

Star-shaped Triphenylamine-thienylenevinylenes Hybrid Systems with Internal Charge-transfer as Donor Materials for Heterojunction Solar Cells

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Experimental

Synthesis

Tris[4-(2-thienyl)phenyl]amine (9). To a solution of tris(4-bromophenyl)amine **12** (Aldrich) (1g, 2mmol) in 100 mL of toluene, are added 2-tributylstannylthiophene (2.9 mL, 4.5 eq) and Pd(PPh₃)₄ 27mg (1.1 mol %). The mixture is refluxed 12 h under inert atmosphere and cooled to room temp. The solution is washed with brine and dried over MgSO₄. After solvent evaporation the residue is rinsed with petroleum ether and filtrated to give 0.868 g (85%) of a yellow solid M.p. 139°C. ¹H NMR (CDCl₃) 7.50 (d, 2H, ³J=8.00Hz), 7.20 (m, 2H), 7.10 (d, 2H, ³J=8.00Hz), 7.08 (dd, 1H, ³J=3.75Hz, ⁴J=5.00Hz). MS MALDI-TOF calcd for C₃₀H₂₁NS₃ 491, found 491 (M.+)

Tris[4-(5-formyl-2-thienyl)phenyl]amine (8). Tris[4-(2-thienyl)phenyl]amine (**9**) (500 mg, 1mmol) is dissolved in 30mL of 1,2-dichloroethane. DMF (371 mg, 5eq) and POCl₃ (781 mg, 5eq) are added dropwise and the mixture is refluxed 15 h under nitrogen. After cooling to room temp and addition of 50 mL of dichloromethane and 100 mL of a saturated aqueous solution of sodium acetate, the mixture is stirred 2 h at room temp. The organic phase is then washed with water and dried over MgSO₄. Solvent removal and column chromatography (silica gel/dichloromethane) gave 0.53 g (90%) of an orange solid. M.p. 230°C. ¹H NMR (CDCl₃) 9.90 (s, 1H), 7.70 (d, 1H, ³J=3.75Hz), 7.60 (d, 1H, ³J=3.75Hz), 7.30 (d, 2H, ³J=8.00Hz), 7.20 (d, 2H, ³J=8.00 Hz). ¹³C NMR (CDCl₃) 182.7, 153.6, 147.5, 142.0, 137.6, 128.4, 127.6, 124.6, 123.6. IR (KBr n (cm⁻¹) 1659 (C=O). MS MALDI-TOF calcd for C₃₃H₂₁NO₃S₃ 575, found 575 (M+.)

Tris{4-[5-(2-thienylethen-2-yl)-2-thienyl]phenyl}amine (1).

Tris[4-(5-formyl-2-thienyl)phenyl]amine **8** (0.3g, 0.5 mmol), and 2-(diethoxyphosphoryl-methyl)thiophene (0.55 g, 5. eq) are dissolved in 50mL of dry THF under nitrogen atmospher. t-BuOK (0.29 g, 5 eq) are added portion wise during 30' after what the solution is stirred 1h.

Addition of methanol leads to the precipitation of 300 mg (70%) of orange solid, M.p. 130°C. ¹H NMR (C₆D₆) 7.50 (d, 2H, ³J=8.00Hz), 7.10 (d, 1H, ³J=15.50 Hz), 7.00 (d, 2H, ³J=8.00Hz), 6.95 (d, 1H, ³J=15.50Hz), 6.90 (d, 1H, ³J=3.75Hz), 6.73 (d, 1H, ³J=3.00Hz), 6.70 (d, 1H, ³J=5.00Hz), 6.65 (m, 2H). ¹³C NMR (CDCl₃): 146.4, 142.6, 142.5, 141.2, 129.1, 127.7, 127.5, 126.5, 126.0, 124.4, 124.3, 123.0, 121.5, 121.1. UV-vis λ_{max} nm (logε) 424 (5.13). HRMS (Fab+, R=7000) calcd for C₄₈H₃₃NS₆ 815.0937 found 815.0973 (M+).

