

Panchromatic Push-Pull Chromophores based on Triphenylamine as Donors for Molecular Solar Cells

**Sandra Gómez Esteban, Pilar de la Cruz,
Ana Aljarilla, Luis M. Arellano and
Fernando Langa***

*Instituto de Nanociencia, Nanotecnología y Materiales
Moleculares (INAMOL), Universidad de Castilla-La
Mancha, 45071-Toledo, Spain*

Fernando.Langa@uclm.es

Table of contents

1- Experimental conditions	S2
2- Synthetic procedures and analytical data	S3
3- ^1H NMR, ^{13}C NMR and MALDI-TOF Spectra of 1 and 2	S6
4- UV-Visible and emission spectroscopies	S12
5- Square Wave plots	S15
6- Frontier Orbitals of 1 and 2	S17
7- Tables S1, S2 and S3	S10

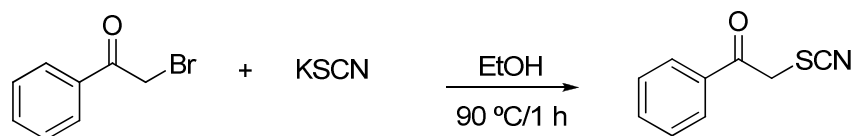
1- Experimental conditions

Synthetic procedures were carried out under inert argon atmosphere, in dry solvent unless otherwise noted. All reagents and solvents were reagent grade and were used without further purification. Chromatographic purifications were performed using silica gel 60 SDS (particle size 0.040-0.063 mm). Analytical thin-layer chromatography was performed using Merck TLC silica gel 60 F254. ^1H NMR spectra were obtained on Bruker TopSpin AV-400 (400 MHz) spectrometer. Chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak (CDCl_3 , 7.27 ppm). ^{13}C NMR chemical shifts are reported relative to the solvent residual peak (CDCl_3 , 77.0 ppm). UV/Vis measurements were carried out on a Shimadzu UV 3600 spectrophotometer. For extinction coefficient determination, solutions of different concentration were prepared in CH_2Cl_2 , HPLC grade, with absorption between 0.1-1 of absorbance using a 1 cm UV cuvette. The emission measurements were carried out on Cary Eclipse fluorescence spectrophotometer. Mass spectra (MALDI-TOF) were recorded on a VOYAGER DETM STR mass spectrometer using dithranol as matrix. Melting points are uncorrected.

Cyclic voltammetry was performed in *o*-dichlorobenzene-acetonitrile (4:1) solutions. Tetrabutylammonium perchlorate (0.1 M as supporting electrolyte) were purchased from Acros and used without purification. Solutions were deoxygenated by argon bubbling prior to each experiment which was run under argon atmosphere. Experiments were done in a one-compartment cell equipped with a platinum working microelectrode ($\varnothing = 2$ mm) and a platinum wire counter electrode. An Ag/AgNO_3 (0.01 M in CH_3CN) electrode was used as reference and checked against the ferrocene/ferrocenium couple (Fc/Fc^+) before and after each experiment.

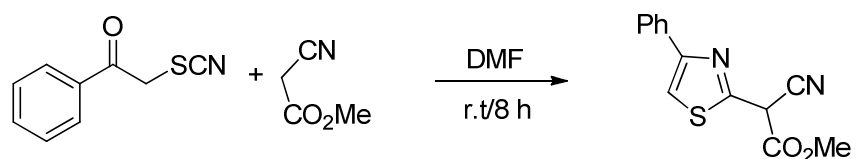
2- Synthesis and analytical data

Synthesis of 2-oxo-2-phenylethylthiocyanate¹



A mixture of 2-bromoacetophenone (Aldrich, 98 %) (1000 mg, 5.05 mmol) and potassium thiocyanate (Aldrich, > 99 %) (634 mg, 6.5 mmol) in ethanol was heated at 85 °C during 1 hour. The reaction was extracted with diethyl ether and the solvent was removed at low pressure. The product was obtained as a yellow solid in a yield of 99% (845 mg, 5.18 mmol). ¹H NMR (400 MHz, CDCl₃) δ/ppm: 7.9 (dd, 2H, *J* = 8.3 Hz; *J* = 1 Hz), 7.7 (dd, 1H, *J* = 8.3 Hz; *J* = 1 Hz), 7.5 (t, 2H, *J* = 8.3 Hz), 4.8 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ/ppm: 190.8, 134.8, 133.9, 129.2, 128.5, 111.9, 43.1.

Synthesis of methyl 2-cyano-2-(4-phenylthiazol-2-yl)acetate (3)



