Electronic Supplementary Material (ESI) for RSC Advances.

ELECTRONIC SUPLEMENTARY INFORMATION FOR

Dye-Sensitized-Solar-Cells based on calix[4]arene scaffold

M. Castillo-Vallés,[a] J. M. Andrés-Castán,[a] J. Garin[a], J. Orduna[a], B. Villacampa[b], S. Franco[a]*, MJ Blesa[a]*

Address:

[a] Departamento de Química Orgánica-ICMA
Universidad de Zaragoza-CSIC
50009, Zaragoza (Spain)
Phone: (+34) 876 553507
FAX: (+34) 976 761194

[b] Departamento de Física de la Materia Condensada-ICMA
Universidad de Zaragoza-CSIC
50009, Zaragoza (Spain)

Corresponding author: mjblesa@unizar.es

TABLE OF CONTENTS

6. NMR spectra

7. Impedance spectroscopy

8. References

1. General Methods:

Infrared measurements were carried out using a Perkin-Elmer Fourier Transform Infrared 1600 spectrometer.

Melting points were obtained on a Gallenkamp apparatus in open capillaries and are uncorrected.

Elemental analysis was performed with a Perkin-Elemer 240C microanalyzer.

NMR studies

^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker ARX300 or a Bruker AV400 at 300 or 400 MHz and 75 or 100 MHz respectively; δ values are given in ppm (relative to TMS) and *J* values in Hz. The apparent resonance multiplicity is described as s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet) and m (multiplet).^{1}H-^{1}H COSY and ^{1}H-^{13}C-HSQC experiments were recorded on a Bruker ARX300 or a Bruker AV400 at 300 or 400 MHz in order to establish peaks assignment.

Mass Spectrometry studies

Electrospray mass spectra were recorded on a Bruker MicroToF-Q spectrometer; accurate mass measurements were achieved using sodium formate as external reference. *MALDI* (Matrix Assisted Laser Desorption Ionization) mass spectra were recorded on Bruker MicroFlex and Autoflex III spectrometers. Exact mass measurements were performed using polyethyleneglycol as internal reference

Absorption and emission

UV-Visible and Fluorescence spectra were recorded with an UV-Vis UNICAM UV4 and Perkin Elmer LS50B spectrophotometer, respectively. Absorption and fluorescence runs were carried out with films and solutions 10^{-5} M CH_2Cl_2.

The emission studies were carried out with a LS-50B fluorimeter with a commercial device for solutions. The cuvette was a fluorescence cell of quartz (Quartz SUPRASIL with transmission values of more than 80 % over a spectral range of between 200 nm and 2500 nm for an empty cell.). The band pass of the monochromator was 1 nm.

The **amounts of dye** adsorbed on anode TiO_2 surface were estimated. We use UV-vis absorption to quantify the concentration of the dye solution. To measure the dye amount, we compared the concentration difference before and after anode film soaking in the solution. By comparing with a standard solution, the amount of dye can be

calculated. We examined dye amount in the devices prepared with **TPA**, **Cx-1-TPA** and **Cx-2-TPA**. The calculated amounts of dye are included in Table 1 in the main text.

To measure the **aggregation of dye**, we study the UV-vis in films before and after anode film soaking in the solution for different period of times in terms of different devices. We examined dye loading capacities in the devices prepared with and without calix[4]arene. The spectra are included in the *Supporting Information* (Figures S.5, S.6 and S.7).

Pulse differential voltammetry measurements were performed with a μ-Autolab type III potentiostat using a glassy carbon working electrode, Pt counter electrode, and Ag/AgCl reference electrode. The experiments were carried out under argon in CH_2Cl_2, with Bu_4NPF_6 as supporting electrolyte (0.1 mol L^{-1}). Scan rate was 0.01 V s^{-1}, modulation amplitude 0.025 V and modulation time 0.05 s^{-1}.

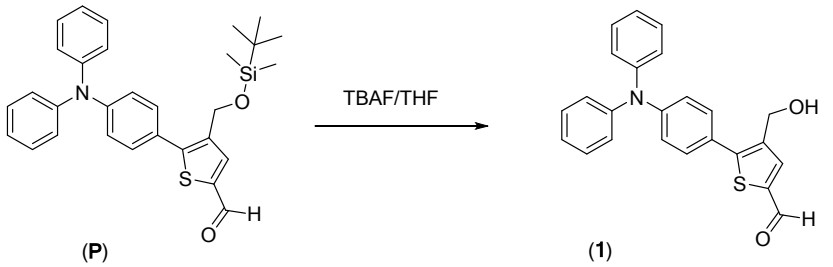
Photovoltaic performance measurements. The *J/V* curves of the cells were carried out using a solar simulator (Abet Technologies model 10500) equipped with a 150W xenon lamp. The illumination intensity was measured to be 100 mW cm^{-2} with a calibrated silicon reference cell (by ReRa) equipped with a KG5 filter. The appropriate filters (KG5) were utilized to faithfully simulate the AM 1.5G spectrum. The applied potential and cell current were measured using a Keithley 2401 digital source meter. The IPCE (incident photon to current conversion efficiency) was measured using a home-made set up consisting of a 150 W xenon lamp, a motorized monochromator and a Keithley 2401 digital source meter. Impedance spectroscopy measurements were carried out using a μ-Autolab type III potenciostate equipped with a FRA module.

2. DSSCs Device Fabrication

Anodes were fabricated by screen printing TiO_2 paste (Dyesol 18NR-AO) on F-doped tin oxide (FTO, with 15 Ω sq^{-1} sheet resistance) conducting glass substrates and they were made using 4 μm thick films. Prior to the deposition of the TiO_2 paste, the conducting glass substrates were immersed in a solution of $TiCl_4$ (40 mM) for 30 minutes and then dried. The TiO_2 electrodes were gradually heated at 325 ºC for 5 min, 375 ºC for 5 min, 450 ºC for 15 min and 500 ºC for 15 min. The heated TiO_2 electrodes were immersed again in a solution of $TiCl_4$ (40 mM) at 70 ºC for 30 min and then washed with ethanol. The electrodes were heated again at 500 ºC for 30 min and cooled before dye absorption. The active area for devices was 0.25 cm^2. The counter electrode was made by spreading a several drops of Platisol T (by Solaronix) onto a conducting glass substrate containing a small hole to allow the introduction of the liquid electrolyte using vacuum, followed by heating at 390 ºC for 15 min. All films were sensitized in 0.1 mM dye solutions in dichloromethane for 5 hours at room temperature (optimized dye loading conditions). The sensitized electrodes were washed with dichloromethane and dried under air. Finally, the working and counter electrodes were sandwiched together using a thin thermoplastic sealing agent (Meltonix 1170-60, by Solaronix) frame that melts at 100 ºC. Electrolyte LP1 was used (0.5 M 1-butyl-3-methylimidazolium iodide (BMII), 0.1 M lithium iodide, 0.05 M iodine and 0.5 M *tert*-butylpyridine in anhydrous acetonitrile).

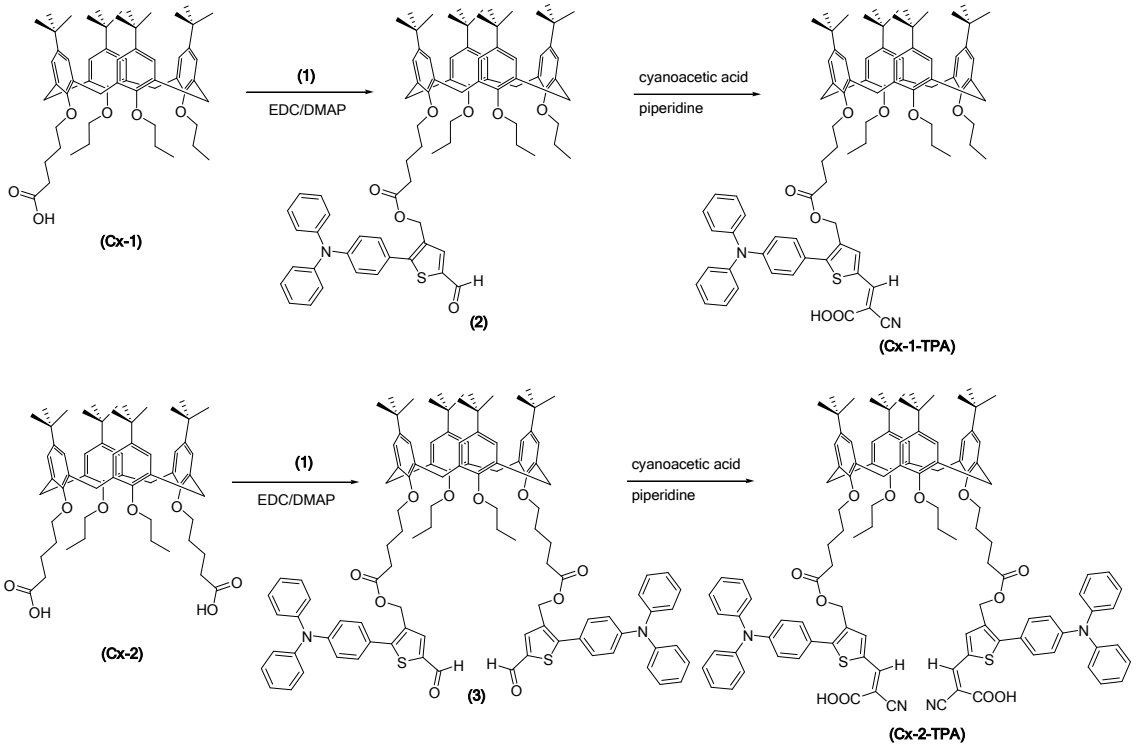
3. Synthetic Details

The *tert*-butyldimethylsilyl group of the compound (**P**), prepared as described in the literature[1], was removed with tetrabutylammonium fluoride in THF at room temperature.



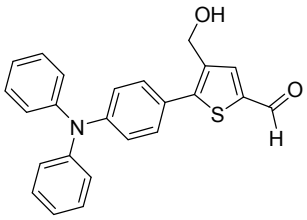
Scheme 1. Preparation of the alcohol (**1**)

The esterification of the hydroxyl group of compound **(1)** with the corresponding the carboxylic acid derivatives of calixarenes **(Cx-1)** and **(Cx-2**), prepaed as described in the literature,[2] was carried out by a Steglich reaction using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide) (EDC) and taking into account the adequate amount of equivalents of calixarene, alcohol and reagents. The aldehydes **(2)** and **(3)** were obtained (Scheme 1). And finally, the desired dyes **(Cx-1-TPA)** and **(Cx-2-TPA)** were obtained by a Knovenagel reaction of the aforementioned aldehydes **(2)** and **(3)** with 2-cyanoacetic acid in the presence of piperidine as shown in **Scheme 1**. All intermediates and final organic dyes have been completely characterized by ^{1}H RMN, ^{13}C RMN and HRMS.



Scheme 2. Synthetic route of the dyes (**Cx-1-TPA**) and (**CX-2-TPA**).

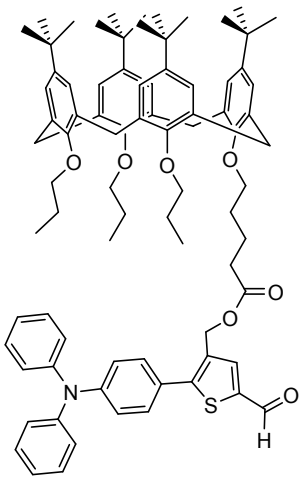
5-(4-(diphenylamino)phenyl)-4-(hydroxymethyl)tiophen-2-carbaldehyde (1)



To a solution of 4-(tert)-butyldimethylsilyloxy)methyl-5-(4-(diphenylamino)phenyl)thiophene-2-carbaldehyde (347 mg, 0.695 mmol) in THF (20mL) at 0ºC of temperature under argon atmosphere, a solution of tetrabutilammonium fosfate (1M THF) (1.39 mL, 1.39 mmol, 2 eq) was slowly added and it was stirred for 3 hours. The mixture of reaction was quenched by the addition of 40 mL of H_2O and 100 mL of NH_4Cl saturated solution (aq). The aqueous phase was recovered with ethyl acetate solution and the organic phase was dyed over dry $MgSO_4$ and the solvent was evaporated by reduced pressure. The residue was purified by flash chromatography using hexane/ethyl acetate (1:1) to yield (238 mg, 87 %) of an orange solid.

