

Supplementary Information

Tunable Photochemical/Redox Properties of (Phenylthio)_ncorannulenes: Application to a Photovoltaic Device

Angela Steinauer,^a Anna M. Butterfield,^a Anthony Linden,^a Agustin Molina-Ontario,^b David C. Buck,^b Robert W. Cotta,^b Luis Echegoyen,^b Kim K. Baldridge^{*a,c} and Jay S. Siegel^{*a,c}

^aDepartment of Chemistry, University of Zurich, 8057 Zurich, Switzerland

^bDepartment of Chemistry, University of Texas at El Paso, 79968 El Paso-TX, USA

^cSchool of Pharmaceutical Science and Technology, Tianjin University, 300072 Nankai District-TJ, China

General methods

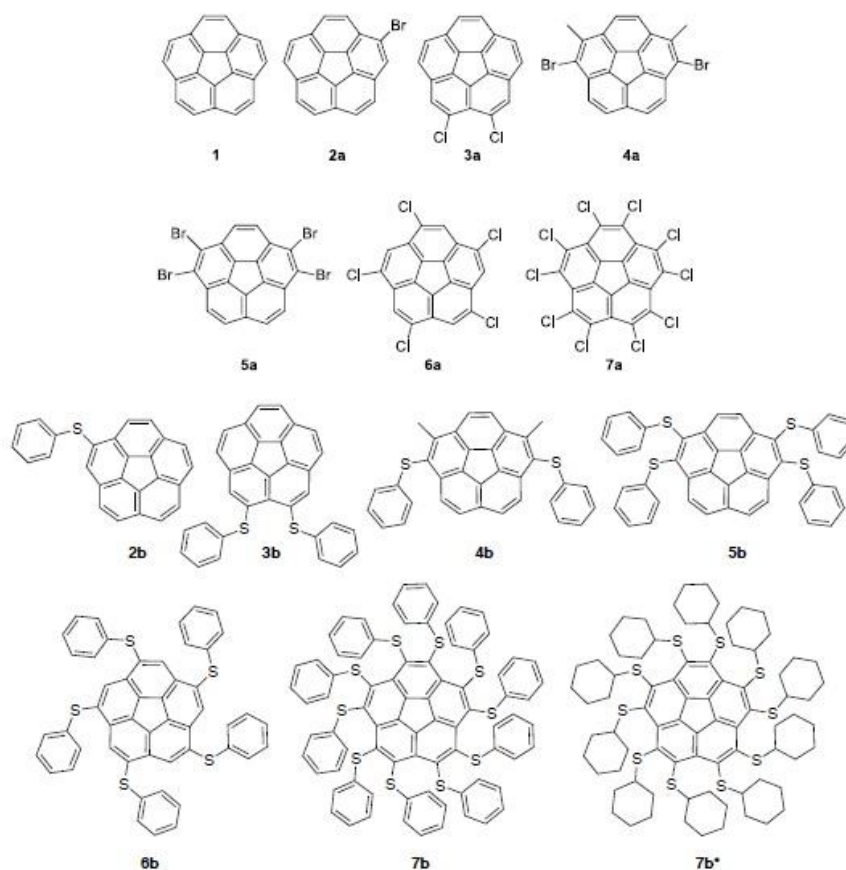
Unless otherwise stated, all chemicals were of reagent grade and purchased from Sigma-Aldrich (St. Louis, MO, USA). Acetonitrile and dichloromethane for UV-Vis measurements were of HPLC grade, THF for voltammetric measurements and 2-methyl-THF for phosphorescence measurements were distilled over CaH₂ prior to use. Electrolyte TBAH was purchased from Fluka (Buchs, Switzerland) and used as received. TCNE was purified by sublimation before used.

Chromatography: silica gel 60 M (Macherey-Nagel GmbH & Co, Düren, Germany). UV-Vis spectra: Agilent 8453 (Santa Clara, CA, USA). IR spectra: KBr from Fluka (Buchs, Switzerland); PerkinElmer Spectrum One, CSI Beam Splitter (Waltham, MA, USA). ¹H NMR and ¹³C NMR spectra in CD₂Cl₂ (Armar Chemicals, Döttingen, Switzerland), Bruker ARX 300/400/500 (Billerica, MA, USA; 300/400/500 MHz); δ in ppm rel. to CD₂Cl₂ (¹H NMR: δ 5.32; ¹³C NMR: δ 54.00); *J* in Hz. Fluorescence emission: Edinburgh Instruments F900 fluorimeter (Livingston, Scotland) equipped with S900 single photon photomultiplier detection system and Xe 900 xenon arc lamp (450 W). Cyclic voltammetry: CHI600C Electrochemical Analyzer, CH Instruments, Inc. (Bee Cave, Tx, USA). Electrodes: non-aqueous Ag/Ag⁺ reference electrode (10 mmol L⁻¹ AgNO₃ in 0.1 mol L⁻¹ Bu₄NPF₆ in acetonitrile), platinum wire counter electrode, glassy carbon working electrode; scan rate = 0.1 V s⁻¹; all E_{1/2} potentials have been directly obtained from cyclic voltammetric curves as averages of the cathodic and anodic peak potentials. For irreversible peaks, the peak potential is given. The internal standard was the ferrocenium/ferrocene couple standard potential (+0.085 V for THF¹ and +0.421 V for ACN²). 1 mmol L⁻¹ compnd. **1-7b*** and 0.07 mol L⁻¹ TBAPF₆ in THF (298 K). Charge-transfer complexes: a stock solution of TCNE (10⁻² mol L⁻¹ in CH₂Cl₂) and saturated solutions of **1-7b*** (concentrations between 6 × 10⁻³ mol L⁻¹ and 2 × 10⁻² mol L⁻¹, in 10⁻² mol L⁻¹ TCNE in CH₂Cl₂) were prepared. UV-Vis spectra of the charge-transfer complex from a 1:1 mix of solutions were measured. HR-EI and HR-ESI were performed by the MS Service of the Institute of Organic Chemistry at the University of Zurich (Switzerland). Bromocorannulene (**2a**),³ 2,3-dichlorocorannulene (**3a**),⁴ 1,6-dibromo-2,5-dimethylcorannulene (**4a**),⁵ 1,2,5,6-tetrabromocorannulene (**5a**),⁶ Sym-1,3,5,7,9-pentachlorocorannulene (**6a**)⁷ and decachlorocorannulene (**7a**)⁸ were prepared according to the literature procedures.

*e-mail: kimb@tju.edu.cn; dean_spst@tju.edu.cn

General synthetic procedure of *n*-(phenylthio)corannulene derivatives (**2b-7b**)

To an appropriate round bottom flask equipped with a reflux condenser, DMI (5-10 mL, dried over molecular sieve = MS) was added. Thiophenol (1.5 equiv./reaction site) and sodium hydride (1.2 equiv./reaction site, 60% in mineral oil) were added and allowed to stir at room temperature for 10 min. The halogenated corannulene derivative (**2a-7a**, 1 equiv.) was added and the solution was warmed to 60 °C for 18 h. The solution was cooled, extracted three times with dichloromethane (15-20 mL) and washed with water. The combined organic layers were dried over magnesium sulfate, filtered, and evaporated. The product was purified by column chromatography (silica gel) with a hexane/dichloromethane mixture as eluent (0-23% dichloromethane, depending on compound). The yield of a light yellow to dark red solid (**2b-7b**) was 28-89%.



Scheme S1.

Mono(phenylthio)corannulene (**2b**)

To a 10 mL round bottom flask equipped with a reflux condenser, DMI (5 mL, dried over MS) was added. Thiophenol (22 mg, 0.20 mmol) and sodium hydride (6 mg, 0.15 mmol, 60% in mineral oil) were added and allowed to stir at room temperature for 10 min. **2a** (41 mg, 0.12 mmol) was added and the solution was warmed to 60 °C for 18 h. The solution was cooled, extracted three times with dichloromethane (15 mL) and washed with water. The organic layer was dried over magnesium sulfate, filtered, and evaporated. The product was purified by column chromatography (silica gel) with hexane as eluent. The yield of a light yellow solid was 12 mg (28%); R_f 0.78 (2:1, hexane/dichloromethane); UV-Vis (acetonitrile) 194 (4.7), 249 (4.7), 256 (λ_{max} , 4.7), 293 (4.4); m.p. 54-55 °C; ^1H NMR (400 MHz, CD_2Cl_2) δ 7.97 (s, 1H), 7.94 (d, J 8.8 Hz, 1H), 7.85-7.78 (m, 5H), 7.73 (d, J 8.8 Hz, 1H), 7.47-7.44 (m, 1H), 7.47-7.44 (m, 2H), 7.33-7.26 (m, 3H); ^{13}C NMR (400 MHz, CD_2Cl_2) δ 137.90, 136.88, 136.46, 136.30, 136.20, 136.03, 133.91, 132.82, 131.95,

131.76, 131.66, 131.62, 131.44, 130.21, 129.81, 128.29, 128.09, 128.05, 128.01, 127.76, 127.64, 127.20, 126.07, 126.62; IR: 3745w, 3442w, 2922w, 1688w, 1580w, 1474w, 1437w, 1262w, 1078w, 1022m, 877w, 828m, 737w, 688w, 675w, 656w, 539w, 463w. HR-EI calcd. for $C_{26}H_{14}S$ $[M]^+$: 358.08162; found: 358.08171.

Di(phenylthio)corannulene (**3b**)

To a 10 mL round bottom flask equipped with a reflux condenser, DMI (5 mL, dried over MS) was added. Thiophenol (43 mg, 0.39 mmol) and sodium hydride (13 mg, 0.33 mmol, 60% in mineral oil) were added and allowed to stir at room temperature for 10 min. **3a** (41 mg, 0.13 mmol) was added and the solution was warmed to 60 °C for 18 h. The solution was cooled, extracted three times with dichloromethane (15 mL) and washed with water. The organic layer was dried over magnesium sulfate, filtered, and evaporated. The product was purified by column chromatography (silica gel) with hexane/dichloromethane (1:10) as eluent. The yield of a light yellow solid was 20 mg (33%); R_f 0.69 (2:1, hexane/dichloromethane); UV-Vis (acetonitrile) 255 (λ_{max} , 4.6), 278 (4.3), 295 (4.3); m.p. 61.1-63.4 °C; 1H NMR (400 MHz, CD_2Cl_2) δ 7.82 (s, 2H), 7.81 (d, J 8.8 Hz, 2H), 7.77 (s, 2H), 7.64 (d, J 8.8 Hz, 2H), 7.39-7.26 (m, 10H); ^{13}C NMR (500 MHz, CD_2Cl_2) δ 137.96, 136.41, 136.01, 135.72, 135.04, 132.56, 131.63, 131.55, 131.24, 130.15, 129.96, 128.57, 127.92, 127.66, 126.71; IR 3744w, 2920m, 2850m, 1631w, 1580w, 1474m, 1438m, 1397w, 1262m, 1082m, 1022m, 880w, 825m, 736m, 688m, 652w, 559w; HR-EI calcd. for $C_{32}H_{18}S_2$ $[M]^+$: 466.08499; found: 466.08535.

Di(methyl)-di(phenylthio)corannulene (**4b**)

To a 10 mL round bottom flask equipped with a reflux condenser, DMI (5 mL, dried over MS) was added. Thiophenol (38 mg, 0.34 mmol) and sodium hydride (11 mg, 0.28 mmol, 60% in mineral oil) were added and allowed to stir at room temperature for 10 min. **4a** (50 mg, 0.115 mmol) was added and the solution was warmed to 60 °C for 18 h. The solution was cooled, extracted three times with dichloromethane (15 mL) and washed with water. The organic layer was dried over magnesium sulfate, filtered, and evaporated. The product was purified by column chromatography (silica gel) with hexane as eluent. The yield of a light yellow solid was 20 mg (35%); R_f 0.74 (2:1, hexane/dichloromethane); UV-Vis (acetonitrile) 201 (4.8), 255 (4.8), 263 (λ_{max} , 4.8), 300 (4.4); m.p. 258.6-259.9 °C; 1H NMR (400 MHz, CD_2Cl_2) δ 7.99 (s, 2H), 7.95 (d, J 9.2 Hz, 2H), 7.72 (d, J 8.8 Hz, 2H), 7.12-7.17 (m, 8H), 7.13-7.09 (m, 2H); ^{13}C NMR (500 MHz, CD_2Cl_2) δ 142.67, 139.05, 136.48, 135.68, 135.30, 134.59, 131.93, 130.93, 129.97 (all quaternary Cs), 129.57, 127.80, 125.97 (phenyl Cs), 128.34, 127.45, 126.16 (C-Hs on corannulene); IR 3745w, 3441w, 2962w, 2922w, 2851w, 1579w, 1476m, 1436m, 1400m, 1371w, 1338w, 1312w, 1292w, 1261m, 1066m, 1085m, 945w, 901w, 795s, 738s, 700m, 688m, 636w, 587w, 519w, 463w; HR-EI calcd. for $C_{34}H_{22}S_2$ $[M]^+$: 494.11629; found: 494.11622.

Tetrakis(phenylthio)corannulene (**5b**)

To a 25 mL round bottom flask equipped with a reflux condenser, DMI (10 mL, dried over MS) was added. Thiophenol (119 mg, 1.08 mmol) and sodium hydride (57 mg, 1.43 mmol, 60% in mineral oil) were added and allowed to stir at room temperature for 10 min. **5a** (100 mg, 0.18 mmol) was added and the solution was warmed to 60 °C for 18 h. The solution was cooled, extracted three times with dichloromethane (20 mL) and washed with water. The organic layer was dried over magnesium sulfate, filtered, and evaporated. The product was purified by column chromatography (silica gel) with hexane as eluent. The yield of a yellow solid was 96 mg (77%); R_f 0.58 (2:1, hexane/dichloromethane); UV-Vis (acetonitrile) 260 (λ_{max} , 4.8), 314 (4.3); m.p. 108.7-109.9 °C; 1H NMR (400 MHz, CD_2Cl_2) δ 7.78 (d, J 8 Hz, 2H), 7.77 (s, 2H), 7.59 (d, J 8 Hz, 2H), 7.42-7.36 (m, 8H), 7.30-7.19 (m, 12H); ^{13}C NMR (500 MHz, CD_2Cl_2) δ 138.96, 138.92, 138.68, 137.71, 137.00, 136.91, 136.14, 134.21, 134.12, 131.64, 129.79, 129.77, 129.30, 129.24, 129.09, 128.86, 128.57, 126.84, 126.81; IR 3052w, 2962m, 2923m, 2853w, 1578m, 1475m, 1437m, 1315w, 1261s, 1195w, 1080s, 1022s, 918w, 799s, 735s, 686m, 591w, 465w; HR-ESI calcd. for $C_{44}H_{26}NaS_4^+$ $[M]^+$: 705.08150; found: 705.08110.

Pentakis(phenylthio)corannulene (**6b**)

To a 25 mL round bottom flask equipped with a reflux condenser, DMI (10 mL, dried over MS) was added. Thiophenol (198 mg, 1.80 mmol) and sodium hydride (58 mg, 1.45 mmol, 60% in mineral oil) were added and allowed to stir at room temperature for 10 min. **6a** (100 mg, 0.24 mmol) was added and the solution was warmed to 60 °C for 18 h. The solution was cooled, extracted three times with dichloromethane (20 mL) and washed with water. The organic layer was dried over magnesium sulfate, filtered, and evaporated. The product was purified by column chromatography (silica gel) with hexane as eluent. The yield of a yellow solid was 57 mg (30%); R_f 0.60 (2:1, hexane/dichloromethane); UV-Vis (acetonitrile) 254 (λ_{max} , 4.9), 344 (4.5); m.p. 161.9-163.7 °C; 1H NMR (400 MHz, CD_2Cl_2) δ 7.82 (s, 5H), 7.31-7.25 (m, 25H); ^{13}C NMR (400 MHz, CD_2Cl_2) δ 136.07, 136.03, 135.94, 132.37, 131.24, 129.95, 129.58, 127.81; IR 3442w, 3053w, 2922w, 2852w, 1724w, 1580m, 1476m, 1438m, 1407m, 1294m, 1170w, 1082m, 1069m, 1023m, 997w, 948m, 877m, 807w, 733s, 703m, 686s, 662w, 541w, 502w, 471w; HR-ESI calcd. for $[C_{50}H_{30}NaS_5]^+$: 813.08487; found: 813.08383.

Decakis(phenylthio)corannulene (**7b**)

To a 25 mL round bottom flask equipped with a reflux condenser, DMI (10 mL, dried over MS) was added. Thiophenol (174 mg, 1.58 mmol) and sodium hydride (50 mg, 1.25 mmol, 60% in mineral oil) were added and allowed to stir at room temperature for 10 min. **7a** (100 mg, 0.10 mmol) was added and the solution was warmed to 60 °C for 18 h. The solution was cooled, extracted three times with dichloromethane (20 mL) and washed with water. The organic layer was dried over magnesium sulfate, filtered, and evaporated. The product was purified by column chromatography (silica gel) with 10:3 hexane/dichloromethane as eluent. The yield of a dark red solid was 124 mg (89%); R_f 0.36 (2:1, hexane/dichloromethane); UV-Vis (acetonitrile) 235 (5.0), 261 (λ_{max} , 5.0), 416 (4.4); m.p. 114.9-117.2 °C; 1H NMR (300 MHz, CD_2Cl_2) δ 7.02-7.00 (m, 30H), 6.81-6.78 (m, 20H); ^{13}C NMR (500 MHz, CD_2Cl_2) δ 142.83, 140.45, 135.47, 134.69, 129.32, 127.87, 126.07; IR 3853w, 3745w, 3053w, 2922w, 2850w, 1580s, 1475s, 1437m, 1284m, 1177w, 1080w, 1067w, 1023m, 985m, 901w, 733s, 697s, 685s, 660w, 471w; HR-ESI calcd. for $[C_{80}H_{50}NaS_{10}]^+$: 1353.10173; found: 1353.10154.

