Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Donor-free oligothiophene based dyes with di-anchor architecture for Dye-Sensitized Solar Cells

John Marques dos Santos,[¶a] Ellie Tanaka,[¶b] Alan A. Wiles,[a] Graeme Cooke*[a] and Neil Robertson*[b]

[a.] *School of Chemistry, Joseph Black Building, University of Glasgow, Glasgow, G12 8QQ, UK.*

[b.] *School of Chemistry, EaStCHEM, University of Edinburgh, King's Buildings, David Brewster Road, Edinburgh, Scotland EH9 3FJ, UK.*

Email: *Graeme.Cooke@glasgow.ac.uk*

Electronic Supporting Information

1. ESI 1 Experimental section.

General: Materials and characterization.

Reagents were purchased from Sigma Aldrich®, Fluorochem®, TCI®, Alfa Aesar®, Acros® or Fisher Scientific® and used as received. Dry solvents were obtained from Innovative Technology inc. Pure Solv 400-5-MD solvent purification system (activated alumina columns) or Sigma Aldrich®. Column chromatography was carried out using silica gel (Sigma-Aldrich) 40 – 63 μm particle size, 60 Å pore size. The solvent system is specified in each experiment. Thin-layer chromatography (TLC) was performed using Merck silica gel 60 covered aluminium plates F254. NMR spectra were obtained with either a Bruker Avance III 400 or a Bruker Avance III 500 spectrometers. Mass spectrometry was obtained from the mass spectrometry service at the University of Glasgow and from the EPSRC UK National Mass Spectrometry Facility at Swansea University. All the spectroscopic (except NMR) and electrochemical data were processed using Origin Pro 8.5 software suite. Density functional theory (DFT) calculations were performed using Gaussian '09 software suite.[1] Molecular geometries were initially optimized semi-empirically (PM6) and then re-optimized by DFT. Global minimum states were confirmed by the absence of imaginary frequencies from vibrational frequency calculations. To facilitate the convergence of the geometry optimizations, long alkyl chains were replaced by methyl units.

2. Molecular design, synthetic procedures and characterization data of new compounds.

The molecules in this study were designed to feature two anchoring (cyanoacrylate) units and an oligothiophene backbone. Two generations of dyes were designed. The first-generation possesses 5 thiophene units with two acetylene residues (**5T2A**, **5T2A-E**), whereas the second-generation is more conjugated and feature 8 thiophene units and an extra diacetylene residue (**8T4A** and **8T4A-E**). EDOT residues were inserted in one dye from each generation (identified by the suffix E). **Fig S1** shows a schematic representation of dyes from both generations in a typical linear conformation and the desired V (first generation) or U (second generation) conformation for this study. The V and U conformations should facilitate the anchoring process at the surface of the TiO_2 semiconductor.

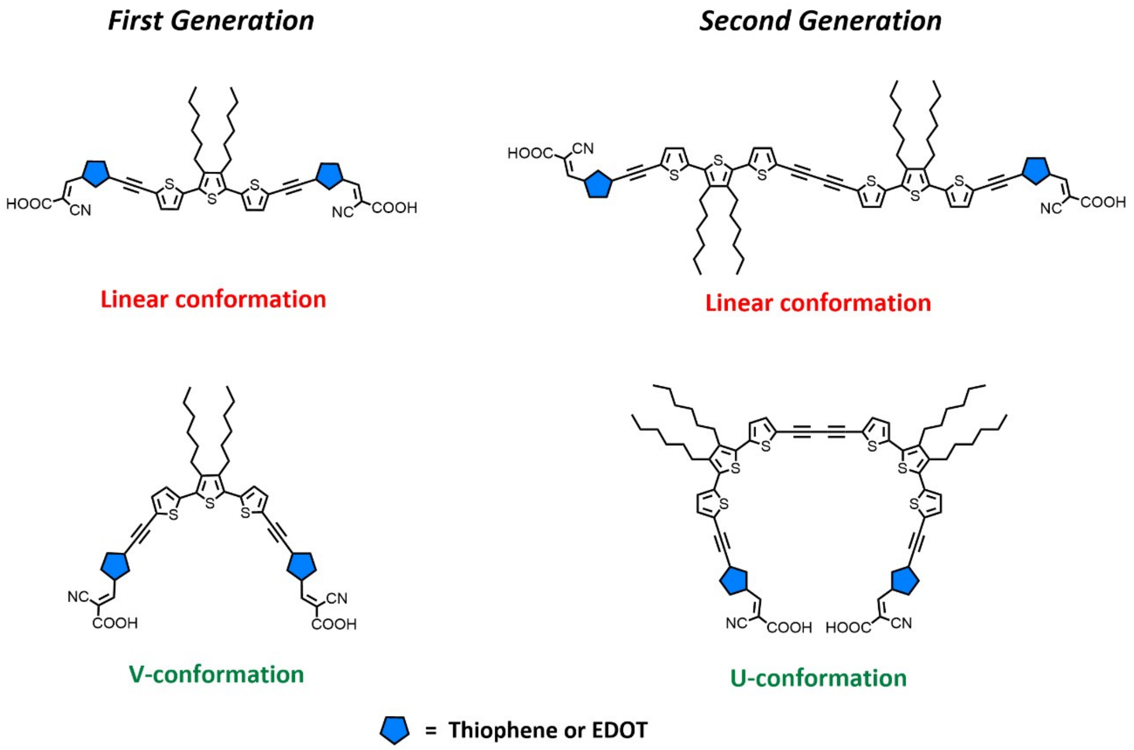
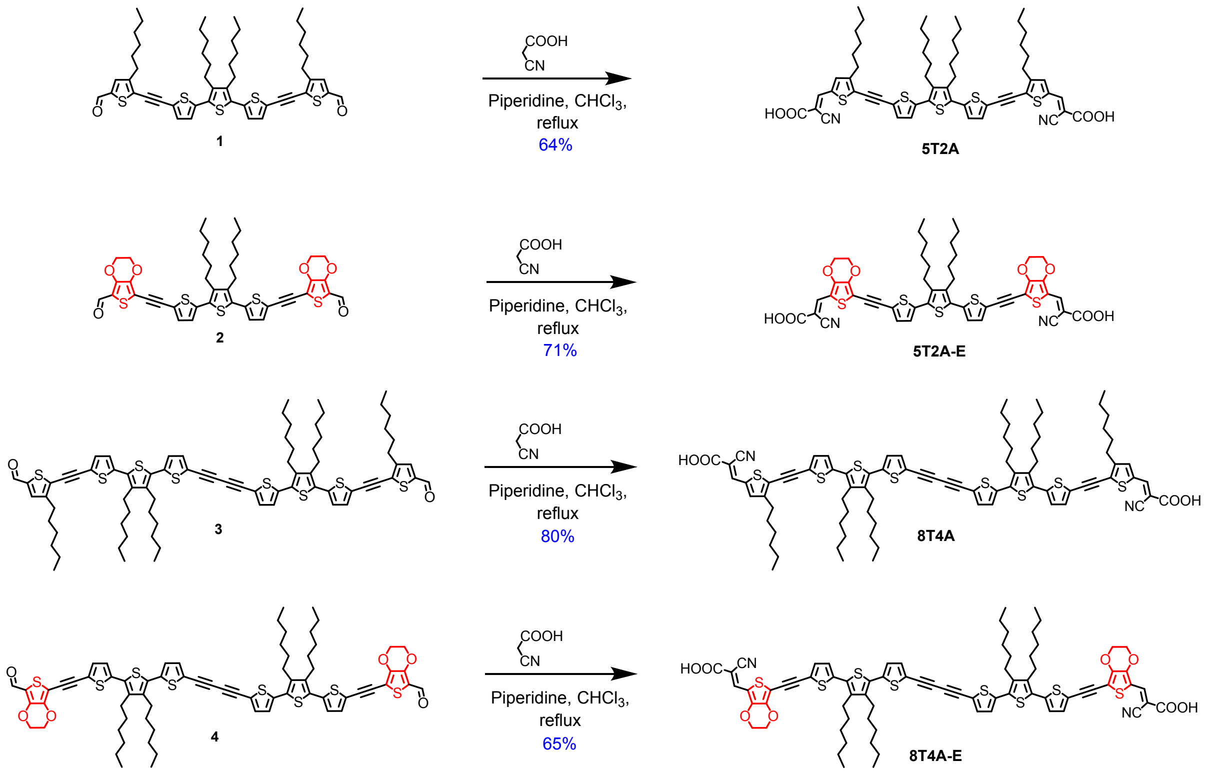


