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Supporting Information

A C_3-Symmetric Triple Oxa[6]helicene with Circularly Polarized Luminescence Featuring Parallel Transition Dipole Moments

Jun Liu,[1] Lihui Jiang,[1] Hao Chang,[1] Haoliang Liu,[2] Xiao-Yu Cao,[2] Yingping Zou,[1] Yunbin Hu*[1]

[1]College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China;

[2]Department of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China.

Contents

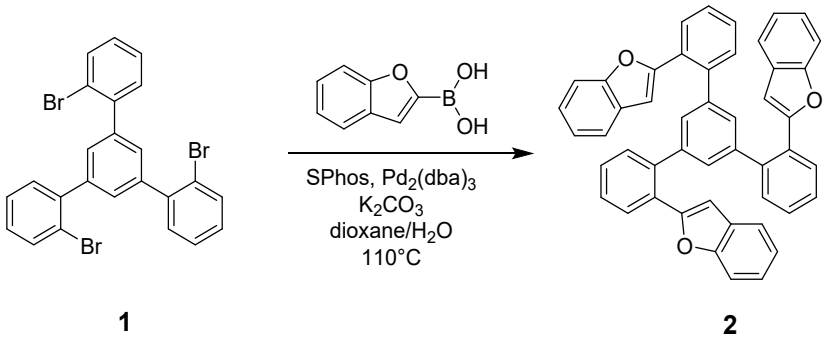
1. Experimental Procedures

General Methods

All starting materials were purchased from Energy Chemical and used as received without further purification. NMR spectra were recorded in $CDCl_3$ on Bruker AV-400 nuclear magnetic resonance spectrometer. Abbreviations: s=singlet, d = doublet, t = triplet, m = multiplet. X-ray crystallography was performed on a Bruker AXS Kappa ApexII Duo Diffractometer. 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 absorption spectra were recorded by UV-2600 Spectrophotometer. Fluorescence spectra were determined by HITACHI F-4600 Fluorescence Spectrophotometer. Absolute photoluminescence quantum yields were recorded on Edinburgh FS5 Fluorescence Spectrometer. Fluorescence lifetimes were determined by 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 an Ag-AgCl electrode as a reference electrode. Optical resolution was performed on a Shimadzu LC-16A instrument equipped with a DAICEL CHIRALPAK IE column. CD spectra were collected on JASCO J-810 circular dichroism spectrometer at 298 K. CPL spectra were obtained using JASCO CPL-300 spectrophotometer at 298 K (emission slit width: 3000 μm, integration time: 4 sec, scan speed: 100 nm/min and accumulations: 3 times).

Synthesis

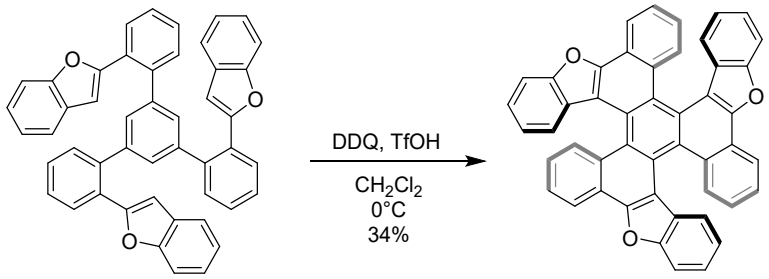
1,3,5-tri(2-bromophenyl)benzene (**1**) was synthesized according to the reported procedure.[1]



1 **2**

1,3,5-Tri(2-benzofuranylphenyl) benzene (2). Under argon atmosphere, 1,3,5-tri(2-bromophenyl)benzene (**1**, 1.00 g, 1.27 mmol), benzofuran-2-boronic acid (656 mg, 4.05 mmol), tris[dibenzylideneacetone]dipalladium(0) ($Pd_2(dba)_3$, 139 mg, 0.152 mmol), 2-

dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos, 249 mg, 0.608 mmol) and potassium carbonate (2.70 g, 19.7 mmol) were suspended in a degassed solvent mixture of dioxane (48 mL) and water (12 mL). The resulting suspension was heated to 110 ºC and stirred for 12 hours. After cooled to room temperature, the reaction mixture was diluted with water and extracted with dichloromethane. The organic phase was dried over Na_2SO_4 and evaporated to dryness. The residue was purified via column chromatography with dichloromethane/petroleum ether (1/3) as eluent to afford **2** as white powder (621 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$, 298K, ppm) δ 7.89 (dd, J = 7.8, 0.9 Hz, 3H), 7.44–7.35 (m, 9H), 7.34 (s, 3H), 7.26–7.21 (m, 6H), 7.17–7.13 (m, 3H), 7.04 (dd, J = 7.6, 0.9 Hz, 3H), 6.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, ppm) δ 155.25, 154.41, 141.91, 140.07, 131.01, 129.06, 129.02, 129.01, 128.58, 128.38, 127.73, 124.28, 122.89, 120.91, 111.15, 105.88. HRMS (MALDI-FT) *m/z*: Calcd for $C_{48}H_{30}O_3$: 654.2195; Found: 654.2189 (M^+).



2 **TO6H**

Triple oxa[6]helicene (TO6H). Under argon atmosphere, compound **2** (500mg, 0.764 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 572 mg, 2.52 mmol) were dissolved in 250 mL of dry degassed dichloromethane. The resulting solution was cooled to 0 ºC and triflic acid (5 mL) 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 dried over Na_2SO_4 and evaporated to dryness. The residue was purified via column chromatography with dichloromethane/petroleum ether (1/4) as eluent, affording the crude product as a yellow solid. The crude product was subjected to recrystallization in tetrahydrofuran/methanol, providing pure **TO6H** as a bright yellow powder (170 mg, 34%). ^{1}H NMR (400 MHz, $CDCl_3$, 298K, ppm) δ 8.75 (d, J = 7.9 Hz, 3H), 8.38 (d, J = 8.4 Hz, 3H), 7.73 (t, J = 7.8 Hz, 6H), 7.29 (dd, J = 16.0, 7.7 Hz, 6H), 6.84 (t, J = 7.6 Hz, 3H), 6.27 (d, J = 7.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 298K, ppm) δ 155.90, 151.23, 131.32, 130.34, 126.79, 126.63, 125.57, 125.33, 125.06, 124.59, 123.33, 121.83, 121.14, 120.62, 117.14, 111.31. HRMS (MALDI-FT) *m/z:* Calcd for $C_{48}H_{30}O_3$: 648.1725; Found: 648.1720 (M^+).

2. X-ray Single Crystallography

Single crystal suitable for X-ray crystallography analysis was obtained by slow diffusion of methanol vapor into the toluene solution of **TO6H** for 3 weeks. The crystal structure was deposited at the Cambridg Crystallographic Data Centre (CCDC) and the data can be obtained free of charge via www.ccdc.cam.ac.uk/structures.

Table S1. Crystal data for **TO6H** (CCDC number: 2171351).

formula	$C_{48}H_{24}O_3$
molecular weight	648.67 g mol^{-1}
absorption	μ =0.086 mm^{-1}
crystal size	0.50 × 0.3 × 0.3 yellow block
space group	P-1(monoclinic)
lattice parameters (calculate from 16522 reflections with 2.35° < θ < 24.99°)	a = 21.582(12)Å α =90° b = 28.06(2)Å β = 120.061(12)° c = 11.830(8)Å γ = 90° v = 6200.51(700)$Å^3$ z = 8 F(000) = 2688.0
temperature	150 k
density	d_{xray} = 1.38966 g cm^{-3}
<u>data collection</u>	
diffractometer	Bruker APEX-II CCD
radiation	Mo-K_α Graphitmonochromator
scan-type	\f and \w scans
scan-width	1°
scan range	2.181° ≤ θ < 28.213° -28° ≤ h ≤ 28°, -37° ≤ k ≤ 37°, -15°≤ l ≤ 13°
number of reflections:	
measured	5988
unique	56830 (R_{int} = 0.0435)
observed	7619(I/s(I) > 2)
<u>Data correction, structure solution and refinement</u>	
corrections	Bruker APEX2
structure solution	program: SHELXS-97 (sheldrick, 2008)
refinement	Program: SHELXS 2014/7 (sheldrick, 2014). refined parameters, weighting scheme: w = 1/[\s^2^(Fo^2^)+(0.0462P)^2^+4.7515P where P = (Fo^2^+2Fc^2^)/3
R-values	wR_2 = 0.1017(R = 0.0435 for observed reflections, 0.0605 for all reflections)
goodness of fit	S = 1.014

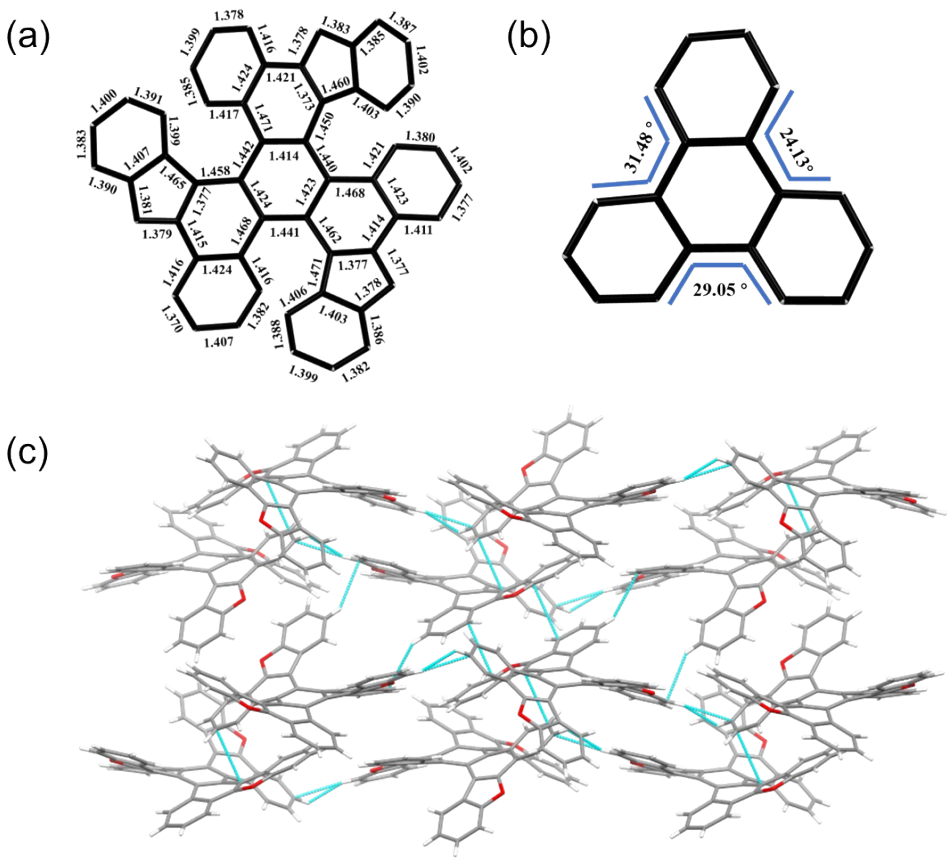


Figure S1. (a) the bond lengths and torsion angles (b) of the **TO6H** in the crystal structure. (c) Molecular packing structure of **TO6H** showing short contacts with blue dotted line.

