Supporting Information

Synthesis, crystal structure and charge transport characteristics of stable *peri*-tetracene analogues

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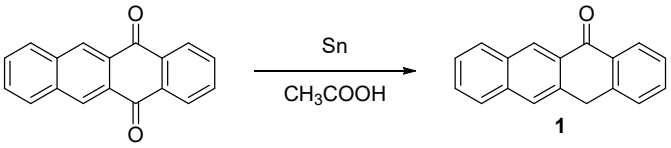
Contents:

Methods S1. Synthesis

Compound **1** was synthesized according to the literature.[1] Compounds **4** was synthesized by modifying the synthesis method of compounds **2** and **3**.[2]

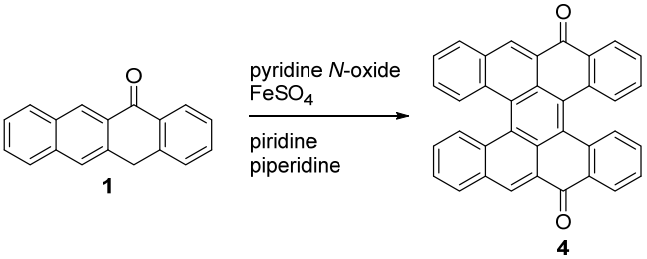
Compound **1**



The mixture of 5,12-naphthacenequinone (8.00 g, 31.0 mmol) and granular tin (16.0 g, 135.0 mmol) in glacial acetic acid (200 ml) was refluxed for 5 h. The solution was filtered on hot at normal pressure to remove tin, treated with conc. HCl (20 ml), concentrated to half its volume, filtered, washed with MeOH, and dried to give **1** as a pale orange solid (6.23 g, 82%).

^{1}H-NMR: δ/ppm (500 MHz, $CDCl_3$) = 8.94 (s, 1H); 8.41 (d, 1H, J = 7.9 Hz); 8.06 (d, 1H, J = 8.2 Hz); 7.93 (s, 1H); 7.87 (d, 1H, J = 8.3 Hz); 7.64–7.58 (m, 2H); 7.54–7.47 (m, 3H). MS (ASAP) m/z (%): 245 (100) [M+H$^+$].

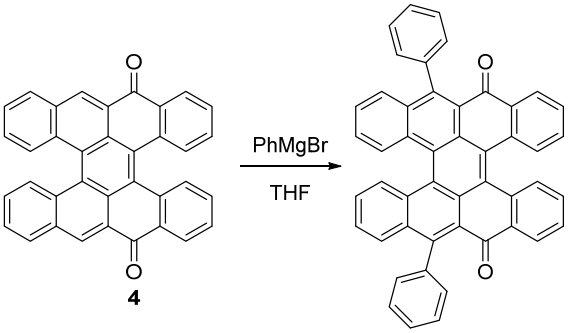
Compound **4**



To a solution of compound **1** (5.88 g, 24.1 mmol) in pyridine (250 ml) and piperidine (25 ml) were added pyridine *N*-oxide (27.9 g, 294 mmol) and $FeSO_4 \cdot 7H_2O$ (0.70 g, 2.52 mmol). The mixture was heated at 120 °C for 48 h, and then treated with 6M HCl (200 ml). The solid was collected by filtration, washed with cold water, MeOH and dried. The crude product was purified by a dry loading column chromatography over silica gel using hexane/DCM (1:3) mixture, then gradually increased to 100% DCM as eluent to give **4** as an orange solid (1.84 g, 32%). The compound **4** shows strong green emission in solution and orange emission in the solid state. The sublimation temperature for **4** is 300 °C.

Mp: >400 °C. ^{1}H-NMR: δ/ppm (500 MHz, $CDCl_3$) = 9.30 (s, 2H); 8.50 (d, 2H, J = 7.7 Hz); 8.37 (d, 2H, J = 8.5 Hz); 8.25 (d, 2H, J = 7.7 Hz); 8.00 (d, 2H, J = 8.0 Hz); 7.64 (dd, 2H, J = 8.0 Hz, J = 7.0 Hz); 7.52 (dd, 2H, J = 8.0 Hz, J = 7.0 Hz); 7.45 (dd, 2H, J = 8.5 Hz, J = 7.0 Hz); 7.38 (dd, 2H, J = 8.0 Hz, J = 7.0 Hz). ^{13}C-NMR: δ/ppm (125 MHz, $CDCl_3$) = 184.34, 137.79, 133.09, 133.03, 132.70, 132.23, 131.98, 131.88, 130.89, 129.79, 129.64, 129.32, 128.33, 128.18, 127.93, 127.56, 126.51, 124.46. MS (ASAP) m/z (%): 483 (100) [M+H$^+$]. Anal. Calcd. For $C_{36}H_{18}O_2$: C, 89.61; H, 3.76; O, 6.63. Found: C, 89.51; H, 3.82.

Compound **5a**

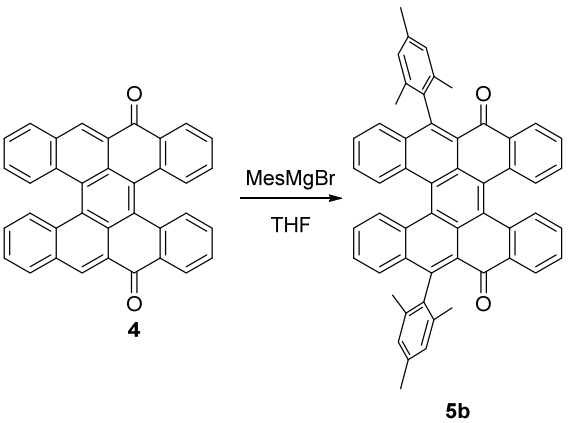


4 **5a**

To a solution of compound **4** (0.193 g, 0.40 mmol) in THF (30 ml) was added the phenyl magnesium bromide solution in ether (3 M, 2 ml, 6 mmol) at 0 °C under N_2 and the reaction mixture was stirred for 4 h at 0 °C and for 24 h at 40 °C. The reaction was quenched with 1N HCl and THF was removed. The reaction mixture was extracted with $CHCl_3$, dried over Na_2SO_4 and the solvent was removed. Although the ASAP-MS showed a peak at m/z 635, indicating formation of the product, the reaction might not be completed at this point. Although a red color fraction on the TLC was separated by column chromatography using hexane/DCM (1:1), orange color fractions gradually appeared. When small amount of DDQ was added to a solution of red solid in DCM, the solution color quickly changed to orange, indicating oxidation to form quinone. Therefore, DDQ was added to the crude product and then the mixture was purified by column chromatography over silica gel using hexane/DCM (1:1) mixture as eluent to give an orange solid (0.122 g, 48%). The product was further purified by recrystallization from DCM layered with MeOH.

The melting point cannot be determined because the decomposition started at ~300 °C. ^{1}H-NMR: δ/ppm (500 MHz, $CDCl_3$, Me_4Si) = 8.29 (d, 2H, J = 8.5 Hz); 8.23 (d, 2H, J = 7.6 Hz); 7.91 (d, 2H, J = 8.0 Hz); 7.741 (d, 2H, J = 8.4 Hz); 7.70–7.59 (m, 6H); 7.52 (br, 2H); 7.46 (dd, 2H, J = 7.5 Hz); 7.42–7.34 (m, 6H); 7.30 (dd, 2H, J = 7.5 Hz). NMR: δ/ppm (125 MHz, $CDCl_3$) = 184.88, 146.41, 141.12, 137.06, 133.10, 132.77, 132.66, 132.53, 131.75, 130.10, 129.64, 129.23, 129.08, 129.00, 128.80, 128.21, 127.95, 127.66, 127.48, 127.25, 127.15, 126.27, 121.27, 77.41, 77.16, 76.9. MS (ASAP) m/z (%): 635 (100) [M+H$^+$]. HRMS/FAB: m/z Calcd. For $C_{48}H_{26}O_2$: m/z 634.19328. Found: 634.1936.

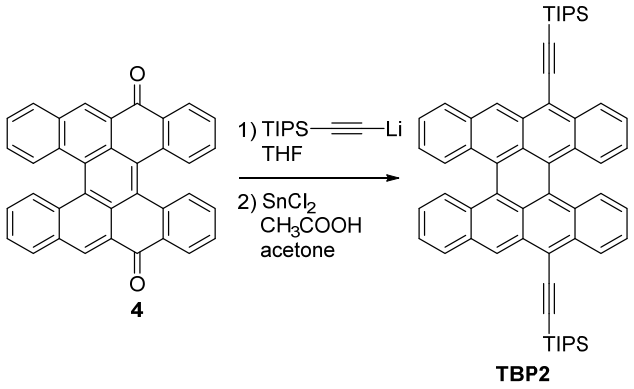
Compound **5b**



4 **5b**

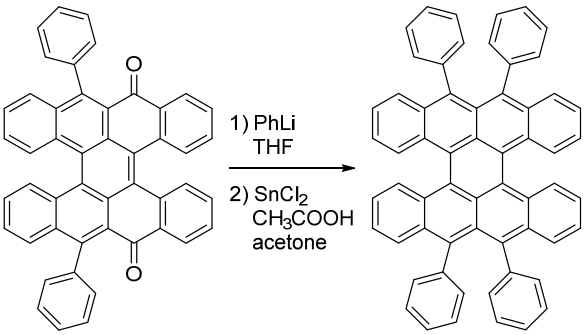
The Grignard reagent was prepared from mesityl bromide (1.20 g, 6.01 mmol) and magnesium (0.21 g, 8.79 mmol) in THF (6 ml). To a solution of compound **4** (0.49 g, 1.02 mmol) in THF under N_2 was added the Grignard reagent at rt, followed by stirring at rt overnight. The reaction mixture was quenched with 1N HCl and the mixture was extracted with DCM, dried over Na_2SO_4 and the solvent was removed. The mixture was purified by column chromatography over silica gel using hexane/DCM (2:1) mixture as eluent to give **5b** as an orange solid (0.61 g, 83%). The product was further purified by recrystallization from DCM layered with MeOH to give red crystals.
The melting point cannot be determined because the decomposition started at ~300 °C. ^{1}H-NMR: δ/ppm (500 MHz, $CDCl_3$, Me_4Si) = 8.28 (dd, 4H, J = 7.0 Hz); 8.00 (d, 2H, J = 8.0 Hz); 7.63 (d, 2H, J = 8.3 Hz); 7.45–7.37 (m, 6H); 7.31 (dd, 2H, J = 7.5 Hz); 7.18 (s, 2H), 7.12 (s, 2H), 2.51 (s, 6H), 1.90 (s, 12H). ^{13}C-NMR: δ/ppm (125 MHz, $CDCl_3$) = 184.64, 146.14, 137.14, 137.09, 136.62, 136.57, 133.49, 132.88, 132.75, 132.66, 131.67, 131.64, 130.36, 129.73, 129.06, 128.87, 128.65, 128.37, 127.92, 127.86, 127.59, 126.13, 121.30, 21.64, 20.53, 20.27. MS (ASAP) m/z (%): 719 (100) [M+H$^+$]. Anal. Calcd. For $C_{54}H_{38}O_2$ + CH_2Cl_2: C, 82.18; H, 5.02; Cl, 8.82; O, 3.98. Found: C, 82.49; H, 4.99. HRMS/FAB: m/z Calcd. For $C_{54}H_{28}O_2$: m/z 718.28718. Found: 718.2868.

TBP2



To a solution of triisopropylsilylacetylene (0.203 g, 1.11 mmol) in dry THF (2 ml) at 0 °C was added *n*-butyllithium (*n*-BuLi, 1.59 M, 0.63 ml, 1.0 mmol). After stirring for 40 min, the mixture was added to a solution of **4** (0.180 g, 0.37 mmol) in THF (5 ml) at 0 °C. The mixture was stirred at rt overnight. The mixture was quenched with 10% hydrochloric acid, and extracted with DCM, washed with water, dried over Na_2SO_4 and the solvent was removed. The solid was dissolved in acetone (3 ml) and a solution of $SnCl_2$ dihydrate (0.230 g, 1.02 mmol) in 50% AcOH/H_2O (3 ml) was added dropwise. The reaction mixture was stirred at 50 °C for 24 h. The resulting solid was filtered and dissolved in DCM in dark, and a solution was washed with water and $NaHCO_3$ aqueous solution, dried over Na_2SO_4, and the solvent was removed. The crude solid was purified by column chromatography over silica gel using degassed hexane/DCM mixture (the ratio of DCM gradually increased from 0%) as eluent and dried in vacuum without heating to give **TBP2** as an olive green solid (trace amount, <1%).
HRMS/FAB: m/z Calcd. For $C_{58}H_{60}Si_2$: m/z 812.42335. Found: 812.4234.

TBP3

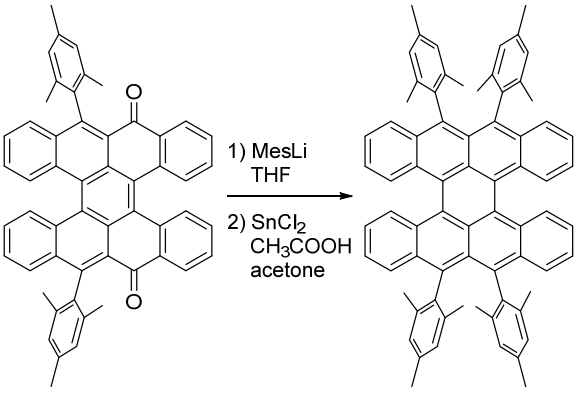


5a **TBP3**

To a solution of **5a** (0.14 g, 0.19 mmol) in THF (5 ml) at −70 °C was added freshly prepared phenyllithium (2 ml, 1 mmol). The mixture was stirred at −70 °C for 30 min and at rt overnight. The mixture was quenched with water and then dilute hydrochloric acid, and extracted with DCM, washed with water, dried over Na_2SO_4 and the solvent was removed. The solid was dissolved in acetone (10 ml) and a solution of $SnCl_2$ dihydrate (0.24 g, 1.06 mmol) in 50% AcOH/H_2O (5 ml) was added dropwise. The reaction mixture was stirred at 50 °C for 24 h. The resulting solid was filtered and dissolved in DCM in dark, and a solution was washed with water and $NaHCO_3$ aqueous solution, dried over Na_2SO_4, and the solvent was removed. The crude solid was purified by column chromatography over silica gel using degassed hexane/DCM mixture (the ratio of DCM gradually increased from 0%) as eluent and dried in vacuum without heating to give **TBP3** as a green solid (trace amount, <1%).

HRMS/FAB: m/z Calcd. For $C_{60}H_{36}$: m/z 756.28170. Found: 756.2816.

TBP4



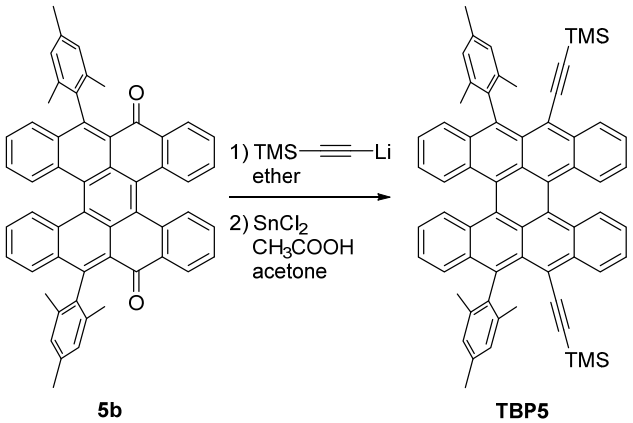
5b **TBP4**

To a solution of mesityl bromide (0.33 g, 1.67 mmol) in THF (5 ml) at −78 °C was added *n*-butyllithium (*n*-BuLi, 1.55 M, 0.85 ml, 1.32 mmol). After stirring for 30 min, a solution of **5b** (0.14 g, 0.20 mmol) in THF (5 ml) was added to the mixture. The mixture was stirred at −78 °C for 1 h and at rt overnight. The mixture was quenched with water and then dilute hydrochloric acid, and extracted with DCM, washed with water, dried over Na_2SO_4 and the solvent was removed. The solid was dissolved in acetone (10 ml) and a solution of $SnCl_2$ dihydrate (0.28 g, 1.26 mmol) in 50% AcOH/H_2O (5 ml) was added dropwise. The reaction mixture was stirred at 50 °C for 24 h. The resulting solid was filtered and dissolved in DCM in dark, and a solution was washed with water and $NaHCO_3$ aqueous solution,

dried over Na_2SO_4, and the solvent was removed. The crude solid was purified by column chromatography over silica gel using degassed hexane/DCM mixture (the ratio of DCM gradually increased from 0%) as eluent, and recrystallization from DCM layered with isopropanol, dried in vacuum without heating to give **TBP4** as a green solid (79.7 mg, 43%).

^{1}H-NMR: δ/ppm (500 MHz, CD_2Cl_2) = 7.40 (d, 4H, J = 8.7 Hz); 7.26 (d, 4H, J = 8.8 Hz); 7.16 (dd, 4H, J = 8.8 Hz, J = 7.5 Hz); 7.086 (dd, 4H, J = 8.7 Hz, J = 7.5 Hz); 6.74 (s, 4H); 6.49 (s, 4H); 7.09 (s, 2H); 2.29 (s, 12H); 1.80 (s, 12H); 1.45 (s, 12H). HRMS/FAB: m/z Calcd. For $C_{72}H_{60}$: m/z 924.46950. Found: 924.4697.

TBP5

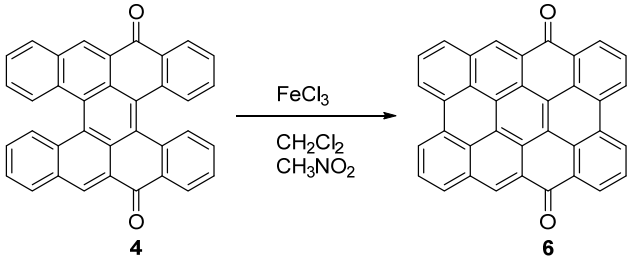


5b **TBP5**

According to the literature, ether is a good solvent to generate the acetylide with TMS group.[3] However, the yields were similar for both ether and THF. To a solution of trimethylsilylacetylene (1.2 ml, 8.0 mmol) in dry THF (10 ml) at −78 °C was added *n*-butyllithium (*n*-BuLi, 1.55 M, 5.2 ml, 8.0 mmol). After stirring for 40 min, the mixture was added to a solution of **5b** (0.57 g, 0.80 mmol) in THF (30 ml) at −78 °C. The mixture was stirred at rt overnight. The mixture was quenched with 10% hydrochloric acid, and extracted with DCM, washed with water, dried over Na_2SO_4 and the solvent was removed. The solid was dissolved in acetone (5 ml) and a solution of $SnCl_2$ dihydrate (0.24 g, 1.1 mmol) in 50% AcOH/H_2O (5 ml) was added dropwise. The reaction mixture was stirred at 50 °C for 24 h. The resulting solid was filtered and dissolved in DCM in dark, and a solution was washed with water and $NaHCO_3$ aqueous solution, dried over Na_2SO_4, and the solvent was removed. The crude solid was purified by column chromatography over silica gel using degassed hexane/DCM mixture (the ratio of DCM gradually increased from 0%) as eluent, and recrystallization from DCM layered with isopropanol, dried in vacuum without heating to give **TBP5** as an olive green solid (17.5 mg, 3%).

^{1}H-NMR: δ/ppm (500 MHz, CD_2Cl_2) = 8.87 (d, 2H, J = 8.8 Hz); 7.62 (d, 2H, J = 8.8 Hz); 7.61 (d, 2H, J = 8.8 Hz); 7.51–7.47 (m, 4H); 7.28 (dd, 2H, J = 8.8 Hz, J = 8.2 Hz); 7.18 (dd, 4H, J = 7.3 Hz); 7.10 (s, 2H); 7.09 (s, 2H); 2.53 (s, 6H); 2.02 (s, 6H); 1.83 (s, 6H); 0.27 (s, 18H). Anal. Calcd. For $C_{64}H_{56}Si_2$: C, 87.22; H, 6.40; Si, 6.37. Found: C, 86.84; H, 6.26. HRMS/FAB: m/z Calcd. For $C_{64}H_{56}Si_2$: m/z 880.39205. Found: 880.3924.

Attempted synthesis of *peri*-tetracene precursor **6**



4 **6**

To a solution of compound **4** (95.4 mg, 0.20 mmol) in anhydrous dichloromethane (50 ml) under N_2, iron chloride (1.01 g, 6.21 mmol) dissolved in degassed nitromethane (5 ml) was added by using dropping funnel. The reaction mixture was stirred for 24 h at room temperature and poured into methanol. The precipitated product was filtered, washed with HCl aq, water and methanol. The analysis of the product obtained by vacuum sublimation at 400 °C indicated the formation of compound **6**. MS (MALDI) m/z: 478 [M^+].

Methods S2. Theoretical calculations

The computations were mainly performed using the computer facilities at the Research Institute for Information Technology, Kyushu University. Molecular orbital calculations were performed using the program Gaussian 16.[4] The geometries were optimized at the B3LYP/6-311G(d,p) level for the singlet and UB3LYP/6-311G(d,p) for the triplet, and these optimized structures are used for the further calculations of the singlet and triplet, respectively, unless otherwise noted according to the literature.[5] The structures of intersecting conformations for two tetracene units are found to be more stable than those of bent conformation for all compounds (Fig. S1). The singlet biradical was investigated by using open-shell broken-symmetry calculations at the UB3LYP/6-311G(d,p) level. The results are summarized in Table S1. The presence of energy minima for the geometry optimization was confirmed by the absence of imaginary modes (no imaginary frequencies). To numerically achieve accurate values, we have used a fine grid. The triisopropylsilyl (TIPS) groups were substituted with trimethylsilyl (TMS) groups. The structures were also optimized at the CAM-B3LYP/6-311+G(d,p), broken symmetry UCAM-B3LYP/6-311+G(d,p), and UCAM-B3LYP/6-311+G(d,p) for closed-shell singlet, open-shell singlet, and triplet, respectively (Table S2).

The singlet biradical factor was calculated by the natural orbital occupation number (NOON) of the LUMO in a spin-unrestricted Hartree-Fock (HF) calculation using 6-31G(d,p) basis set.[6] The broken symmetry UHF/6-31+G(d,p) calculations gave LUMO occupation number. According to the Yamaguchi scheme,[7] the index for singlet biradical character is expressed as

$$y_i = 1 - \frac{2T_i}{1 + T_i^2}$$

where T_i is the orbital overlap between the corresponding orbital pairs and it can be presented using the NOON of HOMO and LUMO.

$$T_i = \frac{n_{HOMO} - n_{LUMO}}{2}$$

The diradical characters by the theoretical calculation are listed in Table S1.

Odd-electron density distribution were calculated using the program Multiwfn,[8] (Fig. S3).

The time-dependent density functional theory (TD-DFT) calculations were conducted at the B3LYP/6-311+G(d,p) level for the excited states calculations (Table S4 and Fig. S4).

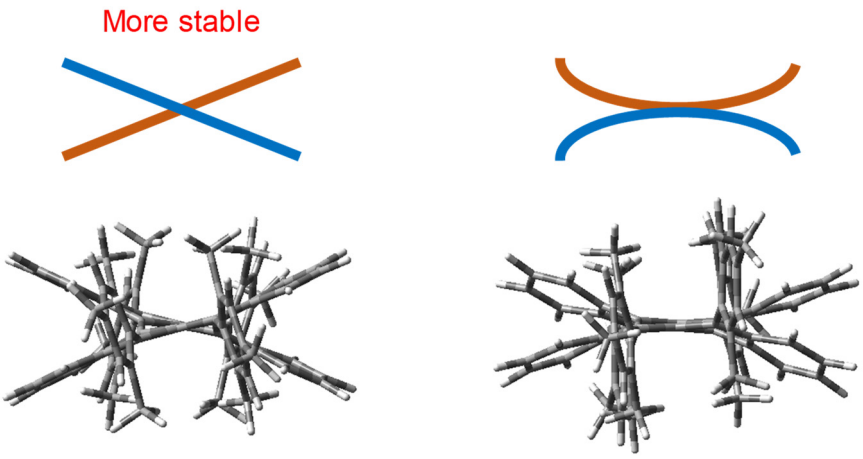


Fig. S1. Two possible conformations.