Figure S1. Schematic representation of first and second-generation dyes in a linear and a V (first generation) or U (second generation)-type conformation.

The synthesis of the dyes **5T2A**, **5T2A-E**, **8T4A** and **8T4A-E** was accomplished as depicted in **Scheme S1**. The di-aldehydes **1**, **2**, **3** and **4** were obtained as previously reported,[2] and then they were reacted with 2-cyanoacetic acid *via* Knoevenagel condensation with yields above 60%.



Scheme S1. Synthesis of **5T2A**, **5T2A-E**, **8T4A** and **8T4A-E.**

Synthesis of **5T2A:**

To a solution of compound **1** (100 mg, 0.110 mmol) and 2-cyanoacetic acid (25 mg; 0.29 mmol) in chloroform (15 mL) under an argon atmosphere was added three drops of piperidine. The mixture was stirred under reflux for 24 h and then allowed to cool to room temperature. The solvent was evaporated under reduced pressure and the resulting solid was washed with hexane and then with a mixture of 10% chloroform in hexane to yield **5T2A** as a violet solid (70 mg, 64%). Mp > 300 °C; ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.37 (s, 2H), 7.85 (s, 2H), 7.46 (d, *J* = 3.9 Hz, 2H), 7.20 (d, *J* = 3.9 Hz, 2H), 2.72–2.62 (m, 8H), 1.65–1.58 (m, 4H), 1.51–1.43 (m, 4H), 1.42–1.36 (m, 4H), 1.33–1.24 (m, 20H), 0.90–0.80 (m, 12H); ^{13}C NMR (101 MHz, $(CD_3)_2SO$) δ 163.1, 148.4, 145.2, 141.0, 139.7, 139.6, 138.0, 135.6, 134.3, 129.2, 126.6, 125.2, 120.5, 116.3, 93.0, 86.8, 30.8, 30.7, 29.7, 29.2, 28.7, 28.5, 28.0, 27.5, 21.9, 13.8, 13.8; *m/z* (MALDI$^+$) 985.3259 [M-H$^-$] ($C_{56}H_{61}N_2O_4S_5$ requires 985.3240).

Synthesis of **5T2A-E:**

To a solution of compound **2** (40 mg, 0.050 mmol) and 2-cyanoacetic acid (10.6 mg; 0.125 mmol) in chloroform (5 mL) under an argon atmosphere was added two drops of piperidine. The mixture was stirred under reflux for 24 h and then allowed to cool to room temperature. The solvent was evaporated under reduced pressure and the resulting solid was washed with hexane and then with a mixture of 10% chloroform in hexane to yield **5T2A-E** as a violet solid (34 mg, 74%). Mp > 300 °C; ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 8.13 (s, 2H), 7.52 (d, *J* = 3.9 Hz, 2H), 7.26 (d, *J* = 3.9 Hz, 2H), 4.44 (m, 8H), 2.75–2.66 (m, 4H), 1.50 (m, 4H), 1.45–1.36 (m, 4H), 1.30 (m, 8H), 0.87 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $(CD_3)_2SO$) δ 163.5, 147.8, 144.4, 141.3, 139.9, 138.2, 134.8, 129.3, 127.0, 120.5, 116.7, 111.7, 105.5, 96.3, 94.0, 85.0, 65.7, 65.0, 30.8, 29.9, 28.8, 27.6, 22.0; *m/z* (MALDI$^+$) 934.1547 [M$^+$] ($C_{48}H_{42}N_2O_8S_5$ requires 934.1545).

Synthesis of **8T4A:**

To a solution of compound **3** (50 mg, 0.038 mmol) and 2-cyanoacetic acid (13.0 mg; 0.153 mmol) in chloroform (5 mL) under an argon atmosphere was added two drops of piperidine. The mixture was stirred under reflux for 24 h and then allowed to cool to room temperature. The solvent was evaporated under reduced pressure and the resulting solid was washed with hexane and then with a mixture of 10% chloroform in hexane to yield **8T4A** as a violet solid (44 mg, 80%). Mp > 300 °C; ^{1}H NMR (500 MHz, THF-d8) 8.11 (s, 2 H), 7.56 (s, 2 H), 7.31 (d, *J* = 3.9, 2 H), 7.27 (d, *J* = 3.9, 2 H), 7.09 (d, *J* = 3.9, 2 H), 7.06 (d, *J* = 3.9, 2 H), 2.71–2.65 (m, 12 H), 1.49 (12 H, t, *J* = 11.0), 1.40–1.34 (m, 8 H), 1.31–1.22 (m, 28 H), 0.85–0.76 (m, 18 H).; ^{13}C NMR (101 MHz, THF-d8) 163.2, 148.5, 143.9, 143.9, 141.4, 141.2, 139.2, 138.6, 137.4, 137.3, 135.3, 133.5, 130.1, 129.7, 126.3, 126.1, 121.8, 121.6, 121.1, 115.8, 92.6, 86.6, 78.7, 77.0, 43.8, 31.5,31.4, 29.9 29.0, 28.7, 24.3, 24.2, 22.5, 22.5, 13.4, 13.4; *m/z* (MALDI$^+$) 1448.4817 [M$^+$] ($C_{84}H_{92}N_2O_4S_8$ requires 1448.4823).