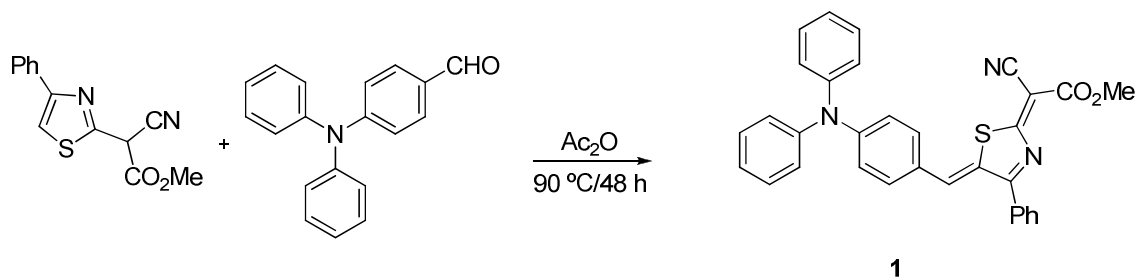
Trimethylamine, 1mL, was added to a stirred solution of methyl cyanoacetate (166 mg, 1.7 mmol) and 4 mL of *N,N*-dimethylformamide. The reaction was then stirred during 15 minutes, and then 2-oxo-2-phenylethylthiocyanate (609 mg, 3.44 mmol) was added and the mixture was stirred at room temperature for 8 hours. Then, distilled water was added (250 mL) and afterwards glacial acetic acid was added dropwise to the solution. The product is obtained as a solid, which was filtered under vacuum and washed with diethyl ether to obtain the compound **3** as a white solid in a 78% yield (342 mg, 1.2 mmol), without further purification (m.p: 174-178°C). ¹H NMR (400 MHz, CDCl₃) δ/ppm: 12.5 (s, 1H), 7.5 (m, 5H), 6.7 (s, 1H), 3.8 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ/ppm: 170.4, 168.6, 140.9, 130.2, 129.5, 128.7, 118.0, 101.9, 64.6, 51.8.

¹ Seybold; G. Patent US4371734, **1983**.

General procedure for the synthesis of **1** and **2**.

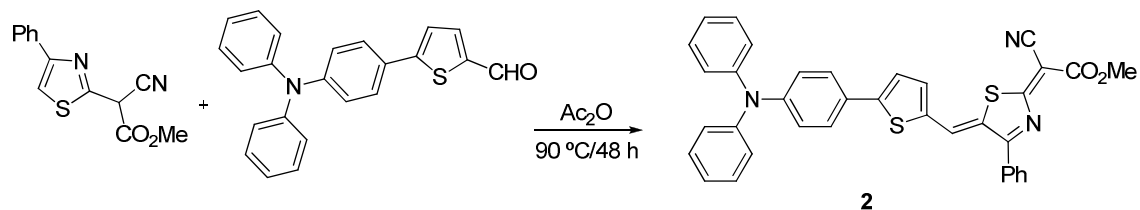
The corresponding aldehyde was added to a stirred solution of methyl 2-cyano-2-(4-phenylthiazol-2-yl) acetate (50 mg, 0.19 mmol) in acetic anhydride under argon atmosphere. The mixture was stirred at 90 °C for 48 h. After cooling to room temperature, the reaction was extracted with diethyl ether, and the organic layer was dried over anhydrous magnesium sulphate. After filtration of the drying agent, the solvent was removed under vacuum. Compounds **1** and **2** were purified by column chromatography using a mixture of hexane/ethyl acetate (2:1). Then, compounds **1** and **2** were recrystallized with petroleum ether.

Synthesis of methyl 2-cyano-2-((Z)-5-(4-(diphenylamino)benzylidene)-4-phenylthiazol-2(5H)-ylidene)acetate (**1**).



From 4-(diphenylamino)benzaldehyde (Aldrich, 97 %) (60 mg, 0.22 mmol). Following the general procedure, a dark blue solid was obtained (m.p: 170-173 °C). Yield 58 %. ¹H NMR (400 MHz, CDCl₃) δ/ppm: 7.8 (d, 2H, *J* = 7.3 Hz), 7.6 (dd, 6H, *J* = 8.8 Hz, *J* = 7.8 Hz), 7.4 (m, 2H), 7.4 (d, 2H, *J* = 7.4 Hz), 7.2 (s, 1H), 7.2 (d, 5H, *J* = 7.8 Hz), 7.0 (d, 2H, *J* = 8.8 Hz), 3.9 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ/ppm: 179.7, 166.1, 165.7, 151.5, 145.6, 140.8, 149.5, 134.1, 133.9, 131.7, 130.5, 129.8, 128.9, 126.4, 125.6, 125.6, 119.8, 119.7, 116.0, 53.5. UV-Vis (CH₂Cl₂) λ_{max}/nm (log ε): 599.0 (4.6), 419.0 (3.8). IR ν/cm⁻¹: 2939, 2368, 2208, 1733, 1961, 1078, 696. MS (*m/z*) (MALDI-TOF): calculated C₃₂H₂₃N₃O₂S: 513.15; found (M+H⁺): 514.17.

Synthesis of methyl 2-cyano-2-((Z)-5-((5-(4-(diphenylamino)phenyl)thiophen-2-yl)methylene)-4-phenylthiazol-2(5H)-ylidene)acetate (2).



From 5-(4-(diphenylamino)phenyl)thiophene-2-carbaldehyde ² (78.2 mg, 0.22 mmol). Following the general procedure a blue solid (m.p: 189-192 °C) was obtained. Yield 27 %. ¹H NMR (400 MHz, CDCl₃) δ/ppm: 7.8 (d, 2H, *J* = 8.4 Hz), 7.8 (s, 1H), 7.6 (m, 1H), 7.6 (m, 4H), 7.5 (d, 1H, *J* = 4 Hz), 7.3 (d, 1H, *J* = 4 Hz), 7.3 (m, 4H), 7.2 (m, 4H), 7.2 (d, 2H, *J* = 8.4 Hz), 7.1 (m, 2H), 3.9 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ/ppm: 178.6, 166.1, 155.8, 149.5, 146.8, 138.7, 137.5, 134.5, 132.1, 131.9, 130.3, 129.8, 129.6, 129.0, 128.6, 128.6, 127.3, 125.7, 125.3, 125.3, 124.2, 122.0, 115.9, 52.7. UV-Vis (CH₂Cl₂) λ_{max}/nm (log ε): 621 (4.5), 351 (4.3). IR ν/cm⁻¹: 2956, 2923, 2850, 2163, 1737, 1461, 1272, 1076, 804. MS (*m/z*) (MALDI-TOF): calculated C₃₆H₂₅N₃O₂S₂: 595.14; found (M+H⁺): 596.22, 566.77, 477.91.

