Supporting Information

for

Construction of a Tetrabenzotetrathia[8]circulene by a "Fold-In" Oxidative Fusion Reaction: Synthesis and Optical Properties

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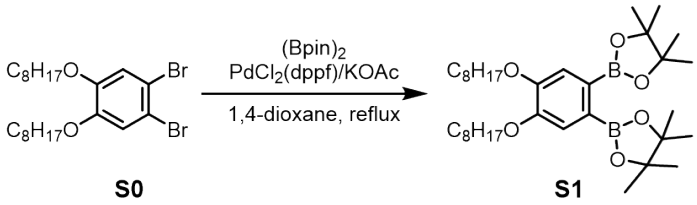
Contents

1. Instrumentation and Materials

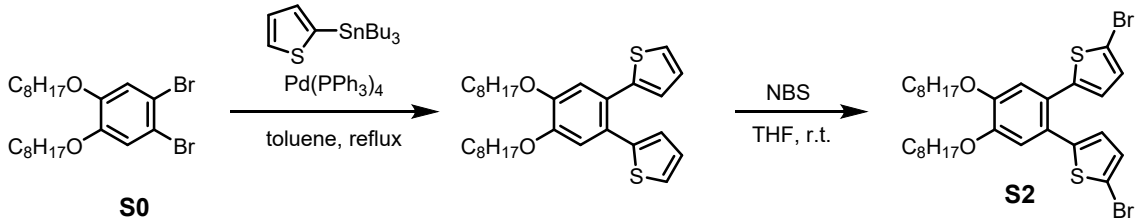
Commercially available solvents and reagents were used without further purification unless otherwise noted. 2,2'-((4,5-Bis(octyloxy)-1,2-phenylene)bis(thiophene-5,2-diyl))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**S1)** and 5,5'-(4,5-bis(octyloxy)-1,2-phenylene)bis(2-bromothiophene) (**S2**) were prepared according to reported procedures.[S1] Spectroscopic grade solvents were used as solvents for all spectroscopic studies. Silica gel column chromatography was performed on Leyan C200012. Thin-layer chromatography (TLC) was carried out on glass sheets coated with silica gel 60 F254 (Leyan C100020). ^{1}H and ^{13}C NMR spectra at room temperature were recorded at ambient temperature and pressure using BRUKER AVANCE III, HD 600 MHz spectrometers. ^{1}H and ^{13}C NMR spectra data at high temperature were recorded on JEOL JNM-ECZ500R 500 Hz nuclear magnetic resonance spectrometer. Chemical shifts are reported in parts per million (ppm, δ) referenced to $CDCl_3$ (δ = 7.26 ppm) for ^{1}H NMR and $CDCl_3$ (δ = 77.16 ppm) or $C_2Cl_4D_2$ (δ = 73.78 ppm) for ^{13}C NMR. Matrix-Assisted Laser Desorption/Ionization Time-of-Flight (MALDI-TOF) mass characterization was conducted on a Bruker UltrafleXtreme TOF/TOF mass spectrometer (Bruker Daltonics, Inc., Billerica, MA). UV-visible absorption spectra were recorded on a UV-2600i spectrometer. Fluorescence spectra and fluorescence lifetimes and were determined by Horiba Fluoro Max+ spectrophotometer at room temperature. Absolute fluorescence quantum yields were measured on a Hamamatsu Photonics C11347-11 with a Quantaurus-QY measurement system. Phosphorescence spectra were recorded by Horiba Fluoro Max+ spectrophotometer at 77 K in 2-methyltetrafuran. The phosphorescence lifetimes and quantum yield were measured using the Edinburgh FLS1000 at 77 K. Cyclic voltammetry curves were recorded on a CHI660E electrochemical workstation with a glassy carbon disc working electrode, a platinum wire counter electrode, and an Ag/AgCl wire reference electrode in dichloromethane (1.0 mM) containing 0.1 M *n*-Bu_4NPF_6 as supporting electrolyte (scan rate: 100 mV s^{-1}) using ferrocene as an external reference.

2. Experimental Section



Synthesis of 2,2'-((4,5-Bis(octyloxy)-1,2-phenylene)bis(thiophene-5,2-diyl))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (S1):

Under N_2 atmosphere, 1,2-dibromo-4,5-bis(octyloxy)benzene **S0** (4.92 g, 10.0 mmol) , $(Bpin)_2$ (5.59 g, 22.0 mmol), $PdCl_2(dppf)$ (0.732 g, 1.0 mmol) and KOAc (4.90 g, 50.0 mmol) were suspended in degassed 1,4-dioxane (150 mL). The resulting suspension was heated to 85 ºC and stirred for 12 hours. After cooled to room temperature, the reaction was quenched with a saturated aqueous NH_4Cl solution, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. After removal of the solvents under vacuum, the residue was purified by column chromatography on silica gel (petroleum ether/dichloromethane/ethyl acetate=30/1/1) to obtain **S1** (2.23 g, 36%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 (s, 2H), 4.03 (t, J = 6.6 Hz, 4H), 1.82-1.77 (m, 4H), 1.48-1.42 (m, 4H), 1.35 (s, 24H), 1.33-1.26 (m, 16H), 0.89 (t, J = 6.6 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ



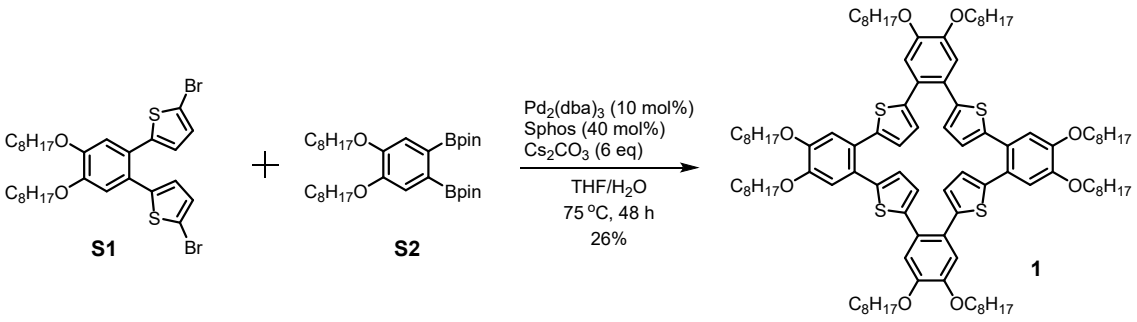
150.0, 118.9, 83.8, 69.1, 31.9, 29.5, 29.40, 29.38, 26.1, 25.0, 22.8, 14.2.

Synthesis of 5,5'-(4,5-bis(octyloxy)-1,2-phenylene)bis(2-bromothiophene) (S2):

Under N_2 atmosphere, 1,2-dibromo-4,5-bis(octyloxy)benzene **S0** (4.92 g, 10.0 mmol), $Pd(PPh_3)_4$ (0.578 g, 0.5 mmol) were suspended in a degassed toluene (150 mL), and then 2-(tributylstannyl)thiophene (7.9 mL, 25.0 mmol) was charged to the mixture by syringe. The resulting reaction mixture was heated reflux and stirred for 12 hours. After cooled to room temperature, the mixture was quenched with a saturated aqueous

KF solution and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. After removal of the solvents under vacuum, the residue was purified by column chromatography on silica gel (petroleum ether/dichloromethane =10/1) to obtain 2,2'-(4,5-bis(octyloxy)-1,2-phenylene)dithiophene (4.59 g, 92%) as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (d, *J* = 6.8 Hz, 2H), 6.99 (s, 2H), 6.95 (t, *J* =6.8 Hz, 2H), 6.84 (d, *J* = 6.8 Hz, 2H), 4.05 (t, *J* = 6.6 Hz, 4H), 1.86-1.81 (m, 4H), 1.50-1.45 (m, 4H), 1.38-1.26 (m, 16H), 0.89 (t, *J* = 6.8 Hz, 6H).

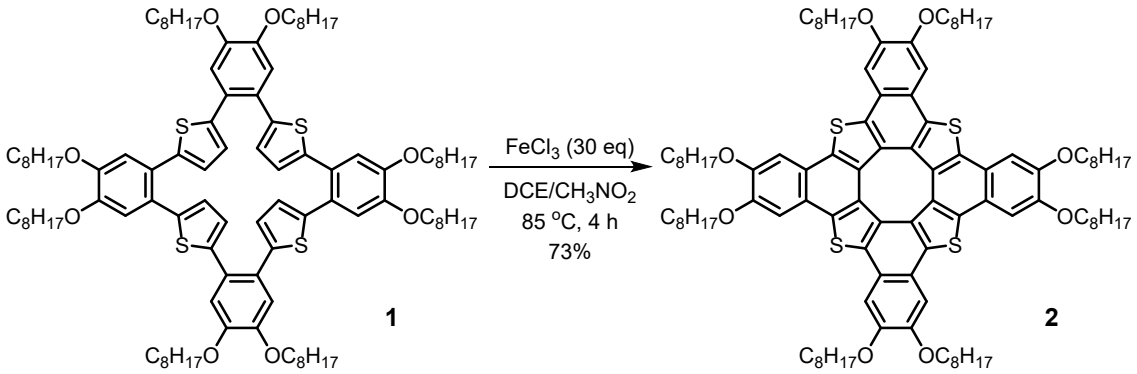
To a solution of 2,2'-(4,5-bis(octyloxy)-1,2-phenylene)dithiophene (2.24 g, 4.5 mmol) in THF (60 mL) was added NBS (1.76 g, 9.9 mmol) at 0 °C under N_2. The reaction mixture was allowed to stir for an additional 2 hours at room temperature. The reaction was then quenched with a saturated aqueous $NaHSO_3$ solution and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. After removal of the solvents under vacuum, the residue was purified by column chromatography on silica gel (petroleum ether/dichloromethane =10/1) to obtain **S2** (2.63 g, 89%) as white solids. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.91 (d, *J* = 6.8 Hz, 2H), 6.89 (s, 2H), 6.62 (d, *J* = 6.8 Hz, 2H), 4.03 (t, *J* = 6.6 Hz, 4H), 1.85-1.80 (m, 4H), 1.49-1.44 (m, 4H), 1.37-1.26 (m, 16H), 0.89 (t, *J* = 6.8 Hz, 6H).