Synthesis of **8T4A-E**:

To a solution of compound **4** (50 mg, 0.038 mmol) and 2-cyanoacetic acid (13.0 mg; 0.153 mmol) in chloroform (5 mL) under an argon atmosphere was added two drops of piperidine. The mixture was stirred under reflux for 24 h and then allowed to cool to room temperature. The solvent was evaporated under reduced pressure and the resulting solid was washed with hexane and then with a mixture of 10% chloroform in hexane to yield **8T4A-E** as a violet solid (44 mg, 80%). Mp > 300 ^{o}C; ^{1}H NMR (400 MHz, THF-d8) δ 8.19 (s, 2H), 7.31 (d, *J* = 3.9 Hz, 2H), 7.27 (d, *J* = 3.9 Hz, 2H), 7.08 (d, *J* = 3.9 Hz, 2H), 7.06 (d, *J* = 3.9 Hz, 2H), 4.34–4.25 (m, 8H), 2.71–2.66 (m, 8H), 1.53–1.45 (m, 8H), 1.41–1.32 (m, 8H), 1.27–1.22 (m, 16H), 0.85–0.78 (m, 12H); ^{13}C NMR (101 MHz, THF-d8) δ 163.0, 147.1, 144.1, 143.3, 142.9, 141.4, 141.1, 139.5, 139.2, 138.6, 135.3, 133.7, 130.1, 129.7, 126..3, 126.1, 121.7, 121.1, 115.8, 112.7, 93.5, 84.6, 78.7, 77.0, 65.5, 65.0, 31.5, 31.5, 30.5, 29.6, 29.4, 29.4, 28.0, 28.0, 27.7, 22.5, 13.4, 13.4.*m/z* (MALDI^{+}) 1396.3061 [M^{+}] ($C_{76}H_{72}N_2O_8S_8$ requires 1396.3054).

3. Spectra.

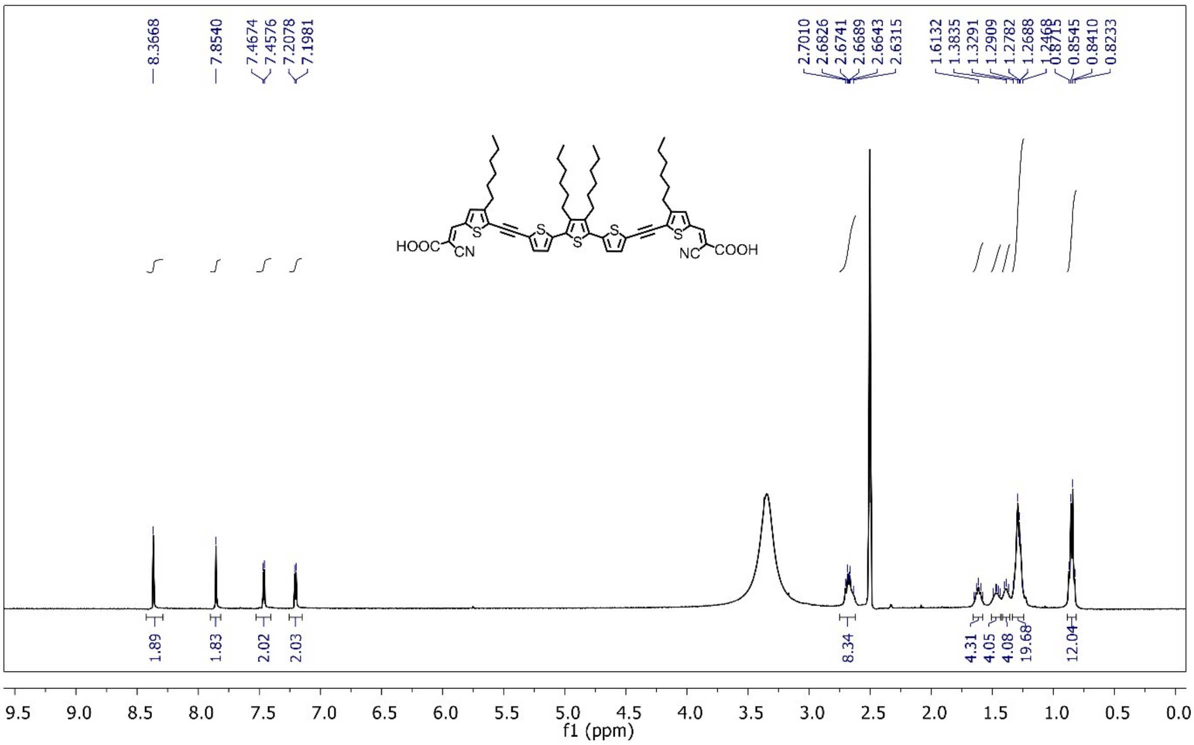


Figure S2. ^{1}H NMR (400 MHz, $(CD_3)_2SO$) of **5T2A**.

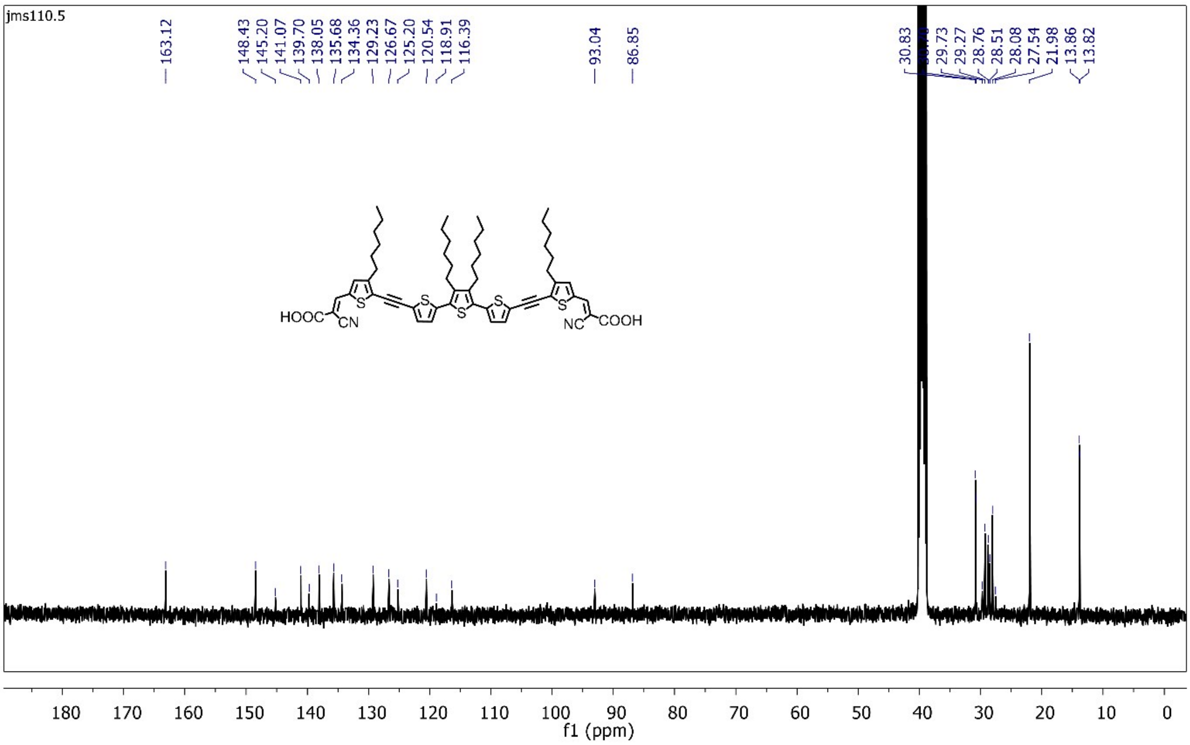


Figure S3. ^{13}C NMR (101 MHz, $(CD_3)_2SO$) of **5T2A**.

