Synthesis of Tetracene Sulfoxide and Tetracene Sulfone *via* a Cascade Cyclization Reaction

Yi-Chun Lin, Chih-Hsiu Lin*

Supporting Material A

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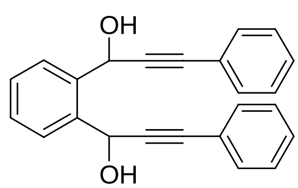
Instruments and General Experimental Set-ups:

Nuclear magnetic resonance spectra were taken on Brucker AMX-400 (400 MHz), Brucker AV-400 (400 MHz), or Brucker AV-500 (500 MHz) spectrometer. Infrared spectrum data were measured on a Thermo Nicolet Avatar 360 E.S.P. FT-IR spectrometer. Samples were pressed into KBr tablet or deposited on KBr pellet from CH_2Cl_2 solution. High resolution mass spectra were taken on JEOL JMS-700 10kV. Ultraviolet-visible spectrum data were obtained with Hitachi U-3310. The samples were dissolved in dichloromethane and placed in a 1 cm quarzt cell. The absorptions were monitored between 200~700 nm. Fluorescence spectra were measured with Hitachi F-4500 spectrometer. Coumarin 6 dye was used as the standard to determine quantum yield. X-ray crystallography was performed on Brucker Ninius X8APEX. Cyclic voltammetry samples were prepared in acetonitrile solution with $TBAPF_6$ as the supporting electrolyte. The measurements were carried out on Bioanalytical System BAS1008 with a scan-rate of 100-150 mV/sec. TGA measurements were performed with Perkin Elmer Pyis 1 TGA.

All reactions are performed under 1 atmosphere of inert gas (dried nitrogen) and well mixed with magnetic stirring devices. Reagent grade chemicals and solvents were used in all reactions. Reaction vessels were dried in oven before use. Diethyl ether and tetrahydrofuran were distilled over metallic sodium with benzophenone radical anion as the indicator. Dichloromethane were distilled from CaH_2. Hexane were dried over P_2O_5 and distilled before use. Flash column chromatography was performed with Merck silica gel 60 (1.11567.9025, 0.040-0.063 mm) as the stationary phase. All ratios of reported mixed eluents are based on volume.

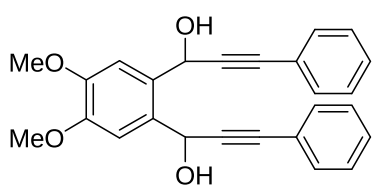
General procedure for the synthesis of *o*-bis-(1-hydroxy-3-phenyl-prop-2-inyl)-benzol derivatives (1a-1m): The solutions of various phenylacetylene derivatives in THF (ca. 15 mmol/30 mL) were cooled to -78 °C. To these solutions were slowly added n-BuLi (2.5 M in hexane, 1.1 equivalents) and the deprotonation reactions were allowed to proceed for 5 min. To these solutions of lithium phenylacetylide were added THF solutions of phthalaldehyde derivatives (ca. 1 g/5 mL). The reactions were warmed back to room temperature before stirred for another 30 min. The reactions were quenched with saturated NH_4Cl and THF was then removed on a rotary evaporator. The residue from each reaction was then extracted with CH_2Cl_2 (×3) and the combined organic extracts were dried over $MgSO_4$. Solvent was removed on a rotary evaporator and the crude products were purified with flash column chromatography (CH_2Cl_2) to furnish the desired products as mixtures of diastereomers. The ratio of various isomers can be determined by ^{1}H NMR spectroscopy.

1a



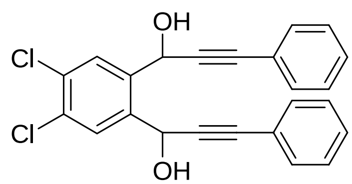
Yield: 87%, isomeric ratio: 1:0.7. ^{1}H NMR (400 MHz, $CDCl_3$):δ6.19 (s), 6.31(s), 6.28~7.50 (m), 6.28~7.50 (m), 7.75 (dd, J = 5.6, 3.2 Hz), 7.92 (dd, J = 5.6, 3.6 Hz).

1b



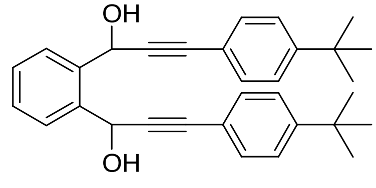
Yield: 49 %. Isomeric ratio: 1: 0.5. IR (KBr) ν (cm^{-1}): 3418, 2933, 2199, 1516, 1489, 1030, 1092, 756. ^{1}H NMR (400 MHz, $CDCl_3$):δ3.09 (d, J = 2.8 Hz), 3.40 (d, J = 4.0 Hz), 3.92 (s), 3.93 (s), 6.11 (d, J = 4.0 Hz), 6.23 (d, J = 2.8 Hz), 7.28~7.34 (m), 7.44~7.49 (m). ^{13}C NMR (125MHz, $CDCl_3$): 55.59, 61.76, 63.31, 86.98, 87.30, 88.17, 88.52, 111.12, 112.42, 122.30, 122.37, 128.30, 128.35, 128.57, 128.64, 130.61, 131.12, 131.70, 148.65, 148.82. HRMS. (M^+), $C_{26}H_{22}O_4$, Calc.: 398.1518; Found: 398.1514.

1c



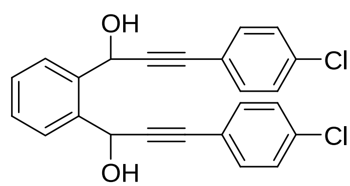
Yield: 41%. Isomeric ratio: 1: 0.5. IR (KBr) ν (cm^{-1}): 3369, 2922, 2221, 1490, 1208, 1031, 755, 689. ^{1}H NMR (400 MHz, $CDCl_3$):δ3.00 (broad s), 3.33 (broad s), 6.11(d, J = 4.4 Hz), 6.21(d, J = 5.6 Hz), 7.31~7.34 (m), 7.45~7.48 (m), 7.83 (s), 7.97 (s). ^{13}C NMR (100MHz, $CDCl_3$): 61.47, 62.65, 86.58, 86.91, 87.94, 88.24, 121.71, 121.78, 128.36, 128.92, 128.98, 129.98, 130.91, 131.77, 131.80, 132.86, 132.97, 137.79, 138.09. HRMS. (M^+), $C_{24}H_{16}O_2Cl_2$, Calc.: 406.0527; Found: 406.0528.

1d



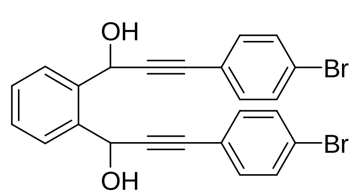
Yield: 86%, isomeric ratio: 1 : 0.3. IR (KBr) ν (cm^{-1}): 3343, 2952, 2870, 2228, 1458, 1266, 1019, 835. ^1H NMR (400 MHz, $CDCl_3$): δ1.28 (s,), 1.29 (s,), 3.09 (d, *J* = 4.8 Hz), 3.48 (d, *J* = 6 Hz), 6.18 (d, *J* = 4.8 Hz), 6.47 (d, *J* = 6 Hz), 7.30~7.44 (m), 7.73 (dd, *J* = 5.6, 3.6 Hz), 7.92 (dd, *J* = 5.6, 3.2 Hz). ^{13}C NMR (100MHz, $CDCl_3$): 31.11, 34.74, 62.46, 63.90, 87.16, 87.45, 87.50, 87.78, 119.28, 119.35, 125.27, 128.05, 129.01, 129.17, 131.53, 138.07, 138.45, 151.89, 151.96. HRMS. (M^+), $C_{32}H_{34}O_2$, Calc.: 450.2559; Found: 450.2567.

1e



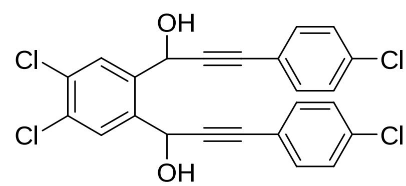
Yield: 55%. Isomeric ratio: 1: 0.4. IR (KBr) ν (cm^{-1}): 3363, 2232, 1489, 1092, 1015, 964, 827, 755. ^1H NMR (400 MHz, $CDCl_3$):δ6.10 (s), 6.24 (s), 7.23~7.27 (m), 7.34~7.42 (m), 7.68 (dd, *J* = 5.6, 3.6 Hz), 7.86 (dd, *J* = 5.6, 3.6 Hz). ^{13}C NMR (100MHz, $CDCl_3$): 62.19, 63.69, 86.17, 86.46, 88.66, 89.02, 120.67, 120.72, 121.72, 128.03, 128.64, 128.94, 129.21, 132.95, 132.98, 134.73, 134.79, 137.66, 138.13. HRMS. (M^+), $C_{24}H_{16}O_2Cl_2$, Calc.: 406.0527; Found: 406.0536.

1f



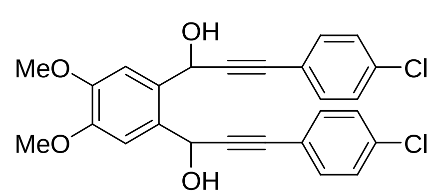
Yield: 45%, isomeric ratio: 1: 1. IR (KBr) ν (cm^{-1}): 3373, 2199, 1486, 1096, 1070, 1011, 823, 754. ^{1}H NMR (400 MHz, $CDCl_3$):δ6.15 (s), 6.26 (s), 7.30~7.34 (m), 7.40~7.46 (m), 7.71 (dd, J = 5.6, 3.6 Hz), 7.87 (dd, J = 5.6, 3.6 Hz). ^{13}C NMR (100MHz, $CDCl_3$): 62.43, 63.73, 86.30, 86.60, 88.70, 89.05, 121.07, 121.12, 123.02, 123.08, 128.06, 129.19, 129.26, 129.29, 131.58, 131.60, 133.13, 133.17, 137.62, 138.01. HRMS. ($[M-OH]^+$), $C_{24}H_{15}OBr_2$, Calc.: 476.9490; Found: 476.9489.

1g



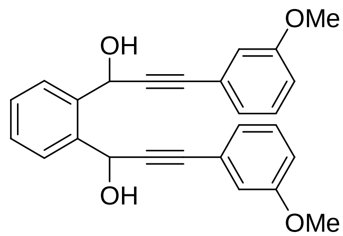
Yield: 60 %. Isomeric ratio: 1: 0.5. IR (KBr) ν (cm^{-1}): 3283, 2226, 1487, 1378, 1204, 1090, 1016, 827. ^{1}H NMR (500 MHz, $CDCl_3$):δ2.89 (d, J = 5.0 Hz), 3.20 (d, J = 6.0 Hz), 6.08 (d, J = 5.0 Hz), 6.17 (d, J = 6.0 Hz), 7.28~7.30 (m), 7.36~7.39 (m), 7.80 (s), 7.93 (s). ^{13}C NMR (100MHz, $CDCl_3$): 61.52, 62.62, 86.90, 87.15, 87.55, 87.85, 120.15, 120.21, 128.79, 129.99, 130.90, 132.99, 133.04, 133.08, 133.15, 135.19, 135.25, 137.61, 137.90. HRMS. (M^+), $C_{24}H_{14}O_2Cl_4$, Calc.: 473.9748; Found: 473.9744.

1h



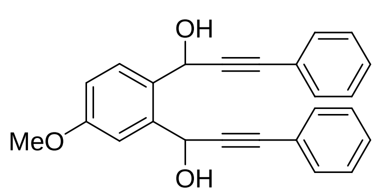
Yield: 62 %. Isomeric ratio: 1:0.5. IR (KBr) ν (cm^{-1}): 3422, 2228, 1517, 1489, 1205, 1090, 827, 760. ^{1}H NMR (500 MHz, $CDCl_3$): δ3.91 (s), 3.92 (s), 6.10 (s), 6.20 (s), 7.26~7.29 (m). ^{13}C NMR (125MHz, $CDCl_3$): 56.05, 62.17, 63.41, 86.06, 86.38, 88.86, 89.20, 111.20, 112.34, 120.63, 120.71, 128.74, 128.77, 130.42, 130.75, 132.91, 134.85, 134.93, 148.97, 149.11. HRMS. ($[M-OH]^+$), $C_{26}H_{19}O_3Cl_2$, Calc.: 449.0711; Found: 449.0706.

1i



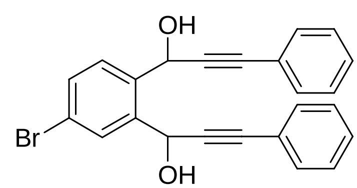
Yield: 64%. Isomeric ratio: 1: 0.3. IR (KBr) ν (cm^{-1}): 3372, 2937, 2228, 1601, 1537, 1482, 1287, 1163, 689. ^{1}H NMR (400 MHz, $CDCl_3$): δ3.76 (s), 3.78 (s), 6.19 (s), 6.30 (s), 6.86~6.90 (m), 7.05~7.09 (m), 7.19~7.23 (m), 7.39~7.44 (m), 7.74 (dd, *J* = 5.6, 3.2 Hz), 7.91 (dd, *J* = 5.6, 3.6 Hz). ^{13}C NMR (125MHz, $CDCl_3$): 55.25, 62.39, 63.84, 87.21, 87.52, 87.85, 115.30, 116.52, 116.57, 123.22, 123.27, 124.30, 128.06, 129.14, 129.22, 129.38, 137.84, 138.24, 159.23. HRMS. ($[M-OH]^+$), $C_{26}H_{21}O_3$, Calc.: 381.1491; Found: 381.1492.