3. Photophysical and Electrochemical Properties

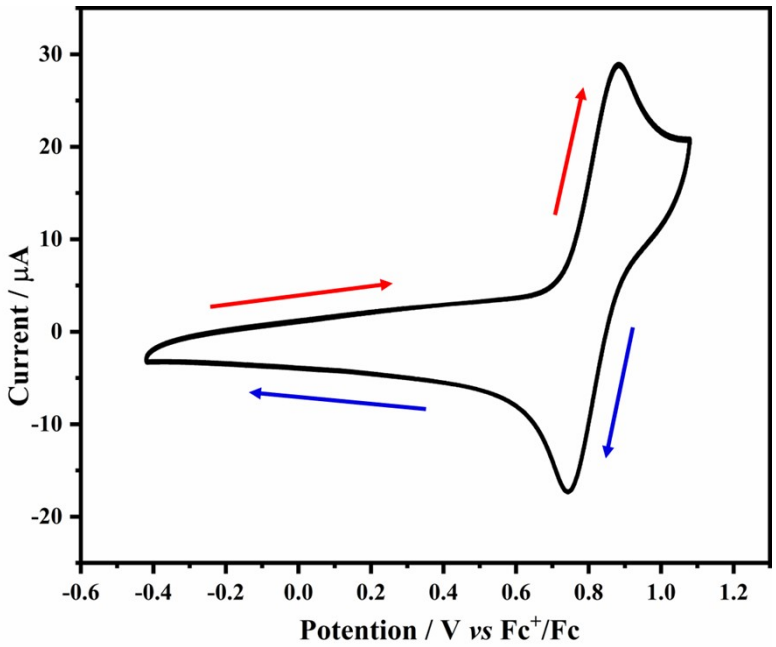


Figure S2. Cyclic voltammograms of **TO6H** in dichloromethane (c =10^{-3} M) with Bu_4NPF_6 (c = 0.1 M) as a supporting electrolyte at a scan rate of 100 mV s^{-1}.

Table S2. Summary of photophysical properties

Compound	λ_{abs} (nm)	λ_{em} (nm)	Stokes shift (cm^{-1})	E_g^{opt} (eV)[a]	Φ_F	τ_F (ns)[b]	k_r ($10^8\ s^{-1}$)[c]	k_{nr} ($10^8\ s^{-1}$)[d]
TO6H	365	490	6989	2.9	5%	5.8	0.084	1.62

[a]Optical band gaps calculated from the onset absorptions: $E_g^{opt} = 1240/\lambda_{abs,onset.}$ [b]Fluorescence lifetimes determined by the fluorescence decay profiles. [b]Radiative decay rate constants calculated by $\Phi_F = k_r \times \tau_F$. [c]Nonradiative rate constants calculated by $k_r + k_{nr} = \tau_F^{-1}$.

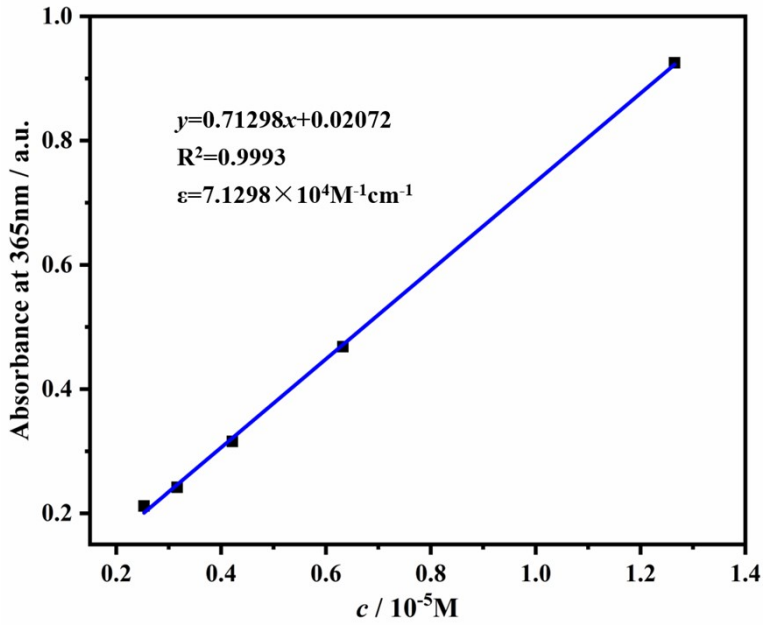


Figure S3. Calibration plot of the absorption molar extinction coefficients ε. (298K, L = 1cm)

4. Chiral HPLC analysis and Chiroptical Properties

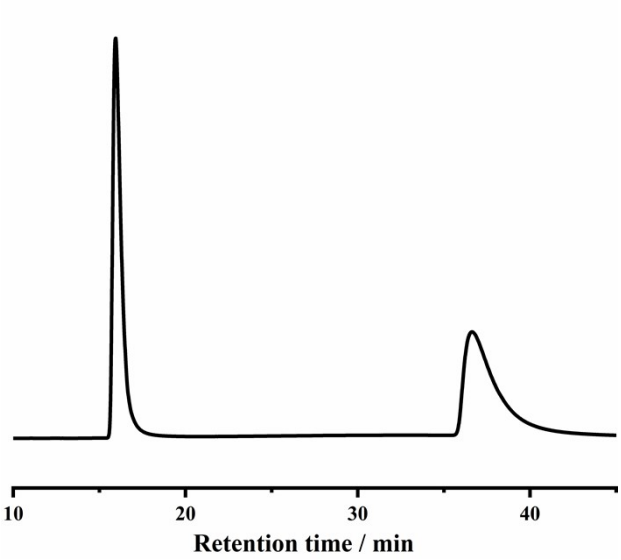


Figure S4. Chiral HPLC trace during the separation of compound **TO6H** using dichloromethane / n-hexane (1/4, v/v) as eluent.

To determine the racemization barrier, the interconversion process from (*P,P,P*)-**TO6H** to (*P,P,P*)-**TO6H** was monitored by chiral HPLC. (*P,P,P*)-**TO6H** is configurationally stable and no racemization was observed after 24 h at room temperature. Thus, the racemization process during the resolution by HPLC can be neglected. Enantiopure sample of (*P,P,P*)-**TO6H** was dissolved in 1, 2-dichlorobenzene and heated at 453 K. Aliquots were periodically removed from the solution and analyzed by chiral HPLC.[2]

The isomerization is a reversible unimolecular reaction and follows first-order kinetics:

$$\upsilon = d(A)/A_0 = kdt$$

where A denotes the concentration of the (*P,P,P*)-**TO6H** and A_0 is the initial concentration thereof. *k* denotes the reaction rate constant. Integration of the first-order rate law yields:

$$\ln(A/A_0) = -k \cdot t$$

Half-life $t_{1/2}$ can be calculated from the following equation:

$$t_{1/2} = \ln 2 / k$$

The free activation enthalpy of enantiomerization is determined from the Eyring equation[3]:

$$\Delta G^{\neq} = -RT\ln(hk/\sigma k_B T)$$

Where R, T, h, k, k_B are gas constant, absolute temperature, Planck's constant, rate constant, and Boltzmann constant, respectively. Parameter σ was assumed as 0.5, as the probability of conversion to (*P,P,P*)- or (*M,M,M*)-enantiomer is equal.

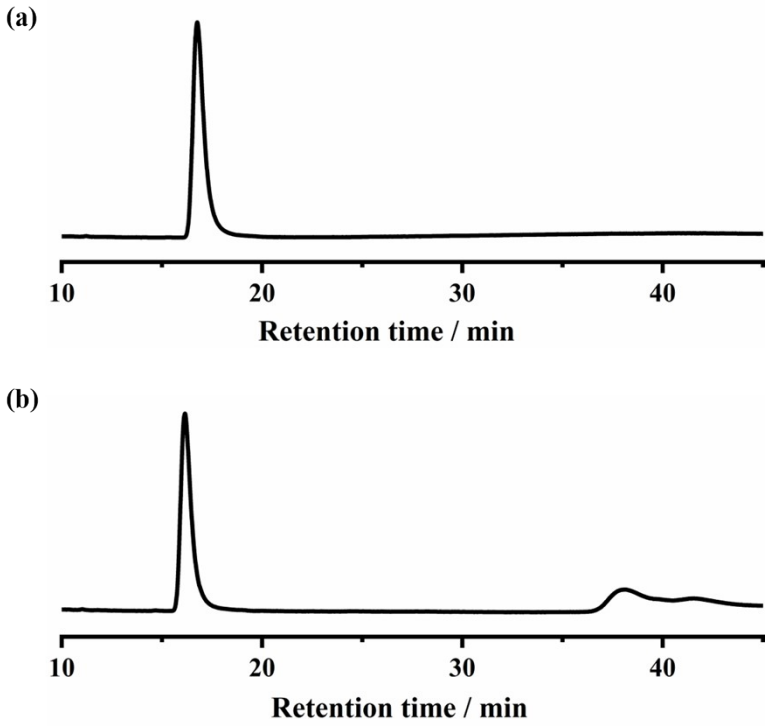


Figure S5. HPLC analysis of the thermal racemization progress of (*P,P,P*)-**TO6H** rich solution after heating at 453K in 1, 2-dichlorobenzene for (a) 0 s and (b) 4000 s

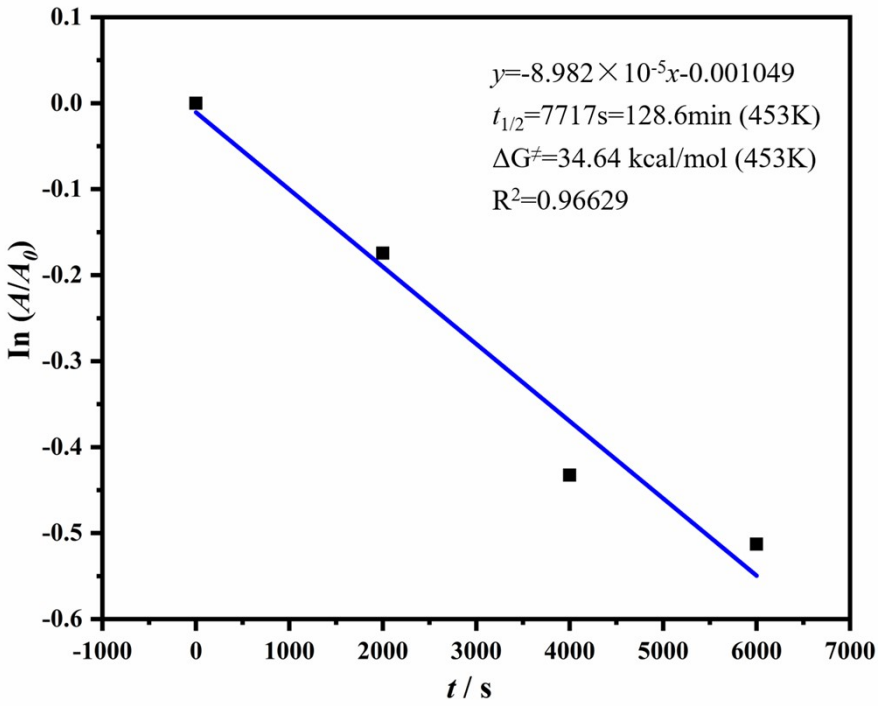


Figure S6. Plot of ln(A/A_0) vs. time for (*P*,*P*,*P*)-**TO6H** at 453 K in 1, 2-dichlorobenzene.

