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Furan-Containing Double Tetraoxa[7]helicene and its Radical Cation

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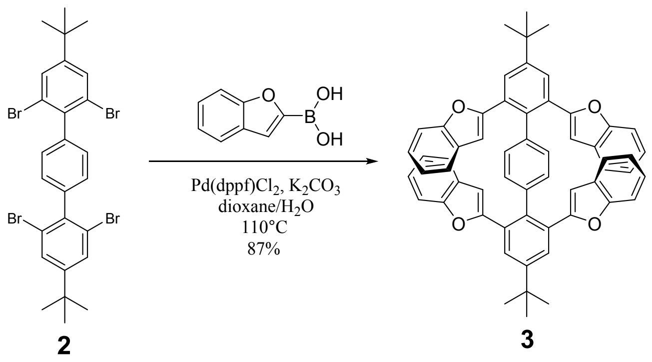
1. Experimental Section

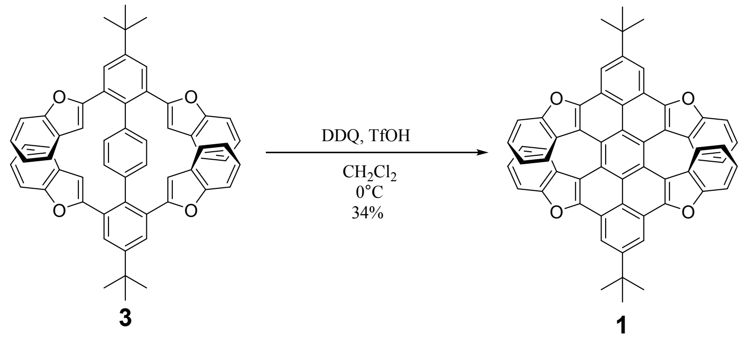
General Methods

All starting materials and reagents were purchased from Energy Chemical and use as received without further purification. ^1H NMR and ^{13}C NMR spectra were measured in CD_2Cl_2 or $CDCl_3$ by Bruker AV-400 nuclear magnetic resonance spectrometer. High resolution mass spectrometry (HRMS) was performed on a SolariX fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer by matrix-assisted laser desorption/ionization (MALDI). UV-Vis-NIR absorption spectra were recorded by UV-2600 Spectrophotometer. Fluorescence spectra were determined by HITACHI F-4600 Fluorescence Spectrophotometer. Absolute photoluminescence quantum yields (excited at 455 nm) were recorded on Edinburgh FS5 Fluorescence Spectrometer. Fluorescence lifetimes were recorded on Edinburgh FLS1000 fluorescence spectrometer. Cyclic voltammetry curves were tested by CHI660E electrochemical workstation and measurements were carried out in dichloromethane containing 0.1 M n-Bu_4NPF_6 as supporting electrolyte (scan rate: 100 mV s^{-1}) using ferrocene as an external reference. A Calomel electrode was used as a working electrode, a platinum wire as a counter electrode and a Ag-AgCl electrode as a reference electrode. EPR spectrum was measured by JEOL JES-FA200 ESR Spectrometer, where the g value was determined by using manganese oxide as the external reference. In situ EPR/UV–vis–NIR spectroelectrochemical experiments were performed in the optical EPR cavity (ER 4104OR, Bruker, Germany). EPR spectra were recorded by the EMXmicro X-band CW spectrometer (Bruker, Germany) at 100 kHz modulation. UV–vis–NIR spectra were measured by the Avantes spectrometer AvaSpec-2048x14-USB2 with the CCD detector and AvaSpec-NIR256-2.2 with the InGaAs detector applying the AvaSpec software. Both the EPR spectrometer and the UV-vis-NIR spectrometer are linked to a HEKA potentiostat PG 390 (HEKA Elektronik, Germany), which triggers both spectrometers. Triggering is performed by the software package PotMaster v2x80. For the spectroelectrochemical experiments a flat cell was used. A laminated gold-μ-mesh (Goodfellow) as the working electrode, a silver chloride coated silver wire as the pseudo reference electrode, and a platinum wire as the counter electrode were used. The EPR and UV–vis–NIR spectra were collected at a continuous potential scan rate (0.003 V/s, a rate allowing successive EPR spectra to be collected). Each UV–vis–NIR spectrum was collected relative to that of the non-charged compound at the initial potential.

Synthetic Procedures



Synthesis of 2,2',2'',2'''-(4,4''-di-tert-butyl-[1,1':4',1''-terphenyl]-2,2'',6,6''-tetrayl) tetrabenzofuran (**3**). Compound **2** (200 mg, 0.304 mmol)[1], benzofuran-2-boronic acid (492 mg, 3.04 mmol), Pd(dppf)Cl$_2$ (35mg, 0.0486mmol), and potassium carbonate (647mg, 4.68mmol) were dissolved in a degassed solvent of dioxane (9.6 mL)/ H_2O (2.4 mL) under argon atmosphere. The resulting solution was heated to 110 ºC and stirred for 1 day. After cooled to room temperature, the reaction mixture was diluted with water and extracted by dichloromethane. The organic phase was collected and evaporated to dryness. The residue was purified via silica column chromatography with dichloromethane/petroleum ether (1/9) as eluent and **3** was obtained as white powder (213 mg, 87%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.05 (s, 4H), 7.49 (dd, J = 12.2, 4.4 Hz, 4H), 7.31 (s, 4H), 7.24–7.19 (m, 4H), 7.14–7.05 (m, 8H), 6.14 (s, J = 0.7 Hz, 4H), 1.51 (s, 18H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 155.06, 154.17, 150.87, 138.56, 135.59, 130.90, 130.63, 128.82, 126.46, 124.25, 122.76, 120.99, 111.05, 106.52, 34.96, 31.32. HRMS (MALDI-TOF) *m*/*z*: Calcd for $C_{58}H_{46}O_4$: 846.3396; Found: 846.3390 (M$^+$)



Synthesis of furan-based double tetraoxa[7]helicene (**1**). Compound **3** (100mg, 0.124mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoqui-none (DDQ) (281mg, 1.24mmol) were dissolved in 10 mL of dry dichloromethane under argon atmosphere. The resulting solution was cooled to 0 ºC and triflic acid (TfOH) (0.2mL) was then added dropwise. After further stirred at 0 ºC for 2 hours, the reaction mixture was successively neutralized by triethylamine, diluted with dichloromethane, and washed with water. The organic phase was collected and evaporated to dryness. The residue was purified via column chromatography with dichloromethane/petroleum ether (1/3) as eluent and **1** was obtained as yellow powder (34 mg, 34%) . ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 9.14 (s, 4H), 7.73 (d, J = 8.2 Hz, 4H), 7.32 (d, J = 7.7 Hz, 4H), 7.22 (t, 4H), 6.72 (t, J = 7.2 Hz, 4H), 1.45 (s,18H). ^{13}C NMR (100 MHz, CD$_2$Cl$_2$) δ 156.02, 151.63, 151.01, 126.90, 125.68, 123.92, 122.80, 122.10, 121.80, 121.65, 119.71, 117.99, 117.81, 111.42, 36.02, 31.92. HRMS (MALDI-TOF) *m*/*z*: Calcd for $C_{58}H_{38}O_4$: 789.2770; Found: 789.2757 (M^+)

Synthesis of $1^{\bullet+}BF_4$ .Compound **1** (50 mg, 0.0626 mmol) and $AgBF_4$(170.56 mg, 0.876 mmol) were added to a reaction tube under argon atmosphere and then 5mL dry dichloromethane (degassed) was added at room temperature . The reaction mixture was stirred for 30 min, and filtered with a membrane filter. The resulting solution was evaporated to dryness by argon flow in argon atmosphere. The residue was washed by n-hexane(degassed) and filtered quickly, then **$1^{\bullet+}BF_4$** was obtained as blackish green solid.

2. X-ray Single Crystallography

The single crystals of compound **1** suitable for X-ray analysis were obtained by diffusing methanol vapor into the tetrahydrofuran solution of compound **1**. The structures were deposited at The Cambridge Crystallographic Data Centre and the data can be obtained free of charge via www.ccdc.cam.ac.uk/structures.