Synthesis of 1:

2,2'-((4,5-Bis(octyloxy)-1,2-phenylene)bis(thiophene-5,2-diyl))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **S1** (1.231 g, 2.1 mmol), 5,5'-(4,5-bis(octyloxy)-1,2-phenylene)bis(2-bromothiophene) **S2** (1.313 g, 2.0 mmol), $Pd_2(dba)_3$ (0.183 g, 0.20 mmol), Sphos (0.328 g, 0.80 mmol), Cs_2CO_3 (3.909 g, 12.0 mmol) were charged into an oven dried Schlenk tube under nitrogen atmosphere, followed by degassed

THF (80 mL) and H_2O (4 mL). The mixture was stirred at 75 ℃ for 12 h. After cooled to room temperature, the reaction was quenched with a saturated aqueous NH_4Cl solution (20 mL) and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. After removal of the solvents under vacuum, the residue was purified by column chromatography on silica gel (petroleum ether /dichloromethane = 2/1) to give **1** (0.862 g, yield: 26%) as yellow-green solids. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.02 (s, 8H), 6.45 (s, 8H), 4.10 (t, J = 6.5 Hz, 16H), 1.89-1.85 (m, 16H), 1.54-1.49 (m, 16H), 1.41-1.26 (m, 64H), 0.90 (t, J = 6.5 Hz, 24H).^{13}C NMR (150 MHz, $CDCl_3$) δ 148.8, 141.6, 127.2, 126.3, 116.4, 69.6, 32.0, 29.5, 29.4, 26.2, 22.8, 14.3. HR-MALDI-TOF-MS: *m/z* calcd. for $C_{104}H_{152}O_8S_4$ $[M]^+$, 1657.0370; found 1657.0347.



Synthesis of 2:

Under N_2 atmosphere, compound **1** (0.663 g, 0.40 mmol) were dissolved in dry degassed 1,2-dichloroethane (150 mL), and the resulting solution was heated to 85 ℃. Then, $FeCl_3$ (1.946 g, 12.0 mmol) in CH_3NO_2 (5 mL) was added dropwise. After further stirred at 85℃ for 4 h, the reaction mixture was cooled down to room temperature, successively quenched with methanol, and extracted with dichloromethane. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. Pure target product **3** was obtained as gray solids by addition of methanol to a toluene solution (0.472 g, 71%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 (s, 8H), 4.16 (s, 16H), 1.89 (s, 16H),1.68(s, 16H), 1.52-1.37 (m, 64H), 1.02 (s, 24H). ^{13}C NMR (125 MHz, 1,1,2,2-tetrachloroethane-d_2, 80 ℃) δ 150.0, 132.9, 128.2, 121.1, 105.8, 69.3, 31.7, 29.6, 29.5, 29.2, 26.2, 22.5, 13.9. HR-MALDI-TOF-MS: *m/z* calcd. for $C_{104}H_{144}O_8S_4$ $[M]^+$, 1648.9744; found 1648.9739.

3. **NMR Spectra**

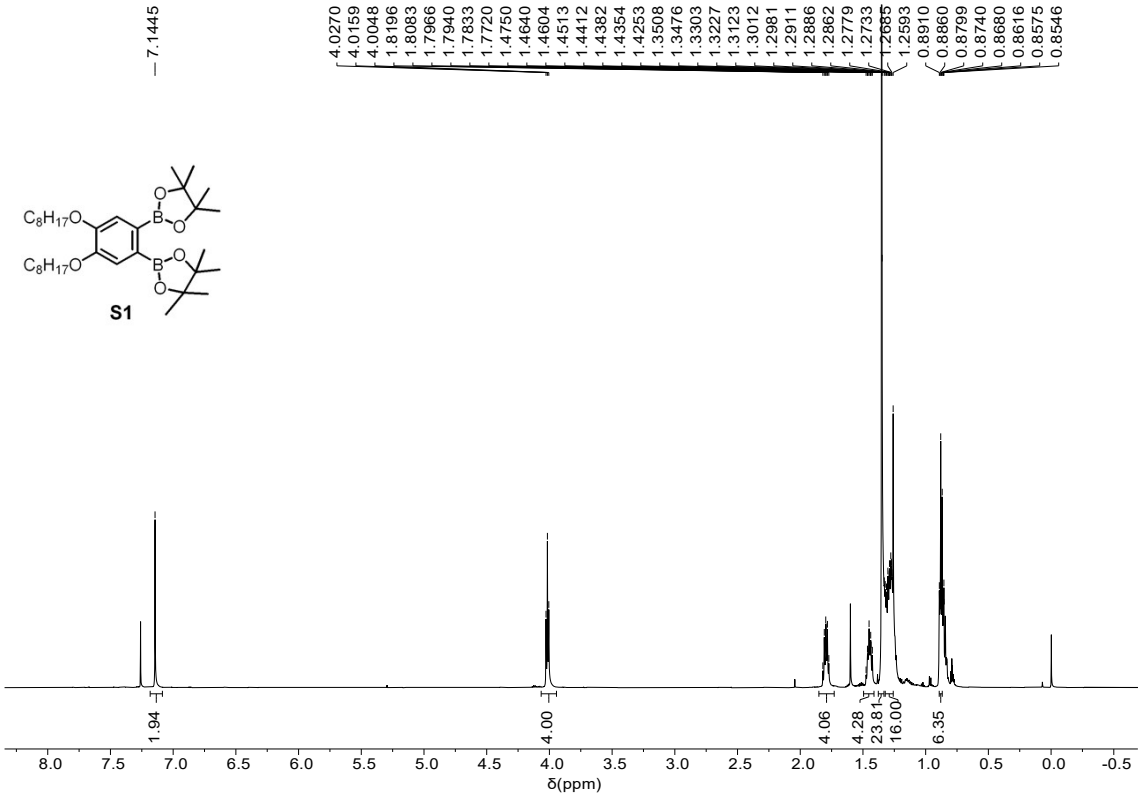


Figure S1. ^{1}H NMR spectra of **S1** in $CDCl_3$ at room temperature.

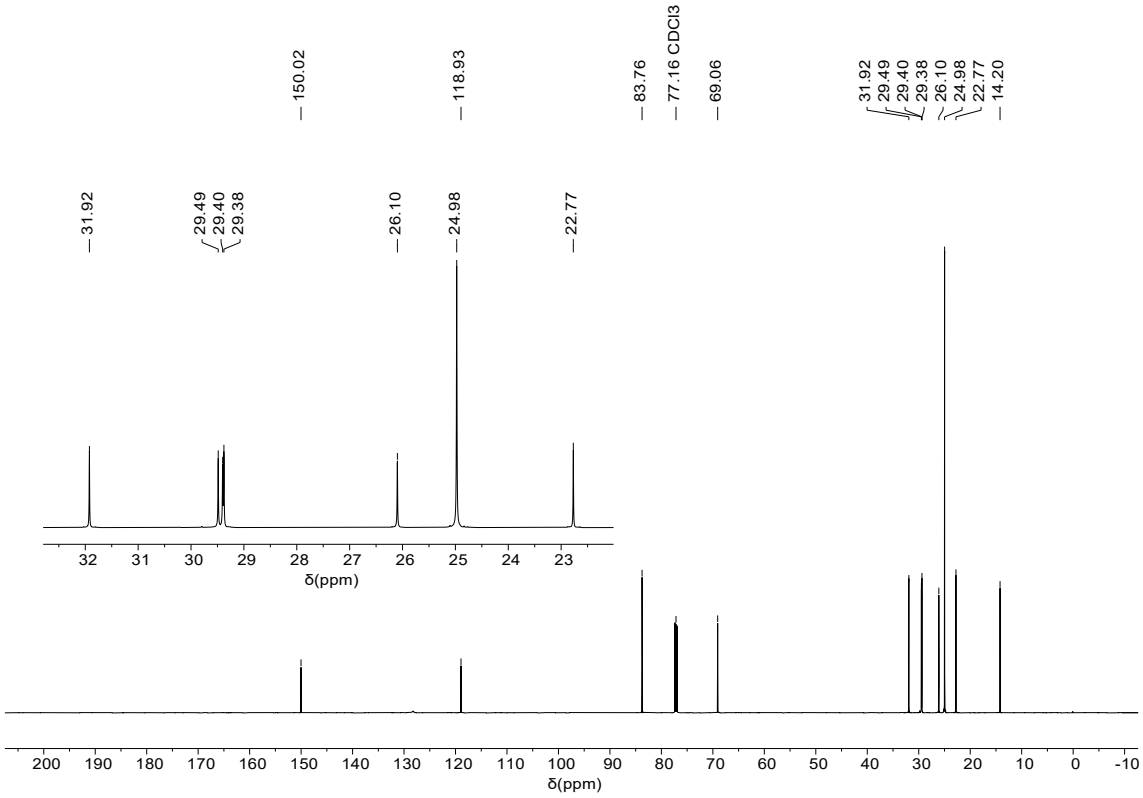


Figure S2. ^{13}C NMR spectra of **S1** in $CDCl_3$ at room temperature.

