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Supporting Information

A Nonalternant azulene-embedded carbon nanohoop featuring anti-kasha emission and tunable properties upon pH stimuli-responsiveness

Xiaonan Li, [a] Luyang Jia, [a] Wenguang Wang, [a] Ying Wang, [a] Di Sun, [b] and Hua Jiang *[a]

[a]College of Chemistry, Beijing Normal University, Beijing 100875 (P.R. China)

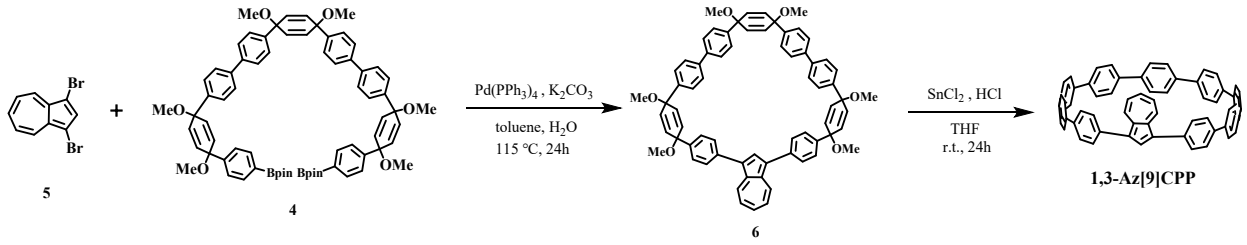
[b]School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100 (P.R. China)

Table of Contents

1. General Procedures and Materials.

All starting chemicals were obtained from commercial sources and used without further purification, unless indicated otherwise. All reactions were performed with dry solvents under Argon in dried glassware with standard vacuum-line techniques. Anhydrous THF, 1,4-dioxane and toluene were obtained from Solvent Purification System. Compound **1**,[1, 2] **2**,[3] **3**,[4] **4**[5] and **5**[6] prepared according to the literatures. Analytical TLC was carried out using tapered silica plates with a preadsorbent zone. NMR spectra were obtained with JEOL Delta (400 MHz and 600 MHz) using dichloromethane-*d* (CD_2Cl_2) and chloroform-*d* ($CDCl_3$) as solvent. The chemical shift references were as follows: (^{1}H) dichloromethane-*d*, 5.32 ppm; (^{13}C) dichloromethane-*d*, 53.84; (^{1}H) chloroform-*d*, 7.26 ppm; (^{13}C) chloroform-*d*, 77.16 ppm. The following abbreviations (or combinations thereof) were used to explain the multiplicities : s = singlet, d = doublet, t = triplet, m = multiplet. Mass spectra (ESI, MALDI) were acquired on GCT and FTICR spectrometer (Bruker Daltonics Inc. APEXII, BIFLEX III), respectively. UV-Vis spectra were recorded on Shimadzu UV-3600 and Fluorescence spectra were measured on FS5. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments were carried out at room temperature with an electrochemical workstation from Chenhua Instruments Co. (Shanghai, China). Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were measured with a glass carbon electrode for 1,1,2,2-tetrachloroethane solution of a sample (1 mM) in the presence of an supporting electrolyte (Bu_4NPF_6, 0.2 M) at room temperature under nitrogen atmosphere and the scan rates at 100 mV/s. The potential was externally calibrated against the Fc/Fc^+ couple at 0.410 V versus a Ag electrode.

2. Synthesis Procedures



To a dried 250 mL flask containing a magnetic stirring bar were added **5** (120 mg, 0.42 mmol, 1.0 eq), **4** (472.1 mg, 0.42 mmol, 1.0 eq), $Pd(PPh_3)_4$ (97 mg, 0.084 mmol, 0.2 eq), K_2CO_3 (3.4 g, 24.64 mmol, 58.7 eq) and 3 drops of Aliquat 336. The flask was evacuated and filled with argon three times. Dry toluene (106 mL) and the degassed distilled water (13 mL) was added via syringe. Then, the mixture was deoxygenated and freeze-pump-thawed (3×) and then was allowed to react at 115 °C for 1 day. After the reaction mixture was cooled, the mixture was extracted with ethyl acetate, washed with water and saturated brine. The combined organic phase was dried over sodium sulfate and consequently concentrated under reduced pressure. The crude product was initially purified by column chromatography on silica gel (PE/EA = 2/1, v/v) to afford a blue solid as the crude macrocyclic precursor 6 that was used in the next step without further purification.

A H_2SnCl_4/THF solution was freshly prepared by dissolving anhydrous $SnCl_2$ (283 mg, 1.49 mmol) in 5.2 mL anhydrous THF under Ar atmosphere and then adding concentrated HCl (aq) (0.2 mL) to the solution. The resulting solution was deoxygenated and stirred for 30 minutes. Crude product **6** (106 mg) was dissolved in anhydrous THF (11 mL) under the Ar atmosphere and the freshly prepared H_2SnCl_4/THF solution was added to this solution. The reaction mixture was stirred at room temperature for 1 day before being quenched with NaOH/H_2O solution. The aqueous layer was extracted with dichloromethane and the organic layers were combined and dried with anhydrous sodium sulfate. After purifying by column chromatography on silica gel (petroleum ether/DCM = 1.5/1, v/v) to get 1,3-Az[9]CPP as a green solid (21 mg, 24 %). M.p. > 300 ℃. ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) δ: 8.70-8.67 (m, 2H), 7.66 (t, J = 10.0 Hz, 1H), 7.62-7.55 (m, 36H), 7.28 (s, 1H), 7.22 (t, J = 9.9 Hz, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2, 298 K) δ: 145.1, 139.4, 138.8, 138.7, 138.6, 138.3, 137.2, 136.8, 136.2, 131.2, 130.1, 127.8, 127.7, 127.7, 124.2. HR-MS (MALDI-TOF) calculated for calculated for $C_{64}H_{42}$ M: 810.3287, found 810.3310.

3. NMR and Mass Spectra

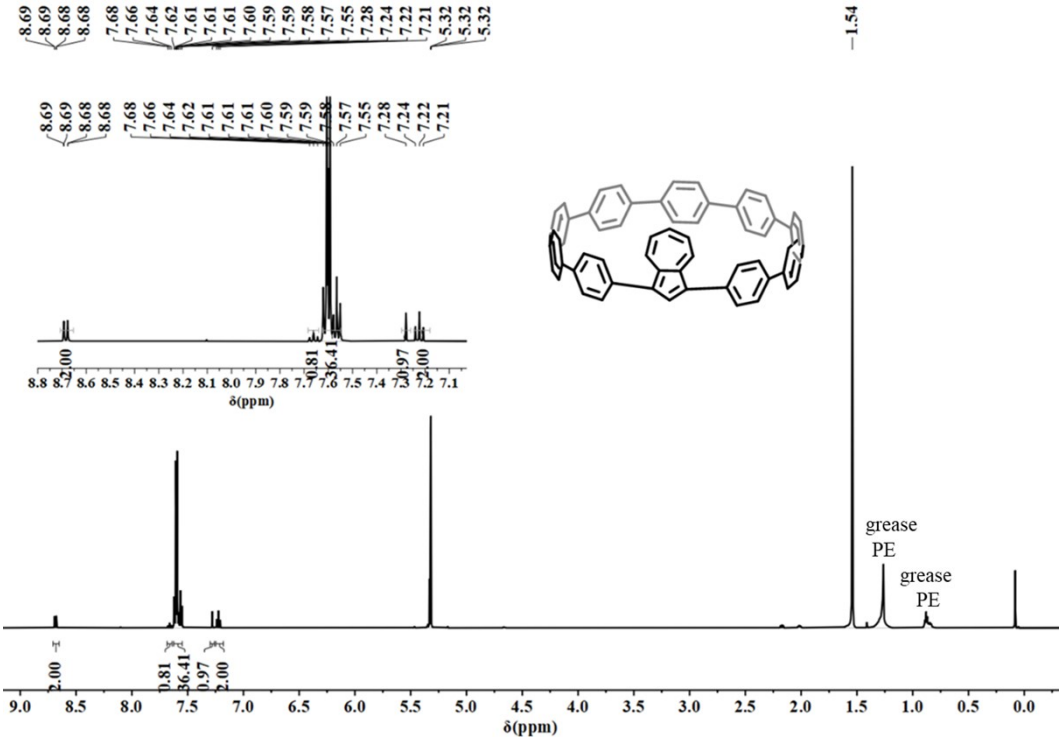


Figure S1. ^{1}H-NMR spectrum of compound **1,3-Az[9]CPP** in CD_2Cl_2 (600 MHz, 298 K)

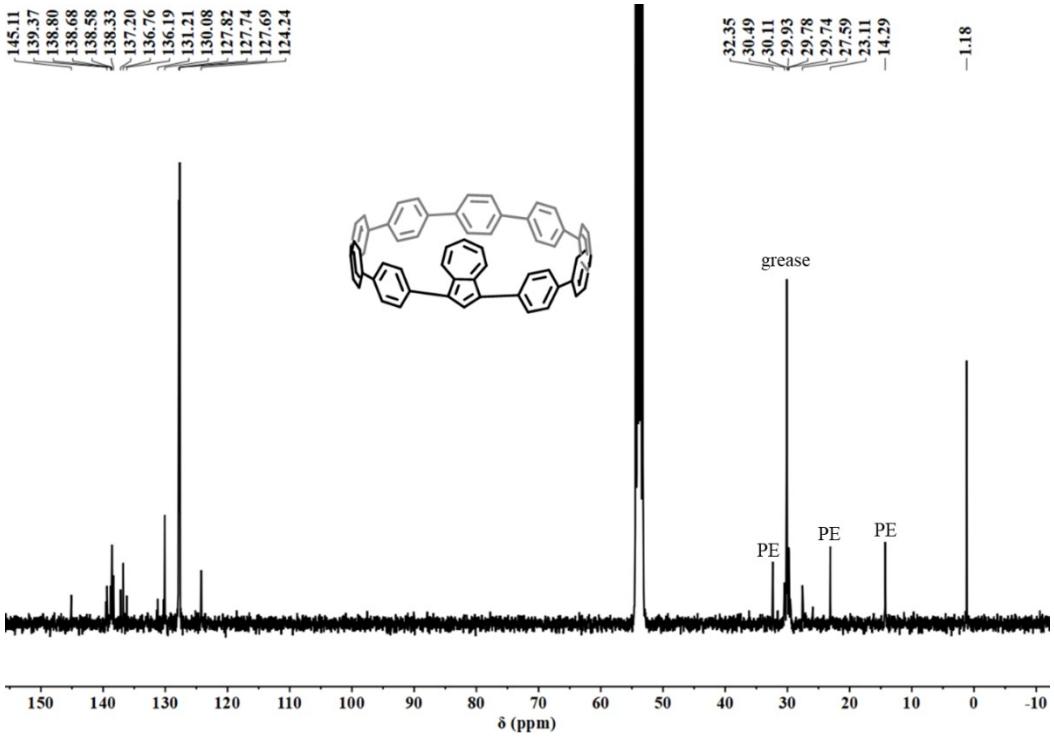


Figure S2. ^{13}C-NMR spectrum of compound **1,3-Az[9]CPP** in CD_2Cl_2 (100 MHz, 298 K)