Table S1. Crystal data for **1**(CCDC number: 2024066)

formula	$C_{58}H_{38}O_{46}$
molecular weight	798.88 gmol^{-1}
absorption	μ = 0.068 mm^{-1}
crystal size	0.22 × 0.35 × 0.4 mm^3 brown block
space group	P1 (triclinic)
lattice parameters	a =11.140(4)Å α = 98.910(10)° b =13.270(3)Å β = 90.453(7)° c =16.669(5)Å γ = 99.668(7)° V = 2398.3(13)Å^3 z =2 F(000) = 836
Temperature	-123.15°C
density	d_{xray} = 1.106 gcm^{-3}
radiation	Mo-K$_\alpha$ Graphitmonochromator
Scan – type	\f and \w scans
scan range ,	$2° \leq \theta < 26°$ $-13 \leq h \leq 13$ $-16 \leq k \leq 16$ $-20 \leq l \leq 20$
number of reflections: measured ,	48349
unique ,	9806 (R_{int} = 0.0666)
observed ,	6187 ($\lvert I\rvert/\sigma(I) > 2.0$)

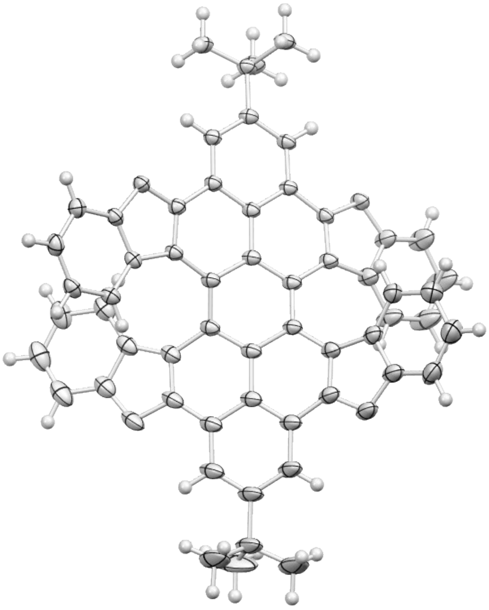


Figure S1 ORTEP drawing of **1** with 50% probability thermal ellipsoids.

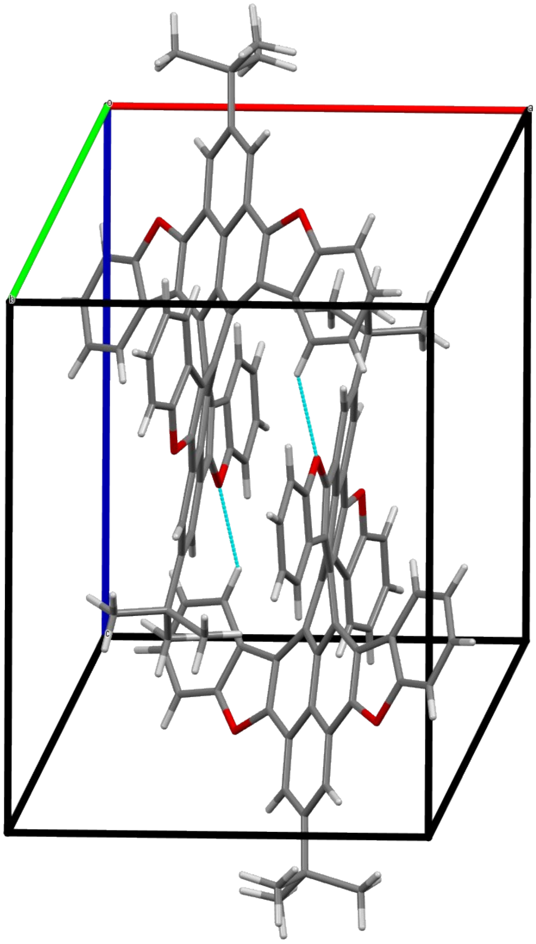


Figure S2. Crystal packing structure of **1** in one unit cell. (CH···O short contacts are shown in dotted blue line)

3. DFT Calculations

DFT calculations were performed using the Gaussian 09 software package. The geometries, molecular orbitals, and MO energies of **1** were calculated at the B3LYP/6-311G(d,p) level.. The UV-vis absorption and CD spectra were simulated by time-dependent DFT (TD-DFT) calculations at the same level of theory. Spin density calculation of the radical cation: B3LYP/def2-TZVPP for optimization, then spin density hfc calculations with B3LYP functional and composite basis, def2-TZVPP for C and O and EPR-III for H. Solvent correction was included n hfc calculations of cation with C-PCM model, calculations were performend with Orca suite.

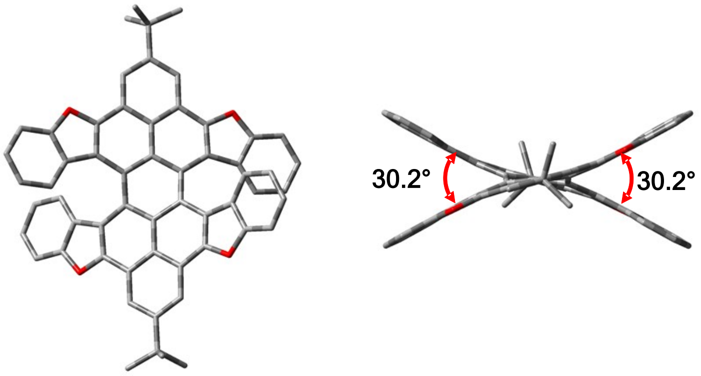


Figure S3. Top and side views of optimized geometry of **1** (all the hydrogen atoms are omitted for simplicity).

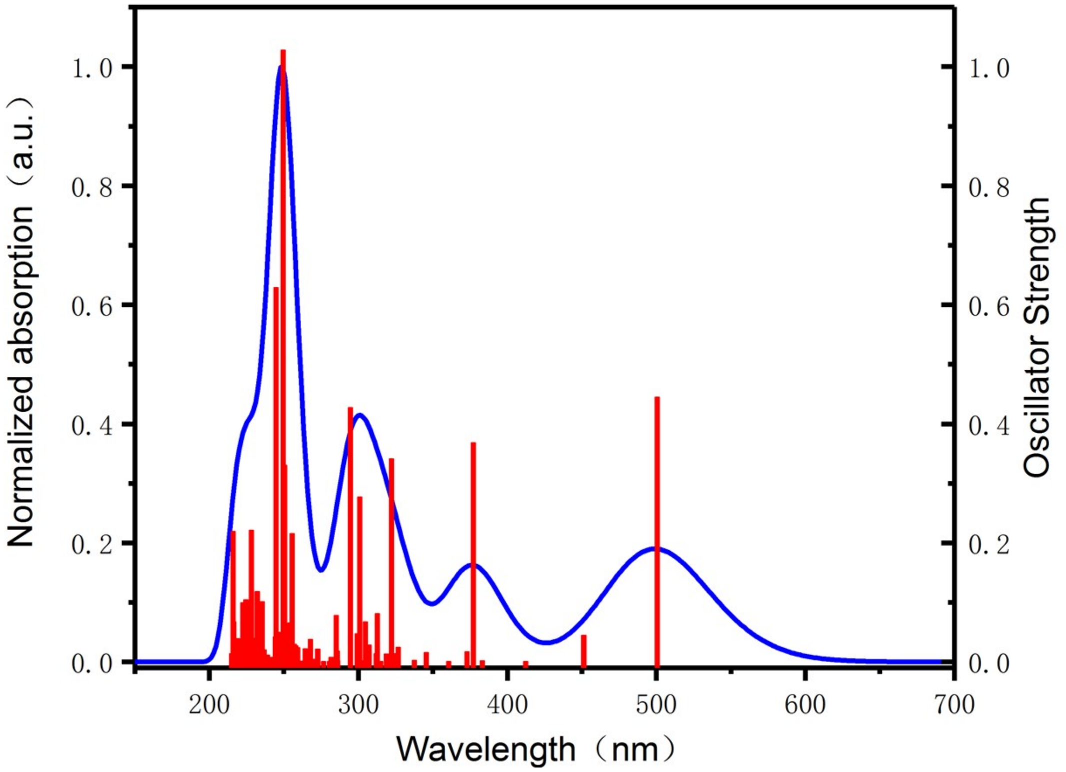


Figure S4. Simulated UV-vis spectrum and vertical transitions of **1** by TD-DFT calculation.