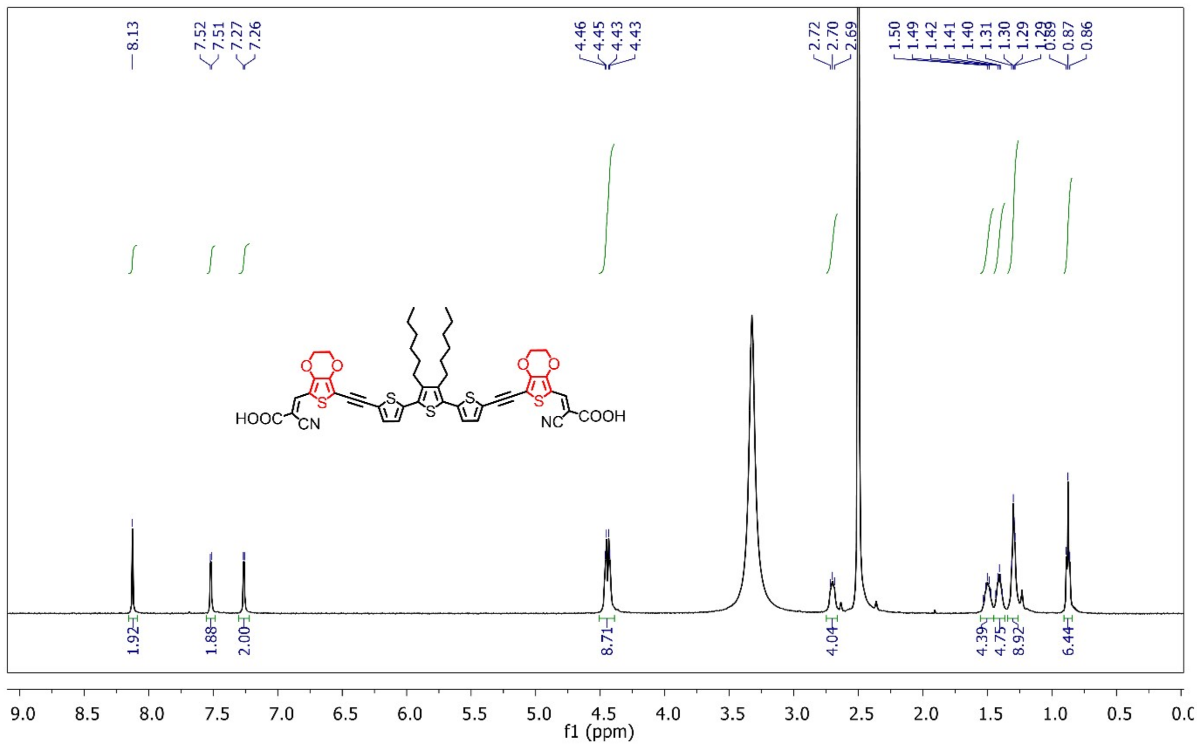


Figure S4. ^{1}H NMR (400 MHz, $(CD_3)_2SO$) of **5T2A-E**.

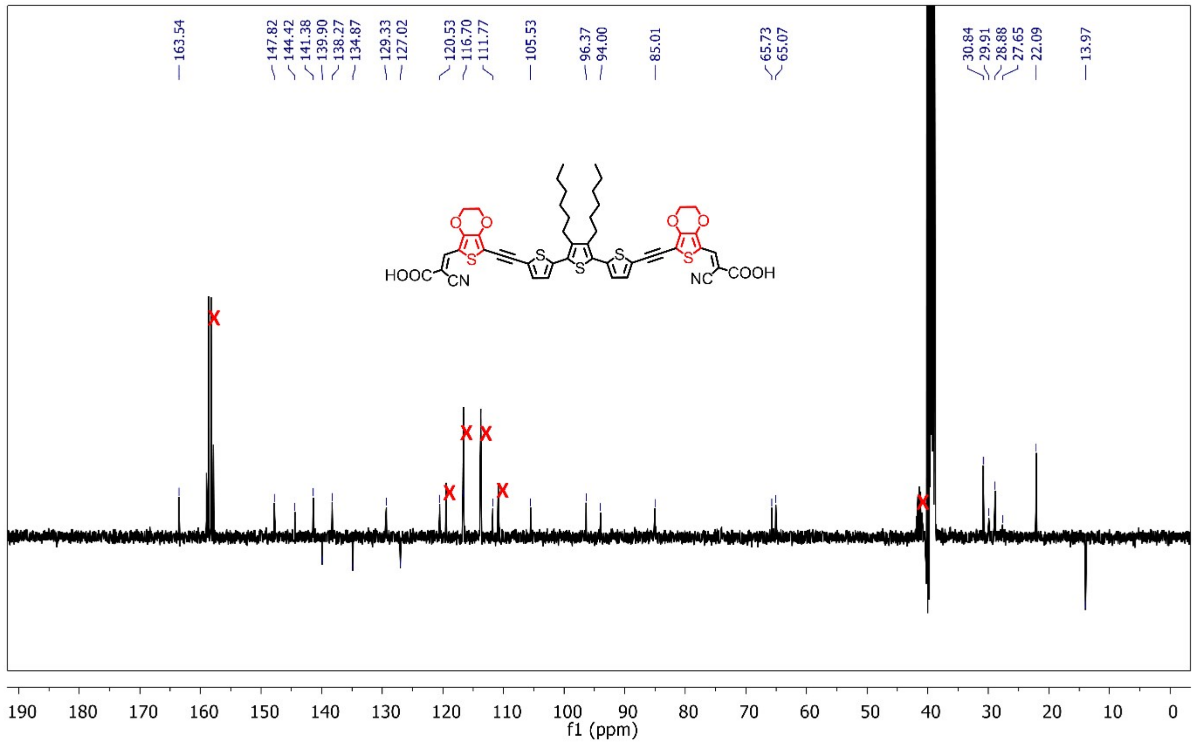


Figure S5. ^{13}C NMR (101 MHz, $(CD_3)_2SO$ + acetic acid-d4) of **5T2A-E**.