Table S1. Converged energies, relative energies and the biradical character (y_0)

Compd	Closed-shell (CS) singlet [a)]	Open-shell (OS) singlet[a)]	Triplet[a)]	$\Delta E_{(OS-CS)}$[b)]	ΔE_{S-T}[c)]	y_0[d)]
TBP1	−2396.97928470	−2396.97931119	−2396.96719001	0.017	7.61	0.60
TBP2	−2354.07046119	−2354.07066145	−2354.06047388	0.126	6.39	0.62
TBP3	−2308.60185040	−2308.60187009	−2308.59002936	0.012	7.43	0.60
TBP4	−2780.50975322	−2780.50975322	−2780.49635406	0.000	8.41	0.59
TBP5	−3052.21068463	−3052.21085771	−3052.20079995	0.109	6.31	0.62

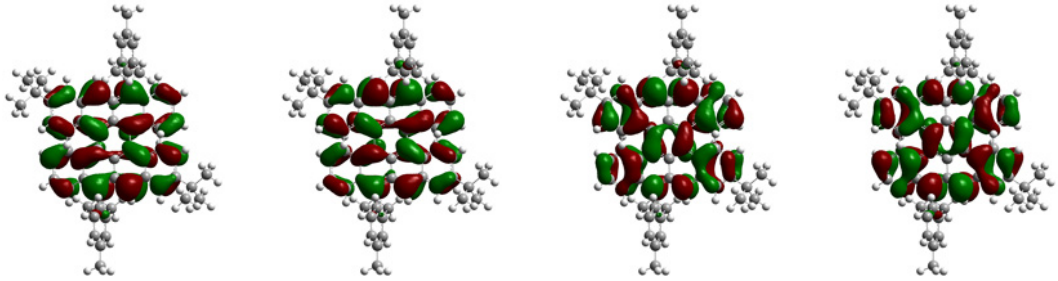
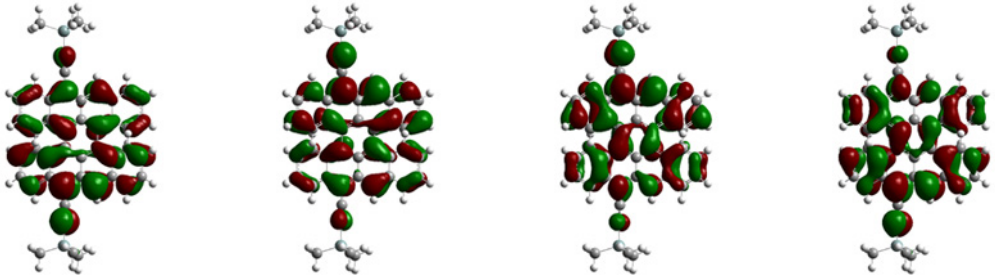
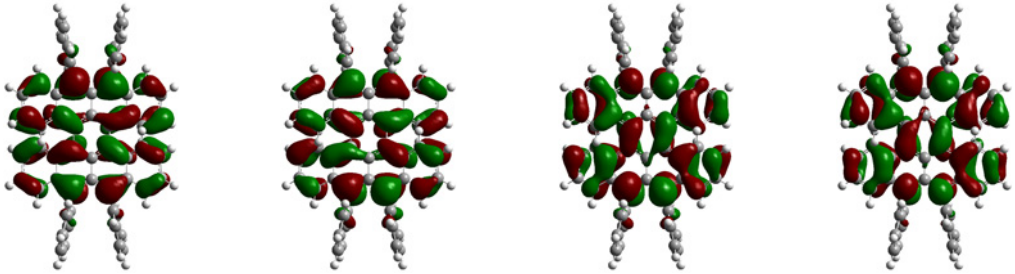
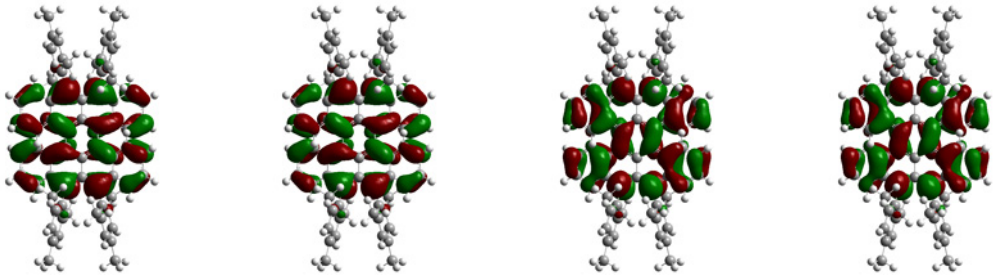
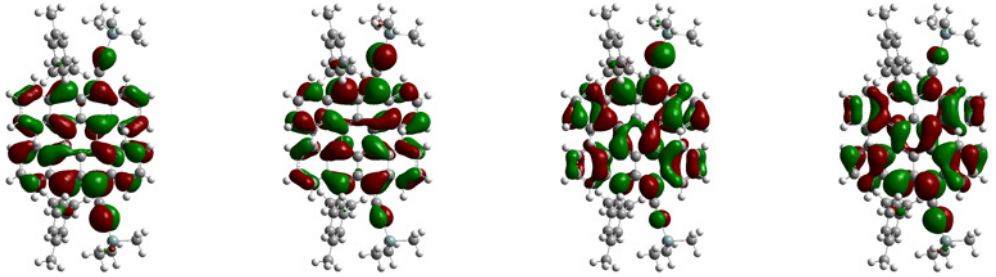
[a] at the B3LYP/6-311G(d,p) (hartrees). [b] CS singlet energy minus OS broken symmetry singlet energy (kcal/mol). [c] Unrestricted triplet energy minus singlet energy (kcal/mol). [d] at the UHF/6-31G(d,p).

Table S2. Converged energies and relative energies

Compd	Closed-shell (CS) singlet [a)]	Open-shell (OS) singlet[a)]	Triplet[a)]	$\Delta E_{(OS-CS)}$[b)]	ΔE_{S-T}[c)]
TBP1	−2395.57627761	−2395.58096327	−2395.56988597	2.94	6.95
TBP2	−2353.00124766	−2353.00728271	−2352.99780725	3.79	5.95
TBP3	−2307.28142474	−2307.28631188	−2307.27564848	3.07	6.69
TBP4	−2778.89752904	−2778.90157287	−2778.88978245	2.54	7.40
TBP5	−3050.73421078	−3050.74015609	−3050.73071432	3.73	5.92

[a] at the CAM-B3LYP/6-311G(d,p) (hartrees). [b] CS singlet energy minus OS broken symmetry singlet energy (kcal/mol). [c] Unrestricted triplet energy minus singlet energy (kcal/mol).

Table S3. Molecular orbitals at the B3LYP/6-311G(d,p)

	HOMO (α-spin)	HOMO (β-spin)	LUMO (α-spin)	LUMO (β-spin)
TBP1				
	−4.446 eV		−2.825 eV	
TBP2				
	−4.671 eV		−3.140 eV	
TBP3				
	−4.524 eV		−2.900 eV	
TBP4				
	−4.515 eV		−2.871 eV	
TBP5				
	−4.629 eV		−3.100 eV	

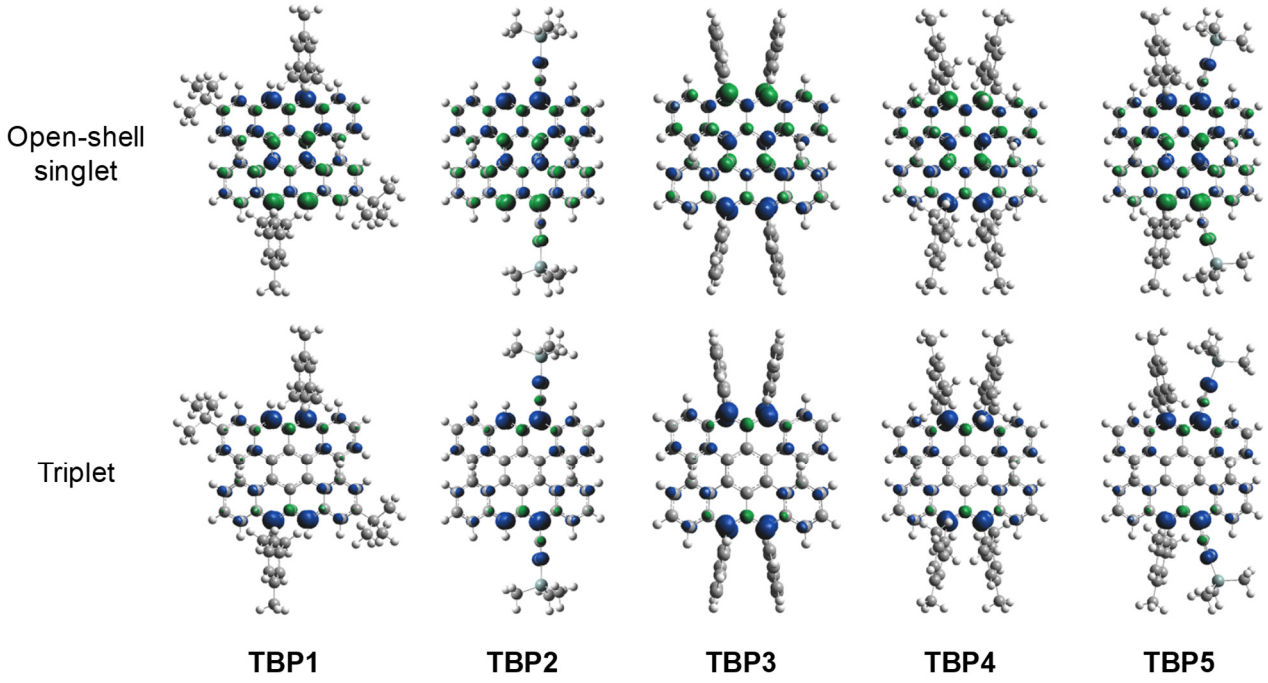


Fig. S2. Spin density distribution for the open-shell singlet and triplet states calculated at the CAM-B3LYP/6-311+G(d,p).

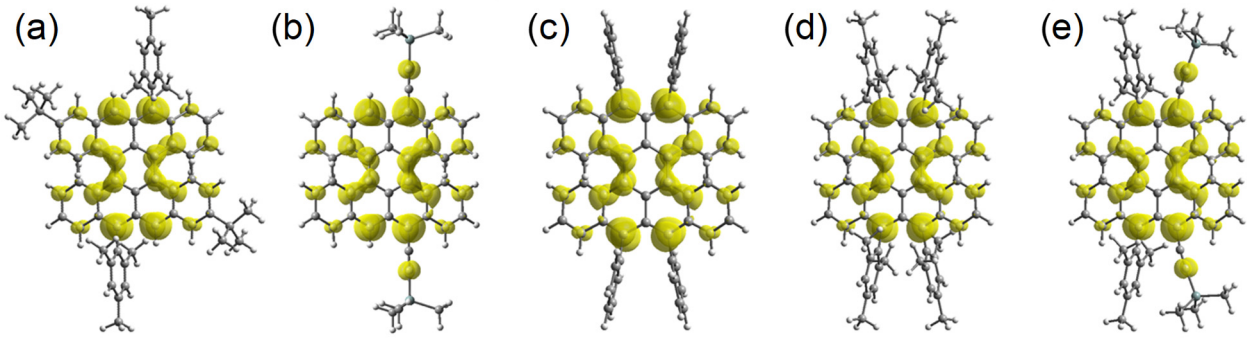


Fig. S3. Odd-electron density maps calculated at LC-UBLYP/6-311+G(d,p) with a contour value of 0.001 a.u.. (a) **TBP1**, (b) **TBP2**, (c) **TBP3**, (d) **TBP4**, and (e) **TBP5**.

Table S4. Calculated vertical excitation energies (VEE) for singlet and triplet excited states, wavelength, and oscillator strength (*f*) at the B3LYP/6-311+G(d,p) level and broken symmetry UB3LYP/6-311+G(d,p)

Compound	Excited States	B3LYP/6-311+G(d,p)				UB3LYP/6-311+G(d,p)			
		S	**VEE (eV)**	**Wavelength (nm)**	***f***	***S***	**VEE (eV)**	**Wavelength (nm)**	***f***
TBP1	1	3	−0.1218	−10177.6	0	2.896	0.1772	6996.75	0
	2	3	1.4027	883.89	0	2.989	1.4203	872.93	0
	3	1	1.4633	847.30	0.3255	0.988	1.4687	844.19	0.3218
	4	3	1.9870	623.98	0	2.990	2.0000	619.91	0.0022
	5	3	2.0121	616.18	0	1.067	2.0193	613.99	0
	6	1	2.0146	615.43	0	2.991	2.0252	612.21	0.0015
	7	1	2.2838	542.89	0.0001	1.045	2.2884	541.80	0.0001
	8	3	2.3594	525.49	0	2.994	2.3684	523.49	0
	9	1	2.5992	477.00	0.0006	1.083	2.6039	476.15	0.0007
	10	1	2.9200	424.60	0.0019	1.070	2.9251	423.87	0.0019
TBP2	1	3	−0.2284	−5427.47	0	2.717	0.3297	3760.85	0
	2	1	1.3803	898.26	0.4003	0.978	1.3971	887.44	0.3752
	3	3	1.3884	892.98	0	2.946	1.4535	853.03	0.0026
	4	3	1.8466	671.42	0	2.961	1.8957	654.01	0.0013
	5	3	1.9224	644.95	0	2.960	1.9733	628.30	0.0194
	6	1	1.9594	632.77	0	1.242	1.9767	627.23	0
	7	1	2.2184	558.88	0.0011	1.153	2.2355	554.61	0.0010
	8	3	2.3156	535.44	0	2.760	2.3365	530.63	0.0065
	9	1	2.4014	516.30	0.0402	1.672	2.4336	509.48	0.0327
	10	1	2.8054	441.95	0.0367	1.446	2.8283	438.36	0.0358
TBP3	1	3	−0.1197	−10354.1	0	2.900	0.1742	7115.75	0
	2	3	1.4248	870.16	0	2.985	1.4416	860.03	0.0016
	3	1	1.4719	842.37	0.3888	1.003	1.4773	839.28	0.3828
	4	3	1.9480	636.48	0	2.991	1.9605	632.41	0.0002
	5	3	2.0083	617.35	0	2.990	2.0208	613.55	0.0031
	6	1	2.0431	606.85	0	1.068	2.0473	605.60	0
	7	1	2.2902	541.36	0	1.039	2.2948	540.28	0
	8	3	2.3416	529.48	0	2.990	2.3499	527.62	0
	9	1	2.5564	484.99	0	1.089	2.5613	484.07	0
	10	1	2.8631	433.04	0.0004	1.058	2.8686	432.22	0.0004
TBP4	1	3	0.1456	8517.79	0	3.000	0.1456	8517.96	0
	2	3	1.3950	888.76	0	3.000	1.3950	888.76	0
	3	1	1.4842	835.34	0.4015	1.000	1.4842	835.34	0.4015
	4	3	1.9769	627.17	0	3.000	1.9769	627.17	0
	5	3	2.0066	617.88	0	3.000	2.0066	617.88	0
	6	1	2.0362	608.89	0	1.000	2.0362	608.89	0
	7	1	2.2929	540.74	0	1.000	2.2929	540.74	0
	8	3	2.3488	527.86	0	3.000	2.3488	527.86	0
	9	1	2.5131	493.35	0.0005	1.000	2.5131	493.35	0.0005
	10	1	2.5135	493.27	0.0008	1.000	2.5135	493.27	0.0008
TBP5	1	3	−0.2218	−5590.03	0	2.731	0.3199	3875.30	0
	2	3	1.3066	948.90	0	2.285	1.3618	910.47	0.2135
	3	1	1.3537	915.86	0.4761	2.108	1.3809	897.86	0.2394
	4	3	1.8401	673.78	0	2.959	1.8866	657.17	0.0009
	5	3	1.8627	665.60	0	2.962	1.9106	648.93	0.0186
	6	1	1.8975	653.42	0	1.261	1.9127	648.20	0
	7	1	2.1567	574.87	0.0012	1.146	2.1727	570.64	0.0011
	8	3	2.2859	542.38	0	2.867	2.3112	536.46	0.0026
	9	1	2.3937	517.96	0.0255	1.482	2.4185	512.65	0.0223
	10	1	2.4933	497.27	0.0006	2.516	2.5688	482.66	0.0044

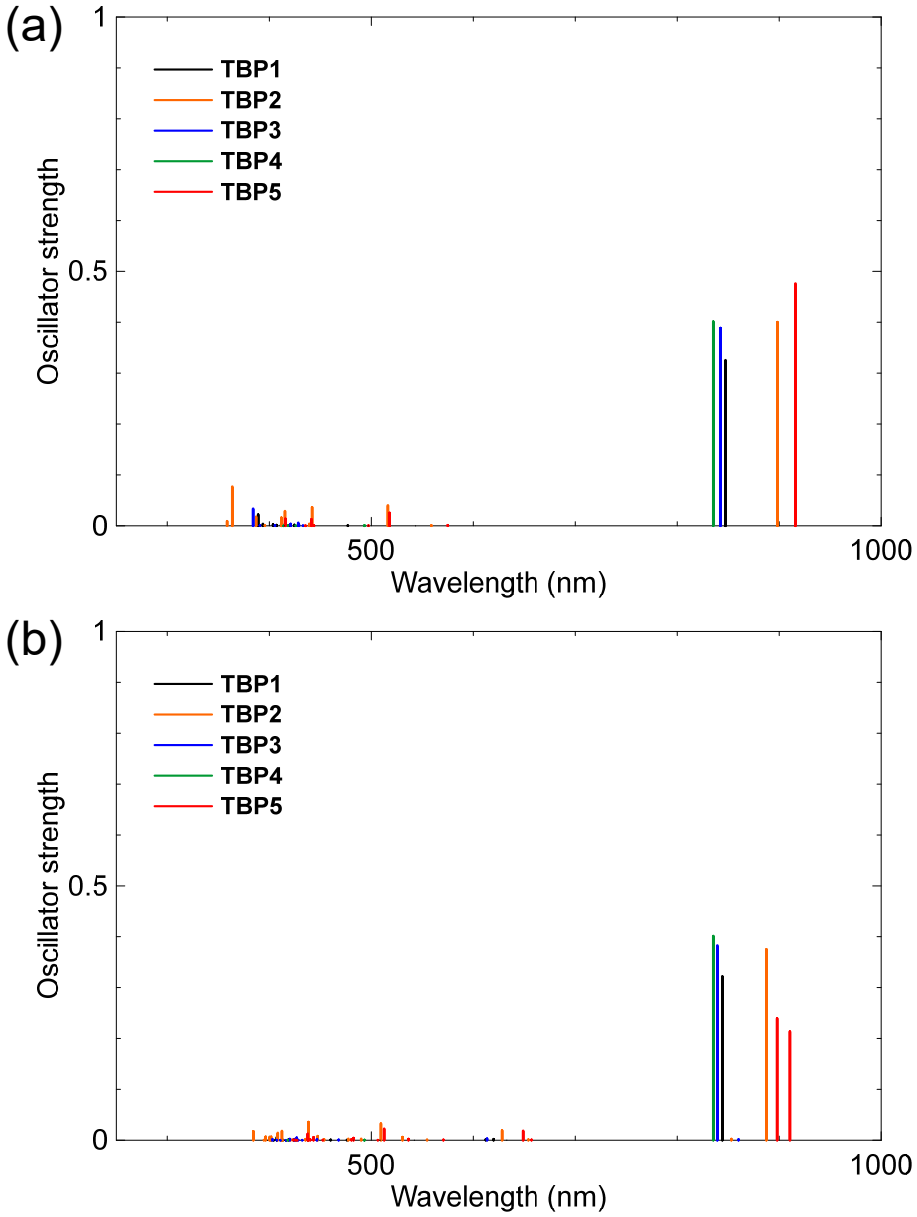


Fig. S4. Simulated absorption spectra at the (a) TD-B3LYP/6-311+G(d,p) and (b) TD-UB3LYP/6-311+G(d,p).

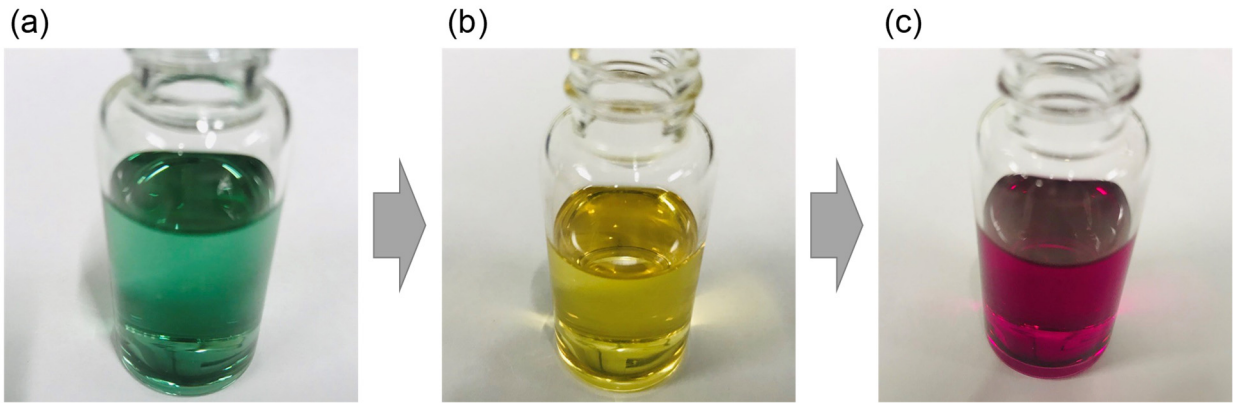


Fig. S5. Photos of **TBP3** solution in dichloromethane. (a) As prepared solution, (b) after 90 min, and (c) after 21 h.

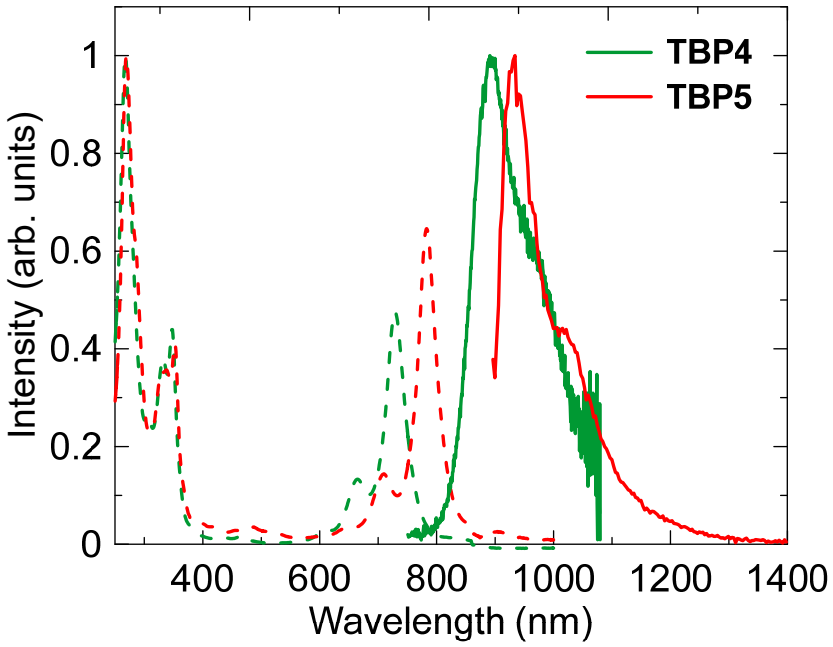


Fig. S6. Emission spectra for **TBP4** and **TBP5** (Dashed lines show absorption spectra). The emission spectra were recorded using PMA-12 C10027-02 (350–1100 nm) for **TBP4** and PMA-12 C10028-01 (900–1650 nm) for **TBP5**, respectively. We could not determine the emission lifetime because of technical difficulties.

