Supporting Information

Through-Space π-Delocalization in a Conjugated Macrocycle Consisting of [2.2]Paracyclophane

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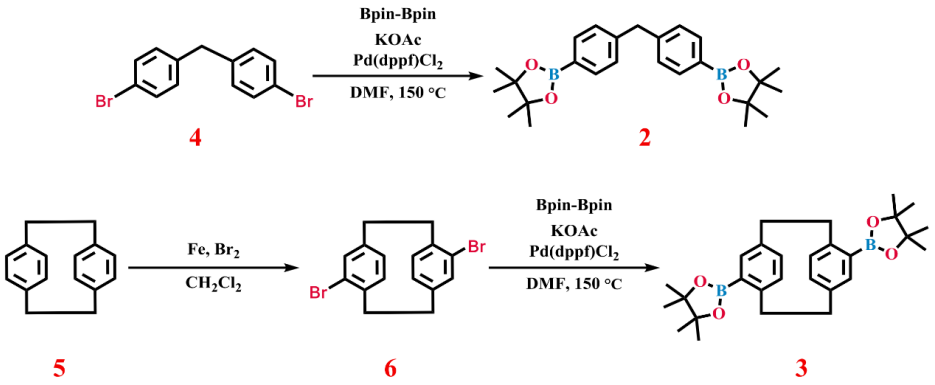
1. General and Materials Information

All anhydrous solvents for syntheses and starting chemicals were purchased from commercial suppliers (Aldrich or Acros) and used without further purification. All glassware was oven-dried and cooled under an inert atmosphere of argon. All air sensitive reactions were carried out under argon atmosphere using standard Schlenk techniques. Flash column chromatography was performed on silica gel (200-300 mesh). NMR spectra were recorded using a Bruker BioSpin (^{1}H 400 MHz, ^{13}C 100 MHz). Chemical shifts are quoted in ppm relative to $CHCl_3$ (δ 7.26 ppm) or tetramethylsilane (δ 0.00 ppm) for ^{1}H NMR and relative to $CDCl_3$ (δ 77.00 ppm) for ^{13}C NMR. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, m = multiplet), coupling constant (Hz), and integration. High-resolution mass spectrum was acquired using MALDI-TOF-MS techniques. FTIR spectra were obtained on Infrared spectrometer (Thermo-Nicolet iS10) equipped with DTGS Detector and EverGlo light source. UV-vis spectra were obtained on a UNIC-3802 spectrophotometer in quartz cuvettes. VT-NMR spectra were recorded using a JEOL JNM-ECZR spectrometer (^{1}H 600 MHz). Variable-temperature UV-vis spectra were recorded using SolidSpec-3700 spectrophotometer with a Shimadzu temperature controller. Variable-temperature fluorescence spectra were obtained on HORIBA JY -Fluorolog-3 spectrometer.

2. Synthetic procedures



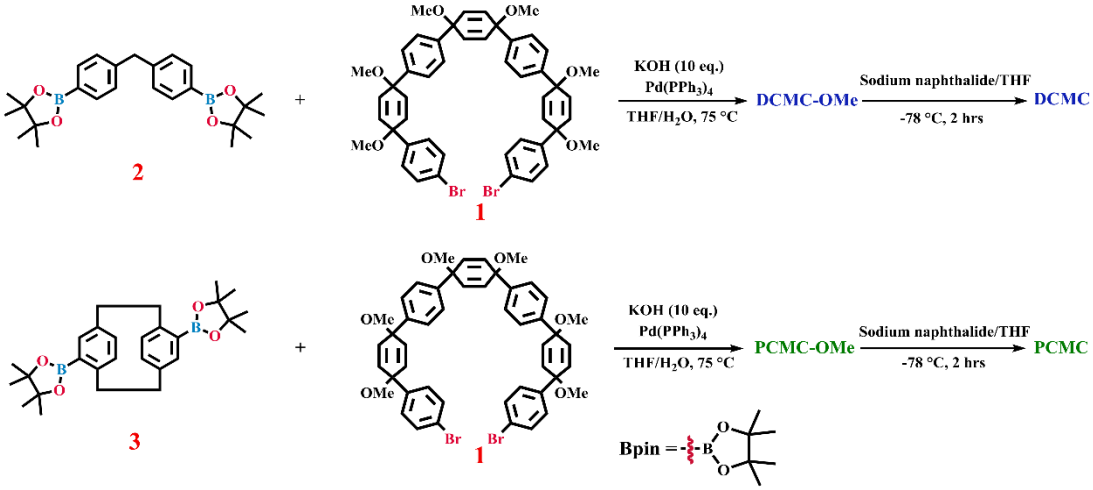
Synthesis of bis(4-borylphenyl)methane (2).

To a mixture of compound **4** (499 mg, 1.53 mmol) which was synthesized according to the literature report, [S1] bis(pinacolato)diboron (2.20 g, 8.58 mmol), and anhydrous KOAc (1.43 g, 14.54 mmol) in a 50 mL flask was added anhydrous dioxane (20 mL). The reaction mixture was degassed by argon bubbling for 15 minutes then $Pd(dppf)Cl_2$ (119 mg, 0.12 mmol) was added and the solution was bubbled with argon for another 15 minutes. The mixture was heated to 100 °C for 36 hours after the flask was sealed. After reaction, the solvent was removed under reduced pressure and the crude product was extracted with CH_2Cl_2, washed twice with brine, dried over anhydrous magnesium sulfate and evaporated to dryness. The product was purified by chromatography on a silica gel column with hexane/CH_2Cl_2 as the eluent (v/v, 4:1) to give pure **2** (515 mg, 1.226 mmol, 80.2%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.71 (d, J = 6.5 Hz, 4H), 7.17 (d, J = 6.2 Hz, 4H), 3.99 (s, 2H), 1.31 (s, 24H).

Synthesis of 4,16-diboryl[2.2]paracyclophane (3).

To a round-bottom flask (50 mL) were added compound **6** (560 mg, 1.53 mmol) which was synthesized following the literature procedure, [S2] bis(pinacolato)diboron (2.20 g, 8.58 mmol), anhydrous KOAc (1.43 g, 14.54 mmol) and dry DMF (15 mL). The mixture was bubbled with argon for 15 minutes then $Pd(dppf)Cl_2$ (119 mg, 0.12 mmol)

was added quickly and the mixture was further degassed by argon bubbling for 15 minutes. The flask was sealed and heated at 150 °C for 36 hours. After reaction, the solvent was removed under reduced pressure and methanol was added to wash the excess bis(pinacolato)diboron. The precipitate was collected by filtration and further purified by silica gel column chromatography with hexane/CH_2Cl_2 as the eluent (v/v, 3:1) to give pure **3** (496 mg, 1.08 mmol, 70.5%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.05 (d, *J* = 1.8 Hz, 2H), 6.45 (dd, *J* = 10.1, 8.1 Hz, 4H), 3.94-3.88 (m, 2H), 3.12-2.92 (m, 6H), 1.38 (d, *J* = 3.6 Hz, 24H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.55, 151.68, 146.31, 145.07, 137.12, 133.09, 129.10, 128.92, 127.72, 125.79, 123.14, 116.39, 107.60, 77.36, 77.25, 77.05, 76.73, 56.66, 56.15, 32.42, 21.17, 19.59. MS (ESI) m/z calcd. for $C_{28}H_{38}B_2O_4$ $[M]^+$: 460.2956, found: 461.3022. IR (KBr) cm^{-1}: 2983.33, 2924.52, 2847.38, 1586.64, 1550.00, 1480.09, 1405.85, 1350.41, 1259.77, 1149.36, 1057.76, 967.60, 853.83, 751.13, 669.66, 628.68, 515.38.



Synthesis of compound 1.

Compound **1** was synthesized according to the reported method in the literature. [S3]

Synthesis of DCMC

Step 1: To a round-bottom flask (500 mL) were added compound **2** (78.15 mg, 0.186 mmol), compound **1** (163.32 mg, 0.186 mmol), THF (250 mL) and H_2O (20 mL), then potassium hydrate (134 mg, 2.388 mmol) and $Pd(PPh_3)_4$ (30.06 mg, 0.026 mmol) was added after argon bubbling for 25 minutes. Then, the mixture was reacted at 75 °C for 48 hours. After cooling to room temperature, solvent was removed under vacuum and the residue was extracted with CH_2Cl_2. The organic layer was dried by anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to afford macrocycle intermediate **DCMC-OMe** as a white solid for the step 2 without further purification.

Step 2: To a 50 mL round-bottom flask (vessel A), sodium metal (274 mg, 11.90 mmol), dry THF (12 mL), and naphthalene (1.00 g, 7.82 mmol) were added under nitrogen and the resultant mixture was stirred at room temperature for 24 hours. To another 250 mL flask (vessel B) containing the dry product **DCMC-OMe** in dry THF (30 mL) was added a solution of sodium napthalenide (2 mL, 2 mmol, 1.0 M in THF) at -78 °C. This resulting mixture was reacted at -78 °C for 2 hours before quenched with 1.5 mL of I_2 solution (1 M in THF). After warmed up to room temperature, the mixture was added

aqueous saturated sodium thiosulfate, extracted with CH_2Cl_2, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. Purification by column chromatography with hexane/CH_2Cl_2 as the eluent (v/v, 4:1) afforded pure **DCMC** (25.97 mg, 20%) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.90-7.65 (m, 6H), 7.55 (d, *J* = 12.2 Hz, 10H), 7.44 (dt, *J* = 27.5, 8.2 Hz, 16H), 7.19 (s, 4H), 3.90 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.19, 138.71, 138.66, 138.46, 138.40, 138.33, 138.10, 138.01, 137.84, 137.78, 137.74, 137.72, 137.57, 137.50, 134.48, 128.52, 127.85, 127.60, 127.54, 127.44, 127.26, 126.85, 126.79, 125.79, 42.11. HR-MS (MALDI-TOF) *m/z* calcd. for $C_{52}H_{38}$ $[M]^+$: 698.2973, found 698.2980. IR (KBr) cm^{-1}: 3021.25, 2921.53, 2850.04, 1903.02, 1637.73, 1587.56, 1482.82, 1388.75, 1261.44, 1111.54, 995.52, 813.01, 724.58, 519.50.

