Supporting Information

Precise synthesis and photophysical properties of a small chiral carbon nanotube segment: Cyclo[7]paraphenylene-2,6-naphthylene

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1. General and Materials Information

All anhydrous solvents for synthesis were used under argon or nitrogen atmosphere, and other chemicals were perchased from commercial suppliers (Acros or Innochem). All the air-sensitive reactions were carried out using the standard Schlenk technique under argon or nitrogen atmosphere. NMR spectra were recorded on a Bruker BioSpin (^{1}H 400 MHz, ^{13}C 100 MHz). Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm) or $CHCl_3$ (δ 7.26 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, m = multiplet, br = broad signal), coupling constant (Hz), and integration. High-resolution mass spectrometry (HR-MS) analyses were carried out using MALDI-TOF-MS techniques (matrix: trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB)). UV-Vis spectra were obtained on a UNIC-3802 spectrophotometer in standard glass cuvettes. Preparative thin-layer chromatography (PTLC) were performed using silica gel GF254 precoated plates and flash chromatography was performed on silica gel (200~300 mesh).

Synthesis of Compound (1) and 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene (2).

Compound **1** was prepared according to the reported method by our group.[S1] 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene **2** was prepared according to the literature.[S2]

Synthesis of compound 3.

To a mixture of **2** (70.65 mg, 0.186 mmol), **1** (163.32 mg, 0.186 mmol), and potassium hydrate (134 mg, 2.388 mmol) in a round-bottom flask (500 mL) was added THF (250 mL) and H_2O (10 mL), then $Pd(PPh_3)_4$ (30.06 mg, 0.026 mmol) were added under argon atmosphere. Thereafter, the solution was heated at 85 °C for 48 hours. Upon cooling to room temperature, solvent was removed under vacuum and the residue was extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to afford crude product **3** as a gray solid for the next step without further purification.

Synthesis of [7]CPPNa$_{2,6}$ (4).

To a round-bottom flask (50 mL, vessel A) containing a magnetic stirring bar were added sodium metal (274 mg, 11.9 mmol), dry THF (12 mL), and naphthalene (1.00 g, 7.82 mmol), and the resultant mixture was stirred at room temperature for 1 day. To another 250-mL round-bottom flask (vessel B) containing the above dry crude product **3** and dry THF (30 mL) was added a solution of sodium naphthalide (2 mL, 2 mmol, 1.0 M in THF) in vessel A at -78 °C. This mixture was kept stirring at -78 °C for 2 hours. Then, 1.5 mL of I_2 solution (1 M in THF) was added. After warmed up to room temperature, the mixture was quenched with aqueous saturated sodium thiosulfate, extracted with CH_2Cl_2, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography with hexane/CH_2Cl_2 as the eluent (v/v, 3:1). Further purification by recrystallization from MeOH and *n*-hexane afforded pure **[7]CPPNa$_{2,6}$** (26 mg, 21%) as yellow solid. Mp:

113-115 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75 (s, 2H), 7.64 (s, 4H), 7.54 (d, J = 8.2 Hz, 4H), 7.46 (brs, 24H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 125.51, 125.85, 127.41, 127.43, 127.47,127.52, 127.58, 127.63, 128.32, 133.30, 136.30, 137.84, 137.86, 137.94, 137.95, 138.01, 138.06. IR (KBr) 722 (w), 732 (w), 752 (m), 802 (w), 811 (w), 821 (m), 945 (w), 999 (w), 1074 (w), 1120 (w), 1212 (w), 1261 (w), 1381 (w), 1462 (m), 1482 (w), 1586 (w), 1631 (w), 1726 (w), 2854 (m), 2871 (w), 2925 (s), 2954 (w) cm^{-1}. HR-MS (MALDI-TOF) *m/z* calcd. for $C_{52}H_{34}$ $[M]^+$: 658.2661, found 658.2612.

