazon.ca) was also used as an irradiation source for comparison. Experiments were performed with minimal exposure to ambient light.

Reproducibility experiments

To demonstrate the reproducibility of the CIE trajectories, thin films prepared from the same mixture were irradiated with 400 nm light (photoreactor). Differences in the initial chromaticity coordinates of trial 1 and 2 using the same mixture (Table S4) are the result of working laboratory conditions, as exposure to light could initiate the conversion of SO to BA premature to the PL measurement. Needless to say, it is difficult to reproduce a mixture (by hand) precisely as the initial chromaticity coordinates between mixture 1 and 2 versus 3 differ. Notably, the change in chromaticity, defined as the magnitude of the vector between the initial and final chromaticity point, was consistent between experiments. The final chromaticity coordinates between trials are also in agreement with each other for the same mixtures.

Table S4. Chromaticity coordinates (*x*, *y*) of thin films prepared from three different solutions containing a 1:1:1 mixing ratio of **1a**, **2a**, **3a** doped into PMMA, before (initial) and after (final) irradiation

Experiment	Entry	Initial (t = 0 s) A	Final (t = 8 s) B	Change in chromaticity $\overrightarrow{\lvert AB \rvert}$[a]
1[b]	Mixture 1, Trial 1	0.372, 0.460	0.271, 0.303	0.126
	Mixture 1, Trial 2	0.373, 0.463	0.273, 0.303	0.126
2[b]	Mixture 2, Trial 1	0.365, 0.454	0.264, 0.287	0.129
	Mixture 2, Trial 2	0.365, 0.456	0.261, 0.281	0.135
	Mixture 3, Trial 1	0.305, 0.355	0.254, 0.293	0.254
	Mixture 3, Trial 2	0.308, 0.360	0.247, 0.289	0.247
	Mixture 3, Trial 3	0.310, 0.365	0.252, 0.295	0.252
	Mixture 3, Trial 4	0.307, 0.359	0.251, 0.292	0.251
3	Mixture 4, phone light[c]	0.310, 0.365	0.255, 0.300	0.051
	Mixture 4, UV flashlight[d]	0.311, 0.367	0.257, 0.303	0.050

[a]Calculated as the distance between the chromaticity coordinates (*x*, *y*) at t = 0 s and t = 8 s.

$$\overrightarrow{AB} = \sqrt{(x_2 - x_1)^2 - (y_2 - y_1)^2}$$

[b]Irradiation by 400 nm light from photoreactor, [c]iPhone7; [d]Vansky

Different formulations

Irradiation experiments using 400 nm light (photoreactor) on thin-films prepared from different mixing ratios of **1a** (B), **2a** (G) and **3a** (R) were performed to demonstrate the possibility of producing different colors upon irradiation from same dyes. The mixing ratios by weight are highlighted in Table S5.

Table S5. Chromaticity coordinates (*x*, *y*) of thin prepared from different mixing ratios of **1a** (B), **2a** (G), **3a** (R) doped into PMMA before (initial) and after (final) irradiation with 400 nm light

Mixing ratio red/blue/green (RGB)	Entry	Initial (t = 0 s) A	Final (t = 8 s) B	Change in chromaticity $\overrightarrow{\lvert AB \rvert}$[a]
1:0:1	Mixture 4, Trial 1	0.386, 0.417	0.240, 0.206	0.101
1:0:1	Mixture 5, Trial 1	0.386, 0.423	0.245, 0.217	0.099
2:1:0	Mixture 6, Trial 1	0.399, 0.475	0.368, 0.462	0.031
1:2:0	Mixture 7, Trial 1	0.329, 0.492	0.312, 0.470	0.017

[a]Calculated as the distance between the chromaticity coordinates (*x*, *y*) at t = 0 s and t = 8 s.