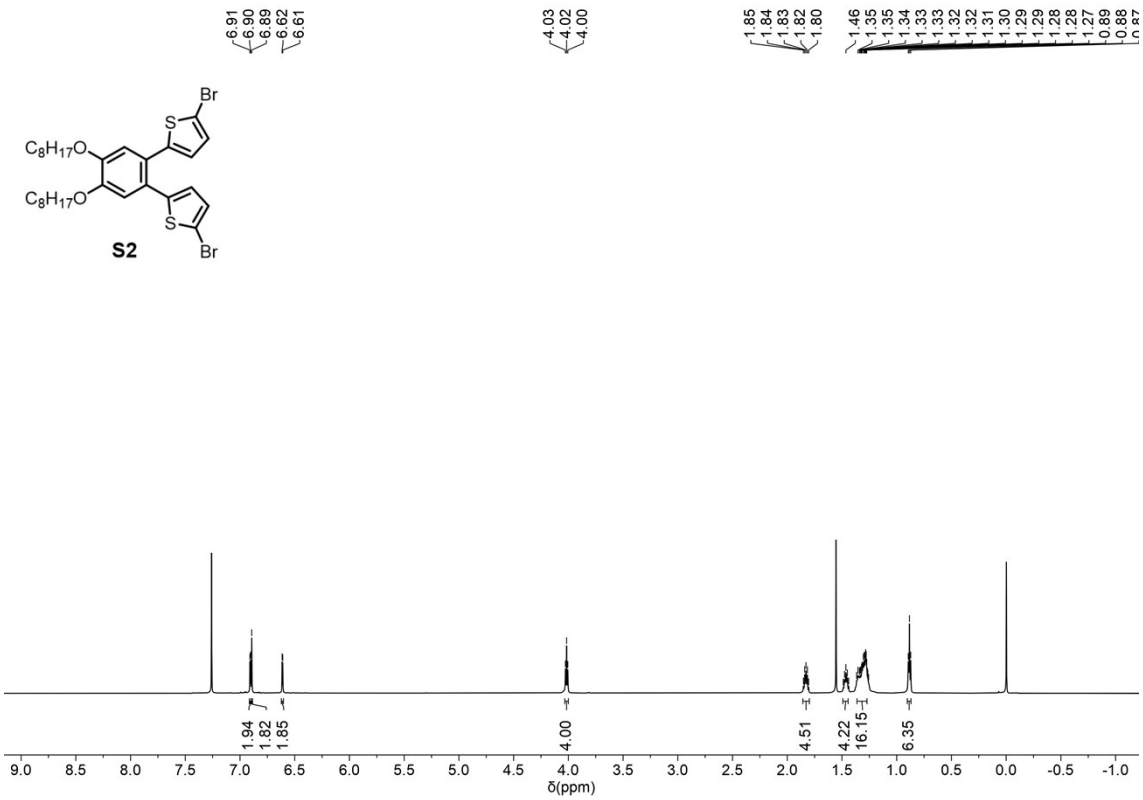


Figure S3. ^{1}H NMR spectra of **S2** in $CDCl_3$ at room temperature.

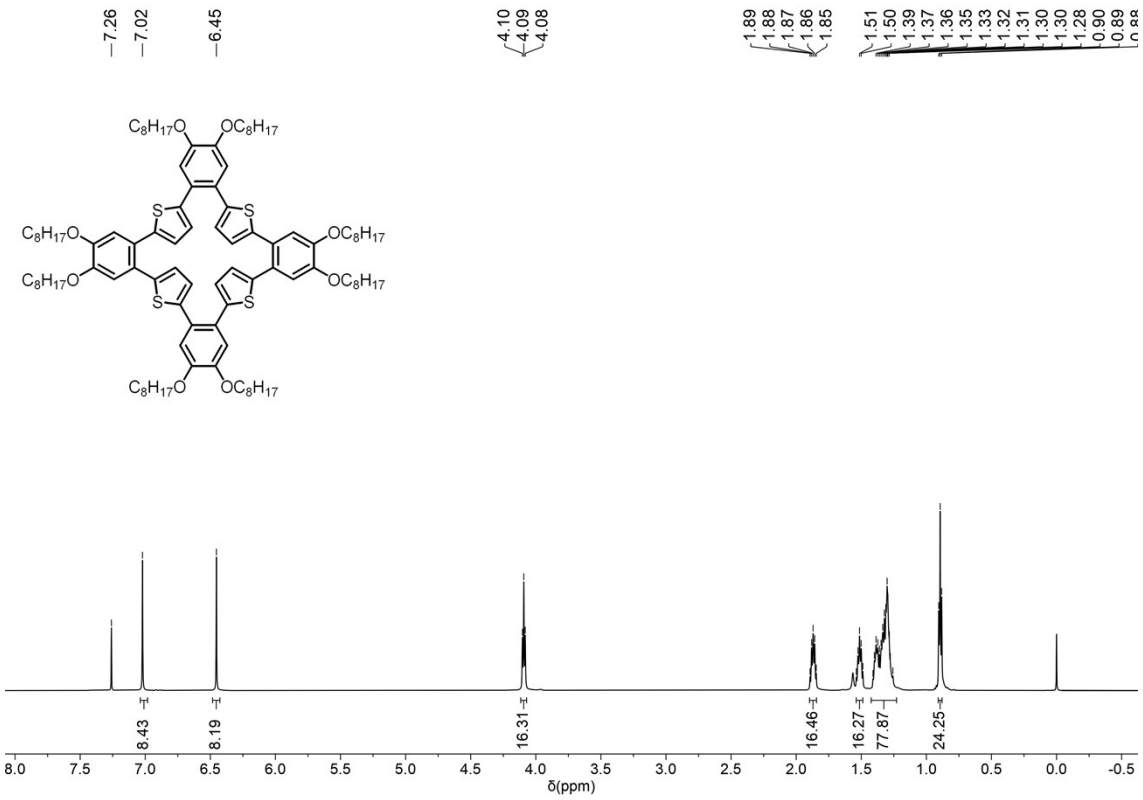


Figure S4. ^{1}H NMR spectra of **1** in $CDCl_3$ at room temperature.

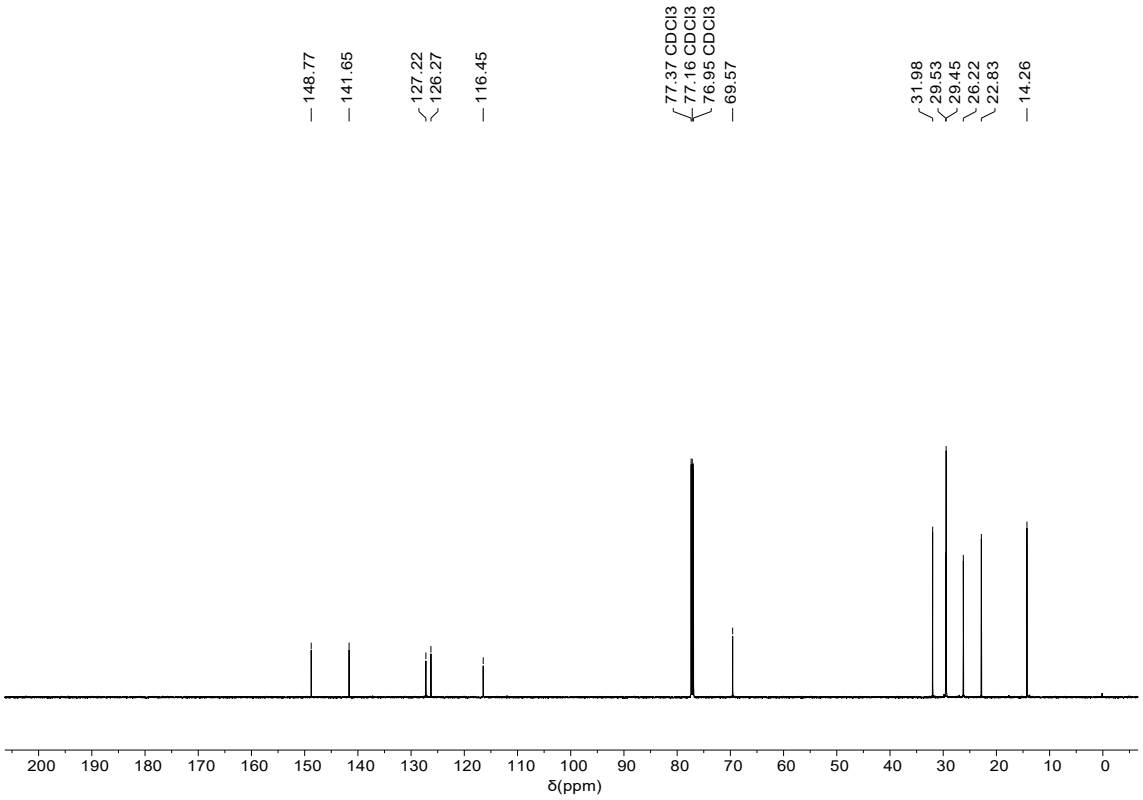


Figure S5. ^{13}C NMR spectra of **1** in $CDCl_3$ at room temperature.

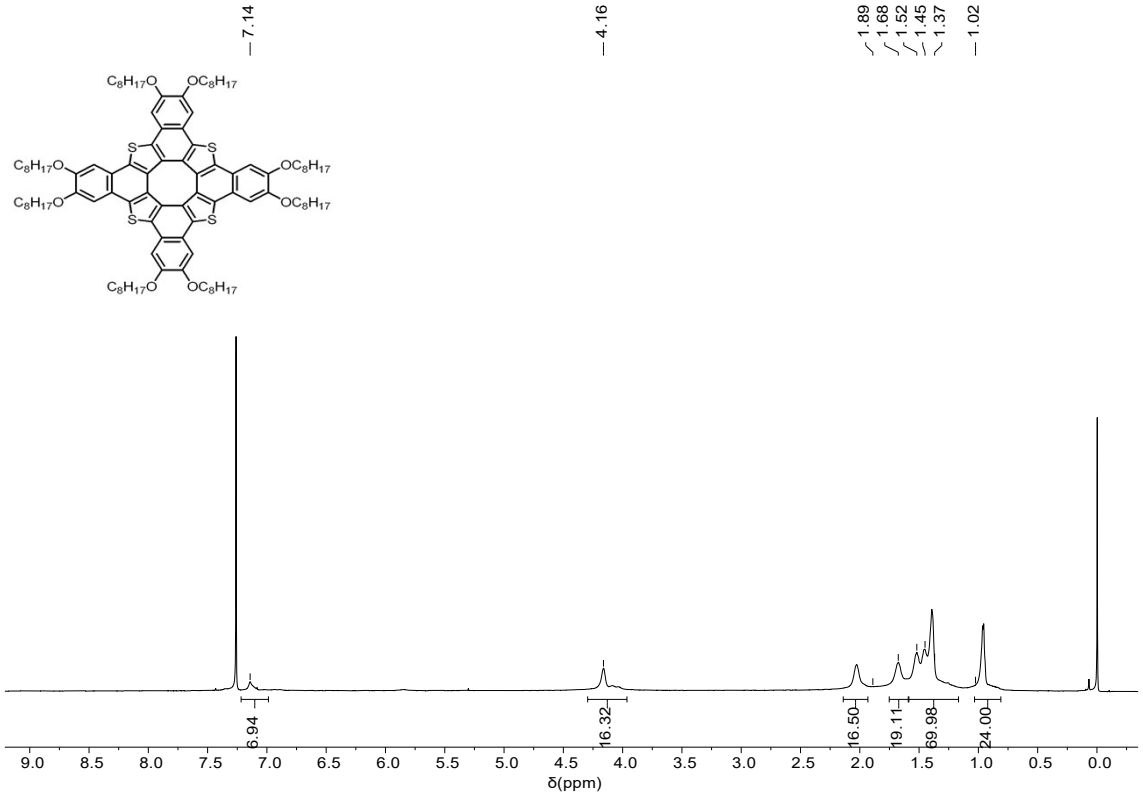


Figure S6. ^{1}H NMR spectra of **2** in $CDCl_3$ at room temperature.