2. Physical characterizations

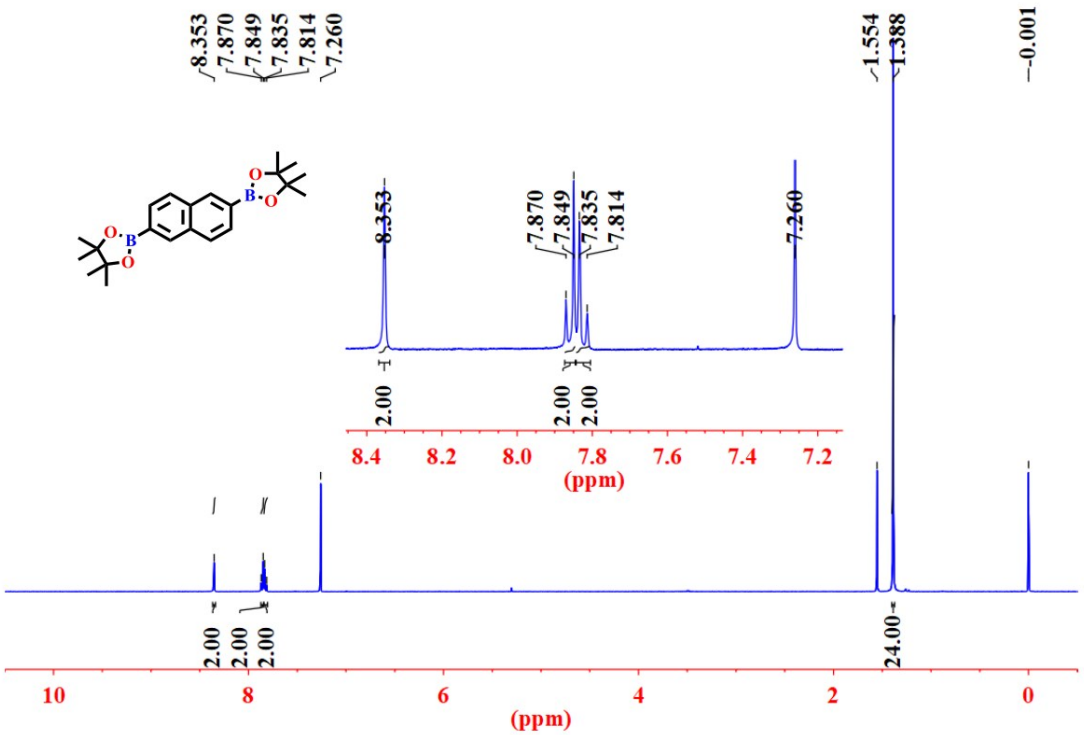

Figure S1. ^{1}H NMR spectrum of 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene in $CDCl_3$.

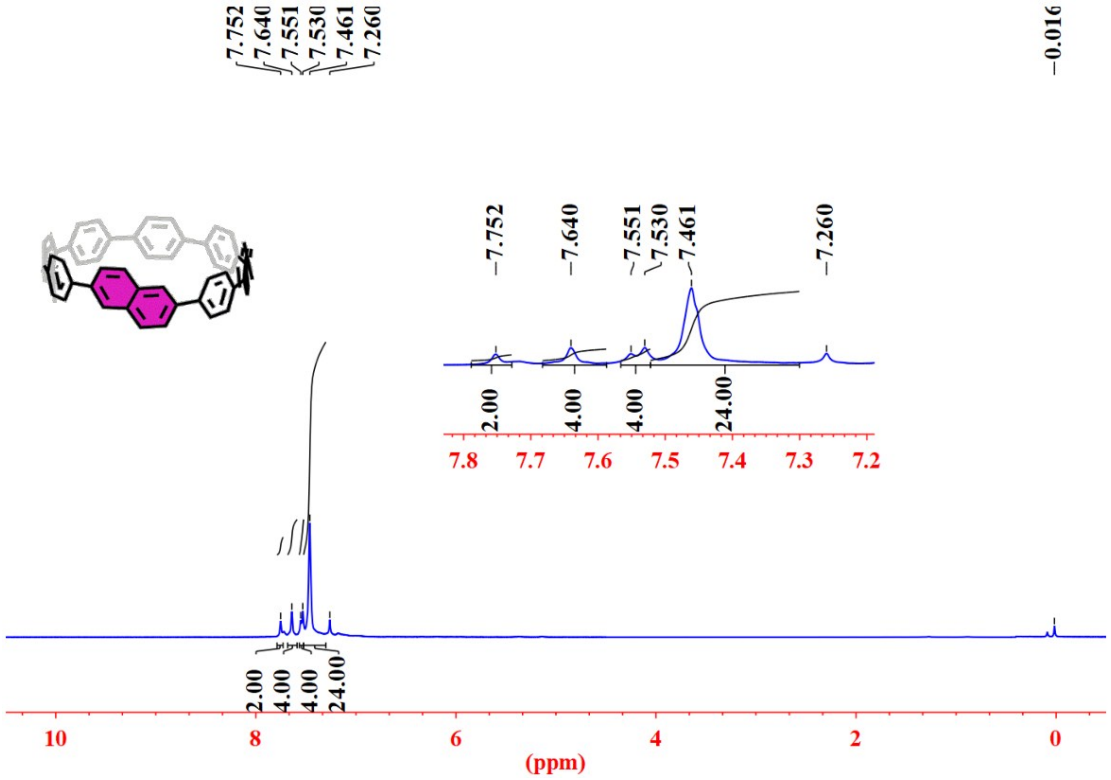

Figure S2. ^{1}H NMR spectrum of **[7]CPPNa$_{2,6}$** in $CDCl_3$.