Decakis(cyclohexylthio)corannulene (**7b***)

To a 25 mL round bottom flask equipped with a reflux condenser, DMI (15 mL, dried over MS) was added. Cyclohexanethiol (275 mg, 2.37 mmol) and sodium hydride (126 mg, 3.16 mmol, 60% in mineral oil) were added and allowed to stir at room temperature for 10 min. **7a** (150 mg, 0.158 mmol) was added and the solution was warmed to 60 °C for 18 h. The solution was cooled, extracted three times with dichloromethane (20 mL) and washed with water. The organic layer was dried over magnesium sulfate, filtered, and removed under reduced pressure. The product was purified by column chromatography (silica gel) with 5:1 hexane/dichloromethane as eluent. The yield of a red solid was 185 mg (84%); R_f 0.24 (2:1, hexane/dichloromethane); UV-Vis (acetonitrile) 270 (λ_{max} , 4.2), 316 (3.9), 380 (4.0); m.p. 135.9-136.3 °C; 1H NMR (500 MHz, $CDCl_3$) δ 3.33 (t, 1H), 1.75-1.15 (m, 10H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 141.95, 133.65, 131.63, 52.26, 33.13, 26.41, 26.14; IR 2925w, 2850w, 1261w, 982w, 742w; MS (MALDI) m/z (%) 1390.5 $[M]^+$ (67), 1307.3 $[M-C_6H_{11}]^+$ (18), $[M-S-C_6H_{11}]^+$ (2).

UV-Vis Spectra

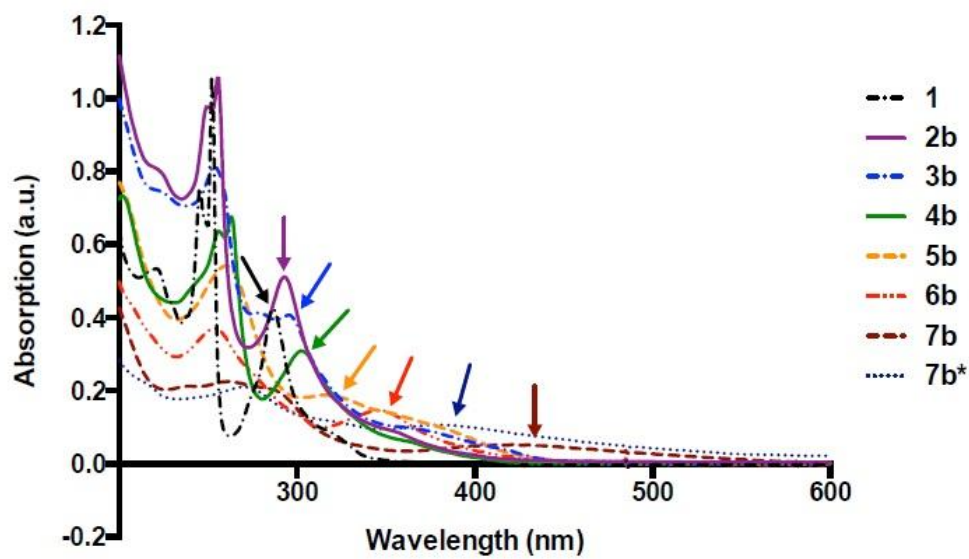


Figure S1. Overview of all spectra. Arrows indicate longest wavelengths of absorption.

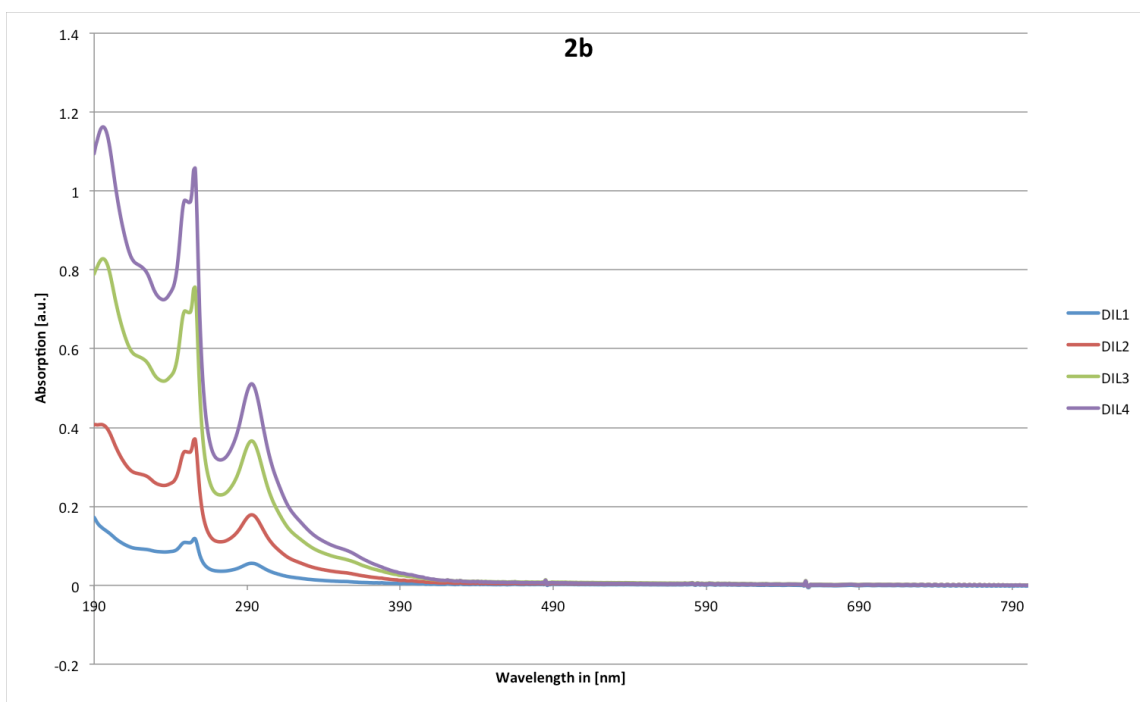


Figure S2. UV-Vis spectra of **2b** at four different concentrations to determine molar extinction coefficients.

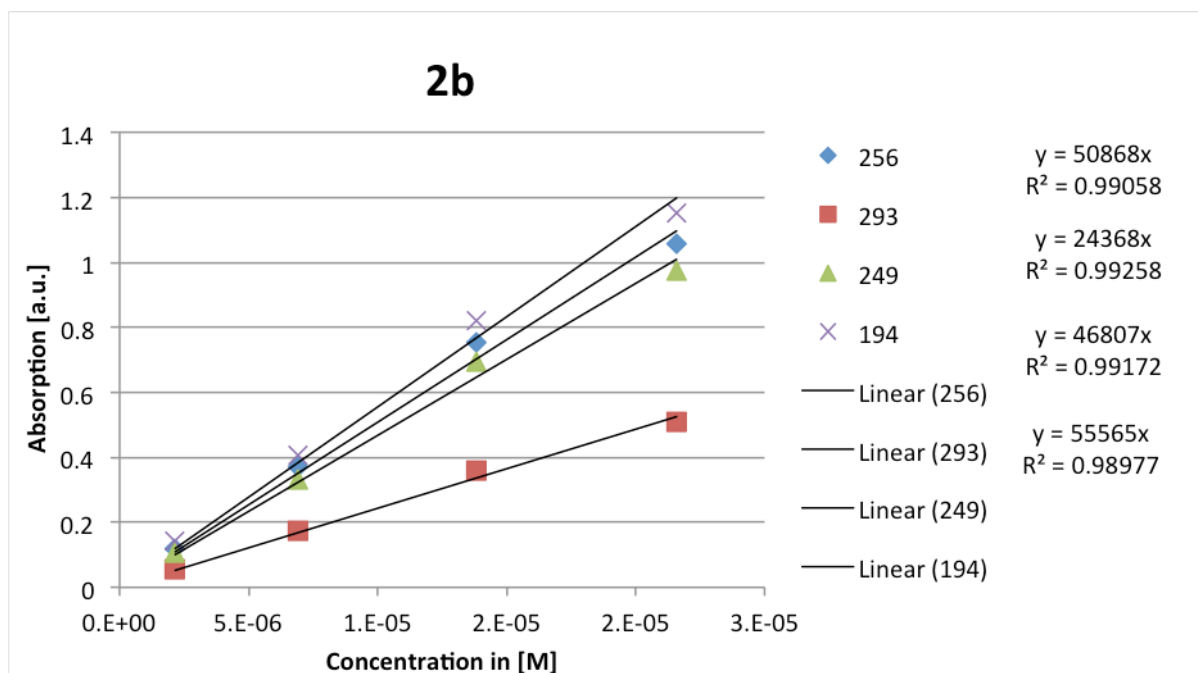


Figure S3. Plot of absorption vs. concentration to determine molar absorptivity of **2b**.

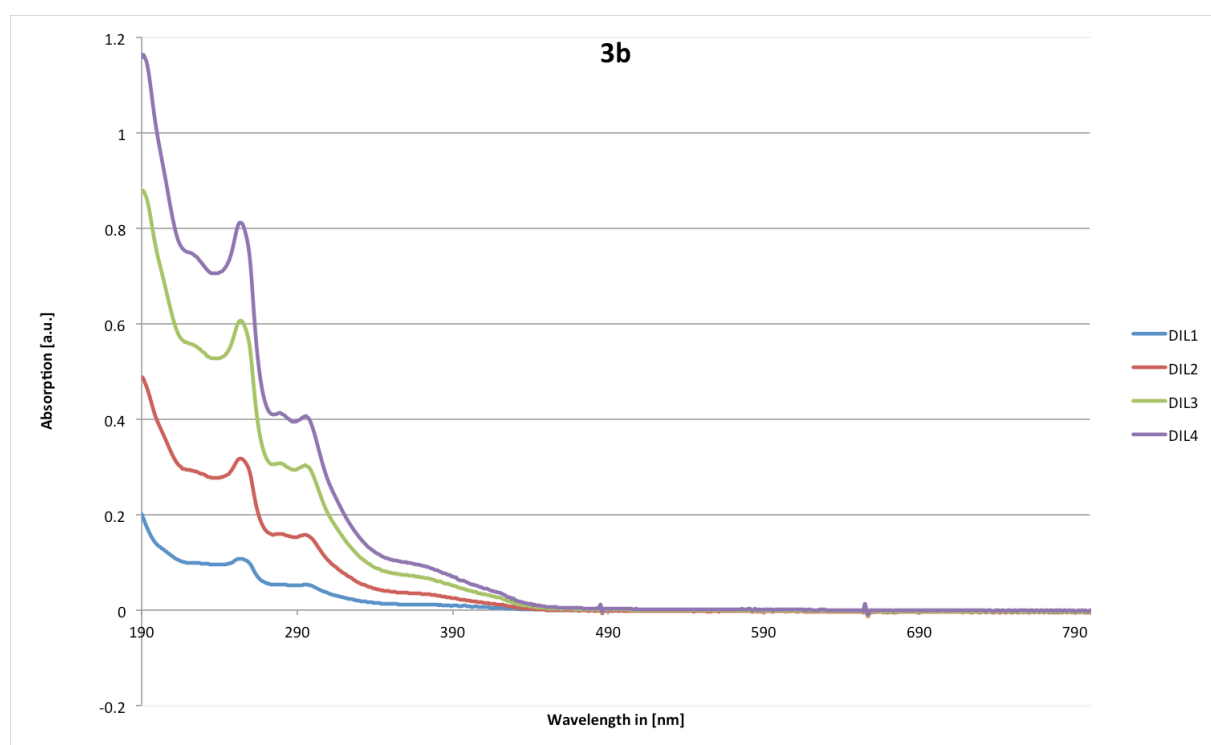


Figure S4. UV-Vis spectra of **3b** at four different concentrations to determine molar extinction coefficients.

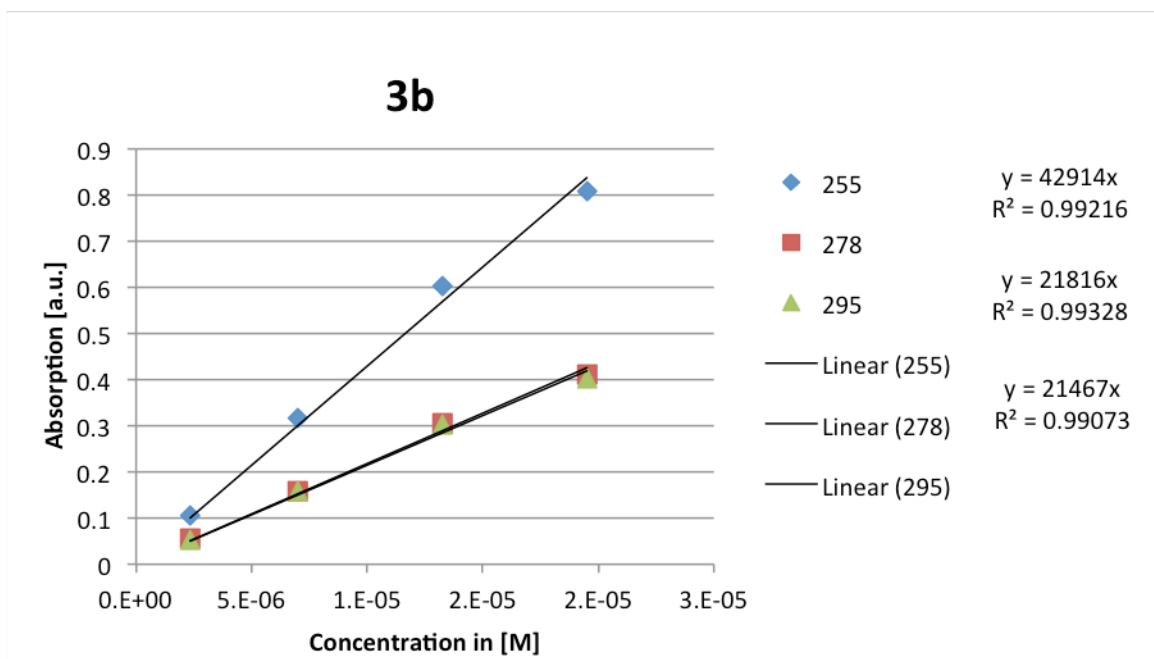


Figure S5. Plot of absorption vs. concentration to determine molar absorptivity of **3b**.

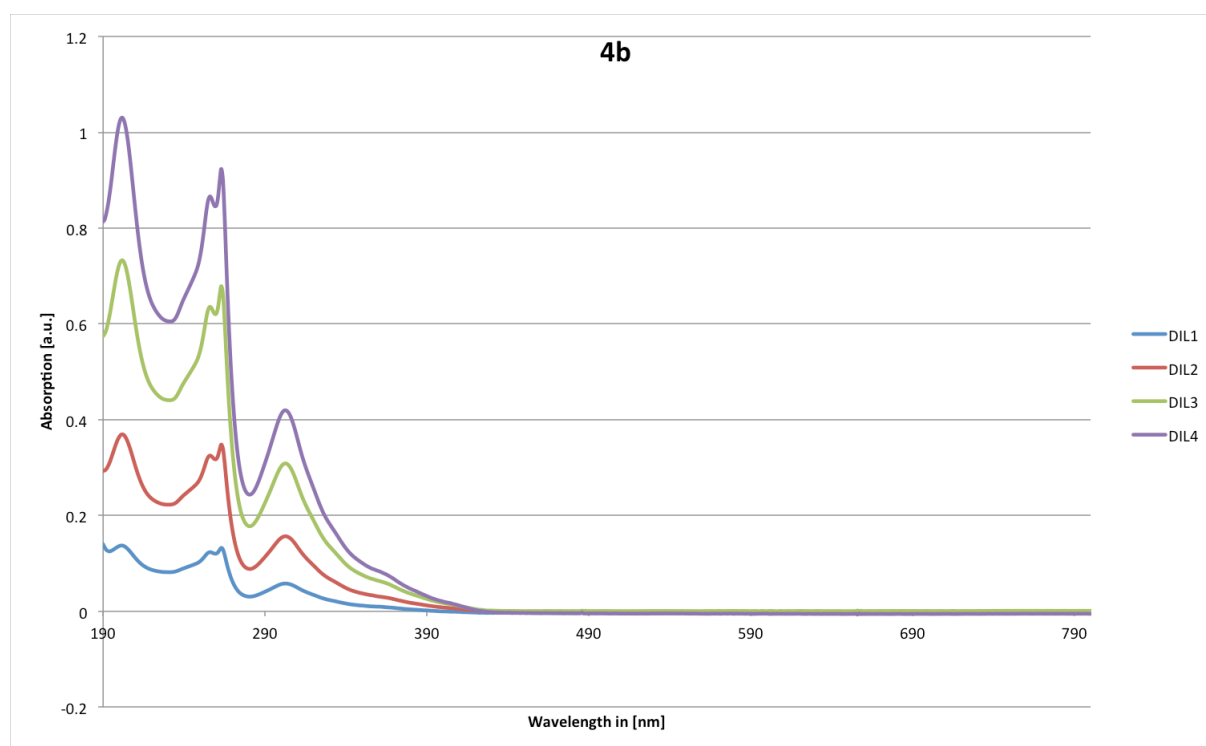


Figure S6. UV-Vis spectra of **4b** at four different concentrations to determine molar extinction coefficients.