Bis{4-[5-(2-thienylethen-2-yl)-2-thienyl]phenyl}-[4-(5-formyl-2-thienyl)phenyl]amine (6).

Prepared according to the same procedure from tris[4-(5-formyl-2-thienyl)phenyl]amine (0.4 g, 0.7 mmol), 2-(diethoxyphosphorylmethyl)thiophene (0.4 g, 2.5 eq) and *t*-BuOK (0.19 g, 2.5 eq). After addition of 150 mL of dichloromethane, the organic phase is washed with water and dried over MgSO₄. Solvent removal and column chromatography (silica gel/dichloromethane:petroleum ether 1:1) gave 0.28g of **1** (50%) and 0.1g (20%) of the targeted compound **6** as a red glassy solid. ¹H NMR (CDCl₃) δ 9.87 (s, 1H), 7.73 (d, 1H, ³J=3.96 Hz), 7.57 (d, 2H, ³J=8.71Hz), 7.53 (d, 4H, ³J=8.62Hz), 7.34 (d, 1H, ³J=3.95 Hz), 7.19 (d, 2H, ³J=4.96Hz), 7.15 (m, 8H), 7.01 (m, 10H). ¹³C NMR (CDCl₃) 183.6, 154.2, 148.2, 146.0, 142.4, 142.4, 141.6, 141.4, 137.7, 129.7, 127.7, 127.4, 127.4, 127.1, 126.6, 126.0, 125.0, 124.4, 123.4, 123.2, 123.2, 121.5, 121.3. IR (KBr) ν(cm⁻¹) 1660 (C=O). MS MALDI-TOF calcd for C₄₃H₂₉NOS₅ 735, found 735 (M+).

Bis[4-(5-formyl-2-thienyl)phenyl]-{4-[5-(2-thienylethen-2-yl)-2-thienyl]phenyl}amine (7).

Prepared according to the same procedure from tris[4-(5-formyl-2-thienyl)phenyl]amine (0.5 g, 0.87 mmol), 2 (diethoxyphosphorylmethyl)thiophene (0.4 g, 2. eq) and *t*-BuOK (0.19 g, 2 eq). After addition of 150 mL of dichloromethane, the organic phase is washed with water and dried over MgSO₄. Solvent removal and column chromatography (silica gel/dichloromethane) gave gave the 90 mg (13%) of compound **1**, 120 mg (19%) of compound **6** and 210 mg (37%) of the target compound **7** as a red glassy solid. ¹H NMR (CDCl₃) 9.87 (s, 2H), 7.73 (d, 2H, ³J=3.96Hz) 7.59 (d, 4H, ³J=9.41Hz), 7.54 (d, 2H, ³J=8.58Hz), 7.34 (d, 2H, ³J=3.94 Hz), 7.17 (m, 8H), 7.02 (m, 5H). ¹³C NMR (CDCl₃) 182.6, 153.9, 147.9, 145.7, 142.4, 142.2, 141.8, 141.7, 137.6, 130.3, 127.8, 127.7, 127.5, 127.4, 126.8, 126.1, 125.4, 124.4, 124.1, 123.4, 121.4. IR (KBr) ν (cm⁻¹) 1660 (C=O). MS MALDI-TOF calcd for C₃₈H₂₅NO₂S₄ 655, found 655 (M+).

Bis{4-[5-(2-thienylethenyl)-2-thienyl]phenyl}{4-[5-(1,3-dioxoinda-2-ylidenemethyl)-2-thienyl]phenyl} amine (2). To a solution of bis{4-[5-(2-thienylethenyl)-2-thienyl]phenyl}-[4-(5-formyl-2-thienyl)phenyl]amine (0.10 g, 0.1 mmol) in 30mL of chloroform are added