Synthesis of PCMC

Step 1: To a round-bottom flask (500 mL) was added compound **3** (85.60 mg, 0.186 mmol), compound **1** (163.32 mg, 0.186 mmol), THF (250 mL) and H_2O (20 mL), then potassium hydrate (134 mg, 2.38 mmol) and $Pd(PPh_3)_4$ (30.06 mg, 0.026 mmol) was added after argon bubbling for 25 minutes. Then, the mixture was reacted at 75 °C for 48 hours. After cooling to room temperature, solvent was removed under vacuum and the residue was extracted with CH_2Cl_2. The organic layer was dried by anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to afford macrocycle intermediate **PCMC-OMe** as a yellow solid for the step 2 without further purification. Step 2: To a 50 mL round-bottom flask (vessel A), sodium metal (274 mg, 11.90 mmol), dry THF (12 mL), and naphthalene (1.00 g, 7.82 mmol) were added under nitrogen and the resultant mixture was stirred at room temperature for 24 hours. To another 250 mL flask (vessel B) containing the intermediate **PCMC-OMe** in dry THF (30 mL) was added a solution of sodium napthalenide (2 mL, 2 mmol, 1.0 M in THF) at -78 °C. This

resulting mixture was reacted at -78 °C for 2 hours before quenched with 1.5 mL of I_2 solution (1 M in THF). After warmed up to room temperature, the mixture was added aqueous saturated sodium thiosulfate, extracted with CH_2Cl_2, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. Purification by column chromatography with hexane/CH_2Cl_2 as the eluent (v/v, 4:1) afforded pure **PCMC** (30.21 mg, 22%) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (s, 2H), 7.65-7.30 (m, 24H), 7.18 (s, 2H), 6.37-6.09 (m, 6H), 3.38 (s, 2H), 2.79 (s, 2H), 2.36 (s, 2H), 1.87 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.75, 138.98, 138.92, 138.27, 138.02, 137.90, 137.84, 137.55, 137.47, 136.14, 134.34, 132.99, 131.51, 128.46, 128.13, 127.61, 127.28, 125.89, 35.88, 34.14. HR-MS (MALDI-TOF) *m/z* calcd. for $C_{58}H_{42}$ $[M]^+$: 738.3286, found 738.3257. IR (KBr) cm^{-1}: 3021.90, 2922.59, 2844.00, 1885.55, 1718.74, 1576.03, 1485.40, 1381.26, 1256.39, 1105.01, 994.60, 810.92, 722.69, 505.25.

3. Computational details and results

All DFT calculations were carried out by using Gaussian 09 software.[S4] The initial structure was fully relaxed by using theoretical level of D3-B3LYP/Def2-TZVP (using Grimme D3 corrected method for van der Waals interactions) and further validated by frequency analysis. Solvent effect was corrected by polarizable continuum model. The tension energy was calculated using the reported computational methods.[S5] As shown in Figure S7, the strain energy was estimated following the formula: Strain energy = *E*(PCMC) + 10**E*(biphenyl) - 9**E*(Terphenyl) - *E*(moiety) for **PCMC**; Strain energy = *E*(DCMC) + 8**E*(biphenyl) - 7**E*(Terphenyl) - *E*(moiety) for **DCMC**. Moreover, TD-DFT with CAM-B3LYP/Def2-TZVP level was used to calculate the UV-vis spectra. Concerning more accuracy of orbital energy by using B3LYP than weak interaction-corrected B3LYP,[S6] B3LYP/Def2-TZVP computational level was used to compute the energy level of frontier orbitals. For the conformation studies of **PCMC**, potential energy surface were scanned based on two twist angles between [2.2]paracyclophane and phenyls using the redundant optimization in the theoretical level of PM6, resulting in two most stable **PCMC** conformations (**PCMC-S0**, **PCMC-S1**). Subsequently, both of them are fully relaxed. Transition states were identified by QST3 method using D3-B3LYP/Def2-TZVP and further validated by frequency analysis (one imaginary frequency).

The geometrical optimization results show that the average twist angles are 26.23º and 27.12º between adjacent phenyls for DCMC and PCMC, respectively (Figures S18). The strain energy is calculated to be 46.22 kcal/mol for DCMC. However, the strain energy is significantly enhanced to 72.58 kcal/mol for PCMC, which is consistent with the theoretical values of cycloparaphenylenes (Figure S19). The frontier molecular orbitals demonstrate that the occupied molecular orbitals and unoccupied molecular

orbitals concentrate on the local π-type bonding orbitals and anti-bonding orbitals (Figures S20-S21), respectively. The HOMO-LUMO gap is 3.42 eV for PCMC and 3.31 eV for DCMC (Figure S22). Time-dependent DFT calculations reveal that the main absorption peaks of PCMC are 293 nm (corresponding to HOMO-2→LUMO), 322 nm (corresponding to HOMO→LUMO+1 and HOMO-1→LUMO), and 348 nm (corresponding to HOMO→LUMO), which are consistent with the experimentally observed peaks (326 nm and 355 nm). Similarly, the absorption peaks in DCMC are 292 nm (corresponding to HOMO-2→LUMO), 311 nm (corresponding to HOMO-1→LUMO), and 357 nm (corresponding to HOMO→LUMO).

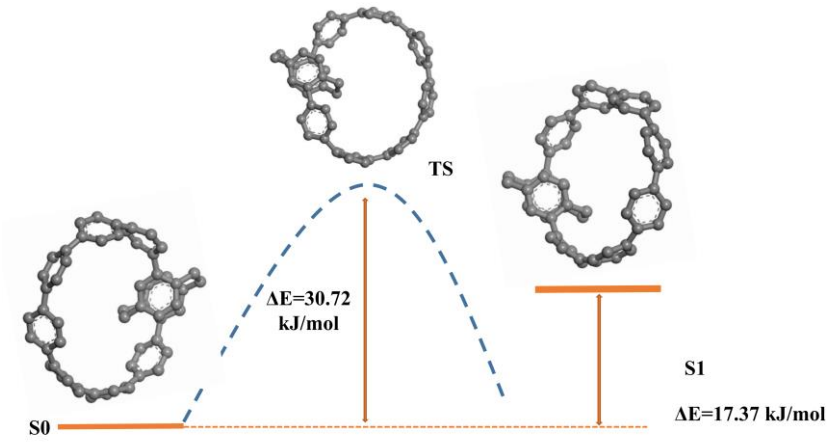


Figure S1. Graphical representation of both enantiomers of **PCMC**. Energy profile of **PCMC-S0**, **PCMC-S1** and **PCMC-TS**.

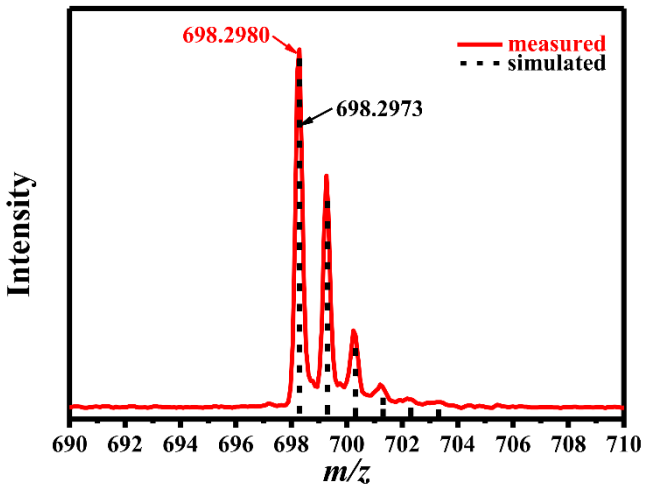


Figure S2. HR-MS (MALDI-TOF) date for **DCMC**.

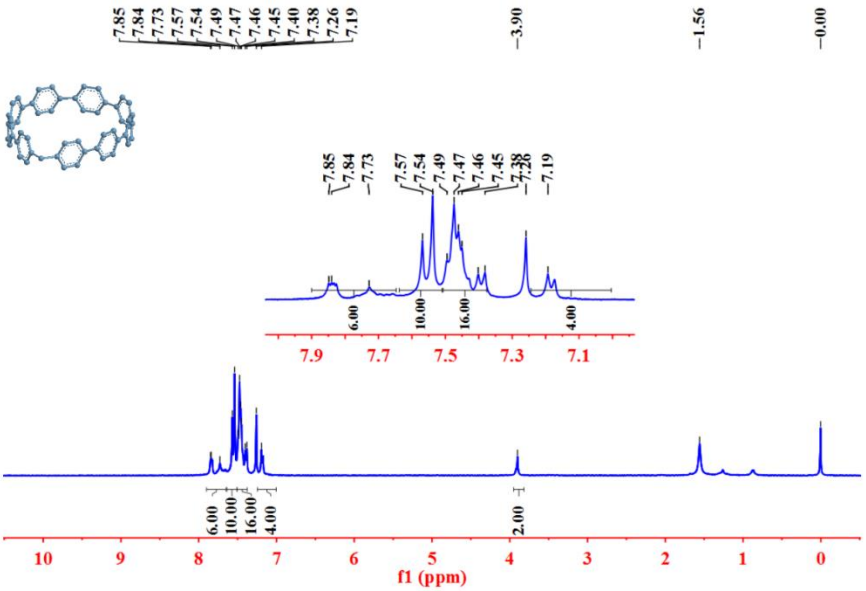


Figure S3. ^{1}H NMR spectrum of **DCMC** in $CDCl_3$.