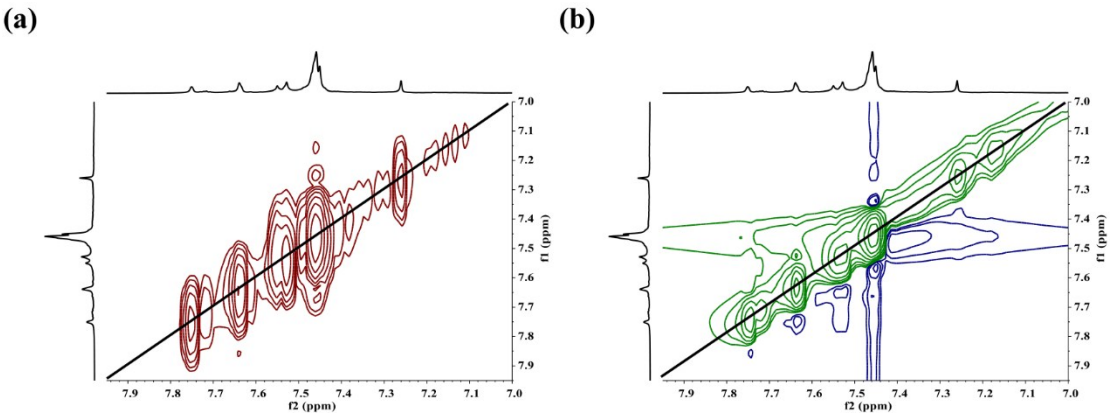

Figure S3. The expanded 2D ^{1}H-^{1}H COSY NMR (a) and 2D NOESY NMR (b) spectra (400 MHz) of **[7]CPPNa$_{2,6}$** in $CDCl_3$.

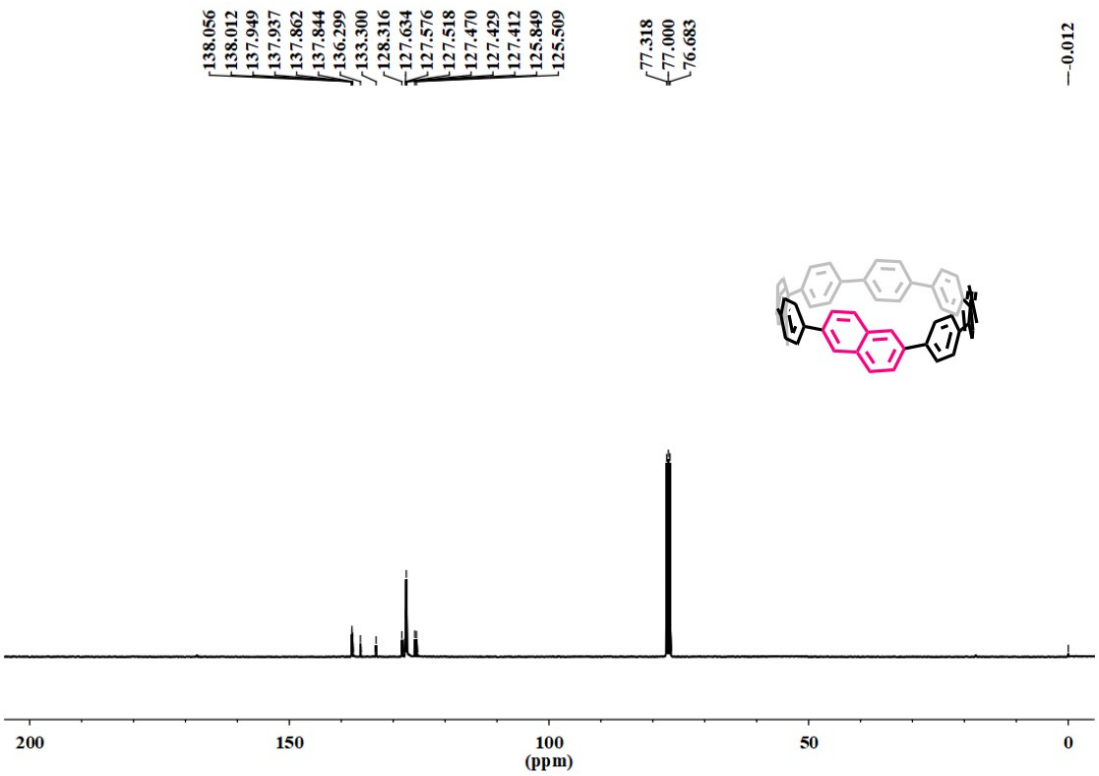

Figure S4. ^{13}C NMR spectrum of **[7]CPPNa$_{2,6}$** in $CDCl_3$.

