

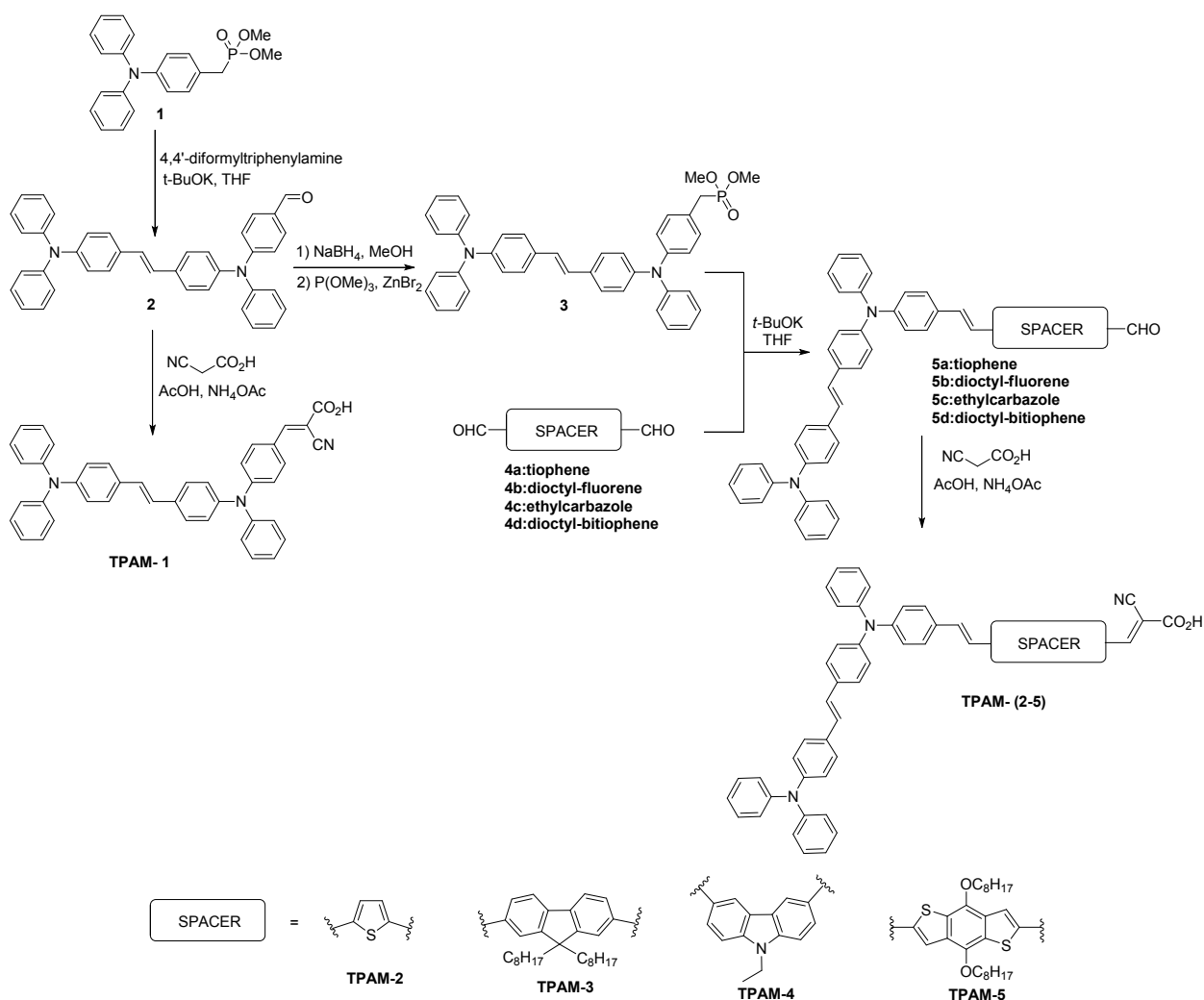
New organic dyes with high IPCE values containing two triphenylamine units as co-donor for efficient dye-sensitized solar cells

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Synthesis and characterization



Scheme S1. Synthesis of TPAM dyes.

Compound 2: The phosphonate **1** (110 mg) and 4,4'-diformyltriphenylamine (167 mg) were heated under reflux in dry THF (17 mL). A solution of *t*-BuOK (34.3 mg) in dry THF (13 mL) was added dropwise over 15 minutes under argon atmosphere. The crude product was further purified by column chromatography on silica gel (Dichloromethane/hexane 2/1). Yellow solid (53%, 80 mg). ¹H -RMN (CDCl₃, 400 MHz) δ: 9.85 (s, 1H), 7.72 (d, *J*=8Hz, 2H), 7.47 (d, *J*=8Hz, 2H), 7.41-7.36 (m, 4H), 7.31-7.27 (m, 4H), 7.23-7.20 (m, 3H), 7.17-7.13 (m, 6H), 7.10-7.04 (m, 6H), 7.01 (d, *J*=8Hz, 2H) ppm; ¹³C -RMN (CDCl₃, 100 MHz) δ: 190.4, 153.2, 147.5, 147.4, 146.1, 145.2, 134.4, 131.4, 131.3, 129.8, 129.4,

129.3, 128.1, 127.5, 127.3, 126.4, 126.1, 126.0, 125.2, 124.6, 123.5, 123.1 ppm; MS (EI): m/z 542 [M^+].