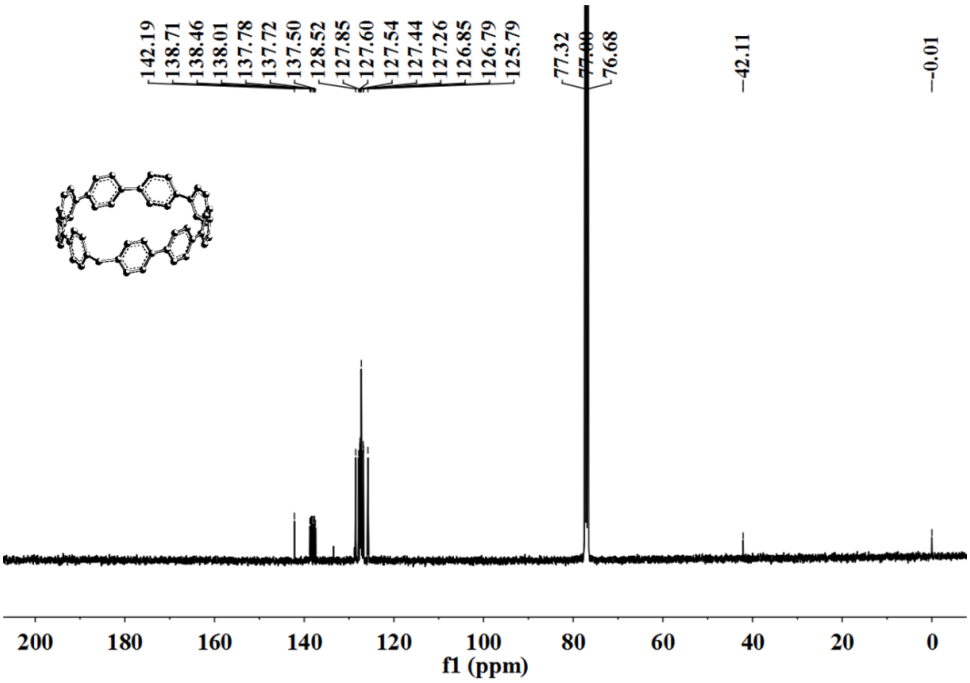


Figure S4. ^{13}C NMR spectrum of **DCMC** in $CDCl_3$.

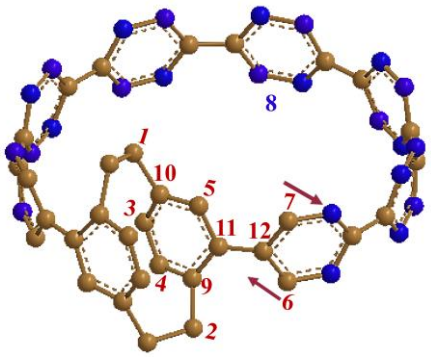


Figure S5. Different types of atoms in **PCMC**. Note: 6 points inside the ring, 7 points outside the ring, 8 represents all blue atoms.

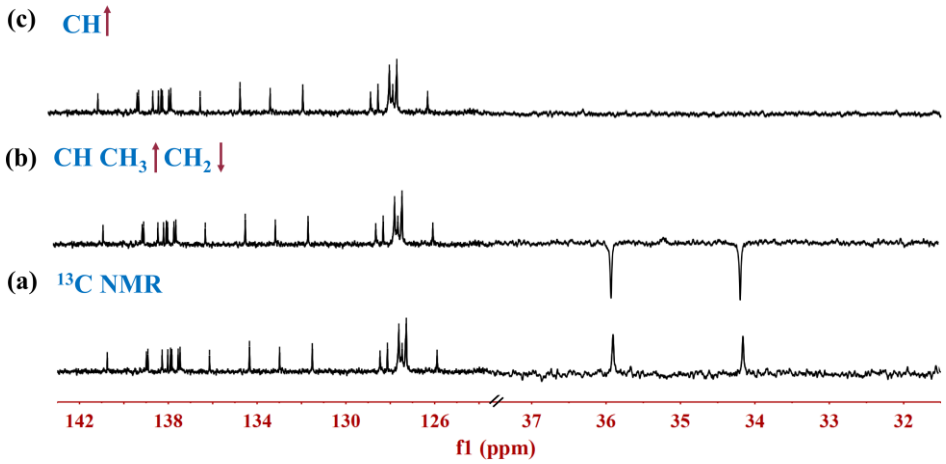


Figure S6. (a) ^{13}C NMR, (b) DEPT-135° NMR, and (c) DEPT-90° NMR spectra of **PCMC** in $CDCl_3$.

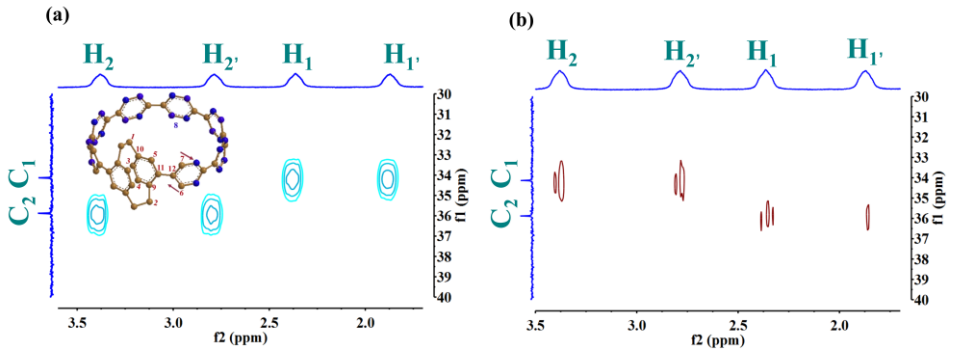


Figure S7. (a) HSQC and (b) HMBC of **PCMC** in the range of 1.8-3.6 ppm in $CDCl_3$.

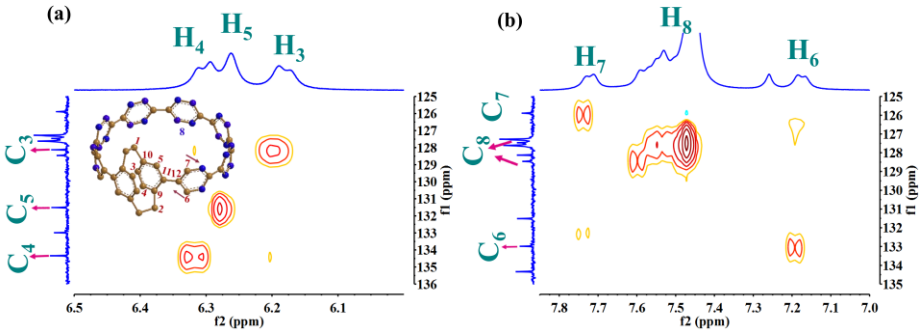


Figure S8. HSQC of **PCMC** in the range of 6.1-6.5 ppm (a) and 7.0-7.8 ppm (b) in $CDCl_3$.

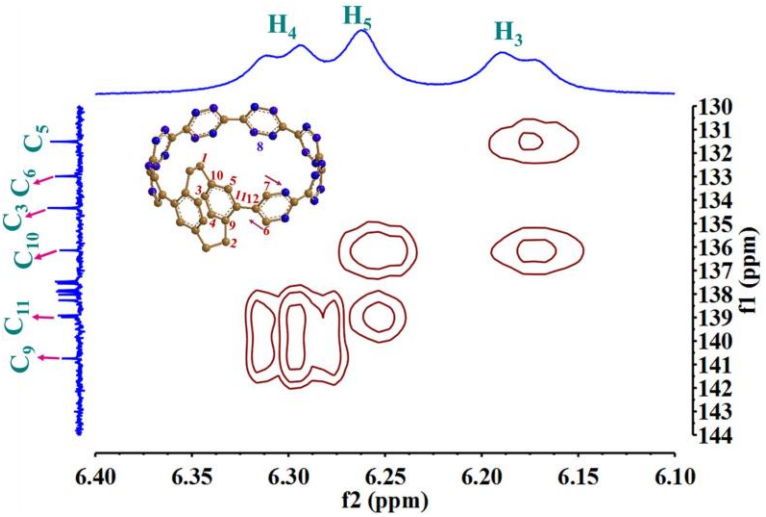


Figure S9. HMBC of **PCMC** in the range of 6.1-6.4 ppm in $CDCl_3$.

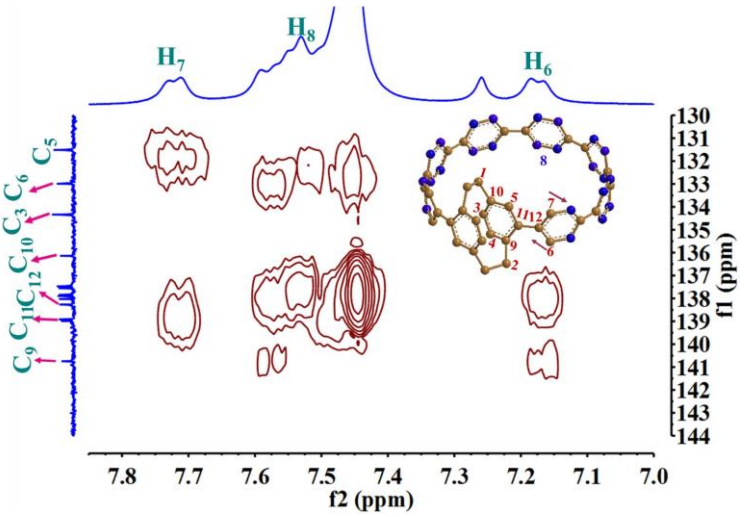


Figure S10. HMBC of **PCMC** in the range of 7.0-7.8 ppm in $CDCl_3$.

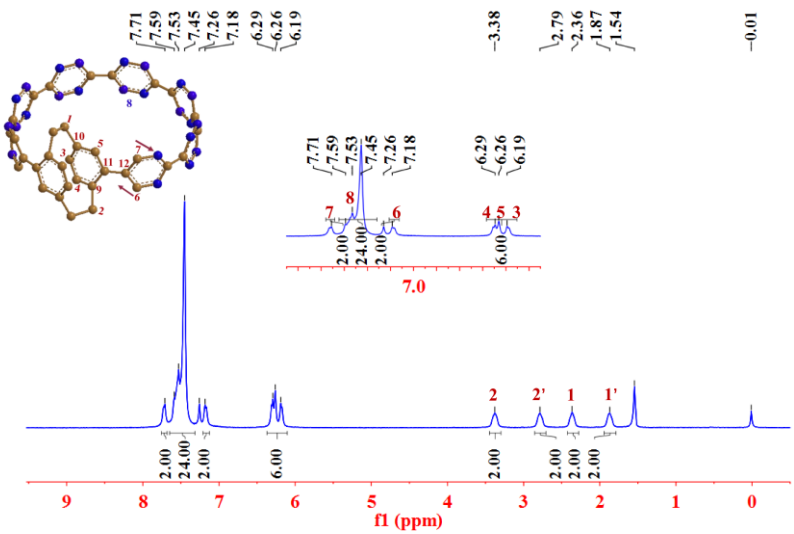


Figure S11. ^{1}H NMR spectrum of **PCMC** in $CDCl_3$.