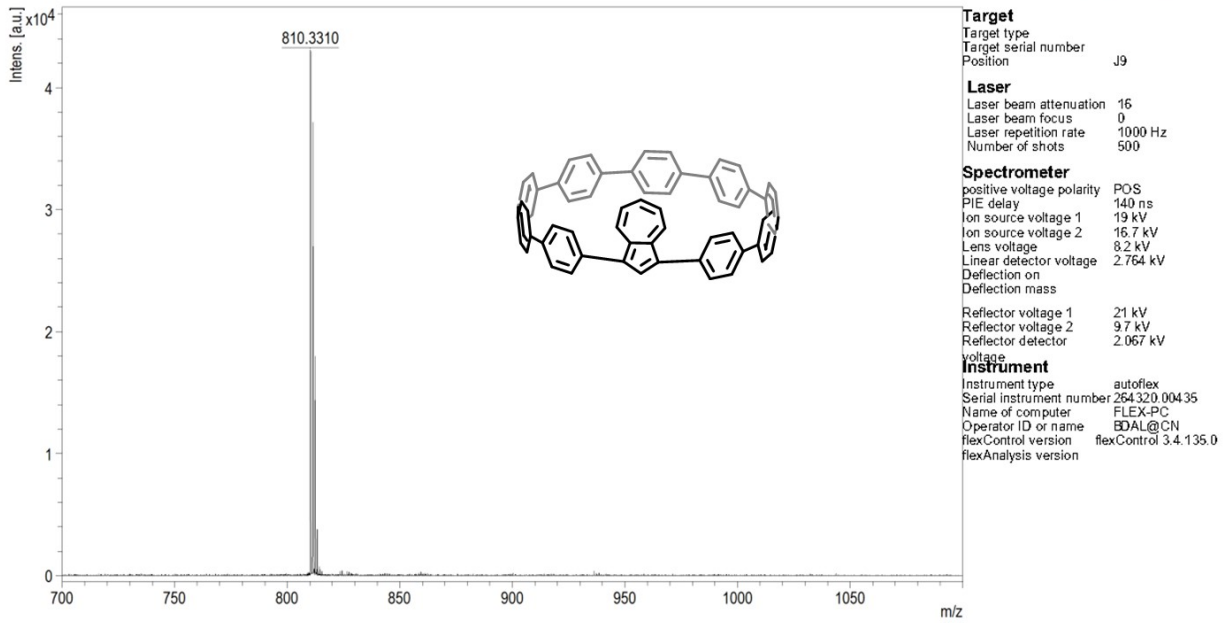


Figure S3. High-resolution mass spectrum (MALDI-TOF) of **1,3-Az[9]CPP**

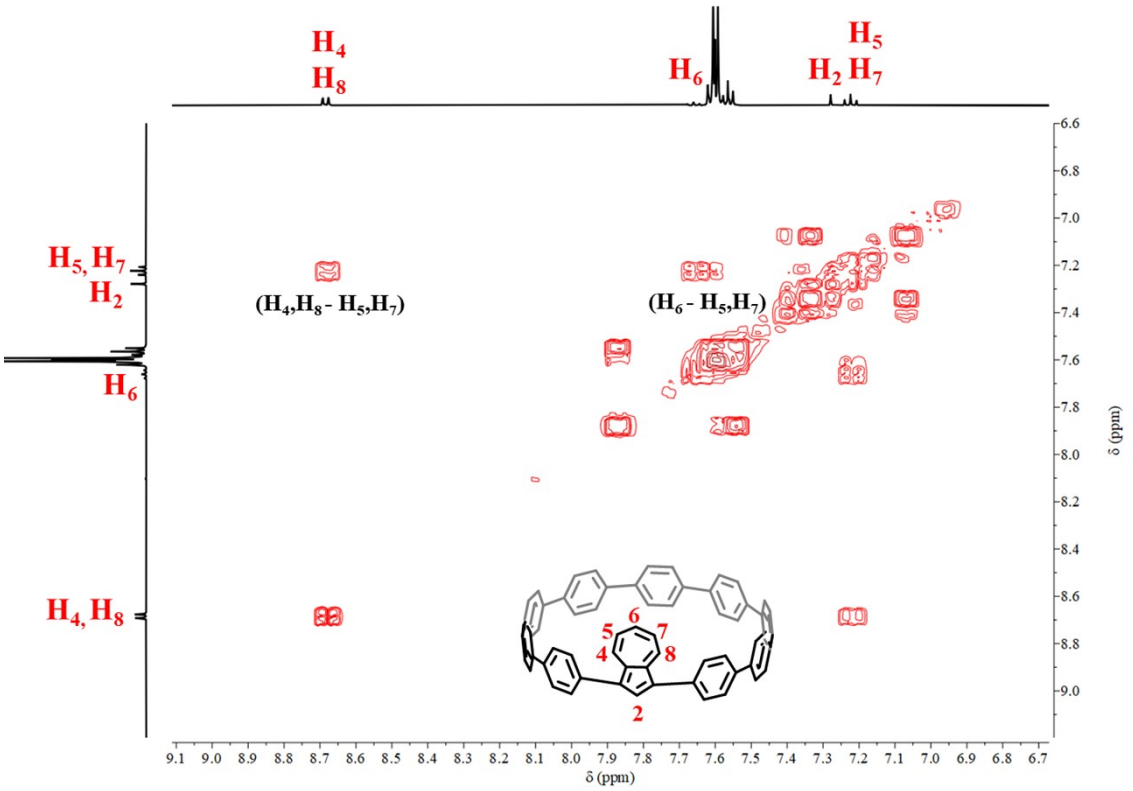


Figure S4. Partial ^{1}H-^{1}H COSY spectrum of compound **1,3-Az[9]CPP** in CD_2Cl_2 (400 MHz, 298 K)

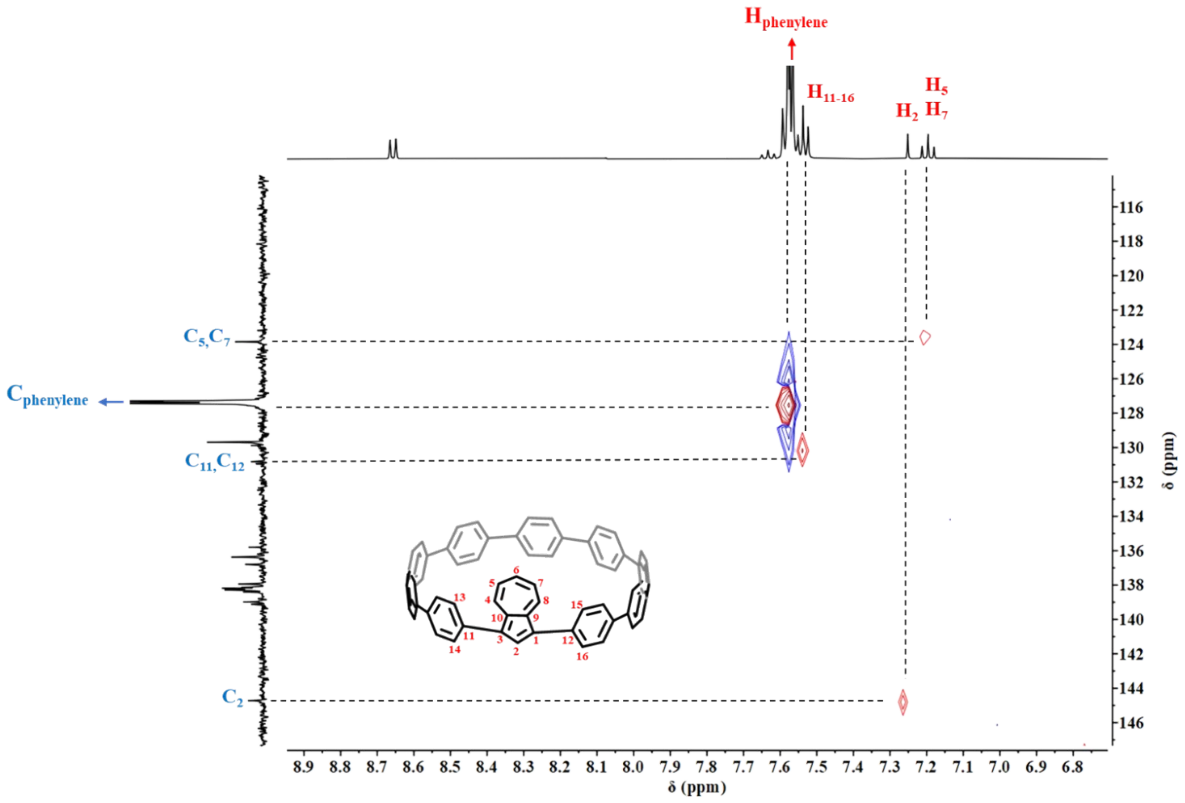


Figure S5. Partial ^{1}H-^{13}C HSQC spectrum of compound **1,3-Az[9]CPP** in CD_2Cl_2 (600 MHz, 298 K)

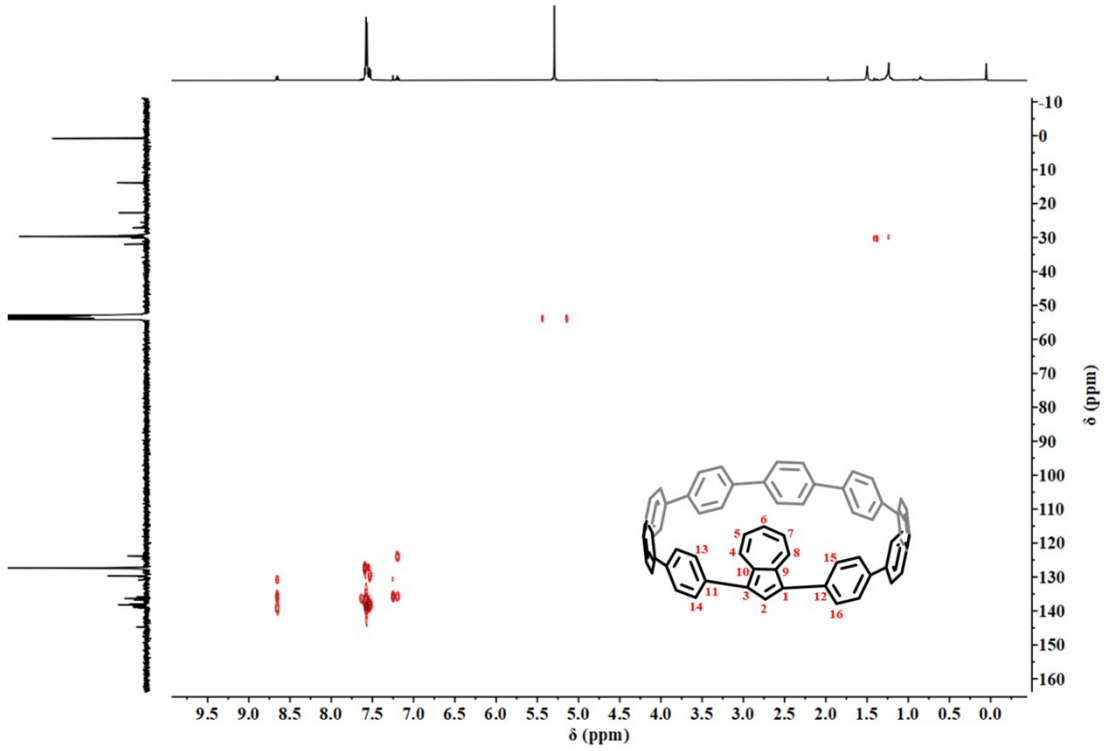


Figure S6. Partial ^{1}H-^{13}C HMBC spectrum of compound **1,3-Az[9]CPP** in CD_2Cl_2 (600 MHz, 298 K)

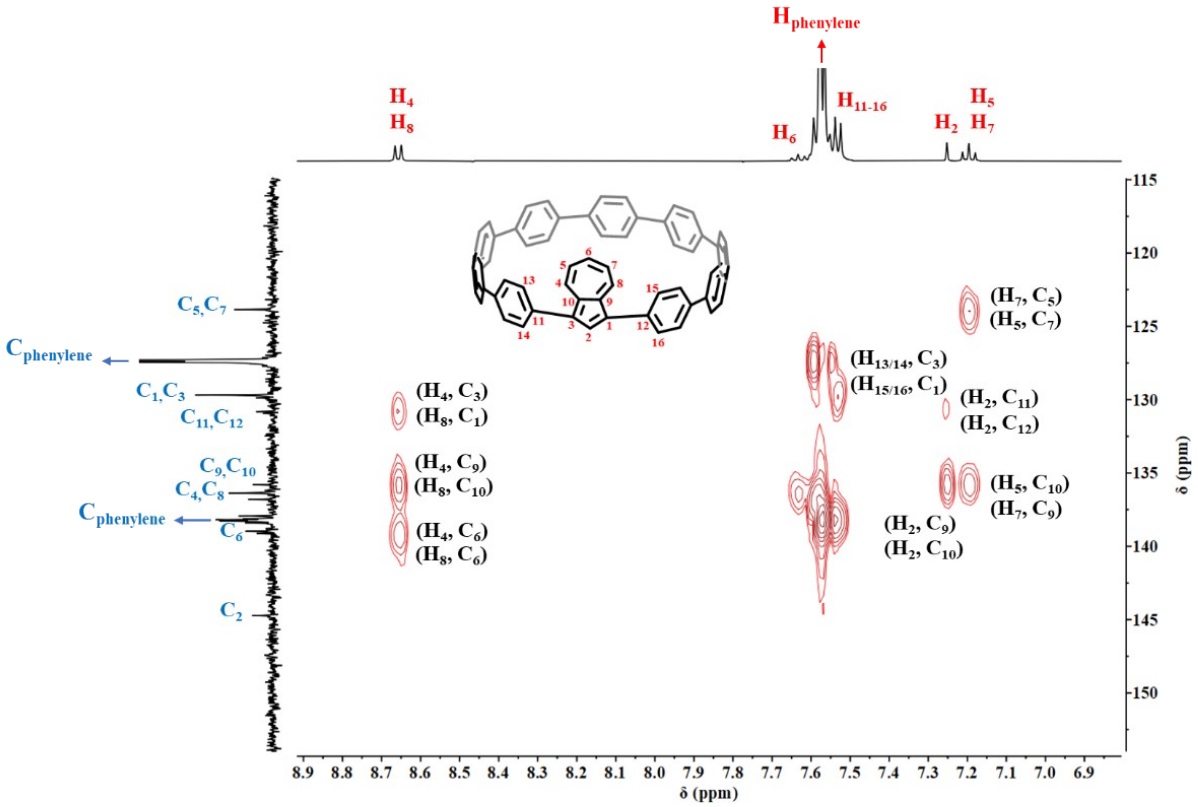


Figure S7. Partial ^{1}H-^{13}C HMBC spectrum of compound **1,3-Az[9]CPP** in CD_2Cl_2 (600 MHz, 298 K)

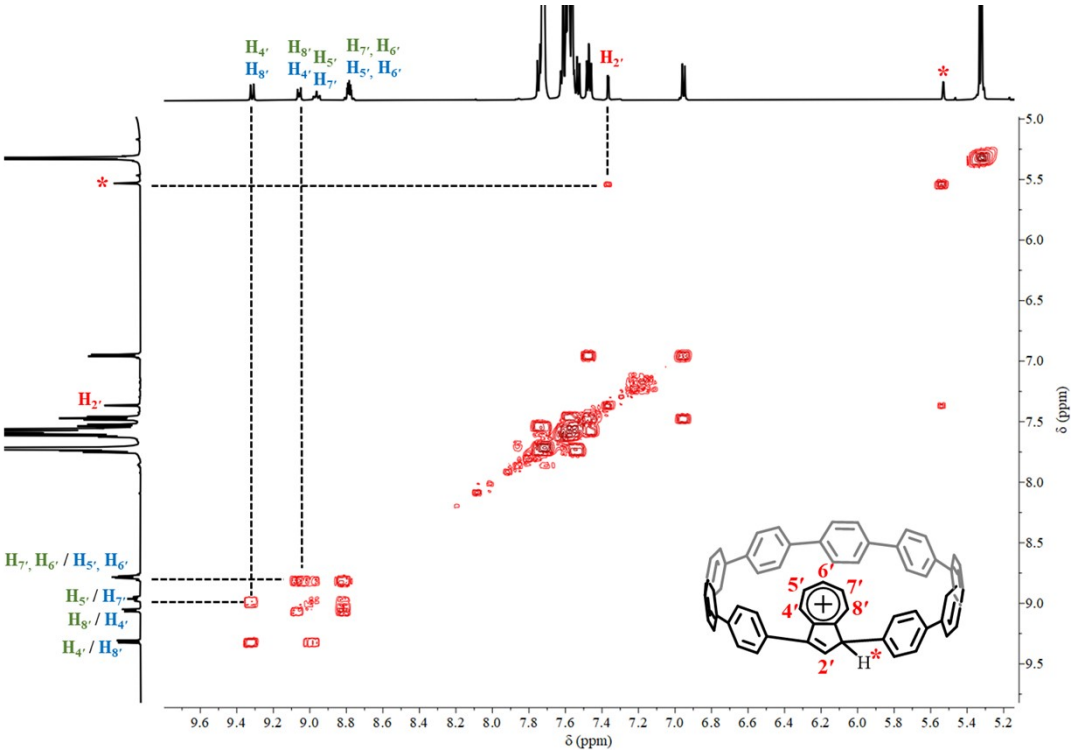


Figure S8. Partial ^{1}H-^{1}H COSY spectrum of compound **1,3-Az[9]CPP-H⁺** in CD_2Cl_2 (400 MHz, 298 K)