Compound 3: The aldehyde **2** (1.0 g, 1.8 mmol) and NaBH₄ (1.5 eq.) were dissolved in a mixture of dichloromethane/methanol 1/1 (10 mL), then the solution was stirred for 30 minutes. The mixture was then dissolved in dichloromethane and washed with water; the combined organic parts were dried over Na₂SO₄, filtered and evaporated. The crude obtained and ZnBr₂ (0.55 g, 2.4 mmol) were dissolved and stirred in P(OMe)₃ (1.4 g, 11.0 mmol, 1.3 mL) under argon atmosphere for 2h. The mixture was then dissolved in dichloromethane and washed with water and HCl 37% (1mL), the combined organic parts were dried over Na₂SO₄, filtered and evaporated. The crude product was further purified by column chromatography on silica gel (Dichloromethane/Ethyl acetate 1/1). yellow oil (73%, 0,855 g). ¹H -RMN (CDCl₃, 400 MHz) δ : 7.39 (*d*, $J=8\text{Hz}$, 4H), 7.30-7.26 (*m*, 6H), 7.20 (*dd*, $J_1=10\text{Hz}$, $J_2=4\text{Hz}$, 2H), 7.15-7.11 (*m*, 6H), 7.09-6.97 (*m*, 11H), 3.74 (*d*, $J=8\text{Hz}$, 6H), 3.15 (*d*, $J=20\text{Hz}$, 2H) ppm; ¹³C -RMN (CDCl₃, 100 MHz) δ : 147.6, 147.4, 147.1, 146.8, 132.1, 131.9, 130.6, 130.5, 129.3, 129.3, 127.2, 126.7, 126.5, 125.3, 124.5, 124.4, 124.2, 123.9, 123.7, 123.1, 123.0, 53.0, 52.9, 32.8, 31.5 ppm; MS (MALDI-TOF): calcd. for C₄₁H₃₇N₂O₃P 636.254; found 636.150 [M^+].

Synthesis of compounds 4a-d

The compounds **4a-c** were prepared according to previously reported synthetic procedures (see *J. Org. Chem.* 2003, **68**, 7254-7265; *Macromolecules* 2006, **39**, 3494-3499 and *European Polymer Journal*. 2000, 36, 957-963, respectively) and showed identical spectroscopic properties to those reported therein.

Compound 4d: The 4,8-bis(octyloxy)benzo[1,2-b:4,5-b']dithiophene (446 mg, 1 mmol) was dissolved in THF (10 mL) at -78 °C, then *n*-BuLi (1 mL) 2.5 M in hexanes was added, after 30 min the reaction was warmed to -10 °C and stirred for 30 min. The reaction was cooled at -78 °C and DMF (0.2 mL in 5 mL of THF) were added, the reaction was stirred for 30 min before the addition of cold water (20 mL). The crude product was further purified by column chromatography on silica gel (Dichloromethane/Hexanes 1/2). yellow solid (79%, 402 mg). ¹H NMR (CDCl₃, 600 MHz), δ (ppm): 10.1 (*s*, 2H), 8.16 (*s*, 2H), 4.33 (*t*, 4H), 1.87 (*m*, 4H), 1.52 (*m*, 8H), 1.38–1.24 (*m*, 16H), 0.86 (*t*, 6H). MS (MALDI-TOF): calcd. for C₂₈H₃₈O₄S₂ 502.2; found 502.7 [M^+].

General procedure for the synthesis of compounds 5a-d

The phosphonate **3** (100 mg, 0.16 mmol) and the corresponding π -conjugated spacer diformylated **4** (1.5 eq) were heated under reflux in dry THF (20 mL). A solution of *t*-

BuOK (27.0 mg, 0.24 mmol) in dry THF (5 mL) was added dropwise over 15 minutes under argon atmosphere. The crude product was further purified by column chromatography on silica gel (Dichloromethane/hexane 2/1).