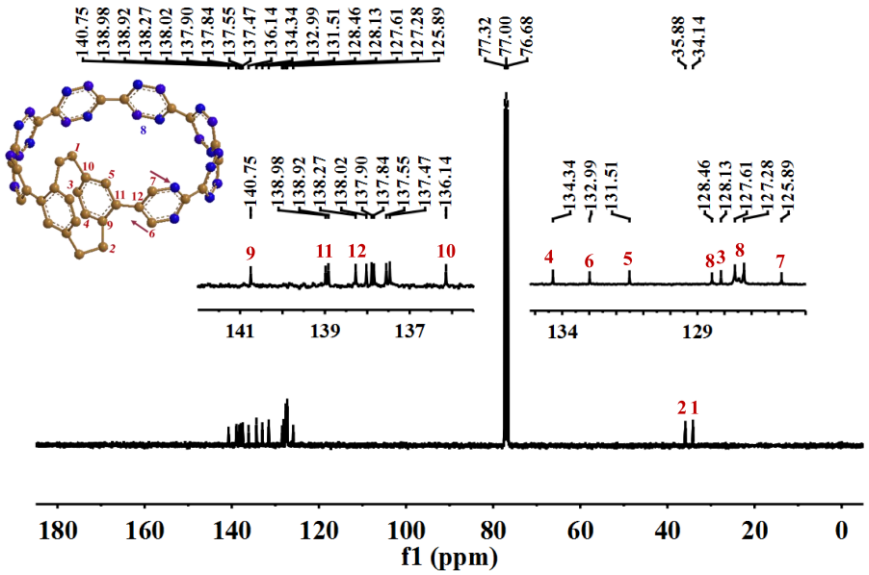


Figure S12. ^{13}C NMR spectrum of **PCMC** in $CDCl_3$.

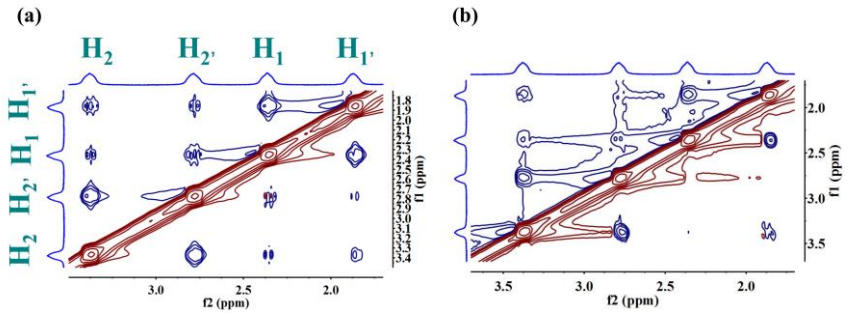


Figure S13. (a) NOESY and (b) ROESY spectra of **PCMC** in the range of 1.8-3.6 ppm in $CDCl_3$.

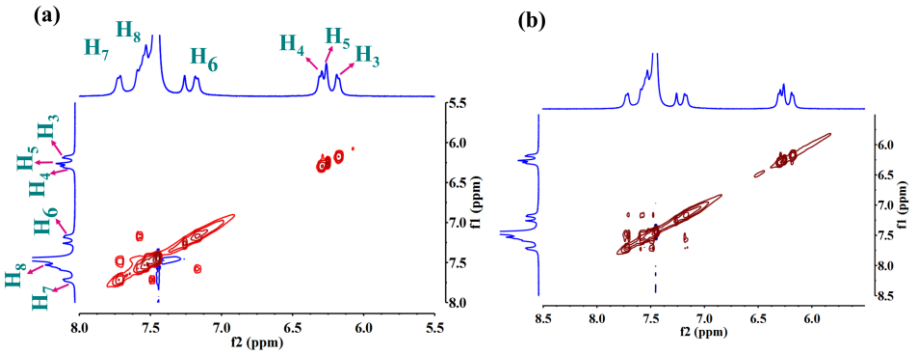


Figure S14. (a) NOESY and (b) ROESY of **PCMC** in the range of 1.5-8.1 ppm in $CDCl_3$.

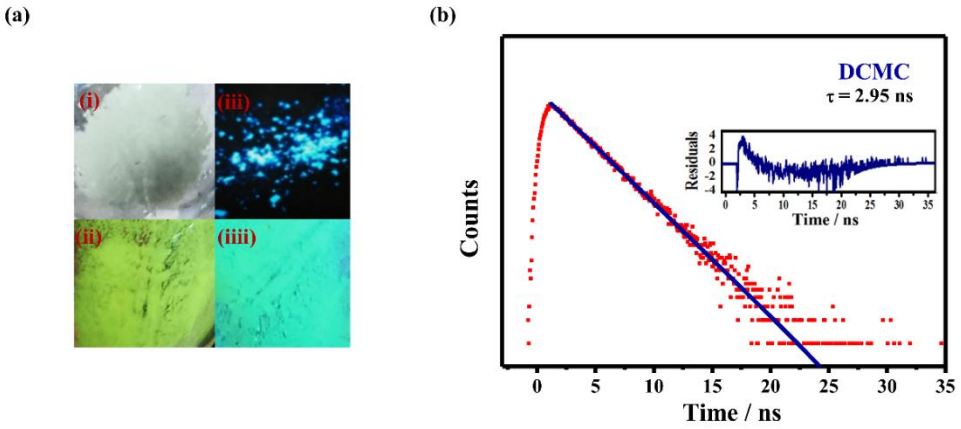


Figure S15. (a) Solid powder of **DCMC** (i) and **PCMC** (ii), fluorescent photographs of **DCMC** (iii) and **PCMC** (iiii) solid under UV irradiation at λ= 365 nm. (b) Emission lifetime decay for **DCMC** in CH_2Cl_2 measured at λ = 458 nm. Insert: curve fitting residuals for **DCMC**.

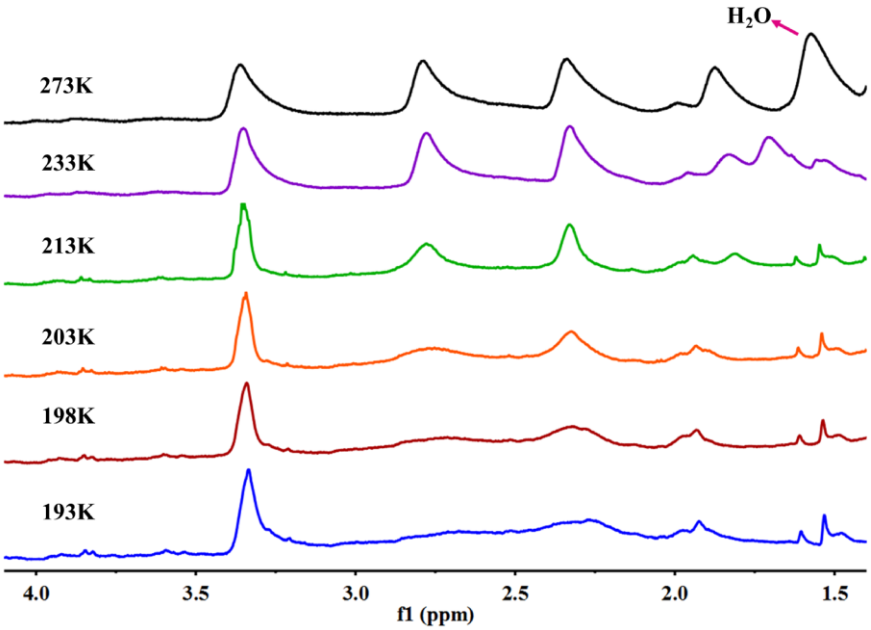


Figure S16. VT-NMR spectra of **PCMC** in the range of 1.4-4.1 ppm in CD_2Cl_2.

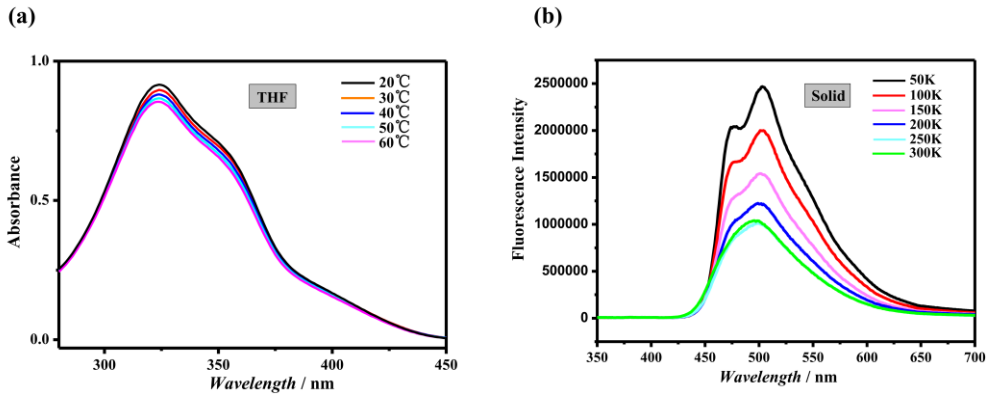


Figure S17. Variable-temperature UV-vis spectra in THF (a) and fluorescence spectra in solid form (b) of **PCMC**.

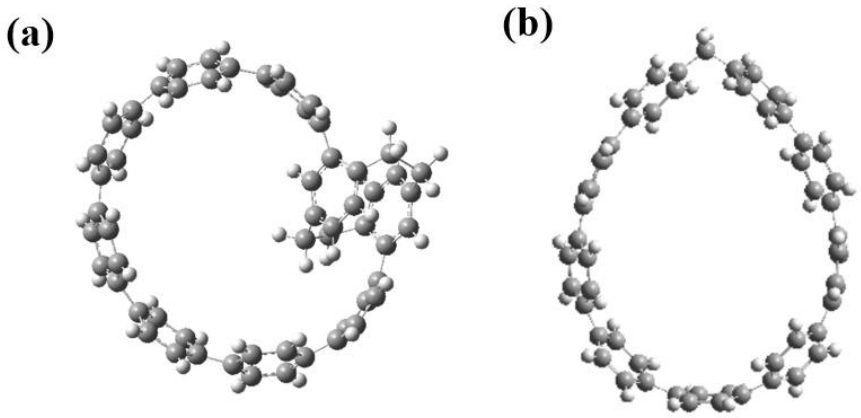


Figure S18. Geometrical optimization structure of **PCMC** (a) and **DCMC** (b).