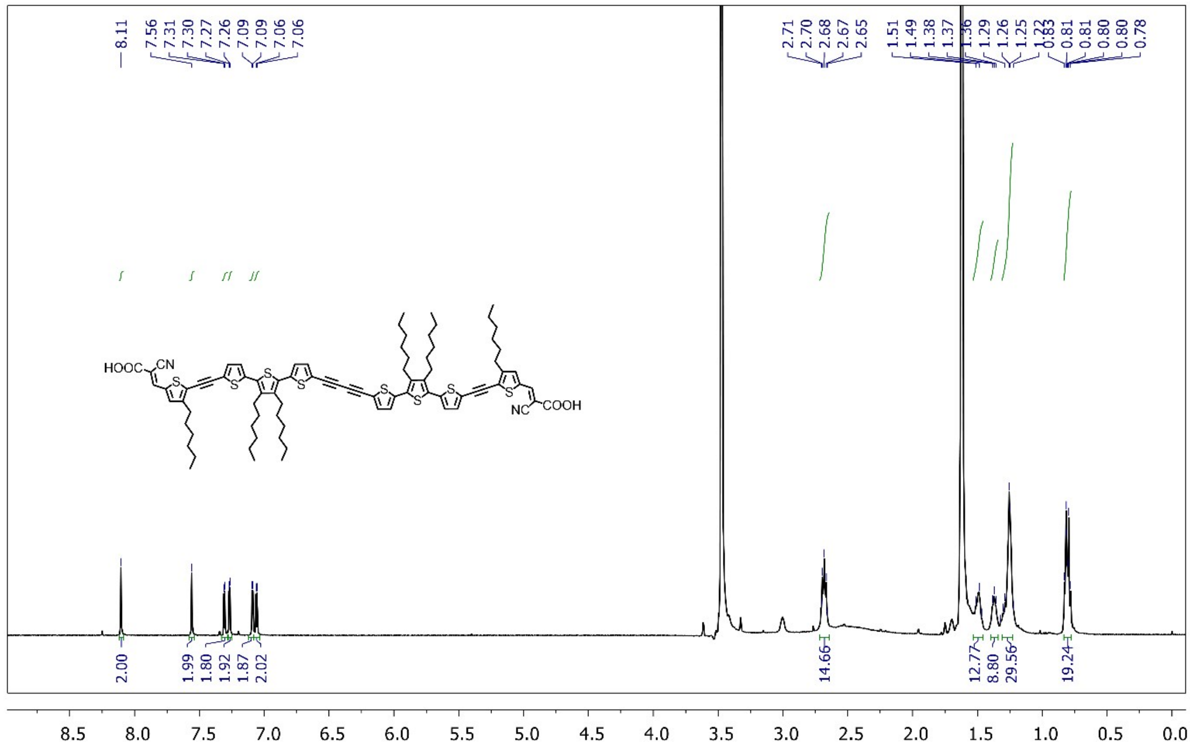


Figure S6. ^{1}H NMR (500 MHz, THF-d8) of **8T4A**.

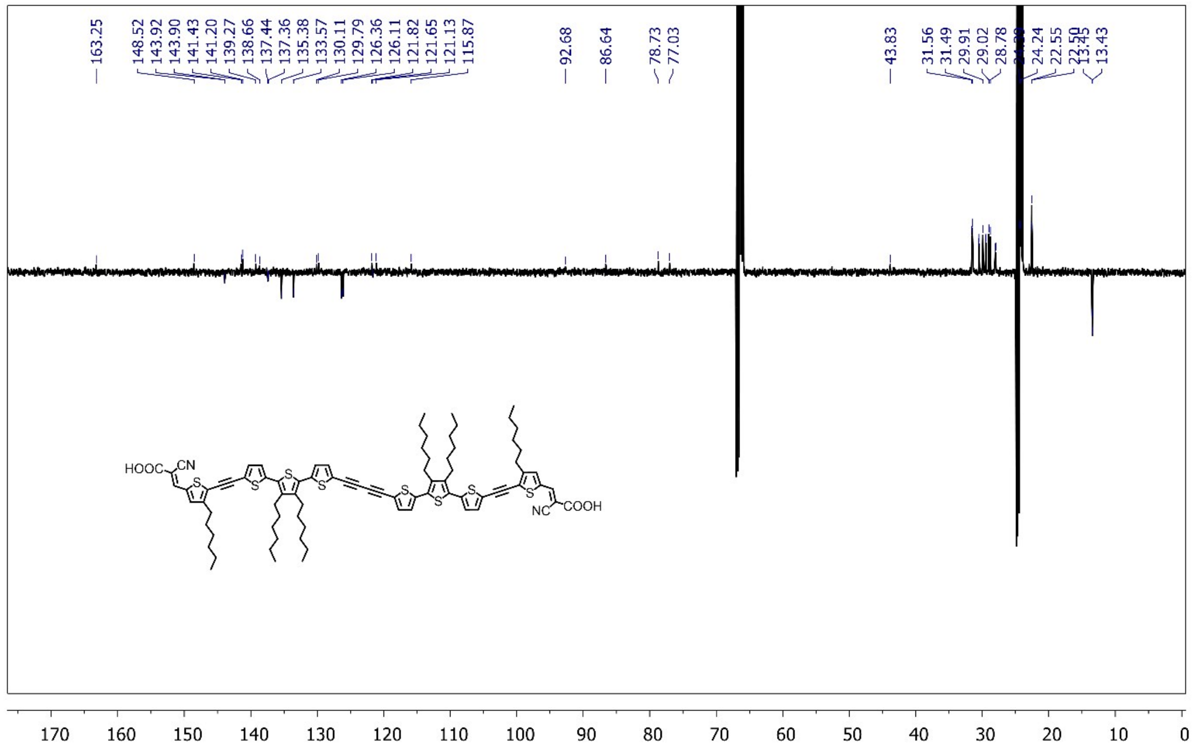


Figure S7. ^{13}C NMR (101 MHz, THF-d8) of **8T4A**.