indanedione (30 mg, 1.5 eq) and 2mL of triethylamine and the mixture is refluxed for 12 h under nitrogen. After cooling to room temperature the solution is washed with water and dried over MgSO₄. Solvent removal and column chromatography (silica gel, 1:1 PE/dichloromethane) gave 50mg (43%) of a red solid. M.p. 222°C. ¹H NMR (CDCl₃): 8.00 (m, 4H), 7.80 (m, 2H), 7.70 (d, 2H, ³J=8.00Hz), 7.55 (d, 4H, ³J=8.00Hz), 7.40 (d, 1H, ³J=3.75 Hz), 7.20 (m, 10H), 7.00 (m, 10H). ¹³CNMR (CDCl₃) 190.5, 189.8, 157.4, 148.4, 145.9, 143.9, 142.4, 142.4, 142, 141.5, 140.5, 136.2, 136, 134.9, 134.7, 129.8, 127.7, 127.6, 127.5, 127.4, 126.7, 126.1, 125.1, 124.4, 124, 123.4, 123.3, 123.2, 122.9, 122.8, 121.5, 121.3. (KBr) ν (cm⁻¹): 1674 (C=O); UV-vis λ_{\max} nm (log ϵ) 419 (4.79), 509. HRMS (Fab+, R=7000) calcd for C₅₂H₃₃NO₂S₅ 863.1141 found 863.1115 (M⁺)

Bis[4-(5-dicyanomethylidenemethyl-2-thienyl)phenyl]-{4-[5-(2-thienylethenyl)-2-thienyl]phenyl}amine (4). To a solution of Bis[4-(5-formyl-2-thienyl)phenyl]-{4-[5-(2-thienylethenyl)-2-thienyl]phenyl}amine (0.2 g, 0.3 mmol) in 15mL of chloroform are added malonodinitrile (0.4 g, 2.05 eq) and two drops of triethylamine and the mixture is refluxed 15 h under nitrogen. After return to room temperature dichloromethane is added, the solution is washed with water and dried over MgSO₄. After solvent removal, the residue is chromatographed (silica gel/dichloromethane) to give 0.11g (48%) of a red solid. M.p. 383°C (dec). ¹H NMR (CDCl₃) δ 7.76 (s, 2H), 7.69 (d, 2H, ³J=4.12Hz), 7.60 (d, 4H, ³J=8.69Hz), 7.56 (d, 2H, ³J=8.58Hz), 7.38 (d, 2H, ³J=4.11Hz), 7.17 (m, 8H) 7.02 (m, 5H). ¹³C NMR (CDCl₃) : 156.0, 150.3, 148.3, 145.1, 142.3, 141.8, 140.3, 133.6, 130.9, 127.8, 127.7, 127.4, 126.9, 126.8, 126.1, 125.9, 124.5, 123.9, 123.9, 123.6, 121.5, 121.3, 114.3, 113.5, 75.8. IR (KBr) ν (cm⁻¹): 2220 (C \equiv N). UV-Vis. λ_{\max} nm (log ϵ) 390, 513 (4.97). HRMS (Fab+, R=7000) calcd for C₄₄H₂₅N₅S₄ 751.1008, found 751.0993 (M+.)

Bis{4-[5-(2-thienylethenyl)-2-thienyl]phenyl}-[4-(5-dicyanomethylidenemethyl-2-thienyl)phenyl]amine (3). Prepared using the procedure already described for **4** from bis{4-[5-(2-thienylethenyl)-2-thienyl]phenyl}-[4-(5-formyl-2-thienyl)phenyl]amine (100mg, 0.14mmol) in 15mL of chloroform, malononitrile (19 mg, 2.1 eq) and two drops of triethylamine. Usual work-up and column chromatography of (silica gel, dichloromethane:petroleum ether 1:1) gives 20 mg (19%) of a red solid. M.p. 386°C (dec). ¹H NMR (CDCl₃) 7.74 (s, 1H), 7.68 (d, 1H, ³J=4.15Hz), 7.57 (d, 2H, ³J=8.74Hz), 7.54 (d, 4H, ³J=8.61 Hz), 7.35 (d, 1H, 3J=4.13Hz), 7.16 (m, 10H), 7.02 (m, 10H), ¹³C NMR (CDCl₃) 156.6, 150.3, 149.0, 145.6, 142.4, 142.2, 141.6, 140.3, 133.3, 130.1, 127.7, 127.4, 126.7, 126.1, 125.8, 125.3, 124.4, 123.6, 123.3, 122.8, 121.4, 121.3, 114.5, 113.6, 75.4. IR (KBr) ν