4. X-ray Crystallography

Crystals suitable for X-ray analysis were obtained by slow diffusion of acetonitrile into 1,1,2,2-tetrachloroethane solution of **1,3-Az[9]CPP** and chlorobenzene solution of **C_{60}@1,3-Az[9]CPP**, respectively. Single crystal X-ray diffraction data were collected on a Super Nova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2[7], the structure was solved with the ShelXT[8] structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization. The disordered solvent molecules were removed with the SQUEEZE routine in PLATON[9] and the solvent-free model was employed for the final refinement. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were positioned by geometric idealization. Details of the crystal data and a summary of the intensity data collection parameters for **1,3-Az[9]CPP** and **C_{60}@1,3-Az[9]CPP** are listed in **Table S1-S2**. Crystallographic data were deposited at the Cambridge Crystallographic Data Center (CCDC 2177150 for **1,3-Az[9]CPP**, 2177151 for **C_{60}@1,3-Az[9]CPP**). The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Crystal Structure Data of compound **1,3-Az[9]CPP** (CCDC number: 2177150).

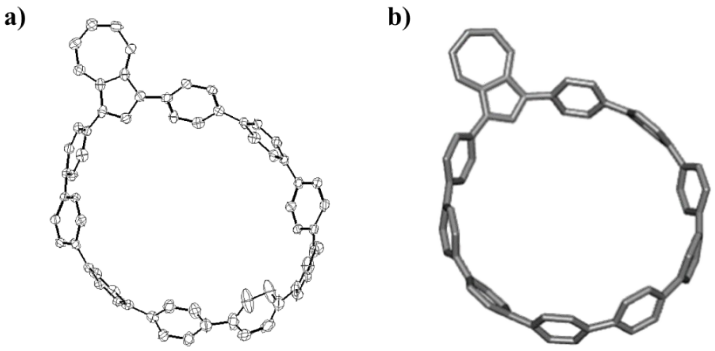


Figure S9. Crystal structure of **1,3-Az[9]CPP** was obtained by slow diffusion of acetonitrile into 1,1,2,2-tetrachloroethane solution. The thermal ellipsoids are set at a 50 % probability level. Hydrogen atoms are omitted for clarity.

Table S1. Crystal data and structure refinement for compound **1,3-Az[9]CPP**.

Identification code	1,3-Az[9]CPP
Empirical formula	$C_{64}H_{42}$
Formula weight	810.97
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	15.6621(4)
b/Å	8.4566(2)
c/Å	20.4458(5)
α/°	90
β/°	108.855(3)
γ/°	90
Volume/Å^3	2562.69(12)
Z	2
ρ_{calc}g/cm^3	1.051
μ/mm^{-1}	0.451
F(000)	852.0
Crystal size/mm^3	0.1 × 0.08 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.608 to 134.128
Index ranges	-18 ≤ h ≤ 18, -9 ≤ k ≤ 10, -24 ≤ l ≤ 23
Reflections collected	18008
Independent reflections	7607 [R_{int} = 0.0349, R_{sigma} = 0.0411]
Data/restraints/parameters	7607/1/577
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0554, wR_2 = 0.1557

Final R indexes [all data]	R_1 = 0.0577, wR_2 = 0.1585
Largest diff. peak/hole / e Å^{-3}	0.33/-0.23
Flack parameter	-5.2(2)

Crystal Structure Data of compound **C_{60}@1,3-Az[9]CPP** (CCDC number: 2177151).

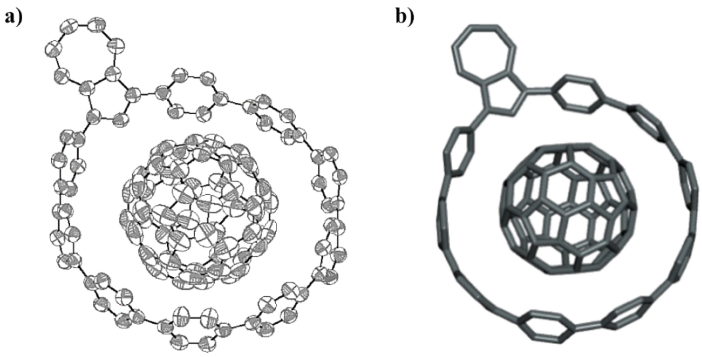


Figure S10. Crystal structure of **C_{60}@1,3-Az[9]CPP** was obtained by slow diffusion of acetonitrile into chlorobenzene solution. The thermal ellipsoids are set at a 50 % probability level. Hydrogen atoms are omitted for clarity.

Table S2. Crystal data and structure refinement for compound **C_{60}@1,3-Az[9]CPP**.

Identification code	**C_{60}@1,3-Az[9]CPP**
Empirical formula	$C_{124}H_{42}$
Formula weight	1531.57
Temperature/K	173.0
Crystal system	monoclinic
Space group	C2/c
a/Å	61.130(4)
b/Å	9.9469(6)
c/Å	31.1453(18)
α/°	90
β/°	102.894(2)
γ/°	90
Volume/Å^3	18460.4(19)
Z	4
ρ_{calc}g/cm^3	1.459
μ/mm^{-1}	2.051
F(000)	8328.0
Crystal size/mm^3	0.04 × 0.03 × 0.02
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.822 to 133.374
Index ranges	-66 ≤ h ≤ 72, -8 ≤ k ≤ 11, -36 ≤ l ≤ 37
Reflections collected	82296
Independent reflections	16164 [R_{int} = 0.0768, R_{sigma} = 0.0709]
Data/restraints/parameters	16164/80/1379
Goodness-of-fit on F^2	1.280
Final R indexes [I>=2σ (I)]	R_1 = 0.1133, wR_2 = 0.3035
Final R indexes [all data]	R_1 = 0.1751, wR_2 = 0.3374
Largest diff. peak/hole / e Å^{-3}	1.55/-0.84

5. Proton-responsive behavior of 1,3-Az[9]CPP by NMR titration experiment

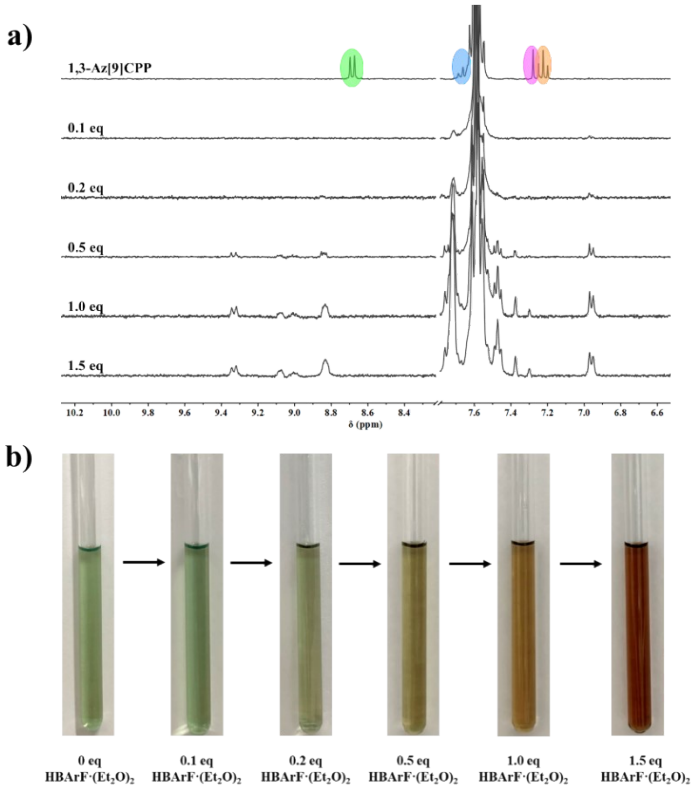


Figure S11. a) ^{1}H-NMR spectra (400 MHz, 298K, CD_2Cl_2) during titration of **1,3-Az[9]CPP** (CD_2Cl_2 , 1 mM) with HBArF·$(Et_2O)_2$**,** b) solution color changes before and after protonation

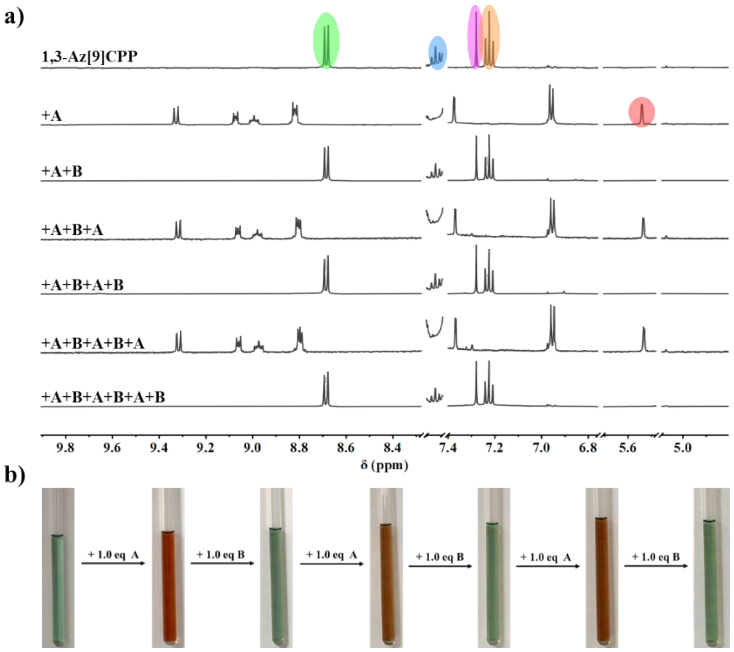


Figure S12. a) ^{1}H-NMR spectra (600 MHz, 298K, CD_2Cl_2) of **1,3-Az[9]CPP** (CD_2Cl_2 , 2 mM) upon addition of HBArF·$(Et_2O)_2$ (A, 1.0 eq for each addition) and DBU (B, 1.0 eq for each addition), b) color changes upon protonation/deprotonation

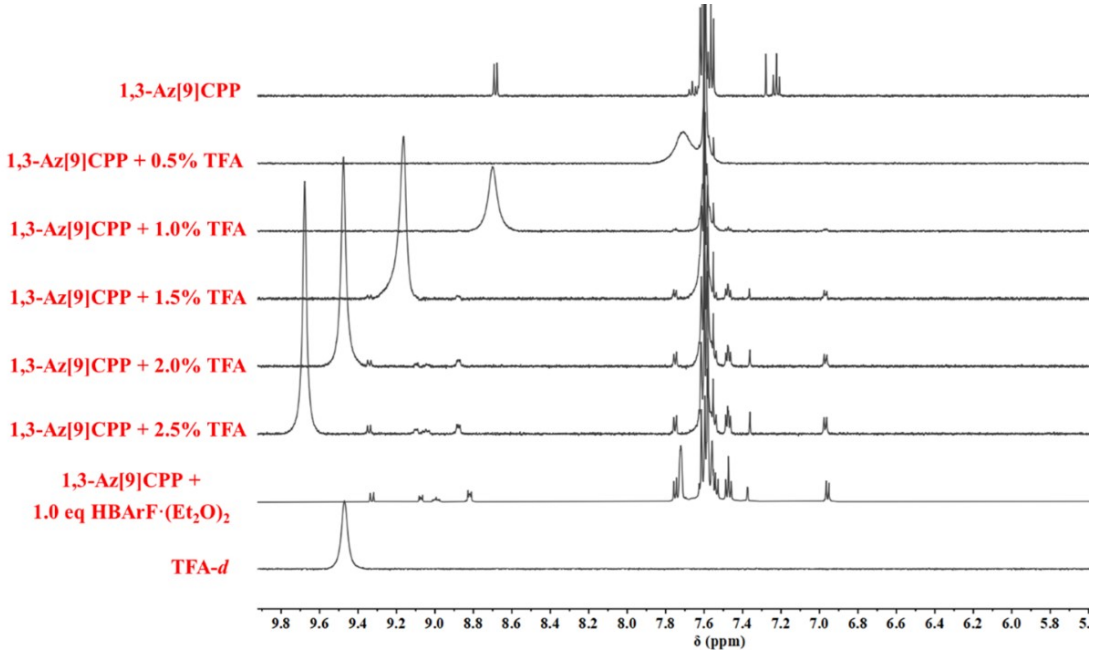


Figure S13. ^{1}H-NMR spectra (600 MHz, 298K, CD_2Cl_2) during titration of **1,3-Az[9]CPP** (CD_2Cl_2 , 1 mM) with TFA-*d*.