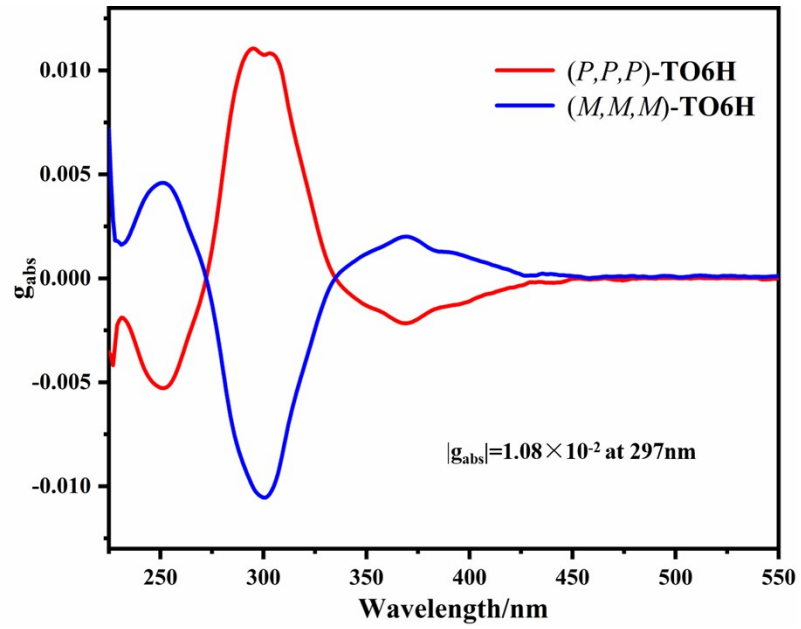


Figure S7. The absorption dissymmetry factor curves of **TO6H** in dichloromethane (c =10^{-5} M)**.**

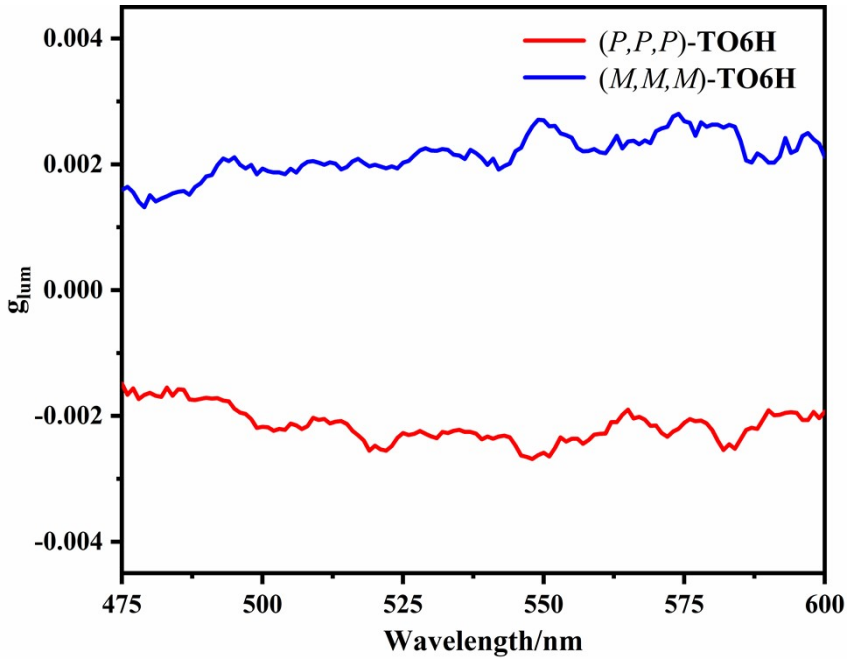


Figure S8. Luminescent dissymmetry factor curves of **TO6H** in dichloromethane (c =10^{-5} M, 298K, excitation wavelength:365nm)

5. Theoretic Calculations

DFT calculations were performed using the Gaussian 16 software package[4]. The ground state (S_0) geometry optimization was carried out at the B3LYP/6-311G(d,p) level of theory to obtain the molecular orbitals. The optimized structures were then subjected to time-dependent (TD) DFT calculations at the same level of theory to obtain the excited states and chiroptical parameters which were used to plot the simulated UV-vis absorption and CD spectra. The lowest excited state (S_1) geometry optimization was carried out by TD-DFT calculations at the cam-B3LYP/6-311G(d,p) level of theory, which was used to plot the fluorescence spectrum and obtain the chiroptical parameters in the S_1 State.

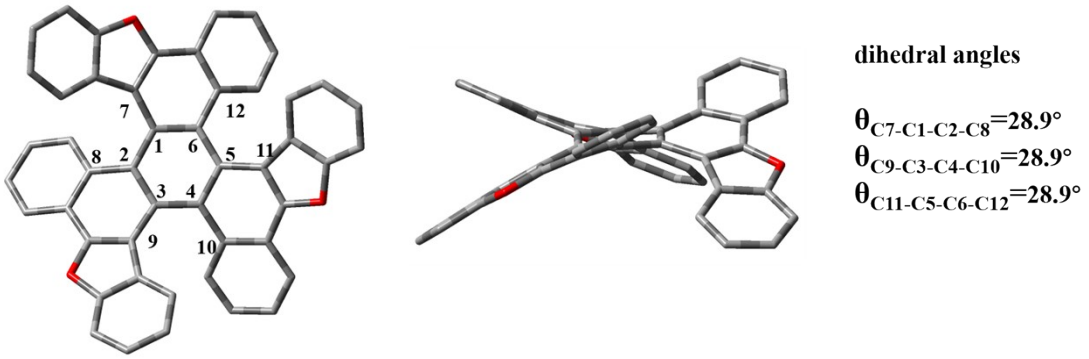


Figure S9. Top and side views of the optimized geometry in the ground state of **TO6H.** (All hydrogen atoms are omitted for clarity, and related dihedral angles are listed)

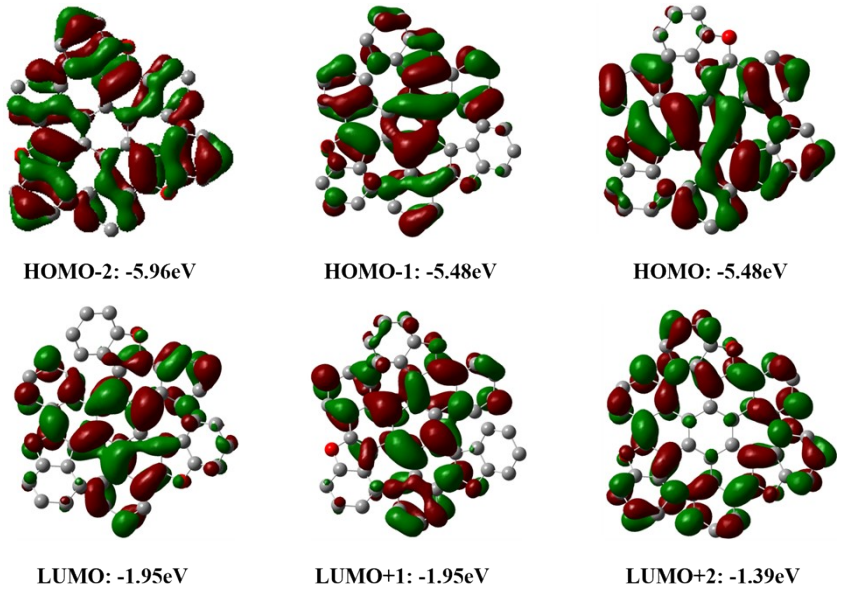


Figure S10. The electron density distribution and energies of molecular orbitals for **TO6H.**

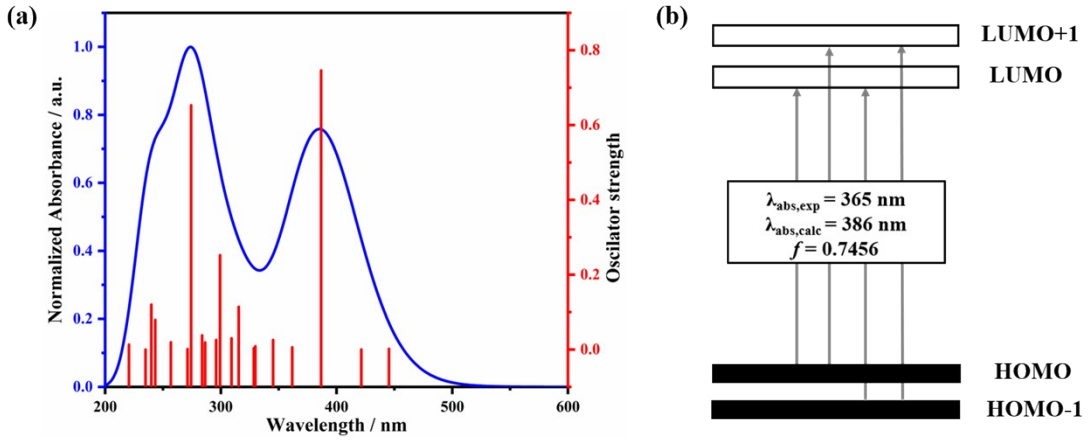
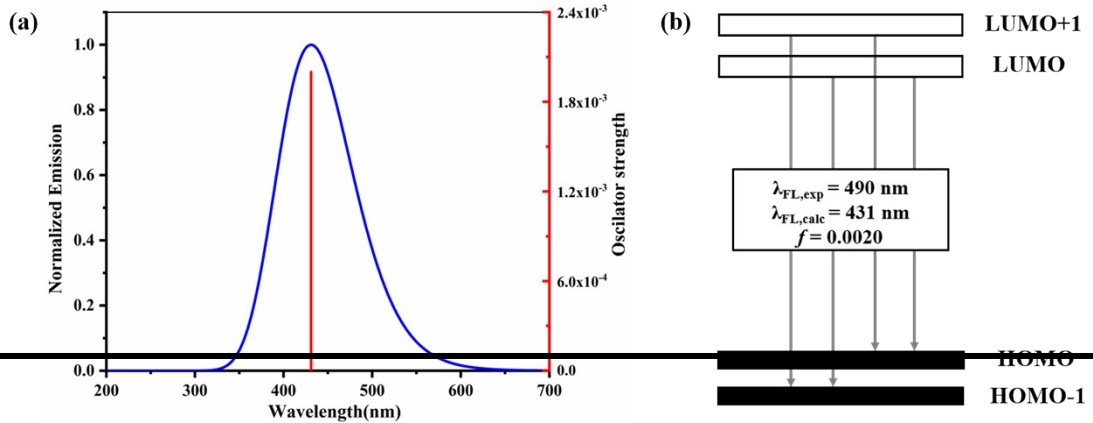


Figure S11. (a) Simulated absorption spectrum (blue line) and calculated oscillator strength (red bar) of **TO6H** at the B3LYP/6-311G (d, p) level. (b) Vertical transitions assigned to the experimental absorption band at 365 nm.