Table S2. Major transitions of **1** calculated by TD-DFT.

excited state	energy (eV)	wavelength (nm)	oscillator strength (*f*)	description
1	2.4766	500.63	0.4445	H→L (0.69445)
				H–1→L+1 (-0.11117)
2	2.7474	451.28	0.0441	H–1→L (0.30635)
				H→L+1 (0.63155)
3	3.0075	412.25	0.0000	H–2→L (-0.25212)
				H→L+2 (0.65656)
4	3.2352	383.23	0.0012	H–3→L (0.69727)
5	3.2877	377.12	0.3679	H–4→L (-0.15937)
				H-1→L (0.59677)
				H→L+1 (-0.29501)
				H→L+5 (0.13953)
6	3.3255	372.83	0.0168	H–4→L (0.67778)
				H–1→L(0.11929)
				H→L+5 (0.11160)
7	3.4375	360.69	0.0003	H–2→L (0.64703)
				H→L+2 (0.24244)
8	3.5884	345.51	0.0152	H–6→L (0.10787)
				H–2→L+1 (0.12969)
				H→L+3 (0.67363)
9	3.6740	337.47	0.0022	H–5→L (0.52178)
				H–1→L+1 (0.10732)
				H→L+4 (0.44621)
10	3.7935	326.83	0.0242	H–8→L (-0.19508)
				H-5→L (0.12958)
				H-1→L (-0.14035)
				H→L+4 (-0.25537)
				H→L+5 (0.57771)

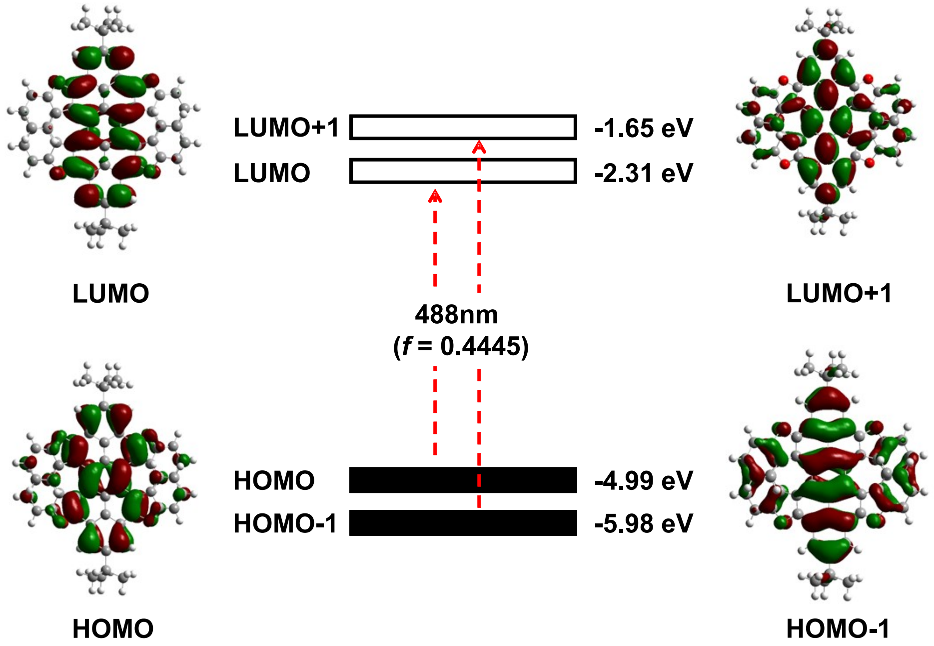


Figure S5. Frontier molecular orbitals and energy diagrams of **1** along with the vertical transitions assigned to the experimental absorption band at 488 nm calculated by TD-DFT at the B3LYP/6-311G(d,p) level.

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

(*P*,*P*)-**1**

	X	Y	Z		X	Y	Z
O	3.329538	3.486303	1.202055	H	7.417559	0.42992	-2.1545
O	3.43952	-3.37723	-1.20007	H	7.403911	-1.28277	-1.72265
O	-3.32958	-3.48627	1.201995	H	8.85263	-0.31517	-1.43208
O	-3.43947	3.377172	-1.20041	C	-2.85741	2.26308	-0.65992
C	2.849277	0.046124	0.00381	C	-3.57558	-1.22927	0.308344
C	3.614529	-1.11588	-0.29962	C	-2.40348	4.186942	-1.59541
C	1.402919	2.392246	0.628255	C	-1.04473	-3.64204	1.286816
C	2.857429	-2.26311	-0.65968	C	-0.00143	4.263157	-1.71917
C	5.717879	0.093502	0.008659	H	0.976485	3.840844	-1.53704
C	1.044682	3.641987	1.286937	C	-2.26843	-4.26449	1.593465
C	2.783323	2.352254	0.665266	C	-5.01187	1.074646	-0.3046
C	2.268363	4.264493	1.593551	H	-5.54049	1.982627	-0.56488
C	1.479634	-2.34595	-0.62398	C	0.134875	-4.26536	1.716985
C	3.575566	1.229291	0.308432	H	1.098927	-3.81156	1.53672
C	-0.13493	4.265185	1.717253	C	0.001501	-4.26313	-1.71921
H	-1.09897	3.811325	1.53701	H	-0.97642	-3.84078	-1.53718
C	5.011876	-1.07466	-0.30432	C	-4.97834	-1.23579	0.318011
H	5.540493	-1.98266	-0.56453	H	-5.47127	-2.16121	0.57949
C	7.256737	0.07851	0.00081	C	-0.1276	5.471812	-2.39296
C	4.978325	1.235821	0.318128	H	0.764835	5.986628	-2.72923
H	5.471245	2.161245	0.579619	C	-5.71788	-0.09348	0.00847
C	1.409453	0.022553	0.003057	C	-2.37939	-5.48148	2.245787
C	-0.04721	5.479993	2.386132	H	-3.34857	-5.91777	2.451781

H	-0.9555	5.967585	2.720485	C	-2.55292	5.397003	-2.25287
C	0.713488	-1.21967	-0.14708	H	-3.5354	5.801618	-2.46053
C	-0.67333	-1.2421	0.153399	C	2.553027	-5.39705	-2.2526
C	0.673323	1.242132	0.153363	H	3.535508	-5.8017	-2.46016
C	1.190653	6.089796	2.637553	C	0.047116	-5.48021	2.3858
H	1.224335	7.040704	3.156336	H	0.955397	-5.96788	2.720061
C	-0.71349	1.219702	-0.14711	C	-1.38414	6.040979	-2.64721
C	-1.40946	-0.02253	0.003041	H	-1.44783	6.988072	-3.17013
C	-1.47962	2.34595	-0.62409	C	-1.19077	-6.08994	2.637272
C	2.403542	-4.18698	-1.59518	H	-1.22448	-7.04088	3.155995
C	-1.1608	3.604364	-1.28679	C	-7.25674	-0.07843	0.000878
C	-1.40294	-2.39222	0.628256	C	0.127715	-5.47179	-2.39297
C	7.765348	-0.96683	1.020632	H	-0.76468	-5.98659	-2.72933
H	8.85938	-0.98845	1.025126	C	1.384272	-6.041	-2.64706
H	7.413272	-1.97298	0.782254	H	1.448	-6.98809	-3.16997
H	7.425741	-0.72374	2.031105	C	-7.76496	0.966341	1.021522
C	2.379286	5.481445	2.245943	H	-8.85899	0.987981	1.026479
H	3.348447	5.917793	2.451903	H	-7.41293	1.972605	0.783516
C	7.855815	1.44625	0.375286	H	-7.42492	0.72269	2.031709
H	7.561513	1.759182	1.380702	C	-7.85579	-1.44638	0.374653
H	7.557322	2.227785	-0.32854	H	-7.56158	-1.7598	1.379942
H	8.94706	1.384778	0.355891	H	-7.55718	-2.22754	-0.32953
C	-2.84928	-0.04611	0.003718	H	-8.94704	-1.38495	0.355202
C	-2.78335	-2.35222	0.665212	C	-7.75921	0.298206	-1.41227
C	1.160845	-3.60436	-1.28671	H	-8.85308	0.316244	-1.43115
C	-3.61452	1.115879	-0.29983	H	-7.41837	-0.42857	-2.15456
C	7.758759	-0.29724	-1.41275	H	-7.40441	1.28387	-1.72176