Molecular weight (g/mol): 385.48. **Melting point:** (ºC): 66-70. **Elemental analysis** found C 74.40, H 4.82, N 3.85, S 8,02 %; molecular formula $C_{24}H_{19}NO_2S$ requires C 74.78, H 4.97, N 3.63, S 8.32 %. **IR** (KBr) cm^{-1}: 1669 (C=O), 1591 (C=C). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ (ppm): 4.73 (s, 2H), 7.10 (tt, J_1=7.4 Hz, J_2=1.2 Hz, 4H), 7.14-7.17 (m, 4H), 7.28-7.40 (m, 4H), 7.38 (dt, J_1=8.8 Hz, J_2=2.4 Hz, 2H), 7.84 (s, 1H), 9.86 (s, 1H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ (ppm): 58.7, 122.0, 123.9, 125.3, 125.6, 129.5, 129.8, 138.1, 138.9, 140.7, 147.1, 149.0, 150.8, 182.7. **HRMS** (ESI^+) m/z: $[2M+Na]^+$: Calculated for $[C_{48}H_{38}N_2O_4S_2Na]^+$: 793.2165. Found: 793.2130.

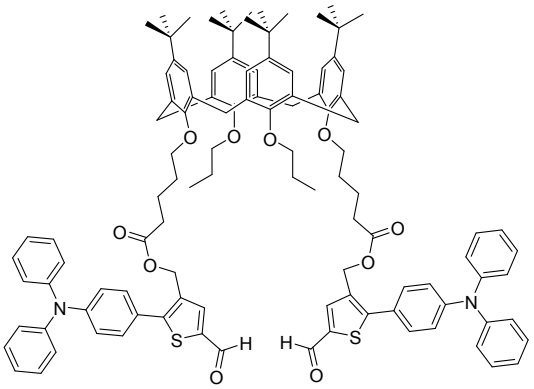
Monoester derivative of the alcohol (1) (2)



To a solution containing the calixarene monoacid derivative **(Cx-1)** 90.8 mg (0.104 mmol) in dry diclorometh ane (24 ml) under nitrogen atmosphere and at 0ºC of temperature, 40 mg (0.104 mmol) of **(1)**, 1.86 mg (0.0156 mmol) 4-dimethylaminopyridine (DMAP) and 24 mg (0.125 mmol) (1.2 eq) of 1-etil-3-(3-dimetilaminopropil)carbodiimida (EDC) were successively added. This mixture was maintained at 0 ºC for 30 minutes. The reaction mixture was stirred at room temperature during 48 hours. After concentration under reduced pressure, the residue was purified by column chromatography (hexane/ethyl acetate: 9/1) on silica gel and the ester was isolated as yellow solid (116 mg, 90 %).

Molecular weight (g/mol): 1242.73. **Melting point** (ºC): 114-117. **Elemental analysis** found C 79.55, H 8.25, N 1.36, S 2.67 %; molecular formula $C_{82}H_{99}NO_7S$ requires C 79.25, H 8.03, N 1.13, S 2.58 %. **IR** (KBr) cm^{-1}: 1741 (C=O), 1482 (C=C), 1201 (C-O). **^{1}H- NMR** (300 MHz, CD_2Cl_2) δ (ppm): 0.93-0.99 (m, 9H), 1.05 (s, 18H), 1.06 (s, 9H), 1.07 (s, 9H), 1.72-1.83 (m, 2H), 1.91-2.09 (m, 8H), 2.45 (t, *J*=7.5 Hz, 2H), 3.06 (d, *J*=4.2 Hz, 2H), 3.10 (d, *J*=4.2 Hz, 2H), 3.73-3.80 (m, 6H), 3.84 (t, 2H), 4.34 (d, J=9.3 Hz, 2H), 4.38 (d, *J*=9 Hz, 2H), 5.12 (s, 2H), 6.75 (s, 2H), 6.76 (s, 2H), 6.78 (s, 4H), 7.04-7.09 (m, 4H), 7.12-7.15 (m, 4H), 7.29-7.32 (m, 4H), 7.35-7.38 (m, 2H), 7.80 (s, 1H), 9.80 (s, 1H). **^{13}C- NMR** (100 MHz, CD_2Cl_2) δ (ppm): 10.7, 10.8, 22.9, 23.9, 24.0, 30.3, 31.6, 31.8, 34.2, 34.3, 34.8, 60.2, 75.2, 77.5, 77.6, 122.4, 124.6, 125.5, 125.6, 125.6, 125.7, 126.0, 130.1, 130.4, 134.3, 134.4, 134.5, 134.6, 140.0, 144.8, 145.0, 147.8, 149.8, 154.2, 154.3, 154.4, 173.6, 183.1. **HMRS (**ESI^+) m/z: $[M+Na]^+$: Calculated $[C_{82}H_{99}NNaO_7S]^+$: 1264.7034, Found: 1264.6989.

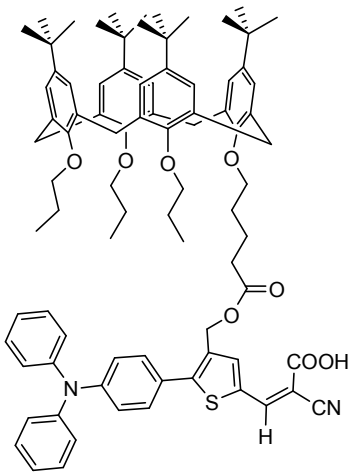
Diester derivative of the alcohol (1) (3)



To a solution of calixarene diacid **(Cx-2)** 155.0 mg (0.166 mmol) in dry dicloromethane (8 mL) under nitrogen atmosphere and at 0ºC of temperature, 128.0 mg (0.332 mmol) of **(1)**, 36.5 mg (0.549 mmol) 4-dimethylaminopyridine (DMAP) and 114.6 mg (0.595 mmol) of 1-ethyl-3-[3-dimethylaminopropyl]carbodiimide hydrochloride (EDC) were successively added. This mixture was maintained at 0ºC during 30 minutes. The reaction mixture was then stirred at room temperature for 5 days. After concentration under reduced pressure, the residue was purified by trituration on MeOH and the ester was isolated as yellow solid (200.0 mg, 72 %).

Molecular weight (g/mol): 1668.23. **Melting point** (ºC): 120-122. **Elemental analysis** found C 77.50, H 7.23, N 1.54, S 3.71 %; molecular formula $C_{108}H_{118}N_2O_{10}S_2$ requires C 77,76, H 7.13, N 1.68, S 3.84 %. **IR** (KBr) cm^{-1}: 1738 (C=O), 1590 (C=C), 1198 (C-O). **^{1}H- NMR** (400 MHz, CD_2Cl_2) δ (ppm): 0.92 (t, *J*=7.6 Hz, 6H), 1.04 (s, 18H), 1.10 (s, 18H), 1.75-1.83 (m, 4H), 1.94-2.02 (m, 8H), 2.45 (t, *J*=7.6 Hz, 4H), 3.08 (d, *J*=12.4 Hz, 4H), 3.77 (t, *J*= 7.6 Hz, 4H), 3.83 (t, *J*=7.2 Hz, 4H), 4.34 (d, *J*=12.4 Hz, 4H), 5.12 (s, 4H), 6.72 (s, 4H), 6.79 (s, 4H), 7.06-7.10 (m, 8H), 7.13-7.15 (m, 8H), 7.27-7.36 (m, 12H), 7.79 (s, 2H), 9.80 (s, 2H). **^{13}C- NMR** (100 MHz, CD_2Cl_2) δ (ppm): 20.2, 21.7, 23.4, 29.7, 31.0, 31.2, 31.3, 34.2, 59.7, 74,7, 77,0, 121,9, 124,0, 125,0, 125,1, 125,3, 125,4, 129,5, 129,9, 133,0, 133,7, 133,9, 139.5, 144.3, 144.4, 147.0, 149.2, 153.5, 173.0, 182.6. **MS** (MALDI$^+$) m/z: $[M+Na]^+$: 1689.9.

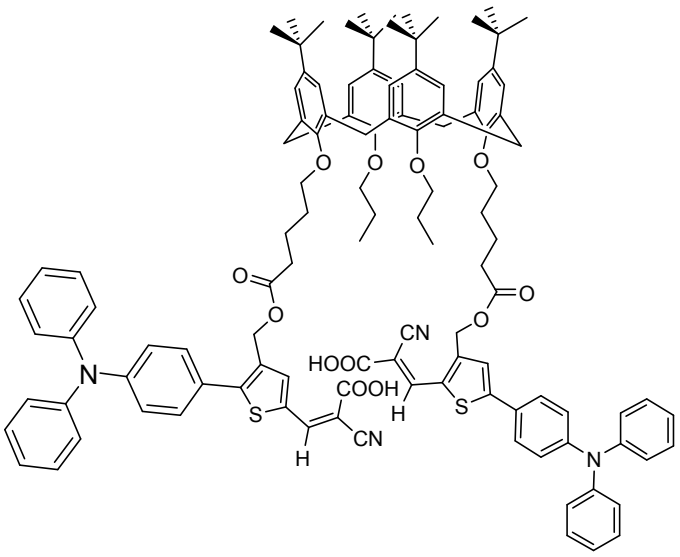
Compound (Cx-1-TPA)



To a solution of compound **(2)** (140 mg , 0.113 mmol)) and 2-cyanoacetic acid (72 mg, 0.847 mmol) in chloroform (10 mL) piperidine (139 μL; 1.427 mmol) was added. The mixture was heated to 65ºC of temperature for 6 days under argon atmosphere and prevented from light, then it was cooled down to room temperature. After concentration under reduced pressure, the resulting solid was solved in CH_2Cl_2, acidified with HCl 0.1 M, and it was washed with water . The resulting solid was filtered and washed with cold MeOH and a red solid was obtained (46 mg, 31 %).

Molecular weight (g/mol): 1309.78. **Melting point** (ºC): 145-150. **Elemental analysis** found C 77.77, H 7.58, N 2.31, S 2.64 %; molecular formula $C_{85}H_{100}N_2O_8S$ requires C 77.95, H 7.70, N 2.14, S 2.45 %. **IR** (KBr) cm^{-1}: 2217 (CΞN), 1740 (C=O), 1586 (C=C), 1199 (C-O). **^{1}H- NMR** (400 MHz, CD_2Cl_2) δ (ppm): 0.95 (t, *J*=4.8 Hz, 9H), 1.04 (s, 18H), 1.06 (s, 9H), 1.07 (s, 9H), 1.73-1.81 (m, 2H), 1.93-2.06 (m, 8H), 2.46 (t, *J*=8 Hz, 2H), 3.06 (d, *J*=4.8 Hz, 2H), 3.09 (d, *J*=4.8 Hz, 2H), 3.74-3.80 (m, 6H), 3.84 (t, *J*=7.2 Hz, 2H), 4.36 (t, *J*=12.4 Hz, 4H), 5.13 (s, 2H), 6.76 (s, 4H), 6.78 (s, 2H), 6.79 (s, 2H), 7.05-7.14 (m, 8H), 7.30 (m, 4H), 7.39 (d, *J*= 8.4 Hz, 2H), 7.81 (s, 1H), 8.32 (s, 1H). **^{13}C-NMR** (100 MHz, CD_2Cl_2) δ (ppm): 10.2, 10.3, 21.6, 21.7, 23.4, 23.5, 29.8, 31.0, 31.2, 31.3, 33.7, 33.8, 34.2, 59.5, 74.7, 77.0, 77.1, 110.1, 121.7, 124.2, 124.7, 124.9, 125.0, 125.1, 125.4, 125.5, 129.5, 129.6, 130.0, 133.2, 133.7, 133.8, 133.9, 134.0, 144.2, 144.3, 144.4, 146.9, 149.5, 153.6, 153.7, 153.8, 173.1. **HRMS** (MALDI$^+$) m/z: $[M+Na]^+$: Calculated $[C_{85}H_{100}N_2O_8SNa]^+$: 1331.7093, Found: 1331.7029.

