Electronic Supplementary Information

Supramolecular Photosensitizers Using Extended Macrocyclic Hosts for Photodynamic Therapy with Distinct Cellular Delivery

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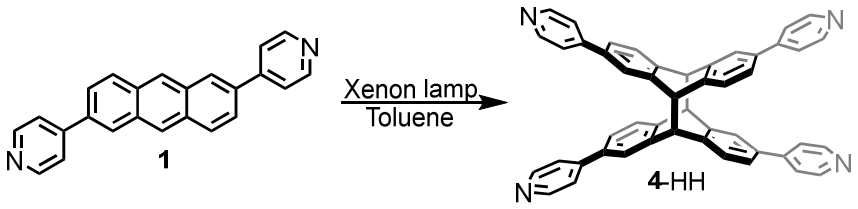
I. General Information

^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance 400 spectrometer at 25 ^{o}C and were internally referenced to residual protio solvent signals (for example, $CDCl_3$ was referenced at 7.26 and 77.16 ppm, respectively, see: G. R. Fulmer, *et al Organometallics* **2010**, *29*, 2176). Data for ^{1}H NMR were reported as follows: chemical shift (δ ppm), integration, multiplicity (br = broad, ovrlp = overlapping, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant (Hz) when applicable. All ^{13}C NMR spectra were recorded with complete proton decoupling. High-resolution mass spectrometry experiments were performed with a Bruker Daltonics Apex IV spectrometer. Confocal fluorescence microscopy images were obtained using a Nikon C1 SI confocal microscopy.

All reactions were carried out using flame-dried glassware under a nitrogen atmosphere unless otherwise noted. Anthracene photodimerizations were conducted under the irradiation of a 300 W xenon lamp (Beijing PerfectLight Technology, PLS-SXE300UV) equipped with a Vis-Ref filter (permitting >320 nm light). Analytical thin layer chromatography (TLC) was performed using 0.25 mm silica gel 60-F plates. Flash chromatography was performed using 200-400 mesh silica gel. HPLC-grade tetrahydrofuran, dichloromethane, diethyl ether, toluene, and hexanes were purified and dried by passing through a PURE SOLV® solvent purification system (Innovative Technology, Inc.). Deionized water was degassed by bubbling with nitrogen balloon for 20 min prior to use as reaction solvent. Chemical reagents were purchased from Strem, Acros, Energy Chemicals, J&K, InnoChem, and Alfa Aesar, and were used as received.

II. Synthesis and Characterization

2.1 Synthesis of AnBox^{4+}



Compound **4**-HH

In nitrogen glove box, compound **1** (prepared according to the literature: *Chem. Lett.* **2011**, *40*, 941, 100 mg, 0.30 mmol) and anhydrous toluene (40 mL) were added in a 100 mL glass heavy-wall pressure vessel equipped with a stir bar. The vessel was capped, transferred out of the glove box, and was stirred under the irradiation of a xenon lamp at 25 °C for 16 h. The solvent was then removed under reduced pressure. The resulting solid was recrystallized using CH_2Cl_2 and petroleum ether to afford compound **4**-HH (77 mg, 77% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.51 (d, *J* = 3.6 Hz, 8H), 7.52–7.47 (m, 12H), 7.27 (d, *J* = 7.6 Hz, 4H), 7.19 (d, *J* = 7.6 Hz, 4H), 4.92 (s, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3, 148.2, 143.95, 143.93, 136.5, 128.2, 126.0, 125.1, 121.6, 53.6;
IR (KBr): 3055, 2932, 2362, 2343, 1597, 1543, 1478, 1404, 1232, 819 cm^{-1};
HRMS (ESI): $[M+H]^+$ calcd for $[C_{48}H_{33}N_4]^+$ 665.2700, found 665.2671.

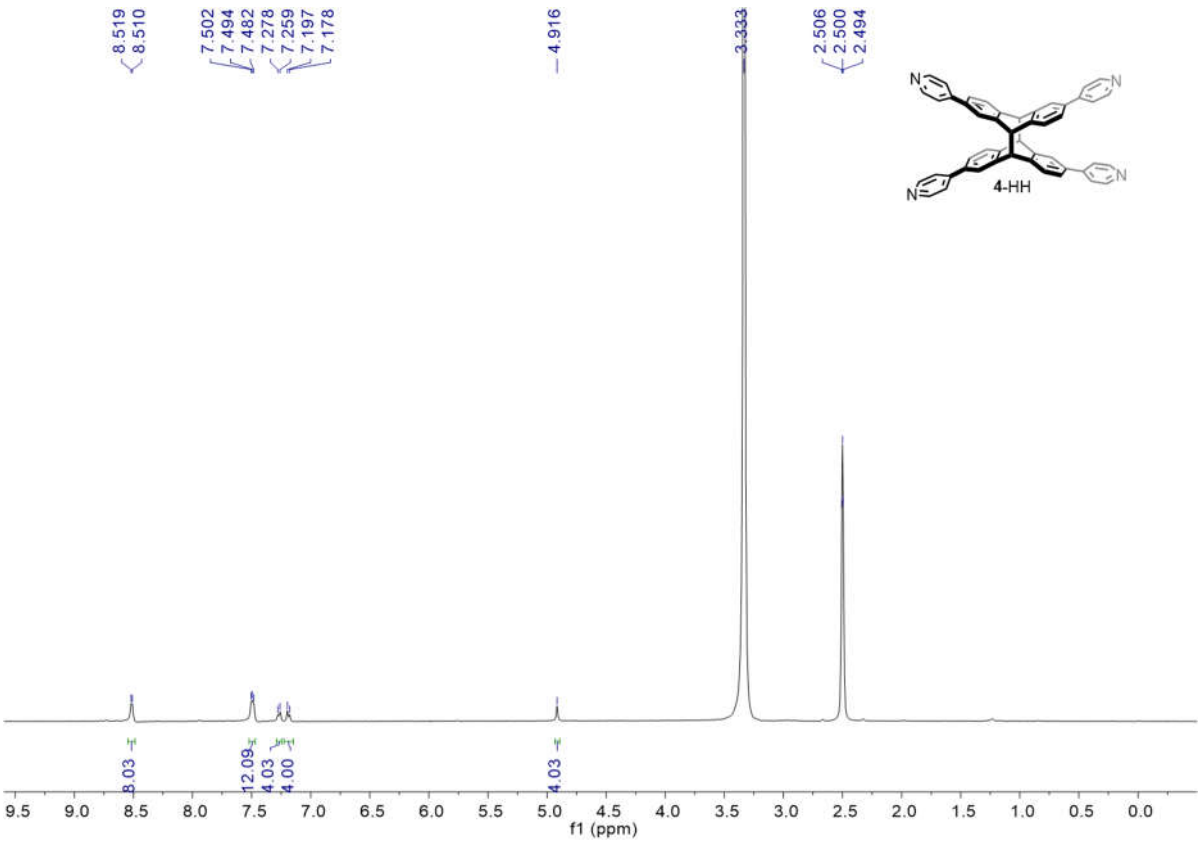


Figure S1. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of compound **4**-HH.

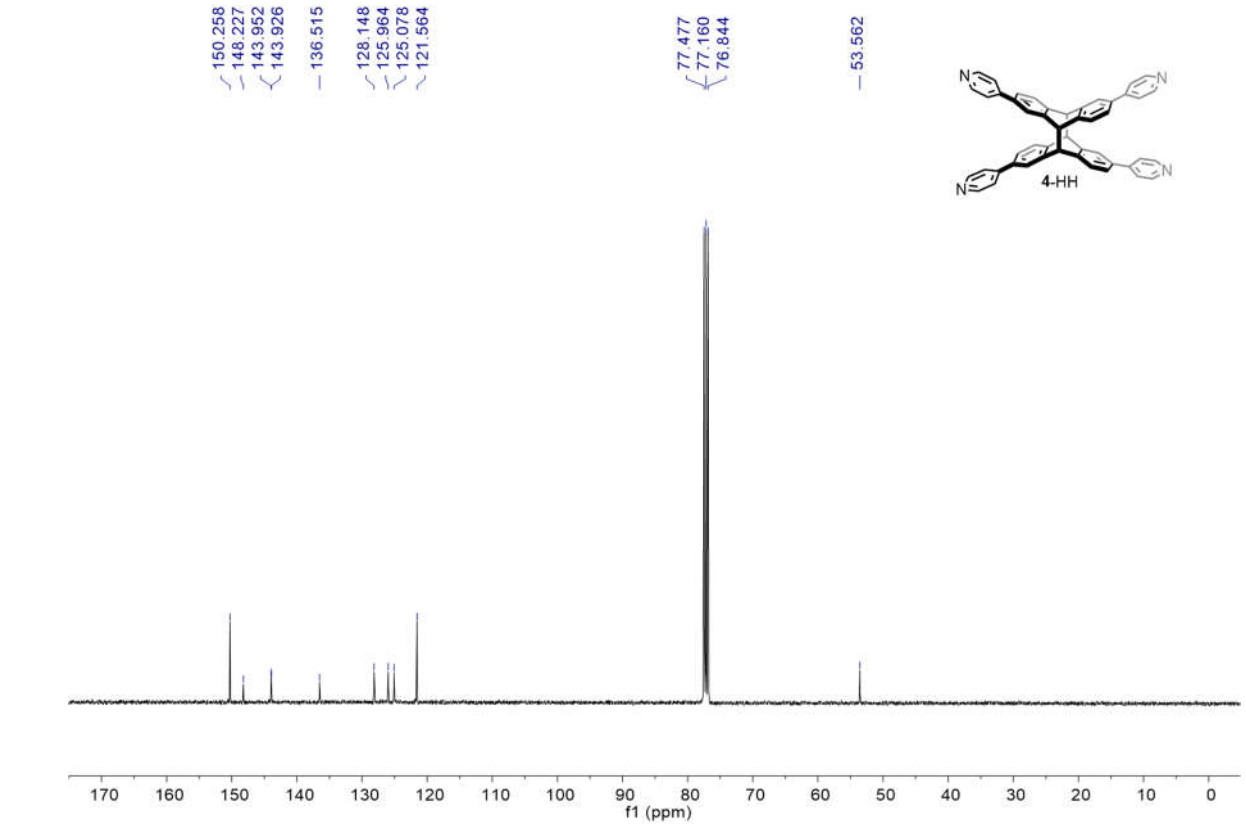
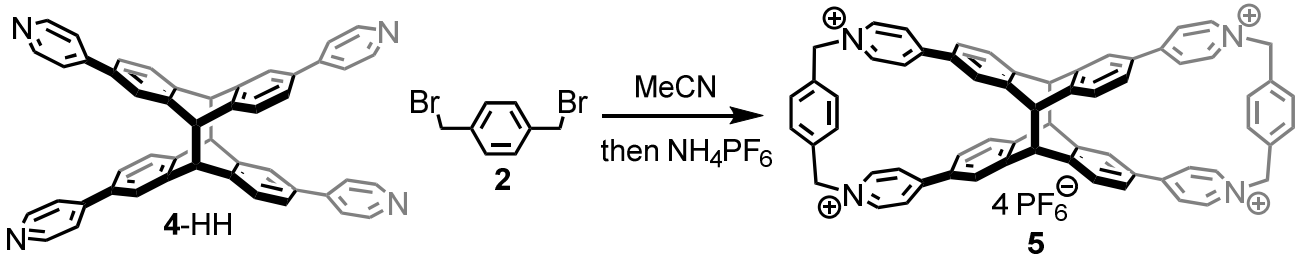


Figure S2. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of compound **4**-HH.



Compound **5**

In air, compound **4-**HH (20 mg, 0.030 mmol, 1.0 equiv), compound **2** (16 mg, 0.06 mmol, 2.0 equiv) and anhydrous CH_3CN (100 mL) were added to a 150 mL glass heavy-wall pressure vessel equipped with a stir bar. The vessel was capped and stirred at 85 °C for 25 h. The mixture was cooled to room temperature, and excess NH_4PF_6 (200 mg) was added to the vessel and sonicated for 10 minutes. The reaction mixture was filtered through a short pad of Celite, followed by concentration under reduced pressure to afford the crude product. The crude product was washed with CH_2Cl_2 three times and water for three times. The resulting solid was mixed with CH_3CN (1 mL) and separated by centrifugation, affording compound **5** (20 mg, 46% yield) as a yellow solid.

^{1}H NMR (400 MHz, CD_3CN) δ 8.50 (d, *J* = 4.0 Hz, 8H), 7.86 (d, *J* = 4.0 Hz, 8H), 7.54 (s, 8H), 7.44 (s, 8H), 7.26 (d, *J* = 8.0 Hz, 4H), 5.60 (s, 8H), 4.89 (s, 4H).
^{13}C NMR (101 MHz, CD_3CN) δ 156.4, 148.3, 145.0, 144.51, 144.48, 139.3, 131.9, 131.0, 130.0, 128.7, 126.7, 125.3, 65.0, 53.3;
IR (KBr): 3436, 3133, 2363, 1637, 1487, 1467, 1410, 1293, 1159 cm^{-1};
HRMS (ESI): $[M-2PF_6]^{2+}$ calcd for $[C_{64}H_{48}F_{12}N_4P_2]^{2+}$ 581.1576, found 581.1580.

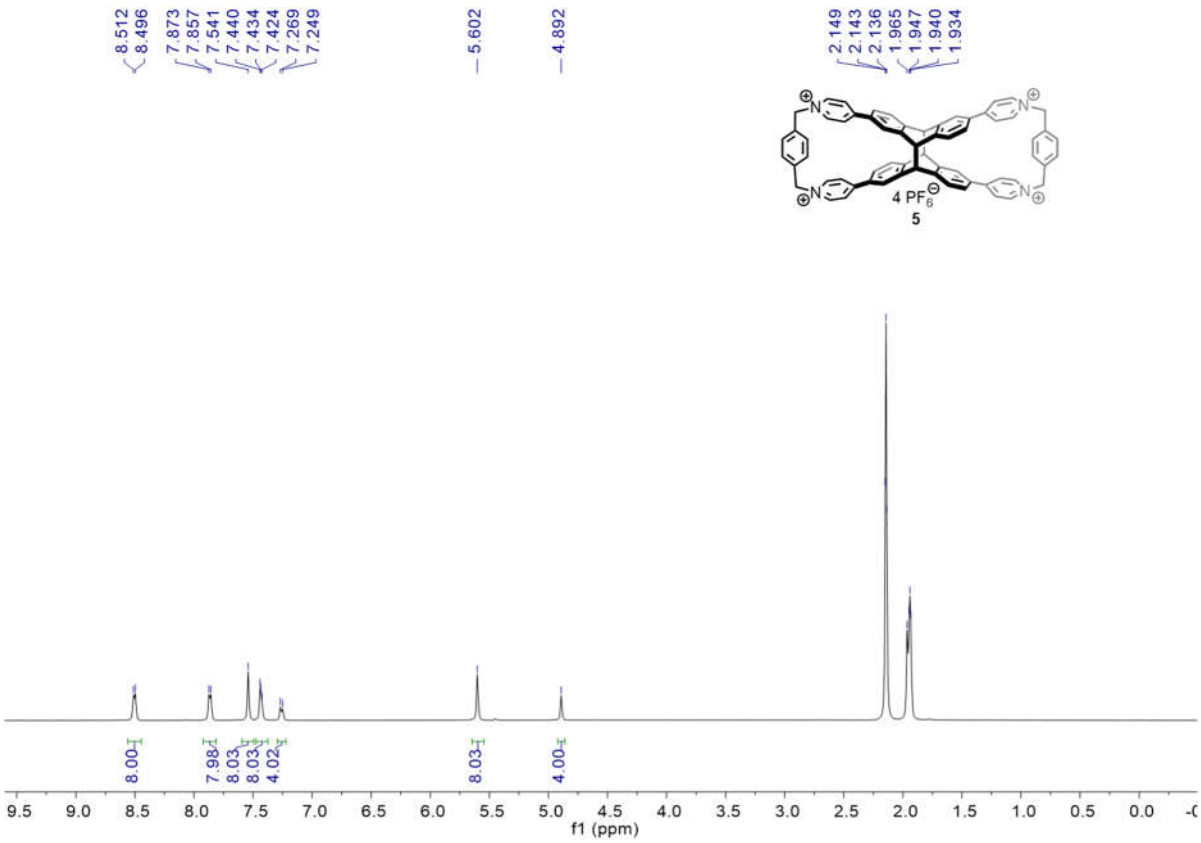


Figure S3. ^{1}H NMR spectrum (CD_3CN, 400 MHz) of compound **5**.