Compound 5a: Red oil (85%, 99.6 mg). ¹H-RMN (CDCl₃, 400 MHz) δ: 9.88 (*s*, 1H), 7.69 (*d*, *J*=4Hz, 1H), 7.44-7.40 (*m*, 6H), 7.35-7.28 (*m*, 7H), 7.19-7.07 (*m*, 17H), 7.05-7.00 (*m*, 2H) ppm; ¹³C-RMN (CDCl₃, 100 MHz) δ: 182.5, 153.2, 148.3, 147.6, 147.2, 147.0, 146.3, 141.0, 137.4, 132.9, 132.6, 131.7, 129.7, 129.5, 129.3, 128.0, 127.3, 127.2, 127.1, 126.3, 126.0, 125.1, 124.6, 124.5, 123.8, 123.7, 123.0, 123.0, 118.9 ppm; MS (MALDI-TOF): calcd. for C₄₅H₃₄N₂OS 650.239; found 650.152 [M⁺].

Compound 5b: Yellow oil (59%, 91 mg). ¹H-RMN (CDCl₃, 400 MHz) δ: 10.08 (*s*, 1H), 7.89-7.83 (*m*, 3H), 7.77 (*d*, *J*=8Hz, 1H), 7.56 (*dd*, *J*₁=8Hz, *J*₂=1.3Hz, 1H), 7.51 (*br*, 1H), 7.47 (*d*, *J*=8Hz, 2H), 7.43-7.39 (*m*, 4H), 7.34-7.32 (*m*, 2H), 7.31-7.30 (*m*, 1H), 7.29-7.28 (*m*, 2H), 7.28-7.27 (*m*, 1H), 7.22-7.17 (*m*, 3H), 7.16-7.15 (*m*, 3H), 7.14-7.00 (*m*, 12H), 2.09-2.04 (*m*, 4H), 1.23-1.07 (*m*, 21H), 0.83 (*t*, *J*=8Hz, 6H), 0.67-0.61 (*m*, 4H) ppm; ¹³C-RMN (CDCl₃, 100 MHz) δ: 192.4, 152.8, 151.7, 147.6, 147.4, 147.3, 147.1, 146.6, 138.9, 138.4, 135.1, 132.4, 131.8, 131.6, 130.7, 129.4, 129.3, 128.6, 127.5, 127.3, 127.2, 127.2, 126.9, 126.5, 125.7, 124.8, 124.5, 124.2, 123.7, 123.4, 123.0, 121.2, 120.8, 119.9, 55.2, 40.3, 31.8, 30.0, 29.2, 23.8, 22.6, 14.1 ppm; MS (MALDI-TOF): calcd. for C₇₀H₇₂N₂O 956.564; found 957.241 [M⁺].

Compound 5c: Yellow oil (58%, 71 mg). ¹H-RMN (CDCl₃, 600 MHz) δ: 10.08 (*s*, 1H), 8.62 (*d*, *J*=6Hz, 1H), 8.25 (*s*, 1H), 8.01 (*dd*, *J*₁=9Hz, *J*₂=6Hz, 1H), 7.69 (*dd*, *J*₁=9Hz, *J*₂=6Hz, 1H), 7.46-7.43 (*m*, 3H), 7.41 (*d*, *J*=12Hz, 1H), 7.37-7.34 (*m*, 4H), 7.28-7.22 (*m*, 7H), 7.20 (*d*, *J*=18Hz, 1H), 7.14-7.13 (*m*, 2H), 7.10-7.09 (*m*, 6H), 7.06 (*d*, *J*=6Hz, 2H), 7.04-6.94 (*m*, 7H), 2.37 (*q*, *J*=6Hz, 2H), 1.46 (*t*, *J*=6Hz, 3H) ppm; ¹³C-RMN (CDCl₃, 150 MHz) δ: 191.8, 147.6, 147.4, 147.1, 146.8, 146.8, 144.0, 140.2, 132.2, 131.9, 130.4, 129.3, 129.3, 128.7, 127.6, 127.2, 127.2, 126.8, 126.6, 126.5, 125.4, 124.6, 124.4, 124.2, 124.1, 124.0, 123.7, 123.6, 123.2, 123.0, 118.6, 109.4, 108.9, 13.9, 8.9 ppm; MS (MALDI-TOF): calcd. for C₅₅H₄₃N₃O 761.340; found 761.337 [M⁺].

Compound 5d: Red oil (49%, 80 mg). ¹H-RMN (CDCl₃, 600 MHz) δ: 8.55 (*s*, 1H), 7.80 (*dd*, *J*₁=9Hz, *J*₂=6Hz, 4H), 7.78-7.75 (*m*, 3H), 7.71-7.68 (*m*, 2H), 7.67-7.64 (*m*, 5H), 5.54-5.53 (*m*, 3H), 7.48-7.46 (*m*, 8H), 7.45-7.38 (*m*, 8H), 4.76-4.63 (*m*, 4H), 2.32-2.24 (*m*, 4H), 1.98-1.93 (*m*, 4H), 1.79-1.68 (*m*, 16H), 1.29-1.26 (*m*, 6H) ppm; ¹³C-RMN (CDCl₃, 150 MHz) δ: 188.6, 151.9, 151.5, 151.2, 151.0, 150.4, 149.3, 148.2, 148.0, 139.8, 138.5, 136.6, 136.1, 136.0, 135.6, 134.7, 134.1, 133.4, 133.2, 132.5, 131.6, 131.1, 131.1, 130.8, 130.4, 130.2, 129.1, 128.8, 128.4, 127.7, 127.4, 127.0, 78.1, 35.8, 34.4, 33.3, 33.2, 30.0, 29.9, 26.5, 17.8 ppm; MS (MALDI-TOF): calcd. for C₆₇H₆₈N₂O₃S₂ 1012.467; found 1012.569 [M⁺].