Compound (Cx-2-TPA)



To a solution of compound **(3)** (172 mg, 0.103 mmol) and 2-cyanoacetic acid (76.2 mg , 0.893 mmol) in chloroform (12 mL) piperidine (216.1 μL; 2.229 mmol) was added. The mixture was heated at 65ºC of temperature for 4 days under argon atmosphere and prevented for ligth, and then it was cooled down to room temperature. After concentration under reduced pressure, the resulting solid was solved with CH_2Cl_2, acidified with HCl 0.1 M, and was washed with water. The solution was dried and the solvent was removed under reduced pressure. The resulting solid was filtered and washed with cold MeOH and a red solid was obtained (55 mg, 30 %).

Molecular weight (g/mol): 1802.32. **Melting point** (ºC): 160-162. **Elemental analysis** found C 76.07, H 6.43, N 3.44, S 3,71 %; molecular formula $C_{114}H_{120}N_4O_{12}S_2$ requires C 75.97, H 6.71, N 3.11, S 3.56 %. **IR** (KBr) cm^{-1}: 2218 (CΞN), 1736 (C=O), 1585 (C=C), 1197 (C-O). **^{1}H-NMR** (400 MHz, CD_2Cl_2) δ (ppm): 0.92-0.97 (m, 6H), 0.97 (s, 18H), 1.13 (s, 18H), 1.70-1.75 (m, 4H), 1.89-1.97(m,4H), 2.03-2.08 (m, 4H), 2.42-2.51 (m, 4H), 3.07 (d, *J*=12 Hz, 4H), 3.67-3.73 (m, 4H), 3.83-3.91 (m, 4H), 4.33 (d, *J*=12,4 Hz, 4H), 5.06 (s, 4H), 6.66 (s, 4H), 6.87 (s, 4H), 6.98-7.01 (m, 4H), 7.07-7.09 (m, 12H), 7.24-7.30 (m, 12H), 7.75 (s, 2H), 8.27 (s, 2H). **^{13}C-NMR** (100 MHz, CD_2Cl_2) δ (ppm): 10.4, 21.6, 23.5, 29.8, 31.0, 31.2, 31.4, 33.7, 34.2, 60.0, 74.7, 77.2, 121.6, 124.1, 124.9, 125.2, 125.5, 129.6, 129.9, 133.3, 134.5, 144.6, 146.9, 149.3, 153.4. **M.S.** (MALDI$^+$) m/z: $[M+Na]^+$: 1823.9.

4. Absoption and emission spectra

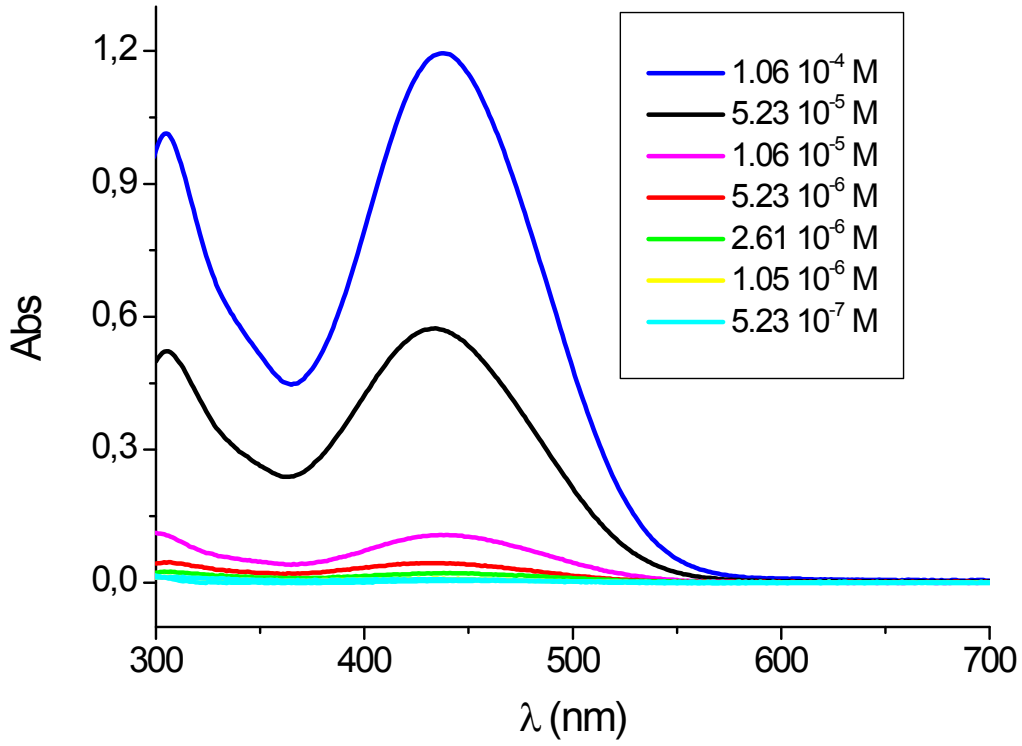


Figure S.1. Concentration dependence of (**TPA**) dye. Absoption spectra.

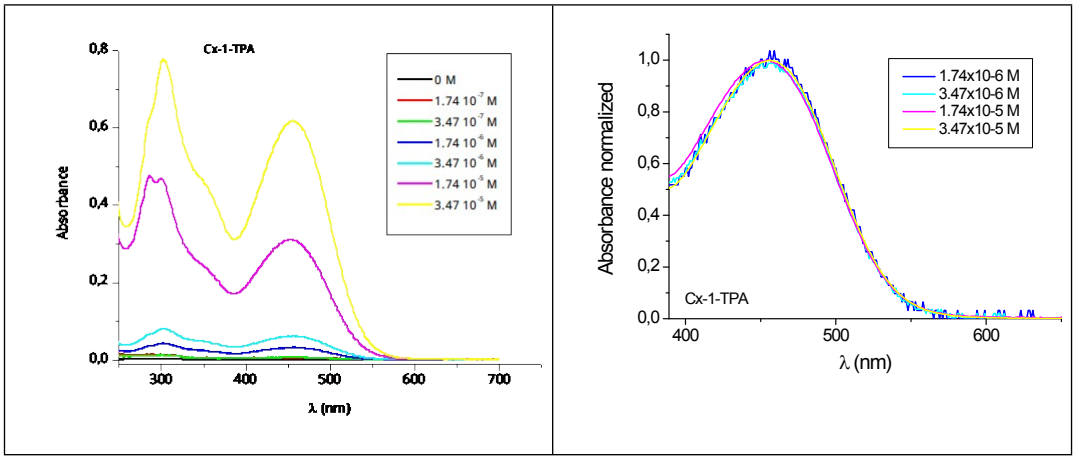


Figure S.2. a) Concentration dependence of (**Cx-1-TPA**) dye. Absoption spectra. b) Normalized spectra of (**Cx-1-TPA**) dye at different CH_2Cl_2 solutions.

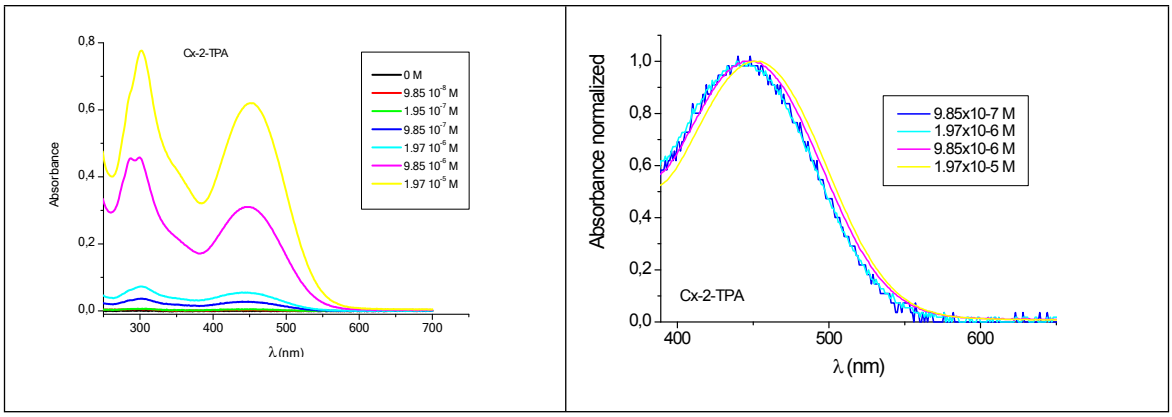


Figure S.3. a) Concentration dependence of (**Cx-2-TPA**) dye. Absoption spectra. b) Normalized spectra of (**Cx-2-TPA**) dye at different CH_2Cl_2 solutions.

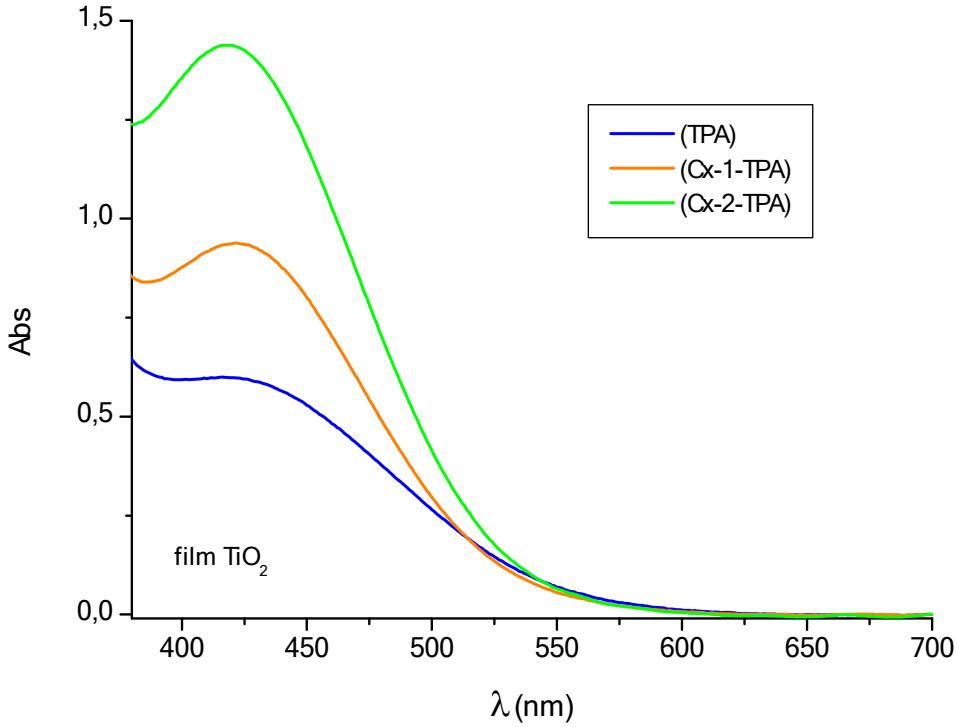


Figure S.4. UV-visible spectra of the dyes (**TPA**), (**Cx-1-TPA**) and (**Cx-2-TPA**) on film.

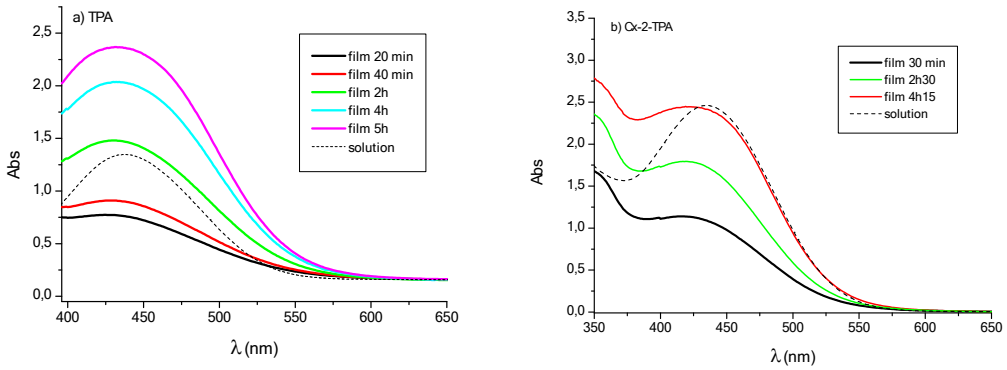


Figure S.5. a) UV-visible spectra of films with (**TPA**) dye at different absorption times and also the CH_2Cl_2 solution of this dye. and b) UV-visible spectra of films with (**Cx-2-TPA**) dye at different absorption times and also the CH_2Cl_2 solution of this dye

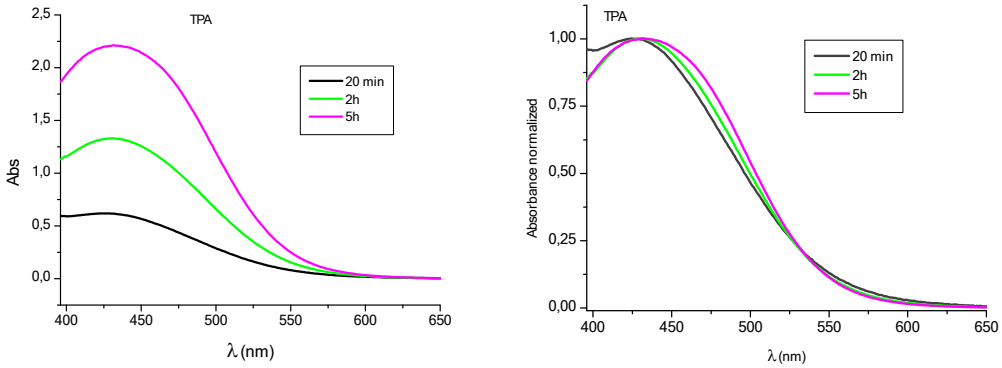


Figure S.6. UV-visible spectra of films with (**TPA**) dye at different absorption times.