1j



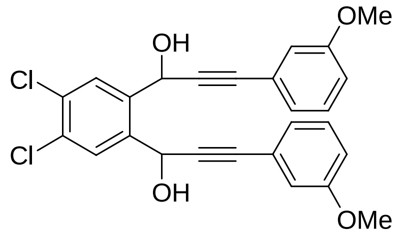
Yield: 79%, Isomeric ratio can not be accurately determined by NMR spectroscopy. IR (KBr) ν (cm^{-1}): 3365, 2837, 2226, 1609, 1490, 1030, 756, 690. ^1H NMR (400 MHz, $CDCl_3$):δ3.84 (s), 3.85 (s), 6.11 (s), 6.16 (s), 6.24 (s), 6.26 (s), 6.89 (dd, J = 8.4, 2.8 Hz), 6.92 (dd, J = 8.4, 2.4 Hz), 7.28~7.32 (m), 7.46~7.50 (m), 7.66 (d, J = 8.4 Hz), 7.84 (d, J = 8.4 Hz). ^{13}C NMR (100MHz, $CDCl_3$):55.33, 61.89, 62.15, 63.33, 63.76, 87.01, 87.22, 87.39, 87.51, 87.65, 87.99, 88.04, 88.38, 113.47, 113.72, 113.80, 115.23, 122.27, 122.32, 122.34, 122.40, 128.27, 128.30, 128.53, 128.59, 128.64, 129.68, 130.00, 130.52, 130.74, 131.75, 131.77, 139.61, 139.91, 159.78, 159.88. HRMS. (M^+), $C_{25}H_{20}O_3$, Calc.:368.1412; Found:368.1407.

1k



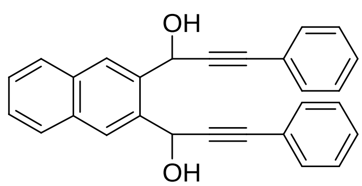
Yield: 63%. Isomeric ratio can not be accurately determined by NMR spectroscopy. IR (KBr) ν (cm^{-1}): 3353, 3062, 2230, 1489, 1084, 1031, 964, 754. ^1H NMR (400 MHz, $CDCl_3$):δ6.13 (s), 6.15 (s), 6.24(s), 7.29~7.33 (m, 10H), 7.45~7.50 (m), 7.54 (dd, J = 8.4, 2.0 Hz), 7.62 (d, J = 8.4), 7.78 (d, J = 8.4), 7.88 (d, J = 2.0), 8.03 (d, J = 2.0). ^{13}C NMR (100MHz, $CDCl_3$): 61.62, 61.69, 63.05, 87.03, 87.26, 87.38, 87.47, 87.57, 87.67, 87.74, 87.95, 121.92, 121.97, 122.03, 122.89, 123.02, 128.26, 128.28, 128.68, 128.73, 128.76, 129.74, 130.77, 130.87, 131.72, 131.75, 131.78, 131.93, 131.98, 136.78, 137.25, 139.85, 140.25. HRMS. ($[M-OH]^+$), $C_{24}H_{16}OBr$, Calc.: 399.0385; Found: 399.0376.

1l



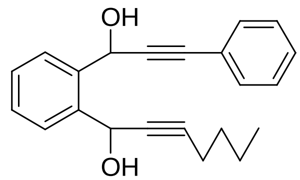
Yield: 72 %. Isomeric ratio: 1:0.6. IR (KBr) ν (cm^{-1}) 3389, 2228, 1603, 1574, 1287, 1165, 1046, 780. ^{1}H NMR (400 MHz, $CDCl_3$):δ3.77 (s), 3.78 (s), 6.10 (s), 6.20 (s), 6.88~7.22 (m), 7.82 (s, 2H), 7.96 (s). ^{13}C NMR (100MHz, $CDCl_3$): 55.26, 61.38, 62.60, 86.45, 87.78, 87.81, 88.09, 115.46, 115.49, 116.63, 116.68, 122.70, 122.76, 124.30, 124.33, 129.46, 129.93, 130.89, 132.85, 132.94, 137.74, 138.06, 159.22. HRMS. ($[M-OH]^+$), $C_{26}H_{19}O_3Cl_2$, Calc.: 449.0711; Found: 449.0710.

1m



Yield: 79%. Isomeric ration: 1: 0.5. IR (KBr) ν (cm^{-1}): 3361, 3057, 2231, 1490, 1443, 796, 753, 690. ^{1}H NMR (400 MHz, $CDCl_3$):δ6.33 (s), 6.47 (s), 7.32~7.35 (m), 7.50~7.55 (m), 7.89~7.91 (m), 8.21 (s), 8.39 (s). ^{13}C NMR (125MHz, $CDCl_3$): δ62.72, 64.30, 87.59, 87.78, 88.11, 122.32, 126.87, 126.99, 127.77, 127.97, 128.10, 128.34, 128.65, 128.71, 128.97, 131.79, 131.83, 133.08, 135.42, 135.63. HRMS. (M^+), $C_{28}H_{20}O_2$, Calc.:388.1463; Found: 388.1461.

1n

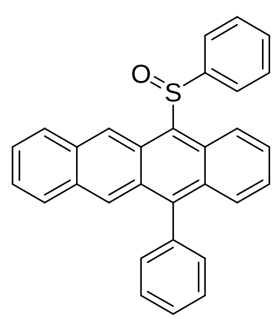


THF solutions of 1-hexyne (1.11 mL, 9.69 mmol in 10 mL THF) and phenylacetylene (0.82 mL, 7.46 mmol in 10 mL THF) are placed in two 100 mL round bottom flasks respectively. n-BuLi (2.5 M in hexane, 3.88 mL, 9.69 mmol) was added to the hexyne solution at -78 °C and this deprotonation reaction was stirred for 5 min. (deprotonation of phenylacetylene was also accomplished accordingly). To this solution was then added a THF solution of phthaldehyde (1 g, 7.46 mmol in 5 mL). The mixture was stirred for a few minuets at -78 °C before the solution of lithium phenylacetylide was added. The reaction was warmed back to room temperature and stirred for 1 hr before quenched with saturated NH_4Cl solution. The solvent was removed on rotary evaporator and the residue was extracted with CH_2Cl_2 several times. The combined organic phase was dried over $MgSO_4$ and concentrated. The crude product was purified with flash chromatography (CH_2Cl_2) to furnish the desired product (contaminated with small amount of compound **1a** as a colorless viscous oil (1.9 g, 74 %). At least three diastereomers can be distinguished in ^{1}H NMR spectrum.

IR (KBr) ν (cm^{-1}): 3350, 2957, 2231, 1490, 1443, 1095, 997, 756. ^{1}H NMR (400 MHz, $CDCl_3$):δ0.88~0.93 (m), 1.40~1.45 (m), 1.51~1.56 (m), 2.28~2.32 (m), 5.89 (s, 1H), 5.94 (s, 1H), 6.01 (s, 1H), 6.06 (s, 1H), 6.14 (s, 1H), 6.26 (s, 1H), 7.31~7.50 (m), 7.65~7.67 (m), 7.71~7.73 (m), 7.81~7.85 (m, 1H), 7.89~7.93 (m, 1H). ^{13}C NMR (125MHz, $CDCl_3$): 13.53, 18.51, 21.97, 30.51, 30.55, 62.00, 62.10, 62.22, 63.46, 63.61, 63.65, 63.78, 78.74, 79.12, 86.98, 87.41, 87.73, 88.11, 88.47, 88.69, 88.85, 122.33, 122.41, 127.82, 127.88, 127.97, 128.25, 128.51, 128.58, 128.76, 128.89, 128.93, 129.09, 131.73, 137.89, 138.28, 138.72. HRMS. ($[M\text{-}OH]^+$), $C_{22}H_{21}O$, Calc.:301.1591;Found: 301.1593.

General procedure for the synthesis of 5-phenylsulfoxide-12-phenyl tetracene derivatives (2a-2n) *via* cascade cyclization reactions: In round bottom flasks, bis-phenylacetylene diol adducts (**1a-1n**) and Et_3N (2.5 equivalents) were dissolved in CH_2Cl_2 (10 mM -30 mM). The mixed solutions were immersed in an ice bath then 2.5 equivalents of phenylsulfenyl chloride was slowly added. The reaction was refluxed for 4 hr before quenched with water and extracted with CH_2Cl_2 (3×). The combined organic extracts was dried over $MgSO_4$ and concentrated. The crude products were purified with flash chromatography (CH_2Cl_2 and hexane mixtures as eluents) to give the tetracene derivatives as orange powders

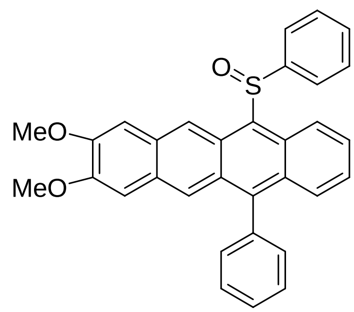
2a



Yield: 79 %. IR (KBr) ν (cm^{-1}) 2924, 2853, 1442, 1080, 1044, 876, 744, 701. ^1H NMR (400 MHz, $CDCl_3$): δ7.26~7.51 (m, 10H), 7.62~7.66 (m, 5H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 8.28 (s, 1H), 8.96 (d, *J* = 9.2 Hz, 1H) , 9.64 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$): 122.68, 123.17, 124.29, 124.87, 125.77, 126.37, 127.19, 127.61, 128.00, 128.06, 128.22, 128.48, 128.90, 129.19, 129.60, 130.76, 130.80, 130.89, 131.69, 131.84, 132.08, 138.10, 143.95, 145.16. HRMS. (M^+),

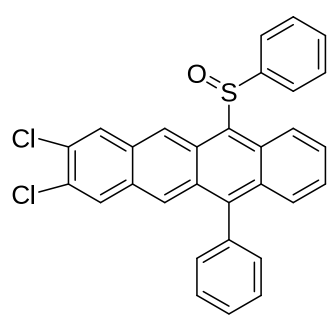
$C_{30}H_{20}OS$, Calc.: 428.1235; Found: 428.1234.

2b



Yield: 57 %. IR (KBr) ν (cm^{-1}): 2924, 1491, 1431, 1305, 1239, 1045, 755, 702. ^{1}H NMR (400 MHz, $CDCl_3$): δ3.93 (s, 3H), 4.02 (s, 3H), 6.91 (s, 1H), 7.10 (s, 1H), 7.24~7.46 (m, 7H), 7.60~7.65 (m, 6H), 8.03 (s, 1H), 9.91 (d, *J* = 9.2 Hz, 1H), 9.39 (s, 1H). ^{13}C NMR (125MHz, $CDCl_3$): 55.92, 56.03, 104.37, 104.61, 119.79, 123.15, 124.32, 124.46, 124.54, 127.23, 127.94, 127.97, 128.36, 128.53, 128.61, 128.98, 129.63, 130.01, 130.62, 130.91, 130.96, 138.56, 143.16, 145.31, 150.74, 151.26. HRMS. (M^+), $C_{32}H_{24}O_3S$, Calc.: 488.1446; Found: 488.1454.

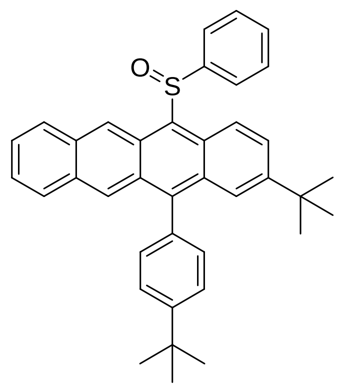
2c



Yield: 65 %. IR (KBr) ν (cm^{-1}): 2925, 1441, 1107, 1081, 1045, 899, 756, 703. ^{1}H

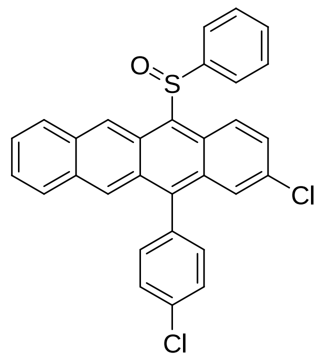
NMR (400 MHz, $CDCl_3$):δ7.33~7.43 (m, 6H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.62~7.67 (m, 6H), 7.88 (s, 1H), 8.06 (s, 1H), 8.18 (s, 1H), 8.95 (d, *J* = 8.8 Hz, 1H), 9.58 (s, 1H). ^{13}C NMR (125MHz, $CDCl_3$): 122.15, 123.04, 124.18, 125.34, 126.60, 128.00, 128.15, 128.25, 128.52, 128.57, 128.66, 128.91, 129.00, 129.05, 129.33, 129.50, 129.76, 130.13, 130.20, 130.59, 130.69, 130.78, 132.13, 137.56, 144.08, 144.77. HRMS. ($M+H^+$), $C_{30}H_{19}OCl_2S$, Calc.: 497.0534; Found: 497.0530.