6. Proton-responsive behavior of 1,3-Az[9]CPP by UV-Vis titration experiment

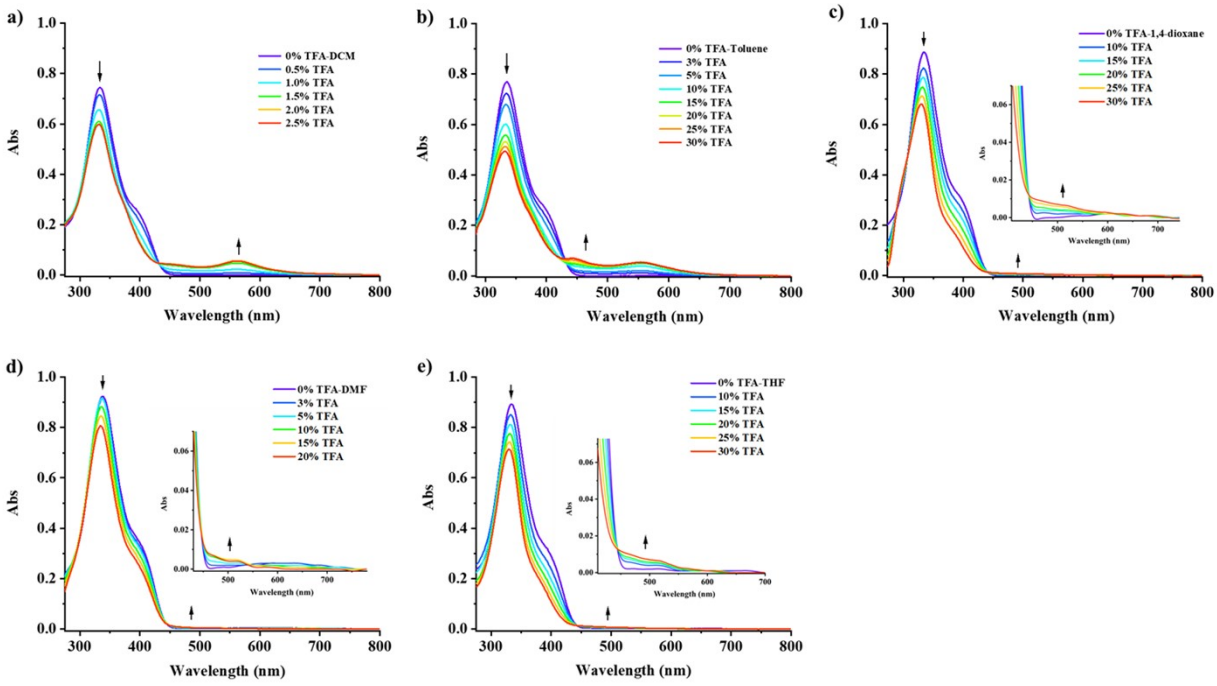


Figure S14. The UV-Vis spectra of **1,3-Az[9]CPP** (1.0×10^{-5} M) upon addition of TFA in a) DCM, b) toluene, c) 1,4-dioxane, d) DMF and e) THF.

7. Fluorescence spectra of 1,3-Az[9]CPP and 1,3-Az[9]CPP-H$^+$

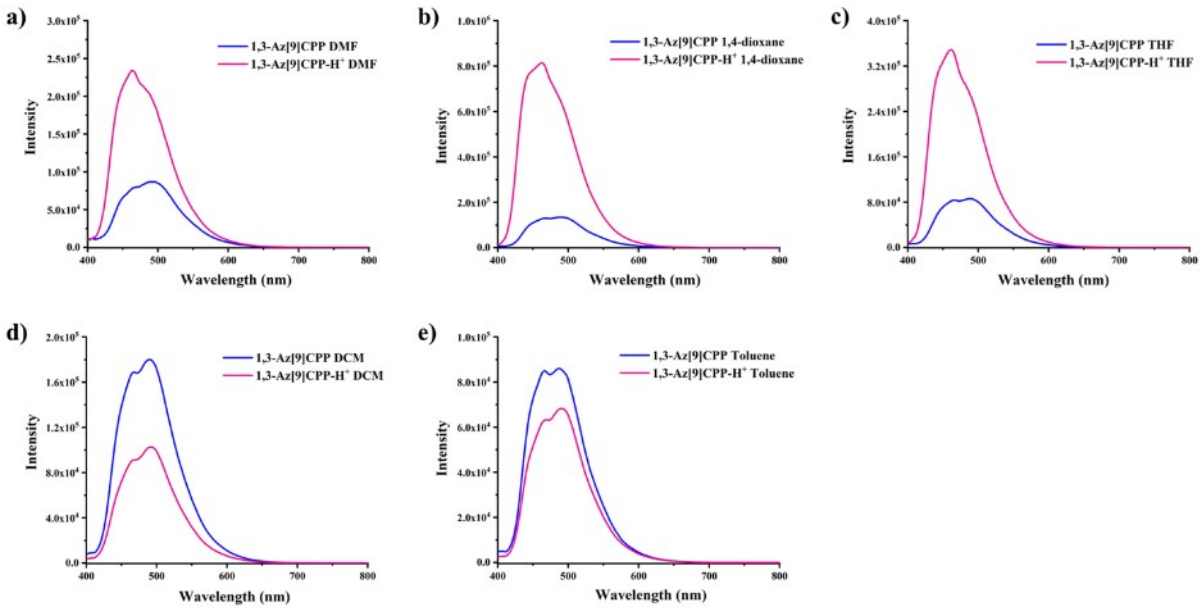


Figure S15. Fluorescence spectra of **1,3-Az[9]CPP** and **1,3-Az[9]CPP-H$^+$** (1.0×10^{-5} M) in a) DMF, c) 1,4-dioxane, c) THF, d) DCM, e) toluene.

8. UV-Vis titration experiments of complexation between 1,3-Az[9]CPP-H$^+$ with C_{70}

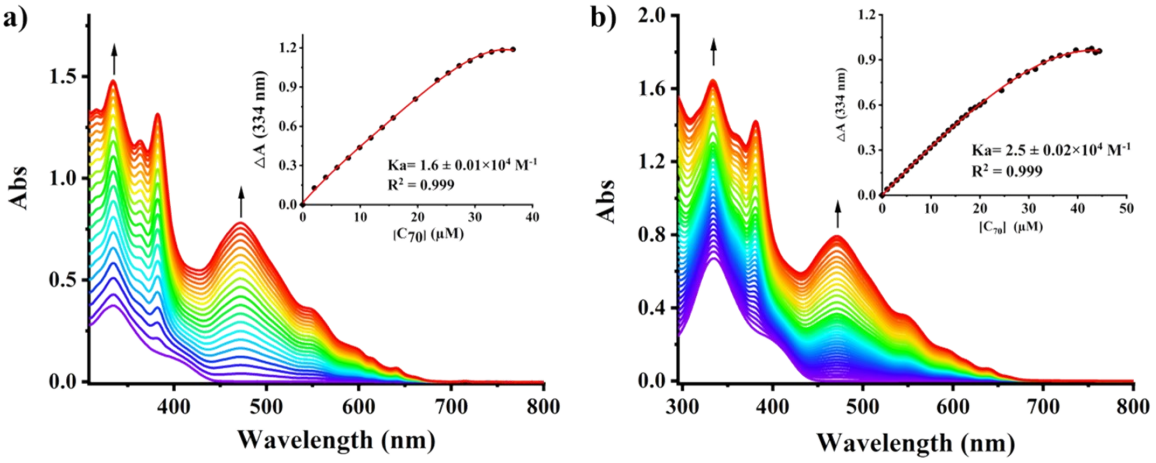


Figure S16. UV-Vis spectra in toluene of a) **1,3-Az[9]CPP** (1.0×10^{-5} M) in the presence of C_{70} (0-3.66×10^{-5} M), $K_a = 1.6 \times 10^4$ M^{-1}, b) **1,3-Az[9]CPP-H$^+$** (1.0×10^{-5} M) in the presence of C_{70} (0-4.44×10^{-5} M) $K_a = 2.5 \times 10^4$ M^{-1}.

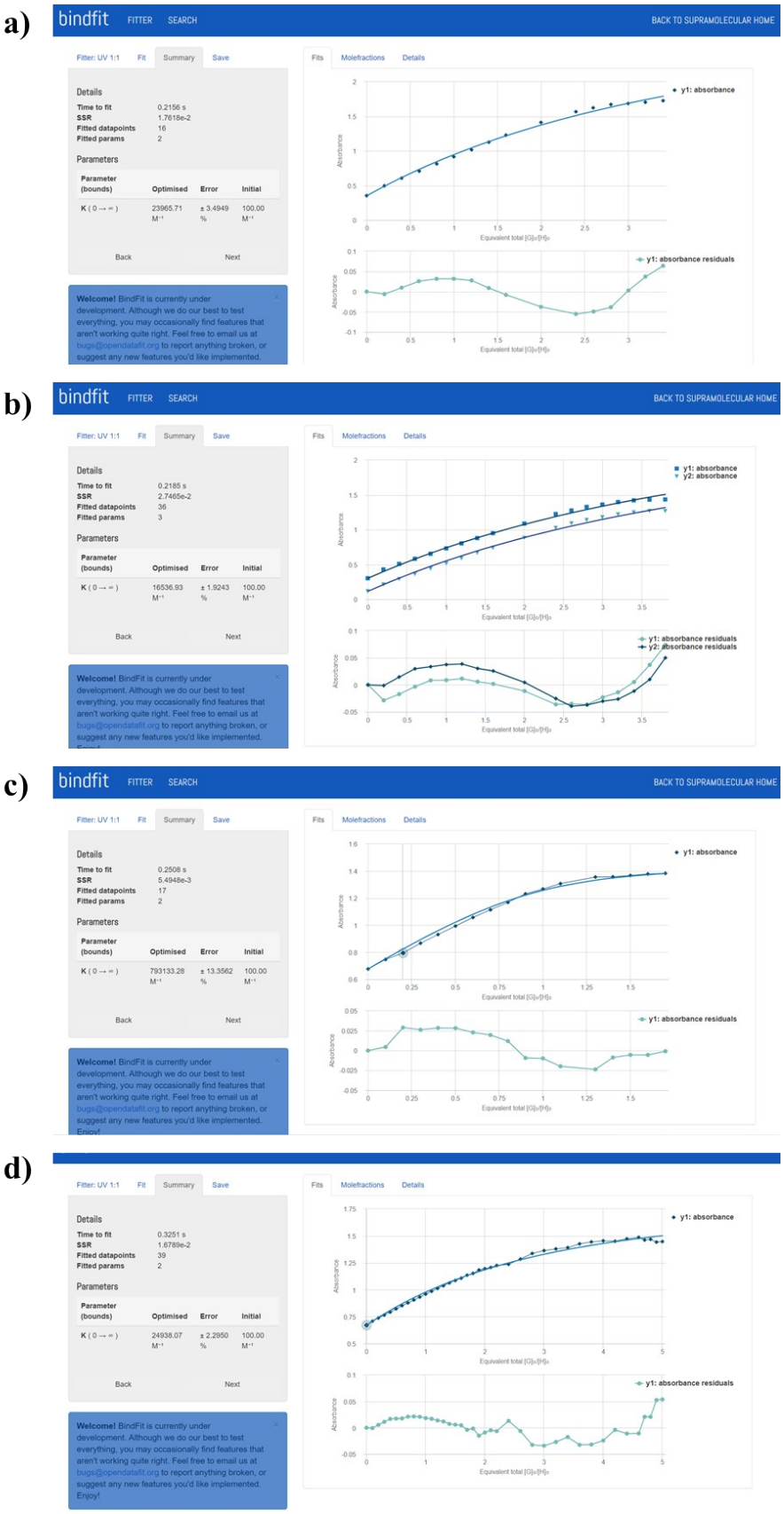


Figure S17. Global fitting with the experimental data of a) **1,3-AZ[9]CPP** and C_{60}, b) **1,3-AZ[9]CPP** and C_{70}, c) **1,3-AZ[9]CPP-H$^+$** and C_{60}, d) **1,3-AZ[9]CPP-H$^+$** and C_{70}, UV-Vis titration experiments by the bindfit program available from the Internet website http://supramolecular.org. [9]

9. NMR titration experiments of complexation between 1,3-Az[9]CPP-H$^+$ with C_{60} and C_{70}

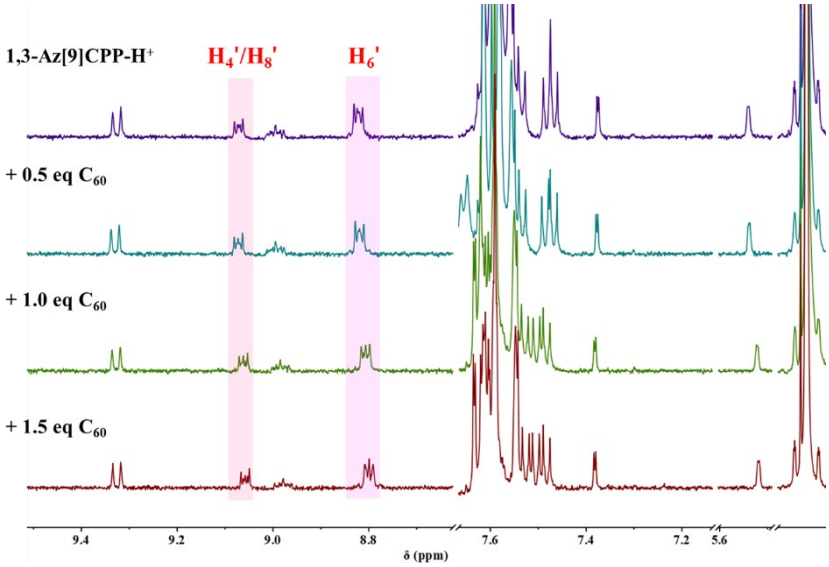


Figure S18. ^{1}H-NMR spectra (600 MHz, 298K, CD_2Cl_2) during titration of **1,3-Az[9]CPP** (CD_2Cl_2 , $C_{\text{1,3-Az[9]CPP}}$ = 1 mM) with C_{60} (CS_2, C_{C60}=0.01 M)