General procedure for the synthesis of new dyes

The corresponding aldehyde (**2**, **5a-d**) (50 mg), 3-cyanoacetic acid (4 eq.), ammonium acetate (100 mg), and glacial acetic acid (15 mL) were stirred and heated at 120 °C for 10 h. The acetic acid was evaporated and the solid was washed with water and filtered. The solid obtained was purified further by crystallization from ethanol and column chromatography (**TPAM-3** and **TPAM-5**).

TPAM-1. Red solid, (40 mg, 71%), mp > 350 °C. ¹H-NMR (DMSO-*d*₆, 400 MHz) δ: 7.97 (*s*, 1H), 7.79 (*d*, *J*=8Hz, 2H), 7.49 (*d*, *J*=8Hz, 2H), 7.40 (*d*, *J*=8Hz, 2H), 7.34-7.31 (*m*, 2H), 7.23-7.20 (*m*, 4H), 7.15-7.09 (*m*, 3H), 7.03 (*br*, 4H), 6.98-6.93 (*m*, 6H), 6.85 (*br*, 4H) ppm; ¹³C-NMR (DMSO-*d*₆, 100 MHz) δ: 169.7, 161.4, 146.9, 146.7, 145.0, 132.4, 131.4, 130.0, 129.6, 127.7, 127.6, 126.2, 126.0, 125.9, 124.1, 123.3, 123.0, 119.3, 99.5, 63.1 ppm; FTIR (KBr) ν: 3390 (O-H), 2218 (CN), 1718 (C=O), 1506, 1487 cm⁻¹; MS (MALDI-TOF): calcd. for C₄₂H₃₁N₃O₂ 609.241; found 609.237 [M⁺].