2d



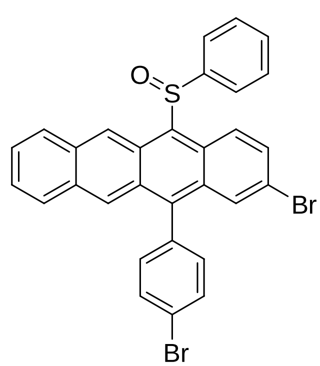
Yield: 70 %. IR (KBr) ν (cm^{-1}): 3053, 2961, 1473, 1365, 1265, 1046, 742, 695. ^{1}H NMR (400 MHz, $CDCl_3$):δ1.49 (s, 9H), 1.52 (s, 9H), 7.29~7.39 (m, 8H), 7.52 (d, *J* = 2.4 Hz, 1H), 7.58~7.68 (m, 5H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 8.35 (s, 1H), 8.87 (d, *J* = 9.2 Hz, 1H), 9.58 (s, 1H). ^{13}C NMR (125MHz, $CDCl_3$): 30.37, 31.48, 34.84, 34.92, 122.09, 122.63, 122.97, 124.49, 125.26, 125.55, 126.14, 127.23, 127.56, 128.13, 128.40, 128.58, 128.96, 129.58, 129.72, 130.61, 130.66, 130.86, 131.12, 131.95, 135.27, 143.89, 145.48, 146.90, 151.03. HRMS. (M^+), $C_{38}H_{36}OS$, Calc.: 540.2487; Found: 540.2483.

2e



Yield : 68 %. IR (KBr) ν (cm^{-1}): 3053, 1487, 1441, 1084, 1046, 875, 737, 691. ^1H NMR (400 MHz, $CDCl_3$): δ7.33~7.45 (m, 8H), 7.57~7.65 (m, 5H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.96 (t, *J* = 8.4 Hz, 1H), 8.22 (s, 1H), 8.98 (d, *J* = 9.6 Hz, 1H), 9.63 (s, 1H). ^{13}C NMR (125MHz, $CDCl_3$): 122.99, 124.25, 125.28, 125.60, 126.42, 126.79, 128.22, 128.55, 128.77, 129.08, 129.15, 129.29, 129.43, 129.52, 129.60, 129.68, 129.91, 131.50, 131.53, 132.19, 132.35, 133.52, 134.67, 135.96, 141.33, 144.89. HRMS. (M^+), $C_{30}H_{19}OCl_2S$, Calc.: 497.0534; Found: 497.0541.

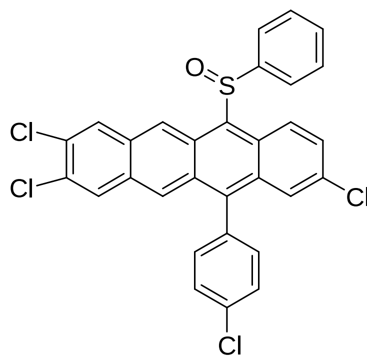
2f



Yield: 39 %. IR (KBr) ν (cm^{-1}): 3062, 1584, 1482, 1443, 1079, 1047, 1012, 741. ^1H NMR (400 MHz, $CDCl_3$): δ7.32~7.52 (m, 7H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.79 (d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 8.4 Hz, 1H), 8.22 (s, 1H), 8.90 (d, *J* = 9.6 Hz, 1H), 9.63 (s, 1H). ^{13}C NMR

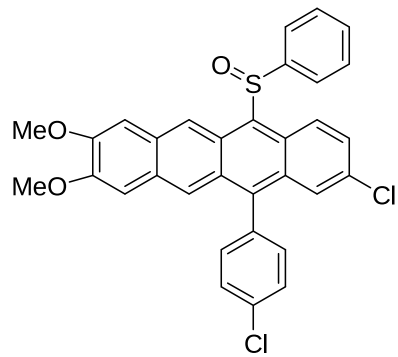
(125MHz, $CDCl_3$): 120.10, 122.88, 123.01, 124.27, 125.19, 126.51, 126.90, 126.92, 128.27, 128.61, 129.14, 129.36, 129.97, 131.08, 131.57, 132.15, 132.42, 132.52, 133.59, 136.44, 141.37, 144.82. HRMS. (M^+), $C_{30}H_{18}OBr_2S$, Calc.: 583.9445; Found: 583.9430.

2g



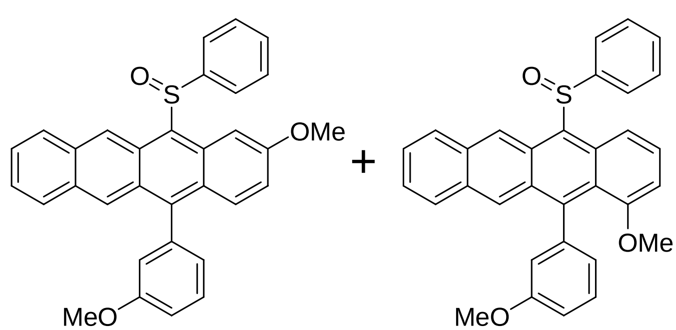
Yield: 42 %. IR (KBr) ν (cm^{-1}): 3062, 1441, 1107, 1085, 1047, 982, 809, 746. ^1H NMR (400 MHz, $CDCl_3$): 7.34~7.45 (m, 6H), 7.58~7.60 (m, 3H), 7.64 (d, J = 7.6 Hz, 2H), 7.92 (s, 1H), 8.08 (s, 1H), 8.12 (s, 1H), 8.96 (d, J = 9.6 Hz, 1H), 9.57 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$): 122.49, 124.15, 125.17, 125.63, 126.20, 128.06, 128.64, 128.97, 129.21, 129.27, 129.37, 129.66, 129.75, 130.00, 130.11, 130.37, 130.99, 131.31, 132.03, 132.06, 132.09, 133.82, 134.92, 135.41, 141.47, 144.49. HRMS. (M^+), $C_{30}H_{16}OCl_4S$, Calc.: 563.9676; Found: 563.9666.

2h



Yield: 47 %. IR (KBr) ν (cm^{-1}): 2934, 1490, 1430, 1305, 1233, 1154, 1083, 1016. ^{1}H NMR (400 MHz, $CDCl_3$): δ3.96 (s,3H), 4.03 (s, 3H), 6.93 (s, 1H), 7.12 (s, 1H), 7.35~7.39 (m, 6H), 7.55 (d, *J* = 2 Hz, 1H), 7.59~7.65 (m, 4H), 7.95 (s, 1H), 8.92 (d, *J* = 9.6 Hz, 1H), 9.37 (s, 1H). ^{13}C NMR (125MHz, $CDCl_3$): 55.99, 56.06, 104.25, 104.54, 119.88, 123.80, 124.31, 125.18, 125.54, 128.27, 128.82, 129.08, 129.11, 129.20, 129.87, 130.26, 130.98, 132.16, 132.24, 134.43, 136.29, 140.46, 144.95, 151.20, 151.54. HRMS. (M^+), $C_{32}H_{22}O_3Cl_2S$, Calc.: 556.0667; Found: 556.0670.

2i and **2i'**

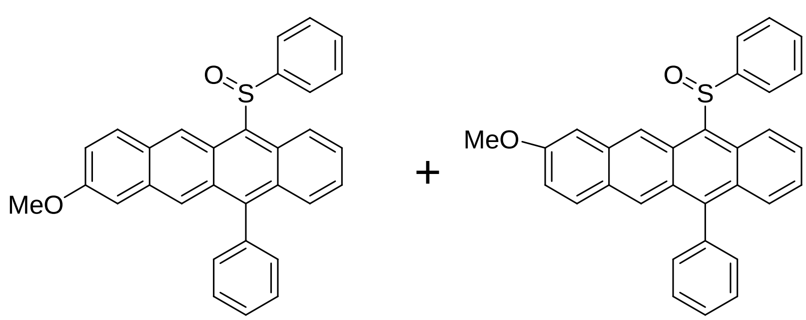


Yield of **2i**: 35 %, yield of **2i'**: 12 %.

2i IR (KBr) ν (cm^{-1}) 2925, 1620, 1458, 1434, 1233, 1042, 739, 701. ^{1}H NMR (500 MHz, $CDCl_3$): δ3.86 (s, 3H), 3.87 (s, 3H), 6.93~6.98 (m, 2H), 7.02 (t, *J* = 6.5 Hz, 1H), 7.13 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.30~7.42 (m, 5H), 7.52 (t, *J* = 8 Hz, 1H), 7.57 (d, *J* = 9.5 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 8.13 (s, 1H), 8.29 (s, 1H), 9.52 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$): 55.37, 55.53, 99.06, 113.83, 113.86, 116.22, 120.90, 123.25, 123.32, 124.42, 124.51, 125.42, 126.55, 127.51, 128.38, 128.43, 128.93, 128.97, 129.62, 129.98, 130.40, 132.44, 139.56, 144.03, 145.16, 158.70, 159.65, 159.67. HRMS. (M^+), $C_{32}H_{24}O_3S$, Calc.: 488.1446; Found: 488.1440.

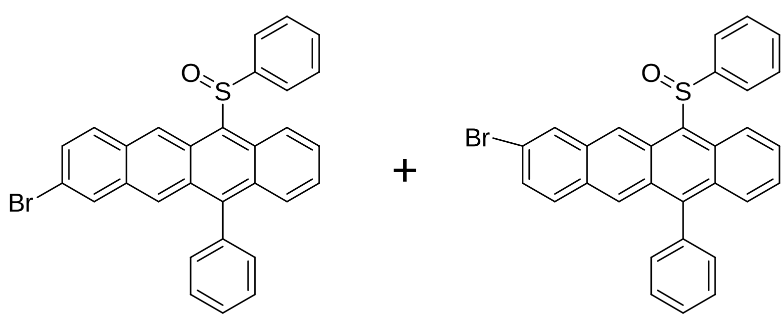
2i' IR (KBr) ν (cm^{-1}) 2925, 1581, 1544, 1463, 1243, 1044, 742, 701. ^{1}H NMR (500 MHz, $CDCl_3$):δ3.45 (s, 3H), 3.83 (s, 3H), 6.56 (d, *J* = 7.5 Hz, 1H), 6.87 (broad s, 1H), 6.92 (dd, *J* = 7, 2.5 Hz, 1H), 7.02 (dd, *J* = 8, 2 Hz, 1H), 7.28~7.42 (m, 7H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 1H), 8.23 (s, 1H), 8.54 (d, *J* = 9 Hz, 1H), 9.59 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$): 55.34, 55.48, 102.99, 112.32, 112.35, 114.60, 115.83, 122.04, 124.41, 125.59, 126.55, 128.06, 128.12, 128.26, 128.38, 128.65, 128.97, 129.62, 130.68, 131.49, 132.19, 142.73, 144.01, 145.20, 157.39, 158.79, 158.82. HRMS. (M^+), $C_{32}H_{24}O_3S$, Calc.: 488.1446; Found: 488.1440.

2j and **2j'**



Combined yield: 39 %. Isomeric ratio: 1: 0.3. IR (KBr) ν (cm^{-1}): 2929, 1630, 1468, 1443, 1233, 1043, 746, 699. ^{1}H NMR (400 MHz, $CDCl_3$): δ3.85 (s), 3.94 (s), 6.90 (s), 7.02 (d, *J* = 8 Hz), 7.09 (d, *J* = 8 Hz), 7.25~7.48 (m), 7.62~7.65 (m), 7.83 (d, *J* = 9.5 Hz), 8.09 (s), 8.19 (s), 8.92~8.95 (m), 9.43 (s), 9.55 (s). ^{13}C NMR (125MHz, $CDCl_3$): 55.22, 55.32, 102.83, 103.09, 119.96, 121.93, 122.53, 122.71, 123.14, 123.28, 124.38, 124.46, 124.68, 124.92, 126.75, 127.14, 127.21, 127.42, 127.52, 127.62, 127.69, 127.89, 127.96, 128.05, 128.11, 128.13, 128.34, 128.48, 128.53, 128.71, 128.94, 129.23, 129.34, 129.48, 129.61, 129.71, 129.79, 129.87, 130.07, 130.26, 130.55, 130.66, 130.73, 130.84, 130.89, 130.94, 131.17, 132.06, 132.12, 133.48, 138.26, 138.50, 142.90, 144.25, 145.35, 157.49, 158.00. HRMS. (M^+), $C_{31}H_{22}O_2S$, Calc.:458.1341; Found: 458.1344.