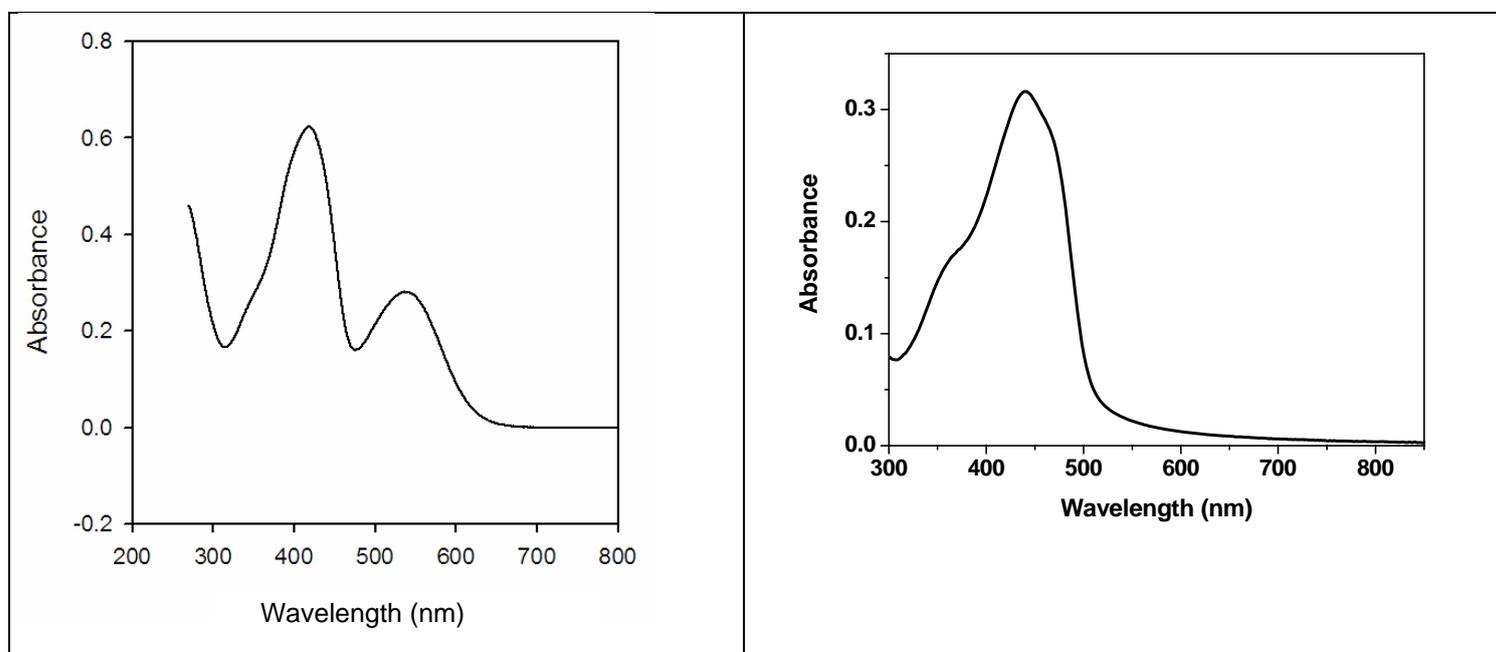
(cm^{-1}) 2220 (CN), UV-Vis. λ_{max} nm ($\log\epsilon$) 415 (4.79). HRMS (Fab+, R=7000) calcd for $\text{C}_{46}\text{H}_{29}\text{N}_3\text{S}_5$ 783.0965, found 783.0939 (M^+).