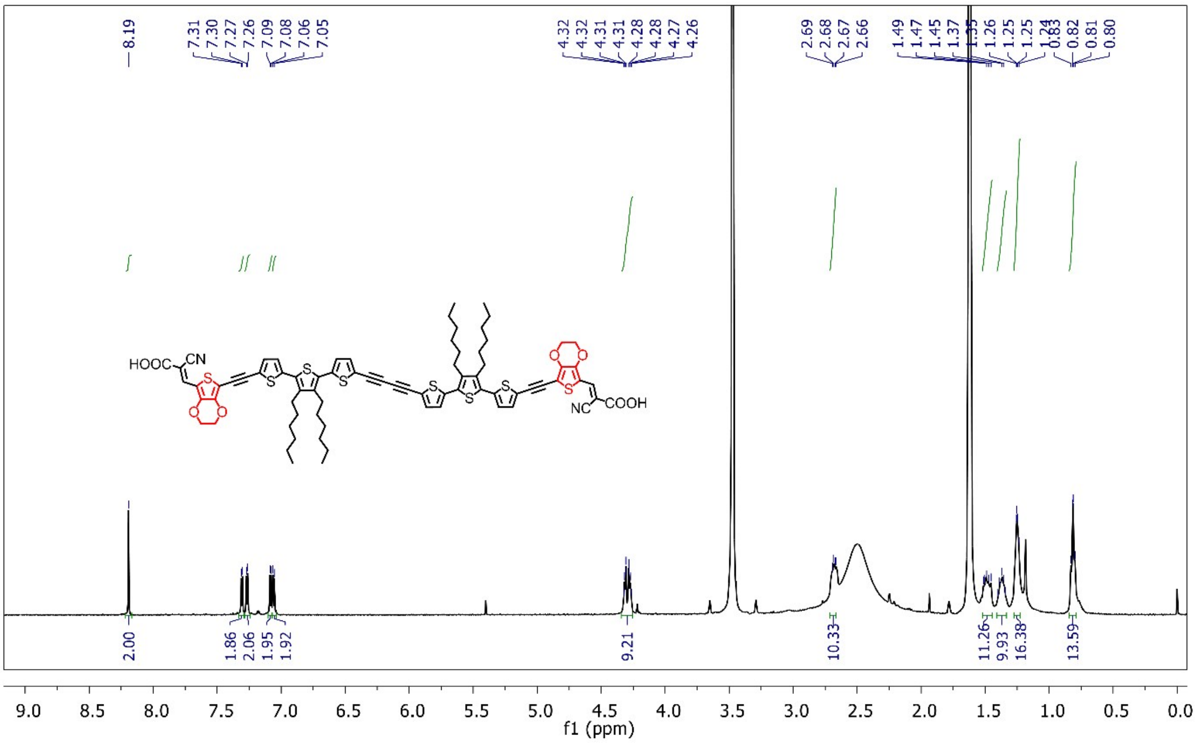


Figure S8. ^{1}H NMR (400 MHz, THF-d8) of **8T4A-E**.

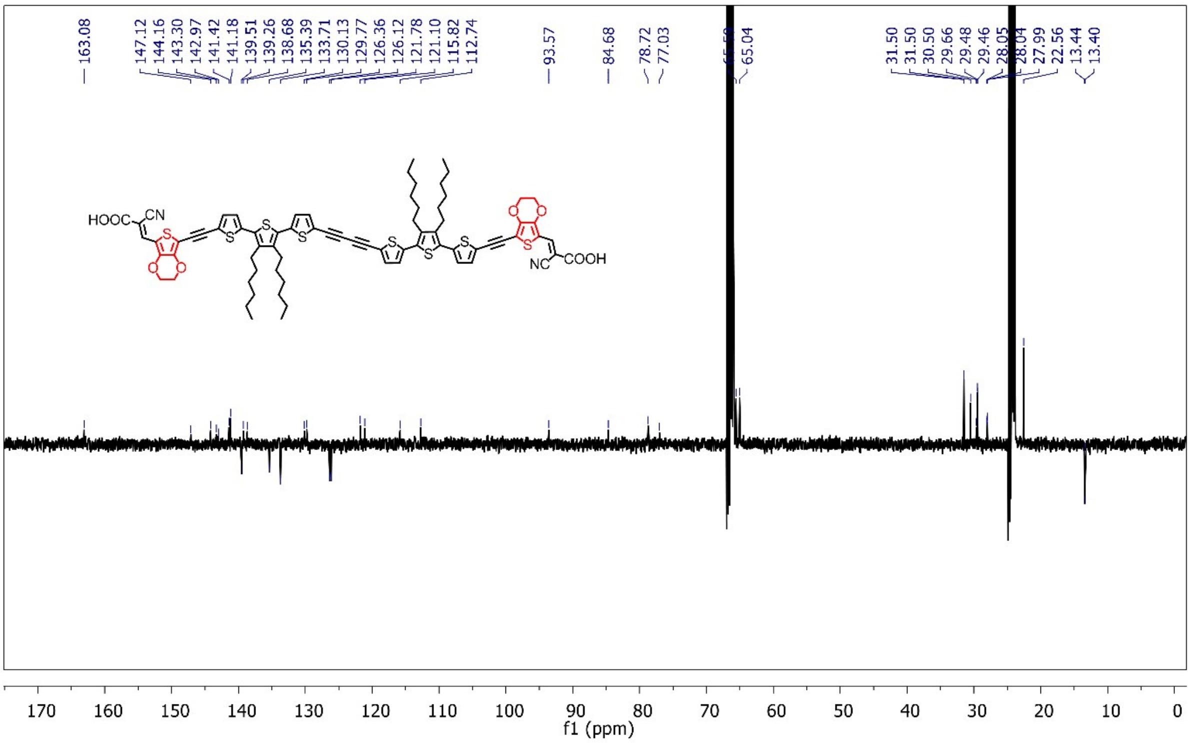


Figure S9. ^{13}C NMR (101 MHz, THF-d8) of **8T4A-E**.

4. Electrochemistry.

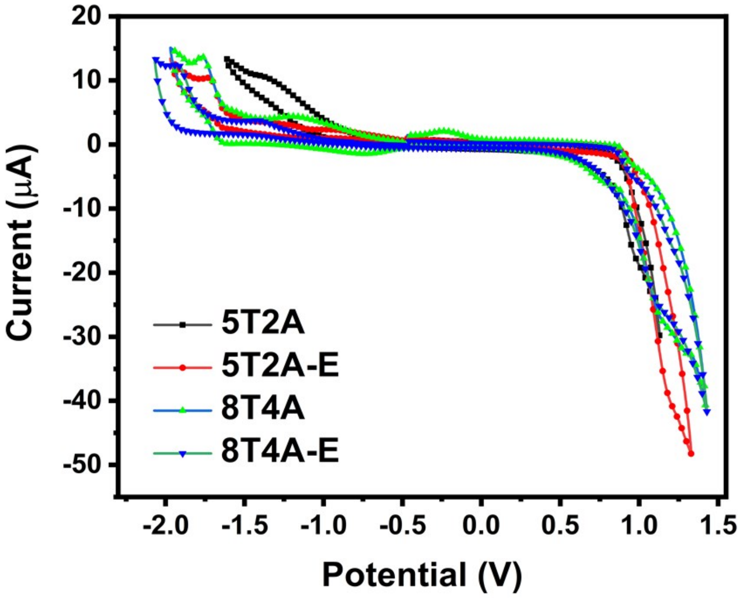


Figure S10. Cyclic voltammograms of **5T2A**, **5T2A-E**, **8T4A** and **8T4A-E**, recorded in THF (1 x 10^{-3} M) and calibrated versus the ferrocene/ferrocenium (Fc/Fc$^+$) redox couple.