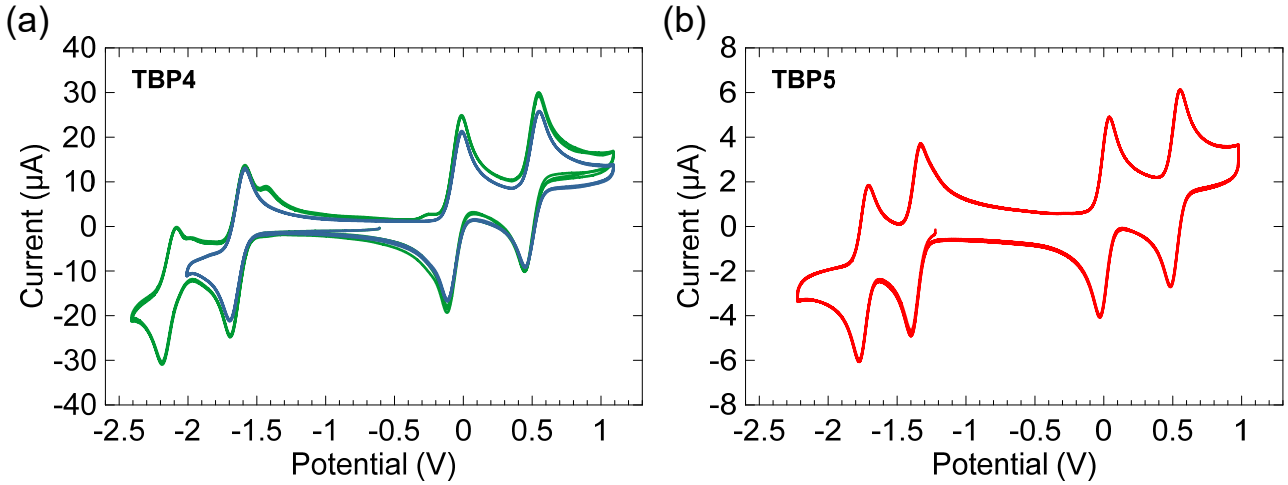


Fig. S7. Cyclic voltammograms (CV) in dichloromethane for (a) **TBP4** and (b) **TBP5** (vs Fc/Fc^+).

Table S5. Electrochemical properties

Compound	E_{ox}^1 (V)	E_{ox}^2 (V)	E_{red}^1 (V)	E_{red}^2 (V)	HOMO (eV)[b)]	LUMO (eV)[b)]	E_g^{redox} (eV)[c)]
TBP4	−0.07	0.50	−1.64	−2.14	−4.73	−3.16	1.57
TBP5	0.00	0.52	−1.37	−1.74	−4.80	−3.43	1.37

[a)] In dichloromethane at room temperature vs Fc/Fc^+. [b)] Estimated versus the vacuum level from $E_{HOMO} = -4.80 - E_{ox}$ (vs Fc/Fc^+) or $E_{LUMO} = -4.80 - E_{red}$ (vs Fc/Fc^+). [c)] Transfer gap calculated by redox potentials.

Methods S3. X-ray crystallographic structure determinations

X-ray diffraction data for **5b** and **TBP5** were collected on a Rigaku AFC HyPix-6000 diffractometer with Mo-Kα radiation (λ = 0.71075 Å) at 100 K. Single crystals suitable for X-ray analysis were grown by recrystallization from dichloromethane layered with MeOH. Data collection, cell refinement, and data reduction were carried out using the software CrysAlisPro. The structure was solved by direct methods using the program SHELXT and refined by full-matrix least squares methods on F^2 using SHELXL-2018.[9] All materials for publication were prepared using the software Olex2.[10] All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were calculated geometrically and refined as a riding model. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre (CCDC): Deposition numbers CCDC 2025243-2025244. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

Table S6. Crystal data and structure refinement for **5b**

CCDC number	2025243	
Identification code	Compd5b	
Empirical formula	$2(CH_2Cl_2)\cdot 2(C_{54}H_{38}O_2)$	
Formula weight	1607.54	
Temperature	100 K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic,	
Space group	$P2_1/c$	
Unit cell dimensions	a = 14.5132 (6)	α = 90
	b = 21.9543 (9)	β = 94.230 (4)
	c = 12.9943 (6)	γ = 90
Volume	4129.1 (3)	
Z	2	
Density (calculated)	1.293 g/cm^3	
Absorption coefficient	0.20 mm^{-1}	
F(000)	1680	
Crystal size	0.28 × 0.09 × 0.04 mm^3	
Theta range for data collection	2.233 to 27.483°.	
Index ranges	−18<=h<=18, −28<=k<=24, −15<=l<=16	
Reflections collected	36370	
Independent reflections	9472 [R(int) = 0.039]	
Completeness to theta = 27.483°	99.91	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.782	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9472 / 0 / 538	
Goodness-of-fit on F^2	1.063	
Final R indices [I>2sigma(I)]	R_1 = 0.048, wR_2 = 0.1278	
R indices (all data)	R_1 = 0.069, wR_2 = 0.1397	
Largest diff. peak and hole	0.43 and −0.54 e.Å^{-3}	

Table S7. Crystal data and structure refinement for **TBP5**

CCDC number	2025244	
Identification code	TBP5	
Empirical formula	$CH_2Cl_2 \cdot C_{64}H_{56}Si_2$	
Formula weight	966.19	
Temperature	100 K	
Wavelength	0.71075 Å	
Crystal system	Triclinic,	
Space group	*P*-1	
Unit cell dimensions	a = 11.6467 (3)	α = 92.613 (2)
	b = 13.8960 (4)	β = 102.408 (2)
	c = 16.8565 (4)	γ = 104.007 (2)
Volume	2571.41 (12)	
Z	2	
Density (calculated)	1.248 g/cm^3	
Absorption coefficient	0.22 mm^{-1}	
F(000)	1020	
Crystal size	0.26 × 0.13 × 0.11 mm^3	
Theta range for data collection	2.071 to 27.484°.	
Index ranges	−14<=h<=15, −17<=k<=18, −21<=l<=21	
Reflections collected	44915	
Independent reflections	11784 [R(int) = 0.033]	
Completeness to theta = 27.484°	99.92	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.813	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11784 / 0 / 634	
Goodness-of-fit on F^2	1.064	
Final R indices [I>2sigma(I)]	R_1 = 0.0464, wR_2 = 0.1257	
R indices (all data)	R_1 = 0.0568, wR_2 = 0.1329	
Largest diff. peak and hole	0.65 and −0.91 e.Å^{-3}	

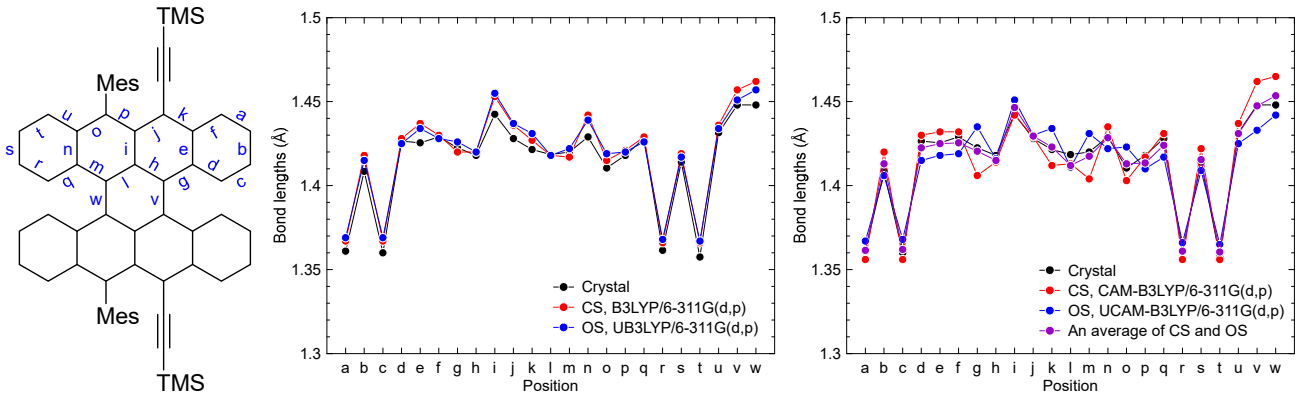


Fig. S8. The bond lengths of **TBP5** in the crystal and calculations

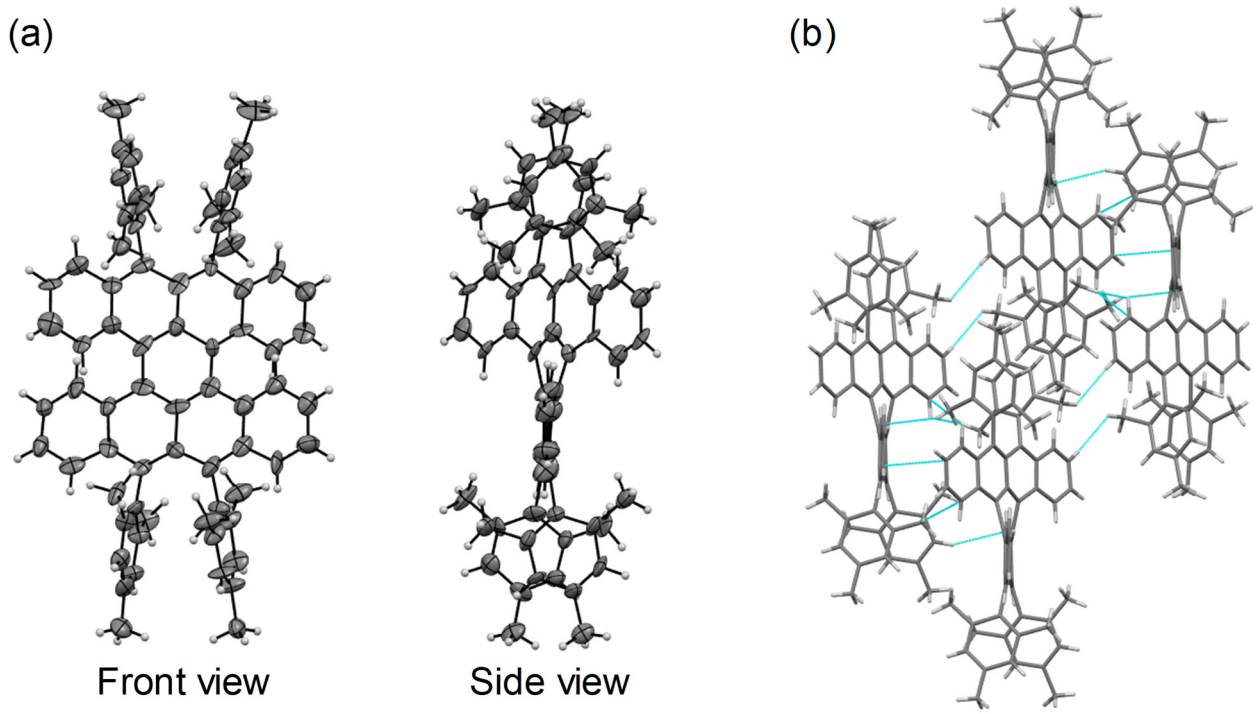


Fig. S9. X-ray single crystal structure of **TBP4**. (a) Molecular structure and (b) packing structure.

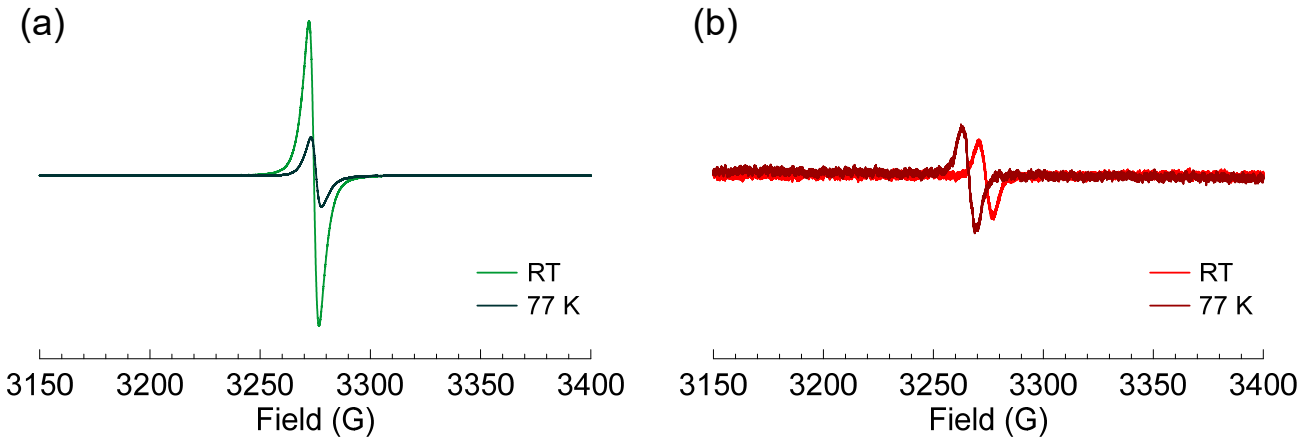


Fig. S10. ESR spectra in powder at rt and 77 K for (a) **TBP4** and (b) **TBP5**. The signals appeared at g = 2.003 for both compounds.

Methods S4. OFET fabrications

Bottom-gate/top-contact (BG/TC) OFETs were constructed on heavily doped n-type silicon wafers covered with thermally grown silicon dioxide (300 nm) which was cleaned by piranha solution. The silicon dioxide acts as a gate dielectric layer. and the silicon wafer serves as a gate electrode. The cross-linked PVP (poly-4-vinylphenol) was prepared by spin-coating from a solution of PVP (Aldrich 436224. M_w ~25.000. 1.0 wt%) and poly(melamine-co-formaldehyde) (M_n ~432. 1.0 wt%) in propylene glycol monomethyl ether acetate (PGMEA) at the rotational speed of 500 rpm for 5 s and then 4000 rpm for 60 s. followed by the cross-linkage at temperatures of 150 °C for 60 min under nitrogen atmosphere. Organic semiconductor layers were formed by drop-casting (see Fig. S11) from a 0.1–0.3 wt% solution of **TBP5** in *o*-dichlorobenzene (ODCB) at 60 °C. Top-contact gold source-drain electrodes (50 nm) were deposited through a shadow mask with L = 50, 100, 150 and 200 μm and W = 2000 μm. The actual lengths of L/W were measured by the optical microscope.

The FET measurements were carried out at room temperature in a glovebox without exposure to air with a semiconductor parameter analyzer (B1500. Agilent). Mobilities (μ) were calculated in the saturation regime by the relationship: $\mu_{sat} = (2I_D L)/[WC_i(V_G - V_{th})^2]$ where I_D is the source-drain saturation current; C_i is the capacitance of the insulating layer; V_G is the gate voltage and V_{th} is the threshold voltage. The latter can be estimated as the intercept of the linear section of the plot of V_G $(I_D)^{1/2}$.

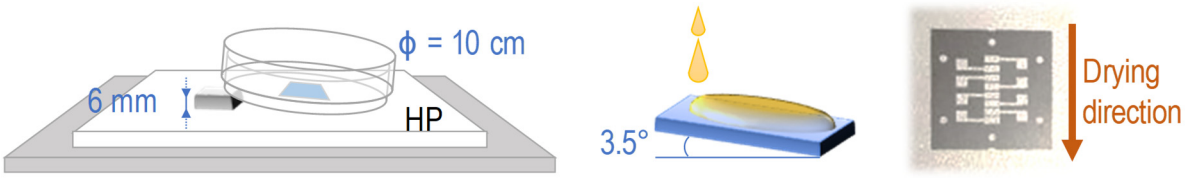


Fig. S11. Schematic image of the drop-casting procedure. The substrates were placed inside the petri-dish with the saturated solvent vapor at 60 °C. then 30 μL of the semiconductor solution was drop-casted.

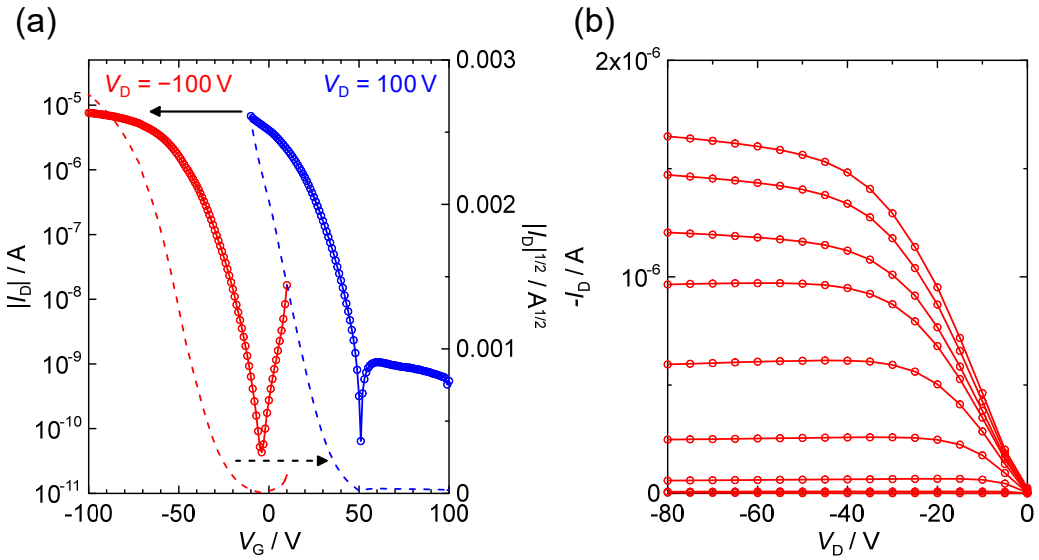


Fig. S12. OFET characteristics. (a) Transfer and (b) output characteristics of a BG/TC device with a drop-casted film of **TBP5** from 0.1 wt% ODCB solution.

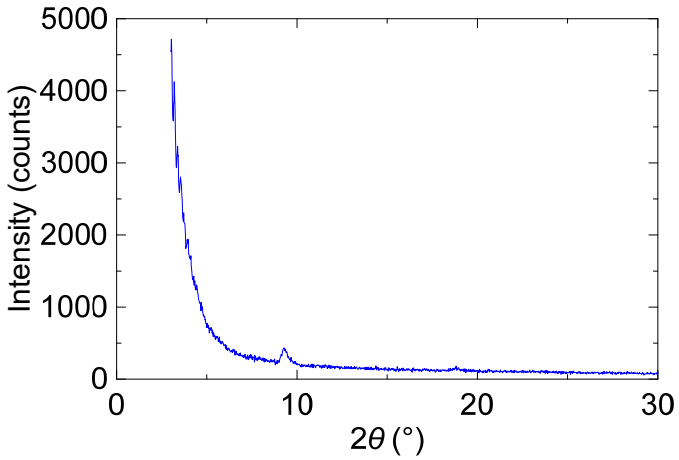


Fig. S13. Out-of-plane X-ray diffractograms for the films of **TBP5**.

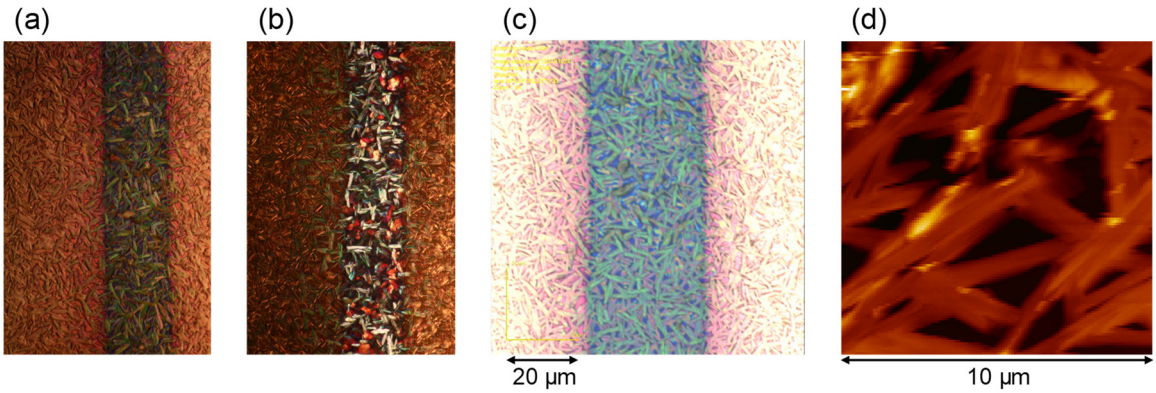


Fig. S14. Microscope images for the films of **TBP5**. (a) The bright-field microscope image, (b) the cross-polarlized microscope image, (c) laser microscope image, and (d) atomic force microscope (AFM) image.

Table S8. Materials

Reagents	CAS No.	Supplier, code and Grade
5,12-Naphthacenequinone	1090-13-7	Tokyo Kasei Co., Ltd., N0603, >98.0%
Tin	7440-31-5	Sigma-Aldrich Chemical Co., 30-2400
Acetic acid	64-19-7	WAKO Chemical Industries, 014-00261, >99.0%
Pyridine *N*-oxide	694-59-7	Tokyo Kasei Co., Ltd., P0557, >98.0%
Iron(II) sulfate heptahydrate	7782-63-0	WAKO Chemical Industries, 098-01085
Piperidine	110-89-4	Tokyo Kasei Co., Ltd., P0453, >99.0%
Pyridine	110-86-1	WAKO Chemical Industries, 166-05316
Phenylmagnesiumbromide, 1.0M in THF	100-58-3	Sigma-Aldrich Chemical Co., 331376
Phenylmagnesiumbromide, 3.0M in Et_2O	100-58-3	Sigma-Aldrich Chemical Co., 171565
2-Mesitylmagnesiumbromide, 1.0M in THF	2633-66-1	Sigma-Aldrich Chemical Co., 227234
Mesityl bromide	576-83-0	Tokyo Kasei Co., Ltd., B1261, >99.0%
Magnesium	7439-95-4	WAKO Chemical Industries, 139-06045
(Triisopropylsilyl)acetylene	89343-06-6	WAKO Chemical Industries, 320-58801, >95.0%
n-Butyllithium	109-72-8	Kanto Chemicals, 04937-25, 1.6 mol/l
Tin(II) chloride	7772-99-8	WAKO Chemical Industries, 204-11491, >99.9%
Bromobenzene	108-86-1	WAKO Chemical Industries, 020-02545, >98.0%
Trimethylsilylacetylene	1066-54-2	Tokyo Kasei Co., Ltd., T1239, >98.0%
Iron(III) chloride	7705-08-0	WAKO Chemical Industries, 097-01675

Table S9. Instruments

Instruments	Brands and Types	Conditions
Sublimation	ALS technology	Three-zone sublimation apparatus.
Elemental Analysis	Yanaco MT-5 CHN corder	
MS	Waters 3100 Mass Spectrometer	Direct probe ionization, ASAP-MS.
MS	Shimadzu AXIMA Confidence	MALDI-MS, Reflection mode
HRMS	JEOL JMS-700	Ion mode: FAB+, inlet: direct, calibration standard: PEG 400
NMR	Bruker AVANCE III 500 MHz spectrometer	Chemical shifts were calibrated to the corresponding deuterated solvents. 7.26 ppm for $CDCl_3$ and 5.32 ppm for CD_2Cl_2 in ^1H NMR, and 77.2 ppm for $CDCl_3$ in ^{13}C NMR
UV-Vis	Perkin-Elmer Lambda 950-PKA UV–vis spectrophotometer	The light source consisted of Deuterium (D2) and Tungsten Iodide (50W) lamps for the ultraviolet and visible regions.
PL	PMA12 C10027-02 PMA12 C10028-01	the excitation wavelength was set to the absorption maximum
PL quantum Yield	Hamamatsu Photonics Quantaurus-QY C11347-01 Hamamatsu Photonics Quantaurus-QY Plus C13534-21	Absolute PL quantum yield. The measurement error for the obtained values on this instrument is ±3%.
ESR	JEOL JES-FA200 spectrometer	at room temperature
CV	BAS 608D + DPV Electrochemical system	Supporting electrolyte: tetrabutylammonium hexafluorophosphate ($TBAPF_6$) (0.1 M) in dichloromethane. Working electrode: a glassy carbon, Auxiliary electrode: a platinum wire, Reference electrode: an $Ag/AgNO_3$. Calibration: ferrocenium-ferrocene (Fc/Fc^+) as a standard. Scan rate: 100 mV s^{-1} for cyclic voltammograms.
UV/ozone	Nippon Laser & Electronics Lab. NL-UV253	15 min
Spin-coater	Active Co., Ltd., ACT-220D II	at room temperature
XRD	Rigaku Ultima IV diffractometer	40 kV and 40 mA using CuKα radiation.
AFM	Bruker 3100 apparatus	Tapping mode using a silicon tip A resonance of around 500 kHz
Laser scanning microscope	Olympus LEXT	
Polarized microscope	Nikon Eclipse LV150N	
Melting point	BUCHI melting point M-565	A heating rate of 10 °C per minute
TG-DTA	Bruker TG-DTA 2400SA,	Under a N_2 atmosphere with a heating rate of 10 °C per minute.