² Marinado, T.; Hagberg, D.; Hedlun, M.; Edvinsson, T.; Johansson, E.; Boschloo, G.; Rensmo, H.; Brinck, T.; Sun, L.; Hagfeldt, A. *Phys. Chem. Chem. Phys.* **2009**, *11*, 133.

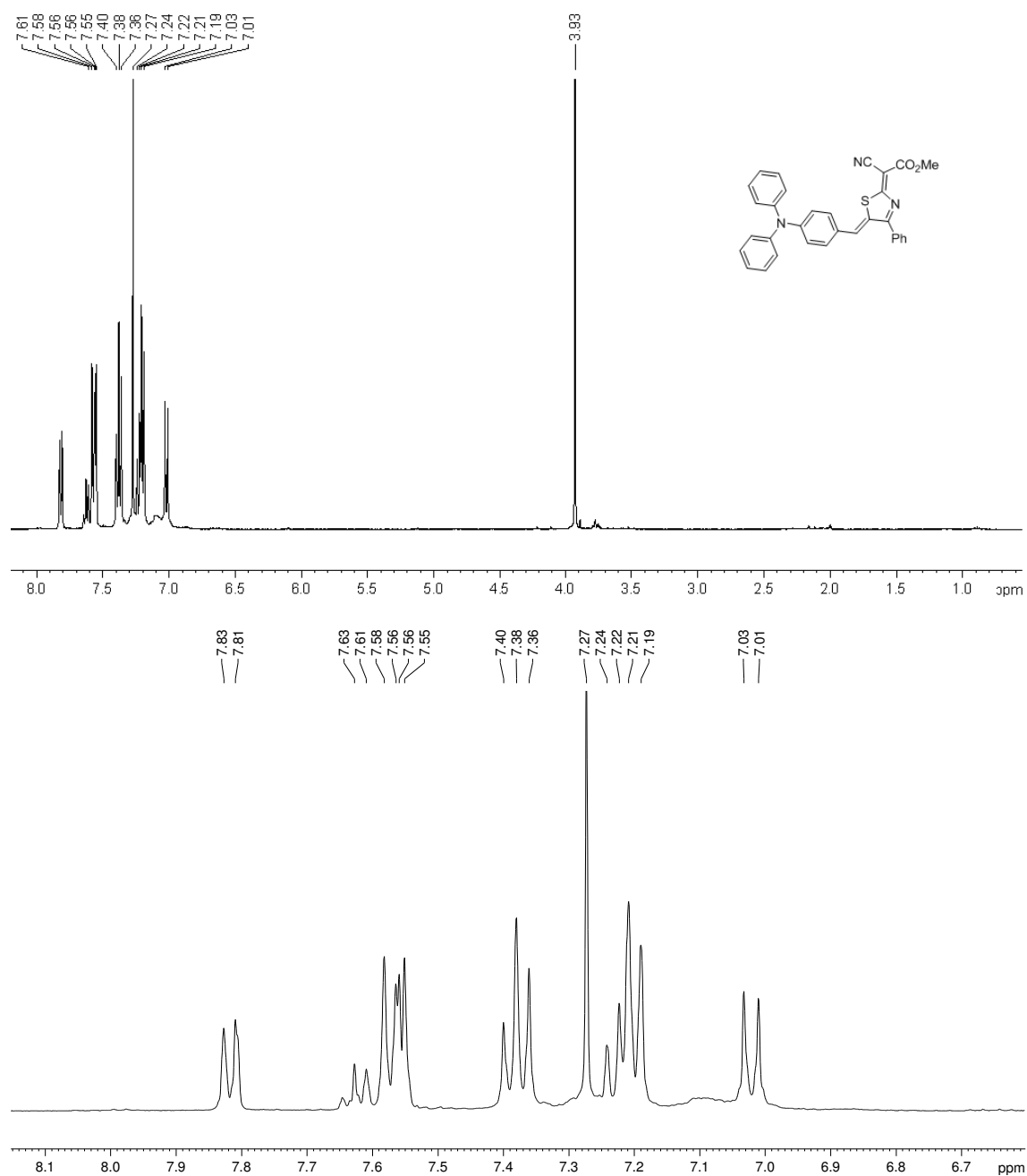


Figure S1. ^1H NMR (400 MHz, CDCl_3) of compound **1**.