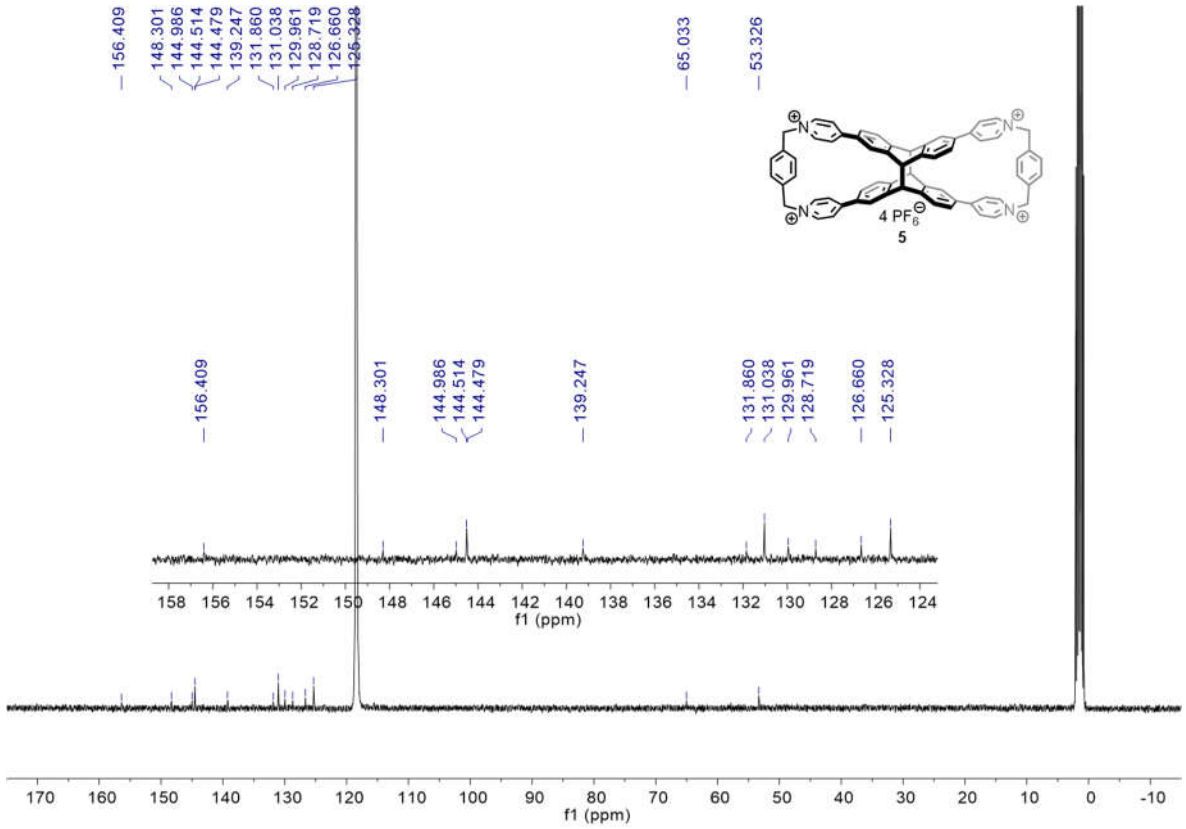
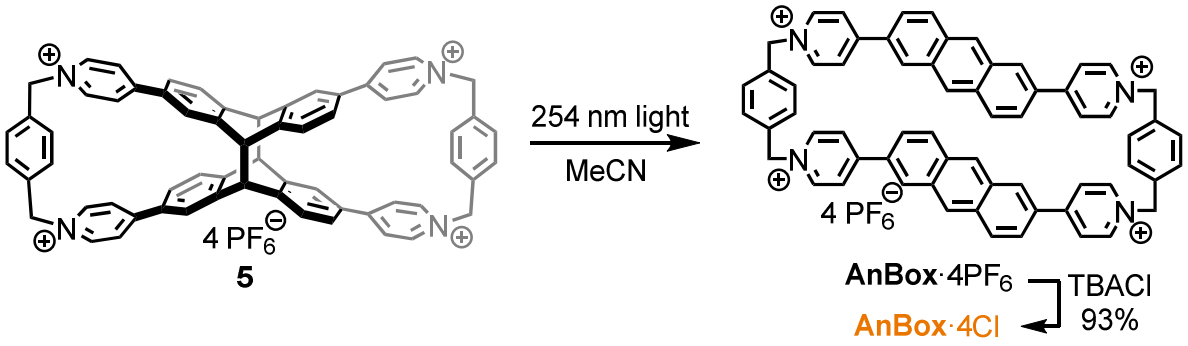


Figure S4. ^{13}C NMR spectrum (CD_3CN, 101 MHz) of compound **5**.



AnBox·4PF_6

In a nitrogen-filled glove box, compound **5** (20 mg, 0.014 mmol, 1.0 equiv) and anhydrous CH_3CN (20 mL) were added to a 50 mL quartz tube equipped with a stir bar. The tube was capped with a septum, transferred out of glove box, and irradiated under 254 nm UV-light at 25 °C for 2 h. The solvent was removed under reduced pressure, and the resulting crude product was recrystallized by CH_3CN/CH_2Cl_2. **AnBox·4PF$_6$** (18 mg, 90% yield) was obtained as an orange solid. Characterization data were identical to the literature (*J. Am. Chem. Soc.* ***2020****, 142, 7956*).

^{1}H NMR (400 MHz, CD_3CN) δ 8.80 (d, *J* = 8.0 Hz, 8H), 8.53 (s, 8H), 8.29 (d, *J* = 8.0 Hz, 8H), 8.14 (d, *J* = 9.0 Hz, 4H), 7.82 (d, *J* = 9.0 Hz, 4H), 7.66 (s, 8H), 5.70 (s, 8H).

AnBox·4Cl

AnBox·4PF_6 (10 mg, 0.007 mmol, 1.0 equiv), TBACl·H_2O (41 mg, 0.14 mmol, 20 equiv) and anhydrous CH_3CN (7 mL) were added to a 40 mL vial equipped with a stir bar. The reaction mixture was stirred for 2 h. The precipitates were collected by centrifugation followed by washing with CH_3CN for three times to afford **AnBox**·4Cl (6.5 mg, 93% yield) as an orange solid.

^{1}H NMR (400 MHz, CD_3OD) δ 9.13 (d, J = 6.5 Hz, 8H), 8.63 (s, 4H), 8.55 (s, 4H), 8.46 (d, J = 6.4 Hz, 8H), 8.10 (d, J = 8.9 Hz, 4H), 7.88 (dd, J = 9.2, 1.9 Hz, 4H), 7.80 (s, 8H), 5.85 (s, 8H).
^{13}C NMR (101 MHz, CD_3OD) δ 155.3, 145.4, 145.3, 137.9, 133.7, 133.6, 131.7, 131.63, 131.58, 126.5, 124.3, 64.6;
IR (KBr): 3024, 2366, 1637, 1618, 1521, 1466, 1157, 1023, 790 cm^{-1};
HRMS (ESI): $[M-2Cl]^{2+}$ calcd for $[C_{64}H_{48}Cl_2N_4]^{2+}$ 471.1622, found 471.1644.

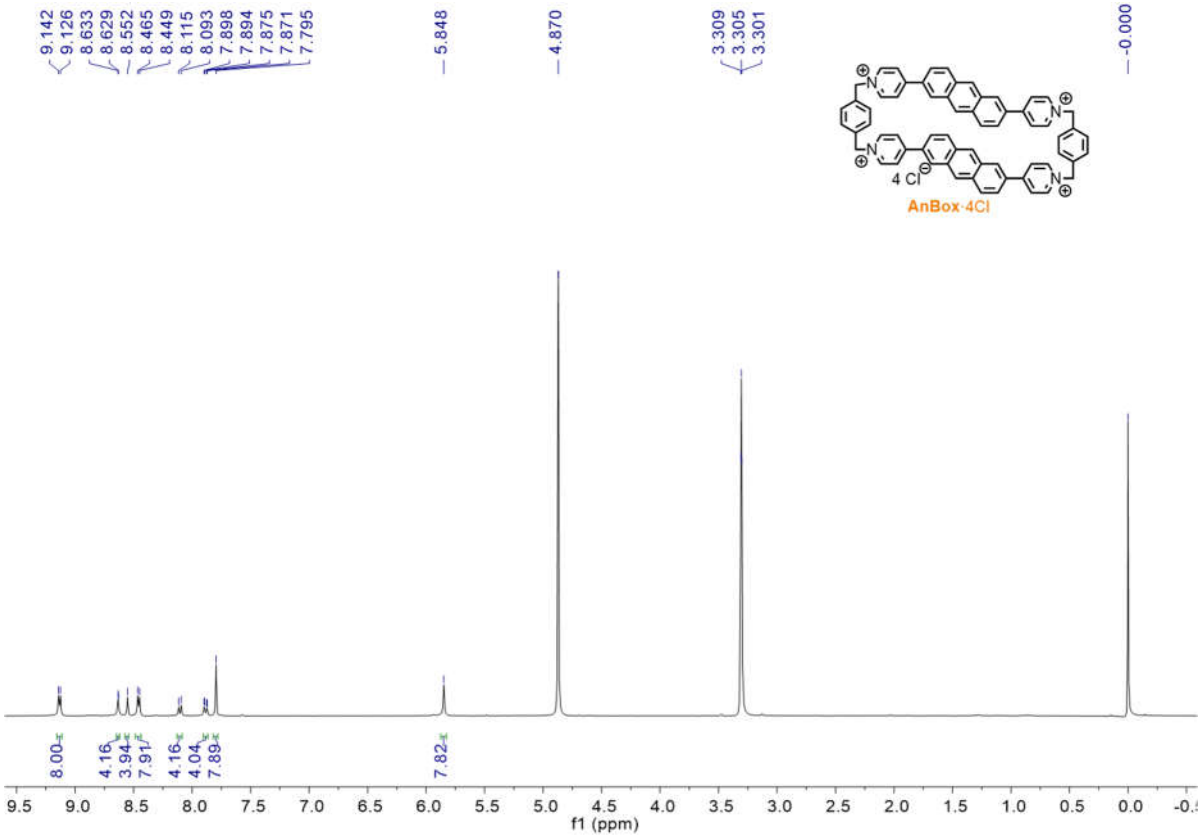


Figure S5. [1]H NMR spectrum (CD_3OD, 400 MHz) of **AnBox**·4Cl.

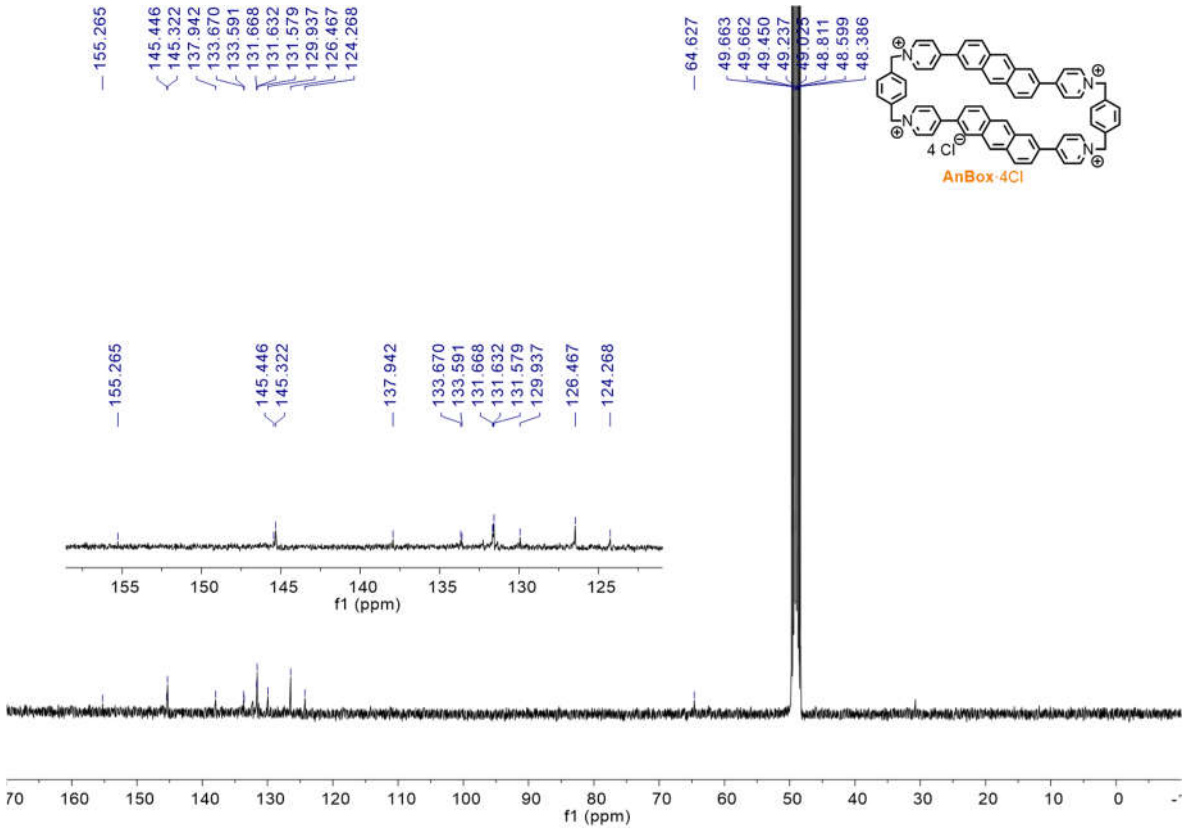


Figure S6. [13]C NMR spectrum (CD_3OD, 101 MHz) of **AnBox**·4Cl.

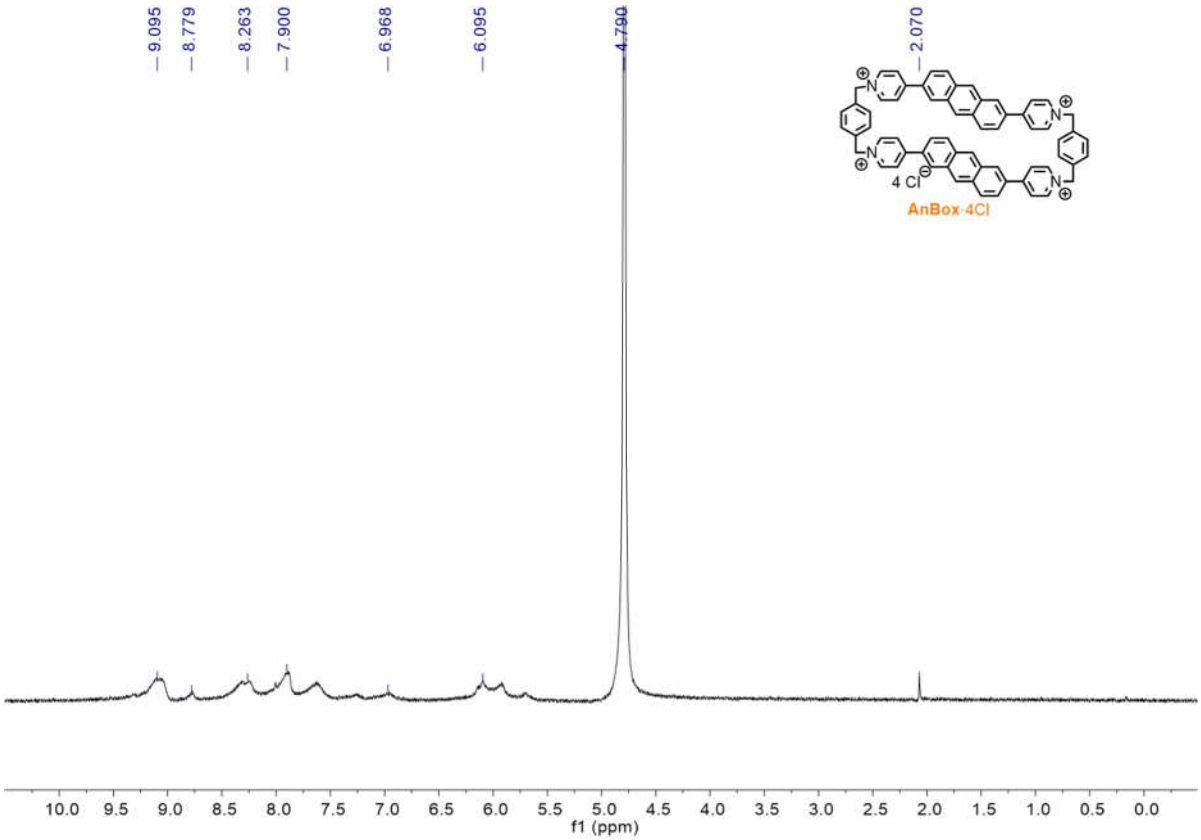


Figure S7. ^{1}H NMR spectrum (D_2O, 400 MHz) of **AnBox**·4Cl, showing broadened peaks.