Table S10. Optimized geometry for the closed-shell singlet of **TBP1** at the B3LYP/6-311G(d,p)

Atom	X	Y	Z	Atom	X	Y	Z
C	0.7439812	-4.6591312	-2.1593320	H	7.2726072	-3.0322868	1.4631205
C	2.1459164	-4.8882468	-2.1325078	C	-4.8366577	1.9202524	-0.6322140
C	2.9838786	-3.9358537	-1.6289064	C	-5.6336543	1.6184074	-1.7537094
C	2.4833975	-2.6963475	-1.1078927	C	-5.4357634	2.4348697	0.5340243
C	1.0496277	-2.5083862	-1.0408098	C	-7.0116715	1.8385723	-1.6878655
C	0.2207120	-3.5152435	-1.6233690	C	-6.8171005	2.6388206	0.5569828
C	3.3566815	-1.6869549	-0.6708270	C	-7.6240139	2.3499978	-0.5437656
C	2.8310696	-0.4240333	-0.2929428	H	-7.6210393	1.6013641	-2.5551609
C	1.4007159	-0.2079540	-0.3036735	H	-7.2729401	3.0324179	1.4609553
C	0.5212864	-1.3078333	-0.4890633	C	4.6065031	-2.7650908	1.7550378
C	3.6631388	0.6377684	0.1013943	H	4.0585897	-1.8901272	2.1159834
C	3.1420074	1.8610069	0.5193759	H	3.8633029	-3.5368026	1.5343457
C	1.7245869	2.1076324	0.4270145	H	5.2386687	-3.1278714	2.5676254
C	0.8778405	1.1035197	-0.1240081	C	5.0231035	-1.0640623	-3.0182910
C	3.9977591	2.8782438	1.0432313	H	4.2877996	-1.7535637	-3.4427876
C	3.5238176	4.0673017	1.5369689	H	4.5027316	-0.1203163	-2.8327895
C	2.1069271	4.2558948	1.5241407	H	5.7916259	-0.8840016	-3.7722654
C	1.2534196	3.3289933	0.9877779	C	9.1112915	-2.6095909	-0.5044767
C	-0.5211828	1.3077176	-0.4894794	H	9.5116966	-2.4921464	0.5053229
C	-1.4006520	0.2078811	-0.3040223	H	9.3405954	-3.6304380	-0.8297972
C	-0.8778149	-1.1035505	-0.1239391	H	9.6518486	-1.9278075	-1.1652056
C	-2.8310077	0.4239628	-0.2936469	C	-4.6069072	2.7652296	1.7535152
C	-3.6631606	-0.6377467	0.1007632	H	-4.0590920	1.8903011	2.1146946
C	-3.1421175	-1.8608872	0.5191395	H	-3.8636427	3.5369017	1.5329002
C	-1.7246779	-2.1075339	0.4271377	H	-5.2392542	3.1281210	2.5659122
C	-1.0494066	2.5081432	-1.0416154	C	-5.0224306	1.0636386	-3.0197080
C	-2.4831620	2.6960880	-1.1090488	H	-4.2870187	1.7530821	-3.4441124
C	-3.3565392	1.6867964	-0.6719357	H	-4.5021159	0.1199054	-2.8339830
C	-3.9979815	-2.8780042	1.0430488	H	-5.7907825	0.8835068	-3.7738393
C	-3.5241456	-4.0669437	1.5371667	C	-9.1111776	2.6095094	-0.5070055
C	-2.1072507	-4.2555411	1.5246845	H	-9.5118815	2.4917915	0.5026451
C	-1.2536302	-3.3287641	0.9882897	H	-9.3403619	3.6304551	-0.8321007
C	-0.2203662	3.5148680	-1.6242271	H	-9.6515565	1.9279241	-1.1680824
C	-0.7435211	4.6586317	-2.1605658	C	4.4919002	5.1245718	2.1028153
C	-2.1454627	4.8877503	-2.1340990	C	5.4927404	5.5454644	1.0019277
C	-2.9835322	3.9354718	-1.6304596	H	6.1883804	6.2973456	1.3876187
H	0.0875126	-5.3891205	-2.6191783	H	6.0811955	4.6974460	0.6448597
H	2.5493409	-5.8095223	-2.5377829	H	4.9699232	5.9746802	0.1428592
H	4.0551928	-4.0916416	-1.6389222	C	3.7597045	6.3889811	2.5903475
H	-0.8464305	-3.3494303	-1.6638840	H	3.2005146	6.8722512	1.7845487
H	4.7361435	0.4900627	0.1110217	H	3.0654377	6.1701074	3.4061007
H	5.0603349	2.6601758	1.0601748	H	4.4892652	7.1116708	2.9655054
H	1.6808353	5.1498356	1.9592525	C	5.2684207	4.5276084	3.2992292
H	0.1896922	3.5187655	1.0168494	H	4.5836703	4.2184824	4.0936081
H	-4.7361670	-0.4900372	0.1101312	H	5.8542223	3.6539469	3.0050689
H	-5.0605620	-2.6599358	1.0597029	H	5.9580397	5.2697156	3.7137324
H	-1.6812538	-5.1493764	1.9601067	C	-4.4923516	-5.1241000	2.1030110
H	-0.1899088	-3.5185274	1.0176364	C	-3.7602573	-6.3883882	2.5910111
H	0.8467854	3.3490464	-1.6644726	H	-3.2009799	-6.8719178	1.7854308
H	-0.0869545	5.3885166	-2.6204379	H	-3.0660915	-6.1692859	3.4067897
H	-2.5488012	5.8089309	-2.5396754	H	-4.4898906	-7.1109476	2.9662811
H	-4.0548446	4.0912539	-1.6407465	C	-5.4929036	-5.5452419	1.0019668
C	4.8367925	-1.9203980	-0.6307390	H	-6.1886764	-6.2970010	1.3876567
C	5.6340442	-1.6186801	-1.7520899	H	-6.0812107	-4.6972914	0.6444992
C	5.4356351	-2.4348662	0.5356978	H	-4.9698672	-5.9747116	0.1431529
C	7.0120468	-1.8388210	-1.6859031	C	-5.2691797	-4.5268917	3.2991093
C	6.8169707	-2.6388017	0.5589969	H	-4.5846276	-4.2175727	4.0935811
C	7.6241326	-2.3501031	-0.5415994	H	-5.8549447	-3.6533126	3.0046243
H	7.6216116	-1.6017087	-2.5530866	H	-5.9588832	-5.2689243	3.7136048

Table S11. Optimized geometry for the open-shell singlet of **TBP1** at the UB3LYP/6-311G(d,p)

Atom	X	Y	Z	Atom	X	Y	Z
C	0.7449927	-4.6612965	-2.1594781	H	7.2711895	-3.0309570	1.4695066
C	2.1455571	-4.8916041	-2.1291139	C	-4.8357460	1.9222153	-0.6281962
C	2.9832747	-3.9392045	-1.6228954	C	-5.6328948	1.6231589	-1.7503400
C	2.4822530	-2.7003576	-1.1032849	C	-5.4346028	2.4347445	0.5390923
C	1.0497095	-2.5115162	-1.0393752	C	-7.0107917	1.8438899	-1.6840522
C	0.2216032	-3.5159120	-1.6244353	C	-6.8158316	2.6393872	0.5624616
C	3.3559053	-1.6887192	-0.6672378	C	-7.6228769	2.3532657	-0.5388933
C	2.8302508	-0.4247032	-0.2936165	H	-7.6202730	1.6088313	-2.5518507
C	1.3995163	-0.2081417	-0.3045588	H	-7.2714825	3.0313382	1.4672411
C	0.5201431	-1.3083031	-0.4886156	C	4.6051874	-2.7616207	1.7609114
C	3.6630841	0.6376089	0.0969748	H	4.0577879	-1.8855174	2.1198724
C	3.1429620	1.8632336	0.5136595	H	3.8615349	-3.5334011	1.5419571
C	1.7265051	2.1097879	0.4238341	H	5.2371453	-3.1229467	2.5743130
C	0.8774012	1.1039412	-0.1261432	C	5.0225303	-1.0713424	-3.0161021
C	3.9995703	2.8790747	1.0364798	H	4.2858935	-1.7607801	-3.4383707
C	3.5264584	4.0685934	1.5323054	H	4.5037805	-0.1262680	-2.8327509
C	2.1106627	4.2569501	1.5221201	H	5.7909254	-0.8944410	-3.7709569
C	1.2560712	3.3292190	0.9865346	C	9.1100348	-2.6135676	-0.4990739
C	-0.5200339	1.3081733	-0.4890098	H	9.5104853	-2.4942904	0.5104945
C	-1.3994488	0.2080516	-0.3049208	H	9.3388103	-3.6351867	-0.8223436
C	-0.8773749	-1.1039931	-0.1261009	H	9.6509372	-1.9333838	-1.1611722
C	-2.8301851	0.4246195	-0.2943441	C	-4.6055426	2.7620684	1.7592707
C	-3.6631078	-0.6376077	0.0962849	H	-4.0582187	1.8860560	2.1185682
C	-3.1430801	-1.8631350	0.5133728	H	-3.8618433	3.5337920	1.5402740
C	-1.7266015	-2.1097081	0.4239323	H	-5.2376686	3.1236026	2.5724491
C	-1.0494741	2.5112837	-1.0401118	C	-5.0218921	1.0705779	-3.0174006
C	-2.4820024	2.7001116	-1.1043926	H	-4.2851659	1.7599019	-3.4396986
C	-3.3557548	1.6885576	-0.6683474	H	-4.5031832	0.1255497	-2.8336943
C	-3.9998074	-2.8788504	1.0362415	H	-5.7901319	0.8934803	-3.7723674
C	-3.5268079	-4.0682443	1.5324730	C	-9.1099164	2.6134637	-0.5016128
C	-2.1110095	-4.2565971	1.5226681	H	-9.5106412	2.4940621	0.5078335
C	-1.2562956	-3.3289945	0.9870546	H	-9.3385896	3.6351296	-0.8248063
C	-0.2212269	3.5155830	-1.6251366	H	-9.6506495	1.9333732	-1.1639434
C	-0.7444900	4.6608722	-2.1605068	C	4.4960474	5.1249793	2.0969487
C	-2.1450631	4.8911782	-2.1305270	C	5.4938616	5.5472977	0.9938696
C	-2.9829009	3.9388665	-1.6243414	H	6.1907038	6.2985105	1.3786877
H	0.0885163	-5.3906089	-2.6203729	H	6.0811278	4.6997072	0.6338285
H	2.5495748	-5.8130297	-2.5334477	H	4.9686854	5.9778918	0.1369091
H	4.0545075	-4.0956753	-1.6305557	C	3.7651391	6.3886588	2.5882350
H	-0.8453411	-3.3493332	-1.6672183	H	3.2040767	6.8732206	1.7845206
H	4.7359279	0.4889468	0.1072977	H	3.0727959	6.1684485	3.4052642
H	5.0621334	2.6608445	1.0517587	H	4.4956280	7.1107338	2.9627973
H	1.6848626	5.1507335	1.9578483	C	5.2758572	4.5263811	3.2904469
H	0.1924077	3.5191126	1.0174170	H	4.5932575	4.2162918	4.0863002
H	-4.7359538	-0.4889415	0.1063324	H	5.8608662	3.6530768	2.9936330
H	-5.0623756	-2.6606243	1.0512118	H	5.9666501	5.2679358	3.7039701
H	-1.6853075	-5.1502673	1.9587244	C	-4.4965288	-5.1245068	2.0971215
H	-0.1926392	-3.5188739	1.0182435	C	-3.7657421	-6.3881098	2.5887848
H	0.8457297	3.3490032	-1.6676206	H	-3.2046572	-6.8729191	1.7852362
H	-0.0879033	5.3901093	-2.6213638	H	-3.0734403	-6.1677331	3.4058051
H	-2.5489852	5.8125328	-2.5351181	H	-4.4963065	-7.1100395	2.9634797
H	-4.0541315	4.0953371	-1.6322814	C	-5.4941257	-5.5470049	0.9939135
C	4.8358883	-1.9223656	-0.6267167	H	-6.1910809	-6.2981133	1.3787313
C	5.6332729	-1.6235872	-1.7487697	H	-6.0812771	-4.6994582	0.6335809
C	5.4345000	-2.4346065	0.5408216	H	-4.9687841	-5.9777882	0.1371496
C	7.0111544	-1.8442994	-1.6821387	C	-5.2765716	-4.5256846	3.2903545
C	6.8157269	-2.6392357	0.5645331	H	-4.5941247	-4.2154277	4.0862733
C	7.6230016	-2.3533860	-0.5367218	H	-5.8615451	-3.6524508	2.9932649
H	7.6208165	-1.6094611	-2.5498702	H	-5.9674268	-5.2671712	3.7038959

Table S12. Optimized geometry for the triplet of **TBP1** at the UB3LYP/6-311G(d,p)

Atom	X	Y	Z	Atom	X	Y	Z
C	0.7628239	-4.6929999	-2.1612752	H	7.2510868	-3.0121181	1.5604134
C	2.1421410	-4.9407350	-2.0757605	C	-4.8217239	1.9496578	-0.5684302
C	2.9750934	-3.9878189	-1.5310491	C	-5.6202214	1.6912052	-1.6998752
C	2.4662648	-2.7577631	-1.0337259	C	-5.4180910	2.4311536	0.6133351
C	1.0502644	-2.5560117	-1.0202128	C	-6.9965356	1.9192106	-1.6276138
C	0.2367396	-3.5245212	-1.6424697	C	-6.7978487	2.6448898	0.6421932
C	3.3436237	-1.7135450	-0.6120797	C	-7.6059663	2.3979227	-0.4677968
C	2.8194520	-0.4341103	-0.3046334	H	-7.6069417	1.7152338	-2.5026196
C	1.3823334	-0.2104451	-0.3194861	H	-7.2514162	3.0124619	1.5581949
C	0.5041625	-1.3130707	-0.4852324	C	4.5867107	-2.7131245	1.8449829
C	3.6615647	0.6355100	0.0282091	H	4.0532421	-1.8194415	2.1809107
C	3.1572264	1.8949148	0.4271172	H	3.8310494	-3.4793129	1.6484167
C	1.7532822	2.1404596	0.3767132	H	5.2149117	-3.0618537	2.6667774
C	0.8709127	1.1084328	-0.1581174	C	5.0123205	-1.1713107	-2.9801428
C	4.0253301	2.8901419	0.9365151	H	4.2503100	-1.8537063	-3.3671618
C	3.5640069	4.0856324	1.4642118	H	4.5247412	-0.2041882	-2.8280930
C	2.1646819	4.2695748	1.4945278	H	5.7768395	-1.0471426	-3.7493220
C	1.2938955	3.3294258	0.9701124	C	9.0912493	-2.6675905	-0.4211444
C	-0.5040591	1.3129551	-0.4856294	H	9.4930230	-2.5229102	0.5845652
C	-1.3822661	0.2103660	-0.3198317	H	9.3126786	-3.6994465	-0.7157620
C	-0.8708806	-1.1084764	-0.1580620	H	9.6366416	-2.0100694	-1.1021920
C	-2.8193876	0.4340359	-0.3053372	C	-4.5871053	2.7135079	1.8434048
C	-3.6615725	-0.6355100	0.0275610	H	-4.0537150	1.8198930	2.1796374
C	-3.1573209	-1.8948264	0.4268576	H	-3.8313966	3.4796493	1.6468388
C	-1.7533659	-2.1403838	0.3768083	H	-5.2154812	3.0624158	2.6649896
C	-1.0500443	2.5557806	-1.0209958	C	-5.0116820	1.1706690	-2.9814848
C	-2.4660413	2.7575303	-1.0348577	H	-4.2495765	1.8529709	-3.3684814
C	-3.3434919	1.7134035	-0.6131767	H	-4.5241517	0.2035701	-2.8291279
C	-4.0255346	-2.8899395	0.9362912	H	-5.7760361	1.0463524	-3.7508041
C	-3.5643255	-4.0853143	1.4643496	C	-9.0911513	2.6675332	-0.4236838
C	-2.1650072	-4.2692513	1.4950061	H	-9.4932063	2.5227203	0.5818955
C	-1.2941076	-3.3292187	0.9705705	H	-9.3124763	3.6994371	-0.7182119
C	-0.2363836	3.5241556	-1.6432836	H	-9.6363691	2.0101199	-1.1049735
C	-0.7623544	4.6925238	-2.1624531	C	4.5548581	5.1292561	2.0113995
C	-2.1416895	4.9402787	-2.0772891	C	5.5153464	5.5658064	0.8809071
C	-2.9747607	3.9874802	-1.5325537	H	6.2287522	6.3074587	1.2535864
H	0.1072954	-5.4133043	-2.6371899	H	6.0858465	4.7222173	0.4860018
H	2.5551890	-5.8658118	-2.4621268	H	4.9622596	6.0130777	0.0504637
H	4.0444540	-4.1547291	-1.5029050	C	3.8438911	6.3857262	2.5471395
H	-0.8265009	-3.3461911	-1.7213987	H	3.2597311	6.8852499	1.7695136
H	4.7320289	0.4732733	0.0515112	H	3.1760756	6.1518850	3.3806194
H	5.0875595	2.6703056	0.9280780	H	4.5874111	7.0995452	2.9117562
H	1.7432235	5.1605047	1.9402450	C	5.3735664	4.5098710	3.1678740
H	0.2312184	3.5192512	1.0298437	H	4.7176874	4.1907304	3.9823689
H	-4.7320416	-0.4732669	0.0505975	H	5.9452661	3.6392097	2.8389816
H	-5.0877618	-2.6701037	0.9275803	H	6.0811002	5.2430563	3.5676045
H	-1.7436451	-5.1600835	1.9410099	C	-4.5552943	-5.1288138	2.0115612
H	-0.2314434	-3.5190312	1.0305733	C	-3.8444437	-6.3851735	2.5477146
H	0.8268737	3.3458075	-1.7219431	H	-3.2601208	-6.8848610	1.7703161
H	-0.1067223	5.4127257	-2.6383802	H	-3.1768034	-6.1511605	3.3812867
H	-2.5546528	5.8652734	-2.4639419	H	-4.5880424	-7.0989144	2.9123236
H	-4.0441267	4.1543979	-1.5046758	C	-5.5155582	-5.5656026	0.8809705
C	4.8218468	-1.9497865	-0.5669633	H	-6.2290426	-6.3071706	1.2536671
C	5.6205890	-1.6915687	-1.6982919	H	-6.0859752	-4.7220966	0.4857679
C	5.4179599	-2.4310258	0.6150326	H	-4.9623074	-6.0130564	0.0507345
C	6.9968876	-1.9195461	-1.6256828	C	-5.3742302	-4.5091720	3.1677373
C	6.7977151	-2.6447445	0.6442354	H	-4.7185119	-4.1898603	3.9822944
C	7.6060707	-2.3980058	-0.4656297	H	-5.9458558	-3.6385769	2.8385411
H	7.6074824	-1.7157501	-2.5005993	H	-6.0818504	-5.2422648	3.5674847

Table S13. Optimized geometry for the closed-shell singlet of **TBP2** at the B3LYP/6-311G(d,p)

Atom	X	Y	Z	Atom	X	Y	Z
C	1.4133923	4.9084173	1.8697703	C	8.5970841	-2.6823248	-0.2117242
C	2.8352476	4.9037837	1.8899398	C	8.7508349	0.1662569	-1.4113536
C	3.5159123	3.8226552	1.4107431	C	8.5488249	-0.2116802	1.6529195
C	2.8234162	2.6922093	0.8726040	C	-8.5491450	-0.2112867	-1.6523712
C	1.3849826	2.7339926	0.7627252	C	-8.5970718	-2.6823766	0.2116438
C	0.7172183	3.8667049	1.3195119	C	-8.7505971	0.1659068	1.4120337
C	3.5212400	1.5564345	0.4669617	H	0.8753642	5.7411625	2.3082772
C	2.8561929	0.3912315	0.0662881	H	3.3701656	5.7472473	2.3114293
C	1.4140126	0.3980088	0.0219998	H	4.5991501	3.7859547	1.4538780
C	0.7034396	1.6188388	0.1952338	H	-0.3632089	3.8858024	1.3310180
C	3.5626504	-0.7966531	-0.2906100	H	4.6039438	1.5594026	0.4945160
C	2.8495633	-1.9263476	-0.7579577	H	4.6141177	-3.0622963	-1.2739464
C	1.4090493	-1.9371363	-0.7165115	H	3.3818327	-4.9774402	-2.2063021
C	0.7066603	-0.8198543	-0.1722109	H	0.8875350	-4.9166694	-2.3135586
C	3.5316769	-3.0685477	-1.2776236	H	-0.3410816	-3.0338183	-1.3682231
C	2.8448841	-4.1280282	-1.7994163	H	-4.6039527	1.5593745	-0.4945759
C	1.4271159	-4.1024257	-1.8436381	H	-4.5991855	3.7859440	-1.4539071
C	0.7379843	-3.0465334	-1.3123242	H	-3.3702218	5.7472537	-2.3114459
C	-0.7066429	-0.8198645	0.1720638	H	-0.8754208	5.7411834	-2.3083247
C	-1.4140082	0.3979938	-0.0221221	H	0.3631748	3.8858161	-1.3311013
C	-0.7034482	1.6188340	-0.1953406	H	0.3411279	-3.0338479	1.3680160
C	-2.8561892	0.3912063	-0.0663952	H	-0.8874640	-4.9167349	2.3133105
C	-3.5212495	1.5564114	-0.4670413	H	-3.3817620	-4.9775273	2.2060670
C	-2.8234391	2.6921973	-0.8726732	H	-4.6140694	-3.0623675	1.2737781
C	-1.3850051	2.7339890	-0.7628099	H	9.6872308	-2.7527728	-0.1427087
C	-1.4090185	-1.9371644	0.7163470	H	8.1696627	-3.3149355	0.5709030
C	-2.8495310	-1.9263868	0.7578107	H	8.2960170	-3.0952907	-1.1784326
C	-3.5626321	-0.7966859	0.2904996	H	9.8449348	0.1606001	-1.3748442
C	-3.5159476	3.8226480	-1.4107863	H	8.4175261	1.2044108	-1.3296237
C	-2.8352942	4.9037867	-1.8899757	H	8.4449830	-0.2054053	-2.3930120
C	-1.4134384	4.9084286	-1.8698234	H	8.2133867	0.8209738	1.7824046
C	-0.7172525	3.8667126	-1.3195875	H	8.1247172	-0.8048607	2.4674683
C	-0.7379387	-3.0465703	1.3121261	H	9.6383819	-0.2256401	1.7576807
C	-1.4270563	-4.1024834	1.8434171	H	-9.6387157	-0.2253590	-1.7569778
C	-2.8448240	-4.1280973	1.7992051	H	-8.2138609	0.8214450	-1.7816309
C	-3.5316297	-3.0686073	1.2774495	H	-8.1250816	-0.8041979	-2.4671385
C	-4.9768781	-0.8258532	0.2097779	H	-9.6872398	-2.7527849	0.1429226
C	-6.1932351	-0.8479173	0.1394619	H	-8.2957316	-3.0956513	1.1781342
Si	-8.0319341	-0.8933398	0.0275529	H	-8.1698888	-3.3147506	-0.5713053
C	4.9768948	-0.8258138	-0.2098490	H	-8.4447103	-0.2060958	2.3935521
C	6.1932486	-0.8478643	-0.1394806	H	-8.4171630	1.2040429	1.3305960
Si	8.0319258	-0.8933342	-0.0272638	H	-9.8447007	0.1603984	1.3756135

Table S14. Optimized geometry for the open-shell singlet of **TBP2** at the UB3LYP/6-311G(d,p)