$$\overrightarrow{AB} = \sqrt{(x_2 - x_1)^2 - (y_2 - y_1)^2}$$

Detection of fluorescence color change using smartphone app

A user-friendly smartphone app called “Colorimeter” was purchased on an android smartphone (OnePlus 3T, equipped with a 16 megapixel camera) from the Google Play Store for 0.99$ CAD. Information about the app can be found at http://researchlabtools.blogspot.com/. Whatman filter paper (diameter = 42.5 cm) were used as paper substrates for the fabrication of the patches. 10 μL of the fluorescent ink was dropped in the middle of the of the filter paper. The smartphone was held with a tripod and placed approximately 15 cm above the filter paper. A hand-lamp (365 nm) was held at approximately 45° angle above the filter paper and was used to irradiate the filter papers for approximately 1 minute until no change in color was measured using the app.

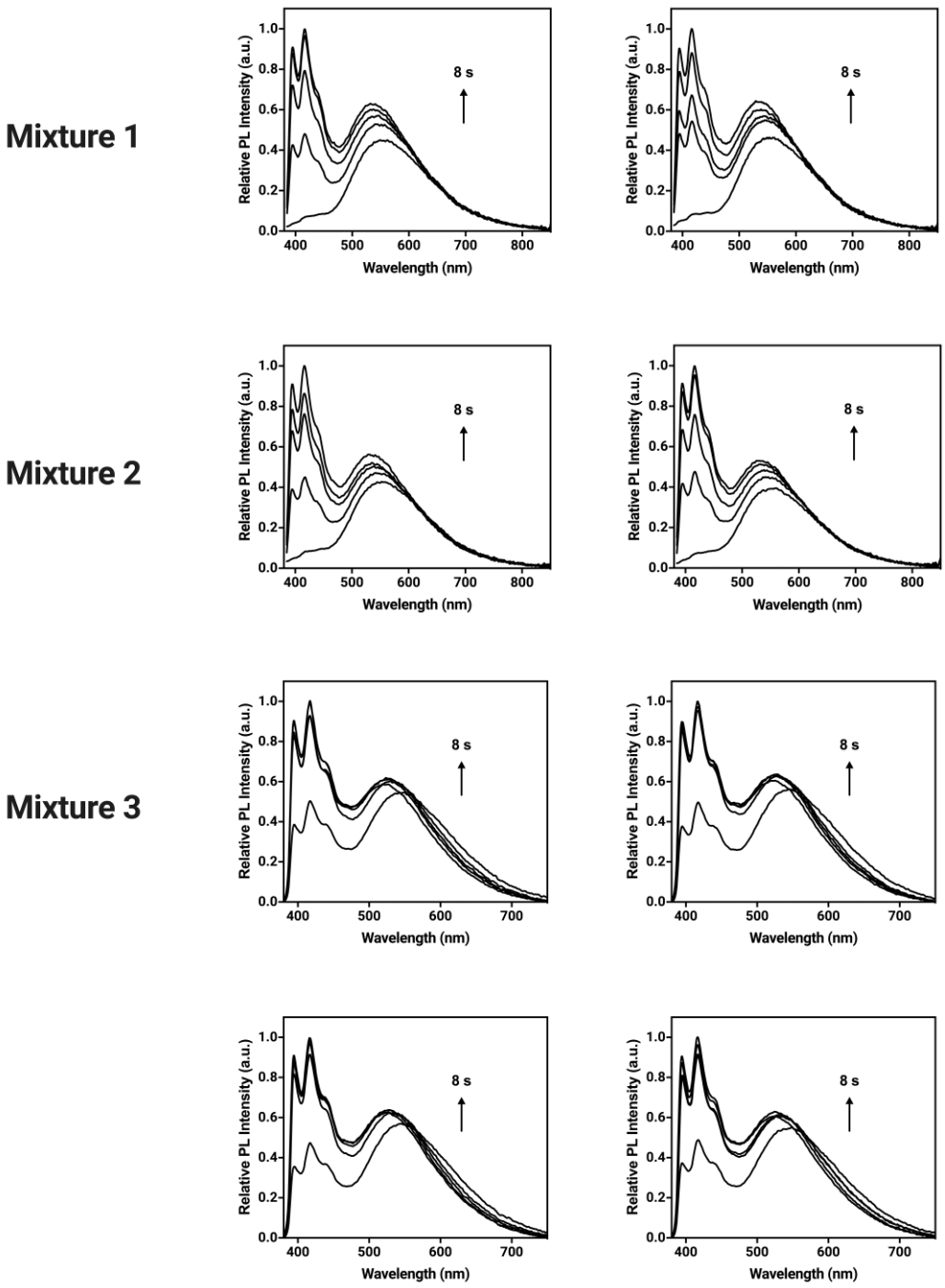


Figure S17. Normalized PL spectra of thin films prepared with doped PMMA (total concentration = 1 wt%). The mixing ratio of RGB was 1:1:1 (by weight) for all mixtures. λ_{exc} = 365 nm.

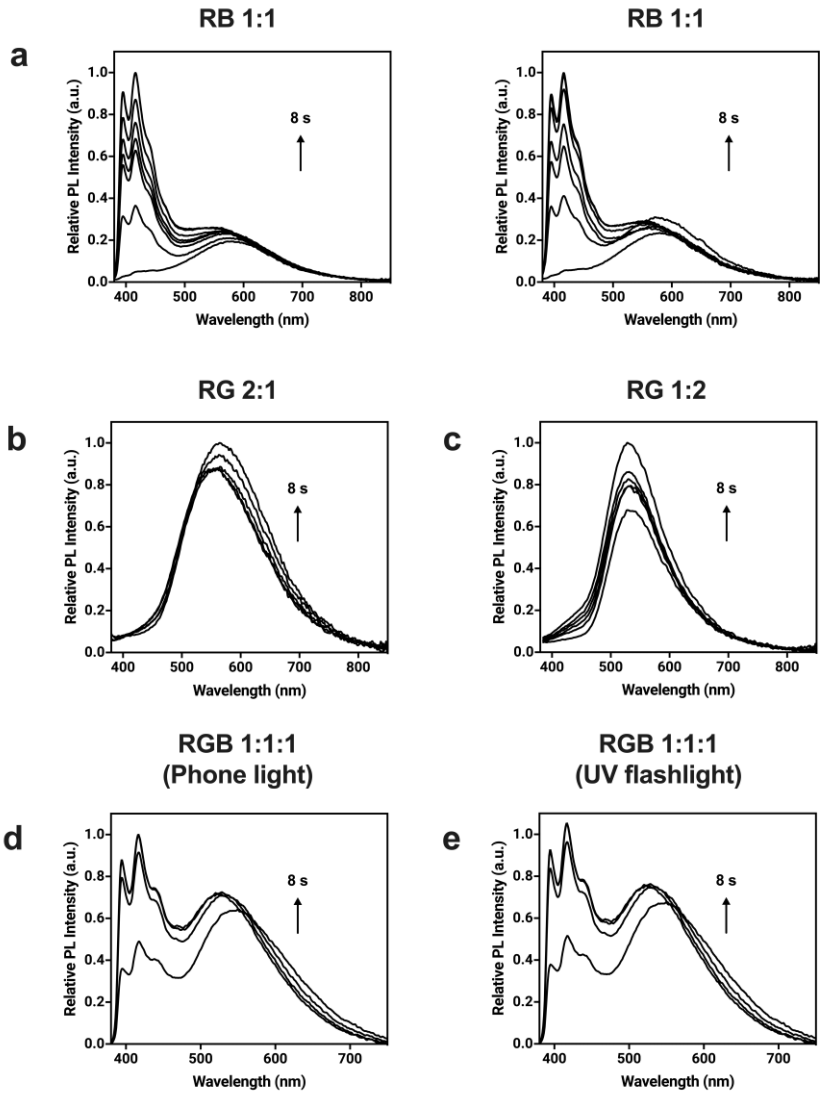


Figure S18. Normalized PL spectra of thin films prepared with doped PMMA (total concentration = 1 wt%). The mixing ratios are a) RB 1:1, b) RG 2:1 c) RG 1:2 d-e) RGB 1:1:1. a-c) A 400 nm photoreactor, d) an iPhone 7 and e) UV flashlight (Vansky, Amazon.ca) were used to irradiate the thin films.