TS

	X	Y	Z		X	Y	Z
C	3.0417112	2.1670132	-0.3114900	C	2.8339872	-0.2014580	-0.1237580
C	1.8564771	2.3994962	0.3636950	C	3.4662943	-1.4728071	-0.1910710
C	0.8805751	1.2957731	0.4318400	C	4.7942934	-1.6078711	-0.6113870
C	1.4545351	-0.0374110	0.2729970	C	5.5542344	-0.5100910	-1.0235241
C	0.6525430	-1.2215881	0.4342600	C	4.9392574	0.7413761	-0.9902451
C	1.2585191	-2.5216092	0.1866880	C	7.0037335	-0.7147311	-1.4958061
C	2.6261052	-2.5919052	0.0242820	C	7.6762426	0.6082460	-1.9047011
C	-2.4080912	2.4608952	-0.8202631	C	7.8306836	-1.3448991	-0.3513210
C	-1.3882581	2.5988322	0.1040080	C	7.0153915	-1.6614651	-2.7188042
C	-0.5499010	1.4036571	0.3577460	O	3.0794592	-3.8573883	-0.2142560
C	-1.3083791	0.1893320	0.2834730	O	3.7955533	3.2891613	-0.5046690
C	-0.7307391	-1.0586131	0.6478861	O	-3.0324662	3.6475623	-1.1124771
C	-1.6623981	-2.0656412	1.0982931	O	-3.7422043	-2.9989822	1.2314921
C	-2.9734602	-2.0065332	0.6840981	H	0.3685410	-3.3084053	2.9240332
C	-2.9111502	-3.6812913	2.0900682	H	-4.3081543	-5.1115024	2.8933532
C	-1.6083161	-3.1510212	2.0586162	H	-0.2707220	-5.1798184	4.4108513
C	-0.6422100	-3.6955293	2.9132642	H	-2.5623362	-6.0906645	4.3937703
C	-3.2930963	-4.7351594	2.9035282	H	2.9288962	-6.5070215	-0.7617251
C	-1.0075851	-4.7475334	3.7439643	H	-1.3605421	-3.9840493	-0.3845000
C	-2.3116152	-5.2667574	3.7359273	H	0.7260981	-7.6505426	-1.1313801
C	0.7900081	-3.8772793	-0.1359710	H	-1.3724411	-6.3511195	-0.9809741
C	1.9602921	-4.6385134	-0.3227930	H	-0.9709081	4.0050313	2.7202762
C	1.9874762	-5.9844205	-0.6489240	H	-3.7998773	6.2273585	-0.7090071
C	-0.4270370	-4.5208053	-0.4155770	H	-3.1820042	7.4309036	1.4038081
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C	2.0160982	3.7820833	0.8338951	H	-7.4727706	-1.5435281	-1.2095481
C	1.5086181	4.5704414	1.8713161	H	-7.5998876	0.9949251	-0.8814081
C	3.7051723	5.5425944	0.3917000	H	-6.9264205	2.0881572	-2.0939852
C	2.0276042	5.8378994	2.1067382	H	-8.3287146	1.0910141	-2.4928892
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C	-5.1321274	0.0064520	-1.6669501	H	8.7000087	0.4112550	-2.2334122
C	-6.4608915	-0.0346010	-2.4424672	H	7.1518496	1.0932501	-2.7324252
C	-7.2055256	-1.3687191	-2.2551452	H	7.8394906	-0.6945851	0.5275420
C	-7.3805996	1.1058661	-1.9467661	H	7.4298726	-2.3142832	-0.0465900
C	-6.1789225	0.1522340	-3.9513253	H	8.8656647	-1.4974461	-0.6721231
C	3.6217023	0.8968061	-0.5390650	H	6.4394385	-1.2380211	-3.5460613

(*P*,*M*)-**1**

	X	Y	Z		X	Y	Z
C	-4.99347	-1.14592	-0.30589	C	0.06607	4.27567	1.71699
C	-3.59594	-1.16429	-0.30171	C	-0.04119	5.48761	2.38822
C	-2.84962	0.01022	0.00113	C	-1.28878	6.07624	2.64204
C	-3.59499	1.181	0.3072	C	-2.46748	5.44896	2.25027
C	-4.99798	1.16452	0.31765	C	-7.25701	-0.02931	-0.00042
C	-5.71863	0.01077	0.00765	C	-7.87813	1.32887	0.37292
C	-1.40963	0.01096	-0.00161	C	-7.75265	-0.41429	-1.41375
C	-0.69276	-1.22059	-0.15084	C	-7.74873	-1.08198	1.02017
C	0.69276	-1.22059	0.15083	C	7.25701	-0.0293	0.00042
C	1.40963	0.01096	0.0016	C	7.74874	-1.08195	-1.02018
C	0.69422	1.24151	-0.14982	C	7.87813	1.3289	-0.37289
C	-0.69422	1.24151	0.14982	C	7.75265	-0.4143	1.41375
C	2.84962	0.01022	-0.00113	H	-5.50751	-2.06225	-0.56616
C	3.59594	-1.16429	0.30171	H	-5.50556	2.08171	0.58005
C	4.99347	-1.14591	0.30589	H	5.50752	-2.06224	0.56617
C	5.71863	0.01078	-0.00765	H	5.50555	2.08172	-0.58005
C	4.99798	1.16453	-0.31765	H	-3.44086	-5.85128	-2.45684
C	3.59499	1.18101	-0.30721	H	-1.33439	-7.00422	-3.16565
C	-1.44156	2.3788	0.62684	H	0.86167	-5.96547	-2.72808
C	-2.82133	2.31617	0.66483	H	1.03854	-3.81457	-1.5393
C	-2.82002	-2.2994	-0.66139	H	-1.03853	-3.81457	1.53929
C	-1.44126	-2.35979	-0.62614	H	-0.86166	-5.96547	2.72808
C	2.82133	2.31617	-0.66484	H	1.33439	-7.00421	3.16565
C	1.44155	2.3788	-0.62685	H	3.44086	-5.85127	2.45685
C	1.44127	-2.35979	0.62614	H	3.44358	5.86873	-2.45789
C	2.82003	-2.29939	0.66139	H	1.33778	7.02545	-3.16272
O	-3.38415	-3.42331	-1.20056	H	-0.85922	5.98962	-2.72261
C	-2.3353	-4.21666	-1.59498	H	-1.03735	3.83825	-1.53505
C	-1.1022	-3.61331	-1.28783	H	1.03735	3.83826	1.53504
C	-1.10342	3.63358	1.2868	H	0.85921	5.98962	2.72259
C	-2.33696	4.23526	1.59546	H	-1.33778	7.02545	3.16271