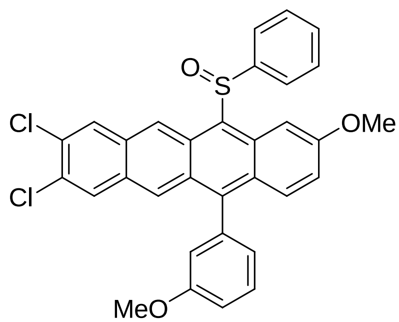
2k and **2k'**



Combined yield: 57 %. Isomeric ratio: 1: 1.

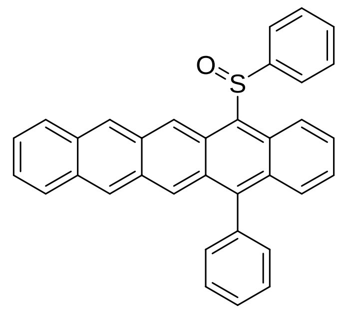
IR (KBr) ν (cm^{-1}): 3055, 2922, 1440, 1080, 1045, 888, 753, 701. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.30~7.44 (m), 7.51 (dd, *J* = 8.4, 6.8 Hz), 7.50~7.54 (m), 7.59~7.67 (m), 7.80 (d, *J* = 8 Hz), 7.93 (s), 8.12 (s), 8.18 (s), 8.25 (s), 8.95 (d, *J* = 9.2 Hz), 8.96 (d, *J* = 9.2 Hz), 9.55 (s), 9.63 (s). ^{13}C NMR (125MHz, $CDCl_3$): 120.17, 120.86, 122.02, 123.23, 123.29, 124.38, 125.22, 125.32, 126.42, 127.76, 127.95, 128.06, 128.09, 128.14, 128.28, 128.63, 129.05, 129.08, 129.35, 129.42, 129.49, 129.65, 129.79, 129.91, 129.96, 130.02, 130.16, 130.27, 130.77, 130.84, 130.91, 131.43, 132.19, 132.39, 132.53, 137.95, 144.05, 144.22, 145.16, 145.21. HRMS. ($[M+H]^+$), $C_{30}H_{20}OBrS$, Calc.: 507.0418; Found: 507.0422.

2l



Yield: 57 %. IR (KBr) ν (cm^{-1}) 2931, 1573, 1462, 1433, 1285, 1227, 1107, 737. ^1H NMR (400 MHz, $CDCl_3$):δ3.87 (s, 3H), 3.88 (s, 3H), 6.98~7.06 (m, 6H), 7.10~7.15 (m, 3H), 7.53 (t, J = 8 Hz, 1H), 7.60 (d, J = 9.6 Hz, 1H), 7.94 (s, 1H), 8.02 (d, J = 2.4 Hz, 1H), 8.09 (s, 1H), 8.19 (s, 1H), 9.35 (s, 1H). ^{13}C NMR (125MHz, $CDCl_3$): 55.36, 55.39, 102.06, 113.72, 116.52, 121.39, 122.22, 123.47, 124.34, 125.16, 126.43, 126.53, 127.34, 128.86, 128.88, 128.92, 128.99, 129.30, 129.65, 129.68, 130.14, 130.46, 132.98, 137.05, 138.23, 139.62, 158.75, 159.72. HRMS. ($[M+H]^+$), $C_{32}H_{23}O_3Cl_2S$, Calc.: 557.0745; Found: 557.0729.

2m

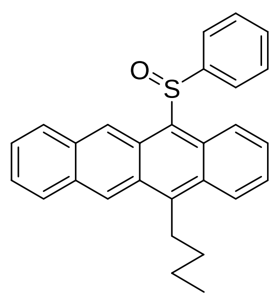


Yield of impure pentacene derivative **2m**: 9 %.

IR (KBr) ν (cm^{-1}) 2923, 2852, 1441, 1080, 1045, 888, 746, 702. ^{1}H NMR (500 MHz, $CDCl_3$): δ7.27~7.74 (m , 15 H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.91 (d, *J* = 8 Hz, 1H), 8.44 (s, 1H), 8.58 (s, 1H), 8.62 (s, 1H), 8.91 (d, *J* = 9 Hz, 1H), 9.94 (s, 1H).

HRMS. (M^+), $C_{34}H_{22}OS$, Calc.: 478.1391; Found: 478.1390.

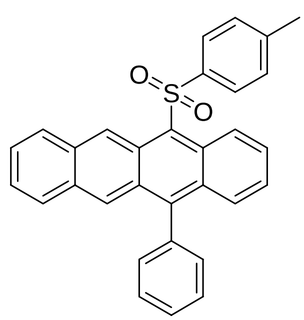
2n



Yield: 10 %. IR (KBr) ν (cm^{-1}) 2956, 2925, 1626, 1442, 1080, 1043, 746, 690. ^{1}H NMR (500 MHz, $CDCl_3$):δ1.06 (t, *J* = 7.5 Hz, 3H), 1.65~1.69 (m, 2H), 1.88~1.91 (m, 2H), 3.81 (t, *J* = 8 Hz, 2H), 7.27~7.49 (m), 7.56 (d, *J* = 7.5 Hz), 7.92~7.94 (m, 1H), 7.99~8.00 (m, 1H), 8.33 (d, *J* = 9 Hz, 1H), 8.96 (s, 2H), 9.61 (s, 1H). ^{13}C NMR (125MHz, $CDCl_3$): 14.02, 23.48, 28.93, 33.63, 123.41, 124.03, 124.21, 124.32, 125.09, 125.45, 125.89, 126.29, 127.43, 128.30, 128.32, 128.40, 128.45, 128.88, 129.50, 130.41, 131.04, 131.98, 143.41, 145.36. HRMS. ($[M+H]^+$), $C_{28}H_{25}OS$, Calc.: 409.1626; Found: 409.1633.

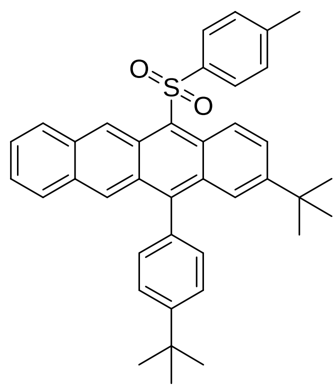
General procedure for the synthesis of 5-phenylsulphonyl-12-phenyl tetracene derivatives (3a, 3d, 3e, 3f, 3i, 3j, and 3k) *via* cascade cyclization reaction: To CH_2Cl_2 solutions of bis-phenylacetylene adducts (**1a, 1d, 1e, 1f, 1i, 1j,** and **1k**) were slowly added 2.5 equivalents of Et_3N and *p*-toluenesulfinyl chloride respectively at 0°C. The mixed solutions were then refluxed for 6 hr before quenched with water and extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$ and concentrated *in vacuo*. The crude products were purified with flash chromatography (CH_2Cl_2/hexane = 2:1) to provide the tetracene products as red-orange powders.

3a



Yield: 66 %. IR (KBr) ν (cm^{-1}): 3054, 2923, 1490, 1303, 1148, 755, 673, 582. ^1H NMR (400 MHz, $CDCl_3$):δ2.32 (s, 3H), 7.21~7.23 (m, 2H), 7.25~7.29 (m, 1H), 7.33~7.37 (m, 1H), 7.40~7.45 (m, 3H), 7.52~7.56 (m, 1H), 7.62~7.65 (m, 4H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 9.6 Hz, 2H), 8.02 (d, *J* = 8.8 Hz, 1H), 8.26 (s, 1H), 9.47 (d, J = 8.4 Hz, 1H), 10.12 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$): 21.49, 124.48, 124.55, 124.68, 125.98, 126.09, 126.75, 127.29, 127.70, 128.03, 128.25, 128.33, 128.45, 128.58, 129.13, 129.24, 129.41, 129.66, 130.48, 130.66, 131.68, 132.57, 138.41, 141.80, 143.51, 147.14. HRMS. (M^+), $C_{31}H_{22}O_2S$, Calc.: 458.1341; Found: 458.1344.

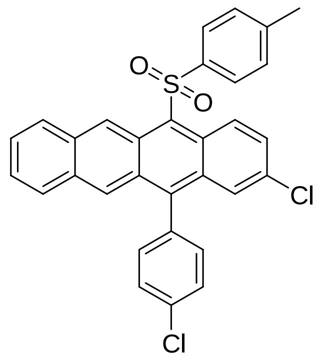
3d



Yield: 42 %. IR (KBr) ν (cm^{-1}): 2962, 1324, 1303, 1149, 1084, 685, 654, 592.

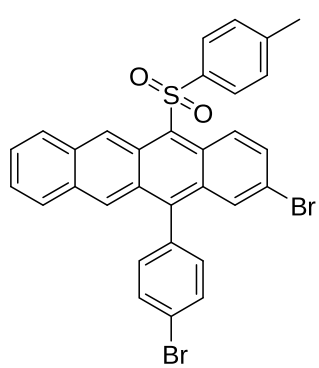
^{1}H NMR (400 MHz, $CDCl_3$): δ1.22 (s, 9H), 1.48 (s, 9H), 2.32 (s, 3H), 7.21~7.23 (m, 2H), 7.31~7.35 (m, 3H), 7.52 (t, J = 7.2 Hz, 1H), 7.49 (d, J = 2 Hz, 1H), 7.62~7.66 (m, 3H), 7.76 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.4 Hz, 2H), 8.01 (d, J = 8.4 Hz, 1H), 8.33 (s, 1H), 9.39 (d, J = 9.6 Hz, 1H), 10.07 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$): 21.46, 30.23, 31.44, 34.69, 34.82, 122.25, 124.28, 124.35, 125.25, 125.78, 125.96, 126.44, 127.25, 127.49, 127.57, 128.06, 128.34, 129.08, 129.47, 129.63, 129.84, 130.30, 130.35, 130.66, 132.32, 135.42, 143.38, 146.33, 147.04, 151.12. HRMS. (M^+), $C_{39}H_{38}O_2S$, Calc.: 570.2593; Found: 570.2596.

3e



Yield: 38 %. IR (KBr) ν (cm^{-1}): 2924, 1319, 1488, 1449, 1086, 810, 680, 648. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.22 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.39 (t, *J* = 8 Hz, 1H), 7.43~7.48 (m, 2H), 7.55 (d, *J* = 2 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 8.01 (d, *J* = 8.4 Hz, 1H), 8.18 (s, 1H), 9.52 (d, *J* = 9.6 Hz, 1H), 10.09 (s, 1H). ^{13}C NMR (125MHz, $CDCl_3$): 21.50, 124.93, 125.59, 125.98, 126.69, 126.78, 126.85, 127.10, 127.29, 127.93, 129.13, 129.22, 129.33, 129.45, 129.53, 129.77, 130.17, 130.99, 131.15, 132.00, 132.70, 134.80, 136.16, 136.47, 141.36, 143.88, 144.42. HRMS. (M^+), $C_{31}H_{20}O_2Cl_2S$, Calc.: 526.0561; Found: 526.0562.

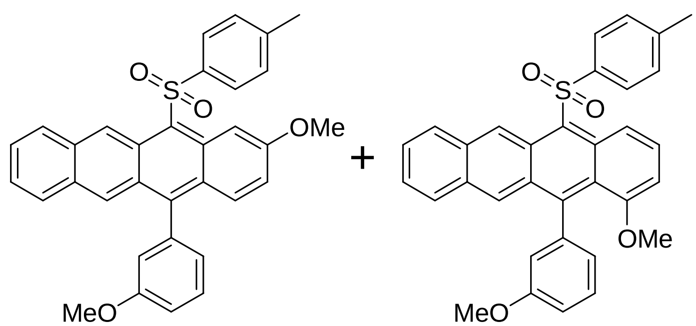
3f



Yield: 35 %. IR (KBr) ν (cm^{-1}): 2921, 1484, 1319, 1149, 1083, 809, 730, 680. ^{1}H NMR (400 MHz, $CDCl_3$): δ2.32 (s, 3H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* =

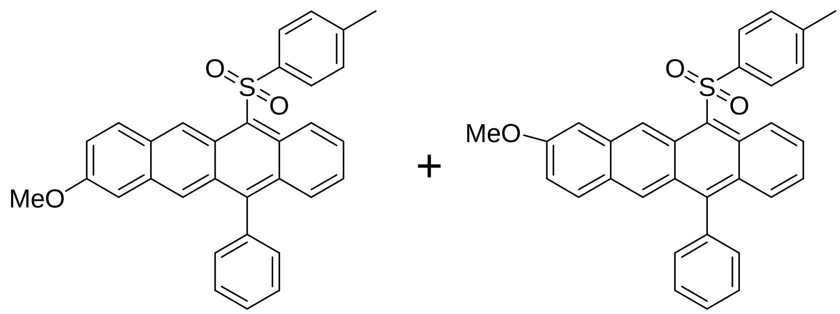
8.4 Hz, 2H), 7.39 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.57 (dd, J = 10, 1.6 Hz, 1H), 7.74~7.76 (m, 2H), 7.79 (d, J = 8 Hz, 2H), 7.89 (d, J = 8 Hz, 2H), 8.01 (d, J = 8.4 Hz, 1H), 8.19 (s, 1H), 9.44 (d, J = 10 Hz, 1H), 10.09 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$): 21.52, 119.74, 123.01, 124.95, 125.99, 126.68, 126.73, 126.91, 127.15, 127.32, 127.94, 129.09, 129.16, 129.45, 129.62, 129.78, 129.94, 130.12, 131.04, 131.71, 132.17, 132.30, 132.75, 136.65, 141.37, 143.89, 144.39. HRMS. (M^+), $C_{31}H_{20}O_2Br_2S$, Calc.: 613.9551; Found: 613.9554.