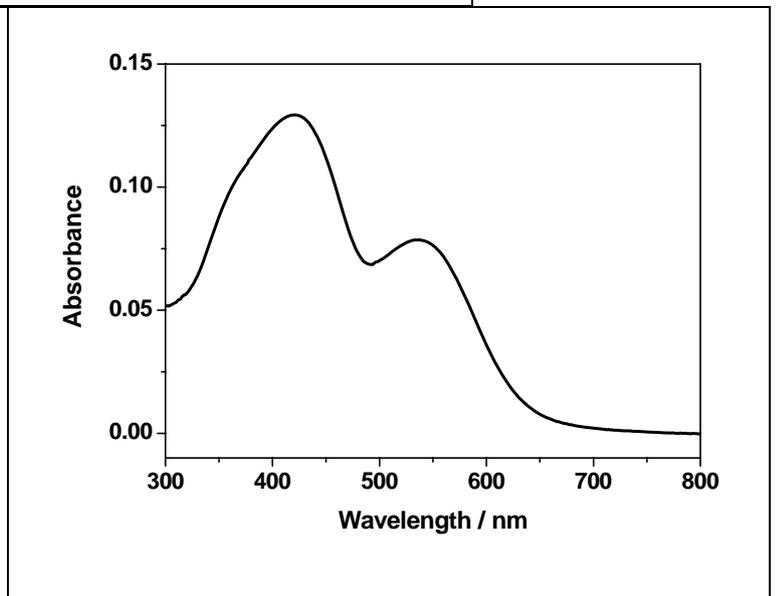
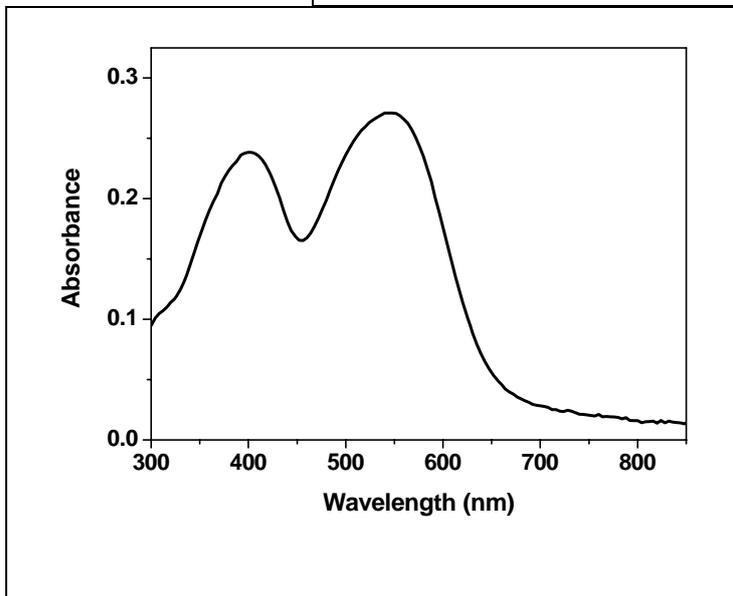
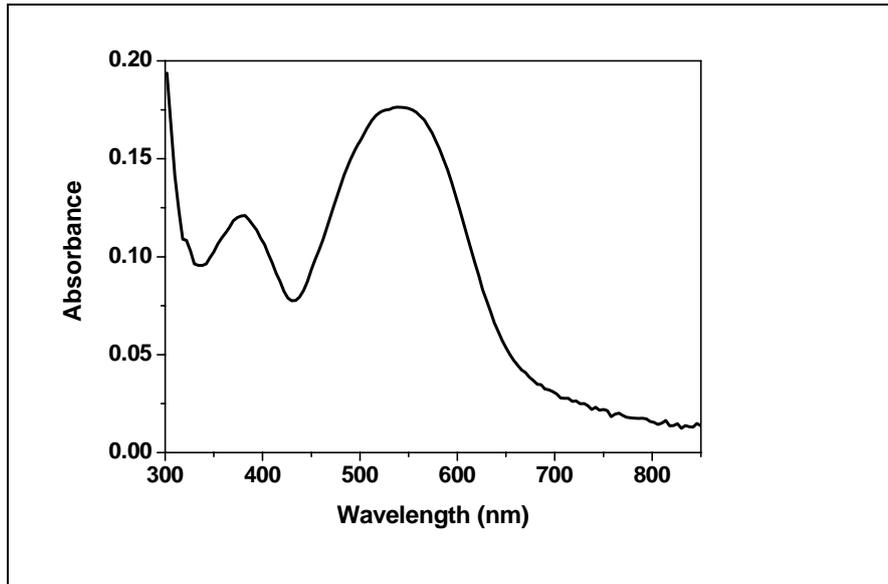
Tris(4-(5-dicyanomethylidenemethyl-2-thienyl)phenyl)amine (5). Prepared using the procedure already described for **4** from 200 mg of compound **8** in 15mL of chloroform. Malononitrile (70mg, 3.06eq) and two drops of triethylamine. Usual work-up and column chromatography eluting with dichloromethane then with 20:1 dichloromethane/ethyl acetate gave 0.19g (76%) of a red solid. M.p. 325°C (dec). ^1H NMR (CDCl_3): 7.79 (s, 1H), 7.71 (d, 1H, $^3J=4.13\text{Hz}$), 7.64 (d, 2H, $^3J=8.69\text{Hz}$), 7.41 (d, 1H, $^3J=4.09\text{Hz}$), 7.20 (d, 2H, $^3J=8.69\text{Hz}$). ^{13}C NMR (CDCl_3) (155.6, 150.4, 147.8, 140.2, 133.9, 128.0, 127.8, 124.8, 124.1, 114.2, 113.4, 76.3. IR (KBr) ν (cm^{-1}) 2220 ($\text{C}\equiv\text{N}$), UV-vis λ_{max} nm ($\log\epsilon$) 368, 509 (5.09). HRMS (Fab+, R=7000) calcd for $\text{C}_{42}\text{H}_{21}\text{N}_7\text{S}_3$ 719.1021, found 719.1020 (M^+).