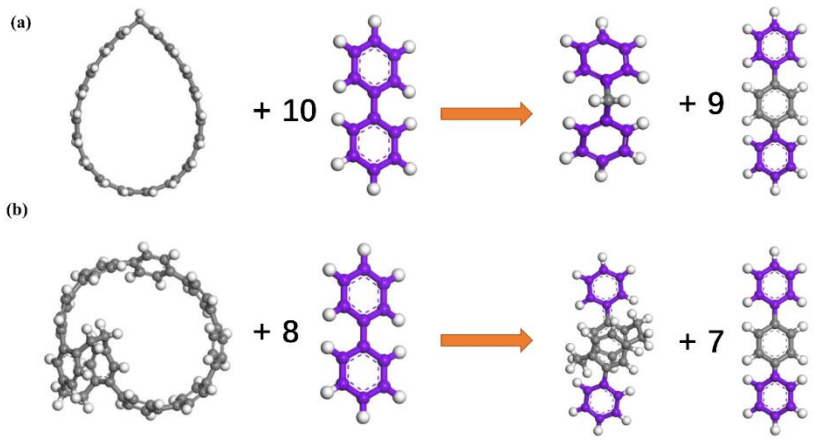


Figure S19. Homodesmotic reactions used by strain-energy calculation: **PCMC** (a) and **DCMC** (b).

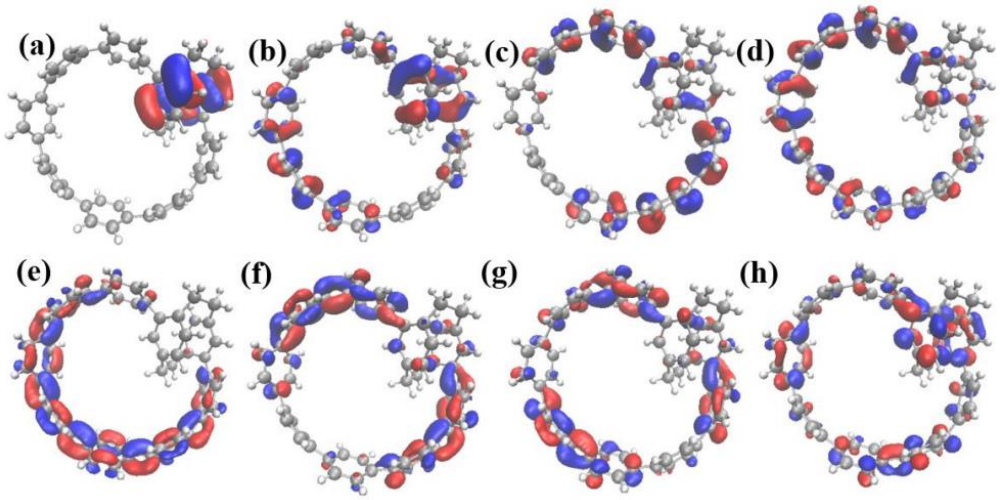


Figure S20. Frontier orbitals of **PCMC**: HOMO-3 (a), HOMO-2 (b), HOMO-1 (c), HOMO (d), LUMO (e), LUMO+1 (f), LUMO+2 (g) and LUMO+3 (h).

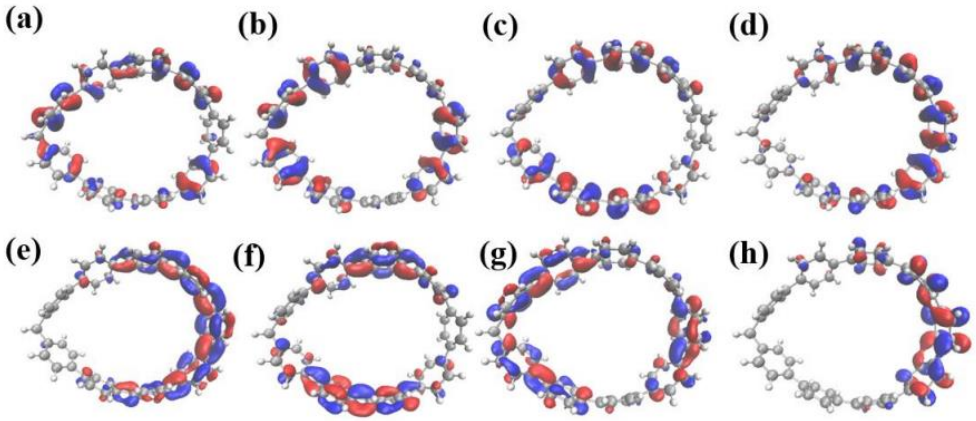


Figure S21. Frontier orbitals of **DCMC**: HOMO-3 (a), HOMO-2 (b), HOMO-1 (c), HOMO (d), LUMO (e), LUMO+1 (f), LUMO+2 (g) and LUMO+3 (h).

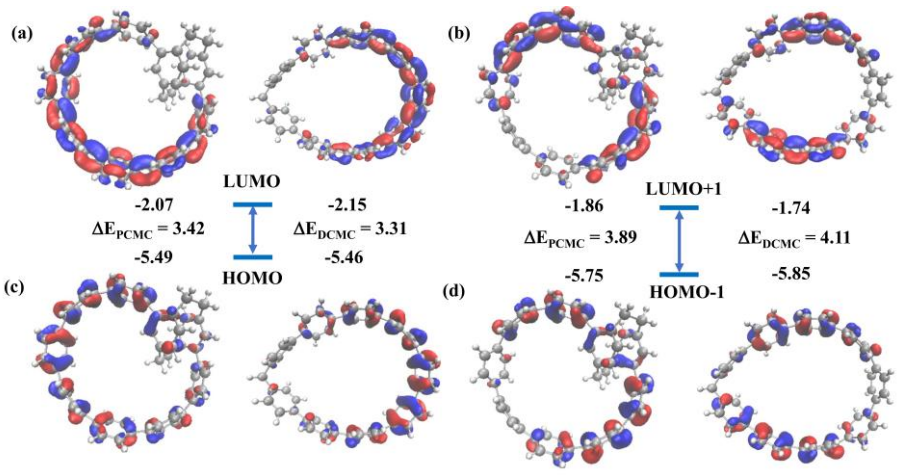


Figure S22. (a) LUMO energy level of **PCMC** (left) and **DCMC** (right). (b) LUMO+1 of **PCMC** (left) and **DCMC** (right). (c) HOMO of **PCMC** (left) and **DCMC** (right). (d) HOMO-1 of **PCMC** (left) and **DCMC** (right).

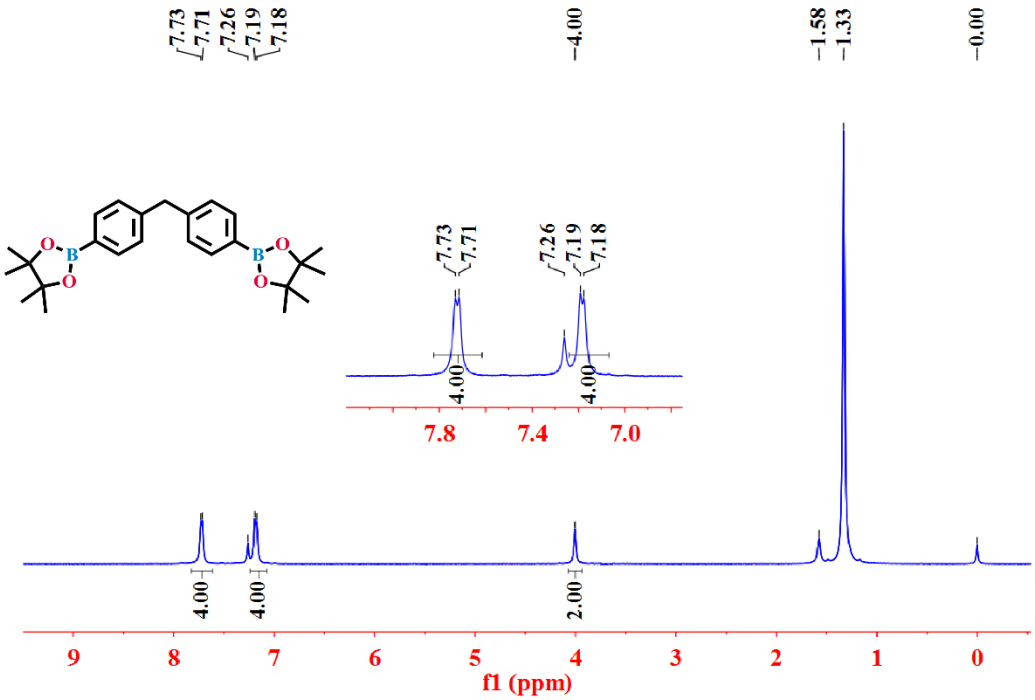


Figure S23. ^{1}H NMR spectrum of **2** in $CDCl_3$.