O	-3.38557	3.44048	1.20348	H	-3.44359	5.86873	2.45788
C	1.10221	-3.6133	1.28783	H	-8.96825	1.25011	0.35265
C	2.3353	-4.21665	1.59499	H	-7.58957	1.6469	1.37839
O	3.38416	-3.4233	1.20056	H	-7.59146	2.11469	-0.33104
O	3.38557	3.44049	-1.20348	H	-8.84606	-0.45044	-1.43297
C	2.33696	4.23527	-1.59546	H	-7.38137	-1.39396	-1.72296
C	1.10342	3.63359	-1.28681	H	-7.4236	0.31797	-2.15596
C	-2.4651	-5.43012	-2.25039	H	-7.41201	-0.83344	2.03027
C	-1.28605	-6.05532	-2.64435	H	-8.84232	-1.12038	1.02558
C	-0.03893	-5.46497	-2.39197	H	-7.38147	-2.08266	0.78173
C	0.06765	-4.25333	-1.72015	H	8.84232	-1.12034	-1.02559
C	-0.06764	-4.25333	1.72015	H	7.38148	-2.08264	-0.78176
C	0.03893	-5.46497	2.39197	H	7.41202	-0.83339	-2.03028
C	1.28606	-6.05531	2.64436	H	8.96825	1.25013	-0.35263
C	2.46511	-5.43011	2.25039	H	7.59146	2.1147	0.33109
C	2.46747	5.44896	-2.25028	H	7.58956	1.64694	-1.37835
C	1.28877	6.07624	-2.64205	H	7.38136	-1.39397	1.72294
C	0.04118	5.48761	-2.38823	H	8.84606	-0.45045	1.43297
C	-0.06607	4.27567	-1.717	H	7.42359	0.31795	2.15597

4. In situ Spectroelectrochemistry

The absorption bands at 265, 314, 335, 425, 685 and 1058 nm appear during the first redox peak in CV. Their intensities show the same potential profile as that of the ESR signal and can be therefore attributed to the radical cation. During the second redox peak in CV the bands at 820 and 955 nm are dominant. The bands at 314 and 425 nm are shifted to low wavelengths. Isosbestic points at 278, 300, 346, 385, 437 and 324 nm are observed for the 1st conversion as well as 642, 712 and 1015 nm for the 2nd conversion (Figure S6).

It should be also mentioned that the CV of **1** shows an additional reversible redox couple at the half-wave potential of 0.21 V vs Fc/Fc$^+$. This redox wave is well pronounced when the potential sweep is extended to more positive values (formation of dication) (Figure S7). The current intensity increases with increasing the cycle number. This points to low stability of the dication and formation of a significant amount of the byproduct. The EPR/UV-Vis-NIR spectroelectrochemical experiment was performed with a thin-layer spectroelectrochemical cell at a low scan rate (3 mV s^{-1}) where conditions lead to accumulation of the product near the electrode surface. Additional redox couple is absent in the CV recorded in bulk solution at 100 mV s^{-1}.

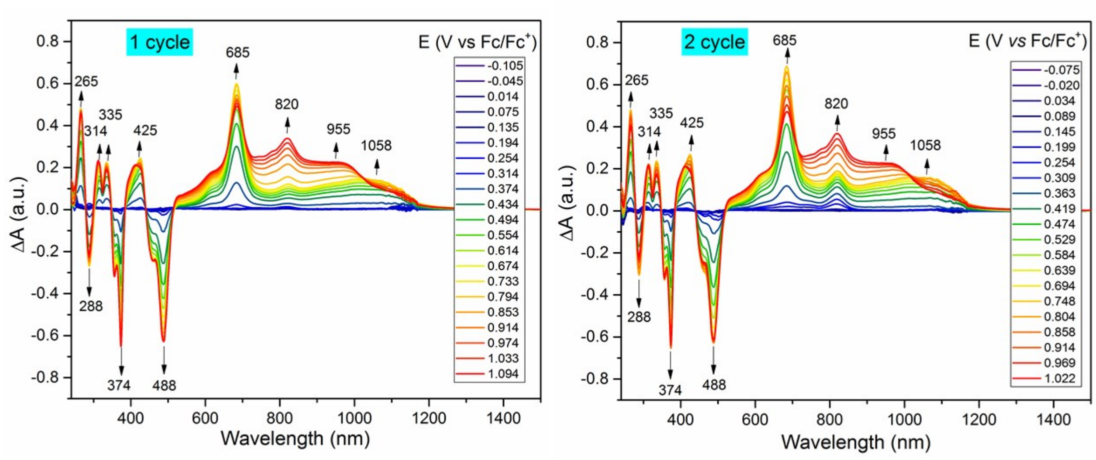


Figure S6. In situ UV-Vis-NIR spectra measured during the first (left) and second (right) cycle of electrochemical oxidation of **1** in DCM solution (reference spectrum: **1** in electrolyte solution).

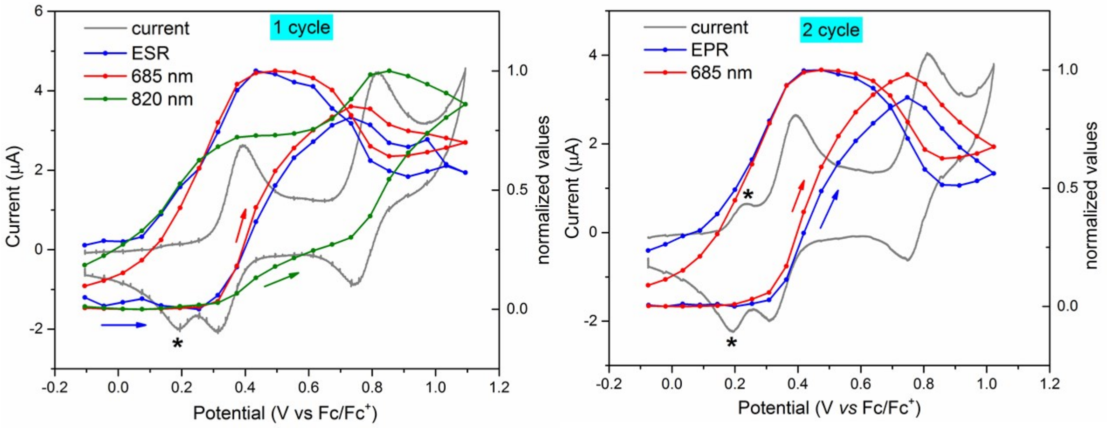


Figure S7. Potential profiles of the absorption band and the EPR intensities (The representative bands at 685 and 820 nm are presented). Additional electrochemical redox couples are marked by (*). The second voltammetric cycle is shown in the right.

5. Optical Resolution and Chiroptical Properties

Optical resolution of the enantiomers was performed on a Shimadzu LC-16A instrument equipped with a DAICEL CHIRALPAK IE column. A mixture of ethyl acetate/methnol (1:4, v/v) was used as the eluent. CD spectra were collected on JASCO J-810 circular dichroism spectrometer at 298 K. CPL spectra were obtained using JASCO CPL-200 spectrophotometer at 298 K.

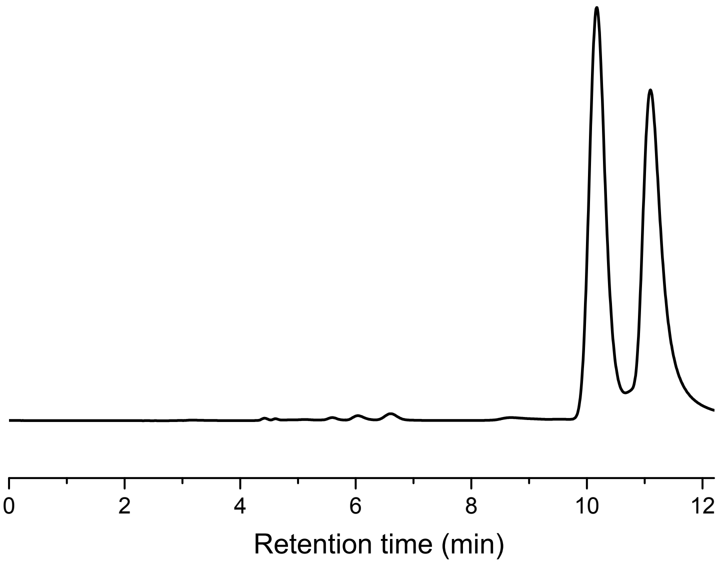


Figure S8. Chiral HPLC trace during the separation of compound **1** using ethyl acetate/methnol (1:4, v/v) as elutents, monitored at 290 nm.