PCBM was synthesized according to a known procedure.²⁹ Fullerene C_{60} (99+%) was purchased from Merck and used without further purification. Indium–tin–oxide (ITO) coated glass substrates (Solems) with a sheet resistance of 40 ohm/square were cleaned in ultrasonic bath with aqueous detergent, acetone and ethanol dried in an oven and treated 15 min with an UV-ozone cleaner (Jelight 42-220, $28\text{W}/\text{cm}^2$). ITO substrates were then spin-coated with a 60 nm film of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (Baytron P®) and dried at 115°C for 15 min. Layers of the donor and C_{60} were thermally evaporated in a Plassys ME300 chamber at a pressure of about 10^{-6} mbar and at rate of $\sim 1.5 \text{ \AA s}^{-1}$. A glass slide placed near the ITO substrates was used to obtain samples for UV-Vis absorption spectra. The devices were completed by the evaporation of aluminium films (ca. 60 nm thick) as negative electrodes. A shadow mask with openings of 6 mm diameter was used to define a device's area of 0.28 cm^2 . After their fabrication, the devices were stored and characterised in a glove-box (200B, MBraun). The J-V curves were recorded in dark and under various light intensities using a Keithley 236 source-measure unit and a home-made acquisition program. Power conversion efficiencies were measured with a Steuernagel Solar constant 575 simulator. Light intensity was measured with a calibrated broadband optical power meter (Melles Griot) and was varied with neutral density filters. The devices were illuminated through the ITO electrode side. The efficiency values were neither corrected for a possible spectral mismatch of the light source with the solar spectrum nor for the absorption/reflection losses at the various interfaces. EQE was measured with a Perkin Elmer 7225 lock-in

amplifier under monochromatic illumination at variable wavelength at a chopping frequency of 100 Hz. The light source was a tungsten lamp (Acton SpectraPro150).

Absorption spectra were recorded with a Perkin Elmer Lambda 19 UV-Visible-Near IR spectrophotometer. Cyclic voltammetry was performed with platinum electrodes in a three-electrode cell using an EGG 273 potentiostat.