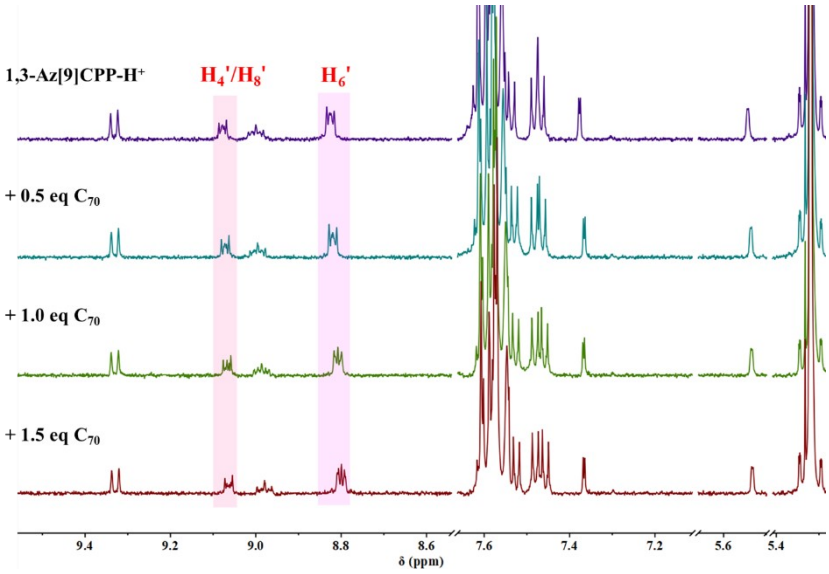


Figure S19. ^{1}H-NMR spectra (600 MHz, 298K, CD_2Cl_2) during titration of **1,3-Az[9]CPP** (CD_2Cl_2 , $C_{\text{1,3-Az[9]CPP}}$ = 1 mM) with C_{70} (CS_2, C_{C70}=0.01 M)

10. Theoretical Calculations

All the DFT calculations were performed with Gaussian 16 program[10]. The geometries of ground state of 1,3-Az[9]CPP and 1,3-Az[9]CPP-H$^+$ were optimized at the B3LYP/6-31g(d, p) level with D3BJ empirical dispersion correction. Time-dependent (TD)-DFT calculations were carried out for the excited states at ωB97XD/ 6-31g(d,p) level of theory. All the calculations were performed with the correction of the polarizable continuum model (PCM) to consider the solvent effect of dichloromethane. Harmonic vibration frequency were calculated at the same level to verify these stationary points as local minima (i.e., no imaginary frequency).The UV-Vis absorption spectrums were drawn by the Multiwfn software[11].

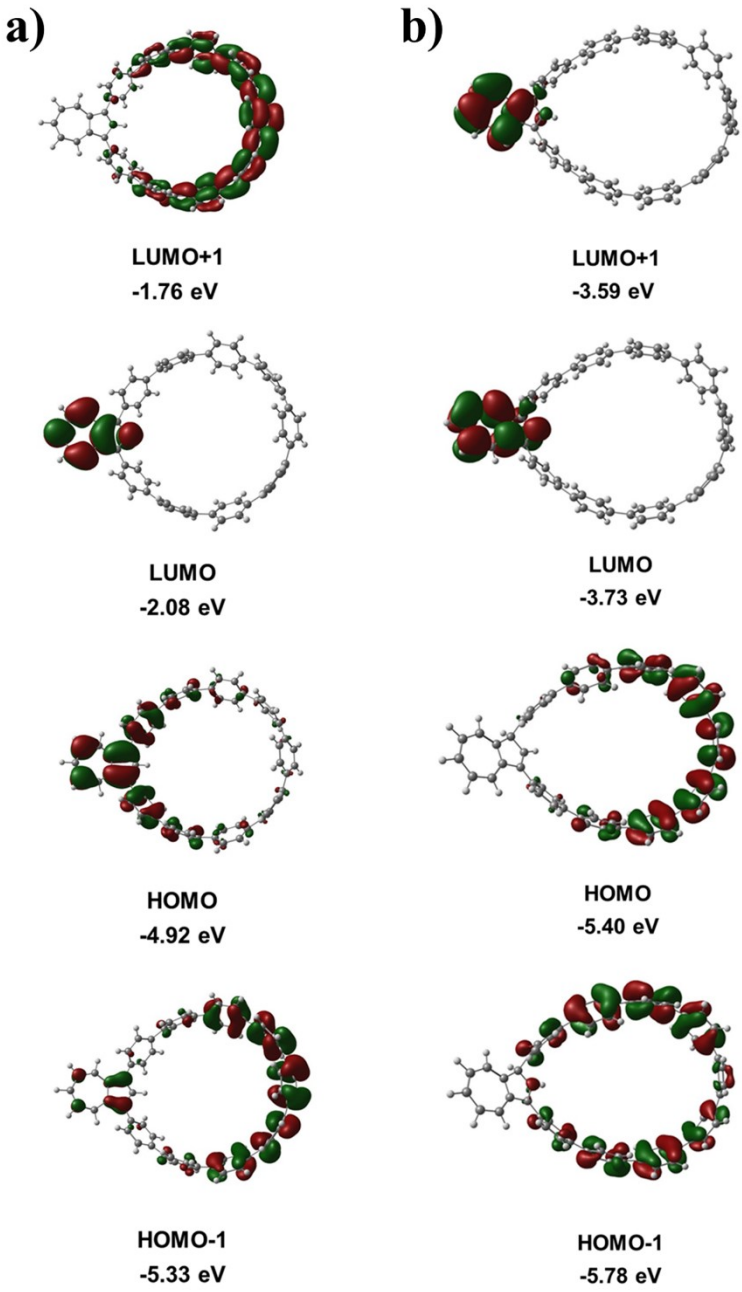


Figure S20. Frontier molecular orbitals (FMOs) of a) **1,3-Az[9]CPP** and b) **1,3-Az[9]CPP-H$^+$**.

Table S3. The electrochemical data of **1,3-Az[9]CPP** and **1,3-Az[9]CPP-H$^+$**

	E_{HOMO} [a] (eV)	E_{LUMO} [a] (eV)	$E_{HOMO-LUMO}$ [a] (eV)
1,3-Az[9]CPP	-4.92	-2.08	2.84
1,3-Az[9]CPP-H$^+$	-5.40	-3.73	1.67

[a] Estimated from DFT calculations at the B3LYP-D3BJ/6-31g(d, p) level

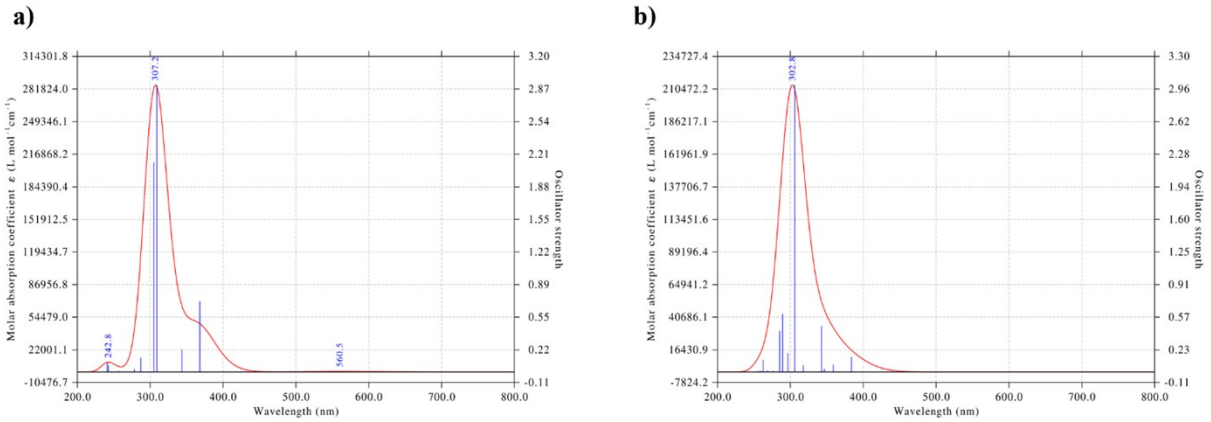


Figure S21. TD-DFT-calculated UV-Vis absorption spectra of (a) **1,3-Az[9]CPP**, (b) **1,3-Az[9]CPP-H**$^{+}$ along with the oscillator strengths at the ωB97XD/ 6-31g(d, p) level.

Table S4. Major electronic transitions of **1,3-Az[9]CPP** calculated by TD-DFT method at the ωB97XD/ 6-31g(d,p) level.

Excited state	Energy (eV)	Wavelength (nm)	Osc. Strength (f)	Major contributions
1	2.2118	560.56	0.0089	H → L 83.5% H-1 → L 7.9% H-4 → L 5.1%
2	3.3671	368.22	0.7165	H → L+2 65.7% H → L+3 9.4% H-3 → L 6.7%
3	3.6084	343.60	0.2296	H-1 → L+1 47.5% H → L+1 15.8% H-2 → L+2 9.4% H-2 → L+3 7.7%
4	4.0119	309.04	2.9106	H-2 → L+1 25.2% H-3 → L 9.7% H-1 → L+3 9.7% H → L+3 9.0% H → L+2 5.8% H-1 → L+2 5.8% H-5 → L 5.3% H-2 → L 5.1%
5	4.063	305.15	2.1264	H → L+4 34.6% H-1 → L+1 18.5% H-2 → L+2 10.4% H-3 → L+2 7.8% H → L+1 5.6% H-4 → L+1 5.4%

6	4.316	287.27	0.1446	H-3 → L 25.6% H-2 → L 12.7% H-5 → L 10.0% H-2 → L+1 8.7% H-1 → L+3 8.4% H → L+2 7.9% H-1 → L+2 5.9% H-3 → L+1 5.8%
7	4.4558	278.25	0.0293	H-3 → L+2 27.7% H-5 → L+2 15.3% H-2 → L+2 11.7% H → L+4 8.2% H-3 → L+3 7.7%
8	4.665	265.78	0.0025	H-1 → L+5 25.9% H-7 → L+1 15.5% H-1 → L+6 13.6% H-2 → L+7 6.0%
9	4.7204	262.66	0.0000	H-1 → L+4 18.8% H-4 → L+1 17.3% H-2 → L+3 11.9% H → L+8 7.6% H-2 → L+2 5.9%
10	4.7408	261.53	0.0029	H-1 → L+7 19.0% H-9 → L+1 10.1% H-2 → L+5 7.8% H → L+7 6.7%
11	4.7775	259.52	0.0012	H → L+9 22.1% H → L+11 5.9% H → L+13 5.3%
12	4.8055	258.00	0.0035	H → L+10 22.0% H-2 → L+9 9.5% H-8 → L+2 7.0% H → L+12 6.6% H → L+8 6.2%
13	4.8164	257.42	0.0083	H-2 → L+4 9.6% H → L+9 5.7% H-2 → L 5.1%
14	4.8789	254.12	0.0036	H-1 → L+11 11.2% H → L+11 7.1% H-11 → L+1 7.1% H-13 → L+1 6.6%
15	4.9344	251.26	0.0043	H → L+12 12.6% H-14 → L+1 5.8% H-11 → L+2 5.3%

16	4.9676	249.59	0.0020	H → L+13 14.3% H-2 → L+12 7.9% H-13 → L+1 7.4% H-12 → L+2 5.8% H-11 → L+4 5.7%
17	5.0012	247.91	0.0031	H-14 → L+1 16.0% H-1 → L+14 9.3% H-2 → L+13 7.0% H-13 → L+3 5.2%
18	5.0223	246.87	0.0046	H-15 → L+1 24.5% H-1 → L+15 15.5% H-14 → L+3 7.9% H-2 → L+14 5.1%
19	5.1114	242.56	0.0648	H-5 → L 32.6% H-2 → L 29.7% H-16 → L 12.6%
20	5.1420	241.12	0.0902	H-4 → L 26.7% H-1 → L 12.5% H → L 8.1% H-6 → L 7.6% H-17 → L 6.4%

Table S5. Major electronic transitions of **1,3-Az[9]CPP-H**$^{+}$ calculated by TD-DFT method at the ωB97XD/ 6-31g(d, p) level.