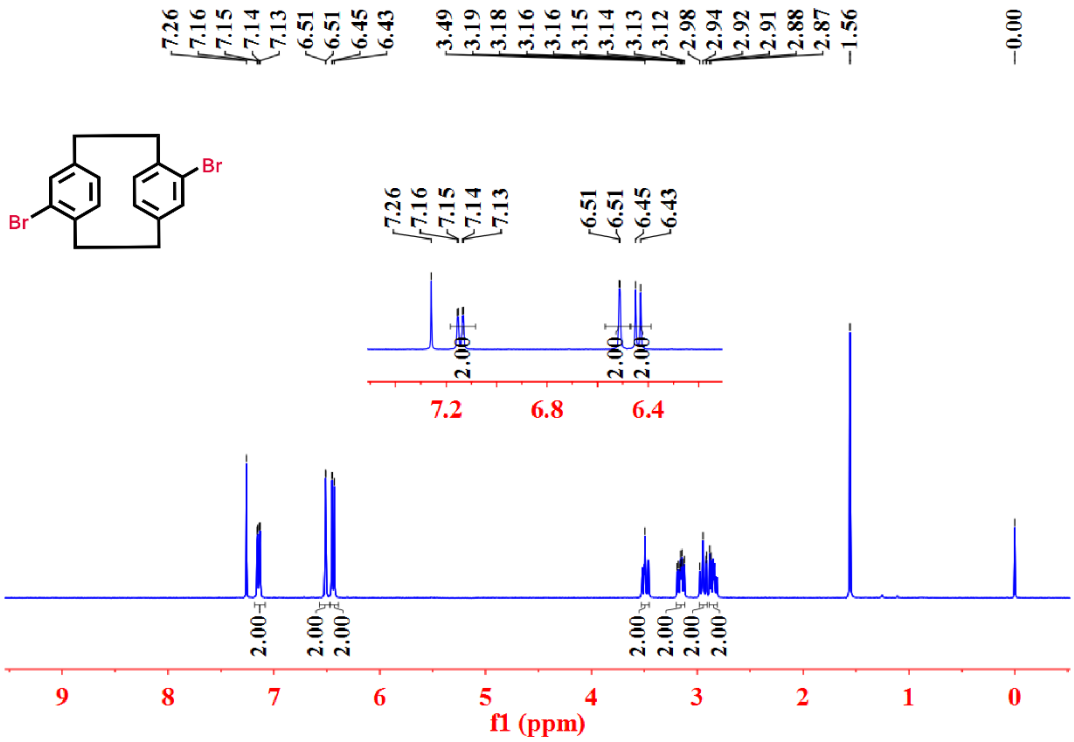


Figure S24. ^{1}H NMR spectrum of 4,16-dibromo[2.2]paracyclophane (**6**) in $CDCl_3$.

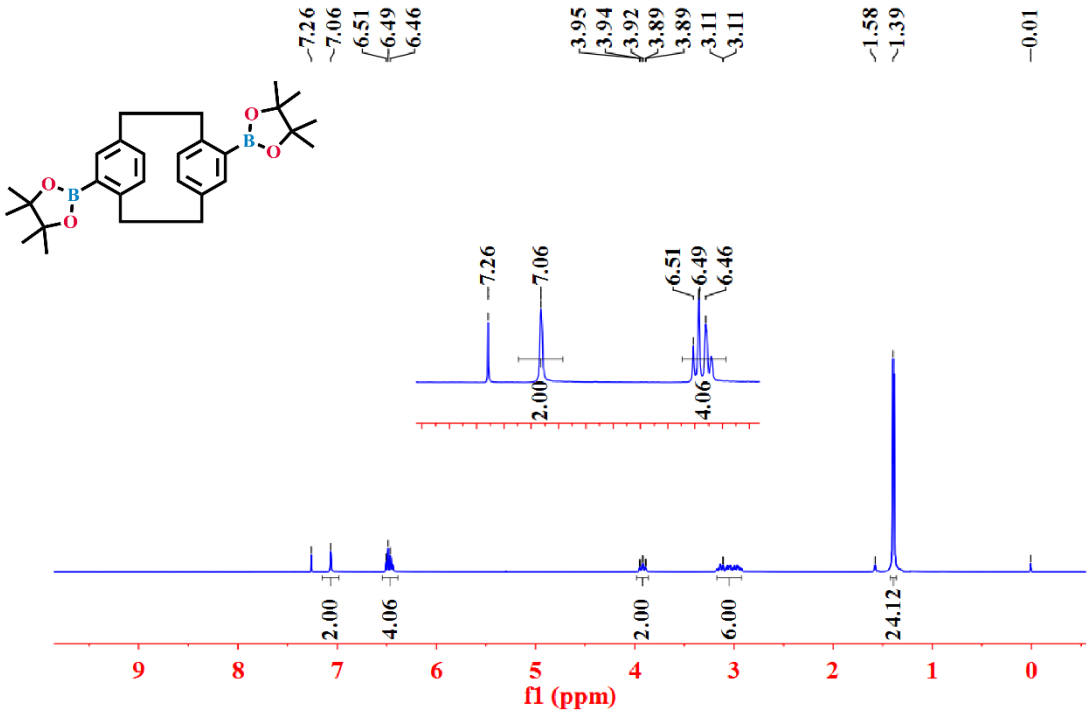


Figure S25. ^{1}H NMR spectrum of **3** in $CDCl_3$.

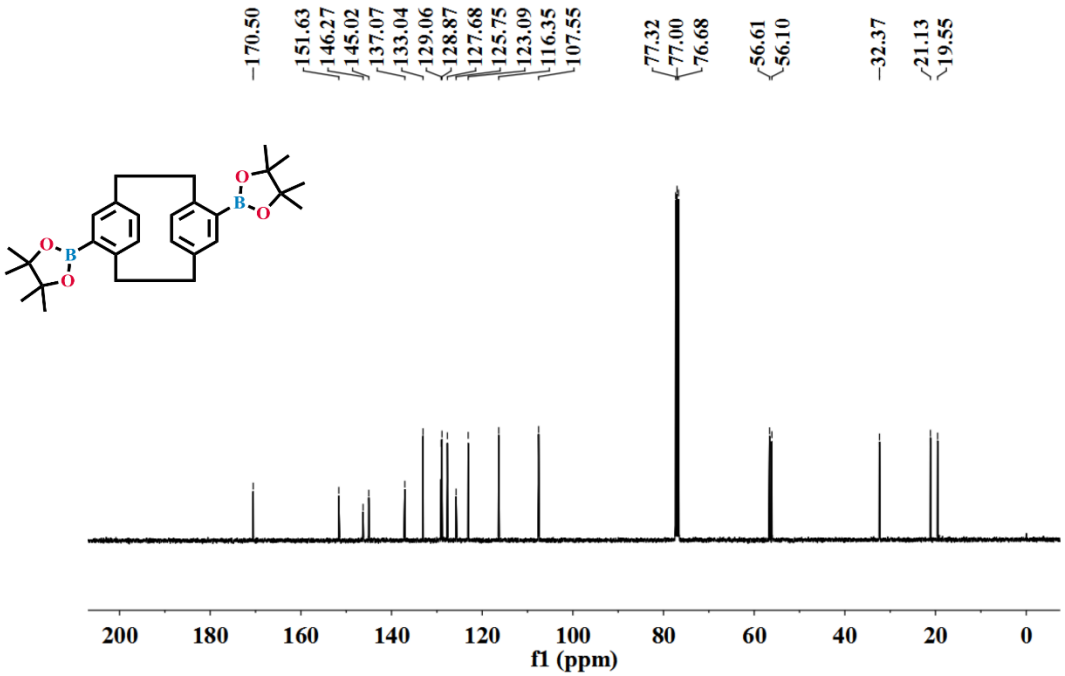


Figure S26. ^{13}C NMR spectrum of **3** in $CDCl_3$.

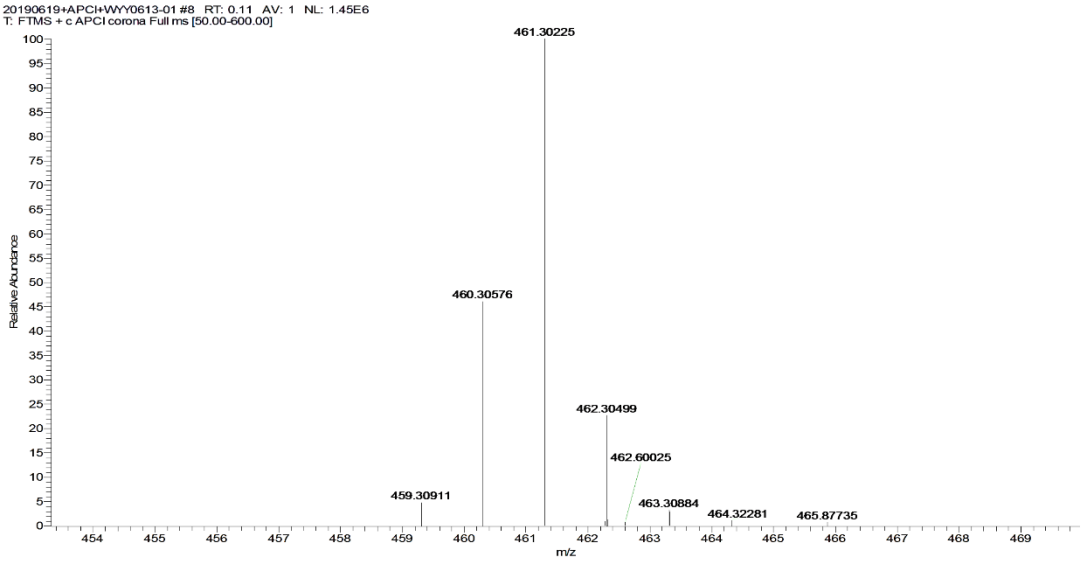


Figure S27. HR-MS (ESI) date for **3**.

Table S1. Summary of spectroscopic data for **PCMC** and **DCMC** in a series of solvents.

compd/solvent	λ_{abs} (nm)	λ_{PL} (nm)	Φ_F
PCMC/hexane	324,354,396	466	0.48
PCMC/toluene	325,354,397	461,480	0.41
PCMC/THF	325,356,398	482	0.34
PCMC/DCM	326,355,398	488	0.31
PCMC/DMSO	327,355,399	499	0.37
DCMC/hexane	320,370	445,456	0.43
DCMC/toluene	321,370	446,458	0.35
DCMC/THF	322,375	450,462	0.36
DCMC/DCM	323,380	458	0.37
DCMC/DMSO	332,391	460	0.41

Table S2. Orbital energy level of **PCMC** and **DCMC**.

Molecule	PCMC	DCMC
LUMO+3	-1.0471	-0.9636
LUMO+2	-1.3511	-1.4664
LUMO+1	-1.8607	-1.7364
LUMO	-2.0675	-2.1473
HOMO	-5.4910	-5.4578
HOMO-1	-5.7482	-5.8475
HOMO-2	-5.9759	-6.0690
HOMO-3	-6.1640	-6.6902
E(HOMO-LUMO)	3.4235	3.3106

Table S3. Energy of moiety and strain energy in the calculation **DCMC** and **PCMC** using theoretical level of D3-B3LYP/Def2-TZVP.