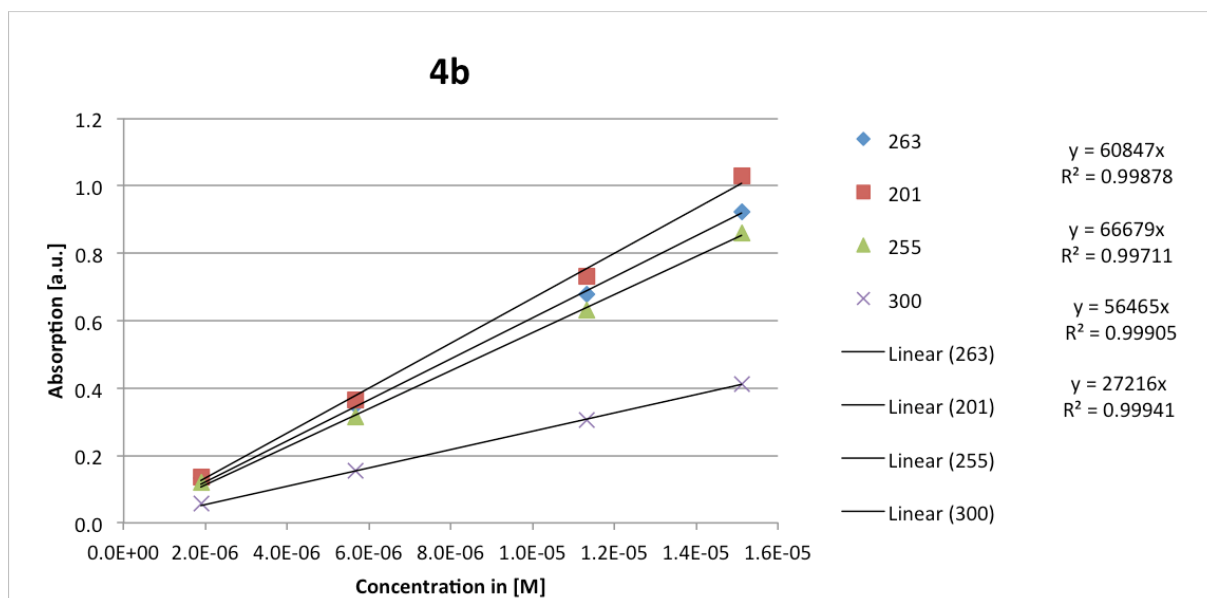


Figure S7. Plot of absorption vs. concentration to determine molar absorptivity of **4b**.

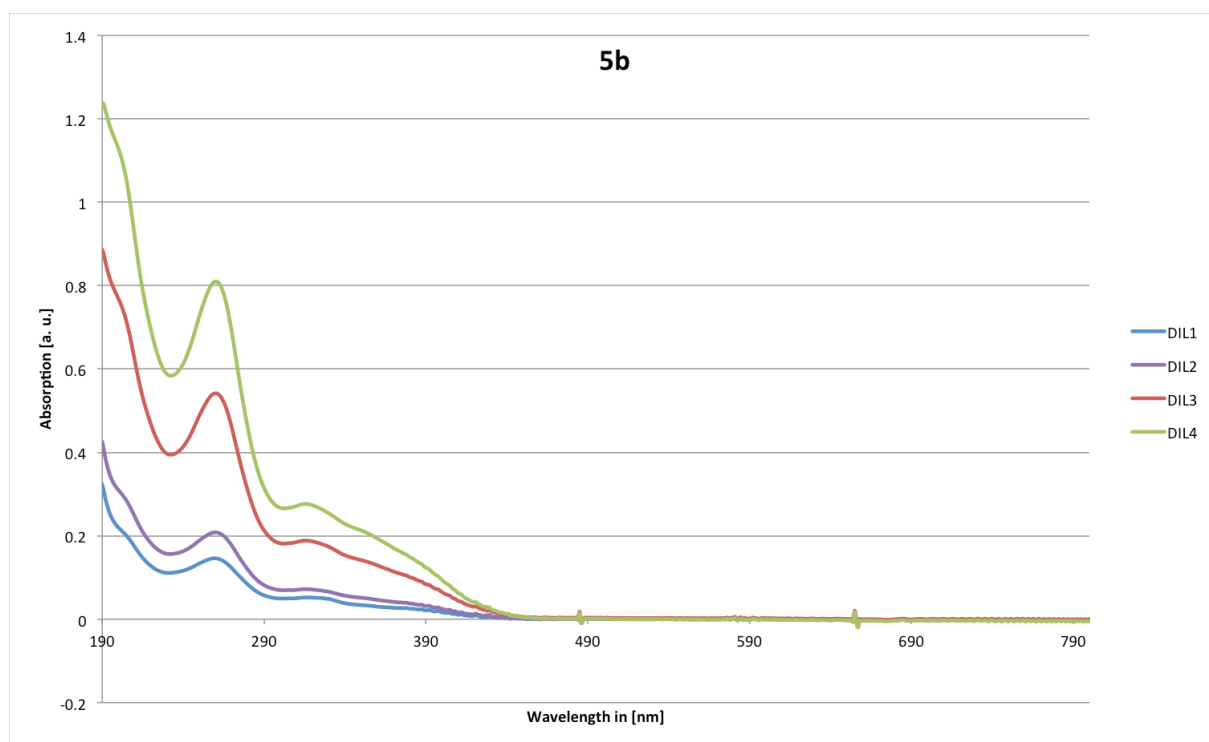


Figure S8. UV-Vis spectra of **5b** at four different concentrations to determine molar extinction coefficients.

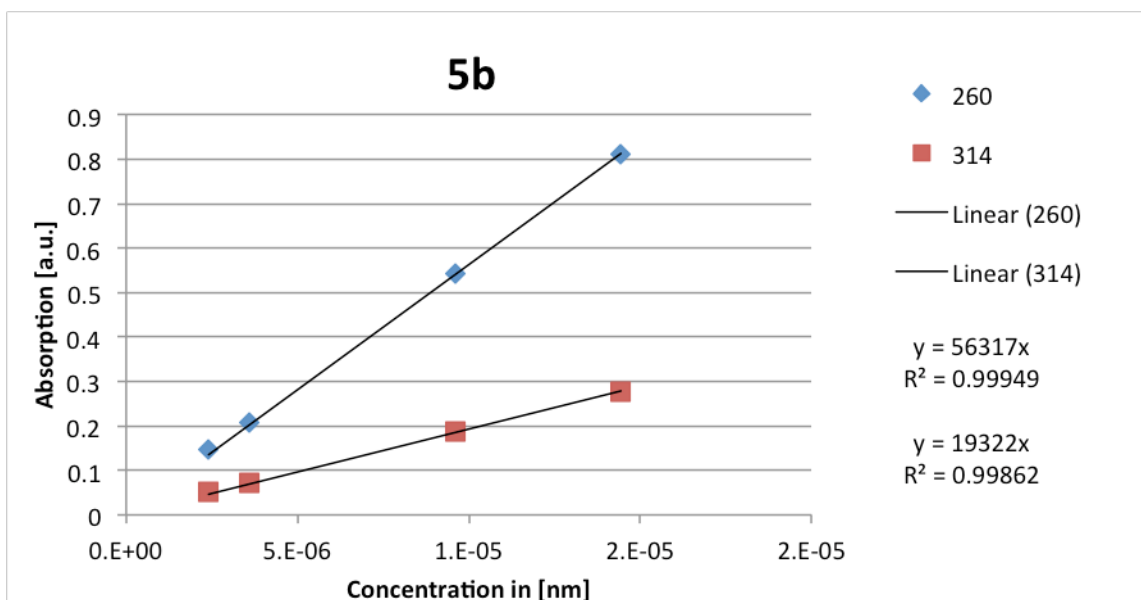


Figure S9. Plot of absorption vs. concentration to determine molar absorptivity of **5b**.

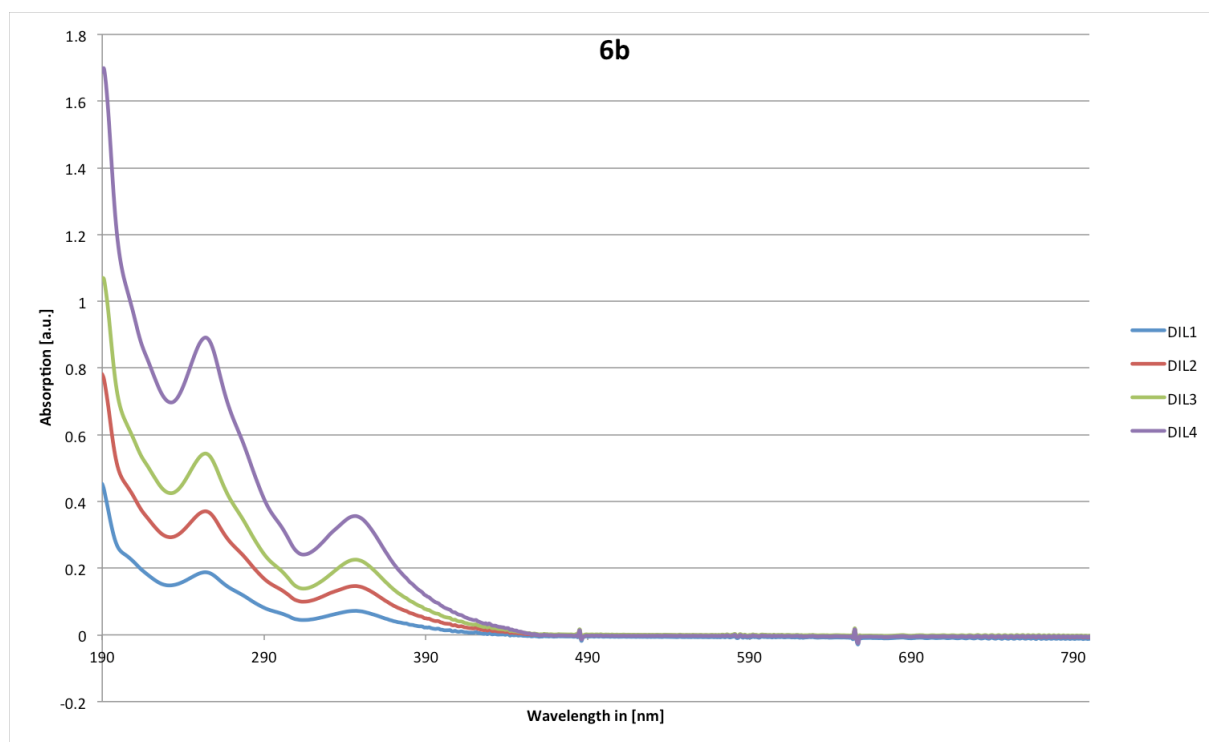


Figure S10. UV-Vis spectra of **6b** at four different concentrations to determine molar extinction coefficients.

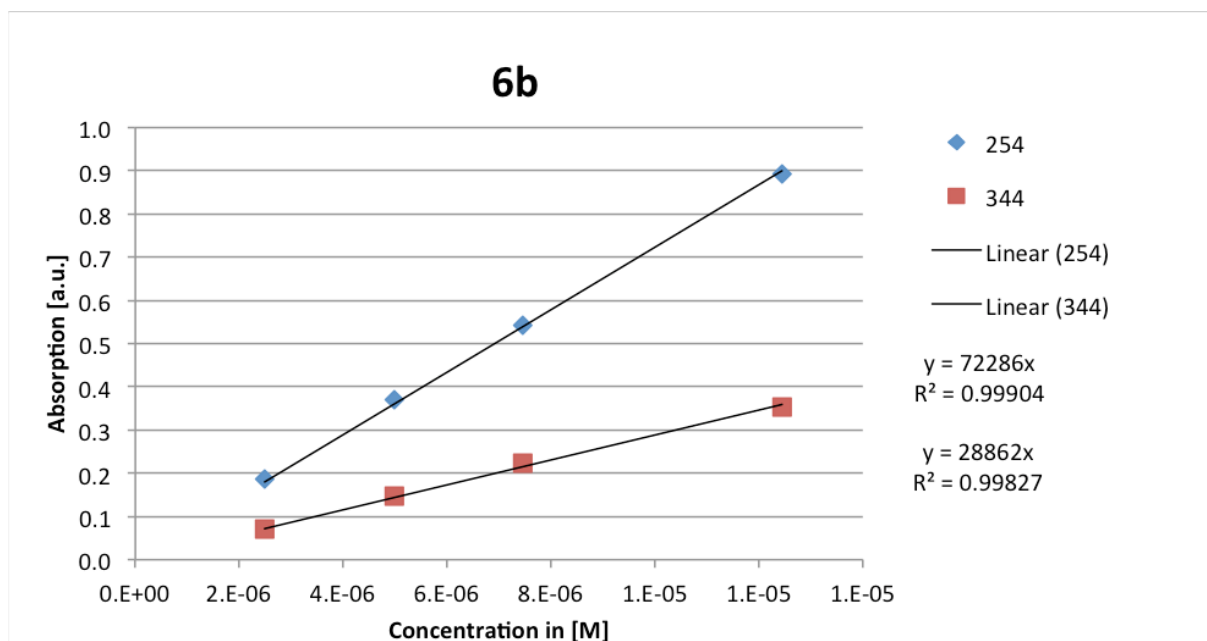


Figure S11. Plot of absorption vs. concentration to determine molar absorptivity of **6b**.

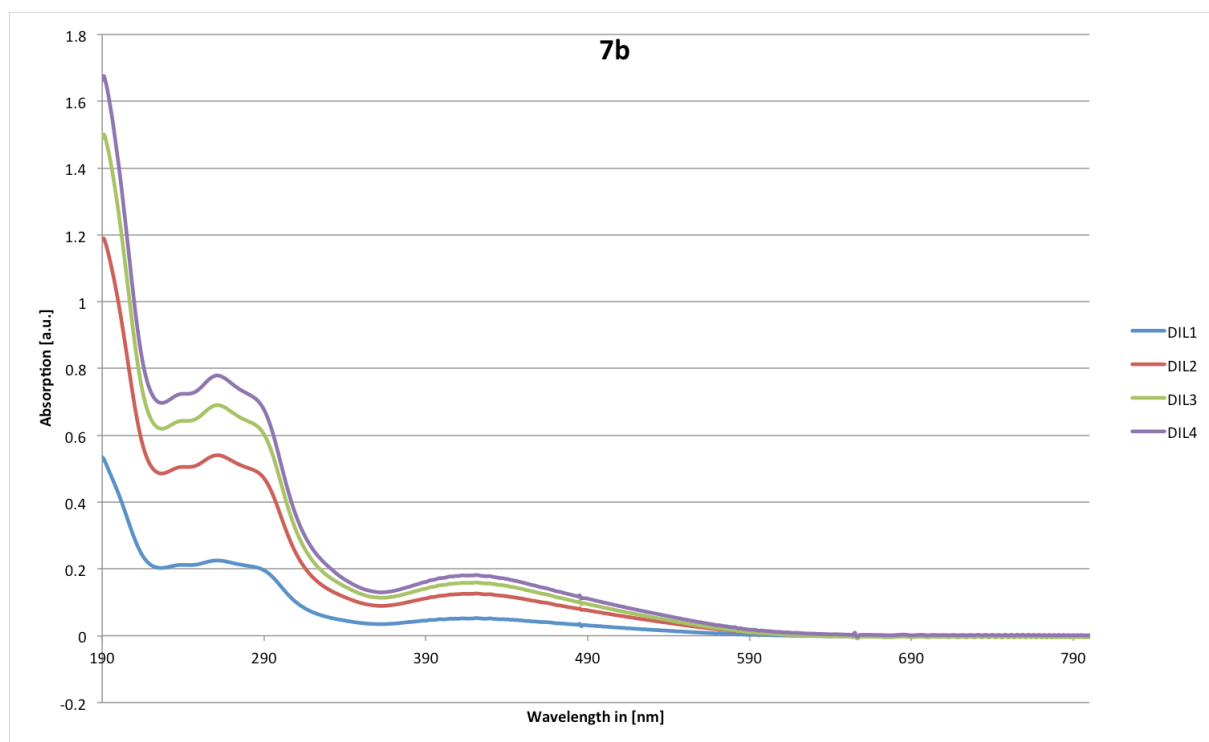


Figure S12. UV-Vis spectra of **7b** at four different concentrations to determine molar extinction coefficients.