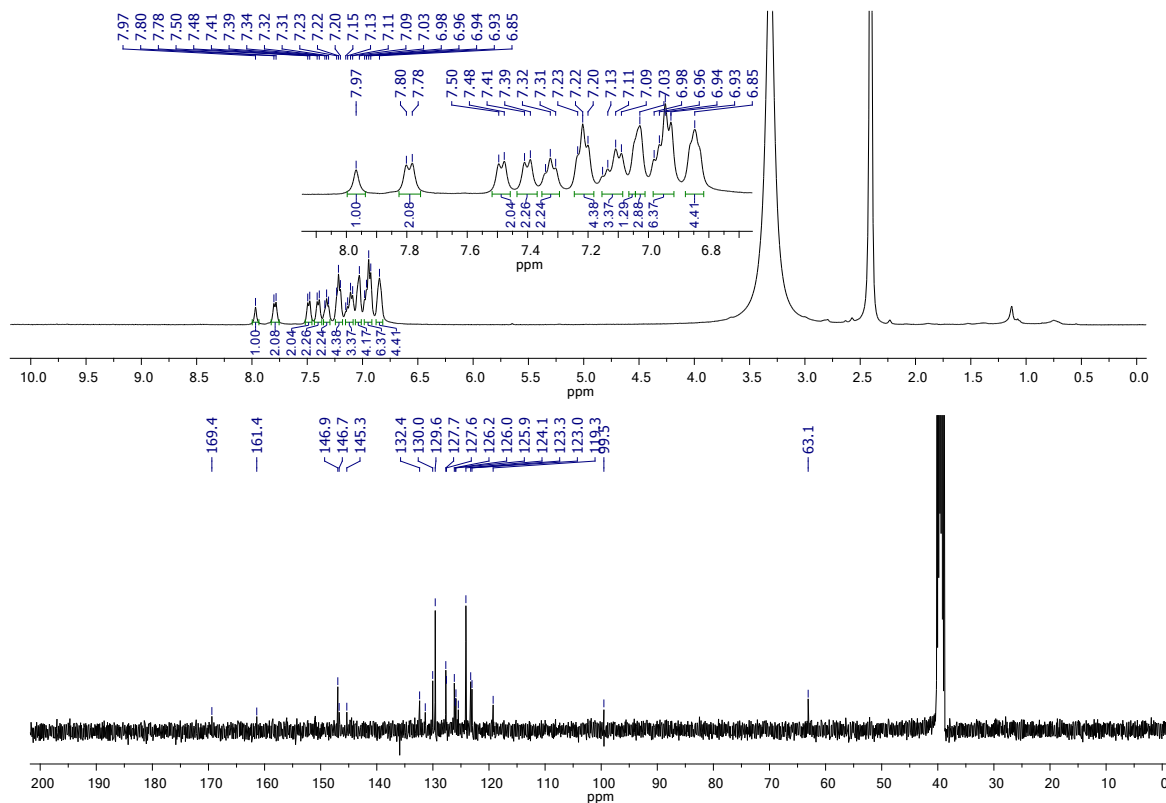
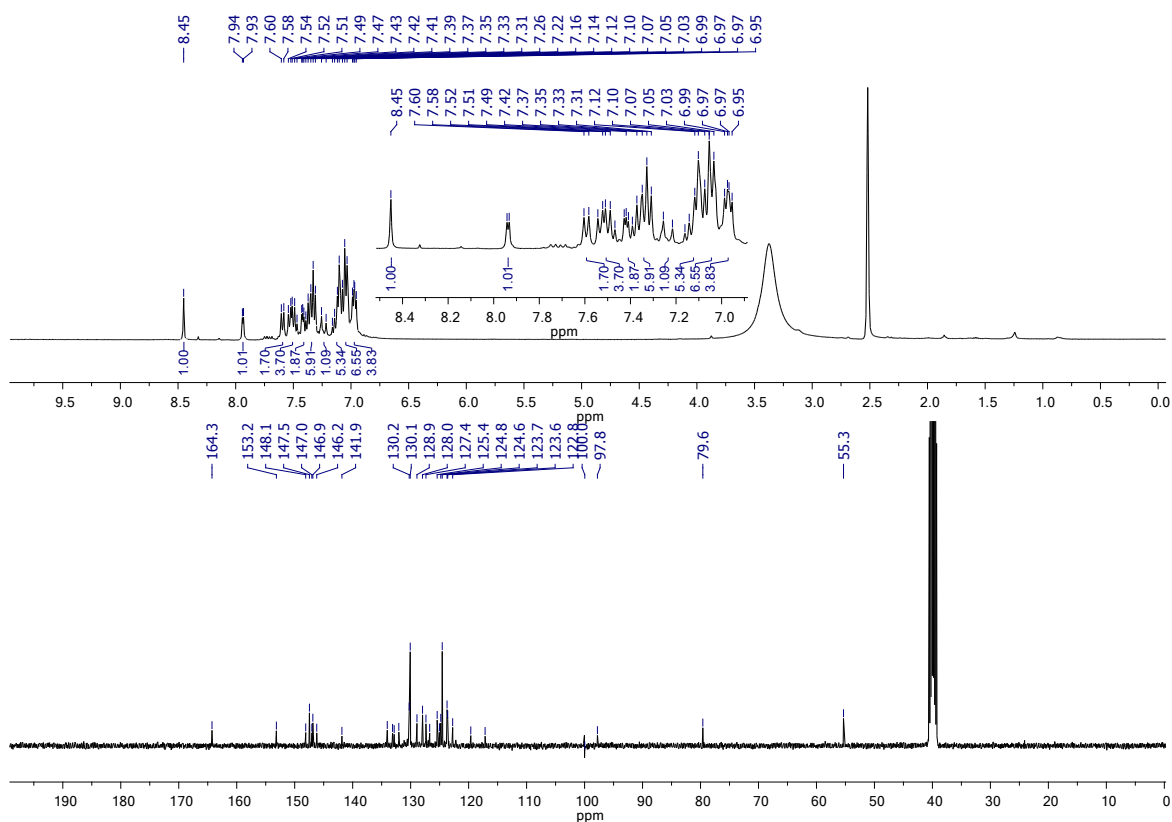


Fig S1. ^1H and ^{13}C -NMR spectra of **TPAM-1** ($\text{DMSO-}d_6$, 400 MHz, 25 $^\circ\text{C}$).

TPAM-2. Black solid, (32 mg, 48%), mp > 350 $^\circ\text{C}$. ^1H -NMR ($\text{DMSO-}d_6$, 400 MHz) δ : 8.45 (s, 1H), 7.94 (d, $J=4\text{Hz}$, 1H), 7.59 (d, $J=8\text{Hz}$, 2H), 7.54-7.47 (m, 4H), 7.43-7.41 (m, 2H), 7.37-7.31 (m, 6H), 7.24 (d, $J=16\text{Hz}$, 1H), 7.16-7.10 (m, 6H), 7.07-7.03 (m, 7H), 6.99-6.95 (m, 4H) ppm; ^{13}C -NMR ($\text{DMSO-}d_6$, 100 MHz) δ : 164.3, 153.2, 148.1, 147.5, 147.0, 146.9, 146.2, 134.0, 133.1, 132.8, 132.0, 130.3, 130.1, 128.9, 128.0, 127.9, 127.4, 126.7, 125.4, 125.0, 124.8, 124.6, 123.7, 123.6, 122.8, 122.2, 117.2, 100.0, 97.9, 79.3, 55.6 ppm; FTIR (KBr) ν : 3398 (O-H), 2230 (CN), 1709 (C=O), 1431 cm^{-1} ; MS (MALDI-TOF): calcd. for $\text{C}_{48}\text{H}_{35}\text{N}_3\text{O}_2\text{S}$ 717.245; found 717.235 [M^+].