3i and **3i'**



Combined yield: 73 %. Isomeric ratio: 1: 0.85. IR (KBr) ν (cm^{-1}) 2924, 1622, 1582, 1458, 1285, 1142, 1083, 585. ^{1}H NMR (400 MHz, $CDCl_3$): δ2.32 (s), 2.33 (s), 3.42 (s), 3.81 (s), 3.82 (s), 3.85 (s), 3.97 (s), 6.54 (d, J = 7.2 Hz), 6.83 (dd, J = 2.4, 1.6 Hz), 6.90 (d, J = 7.6 Hz), 6.93~7.04 (m), 7.13 (dd, J = 8.4, 2.4 Hz), 7.20 (d, J = 3.2Hz), 7.21 (d, J = 3.2Hz), 7.32~7.43 (m), 7.50~7.57 (m), 7.73 (t, J = 9.2 Hz), 7.90 (dd, J = 8, 1.2 Hz), 7.99 (d, J = 8.4Hz), 8.25 (d, J = 2.8 Hz), 8.74 (d, J = 2.4 Hz), 8.90 (d, J = 9.6 Hz), 10.00 (s), 10.04 (s). ^{13}C NMR (125MHz, $CDCl_3$): 21.45, 55.32, 55.48, 100.62, 102.86, 112.32, 113.89, 114.36, 116.03, 117.15, 120.29, 121.77, 123.03, 123.64, 123.81, 124.51, 125.62, 125.77, 125.86, 126.28, 126.69, 126.82, 127.57, 127.67, 127.80, 128.02, 128.14, 128.36, 128.55, 128.86, 128.98, 129.27, 129.52, 129.58, 129.88, 129.94, 130.16, 132.49, 132.66, 133.27, 133.85, 139.71, 141.88, 141.97, 143.33, 144.16, 145.42, 146.92, 157.26, 158.83, 159.37, 159.61. HRMS. (M^+), $C_{33}H_{26}O_4S$, Calc.: 518.1552; Found: 518.1559.

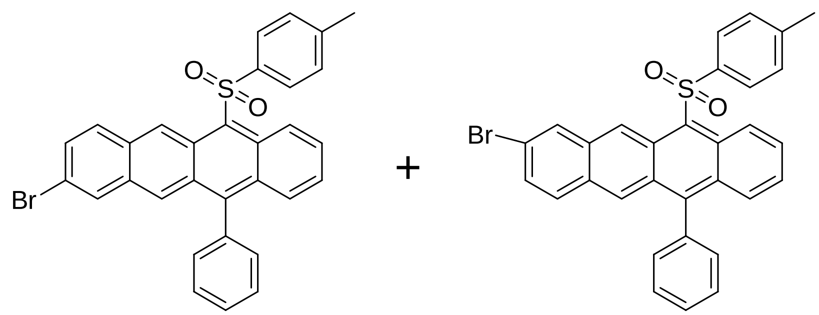
3j and **3j'**



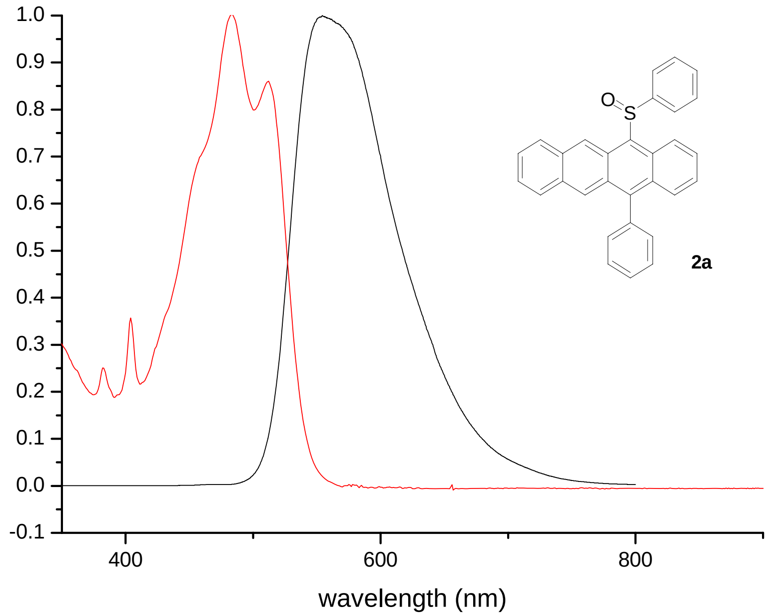
Combined yield: 74 %. Isomeric ratio: 1: 0.7.

IR (KBr) ν (cm^{-1}): 2925, 1633, 1469, 1429, 1303, 1147, 673, 582. ^{1}H NMR (400 MHz, $CDCl_3$): δ2.32 (s), 2.33 (s), 3.86 (s), 3.97 (s), 6.88 (d, *J* = 2 Hz), 7.04 (dd, *J* = 9.2, 2.4 Hz), 7.12 (dd, *J* = 9.2, 2.4 Hz), 7.20~7.27 (m), 7.40~7.43 (m), 7.49~7.54 (m), 7.59~7.64 (m), 7.91~7.95 (m), 8.06 (s), 8.17 (s), 9.38 (d, *J* = 9.2 Hz), 9.43 (d, *J* = 9.2 Hz), 9.98 (s), 10.05 (s), 8.92~8.95 (m), 9.43 (s), 9.55 (s). ^{13}C NMR (125MHz, $CDCl_3$): 21.36, 22.54, 55.16, 55.30, 102.35, 103.48, 121.47, 122.15, 122.82, 124.05, 124.30, 124.44, 124.47, 124.55, 124.62, 125.82, 125.86, 126.68, 126.98, 127.21, 127.55, 127.87, 127.99, 128.04, 128.13, 128.22, 128.32, 128.45, 128.51, 128.76, 129.49, 129.56, 129.72, 130.52, 130.58, 130.71, 130.82, 131.49, 131.70, 133.98, 138.32, 138.56, 141.78, 141.86, 143.35, 143.40, 145.95, 147.34, 157.56, 158.19. HRMS. (M^+), $C_{32}H_{24}O_3S$, Calc.: 488.1446; Found: 488.1432.

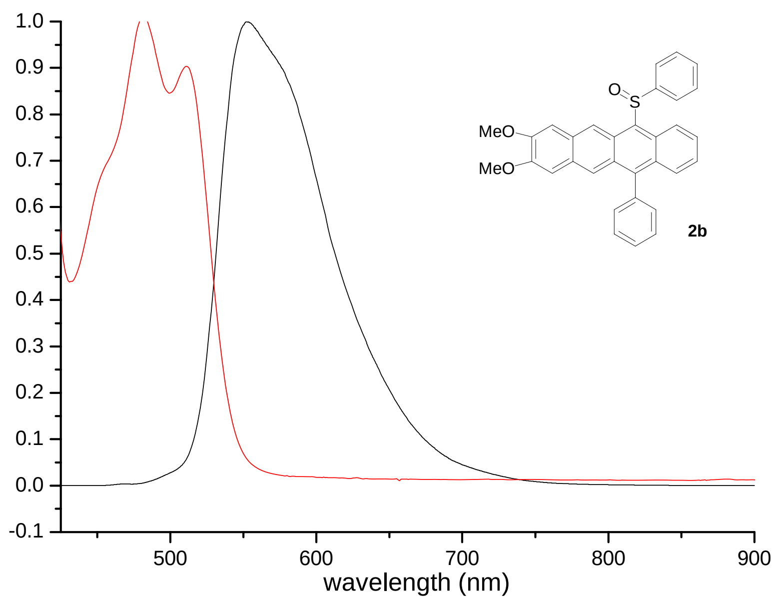
3k and **3k'**



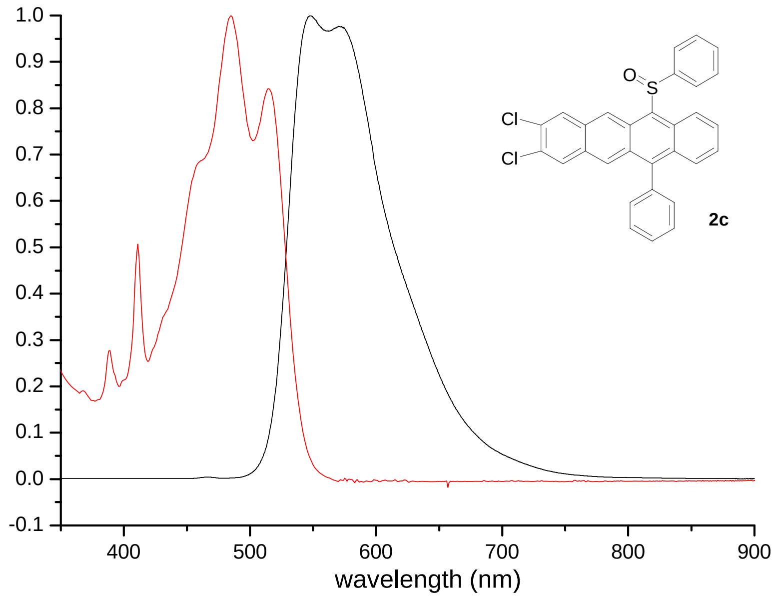
Combined yield: 53 %. Isomeric ratio: 1 : 0.55. IR (KBr) ν (cm^{-1}): 2923, 1309, 1149, 1083, 756, 703, 677, 580. ^1H NMR (500 MHz, $CDCl_3$): δ2.33 (s), 2.34 (s), 7.21~7.23 (m), 7.26~7.29 (m), 7.37~7.40 (m), 7.45(d, *J* = 9.5 Hz), 7.53~7.65 (m), 7.89~7.94 (m), 8.16 (s), 8.21 (s), 8.23 (s), 9.44 (d, *J* = 9.5 Hz), 9.48 (d, *J* = 9.5 Hz), 10.02 (s), 10.13 (s). ^{13}C NMR (125MHz, $CDCl_3$) : 21.49, 22.63, 120.47, 121.20, 123.71, 124.78, 124.83, 124.94, 125.01, 126.00, 126.37, 127.73, 127.81, 128.12, 128.24, 128.29, 128.42, 128.66, 128.78, 128.89, 129.27, 129.56, 129.65, 129.72, 129.76, 129.91, 130.30, 130.62, 130.69, 130.85, 130.98, 131.83, 132.13, 132.98, 138.20, 141.78, 141.82, 143.64, 147.10, 147.28. HRMS. (M^+), $C_{31}H_{21}O_2BrS$, Calc.: 536.0446; Found: 536.0442.