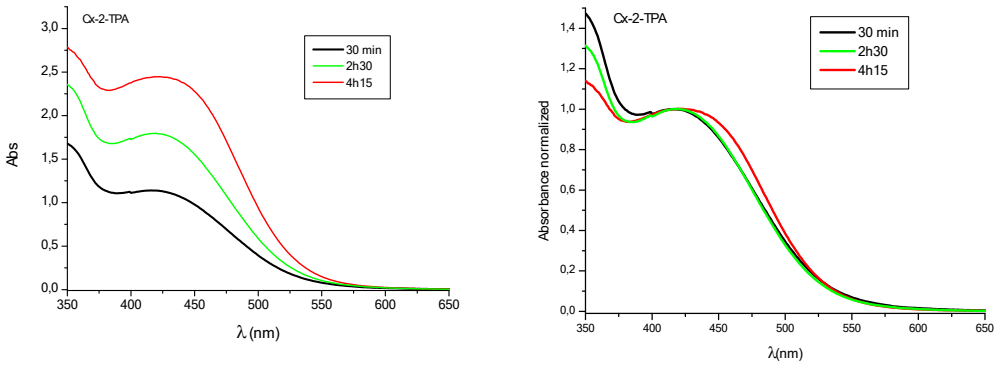


Figure S.7. UV-visible spectra of films with (**Cx-2-TPA**) dye at different absorption times.

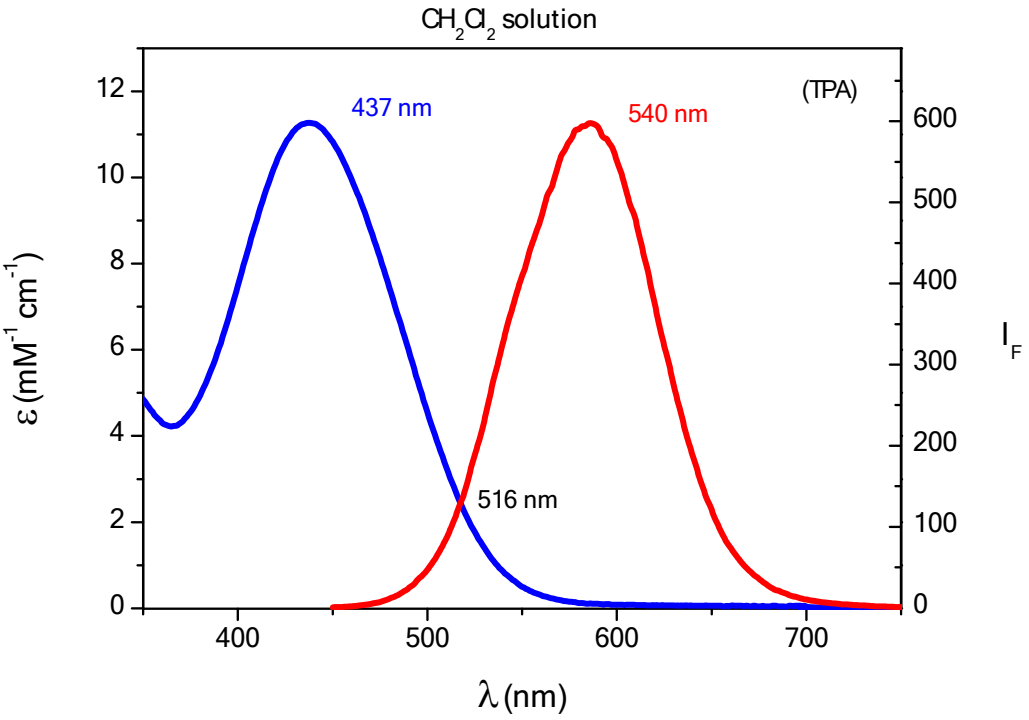


Figure S.8. UV-visible and emission spectra of (**TPA**) dye in CH_2Cl_2 solution

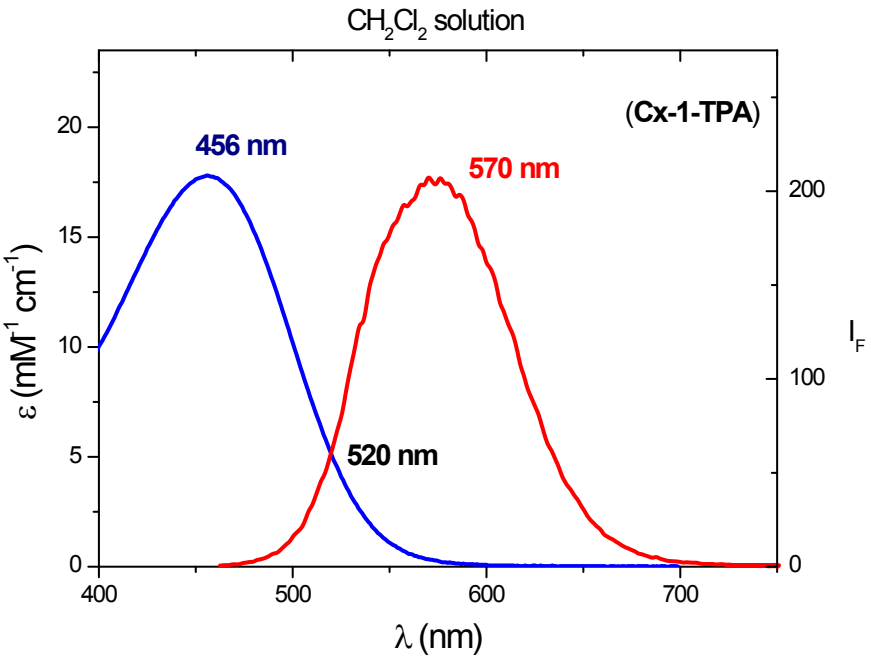


Figure S.9. UV-visible and emission spectra of (**Cx-1-TPA**) dye in CH_2Cl_2 solution

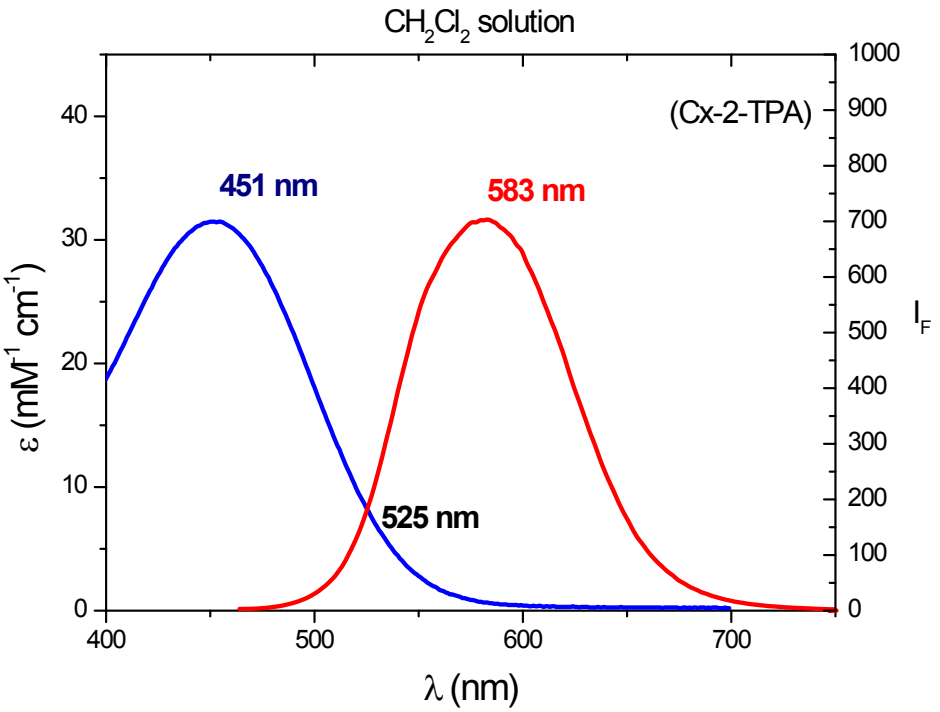


Figure S.10. UV-visible and emission spectra of (**Cx-2-TPA**) dye in CH_2Cl_2 solution

5. Diferential Pulse Voltammetry

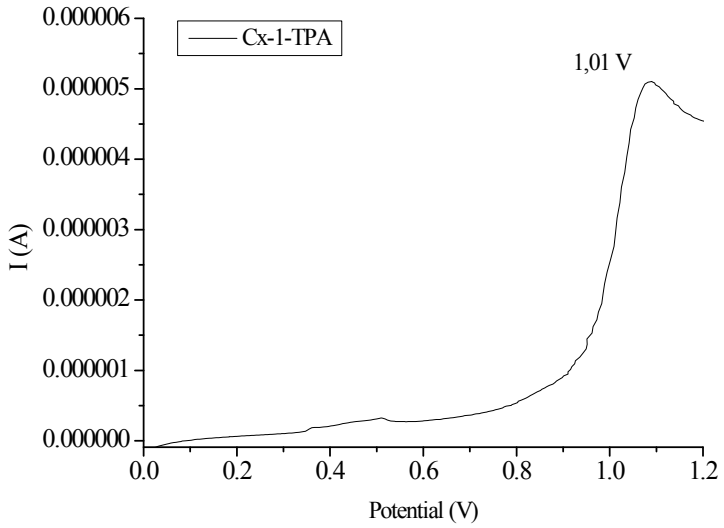


Figure S.11. Differential Pulse Voltammogram of the dye (**Cx-1-TPA**).

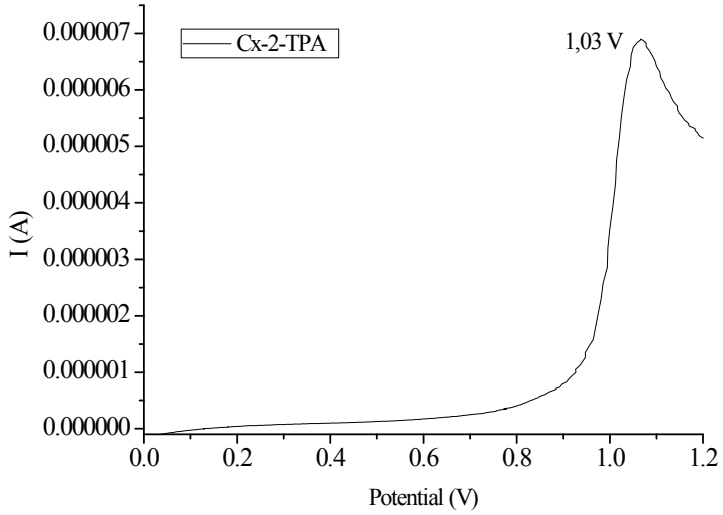


Figure S12. Differential Pulse Voltammogram of the dye (**Cx-2-TPA**).