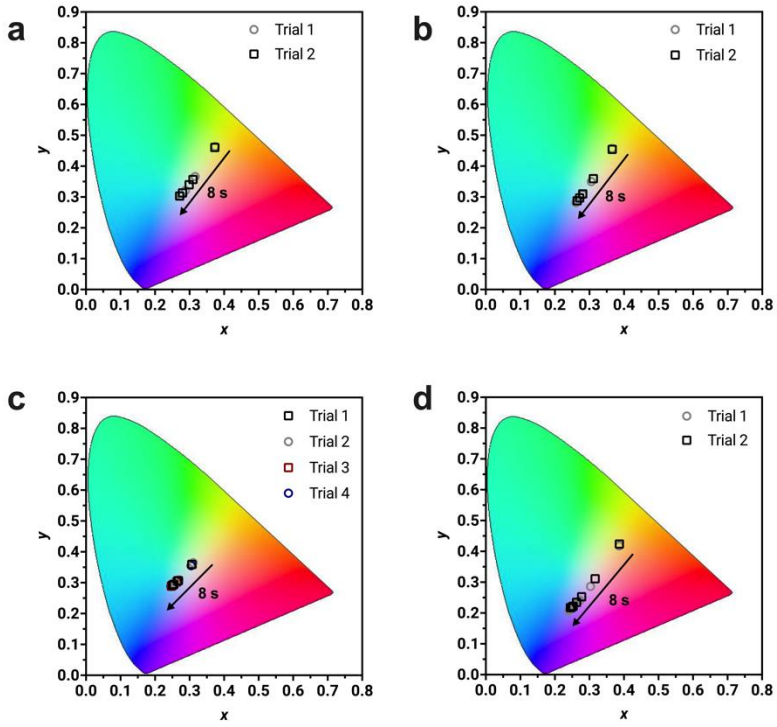


Figure S19. Chromaticity coordinates in CIE 1931 diagram of doped PMMA films (total concentration = 1 wt %) prepared from a) mixture 1, b) mixture 2, c) mixture 3, d) mixture 4 and 5.

References

1 H. Wang, A. G. Chen, A. X. Xu and S. Jia, Synthesis and Properties of the Bipolar Triphenylamine- benzimidazole Derivatives, *Aust. J. Chem.*, 2010, **63**, 712–718.

2 J. W. Jo, J. W. Jung, H. W. Wang, P. Kim, T. P. Russell and W. H. Jo, Fluorination of polythiophene derivatives for high performance organic photovoltaics, *Chem. Mater.*, 2014, **26**, 4214–4220.

3 Q. Wang, J. U. Wallace, T. Y.-H. Lee, J. J. Ou, Y.-T. Tsai, Y.-H. Huang, C.-C. Wu, L. J. Rothberg and S. H. Chen, Evaluation of propylene-, meta-, and para-linked triazine and tert-butyltriphenylamine as bipolar hosts for phosphorescent organic light-emitting diodes, *J. Mater. Chem. C*, 2013, **1**, 2224.

4 P. Xue, B. Yao, X. Liu, J. Sun, P. Gong, Z. Zhang, C. Qian, Y. Zhang and R. Lu, Reversible mechanochromic luminescence of phenothiazine-based 10,10′-bianthracene derivatives with different lengths of alkyl chains, *J. Mater. Chem. C*, 2015, **3**, 1018–1025.

5 P. R. Christensen and M. O. Wolf, Photopatterned Multidimensional Fluorescent Images, *Adv. Funct. Mater.*, 2016, **26**, 8471–8477.

6 P. Natarajan and M. Schmittel, Photoluminescence, redox properties, and electrogenerated chemiluminescence of twisted 9,9′-bianthryls, *J. Org. Chem.*, 2013, **78**, 10383–10394.