Supporting Information

Low energy loss (0.42 eV) and efficiency over 15% enabled by non-fullerene acceptors containing N-bis(trifluoromethyl)phenylbenzotriazole as core in binary solar cells

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1. General Remarks.

Experimental conditions. Anhydrous solvents were dried by purification system Pure-Sov 400. Chromatographic purifications were performed using silica gel 60 Merk 230-400 mesh ASTM. Analytical thin-layer chromatography was performed using ALUGRAM ® SIL G/UV_{254} silica gel 60. Nuclear magnetic resonance ^{1}H NMR and ^{13}C NMR were performed using Bruker Innova 400 Hz. Chemical shifts (δ) values are denoted in ppm. Residual solvent peaks being used as the internal standard ($CHCl_3$, δ = 7.27 ppm; CD_2Cl_2, δ = 5.32 ppm). ^{13}C NMR chemical shifts are reported relative to the solvent residual peaks ($CDCl_3$, δ = 77.00 ppm; CD_2Cl_2, δ = 54 ppm). MALDI-TOF spectra were obtained in VOYAGER DETM STR spectrometry, using Dithranol [1,8-dihydroxy-9(10H)-anthracenone] as matrix. Fourier transform infrared spectrophotometer (FT-IR) Jasco FT/IR-6800 spectrometer was used ATR (Attenuated Total Reflection) method, in each case the most characteristic bands are indicated for each compound. Absorption spectra were performed on Shimadzu UV 3600 spectrophotometer. Solutions of different concentration were prepared in CH_2Cl_2, toluene, benzonitrile or THF spectroscopy grade, with absorbance between 0.2 and 0.5 using a 1 cm UV cuvette. Thermogravimetric analyses were performed using a TGA/DSC Linea Excellent instrument by Mettler-Toledo and collected under inert atmosphere of nitrogen with a scan rate of 10 °C min^{-1}. The weight changes were recorded as a function of temperature.

Electrochemical Measurements: Reduction (E_{red}) and oxidation potentials (E_{ox}) were measured by cyclic voltammetry with a potentiostat BAS CV50W in a conventional three-electrode cell equipped with a glassy carbon working electrode, a platinum wire counter electrode, and an $Ag/AgNO_3$ reference electrode at scan rate of 100 mV/s. The E_{red} and E_{ox} were expressed vs. Fc/Fc^+ used as external reference. In each case, the measurements were done in a deaerated solution containing 1 mM of the sample compound in 0.1 M of (n-Bu)$_4NClO_4$ in CH_2Cl_2 (4:1) as an electrolyte solution.

Computational Details: Theoretical calculations were carried out within the density functional theory (DFT) framework by using the Gaussian 09, applying density functional theory at the B3LYP level. The basis set of 6-31G* was used in the calculations (Supercomputation Service of UCLM).

Device Fabrication and characterization

The solution processed organic solar cells were fabricated on the ITO coated glass substrate with structure ITO/PESOT:PSS/active layer (P1 or P2:**TOCR1** or

TOCR2)/PFN/Al. The ITO coated glass substrates were cleaned in detergent, and subsequently ultra-sonicated in deionized water, acetone and isopropyl alcohol and dried *in vacuum* oven to remove all the traces of residues. The photovoltaic performance optimization process was started with identifying the donor to acceptor ratio (weight percentage, varying from 1:0.4 to 1:1.3) and after that solvent vapor annealing was applied to maximize the performance of the OSCs. The D-A conjugated polymers P1 and P2 were used as donor (D) and the total concentration of D:A blend mixture was 16 mg/mL in chloroform. The devices were fabricated by depositing PEDOT:PSS as hole transport layer having thickness of 35-40 nm. The active layer was deposited by spin coating (2500 rpm, 60 s) on the top of PEDOT:PSS layer under ambient conditions. For the solvent vapor annealing (SVA), the optimized (as cast 1:1.2 D/A wt ratio) was exposed to the THF vapours for 40s. A thin layer of PFN was spin coated on the top of the active layer from the methanol solution. The aluminium (Al) electrode was deposited onto the top of PFN layer *via* thermal evaporation at the pressure less than 10^{-5} Torr. The current-voltage characteristics of the OSCs were measured under illumination intensity of 100 mW/cm^2 (AM1.5 G) using a solar simulator and a Keithley 2400 source meter unit. The External quantum efficiency (EQE) measurements were performed using Bentham EQE system.

2. Synthesis and characterization of TOCR1 and TOCR2.

- Synthesis of **2**:

A mixture of **1** (0.1 g, 0,2 mmol), tributyl(4,4-dihexyl-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)stannane (0.29 g, 0.44 mmol), $PdCl_2(PPh_3)_2$ (0.0129 g, 0.018 mmol), LiCl (0.026 g, 0.61 mmol) and CH_3CN (1 mL) was irradiated under argon in a microwave reactor at 110 °C for 20 min. The solvent was removed under reduced pressure and the residue was purified by means of column chromatography on silica gel employing hexane as the eluent to give pure product 2 as a viscous purple syrup. ^{1}H-NMR (500 MHz, $CDCl_3$) δ/ppm: 8.97 (s, 2H), 8.02 (s, 1H), 7.99 (s, 2H), 7.69 (s, 2H), 7.25 (d, *J* = 4.9 Hz, 2H), 6.99 (d, *J*= 4.9 Hz, 2H), 1.96 – 1.89 (m, 8H), 1.24-1.07 (m, 32H), 0.8 (t, *J* = 7 Hz, 12H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ/ppm: 159.0, 143.4, 141.1, 139.0, 138.1, 136.5, 133.5, 133.2, 128.4, 125.8, 124.0, 123.3, 121.8, 121.5, 120.6, 118.6, 53.8, 37.8, 31.6, 29.7, 24.6, 22.6, 14.0. MS (MALDI-TOF) (m/z): calculated 1019.38 $[M]^+$ for $C_{56}H_{63}F_6N_3S_4$; found 1020.38.

- Synthesis of **3**:

Under argon atmosphere, 1,2-dichloroethane (9.3 mL, previously dried with anhydrous $MgSO_4$ for 30 minutes) was added to compound **2** (0.11 mmol, 116 mg). Subsequently, anhydrous DMF (0.66 mmol, 50 µL) and $POCl_3$ (0.66 mmol, 60 µL) were added. The reaction mixture was monitored by TLC turning purple after 12 hours at room temperature. Next, the reaction was quenched with a saturated sodium acetate solution, and it was stirred over 1 hour. At that time, the reaction turned pink. The crude was extracted with CH_2Cl_2 (3 x 40 mL), the organic phase was dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The reaction crude was purified by column chromatography (silica gel, CH_2Cl_2/ethyl acetate 9:1). A reddish solid **2** was obtained (103 mg, 87%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ/ppm: 9.88 (s, 2H), 8.95 (d, *J* = 1.6 Hz, 2H), 8.05 (s, 3H), 7.76 (s, 2H), 7.64 (s, 2H), 2.06 – 1.92 (m, 8H), 1.32 – 1.09 (m, 34H), 0.81 (t, *J* = 6.5 Hz, 12H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ/ppm: 182.60, 163.29, 158.70, 147.24, 144.06, 143.53, 143.17, 140.83, 137.05, 133.63, 133.29, 130.02, 124.32, 124.12, 122.60, 121.56, 121.41, 120.63, 54.22, 37.63, 31.56, 29.66, 24.74, 22.63, 13.99. MS (MALDI-TOF) (m/z): calculated 1075.37 $[M]^+$ for $C_{58}H_{63}F_6N_3O_2S_4$; found 1075.39.

- Synthesis of **TOCR1**:

Under argon atmosphere, anhydrous DMF (8 mL) was added over compound **2** (0.05 mmol, 59 mg) and tetracyanoethylene (TCNE) (0.69 mmol, 89 mg). Subsequently, the reaction was heated to 120 °C and was quenched with H_2O after disappeared the starting

material. Then, the crude was extracted with $CHCl_3$ (3 x 20 mL), and the organic phase was dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The reaction crude was purified by GPC in dichloromethane. A navy blue solid **TOCR1** was obtained after washing with MeOH (50 mg, 82 %). ^{1}H-NMR (400 MHz, CD_2Cl_2) δ/ppm: 9.01 (s, 2H), 8.13 (s, 1H), 8.11 (s, 2H), 7.95 (s, 2H), 7.89 (s, 2H), 2.07 (m, 8H), 1.40 – 0.97 (m, 32H), 0.81 (t, *J* = 6.9 Hz, 5H). ^{13}C-NMR (100 MHz, CD_2Cl_2) δ/ppm: 167.66, 160.59, 154.61, 148.77, 142.99, 140.70, 137.26, 136.22, 133.51, 133.17, 132.18, 131.12, 125.04, 124.75, 124.21, 123.15, 121.78, 121.50, 120.90, 113.84, 113.48, 113.36, 75.98, 54.83, 37.71, 31.50, 29.48, 24.63, 22.57, 13.74. FT-IR (ATR) ν/ cm^{-1}: 3077, 2926, 2854, 2212, 1474, 1331, 1276, 1135. MS (MALDI-TOF) (m/z): calculated 1221.38 $[M]^+$ for $C_{66}H_{61}F_6N_9O_2S_4$, found 1221.29.

- Synthesis of **TOCR2**:

A catalytic amount of pyridine (0.5 mL) was added to a solution of compound **3** (0.09 mmol, 103 mg) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)-malononitrile (0.63 mmol, 145 mg) in $CHCl_3$ (7.5 mL), and the mixture was stirred under inert and anhydrous conditions at 65 ºC. After monitoring by TLC, it was concentrated under reduced pressure after 2 hours of reaction. The reaction crude was purified by column chromatography (silica gel, 100% $CHCl_3$) and after washed with MeOH and *n*-hexane. A dark blue solid **TOCR2** was obtained (85 mg, 63 %). ^{1}H-NMR (400 MHz, $CDCl_3$, 323 K) δ/ppm: 8.94 (s, 5H), 8.54 (s, 2H), 8.07 (s, 2H), 7.87 (s, 2H), 7.69 (s, 4H), 2.03 (m, 8H), 1.16 (m, 34H), 0.81 (t, 12H). FT-IR (ATR) ν/ cm^{-1}: 3076, 2927, 2854, 2217, 1687, 1528, 1470, 1391, 1275, 1124. MS (MALDI-TOF) (m/z): calculated 1499.41 $[M]^+$ for $C_{82}H_{67}F_{10}N_7O_2S_4$, found 1499.31.