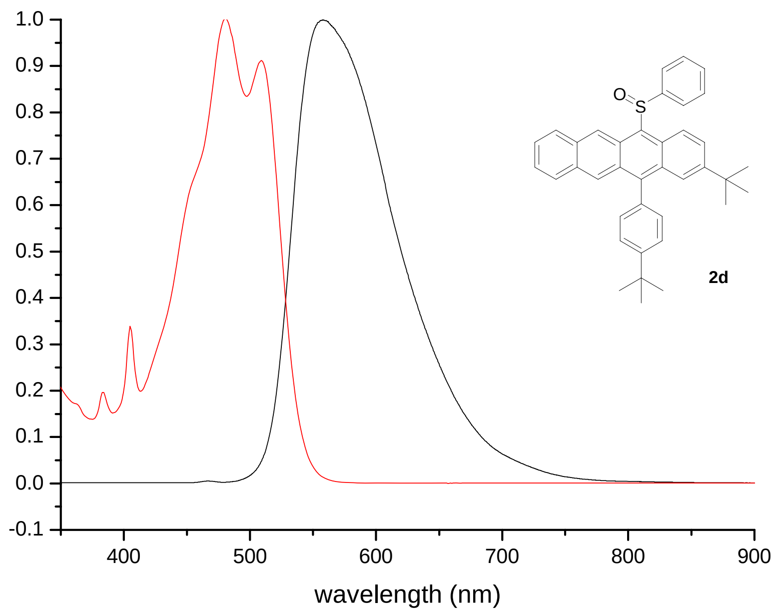
UV and PL spectrum of 2a



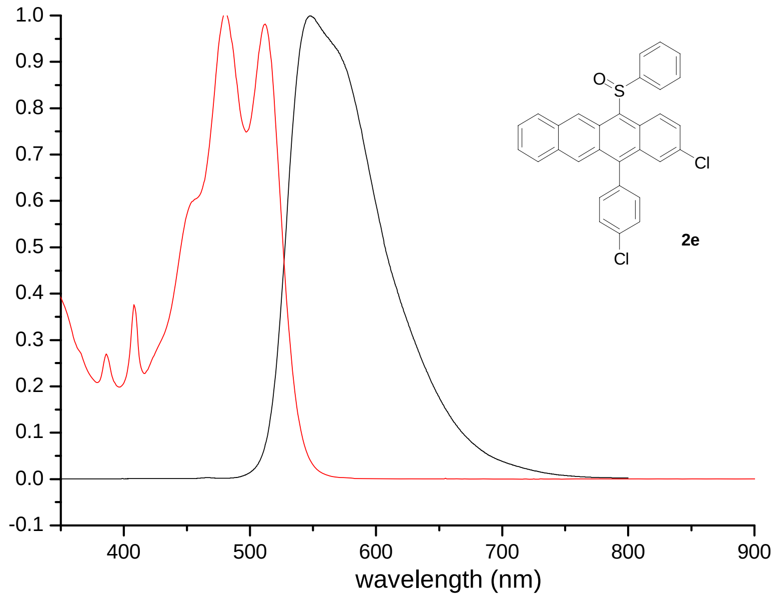
UV and PL spectrum of 2b



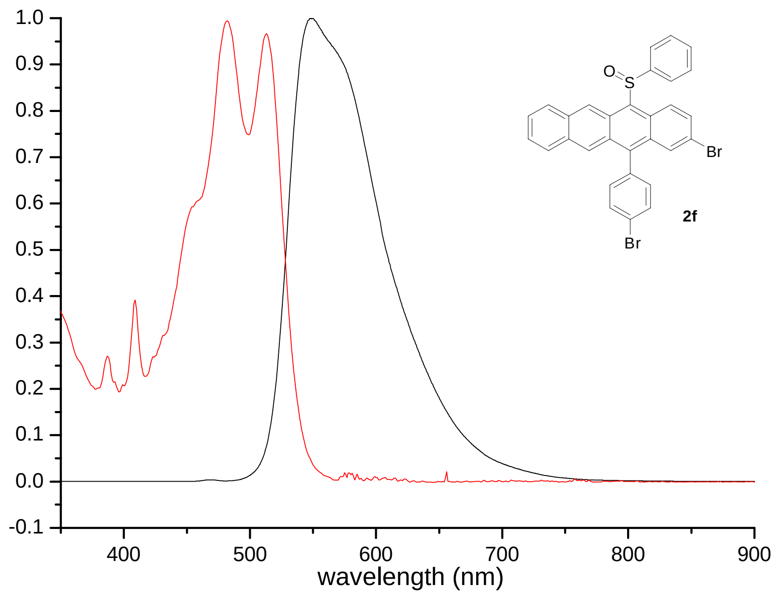
UV and PL spectrum of 2c



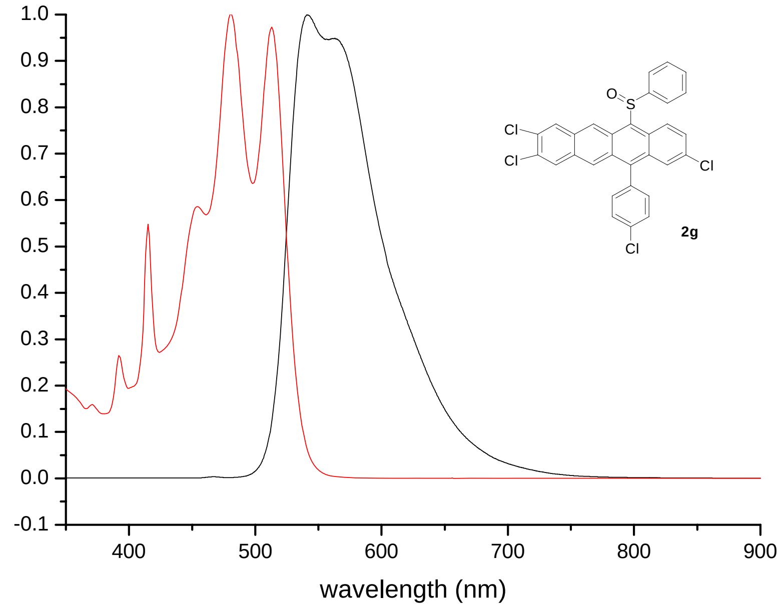
UV and PL spectrum of 2d



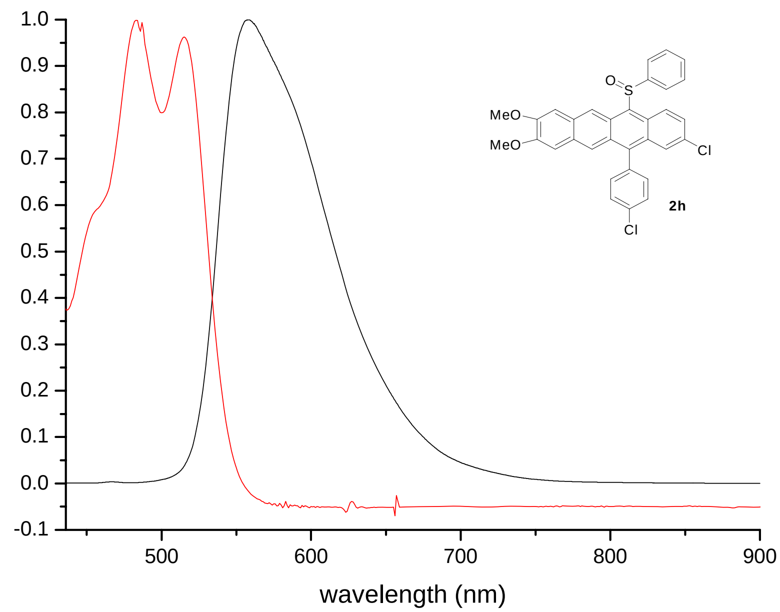
UV and PL spectrum of 2e



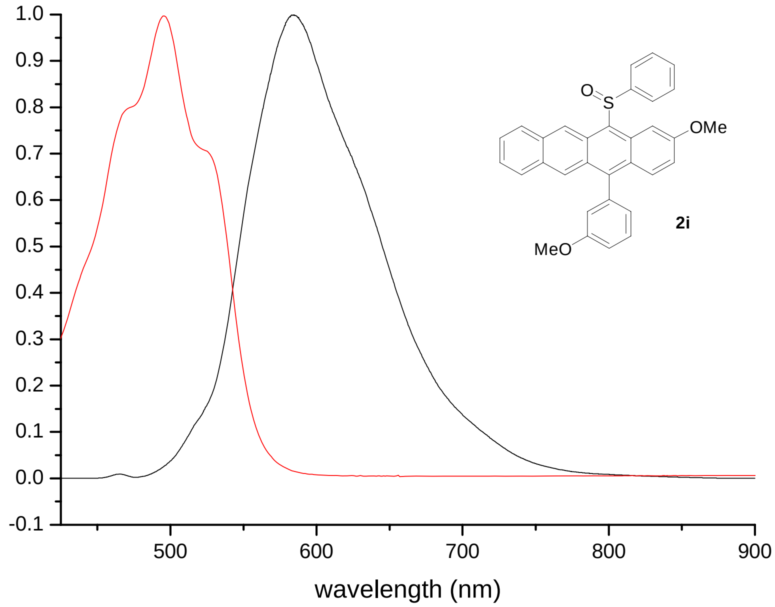
UV and PL spectrum of 2f



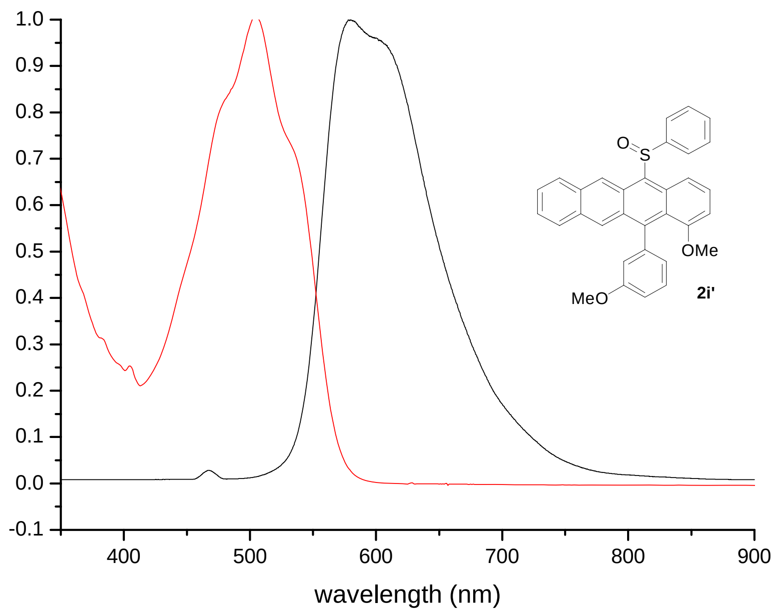
UV and PL spectrum of 2g



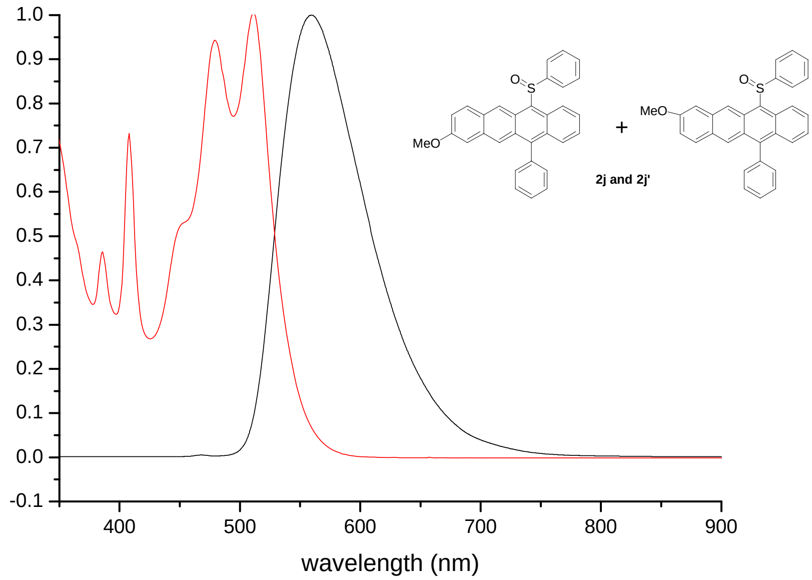
UV and PL spectrum of 2h



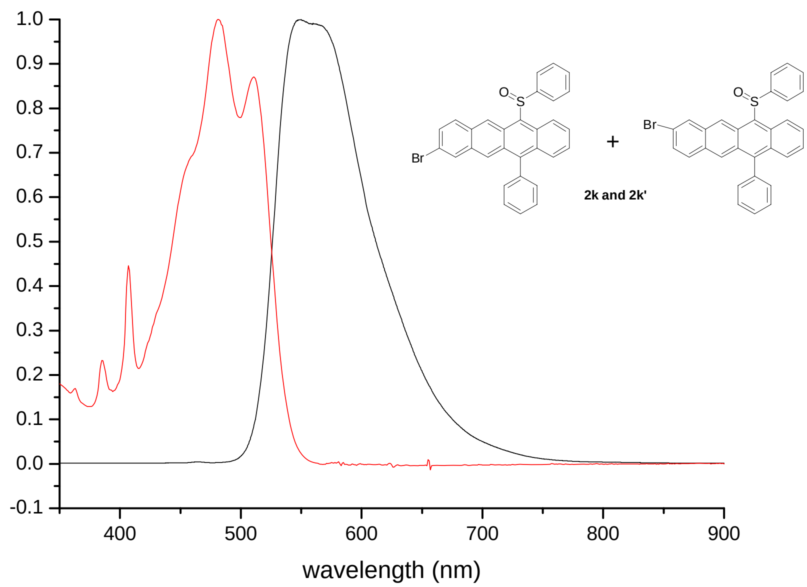
UV and PL spectrum of 2i



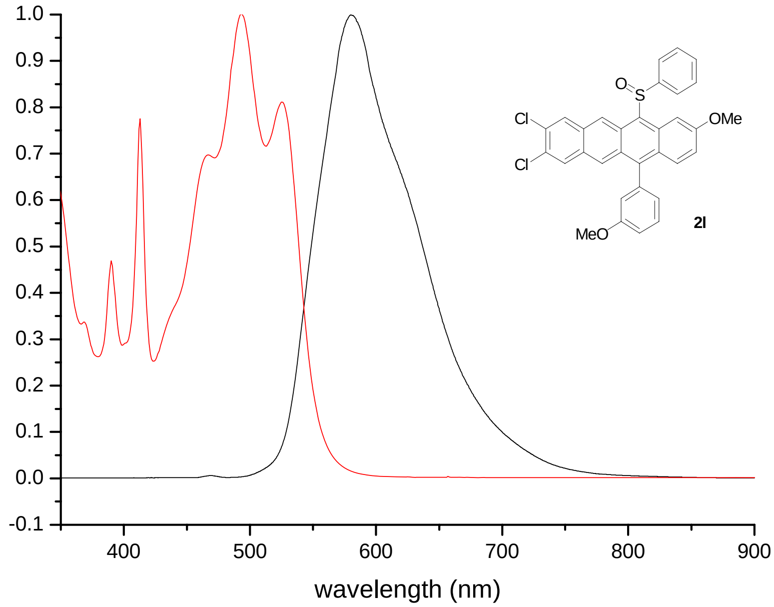
UV and PL spectrum of 2i’