2H), 7.73 (*d*, $J=8\text{Hz}$, 1H), 7.58 (*d*, $J=8\text{Hz}$, 2H), 7.50 (*t*, $J=8\text{Hz}$, 4H), 7.39-7.30 (*m*, 7H), 7.26 (*d*, $J=16\text{Hz}$, 1H), 7.09-7.03 (*m*, 15H), 6.96 (*d*, $J=8\text{Hz}$, 2H), 4.53 (*q*, $J=4\text{Hz}$, 2H), 1.36 (*t*, $J=4\text{Hz}$, 3H) ppm; ^{13}C -NMR (DMSO- d_6 , 100 MHz) δ : 164.6, 147.5, 147.3, 146.9, 146.7, 146.5, 143.0, 140.3, 132.6, 132.4, 132.2, 130.6, 130.1, 130.0, 128.1, 127.9, 127.0, 126.8, 126.5, 125.9, 125.8, 124.8, 124.5, 124.1, 124.0, 123.9, 123.7, 123.6, 123.2, 123.1, 123.0, 119.1, 110.9, 110.8, 55.4, 31.2, 14.3 ppm; FTIR (KBr) ν : 3414 (O-H), 2923, 2220 (CN), 1606 (C=O), 1190 cm^{-1} ; MS (MALDI-TOF): calcd. for $\text{C}_{58}\text{H}_{44}\text{N}_4\text{O}_2$ 828.346; found 828.389 [M^+].

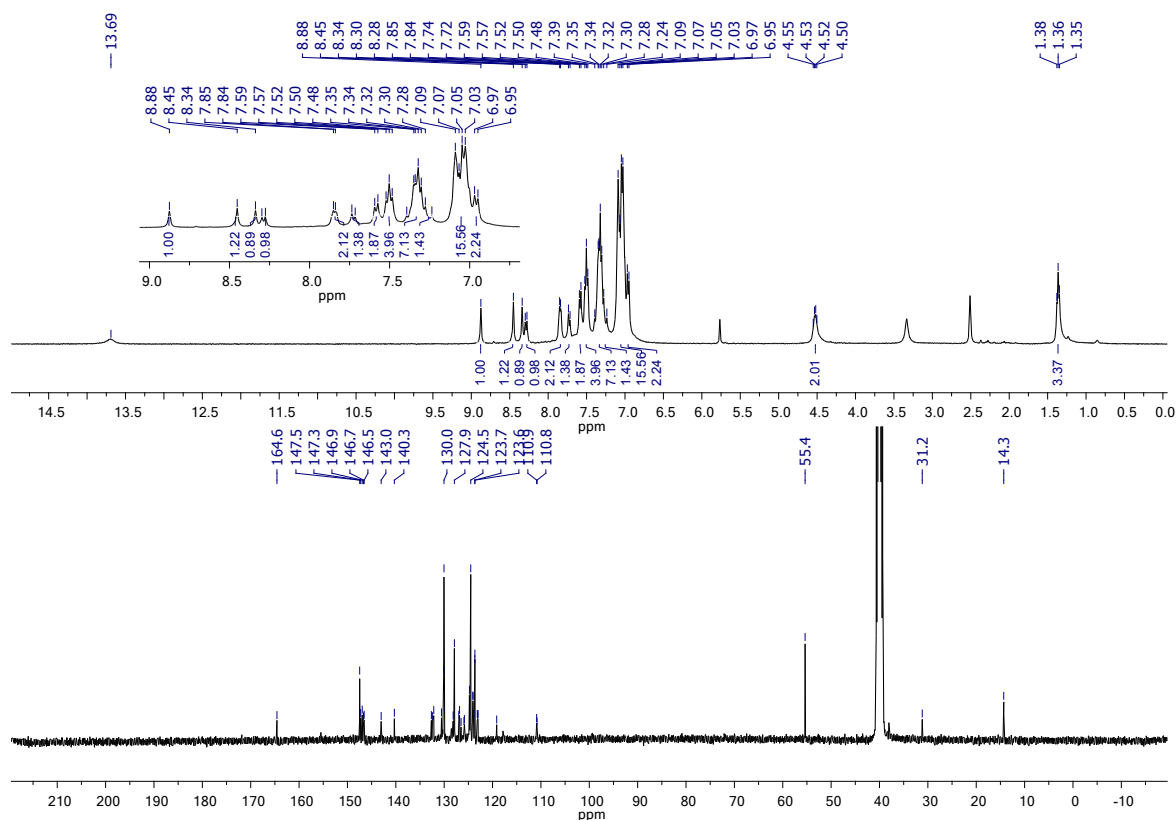


Fig S4. ^1H and ^{13}C -NMR spectra of **TPAM-4** (DMSO- d_6 , 400 MHz, 25 $^\circ\text{C}$).