3. ^{1}H NMR, ^{13}C NMR, FT-IR and MALDI-TOF spectra.

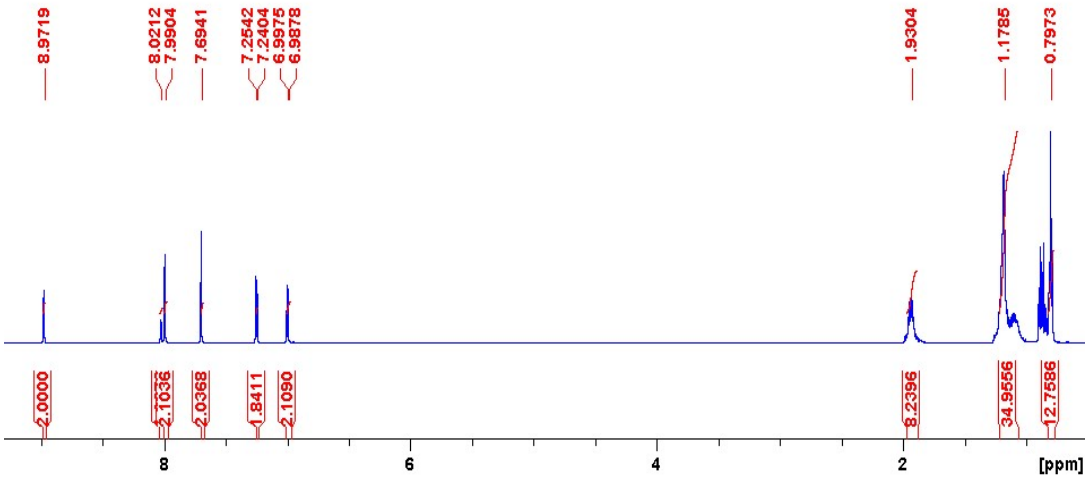


Figure S1. ^{1}H-NMR (500MHz, $CDCl_3$) spectrum of **2**.

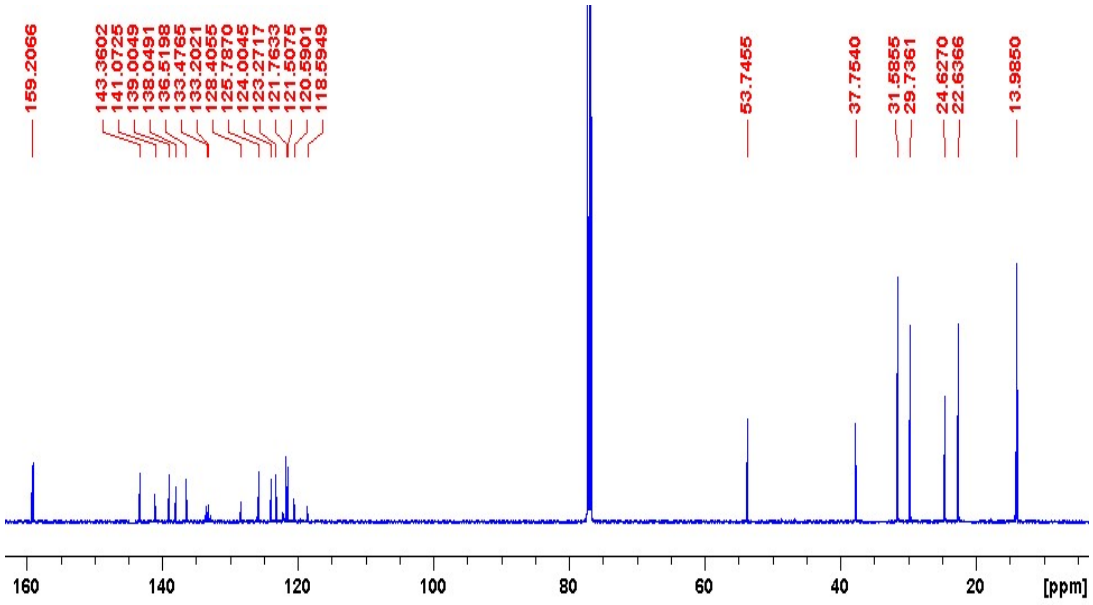


Figure S2. ^{13}C-NMR (125MHz, $CDCl_3$) spectrum of compound **2**.

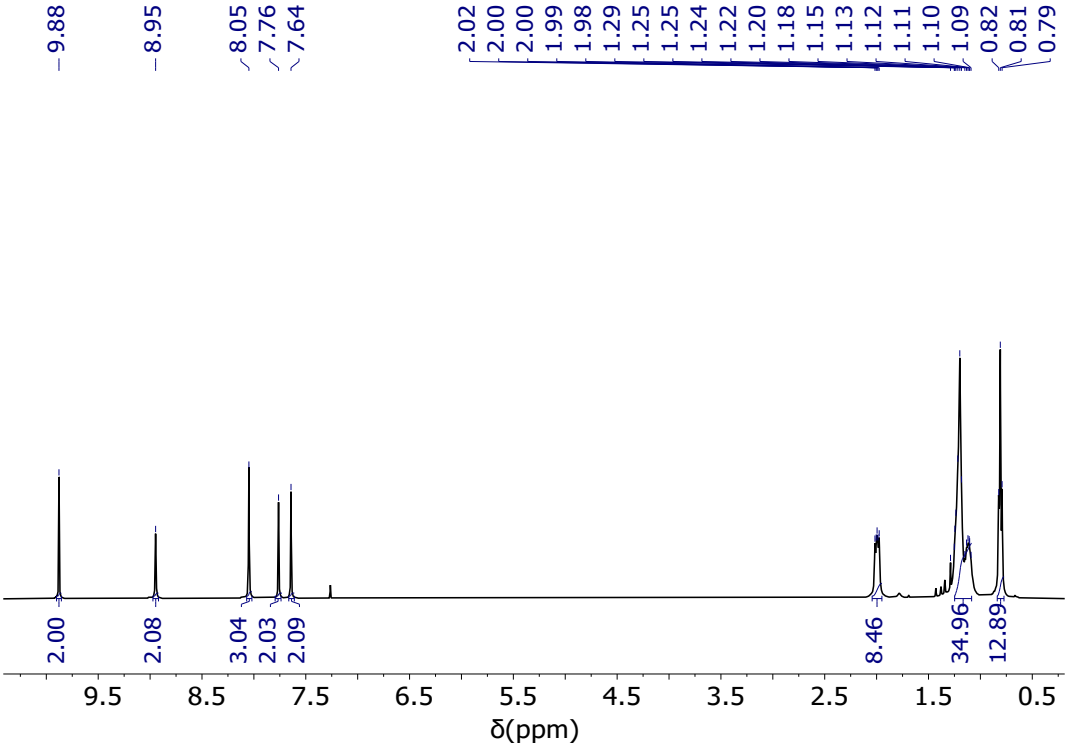


Figure S3. ^{1}H-NMR (400MHz, $CDCl_3$) spectrum of **3**

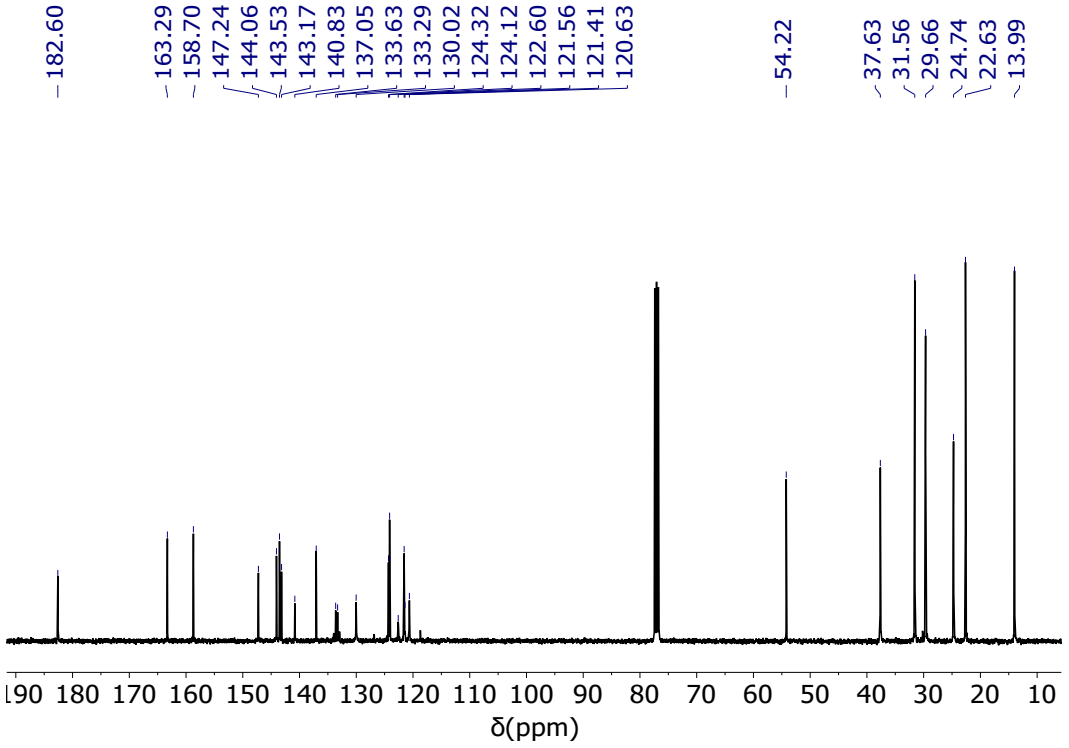


Figure S4. ^{13}C-NMR (100MHz, $CDCl_3$) spectrum of compound **3**.