	DCMC	PCMC
DCMC/PCMC	-2119.748582	-2236.460915
Moiety	-502.85371	-1081.939693
Byphen	-463.5238957	-463.5238957
Triphen	-694.6897217	-694.6897217
Strain Energy (kcal / mol)	46.22	72.58

Table S4. Main electronic transitions of **PCMC** and **DCMC** obtained by TD-DFT with f_{os}> 0.10.

λ_{exp}/nm	λ_{DFT}/nm	transitions	f_{os}
PCMC			
355	348.55	HOMO→LUMO (55%) HOMO → LUMO+1 (14%) HOMO-1 → LUMO+1 (31%)	0.1044
325	322.22	HOMO-1→LUMO+1 (12%) HOMO-1→LUMO (42%) HOMO →LUMO+1 (46%)	1.4882
	293.68	HOMO-2→LUMO (37%) HOMO-1→LUMO (32%)	1.4957
DCMC			
320	357.64	HOMO → LUMO (61%)	0.4318
	311.58	HOMO-1→LUMO (45%)	2.7163
	292.69	HOMO-2→LUMO (39%)	1.0433

Table S5. Relaxed structure of **PCMC-S0, PCMC-S1** and **PCMC-TS** and **DCMC**

PCMC-S0							
C	-2.067931	-5.215815	-0.963862	H	-5.571977	-0.653533	-2.293515
C	-2.291533	-5.601620	1.393945	H	-7.124650	1.977626	1.591210
C	-4.126681	-4.367272	0.158580	H	-5.505418	4.023187	-2.253414
C	-2.868435	-5.152754	0.190494	H	-3.317826	4.571724	2.138443
C	-4.848976	-4.142507	-1.028956	H	-5.262506	3.152941	1.950042
C	-5.341259	-2.504992	1.153309	H	-3.547585	5.465027	-2.062581
C	-4.470363	-3.580853	1.272318	H	-1.551697	5.853633	2.155918
C	-5.905274	-2.159041	-0.087298	H	0.840994	3.977698	-1.740221
C	-5.715734	-3.060439	-1.150824	H	-1.444996	4.781663	-2.009379
C	-6.880806	0.022067	0.759200	H	0.710720	4.962051	2.433193
C	-6.360110	-0.761799	-0.287386	H	3.358106	-3.452594	2.199257
C	-5.864458	1.299220	-1.482211	H	1.944613	-6.535396	-1.392121
C	-5.961569	-0.086939	-1.454290	H	4.120486	-5.435323	-1.542259
C	-6.789751	1.410112	0.728492	H	1.214626	-4.574929	2.360837
C	-5.485702	3.382462	-0.186207	H	-0.103683	-5.429649	-1.777414
C	-6.164423	2.072187	-0.345799	H	-0.507959	-6.167950	2.436340
C	-5.039387	4.148279	-1.280744	H	4.716332	-3.454317	-2.187068
C	-3.814744	4.509194	1.177002	H	5.295628	-1.151840	-2.736275
C	-4.932026	3.691680	1.068799	H	5.812142	-0.270368	1.423263
C	-3.199813	5.055866	0.035592	H	5.334277	-2.596694	1.982417
C	-3.922215	4.971320	-1.171246	C	5.627703	1.996409	-0.252928
C	-1.034435	5.457553	1.287672	C	5.087681	0.923036	-0.981347
C	-1.730464	5.277376	0.076372	C	3.949084	1.171924	-1.794597
C	0.327919	4.406966	-0.885646	C	3.652539	2.507201	-2.095700
C	-0.969295	4.880747	-1.039631	C	4.223393	3.561131	-1.389969
C	0.260178	4.966944	1.444945	C	5.106037	3.294141	-0.338133
C	0.906069	4.296838	0.390905	C	5.232820	4.272015	0.813284
C	4.838121	-3.184794	-0.042469	C	2.828691	0.155692	-2.007670
C	3.091574	-4.167217	1.428938	C	1.848331	3.185767	0.686187
C	3.890584	-4.283322	0.276515	C	1.486032	1.953581	0.121961
C	2.256663	-5.871561	-0.591454	C	2.191174	0.779176	0.377776
C	3.495101	-5.242126	-0.676602	C	3.067903	0.801225	1.466245
C	1.861802	-4.806590	1.521517	C	3.470342	2.019917	2.012487
C	-0.097591	-5.777425	0.351141	C	2.987226	3.237911	1.521852
C	1.368304	-5.585459	0.460972	C	3.860448	4.473320	1.596334
C	-0.715056	-5.524688	-0.886075	C	2.198899	-0.336346	-0.643481
C	-0.934902	-5.900583	1.474473	H	6.382148	1.782293	0.500025
C	4.990213	-2.780740	-1.382527	H	2.830867	2.718530	-2.775142
C	5.298989	-1.463774	-1.697363	H	3.844770	4.568919	-1.538481
C	5.428616	-0.491814	-0.690573	H	5.568721	5.259644	0.477738
C	5.596092	-0.968245	0.621705	H	5.984498	3.899627	1.515879

C	5.312467	-2.294412	0.940349	H	3.109694	-0.727739	-2.581033
H	-2.470671	-4.887870	-1.915925	H	2.042634	0.660447	-2.577387
H	-2.894064	-5.650856	2.295357	H	0.682682	1.937978	-0.608106
H	-4.680030	-4.778870	-1.891889	H	3.546835	-0.115198	1.786809
H	-5.469029	-1.841444	2.001895	H	4.293977	2.028781	2.722582
H	-3.947833	-3.721830	2.212030	H	3.322737	5.317555	1.156763
H	-6.195965	-2.873397	-2.106524	H	4.107807	4.749930	2.627313
H	-7.283541	-0.461166	1.644179	H	2.774221	-1.183329	-0.263305
H	-5.397770	1.768139	-2.341653	H	1.189326	-0.701879	-0.864035

PCMC-S1

C	-6.244832	-0.328736	-1.211456	H	-2.904787	4.374302	-2.224996
C	-6.841524	-0.329849	1.111553	H	-1.029343	6.548126	1.798102
C	-6.168122	1.844776	-0.004970	H	1.459896	6.108241	-2.044727
C	-6.531071	0.406799	-0.047806	H	2.951337	4.192072	2.255878
C	-6.102604	2.644262	-1.161964	H	0.748483	5.183714	2.092331
C	-4.769117	3.493103	1.116480	H	3.688831	5.126234	-1.877919
C	-5.564755	2.354932	1.158348	H	5.003753	3.547950	2.321828
C	-4.535934	4.172847	-0.091684	H	5.404075	0.864562	-1.794954
C	-5.300398	3.780675	-1.205827	H	4.491465	3.080925	-1.919631
C	-2.775472	5.708118	0.888975	H	5.852186	1.269871	2.453034
C	-3.322052	5.016549	-0.207728	H	-2.677463	-4.483074	2.135845
C	-1.177345	5.260684	-1.334893	H	-5.698486	-4.485546	-1.772071
C	-2.517999	4.893169	-1.354302	H	-3.640089	-5.798604	-1.843432
C	-1.434461	6.077657	0.907623	H	-4.727170	-3.193936	2.211141
C	0.889509	5.664068	-0.007174	H	-5.672467	-2.206160	-2.045948
C	-0.580696	5.769408	-0.168130	H	-6.803784	-2.227832	2.101201
C	1.784244	5.698994	-1.092862	H	-1.630437	-4.942871	-2.247219
C	2.662752	4.652597	1.318038	H	0.624206	-4.059068	-2.484511
C	1.398799	5.219353	1.225048	H	1.398866	-4.881189	1.654443
C	3.484800	4.506323	0.185666	H	-0.864178	-5.767972	1.902752
C	3.054670	5.137673	-0.997159	C	3.009266	-3.050125	-1.610220
C	5.063851	2.958766	1.412496	C	2.122907	-3.159074	-0.528044
C	4.540805	3.464497	0.206112	C	1.953447	-2.025999	0.318035
C	5.329061	1.423938	-0.875335	C	2.296986	-0.787955	-0.223135
C	4.816902	2.718268	-0.950428	C	3.065515	-0.682301	-1.376838
C	5.553192	1.662057	1.486289	C	3.617319	-1.830986	-1.948574
C	5.551716	0.801962	0.365647	C	4.926930	-1.738850	-2.701560
C	-1.475306	-5.323755	-0.124890	C	1.639008	-2.087529	1.794297
C	-3.355120	-4.542084	1.291167	C	5.464869	-0.670573	0.598299
C	-2.934770	-5.168026	0.103636	C	4.648684	-1.018083	1.700197
C	-5.048442	-4.492742	-0.902368	C	4.203680	-2.315947	1.939534
C	-3.875258	-5.240190	-0.942626	C	4.832822	-3.344634	1.232022

C	-4.529843	-3.801388	1.334353	C	5.658536	-3.034477	0.158544
C	-6.125874	-2.404619	0.054987	C	5.858199	-1.715447	-0.275665
C	-5.333315	-3.651688	0.190134	C	6.206311	-1.560036	-1.741083
C	-6.048532	-1.703263	-1.161574	C	2.891788	-2.564006	2.653635
C	-6.641924	-1.706202	1.162793	H	3.269646	-3.951250	-2.160277
C	-0.965575	-4.981359	-1.391223	H	2.062135	0.114394	0.334463
C	0.319556	-4.473551	-1.528694	H	3.366651	0.297396	-1.719313
C	1.146999	-4.276357	-0.407191	H	4.907042	-0.894270	-3.398451
C	0.740167	-4.885797	0.793348	H	5.079144	-2.641832	-3.299424
C	-0.547851	-5.402441	0.930565	H	0.794547	-2.741044	2.027394
H	-6.018300	0.192502	-2.135190	H	1.367626	-1.080507	2.123152
H	-7.160691	0.188337	2.010443	H	4.183123	-0.213231	2.257604
H	-6.623914	2.334074	-2.062104	H	4.564299	-4.380347	1.421057
H	-4.208758	3.770113	2.003043	H	6.026883	-3.841807	-0.468994
H	-5.596748	1.778473	2.076403	H	6.688519	-0.604751	-1.950446
H	-5.212036	4.329186	-2.138617	H	6.927451	-2.334586	-2.017058
H	-3.387865	5.896333	1.765454	H	2.796199	-3.635287	2.857134
H	-0.557269	5.017183	-2.191066	H	2.846848	-2.049264	3.619156