TPAM-5. Red solid, (75 mg, 54%), mp > 350 $^\circ\text{C}$. ^1H -NMR (DMSO- d_6 , 400 MHz) δ : 8.40 (*s*, 1H), 8.27 (*s*, 1H), 7.57-7.48 (*m*, 8H), 7.37 (*d*, $J=8\text{Hz}$, 2H), 7.33 (*d*, $J=8\text{Hz}$, 2H), 7.31 (*d*, $J=8\text{Hz}$, 2H), 7.14 (*d*, $J=8\text{Hz}$, 2H), 7.11-7.01 (*m*, 12H), 6.99 (*d*, $J=8\text{Hz}$, 2H), 6.96 (*d*, $J=8\text{Hz}$, 2H), 4.33-4.24 (*m*, 4H), 1.83-1.77 (*m*, 4H), 1.55-1.48 (*m*, 4H), 1.33-1.23 (*m*, 16H), 0.87-0.84 (*m*, 6H) ppm; ^{13}C -NMR (DMSO- d_6 , 100 MHz). δ : 147.7, 147.5, 147.0, 146.3, 145.3, 143.4, 132.9, 132.1, 131.7, 130.6, 130.2, 130.0, 129.9, 128.7, 128.5, 128.0, 127.9, 127.2, 126.7, 125.3, 124.6, 124.5, 124.4, 123.7, 123.1, 55.4, 31.7, 30.4, 29.2, 29.1, 26.0,

25.8, 22.6, 14.4 ppm; FTIR (KBr) ν : 3350 (O-H), 2922, 2213 (CN), 1589 (C=O), 1273 cm^{-1} ; MS (MALDI-TOF): calcd. for $\text{C}_{70}\text{H}_{69}\text{N}_3\text{O}_4\text{S}_2$ 1079.472; found 1079.566 [M^+].