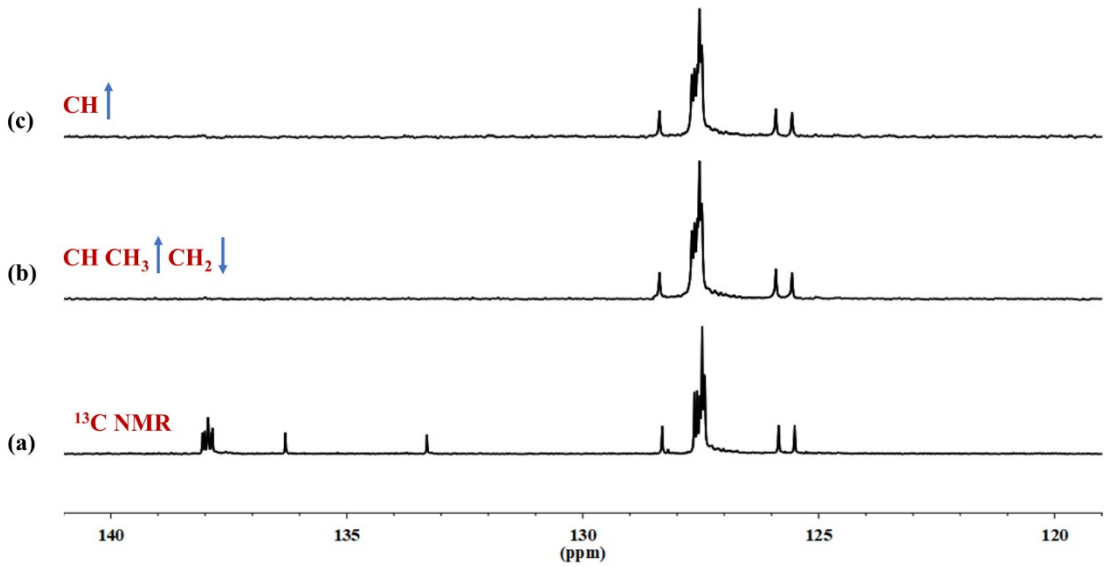

Figure S5. Aromatic region of ^{13}C NMR (a), DEPT-135° NMR (b), DEPT-90° NMR (c) spectrum of **[7]CPPNa$_{2,6}$** in $CDCl_3$.

3. Emission profiles of [7]CPPNa$_{2,6}$ in nitrogen atmosphere and air (Figure S6)

Photoluminescence of **[7]CPPNa$_{2,6}$** was recorded after bubbling of nitrogen or air for 20 min (CH_2Cl_2, 1.0×10^{-5} M).

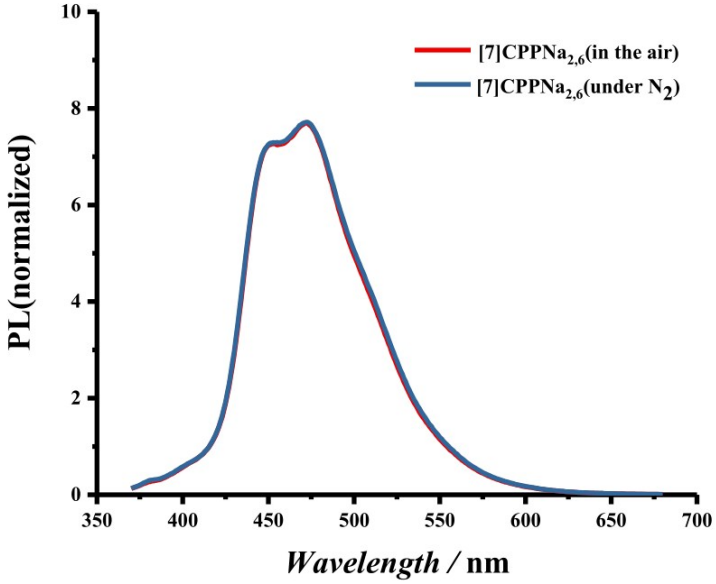

Figure S6. Normalized emission profiles of **[7]CPPNa$_{2,6}$** in nitrogen atmosphere (blue) and in the air (red).

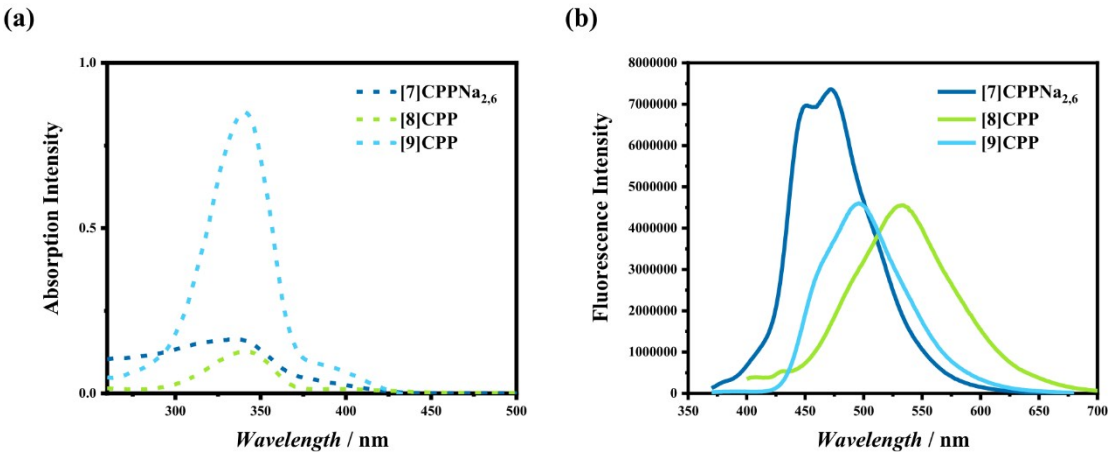

Figure S7. UV-Vis absorption (a) and fluorescence spectra (b) for **[7]CPPNa$_{2,6}$** (blue), **[8]CPP** (yellow) and **[9]CPP** (cyan) in CH_2Cl_2 (1.0×10^{-5} M).