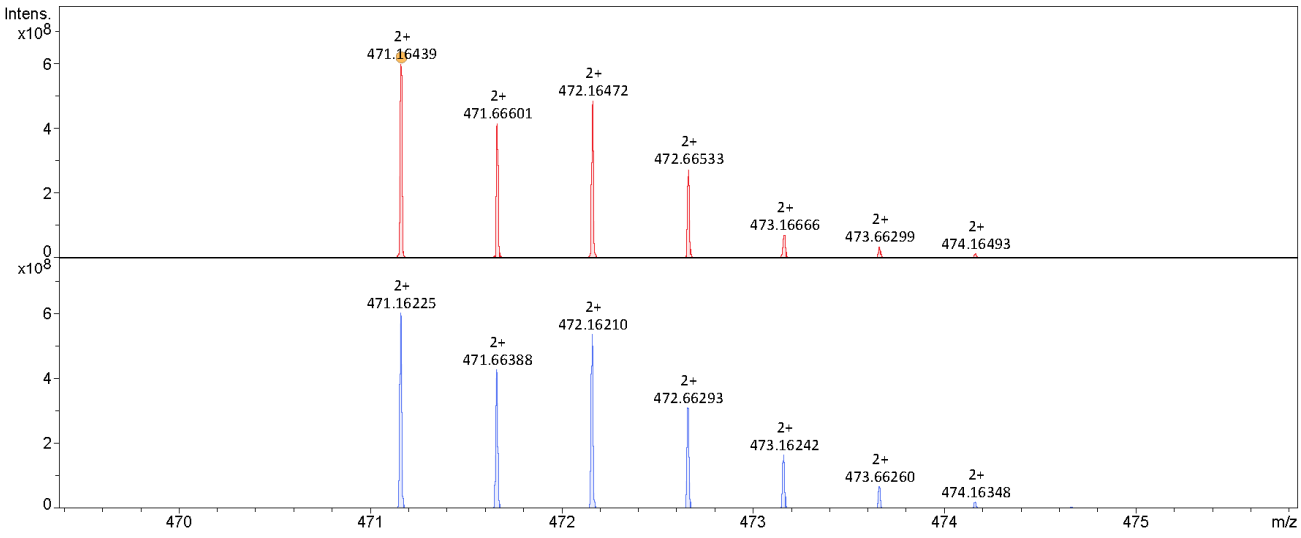
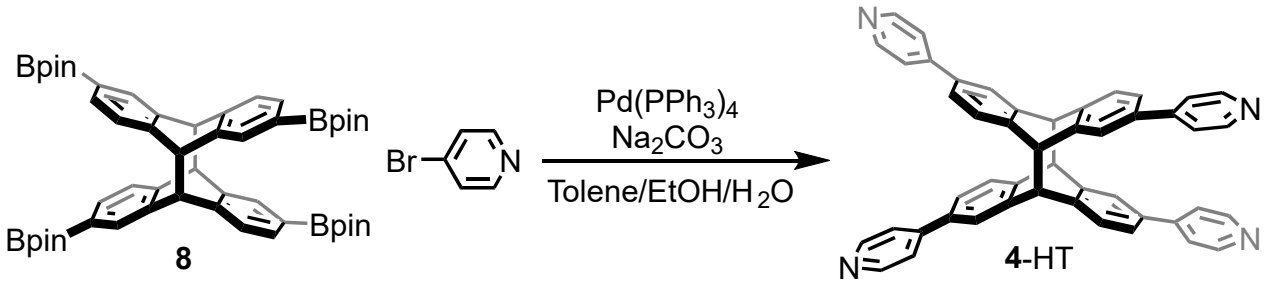


Figure S8. Measured (top) and simulated (bottom) HRMS data for **AnBox**·4Cl.

2.2 Synthesis and Characterization of ExAnBox^{4+}



Compound **4**-HT

In a nitrogen-filled glove box, compound **8** (172 mg, 0.20 mmol, 1.0 equiv, prepared according to the literature: *J. Am. Chem. Soc*. **2016**, *138*, 11144), 4-bromopyridine (190 mg, 1.20 mmol, 6.0 equiv), $Pd(PPh_3)_4$ (46 mg, 0.040 mmol, 20 mol%), Na_2CO_3 (170 mg, 1.60 mmol, 8.0 equiv), and toluene (8.0 mL) were added to a 40 mL glass vial equipped with a stir bar. The vial was sealed with a teflon-lined septum cap and transferred out of glove box. Degassed EtOH (4.0 mL) and degassed H_2O (2.0 mL) were sequentially added to the reaction vial via a syringe, and the puncture in the septum cap was covered with vacuum grease. The reaction mixture was stirred at 80 °C for 42 h before it was cooled down to room temperature. The solvents were removed under reduced pressure. The crude product was recrystallized using hot ethyl acetate, and compound **4**-HT (110 mg, 83% yield) was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.1 Hz, 8H), 7.38–7.27 (m, 12H), 7.12 (s, 8H), 4.79 (s, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3, 148.1, 144.1, 143.9, 136.2, 128.1, 125.9, 124.9, 121.5, 53.6;
IR (KBr): 3027, 2922, 2343, 1598, 1478, 1402, 897, 824 cm^{-1};
HRMS (ESI): $[M+H]^+$ calcd for $[C_{48}H_{33}N_4]^+$ 665.2700, found 665.2687.

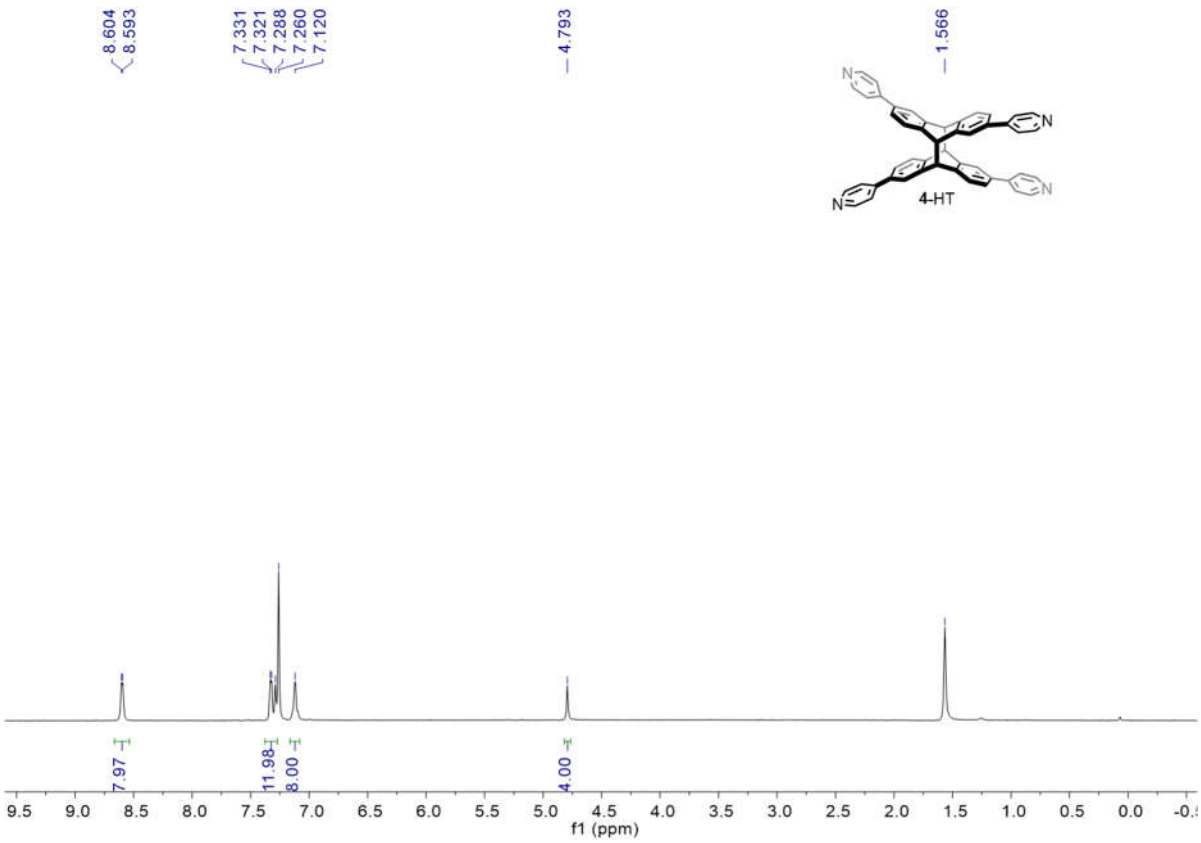


Figure S9. [1]H NMR spectrum ($CDCl_3$, 400 MHz) of compound **4**-HT.

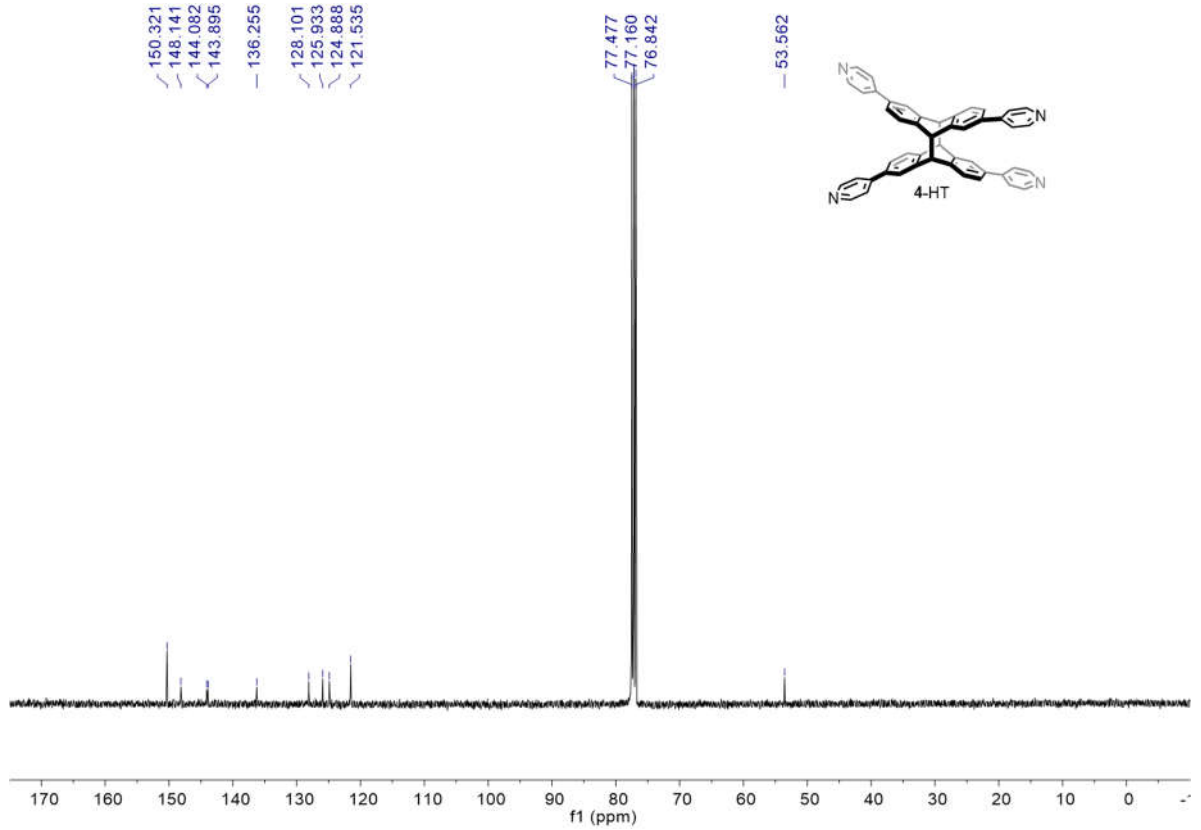
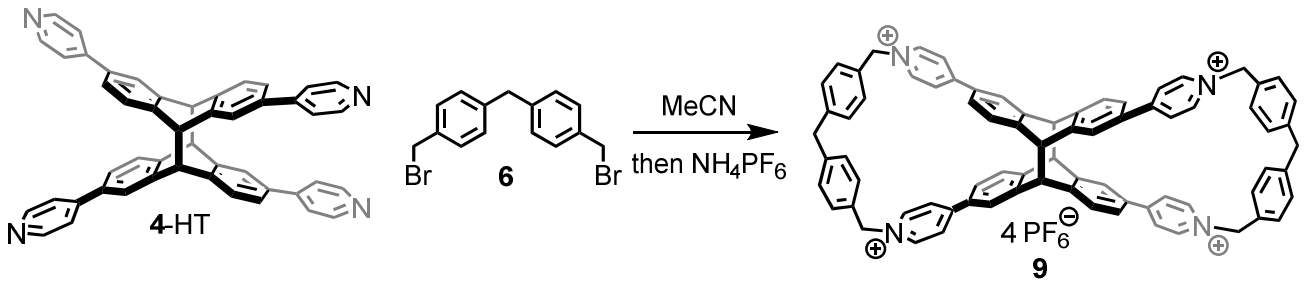


Figure S10. [13]C NMR spectrum ($CDCl_3$, 101 MHz) of compound **4**-HT.



Compound **9**

In air, compound **4**-HT (133 mg, 0.20 mmol, 1.0 equiv), compound **6** (142 mg, 0.40 mmol, 2.0 equiv) and anhydrous CH_3CN (200 mL) were added to a 350 mL glass heavy-wall pressure vessel equipped with a stir bar. The vessel was capped and stirred at 85 °C for 20 h. The mixture was cooled to room temperature, and excess NH_4PF_6 (1.70 g) was added to the vessel and sonicated for 10 minutes. The supernatant was collected by centrifugation, followed by concentration under reduced pressure to afford the crude product. The crude product was recrystallized using CH_3CN/H_2O for three times, then the precipitate was washed with water for three times and air-dried. Compound **9** (130 mg, 40% yield) was obtained as a light-yellow solid.

^{1}H NMR (400 MHz, CD_3CN) δ 8.70 (d, *J* = 4.7 Hz, 8H), 7.81 (d, *J* = 4.6 Hz, 8H), 7.52–7.40 (m, 12H), 7.35 (d, *J* = 5.0 Hz, 12H), 7.13 (d, *J* = 7.7 Hz, 4H), 5.56–5.52 (m, 8H), 4.95 (s, 4H), 3.94 (s, 4H).
^{13}C NMR (101 MHz, CD_3CN) δ 158.0, 147.9, 145.0, 144.5, 144.4, 133.5, 133.1, 130.5, 130.0, 129.2, 128.2, 127.8, 126.7, 64.9, 53.4, 42.1;
IR (KBr): 2922, 1638, 1485, 1222, 1160, 850 cm^{-1};
HRMS (ESI): $[M-2PF_6]^{2+}$ calcd for $[C_{78}H_{60}F_{12}N_4P_2]^{2+}$ 671.2045, found 671.2052.

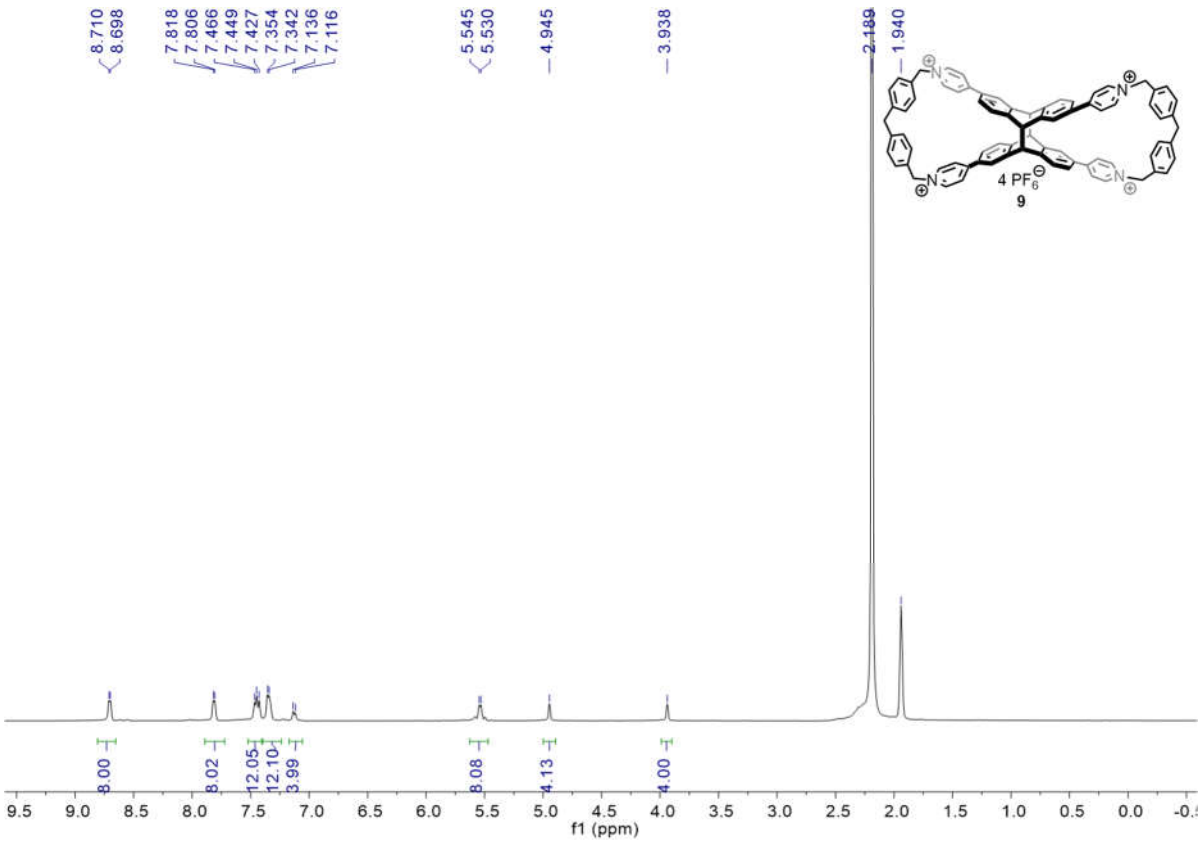


Figure S11. ^{1}H NMR spectrum (CD_3CN, 400 MHz) of compound **9**.