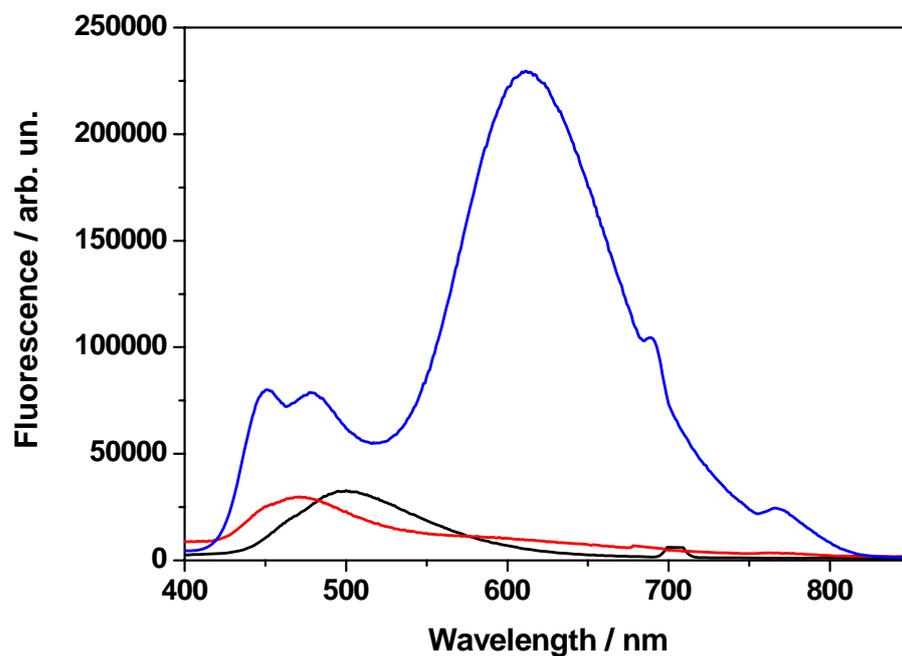
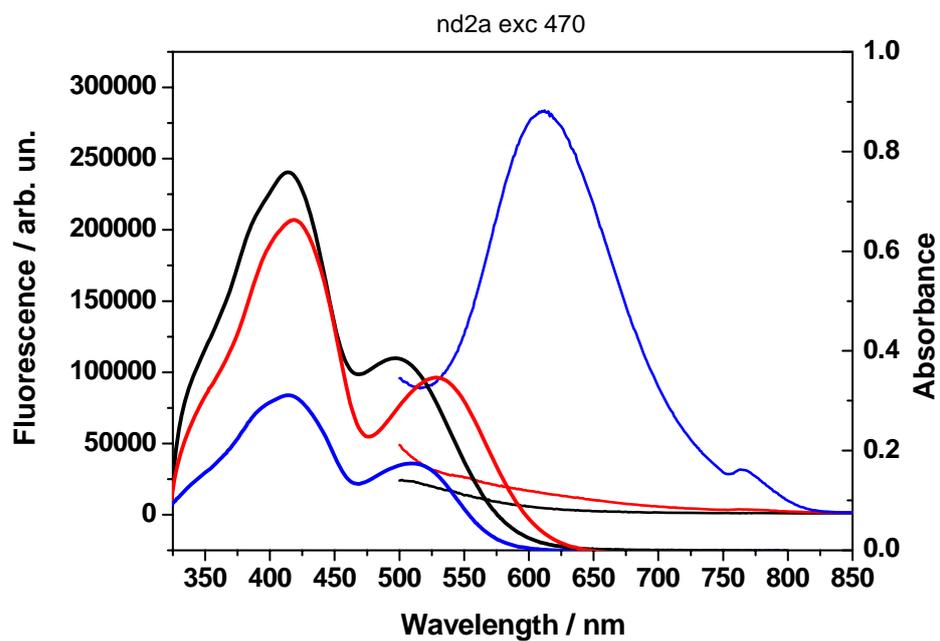