Atom	X	Y	Z	Atom	X	Y	Z
C	1.4267565	4.9163454	1.8614039	C	8.5921352	-2.6890773	-0.2099326
C	2.8461560	4.9132661	1.8688665	C	8.7504730	0.1606714	-1.4062673
C	3.5236106	3.8311547	1.3819004	C	8.5466798	-0.2204889	1.6574861
C	2.8270229	2.7031805	0.8495057	C	-8.5469380	-0.2204642	-1.6571802
C	1.3906510	2.7440910	0.7514471	C	-8.5921528	-2.6890702	0.2102184
C	0.7267383	3.8718256	1.3158960	C	-8.7502404	0.1606699	1.4066092
C	3.5220180	1.5610130	0.4454283	H	0.8906515	5.7482109	2.3038793
C	2.8545239	0.3941747	0.0577598	H	3.3849317	5.7562813	2.2862995
C	1.4112362	0.4014558	0.0165494	H	4.6071714	3.7946859	1.4165160
C	0.7026202	1.6233520	0.1890800	H	-0.3535835	3.8902566	1.3365033
C	3.5612733	-0.7975115	-0.2881384	H	4.6047631	1.5621254	0.4708906
C	2.8468559	-1.9332624	-0.7513469	H	4.6114498	-3.0690395	-1.2616375
C	1.4093596	-1.9414569	-0.7146096	H	3.3796821	-4.9830215	-2.2005416
C	0.7036796	-0.8178921	-0.1714413	H	0.8863523	-4.9169399	-2.3164226
C	3.5289938	-3.0736171	-1.2687502	H	-0.3405332	-3.0297891	-1.3743553
C	2.8419444	-4.1333467	-1.7952783	H	-4.6047686	1.5620963	-0.4709615
C	1.4272209	-4.1043009	-1.8452285	H	-4.6071934	3.7946683	-1.4165600
C	0.7383760	-3.0445098	-1.3150225	H	-3.3849680	5.7562836	-2.2863186
C	-0.7036671	-0.8179000	0.1713404	H	-0.8906877	5.7482325	-2.3038966
C	-1.4112331	0.4014452	-0.0166333	H	0.3535608	3.8902758	-1.3365422
C	-0.7026265	1.6233491	-0.1891481	H	0.3405617	-3.0298106	1.3742157
C	-2.8545207	0.3941537	-0.0578441	H	-0.8863099	-4.9169878	2.3162478
C	-3.5220235	1.5609915	-0.4454993	H	-3.3796392	-4.9830868	2.2003630
C	-2.8270370	2.7031693	-0.8495619	H	-4.6114209	-3.0690966	1.2614946
C	-1.3906655	2.7440898	-0.7515015	H	9.6821486	-2.7611683	-0.1405325
C	-1.4093390	-1.9414794	0.7144893	H	8.1634989	-3.3219701	0.5718030
C	-2.8468353	-1.9332963	0.7512264	H	8.2908838	-3.1005012	-1.1772381
C	-3.5612612	-0.7975422	0.2880388	H	9.8445431	0.1535051	-1.3691817
C	-3.5236328	3.8311449	-1.3819432	H	8.4185591	1.1991971	-1.3235838
C	-2.8461862	4.9132673	-1.8688955	H	8.4446515	-0.2095128	-2.3884910
C	-1.4267867	4.9163575	-1.8614318	H	8.2125584	0.8124502	1.7880711
C	-0.7267609	3.8718364	-1.3159361	H	8.1214701	-0.8140469	2.4711847
C	-0.7383474	-3.0445383	1.3148822	H	9.6361796	-0.2360519	1.7626302
C	-1.4271845	-4.1043444	1.8450683	H	-9.6364544	-0.2360115	-1.7621543
C	-2.8419077	-4.1334003	1.7951160	H	-8.2128231	0.8124719	-1.7878050
C	-3.5289649	-3.0736663	1.2686071	H	-8.1218632	-0.8140185	-2.4709519
C	-4.9742549	-0.8272161	0.2074250	H	-9.6821793	-2.7611356	0.1409970
C	-6.1909290	-0.8513839	0.1367269	H	-8.2907510	-3.1005144	1.1774684
Si	-8.0295031	-0.8994893	0.0238974	H	-8.1636600	-3.3219619	-0.5715967
C	4.9742685	-0.8271697	-0.2075435	H	-8.4442787	-0.2095361	2.3887810
C	6.1909403	-0.8513379	-0.1368036	H	-8.4183100	1.1991875	1.3238890
Si	8.0294952	-0.8994862	-0.0236799	H	-9.8443164	0.1535353	1.3696917

Table S15. Optimized geometry for the triplet of **TBP2** at the UB3LYP/6-311G(d,p)

Atom	X	Y	Z	Atom	X	Y	Z
C	1.4993644	4.9558650	1.8146320	C	8.5638220	-2.7277740	-0.2036449
C	2.9055633	4.9583061	1.7581799	C	8.7515532	0.1329630	-1.3692014
C	3.5640661	3.8708036	1.2328079	C	8.5300233	-0.2782939	1.6889843
C	2.8460935	2.7557694	0.7287900	C	-8.5299406	-0.2782405	-1.6889806
C	1.4194220	2.7941332	0.6918178	C	-8.5639162	-2.7277745	0.2035771
C	0.7783400	3.8988503	1.2944329	C	-8.7514717	0.1329401	1.3692152
C	3.5250222	1.5827551	0.3310327	H	0.9753619	5.7847014	2.2766802
C	2.8471101	0.4103867	0.0088282	H	3.4642817	5.7989101	2.1535765
C	1.3979257	0.4217811	-0.0155780	H	4.6481651	3.8339138	1.2247345
C	0.6996544	1.6468510	0.1573278	H	-0.3001673	3.9149656	1.3625079
C	3.5533119	-0.8008466	-0.2808945	H	4.6079380	1.5742563	0.3476714
C	2.8316029	-1.9630645	-0.7276111	H	4.5937229	-3.0983693	-1.2192613
C	1.4073350	-1.9573914	-0.7127634	H	3.3602930	-5.0033851	-2.1903118
C	0.6887517	-0.8034910	-0.1717003	H	0.8721801	-4.9097877	-2.3417763
C	3.5113057	-3.0935718	-1.2401052	H	-0.3430687	-3.0011910	-1.4104406
C	2.8206181	-4.1523337	-1.7906507	H	-4.6079845	1.5741135	-0.3476679
C	1.4207033	-4.1056666	-1.8649590	H	-4.6482806	3.8337681	-1.2247353
C	0.7350586	-3.0273221	-1.3364301	H	-3.4644572	5.7987994	-2.1535799
C	-0.6887252	-0.8035121	0.1717087	H	-0.9755368	5.7846673	-2.2766816
C	-1.3979367	0.4217380	0.0155852	H	0.3000494	3.9149725	-1.3625050
C	-0.6997031	1.6468293	-0.1573218	H	0.3431619	-3.0011817	1.4104475
C	-2.8471206	0.4102991	-0.0088214	H	-0.8720284	-4.9098166	2.3417805
C	-3.5250689	1.5826459	-0.3310284	H	-3.3601383	-5.0034904	2.1903151
C	-2.8461761	2.7556804	-0.7287874	H	-4.5936264	-3.0985111	1.2192670
C	-1.4195058	2.7940883	-0.6918142	H	9.6528402	-2.8093700	-0.1293419
C	-1.4072733	-1.9574348	0.7127710	H	8.1261269	-3.3653638	0.5692120
C	-2.8315412	-1.9631514	0.7276187	H	8.2643519	-3.1265503	-1.1767737
C	-3.5532854	-0.8009552	0.2809027	H	9.8453162	0.1163172	-1.3263117
C	-3.5641827	3.8706915	-1.2328080	H	8.4279750	1.1733636	-1.2774060
C	-2.9057131	4.9582133	-1.7581814	H	8.4480336	-0.2244280	-2.3568498
C	-1.4995141	4.9558156	-1.8146323	H	8.2024425	0.7554539	1.8293168
C	-0.7784574	3.8988240	-1.2944309	H	8.0974378	-0.8774548	2.4946454
C	-0.7349645	-3.0273457	1.3364366	H	9.6189882	-0.3026700	1.7981248
C	-1.4205762	-4.1057119	1.8649641	H	-9.6189056	-0.3025484	-1.7981346
C	-2.8204895	-4.1524218	1.7906554	H	-8.2022968	0.7554924	-1.8292756
C	-3.5112093	-3.0936804	1.2401111	H	-8.0973813	-0.8774009	-2.4946560
C	-4.9594136	-0.8353937	0.1990596	H	-9.6529394	-2.8092963	0.1292670
C	-6.1775770	-0.8716777	0.1235061	H	-8.2644767	-3.1265992	1.1766955
Si	-8.0146407	-0.9357499	0.0013944	H	-8.1262597	-3.3653704	-0.5692967
C	4.9594410	-0.8352423	-0.1990524	H	-8.4479884	-0.2245024	2.3568561
C	6.1776046	-0.8715208	-0.1234984	H	-8.4278205	1.1733213	1.2774558
Si	8.0146651	-0.9357194	-0.0014057	H	-9.8452353	0.1163712	1.3263121

Table S16. Optimized geometry for the closed-shell singlet of **TBP3** at the B3LYP/6-311G(d,p)

Atom	X	Y	Z	Atom	X	Y	Z
C	-1.3698894	-4.5292983	1.7674894	H	-0.3710143	3.3613554	1.4407161
C	-2.7760798	-4.6242312	1.5985516	H	0.8270244	5.3331183	2.2514969
C	-3.4772484	-3.5815248	1.0642111	H	3.2978271	5.5200788	1.9162981
C	-2.8289807	-2.3630901	0.6681112	H	4.5506115	3.6552216	0.9656042
C	-1.3869251	-2.3312230	0.7103736	C	4.9970453	-1.4589504	0.1482276
C	-0.7012754	-3.4252901	1.3186552	C	6.0187988	-1.5754048	-0.8006759
C	-3.5609909	-1.2409688	0.2201339	C	5.3135343	-1.6598505	1.4976527
C	-2.8920639	0.0000304	0.0000517	C	7.3220639	-1.8704855	-0.4100175
C	-1.4349562	0.0000224	0.0000948	H	5.7913877	-1.4218245	-1.8488159
C	-0.7075052	-1.2045777	0.1774685	C	6.6158402	-1.9594666	1.8894376
C	-3.5609686	1.2410357	-0.2200702	H	4.5278687	-1.5872902	2.2416711
C	-2.8289185	2.3631486	-0.6680189	C	7.6255488	-2.0651208	0.9360075
C	-1.3868599	2.3312523	-0.7102208	H	8.1020009	-1.9467475	-1.1594455
C	-0.7074819	1.2046122	-0.1772600	H	6.8392061	-2.1155829	2.9392511
C	-3.4771380	3.5815834	-1.0642107	H	8.6403698	-2.2983668	1.2382694
C	-2.7759197	4.6242540	-1.5985563	C	4.9970425	1.4588954	-0.1482518
C	-1.3697237	4.5292830	-1.7674265	C	5.3134098	1.6597466	-1.4977134
C	-0.7011581	3.4252749	-1.3185240	C	6.0188790	1.5753932	0.8005556
C	0.7074783	1.2046085	0.1774092	C	6.6156796	1.9593502	-1.8896271
C	1.4349329	-0.0000036	0.0001057	H	4.5276767	1.5871599	-2.2416577
C	0.7074547	-1.2046010	-0.1771938	C	7.3221091	1.8704584	0.4097678
C	2.8920464	-0.0000167	0.0000811	H	5.7915632	1.4218535	1.8487223
C	3.5609384	-1.2410248	-0.2200522	C	7.6254736	2.0650414	-0.9362918
C	2.8288818	-2.3631487	-0.6679464	H	6.8389511	2.1154271	-2.9394665
C	1.3868250	-2.3312737	-0.7101001	H	8.1021125	1.9467508	1.1591235
C	1.3868871	2.3312782	0.7102766	H	8.6402669	2.2982776	-1.2386540
C	2.8289442	2.3631290	0.6680650	C	-4.9970399	1.4589242	0.1483635
C	3.5609663	1.2409866	0.2201595	C	-6.0188927	1.5755169	-0.8004176
C	3.4771191	-3.5815706	-1.0641397	C	-5.3134036	1.6595948	1.4978544
C	2.7759013	-4.6242774	-1.5984143	C	-7.3221195	1.8705350	-0.4095839
C	1.3696941	-4.5293478	-1.7672162	H	-5.7915914	1.4220891	-1.8486035
C	0.7011216	-3.4253362	-1.3183298	C	-6.6156698	1.9591511	1.8898143
C	0.7012285	3.4253698	1.3185071	H	-4.5276666	1.5869109	2.2417846
C	1.3698386	4.5293815	1.7673360	C	-7.6254725	2.0649595	0.9365007
C	2.7760382	4.6242906	1.5984578	H	-8.1021312	1.9469084	-1.1589231
C	3.4772151	3.5815610	1.0641766	H	-6.8389328	2.1150994	2.9396745
H	-0.8270845	-5.3330168	2.2516912	H	-8.6402642	2.2981553	1.2389000
H	-3.2978688	-5.5200230	1.9163815	C	-4.9970291	-1.4588679	-0.1484092
H	-4.5506376	-3.6552110	0.9655744	C	-5.3132798	-1.6595806	-1.4979205
H	0.3709642	-3.3612618	1.4408897	C	-6.0189509	-1.5754723	0.8002954
H	-4.5505297	3.6552969	-0.9656434	C	-6.6155104	-1.9591617	-1.8899781
H	-3.2976726	5.5200441	-1.9164504	H	-4.5274837	-1.5869064	-2.2417894
H	-0.8268784	5.3329695	-2.2516362	C	-7.3221434	-1.8705103	0.4093628
H	0.3710859	3.3612129	-1.4407118	H	-5.7917346	-1.4220221	1.8484970
H	4.5505206	-3.6552450	-0.9656292	C	-7.6253877	-2.0649614	-0.9367426
H	3.2976636	-5.5200622	-1.9163075	H	-6.8386862	-2.1151363	-2.9398530
H	0.8268453	-5.3330633	-2.2513739	H	-8.1022132	-1.9468795	1.1586417
H	-0.3711264	-3.3613006	-1.4404869	H	-8.6401522	-2.2981773	-1.2392173

Table S17. Optimized geometry for the open-shell singlet of **TBP3** at the UB3LYP/6-311G(d,p)

Atom	X	Y	Z	Atom	X	Y	Z
C	1.3740089	-4.5316128	-1.7644422	H	0.3674375	3.3621024	-1.4428902
C	2.7786036	-4.6273302	-1.5907945	H	-0.8319309	5.3349367	-2.2501228
C	3.4785534	-3.5842057	-1.0537587	H	-3.3013636	5.5231731	-1.9068606
C	2.8292966	-2.3665344	-0.6600911	H	-4.5515923	3.6582632	-0.9516210
C	1.3884746	-2.3341475	-0.7065614	C	-4.9956379	-1.4575331	-0.1596010
C	0.7044428	-3.4263710	-1.3174951	C	-6.0196329	-1.5820061	0.7859437
C	3.5605912	-1.2416883	-0.2133076	C	-5.3090436	-1.6473329	-1.5113838
C	2.8911001	-0.0000046	0.0000247	C	-7.3219164	-1.8740692	0.3898591
C	1.4337403	-0.0000028	0.0000345	H	-5.7948376	-1.4366202	1.8358101
C	0.7068443	-1.2052991	-0.1756779	C	-6.6103667	-1.9440693	-1.9086055
C	3.5605958	1.2416806	0.2133341	H	-4.5217328	-1.5683069	-2.2529946
C	2.8293104	2.3665309	0.6601178	C	-7.6222512	-2.0577494	-0.9584182
C	1.3884891	2.3341481	0.7066127	H	-8.1035988	-1.9564580	1.1368169
C	0.7068482	1.2052961	0.1757480	H	-6.8312685	-2.0915725	-2.9601835
C	3.4785797	3.5842030	1.0537602	H	-8.6363280	-2.2886747	-1.2649307
C	2.7786443	4.6273340	1.5908013	C	-4.9956410	1.4575424	0.1595996
C	1.3740530	4.5316210	1.7644801	C	-5.3090793	1.6473574	1.5113727
C	0.7044739	3.4263783	1.3175543	C	-6.0196098	1.5820204	-0.7859727
C	-0.7068426	1.2052931	-0.1757019	C	-6.6104108	1.9441050	1.9085588
C	-1.4337383	0.0000001	0.0000364	H	-4.5217881	1.5683321	2.2530042
C	-0.7068459	-1.2052951	0.1757726	C	-7.3219015	1.8740956	-0.3899238
C	-2.8910982	0.0000009	0.0000286	H	-5.7947877	1.4366289	-1.8358325
C	-3.5605944	-1.2416792	0.2133658	C	-7.6222701	2.0577852	0.9583447
C	-2.8293074	-2.3665226	0.6601673	H	-6.8313385	2.0916174	2.9601301
C	-1.3884856	-2.3341385	0.7066569	H	-8.1035636	1.9564869	-1.1369025
C	-1.3884742	2.3341284	-0.7066119	H	-8.6363530	2.2887203	1.2648294
C	-2.8292957	2.3665153	-0.6601383	C	4.9956370	1.4575334	-0.1596421
C	-3.5605889	1.2416807	-0.2133287	C	6.0196320	1.5820472	0.7858970
C	-3.4785730	-3.5841903	1.0538309	C	5.3090373	1.6473002	-1.5114306
C	-2.7786341	-4.6273127	1.5908846	C	7.3219117	1.8741121	0.3898012
C	-1.3740421	-4.5315966	1.7645546	H	5.7948397	1.4366927	1.8357683
C	-0.7044663	-3.4263598	1.3176094	C	6.6103565	1.9440382	-1.9086638
C	-0.7044467	3.4263353	-1.3175803	H	4.5217255	1.5682462	-2.2530373
C	-1.3740167	4.5315634	-1.7645559	C	7.6222419	2.0577554	-0.9584821
C	-2.7786114	4.6272831	-1.5909065	H	8.1035945	1.9565322	1.1367550
C	-3.4785575	3.5841723	-1.0538396	H	6.8312544	2.0915138	-2.9602466
H	0.8319195	-5.3349997	-2.2499829	H	8.6363156	2.2886826	-1.2650034
H	3.3013528	-5.5232308	-1.9067231	C	4.9956417	-1.4575392	0.1596343
H	4.5515873	-3.6582992	-0.9515383	C	5.3090651	-1.6473862	1.5114063
H	-0.3674422	-3.3621409	-1.4428007	C	6.0196267	-1.5819672	-0.7859270
H	4.5516126	3.6582899	0.9515193	C	6.6103954	-1.9441261	1.9086016
H	3.3014029	5.5232349	1.9067137	H	4.5217622	-1.5683959	2.2530292
H	0.8319766	5.3350120	2.2500283	C	7.3219179	-1.8740319	-0.3898684
H	-0.3674076	3.3621517	1.4428870	H	5.7948176	-1.4365444	-1.8357853
H	-4.5516057	-3.6582818	0.9515941	C	7.6222700	-2.0577605	0.9583984
H	-3.3013904	-5.5232099	1.9068115	H	6.8313107	-2.0916669	2.9601716
H	-0.8319625	-5.3349806	2.2501109	H	8.1035924	-1.9563851	-1.1368383
H	0.3674163	-3.3621311	1.4429339	H	8.6363526	-2.2886877	1.2648903

Table S18. Optimized geometry for the triplet of **TBP3** at the UB3LYP/6-311G(d,p)

Atom	X	Y	Z	Atom	X	Y	Z
C	1.4498779	-4.5643213	-1.7193644	H	0.3023677	3.3748933	-1.4795674
C	2.8265284	-4.6699881	-1.4686340	H	-0.9223546	5.3637335	-2.2268919
C	3.5029891	-3.6200458	-0.8853633	H	-3.3653704	5.5667615	-1.7532717
C	2.8364331	-2.4167914	-0.5280951	H	-4.5683726	3.6995135	-0.7238527
C	1.4154926	-2.3781846	-0.6469992	C	-4.9669520	-1.4212776	-0.3561599
C	0.7623974	-3.4409864	-1.3028337	C	-6.0285751	-1.6853028	0.5182206
C	3.5522129	-1.2486450	-0.0947295	C	-5.2275236	-1.4057382	-1.7331549
C	2.8751195	-0.0000090	0.0000617	C	-7.3117571	-1.9168986	0.0311571
C	1.4144332	-0.0000051	0.0000636	H	-5.8502165	-1.6877319	1.5867703
C	0.6970746	-1.2148716	-0.1503692	C	-6.5096053	-1.6435692	-2.2216839
C	3.5522181	1.2486290	0.0947991	H	-4.4130386	-1.2128092	-2.4225055
C	2.8364467	2.4167952	0.5281165	C	-7.5572238	-1.8998785	-1.3404838
C	1.4155087	2.3781989	0.6470466	H	-8.1223433	-2.1067309	0.7259241
C	0.6970798	1.2148677	0.1504756	H	-6.6877270	-1.6325626	-3.2914968
C	3.5030193	3.6200560	0.8853286	H	-8.5566458	-2.0842467	-1.7183514
C	2.8265737	4.6700295	1.4685605	C	-4.9669591	1.4212911	0.3561813
C	1.4499235	4.5643867	1.7193061	C	-5.2275241	1.4061281	1.7331822
C	0.7624284	3.4410380	1.3028354	C	-6.0286144	1.6849450	-0.5182730
C	-0.6970221	1.2148699	-0.1503612	C	-6.5096234	1.6439923	2.2216474
C	-1.4143801	0.0000018	0.0000613	H	-4.4130168	1.2134835	2.4225859
C	-0.6970282	-1.2148730	0.1504681	C	-7.3118170	1.9165578	-0.0312715
C	-2.8750656	0.0000073	0.0000600	H	-5.8502659	1.6870546	-1.5868256
C	-3.5521698	-1.2486210	0.0948368	C	-7.5572721	1.8999348	1.3403764
C	-2.8363986	-2.4167877	0.5281448	H	-6.6877374	1.6332926	3.2914647
C	-1.4154575	-2.3782016	0.6470489	H	-8.1224275	2.1060944	-0.7260909
C	-1.4154371	2.3781889	-0.6469829	H	-8.5567096	2.0843209	1.7181943
C	-2.8363818	2.4167850	-0.5281147	C	4.9669493	1.4213192	-0.3563456
C	-3.5521646	1.2486341	-0.0947717	C	6.0286844	1.6852316	0.5179333
C	-3.5029858	-3.6200199	0.8854227	C	5.2273471	1.4059643	-1.7333756
C	-2.8265419	-4.6699871	1.4686676	C	7.3118043	1.9168914	0.0307363
C	-1.4498826	-4.5643593	1.7193717	H	5.8504638	1.6875197	1.5865061
C	-0.7623801	-3.4410317	1.3028558	C	6.5093632	1.6438715	-2.2220382
C	-0.7623344	3.4409970	-1.3027997	H	4.4127734	1.2131321	-2.4226480
C	-1.4498160	4.5643207	-1.7193596	C	7.5570946	1.9000622	-1.3409385
C	-2.8264788	4.6699671	-1.4686867	H	8.1224794	2.1066308	0.7254247
C	-3.5029458	3.6200198	-0.8854319	H	6.6873467	1.6330139	-3.2918756
H	0.9224229	-5.3637314	-2.2269077	H	8.5564676	2.0844848	-1.7189092
H	3.3654159	-5.5667958	-1.7531849	C	4.9669564	-1.4213398	0.3563704
H	4.5684060	-3.6995602	-0.7237357	C	5.2273542	-1.4063217	1.7334045
H	-0.3022986	-3.3748723	-1.4796329	C	6.0287149	-1.6849274	-0.5179787
H	4.5684378	3.6995469	0.7236930	C	6.5093874	-1.6442634	2.2220046
H	3.3654725	5.5668435	1.7530698	H	4.4127646	-1.2137394	2.4227278
H	0.9224806	5.3638245	2.2268184	C	7.3118542	-1.9166081	-0.0308425
H	-0.3022665	3.3749413	1.4796484	H	5.8504980	-1.6869324	-1.5865531
H	-4.5684137	-3.6994889	0.7238303	C	7.5571406	-1.9001322	1.3408372
H	-3.3654495	-5.5667803	1.7532260	H	6.6873687	-1.6336794	3.2918452
H	-0.9224409	-5.3637878	2.2268995	H	8.1225469	-2.1060889	-0.7255811
H	0.3023174	-3.3749415	1.4796536	H	8.5565282	-2.0845750	1.7187594