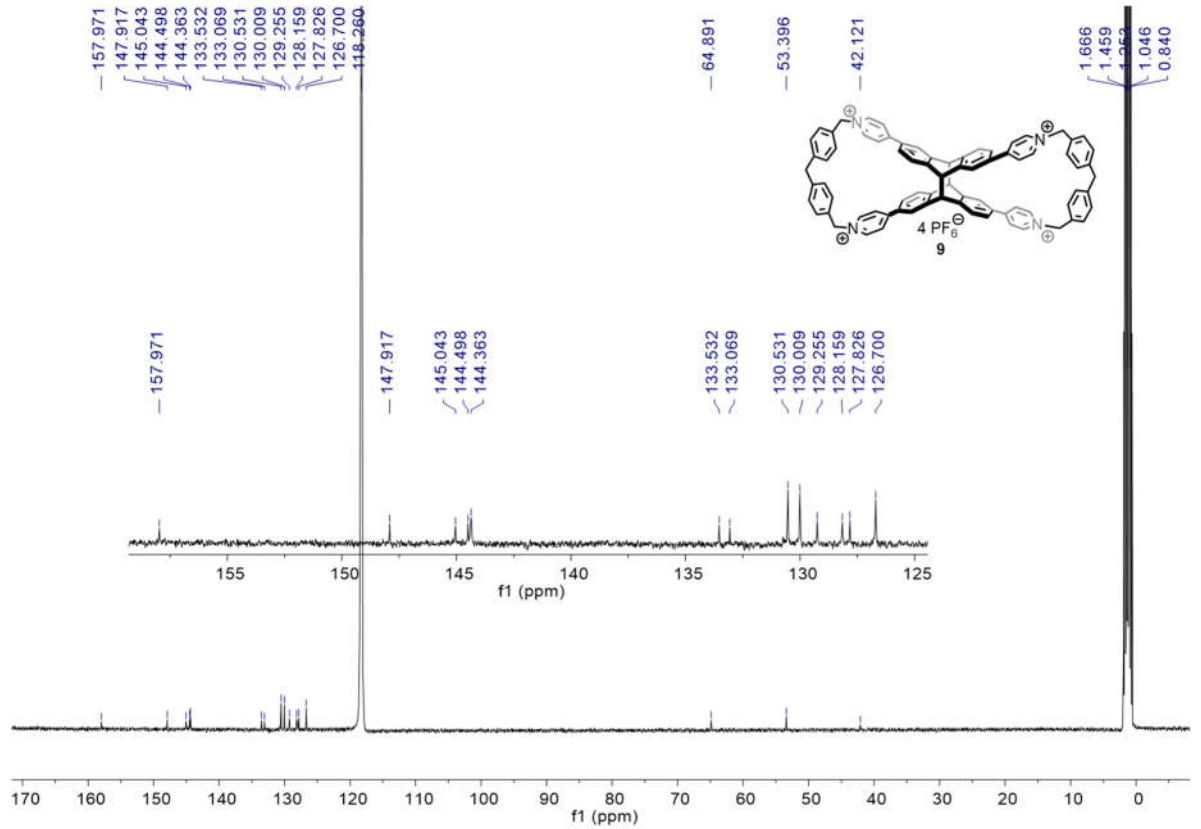
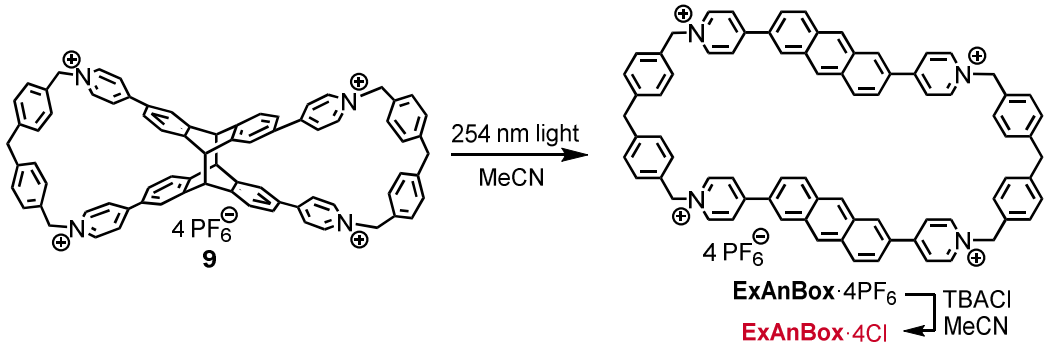


Figure S12. ^{13}C NMR spectrum (CD_3CN, 101 MHz) of compound **9**.



ExAnBox·4PF_6

In a nitrogen-filled glove box, compound **9** (40 mg, 0.024 mmol, 1.0 equiv) and anhydrous CH_3CN (30 mL) were added to a 50 mL quartz tube equipped with a stir bar. The quartz tube was capped with a septum, transferred out of glove box, and irradiated under 254 nm UV-light at 25 °C for 2 h. The solvent was removed under reduced pressure and the resulting crude product was recrystallized by CH_3CN/CH_2Cl_2, affording **ExAnBox**·4PF_6 (38 mg, 95% yield) as an orange solid.

^{1}H NMR (400 MHz, CD_3CN) δ 8.73 (d, *J* = 4.5 Hz, 8H), 8.66 (s, 8H), 8.35 (s, 8H), 8.18 (d, *J* = 8.6 Hz, 4H), 7.87 (d, *J* = 9.1 Hz, 4H), 7.43 (s, 16H), 5.67 (s, 8H), 4.05 (s, 4H).
^{13}C NMR (101 MHz, CD_3CN) δ 157.1, 145.2, 144.2, 133.3, 133.2, 132.7, 132.2, 131.3, 131.2, 130.8, 130.5, 129.8, 126.5, 124.7, 64.4, 41.8;
IR (KBr): 3662, 3129, 3056, 1638, 1520, 1466, 1157, 840 cm^{-1};
HRMS (ESI): $[M-2PF_6]^{2+}$ calcd for $[C_{78}H_{60}F_{12}N_4P_2]^{2+}$ 671.2045, found 671.2054.

ExAnBox·4Cl

ExAnBox·4PF_6 (49 mg, 0.030 mmol, 1.0 equiv), TBACl·H_2O (177 mg, 0.60 mmol, 20 equiv) and anhydrous CH_3CN (7 mL) were added to a 40 mL vial equipped with a stir bar. The reaction mixture was stirred at 25 °C for 24 h. The precipitates were collected by centrifugation, followed by washing using CH_3CN for three times to afford **ExAnBox**·4Cl (29 mg, 80% yield) as an orange solid.

^{1}H NMR (400 MHz, CD_3OD) δ 9.00 (s, 8H), 8.84 (s, 4H), 8.75 (s, 4H), 8.55 (s, 8H), 8.18 (d, *J* = 8.0 Hz, 4H), 7.97 (d, *J* = 8.9 Hz, 4H), 7.62–7.34 (m, 16H), 5.80 (s, 8H), 4.06 (s, 4H).
^{13}C NMR (101 MHz, CD_3OD) δ 145.6, 144.8, 133.9, 133.9, 133.1, 132.7, 131.6, 131.5, 131.1, 130.7, 130.0, 126.5, 124.8, 64.6, 57.5.;
IR (KBr): 3023, 2919, 1636, 1618, 1520, 1464, 1401, 1156, 871, 786 cm^{-1};
HRMS (ESI): $[M-2Cl]^{2+}$ calcd for $[C_{78}H_{60}Cl_2N_4]^{2+}$ 561.2092, found 561.2117.

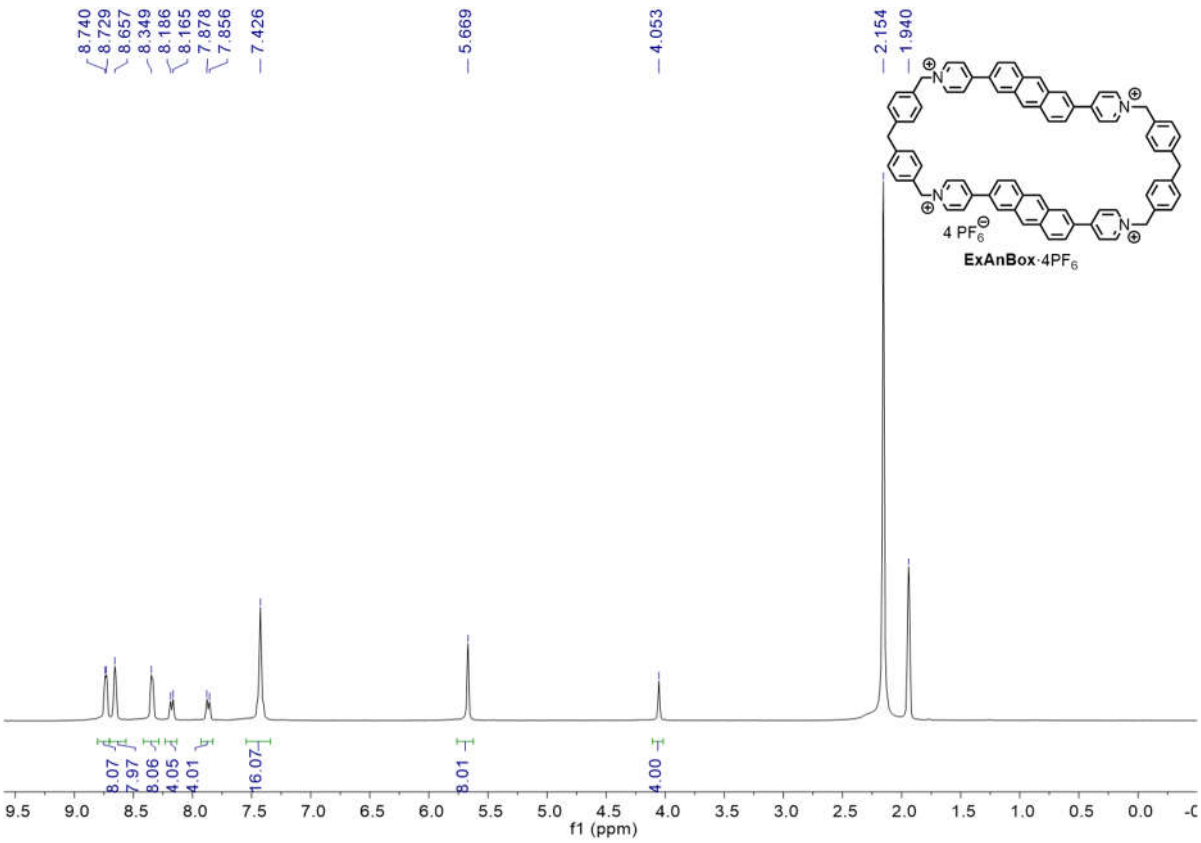


Figure S13. ^{1}H NMR spectrum (CD_3CN, 400 MHz) of **ExAnBox**·4PF_6.

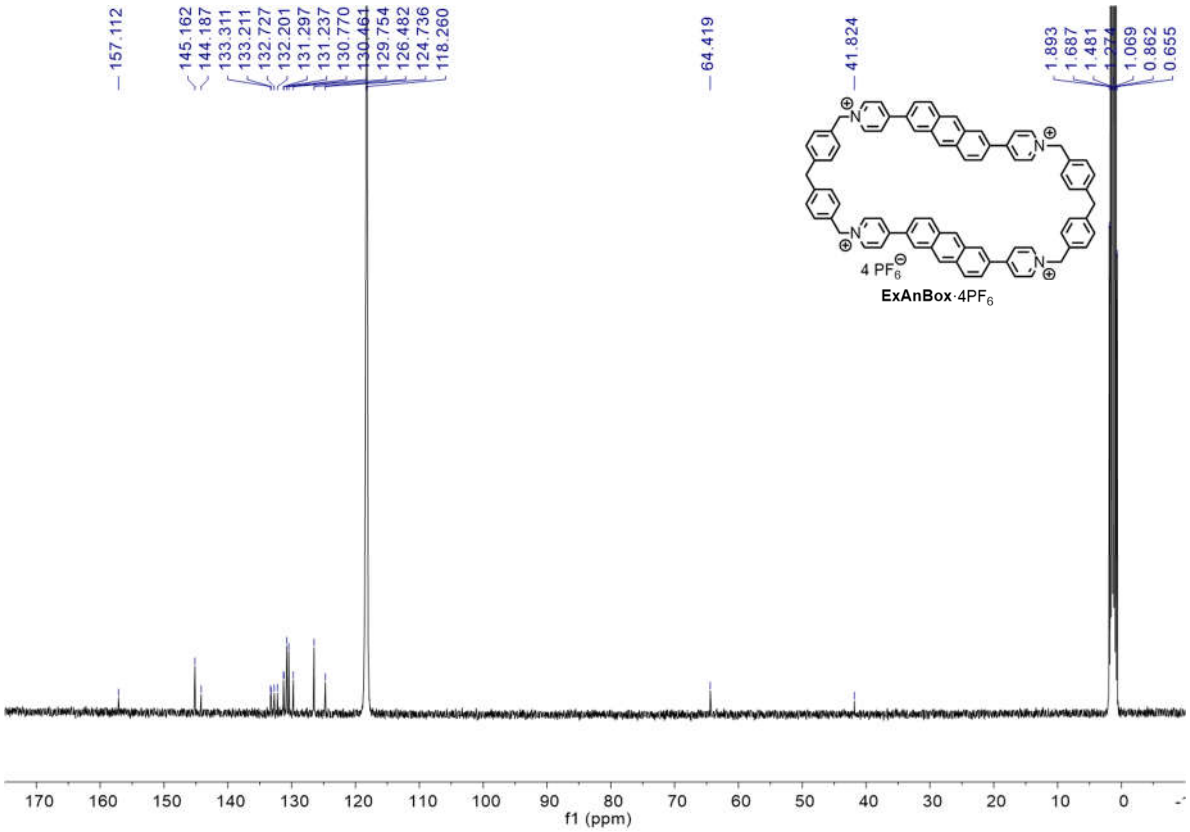


Figure S14. ^{13}C NMR spectrum (CD_3CN, 101 MHz) of **ExAnBox**·4PF_6.

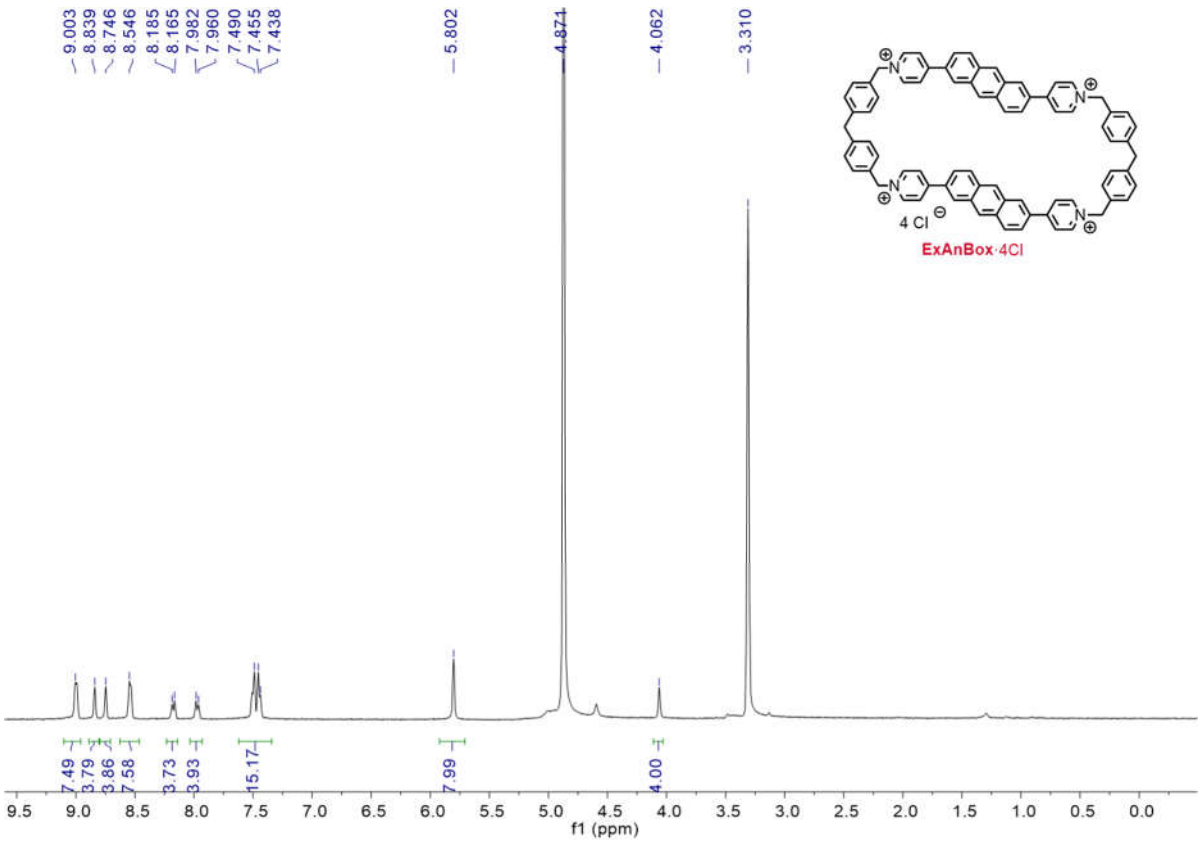


Figure S15. ^{1}H NMR spectrum (CD_3OD, 400 MHz) of **ExAnBox**·4Cl.