4. Computational Details

All density functional theory calculations were performed by using Gaussian 09 software.[S3] Geometrical optimization were carried out by CAM-B3LYP/Def2-TZVP and further validated by frequency analysis. Solvent effect was corrected by polarizable continuum model. The tension energy was calculated using the reported computational methods.[S4] As shown in Figure S7, the strain energy was obtained according to the following formula: Strain energy = E(**[7]CPPNa$_{2,6}$**) + 8*E(biphenyl) – 7*E(Terphenyl) – E(naphthalene-diphenyl). Based on the relaxed structure, time-dependence 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 CAM-B3LYP,[S5] B3LYP/Def2-TZVP computational level was used to identify the energy level of frontier orbitals. Moreover, as reference compounds for comparison, frontier molecular orbital energy of [8]CPP and [9]CPP molecules were calculated.

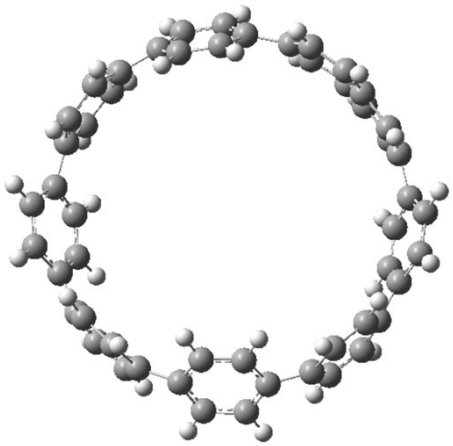

Figure S8. The relaxed structure of **[7]CPPNa$_{2,6}$**.

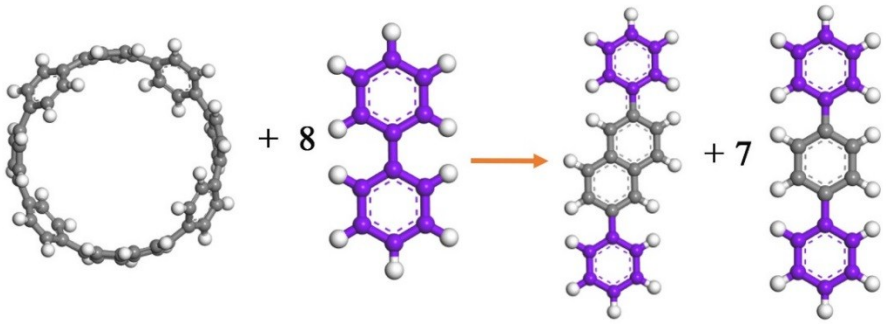

Figure S9. Strain-energy based homodesmotic reactions.

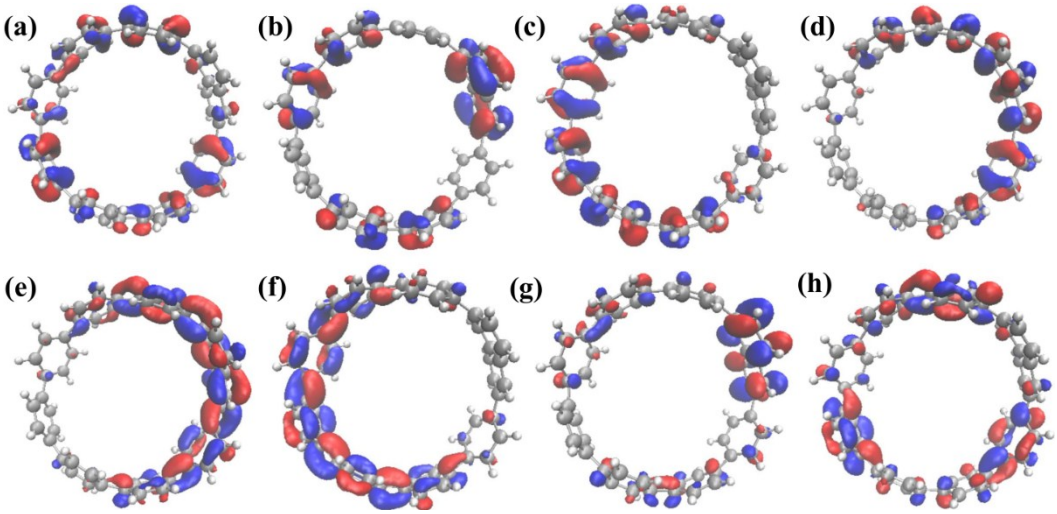

Figure S10. Frontier molecular orbitals of **[7]CPPNa$_{2,6}$**: (a) HOMO-3, (b) HOMO-2, (c) HOMO-1, (d) HOMO, (e) LUMO, (f) LUMO+1, (g) LUMO+2 and (h) LUMO+3.