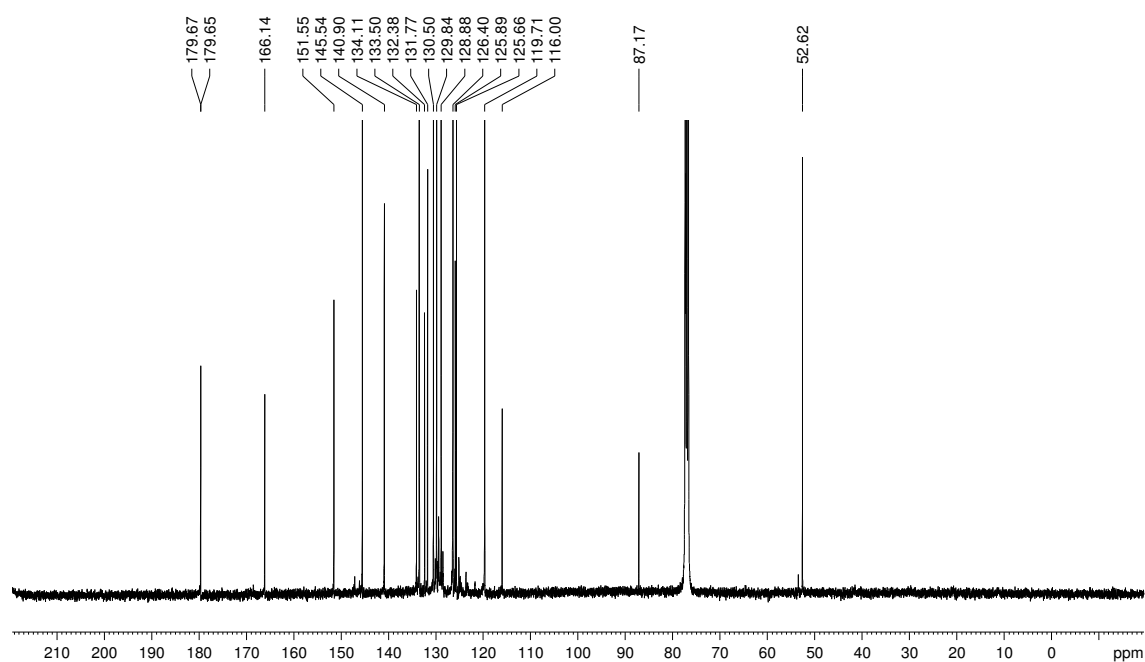


Figure S2. ^{13}C NMR (100 MHz, CDCl_3) of compound **1**.

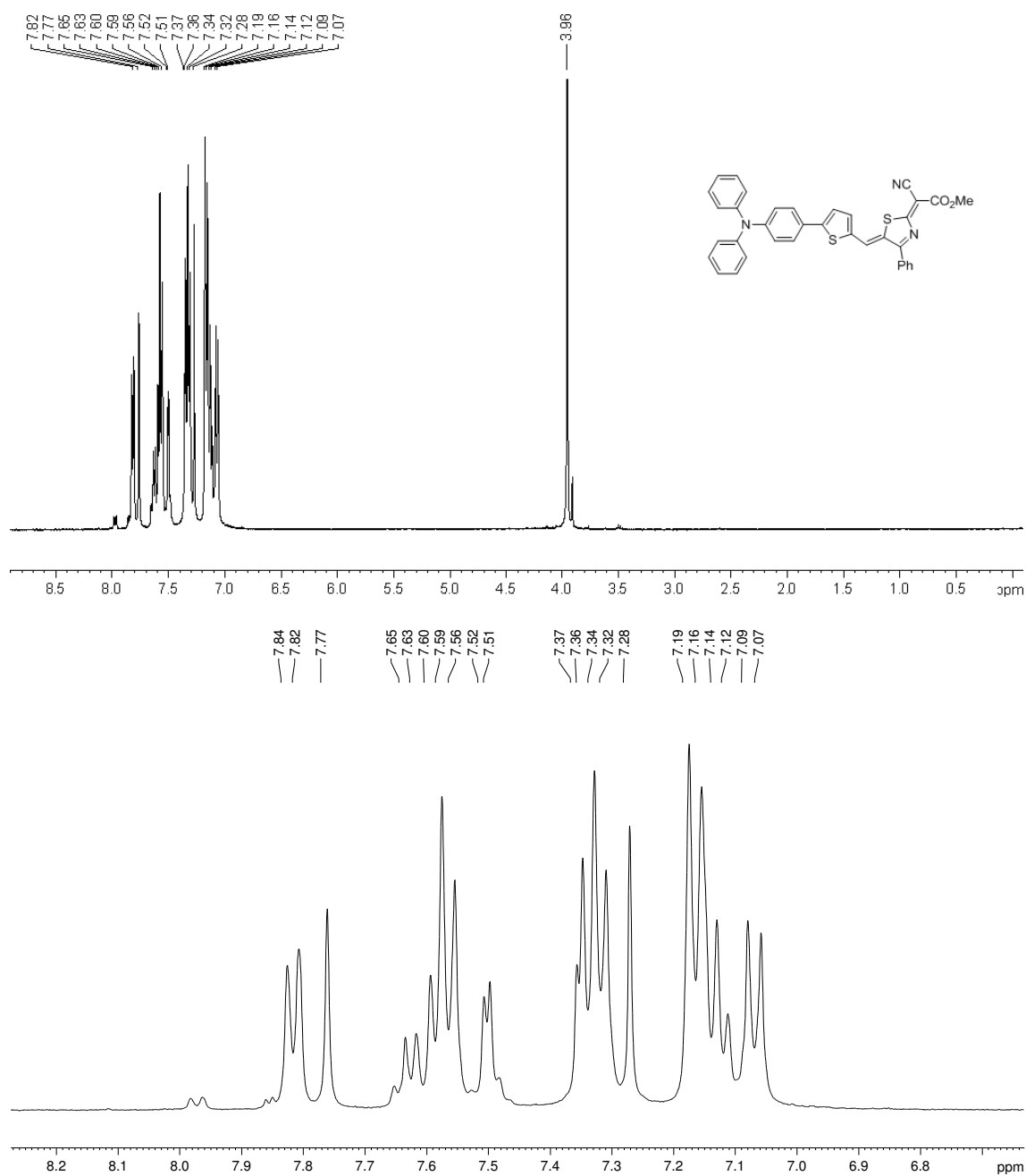


Figure S3. ^1H NMR (400 MHz, CDCl_3) of compound **2**.