5. Computational studies.

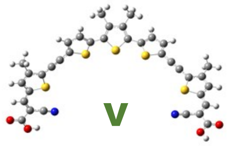
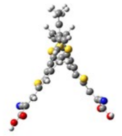
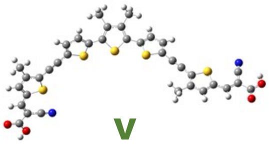
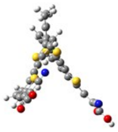
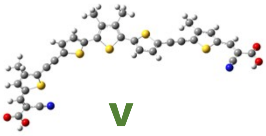
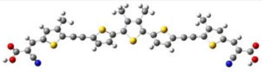
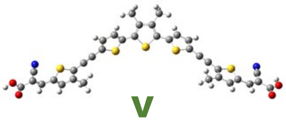
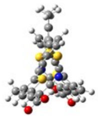
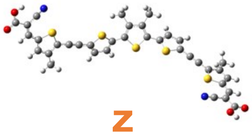
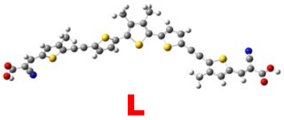
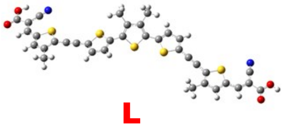
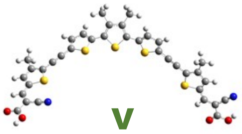
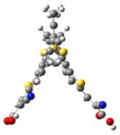
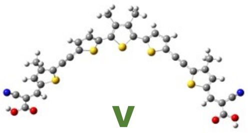
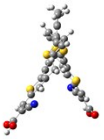
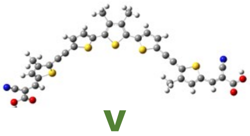
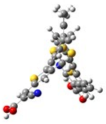
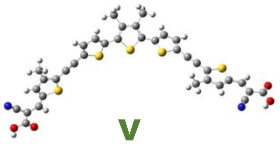
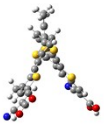
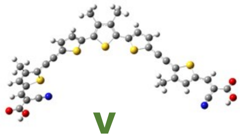
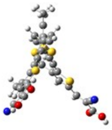
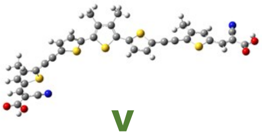
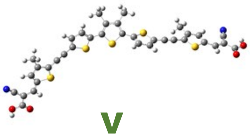
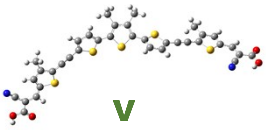
Table S1. List of possible conformers of **5T2A** (with their assigned L, U or Z conformation) and their respective energy (kCal/mol), number of degenerate isomers and relative population at 300 K, calculated at the ωB97X-D/6-31+G(d,p) level of theory in toluene. Conformers highlighted in orange are transition states and displayed a negative frequency.

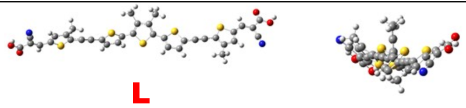
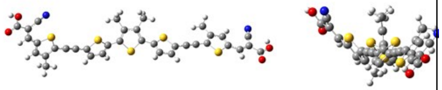
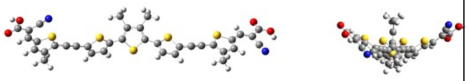
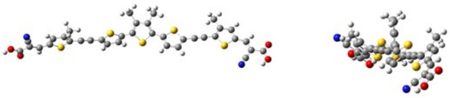
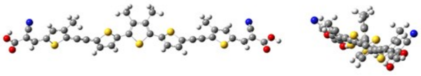
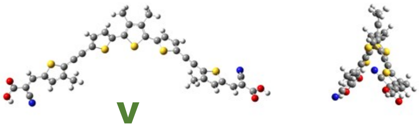
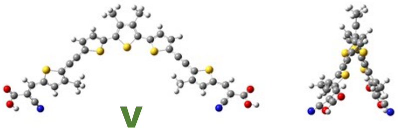
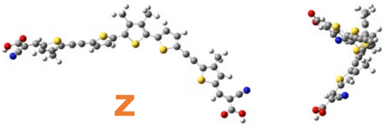
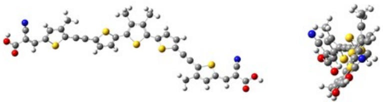
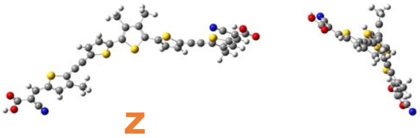
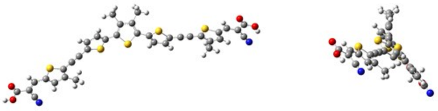
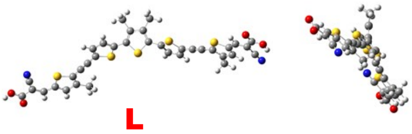
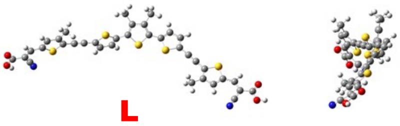
Compound	Conformation	Energy (kCal/mol)	Degen.	pi/p0 (300 K)
33	Z	-2375276.561	2	1.000
24	L	-2375276.122	2	0.479
26	V	-2375275.561	2	0.187
32	L	-2375275.412	2	0.145
19	L	-2375275.397	2	0.142
22	L	-2375275.143	2	0.093
3	V	-2375275.121	2	0.089
8	L	-2375275.019	2	0.075
28	Z	-2375275.003	2	0.073
34	L	-2375274.905	2	0.062
21	L	-2375274.884	2	0.060
13	V	-2375274.854	2	0.057
35	L	-2375274.822	2	0.054
29	Z	-2375274.727	2	0.046
36	L	-2375274.673	2	0.042
14	V	-2375274.627	2	0.039
30	Z	-2375274.607	2	0.038
4	L	-2375274.582	2	0.036
7	Z	-2375274.504	2	0.032
16	V	-2375274.498	2	0.031
20	L	-2375274.498	2	0.031
10	L	-2375274.489	2	0.031
27	V	-2375274.616	1	0.019
6	V	-2375274.547	1	0.017
11	V	-2375274.077	2	0.015
9	L	-2375274.434	1	0.014
31	L	-2375273.834	2	0.010
15	V	-2375273.732	2	0.009
1	V	-2375273.815	1	0.005
5	L	-2375273.742	1	0.004
12	V	-2375273.729	1	0.004
18	V	-2375273.141	2	0.003
23	L	-2375273.544	1	0.003
2	V	-2375273.006	2	0.003
17	V	-2375272.565	2	0.001
25	L	-2375271.57	1	0.000

Table S2. List of possible conformers of **5T2A** (with their assigned L, U or Z conformation) and their respective energy (kCal/mol), number of degenerate isomers and relative population at 300 K, calculated at the ωB97X-D/6-31+G(d,p) level of theory in THF. Conformers highlighted in orange are transition states and displayed a negative frequency.