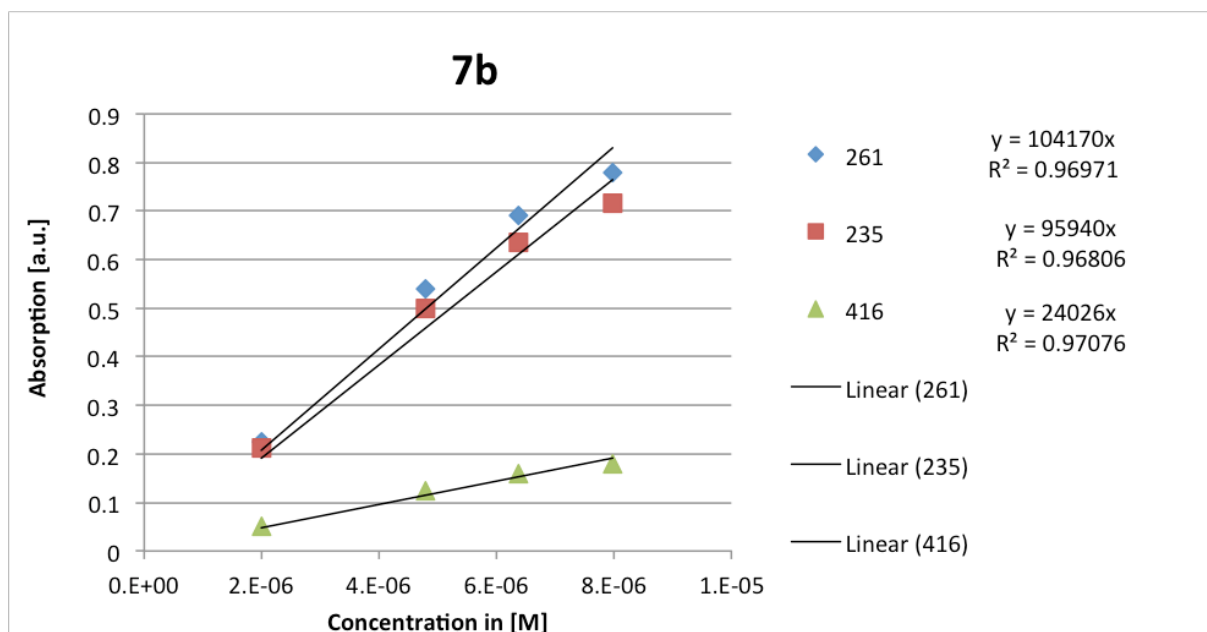


Figure S13. Plot of absorption vs. concentration to determine molar absorptivity of **7b**.

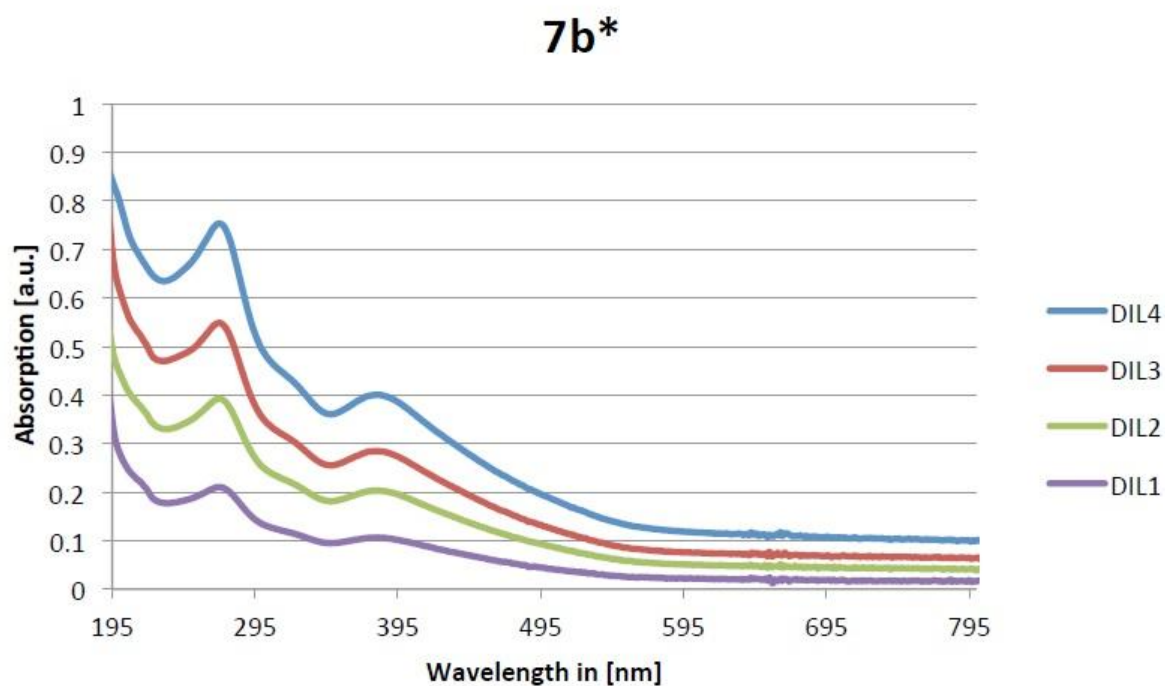


Figure S14. UV-Vis spectra of **7b*** at four different concentrations to determine molar extinction coefficients.

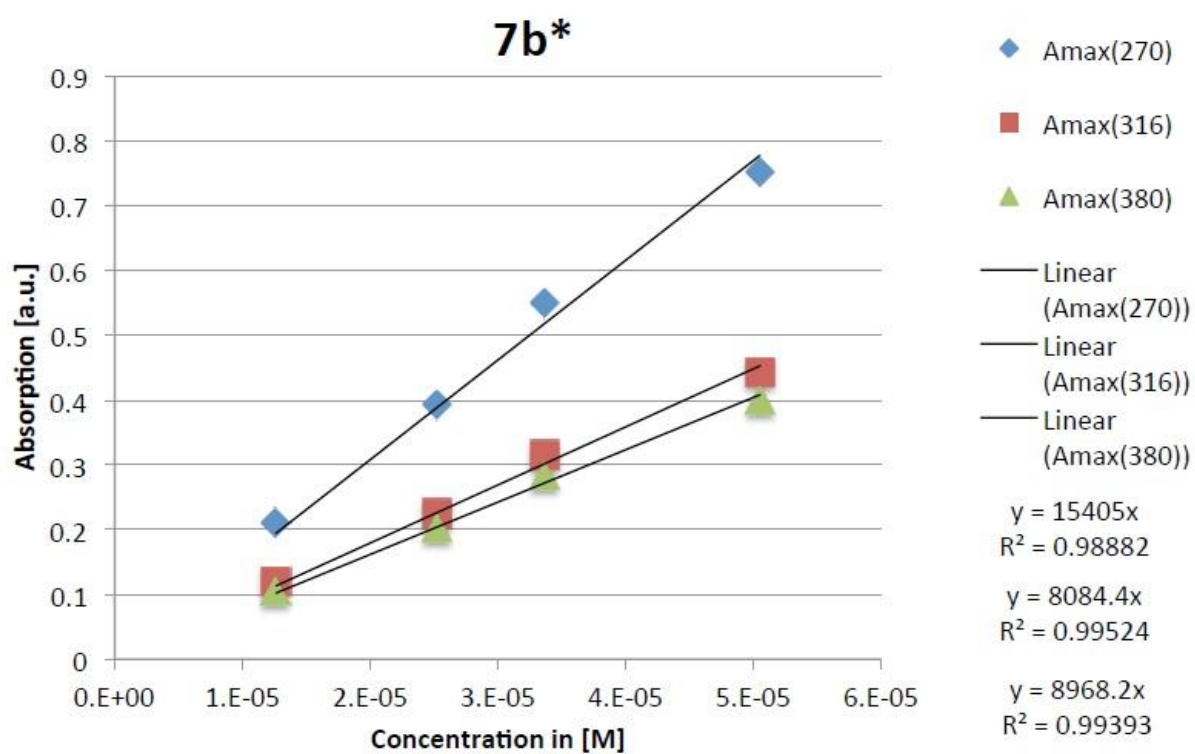


Figure S15. Plot of absorption vs. concentration to determine molar absorptivity of **7b***.

Cyclic voltammetry

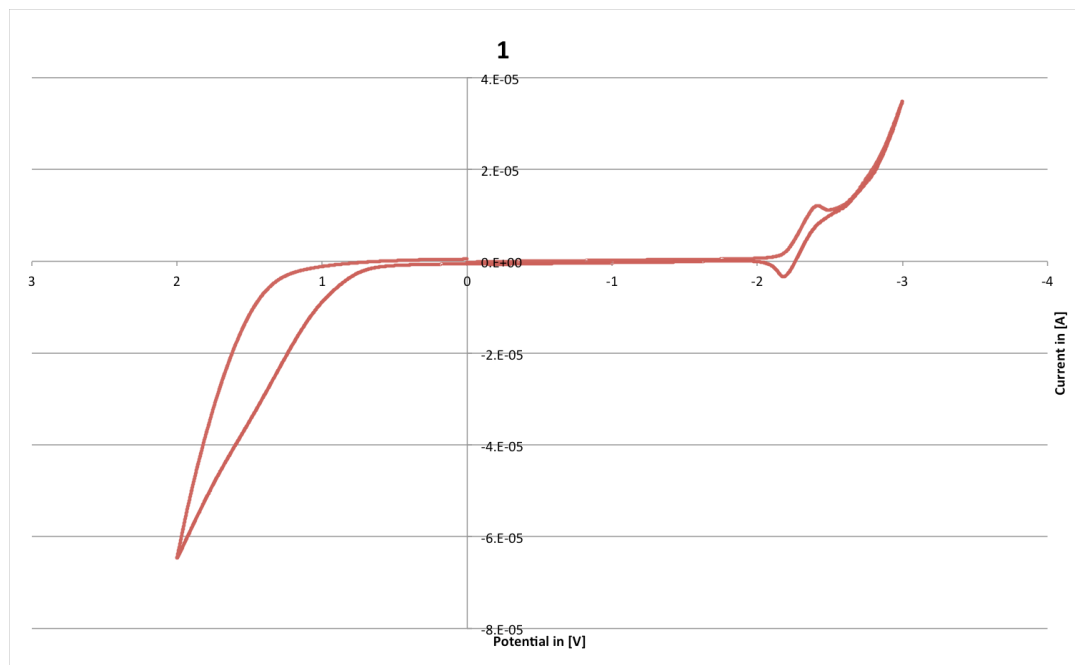


Figure S16. Cyclic voltammogram of **1**. Scan rate = 0.1 V s^{-1} ; 1 mmol L^{-1} in a 0.07 TBAH/THF solution; $T = 298 \text{ K}$. Glassy carbon working electrode; reference electrode Ag/Ag⁺ in ACN; platinum wire counter electrode.

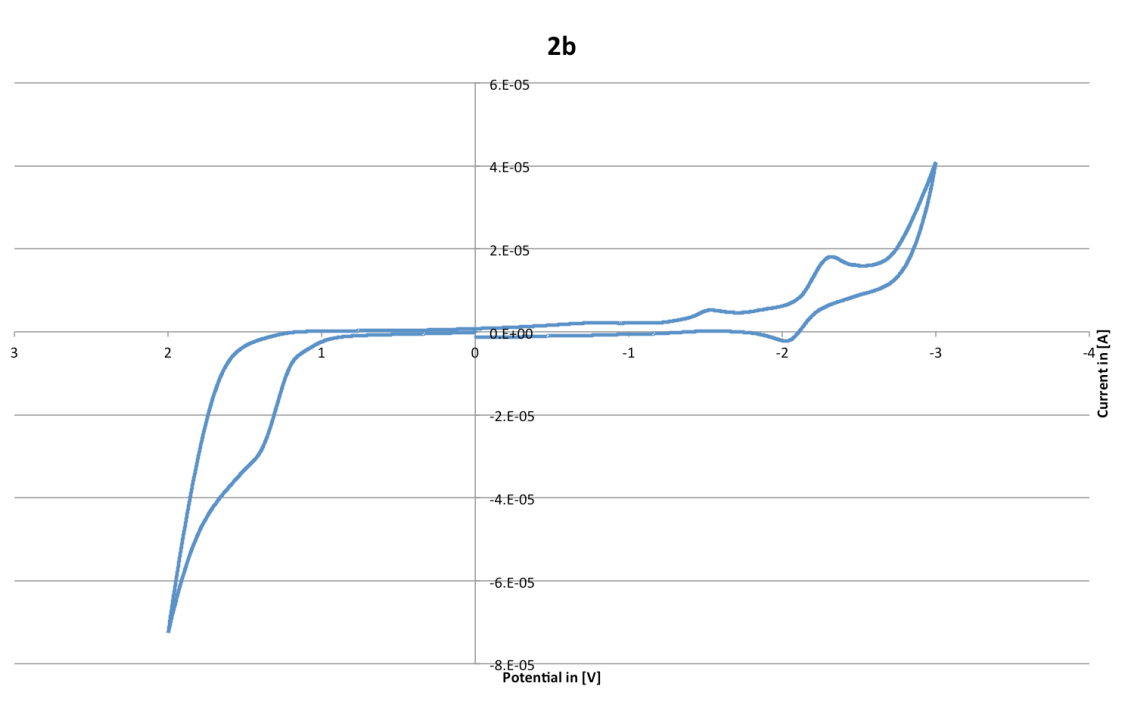


Figure S17. Cyclic voltammogram of **2b**. Scan rate = 0.1 V s^{-1} ; 1 mmol L^{-1} in a 0.07 TBAH/THF solution; $T = 298 \text{ K}$. Glassy carbon working electrode; reference electrode Ag/Ag^+ in ACN; platinum wire counter electrode.

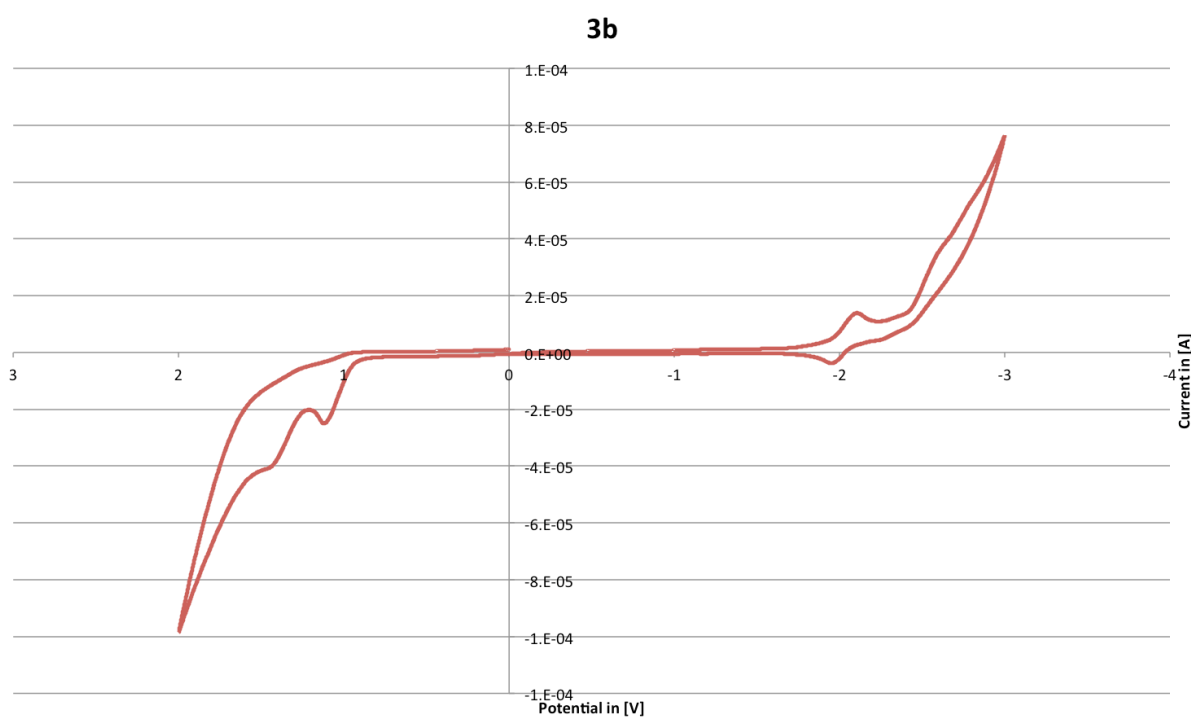


Figure S18. Cyclic voltammogram of **3b**. Scan rate = 0.1 V s^{-1} ; 1 mmol L^{-1} in a 0.07 TBAH/THF solution; $T = 298 \text{ K}$. Glassy carbon working electrode; reference electrode Ag/Ag^+ in ACN; platinum wire counter electrode.