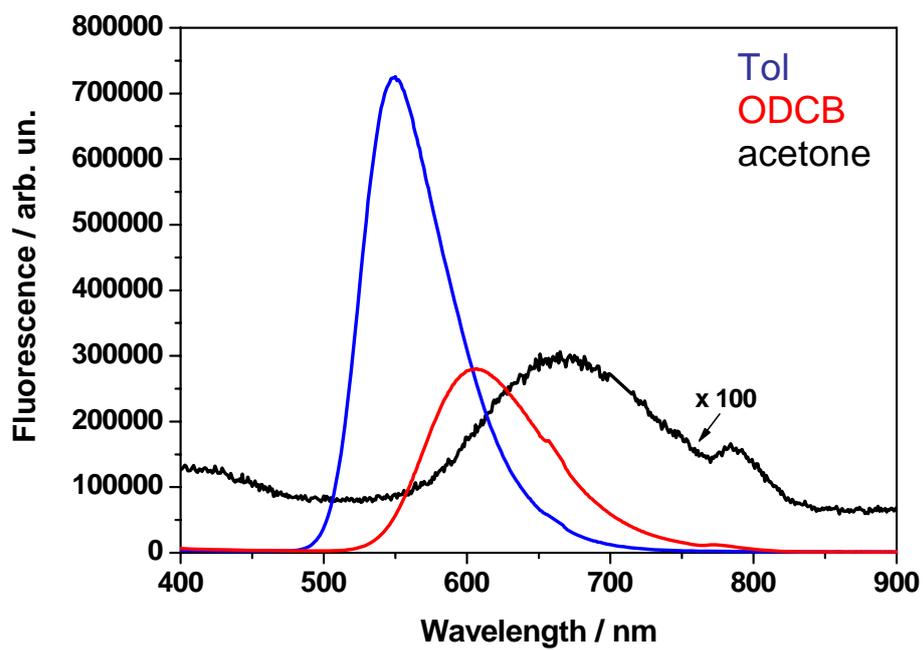
UV-vis spectra of thin films deposited on glass by thermal evaporation under vacuum

Top left (2), right (1), bottom left (3), right (4)

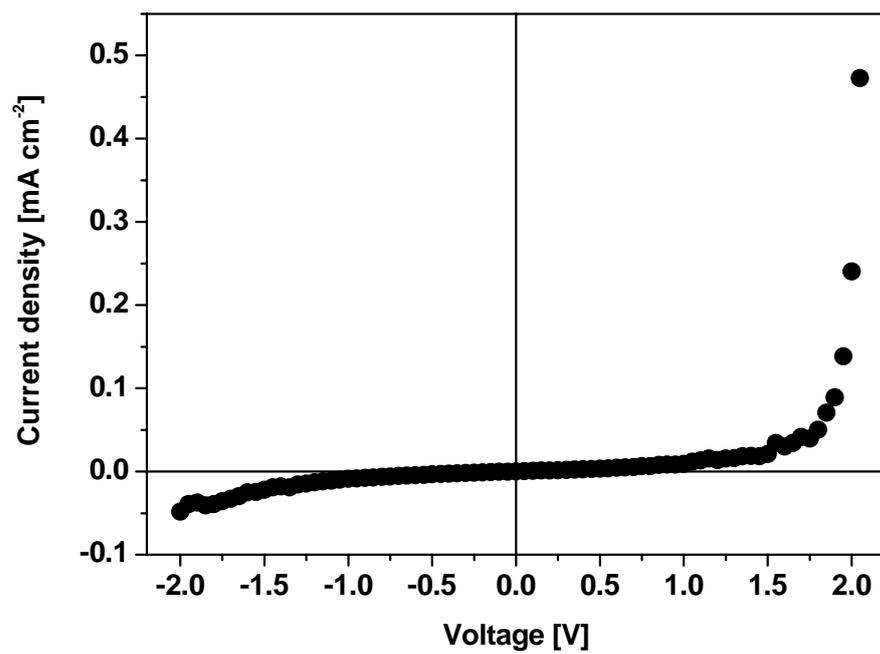
UV-vis spectrum of thin film of **5** deposited on glass by thermal evaporation under vacuum



Fluorescence emission spectra of compound **3** (top) and **4** (bottom) blue toluene, black: dichlorobenzene, red: acetone. Excitation wavelength top 470 nm, bottom 370 nm



Fluorescence emission spectra of compound **5**: blue toluene, black: dichlorobenzene, red: acetone. Excitation wavelength 370 nm.



Current voltage curve of the cell ITO/1(25nm) /C₆₀ (25 nm) /Al (60 nm)