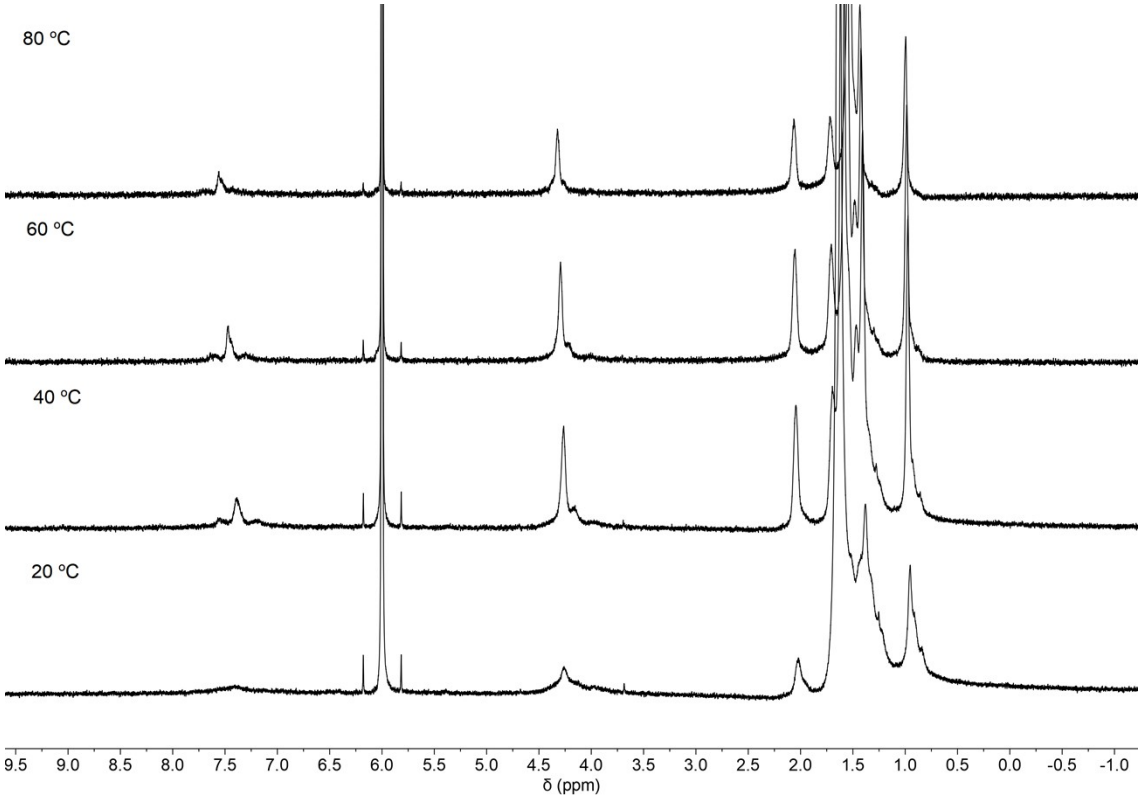


Figure S7. ^{1}H NMR spectra of **2** in 1,1,2,2-tetrachloroethane-d_2 at different temperatures.

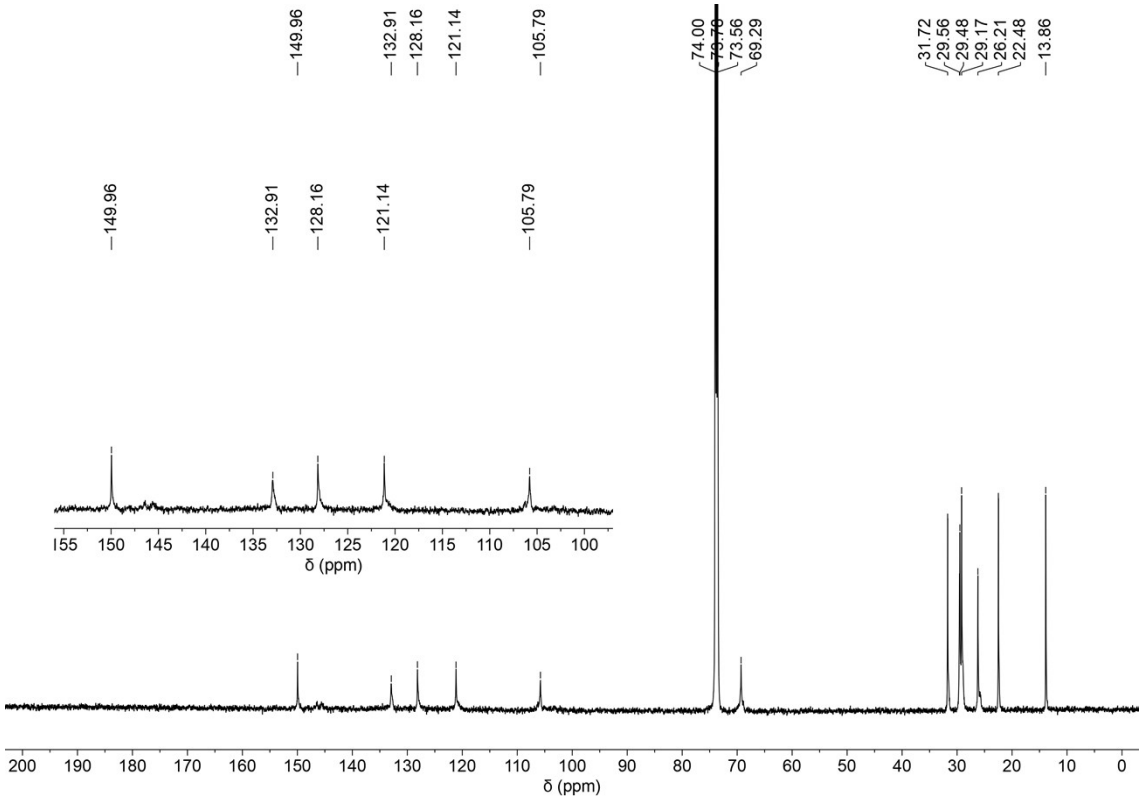


Figure S8. ^{13}C NMR spectra of **2** in 1,1,2,2-tetrachloroethane-d_2 at 80℃.

4. Mass Spectra

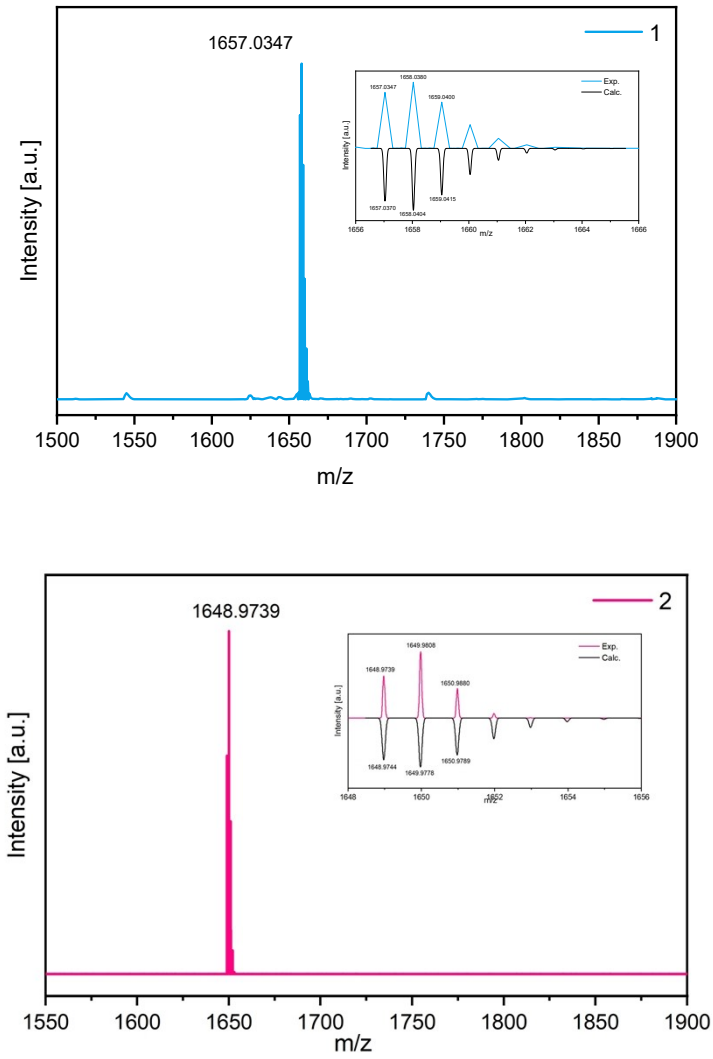


Figure S9. HR-MALDI-TOF-MS of **1** and **2**.

5. Decay Profiles

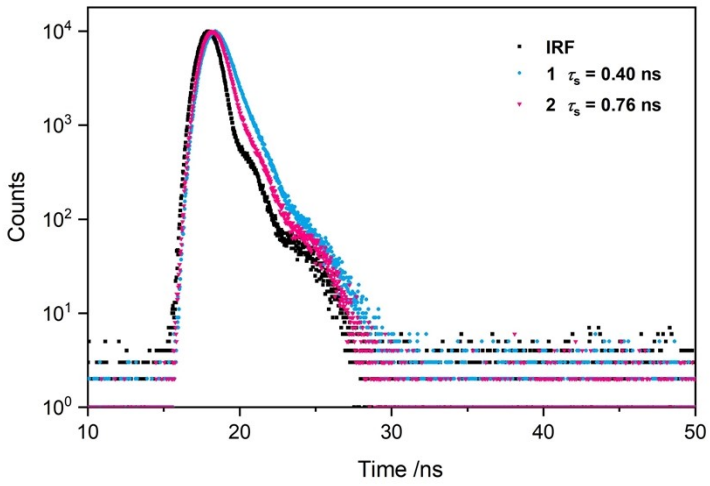


Figure S10. The transient fluorescence decay profiles of **1** and **2** in CH_2Cl_2 at room temperature.