Excited state	Energy (eV)	Wavelength (nm)	Osc. Strength (f)	Major contributions
1	3.2298	383.88	0.1585	H-3 → L 34.8% H-1 → L 30.0% H-12 → L 14.8% H-2 → L 6.4%
2	3.456	358.75	0.0768	H-3 → L+1 30.2% H-1 → L+1 24.4% H-12 → L+1 15.5% H-2 → L+1 10.4%
3	3.5773	346.59	0.0330	H-2 → L 36.2% H → L 24.3% H-4 → L 8.4% H → L+2 5.4%
4	3.6180	342.69	0.4819	H → L+2 52.9% H-1 → L+3 6.6% H → L+3 5.8%
5	3.9026	317.7	0.0707	H-2 → L+1 33.1% H → L+1 27.5% H-1 → L+1 9.5% H-4 → L+1 7.7%

				H-3 → L+1 6.5%
6	4.0536	305.86	3.0016	H-1 → L+2 28.0% H → L+3 22.9% H → L+5 8.5% H-1 → L+3 7.6% H-2 → L+3 6.9%
7	4.1794	296.66	0.1972	H → L 23.1% H-1 → L 17.5% H-12 → L 10.0% H-15 → L 8.5% H-1 → L+3 5.3%
8	4.2848	289.36	0.6079	H → L 32.8% H-2 → L+2 12.4% H-1 → L+3 11.3% H → L+4 8.5% H-2 → L 7.5%
9	4.3464	285.26	0.4301	H-1 → L 14.3% H → L 13.8% H-1 → L+3 10.0% H-2 → L+2 9.5% H-12 → L 8.5% H → L+4 6.5% H-16 → L 6.0% H-2 → L 5.4%
10	4.4364	279.47	0.0006	H → L+1 37.7% H-1 → L+1 21.4% H-15 → L+1 8.5% H-12 → L+1 6.7%
11	4.4886	276.22	0.0119	H-13 → L 84.9%
12	4.6119	268.84	0.0151	H → L+8 22.1% H → L+1 9.2% H-5 → L+2 8.5% H-2 → L+1 5.5%
13	4.6131	268.77	0.0072	H → L+1 19.3% H-2 → L+1 11.5% H → L+8 11.0% H-1 → L+1 9.2% H-12 → L+1 6.8% H-16 → L+1 5.8%
14	4.6312	267.72	0.0009	H-14 → L 89.8%
15	4.7228	262.52	0.1287	H-2 → L+3 18.1% H-1 → L+4 16.9%

				H → L+5 13.3% H-3 → L+2 12.8%
16	4.7683	260.02	0.0099	H → L+9 18.4% H-6 → L+3 6.5% H-1 → L+9 5.8% H-6 → L+2 5.5%
17	4.7988	258.37	0.0098	H-1 → L 22.3% H-3 → L 21.7% H-13 → L+1 12.6% H-17 → L 6.5% H-21 → L+1 6.1% H-15 → L 5.5%
18	4.8322	256.58	0.0061	H-13 → L+1 72.4%
19	4.8536	255.45	0.0035	H-7 → L+2 14.5% H → L+11 10.0% H → L+14 9.7% H-1 → L+9 5.4%
20	4.8955	253.26	0.0047	H-2 → L+6 12.2% H-9 → L+2 8.8% H-1 → L+6 8.1%

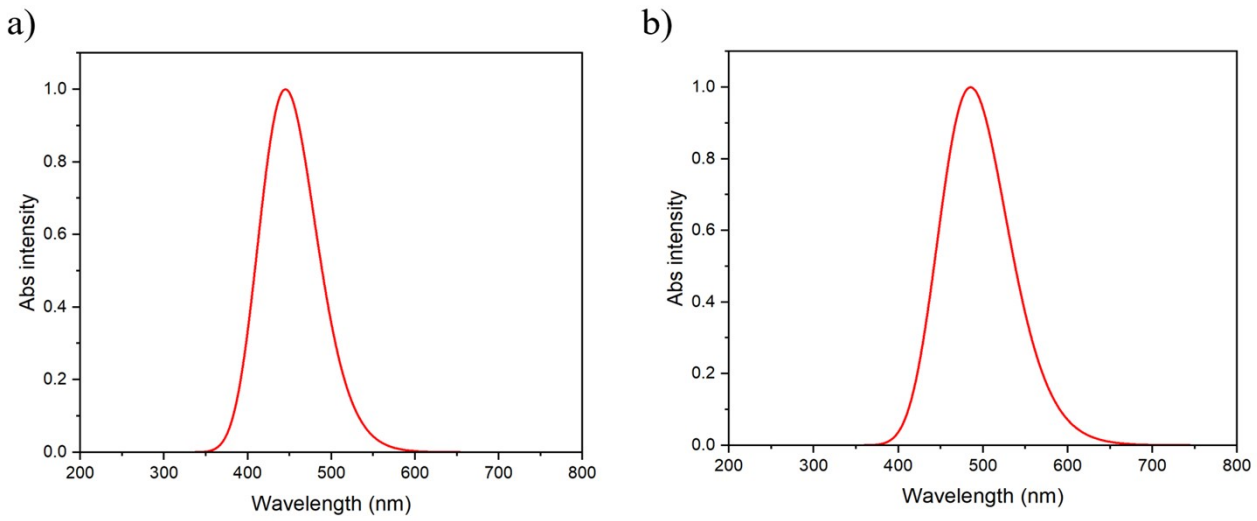
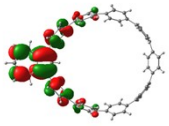
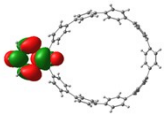
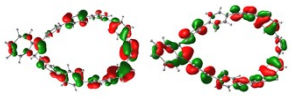
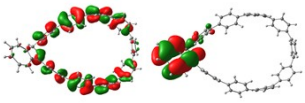
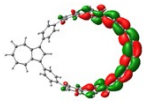
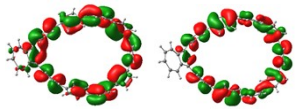
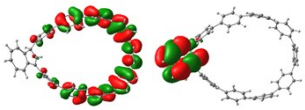


Figure S22. a) The $S_2 \rightarrow S_0$ fluorescence of **1,3-Az[9]CPP**, b) the $S_1 \rightarrow S_0$ fluorescence of **1,3-Az[9]CPP-H$^+$** calculated by TD-DFT method at the ωB97XD/ 6-31g(d, p) level.

Table S6. TD-DFT-calculated FMOs and electronic transitions of **1,3-Az[9]CPP** and **1,3-Az[9]CPP-H$^+$**.

Excited State ($S_n \rightarrow S_0$)	1,3-Az[9]CPP		1,3-Az[9]CPP-H$^+$	
S_1	 HOMO  LUMO	1.5533 eV f = 0.0043 798 nm H→L 92.8%	 HOMO-10 HOMO-3  HOMO-1 LUMO	2.5447 eV f = 0.3737 485 nm H-1→L 42.8% H-3→L 39.5% H-10→L 5.6%
S_2	 HOMO-1  HOMO  LUMO	2.7853 eV f = 1.1896 445 nm H→L 65.9% H-1→L 22.0%	 HOMO-4 HOMO-2  HOMO LUMO	3.0945 eV f = 0.0225 401 nm H-2→L 43.0% H→L 28.5% H-4→L 16.5%

Cartesian coordinates

Optimized S_0 geometry of 1,3-Az[9]CPP

1	C	-1.429858	-6.555819	0.425526
2	C	-2.097065	5.939765	1.497436
3	H	-1.531584	5.620277	2.366312
4	C	4.769104	4.474285	-0.632740
5	H	4.688389	5.122124	-1.500191
6	C	2.728751	5.554787	0.413126
7	C	-2.097463	-5.940010	1.497485
8	H	-1.532027	-5.620740	2.366470
9	C	0.827954	-6.556188	1.562055
10	H	0.383141	-6.909279	2.487310

11	C	2.139201	-6.093221	1.571705
12	H	2.694815	-6.098408	2.504155
13	C	2.006045	-5.663951	-0.787677
14	H	2.426978	-5.264141	-1.704152
15	C	-2.209710	-6.953548	-0.674699
16	H	-1.746228	-7.494584	-1.494058
17	C	-3.434301	5.580389	1.399652
18	H	-3.866205	4.987281	2.197295
19	C	2.006410	5.664036	-0.787606
20	H	2.427343	5.264281	-1.704105
21	C	-5.416369	5.053395	-0.016357
22	C	4.768828	-4.474407	-0.632801
23	H	4.688073	-5.122220	-1.500267
24	C	6.359394	-1.164026	0.267410
25	C	0.828292	6.556126	1.562170
26	H	0.383452	6.909165	2.487433
27	C	2.728426	-5.554827	0.413051
28	C	-1.429500	6.555847	0.425606
29	C	0.050201	-6.506268	0.391543
30	C	2.139519	6.093129	1.571813
31	H	2.695129	6.098248	2.504266
32	C	5.653025	-3.398735	-0.673029
33	H	6.214617	-3.209785	-1.582026
34	C	4.996230	2.785246	1.556743
35	H	5.069026	2.122889	2.413657
36	C	0.050561	6.506305	0.391629
37	C	-3.434698	-5.580600	1.399752
38	H	-3.866587	-4.987712	2.197566
39	C	6.359481	1.163778	0.267419
40	C	3.926212	4.683992	0.472585
41	C	-5.416698	-5.053190	-0.016281
42	C	8.522495	-1.591252	-0.913736
43	H	8.338285	-2.654651	-0.779401
44	C	4.109115	3.851801	1.591724
45	H	3.481623	3.985208	2.466539
46	C	0.696442	-6.131065	-0.798606
47	H	0.128775	-6.083456	-1.722174
48	C	5.736993	2.488735	0.397524
49	C	-3.554129	-6.604569	-0.766343
50	H	-4.108134	-6.889222	-1.654956
51	C	5.653235	3.398560	-0.672996
52	H	6.214791	3.209597	-1.582011
53	C	0.696814	6.131194	-0.798530
54	H	0.129166	6.083685	-1.722117
55	C	7.541271	-0.750054	-0.402062

56	C	-2.209358	6.953815	-0.674524
57	H	-1.745863	7.495008	-1.493774
58	C	4.108894	-3.851958	1.591693
59	H	3.481406	-3.985367	2.466511
60	C	7.541417	0.749731	-0.401900
61	C	3.925931	-4.684095	0.472524
62	C	5.736830	-2.488949	0.397517
63	C	-4.175362	5.827746	0.229848
64	C	4.996071	-2.785451	1.556738
65	H	5.068912	-2.123121	2.413669
66	C	8.522823	1.590839	-0.913388
67	H	8.338802	2.654249	-0.778891
68	C	-4.175726	-5.827623	0.229861
69	C	5.686546	-0.000106	0.682982
70	H	4.717218	-0.000076	1.166197
71	C	-3.553793	6.604881	-0.766214
72	H	-4.107843	6.889707	-1.654747
73	C	-6.122968	4.434139	1.031108
74	H	-5.956269	4.746334	2.056535
75	C	-6.123049	-4.433720	1.031232
76	H	-5.956194	-4.745767	2.056677
77	C	-7.128603	-2.831545	-0.504794
78	C	-6.947388	-3.339537	0.794292
79	H	-7.361465	-2.806933	1.643918
80	C	-5.766380	-4.675296	-1.325816
81	H	-5.285417	-5.151805	-2.172995
82	C	9.713168	1.264225	-1.569881
83	H	10.320206	2.107252	-1.887433
84	C	-6.947354	3.339991	0.794149
85	H	-7.361638	2.807539	1.643770
86	C	-7.128370	2.831850	-0.504906
87	C	9.712904	-1.264740	-1.570172
88	H	10.319774	-2.107823	-1.887894
89	C	-5.765812	4.675362	-1.325912
90	H	-5.284592	5.151719	-2.173035
91	C	10.229891	-0.000281	-1.862030
92	H	11.183410	-0.000320	-2.385328
93	C	-6.613754	-3.600516	-1.564383
94	H	-6.798087	-3.299841	-2.590346
95	C	-6.613237	3.600630	-1.564502
96	H	-6.797383	3.299830	-2.590460
97	C	-7.552149	-1.425175	-0.704185
98	C	-7.552014	1.425506	-0.704249
99	C	-8.288147	-0.696178	0.248762
100	H	-8.818228	-1.220143	1.037959

101	C	-8.288083	0.696613	0.248729
102	H	-8.818128	1.220655	1.037897
103	C	-6.970650	0.693348	-1.754643
104	H	-6.392977	1.206838	-2.514353
105	C	-6.970717	-0.693114	-1.754615
106	H	-6.393105	-1.206704	-2.514303

Optimized S_0 geometry of 1,3-Az[9]CPP-H$^+$

1	C	1.788872	6.046550	0.112247
2	C	1.792556	-6.159742	1.019348
3	H	1.233145	-6.311446	1.936981
4	C	-4.933256	-3.283998	-0.740146
5	H	-4.620145	-3.421423	-1.769288
6	C	-3.005316	-4.702542	0.035186
7	C	2.441839	5.641779	1.287553
8	H	1.860108	5.448603	2.182905
9	C	-0.518013	6.226709	1.138240
10	H	-0.114393	6.758159	1.994377
11	C	-1.839361	5.793168	1.166756
12	H	-2.443384	6.008416	2.042042
13	C	-1.587658	4.878847	-1.040773
14	H	-1.963070	4.304645	-1.880443
15	C	2.588439	6.296190	-1.016053
16	H	2.131234	6.676236	-1.924544
17	C	3.175922	-6.026004	1.087588
18	H	3.663053	-6.110340	2.053489
19	C	-2.138822	-4.237740	-0.968047
20	H	-2.445498	-3.417477	-1.607525
21	C	5.276101	-5.069525	0.049491
22	C	-4.378767	3.854503	-0.879793
23	H	-4.111473	4.206963	-1.869743
24	C	-6.625456	1.224654	0.637781
25	C	-1.247175	-6.238563	0.738543
26	H	-0.918278	-7.029446	1.405319
27	C	-2.383571	5.046858	0.105586
28	C	1.104404	-5.974758	-0.192365
29	C	0.313883	5.943424	0.041417
30	C	-2.545681	-5.747887	0.855305
31	H	-3.203345	-6.170505	1.608352
32	C	-5.403617	2.921790	-0.756592
33	H	-5.870480	2.538606	-1.657757
34	C	-5.801938	-2.939166	1.874481
35	H	-6.122213	-2.796877	2.902547
36	C	-0.351808	-5.705697	-0.204954