Figure S12. (a) Simulated fluorescence spectra and calculated oscillator strength (red bar) of **TO6H** at the cam-B3LYP/6-311G (d, p) level. (b) Vertical transitions assigned to the experimental fluorescence band at 490 nm.



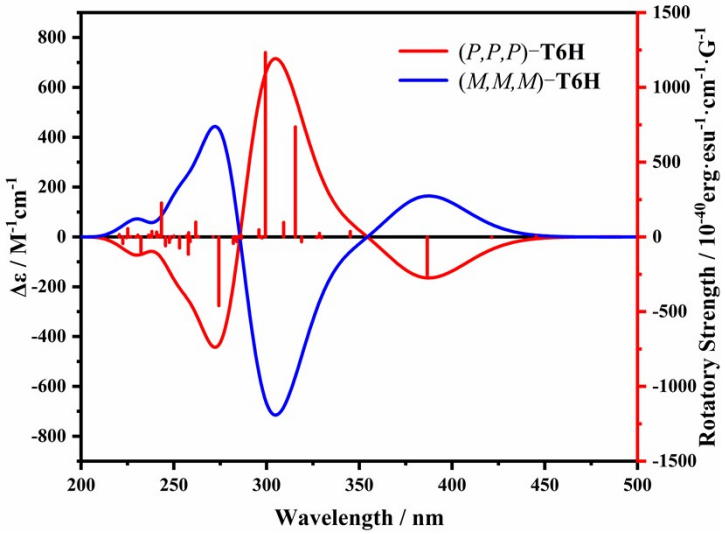


Figure S13. Simulated CD spectra and calculated rotatory strength (red bar) for the isomers of **TO6H** at the B3LYP/6-311G (d, p) level.

Table S3. Excited states of **TO6H** calculated by TD-DFT at the B3LYP/6-311G (d, p) level for the geometry optimized in the S_0 state (H represents HOMO, and L represents LUMO).

excited state	energy (eV)	wavelength (nm)	oscillator strength (*f*)	description
S_1	2.7839	445.36	0.0020	H-1→L(0.19401) H-1→L+1(-0.45548) H→L(0.45557) H→L+1(0.19403)
S_2	2.9422	421.40	0.0001	H-1→L(0.45750) H-1→L+1(0.19377) H→L(-0.19387) H→L+1(0.45750)
S_3	3.2067	386.64	0.7462	H-1→L(-0.22935) H-1→L+1(0.43389) H→L(0.22941) H→L+1(0.45750)
S_4	3.2068	386.63	0.7456	H-1→L(0.43384) H-1→L+1(0.22938) H→L(0.22935) H→L+1(-0.43380)
S_5	3.4275	361.73	0.0061	H-2→L(0.59701) H-2→L+1(-0.19858) H-1→L+2(-0.18480) H→L+2(0.20761)
S_6	3.4275	361.73	0.0060	H-2→L(0.19859) H-2→L+1(0.59700) H-1→L+2(-0.20755) H→L+2(-0.18489)
S_7	3.5920	345.17	0.0256	H-2→L(-0.15093) H-2→L+1(0.24175)

S_8	3.5920	345.16	0.0257	H→L+2(0.60476) H-2→L(0.24163) H-2→L+1(0.15090) H-1→L+2(0.60486) H-4→L(-0.10493) H-4→L+1(0.26401)
S_9	3.7598	329.76	0.0089	H-3→L(-0.26289) H-3→L+1(-0.10397) H-1→L+2(-0.14997) H-1→L+4(0.38504) H→L+3(0.38778)
S_{10}	3.7599	329.75	0.0089	H-4→L(0.26354) H-4→L+1(0.10405) H-3→L(-0.10444) H-3→L+1(0.26322) H-1→L+3(0.38691) H→L+2(-0.15009) H→L+4(-0.38608)

Table S4. Excited states of **TO6H** calculated at the cam-B3LYP/6-311G (d, p) level for the geometry optimized in the S_1 state (H represents HOMO, and L represents LUMO).

excited state	energy (eV)	wavelength (nm)	oscillator strength (*f*)	description
S_1	2.8765	431.02	0.0020	H-1→L(-0.24913) H-1→L+1(0.41099) H→L(0.41109) H→L+1(0.24911)
S_2	3.1053	399,27	0.0005	H-1→L+1(0.25132) H→L(0.25144) H-1→L(0.41539) H→L+1(-0.41533)
S_3	3.5603	348.24	0.7900	H-1→L+1(-0.43627) H→L(0.43614) H→L+1(-0.20608) H-1→L(-0.20609)

Table S5. Chiroptical parameters of (*P*,*P*,*P*)-**TO6H** calculated by TD-DFT at B3LYP/6-311G (d, p) level of theory for the geometry optimized in S_0 state.

excited state	$\lvert\boldsymbol{\mu}\rvert$ (10^{-20} esu·cm)	$\lvert\boldsymbol{m}\rvert$ (10^{-20} erg/Gauss)	cosθ	$g_{abs,cal}$	wavelength (nm)
S_1	43.11242	0.17788	1	0.0165	445.36
S_2	8.0381	0.55069	-0.99992	-0.27274	421.40
S_3	783.90437	1.06215	-0.61233	-0.00332	386.64
S_4	783.54148	1.06132	-0.61255	-0.00332	386.63
S_5	68.27975	0.40025	0.36065	0.00846	361.73
S_6	67.78065	0.40097	0.35413	0.00838	361.73
S_7	137.30985	1.05213	0.44722	0.01371	345.17
S_8	137.34087	1.05228	0.44683	0.01369	345.16

S_9	78.9325	0.17667	-0.88096	-0.00789	329.76
S_{10}	78.92073	0.17718	-0.88400	-0.00794	329.75

$\boldsymbol{\mu}$: transition electric dipole moments.
$\boldsymbol{m}$: transition magnetic dipole moments.
θ: angle between $\boldsymbol{\mu}$ and $\boldsymbol{m}$.
$g_{abs,cal}$: absorption dissymmetry factor calculated by $g_{abs,cal} = 4\cos\theta|\boldsymbol{\mu}||\boldsymbol{m}|/(|\boldsymbol{\mu}|^2+|\boldsymbol{m}|^2)$.

Table S6. Chiroptical parameters of (*P*,*P*,*P*)-**TO6H** calculated at cam-B3LYP/6-311G(d,p) level of theory for the geometry optimized in S_1 state.

compound	$\lvert\boldsymbol{\mu}\rvert$ (10^{-20} esu·cm)	$\lvert\boldsymbol{m}\rvert$ (10^{-20} erg/Gauss)	cosθ	$g_{lum,cal}$	wavelength (nm)
TO6H	42.40024	0.03116	-1	0.00294	431.02

$\boldsymbol{\mu}$: transition electric dipole moments.
$\boldsymbol{m}$: transition magnetic dipole moments
θ: angle between $\boldsymbol{\mu}$ and $\boldsymbol{m}$.
$g_{lum,cal}$: luminescence dissymmetry factor calculated by $g_{lum,cal} = 4\cos\theta|\boldsymbol{\mu}||\boldsymbol{m}|/(|\boldsymbol{\mu}|^2+|\boldsymbol{m}|^2)$.

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

(*P*,*P*,*P*)-**TO6H**

	X	Y	Z		X	Y	Z
O	1.257457	4.760837	0.318795	C	1.226657	0.727186	-0.49782
O	3.494458	-3.46941	0.3185	C	-0.00525	1.419735	-0.36895
O	-4.75189	-1.29137	0.318428	C	-1.24315	0.698685	-0.49798
C	0.00659	4.928765	0.85907	C	-2.49528	1.351855	-0.88012
C	-0.42105	6.074132	1.509597	C	-2.535	2.586806	-1.56719
H	0.222037	6.941279	1.590481	H	-1.61057	3.092325	-1.80581
C	-1.69705	6.03832	2.063763	C	-3.72974	3.149859	-1.97172
H	-2.07633	6.908156	2.587198	H	-3.71853	4.092277	-2.50707
C	-2.48897	4.88555	1.966958	C	-4.95217	2.511572	-1.70584
H	-3.47181	4.877423	2.423617	H	-5.88456	2.970471	-2.0137
C	-2.04364	3.751395	1.297362	C	-4.95531	1.280036	-1.08586
H	-2.6736	2.875619	1.240773	H	-5.88018	0.744771	-0.9093
C	-0.77049	3.765369	0.709234	C	3.646216	-1.21545	0.709142
C	0.085403	2.819538	-0.00266	C	-3.73961	0.678996	-0.70381
C	1.29016	3.477292	-0.14963	C	-3.6566	-0.62134	-0.14995
C	2.457873	2.899047	-0.70334	C	-2.48461	-1.3358	-0.00274
C	3.58633	3.651346	-1.08513	C	-1.22699	-0.71445	-0.36901
H	3.585226	4.719918	-0.90847	C	0.016425	-1.42598	-0.49785
C	4.651367	3.032886	-1.70503	C	1.23214	-0.7054	-0.3689
H	5.515037	3.610916	-2.01271	C	2.399088	-1.4838	-0.00262
C	4.592907	1.655128	-1.97109	C	2.366381	-2.85601	-0.14963
H	5.403502	1.174232	-2.5064	C	1.281743	-3.57817	-0.70329
C	3.507848	0.901972	-1.56678	C	1.369072	-4.93159	-1.0851
H	3.483441	-0.15135	-1.8055	H	2.295054	-5.46489	-0.90844
C	2.418417	1.48501	-0.87978	C	0.300984	-5.54473	-1.70503