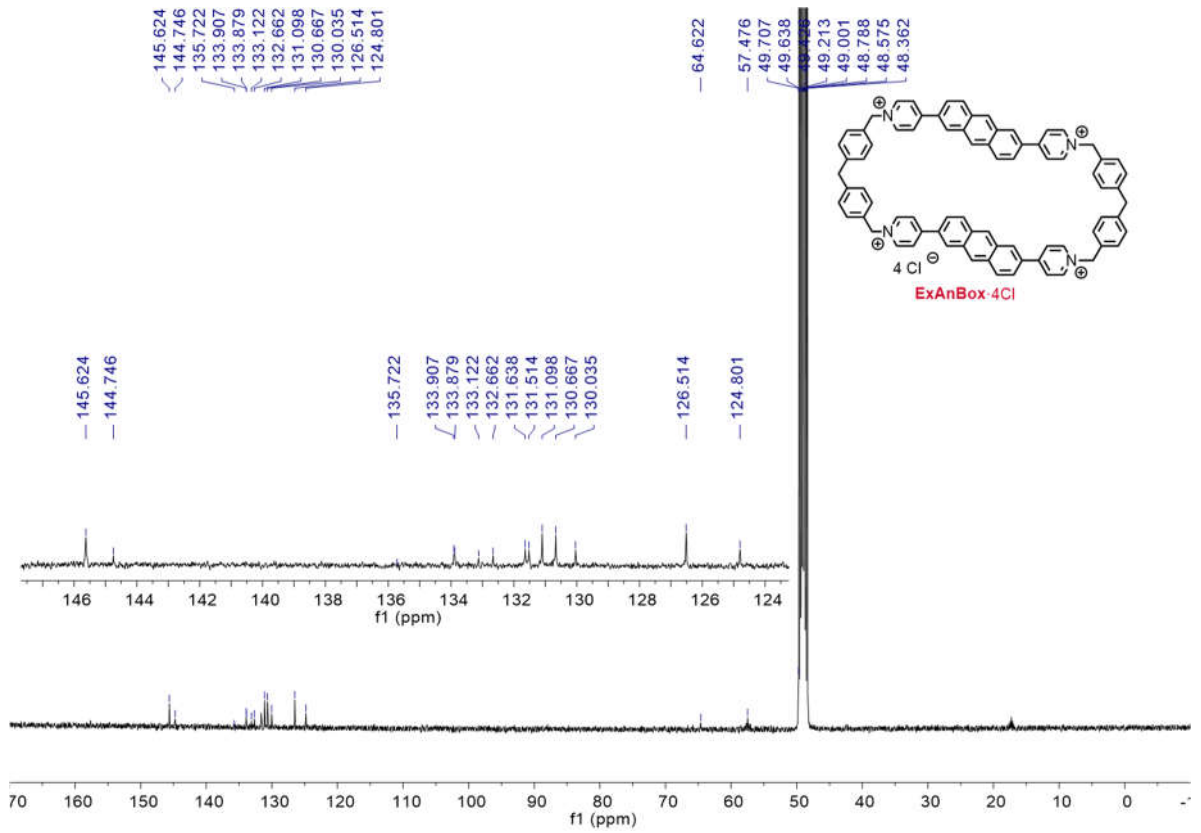


Figure S16. ^{13}C NMR spectrum (CD_3OD, 101 MHz) of **ExAnBox**·4Cl.

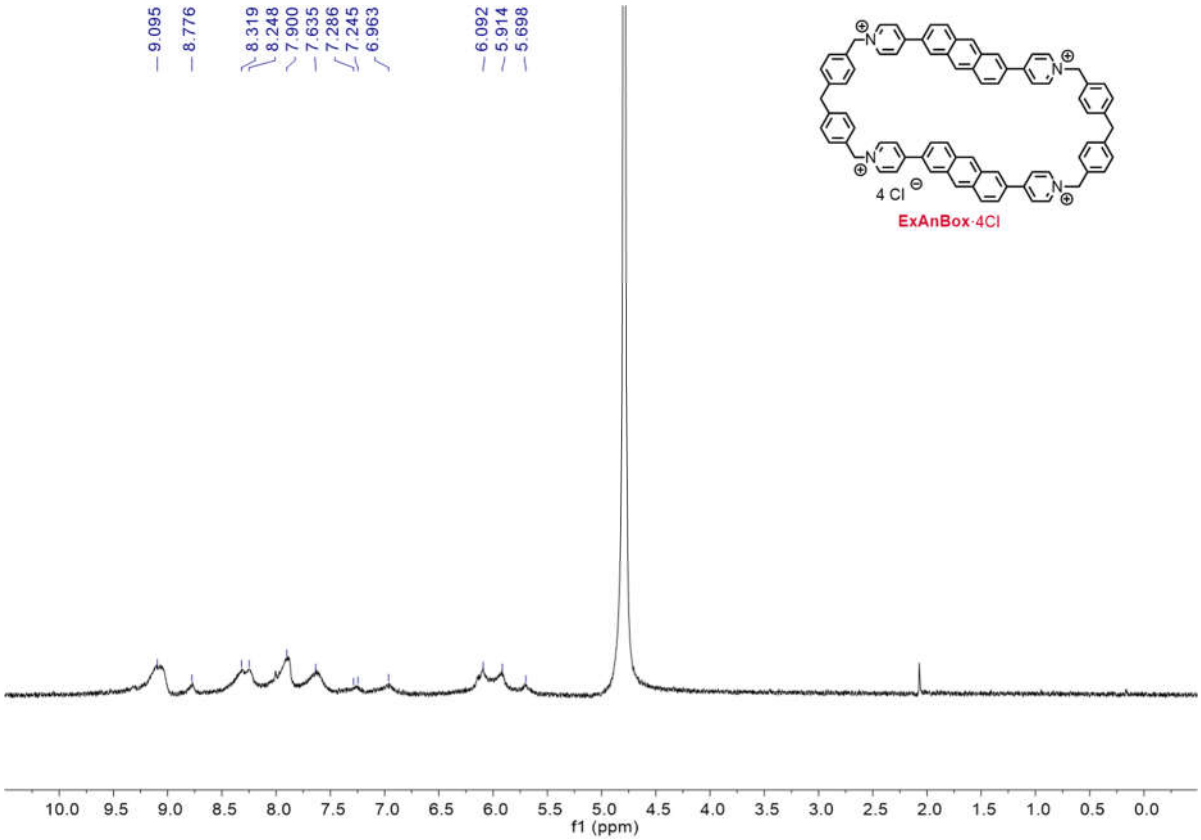


Figure S17. ^{1}H NMR spectrum (D_2O, 400 MHz) of **ExAnBox**·4Cl, showing broadened peaks.

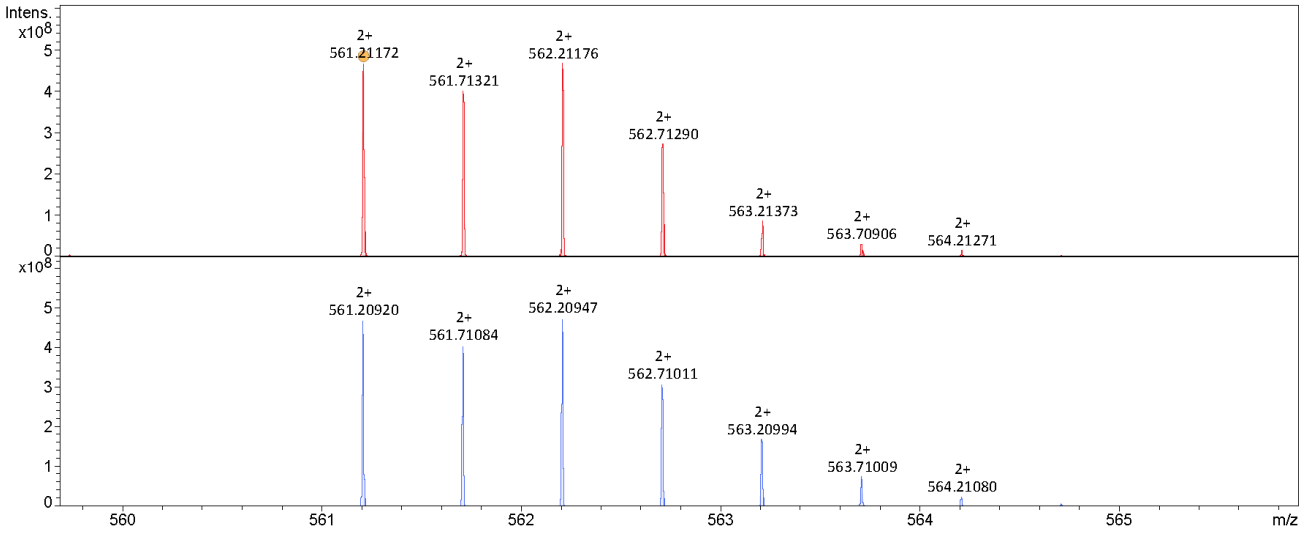
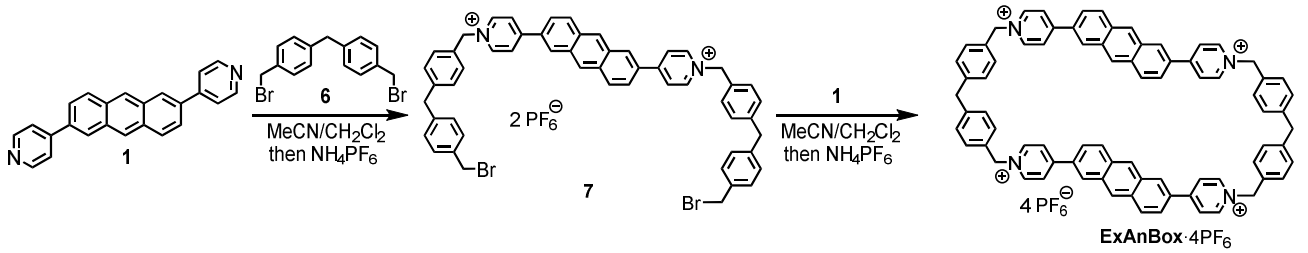


Figure S18. Measured (top) and simulated (bottom) HRMS data for **ExAnBox**·4Cl.



ExAnBox·4PF_6 (using the consecutive nucleophilic substitution approach)

Step 1: Compound **6** (354 mg, 1.0 mmol, 10 equiv) was dissolved in mixed solvents (10 mL, CH_3CN: CH_2Cl_2 = 2:1) in a 40 mL vial. The vial was sealed with a teflon-lined septum cap, and was heated at 60 °C until the solid was dissolved. Then the suspension of compound **1** (33 mg, 0.1 mmol, 1.0 equiv, in 10 mL CH_3CN) was added to the solution, and the reaction mixture was stirred at 90 °C for 48 h. The reaction mixture was cooled to room temperature, and the solvents were removed under reduced pressure. The resulting solid was washed with CH_2Cl_2 for three times before it was dispersed in hot CH_3OH and excess aqueous solution of NH_4PF_6 was added. The precipitate was washed with deionized water for three times, and the intermediate compound **7** (58.0 mg, 40% yield) was obtained as an orange solid.

Step 2: Compound **7** (23.4 mg, 0.02 mmol, 1.0 equiv), compound **1** (6.6 mg, 0.02 mmol, 1.0 equiv), and tetrabutylammonium iodide (3.6 mg, 5 mol%) were dissolved in mixed solvents (6 mL, CH_3CN: CH_2Cl_2 = 5:1) in a 40 mL vial. The vial was sealed with a teflon-lined septum cap, and the reaction mixture was stirred at 90 °C for 48 h before it was cooled to room temperature. Excess NH_4PF_6 was added to the reaction mixture which was then heated at 90 °C for another 0.5 h. The reaction mixture was cooled to room temperature and filtered. The supernatant was concentrated under reduced pressure. NMR analysis of the resulting crude solid showed an NMR yield of 21% for the desired product, along with large amounts of insoluble by-products. However, further purification by various recrystallization methods were unsuccessful to afford pure **ExAnBox**·4PF_6.

III. Host-Guest Chemistry

3.1 ^{1}H-NMR experiments.

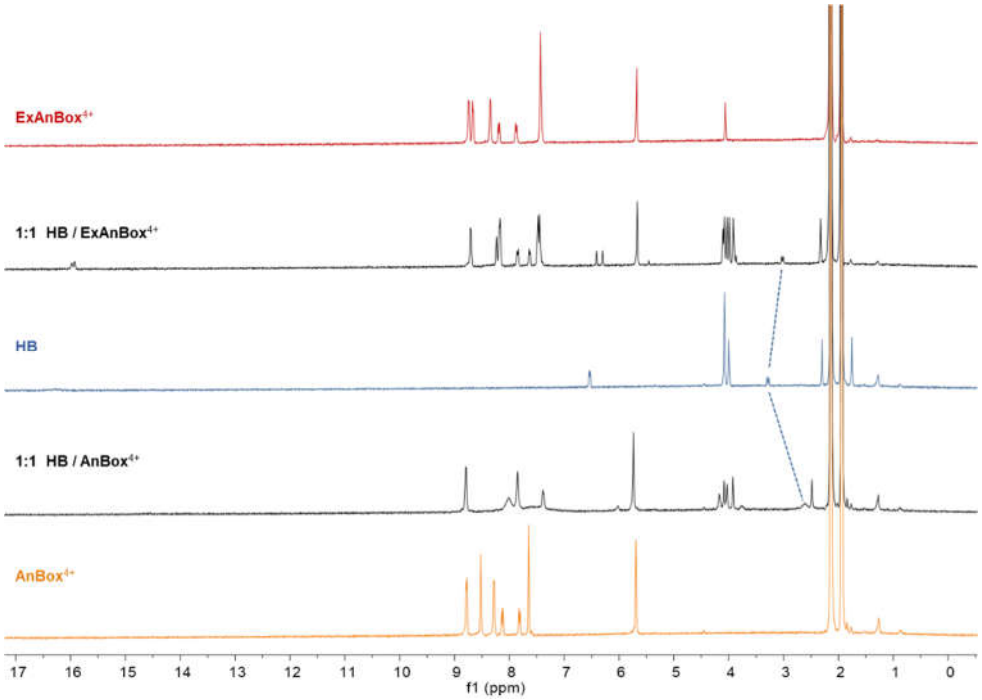


Figure S19. ^{1}H NMR spectra (400 MHz, 298 K) of **AnBox**$^{4+}$ (0.5 mM), **ExAnBox**$^{4+}$ (0.5 mM)**, HB** (0.5 mM) and their equimolar mixtures in CD_3CN.

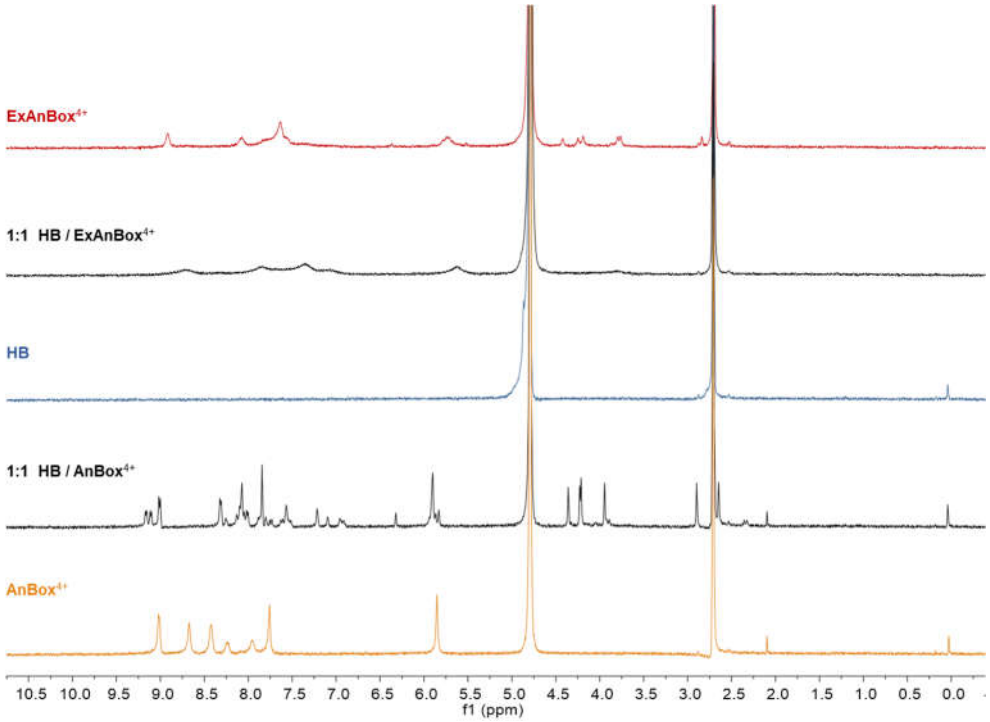


Figure S20. ^{1}H NMR spectra (400 MHz, 298 K) of **AnBox**$^{4+}$ (0.5 mM), **ExAnBox**$^{4+}$ (0.5 mM)**, HB** (0.5 mM) and their equimolar mixtures in the mixed solvents of DMSO-d_6/D_2O (1:4).