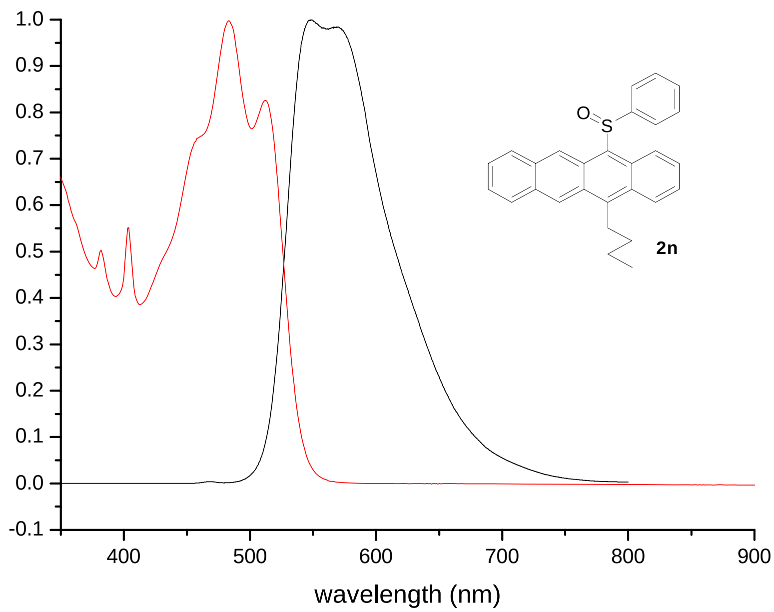
UV and PL spectrum of 2j and 2j' mixture



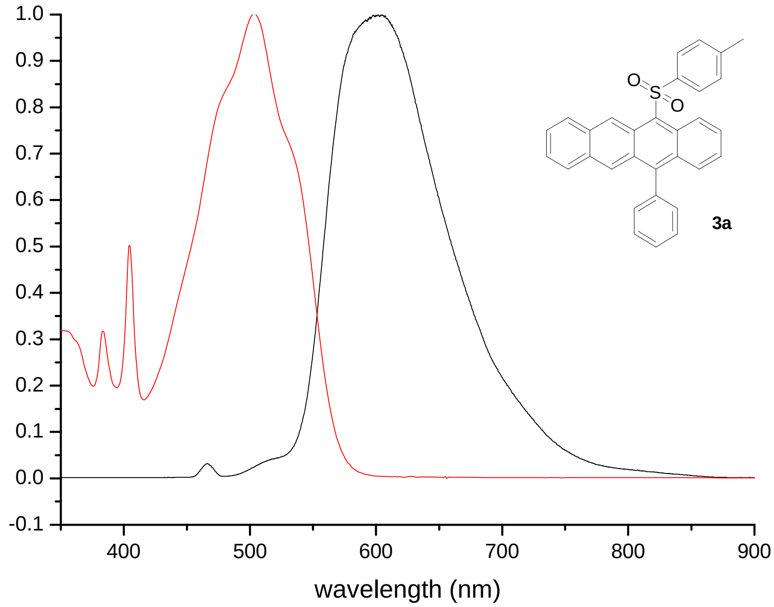
UV and PL spectrum of 2k and 2k' mixture