	X	Y	Z		X	Y	Z
H	0.369766	-6.5817	-2.01273	H	-4.94489	-5.25176	2.58754
C	-0.86298	-4.80524	-1.97108	C	-5.05012	-3.40144	1.509567
H	-1.68473	-5.2668	-2.50641	H	-6.12264	-3.27804	1.590338
C	-0.97274	-3.48898	-1.56673	C	4.265383	-2.47007	0.858657
H	-1.87272	-2.94119	-1.80551	C	5.471315	-2.67235	1.508843
C	0.076865	-2.83701	-0.87972	H	5.900878	-3.66282	1.589474
C	-4.27196	-2.45853	0.858942	C	6.078298	-1.5494	2.063017
C	-2.87587	-2.54984	0.709272	H	7.021394	-1.6558	2.586184
C	-2.22728	-3.64539	1.297568	C	5.475717	-0.28726	1.966597
H	-1.15386	-3.75312	1.241038	H	5.960076	0.567974	2.423271
C	-2.98688	-4.59799	1.967282	C	4.270638	-0.10592	1.297365
H	-2.48846	-5.44505	2.424062	H	3.826917	0.877428	1.241178
C	-4.38117	-4.48848	2.063996				

TS-1

	X	Y	Z		X	Y	Z
O	-0.90399	4.548102	1.412028	C	-1.28292	0.326802	-0.80248
O	4.366053	-1.83808	1.065557	C	-2.54975	0.523184	-1.48523
O	-4.01654	-2.69633	-0.56025	C	-2.86362	1.718804	-2.16792
C	-2.199	4.103549	1.513038	H	-2.16004	2.540592	-2.14862
C	-3.1945	4.760547	2.215709	C	-4.04239	1.845355	-2.87736
H	-2.99726	5.706854	2.70323	H	-4.25439	2.770617	-3.4006
C	-4.4359	4.135202	2.274491	C	-4.96275	0.785098	-2.93338
H	-5.24809	4.607159	2.814878	H	-5.88754	0.899217	-3.48707
C	-4.63906	2.89529	1.654841	C	-4.67907	-0.40735	-2.29805
H	-5.60914	2.417592	1.728443	H	-5.36905	-1.24111	-2.34188
C	-3.62592	2.259267	0.945485	C	4.370693	-0.01209	-0.31267
H	-3.81853	1.302315	0.486233	C	-3.47179	-0.55652	-1.59025
C	-2.36808	2.873712	0.847865	C	-3.10248	-1.72843	-0.88037
C	-1.05469	2.564591	0.276423	C	-1.85646	-1.96185	-0.33233
C	-0.24247	3.594376	0.696858	C	-0.80486	-0.9698	-0.53789
C	1.131887	3.681806	0.388496	C	0.611696	-1.17493	-0.4216
C	1.880911	4.860935	0.567579	C	1.537122	-0.07407	-0.41561
H	1.416458	5.697752	1.074473	C	2.957595	-0.4539	-0.13177
C	3.158381	4.9589	0.054968	C	3.114472	-1.64836	0.564283
H	3.732048	5.869379	0.183182	C	2.276136	-2.78703	0.408836
C	3.673484	3.894087	-0.69645	C	2.724267	-4.09685	0.6679
H	4.633632	3.988607	-1.19061	H	3.626389	-4.24189	1.248046
C	2.947529	2.725451	-0.83033	C	2.064381	-5.16809	0.096175
H	3.286517	1.954149	-1.48515	H	2.416767	-6.17822	0.270356
C	1.703289	2.529928	-0.22729	C	0.982464	-4.93923	-0.76611
C	0.958076	1.271637	-0.36401	H	0.512789	-5.77183	-1.27655
C	-0.45706	1.407682	-0.36142	C	0.502352	-3.65623	-0.9675

	X	Y	Z		X	Y	Z
H	-0.33372	-3.501	-1.63453	H	-5.00749	-4.86972	0.754294
C	1.095532	-2.55261	-0.32746	C	5.135909	-0.85334	0.523752
C	-3.37624	-3.53695	0.312997	C	6.509407	-0.79971	0.70079
C	-2.0432	-3.13572	0.517989	H	6.993915	-1.46796	1.401366
C	-1.29913	-3.82295	1.488587	C	7.215169	0.080071	-0.10586
H	-0.28368	-3.53404	1.719575	H	8.292932	0.151433	-0.02261
C	-1.88879	-4.88429	2.164491	C	6.531128	0.814582	-1.08137
H	-1.31616	-5.41479	2.916327	H	7.091103	1.422898	-1.78212
C	-3.20557	-5.28472	1.895159	C	5.147936	0.76677	-1.19989
H	-3.63363	-6.12176	2.434276	H	4.71529	1.296687	-2.03217
C	-3.97801	-4.60468	0.959301				

(*P,P,M*)-**TO6H**

	X	Y	Z		X	Y	Z
C	-3.53213	-1.6221	3.16334	C	0.245169	-3.57886	-0.51335
C	-2.43287	-1.48669	2.338184	C	-1.97063	-3.41509	-0.1367
C	-2.3707	-0.46042	1.36992	C	-1.60513	-4.73723	-0.45509
C	-3.45914	0.46083	1.316317	O	-0.25636	-4.84046	-0.66946
C	-4.59444	0.280778	2.130554	C	-3.3455	-3.14136	-0.04651
C	-4.63098	-0.75339	3.043589	C	-4.25945	-4.17673	-0.20886
C	-1.19078	-0.24815	0.549552	C	-3.84503	-5.49076	-0.46101
C	-0.29201	-1.29361	0.120453	C	-2.49383	-5.78969	-0.59782
C	1.01771	-0.92568	-0.27984	C	-2.37931	2.967243	-1.07349
C	1.453813	0.428308	-0.00656	C	-3.7582	3.200942	-0.92738
C	0.486382	1.467785	0.053665	O	-4.30932	2.344005	-0.00528
C	-0.90695	1.070283	0.116084	C	-1.67468	3.714398	-2.02615
C	1.86212	-1.86445	-0.99967	C	-2.3632	4.665411	-2.77067
C	0.913687	2.852039	0.272307	C	-3.73547	4.887801	-2.58271
C	1.526033	-3.24756	-1.01296	C	-4.46119	4.149474	-1.65163
C	2.349736	-4.19325	-1.66265	C	4.030956	0.03078	0.651771
C	3.458986	-3.77547	-2.36277	C	5.032752	1.008801	0.784268
C	3.743689	-2.40119	-2.45637	O	4.536807	2.263412	0.531172
C	2.967308	-1.4738	-1.79393	C	4.362131	-1.29141	0.980638
C	2.30536	3.179331	0.254074	C	5.660159	-1.58012	1.386501
C	2.754772	4.508992	0.407051	C	6.641305	-0.58214	1.467217
C	1.855976	5.521985	0.648675	C	6.336621	0.742398	1.167918
C	0.494945	5.207225	0.793386	H	-3.54548	-2.40722	3.910409
C	0.043898	3.914185	0.621569	H	-1.59445	-2.16225	2.445898
C	-2.07151	1.881596	-0.15354	H	-5.41616	0.981788	2.047824
C	-3.28591	1.536431	0.410452	H	-5.49521	-0.88171	3.684974
C	2.829926	0.761948	0.253162	H	2.065382	-5.23755	-1.63712
C	3.204319	2.090647	0.268803	H	4.086414	-4.49715	-2.873
C	-0.71029	-2.66407	-0.09977	H	4.579062	-2.06365	-3.05893

	X	Y	Z		X	Y	Z
H	3.200843	-0.42434	-1.89777	H	-0.61582	3.556198	-2.18151
H	3.819458	4.702372	0.371181	H	-1.82894	5.248102	-3.51201
H	2.1985	6.54302	0.770655	H	-4.24208	5.639077	-3.17714
H	-0.21482	5.983562	1.055154	H	-5.52386	4.292005	-1.5019
H	-1.0019	3.718034	0.782793	H	3.625097	-2.07964	0.927226
H	-3.70747	-2.14112	0.12845	H	5.918881	-2.60063	1.643725
H	-5.31855	-3.95705	-0.14086	H	7.64619	-0.84098	1.779865
H	-4.58228	-6.27706	-0.57358	H	7.067152	1.537409	1.247219
H	-2.13958	-6.78525	-0.83318				

TS-2

	X	Y	Z		X	Y	Z
O	3.265111	3.642487	1.173339	C	-0.08588	2.667763	-2.16737
O	1.113433	-4.69157	-0.87208	H	0.956341	2.728209	-1.89166
O	-4.49118	0.930392	-1.37259	C	-0.5175	3.333421	-3.29473
C	2.19611	4.491851	1.024399	H	0.190836	3.919139	-3.8695
C	2.232299	5.85539	1.263697	C	-1.8578	3.249127	-3.71506
H	3.14958	6.344756	1.565553	H	-2.18522	3.783475	-4.59934
C	1.033927	6.547673	1.112813	C	-2.74278	2.464439	-3.01019
H	1.009696	7.616	1.293466	H	-3.77356	2.362044	-3.32448
C	-0.14196	5.880248	0.742074	C	2.436609	-2.83303	-1.12031
H	-1.06287	6.443234	0.644563	C	-2.30654	1.767394	-1.86411
C	-0.15246	4.511877	0.494649	C	-3.15645	0.941701	-1.09679
H	-1.07007	4.017713	0.209057	C	-2.80326	0.142471	-0.01459
C	1.04285	3.79206	0.626503	C	-1.35365	0.001427	0.23387
C	1.461809	2.400998	0.504284	C	-0.61463	-1.22523	0.572822
C	2.791458	2.390043	0.88701	C	0.766314	-1.26059	0.246821
C	3.555235	1.225253	1.119789	C	1.292767	-2.48562	-0.28594
C	4.877456	1.275312	1.615326	C	0.539083	-3.64239	-0.21334
H	5.355009	2.241022	1.724439	C	-0.65456	-3.73938	0.536581
C	5.5241	0.117652	1.981282	C	-1.23691	-4.96314	0.922843
H	6.537043	0.155202	2.365132	H	-0.82922	-5.88324	0.522229
C	4.848397	-1.11315	1.890185	C	-2.26374	-4.98243	1.843796
H	5.337739	-2.02211	2.220898	H	-2.69962	-5.92435	2.155616
C	3.563254	-1.17901	1.395108	C	-2.68744	-3.77961	2.430564
H	3.066466	-2.13684	1.362761	H	-3.41796	-3.7966	3.231374
C	2.879391	-0.02215	0.945916	C	-2.15605	-2.57443	2.011846
C	1.522111	-0.03829	0.425038	H	-2.40142	-1.66252	2.527687
C	0.816528	1.155928	0.207481	C	-1.18993	-2.49784	0.999151
C	-0.54928	1.062315	-0.27578	C	-5.07421	0.196322	-0.38595
C	-0.97459	1.879881	-1.39112	C	-4.11427	-0.29105	0.526771