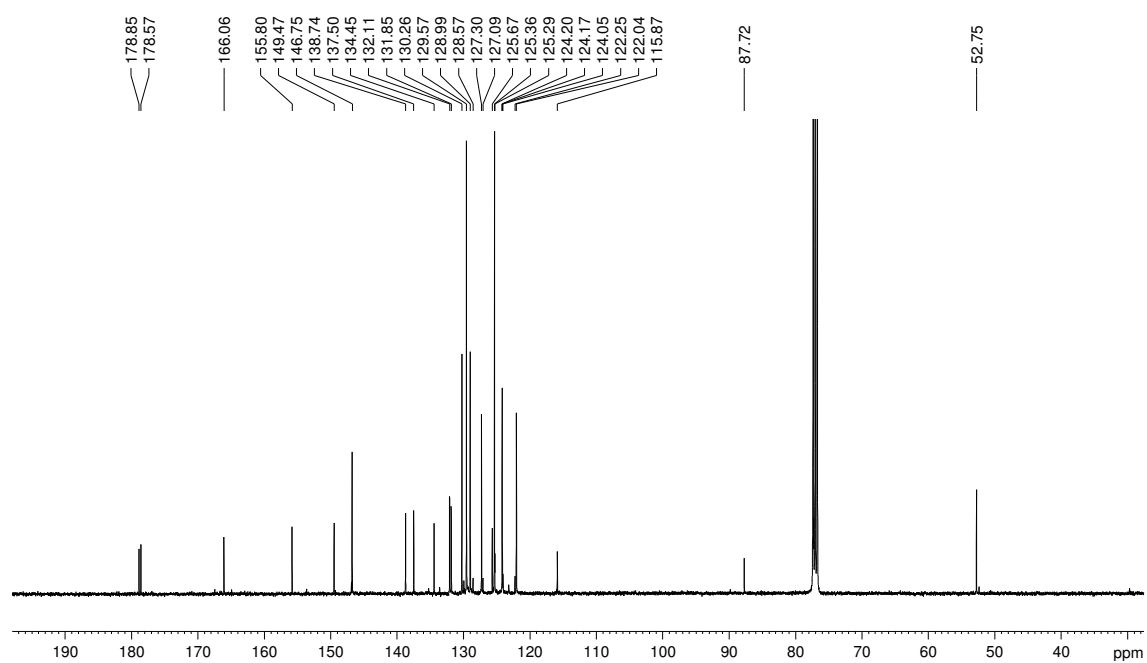


Figure S4. ¹³C NMR (100.59 MHz, CDCl₃) of compound **2**.

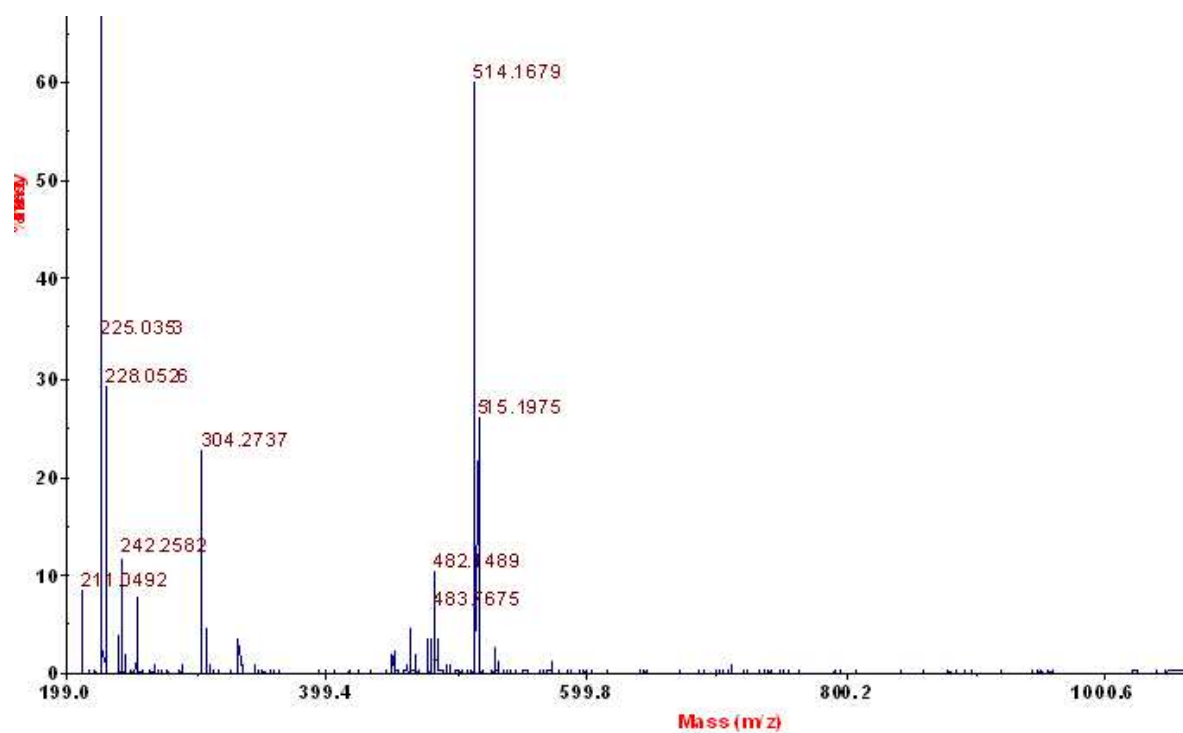


Figure S5. MALDI-MS spectrum of compound **1** (Matrix: Ditrinol).