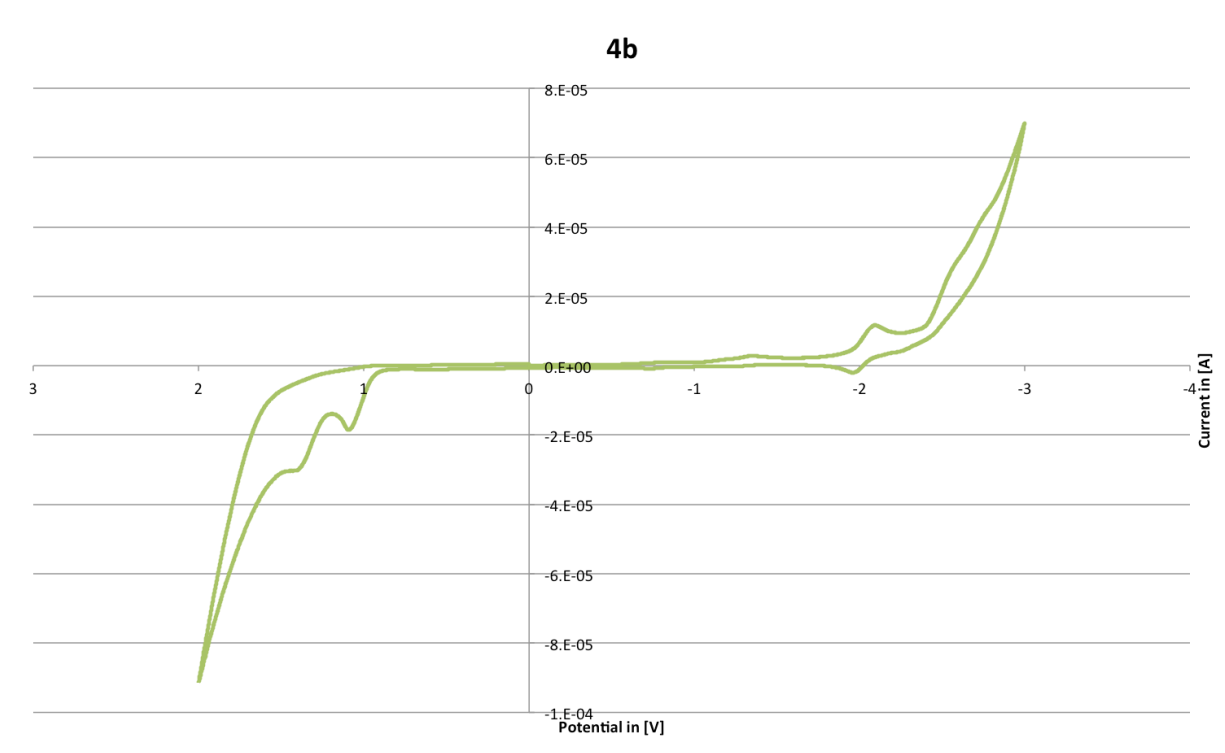


Figure S19. Cyclic voltammogram of **4b**. Scan rate = 0.1 V s^{-1} ; 1 mmol L^{-1} in a 0.07 TBAH/THF solution; $T = 298 \text{ K}$. Glassy carbon working electrode; reference electrode Ag/Ag^+ in ACN; platinum wire counter electrode.

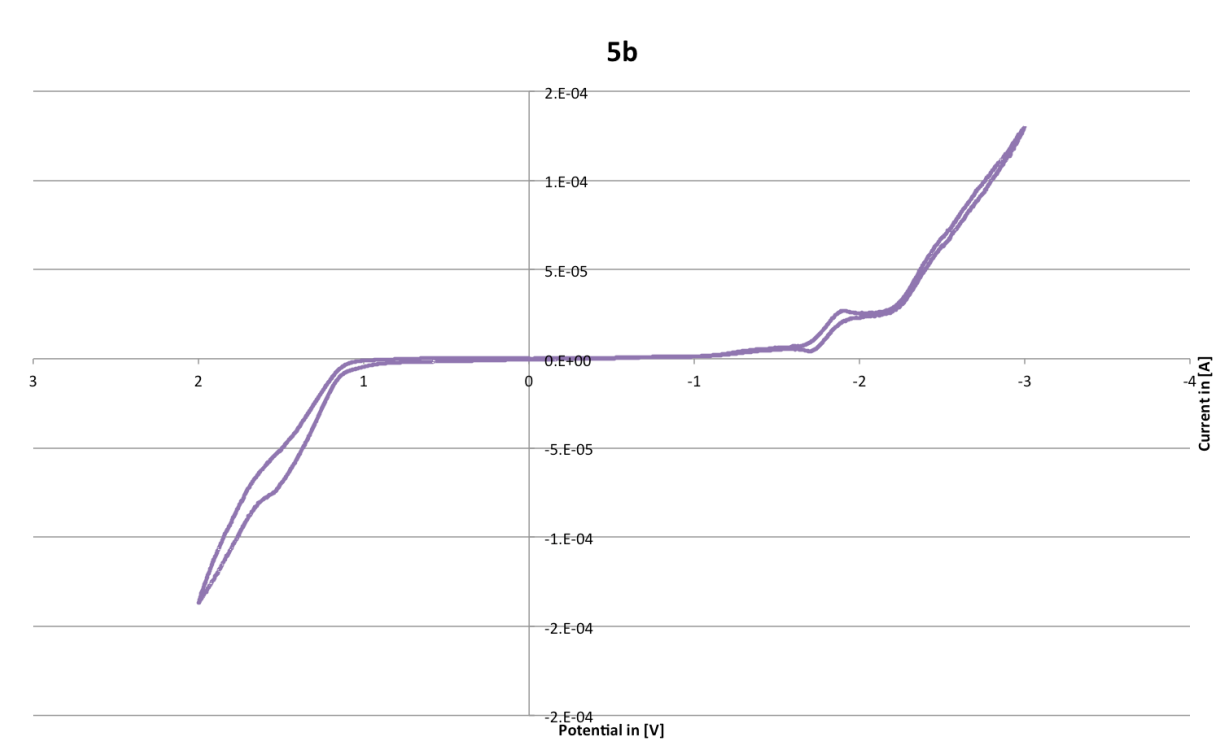


Figure S20. Cyclic voltammogram of **5b**. Scan rate = 0.1 V s^{-1} ; 1 mmol L^{-1} in a 0.07 TBAH/THF solution; $T = 298 \text{ K}$. Glassy carbon working electrode; reference electrode Ag/Ag^+ in ACN; platinum wire counter electrode.

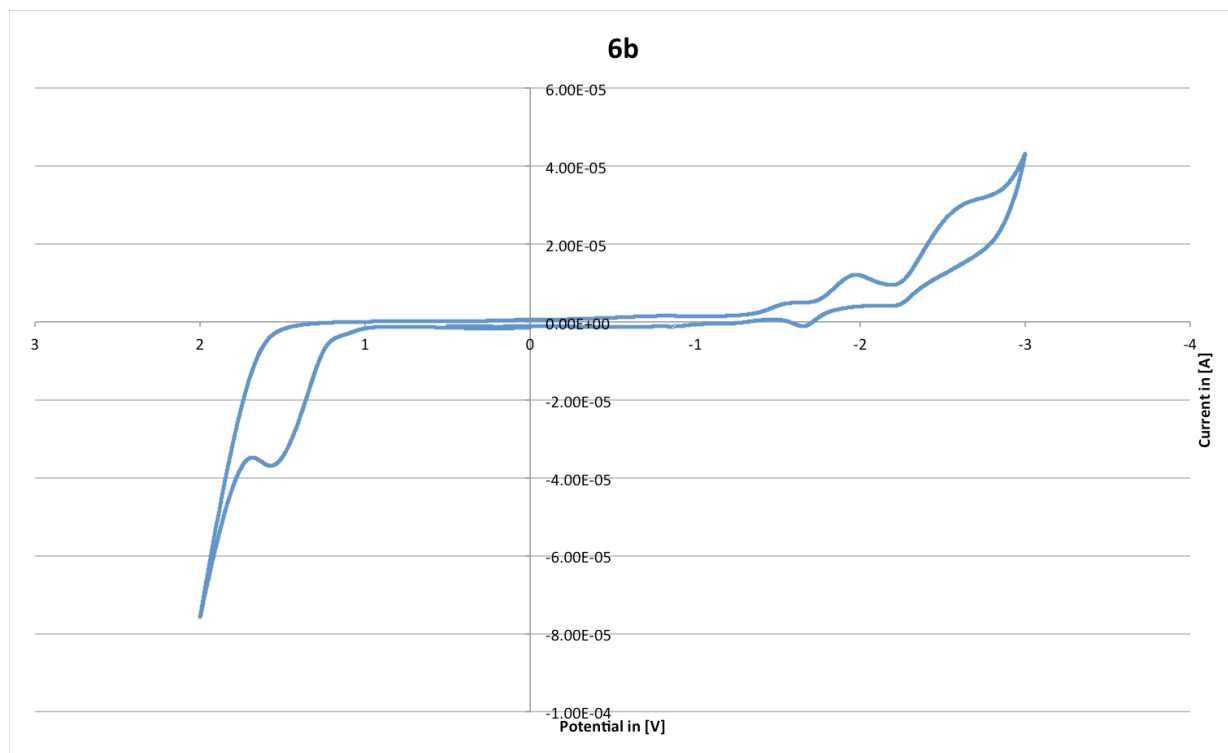


Figure S21. Cyclic voltammogram of **6b**. Scan rate = 0.1 V s^{-1} ; 1 mmol L^{-1} in a 0.07 TBAH/THF solution; $T = 298 \text{ K}$. Glassy carbon working electrode; reference electrode Ag/Ag^+ in ACN; platinum wire counter electrode.

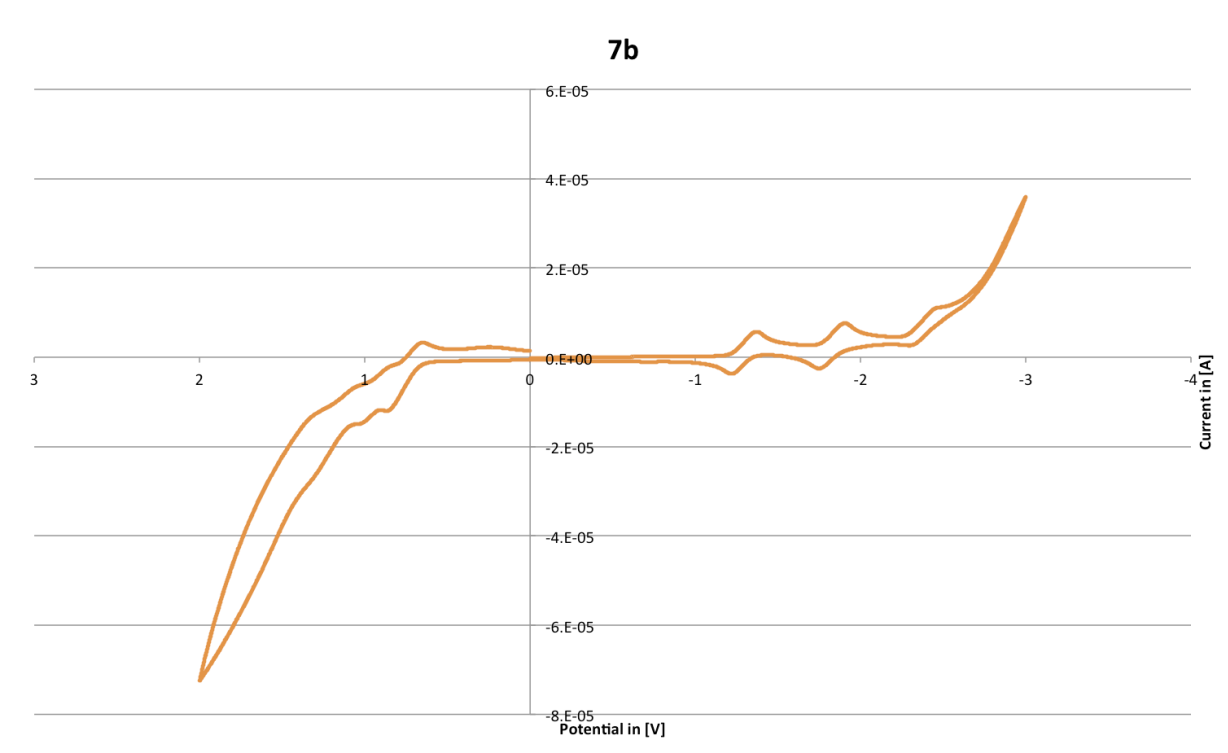


Figure S22. Cyclic voltammogram of **7b**. Scan rate = 0.1 V s^{-1} ; 1 mmol L^{-1} in a 0.07 TBAH/THF solution; $T = 298 \text{ K}$. Glassy carbon working electrode; reference electrode Ag/Ag^+ in ACN; platinum wire counter electrode.

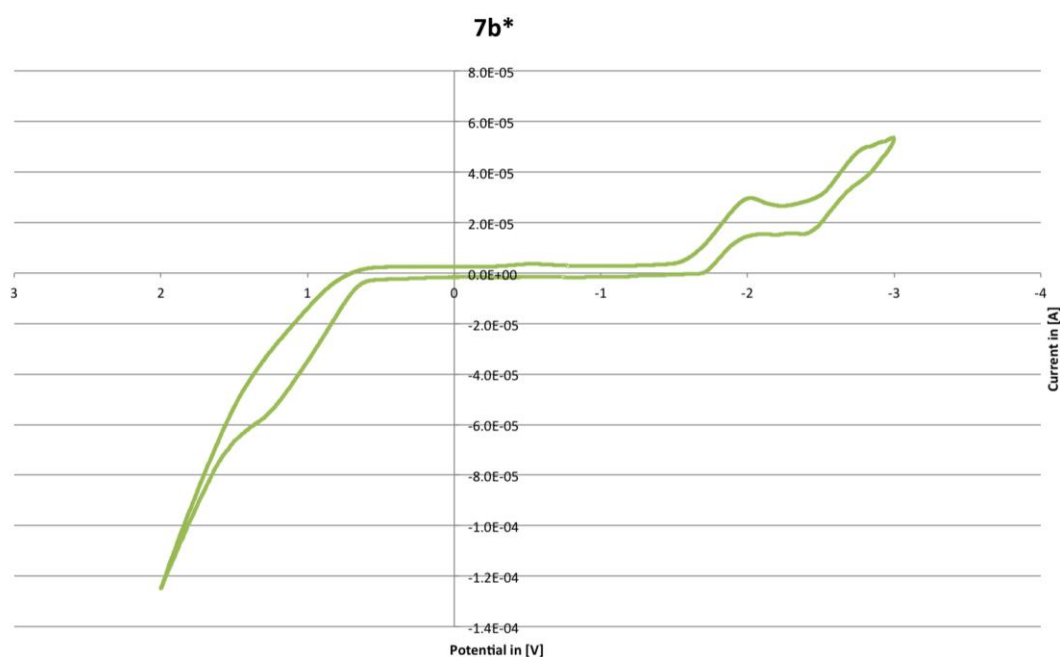


Figure S23. Cyclic voltammogram of **7b***. Scan rate = 0.1 V s^{-1} ; 1 mmol L^{-1} in a 0.07 TBAH/THF solution; $T = 298 \text{ K}$. Glassy carbon working electrode; reference electrode Ag/Ag^+ in ACN; platinum wire counter electrode.

Fluorescence-phosphorescence

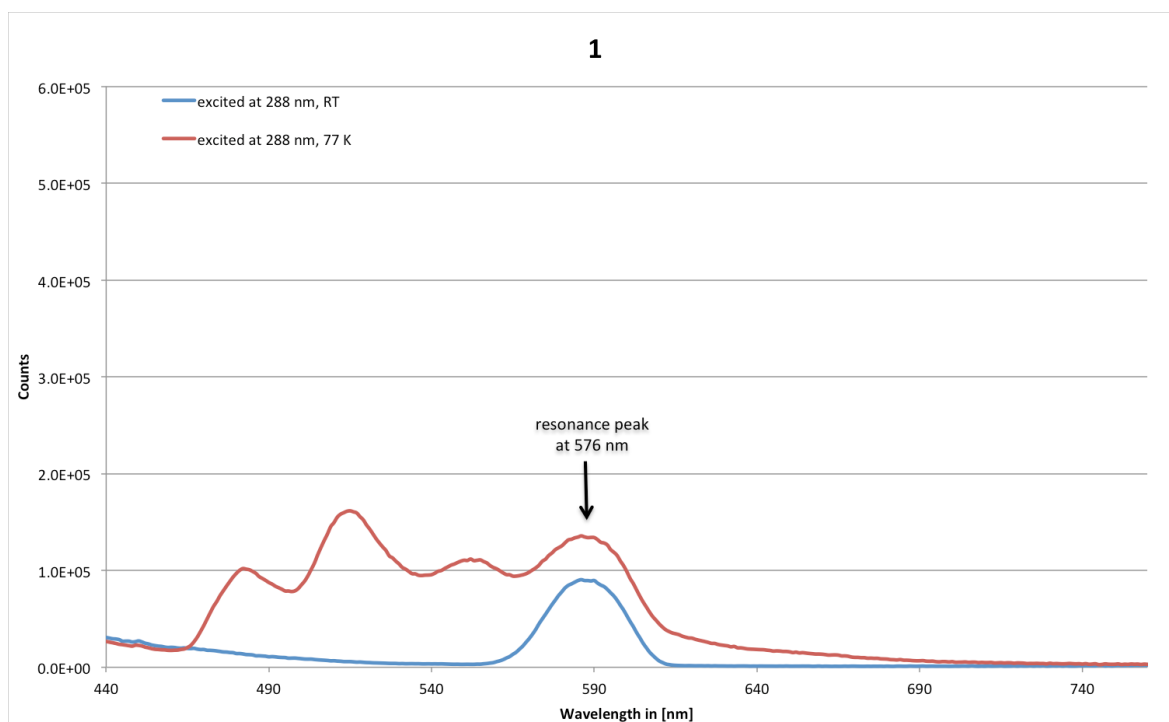


Figure S24. Emission scan of **1** at r.t. and at 77 K with $\lambda_{\text{ex}} = 288$. Second-order diffraction peak at 576 nm.