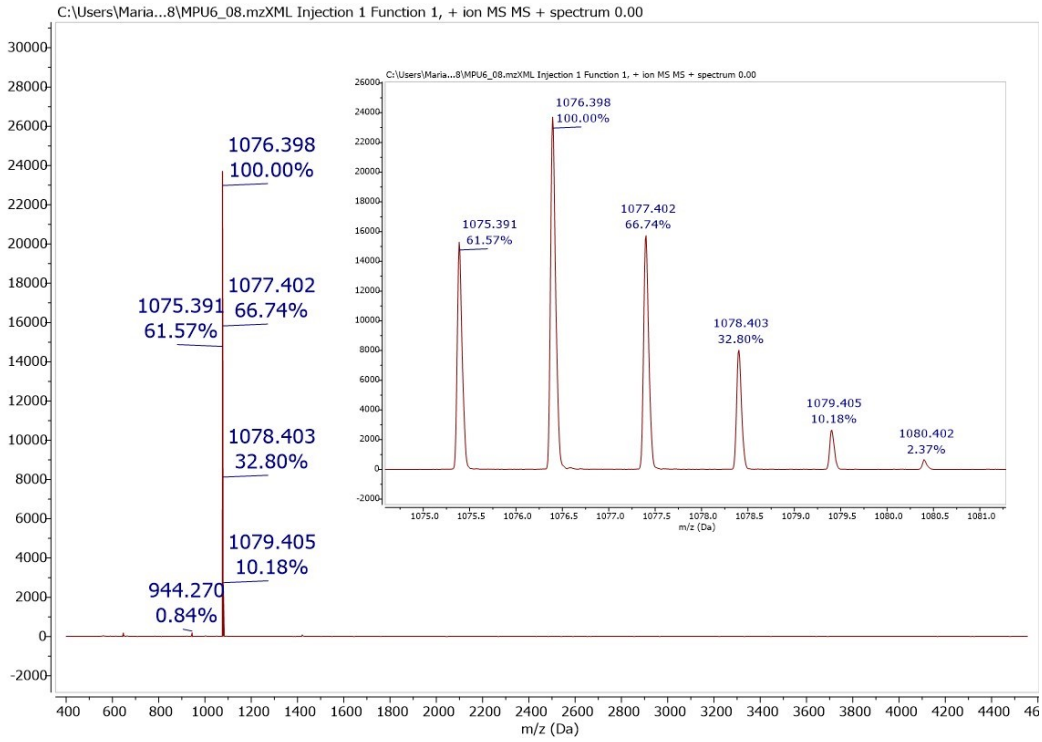


Figure S5. MALDI-TOF MS spectrum of compound **3** (Matrix: Dithranol).

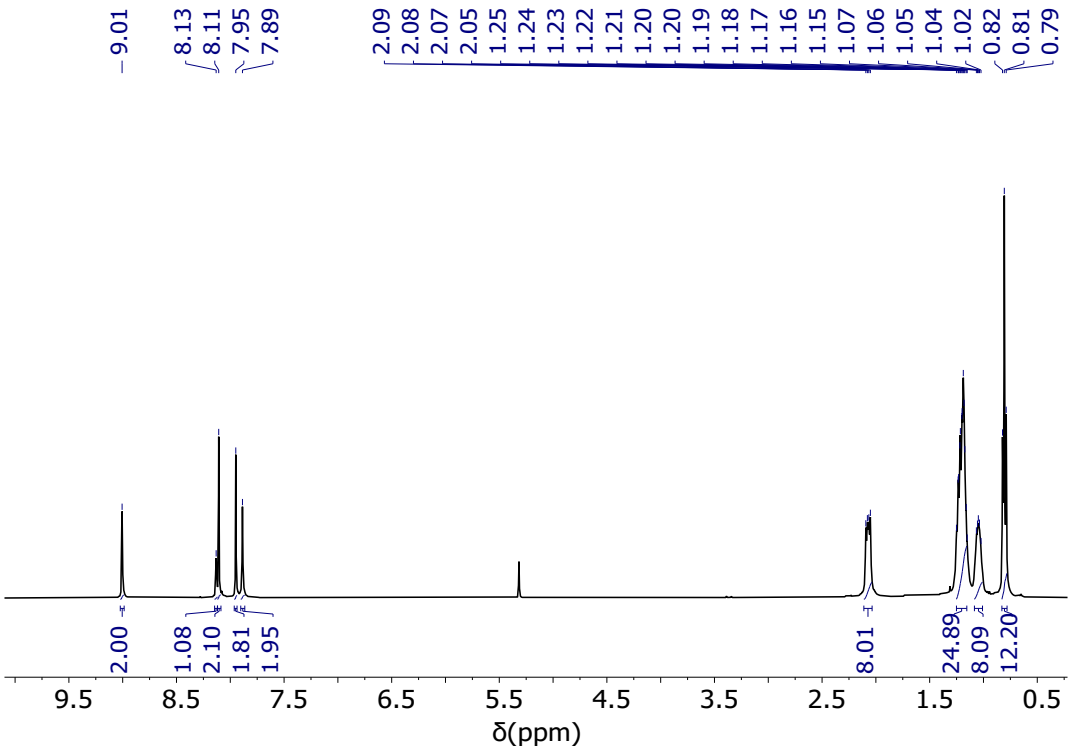


Figure S6. ^{1}H-NMR (400MHz, CD_2Cl_2) spectrum of **TOCR1.**

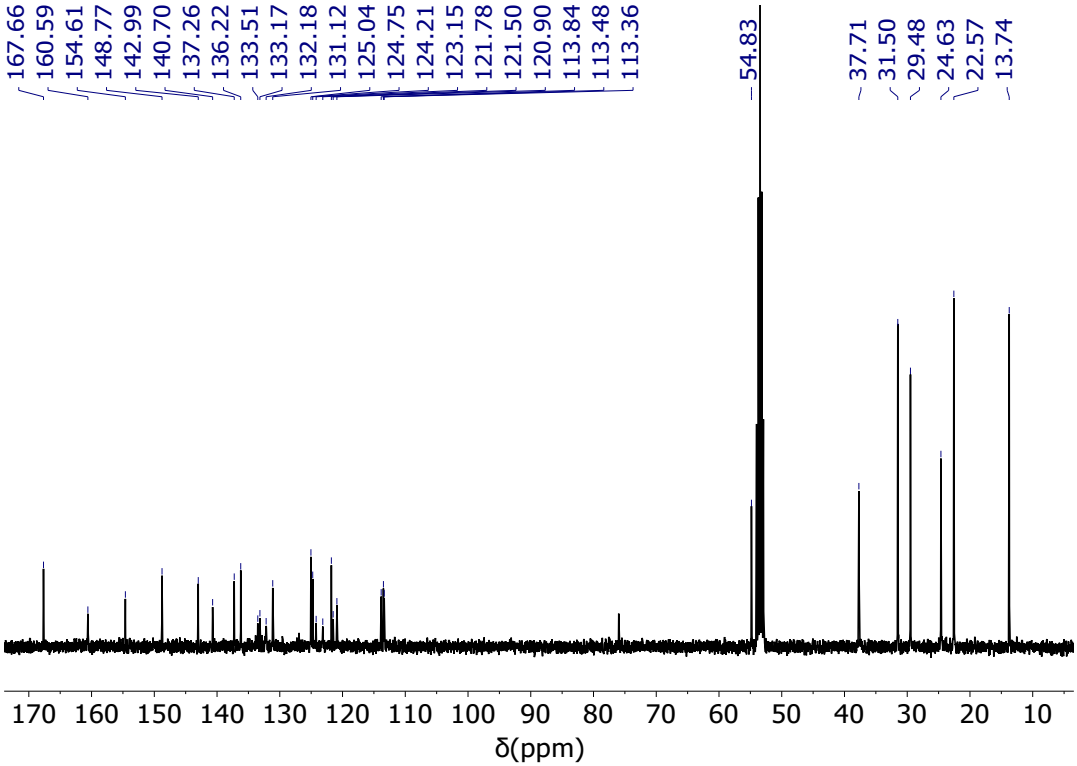


Figure S7. ^{13}C-NMR (100MHz, $CDCl_3$) spectrum of compound **TOCR1**.

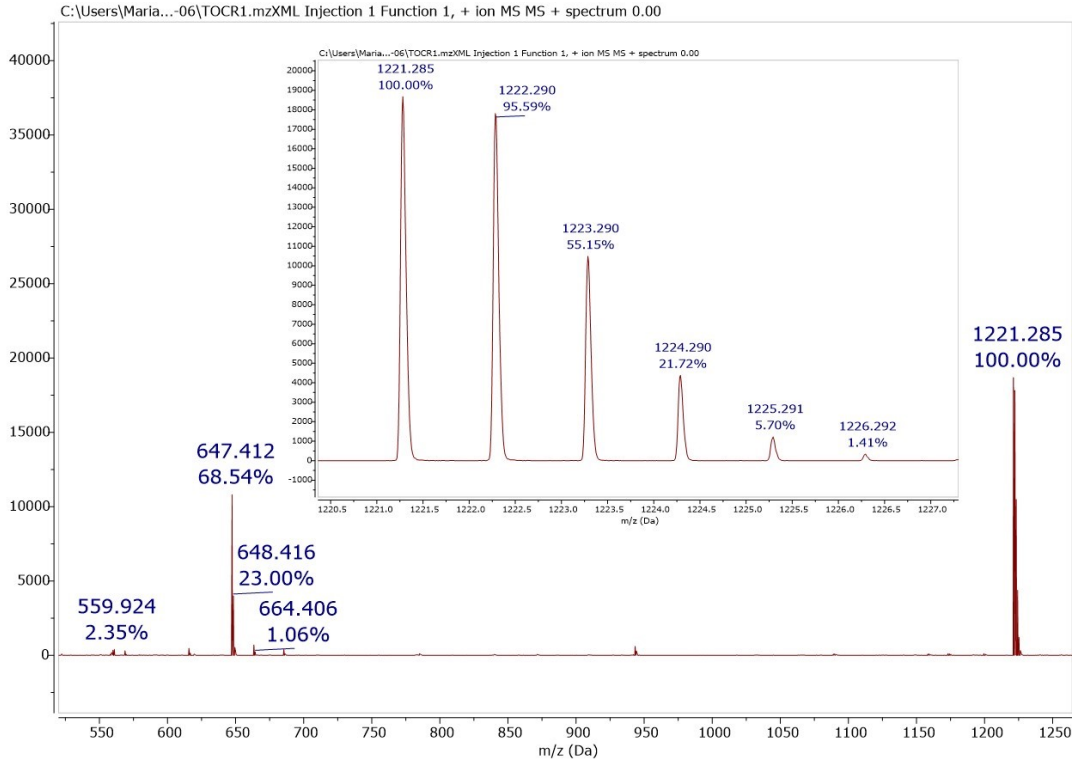


Figure S8. MALDI-TOF MS spectrum of **TOCR1** (Matrix: Dithranol).