PCMC-TS

C	2.702446	-5.633502	1.095898	H	6.641741	0.038821	2.313028
C	2.699018	-4.960204	-1.208099	H	6.518913	1.979752	-2.222537
C	4.573669	-4.168136	0.216046	H	5.765456	4.479557	1.702020
C	3.372105	-5.014549	0.024507	H	2.834913	4.516685	-2.268854
C	4.663258	-3.388601	1.381763	H	4.849278	3.202178	-2.304253
C	6.283821	-2.739538	-0.771138	H	3.725709	5.804463	1.736070
C	5.475808	-3.871833	-0.821738	H	1.050313	5.772714	-2.104746
C	6.214352	-1.840731	0.311546	H	-0.594971	4.258208	2.281916
C	5.459662	-2.252285	1.426166	H	1.644502	5.076199	2.093729
C	6.699405	0.198594	-1.068227	H	-1.193280	4.927332	-1.926958
C	6.614238	-0.415635	0.195787	H	-3.363231	-5.115595	-2.441511
C	6.400846	1.812881	1.157396	H	-0.993112	-5.200699	1.895434
C	6.604124	0.446451	1.308632	H	-3.226265	-4.235897	1.761100
C	6.531575	1.569814	-1.218502	H	-1.132660	-6.113495	-2.304814
C	5.432904	3.634267	-0.265521	H	0.864718	-6.422036	1.856979
C	6.231430	2.391702	-0.115080	H	0.843350	-5.129712	-2.244479
C	5.134428	4.483671	0.819041	H	-3.670716	-2.775026	-2.358291
C	3.489035	4.560101	-1.405367	H	-4.645240	-0.570022	-2.215184
C	4.649523	3.800114	-1.423045	H	-6.656366	-1.670973	1.413313
C	3.049547	5.192292	-0.227793	H	-5.615609	-3.887557	1.306215
C	3.969158	5.244565	0.838324	C	-5.706096	1.484883	-1.092498
C	0.698088	5.448363	-1.130382	C	-5.765374	0.573769	-0.014307
C	1.590993	5.386844	-0.044957	C	-5.586328	1.088532	1.298388

C	-0.278158	4.614801	1.310113	C	-5.621805	2.482002	1.461575
C	1.020163	5.094127	1.206803	C	-5.482536	3.343093	0.383771
C	-0.600530	4.961493	-1.024693	C	-5.384832	2.830295	-0.916203
C	-1.080675	4.385416	0.170640	C	-4.684336	3.641383	-1.984769
C	-4.481617	-3.481249	-0.487931	C	-4.977194	0.321724	2.466179
C	-2.854478	-5.146208	-1.482741	C	-2.076800	3.272720	0.204671
C	-3.444733	-4.533495	-0.362920	C	-2.346443	2.632280	1.432157
C	-1.519554	-5.237333	0.947846	C	-2.803367	1.315789	1.529878
C	-2.794115	-4.686195	0.873179	C	-2.763717	0.550917	0.363434
C	-1.584111	-5.707764	-1.404974	C	-2.694787	1.211478	-0.858276
C	0.636246	-5.763735	-0.190443	C	-2.543907	2.596511	-0.966130
C	-0.844265	-5.668326	-0.207929	C	-3.163402	3.216073	-2.206404
C	1.365413	-6.004079	0.989313	C	-3.497856	0.794420	2.768290
C	1.361549	-5.322874	-1.311671	H	-5.741312	1.093662	-2.104215
C	-4.344255	-2.556258	-1.536437	H	-5.553758	2.887432	2.467828
C	-4.900241	-1.288297	-1.447314	H	-5.319878	4.402590	0.559847
C	-5.627115	-0.878841	-0.312920	H	-4.703079	4.695993	-1.693726
C	-5.981005	-1.896175	0.594874	H	-5.185255	3.563785	-2.955836
C	-5.402005	-3.163530	0.525449	H	-4.950012	-0.744019	2.261858
H	3.213590	-5.764749	2.044766	H	-5.571431	0.452400	3.377494
H	3.183338	-4.497165	-2.061421	H	-2.217618	3.189953	2.354162
H	3.994651	-3.589424	2.212128	H	-2.974118	-0.512771	0.388963
H	6.918681	-2.515994	-1.622234	H	-2.892967	0.648214	-1.763870
H	5.496833	-4.495726	-1.710171	H	-2.647312	4.093320	-2.595872
H	5.379385	-1.607976	2.293664	H	-3.141670	2.463800	-3.000641
H	6.772286	-0.409447	-1.963225	H	-2.963912	-0.055746	3.209527
H	6.243571	2.409265	2.049311	H	-3.510450	1.585741	3.523947

DCMC

C	-6.049631	-3.203652	1.065955	C	5.154724	-4.417363	0.910061
C	-5.175398	-3.341045	-0.017605	C	4.554558	-4.005974	-1.362270
C	-5.410316	-2.525633	-1.134337	C	-2.005032	-5.108877	-1.063006
C	-6.416499	-1.576045	-1.135264	C	-3.281846	-4.576322	-1.119565
C	-7.231136	-1.384907	-0.018758	C	-3.963875	-4.188759	0.040599
C	-7.051691	-2.239422	1.066424	C	-3.359349	-4.509292	1.262971
C	-5.421475	3.132921	-0.079193	C	-2.091206	-5.063031	1.320153
C	-6.169479	2.783428	-1.207534	C	-8.175066	-0.198798	0.040875
C	-7.122387	1.775242	-1.148930	H	-5.936568	-3.836856	1.935662
C	-7.356336	1.074651	0.033436	H	-4.757333	-2.587436	-1.993432
C	-6.679674	1.486320	1.181803	H	-6.530593	-0.931554	-1.997689
C	-5.733893	2.499033	1.129642	H	-7.684136	-2.133320	1.939659
C	6.125850	-3.432721	0.830802	H	-5.984618	3.284824	-2.148848

C	5.517530	-3.014819	-1.436498	H	-7.661642	1.501247	-2.047661
C	6.809637	-1.248865	-0.232799	H	-6.850688	0.966797	2.117045
C	6.246912	-2.617878	-0.306387	H	-5.175637	2.749334	2.022364
C	7.042607	-0.638846	1.009543	H	6.730537	-3.240094	1.705926
C	6.753215	0.977036	-1.202115	H	5.594961	-2.457185	-2.358063
C	6.812265	-0.398431	-1.348425	H	7.131406	-1.240015	1.903009
C	6.715652	1.571197	0.066615	H	6.595894	1.581099	-2.085277
C	7.007137	0.736684	1.154644	H	6.733971	-0.805776	-2.346177
C	5.892086	3.810326	-0.788974	H	7.094381	1.153445	2.148942
C	6.052411	2.879552	0.248076	H	6.525283	3.757638	-1.664957
C	4.248874	4.004136	1.419686	H	3.590692	4.013644	2.276510
C	5.272641	3.076157	1.395513	H	5.367139	2.399645	2.232677
C	4.865980	4.742654	-0.763442	H	4.733951	5.391776	-1.618929
C	2.597016	5.369882	0.170534	H	2.204899	5.598179	2.278993
C	3.950515	4.788940	0.298748	H	0.181637	5.560080	-2.206107
C	1.775616	5.580888	1.286559	H	2.578129	5.344036	-1.984076
C	0.610176	5.559759	-1.213322	H	-0.198736	5.702651	2.060872
C	1.985329	5.459348	-1.087112	H	-1.451852	4.237447	-2.098463
C	-0.226006	5.554138	-0.089177	H	-4.481541	5.021850	1.702435
C	0.399005	5.658065	1.160790	H	-2.288598	6.079064	1.682390
C	-2.117990	4.455927	-1.276064	H	-3.646785	3.216068	-2.088139
C	-1.662502	5.217990	-0.192129	H	0.308853	-6.427829	-1.756779
C	-3.822581	4.850422	0.860860	H	2.758795	-4.489002	2.046271
C	-2.572001	5.450568	0.848718	H	0.360269	-4.729822	2.180742
C	-3.370292	3.868030	-1.270309	H	2.719598	-6.156775	-1.898613
C	-4.229437	4.001265	-0.174774	H	5.029996	-4.956750	1.840224
C	-1.346846	-5.305408	0.158035	H	3.919909	-4.177916	-2.221294
C	0.833772	-5.998424	-0.914062	H	-1.486783	-5.301415	-1.992055
C	0.113759	-5.536139	0.197667	H	-3.728248	-4.410078	-2.090215
C	2.237048	-4.951594	1.219467	H	-3.853270	-4.257176	2.191253
C	0.862211	-5.087954	1.293339	H	-1.655308	-5.251852	2.291488
C	2.209799	-5.850969	-0.993972	H	-8.783654	-0.261353	0.943939
C	4.269751	-4.647137	-0.151460	H	-8.852076	-0.207792	-0.815631
C	2.933828	-5.246058	0.041297				

References:

(S1) Tour, J. M.; Rawlett, A. M.; Kozaki, M.; Yao, Y. X.; Jagessar, R. C.; Dirk, S. M.; Price, D. W.; Reed, M. A.; Zhou, C. W.; Chen, J.; Wang, W. Y.; Campbell, I. *Chem. Eur. J.* **2001**, *7*, 5118-5134.

(S2) Braun, C.; Brase, S.; Schafer, L. L. *Eur. J. Org. Chem.* **2017**, 1760-1764.

(S3) Huang, Q.; Zhuang, G.; Jia, H.; Qian, M.; Cui, S.; Yang, S.; Du, P. W. *Angew. Chem., Int. Ed.* **2019**, *58*, 6244-6249.

(S4) Frisch, M.; Trucks, G.; Schlegel, H. B.; Scuseria, G.; Robb, M.; Cheeseman, J.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. et. al. Gaussian 09, Revision A. 02, Gaussian. *Inc., Wallingford, CT* **2009**.

(S5) Segawa, Y.; Omachi, H.; Itami, K. *Org. Lett.* **2010**, *12*, 2262-2265.

(S6) McCormick, T. M.; Bridges, C. R.; Carrera, E. I.; Di Carmine, P. M.; Gibson, G. L.; Hollinger, J.; Kozycz, L. M.; Seferos, D. S. *Macromolecules* **2013**, *46*, 3879-3886.