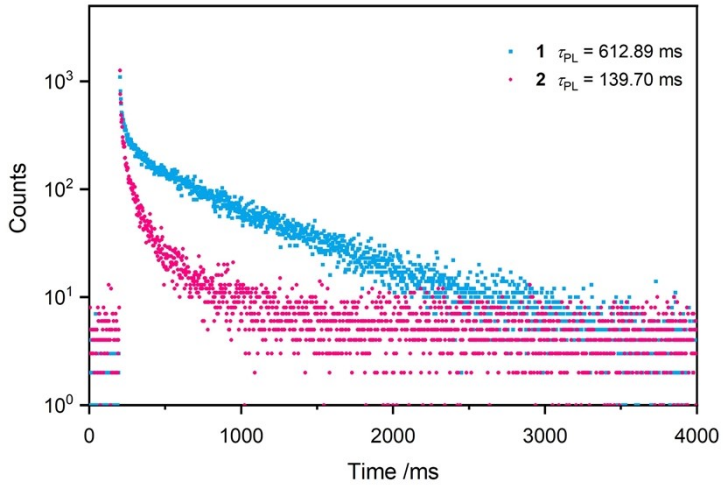


Figure S11. The transient phosphorescence decay profiles of **1** and **2** in 2-methyltetrahydrofuran at 77K.

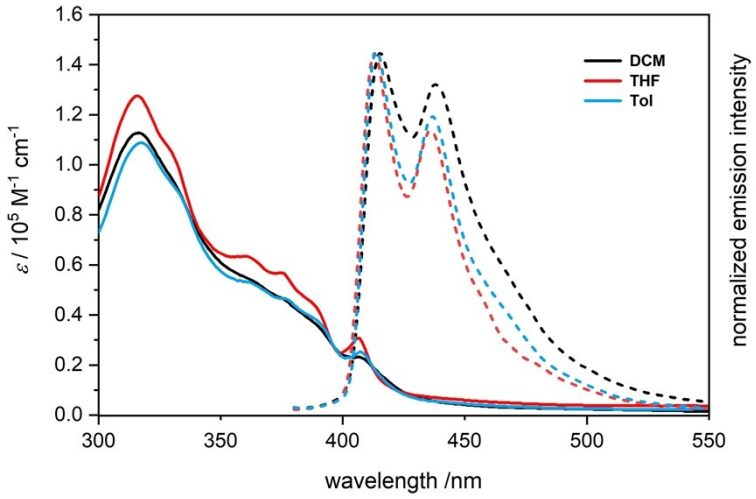


Figure S12. Absorption and emission spectra of **2** in different solvents.

Table S1 Summary of optical and electrochemical properties.

	λ_{abs} [a] (nm)	λ_{FL} [a] (nm)	λ_{PL} [b] (nm)	E_g^{opt} [c] (eV)	Φ_{FL} [d] (%)	Φ_{PL} [e] (%)	τ_{FL} [f] (ns)	τ_{PL} [g] (ms)	k_r [h] (10^8 s^{-1})	k_{nr} [h] (10^9 s^{-1})	E_{HOMO}^{cv} [i] (eV)	E_{LUMO}^{cv} [i] (eV)
1	330	520	550	3.36	5.80	5.3	0.40	612.89	1.45	2.36	-5.11	-3.56
2	316 407	416 438	565	2.88	3.00	11.7	0.76	139.70	0.40	1.28	-5.17	-3.55

[a] Absorption and emission spectra were recorded in CH_2Cl_2 (1 x 10^{-5} M). [b] Phosphorescence spectra were recorded in 2-methyltetrahydrofuran at 77 K. [c] Optical band gaps were calculated from the absorption spectra using the equation $E_g^{opt} = 1240/\lambda_{offset}$. [d] Measured in a CH_2Cl_2 solution and determined using the absolute quantum yield method. [e] Measured in a 2-MeTHF solution at 77K. [f] Single-exponential fitting of transient decay profile. [g] Triple-exponential fitting of transient decay profile. [h] Radiative (k_r) and nonradiative (k_{nr}) decay rate constants are calculated by the equations $k_r = \Phi_{PL}/\tau_s$ and $k_{nr} = (1 - \Phi_{PL})/\tau_s$. [i] Frontier molecular orbital energy levels from cyclic voltammetry were estimated as: E_{HOMO}^{cv} (eV) = $-(E_{onset}^{ox}-E_{Fc}/_{Fc+}+4.8)$ (eV), E_{LUMO}^{cv} (eV) = $-(E_{onset}^{red}-E_{Fc/Fc+}+4.8)$ (eV).

6. DFT Calculations

All calculations were carried out using the *Gaussian 16* program. [S2] The structures were fully optimized without any symmetry restriction. Calculations were performed by the density functional theory (DFT) method with restricted B3LYP (Becke's three-parameter hybrid exchange functionals and the Lee-Yang-Parr correlation functional) [S3] level, employing a basis set of 6-311G(d, p). TD-DFT and NICS calculations were performed at the B3LYP/6-311G(d, p) level based on the optimized geometry.

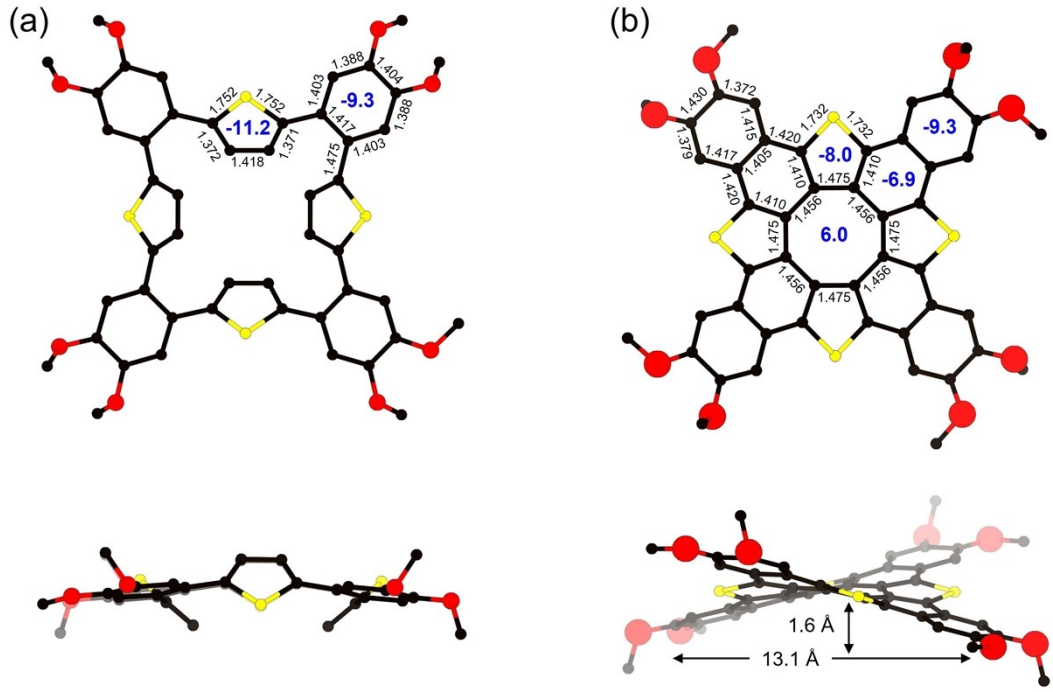


Figure S13. Optimized geometry of (a) **1** and (b) **2** with selected bond length (Å) and NICS (0) values (in blue) calculated at the B3LYP-6-311G(d,p) level. Octyloxy groups were replaced by methoxy groups.

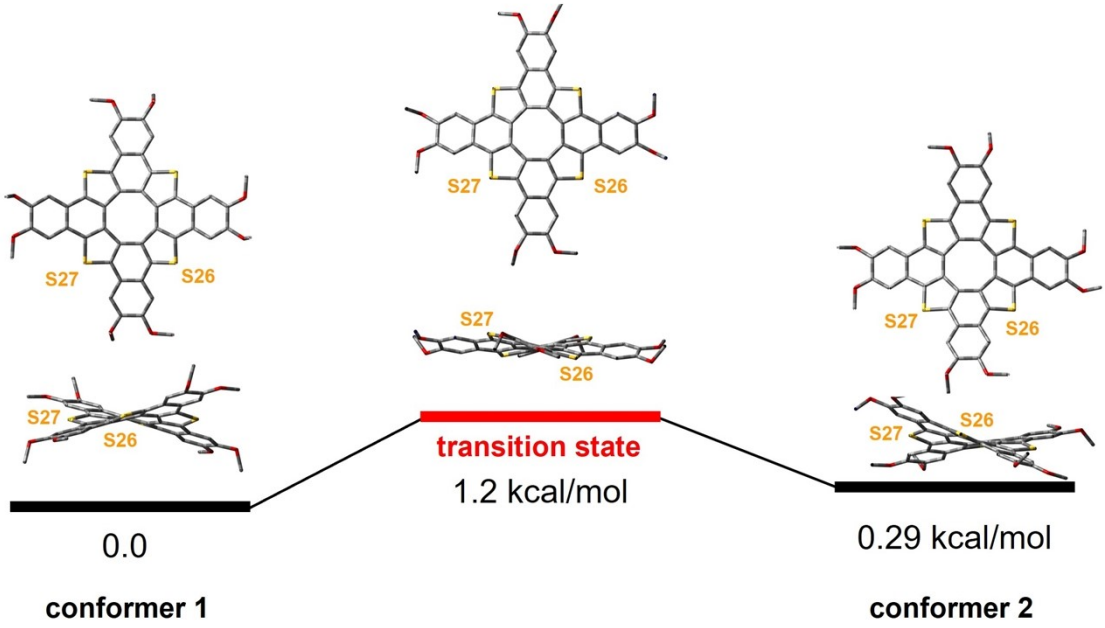


Figure S14. Saddle-to-saddle inversion of **2** with relative Gibbs free energy calculated at the B3LYP-6-311G(d,p) level.