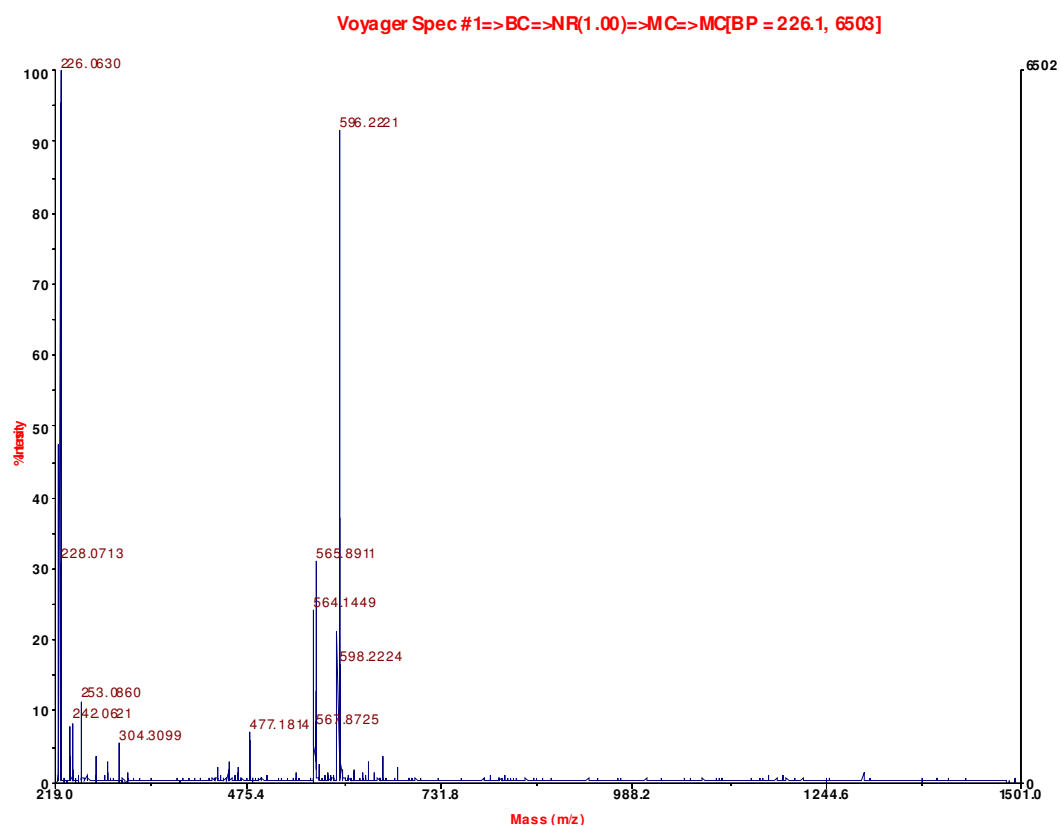


Figure S6. MALDI-MS spectrum of compound **2** (Matrix: Ditrinol).

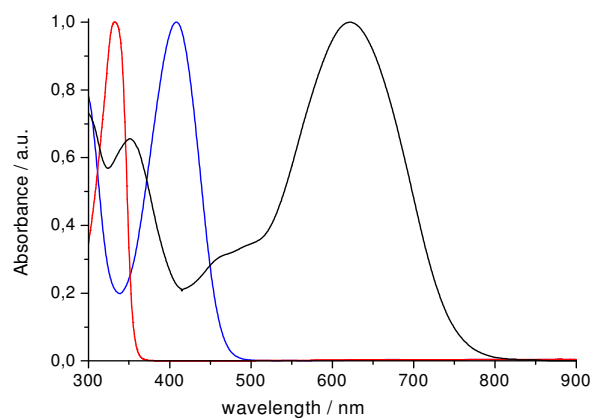


Figure S7. UV-vis spectra of compound **2** (black) and its corresponding precursors, thiazol **3** (red) and TPA-CHO (blue).

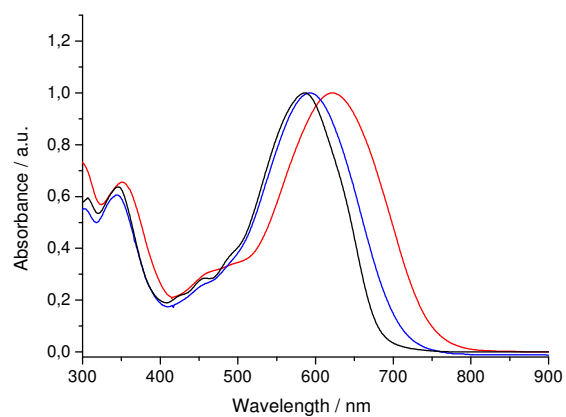


Figure S8. UV-vis spectra of compounds **1** (left) and **2** (right) in solvents with different polarity: cyclohexane (black), diethyl ether (blue) and dichloromethane (red).