	X	Y	Z		X	Y	Z
C	-4.65367	-0.84699	1.703599	C	3.125748	-4.91576	-2.24455
H	-4.03672	-1.1316	2.533949	H	2.945161	-5.96162	-2.45801
C	-6.0267	-0.99942	1.850327	C	4.216006	-4.22632	-2.76882
H	-6.40704	-1.43281	2.768113	H	4.919003	-4.74835	-3.40734
C	-6.92519	-0.59155	0.857767	C	4.409778	-2.86573	-2.49105
H	-7.99062	-0.73368	0.994073	H	5.261277	-2.35284	-2.92291
C	-6.44743	0.041567	-0.27994	C	3.53376	-2.15982	-1.67348
H	-7.101	0.436336	-1.04746	H	3.700233	-1.11071	-1.47252
C	2.263252	-4.19256	-1.43836				

(*P,M,M*)-**TO6H**

	X	Y	Z		X	Y	Z
O	-4.53681	2.263407	0.531172	C	-3.74368	-2.40119	-2.45637
O	4.309315	2.34401	-0.00529	H	-4.57906	-2.06365	-3.05893
O	0.256361	-4.84046	-0.66945	C	-3.45898	-3.77547	-2.36277
C	-5.03275	1.008795	0.784266	H	-4.08641	-4.49715	-2.873
C	-6.33662	0.742391	1.167914	C	-2.34973	-4.19325	-1.66265
H	-7.06715	1.537401	1.247216	H	-2.06538	-5.23755	-1.63712
C	-6.64131	-0.58215	1.467212	C	2.379307	2.967248	-1.07349
H	-7.64619	-0.84099	1.779859	C	-1.52603	-3.24756	-1.01296
C	-5.66016	-1.58013	1.386496	C	-0.24517	-3.57886	-0.51335
H	-5.91888	-2.60064	1.64372	C	0.710289	-2.66407	-0.09977
C	-4.36213	-1.29142	0.980635	C	0.292016	-1.29361	0.120454
H	-3.6251	-2.07965	0.927223	C	1.190777	-0.24815	0.549551
C	-4.03096	0.030775	0.651769	C	0.906947	1.070284	0.116084
C	-2.82993	0.761945	0.253163	C	2.071509	1.881599	-0.15354
C	-3.20432	2.090644	0.268805	C	3.28591	1.536435	0.410446
C	-2.30536	3.179329	0.254078	C	3.459144	0.460834	1.31631
C	-2.75478	4.508989	0.407059	C	4.594443	0.280783	2.130545
H	-3.81946	4.702368	0.371189	H	5.416166	0.981793	2.047812
C	-1.85598	5.521982	0.648685	C	4.630986	-0.75338	3.04358
H	-2.19851	6.543016	0.770667	H	5.49522	-0.8817	3.684963
C	-0.49495	5.207223	0.793396	C	3.532134	-1.6221	3.163334
H	0.214818	5.98356	1.055167	H	3.545488	-2.40722	3.910405
C	-0.0439	3.914183	0.621576	C	2.432874	-1.48668	2.338181
H	1.001894	3.718034	0.7828	H	1.594456	-2.16225	2.445897
C	-0.91369	2.852037	0.272312	C	2.370703	-0.46042	1.369916
C	-0.48638	1.467785	0.053667	C	1.605131	-4.73724	-0.45509
C	-1.45381	0.428307	-0.00656	C	1.970637	-3.41509	-0.13669
C	-1.01771	-0.92568	-0.27984	C	3.345505	-3.14136	-0.04651
C	-1.86212	-1.86445	-0.99967	H	3.707477	-2.14112	0.128448
C	-2.9673	-1.4738	-1.79393	C	4.259453	-4.17673	-0.20885
H	-3.20084	-0.42434	-1.89777	H	5.318554	-3.95705	-0.14086

	X	Y	Z		X	Y	Z
C	3.845033	-5.49076	-0.46101	C	3.735461	4.88781	-2.58271
H	4.582283	-6.27706	-0.57357	H	4.242068	5.639088	-3.17714
C	2.493829	-5.78969	-0.59781	C	2.363186	4.66542	-2.77067
H	2.139585	-6.78525	-0.83318	H	1.828928	5.248112	-3.512
C	3.758192	3.200948	-0.92738	C	1.674673	3.714405	-2.02614
C	4.461184	4.149482	-1.65163	H	0.615806	3.556204	-2.18151
H	5.523851	4.292014	-1.50191				

TS-3

	X	Y	Z		X	Y	Z
O	2.071009	-4.55949	0.357562	C	5.217158	1.370967	1.822866
O	-4.71722	0.433938	1.453318	H	6.181638	1.662634	2.2221
O	2.957092	3.798358	-0.99202	C	4.582631	2.166779	0.891689
C	3.289827	-3.97652	0.124043	H	5.020529	3.101955	0.564381
C	4.479452	-4.67679	0.013537	C	3.314741	1.800024	0.397881
H	4.511964	-5.74522	0.185097	C	2.50827	2.652234	-0.39728
C	5.601016	-3.94785	-0.36882	C	1.148999	2.468963	-0.5599
H	6.5536	-4.45176	-0.48336	C	0.538347	1.260299	-0.08884
C	5.501262	-2.57649	-0.63867	C	-0.87398	1.077022	0.168533
H	6.379249	-2.0352	-0.97142	C	-1.45601	-0.20352	-0.05262
C	4.301268	-1.89016	-0.49026	C	-2.93391	-0.26786	0.169638
H	4.258917	-0.8355	-0.71676	C	-3.41627	0.636014	1.103065
C	3.159229	-2.58763	-0.06529	C	-2.77796	1.80674	1.573418
C	1.735878	-2.30128	0.135588	C	-3.39734	2.665487	2.503498
C	1.156356	-3.54632	0.276165	H	-4.36169	2.386259	2.907293
C	-0.19574	-3.81481	-0.04404	C	-2.78095	3.838397	2.877497
C	-0.68192	-5.12501	-0.22444	H	-3.25231	4.504523	3.590669
H	-0.09604	-5.95496	0.149884	C	-1.52741	4.152324	2.332003
C	-1.83771	-5.34096	-0.94715	H	-1.01801	5.060218	2.63458
H	-2.20728	-6.34848	-1.09846	C	-0.91482	3.312019	1.423049
C	-2.47534	-4.25329	-1.5615	H	0.064176	3.586736	1.071283
H	-3.31667	-4.42097	-2.22376	C	-1.52504	2.109237	0.986762
C	-2.01852	-2.96839	-1.33779	C	1.854582	4.366617	-1.59104
H	-2.42614	-2.13497	-1.87491	C	0.701147	3.596688	-1.35883
C	-0.94212	-2.68906	-0.49355	C	-0.51199	4.020786	-1.91297
C	-0.51503	-1.3252	-0.20276	H	-1.4208	3.454659	-1.75455
C	0.871542	-1.13135	0.10283	C	-0.52419	5.1873	-2.6701
C	1.393716	0.199435	0.249314	H	-1.45563	5.528548	-3.10658
C	2.713887	0.558157	0.769663	C	0.644464	5.934312	-2.87964
C	3.3701	-0.19546	1.765962	H	0.600347	6.839894	-3.47324
H	2.900588	-1.0916	2.14627	C	1.863869	5.531032	-2.33992
C	4.58465	0.206953	2.28863	H	2.777656	6.090379	-2.49511
H	5.050893	-0.38548	3.067259	C	-5.1854	-0.52795	0.615152

	X	Y	Z		X	Y	Z
C	-6.51765	-0.91162	0.602825	H	-6.35102	-2.64891	-2.29284
H	-7.1974	-0.53311	1.355692	C	-4.67692	-1.70805	-1.36886
C	-6.92959	-1.73181	-0.4353	H	-4.06949	-1.96348	-2.21772
H	-7.96194	-2.0537	-0.50119	C	-4.17885	-0.96987	-0.27092
C	-6.01308	-2.08299	-1.43238				

(*M,M,M*)-**TO6H**

	X	Y	Z	H	-1.78737	6.342652	-2.0153
O	-4.91472	-0.3202	0.316593	C	-0.30587	5.107743	-1.08688
O	2.734884	-4.09569	0.317691	H	0.397005	5.9129	-0.912
O	2.180137	4.416287	0.31631	C	0.051014	3.799834	-0.70331
C	-4.83989	0.939323	0.857745	C	1.311735	3.469413	-0.14999
C	-5.88265	1.578752	1.507144	C	1.787989	2.182256	-0.00142
H	-6.85728	1.114275	1.586342	C	0.936433	1.066861	-0.36554
C	-5.60302	2.823714	2.062507	C	1.396039	-0.28977	-0.49465
H	-6.38446	3.362803	2.585063	C	0.455691	-1.34467	-0.36571
C	-4.31933	3.379288	1.96803	C	0.995971	-2.63957	-0.00084
H	-4.12308	4.341867	2.4256	C	2.348811	-2.87067	-0.14931
C	-3.29093	2.724665	1.299557	C	3.26511	-1.94425	-0.70338
H	-2.31031	3.174441	1.244886	C	4.576283	-2.28928	-1.08661
C	-3.5486	1.478427	0.710129	H	4.922254	-3.3004	-0.91093
C	-2.78406	0.457215	-0.00147	C	5.382272	-1.35815	-1.70672
C	-3.66074	-0.59858	-0.15033	H	6.386444	-1.62434	-2.01554
C	-3.31671	-1.85542	-0.70434	C	4.879512	-0.07376	-1.97141
C	-4.27104	-2.81821	-1.08809	H	5.489658	0.644652	-2.50652
H	-5.31973	-2.61226	-0.91266	C	3.609095	0.286158	-1.56564
C	-3.86762	-3.98163	-1.70853	H	3.243985	1.274747	-1.80293
H	-4.60025	-4.71801	-2.01769	C	2.76871	-0.61952	-0.87854
C	-2.50399	-4.18831	-1.97332	C	3.233877	3.721812	0.85674
H	-2.18689	-5.07553	-2.50908	C	3.055194	2.333968	0.709111
C	-1.55708	-3.26824	-1.56702	C	4.006235	1.487787	1.297729
H	-0.51839	-3.44611	-1.80454	H	3.905725	0.413646	1.242784
C	-1.92119	-2.08804	-0.87921	C	5.087585	2.051193	1.965743
C	-0.94912	-1.06441	-0.49485	H	5.823407	1.399982	2.422839
C	-1.39237	0.27746	-0.36575	C	5.248127	3.440709	2.060327
C	-0.44735	1.353932	-0.49427	H	6.105855	3.847961	2.582597
C	-0.84831	2.707588	-0.87755	C	4.309339	4.305243	1.505579
	X	Y	Z	H	4.394216	5.381557	1.584776
H	-2.72712	2.171824	-1.80031	C	1.606645	-4.66096	0.858499
C	-2.37702	4.262486	-1.96975	C	1.57453	-5.88376	1.507859
H	-3.30455	4.431608	-2.50437	H	2.46438	-6.49514	1.587325
C	-1.51568	5.340046	-1.70621	C	0.356471	-6.2646	2.062674