The cartesian coordinates of the optimized structure was listed as follows:

1:

	X	Y	Z		X	Y	Z
C	4.314296	-1.52588	-0.16178	C	2.75338	3.611952	-0.09377
C	5.711795	-1.52535	-0.28138	C	2.855175	2.161146	-0.33653
H	6.236028	-0.60299	-0.5002	C	2.115305	1.367101	-1.17492
C	6.467364	-2.68584	-0.17764	H	1.303316	1.75471	-1.77503
C	5.816388	-3.90513	0.067326	C	2.527688	0.010268	-1.19293
C	4.433442	-3.92022	0.192502	H	2.064109	-0.74923	-1.8077
H	3.959664	-4.86961	0.410619	C	3.590354	-0.25783	-0.36869
C	3.657397	-2.75585	0.094559	S	1.253129	-4.08739	-0.48382
C	2.204147	-2.85699	0.322565	S	-4.04623	-1.25972	0.41021
C	1.403632	-2.12097	1.157986	S	-1.20829	4.048114	-0.43766
C	1.786801	-1.31224	1.76538	S	4.089594	1.204223	0.456203
C	0.046862	-2.53461	1.164686	O	7.834615	-2.60449	-0.29317
H	-0.71685	-2.07529	1.777569	O	6.507589	-5.08932	0.161904
C	-0.2156	-3.59309	0.333183	O	-2.54044	-7.8354	0.165746
C	-1.48204	-4.31383	0.109986	O	-4.96531	-6.61386	-0.27879
C	-1.48919	-5.71401	0.222543	O	-7.78764	2.55749	-0.32195
H	-0.56947	-6.24397	0.437881	O	-6.46498	5.036013	0.183068
C	-2.64192	-6.47203	0.099291	O	5.084517	6.464355	-0.1401
C	-3.86741	-5.81827	-0.14721	O	2.600063	7.784469	0.338651
C	-3.87707	-4.43266	-0.26821	C	7.331494	-5.21979	1.330586
H	-4.79949	-3.92132	-0.50524	H	7.806772	-6.19745	1.257646
C	-2.70555	-3.66185	-0.15994	H	8.092665	-4.43702	1.368013
C	-2.80744	-2.20868	-0.3877	H	6.717783	-5.18105	2.236657
C	-2.06299	-1.40427	-1.21154	C	8.380466	-3.20761	-1.47642
H	-1.2473	-1.78502	-1.81092	H	8.149354	-4.27447	-1.51991
C	-2.47507	-0.04686	-1.21556	H	7.993845	-2.70983	-2.37188
H	-2.00718	0.719545	-1.81847	H	9.458822	-3.0628	-1.41959
C	-3.54288	0.212308	-0.39557	C	-3.20953	-8.47582	1.259246
C	-4.26816	1.477694	-0.17765	H	-2.84348	-8.08656	2.215865
C	-5.66459	1.479395	-0.30863	H	-4.29117	-8.34622	1.195945
H	-6.18677	0.560429	-0.5457	H	-2.96075	-9.5337	1.18208
C	-6.42145	2.638018	-0.19372	C	-6.21474	-6.00334	-0.57815
C	-5.77283	3.853491	0.075253	H	-6.93329	-6.8184	-0.64406
C	-4.39089	3.86665	0.211224	H	-6.17981	-5.47322	-1.53567
H	-3.91923	4.812733	0.447554	C	-8.32504	3.18367	-1.49721
C	-3.61373	2.704027	0.101642	H	-8.09484	4.251341	-1.51769
C	-2.16217	2.802483	0.341045	H	-7.93081	2.704261	-2.39936

C	-1.36518	2.051345	1.166577	H	-9.40364	3.036696	-1.45163
H	-1.75018	1.230551	1.756246	C	-7.29677	5.148491	1.348069
C	-0.00854	2.464146	1.186065	H	-6.68922	5.095697	2.257556
H	0.752917	1.992133	1.791911	H	-7.77165	6.127139	1.287036
C	0.256553	3.538171	0.375637	H	-8.05816	4.365259	1.368245
C	1.523629	4.265028	0.173415	C	3.208128	8.318691	1.524732
C	1.522695	5.661156	0.307927	H	4.275455	8.088529	1.560787
H	0.600781	6.182426	0.535455	H	3.061658	9.397369	1.479846
C	2.682271	6.418736	0.208213	H	2.715013	7.922052	2.418383
C	3.90119	5.771455	-0.0482	C	5.209634	7.30142	-1.3001
C	3.916766	4.389886	-0.18787	H	5.167436	6.697813	-2.21276
H	4.865719	3.919292	-0.41463	H	4.426277	8.062451	-1.32574
H	-6.52271	-5.30998	0.211858	H	6.187311	7.776434	-1.2259

Conformer 1 of **2:**

	X	Y	Z		X	Y	Z
C	0.70962	1.75095	-0.16957	O	-7.67438	1.335023	1.777972
C	-0.74687	1.7367	-0.16488	O	-7.70255	-1.38901	1.793674
C	-1.75096	0.70959	0.1696	O	1.389129	-7.70222	-1.79495
C	-1.73671	-0.7469	0.16466	O	-1.33491	-7.67406	-1.77942
C	-0.70958	-1.75093	-0.16993	O	7.702121	1.388815	1.795663
C	0.74691	-1.73668	-0.16489	O	7.673955	-1.33522	1.779675
C	1.75092	-0.70961	0.16995	H	2.409141	5.442869	-1.17577
C	1.73667	0.74688	0.16516	H	-2.54244	5.353149	-1.11513
C	1.30784	3.0101	-0.3825	H	5.44267	-2.40906	1.176881
C	0.65467	4.20706	-0.77815	H	5.352962	2.542508	1.115891
C	-0.75027	4.19521	-0.77131	H	-2.40886	-5.44274	-1.17694
C	-1.37369	2.98345	-0.37024	H	2.542703	-5.35303	-1.1151
C	3.01003	-1.30782	0.38313	H	-5.44296	2.408935	1.175822
C	4.20693	-0.65462	0.77894	H	-5.35323	-2.54263	1.114336
C	4.19508	0.75032	0.772	C	-2.80818	7.778809	-1.73721
C	2.98339	1.37371	0.37069	H	-3.27518	7.088662	-2.44815
C	-1.30775	-3.01006	-0.38314	H	-3.1754	7.566701	-0.72766
C	-0.65448	-4.20698	-0.77877	H	-3.06079	8.802552	-2.00702
C	0.75045	-4.19512	-0.77159	C	1.251796	8.142818	-3.13048
C	1.37378	-2.98341	-0.37024	H	1.61426	7.37732	-3.82551
C	-3.01013	1.30777	0.38254	H	0.230867	8.427619	-3.39055
C	-4.20712	0.65453	0.77799	H	1.90109	9.015975	-3.18433
C	-4.19526	-0.7504	0.77091	C	7.778519	2.808298	1.738356
C	-2.98348	-1.37376	0.36982	H	7.566579	3.175444	0.728752

S	2.9986	3.06334	-0.01184	H	7.088254	3.275343	2.449148
S	3.06334	-2.9986	0.01258	H	8.802217	3.060924	2.008317
S	-2.9986	-3.06334	-0.01289	C	8.142294	-1.25159	3.13197
S	-3.06334	2.9986	0.01217	H	8.427055	-0.23064	3.392019
C	1.32721	5.39642	-1.14785	H	7.376679	-1.614	3.826901
C	0.63771	6.53381	-1.4861	H	9.01544	-1.90088	3.186012
C	-0.79238	6.52586	-1.46336	C	-7.77893	-2.80849	1.736209
C	-1.46152	5.37093	-1.11795	H	-7.56675	-3.17554	0.726619
C	5.39623	-1.32713	1.14888	H	-7.08883	-3.2756	2.447117
C	6.53356	-0.63761	1.48728	H	-8.80269	-3.06114	2.005906
C	6.52562	0.79247	1.46444	C	-8.14304	1.251256	3.130149
C	5.37074	1.46159	1.11879	H	-8.42786	0.230282	3.39003
C	-1.32693	-5.3963	-1.14876	H	-7.37759	1.613605	3.825295
C	-0.63735	-6.53365	-1.48697	H	-9.0162	1.900538	3.184051
C	0.79273	-6.5257	-1.46388	C	-1.25104	-8.14247	-3.13168
C	1.46179	-5.3708	-1.11819	H	-1.61334	-7.3769	-3.82671
C	-5.39651	1.32701	1.14772	H	-0.23005	-8.42724	-3.39154
C	-6.53392	0.63745	1.48578	H	-1.90033	-9.01562	-3.18579
C	-6.52597	-0.79263	1.46279	C	2.808603	-7.77862	-1.7374
C	-5.37101	-1.46172	1.11735	H	3.275765	-7.08839	-2.44815
O	1.33533	7.67426	-1.77826	H	3.17558	-7.56662	-0.72774
O	-1.3887	7.70242	-1.79443	H	3.061275	-8.80233	-2.00726

Conformer-2 of **2:**

	X	Y	Z		X	Y	Z
C	-1.14698	-1.50484	0.149946	O	-0.70912	-7.75761	1.921424
C	0.262763	-1.87011	0.181205	O	7.03095	-3.33137	-1.79845
C	1.50485	-1.14699	-0.14983	O	7.757683	-0.70922	-1.92111
C	1.870114	0.262754	-0.18116	O	0.709145	7.757778	1.920742
C	1.14698	1.504858	0.149792	O	3.331298	7.031037	1.798221
C	-0.26276	1.870124	0.181041	O	-7.75771	0.709044	-1.92106
C	-1.50485	1.146972	-0.14991	O	-7.03097	3.331203	-1.79867
C	-1.87012	-0.26277	-0.1811	H	-3.77732	-4.6427	1.036554
C	-2.05724	-2.56676	0.331833	H	1.033109	-5.79847	1.256679
C	-1.74959	-3.89181	0.738696	H	-4.64276	3.777282	-1.03645
C	-0.38945	-4.23917	0.793894	H	-5.79854	-1.03316	-1.25635
C	0.538951	-3.2332	0.415091	H	3.777336	4.642801	1.036063
C	-2.56678	2.057227	-0.33177	H	-1.03309	5.798578	1.2562
C	-3.89185	1.749563	-0.73856	H	4.642752	-3.77738	-1.03615
C	-4.23922	0.389417	-0.79369	H	5.798514	1.033045	-1.25655