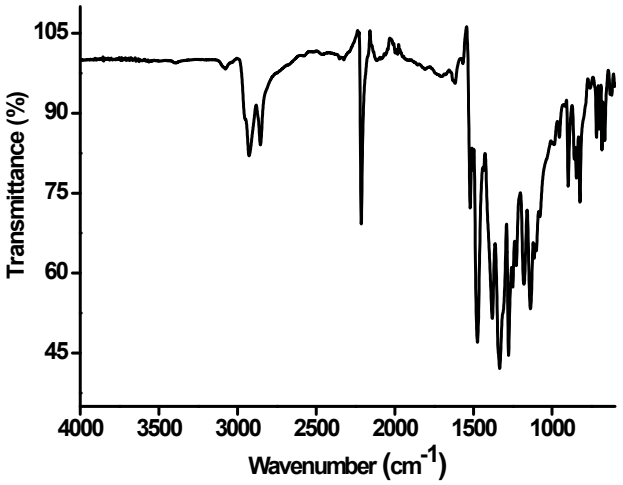


Figure S9. FT-IR (ATR) spectrum of **TOCR1**.

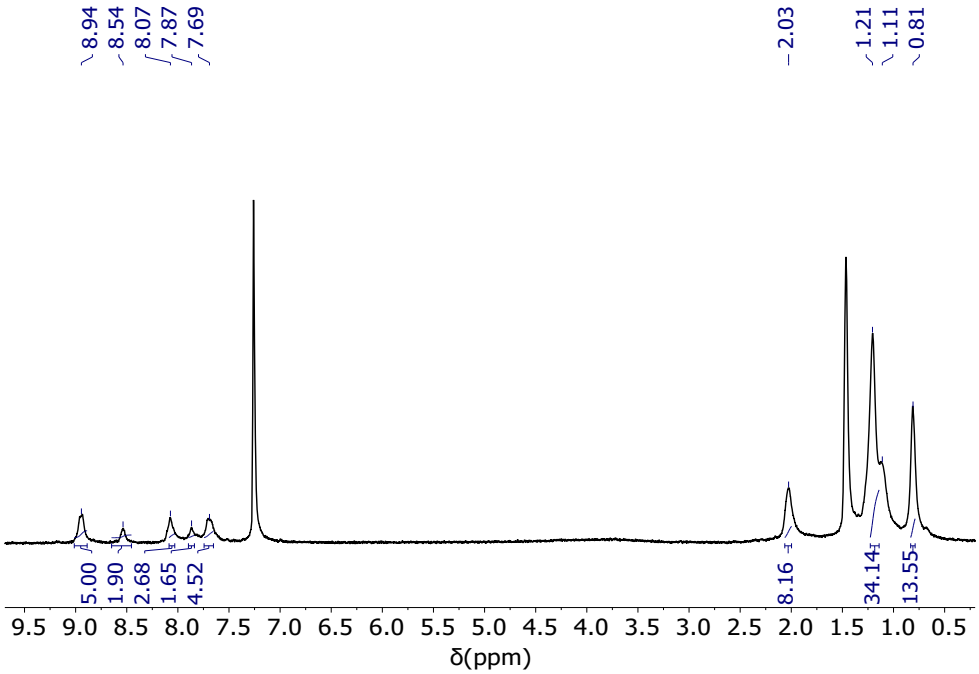


Figure S10. ^{1}H-NMR (400MHz, $CDCl_3$) spectrum of **TOCR2.**

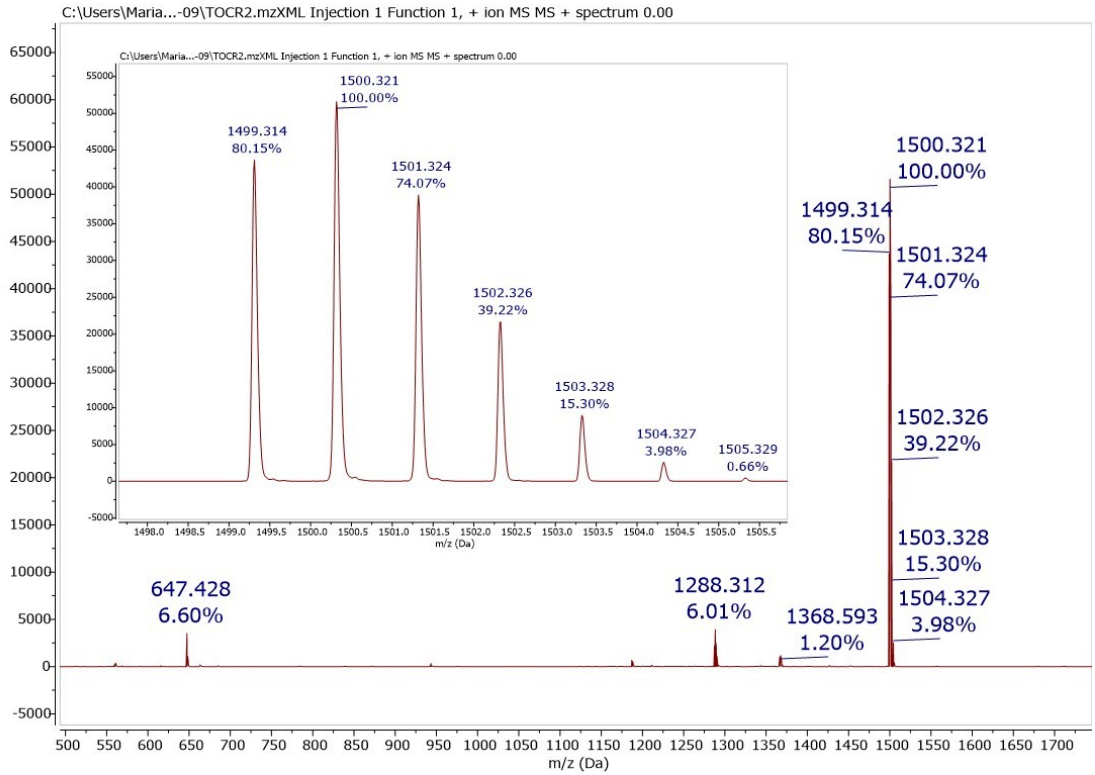


Figure S11. MALDI-TOF MS spectrum of **TOCR2** (Matrix: Dithranol).

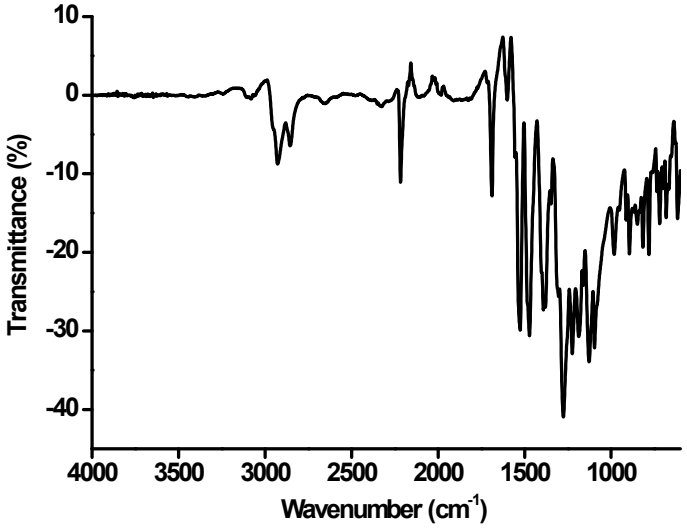


Figure S12. FT-IR (ATR) spectrum of **TOCR2**.

4. Thermogravimetric Analysis (TGA) of TOCR1 and TOCR2.

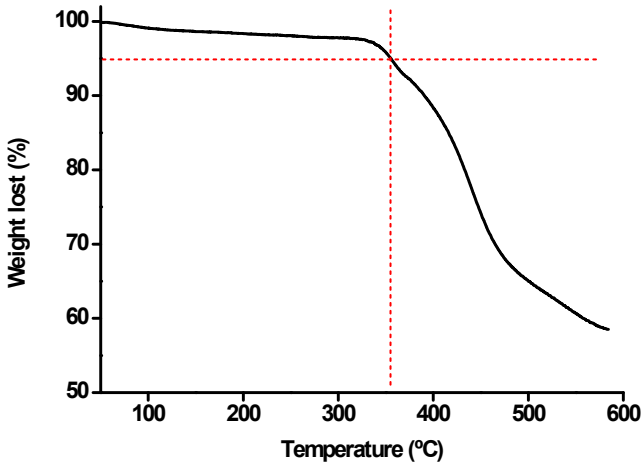


Figure S13. TGA of **TOCR1**.

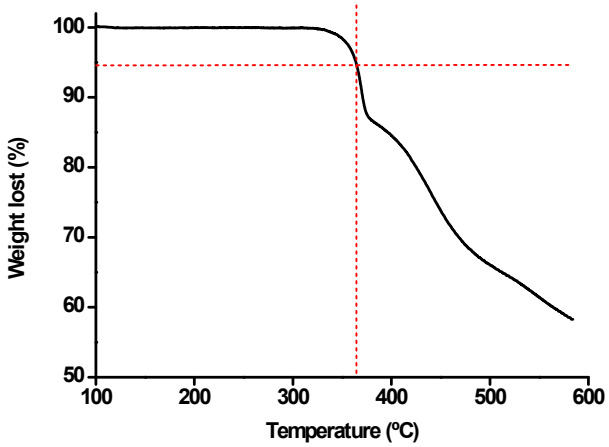


Figure S14. TGA of **TOCR2**.