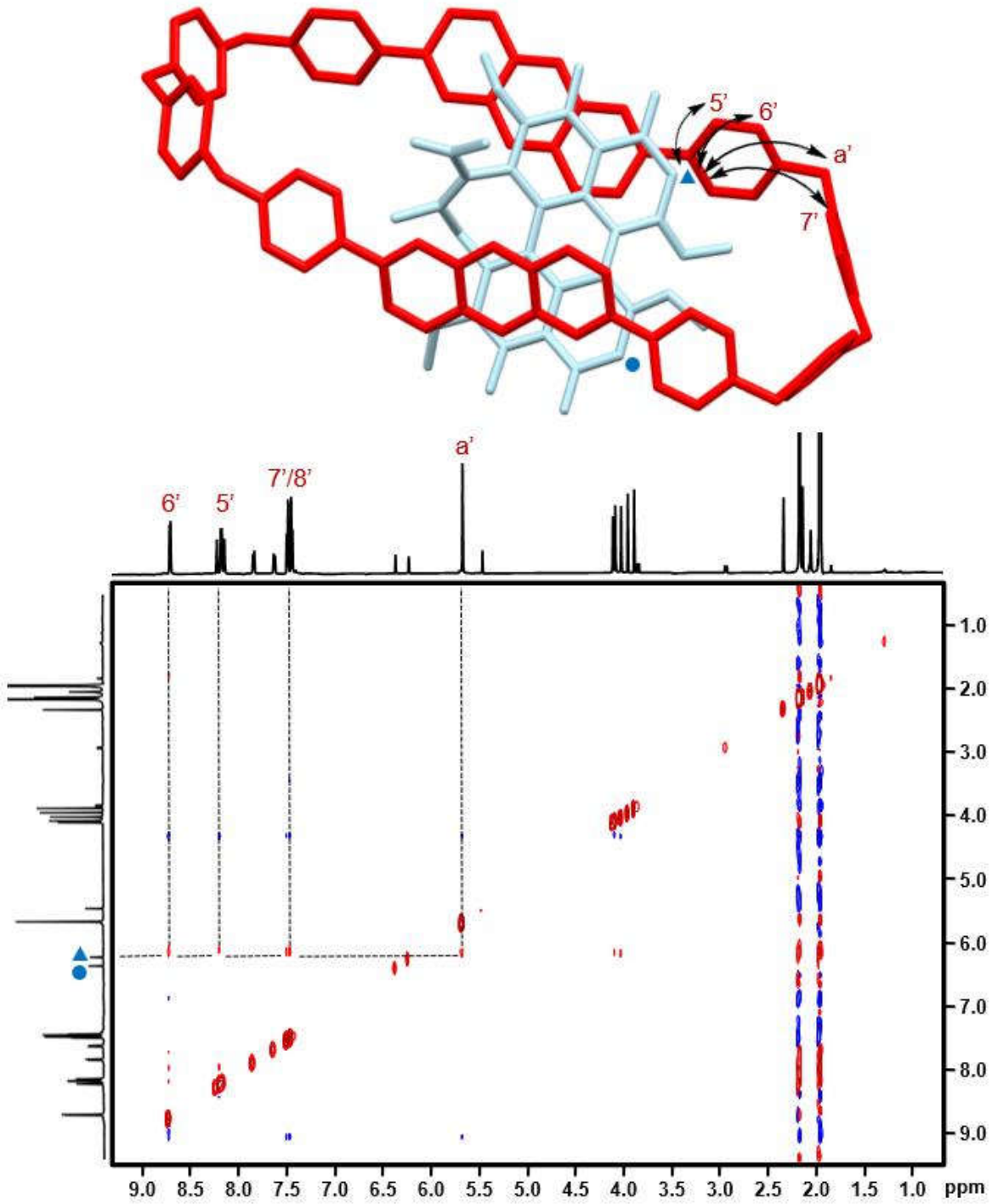


Figure S21. NOESY NMR spectrum (600 MHz, 298 K) of **ExAnBox**$^{4+}$ (0.5 mM) in the presence of **HB** (0.5 mM) in CD_3CN. The highlighted correlations between **ExAnBox**$^{4+}$ and **HB** signals are consistent with the computationally optimized host-guest structure (*cf*. Figure 5d).

Note: Due to severe signal broadening (*cf*. Figure S19), the NOESY and ROESY NMR for **AnBox**$^{4+}$ in the presence of **HB** in CD_3CN were unsuccessful.

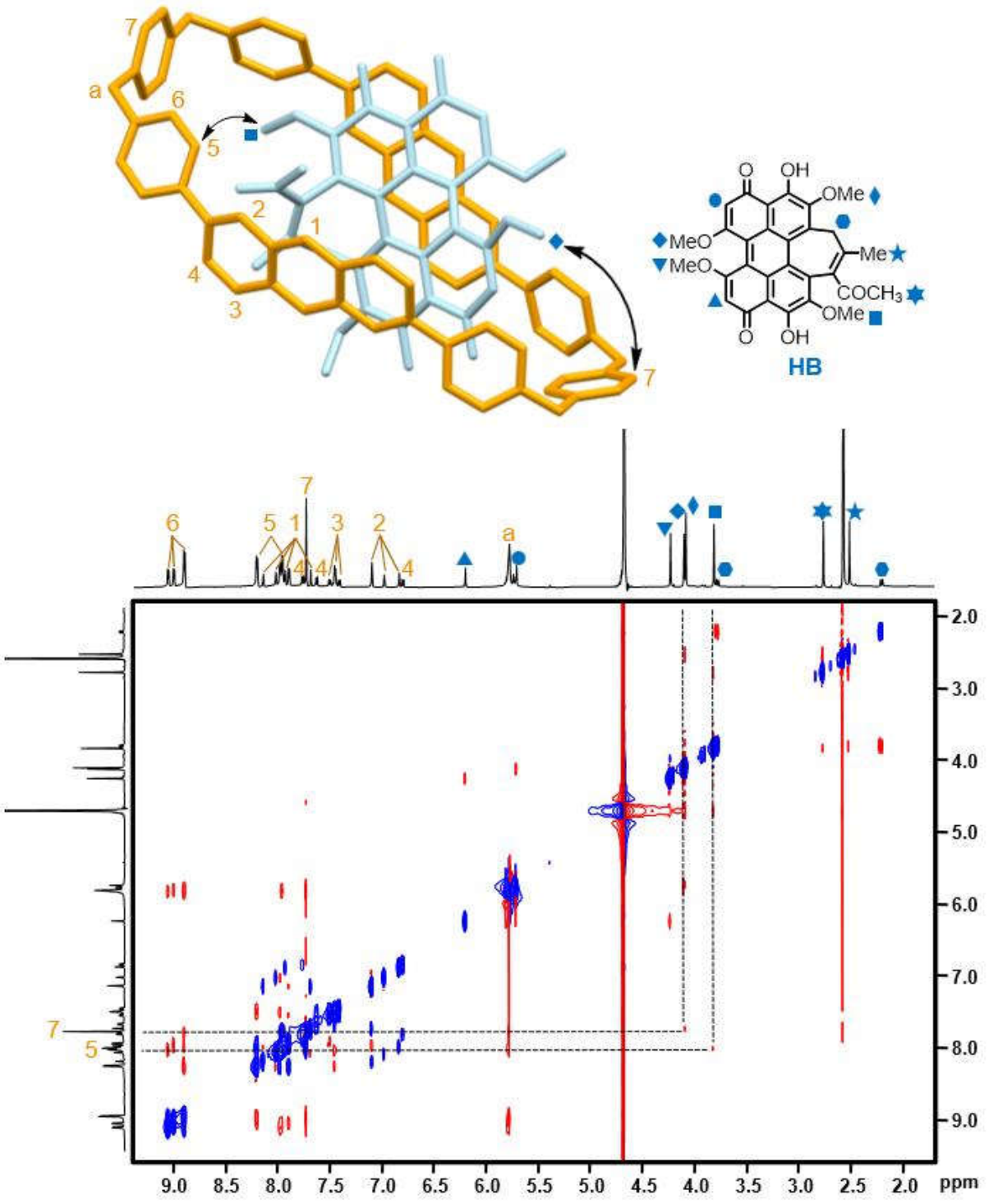


Figure S22. ROESY NMR spectrum (600 MHz, 298 K) of **AnBox**$^{4+}$ (0.5 mM) in the presence of **HB** (0.5 mM) in the mixed solvents of DMSO-d_6/D_2O (1:4). The highlighted correlations between **AnBox**$^{4+}$ and **HB** signals are consistent with the computationally optimized host-guest structure (*cf*. Figure 4d).

Note: Due to severe signal broadening (*cf*. Figure S20), the NOESY and ROESY NMR for **ExAnBox**$^{4+}$ in the presence of **HB** in mixed DMSO-d_6/D_2O (1:4) were unsuccessful.

3.2 Photophysical properties.

UV-Vis spectra were recorded in 1 cm quartz cuvette using a Hitachi U-3900 spectrophotometer. Fluorescence spectra were measured using a Horiba Fluoremax+ spectrometer.

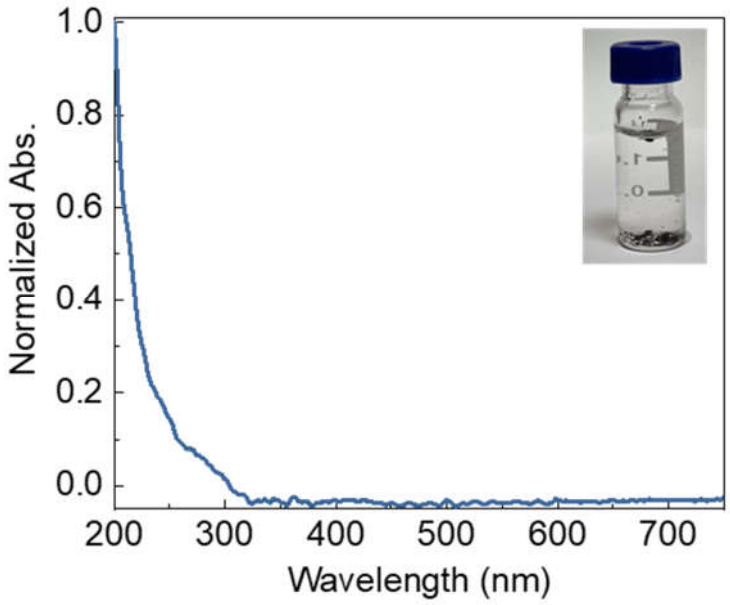


Figure S23. UV-vis absorption spectra of **HB** in H_2O at 25 ˚C, exhibiting minimal absorption.

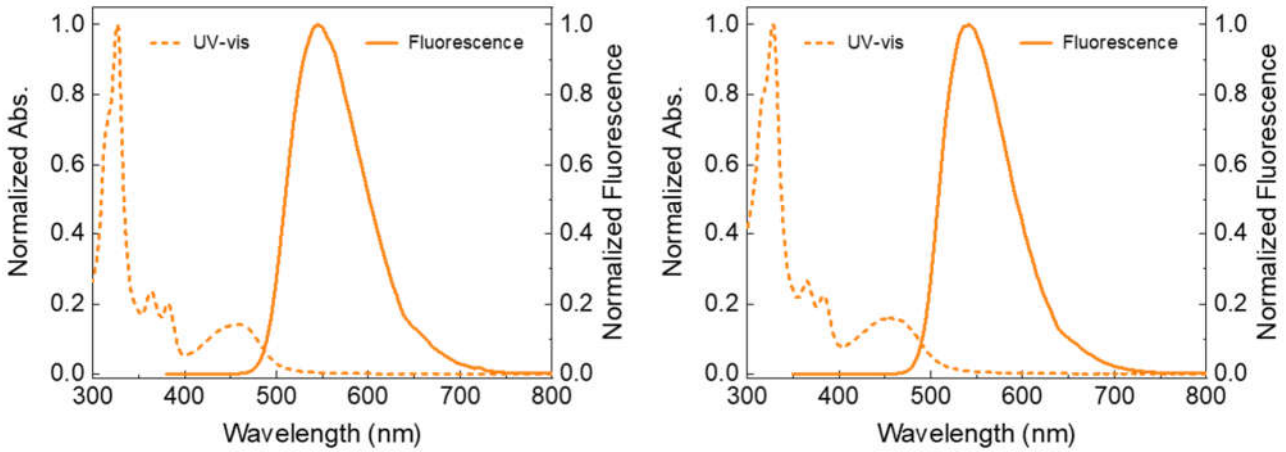


Figure S24. Normalized UV-vis absorption and fluorescence spectra of **AnBox**$^{4+}$ in CH_3CN (left) and 1:4 DMSO/H_2O (right) at 25 ˚C.

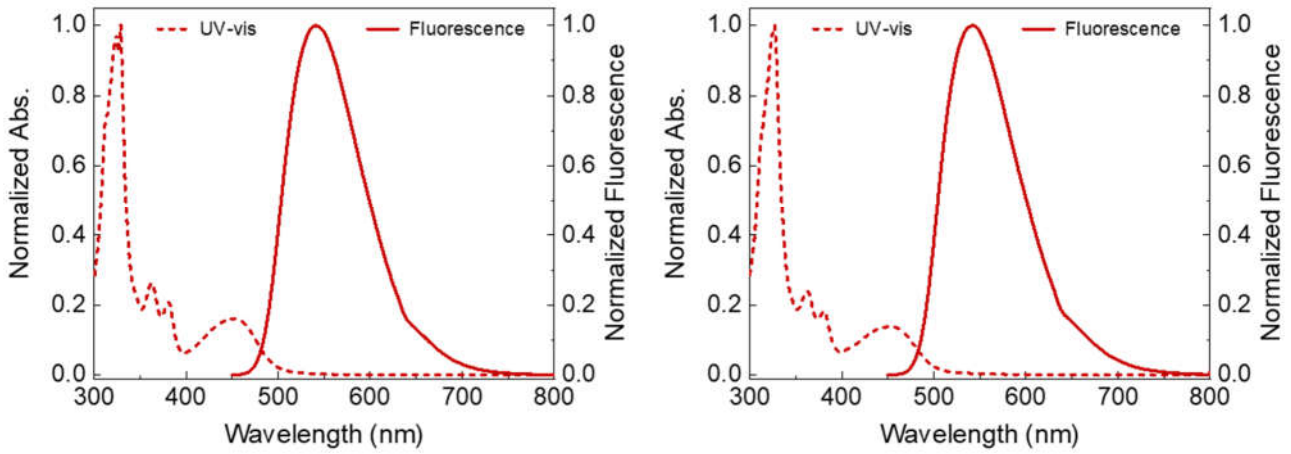


Figure S25. Normalized UV-vis absorption and fluorescence spectra of **ExAnBox**$^{4+}$ in CH_3CN (left) and 1:4 DMSO/H_2O (right) at 25 ˚C.

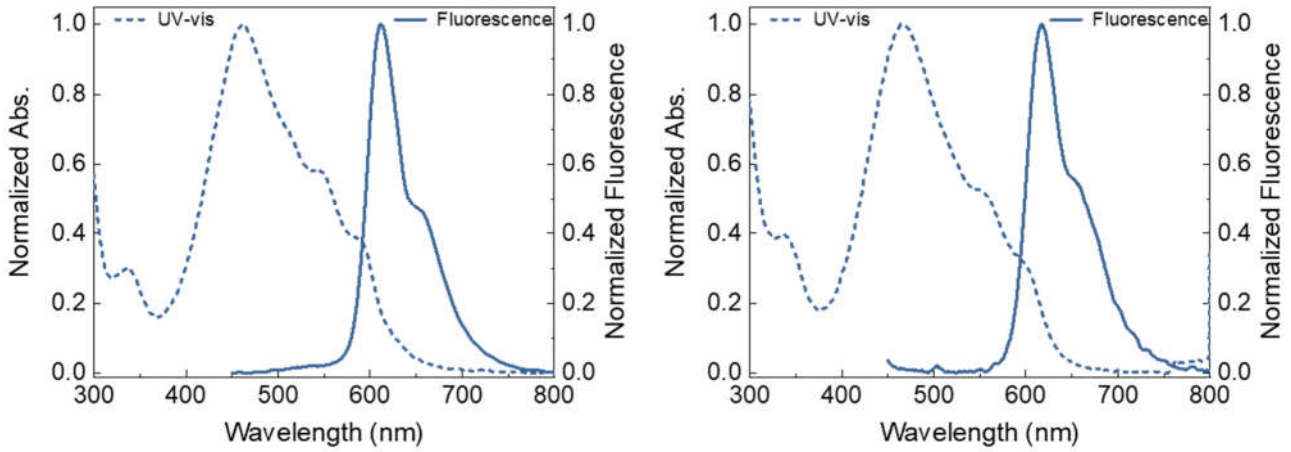


Figure S26. Normalized UV-vis absorption and fluorescence spectra of **HB** in CH_3CN (left) and 1:4 DMSO/H_2O (right) at 25 ˚C.

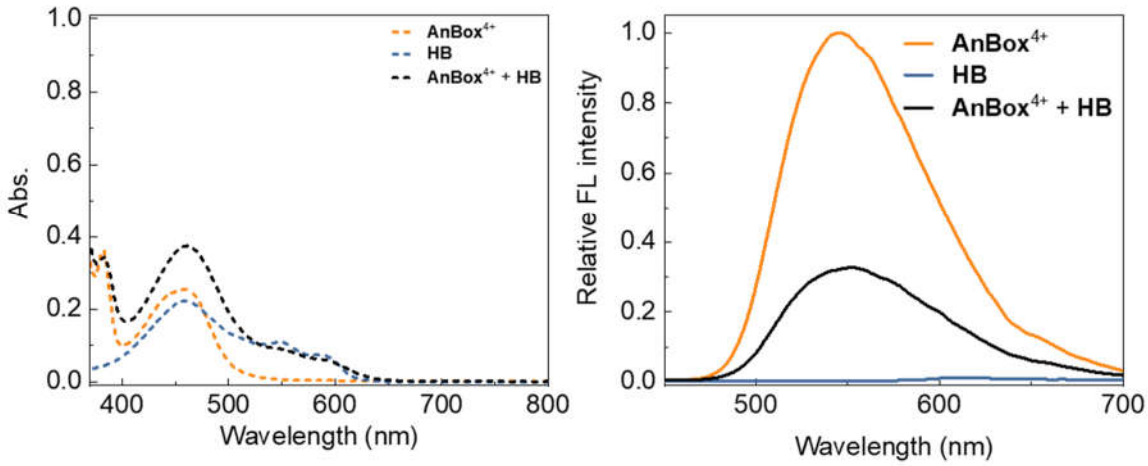


Figure S27. (left) UV-vis absorption spectra and (right) fluorescence spectra (1×10^{-5} M, λ_{ex} = 350 nm) of **AnBox**$^{4+}$, **HB** and their equimolar mixture in CH_3CN at 25 ˚C.