Compound	Conformation	Energy (kCal/mol)	Degen.	pi/p0 (300 K)
4	L	-2375284.888	2	1.000
8	L	-2375283.118	2	0.051
19	L	-2375282.934	2	0.038
3	V	-2375282.862	2	0.033
26	V	-2375282.766	2	0.028
2	V	-2375282.336	2	0.014
13	V	-2375282.24	2	0.012
28	Z	-2375282.21	2	0.011
18	V	-2375282.183	2	0.011
7	Z	-2375282.117	2	0.010
24	L	-2375282.001	2	0.008
17	V	-2375281.962	2	0.007
10	L	-2375281.844	2	0.006
32	L	-2375281.671	2	0.005
21	L	-2375281.639	2	0.004
11	V	-2375281.622	2	0.004
35	L	-2375281.61	2	0.004
9	L	-2375281.984	1	0.004
34	L	-2375281.423	2	0.003
16	V	-2375281.405	2	0.003
36	L	-2375281.324	2	0.003
29	Z	-2375281.25	2	0.002
30	Z	-2375281.181	2	0.002
6	V	-2375281.496	1	0.002
15	V	-2375281.081	2	0.002
27	V	-2375281.415	1	0.001
20	L	-2375280.903	2	0.001
14	V	-2375280.903	2	0.001
31	L	-2375280.795	2	0.001
1	V	-2375281.036	1	0.001
5	L	-2375280.918	1	0.001
22	L	-2375280.494	2	0.001
33	Z	-2375280.445	2	0.001
23	L	-2375280.754	1	0.000
12	V	-2375280.383	1	0.000
25	L	-2375278.303	1	0.000

Table S3. List of pictures of **5T2A** conformers computed at 300 K in THF at the ωB97X-D/6-31+G(d,p) level of theory.

Comp.	Conformation	Side view	Comp.	Conformation	Side view
1	 V		2	 V	
3	 V		4	 L	
5	 L		6	 V	
7	 Z		8	 L	
9	 L		10	 L	
11	 V		12	 V	
13	 V		14	 V	
15	 V		16	 V	
17	 V		18	 V	

19	 **L**	**20**	 **L**
21	 **L**	**22**	 **L**
23	 **L**	**24**	 **L**
25	 **L**	**26**	 **V**
27	 **V**	**28**	 **Z**
29	 **Z**	**30**	 **Z**
31	 **L**	**32**	 **L**
33	 **Z**	**34**	 **L**
35	 **L**	**36**	 **L**

6. Solar cell characterization.

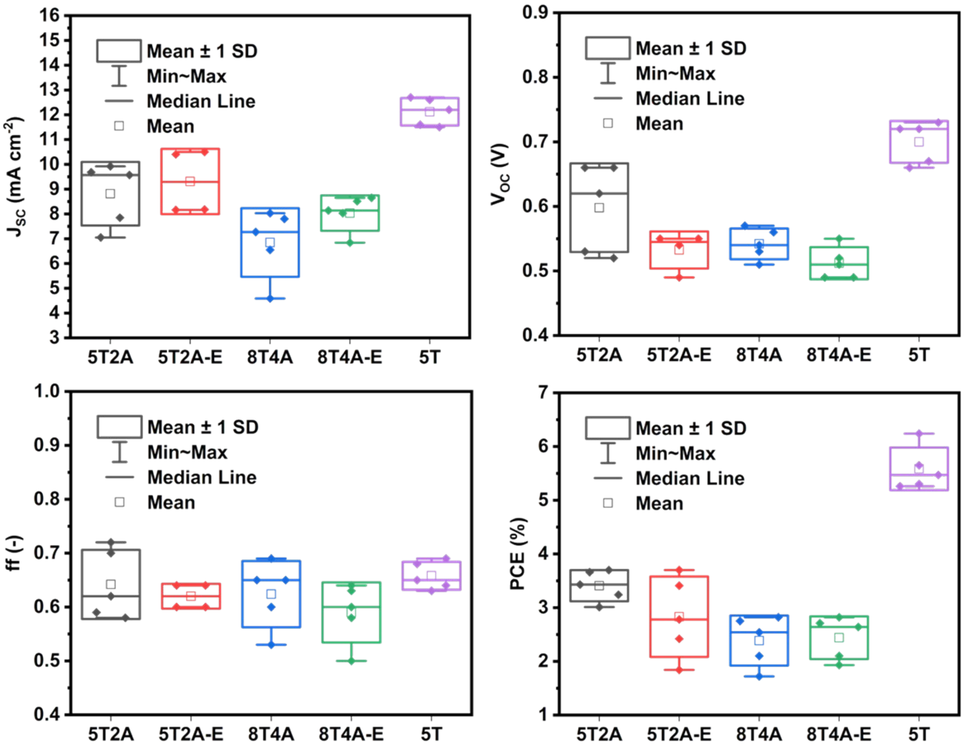


Figure S11 Performance statistics of 5 DSSCs for each studied dye.

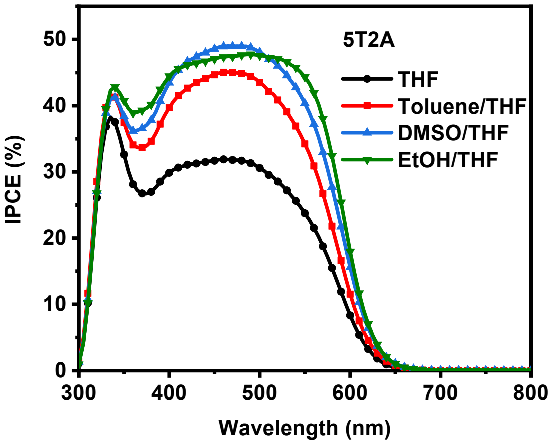


Figure S12. IPCE curves of DSSCs employing **5T2A** dye and I^-/I_3^- electrolyte with different dye bath systems.

Table S4. Optimized dye bath conditions for each dye.

Dye	Concentration	Solvent system
5T2A	0.1 M	Ethanol/THF 4:1
5T2A-E	0.1 M	Ethanol/THF 4:1
8T4A	0.1 M	Ethanol/THF 1:1
8T4A-E	0.1 M	Ethanol/THF 1:1
5T	0.1 M	Ethanol/chloroform 7:3

*All systems contained chenodeoxycholic acid 0.4 M.

7. References

1. Frisch, M. J. *et al.* Gaussian 09. Gaussian, Inc., Wallingford CT. (2009).

2. dos Santos, J.M. Neophytou, M. Wiles, A. Howells, C.T. Ashraf, R. S. McCulloch, I. Cooke, G., *Dye. Pigment.*, 2021, 109152.