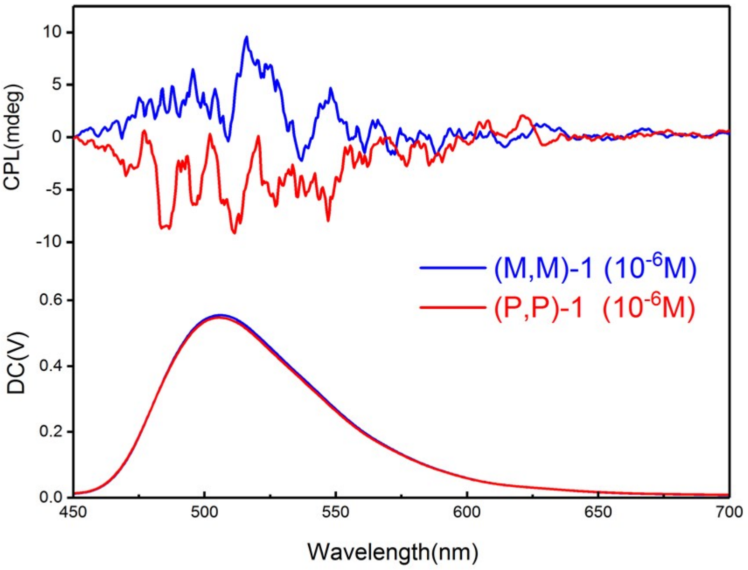


Figure S9. CPL spectra of (*M*,*M*)-**1** and (*P*,*P*)-**1** in DCM (c=10^{-6} M) excited at 375 nm with g_{lum} = –0.000754131 for (*P*,*P*)-**1**at 506 nm.

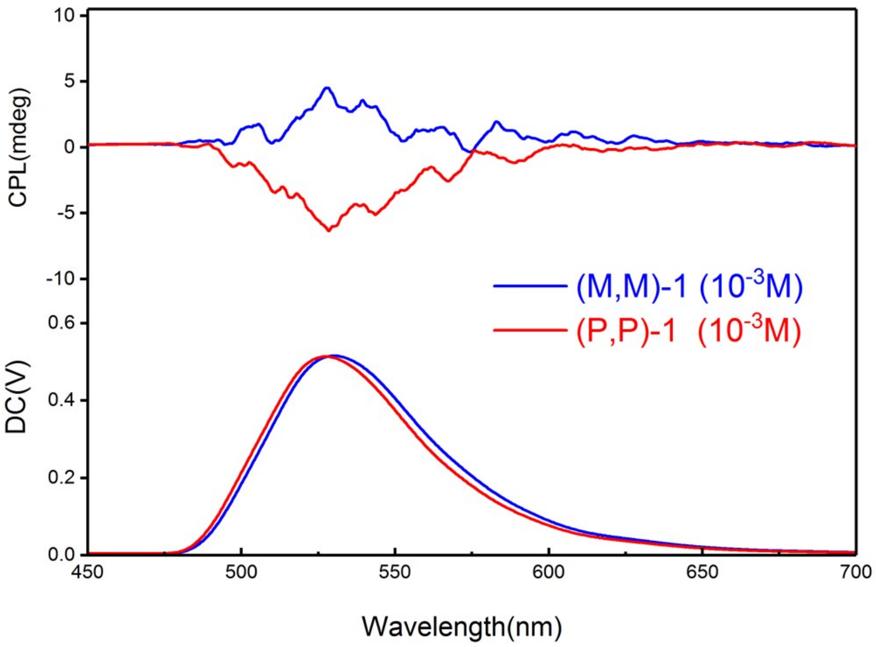


Figure S10. CPL spectra of (*M*,*M*)-**1** and (*P*,*P*)-**1** in DCM (c=10^{-3} M) excited at 375 nm with g_{lum} = 0.000518326 for (*M*,*M*)-**1**at 530 nm.

6. NMR and HRMS spectra

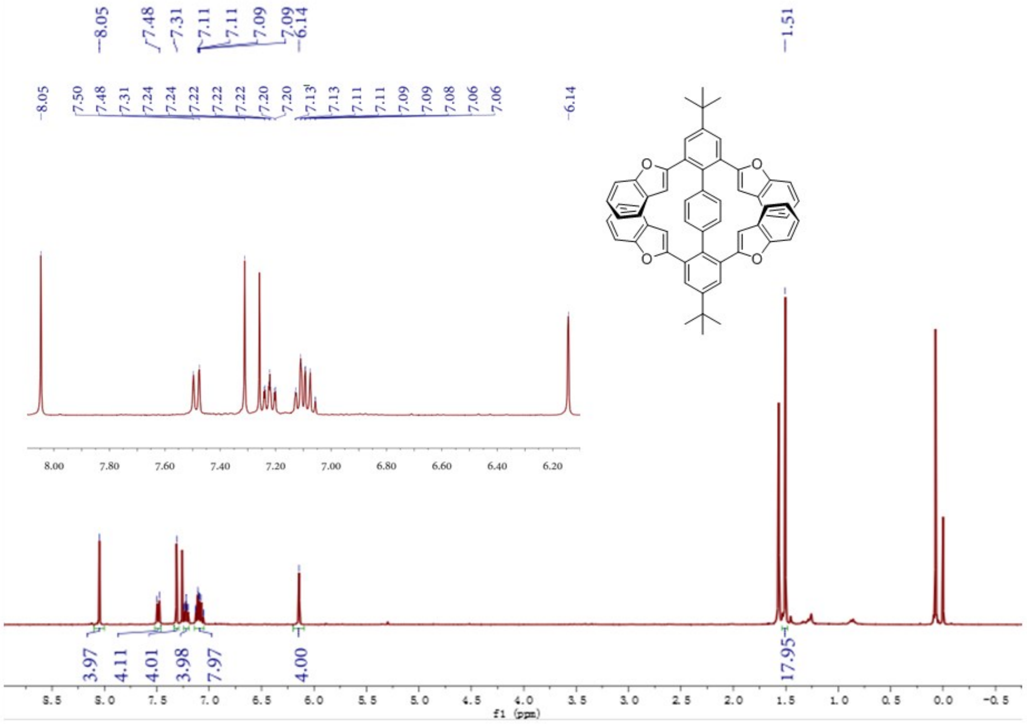


Figure S11. ^{1}H NMR spectrum of **3** (400 MHz, $CDCl_3$).