5. Absorption spectrum in solution

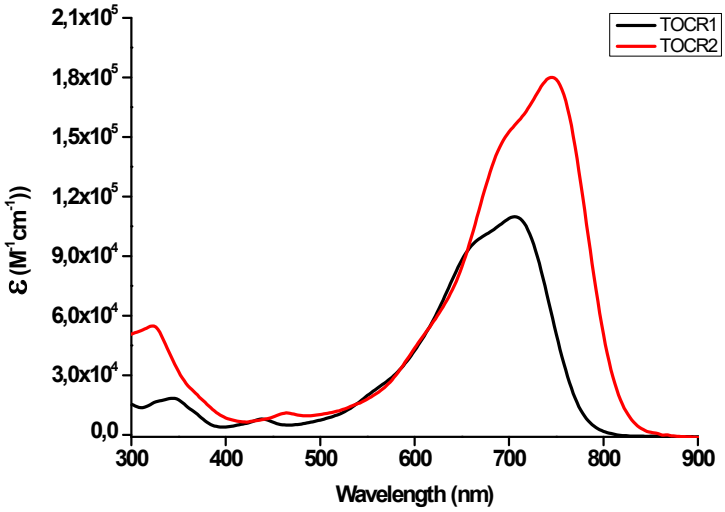


Figure S15. Absorption spectrum of **TOCR1** (CH_2Cl_2, 3.7 x 10^{-6} M) and **TOCR2** (CH_2Cl_2, 2.2 x 10^{-6} M).

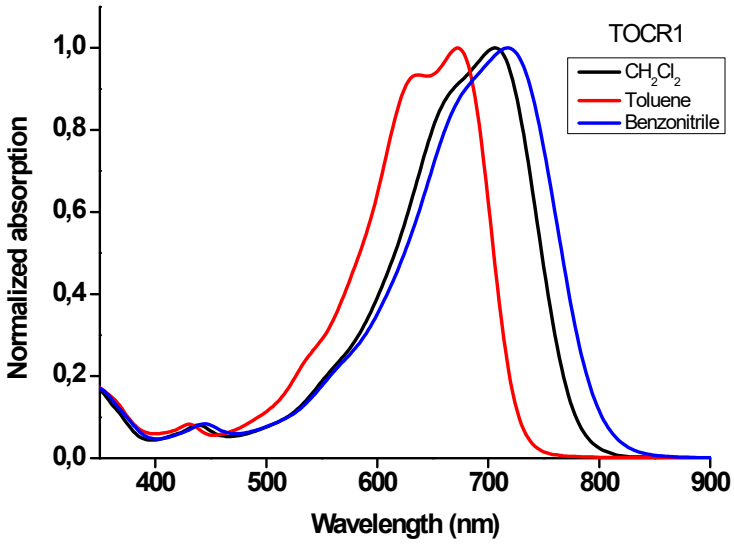


Figure S16. Normalized absorption spectra of **TOCR1** in CH_2Cl_2 (c: 3.68 x 10^{-6}M), toluene (c: 3.06 x 10^{-6}M) and benzonitrile (c: 4.55 x 10^{-6}M).

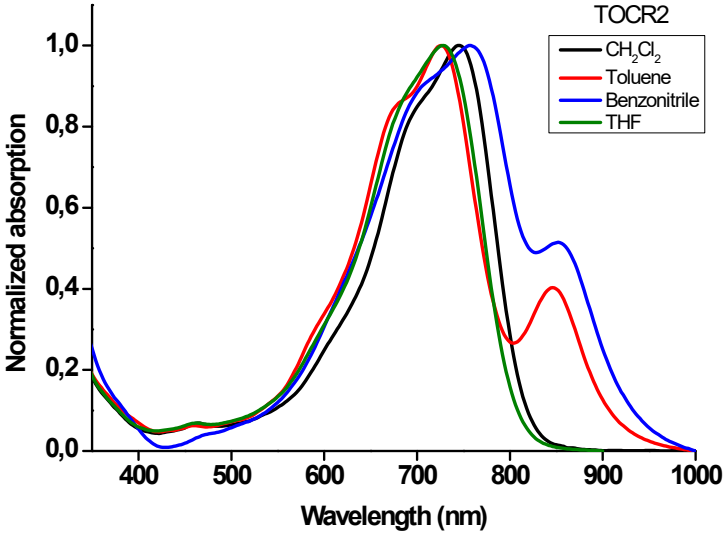


Figure S17. Normalized absorption spectra of **TOCR2** in CH_2Cl_2 (c: 2.20 x 10^{-6}M), toluene (c: 3.66 x 10^{-6}M), benzonitrile (c: 8.79 x 10^{-6}M) and tetrahydrofuran (c: 6.66 x 10^{-6}M).

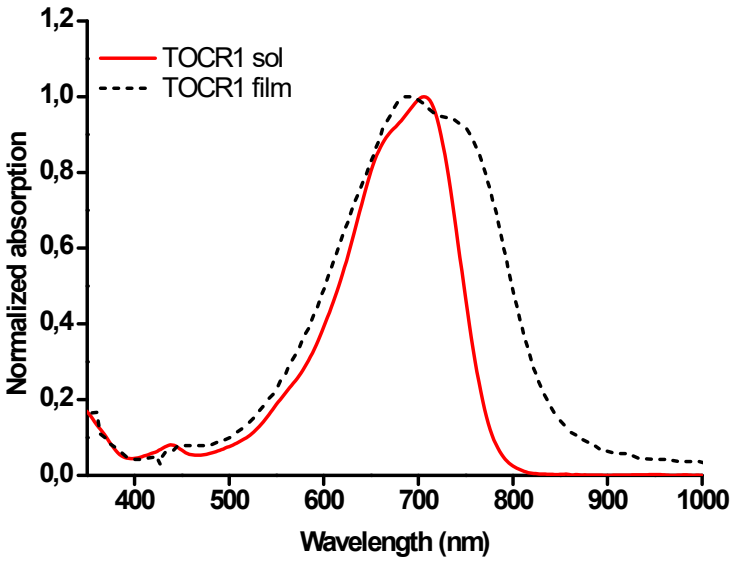


Figure S18 Absorption spectrum of **TOCR1** in solution and in film.

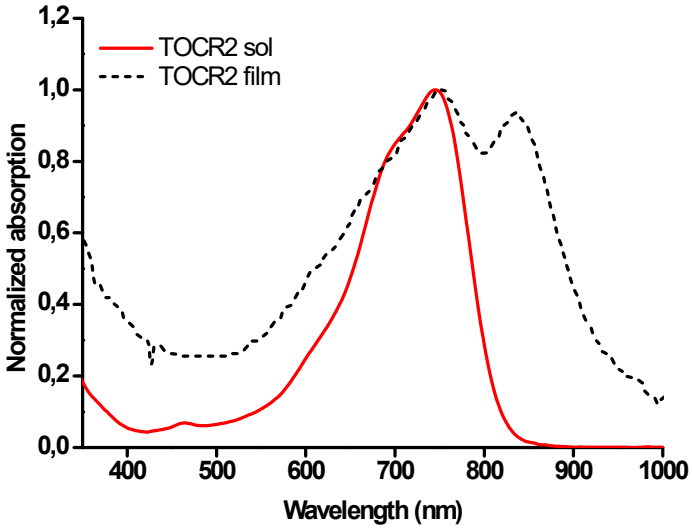


Figure S19. Absorption spectrum of **TOCR2** in solution and in film.

6. Electrochemical Studies

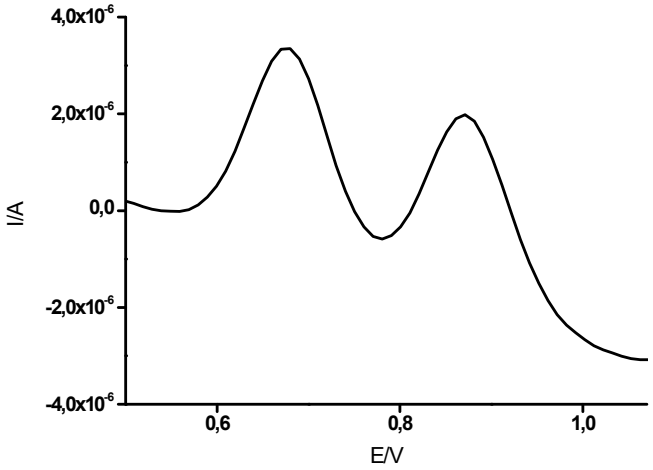


Figure S20. OSWV (oxidation side) of **TOCR1.**

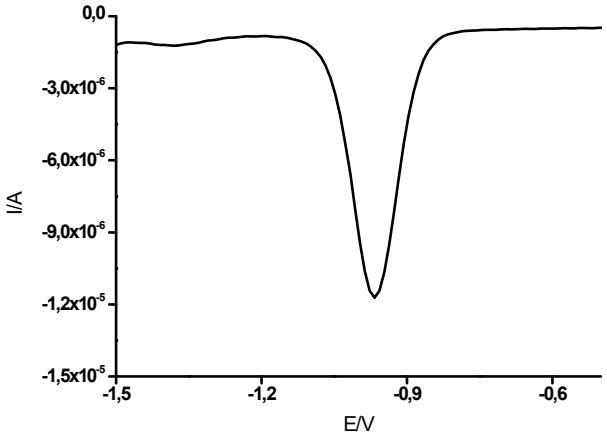


Figure S21. OSWV (reduction side) of **TOCR1.**

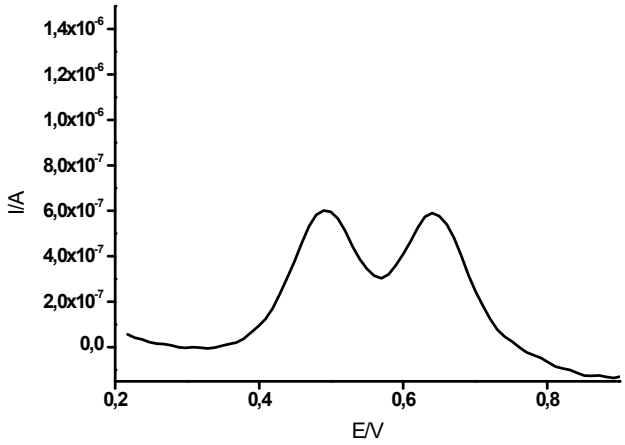


Figure S22. OSWV (oxidation side) of **TOCR2**.