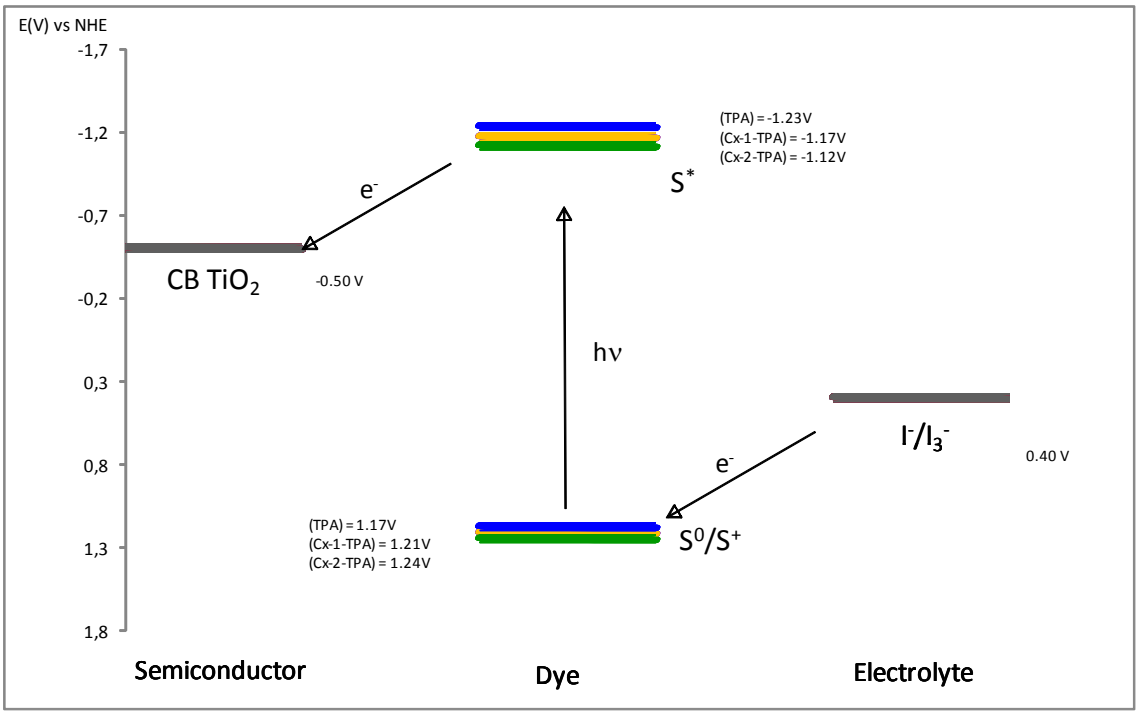


Figure S.13. Energy diagram of compounds (**TPA**), (**Cx-1-TPA**) and (**Cx-2-TPA**).

6. NMR spectra

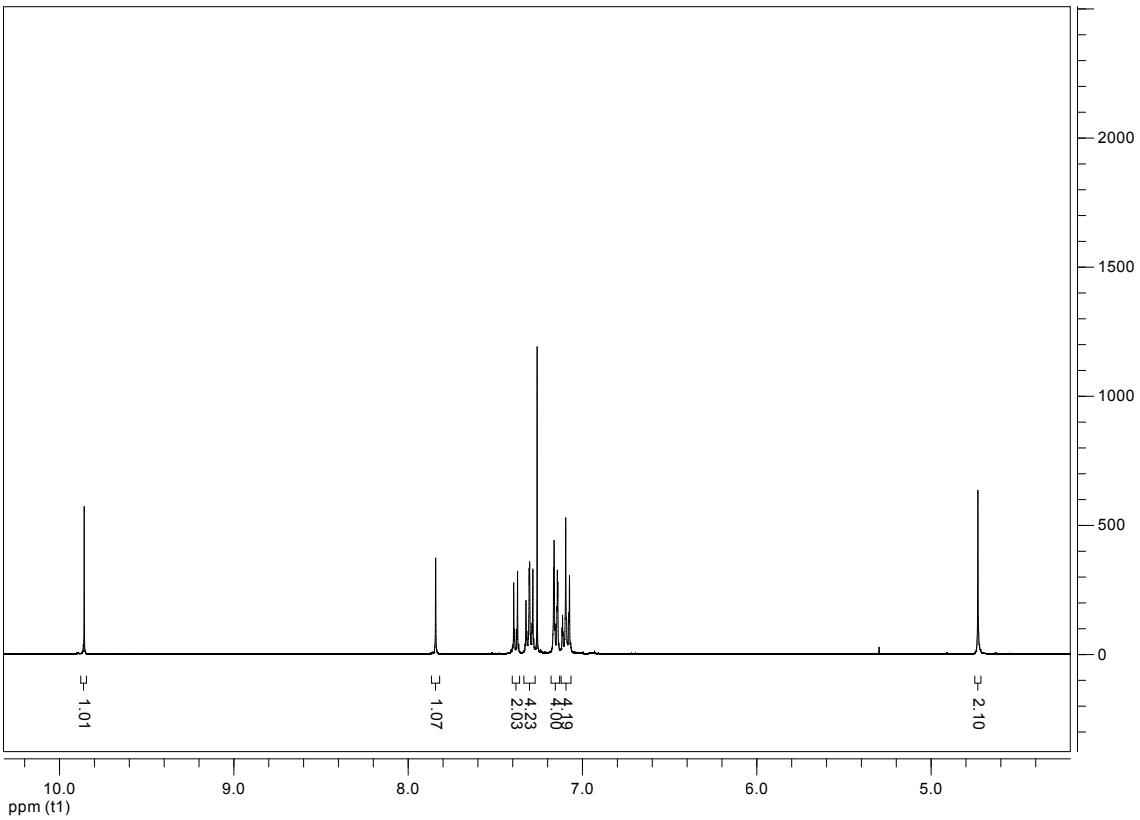


Figure S.14. ^{1}H-NMR spectrum of compound (**1**) (400 MHz, $CDCl_3$).

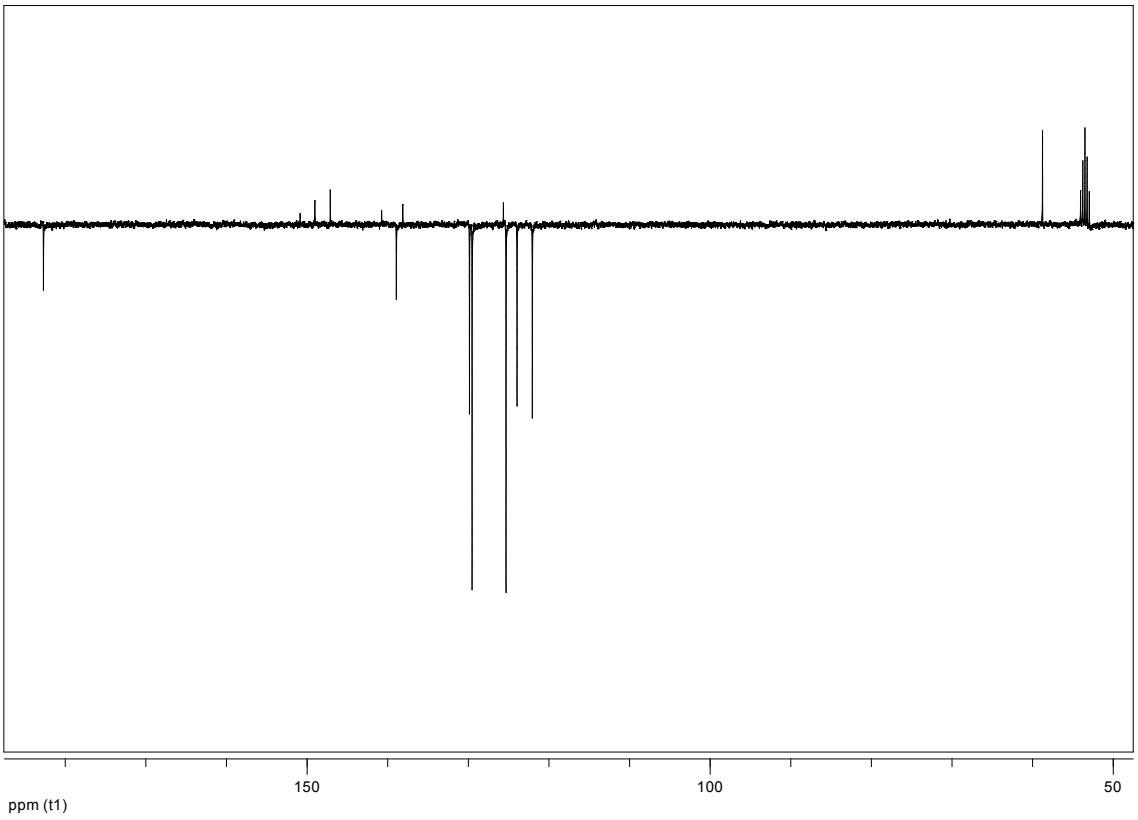


Figure S.15. ^{13}C-NMR spectrum of compound (**1**) (400 MHz, CD_2Cl_2).

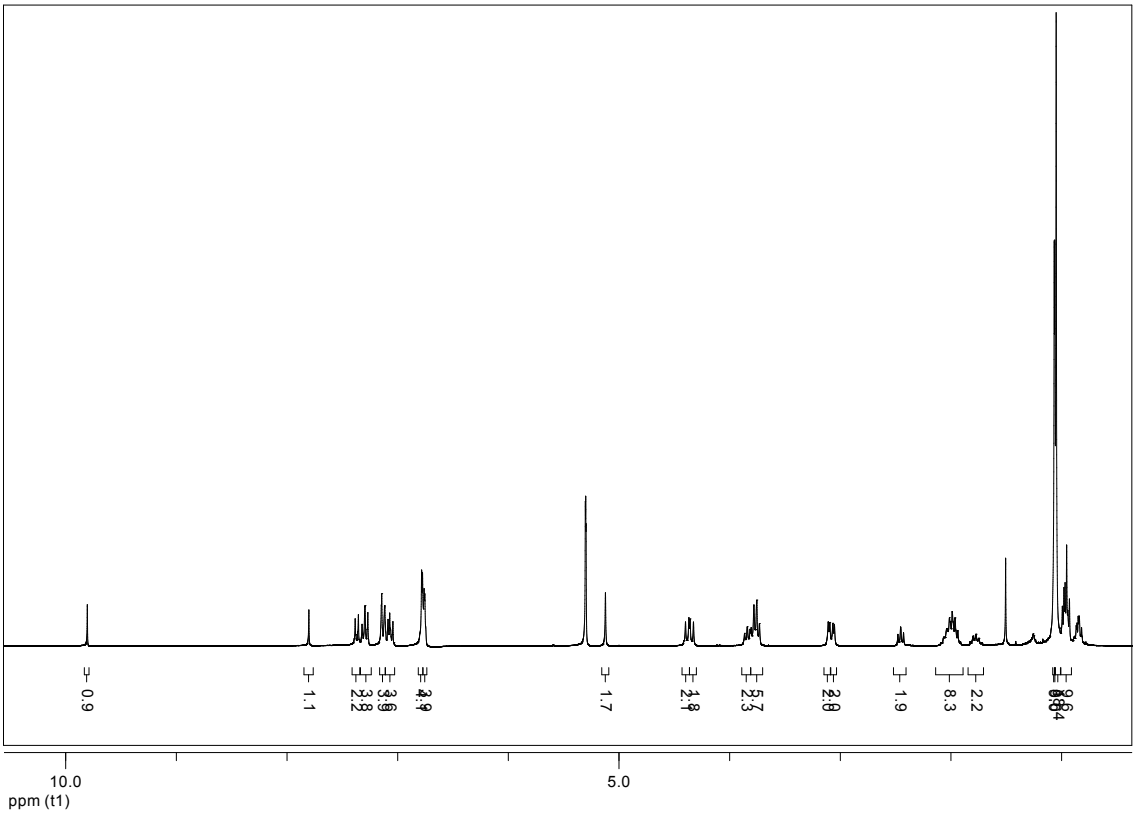


Figure S.17. ^{1}H-NMR spectrum of compound (**2**) (400 MHz, CD_2Cl_2).