Table S19. Optimized geometry for the closed-shell singlet of **TBP4** at the B3LYP/6-311G(d,p)

Atom	X	Y	Z	Atom	X	Y	Z
C	-1.3131711	-4.4928999	1.8518877	H	7.0218416	2.6517756	-2.4385607
C	-2.7271432	-4.5771062	1.7545719	H	8.0430150	1.7156948	1.6057192
C	-3.4438080	-3.5403611	1.2297757	C	-5.0239523	1.4963324	-0.0619525
C	-2.8067135	-2.3387794	0.7657977	C	-5.9819250	1.4439147	-1.0908571
C	-1.3654252	-2.3161425	0.7518015	C	-5.4038225	1.9708129	1.2128458
C	-0.6590546	-3.4039129	1.3501610	C	-7.3095201	1.7747472	-0.8062904
C	-3.5629278	-1.2346607	0.3089123	C	-6.7394295	2.2934856	1.4524957
C	-2.9050947	-0.0000003	0.0000016	C	-7.7150991	2.1865754	0.4603781
C	-1.4435024	-0.0000009	-0.0000141	H	-8.0429569	1.7159830	-1.6057985
C	-0.7062123	-1.1971075	0.1874015	H	-7.0218905	2.6516638	2.4386003
C	-3.5629402	1.2346423	-0.3088780	C	-5.0239358	-1.4963529	0.0619906
C	-2.8067453	2.3387827	-0.7657653	C	-5.4037951	-1.9708359	-1.2128214
C	-1.3654603	2.3161436	-0.7518225	C	-5.9819192	-1.4439378	1.0908771
C	-0.7062220	1.1971106	-0.1874382	C	-6.7393963	-2.2934849	-1.4524941
C	-3.4438450	3.5403750	-1.2296854	C	-7.3095157	-1.7747722	0.8062930
C	-2.7271927	4.5771258	-1.7544988	C	-7.7150782	-2.1865803	-0.4603819
C	-1.3132306	4.4929057	-1.8518992	H	-7.0218245	-2.6516711	-2.4386077
C	-0.6591036	3.4039036	-1.3502140	H	-8.0429715	-1.7160218	1.6057796
C	0.7062135	1.1971107	0.1874298	C	5.6154555	-1.1099365	-2.5180869
C	1.4435008	0.0000091	-0.0000287	H	6.3422340	-0.4235329	-2.9574404
C	0.7062199	-1.1970958	-0.1874809	H	5.6067799	-2.0181396	-3.1309921
C	2.9050944	0.0000040	-0.0000235	H	4.6278392	-0.6599508	-2.5960876
C	3.5629329	-1.2346300	-0.3089392	C	4.3825622	-2.2158225	2.3011821
C	2.8067337	-2.3387501	-0.7658724	H	3.8049979	-3.1221458	2.0887710
C	1.3654496	-2.3161153	-0.7519059	H	4.8712255	-2.3540785	3.2677155
C	1.3654385	2.3161282	0.7518571	H	3.6644048	-1.3999600	2.3952500
C	2.8067255	2.3387634	0.7658257	C	9.1623778	-2.4981337	0.7556975
C	3.5629303	1.2346528	0.3089041	H	9.6853407	-1.6119948	1.1323478
C	3.4438358	-3.5403108	-1.2298599	H	9.2564923	-3.2788303	1.5146492
C	2.7271821	-4.5770484	-1.7547017	H	9.6901308	-2.8315889	-0.1410096
C	1.3132168	-4.4928425	-1.8520504	C	9.1624129	2.4980969	-0.7556052
C	0.6590889	-3.4038659	-1.3503067	H	9.6899299	2.8324248	0.1409210
C	0.6590817	3.4038805	1.3502661	H	9.6855996	1.6117053	-1.1313489
C	1.3132076	4.4928585	1.8519977	H	9.2565523	3.2781410	-1.5152172
C	2.7271764	4.5770754	1.7546370	C	5.6153829	1.1100169	2.5181029
C	3.4438287	3.5403413	1.2298031	H	6.3423327	0.4239097	2.9576355
H	-0.7543891	-5.2912287	2.3268421	H	5.6063499	2.0182953	3.1308968
H	-3.2409840	-5.4592220	2.1201223	H	4.6279028	0.6597295	2.5960636
H	-4.5214058	-3.6065518	1.1831892	C	4.3826362	2.2157978	-2.3012118
H	0.4177757	-3.3445257	1.4231624	H	3.8051367	3.1221889	-2.0888921
H	-4.5214394	3.6065912	-1.1830481	H	4.8713113	2.3539451	-3.2677574
H	-3.2410502	5.4592572	-2.1199892	H	3.6644173	1.3999866	-2.3952217
H	-0.7544691	5.2912295	-2.3268851	C	-5.6153989	-1.1101402	2.5181600
H	0.4177222	3.3444909	-1.4232643	H	-6.3416688	-0.4230064	2.9572202
H	4.5214315	-3.6065216	-1.1832489	H	-5.6076682	-2.0182253	3.1312514
H	3.2410419	-5.4591494	-2.1202600	H	-4.6274068	-0.6609930	2.5962728
H	0.7544450	-5.2911592	-2.3270368	C	-4.3826463	-2.2155843	-2.3012698
H	-0.4177404	-3.3444715	-1.4233231	H	-3.8049607	-3.1218473	-2.0889265
H	-0.4177462	3.3444896	1.4232987	H	-4.8713455	-2.3538634	-3.2677822
H	0.7544334	5.2911700	2.3269908	H	-3.6645942	-1.3996300	-2.3953438
H	3.2410257	5.4591900	2.1201775	C	-4.3826953	2.2155173	2.3013156
H	4.5214233	3.6065444	1.1831813	H	-3.8049982	3.1217855	2.0890044
C	5.0239350	-1.4963394	-0.0619705	H	-4.8714026	2.3537923	3.2678271
C	5.9819793	-1.4437798	-1.0908198	H	-3.6646591	1.3995537	2.3953946
C	5.4037428	-1.9709241	1.2127933	C	-5.6153686	1.1101777	-2.5181352
C	7.3095579	-1.7745707	-0.8061997	H	-6.3420446	0.4236751	-2.9575101
C	6.7393612	-2.2935506	1.4525080	H	-5.6068557	2.0183972	-3.1310220
C	7.7150760	-2.1864983	0.4604729	H	-4.6276852	0.6603427	-2.5961767
H	8.0430585	-1.7157127	-1.6056390	C	-9.1623970	2.4982639	0.7555592
H	7.0217526	-2.6518004	2.4386061	H	-9.2564998	3.2787491	1.5147253
C	5.0239363	1.4963474	0.0619689	H	-9.6900433	2.8320280	-0.1410996
C	5.4037821	1.9709136	-1.2127978	H	-9.6854754	1.6120572	1.1318883
C	5.9819523	1.4437952	1.0908360	C	-9.1623576	-2.4983026	-0.7556188
C	6.7394046	2.2935303	-1.4524740	H	-9.6906916	-2.8294583	0.1415883
C	7.3095478	1.7745682	0.8062485	H	-9.6847582	-1.6128365	-1.1346242
C	7.7151010	2.1864798	-0.4604125	H	-9.2564145	-3.2807246	-1.5128109

Table S20. Optimized geometry for the open-shell singlet of **TBP4** at the UB3LYP/6-311G(d,p)

Atom	X	Y	Z	Atom	X	Y	Z
C	-1.3131712	-4.4929002	1.8518878	H	7.0218421	2.6517757	-2.4385608
C	-2.7271434	-4.5771065	1.7545720	H	8.0430156	1.7156950	1.6057193
C	-3.4438083	-3.5403614	1.2297758	C	-5.0239527	1.4963325	-0.0619525
C	-2.8067137	-2.3387796	0.7657978	C	-5.9819254	1.4439148	-1.0908572
C	-1.3654252	-2.3161426	0.7518015	C	-5.4038229	1.9708130	1.2128459
C	-0.6590547	-3.4039132	1.3501611	C	-7.3095206	1.7747473	-0.8062905
C	-3.5629280	-1.2346608	0.3089123	C	-6.7394299	2.2934858	1.4524959
C	-2.9050949	-0.0000003	0.0000016	C	-7.7150996	2.1865756	0.4603781
C	-1.4435025	-0.0000009	-0.0000141	H	-8.0429574	1.7159832	-1.6057986
C	-0.7062124	-1.1971076	0.1874015	H	-7.0218910	2.6516640	2.4386005
C	-3.5629405	1.2346424	-0.3088780	C	-5.0239361	-1.4963530	0.0619906
C	-2.8067455	2.3387828	-0.7657654	C	-5.4037955	-1.9708360	-1.2128215
C	-1.3654604	2.3161438	-0.7518226	C	-5.9819196	-1.4439379	1.0908772
C	-0.7062221	1.1971107	-0.1874382	C	-6.7393968	-2.2934851	-1.4524942
C	-3.4438453	3.5403752	-1.2296855	C	-7.3095162	-1.7747723	0.8062930
C	-2.7271929	4.5771261	-1.7544989	C	-7.7150787	-2.1865804	-0.4603820
C	-1.3132307	4.4929061	-1.8518993	H	-7.0218250	-2.6516713	-2.4386079
C	-0.6591036	3.4039038	-1.3502141	H	-8.0429720	-1.7160219	1.6057797
C	0.7062135	1.1971108	0.1874298	C	5.6154559	-1.1099366	-2.5180871
C	1.4435009	0.0000091	-0.0000287	H	6.3422345	-0.4235329	-2.9574406
C	0.7062200	-1.1970959	-0.1874809	H	5.6067803	-2.0181397	-3.1309923
C	2.9050946	0.0000040	-0.0000235	H	4.6278396	-0.6599509	-2.5960878
C	3.5629332	-1.2346301	-0.3089393	C	4.3825625	-2.2158227	2.3011823
C	2.8067339	-2.3387503	-0.7658724	H	3.8049982	-3.1221460	2.0887712
C	1.3654497	-2.3161155	-0.7519059	H	4.8712259	-2.3540787	3.2677157
C	1.3654386	2.3161284	0.7518572	H	3.6644051	-1.3999601	2.3952502
C	2.8067258	2.3387636	0.7658257	C	9.1623785	-2.4981339	0.7556976
C	3.5629306	1.2346529	0.3089041	H	9.6853414	-1.6119950	1.1323478
C	3.4438360	-3.5403110	-1.2298600	H	9.2564930	-3.2788305	1.5146493
C	2.7271823	-4.5770487	-1.7547019	H	9.6901315	-2.8315891	-0.1410096
C	1.3132169	-4.4928428	-1.8520506	C	9.1624135	2.4980970	-0.7556053
C	0.6590890	-3.4038661	-1.3503068	H	9.6899306	2.8324250	0.1409210
C	0.6590817	3.4038807	1.3502662	H	9.6856003	1.6117055	-1.1313490
C	1.3132077	4.4928588	1.8519978	H	9.2565530	3.2781413	-1.5152173
C	2.7271766	4.5770757	1.7546371	C	5.6153833	1.1100170	2.5181031
C	3.4438290	3.5403415	1.2298032	H	6.3423332	0.4239097	2.9576357
H	-0.7543892	-5.2912290	2.3268423	H	5.6063503	2.0182955	3.1308970
H	-3.2409843	-5.4592223	2.1201225	H	4.6279031	0.6597295	2.5960638
H	-4.5214062	-3.6065521	1.1831893	C	4.3826365	2.2157980	-2.3012120
H	0.4177757	-3.3445260	1.4231625	H	3.8051370	3.1221891	-2.0888923
H	-4.5214397	3.6065915	-1.1830482	H	4.8713116	2.3539453	-3.2677577
H	-3.2410505	5.4592576	-2.1199893	H	3.6644175	1.3999867	-2.3952219
H	-0.7544691	5.2912298	-2.3268853	C	-5.6153993	-1.1101402	2.5181602
H	0.4177223	3.3444912	-1.4232644	H	-6.3416693	-0.4230065	2.9572204
H	4.5214318	-3.6065219	-1.1832490	H	-5.6076686	-2.0182254	3.1312517
H	3.2410421	-5.4591498	-2.1202602	H	-4.6274071	-0.6609930	2.5962730
H	0.7544451	-5.2911595	-2.3270369	C	-4.3826467	-2.2155845	-2.3012699
H	-0.4177405	-3.3444718	-1.4233232	H	-3.8049610	-3.1218475	-2.0889267
H	-0.4177462	3.3444899	1.4232988	H	-4.8713458	-2.3538635	-3.2677824
H	0.7544335	5.2911704	2.3269909	H	-3.6645945	-1.3996301	-2.3953440
H	3.2410259	5.4591904	2.1201776	C	-4.3826956	2.2155175	2.3013157
H	4.5214236	3.6065446	1.1831813	H	-3.8049985	3.1217857	2.0890045
C	5.0239354	-1.4963395	-0.0619705	H	-4.8714030	2.3537925	3.2678274
C	5.9819798	-1.4437799	-1.0908199	H	-3.6646594	1.3995538	2.3953948
C	5.4037432	-1.9709242	1.2127934	C	-5.6153690	1.1101778	-2.5181354
C	7.3095585	-1.7745709	-0.8061998	H	-6.3420451	0.4236751	-2.9575103
C	6.7393617	-2.2935508	1.4525081	H	-5.6068561	2.0183974	-3.1310223
C	7.7150766	-2.1864985	0.4604729	H	-4.6276856	0.6603427	-2.5961768
H	8.0430590	-1.7157128	-1.6056392	C	-9.1623977	2.4982641	0.7555592
H	7.0217531	-2.6518006	2.4386063	H	-9.2565005	3.2787493	1.5147254
C	5.0239366	1.4963475	0.0619689	H	-9.6900440	2.8320282	-0.1410996
C	5.4037824	1.9709137	-1.2127978	H	-9.6854761	1.6120573	1.1318884
C	5.9819528	1.4437953	1.0908360	C	-9.1623582	-2.4983028	-0.7556188
C	6.7394051	2.2935304	-1.4524741	H	-9.6906923	-2.8294586	0.1415883
C	7.3095484	1.7745683	0.8062486	H	-9.6847589	-1.6128366	-1.1346243
C	7.7151015	2.1864800	-0.4604125	H	-9.2564152	-3.2807249	-1.5128110

Table S21. Optimized geometry for the triplet of **TBP4** at the UB3LYP/6-311G(d,p)

Atom	X	Y	Z	Atom	X	Y	Z
C	-1.3725790	-4.5295745	1.8103957	H	6.9538663	2.4743055	-2.6985428
C	-2.7609621	-4.6324417	1.6328299	H	8.0532505	1.8713160	1.3883911
C	-3.4610726	-3.5901745	1.0646255	C	-5.0117335	1.4954299	0.0806822
C	-2.8095214	-2.3983464	0.6415260	C	-5.9878251	1.5361165	-0.9321975
C	-1.3869870	-2.3639273	0.6962763	C	-5.3654255	1.8708598	1.3960260
C	-0.7045978	-3.4163390	1.3407289	C	-7.3062716	1.8584012	-0.5991674
C	-3.5578997	-1.2482277	0.2077434	C	-6.6922384	2.1910212	1.6829250
C	-2.8940786	0.0000376	-0.0001191	C	-7.6855164	2.1746413	0.7024911
C	-1.4251720	0.0000188	-0.0001664	H	-8.0534007	1.8714260	-1.3880404
C	-0.6954790	-1.2057854	0.1619584	H	-6.9535443	2.4742545	2.6987885
C	-3.5578905	1.2483180	-0.2078627	C	-5.0117840	-1.4953389	-0.0805813
C	-2.8095108	2.3984763	-0.6415663	C	-5.3656760	-1.8708206	-1.3958654
C	-1.3869800	2.3640210	-0.6964362	C	-5.9876972	-1.5360723	0.9324549
C	-0.6954582	1.2058094	-0.1622877	C	-6.6925173	-2.1910448	-1.6825357
C	-3.4610476	3.5904052	-1.0644077	C	-7.3061912	-1.8584203	0.5996515
C	-2.7609475	4.6327309	-1.6325186	C	-7.6856383	-2.1746916	-0.7019339
C	-1.3725868	4.5298336	-1.8102343	H	-6.9539781	-2.4743166	-2.6983495
C	-0.7046068	3.4165047	-1.3407897	H	-8.0531825	-1.8714766	1.3886534
C	0.6954817	1.2057644	0.1620924	C	5.6543630	-1.3060473	-2.3884364
C	1.4251662	-0.0000188	-0.0002098	H	6.3585446	-0.6064986	-2.8434004
C	0.6954493	-1.2057863	-0.1624766	H	5.7167274	-2.2467255	-2.9461624
C	2.8940684	-0.0000382	-0.0002046	H	4.6480697	-0.9150121	-2.5252166
C	3.5578765	-1.2483089	-0.2080540	C	4.3238439	-2.0084994	2.4835160
C	2.8094970	-2.3984042	-0.6418907	H	3.7029662	-2.8946281	2.3127964
C	1.3869668	-2.3639221	-0.6967927	H	4.7968424	-2.1188002	3.4613379
C	1.3870244	2.3638605	0.6964548	H	3.6471570	-1.1536772	2.5260969
C	2.8095554	2.3983058	0.6415659	C	9.1230535	-2.4817821	1.0460261
C	3.5579019	1.2482099	0.2076893	H	9.6516728	-1.5773803	1.3672933
C	3.4610292	-3.5902954	-1.0648474	H	9.1930589	-3.2064639	1.8610840
C	2.7609299	-4.6325290	-1.6331253	H	9.6617185	-2.8859712	0.1856739
C	1.3725791	-4.5295724	-1.8109026	C	9.1231930	2.4818129	-1.0457343
C	0.7045994	-3.4162969	-1.3413307	H	9.6616615	2.8862612	-0.1853800
C	0.7046733	3.4162178	1.3410355	H	9.6519647	1.5773890	-1.3666883
C	1.3726768	4.5294476	1.8106833	H	9.1932714	3.2063086	-1.8609504
C	2.7610373	4.6323648	1.6329505	C	5.6540839	1.3060396	2.3882921
C	3.4611183	3.5901433	1.0646274	H	6.3582061	0.6065171	2.8433866
H	-0.8230649	-5.3212888	2.3065726	H	5.7163610	2.2467450	2.9459830
H	-3.2891479	-5.5195294	1.9641181	H	4.6477727	0.9150036	2.5249452
H	-4.5341173	-3.6657650	0.9612521	C	4.3241706	2.0084263	-2.4838130
H	0.3669619	-3.3482233	1.4671458	H	3.7033006	2.8945768	-2.3131752
H	-4.5340757	3.6660390	-0.9609087	H	4.7972789	2.1186999	-3.4615849
H	-3.2891271	5.5198972	-1.9636064	H	3.6474619	1.1536260	-2.5264560
H	-0.8230859	5.3216044	-2.3063356	C	-5.6539813	-1.3061784	2.3884589
H	0.3669403	3.3483735	-1.4673006	H	-6.3579456	-0.6064989	2.8435578
H	4.5340516	-3.6659617	-0.9613020	H	-5.7164656	-2.2468653	2.9461577
H	3.2891014	-5.5196660	-1.9643044	H	-4.6475827	-0.9153618	2.5250995
H	0.8230907	-5.3212586	-2.3071527	C	-4.3242871	-2.0083738	-2.4837335
H	-0.3669413	-3.3481184	-1.4678742	H	-3.7034220	-2.8945422	-2.3131690
H	-0.3668729	3.3480574	1.4675513	H	-4.7974367	-2.1185889	-3.4614922
H	0.8232051	5.3211197	2.3069740	H	-3.6475729	-1.1535766	-2.5263564
H	3.2892310	5.5194633	1.9641977	C	-4.3238594	2.0084100	2.4837234
H	4.5341493	3.6657725	0.9611306	H	-3.7029564	2.8945203	2.3130035
C	5.0117136	-1.4954395	0.0804815	H	-4.7968487	2.1187196	3.4615490
C	5.9878146	-1.5360637	-0.9323887	H	-3.6471986	1.1535661	2.5262949
C	5.3654043	-1.8709158	1.3958155	C	-5.6543592	1.3062120	-2.3882584
C	7.3062647	-1.8583449	-0.5993655	H	-6.3584228	0.6065556	-2.8432391
C	6.6922185	-2.1910728	1.6827078	H	-5.7169074	2.2469012	-2.9459441
C	7.6855036	-2.1746442	0.7022803	H	-4.6479978	0.9153625	-2.5250726
H	8.0533987	-1.8713095	-1.3882345	C	-9.1230656	2.4817824	1.0462397
H	6.9535229	-2.4743371	2.6985630	H	-9.1930666	3.2064774	1.8612865
C	5.0117703	1.4953141	-0.0807115	H	-9.6617340	2.8859584	0.1858837
C	5.3656067	1.8708142	-1.3959970	H	-9.6516838	1.5773861	1.3675235
C	5.9877392	1.5359878	0.9322824	C	-9.1232195	-2.4819321	-1.0454595
C	6.6924482	2.1910136	-1.6827246	H	-9.6619879	-2.8852122	-0.1847493
C	7.3062193	1.8583082	0.5994254	H	-9.6516781	-1.5777605	-1.3676357
C	7.6856117	2.1746105	-0.7021763	H	-9.1932969	-3.2073875	-1.8598273

Table S22. Optimized geometry for the closed-shell singlet of **TBP5** at the B3LYP/6-311G(d,p)