H	0.280471	-7.21087	2.585274	H	-1.59446	-3.58941	1.243821
C	-0.76681	-5.43116	1.967565	C	0.493914	-3.81258	0.710331
H	-1.6987	-5.7428	2.424633	C	-2.05337	2.982421	-1.56376
C	-0.71433	-4.21326	1.298997				

6. NMR and HRMS Spectra

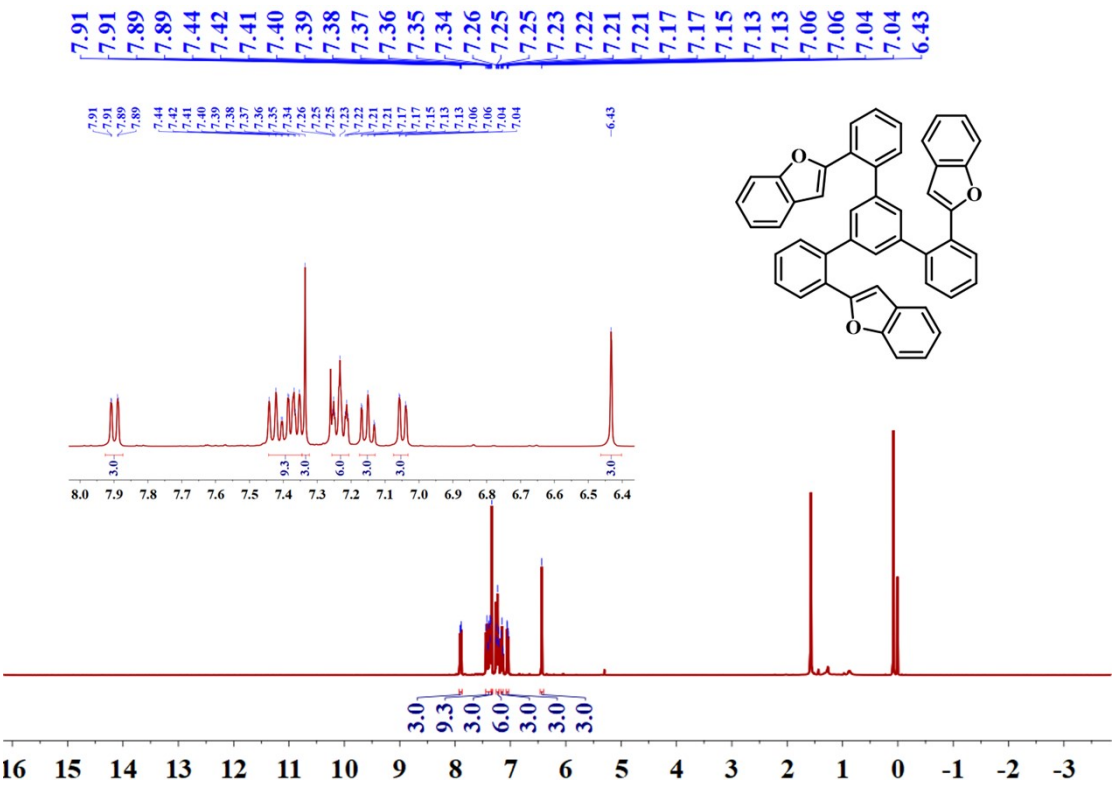


Figure S14. ^{1}H NMR spectrum of **2** (400 MHz, $CDCl_3$, 298K).

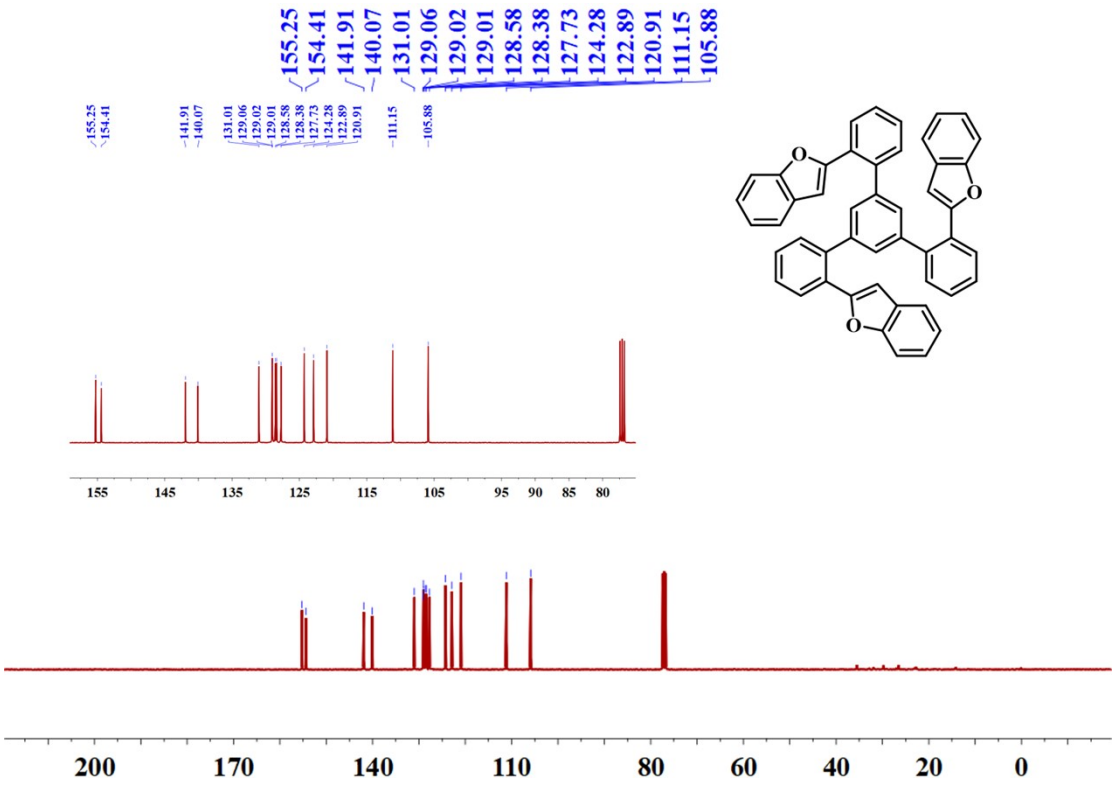
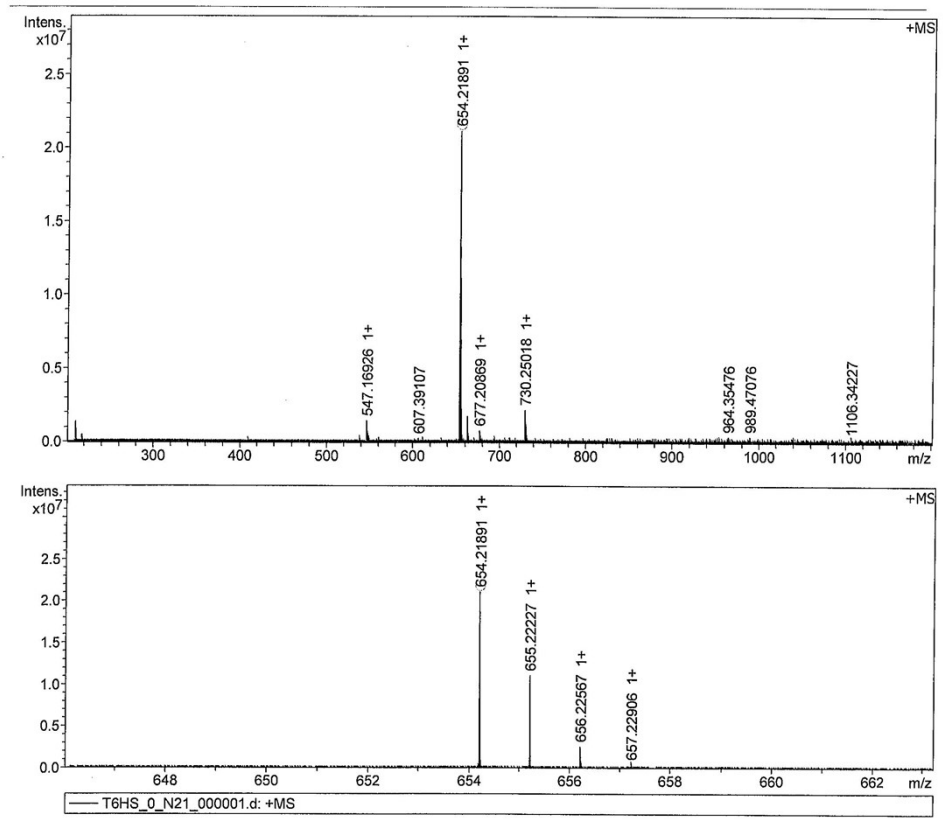


Figure S15. ^{13}C NMR spectrum of **2** (100 MHz, $CDCl_3$, 298K).



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
654.218913	1	C48H30O3	100.00	654.218946	-0.1	0.0	7.7	34.0	odd	ok

Figure S16. HRMS (MALDI-FT) spectrum of **2.**

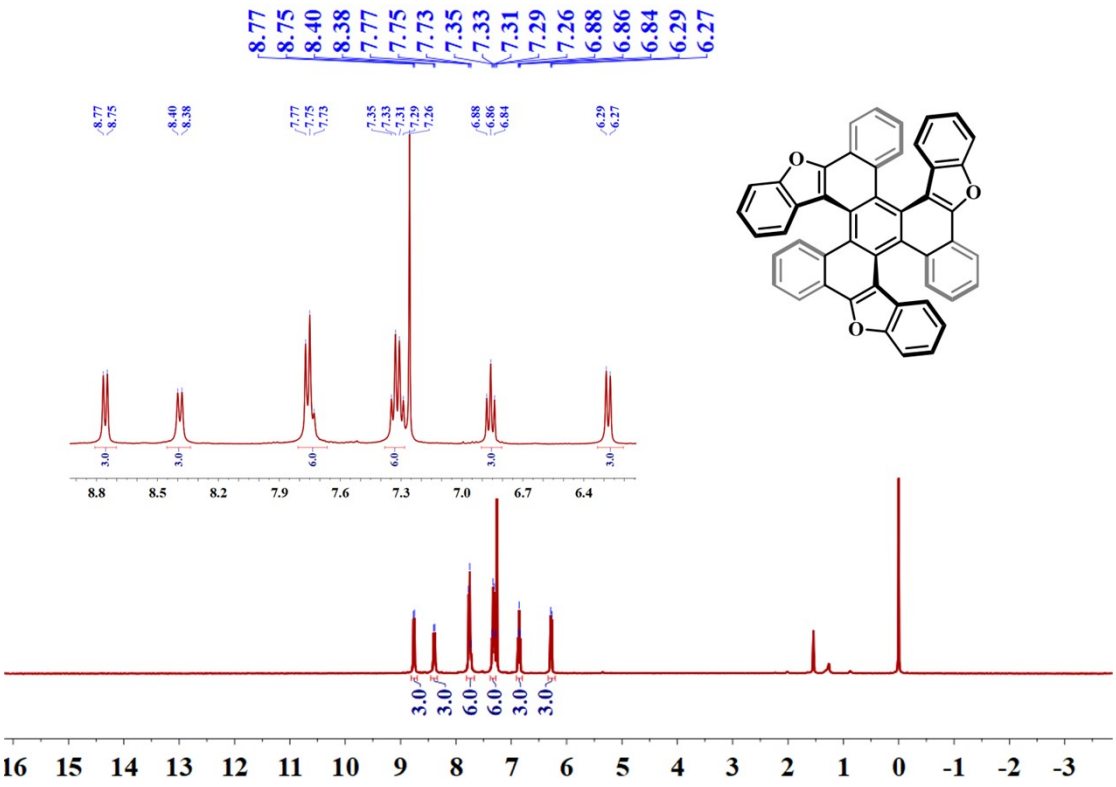


Figure S17. ^{1}H NMR spectrum of **TO6H** (400 MHz, $CDCl_3$, 298K).