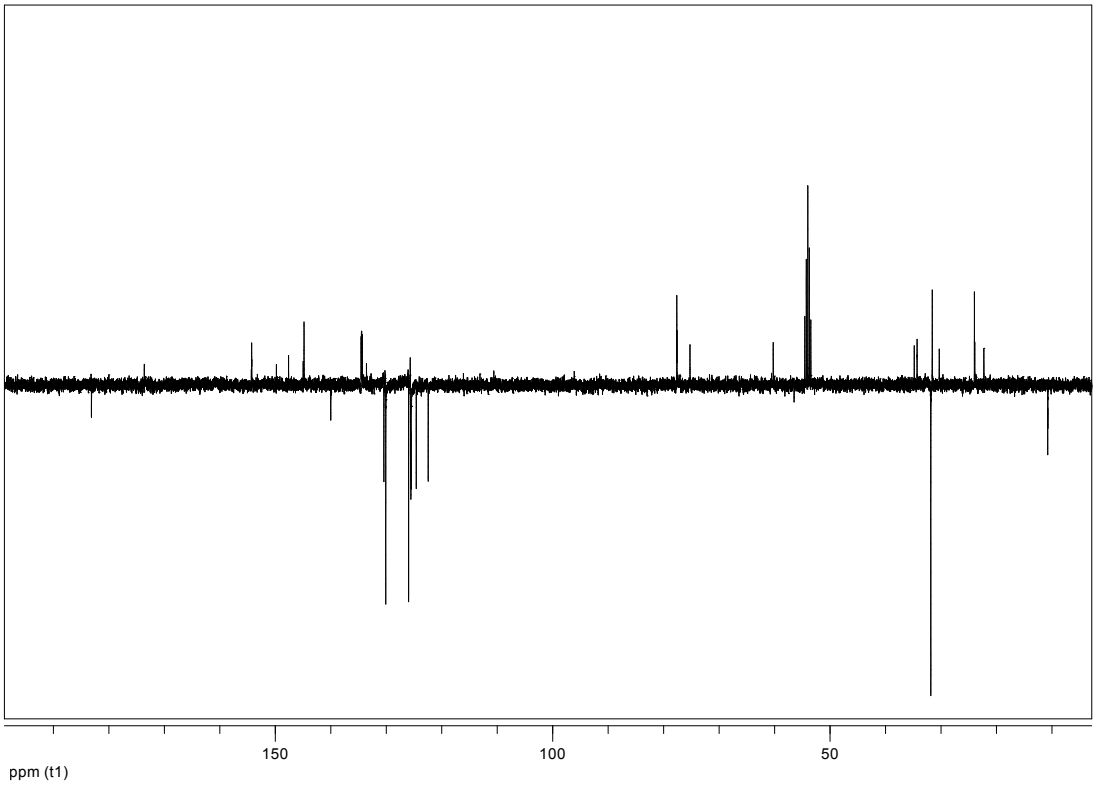


Figure S.18. ^{13}C-NMR spectrum of compound (**2**) (400 MHz, CD_2Cl_2).

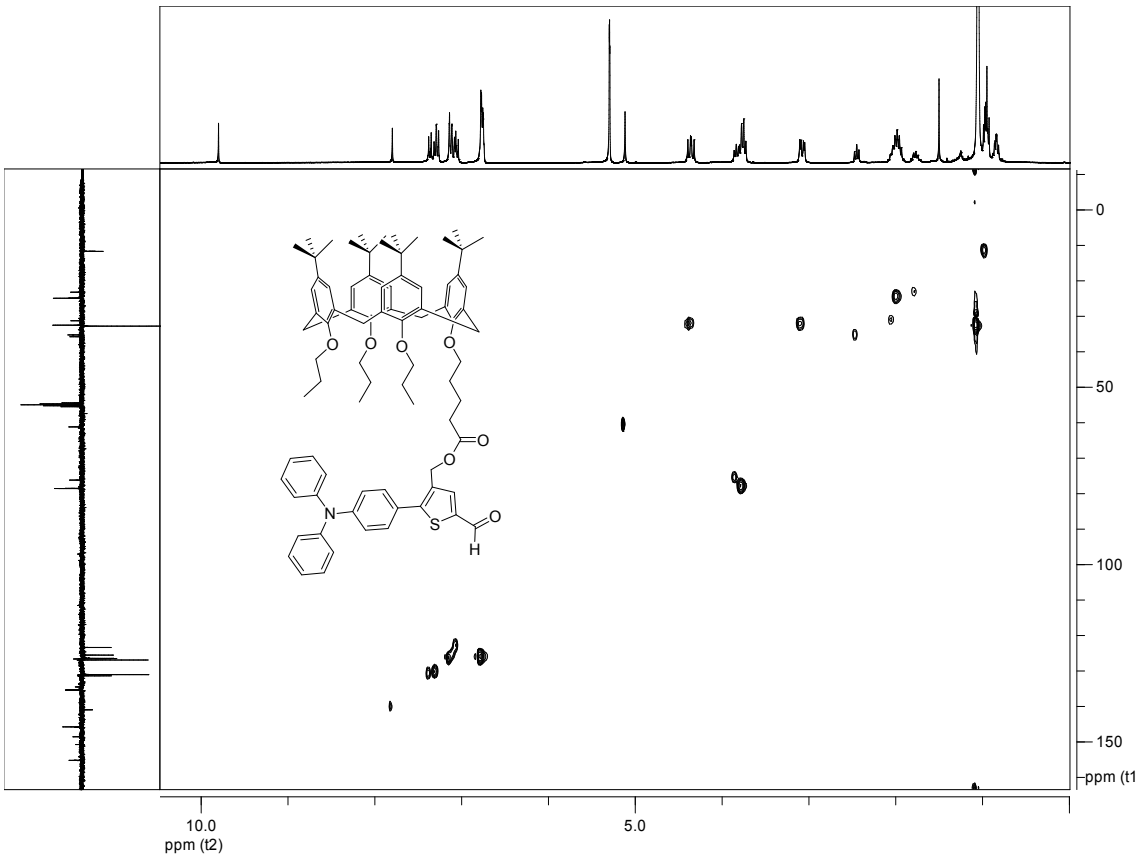


Figure S.18. ^{1}H-^{13}C HSQC spectrum of compound (**2**).

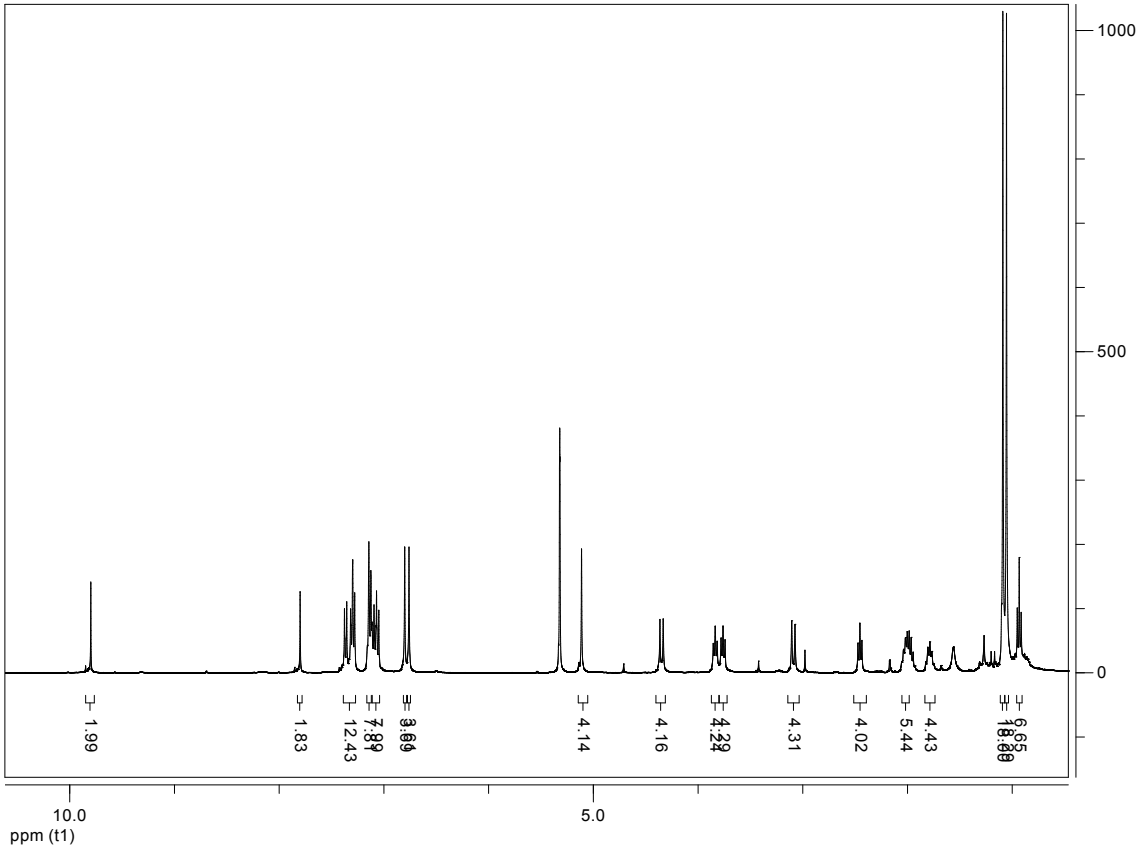


Figure S.19. ^{1}H-NMR spectrum of compound (**3**) (400 MHz, CD_2Cl_2).

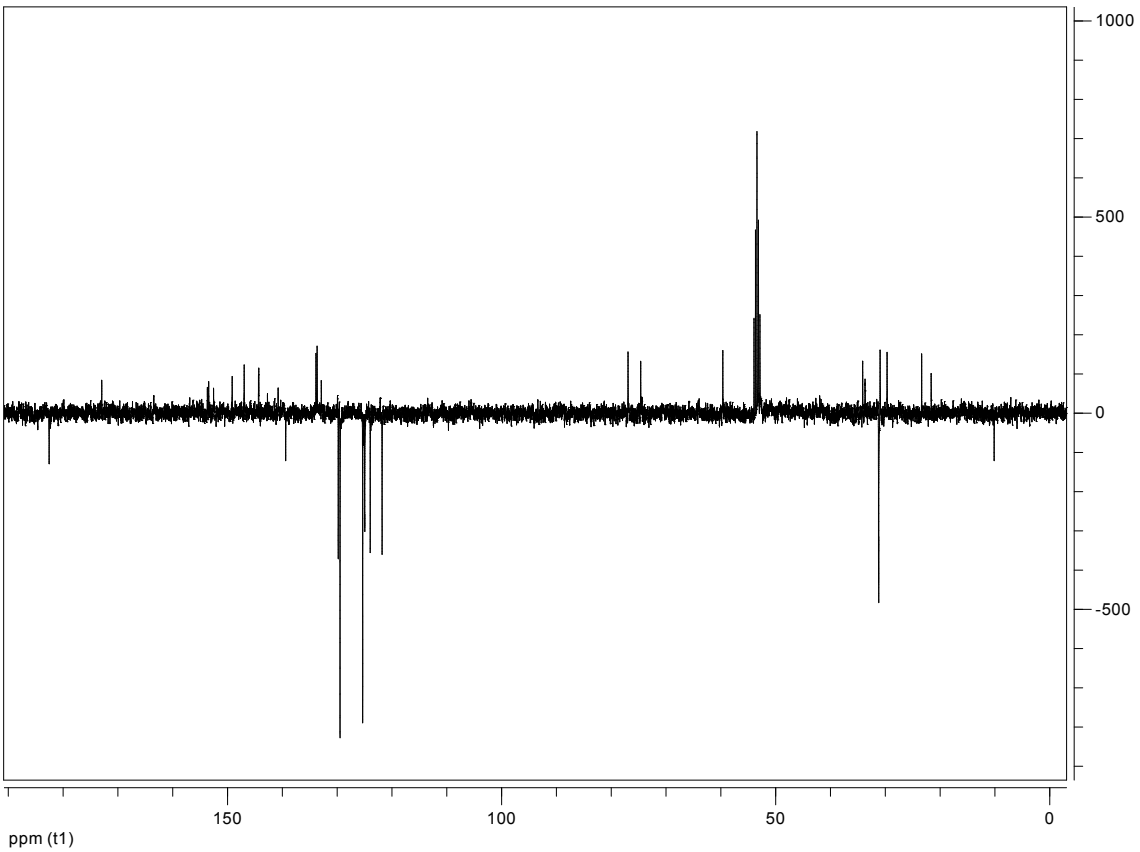


Figure S.20. ^{13}C-NMR spectrum of compound (**3**) (400 MHz, CD_2Cl_2).