Atom	X	Y	Z	Atom	X	Y	Z
C	1.2576149	4.3542838	1.9980413	C	5.7773053	-1.1499542	-1.6112651
C	2.6739943	4.3885494	2.0474560	C	5.7055195	-1.9282784	0.6968164
C	3.4064266	3.3578679	1.5289964	C	7.1430779	-1.4304415	-1.6396384
C	2.7806222	2.2248981	0.9214833	C	7.0756311	-2.1902229	0.6274273
C	1.3478077	2.2268967	0.8076843	C	7.8123384	-1.9591041	-0.5336084
C	0.6207951	3.3091270	1.3896755	H	7.6977128	-1.2376000	-2.5536019
C	3.5465890	1.1277231	0.4265993	H	7.5759861	-2.5950359	1.5022913
C	2.8871467	-0.0755898	0.0022005	C	-9.2809613	-2.3032705	0.6088154
C	1.4338163	-0.0822146	0.0121263	H	-9.8384396	-1.5605718	1.1855031
C	0.6996322	1.1177800	0.2024723	H	-9.7284242	-2.3657616	-0.3855880
C	3.5580705	-1.2547352	-0.4200132	H	-9.4318375	-3.2721606	1.0975181
C	2.8099920	-2.3701944	-0.8659811	C	-5.1047363	-0.5688643	2.8320582
C	1.3714212	-2.3894445	-0.7724287	H	-5.8191600	-0.4512501	3.6489502
C	0.7062446	-1.2826498	-0.1883046	H	-4.2877212	-1.2039048	3.1856109
C	3.4575241	-3.5278942	-1.4154709	H	-4.6774167	0.4142593	2.6145135
C	2.7443923	-4.5780459	-1.9187401	C	-4.9530176	-2.2071867	-1.9760118
C	1.3255756	-4.5446152	-1.9164902	H	-4.1440919	-2.9262389	-1.8169668
C	0.6672405	-3.4894437	-1.3512605	H	-5.6204930	-2.6133051	-2.7382489
C	-0.7062502	-1.2826517	0.1882855	H	-4.4984825	-1.2965538	-2.3765223
C	-1.4338109	-0.0821987	-0.0120880	C	4.9529237	-2.2071445	1.9760913
C	-0.6996153	1.1178024	-0.2023510	H	4.1439407	-2.9261285	1.8170337
C	-2.8871408	-0.0755650	-0.0021751	H	5.6203542	-2.6133182	2.7383380
C	-3.5465715	1.1277657	-0.4265429	H	4.4984584	-1.2964747	2.3765972
C	-2.7805906	2.2249842	-0.9213116	C	5.1048192	-0.5690062	-2.8320363
C	-1.3477782	2.2269744	-0.8074775	H	5.8192684	-0.4514359	-3.6489121
C	-1.3714348	-2.3894607	0.7723728	H	4.2878006	-1.2040409	-3.1855902
C	-2.8100038	-2.3701902	0.8659544	H	4.6775160	0.4141341	-2.6145355
C	-3.5580748	-1.2547145	0.4200157	C	9.2809500	-2.3033775	-0.6085970
C	-3.4063813	3.3580050	-1.5287468	H	9.4318684	-3.2720734	-1.0976698
C	-2.6739382	4.3887330	-2.0470976	H	9.8385258	-1.5604630	-1.1849156
C	-1.2575600	4.3544630	-1.9976536	H	9.7282777	-2.3662703	0.3858408
C	-0.6207539	3.3092546	-1.3893629	C	4.9537638	1.3186696	0.3989906
C	-0.6672606	-3.4894893	1.3511573	C	6.1176073	1.6803101	0.4384799
C	-1.3256009	-4.5446607	1.9163807	C	-4.9537569	1.3186736	-0.3990378
C	-2.7444184	-4.5780608	1.9186756	C	-6.1176077	1.6802795	-0.4386373
C	-3.4575433	-3.5278849	1.4154477	Si	-7.8432343	2.3168160	-0.5236247
H	0.6796885	5.1484030	2.4566786	Si	7.8432207	2.3169081	0.5232753
H	3.1771308	5.2240001	2.5212480	C	8.8349022	1.2911558	1.7544923
H	4.4844438	3.3723523	1.5963418	H	9.8666392	1.6520446	1.8164949
H	-0.4592301	3.2787026	1.3719864	H	8.3974605	1.3488171	2.7550348
H	4.5375746	-3.5494980	-1.4491341	H	8.8559800	0.2398246	1.4591397
H	3.2630310	-5.4299406	-2.3440667	C	8.6247621	2.2405017	-1.1902414
H	0.7644335	-5.3520814	-2.3728616	H	8.0628344	2.8469336	-1.9058432
H	-0.4130101	-3.4661803	-1.3629601	H	9.6523548	2.6171195	-1.1631668
H	-4.4843966	3.3724954	-1.5961175	H	8.6464247	1.2144865	-1.5646547
H	-3.1770645	5.2242255	-2.5208266	C	7.7647896	4.1110502	1.1080091
H	-0.6796226	5.1486208	-2.4562104	H	7.1679798	4.7254261	0.4283067
H	0.4592703	3.2788298	-1.3716572	H	7.3222825	4.1858493	2.1054037
H	0.4129906	-3.4662475	1.3628300	H	8.7690457	4.5442098	1.1567360
H	-0.7644614	-5.3521485	2.3727172	C	-8.6249022	2.2404920	1.1898387
H	-3.2630620	-5.4299510	2.3440054	H	-8.0630278	2.8469584	1.9054527
H	-4.5375934	-3.5494647	1.4491472	H	-9.6524942	2.6171066	1.1626709
C	-5.0506845	-1.4049717	0.4321776	H	-8.6465935	1.2144940	1.5642990
C	-5.7055713	-1.9282625	-0.6967249	C	-8.8347969	1.2909710	-1.7548576
C	-5.7772693	-1.1498434	1.6113272	H	-9.8665323	1.6518457	-1.8169673
C	-7.0756823	-2.1901833	-0.6272826	H	-8.3972724	1.3485785	-2.7553672
C	-7.1430489	-1.4303052	1.6397536	H	-8.8558852	0.2396583	-1.4594427
C	-7.8123504	-1.9590064	0.5337697	C	-7.7648076	4.1109248	-1.1084631
H	-7.5760718	-2.5950178	-1.5021172	H	-7.1680811	4.7253630	-0.4287436
H	-7.6976528	-1.2374153	2.5537256	H	-7.3222112	4.1856752	-2.1058220
C	5.0506782	-1.4050209	-0.4321250	H	-8.7690733	4.5440483	-1.1573088

Table S23. Optimized geometry for the open-shell singlet of **TBP5** at the UB3LYP/6-311G(d,p)

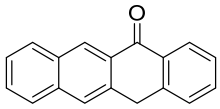
Atom	X	Y	Z	Atom	X	Y	Z
C	1.2592814	4.3556928	1.9979652	C	5.7825489	-1.1721951	-1.5834626
C	2.6732140	4.3944601	2.0389066	C	5.7017737	-1.9176398	0.7351958
C	3.4056607	3.3641409	1.5144783	C	7.1483392	-1.4530408	-1.6025222
C	2.7789770	2.2325759	0.9105664	C	7.0721716	-2.1805435	0.6748447
C	1.3487640	2.2310899	0.8036421	C	7.8133321	-1.9659386	-0.4864833
C	0.6221469	3.3065797	1.3916976	H	7.7065350	-1.2732653	-2.5169854
C	3.5457476	1.1296527	0.4173889	H	7.5691090	-2.5729196	1.5572860
C	2.8855618	-0.0787881	0.0075156	C	-9.2821864	-2.3113173	0.5510260
C	1.4310664	-0.0860259	0.0159450	H	-9.8420267	-1.5766296	1.1356314
C	0.6971739	1.1157327	0.2003600	H	-9.7256921	-2.3602136	-0.4459061
C	3.5588548	-1.2607259	-0.3988952	H	-9.4348481	-3.2868189	1.0258165
C	2.8130132	-2.3840715	-0.8408443	C	-5.1149298	-0.6075210	2.8144946
C	1.3765556	-2.4006737	-0.7604964	H	-5.8319294	-0.5034932	3.6309742
C	0.7053712	-1.2878101	-0.1823822	H	-4.2973074	-1.2455089	3.1612008
C	3.4643480	-3.5421396	-1.3793734	H	-4.6896590	0.3797596	2.6122186
C	2.7542163	-4.5935232	-1.8893055	C	-4.9441060	-2.1786412	-2.0152359
C	1.3380173	-4.5557934	-1.9038738	H	-4.1342247	-2.8979839	-1.8623961
C	0.6762207	-3.4957434	-1.3468898	H	-5.6079781	-2.5764710	-2.7849524
C	-0.7053789	-1.2878114	0.1823784	H	-4.4900215	-1.2621047	-2.4025646
C	-1.4310676	-0.0860165	-0.0159115	C	4.9440563	-2.1787829	2.0152099
C	-0.6971672	1.1157443	-0.2002822	H	4.1341714	-2.8981098	1.8623152
C	-2.8855634	-0.0787714	-0.0074864	H	5.6079137	-2.5766642	2.7849124
C	-3.5457410	1.1296829	-0.4173365	H	4.4899738	-1.2622662	2.4025873
C	-2.7789613	2.2326254	-0.9104557	C	5.1149673	-0.6074063	-2.8144348
C	-1.3487493	2.2311301	-0.8035198	H	5.8319840	-0.5033250	-3.6308926
C	-1.3765679	-2.4006870	0.7604628	H	4.2973566	-1.2453783	-3.1611972
C	-2.8130249	-2.3840772	0.8408163	H	4.6896860	0.3798594	-2.6121085
C	-3.5588618	-1.2607172	0.3988962	C	9.2821888	-2.3112958	-0.5509798
C	-3.4056359	3.3642205	-1.5143216	H	9.4349071	-3.2865735	-1.0262102
C	-2.6731811	4.3945614	-2.0386957	H	9.8420976	-1.5763351	-1.1351794
C	-1.2592489	4.3557846	-1.9977499	H	9.7255784	-2.3606505	0.4459802
C	-0.6221232	3.3066412	-1.3915255	C	4.9509379	1.3235584	0.3812557
C	-0.6762377	-3.4957746	1.3468284	C	6.1138951	1.6904700	0.4103026
C	-1.3380390	-4.5558320	1.9037927	C	-4.9509333	1.3235847	-0.3812390
C	-2.7542384	-4.5935501	1.8892338	C	-6.1138897	1.6904952	-0.4103403
C	-3.4643654	-3.5421503	1.3793284	Si	-7.8378218	2.3336854	-0.4787195
H	0.6804868	5.1476431	2.4592387	Si	7.8378228	2.3336839	0.4785683
H	3.1776256	5.2306004	2.5100890	C	8.8373281	1.3293605	1.7210657
H	4.4840256	3.3809907	1.5761419	H	9.8681929	1.6942172	1.7736267
H	-0.4579308	3.2733166	1.3796989	H	8.4035776	1.4006998	2.7223351
H	4.5446678	-3.5659224	-1.4013522	H	8.8603880	0.2737794	1.4414557
H	3.2763196	-5.4472898	-2.3065268	C	8.6129040	2.2341044	-1.2367371
H	0.7787732	-5.3623026	-2.3642259	H	8.0460116	2.8276520	-1.9591922
H	-0.4038142	-3.4701708	-1.3701405	H	9.6391610	2.6149157	-1.2193210
H	-4.4840005	3.3810779	-1.5759916	H	8.6371945	1.2026968	-1.5958825
H	-3.1775861	5.2307272	-2.5098398	C	7.7561618	4.1361109	1.0366633
H	-0.6804478	5.1477519	-2.4589860	H	7.1543854	4.7383421	0.3505182
H	0.4579541	3.2733729	-1.3795203	H	7.3177960	4.2245220	2.0347707
H	0.4037975	-3.4702096	1.3700747	H	8.7592357	4.5730871	1.0744716
H	-0.7787982	-5.3623550	2.3641245	C	-8.6130144	2.2341025	1.2365352
H	-3.2763456	-5.4473205	2.3064423	H	-8.0461761	2.8276574	1.9590269
H	-4.5446855	-3.5659231	1.4013166	H	-9.6392742	2.6149035	1.2190504
C	-5.0513538	-1.4104162	0.4035912	H	-8.6373186	1.2026951	1.5956798
C	-5.7018019	-1.9175691	-0.7351946	C	-8.8372317	1.3293414	-1.7212771
C	-5.7825340	-1.1722413	1.5835032	H	-9.8680892	1.6942062	-1.7739299
C	-7.0721968	-2.1804758	-0.6748326	H	-8.4033992	1.4006542	-2.7225128
C	-7.1483253	-1.4530904	1.6025733	H	-8.8603223	0.2737670	-1.4416448
C	-7.8133366	-1.9659328	0.4865225	C	-7.7561512	4.1361107	-1.0368186
H	-7.5691511	-2.5728033	-1.5572865	H	-7.1544271	4.7383543	-0.3506381
H	-7.7065049	-1.2733615	2.5170552	H	-7.3177231	4.2245221	-2.0348987
C	5.0513463	-1.4104312	-0.4035745	H	-8.7592287	4.5730725	-1.0746925

Table S24. Optimized geometry for the triplet of **TBP5** at the UB3LYP/6-311G(d,p)

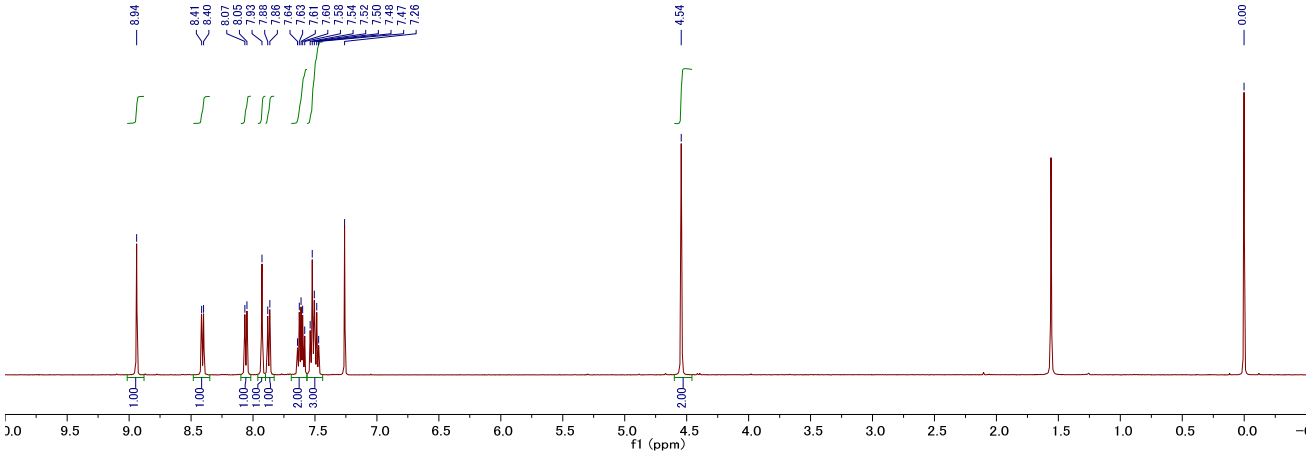
Atom	X	Y	Z	Atom	X	Y	Z
C	1.2557702	4.3439867	2.0135368	C	5.8520221	-1.3721741	-1.2874201
C	2.6561779	4.4097074	2.0109526	C	5.6439897	-1.7936266	1.1040697
C	3.3916217	3.3862220	1.4505777	C	7.2157383	-1.6467363	-1.1938850
C	2.7627650	2.2635414	0.8601646	C	7.0154168	-2.0549710	1.1540876
C	1.3454121	2.2379738	0.7934604	C	7.8184428	-1.9987587	0.0161737
C	0.6189397	3.2740743	1.4156436	H	7.8233772	-1.5901270	-2.0926211
C	3.5347091	1.1368229	0.3665427	H	7.4628104	-2.3201867	2.1075317
C	2.8772668	-0.1086728	0.0664346	C	-9.2872478	-2.3444589	-0.0796498
C	1.4166033	-0.1222431	0.0550075	H	-9.8771326	-1.7130328	0.5897523
C	0.6819900	1.0880146	0.1972318	H	-9.6824101	-2.2285337	-1.0913172
C	3.5671101	-1.3074972	-0.2148000	H	-9.4582596	-3.3839272	0.2215175
C	2.8422775	-2.4780671	-0.6295534	C	-5.2570043	-0.9713729	2.6156500
C	1.4172004	-2.4772971	-0.6619364	H	-6.0211459	-0.9606065	3.3951156
C	0.7038672	-1.3298938	-0.1396723	H	-4.4640891	-1.6555761	2.9295490
C	3.5212356	-3.6495063	-1.0673246	H	-4.8178954	0.0288426	2.5604638
C	2.8414414	-4.7119877	-1.6190221	C	-4.8188648	-1.8821302	-2.3664658
C	1.4466103	-4.6461955	-1.7731306	H	-3.9860385	-2.5821877	-2.2538903
C	0.7557618	-3.5518166	-1.2976886	H	-5.4303098	-2.2164383	-3.2065980
C	-0.7039116	-1.3298532	0.1399636	H	-4.3879032	-0.9116517	-2.6290275
C	-1.4166053	-0.1221822	-0.0547741	C	4.8191900	-1.8822942	2.3663248
C	-0.6819404	1.0880482	-0.1969685	H	3.9862823	-2.5822596	2.2537992
C	-2.8772610	-0.1085949	-0.0663042	H	5.4307207	-2.2167370	3.2063420
C	-3.5346651	1.1369167	-0.3664106	H	4.3883667	-0.9117931	2.6290346
C	-2.7626699	2.2636693	-0.8598710	C	5.2566251	-0.9713200	-2.6158116
C	-1.3453189	2.2380636	-0.7931311	H	6.0205416	-0.9610938	-3.3955051
C	-1.4172987	-2.4771951	0.6622651	H	4.4632521	-1.6551522	-2.9293504
C	-2.8423711	-2.4779701	0.6297299	H	4.8180664	0.0291442	-2.5606736
C	-3.5671519	-1.3074226	0.2148588	C	9.2872880	-2.3443396	0.0788837
C	-3.3914818	3.3864321	-1.4501873	H	9.4582923	-3.3838296	-0.2222139
C	-2.6560013	4.4099511	-2.0104431	H	9.8770327	-1.7129496	-0.5906747
C	-1.2555926	4.3441873	-2.0130147	H	9.6826138	-2.2283025	1.0904745
C	-0.6188068	3.2742026	-1.4152110	C	4.9200598	1.3644937	0.2313171
C	-0.7559076	-3.5516510	1.2981814	C	6.0683123	1.7736280	0.1398808
C	-1.4467937	-4.6459982	1.7736310	C	-4.9200421	1.3645510	-0.2313883
C	-2.8416082	-4.7118313	1.6193361	C	-6.0683214	1.7736502	-0.1401465
C	-3.5213582	-3.6494100	1.0674767	Si	-7.7672764	2.4700871	-0.0063158
H	0.6713427	5.1228086	2.4897616	Si	7.7672717	2.4700521	0.0060696
H	3.1640463	5.2497604	2.4712147	C	8.8672636	1.7053366	1.3318441
H	4.4714724	3.4175581	1.4821801	H	9.8847360	2.1043455	1.2672130
H	-0.4608019	3.2228905	1.4332539	H	8.4840624	1.9215315	2.3329124
H	4.5986486	-3.6884770	-0.9896243	H	8.9163847	0.6198901	1.2203915
H	3.3873316	-5.5847866	-1.9591207	C	8.4557446	2.1157073	-1.7126544
H	0.9114896	-5.4521009	-2.2621816	H	7.8278421	2.5624541	-2.4883148
H	-0.3175180	-3.5114859	-1.4176923	H	9.4642725	2.5287517	-1.8165602
H	-4.4713301	3.4178024	-1.4818063	H	8.5071663	1.0406537	-1.8999398
H	-3.1638355	5.2500667	-2.4706288	C	7.6484883	4.3354018	0.2736589
H	-0.6711355	5.1230327	-2.4891649	H	6.9872314	4.8010949	-0.4620571
H	0.4609327	3.2229858	-1.4328135	H	7.2615939	4.5714847	1.2689909
H	0.3173610	-3.5112771	1.4182846	H	8.6349124	4.8012186	0.1812540
H	-0.9117330	-5.4518518	2.2628327	C	-8.4555822	2.1154584	1.7124109
H	-3.3875168	-5.5846257	1.9594170	H	-7.8275056	2.5619822	2.4880620
H	-4.5987587	-3.6884181	0.9896205	H	-9.4641043	2.5283989	1.8166815
C	-5.0565418	-1.4513476	0.1270214	H	-8.5068705	1.0403368	1.8993794
C	-5.6438334	-1.7935148	-1.1043182	C	-8.8673909	1.7056285	-1.3321419
C	-5.8522208	-1.3721705	1.2871568	H	-9.8848044	2.1047693	-1.2672563
C	-7.0152462	-2.0549203	-1.1545331	H	-8.4843202	1.9220613	-2.3332069
C	-7.2159077	-1.6467914	1.1934275	H	-8.9166625	0.6201659	-1.2209692
C	-7.8184298	-1.9988040	-0.0167286	C	-7.6484941	4.3354247	-0.2739822
H	-7.4624962	-2.3201079	-2.1080521	H	-6.9871383	4.8012402	0.4615644
H	-7.8236707	-1.5902496	2.0920847	H	-7.2617377	4.5713441	-1.2694100
C	5.0565155	-1.4514198	-0.1271721	H	-8.6349060	4.8012574	-0.1815283

Data S1. NMR spectra

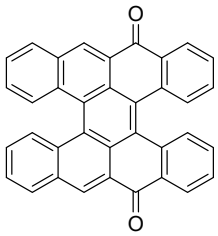
Compound 1



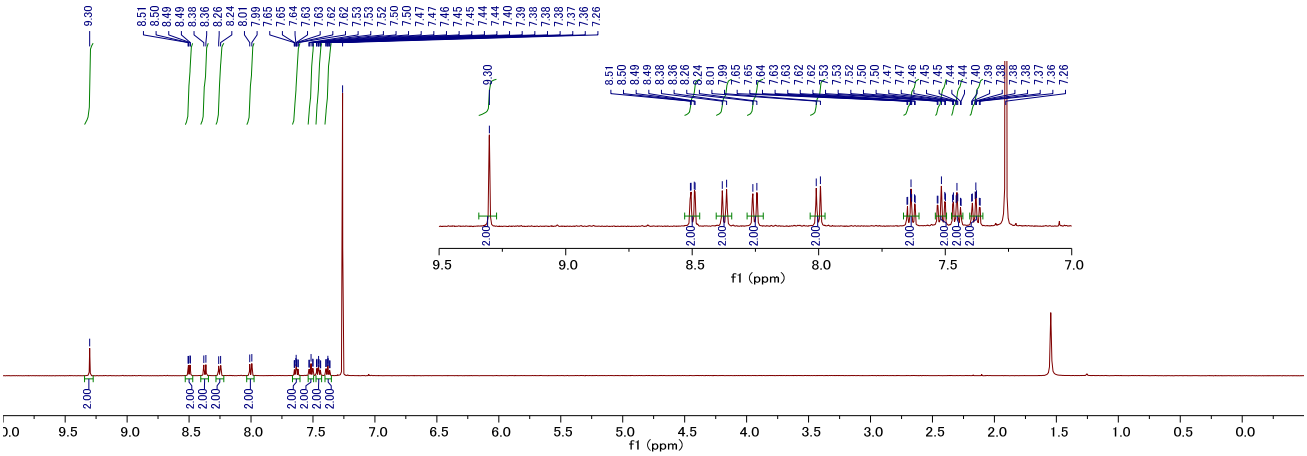
^{1}H-NMR spectrum (500 MHz, $CDCl_3$, 300 K)



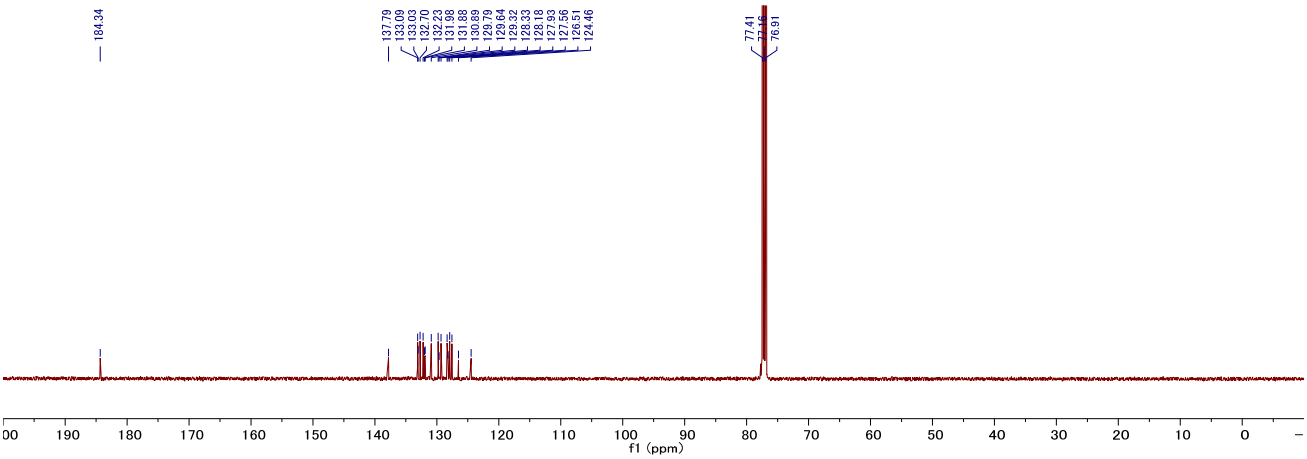
Compound **4**



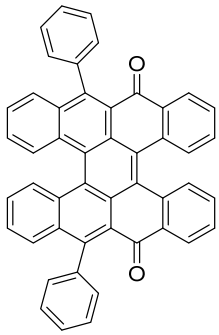
^{1}H-NMR spectrum (500 MHz, $CDCl_3$, 300 K)