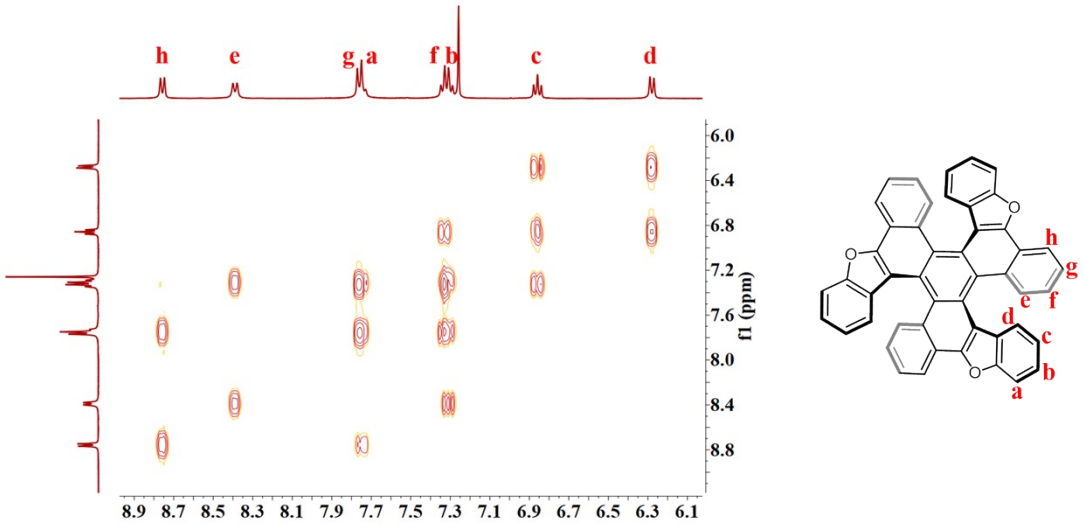


Figure S18. 2D ^{1}H-^{1}H COSY NMR spectrum of **TO6H** (400MHz, $CDCl_3$, 298K).

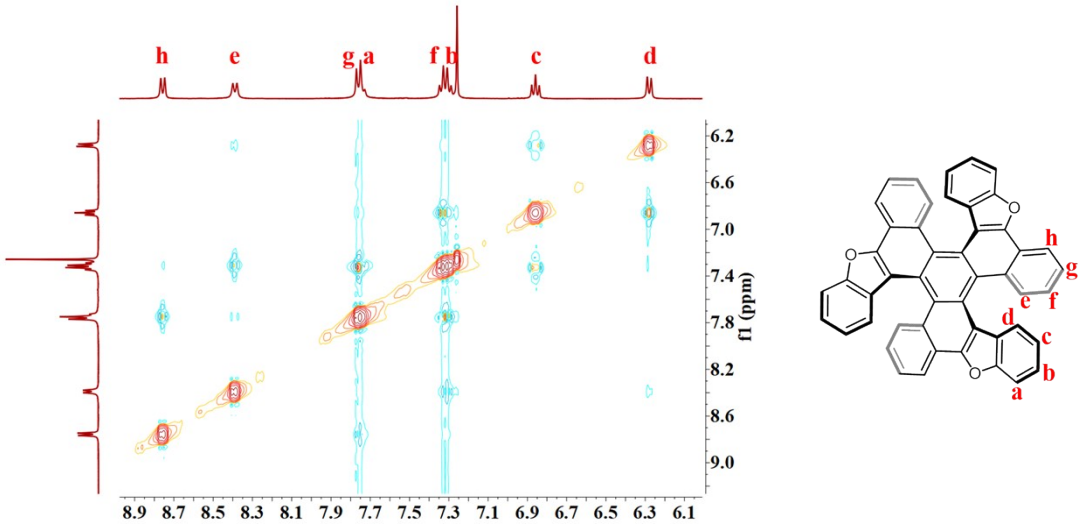


Figure S19. 2D ^{1}H-^{1}H NOESY NMR spectrum of **TO6H** (400MHz, $CDCl_3$, 298K).

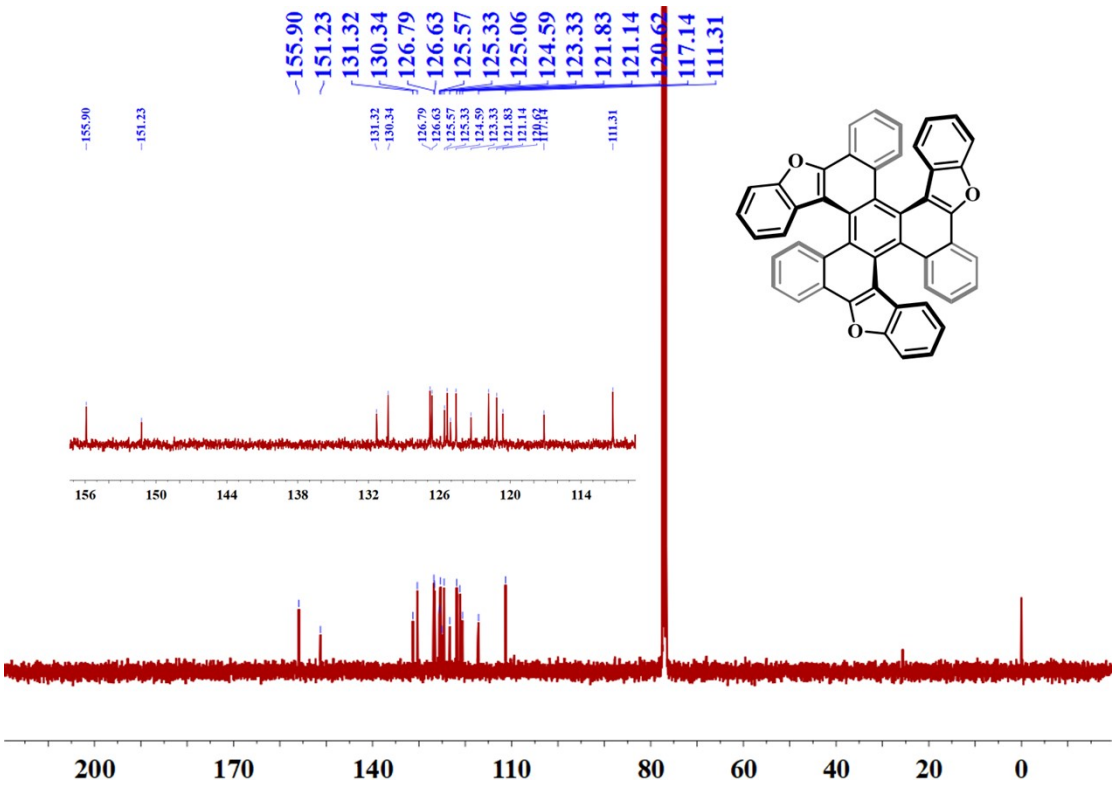
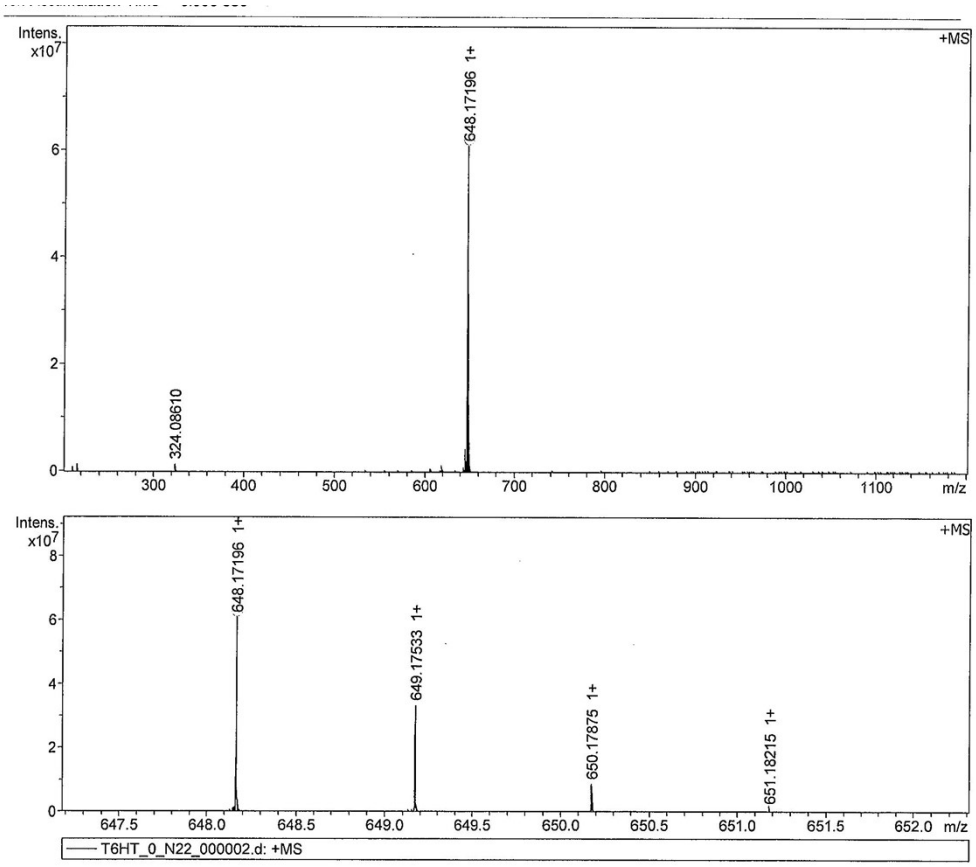


Figure S20. ^{13}C NMR spectrum of **TO6H** (100 MHz, $CDCl_3$, 298K).



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
648.171956	1	C48H24O3	100.00	648.171996	-0.1	0.0	11.9	37.0	odd	ok

Figure S21. HRMS (MALDI-FT) spectrum of **TO6H.**

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