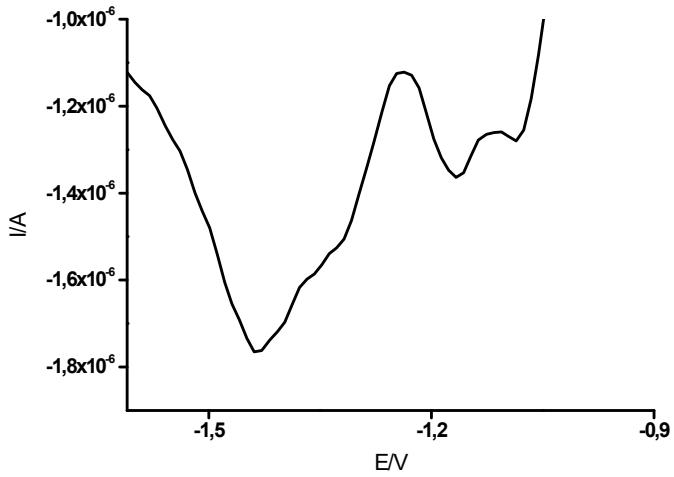


Figure S23. OSWV (reduction side) of **TOCR2.**

7. Theoretical calculations

Table S1. Energetic values of the most relevant conformations of the central fragment in Hartrees and relative values in Kcal/mol calculated at the B3LYP/6-31G(d,p) level.

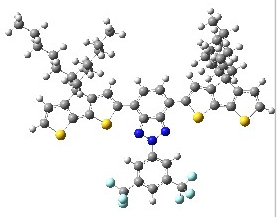
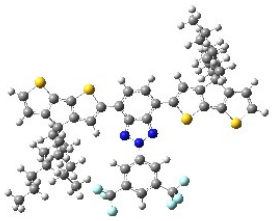
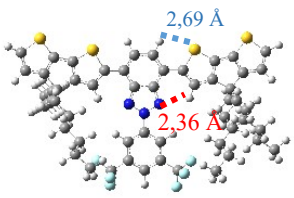
Conformation			
E (Hartrees) **(Kcal/mol)**	-4528,061554 (2,7)	-4528,065188 (0,42)	-4528,068516 (0)

Table S2. Energetic values of the most relevant conformations of the compounds **TOCR1**and **TOCR2** in Hartrees and relative values in Kcal/mol calculated at the B3LYP/6-31G(d,p) level.

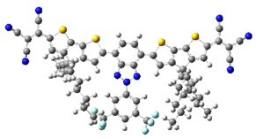
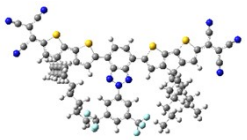
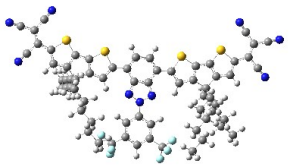
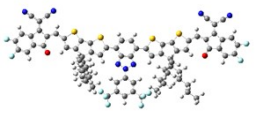
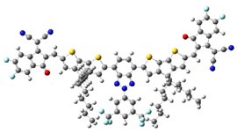
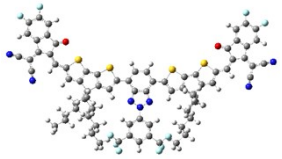
Compound	**Conformations**		
TOCR1			
E (Hartrees) **(Kcal/mol)**	-5236.29892 (0,6)	-5236,299407 (0,29)	-5236,299875 (0)
Compound	**Conformations**		
TOCR2			
E (Hartrees) **(Kcal/mol)**	-6289,959277 (2,67)	-6289,96143 (1,32)	-6289,963536 (0)

Table S3. Cartesian coordinates for optimized geometry of **TOCR1.**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.527921	-0.625805	-0.250229

2	6	0	-0.901660	-0.558870	-0.241480
3	6	0	-1.723626	-1.728184	-0.351427
4	6	0	-1.002189	-2.917430	-0.465672
5	6	0	0.403789	-2.983575	-0.470787
6	6	0	1.235274	-1.867616	-0.363220
7	7	0	1.006206	0.627224	-0.144931
8	7	0	-0.093800	1.376487	-0.078527
9	7	0	-1.259610	0.733156	-0.130380
10	6	0	-0.027025	2.791983	0.036240
11	6	0	1.216666	3.422977	0.031023
12	6	0	1.269816	4.810738	0.153588
13	6	0	0.103595	5.563309	0.281875
14	6	0	-1.131200	4.910894	0.279503
15	6	0	-1.208885	3.526865	0.157072
16	6	0	2.681252	-1.949224	-0.360277
17	6	0	-3.170711	-1.670776	-0.347282
18	16	0	-4.136413	-3.126301	-0.654340
19	6	0	-5.594597	-2.216652	-0.471808
20	6	0	-5.358766	-0.869205	-0.203402
21	6	0	-3.987880	-0.565683	-0.126505
22	6	0	-7.001075	-2.449856	-0.491881
23	6	0	-7.665748	-1.245077	-0.232512
24	6	0	-6.670593	-0.099377	-0.046588
25	16	0	-8.067173	-3.778425	-0.743495
26	6	0	-9.465757	-2.709268	-0.497815
27	6	0	-9.050611	-1.391372	-0.239531
28	16	0	3.499505	-3.506467	-0.586285
29	6	0	5.039255	-2.735318	-0.442254
30	6	0	4.937653	-1.359545	-0.245984
31	6	0	3.602779	-0.919855	-0.189851
32	6	0	6.414426	-3.106696	-0.437301
33	6	0	7.197973	-1.963118	-0.232354
34	6	0	6.318354	-0.717615	-0.088890
35	16	0	7.336561	-4.546984	-0.635885
36	6	0	8.561614	-2.251460	-0.257230
37	6	0	2.605174	5.511067	0.087361
38	9	0	2.619588	6.625097	0.845081
39	9	0	2.896612	5.883620	-1.178979
40	9	0	3.610326	4.711580	0.507977
41	6	0	-2.387912	5.738471	0.396635
42	9	0	-3.488654	4.971081	0.554104
43	9	0	-2.577010	6.496685	-0.706041
44	9	0	-2.321885	6.580939	1.447246
45	6	0	-4.324243	6.189532	-3.924374
46	6	0	-5.468087	5.208887	-3.648143
47	6	0	-5.082789	4.105202	-2.655750
48	6	0	-6.195805	3.080027	-2.406284
49	6	0	-5.825424	2.043478	-1.335550
50	6	0	-6.883657	0.941088	-1.194521
51	6	0	-6.748067	-0.666809	7.675826
52	6	0	-6.865582	0.246679	6.452244
53	6	0	-6.715297	-0.501814	5.122123
54	6	0	-6.832608	0.406111	3.891864
55	6	0	-6.681886	-0.346917	2.563365

56	6	0	-6.803852	0.578719	1.346135
57	6	0	10.387085	3.087941	5.306625
58	6	0	9.065163	2.415067	4.925651
59	6	0	9.067480	1.840810	3.503517
60	6	0	7.746700	1.165502	3.114919
61	6	0	7.752866	0.589338	1.691708
62	6	0	6.420232	-0.078280	1.330124
63	6	0	4.936547	5.912578	-3.874270
64	6	0	5.857285	4.705310	-3.673413
65	6	0	5.348894	3.720844	-2.612539
66	6	0	6.250996	2.492809	-2.440207
67	6	0	5.780569	1.541085	-1.330873
68	6	0	6.648904	0.279361	-1.241025
69	1	0	-1.540915	-3.856397	-0.546213
70	1	0	0.850644	-3.969163	-0.556012
71	1	0	2.121112	2.837738	-0.061529
72	1	0	0.156350	6.640154	0.392041
73	1	0	-2.163870	3.020869	0.158452
74	1	0	-3.573201	0.408904	0.085683
75	1	0	-9.764384	-0.595122	-0.064771
76	1	0	3.284341	0.099146	-0.025264
77	1	0	9.356929	-1.525586	-0.142851
78	1	0	-4.638308	6.992231	-4.599049
79	1	0	-3.965982	6.649725	-2.997365
80	1	0	-3.471764	5.680666	-4.388990
81	1	0	-5.797643	4.752798	-4.591501
82	1	0	-6.335814	5.756993	-3.257111
83	1	0	-4.788883	4.565203	-1.702824
84	1	0	-4.189968	3.581039	-3.027144
85	1	0	-6.433513	2.565549	-3.347861
86	1	0	-7.115000	3.601055	-2.104213
87	1	0	-5.675988	2.563702	-0.380873
88	1	0	-4.861823	1.590032	-1.598755
89	1	0	-6.948592	0.394017	-2.142579
90	1	0	-7.868482	1.400310	-1.036803
91	1	0	-6.859631	-0.103508	8.607754
92	1	0	-7.518673	-1.445780	7.664310
93	1	0	-5.773768	-1.167805	7.704848
94	1	0	-6.104701	1.036993	6.510387
95	1	0	-7.836618	0.759734	6.470210
96	1	0	-7.476607	-1.292575	5.063704
97	1	0	-5.743669	-1.016005	5.103334
98	1	0	-6.071610	1.197488	3.951007
99	1	0	-7.804523	0.919228	3.911490
100	1	0	-7.442777	-1.135415	2.507347
101	1	0	-5.709460	-0.855317	2.544269
102	1	0	-6.043847	1.365361	1.419873
103	1	0	-7.774473	1.091677	1.373862
104	1	0	10.353719	3.486309	6.325659
105	1	0	11.221839	2.380131	5.253540
106	1	0	10.617480	3.920081	4.631793
107	1	0	8.244175	3.138660	5.022062
108	1	0	8.844685	1.610045	5.639732
109	1	0	9.888584	1.116517	3.406896