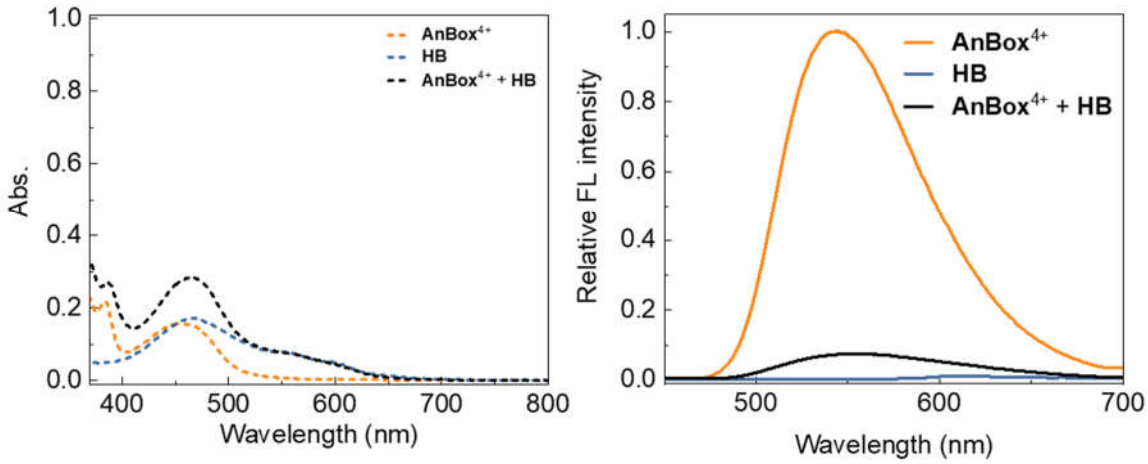


Figure S28. (left) UV-vis absorption spectra and (right) fluorescence spectra (1×10^{-5} M, λ_{ex} = 350 nm) of **AnBox**$^{4+}$, **HB** and their equimolar mixture in the mixed solvents of DMSO/H_2O (1:4) at 25 ˚C.

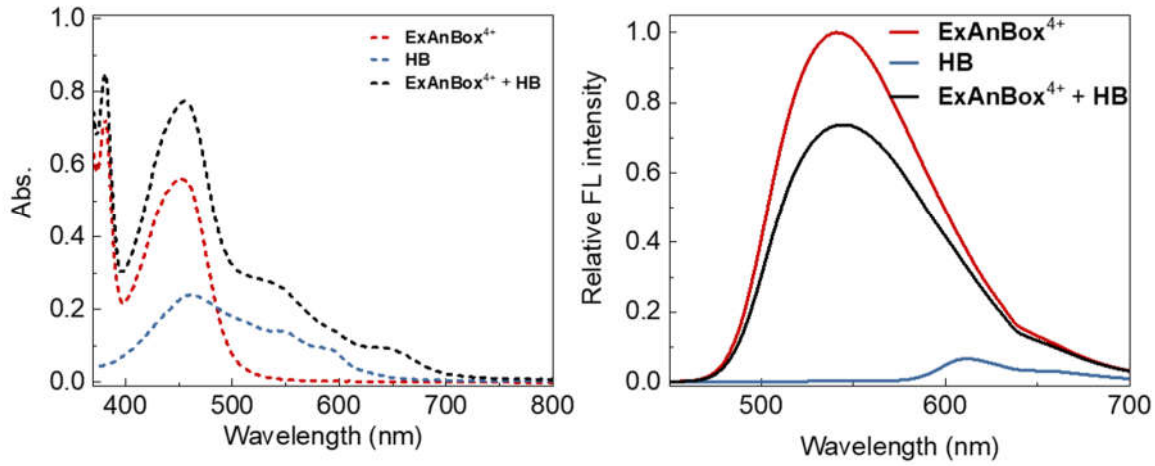


Figure S29. (left) UV-vis absorption spectra and (right) fluorescence spectra (1×10^{-5} M, λ_{ex} = 350 nm) of **ExAnBox**$^{4+}$, **HB** and their equimolar mixture in CH_3CN at 25 ˚C.

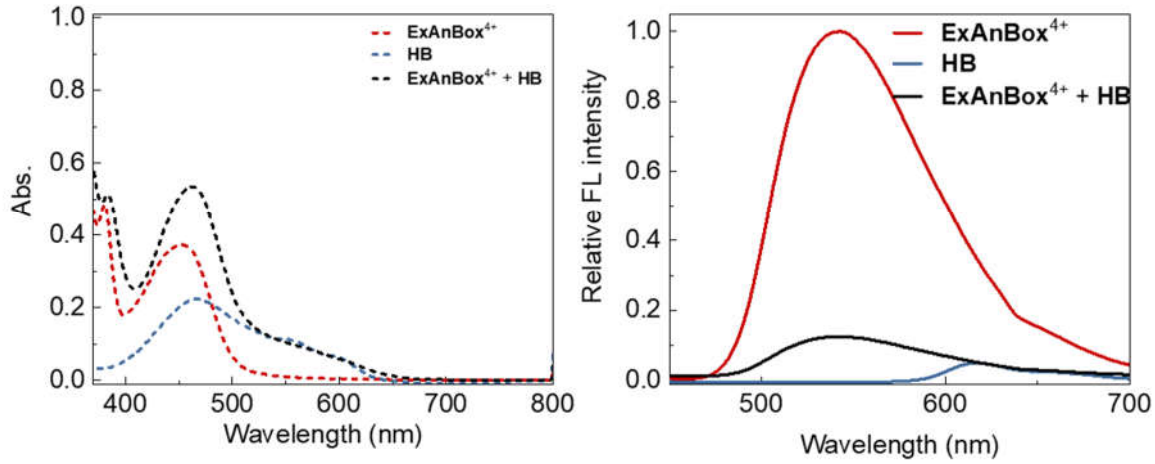


Figure S30. (left) UV-vis absorption spectra and (right) fluorescence spectra (1×10^{-5} M, λ_{ex} = 350 nm) of **ExAnBox**$^{4+}$, **HB** and their equimolar mixture in the mixed solvents of DMSO/H_2O (1:4) at 25 ˚C.

3.3 Fluorescence titration of $AnBox^{4+}$and $ExAnBox^{4+}$ with HB.

For fluorescence titrations, 1×10^{-5} M solution of **$AnBox^{4+}$**or **$ExAnBox^{4+}$** was prepared in the mixed solvents of DMSO/H_2O (1:4). This solution was placed in a cuvette (3 mL) at 25 ˚C. The sample was then titrated with a solution of **HB**. Titration curve-fitting and association constant values were calculated employing the BindFit program. The 1:1 host-guest binding stoichiometry was chosen in the BindFit program (*Chem. Commun*. **2016**, *52*, 12792). This program employs a nonlinear least-squares regression analysis and is available free of cost online through the following link: http://supramolecular.org. The fluorescence titration experiments were repeated in duplicate.

Table S1. Calculated binding constants of **$AnBox^{4+}$**and **$ExAnBox^{4+}$** for **HB** based on fluorescence titrations.

K	CH_3CN		20% DMSO/H_2O	
	$AnBox^{4+}$	**$ExAnBox^{4+}$**	**$AnBox^{4+}$**	**$ExAnBox^{4+}$**
1	4.24×10^5	3.39×10^4	1.73×10^7	1.67×10^7
2	4.26×10^5	3.15×10^4	1.72×10^7	2.24×10^7
Average	4.25×10^5	3.27×10^4	1.73×10^7	1.96×10^7
Standard deviation	1.39×10^3	1.69×10^3	9.82×10^4	4.04×10^6

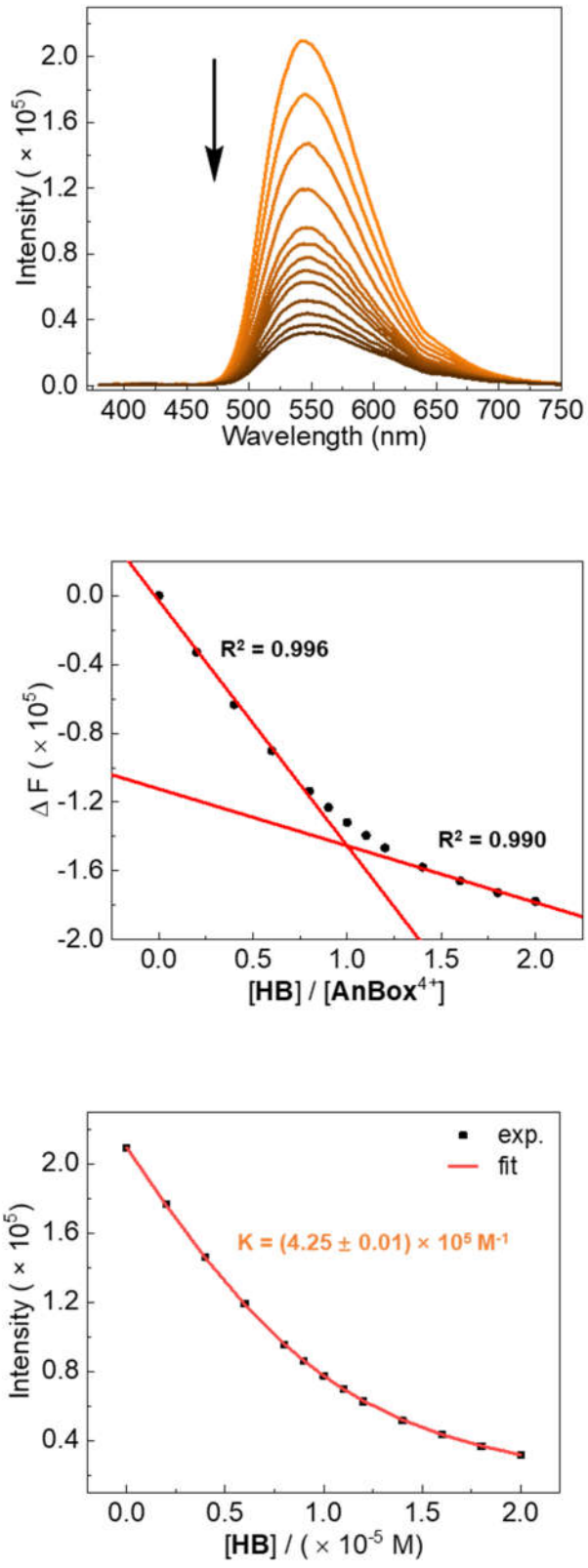


Figure S31. Fluorescence titration of **AnBox**$^{4+}$ (1×10^{-5} M, λ_{ex} = 350 nm) with **HB** in CH_3CN solution at 25 ˚C

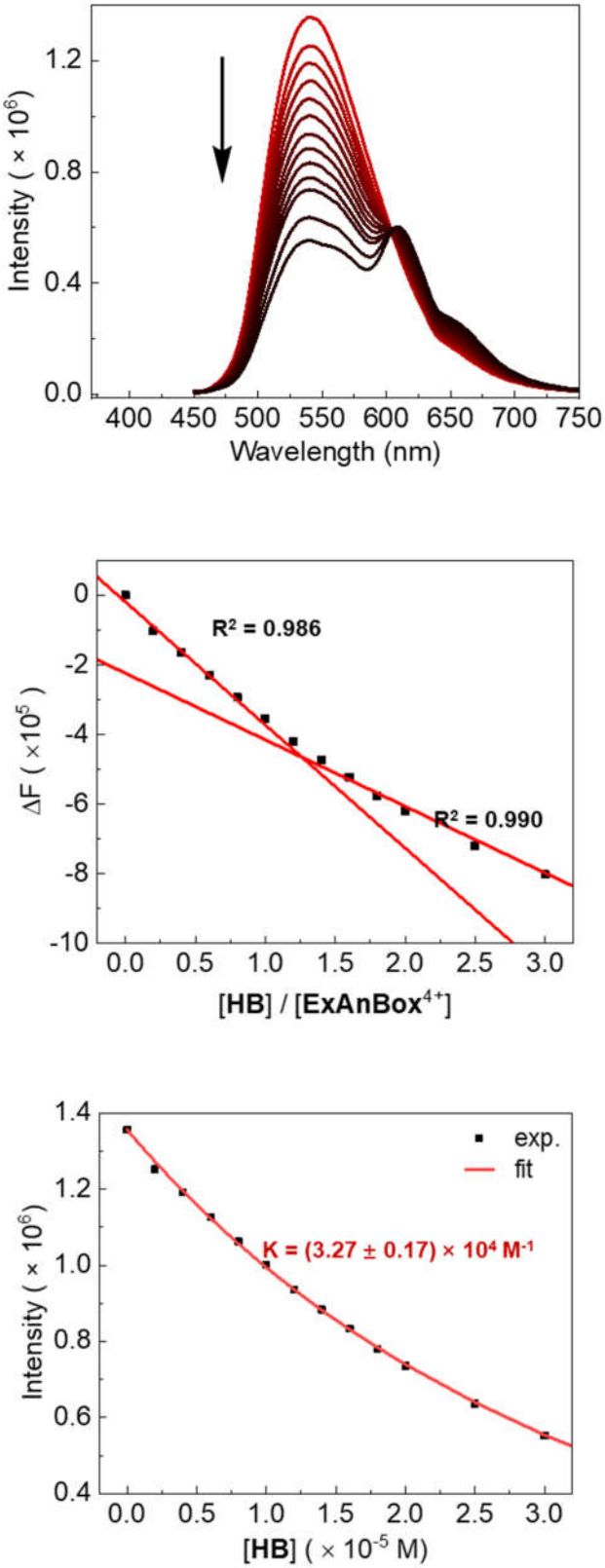


Figure S32. Fluorescence titration of **ExAnBox**$^{4+}$ (1×10^{-5} M, λ_{ex} = 350 nm) with **HB** in CH_3CN solution at 25 ˚C

3.4 Photoactivity tests

General Procedures

25 μL of DPBF solution (1 mg mL^{-1} in DMSO) was added to 1.5 mL of **AnBox**$^{4+}$, **ExAnBox**$^{4+}$, **HB⊂AnBox**$^{4+}$, or **HB⊂ExAnBox**$^{4+}$ solution (20 μM in 50:50 DMSO/H_2O), respectively, and the absorption intensities of DPBF at 415 nm was recorded at various 532 nm laser irradiation times.

10 μL of DHR123 solution (1 mM in DMSO) was added to 1.0 mL of **AnBox**$^{4+}$, **ExAnBox**$^{4+}$, **HB⊂AnBox**$^{4+}$, or **HB⊂ExAnBox**$^{4+}$ solution (10 μM in H_2O), respectively, and the fluorescence intensities of DHR123 at 525 nm was recorded after 532 nm laser irradiation.

Photo-stability tests: 1.5 mL of **HB⊂AnBox**$^{4+}$ and **HB⊂ExAnBox**$^{4+}$ solutions (10 μM in water) were continuously irradiated under 532 nm laser (0.1 W cm^{-2}) for 60 min, respectively, and the absorption intensities of **HB⊂AnBox**$^{4+}$ and **HB⊂ExAnBox**$^{4+}$ solutions at 465 nm were recorded every 10 minutes.

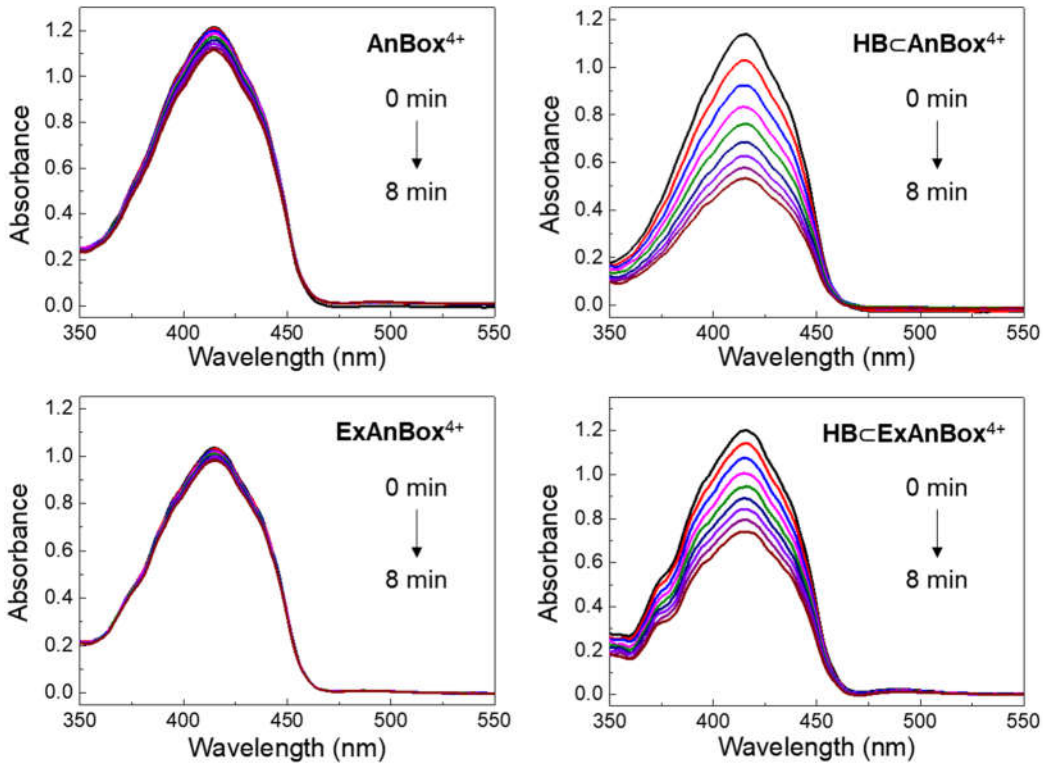


Figure S33. Photodegradation of DPBF with **AnBox**$^{4+}$, **HB⊂AnBox**$^{4+}$, **ExAnBox**$^{4+}$, and **HB⊂ExAnBox**$^{4+}$ (20 μM in 50:50 DMSO/H_2O) under 532 nm laser irradiation, respectively.