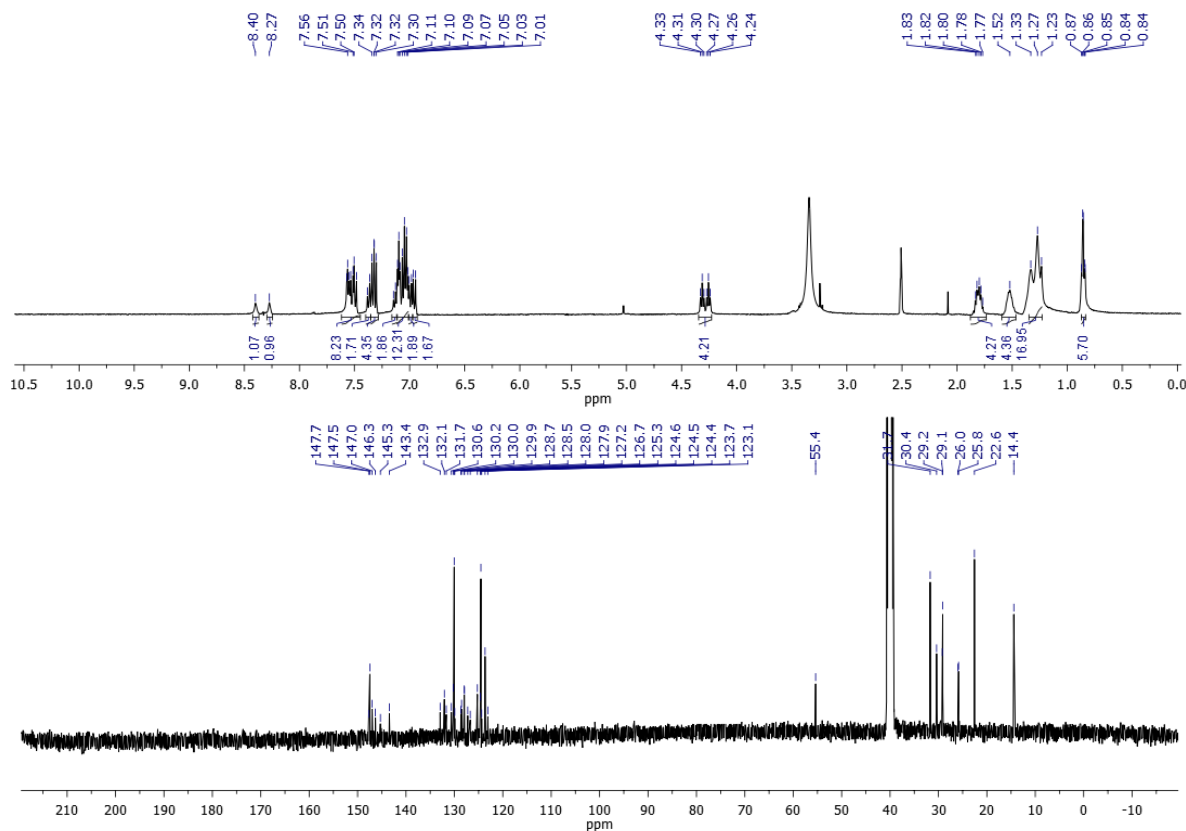


Fig S5. ^1H and ^{13}C -NMR spectra of **TPAM-5** ($\text{DMSO-}d_6$, 400 MHz, 25 °C).

Electrochemical measurements. We employed cyclic voltammetry to determine the redox potentials of these bis-TPA-based dyes; the electrochemical reactions of these compounds were measured under ambient conditions. The electrochemical data are summarized in Table S1.

Table S1. Electrochemical data for dyes **TPAM-(1-5)**^a

Dyes	$E^1_{\text{ox}}/\text{V}^b$	$E^2_{\text{ox}}/\text{V}^b$
TPAM-1	0.352	0.568
TPAM-2	-----	0.300
TPAM-3	0.316	0.572
TPAM-4	0.340	0.500
TPAM-5	0.328	0.572

^a Values obtained from square-wave voltammetry. ^b E_{pa} reported due to chemical irreversibility

All dyes exhibit two waves for oxidation (E_{ox}) with exception of **TPAM-2** that exhibit a electrochemically irreversible oxidation process, consequence of the coalescence of the first and second electron oxidations into a single two-electron wave, corresponding to the HOMO and HOMO-1 energies of the dyes. Figure S6 shows representative cyclic voltammograms for **TPAM-(1-5)** in DCM (0.5 mM) containing tetrabutylammonium hexafluorophosphate (TBAPF₆, 0.1 M). In the case of **TPAM-1**, two oxidation reaction was observed at E_{ox} = +0.352 and +0.568 V corresponding to the formation of [TPAM-1]⁺ and [TPAM-1]⁺⁺. The potentials for the first oxidations of **TPAM-(2-5)** show significant cathodic shifts with increasing electron-donating ability of the amino substituent as compared to these of **TPAM-1**, chain lengthening promotes a decrease in the redox potentials, due to the stabilization of the charges of the oxidized species along the conjugated chain.

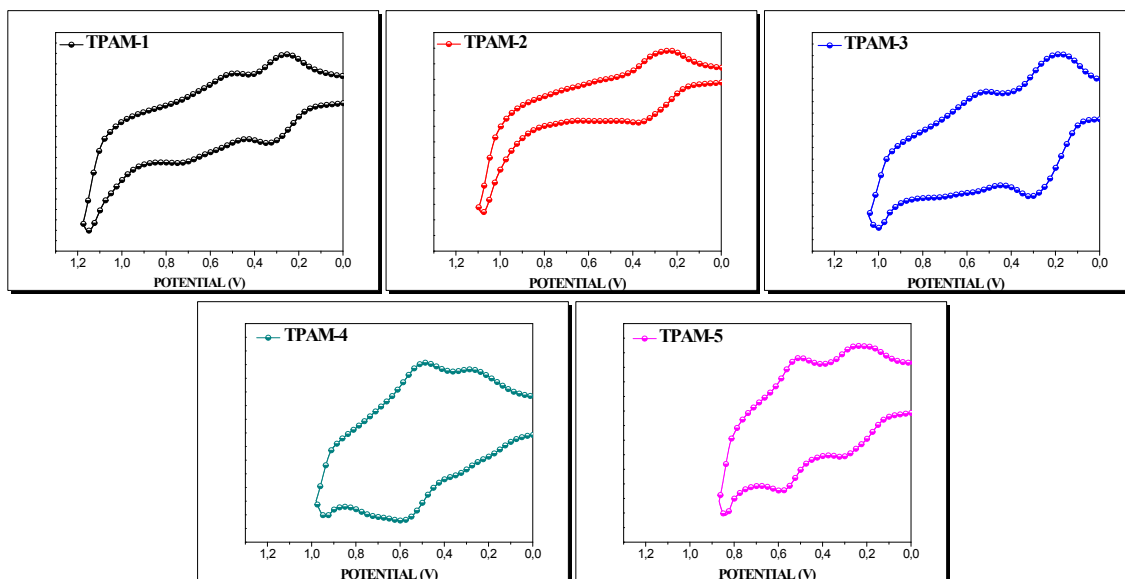


Figure S6. Cyclic voltammograms of **TPAM-(1-5)** in DCM vs Fc/Fc⁺