110	1	0	9.288917	2.645874	2.788333
111	1	0	6.925834	1.890624	3.209444
112	1	0	7.524810	0.361381	3.830458
113	1	0	8.570744	-0.137073	1.607716
114	1	0	7.979273	1.395524	0.982546
115	1	0	5.614560	0.659720	1.426026
116	1	0	6.198760	-0.861826	2.064945
117	1	0	5.338666	6.599058	-4.626174
118	1	0	3.940889	5.599626	-4.208742
119	1	0	4.806540	6.472897	-2.942710
120	1	0	6.860027	5.052544	-3.389688
121	1	0	5.980510	4.175897	-4.628042
122	1	0	4.335571	3.389765	-2.883139
123	1	0	5.247891	4.241390	-1.650995
124	1	0	7.276972	2.821417	-2.222521
125	1	0	6.304173	1.945237	-3.391590
126	1	0	4.738260	1.256813	-1.522972
127	1	0	5.786073	2.080768	-0.375060
128	1	0	7.700376	0.573469	-1.138664
129	1	0	6.580412	-0.268373	-2.188608
130	6	0	8.838210	-3.614768	-0.457803
131	6	0	10.154234	-4.177845	-0.510625
132	6	0	10.534614	-5.503220	-0.702727
133	6	0	-10.832139	-3.135563	-0.554439
134	6	0	-11.345940	-4.405452	-0.802686
135	6	0	11.910099	-5.881959	-0.726562
136	6	0	9.601202	-6.562628	-0.885911
137	6	0	11.219875	-3.224946	-0.338976
138	6	0	-10.526025	-5.542122	-1.053327
139	6	0	-12.752664	-4.643749	-0.819991
140	6	0	-11.794376	-2.090691	-0.319217
141	7	0	13.024841	-6.218326	-0.750151
142	7	0	8.855201	-7.445328	-1.037723
143	7	0	12.048980	-2.422803	-0.195105
144	7	0	-9.874412	-6.486103	-1.260758
145	7	0	-13.895717	-4.865990	-0.839689
146	7	0	-12.536547	-1.217544	-0.123440

Table S4. Cartesian coordinates for optimized geometry of **TOCR2.**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.608904	-0.713356	-0.134375
2	6	0	0.822336	-0.751040	-0.129978
3	6	0	1.620354	0.440015	-0.140807
4	6	0	0.873251	1.618777	-0.159982
5	6	0	-0.533847	1.655854	-0.163020
6	6	0	-1.342695	0.518356	-0.147311
7	7	0	-1.060885	-1.980364	-0.132029
8	7	0	0.054773	-2.709639	-0.126530
9	7	0	1.207155	-2.039970	-0.124912

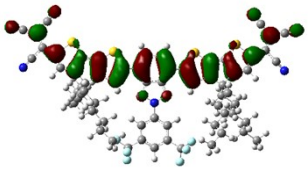
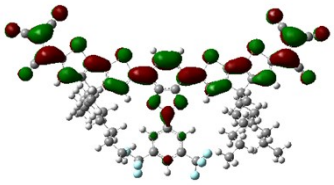
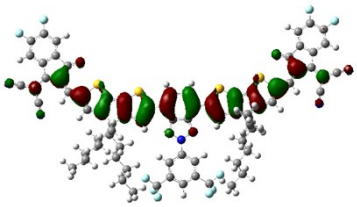
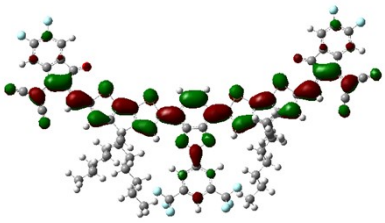
10	6	0	0.017645	-4.130174	-0.127585
11	6	0	-1.214297	-4.784743	-0.143355
12	6	0	-1.238116	-6.178249	-0.132608
13	6	0	-0.054571	-6.914901	-0.104441
14	6	0	1.167067	-6.239153	-0.095824
15	6	0	1.215585	-4.847963	-0.107521
16	6	0	-2.789862	0.569752	-0.139753
17	6	0	3.068124	0.413360	-0.132342
18	16	0	4.003619	1.911229	-0.297545
19	6	0	5.482305	1.022278	-0.181889
20	6	0	5.273601	-0.348152	-0.038450
21	6	0	3.909340	-0.688276	-0.003848
22	6	0	6.882643	1.295854	-0.165084
23	6	0	7.570172	0.082543	-0.005013
24	6	0	6.601849	-1.098837	0.065320
25	16	0	7.911574	2.671924	-0.285017
26	6	0	9.340283	1.618343	-0.117717
27	6	0	8.945716	0.268162	0.017600
28	16	0	-3.641029	2.121910	-0.251268
29	6	0	-5.166022	1.311799	-0.163914
30	6	0	-5.034296	-0.071688	-0.069113
31	6	0	-3.690557	-0.487367	-0.045640
32	6	0	-6.547690	1.661452	-0.134074
33	6	0	-7.305332	0.484489	-0.013437
34	6	0	-6.401618	-0.751092	0.041048
35	16	0	-7.490424	3.099524	-0.226838
36	6	0	-8.668599	0.753913	-0.018271
37	6	0	-2.560451	-6.901451	-0.208954
38	9	0	-2.537866	-8.051411	0.493784
39	9	0	-2.867494	-7.220042	-1.486541
40	9	0	-3.574108	-6.145831	0.267579
41	6	0	2.444137	-7.043180	-0.107356
42	9	0	3.523688	-6.284392	0.182350
43	9	0	2.657795	-7.601407	-1.319905
44	9	0	2.397797	-8.050473	0.787841
45	6	0	4.499275	-7.085880	-4.396232
46	6	0	5.599837	-6.089644	-4.018767
47	6	0	5.167594	-5.101672	-2.928397
48	6	0	6.240463	-4.064029	-2.576080
49	6	0	5.829862	-3.142389	-1.418561
50	6	0	6.853181	-2.026513	-1.167390
51	6	0	6.575490	-1.223969	7.807398
52	6	0	6.734321	-2.020470	6.508998
53	6	0	6.577108	-1.160851	5.248709
54	6	0	6.734325	-1.951331	3.944108
55	6	0	6.577695	-1.086936	2.686018
56	6	0	6.736166	-1.896472	1.392707
57	6	0	-10.393665	-5.007679	5.148927
58	6	0	-9.086531	-4.280671	4.819796
59	6	0	-9.098331	-3.610797	3.440183
60	6	0	-7.792250	-2.881317	3.103259
61	6	0	-7.807956	-2.209439	1.722824
62	6	0	-6.489161	-1.491337	1.410793
63	6	0	-4.891067	-7.076660	-4.190889

64	6	0	-5.835447	-5.904556	-3.908109
65	6	0	-5.344402	-4.983149	-2.784258
66	6	0	-6.271765	-3.789259	-2.527080
67	6	0	-5.818680	-2.905460	-1.356061
68	6	0	-6.712687	-1.671287	-1.177825
69	1	0	1.392408	2.572122	-0.162243
70	1	0	-1.001517	2.635455	-0.168456
71	1	0	-2.131533	-4.212505	-0.157255
72	1	0	-0.083707	-7.997883	-0.078415
73	1	0	2.160702	-4.323646	-0.096357
74	1	0	3.515926	-1.687152	0.116459
75	1	0	9.685143	-0.517892	0.129728
76	1	0	-3.351598	-1.509160	0.043612
77	1	0	-9.457605	0.012593	0.041818
78	1	0	4.847594	-7.802270	-5.147099
79	1	0	4.161737	-7.652044	-3.521750
80	1	0	3.625162	-6.570205	-4.810381
81	1	0	5.913074	-5.532136	-4.911947
82	1	0	6.488618	-6.636580	-3.676220
83	1	0	4.887537	-5.660858	-2.025635
84	1	0	4.256728	-4.578890	-3.255166
85	1	0	6.464326	-3.457726	-3.465011
86	1	0	7.176509	-4.577601	-2.315559
87	1	0	5.690219	-3.752444	-0.517029
88	1	0	4.854408	-2.695797	-1.647969
89	1	0	6.909910	-1.395109	-2.062083
90	1	0	7.849895	-2.469853	-1.041373
91	1	0	6.693157	-1.864746	8.687144
92	1	0	7.322414	-0.425045	7.876089
93	1	0	5.586346	-0.755807	7.867064
94	1	0	5.996749	-2.834335	6.485886
95	1	0	7.719914	-2.505168	6.495028
96	1	0	7.315543	-0.346841	5.271257
97	1	0	5.591183	-0.674459	5.262472
98	1	0	5.995450	-2.765318	3.922118
99	1	0	7.720084	-2.437699	3.931690
100	1	0	7.318079	-0.277652	2.709235
101	1	0	5.592525	-0.603560	2.699798
102	1	0	5.995343	-2.704797	1.386519
103	1	0	7.719194	-2.386198	1.387735
104	1	0	-10.353825	-5.474013	6.138542
105	1	0	-11.244259	-4.316947	5.140807
106	1	0	-10.603487	-5.796659	4.417874
107	1	0	-8.249534	-4.990496	4.869951
108	1	0	-8.886049	-3.521602	5.588097
109	1	0	-9.935423	-2.900207	3.389910
110	1	0	-9.300081	-4.369918	2.670965
111	1	0	-6.955625	-3.592932	3.151328
112	1	0	-7.589834	-2.123320	3.872943
113	1	0	-8.640039	-1.495452	1.685546
114	1	0	-8.016726	-2.969836	0.959652
115	1	0	-5.668620	-2.217901	1.456540
116	1	0	-6.284178	-0.756806	2.199112
117	1	0	-5.280742	-7.718921	-4.987209