37	C	3.794993	5.330358	1.284671
38	H	4.219352	4.900341	2.183809
39	C	-7.264460	-0.985581	1.232876
40	C	-4.271947	-3.976860	0.289022
41	C	5.850391	4.679242	0.014275
42	C	-8.454439	1.763268	-1.031654
43	H	-8.042468	2.765864	-1.076761
44	C	-4.762486	-3.822669	1.596597
45	H	-4.279540	-4.342126	2.417168
46	C	-0.271779	5.322937	-1.074789
47	H	0.343376	5.086153	-1.936495
48	C	-6.378098	-2.174350	0.854854
49	C	3.948292	6.002842	-1.011637
50	H	4.516190	6.171260	-1.920116
51	C	-5.955804	-2.383234	-0.462076
52	H	-6.401584	-1.821066	-1.276075
53	C	-0.846556	-4.727528	-1.085516
54	H	-0.180289	-4.274994	-1.811189
55	C	-7.804886	0.874801	-0.159811
56	C	1.878290	-5.824614	-1.355808
57	H	1.389135	-5.748303	-2.321417
58	C	-4.084010	3.851683	1.504992
59	H	-3.555315	4.169467	2.396376
60	C	-8.191025	-0.461581	0.157892
61	C	-3.653951	4.295844	0.240811
62	C	-5.764552	2.412785	0.501897
63	C	3.929461	-5.682223	-0.049288
64	C	-5.120361	2.937165	1.634128
65	H	-5.402160	2.584190	2.620905
66	C	-9.214421	-1.228031	-0.367656
67	H	-9.291666	-2.240562	0.019033
68	C	4.567586	5.420159	0.111560
69	C	-6.365629	0.188695	1.479495
70	H	-5.537476	0.139645	2.174402
71	C	3.256931	-5.673803	-1.285053
72	H	3.802236	-5.440948	-2.193004
73	C	5.605174	-4.319378	1.192268
74	H	4.979656	-4.380664	2.075792
75	C	6.472380	4.129557	1.150813
76	H	6.207371	4.480204	2.141856
77	C	7.656288	2.480565	-0.201021
78	C	7.338530	3.048465	1.046836
79	H	7.676696	2.574379	1.961325
80	C	6.345531	4.256346	-1.233647
81	H	5.951741	4.682879	-2.149093

82	C	-10.153497	-0.871878	-1.347767
83	H	-10.857922	-1.649885	-1.625144
84	C	6.611282	-3.362124	1.158458
85	H	6.738817	-2.706431	2.013293
86	C	7.328057	-3.105992	-0.023009
87	C	-9.560359	1.525355	-1.835252
88	H	-9.891298	2.369876	-2.432299
89	C	6.137255	-4.959538	-1.058821
90	H	5.977090	-5.584703	-1.931425
91	C	-10.307509	0.347067	-1.995115
92	H	-11.119928	0.402703	-2.712971
93	C	7.238662	3.197347	-1.338021
94	H	7.532291	2.867662	-2.328504
95	C	7.138872	-3.994953	-1.096646
96	H	7.731210	-3.881665	-1.999491
97	C	8.101883	1.067776	-0.290002
98	C	7.949234	-1.771391	-0.190062
99	C	8.568708	0.351243	0.829748
100	H	8.925344	0.883273	1.705380
101	C	8.485685	-1.036708	0.882501
102	H	8.768836	-1.548524	1.797264
103	C	7.702779	-1.072861	-1.384110
104	H	7.305712	-1.604371	-2.242362
105	C	7.772745	0.312686	-1.430900
106	H	7.427059	0.808838	-2.329893
107	H	-7.856628	-1.245025	2.121932

Optimized S_1 geometry of 1,3-Az[9]CPP

1	C	-1.416698	-6.456296	0.135655
2	C	-2.110229	5.993205	1.259704
3	H	-1.567241	5.769276	2.172498
4	C	4.816871	4.325968	-0.637993
5	H	4.743566	4.909164	-1.550807
6	C	2.732542	5.430649	0.271906
7	C	-2.110234	-5.993205	1.259701
8	H	-1.567248	-5.769277	2.172497
9	C	0.840242	-6.573153	1.276945
10	H	0.397824	-7.048647	2.147274
11	C	2.148428	-6.110108	1.349205
12	H	2.703868	-6.234861	2.274015
13	C	2.009888	-5.365562	-0.925130
14	H	2.429486	-4.845237	-1.780221
15	C	-2.161788	-6.735029	-1.017777
16	H	-1.669818	-7.157895	-1.888796
17	C	-3.455619	5.661723	1.182393

18	H	-3.926825	5.185298	2.036160
19	C	2.009886	5.365561	-0.925137
20	H	2.429482	4.845235	-1.780229
21	C	-5.412981	4.998471	-0.191503
22	C	4.816875	-4.325972	-0.637974
23	H	4.743580	-4.909176	-1.550783
24	C	6.430105	-1.133990	0.509485
25	C	0.840249	6.573157	1.276939
26	H	0.397834	7.048653	2.147268
27	C	2.732539	-5.430646	0.271916
28	C	-1.416696	6.456297	0.135657
29	C	0.067188	-6.370587	0.126094
30	C	2.148435	6.110113	1.349195
31	H	2.703878	6.234869	2.274003
32	C	5.726136	-3.276533	-0.578374
33	H	6.322324	-3.039915	-1.453325
34	C	5.012537	2.798883	1.668715
35	H	5.072491	2.197094	2.570047
36	C	0.067191	6.370588	0.126091
37	C	-3.455624	-5.661724	1.182387
38	H	-3.926833	-5.185300	2.036154
39	C	6.430109	1.133994	0.509479
40	C	3.945836	4.587947	0.426614
41	C	-5.412983	-4.998471	-0.191512
42	C	8.587508	-1.602603	-0.750066
43	H	8.414453	-2.659650	-0.577169
44	C	4.112195	3.848028	1.606864
45	H	3.461051	4.035139	2.454646
46	C	0.702813	-5.826381	-0.996210
47	H	0.134328	-5.652907	-1.904351
48	C	5.791906	2.448996	0.553996
49	C	-3.509701	-6.404899	-1.094471
50	H	-4.044040	-6.575285	-2.024523
51	C	5.726132	3.276529	-0.578393
52	H	6.322309	3.039903	-1.453349
53	C	0.702812	5.826380	-0.996214
54	H	0.134323	5.652904	-1.904352
55	C	7.612787	-0.702890	-0.222372
56	C	-2.161788	6.735031	-1.017773
57	H	-1.669820	7.157899	-1.888793
58	C	4.112180	-3.848015	1.606873
59	H	3.461030	-4.035119	2.454652
60	C	7.612794	0.702885	-0.222370
61	C	3.945831	-4.587942	0.426627
62	C	5.791899	-2.448990	0.554008

63	C	-4.160318	5.781340	-0.021381
64	C	5.012522	-2.798868	1.668723
65	H	5.072468	-2.197073	2.570052
66	C	8.587527	1.602590	-0.750057
67	H	8.414486	2.659638	-0.577155
68	C	-4.160320	-5.781339	-0.021388
69	C	5.782941	0.000004	1.016077
70	H	4.813618	0.000007	1.495379
71	C	-3.509702	6.404901	-1.094464
72	H	-4.044043	6.575288	-2.024515
73	C	-6.294140	4.744817	0.868322
74	H	-6.244167	5.349808	1.768906
75	C	-6.294144	-4.744819	0.868313
76	H	-6.244172	-5.349812	1.768896
77	C	-7.203396	-2.809597	-0.282626
78	C	-7.174101	-3.669706	0.823438
79	H	-7.792507	-3.456142	1.690344
80	C	-5.579450	-4.252048	-1.363890
81	H	-4.920594	-4.423546	-2.209154
82	C	9.735604	1.264307	-1.446672
83	H	10.338136	2.107864	-1.778668
84	C	-7.174098	3.669704	0.823445
85	H	-7.792503	3.456139	1.690352
86	C	-7.203395	2.809598	-0.282620
87	C	9.735587	-1.264331	-1.446681
88	H	10.338108	-2.107893	-1.778682
89	C	-5.579449	4.252050	-1.363883
90	H	-4.920594	4.423551	-2.209147
91	C	10.251658	-0.000014	-1.783862
92	H	11.178778	-0.000018	-2.348244
93	C	-6.457563	-3.178503	-1.408543
94	H	-6.458608	-2.541094	-2.286944
95	C	-6.457562	3.178505	-1.408537
96	H	-6.458609	2.541099	-2.286939
97	C	-7.711972	-1.414458	-0.200056
98	C	-7.711971	1.414459	-0.200053
99	C	-7.485886	-0.693851	0.978632
100	H	-7.169133	-1.215740	1.875982
101	C	-7.485885	0.693849	0.978634
102	H	-7.169132	1.215736	1.875985
103	C	-8.128831	0.695006	-1.328255
104	H	-8.383965	1.223539	-2.242098
105	C	-8.128831	-0.695002	-1.328256
106	H	-8.383966	-1.223533	-2.242100

Optimized S_2 geometry of 1,3-Az[9]CPP

1	C	-1.416949	-6.249823	0.170173
2	C	-2.102077	5.800681	1.308828
3	H	-1.551800	5.599803	2.222538
4	C	4.891941	4.373943	-0.688668
5	H	4.800246	4.979543	-1.585649
6	C	2.772359	5.384124	0.256186
7	C	-2.102505	-5.800609	1.308855
8	H	-1.552222	-5.599789	2.222574
9	C	0.836139	-6.411549	1.303201
10	H	0.381629	-6.846264	2.188444
11	C	2.163800	-6.007613	1.354479
12	H	2.719327	-6.132013	2.279360
13	C	2.044251	-5.323460	-0.938800
14	H	2.481446	-4.846865	-1.810493
15	C	-2.180015	-6.499684	-0.982300
16	H	-1.703819	-6.921789	-1.862360
17	C	-3.443995	5.467477	1.255320
18	H	-3.895341	5.014646	2.131132
19	C	2.044665	5.323449	-0.938773
20	H	2.481847	4.846837	-1.810463
21	C	-5.444836	4.845785	-0.084269
22	C	4.891585	-4.374116	-0.688727
23	H	4.799834	-4.979694	-1.585717
24	C	6.560808	-1.159047	0.359904
25	C	0.836578	6.411580	1.303221
26	H	0.382073	6.846305	2.188463
27	C	2.771958	-5.384179	0.256149
28	C	-1.416509	6.249935	0.170172
29	C	0.063019	-6.209111	0.150277
30	C	2.164220	6.007582	1.354512
31	H	2.719742	6.131947	2.279401
32	C	5.819111	-3.337799	-0.664751
33	H	6.409341	-3.134167	-1.553209
34	C	5.142620	2.791651	1.570019
35	H	5.220018	2.165317	2.453706
36	C	0.063463	6.209181	0.150289
37	C	-3.444414	-5.467375	1.255373
38	H	-3.895739	-5.014582	2.131215
39	C	6.560905	1.158728	0.359932
40	C	4.018122	4.585612	0.385257
41	C	-5.445247	-4.845581	-0.084187
42	C	8.788776	-1.589048	-0.673776
43	H	8.591552	-2.653402	-0.558760

44	C	4.211217	3.818255	1.541422
45	H	3.558155	3.961183	2.396731
46	C	0.718387	-5.728367	-0.991411
47	H	0.155088	-5.556872	-1.903149
48	C	5.910947	2.479817	0.440221
49	C	-3.523018	-6.167578	-1.039577
50	H	-4.064275	-6.348061	-1.962645
51	C	5.819392	3.337559	-0.664696
52	H	6.409618	3.133900	-1.553151
53	C	0.718819	5.728416	-0.991395
54	H	0.155519	5.556952	-1.903138
55	C	7.779501	-0.747664	-0.222007
56	C	-2.179556	6.499865	-0.982294
57	H	-1.703342	6.921992	-1.862333
58	C	4.210937	-3.818421	1.541385
59	H	3.557880	-3.961319	2.396702
60	C	7.779589	0.747258	-0.221938
61	C	4.017770	-4.585744	0.385210
62	C	5.910747	-2.480086	0.440181
63	C	-4.174836	5.558238	0.053550
64	C	5.142415	-2.791885	1.569986
65	H	5.219875	-2.165574	2.453685
66	C	8.788963	1.588565	-0.673631
67	H	8.591852	2.652932	-0.558543
68	C	-4.175273	-5.558057	0.053600
69	C	5.862284	-0.000135	0.720166
70	H	4.860393	-0.000098	1.135255
71	C	-3.522569	6.167786	-1.039595
72	H	-4.063821	6.348310	-1.962659
73	C	-6.203575	4.432020	1.039421
74	H	-6.024757	4.888822	2.007634
75	C	-6.203899	-4.431701	1.039532
76	H	-6.025050	-4.888454	2.007762
77	C	-7.373686	-2.736076	-0.279950
78	C	-7.135762	-3.427660	0.950243
79	H	-7.653443	-3.125169	1.853290
80	C	-5.856643	-4.336098	-1.339523
81	H	-5.355598	-4.662549	-2.244568
82	C	10.015946	1.262510	-1.247840
83	H	10.642069	2.104335	-1.528813
84	C	-7.135490	3.428018	0.950133
85	H	-7.653246	3.125614	1.853165
86	C	-7.373377	2.736380	-0.280025
87	C	10.015797	-1.263084	-1.247956
88	H	10.641826	-2.104956	-1.528997

89	C	-5.856134	4.336214	-1.339590
90	H	-5.354971	4.662546	-2.244614
91	C	10.549324	-0.000307	-1.501837
92	H	11.535225	-0.000344	-1.960889
93	C	-6.788788	-3.332322	-1.440623
94	H	-6.990134	-2.921761	-2.422834
95	C	-6.788332	3.332478	-1.440688
96	H	-6.989591	2.921830	-2.422880
97	C	-7.943021	-1.429964	-0.320887
98	C	-7.942851	1.430312	-0.320928
99	C	-8.218870	-0.681840	0.876108
100	H	-8.348273	-1.196575	1.821328
101	C	-8.218784	0.682260	0.876086
102	H	-8.348114	1.197039	1.821292
103	C	-8.051768	0.681582	-1.544740
104	H	-8.085588	1.199546	-2.496764
105	C	-8.051858	-0.681254	-1.544724
106	H	-8.085744	-1.199237	-2.496735