Table S1. Energy of different moiety (unit: Hatree) and strain energy (unit: kcal/mol) of [7]CPPNa$_{2,6}$, [8]CPP and [9]CPP.

Name	[7]CPPNa$_{2,6}$	[8]CPP	[9]CPP
Total energy	-2001.53180120	-1847.916135	-2078.9401014
Biphenyl Energy	-463.19835880	-463.19835880	-463.19835880
Triphenyl Energy	-694.20663170	-694.20663170	-694.20663170
Naphthalene-diphenyl energy	-847.81509160	-	-
Strain energy (kal/mol)	89.63	94.16	84.31

Table S2. Orbital energy level of [7]CPPNa$_{2,6}$, [8]CPP and [9]CPP.

Orbitals	[7]CPPNa$_{2,6}$	[8]CPP	[9]CPP
LUMO+3	-1.1119	-0.9875	-0.9045
LUMO+2	-1.3396	-1.5995	-1.5894
LUMO+1	-2.0294	-1.5995	-1.6621
LUMO	-2.0479	-2.2259	-2.0871
HOMO	-5.5313	-5.3653	-5.5125
HOMO-1	-5.5580	-5.9833	-5.9234
HOMO-2	-6.3346	-5.9833	-5.9827
HOMO-3	-6.4521	-6.9893	-6.8127
Gap (HOMO-LUMO)	3.4834	3.1394	3.4254

Table S3. Main electronic transitions of [7]CPPNa$_{2,6}$ and Naphthalene obtained by TD-DFT with fos > 0.1

λ_{exp} (nm)	λ_{DFT} (nm)	main transitions (coefficient)	f_{os}
[7]CPPNa$_{2,6}$			
335	325.22	HOMO→LUMO (40.1%) HOMO-1→LUMO+1 (42%)	1.7289
	325.54	HOMO→LUMO+1 (-41%) HOMO-1→LUMO (41%)	1.9734
	277.56	HOMO-2→LUMO (19%) HOMO-1→LUMO+5 (39%) HOMO→LUMO+6 (-22%) HOMO-5→LUMO+1 (19%) HOMO→LUMO+2 (17%)	0.1044
	275.24	HOMO-2→LUMO (31%) HOMO-3→LUMO+1 (21%) HOMO-1→LUMO+5 (-27%) HOMO→LUMO+2 (25%)	0.2428

Table S4. Coordinate of relaxed [7]CPPNa$_{2,6}$.

C	-0.688527	0.154905	-5.653249	C	-0.365686	-4.176945	-3.478219
C	1.188009	2.196067	-5.447518	C	0.031258	-4.921509	-2.387126
C	1.609091	0.921785	-5.668649	C	1.872502	-4.138368	-4.269391
C	-0.180123	2.484853	-5.190382	C	0.180123	-2.484853	-5.190382
C	-1.094892	1.486772	-5.418788	C	0.560560	-3.675203	-4.390240
C	0.365686	4.176945	-3.478219	C	-1.188009	-2.196067	-5.447518
C	-0.560560	3.675203	-4.390240	C	0.688527	-0.154905	-5.653249
C	-2.269583	4.888136	-3.176327	C	1.094892	-1.486772	-5.418788
C	-1.872502	4.138368	-4.269391	C	-1.609091	-0.921785	-5.668649
C	-0.031258	4.921509	-2.387126	H	1.918751	2.991591	-5.397782
C	-1.799699	5.525402	-0.766567	H	2.665556	0.710421	-5.777828
C	-1.374233	5.208513	-2.152556	H	-2.148371	1.664322	-5.246166
C	-3.026476	5.064569	-0.287769	H	1.400432	3.871745	-3.534312
C	-1.094892	5.760383	1.534587	H	-3.313603	5.158025	-3.087151
C	-0.894583	5.991792	0.187382	H	-2.618902	3.845589	-4.996354
C	-2.222278	5.077948	1.992790	H	0.712097	5.161748	-1.641158
C	-3.238249	4.858742	1.062019	H	-3.791081	4.742476	-0.981279
C	-1.264149	4.637323	4.298217	H	-0.297794	6.009567	2.221445
C	-2.174331	4.342085	3.280877	H	0.037357	6.443977	-0.122889
C	-2.474452	2.172130	4.305272	H	-4.173688	4.414250	1.373040
C	-2.842322	3.122410	3.376446	H	-0.771801	5.600539	4.322164
C	-0.893047	3.682740	5.229316	H	-2.932008	1.195443	4.241466
C	-0.730132	1.208993	5.765905	H	-3.570739	2.844538	2.628846
C	-1.417721	2.389599	5.187732	H	-0.123368	3.931975	5.948066
C	-1.373967	-0.021285	5.898269	H	-2.454416	-0.070564	5.898077
C	1.373967	0.021285	5.898269	H	2.454416	0.070564	5.898077
C	0.659907	1.204165	5.885965	H	1.207821	2.135674	5.843823
C	0.730132	-1.208993	5.765905	H	-1.207821	-2.135674	5.843823
C	-0.659907	-1.204165	5.885965	H	2.932008	-1.195443	4.241466
C	2.474452	-2.172130	4.305272	H	0.771801	-5.600539	4.322164
C	1.417721	-2.389599	5.187732	H	0.123368	-3.931975	5.948066
C	1.264149	-4.637323	4.298217	H	3.570739	-2.844538	2.628846
C	0.893047	-3.682740	5.229316	H	0.297794	-6.009567	2.221445
C	2.842322	-3.122410	3.376446	H	3.791081	-4.742476	-0.981279
C	2.222278	-5.077948	1.992790	H	4.173688	-4.414250	1.373040
C	2.174331	-4.342085	3.280877	H	-0.037357	-6.443977	-0.122889
C	1.094892	-5.760383	1.534587	H	3.313603	-5.158025	-3.087151
C	3.026476	-5.064569	-0.287769	H	-1.400432	-3.871745	-3.534312
C	3.238249	-4.858742	1.062019	H	-0.712097	-5.161748	-1.641158
C	1.799699	-5.525402	-0.766567	H	2.618902	-3.845589	-4.996354
C	0.894583	-5.991792	0.187382	H	-1.918751	-2.991591	-5.397782