118	1	0	-3.902558	-6.721771	-4.504065
119	1	0	-4.747914	-7.695705	-3.299323
120	1	0	-6.830167	-6.290553	-3.646983
121	1	0	-5.972127	-5.314936	-4.824917
122	1	0	-4.339369	-4.612772	-3.034018
123	1	0	-5.228655	-5.565158	-1.860300
124	1	0	-7.289956	-4.153888	-2.330948
125	1	0	-6.339410	-3.179476	-3.438953
126	1	0	-4.783080	-2.586786	-1.529459
127	1	0	-5.809801	-3.509613	-0.439574
128	1	0	-7.757908	-1.993448	-1.097067
129	1	0	-6.656607	-1.056982	-2.084532
130	6	0	-8.980454	2.128418	-0.118706
131	6	0	-10.328948	2.554992	-0.122879
132	1	0	-10.990878	1.699984	-0.043844
133	6	0	-10.950713	3.786869	-0.204410
134	6	0	-11.319972	6.124406	-0.385150
135	6	0	-12.582165	5.510452	-0.310042
136	6	0	-11.152349	7.498339	-0.500233
137	6	0	-13.733647	6.306592	-0.352147
138	6	0	-12.299761	8.276072	-0.540796
139	6	0	-13.567514	7.681257	-0.467507
140	6	0	-10.263319	5.089718	-0.322681
141	6	0	-12.393422	4.039870	-0.193059
142	8	0	-9.056031	5.301623	-0.364248
143	6	0	-13.428099	3.125080	-0.092050
144	6	0	-14.806970	3.498922	-0.092862
145	6	0	-13.241186	1.713516	0.025764
146	7	0	-15.940863	3.767141	-0.090314
147	7	0	-13.123521	0.557992	0.123853
148	1	0	-10.166932	7.947210	-0.556313
149	1	0	-14.740371	5.915421	-0.300533
150	6	0	10.711374	1.965632	-0.106783
151	1	0	11.319995	1.076694	0.014988
152	6	0	11.406206	3.155541	-0.216192
153	6	0	13.138219	4.776513	-0.343319
154	6	0	11.916116	5.460099	-0.465355
155	6	0	14.335231	5.502324	-0.386615
156	6	0	11.832057	6.836794	-0.628710
157	6	0	13.023899	7.544509	-0.670092
158	6	0	14.252716	6.879654	-0.550204
159	6	0	12.860918	3.324142	-0.183187
160	6	0	10.799285	4.491511	-0.391588
161	8	0	9.607588	4.771859	-0.465264
162	6	0	13.837724	2.354239	-0.032713
163	6	0	15.236017	2.646801	-0.016604
164	6	0	13.565766	0.960355	0.123830
165	7	0	16.383484	2.848436	0.001146
166	7	0	13.378454	-0.182743	0.253915
167	1	0	15.315934	5.055116	-0.300650
168	1	0	10.876092	7.340166	-0.720458
169	9	0	-12.224635	9.607716	-0.650580
170	9	0	-14.641077	8.479676	-0.511613
171	9	0	15.372129	7.612213	-0.597185

172	9	0	13.029564	8.873778	-0.824891

Table S5. Topologies and energy values of frontier molecular orbitals and HOMO-LUMO gaps of the compounds **TOCR1** and **TOCR2** calculated at B3LYP/6-31G(d,p) level.

HOMO (eV)	LUMO (eV)	HOMO-LUMO Gap (eV)
 **-5,77**	 **-3,89**	**1,87**
 **-5,47**	 **-3,62**	**1,85**

Photophysical study

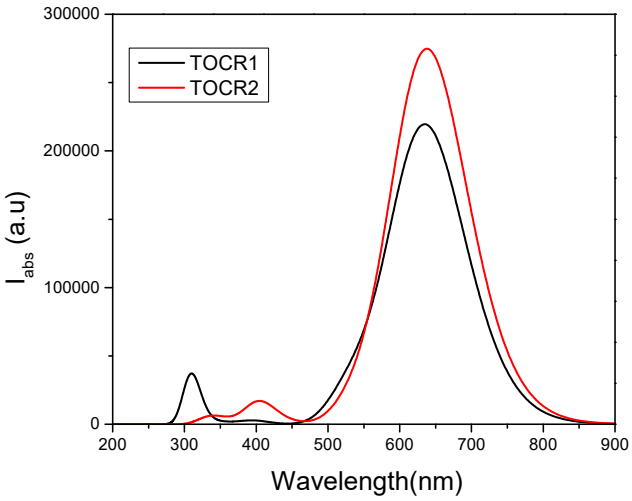


Figure S24. Theoretical absorption spectra of compounds **TOCR1** and **TOCR2** calculated at M062x/6-311+G(2d,p) level in CH_2Cl_2.

Table S6. Electronic transitions associated with the absorption spectra of compounds **TOCR1** and **TOCR2** calculated at M062x/6-311+G(2d,p) level. Only transitions with f≥0.1 and a contribution greater than 10% are described.

Compound	***Electronic transition***	***E(eV)***	***λ (nm)***	***f***	***MO (coefficient %)***
TOCR1	**$S_0 \rightarrow S_1$**	**1,95**	**636,92**	**2,97**	**H→L (82), H-1→L+1 (13)**
	$S_0 \rightarrow S_2$	2,28	543,53	0,51	H-1→L (33), H→L+1 (62)
	$S_0 \rightarrow S_9$	4,00	309,64	0,47	H-6→L (16), H-3→L (18), H-1→L+2 (16)
TOCR2	**$S_0 \rightarrow S_1$**	**1,94**	**639,96**	**3,71**	**H→L (78), H-1→L+1 (15)**
	$S_0 \rightarrow S_2$	2,23	556,04	0,43	H-1→L (37), H→L+1 (53)
	$S_0 \rightarrow S_4$	3,05	407,01	0,19	H-1→L (11), H-1→L+2 (26), H→L+1 (13), H→L+3 (35)

E: Transition energy, λ: Wavelength of the transition, f: Transition oscillator strength, MO: Molecular orbitals involved in the transition (H: HOMO. L: LUMO).

8. Photovoltaic studies

Table S6a. Photovoltaic parameters of the P1:**TOCR1** based PSCs for different weight ratio of P1 and **TOCR1**

D:A weight ratio	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
1:0.4	15.94	0.76	0.52	6.30
1:0.8	16.53	0.77	0.55	7.00
1:1.2	17.09	0.76	0.59	7.66
1:1.3	16.47	0.75	0.56	6.92

Table S6b. Photovoltaic parameters of the P1:**TOCR2** based PSCs for different weight ratio of P1 and **TOCR2**

D:A weight ratio	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
1:0.4	17.98	0.91	0.56	9.16
1:0.8	18.52	0.92	0.60	10.22
1:1.2	19.38	0.91	0.63	11.11
1:1.3	18.64	0.92	0.61	10.46

Table S7a. Photovoltaic parameters of the P2:**TOCR1** based PSCs for different weight ratio of P2 and **TOCR1**

D:A weight ratio	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
1:0.4	17.02	0.83	0.51	7.20
1:0.8	17.94	0.84	0.54	8.14
1:1.2	18.45	0.82	0.57	8.621
1:1.3	17.84	0.83	0.55	8.13

Table S7b. Photovoltaic parameters of the P2:**TOCR2** based PSCs for different weight ratio of P2 and **TOCR2**

D:A weight ratio	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
1:0.4	6.82	0.94	0.43	2.76
1:0.8	7.44	0.95	0.45	3.18
1:1.2	7.14	0.96	0.49	3.36
1:1.3	6.64	0.97	0.48	3.09

Table S8a. Photovoltaic parameters of the PSCs based on P1:**TOCR1** (1:1.2) active layer subjected to SVA treatment for different times.

SVA exposure time	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
10 s	20.15	0.73	0.62	9.12
30 s	20.78	0.72	0.65	9.73
40 s	21.38	0.72	0.67	10.31
50 s	20.85	0.73	0.66	10.04

Table S8b. Photovoltaic parameters of the PSCs based on P1:**TOCR2** (1:1.2) active layer subjected to SVA treatment for different times.

SVA exposure time	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
10 s	23.06	0.87	0.67	12.44
30 s	23.71	0.86	0.69	13.25
40 s	24.22	0.87	0.72	15.17
50 s	23.82	0.88	0.68	14.25

Table S9a. Photovoltaic parameters of the PSCs based on P2:**TOCR1** (1:1.2) active layer subjected to SVA treatment for different times.

SVA exposure time	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
10 s	20.86	0.82	0.61	10.43
30 s	22.41	0.80	0.63	11.29
40 s	23.08	0.78	0.66	11.88
50 s	22.52	0.76	0.63	10.78

Table S9b. Photovoltaic parameters of the PSCs based on P2:**TOCR2** (1:1.2) active layer subjected to SVA treatment for different times.

SVA exposure time	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
10 s	9.02	0.95	0.51	4.37
30 s	9.68	0.95	0.54	4.96
40 s	10.21	0.93	0.57	5.41
50 s	9.86	0.93	0.55	5.04

9. XRD studies

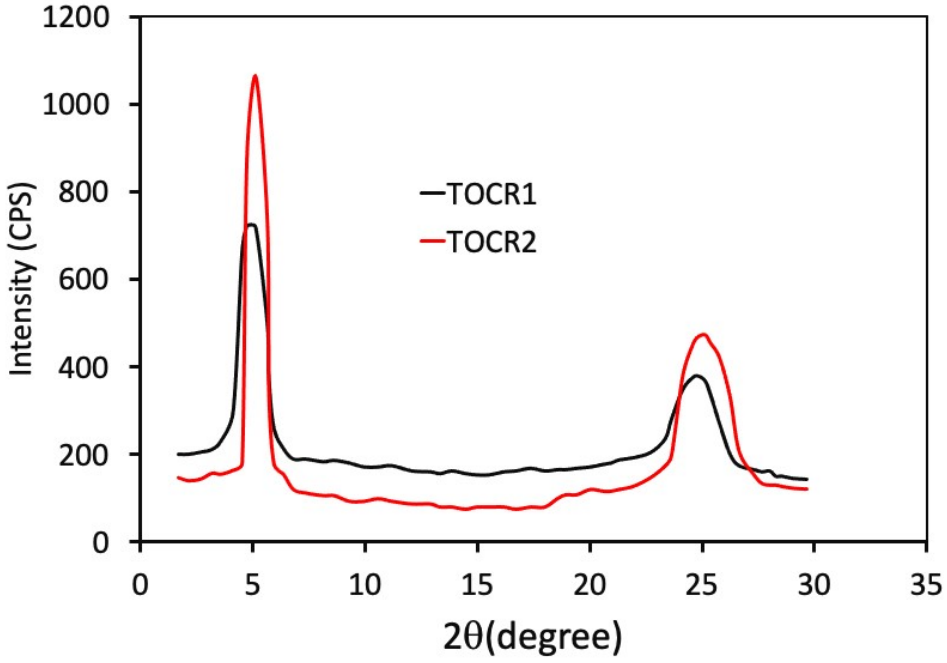


Figure S25. XRD patterns of pristine **TOCR1** and **TOCR2** films.