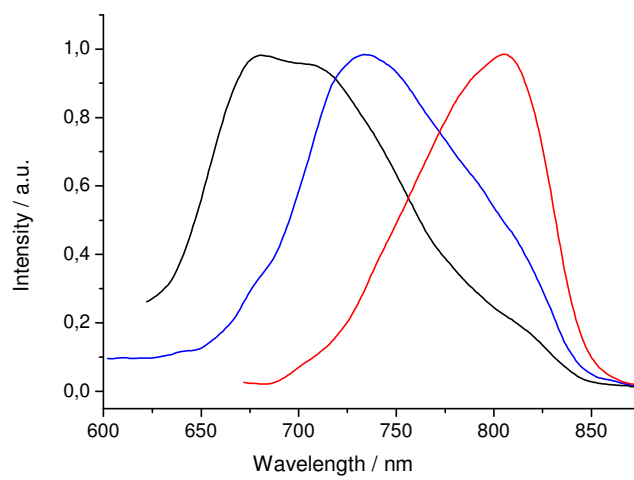


Figure S9. Emission spectra of compound **2** in cyclohexane (black), diethyl ether (blue) and dichloromethane (red).

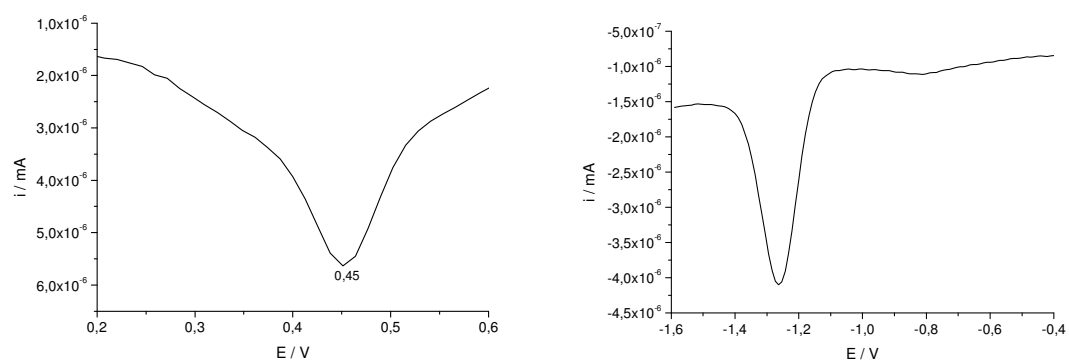


Figure S10. Square Wave Voltammetry plots of compound **1**, cathodic (left) and anodic (right) sides (referred to Fc/Fc⁺).

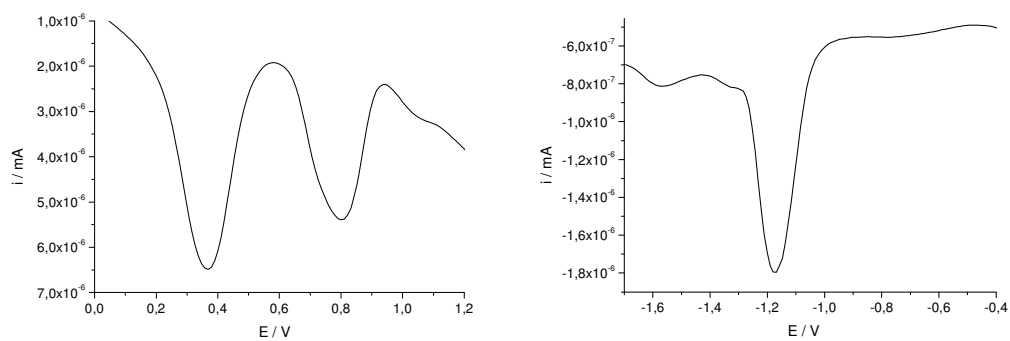


Figure S11. Square Wave Voltammetry plots of compound **2**, cathodic (left) and anodic (right) sides (referred to Fc/Fc⁺).