C	2.269583	-4.888136	-3.176327	H	2.148371	-1.664322	-5.246166
C	1.374233	-5.208513	-2.152556	H	-2.665556	-0.710421	-5.777828

Table S5. Coordinate of relaxed [8]CPP.

C	**4.486870**	**-3.250604**	**1.057847**	**C**	**-0.689429**	**-4.822529**	**1.530821**
C	4.225104	-3.533567	-1.282899	C	0.692036	-5.945411	-0.559483
C	5.282423	-1.416290	-0.434001	C	-0.692036	-5.945411	-0.559483
C	4.764568	-2.792754	-0.230714	C	1.416290	-5.282423	0.434001
C	5.945411	-0.692036	0.559483	C	0.689429	-4.822529	1.530821
C	4.822529	0.689429	-1.530821	C	3.250604	-4.486870	-1.057847
C	4.822529	-0.689429	-1.530821	C	2.792754	-4.764568	0.230714
C	5.282423	1.416290	-0.434001	C	3.533567	-4.225104	1.282899
C	5.945411	0.692036	0.559483	H	4.923486	-2.754542	1.913761
C	4.225104	3.533567	-1.282899	H	4.476159	-3.287947	-2.305604
C	4.764568	2.792754	-0.230714	H	6.396794	-1.208102	1.396546
C	3.533567	4.225104	1.282899	H	4.320997	1.194448	-2.343351
C	4.486870	3.250604	1.057847	H	4.320997	-1.194448	-2.343351
C	3.250604	4.486870	-1.057847	H	6.396794	1.208102	1.396546
C	1.416290	5.282423	0.434001	H	4.476159	3.287947	-2.305604
C	2.792754	4.764568	0.230714	H	3.287947	4.476159	2.305604
C	0.689429	4.822529	1.530821	H	4.923486	2.754542	1.913761
C	-0.692036	5.945411	-0.559483	H	2.754542	4.923486	-1.913761
C	0.692036	5.945411	-0.559483	H	1.194448	4.320997	2.343351
C	-1.416290	5.282423	0.434001	H	-1.208102	6.396794	-1.396546
C	-0.689429	4.822529	1.530821	H	1.208102	6.396794	-1.396546
C	-3.250604	4.486870	-1.057847	H	-1.194448	4.320997	2.343351
C	-2.792754	4.764568	0.230714	H	-2.754542	4.923486	-1.913761
C	-4.486870	3.250604	1.057847	H	-4.923486	2.754542	1.913761
C	-3.533567	4.225104	1.282899	H	-3.287947	4.476159	2.305604
C	-4.225104	3.533567	-1.282899	H	-4.476159	3.287947	-2.305604
C	-5.282423	1.416290	-0.434001	H	-6.396794	1.208102	1.396546
C	-4.764568	2.792754	-0.230714	H	-4.320997	-1.194448	-2.343351
C	-5.945411	0.692036	0.559483	H	-4.320997	1.194448	-2.343351
C	-4.822529	-0.689429	-1.530821	H	-6.396794	-1.208102	1.396546
C	-4.822529	0.689429	-1.530821	H	-4.476159	-3.287947	-2.305604
C	-5.282423	-1.416290	-0.434001	H	-3.287947	-4.476159	2.305604
C	-5.945411	-0.692036	0.559483	H	-4.923486	-2.754542	1.913761
C	-4.225104	-3.533567	-1.282899	H	-2.754542	-4.923486	-1.913761
C	-4.764568	-2.792754	-0.230714	H	-1.194448	-4.320997	2.343351
C	-3.533567	-4.225104	1.282899	H	1.208102	-6.396794	-1.396546
C	-4.486870	-3.250604	1.057847	H	-1.208102	-6.396794	-1.396546
C	-3.250604	-4.486870	-1.057847	H	1.194448	-4.320997	2.343351

C	-1.416290	-5.282423	0.434001	H	2.754542	-4.923486	-1.913761
C	-2.792754	-4.764568	0.230714	H	3.287947	-4.476159	2.305604

Table S6. Coordinate of relaxed [9]CPP.