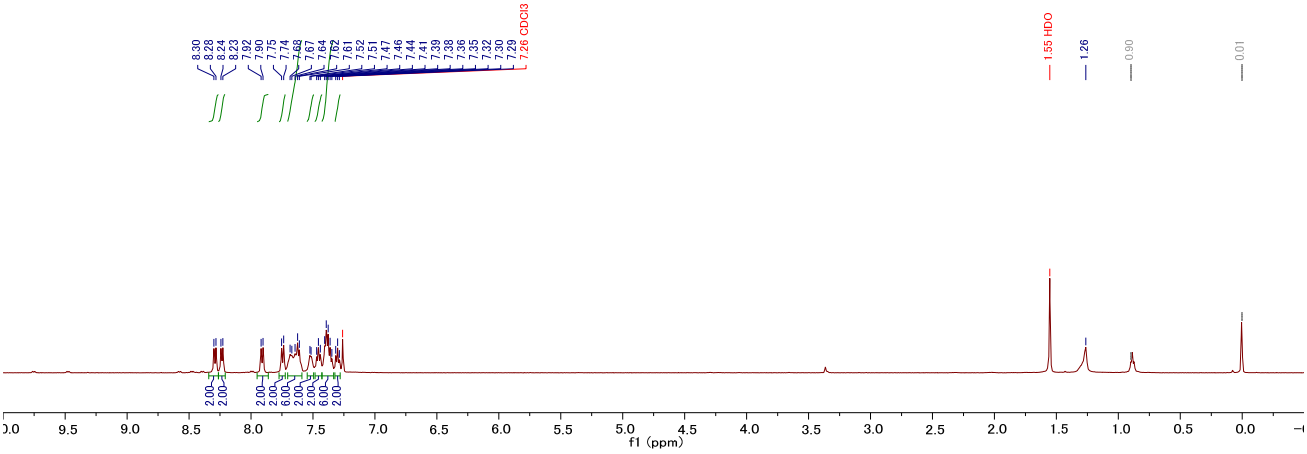
^{13}C-NMR spectra (125 MHz, $CDCl_3$, 300 K)



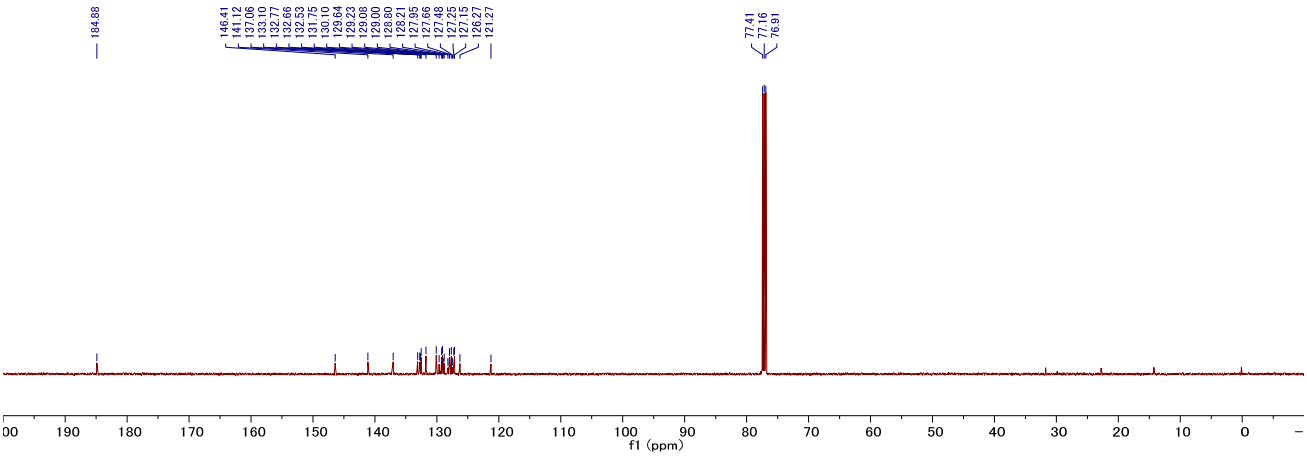
Compound **5a**



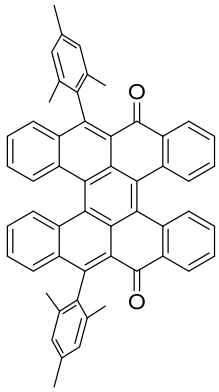
^{1}H-NMR spectrum (500 MHz, $CDCl_3$, 300 K)



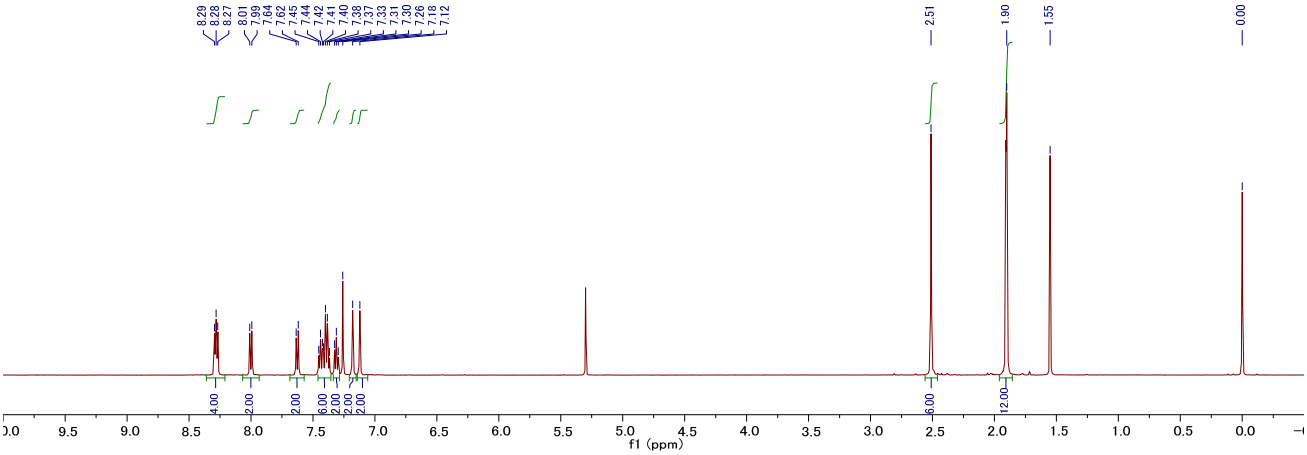
^{13}C-NMR spectra (125 MHz, $CDCl_3$, 300 K)



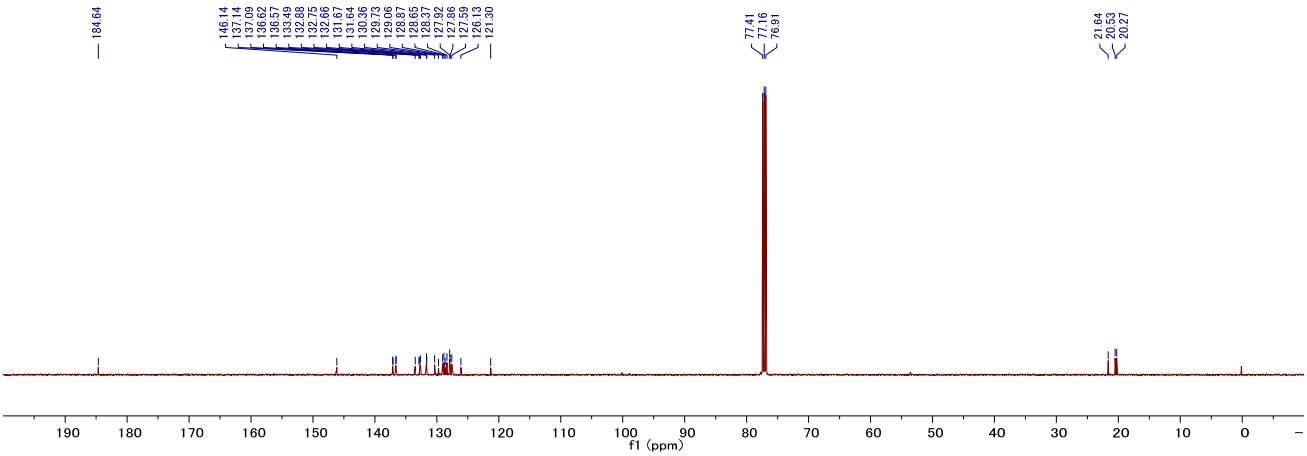
Compound **5b**



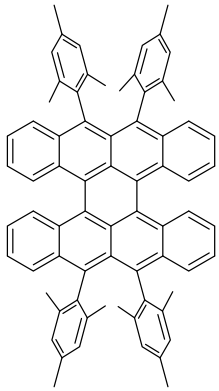
^{1}H-NMR spectrum (500 MHz, $CDCl_3$, 300 K)



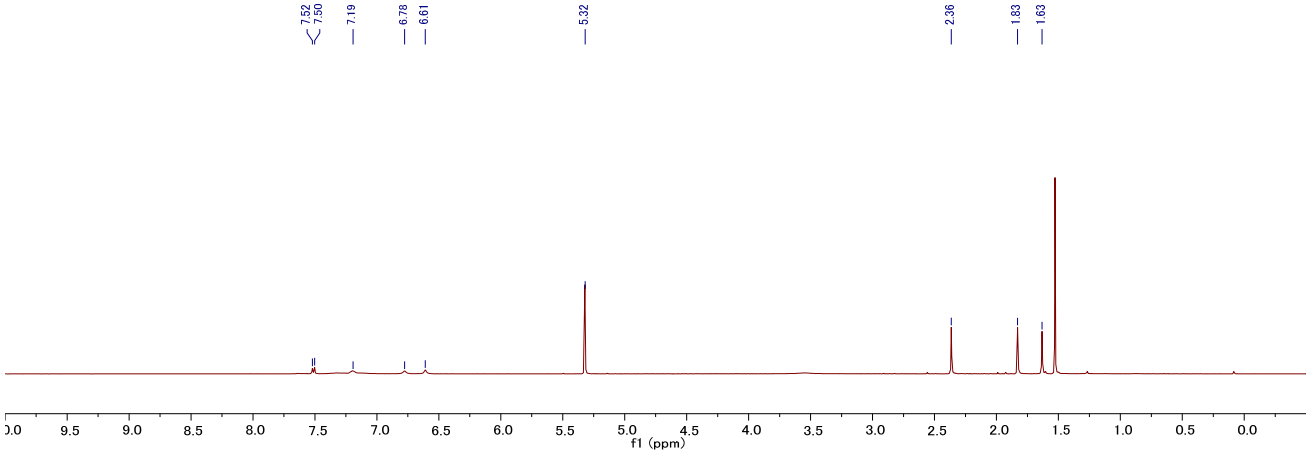
^{13}C-NMR spectra (125 MHz, $CDCl_3$, 300 K)



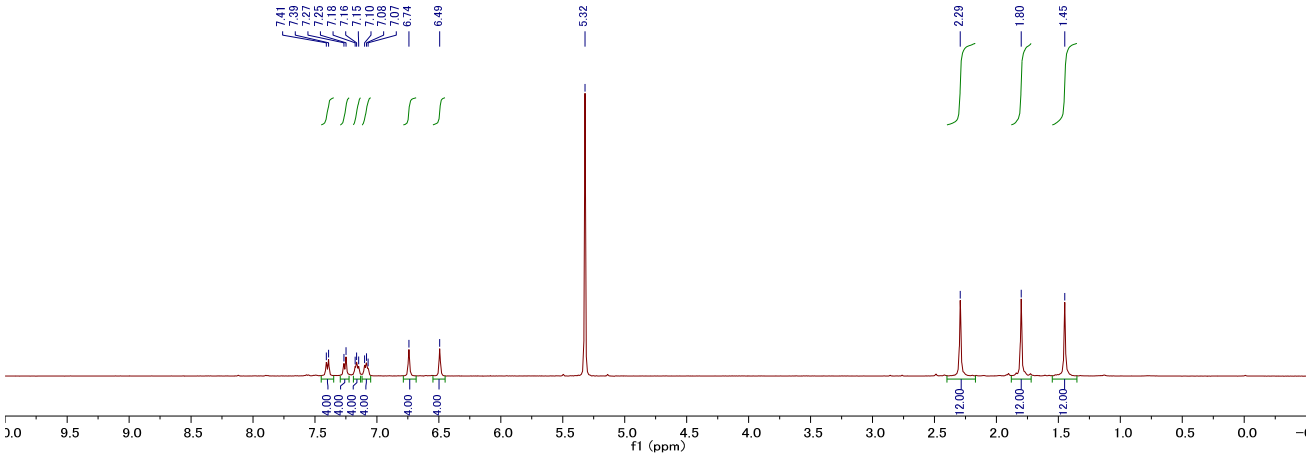
TBP4



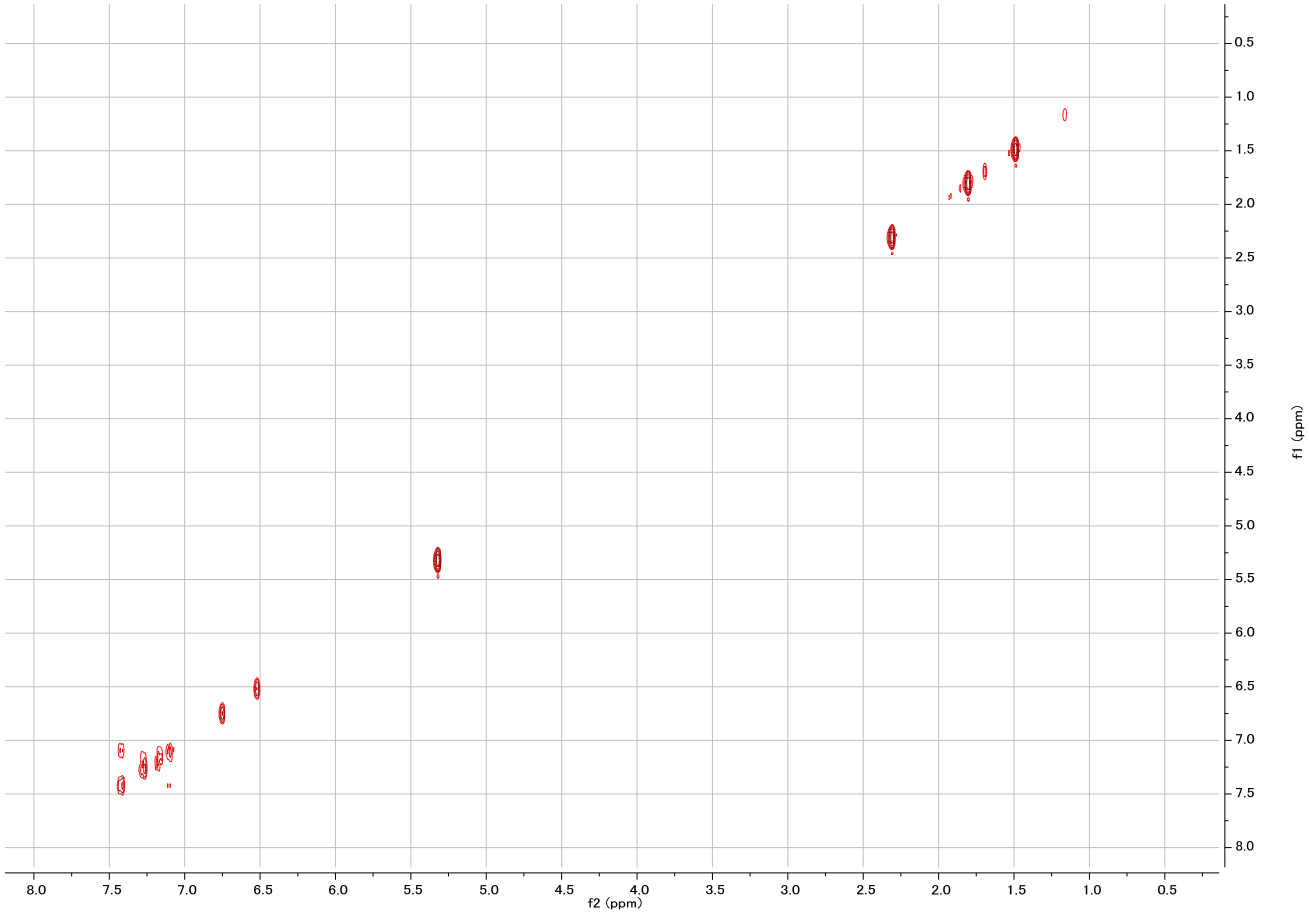
^{1}H-NMR spectrum (500 MHz, CD_2Cl_2, 298 K)



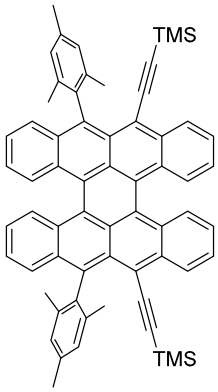
^{1}H-NMR spectrum (500 MHz, CD_2Cl_2, 193 K)



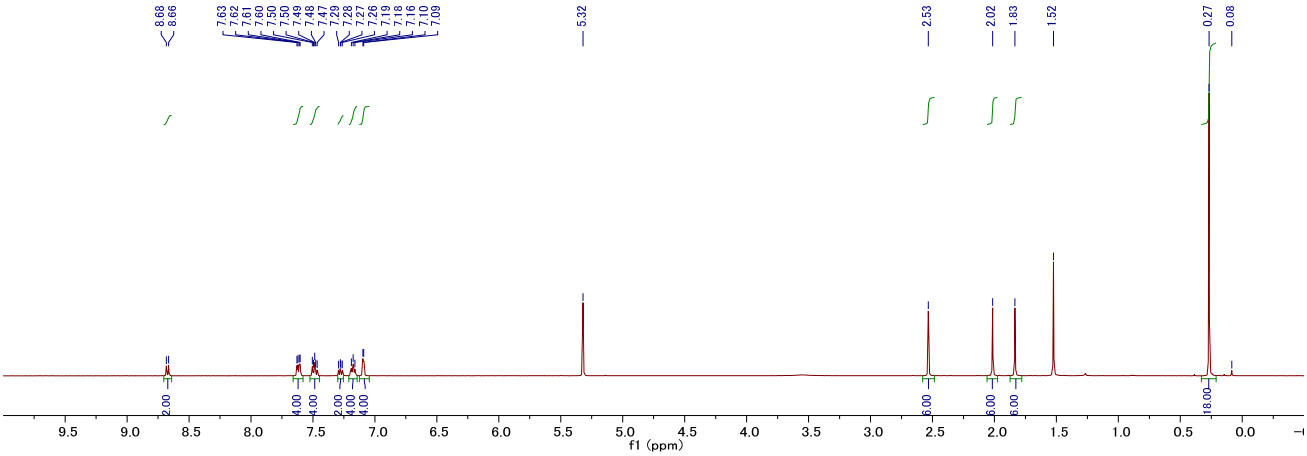
2D ^{1}H-^{1}H COSY NMR spectrum (500 MHz, CD_2Cl_2, 213 K)



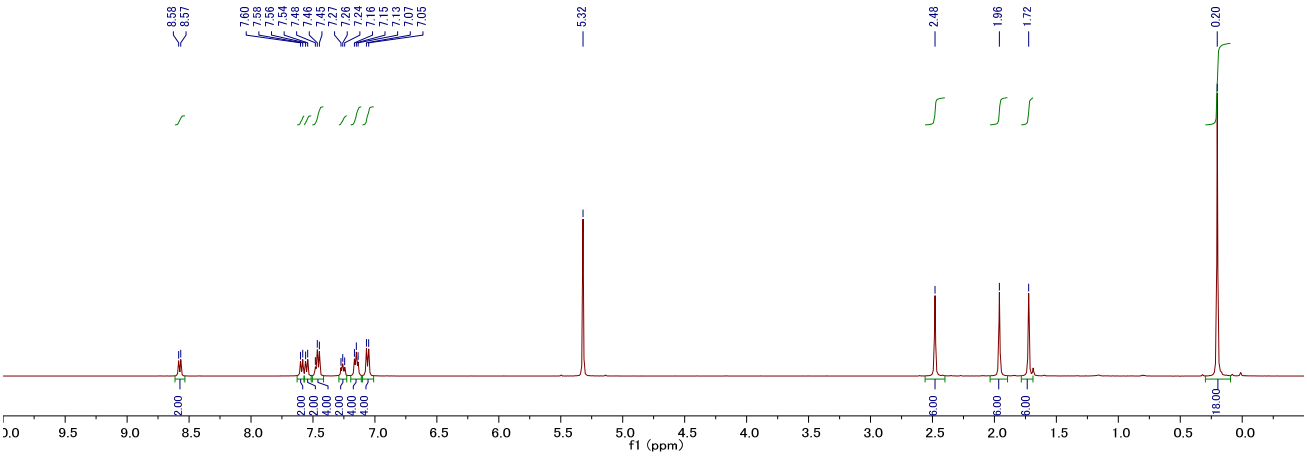
TBP5



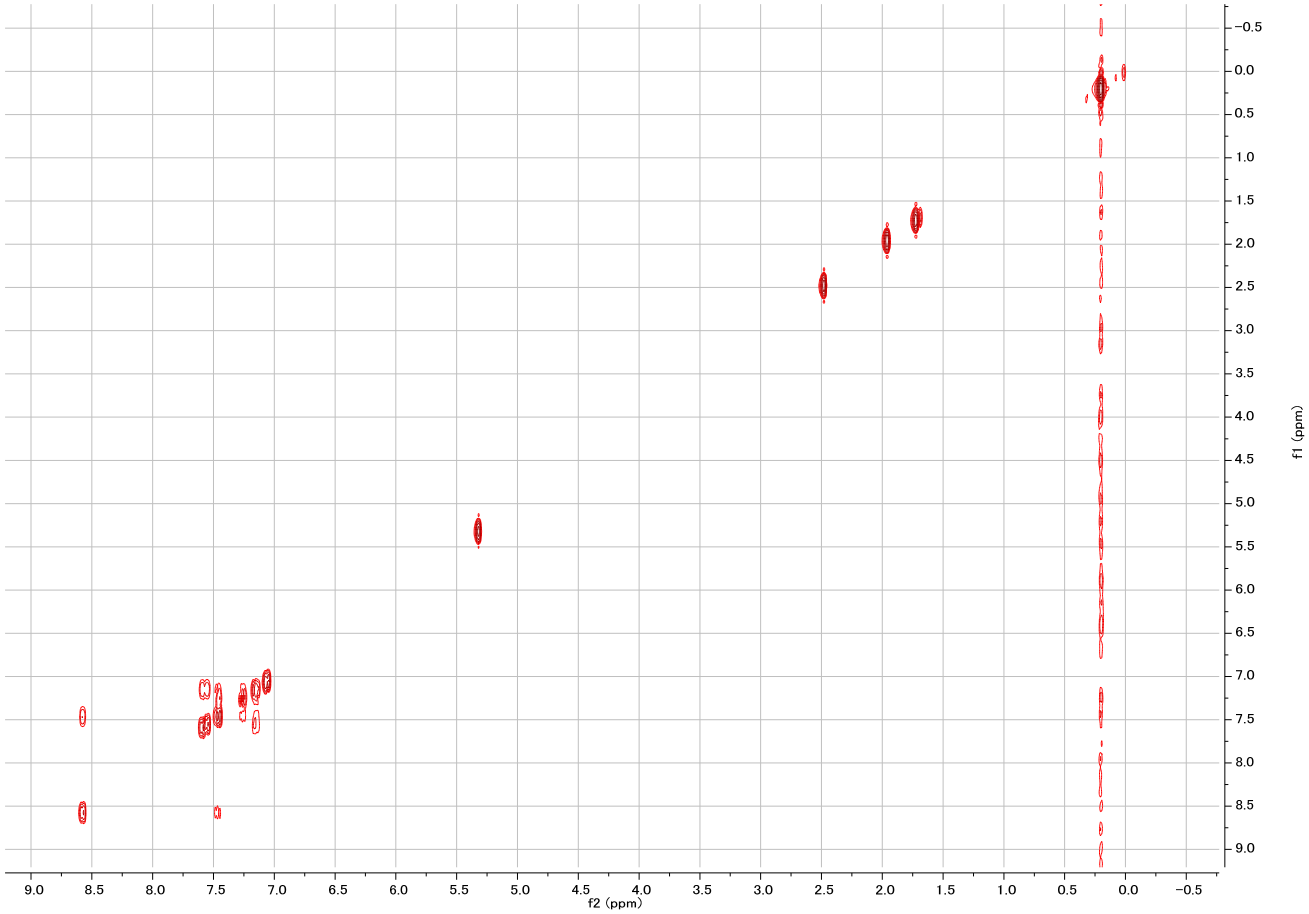
^{1}H-NMR spectrum (500 MHz, CD_2Cl_2, 298 K)



^{1}H-NMR spectrum (500 MHz, CD_2Cl_2, 213 K)



2D ^{1}H-^{1}H COSY NMR spectrum (500 MHz, CD_2Cl_2, 213 K)



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