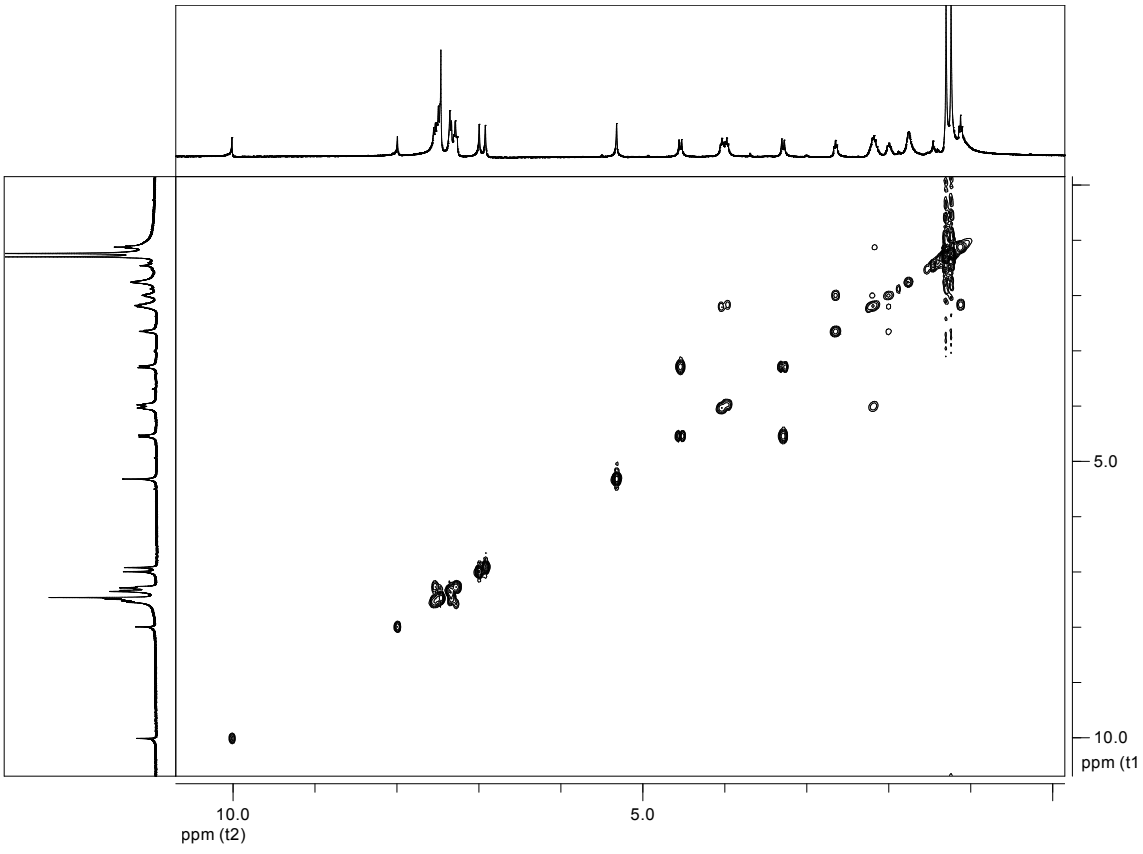


Figure S.21. ^{1}H-^{1}H COSY spectrum of compound (**3**).

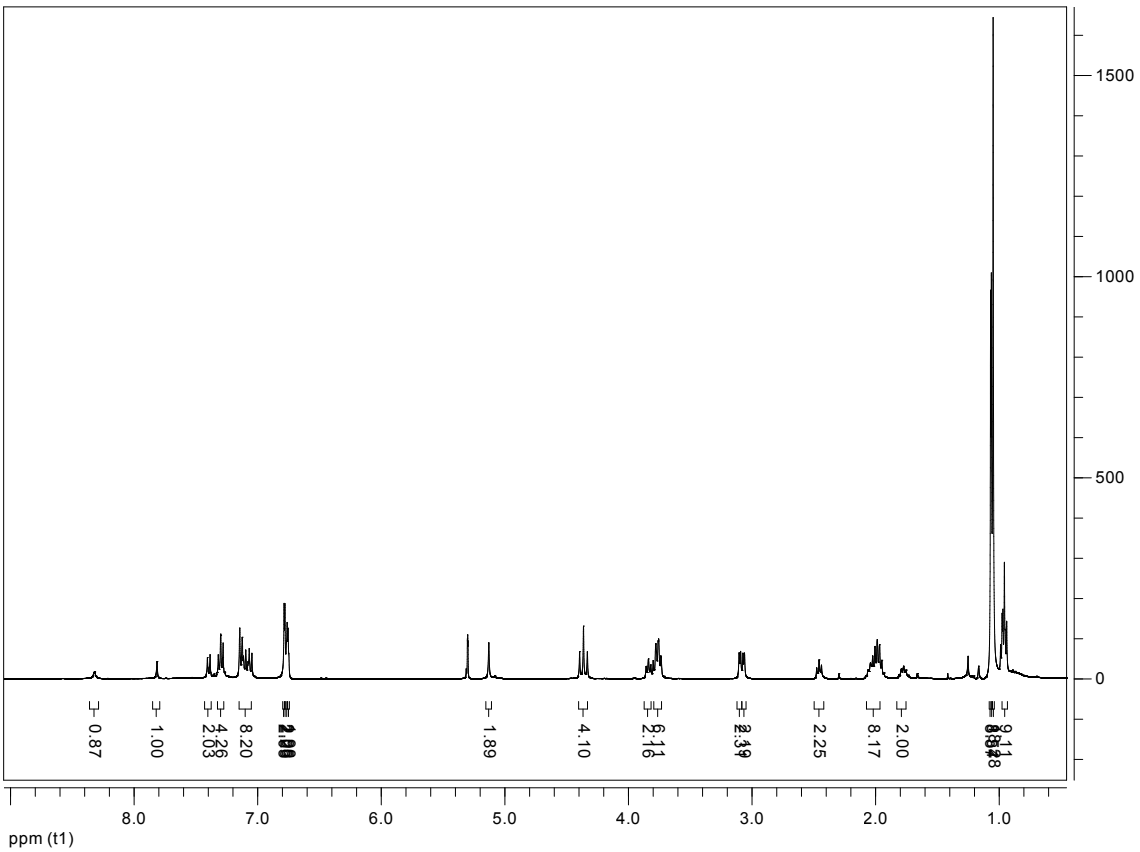


Figure S.22. ^{1}H-NMR spectrum of compound (**Cx-1-TPA**) (400 MHz, CD_2Cl_2).

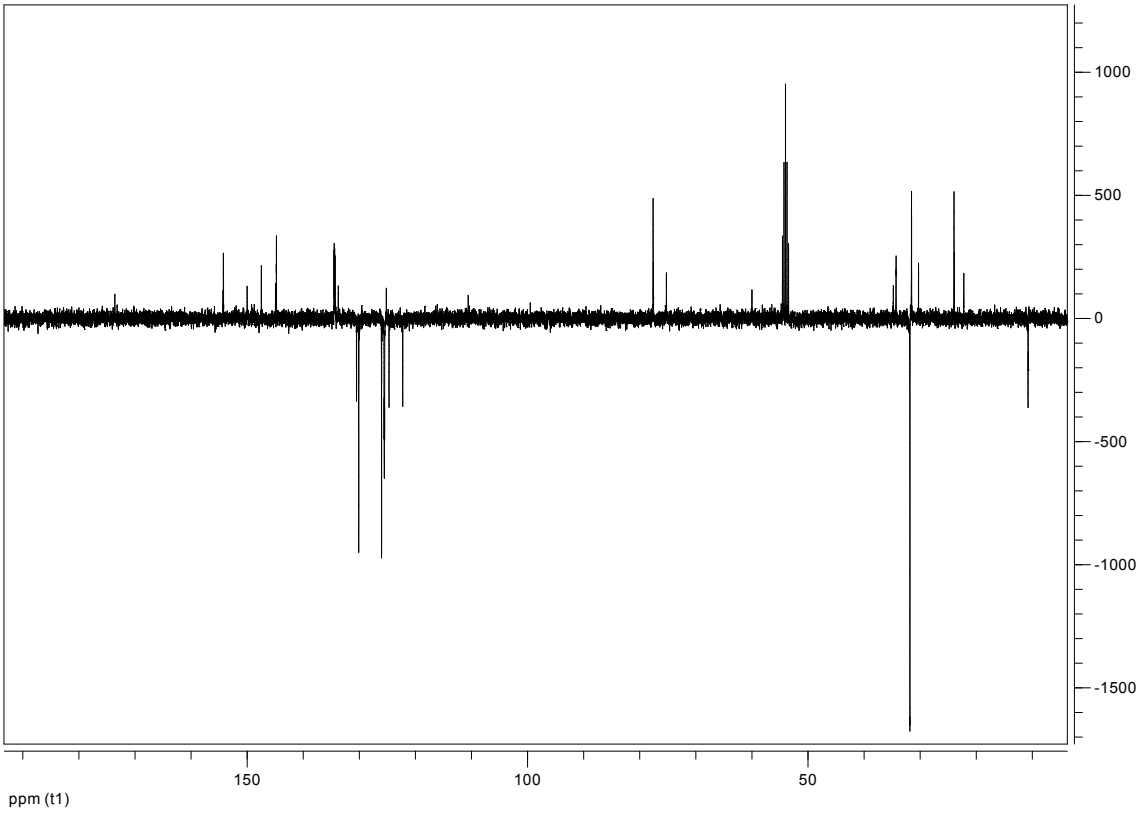


Figure S.23. ^{13}C-NMR spectrum of compound (**Cx-1-TPA**) (400 MHz, CD_2Cl_2).

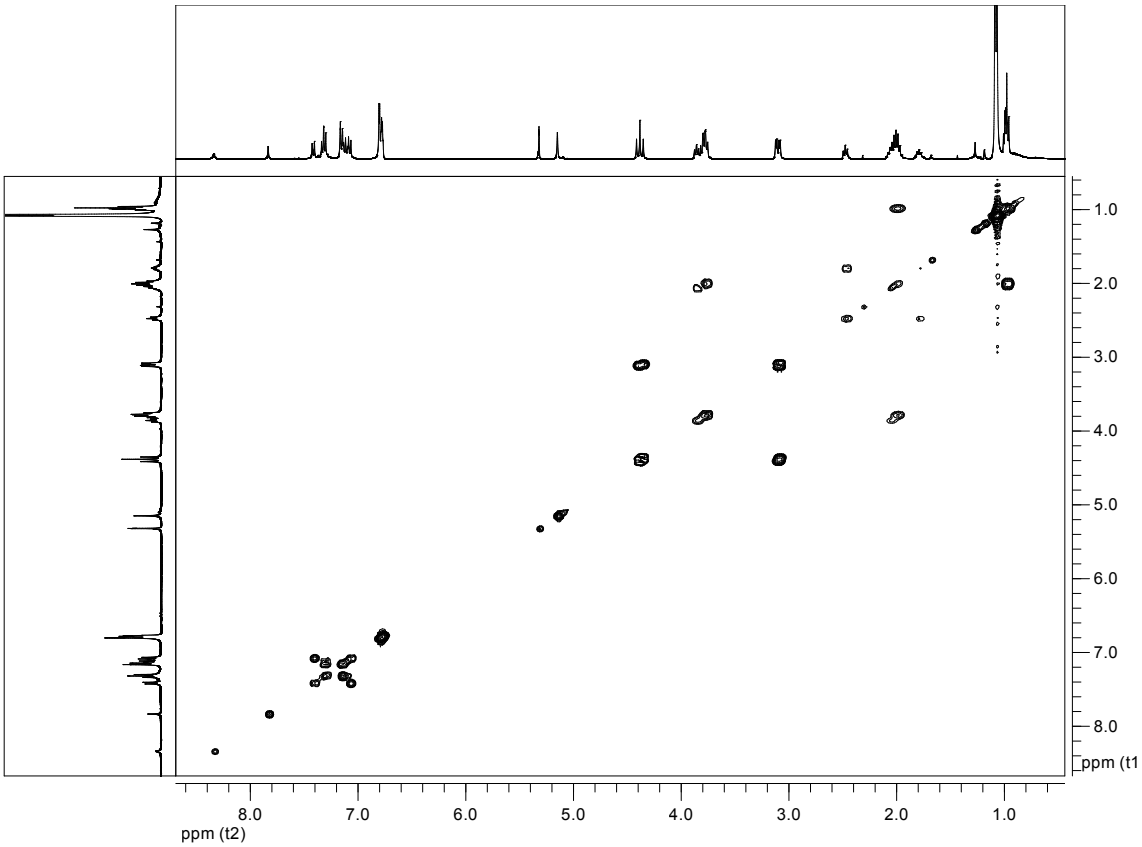


Figure S.24. ^{1}H-^{1}H COSY of compound (**Cx-1-TPA**).