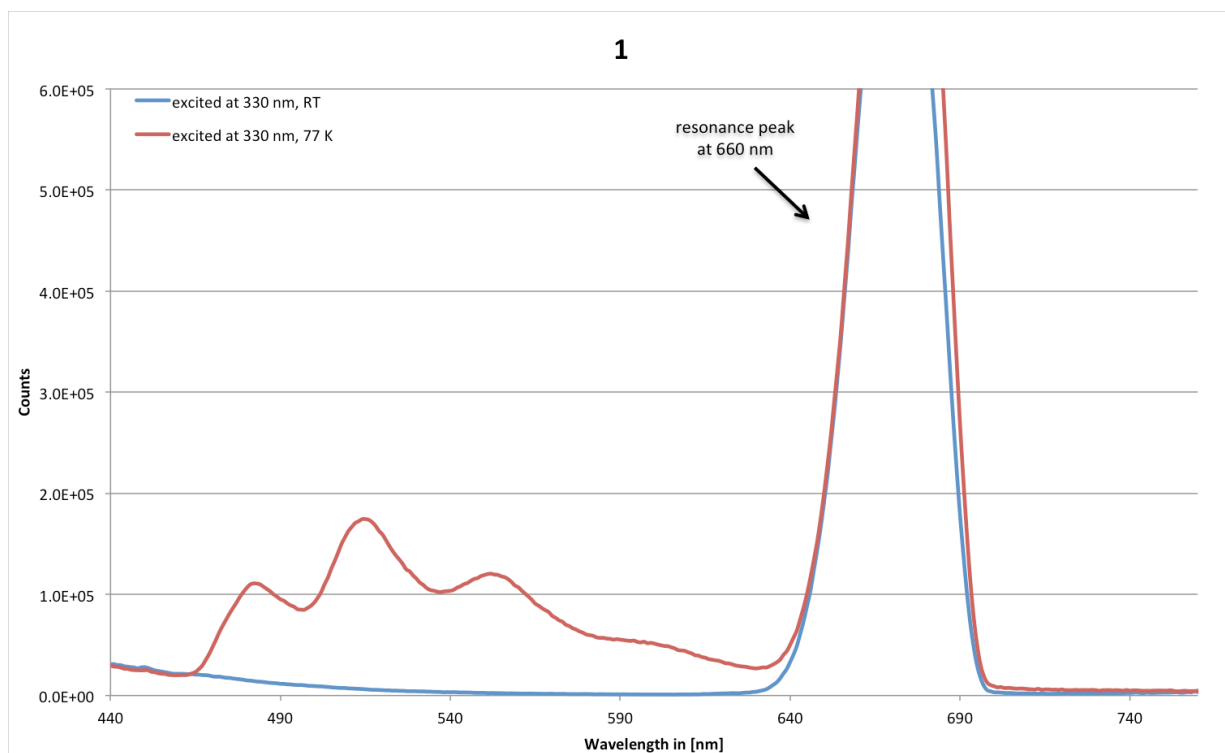


Figure S25. Emission scan of **1** at r.t. and at 77 K with $\lambda_{\text{ex}} = 330$ nm. Second-order diffraction peak at 660 nm.

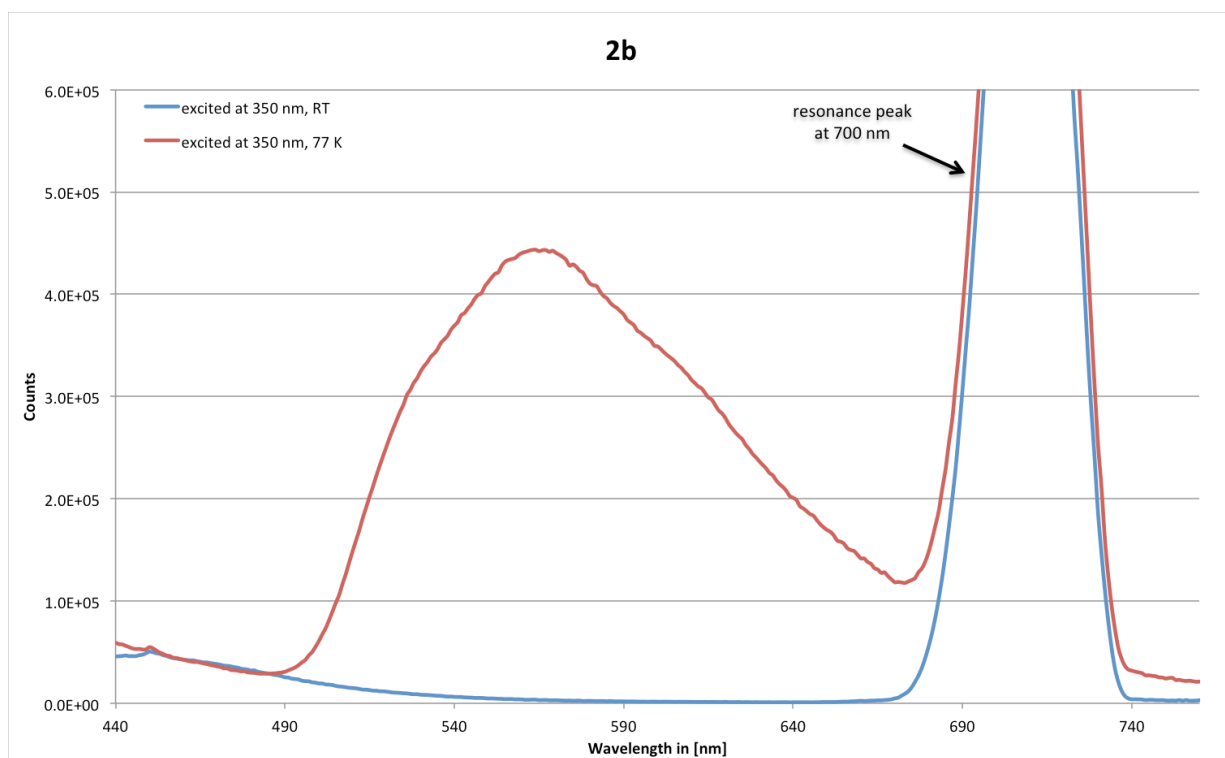


Figure S26. Emission scan of **2b** at r.t. and at 77 K with $\lambda_{\text{ex}} = 350$ nm. Second-order diffraction peak at 700 nm.

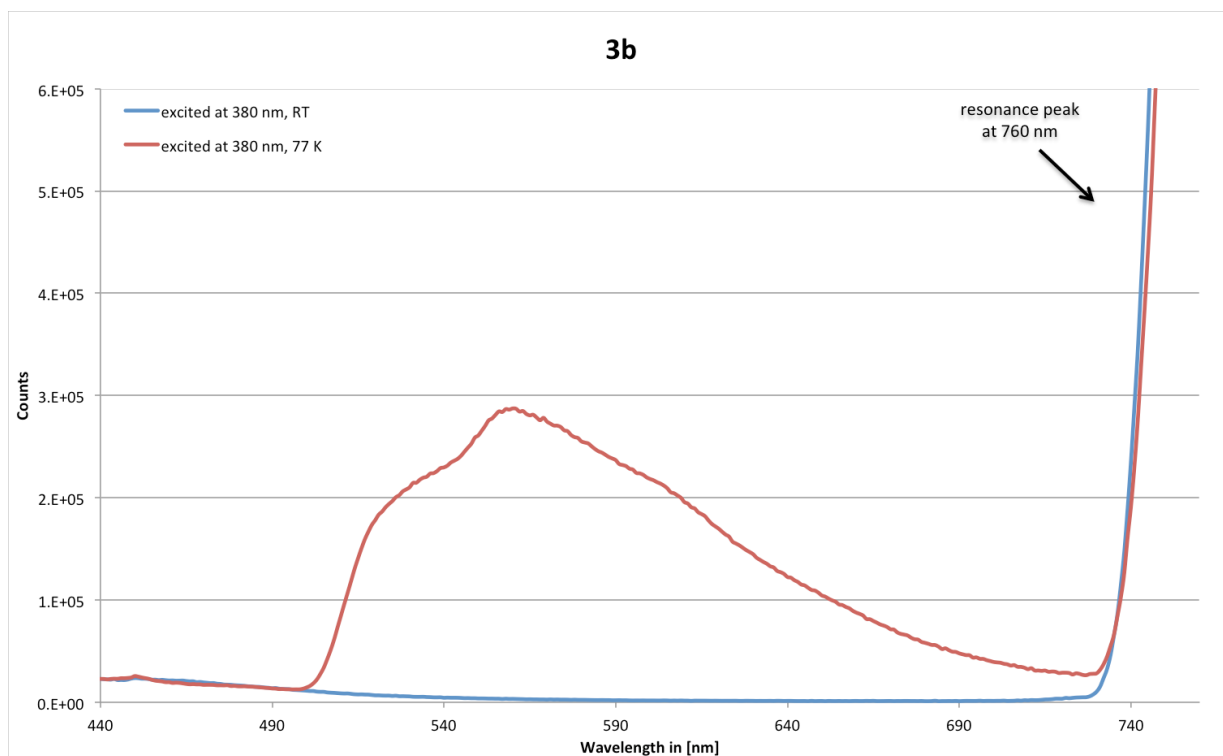


Figure S27. Emission scan of **3b** at r.t. and 77 K with $\lambda_{\text{ex}} = 380$ nm. Second-order diffraction peak at 760 nm.

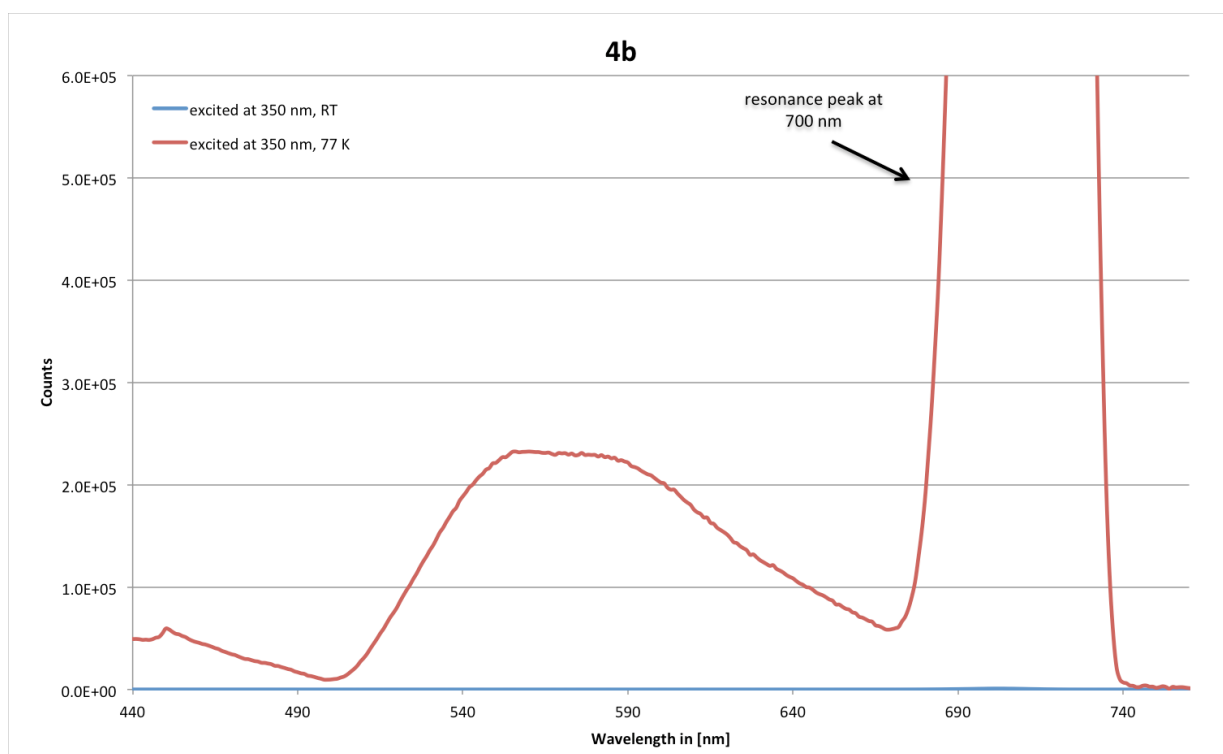


Figure S28. Emission scan of **4b** at r.t. and at 77 K with $\lambda_{\text{ex}} = 350$ nm. Second-order diffraction peak at 700 nm.

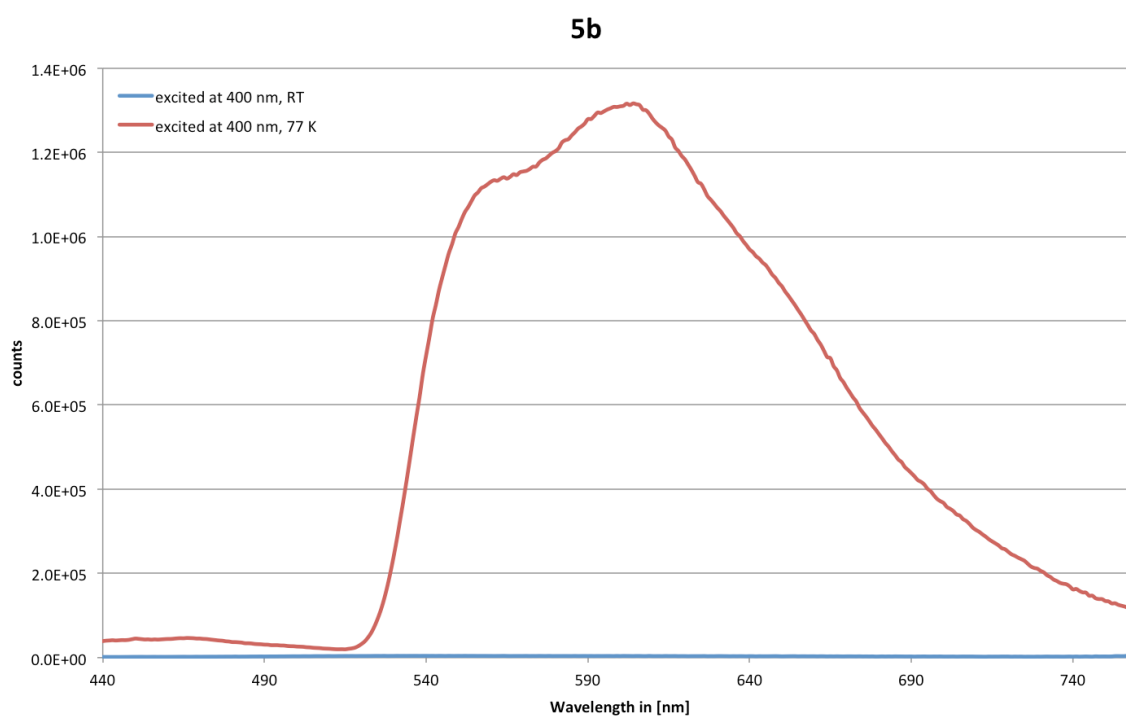


Figure S29. Emission scans of **5b** at r.t. and at 77 K with $\lambda_{\text{ex}} = 400$ nm.

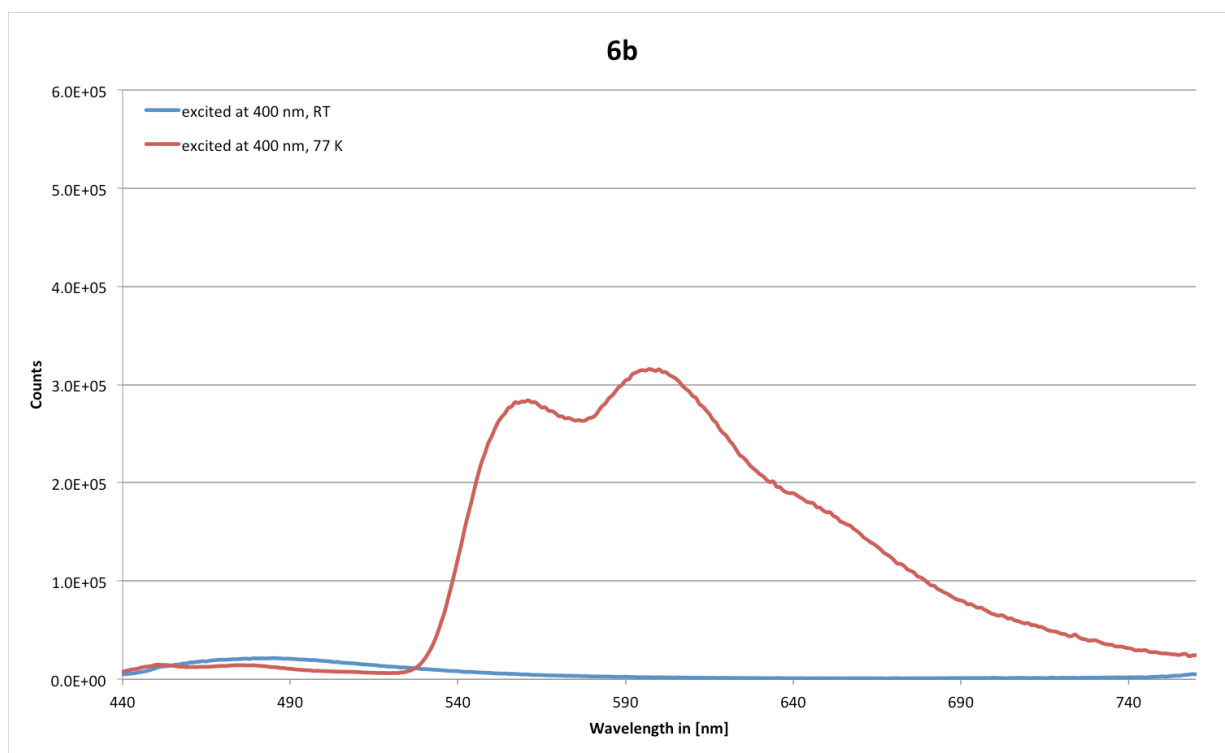


Figure S30. Emission scan of **6b** at r.t. and at 77 K with $\lambda_{\text{ex}} = 400$ nm.