C	**-1.337633**	**-3.164910**	**4.768500**	**C**	**1.236024**	**-5.827197**	**0.356686**
C	0.874912	-3.668958	5.469580	C	0.094351	-6.217581	-0.340035
C	-0.115695	-1.411703	6.036360	C	-1.068957	-6.313500	1.778106
C	-0.214854	-2.796083	5.508345	C	-1.027541	-6.556606	0.417935
C	-1.237910	-0.592567	6.161647	C	1.196104	-5.587725	1.717124
C	1.237910	0.592567	6.161647	C	-0.141795	-4.974860	3.705236
C	1.125380	-0.784133	6.147049	C	0.011651	-5.725718	2.436812
C	0.115695	1.411703	6.036360	C	-1.303837	-4.230258	3.892042
C	-1.125380	0.784133	6.147049	C	0.914078	-4.730357	4.583039
C	1.337633	3.164910	4.768500	H	-2.219241	-2.540958	4.771858
C	0.214854	2.796083	5.508345	H	1.745026	-3.478698	6.083247
C	-0.914078	4.730357	4.583039	H	-2.229224	-1.023638	6.169685
C	-0.874912	3.668958	5.469580	H	2.229224	1.023638	6.169685
C	1.303837	4.230258	3.892042	H	2.033826	-1.368820	6.110533
C	-0.011651	5.725718	2.436812	H	-2.033826	1.368820	6.110533
C	0.141795	4.974860	3.705236	H	2.219241	2.540958	4.771858
C	-1.196104	5.587725	1.717124	H	-1.812907	5.330789	4.525489
C	1.027541	6.556606	0.417935	H	-1.745026	3.478698	6.083247
C	1.068957	6.313500	1.778106	H	2.155486	4.395512	3.246405
C	-0.094351	6.217581	-0.340035	H	-2.064891	5.153616	2.193254
C	-1.236024	5.827197	0.356686	H	1.912887	6.940757	-0.071758
C	1.150092	5.407166	-2.317868	H	1.985887	6.510651	2.318431
C	-0.020439	5.955267	-1.797642	H	-2.135583	5.571641	-0.186398
C	-1.150099	5.250499	-3.817246	H	2.052183	5.403195	-1.721749
C	-1.145646	5.947964	-2.623087	H	-2.066179	5.203968	-4.391680
C	1.145646	4.710722	-3.510435	H	-2.058257	6.428552	-2.295259
C	-0.115874	3.392474	-5.181797	H	2.044423	4.186950	-3.805505
C	-0.029893	4.531196	-4.236093	H	-2.155307	2.954064	-4.677425
C	-1.263421	2.602572	-5.177718	H	1.930380	1.216018	-6.781084
C	1.021318	1.592507	-6.330204	H	1.886555	3.500602	-5.958287
C	0.996291	2.892965	-5.861131	H	-2.112904	0.683994	-5.500711
C	-0.065767	0.738279	-6.141793	H	2.112904	-0.683994	-5.500711
C	-1.239226	1.304044	-5.648253	H	-1.886555	-3.500602	-5.958287
C	1.239226	-1.304044	-5.648253	H	-1.930380	-1.216018	-6.781084
C	0.065767	-0.738279	-6.141793	H	2.155307	-2.954064	-4.677425
C	-0.996291	-2.892965	-5.861131	H	-2.044423	-4.186950	-3.805505
C	-1.021318	-1.592507	-6.330204	H	2.058257	-6.428552	-2.295259
C	1.263421	-2.602572	-5.177718	H	2.066179	-5.203968	-4.391680

C	0.029893	-4.531196	-4.236093	H	-2.052183	-5.403195	-1.721749
C	0.115874	-3.392474	-5.181797	H	2.135583	-5.571641	-0.186398
C	-1.145646	-4.710722	-3.510435	H	-1.985887	-6.510651	2.318431
C	1.145646	-5.947964	-2.623087	H	-1.912887	-6.940757	-0.071758
C	1.150099	-5.250499	-3.817246	H	2.064891	-5.153616	2.193254
C	0.020439	-5.955267	-1.797642	H	-2.155486	-4.395512	3.246405
C	-1.150092	-5.407166	-2.317868	H	1.812907	-5.330789	4.525489

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