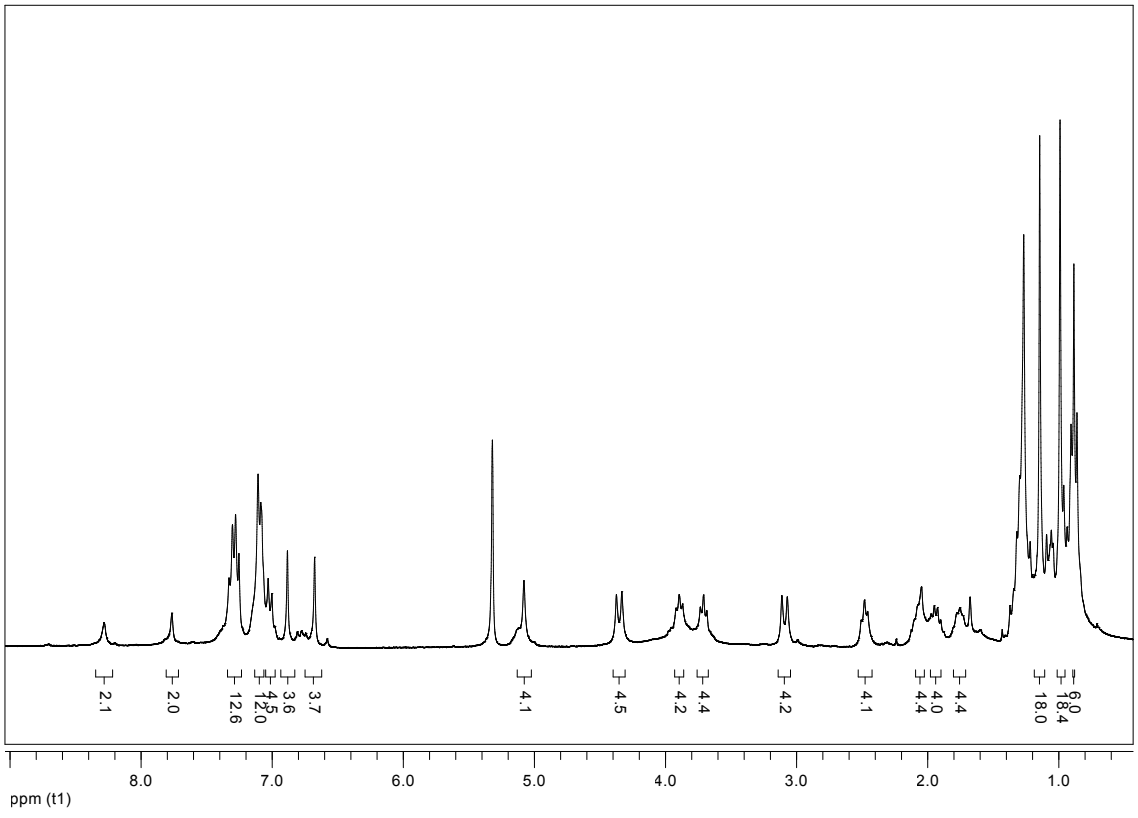


Figure S.25. ^{1}H-NMR spectrum of compound (**Cx-2-TPA)** (400 MHz, CD_2Cl_2).

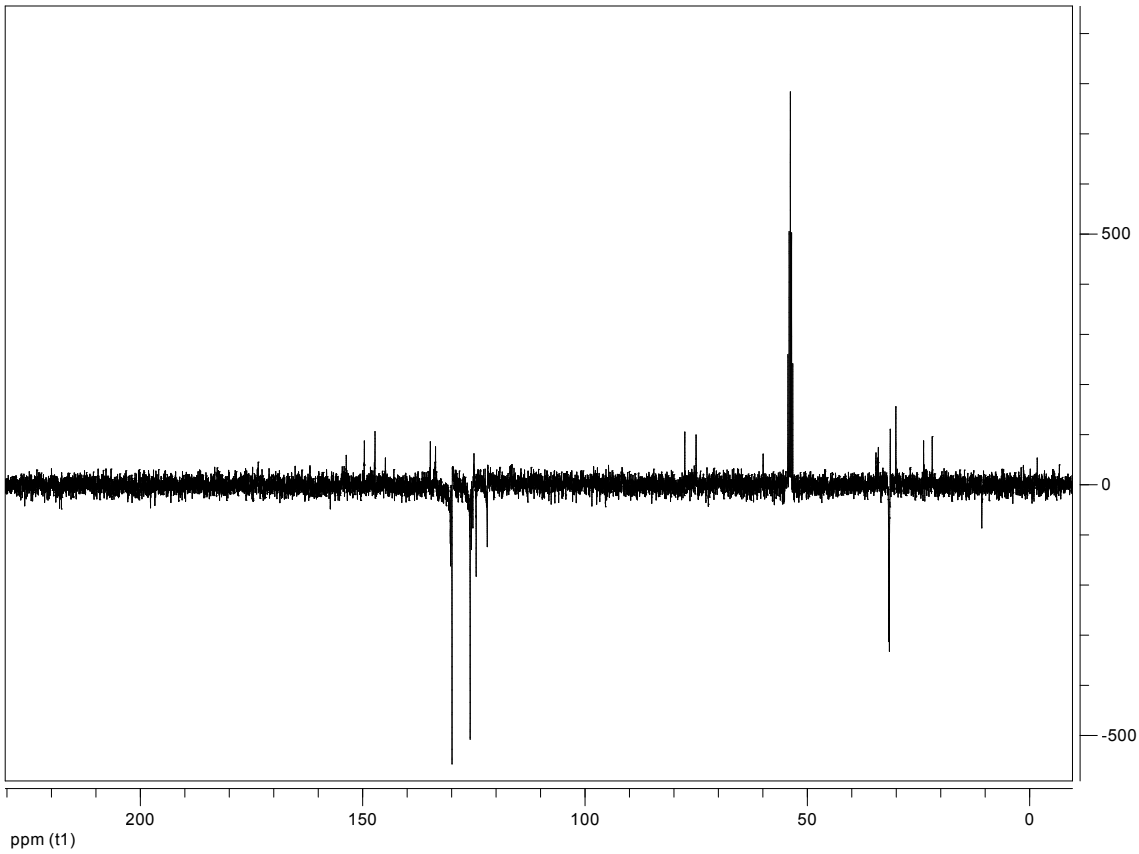


Figure S.26. ^{13}C-NMR spectrum of compound (**Cx-2-TPA)** (400 MHz, CD_2Cl_2).

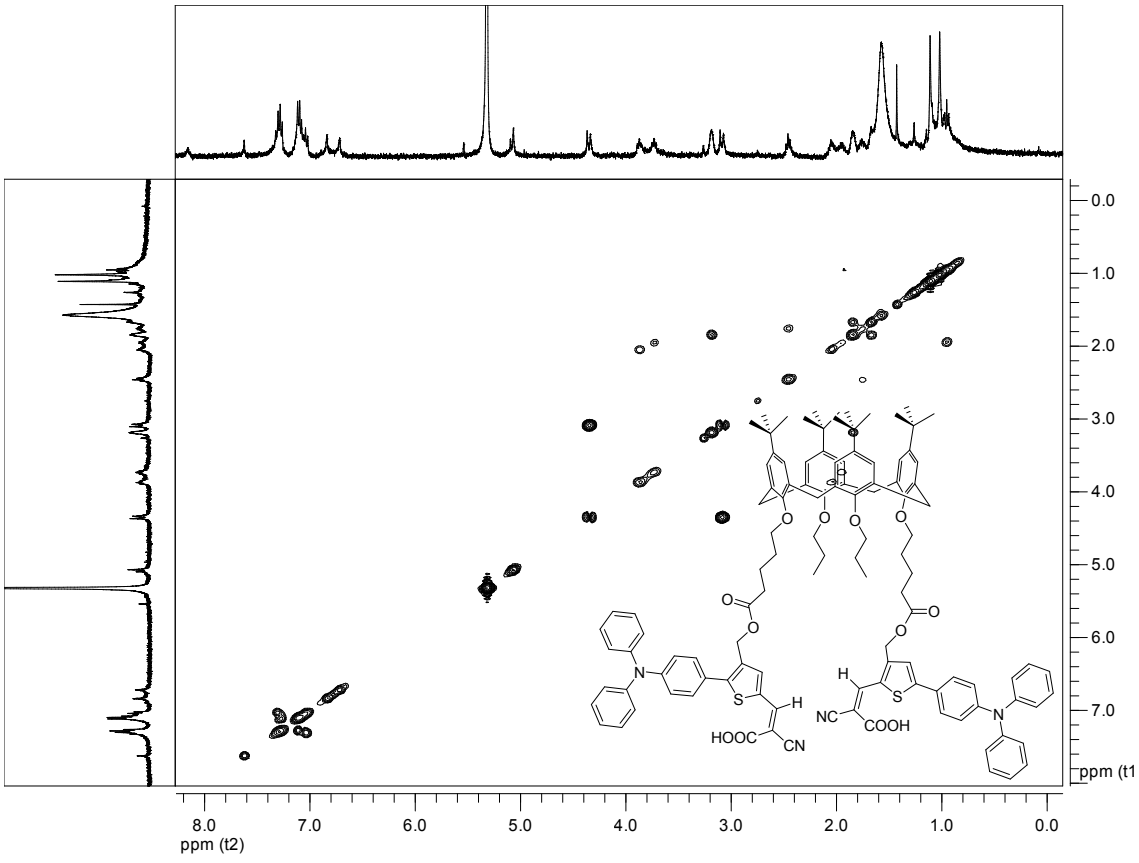


Figure S.27. ^{1}H-^{1}H COSY spectrum of compound (**Cx-2-TPA).**

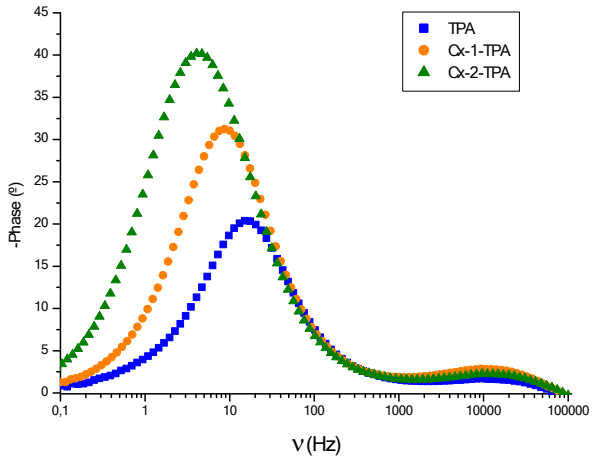


Figure S.28. Bode plot of devices prepared with (**TPA**), (**Cx-1-TPA**) and (**Cx-2-TPA**) dyes.

7. References

1. R. Pérez-Tejada; N. Martínez de Baroja; S. Franco; L. Pellejà; J. Orduna; R. Andreu; J. Garín, *Dyes Pigments*, 2015. Doi: 10.1016/j.dyepig.2015.07.026

2. a) K. Iwamoto, K. Araki, S. Shinkai, *J. Org. Chem*., 1991, **56**, 4955; b) M.J. Blesa, B. Zhao, M., Allain, F. Le Derf, M. Sallé. *Chem. Eur. J.*. 2006, **12**, 1906; c) Y. Rudzevich, K. Fischer, M. Schmidt, V. Böhmer. *Org. Biomol. Chem.,* 2005, 3, 3916; d) I. Bitter, A. Grün, G. Téth, B. Balázs, G. Horváth, L. Töke. *Tetrahedron*, 1998, 54, 3857; e) Y. Rudzevich, Synthesis and characterization of tetraurea derivatives of calix[4]arenes, *PhD Thesis, 2005*.