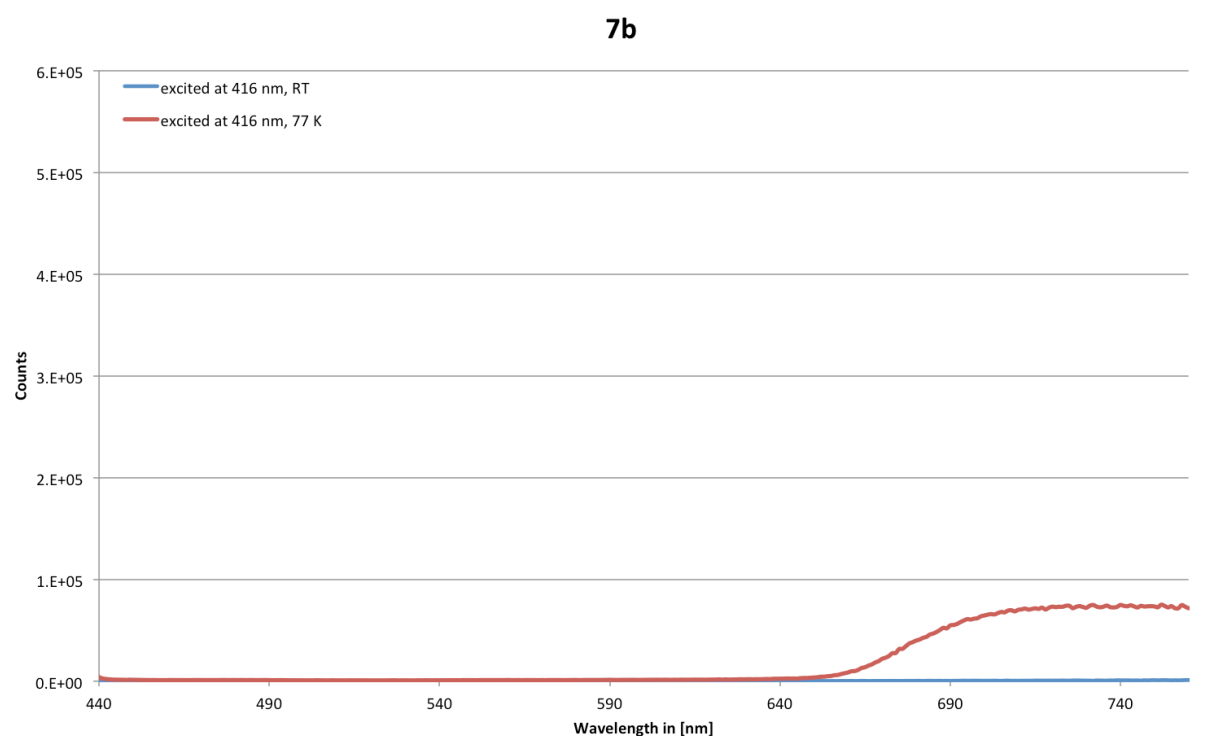


Figure S31. Emission scan of **7b** at r.t. and at 77 K with $\lambda_{\text{ex}} = 416$ nm.

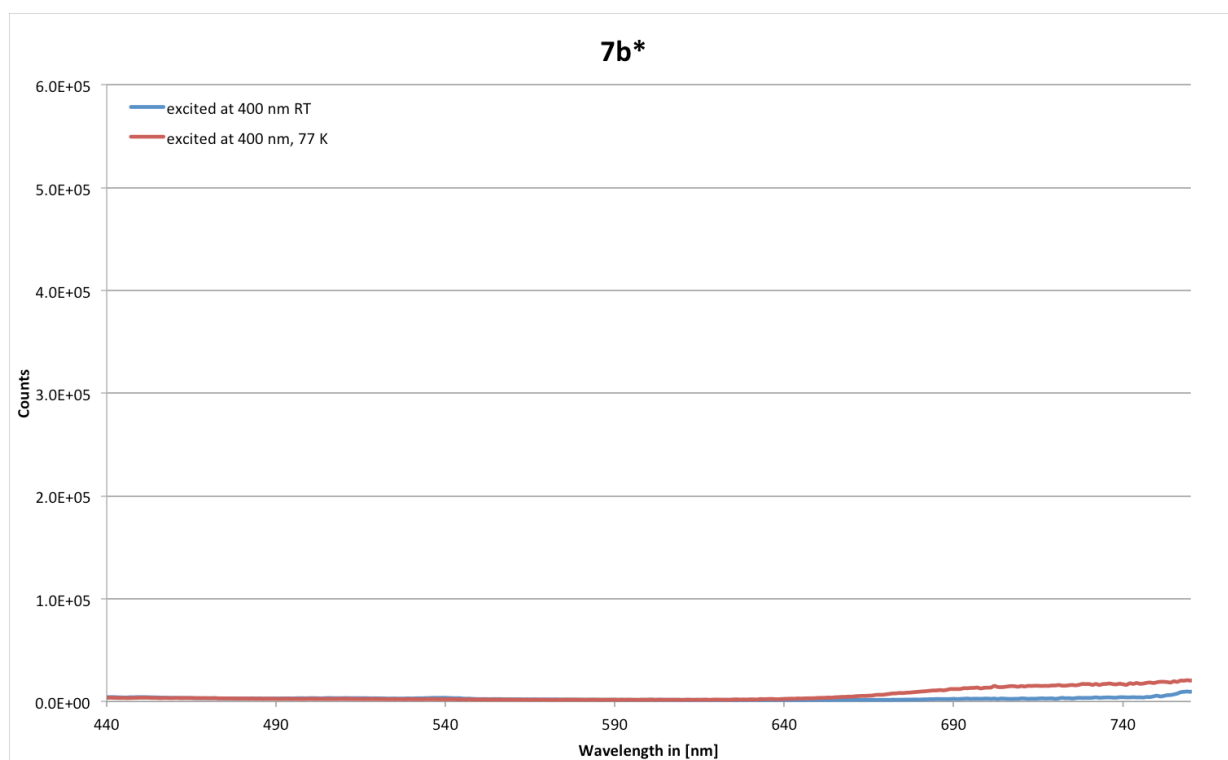


Figure S32. Emission scan of **7b*** at r.t. and at 77 K with $\lambda_{\text{ex}} = 400$ nm.

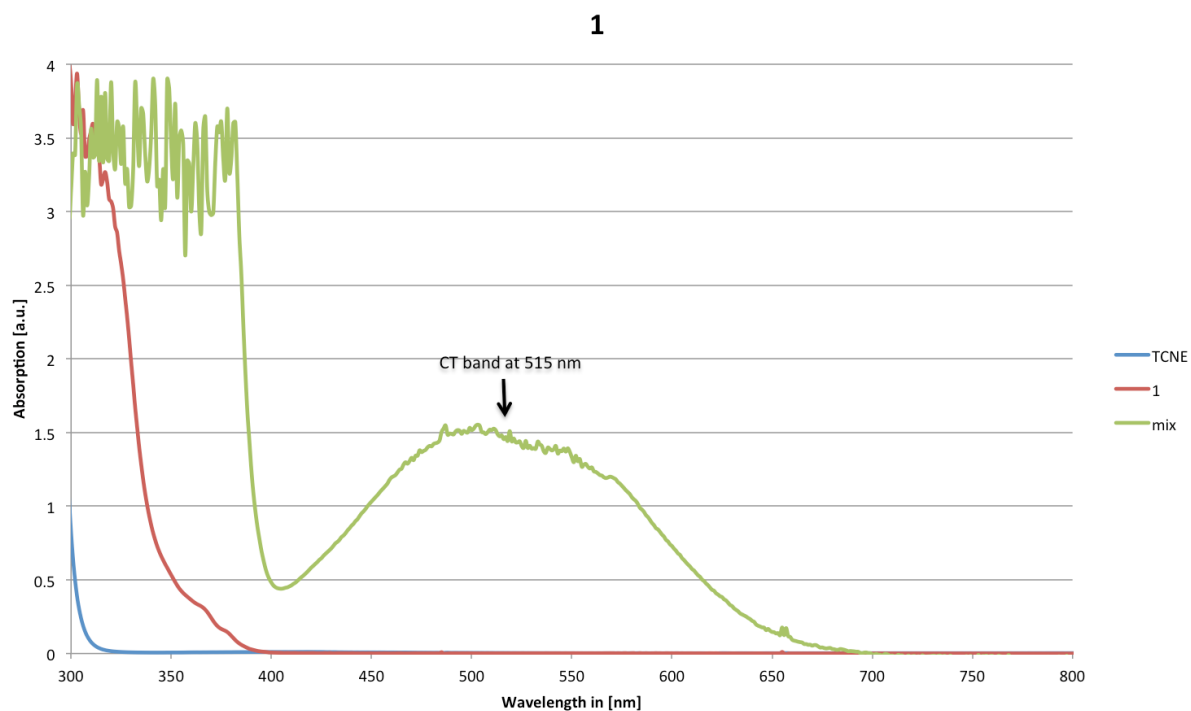


Figure S33. Charge-transfer band of **1** and TCNE at 515 nm.

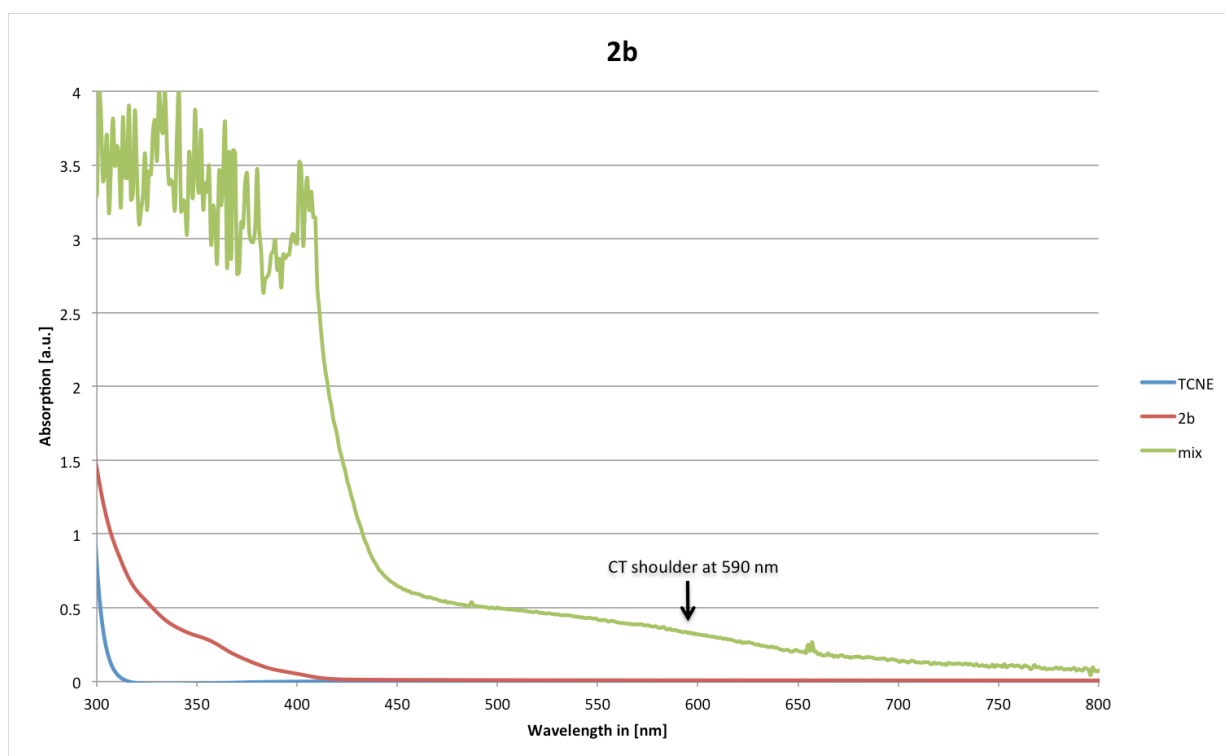


Figure S34. Charge-transfer shoulder of **2b** and TCNE at 590 nm.

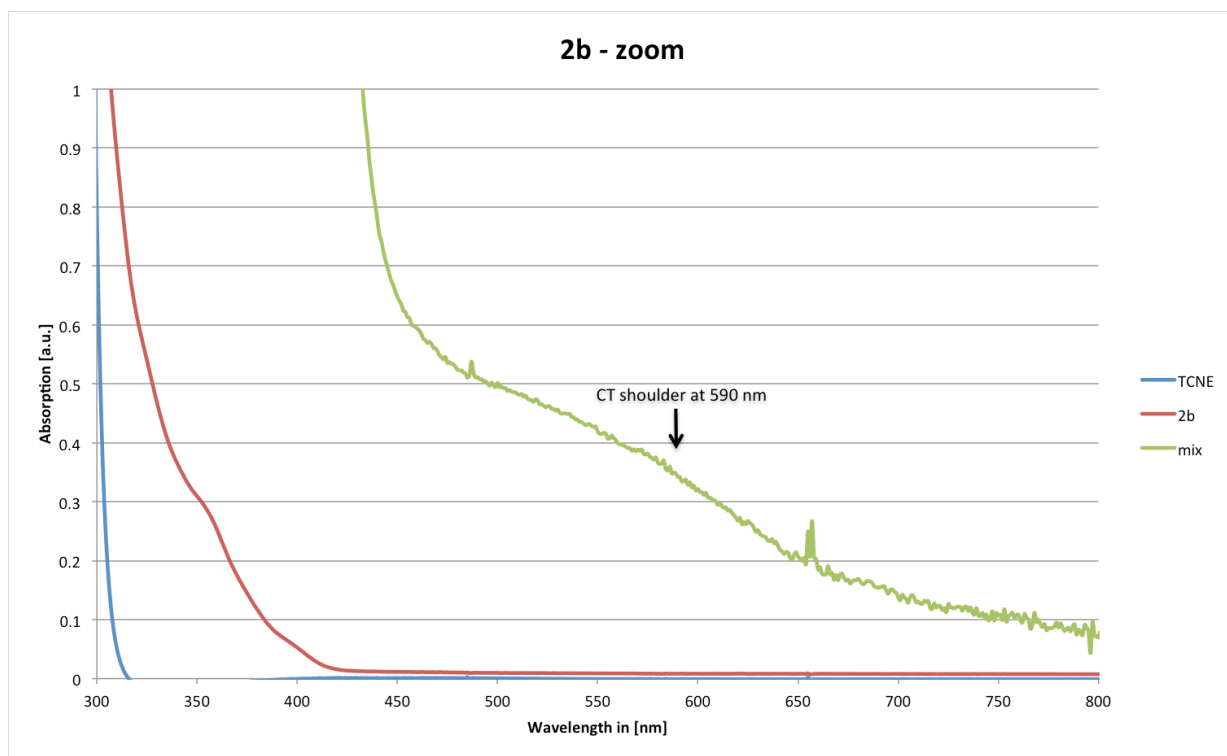


Figure S35. Zoomed in: charge-transfer shoulder of **2b** and TCNE at 590 nm.