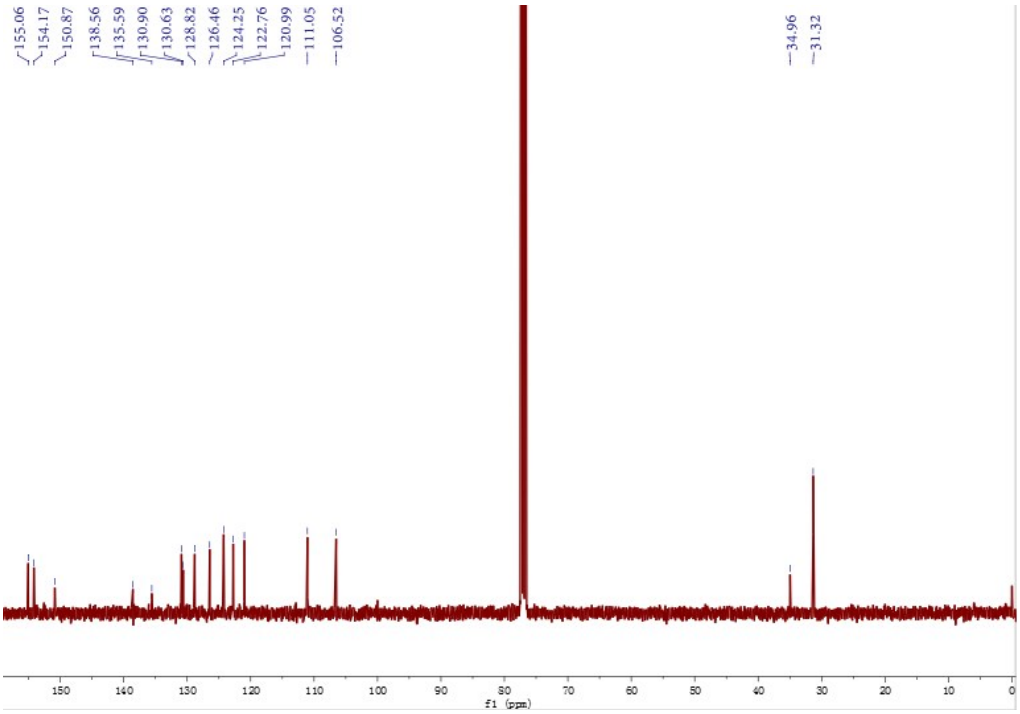
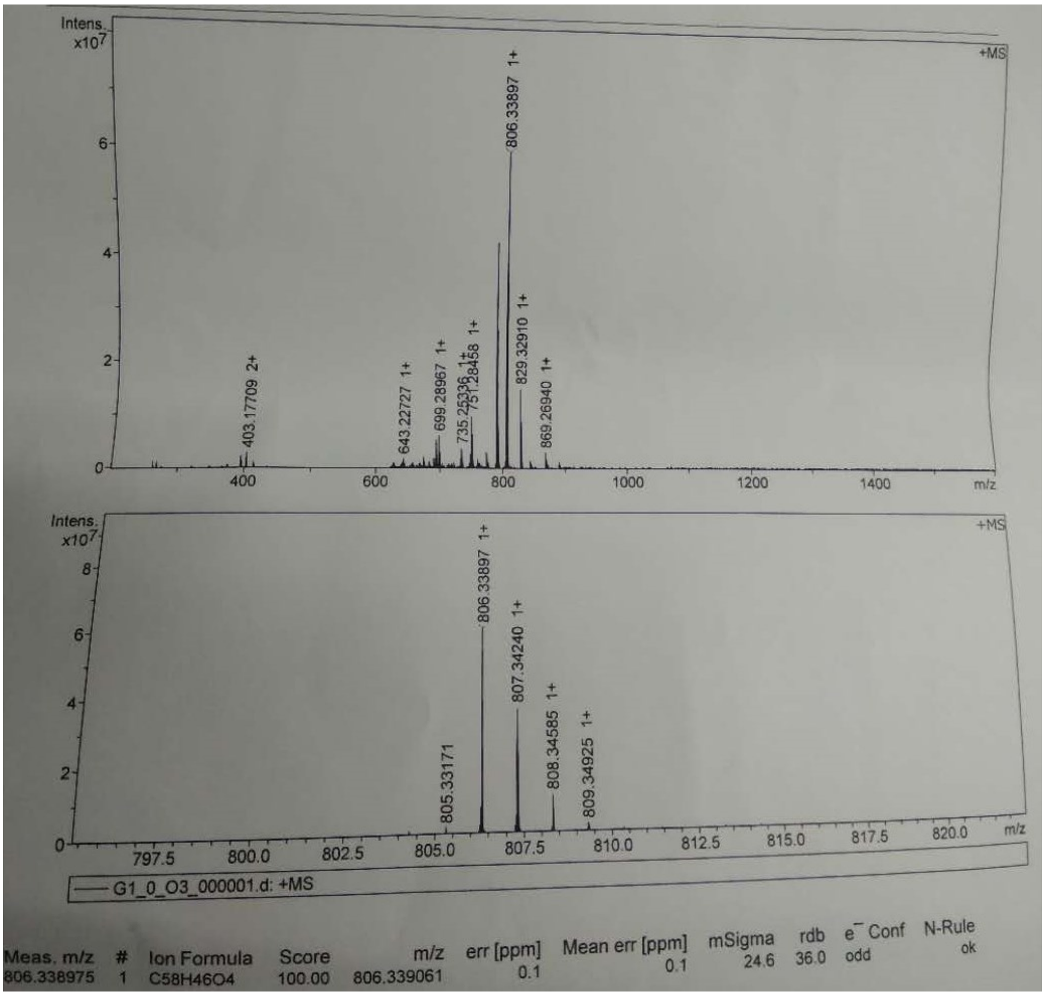


Figure S12. ^{13}C NMR spectrum of **3** (100 MHz, $CDCl_3$)



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
806.338975	1	C58H46O4	100.00	806.339061	0.1	0.1	24.6	36.0	odd	ok

Figure S13. HRMS (MALDI-TOF) spectrum of **3**.

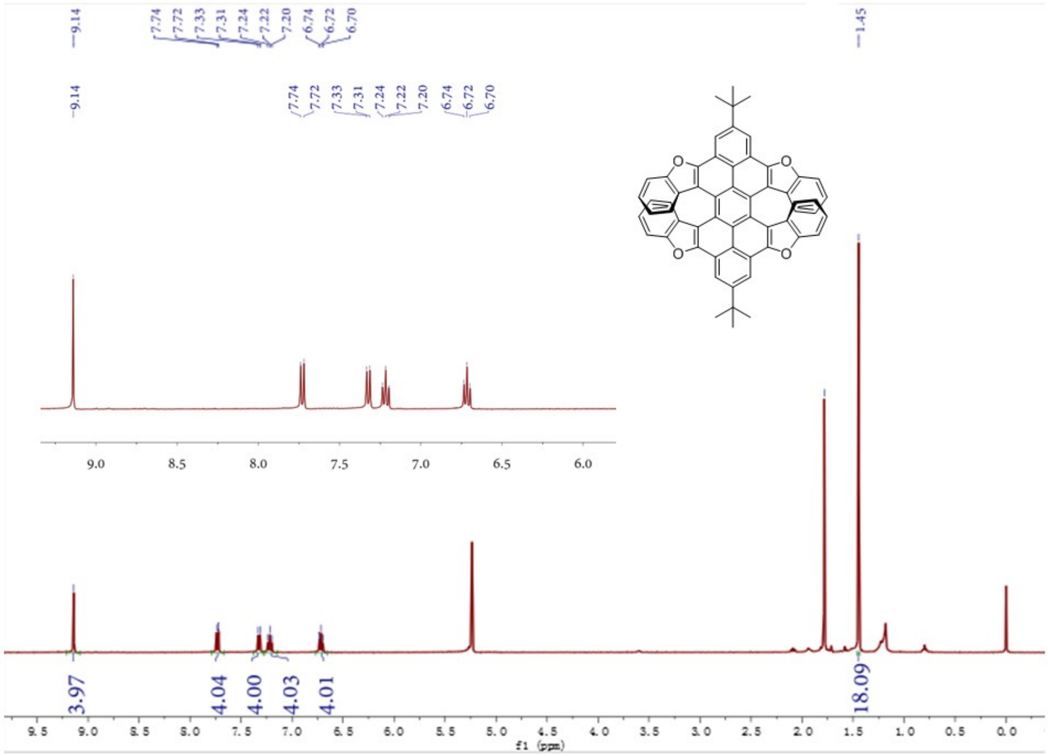


Figure S14. ^{1}H NMR spectrum of **1** (400 MHz, CD_2Cl_2)