Optimized S_1 geometry of 1,3-Az[9]CPP-H$^+$

1	C	-2.031483	-5.573208	-0.133010
2	C	-1.547445	5.842755	0.840300
3	H	-0.994688	6.051598	1.750970
4	C	5.132712	2.679314	-0.622552
5	H	4.792717	2.713164	-1.651138
6	C	3.201009	4.120339	0.064282
7	C	-2.696097	-5.710102	1.092244
8	H	-2.127204	-5.878695	2.001441
9	C	0.322690	-5.922256	0.756902
10	H	-0.028962	-6.679350	1.450929
11	C	1.642029	-5.492541	0.837919
12	H	2.294089	-5.923195	1.591827
13	C	1.274893	-4.020985	-1.022562
14	H	1.613360	-3.241568	-1.697258
15	C	-2.819889	-5.403946	-1.277832
16	H	-2.353891	-5.367740	-2.257506
17	C	-2.935526	5.825015	0.887467
18	H	-3.431238	6.050772	1.826381
19	C	2.325510	3.564342	-0.881745
20	H	2.614568	2.678673	-1.436789
21	C	-5.092661	4.950995	-0.097048
22	C	4.178516	-3.379315	-0.946315
23	H	3.840564	-3.597720	-1.953672
24	C	6.780113	-1.243342	0.714485

25	C	1.483762	5.754140	0.601498
26	H	1.176383	6.625202	1.171203
27	C	2.133113	-4.506301	-0.028512
28	C	-0.861144	5.483484	-0.327010
29	C	-0.560981	-5.369278	-0.180192
30	C	2.762552	5.247922	0.779798
31	H	3.429322	5.739530	1.480840
32	C	5.301878	-2.591100	-0.769640
33	H	5.792608	-2.171747	-1.640692
34	C	6.063947	2.635887	2.005037
35	H	6.423717	2.607930	3.028482
36	C	0.581165	5.143450	-0.282398
37	C	-4.067229	-5.508448	1.189443
38	H	-4.533897	-5.559054	2.168123
39	C	7.714163	0.793929	1.464239
40	C	4.470714	3.441477	0.357870
41	C	-6.118366	-4.412185	0.199732
42	C	8.410211	-1.854493	-1.137988
43	H	7.893543	-2.806281	-1.223635
44	C	4.998641	3.438051	1.672540
45	H	4.517793	4.026276	2.445976
46	C	-0.043428	-4.438660	-1.091265
47	H	-0.700870	-3.968189	-1.813947
48	C	6.677163	1.809755	1.034181
49	C	-4.184390	-5.175643	-1.176817
50	H	-4.735715	-4.922441	-2.076368
51	C	6.201462	1.871375	-0.298320
52	H	6.669728	1.272420	-1.070139
53	C	1.044953	4.060604	-1.043849
54	H	0.368424	3.547284	-1.717903
55	C	7.907390	-0.968957	-0.144207
56	C	-1.619616	5.259441	-1.482929
57	H	-1.123717	5.042733	-2.423875
58	C	3.944810	-3.593000	1.441301
59	H	3.406007	-3.958893	2.308940
60	C	8.528089	0.254086	0.305373
61	C	3.453620	-3.863941	0.152475
62	C	5.745672	-2.250560	0.522514
63	C	-3.689681	5.426679	-0.224229
64	C	5.058204	-2.794839	1.624416
65	H	5.395539	-2.571075	2.631076
66	C	9.602863	0.932026	-0.191353
67	H	9.870763	1.856172	0.312918
68	C	-4.822036	-5.131719	0.070407
69	C	6.732660	-0.298759	1.739262

70	H	5.996533	-0.255731	2.530552
71	C	-3.004928	5.224625	-1.430366
72	H	-3.553703	4.938049	-2.321465
73	C	-5.467864	4.284607	1.075474
74	H	-4.822139	4.314804	1.946655
75	C	-6.322153	-3.603491	1.324450
76	H	-5.667789	-3.694155	2.184725
77	C	-7.961703	-2.265004	0.140128
78	C	-7.227922	-2.554262	1.296867
79	H	-7.247984	-1.863007	2.133070
80	C	-7.010065	-4.256100	-0.871768
81	H	-6.947270	-4.916533	-1.731359
82	C	10.420229	0.571173	-1.314564
83	H	11.198073	1.286051	-1.565583
84	C	-6.565019	3.437131	1.096001
85	H	-6.737684	2.831399	1.979525
86	C	-7.329661	3.217417	-0.056223
87	C	9.467857	-1.674921	-1.985644
88	H	9.672447	-2.489246	-2.672926
89	C	-5.973391	4.884613	-1.186166
90	H	-5.762451	5.449498	-2.089313
91	C	10.354872	-0.550000	-2.089089
92	H	11.091019	-0.622201	-2.884662
93	C	-7.912603	-3.198680	-0.903632
94	H	-8.523312	-3.052247	-1.789805
95	C	-7.071870	4.032475	-1.166774
96	H	-7.687831	3.944395	-2.056932
97	C	-8.417819	-0.860773	-0.042850
98	C	-8.088205	1.940698	-0.143570
99	C	-8.812667	-0.053893	1.033506
100	H	-9.155236	-0.512929	1.956309
101	C	-8.650668	1.325175	0.983671
102	H	-8.872069	1.915273	1.868207
103	C	-7.927882	1.158055	-1.293020
104	H	-7.515775	1.601750	-2.193821
105	C	-8.090704	-0.219758	-1.243638
106	H	-7.800133	-0.810182	-2.106841
107	H	8.312172	1.145764	2.307242

Optimized S_2 geometry of 1,3-Az[9]CPP-H$^+$

1	C	-1.980024	-5.897733	-0.162841
2	C	-1.587338	6.130108	0.874890
3	H	-1.040424	6.321234	1.792254
4	C	5.128093	3.190472	-0.696789

5	H	4.877392	3.359245	-1.737770
6	C	3.192307	4.613574	0.020013
7	C	-2.641766	-5.977521	1.070299
8	H	-2.076641	-6.155311	1.979710
9	C	0.354482	-6.266669	0.764682
10	H	-0.021815	-6.972764	1.497901
11	C	1.676748	-5.855286	0.845044
12	H	2.304274	-6.250875	1.637368
13	C	1.373765	-4.508030	-1.120976
14	H	1.734056	-3.781318	-1.840657
15	C	-2.770583	-5.716291	-1.305934
16	H	-2.314606	-5.728391	-2.290605
17	C	-2.968307	6.017509	0.937243
18	H	-3.461031	6.159108	1.893512
19	C	2.383275	4.202070	-1.055872
20	H	2.722776	3.418871	-1.723748
21	C	-5.076526	5.054995	-0.061364
22	C	4.211812	-3.725098	-0.970213
23	H	3.903354	-3.962725	-1.982186
24	C	6.604179	-1.384109	0.725316
25	C	1.412066	6.123697	0.696635
26	H	1.058556	6.898266	1.368594
27	C	2.203568	-4.927859	-0.069825
28	C	-0.894510	5.883062	-0.319975
29	C	-0.505943	-5.753404	-0.219467
30	C	2.690696	5.625410	0.863696
31	H	3.309702	6.022236	1.661268
32	C	5.269718	-2.860750	-0.776388
33	H	5.751369	-2.404847	-1.634607
34	C	5.833450	2.798475	1.967993
35	H	6.099692	2.628517	3.006232
36	C	0.558910	5.616440	-0.301838
37	C	-3.999082	-5.705076	1.173018
38	H	-4.459178	-5.714287	2.155798
39	C	7.231474	0.800170	1.354638
40	C	4.419215	3.876773	0.316933
41	C	-6.002082	-4.530320	0.179402
42	C	8.432639	-1.960572	-0.942178
43	H	8.010377	-2.961435	-0.990802
44	C	4.850569	3.710069	1.654404
45	H	4.344075	4.237993	2.454080
46	C	0.051415	-4.905394	-1.188291
47	H	-0.579994	-4.471589	-1.955205
48	C	6.436229	2.015820	0.962315
49	C	-4.120243	-5.418378	-1.199630

50	H	-4.666046	-5.161019	-2.101199
51	C	6.121088	2.289861	-0.383416
52	H	6.628078	1.750596	-1.175191
53	C	1.098430	4.684278	-1.204569
54	H	0.473673	4.258814	-1.980980
55	C	7.767606	-1.060738	-0.055294
56	C	-1.658475	5.683766	-1.479566
57	H	-1.170107	5.564736	-2.441057
58	C	3.984866	-3.991172	1.418769
59	H	3.468530	-4.399582	2.280720
60	C	8.189394	0.265879	0.296459
61	C	3.502360	-4.260627	0.122401
62	C	5.681769	-2.507735	0.524589
63	C	-3.713018	5.629559	-0.185729
64	C	5.047051	-3.130382	1.616351
65	H	5.369513	-2.890553	2.624164
66	C	9.222605	1.015842	-0.176789
67	H	9.338370	2.011446	0.241521
68	C	-4.743459	-5.311739	0.051945
69	C	6.292961	-0.369901	1.584935
70	H	5.436813	-0.318667	2.243342
71	C	-3.035970	5.553040	-1.412027
72	H	-3.577581	5.288838	-2.314031
73	C	-5.403039	4.350202	1.104189
74	H	-4.755482	4.405892	1.972448
75	C	-6.172377	-3.715195	1.305614
76	H	-5.520805	-3.830747	2.164777
77	C	-7.773021	-2.321628	0.131917
78	C	-7.042805	-2.636878	1.284210
79	H	-7.040377	-1.949658	2.123901
80	C	-6.887026	-4.336598	-0.892108
81	H	-6.850837	-4.996857	-1.753192
82	C	10.176549	0.651889	-1.199358
83	H	10.884295	1.433275	-1.460337
84	C	-6.450571	3.443148	1.121753
85	H	-6.585013	2.820264	1.999885
86	C	-7.212031	3.196366	-0.027290
87	C	9.522425	-1.734081	-1.724577
88	H	9.859371	-2.569055	-2.330472
89	C	-5.957692	4.947536	-1.147763
90	H	-5.789044	5.536344	-2.044274
91	C	10.302406	-0.523461	-1.862859
92	H	11.103686	-0.579687	-2.593843
93	C	-7.752838	-3.249359	-0.918261
94	H	-8.362021	-3.080012	-1.801310

95	C	-7.005055	4.034171	-1.131918
96	H	-7.622815	3.922964	-2.018117
97	C	-8.214780	-0.911886	-0.033327
98	C	-7.924188	1.894759	-0.114922
99	C	-8.607349	-0.118701	1.054159
100	H	-8.940373	-0.589683	1.974335
101	C	-8.464392	1.262082	1.013864
102	H	-8.690242	1.843233	1.903068
103	C	-7.754596	1.122407	-1.270117
104	H	-7.357055	1.579982	-2.170526
105	C	-7.898123	-0.257922	-1.230055
106	H	-7.607950	-0.838719	-2.099911
107	H	7.770014	1.028323	2.288234

References

(1) (a) Yakura, T.; Omoto, M.; Yamauchi, Y.; Tian, Y.; Ozono, A., Hypervalent iodine oxidation of phenol derivatives using a catalytic amount of 4-iodophenoxyacetic acid and Oxone® as a co-oxidant. *Tetrahedron,* **2010**, *66* (31), 5833-5840; (b) Abdulkarim, A.; Hinkel, F.; Jansch, D.; Freudenberg, J.; Golling, F. E.; Mullen, K., A New Solution to an Old Problem: Synthesis of Unsubstituted Poly(para-phenylene). *J. Am. Chem. Soc.* **2011**, *133* (40), 15800-15802.

(2) Abdulkarim, A.; Hinkel, F.; Jansch, D.; Freudenberg, J.; Golling, F. E.; Mullen, K., A New Solution to an Old Problem: Synthesis of Unsubstituted Poly(para-phenylene). *J. Am. Chem. Soc.* **2016**, *138* (50), 16208-16211.

(3) Darzi, E. R.; Sisto, T. J.; Jasti, R., Selective syntheses of [7]-[12]cycloparaphenylenes using orthogonal Suzuki-Miyaura cross-coupling reactions. *J Org Chem* **2012**, 77 (15), 6624-6628.

(4) Chen, M.; Unikela, K. S.; Ramalakshmi, R.; Li, B.; Darrigan, C.; Chrostowska, A.; Liu, S. Y., A BN-Doped Cycloparaphenylene Debuts. *Angew. Chem. Int. Ed.* **2021**, *60* (3), 1556-1560.

(5) Bredihhin, A.; Dubovik, J., A Convenient Synthesis of Functionalized Azulenes via Negishi Cross-Coupling. *Synthesis* **2015**, *47* (04), 538-548.

(6) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42* (2), 339-341.

(7) Sheldrick, G. M., SHELXT-integrated space-group and crystal-structure determination. *Acta Cryst.* **2015**, A*71*, 3-8.

(8) Spek, A. L., PLATON SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors. *Acta Cryst.* **2015**, C*71*, 9-18.

(9) (a) Thordarson, P., Determining association constants from titration experiments in supramolecular chemistry. *Chem. Soc. Rev.*, **2011**, 40 (3), 1305-1323; (b) Brynn Hibbert, D.; Thordarson, P., The death of the Job plot, transparency, open science and online tools, uncertainty estimation methods and other developments in supramolecular chemistry data analysis. *Chem. Commun.*, **2016**, 52 (87), 12792-12805.

(10) M.J. Frisch, G.W.Trucks, H.B.Schlegel, et al. Gaussian 16, Revision B.01; Gaussian, Inc., Wallingford CT, **2016**.

(11) Lu, T.; Chen, F., Multiwfn: a multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012**, *33* (5), 580-592.