C	-3.23323	-0.53897	-0.4149	C	0.649939	-8.14882	2.075293
C	2.057243	2.566791	0.331564	H	1.18802	-8.10839	1.122013
C	1.749601	3.891877	0.738316	H	1.1623	-7.51981	2.810741
C	0.389458	4.239244	0.793512	H	0.623649	-9.17628	2.433519
C	-0.53895	3.233241	0.414811	C	-3.50749	-8.17699	0.956545
C	2.566774	-2.05726	-0.33163	H	-3.75333	-7.86875	-0.06581
C	3.89184	-1.74963	-0.73845	H	-2.61664	-8.80737	0.950331
C	4.239203	-0.38949	-0.79372	H	-4.34558	-8.73089	1.37812
C	3.233219	0.538931	-0.41501	C	-8.14892	-0.65002	-2.07486
S	-3.69441	-2.1735	-0.07281	H	-7.51995	-1.1624	-2.81032
S	-2.1735	3.694412	0.072787	H	-8.10845	-1.18807	-1.12157
S	3.694407	2.173495	-0.07307	H	-9.1764	-0.62374	-2.43304
S	2.173498	-3.69441	0.073085	C	-8.17704	3.507446	-0.95626
C	-2.71921	-4.87434	1.052451	H	-8.80742	2.616598	-0.94998
C	-2.35792	-6.14507	1.423817	H	-7.86876	3.753327	0.066072
C	-0.97208	-6.49116	1.501112	H	-8.73096	4.345524	-1.37783
C	-0.01645	-5.54975	1.183287	C	8.148885	0.649832	-2.07505
C	-4.8744	2.719173	-1.0523	H	7.519903	1.162142	-2.81056
C	-6.14514	2.357864	-1.42359	H	8.108425	1.187974	-1.12181
C	-6.49124	0.972028	-1.50082	H	9.176361	0.623524	-2.43324
C	-5.54981	0.016405	-1.18301	C	8.177037	-3.50752	-0.95603
C	2.719228	4.874436	1.051964	H	8.807414	-2.61667	-0.94985
C	2.357938	6.145194	1.423229	H	7.868763	-3.7533	0.066323
C	0.972106	6.491294	1.500528	H	8.730949	-4.34564	-1.37753
C	0.016466	5.549853	1.182804	C	3.507491	8.177082	0.955761
C	4.874385	-2.71927	-1.05211	H	3.753313	7.868758	-0.06657
C	6.145124	-2.35799	-1.42345	H	2.616642	8.80746	0.949515
C	6.491219	-0.97216	-1.50082	H	4.345594	8.731013	1.377269
C	5.549793	-0.01651	-1.18309	C	-0.64991	8.148991	2.07461
O	-3.33127	-7.03088	1.798906	H	-1.18801	8.108485	1.121346
H	-0.62361	9.176484	2.43275	H	-1.16225	7.520045	2.810122

Transition state of **2**:

	X	Y	Z		X	Y	Z
C	-1.65937	-0.91398	0.164594	O	-4.03593	-6.97262	-0.23883
C	-0.55192	-1.81704	-0.12935	O	5.313221	-5.95474	-0.75576
C	0.914	-1.65939	-0.16443	O	6.972635	-4.0359	0.239386
C	1.817038	-0.55192	0.129474	O	4.035892	6.972629	-0.23937
C	1.659379	0.914	0.164509	O	5.954639	5.313275	0.756042
C	0.551927	1.817021	-0.12953	O	-6.97263	4.035907	0.238756

C	-0.91399	1.659362	-0.16466	O	-5.31323	5.954586	-0.7567
C	-1.81703	0.551926	0.129388	H	-5.28237	-2.86914	0.98505
C	-2.89803	-1.53645	0.425314	H	-1.66493	-5.77813	-0.73316
C	-3.20218	-2.92057	0.323194	H	-2.86918	5.282298	-0.98529
C	-2.18511	-3.7584	-0.16139	H	-5.77812	1.664948	0.733216
C	-0.90648	-3.16539	-0.3464	H	5.28237	2.869245	0.98479
C	-1.53647	2.898007	-0.42543	H	1.664903	5.778087	-0.73362
C	-2.92058	3.202157	-0.32329	H	2.869186	-5.28247	-0.98446
C	-3.7584	2.185107	0.161391	H	5.778128	-1.66486	0.733466
C	-3.16537	0.906499	0.346481	C	-3.03536	-7.88546	-0.67396
C	2.898042	1.536499	0.425162	H	-2.67269	-7.63344	-1.67639
C	3.202184	2.920607	0.322925	H	-2.19191	-7.91063	0.023914
C	2.185103	3.758394	-0.16173	H	-3.51534	-8.86207	-0.69718
C	0.906486	3.165358	-0.34671	C	-6.781	-5.78831	-0.3141
C	1.536484	-2.89808	-0.42502	H	-6.97871	-4.98497	-1.03253
C	2.920592	-3.20222	-0.32281	H	-6.32302	-6.63786	-0.82352
C	3.758407	-2.1851	0.161713	H	-7.71772	-6.09895	0.147381
C	3.165386	-0.90646	0.346612	C	-7.88545	3.035368	0.673992
S	-4.20112	-0.4328	0.709552	H	-7.91064	2.191865	-0.02383
S	-0.43283	4.201083	-0.70978	H	-7.6334	2.672768	1.676436
S	4.201135	0.432881	0.709514	H	-8.86206	3.515343	0.697205
S	0.432847	-4.20117	-0.70928	C	-5.78834	6.780995	0.313827
C	-4.47414	-3.47818	0.599037	H	-6.63784	6.323022	0.823336
C	-4.73162	-4.81128	0.403013	H	-4.98497	6.978806	1.032199
C	-3.69637	-5.66358	-0.09465	H	-6.09905	7.717663	-0.14771
C	-2.45395	-5.13477	-0.37028	C	7.885461	-3.03529	0.674459
C	-3.47821	4.474088	-0.5992	H	7.910646	-2.1919	-0.0235
C	-4.8113	4.731577	-0.40317	H	7.633409	-2.67253	1.676845
C	-5.66359	3.696353	0.094578	H	8.862069	-3.51526	0.697746
C	-5.13477	2.45395	0.370283	C	5.788339	-6.78096	0.31491
C	4.474134	3.478252	0.59873	H	6.637857	-6.32292	0.82432
C	4.731608	4.811333	0.40261	H	4.984981	-6.97863	1.033334
C	3.69635	5.663598	-0.09511	H	6.099019	-7.71772	-0.14647
C	2.45393	5.134755	-0.37071	C	6.780975	5.788341	-0.31457
C	3.478217	-4.4742	-0.59851	H	6.97875	4.984938	-1.03291
C	4.811305	-4.73166	-0.40243	H	6.322962	6.637809	-0.82409
C	5.663599	-3.69636	0.09515	H	7.717669	6.099084	0.146901
C	5.134775	-2.45391	0.370655	C	3.035322	7.885429	-0.67459
O	-5.95466	-5.31318	0.756477	H	2.672658	7.633322	-1.67699
H	3.515294	8.862037	-0.69788	H	2.191865	7.910648	0.023286

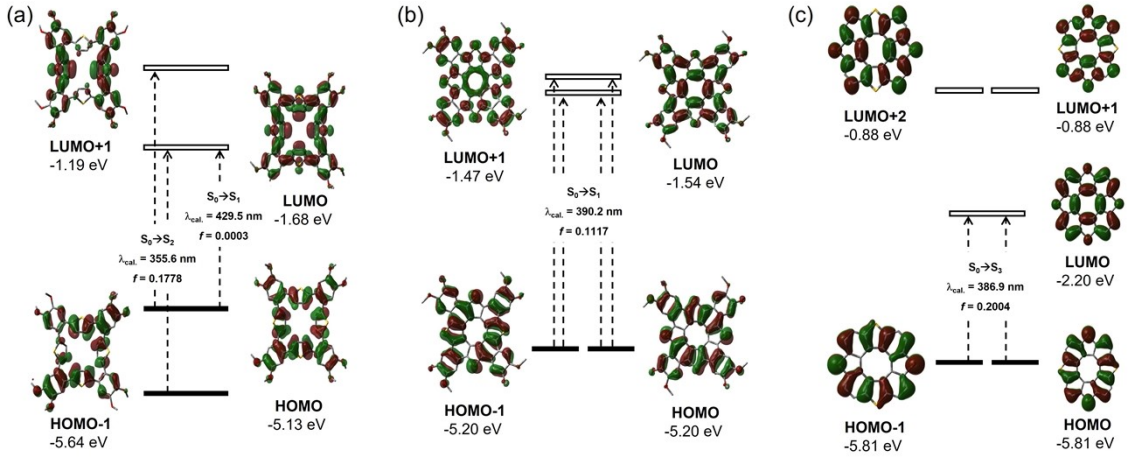


Figure S15. Selected frontier molecular orbitals of (a) **1**, (b) **2** and (c) pristine tetrathia[8]circulene with orbital energy calculated at the B3LYP-6-311G (d, p) level.

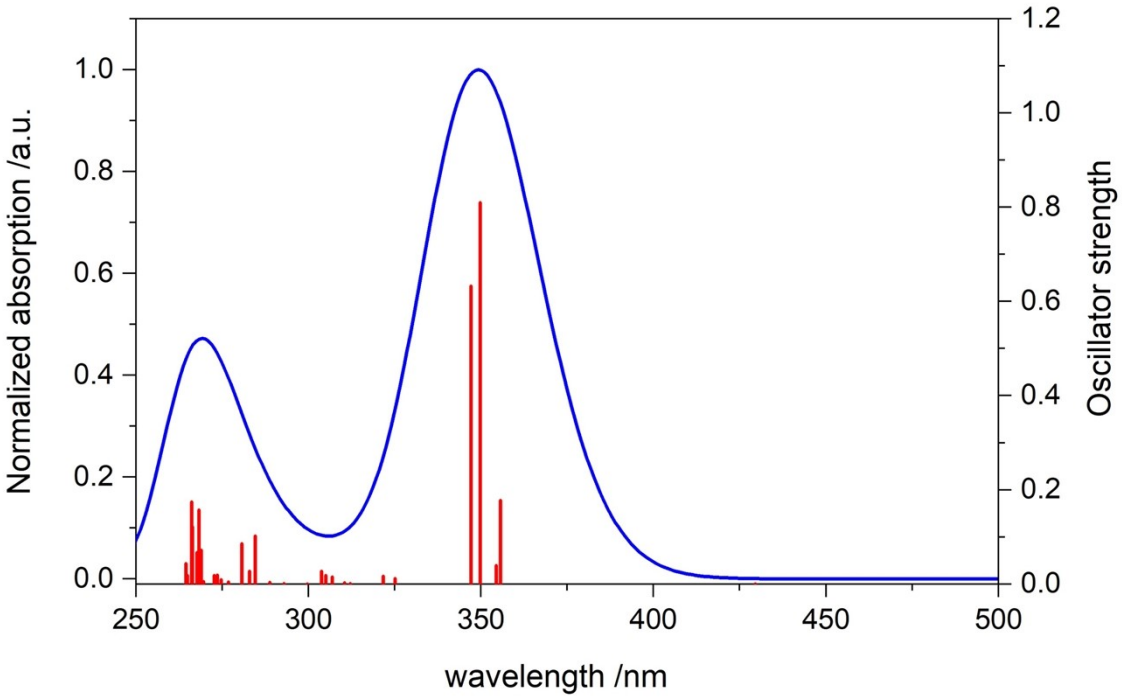


Figure S16. Calculated absorption spectrum (blue line) and oscillator strength (red bars) of **1** calculated at the B3LYP-6-311G (d, p) level.