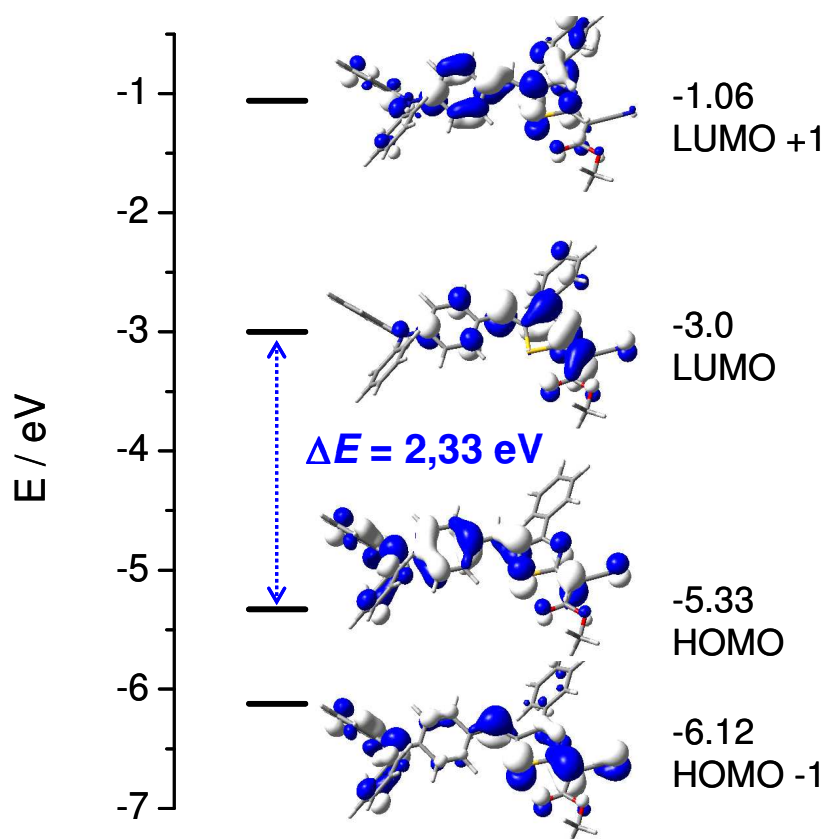


Figure S12. Energy levels of frontier Molecular Orbitals of **1**.

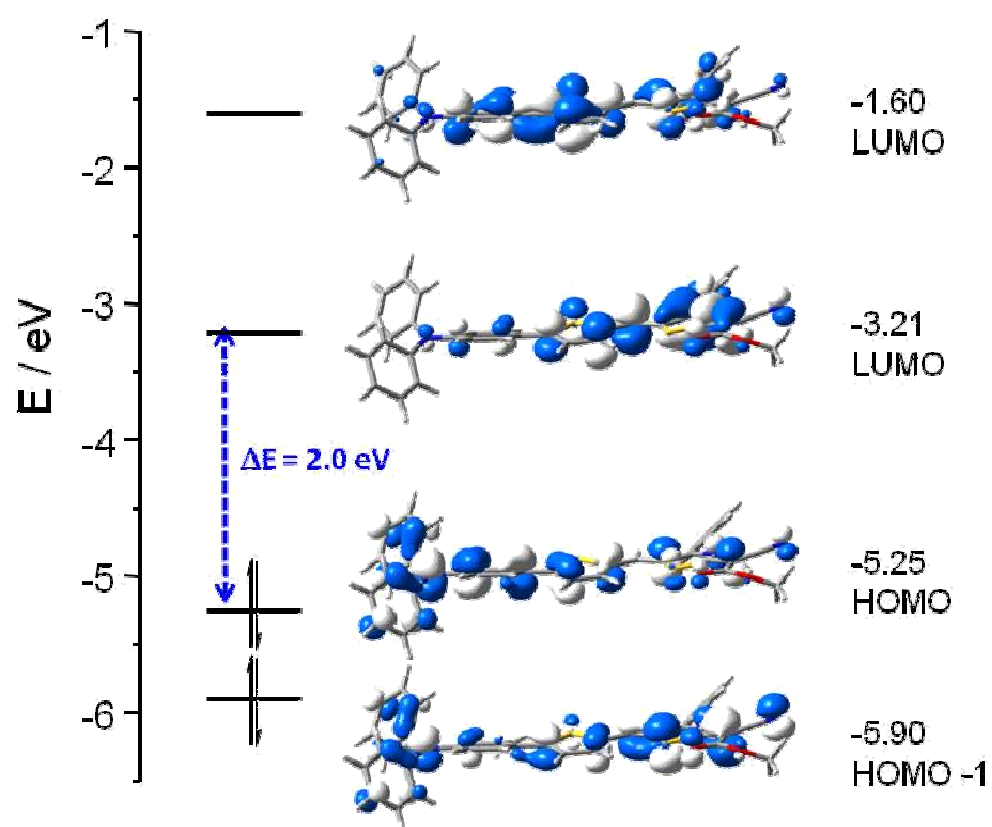


Figure S13. Energy levels of frontier Molecular Orbitals of **2**.

Table S1. Data of UV-Vis spectroscopy and fluorescence emission for **1** and **2**.^a

	Compound 1			Compound 2		
	λ_a / nm (ν_a / cm^{-1})	λ_f / nm (ν_f / cm^{-1})	$\Delta\lambda$ / nm ($\Delta\nu$ / cm^{-1})	λ_a / nm (ν_a / cm^{-1})	λ_f / nm (ν_f / cm^{-1})	$\Delta\lambda$ / nm ($\Delta\nu$ / cm^{-1})
Cyclohexane	553.5 (18083.18)	630.0 (15873.01)	76.5 (2210.2)	586.0 (17064.90)	709.01 (14749.30)	92.0 (2315.6)
Diethyl Ether	565.5 (17699.11)	663.0 (15082.96)	97.5 (2616.2)	594.5 (16835.00)	731.9 (13679.90)	137.40 (3155.1)
Dichloromethane	599.5 (16694.49)	723.0 (13831.26)	123.5 (2863.2)	623.5 (16051.40)	806.02 (12407.00)	182.50 (3644.4)

^a 10^{-5} M, in dichloromethane.

Table S2. Taft constants (π^*) of solvents, absorption maxima and corresponding transition energies (in kcal/mol).

Solvent	π^*	1		2	
		λ (nm)	E (kcal/mol)	λ (nm)	E (kcal/mol)
cyclohexane	0.00	553.5	51.66	586.0	48.8
Diethyl Ether	0.27	565.5	50.50	594.5	48.2
Dichloromethane	0.82	599.5	47.73	623.5	45.9

Table S3. E° , S values and correlation coefficients for compounds (according to $E = E^\circ + S\pi^*$)

Compound	E° (kcal.mol ⁻¹)	S	Correlation coefficient
1	51.97	4.40	0.999
2	48.95	3.63	0.991