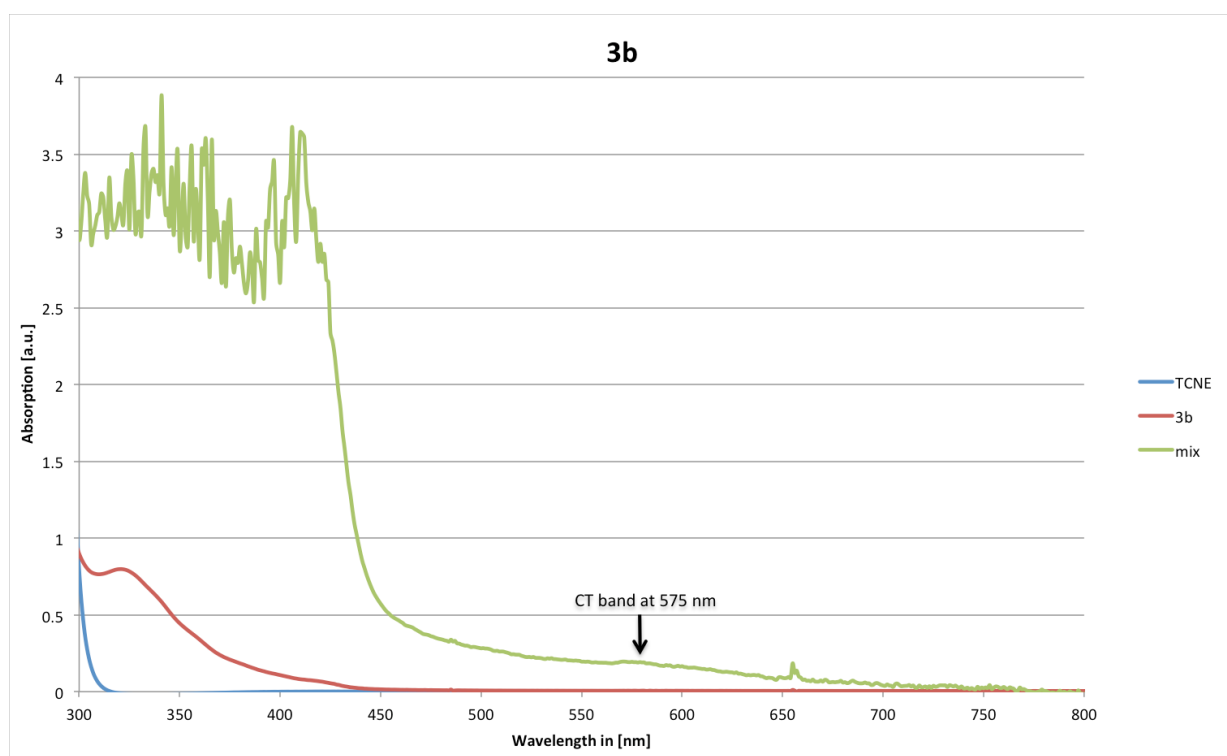


Figure S36. Charge-transfer band of **3b** and TCNE at 575 nm.

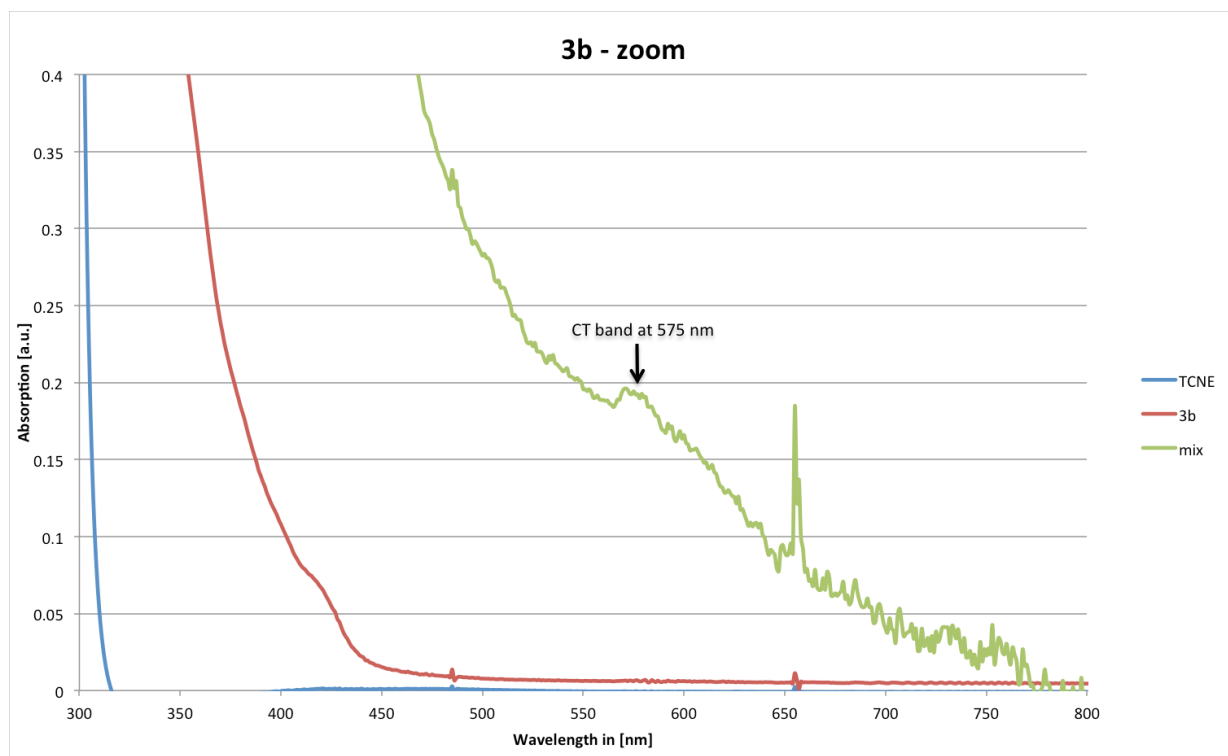


Figure S37. Zoomed in: charge-transfer shoulder of **3b** and TCNE at 575 nm.

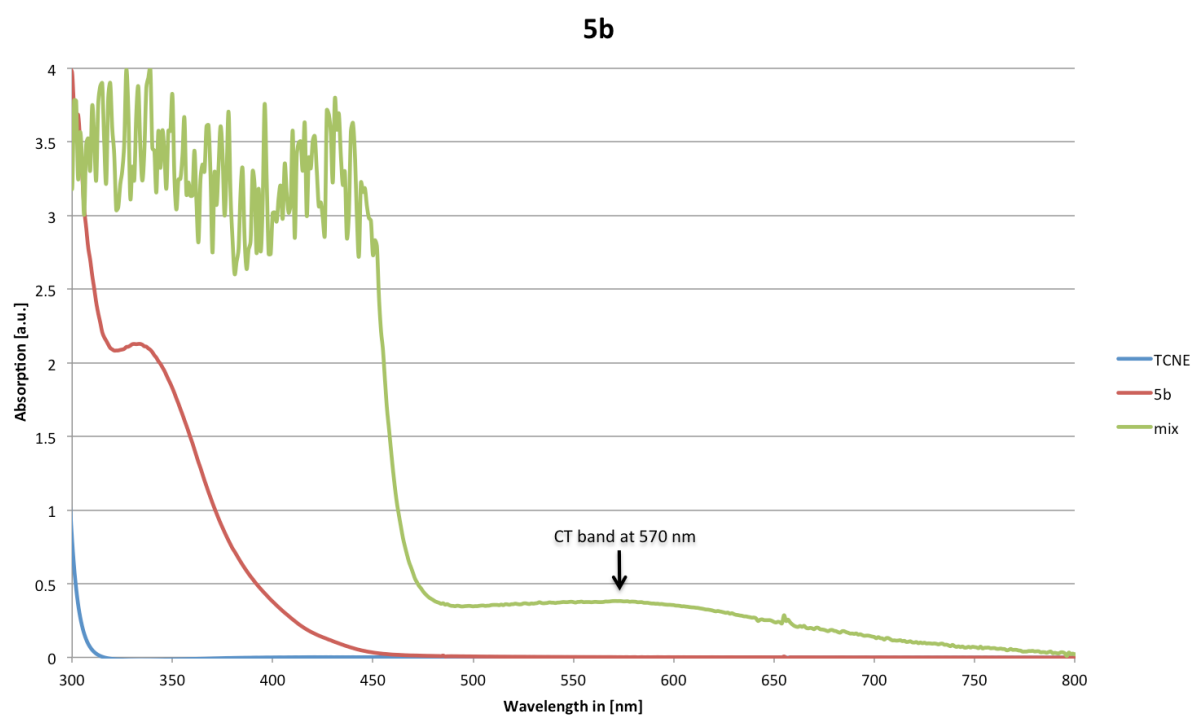


Figure S38. Charge-transfer band of **5b** and TCNE 570 nm.

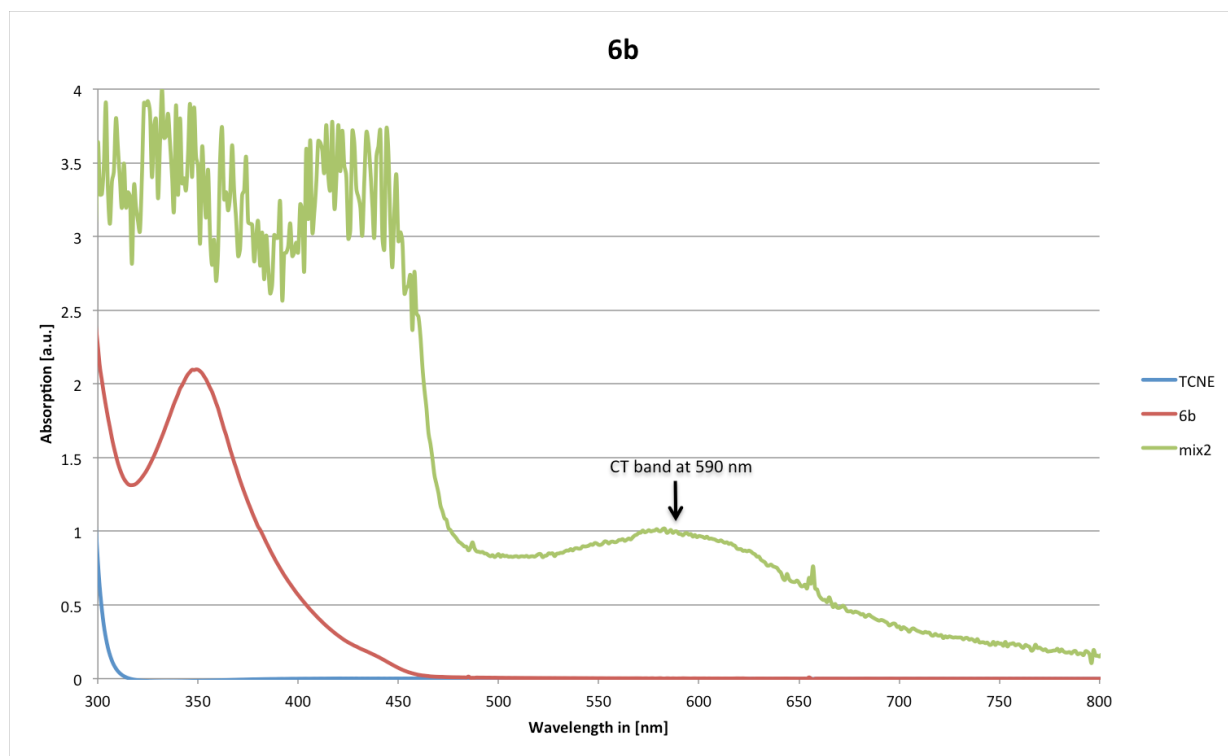


Figure S39. Charge-transfer band of **6b** and TCNE at 590 nm.

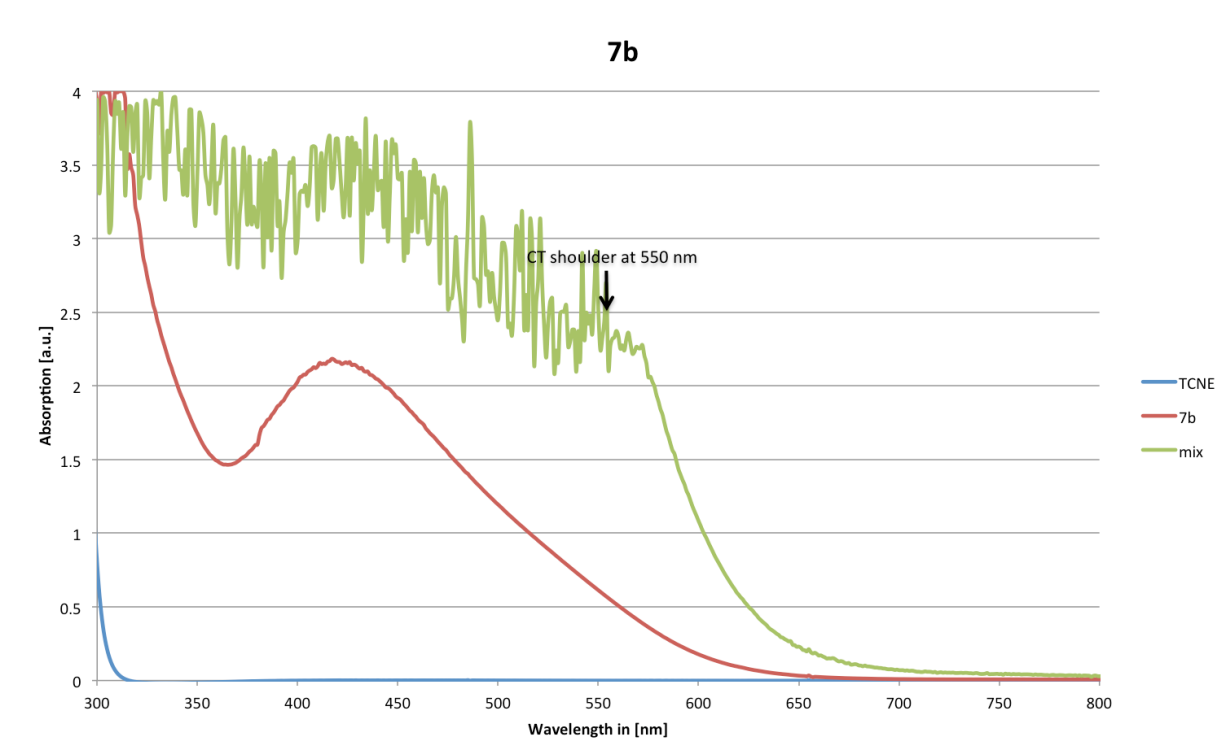


Figure S40. Charge-transfer band of **7b** and TCNE at 550 nm.

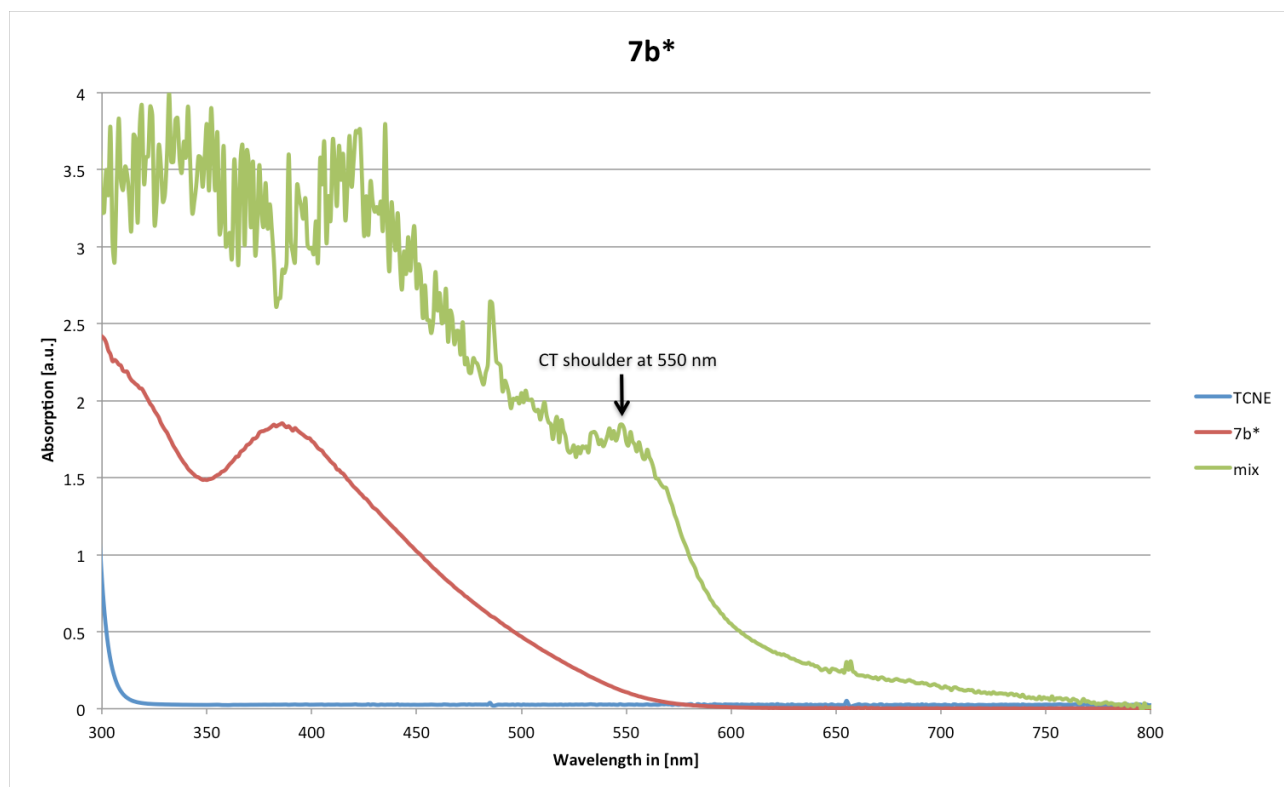


Figure S41. Charge-transfer shoulder of **7b*** and TCNE at 550 nm.

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