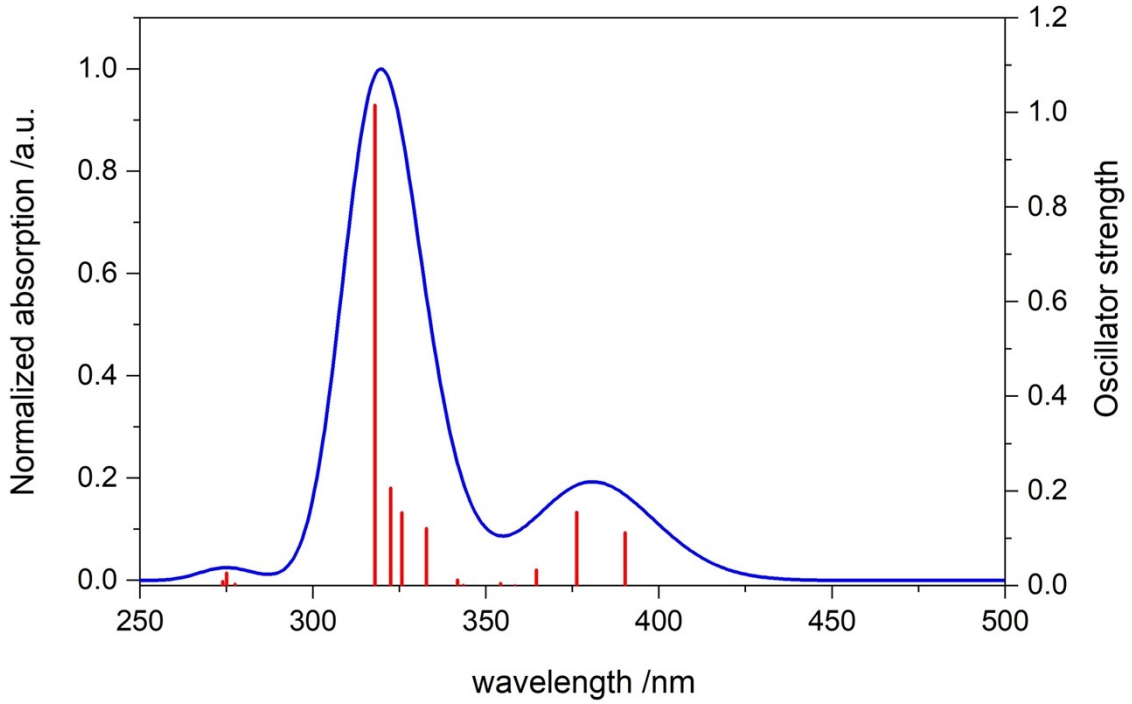


Figure S17. Calculated absorption spectrum (blue line) and oscillator strength (red bars) of **3** calculated at the B3LYP-6-311G (d, p) level.

Table S2. Selected excitation energies of **1** calculated at B3LYP/6-311G (d, p) level. (The first 30 transitions are calculated, and transitions with $f > 0.1$ are listed in the table).

No.	energy (eV)	wavelength (nm)	oscillator strength (*f*)	electronic transition
1	3.4861	355.65	0.1778	H-2 -> L (-0.15678) H-1 -> L (-0.14255) H -> L+1 (0.66384)
2	3.5443	349.81	0.8097	H-1 -> L (0.43980) H -> L+2 (0.54271)
3	3.5726	347.05	0.6329	H-2 -> L (0.67231) H -> L+1 (0.17561)
4	4.3574	284.54	0.1023	H-1 -> L+3 (0.66728)
5	4.6229	268.19	0.1572	H-10 -> L (0.10414) H-9 -> L (-0.16828) H-8 -> L (0.16163) H-7 -> L (0.22447) H-6 -> L (0.28337) H-5 -> L (0.10912) H-3 -> L+1 (0.38551) H-2 -> L+5 (-0.19879) H-1 -> L+4 (0.12133) H-1 -> L+6 (-0.11137)
6	4.6556	266.31	0.1213	H-10 -> L (-0.19095) H-3 -> L+1 (0.25351) H-3 -> L+2 (-0.27140) H-2 -> L+4 (-0.18770) H-2 -> L+5 (0.35133) H-1 -> L+4 (-0.12728) H-1 -> L+6 (0.26545) H -> L+4 (-0.18770)
7	4.6593	266.10	0.1744	H-10 -> L (-0.11289) H-7 -> L (-0.11608) H-4 -> L+1 (-0.15723) H-3 -> L+1 (0.10770) H-3 -> L+2 (0.49590)

H-2 -> L+5 (0.13588)

H-1 -> L+4 (0.13151)

H-1 -> L+6 (0.22222)

H -> L+8 (0.14358)

H -> L+9 (0.17226)

Table S3. Selected excitation energies of **2** calculated at B3LYP/6-311G (d, p) level. (The first 30 transitions are calculated, and transitions with $f > 0.1$ are listed in the table).

No.	energy (eV)	wavelength (nm)	oscillator strength (*f*)	electronic transition
1	3.1772	390.23	0.1117	H-2 -> L+2 (-0.11396) H-2 -> L+3 (-0.11278) H-1 -> L (0.60689) H-1 -> L+1 (-0.22067) H -> L+1 (-0.14629) H -> L+4 (0.14209)
2	3.1772	390.23	0.1117	H-2 -> L+2 (0.11278) H-2 -> L+3 (-0.11396) H-1 -> L+1 (-0.14629) H-1 -> L+1 (-0.17550) H -> L (0.60689) H -> L+1 (0.22068)
3	3.2955	376.22	0.1548	H-1 -> L+1 (-0.17592) H -> L (-0.26551) H -> L+1 (0.61716)
4	3.2995	376.22	0.1548	H-1 -> L (0.26550) H-1 -> L+1 (0.61716) H -> L+1 (0.17592)
5	3.7255	332.80	0.1208	H-4 -> L+3 (-0.11524) H-3 -> L+2 (0.20058) H-3 -> L+3 (-0.24418) H-2 -> L+2 (0.44013) H-2 -> L+3 (0.10785) H-1 -> L+4 (0.27937) H -> L+4 (0.29870)
6	3.7255	332.80	0.1208	H-4 -> L+2 (-0.11525) H-3 -> L+2 (0.24418) H-3 -> L+3 (0.20058) H-2 -> L+2 (-0.10785) H-2 -> L+3 (0.44013) H-1 -> L+4 (-0.29870) H -> L+5 (0.27937)

7	3.8074	325.64	0.1541	H-4 -> L+2 (0.59796) H-4 -> L+3 (0.12776) H-3 -> L+2 (0.15929) H-3 -> L+3 (0.14446) H-2 -> L+2 (-0.15699) H-1 -> L+4 (0.12211) H -> L (0.13818)
8	3.8074	325.64	0.1541	H-4 -> L+2 (-0.12777) H-4 -> L+3 (0.59796) H-3 -> L+2 (0.14446) H-3 -> L+3 (0.15699) H-1 -> L (0.13818) H -> L+4 (-0.12212)
9	3.8447	322.48	0.2059	H-4 -> L (0.53106) H-3 -> L+1 (-0.11252) H-2 -> L+1 (0.39500) H-1 -> L+3 (-0.14141) H -> L+2 (-0.14141)
10	3.9008	317.84	1.0151	H-4 -> L+1 (-0.19890) H-4 -> L+2 (0.19953) H-3 -> L+2 (0.13915) H-2 -> L+2 (-0.25546) H-1 -> L (-0.12181) H-1 -> L+4 (0.37863) H -> L+4 (0.37538)
11	3.9008	317.84	1.0151	H-4 -> L+2 (0.19953) H-4 -> L+3 (0.19890) H-3 -> L+2 (-0.13915) H-2 -> L+3 (-0.25546) H-1 -> L+4 (-0.37538) H -> L (-0.12181) H -> L+4 (0.37862)

7. Electrochemical Properties

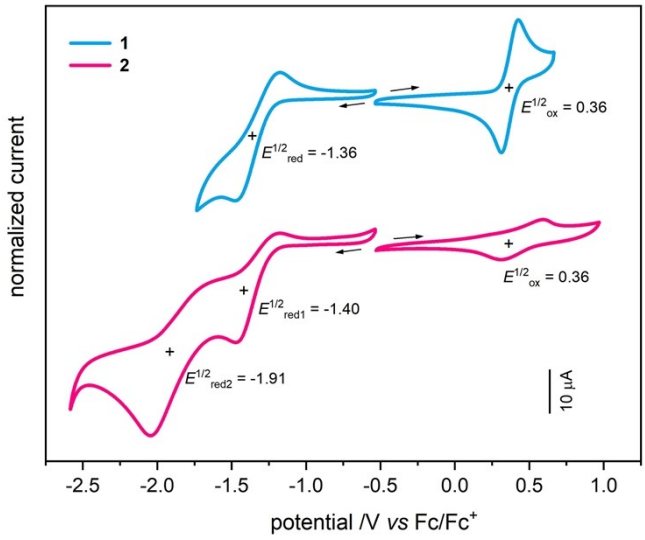


Figure S18. Cyclic voltammograms of **1** and **2** (1.0 mM) measured in CH_2Cl_2 at a scan rate of 100 mV/s. Potentials vs Fc/Fc^+. Working electrode: glassy carbon. Counter electrode: Pt wire. Reference electrode: Ag/AgCl. Supporting electrolyte: 0.1 M Bu_4NPF_6.

8. Supporting References

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