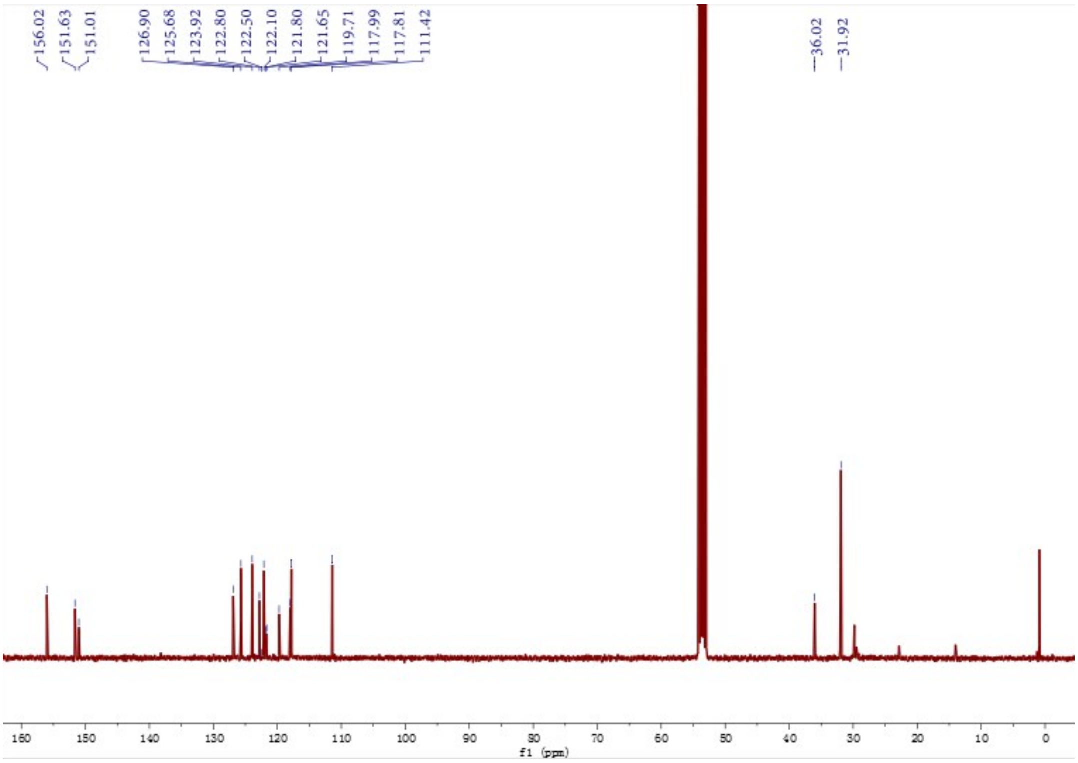
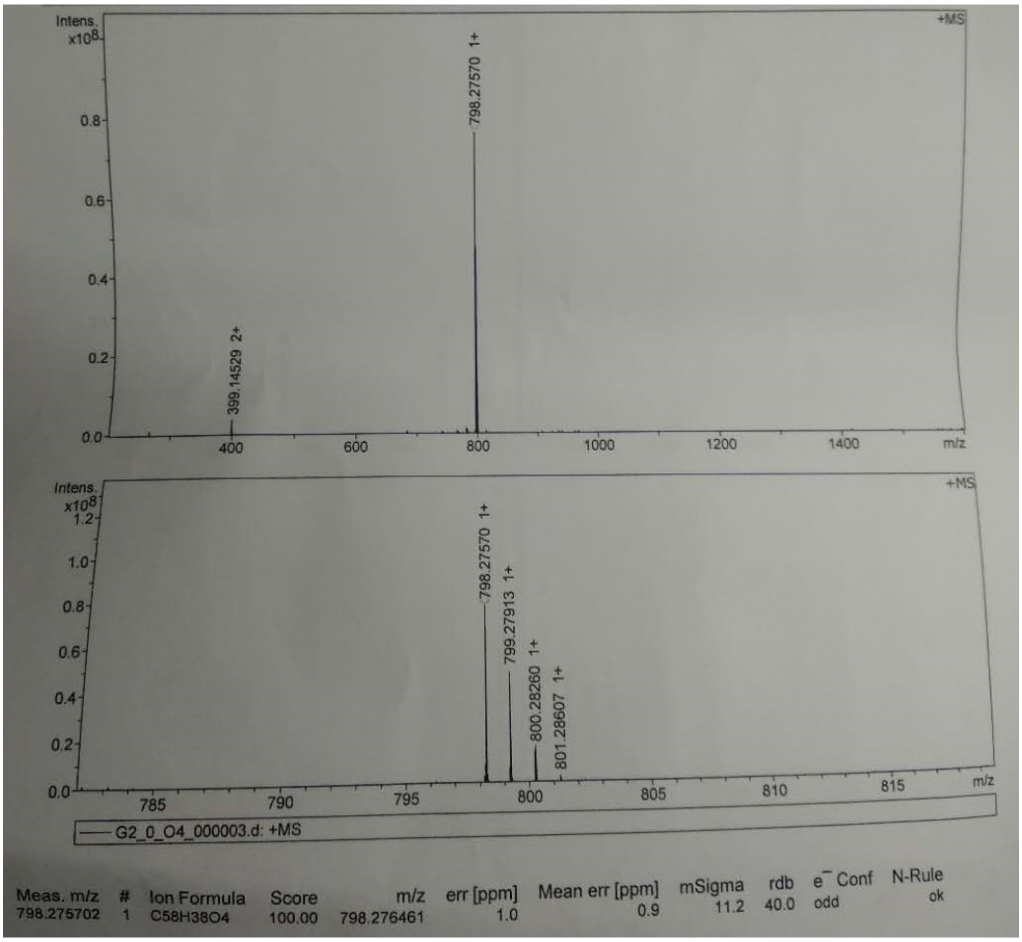


Figure S15. ^{13}C NMR spectrum of **1** (100 MHz, CD_2Cl_2)



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
798.275702	1	C58H38O4	100.00	798.276461	1.0	0.9	11.2	40.0	odd	ok

Figure S16. HRMS (MALDI-TOF) spectrum of **1**

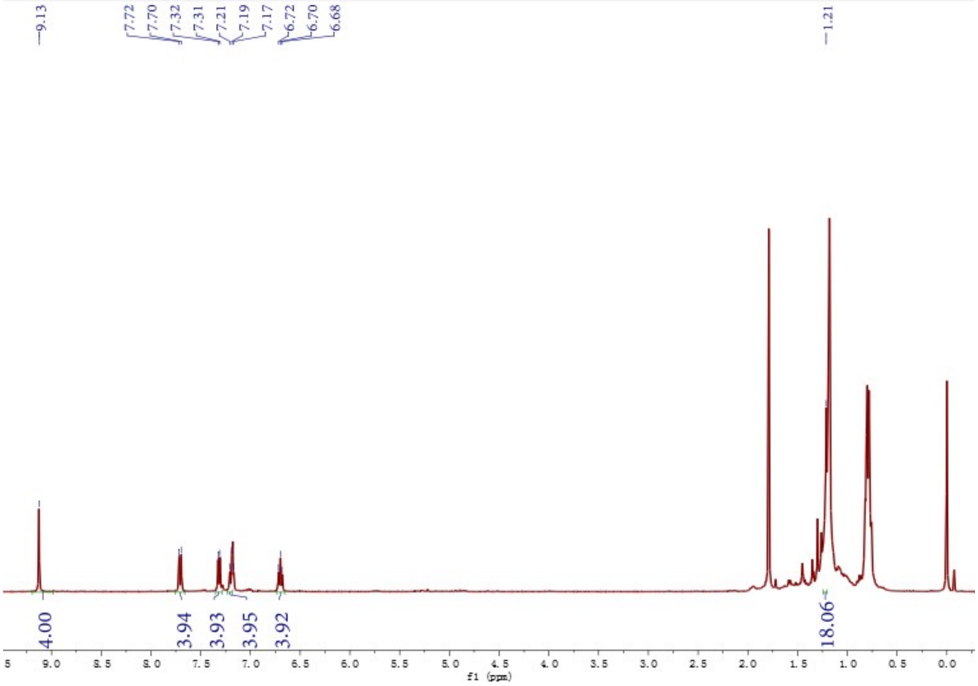


Figure S17. ^{1}H NMR spectrum of **1** obtained after the reduction of $1^{\bullet +}BF_4$ by $SnCl_2$ (400 MHz, $CDCl_3$)

References:

1. Y. Hu, X.-Y. Wang, P.-X. Peng, X.-C. Wang, X.-Y. Cao, X. Feng, K. Müllen, A. Narita, *Angew. Chem. In. Ed.* **2017,** *56*, 3374-3378.