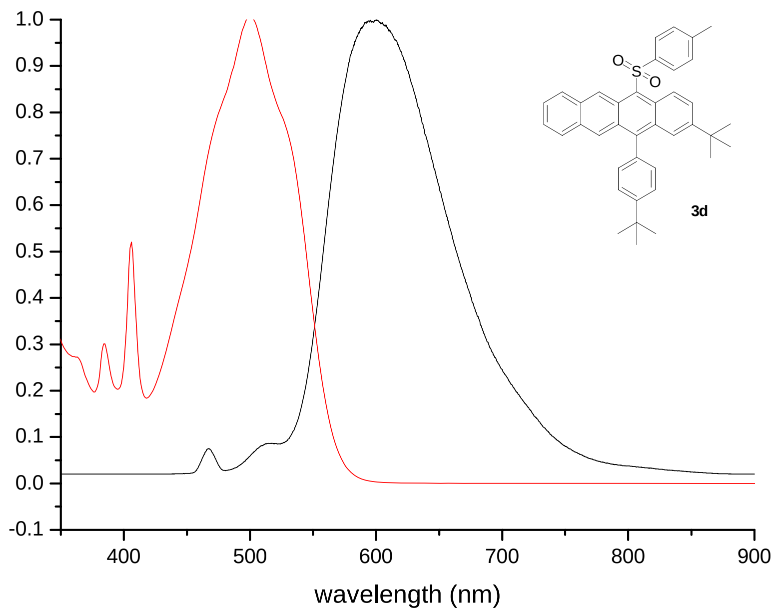
UV and PL spectrum of 2l



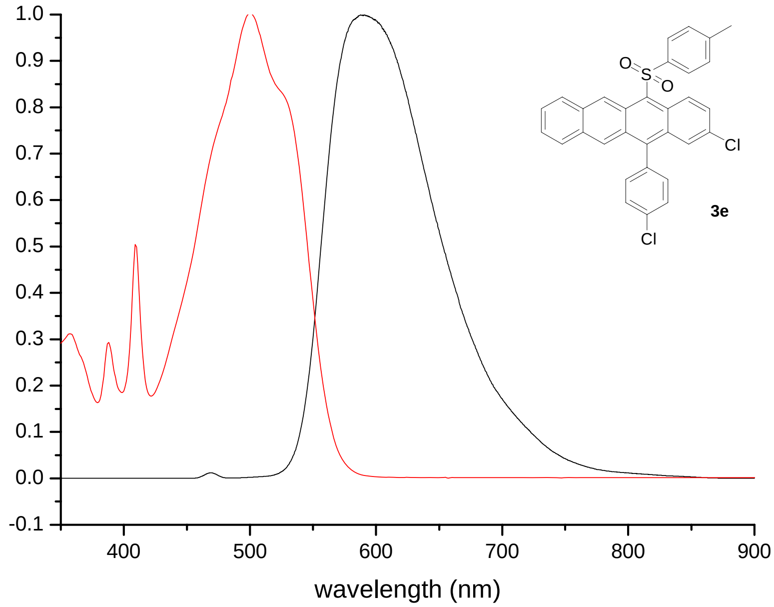
UV and PL spectrum of 2n



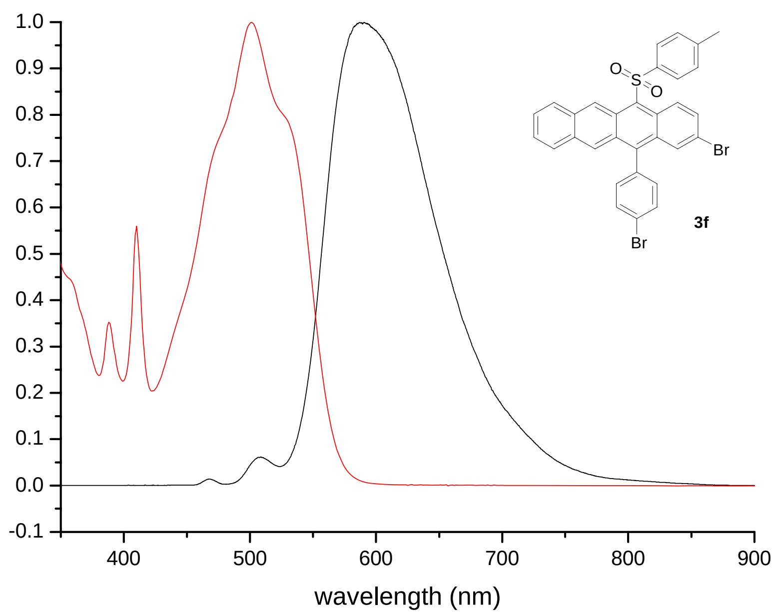
UV and PL spectrum of 3a



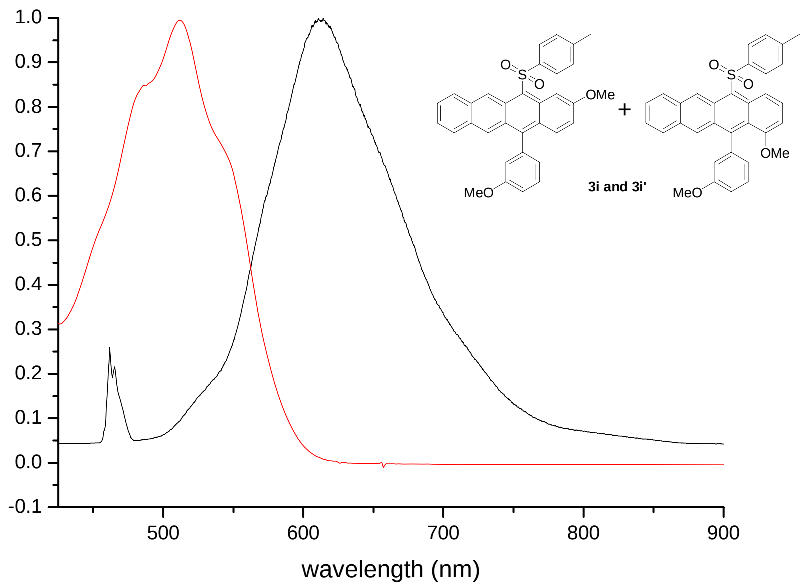
UV and PL spectrum of 3d



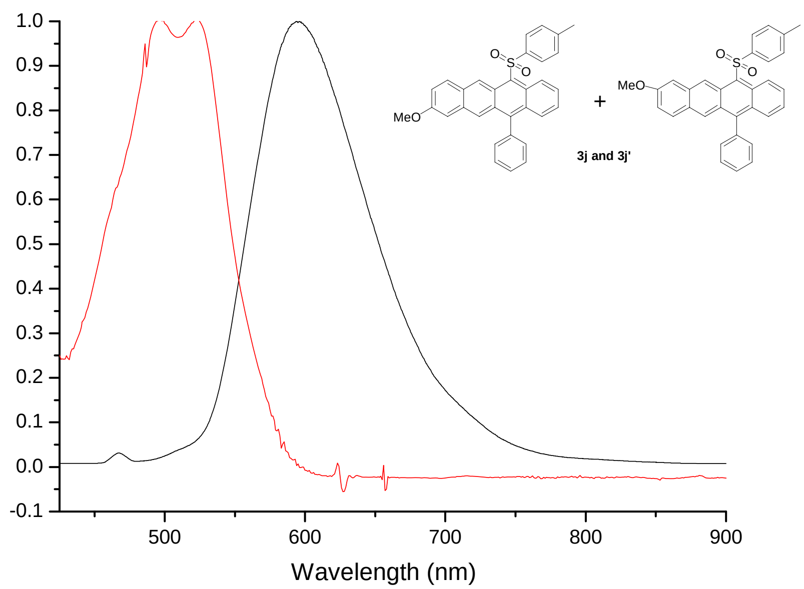
UV and PL spectrum of 3e



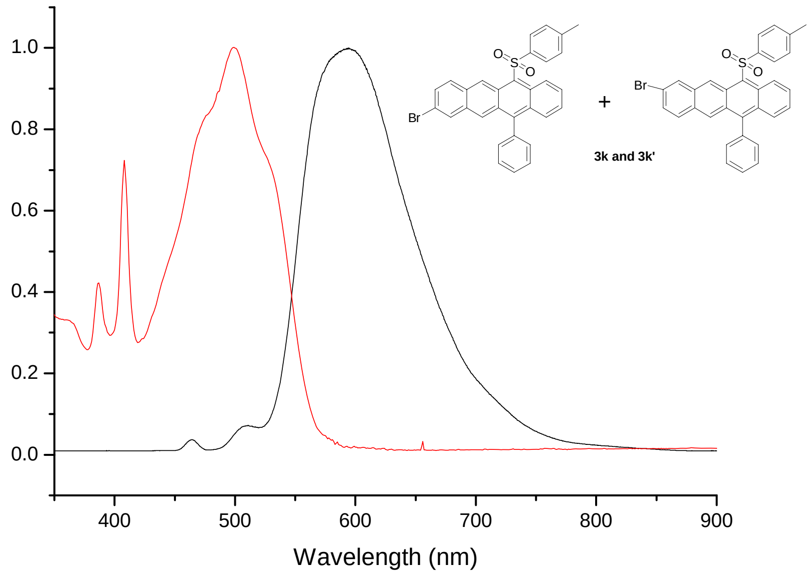
UV and PL spectrum of 3f



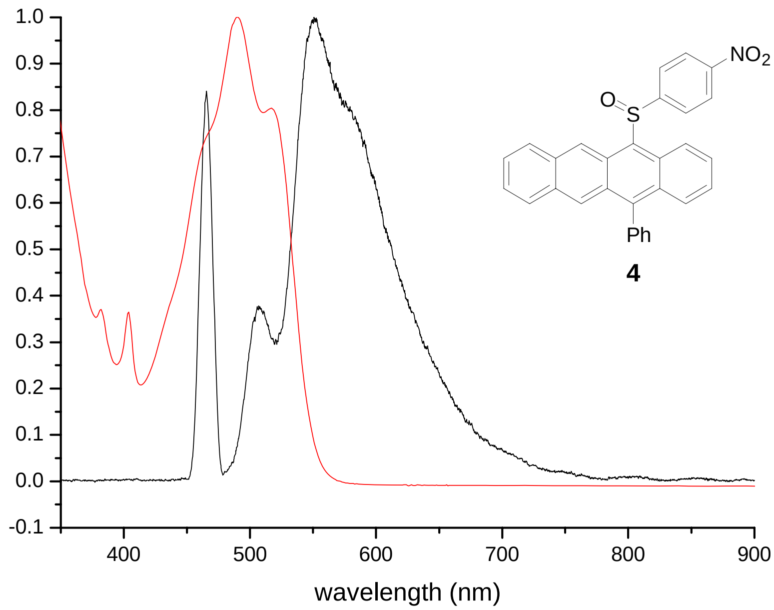
UV and PL spectrum of 3i and 3i' mixture



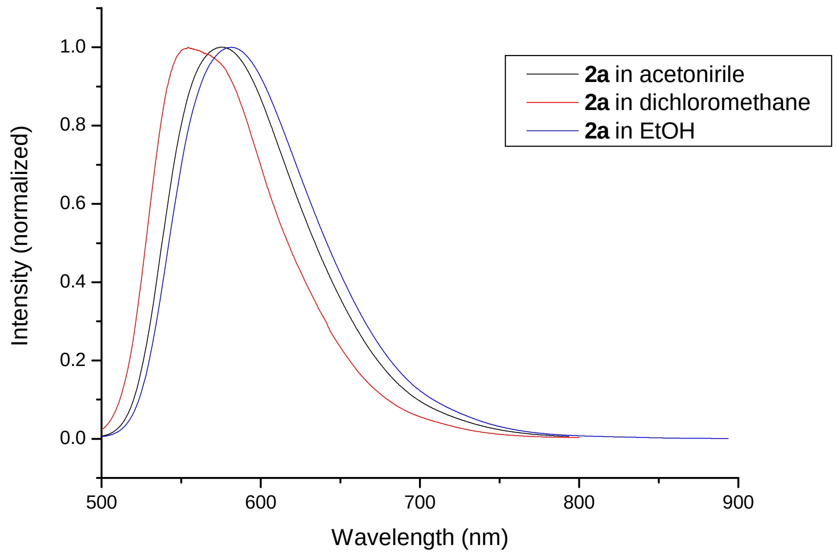
UV and PL spectrum of 3j and 3j' mixture



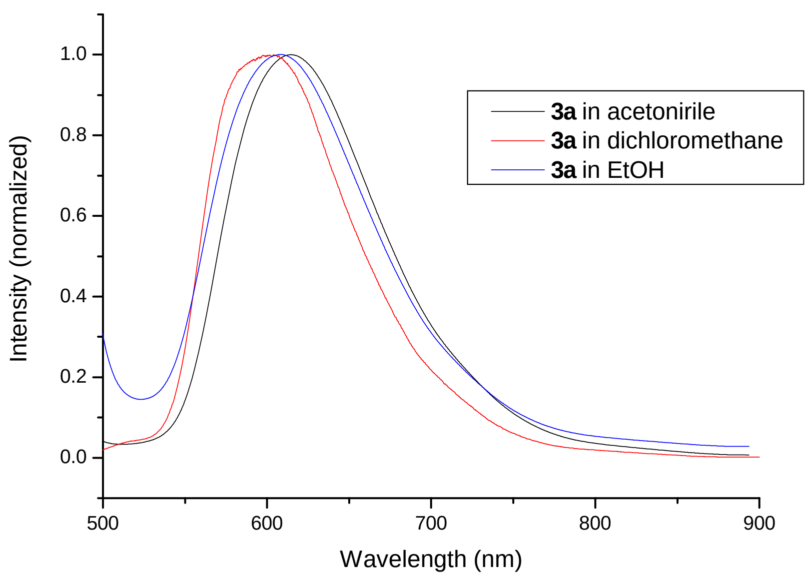
UV and PL spectrum of 3k and 3k' mixture



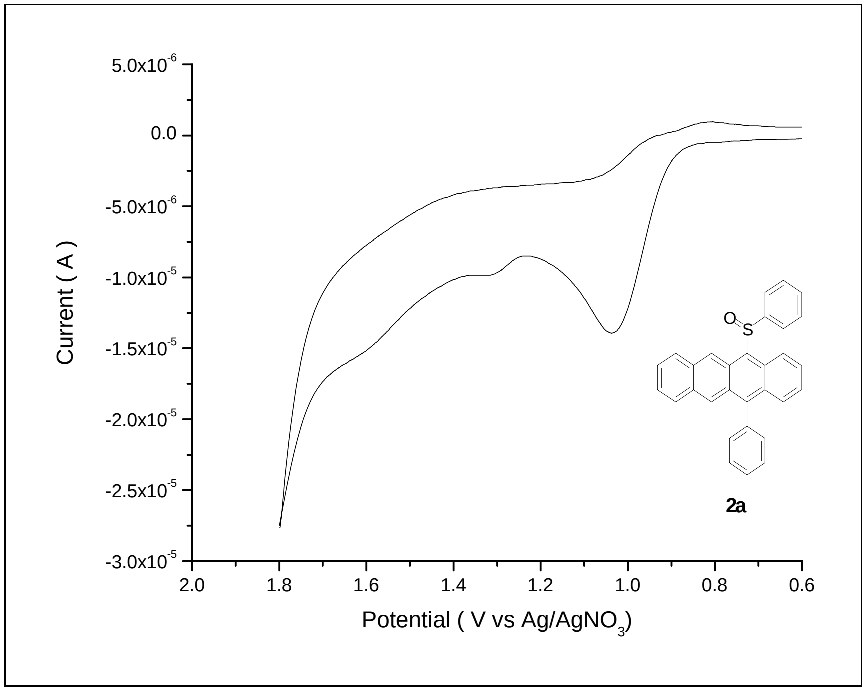
UV and PL spectrum of 4



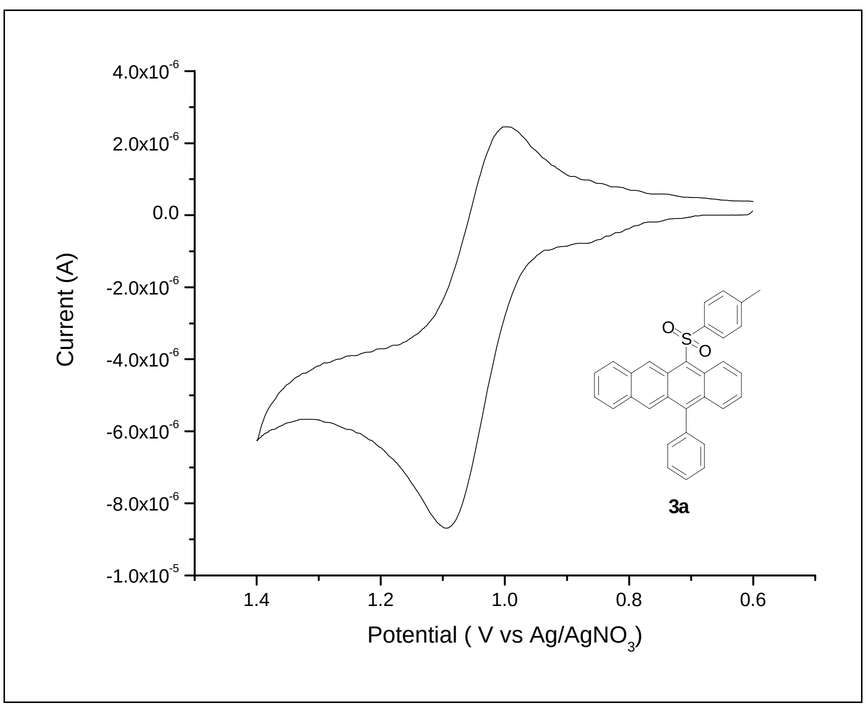
Solvatochromism observed for tetracene sulfoxides **2a**



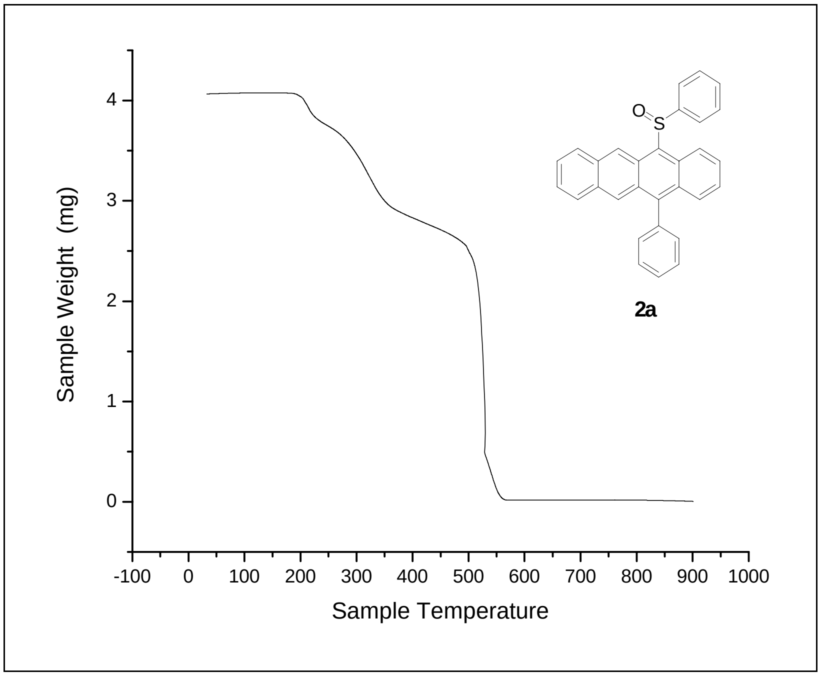
Solvatochromism observed for tetracene sulfone **3a**



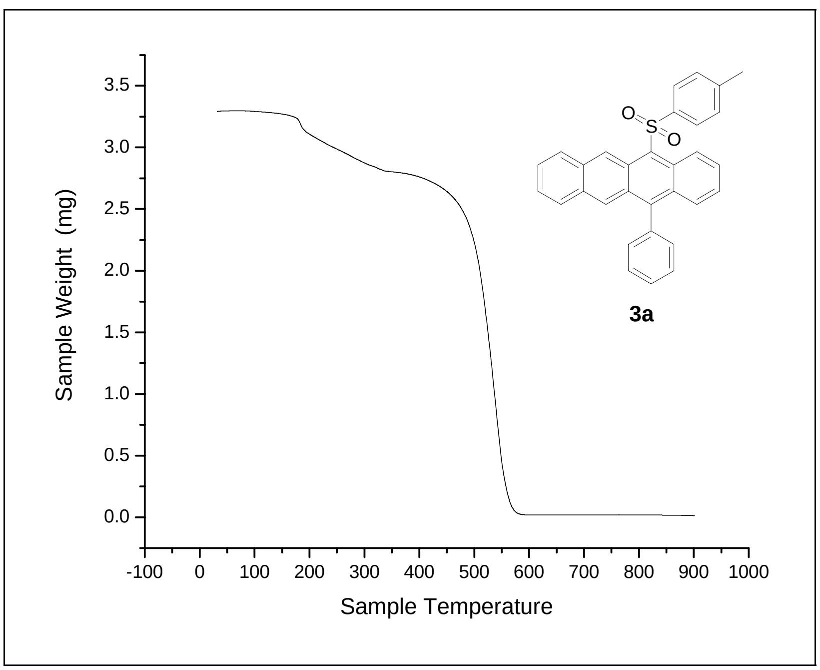
Cyclic voltammogram of tetracene sulfoxide **2a**



Cyclic voltammogram of tetracene sulfone **3a**



TGA of tetracene sulfoxide **2a**



TGA of tetracene sulfone **3a**