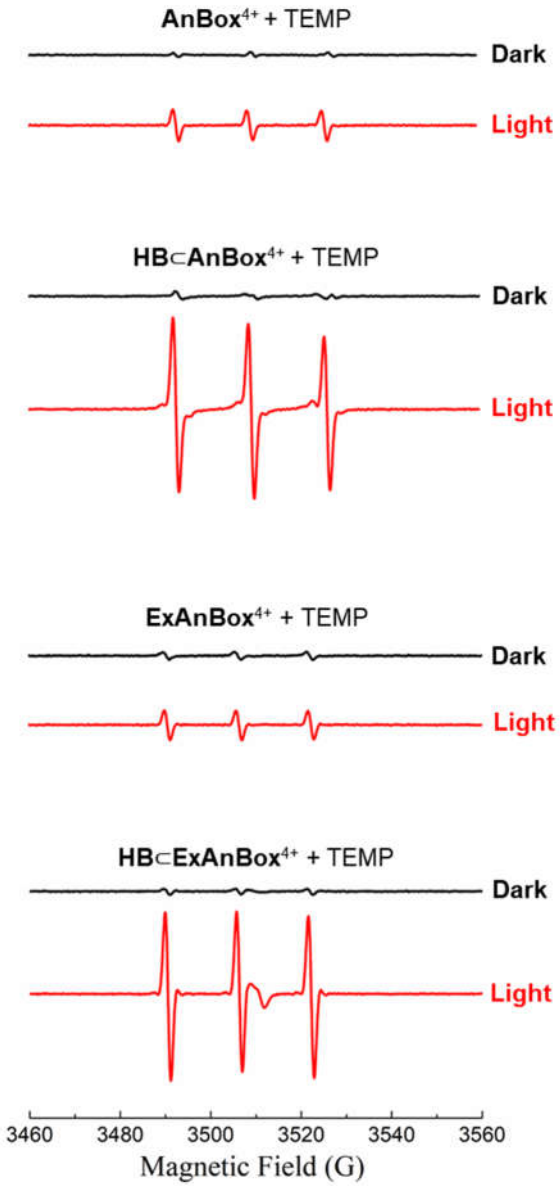


Figure S34. The EPR spectra of **AnBox**$^{4+}$, **HB⊂AnBox**$^{4+}$, **ExAnBox**$^{4+}$, and **HB⊂ExAnBox**$^{4+}$ (0.25 mM in 50:50 DMSO/H_2O, 100 μL) in the presence of 2,2,6,6-tetramethyl-4-piperidone (TEMP, 10 μL), before and after 532 nm laser irradiation (0.1 W cm^{-2}, 10 min). The results verified the generation of $^1O_2$ of both **HB⊂AnBox**$^{4+}$ and **HB⊂ExAnBox**$^{4+}$ under light irradiation.

IV. Photodynamic Therapy-Related Cell Experiment

4.1 *In vitro* imaging and photodynamic therapy

General Procedures

HeLa cells were seeded in confocal dishes and incubated for 24 h in 5% CO_2 at 37 °C. After cells were washed with PBS three times, **HB⊂AnBox**$^{4+}$ or **HB⊂ExAnBox**$^{4+}$ (10 μM in PBS) was added to confocal dishes. Imaging was acquired with confocal microscope at different times (10, 20, 30 min).

HeLa cells were seeded in 96-well plates and incubated for 24 h in 5% CO_2 at 37 °C. For photo-toxicity, cells were incubated with **AnBox**$^{4+}$, **ExAnBox**$^{4+}$, **HB⊂AnBox**$^{4+}$, or **HB⊂ExAnBox**$^{4+}$ of different concentrations (0, 0.025, 0.05, 0.1, 0.25, 0.5, 1, 2.5 μM) for 2 h, and fresh culture medium were exchanged. Then the cells were irradiated by 532 nm laser (0.1 W cm^{-2}, 10 min), and incubated for another 12 h. For dark toxicity, cells were incubated with **AnBox**$^{4+}$, **ExAnBox**$^{4+}$, **HB⊂AnBox**$^{4+}$, or **HB⊂ExAnBox**$^{4+}$ of different concentrations (0, 0.025, 0.05, 0.1, 0.25, 0.5, 1, 2.5 μM) for 24 h, and fresh culture medium were exchanged. The cell viabilities were performed using the standard MTT assay.

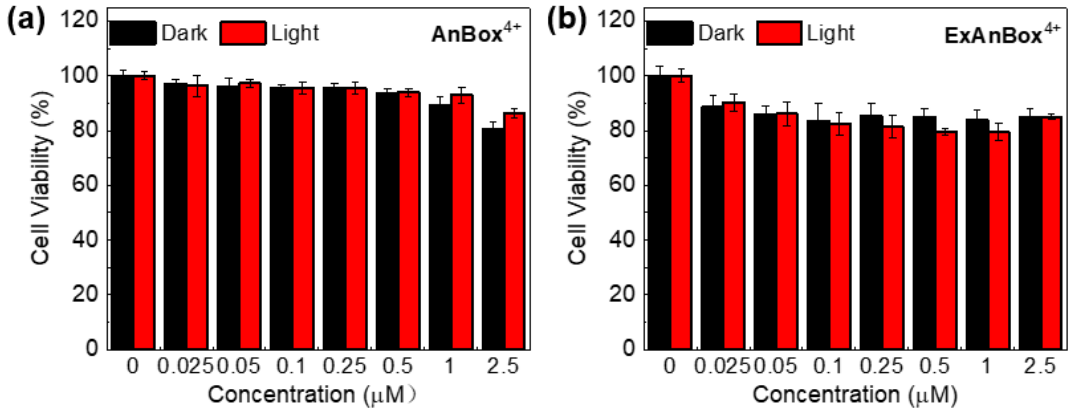


Figure S35. Relative viability of HeLa cells incubated with (a) **AnBox**$^{4+}$ and (b) **ExAnBox**$^{4+}$ in the dark or under 532 nm laser irradiation.

4.2 Calcein AM/PI experiment

The HeLa cells were treated with one of the following conditions: laser only, **AnBox**$^{4+}$ only (2.5 μM), **ExAnBox**$^{4+}$ only (2.5 μM), **HB⊂AnBox**$^{4+}$ only (2.5 μM), **HB⊂ExAnBox**$^{4+}$ only (2.5 μM), **AnBox**$^{4+}$ + 532 nm laser (0.1 W cm^{-2}), **ExAnBox**$^{4+}$ + 532 nm laser (0.1 W cm^{-2}), **HB⊂AnBox**$^{4+}$ + 532 nm laser (0.1 W cm^{-2}), and **HB⊂ExAnBox**$^{4+}$ + 532 nm laser (0.1 W cm^{-2}). Then the Hela cells were co-stained with Calcein AM/PI (10 min), and washed with PBS three times. Imaging was acquired with confocal microscope.

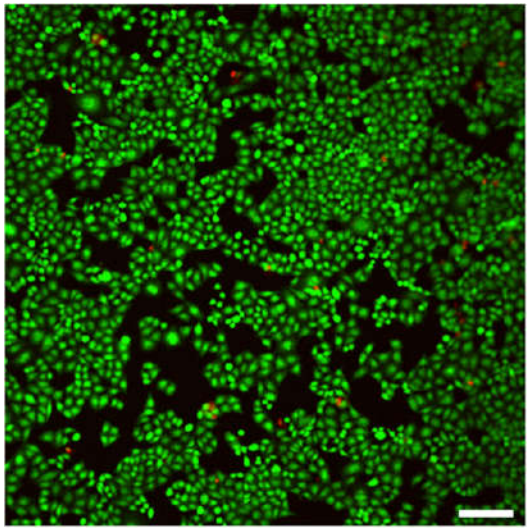


Figure S36. FL images of HeLa cells under 532 nm laser irradiation (0.1 W cm^{-2}) using calcein AM/PI staining. Scale bar: 100 μm.

V. DFT Calculations

5.1 Computational information

The structures of **AnBox**$^{4+}$, **ExAnBox**$^{4+}$, **HB**, and two supramolecular complexes **HB⊂AnBox**$^{4+}$ and **HB⊂ExAnBox**$^{4+}$ were optimized at the B3LYP/6-31+G* level. The dispersion correction with the Grimme's D3 version[S1] was considered. All the calculations were performed with Gaussian 09 software package.[S2] Cartesian coordinates of the optimized structures were listed at the end.

5.2 Optimized geometry

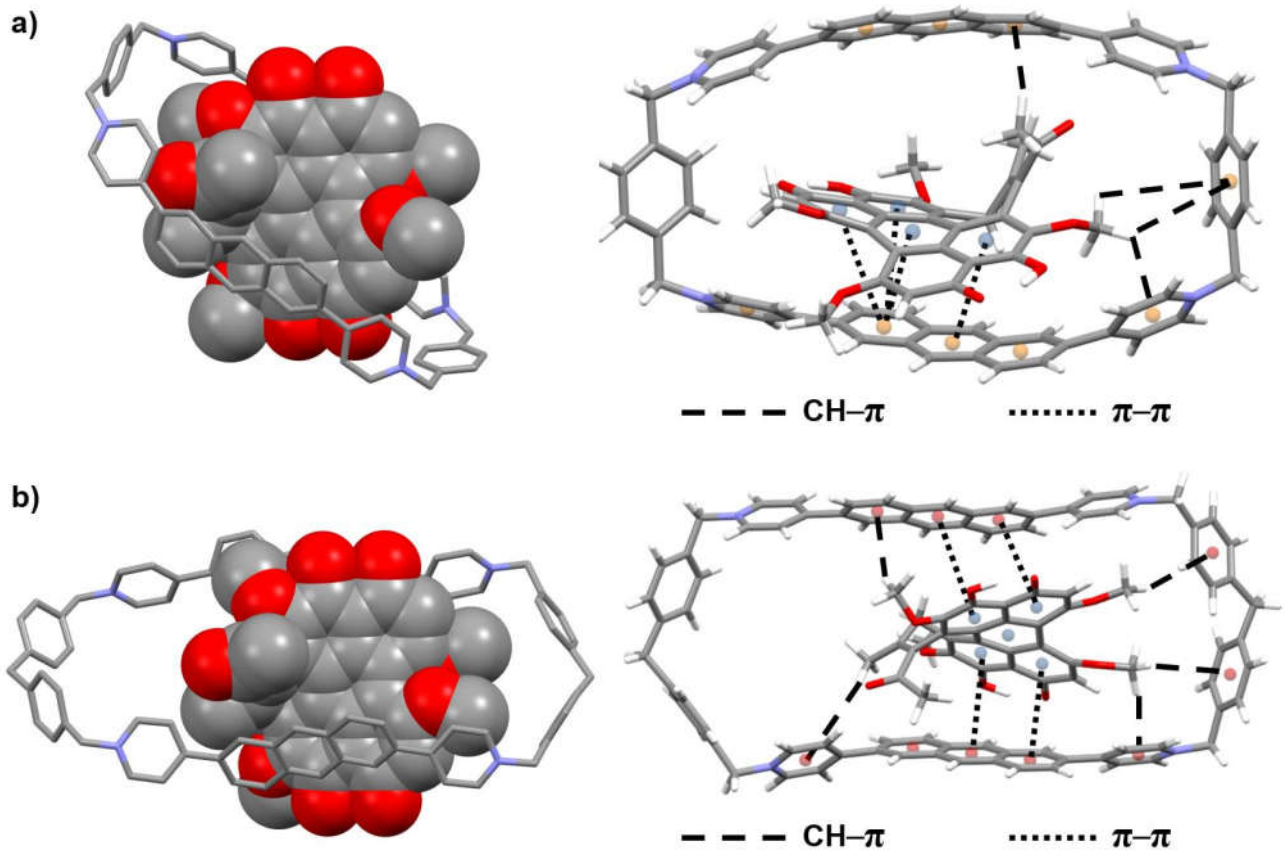


Figure S37. The DFT-optimized structures and non-covalent interactions of a) **HB ⊂ AnBox**$^{4+}$ and b) **HB ⊂ ExAnBox**$^{4+}$.

5.3 Cartesian coordinates (Å) of the optimized structures

AnBox^{4+}

N	7.597765	3.645944	-0.218407	C	-3.886165	4.593552	0.709099
N	-7.938619	3.295146	0.290119	C	-3.33846	4.944576	1.992226
C	9.297366	-2.680879	0.121677	H	-4.001142	5.094391	2.839137
H	9.71641	-3.089649	-0.800544	C	-1.993682	5.135961	2.151507
H	9.917588	-3.029506	0.951136	H	-1.596394	5.414097	3.123976
C	9.219382	-1.166824	0.078454	C	-1.086152	4.967976	1.056108
C	9.7102	-0.395723	1.136816	C	0.301955	5.039938	1.21661
H	10.175285	-0.873589	1.995749	H	0.713916	5.247436	2.201611
C	9.633251	1.001914	1.092419	C	1.173086	4.811279	0.136551
H	10.036267	1.58233	1.918791	C	2.585336	4.749387	0.312654
C	9.069966	1.644886	-0.014073	H	2.980444	4.930498	1.308994
C	8.587618	0.870337	-1.081699	C	-5.304814	4.224535	0.575927
H	8.17022	1.351627	-1.963177	C	-6.037907	4.417994	-0.615991
C	8.660674	-0.519068	-1.035459	H	-5.610349	4.954617	-1.455599
H	8.301032	-1.099185	-1.882268	C	-7.331594	3.947916	-0.733286
C	9.008085	3.160459	-0.076241	H	-7.916629	4.085079	-1.635726
H	9.42442	3.616785	0.825455	C	-7.285052	3.141187	1.469982
H	9.564725	3.550844	-0.931819	H	-7.825649	2.621393	2.252662
C	7.162357	4.211235	-1.371831	C	-5.996201	3.598069	1.639309
H	7.909111	4.389592	-2.137554	H	-5.51407	3.424825	2.594427
C	5.831588	4.536867	-1.55198	N	-7.597774	-3.645967	-0.21839
H	5.54381	4.999178	-2.489278	N	7.938623	-3.295149	0.290143
C	4.880785	4.284002	-0.537799	C	-9.297358	2.680875	0.12163
C	5.389112	3.75716	0.673183	H	-9.716382	3.089632	-0.800606
H	4.731343	3.538531	1.506421	H	-9.917599	3.029512	0.95107
C	6.724355	3.446045	0.802865	C	-9.219371	1.166819	0.078428
H	7.135071	2.999673	1.701245	C	-9.71032	0.395726	1.136733
C	3.436984	4.479629	-0.74759	H	-10.175501	0.873599	1.995612
C	2.882011	4.323073	-2.065738	C	-9.633371	-1.001911	1.092352
H	3.535499	4.120459	-2.908211	H	-10.036482	-1.582322	1.918682
C	1.530408	4.367075	-2.268281	C	-9.069952	-1.644891	-0.014067
H	1.125956	4.220472	-3.266234	C	-8.587469	-0.870349	-1.081636
C	0.625055	4.575738	-1.179901	H	-8.169958	-1.351643	-1.963059
C	-0.763077	4.520269	-1.343267	C	-8.660527	0.519056	-1.035412
H	-1.175317	4.328644	-2.331432	H	-8.300772	1.099167	-1.882177
C	-1.631786	4.67808	-0.250406	C	-9.008084	-3.160468	-0.076217
C	-3.040049	4.507006	-0.384415	H	-9.424416	-3.616775	0.82549
H	-3.425263	4.232311	-1.363004	H	-9.564742	-3.550861	-0.931781

C	-7.162364	-4.211216	-1.371835
H	-7.909119	-4.389549	-2.137562
C	-5.831595	-4.536839	-1.551994
H	-5.543815	-4.999118	-2.489307
C	-4.880792	-4.284003	-0.537805
C	-5.38912	-3.757207	0.673197
H	-4.731353	-3.538605	1.506442
C	-6.724365	-3.446101	0.80289
H	-7.135082	-2.999763	1.701285
C	-3.43699	-4.479616	-0.747604
C	-2.882019	-4.323014	-2.065748
H	-3.535509	-4.120377	-2.908214
C	-1.530416	-4.367	-2.268293
H	-1.125967	-4.220362	-3.266242
C	-0.625061	-4.575694	-1.179922
C	0.763071	-4.520211	-1.343288
H	1.175309	-4.328551	-2.331447
C	1.631782	-4.678055	-0.250434
C	3.040044	-4.506971	-0.384439
H	3.425255	-4.232239	-1.363019
C	3.886163	-4.593554	0.70907
C	3.338461	-4.944623	1.992186
H	4.001146	-5.094463	2.83909
C	1.993684	-5.136017	2.151463
H	1.596399	-5.414186	3.123923
C	1.086151	-4.967999	1.056072
C	-0.301955	-5.039972	1.216573
H	-0.713914	-5.247505	2.201568
C	-1.173089	-4.811282	0.136522
C	-2.585339	-4.749405	0.31263
H	-2.980445	-4.93055	1.308964
C	5.304812	-4.224532	0.57591
C	6.037905	-4.417948	-0.616015
H	5.610347	-4.954537	-1.455644
C	7.331595	-3.947872	-0.733288
H	7.916631	-4.085005	-1.635732
C	7.285054	-3.14123	1.470011
H	7.825654	-2.621474	2.252715
C	5.9962	-3.59811	1.639317
H	5.514068	-3.424902	2.594442

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N	-7.754914	-5.486987	0.18626
N	8.015343	-5.363035	0.318714
C	-9.485879	5.181419	0.075478
H	-9.745169	5.862984	-0.739002
H	-10.004665	5.527167	0.974176
C	-9.23527	-5.25526	0.355287
H	-9.452359	-5.391204	1.418263
H	-9.732549	-6.058959	-0.191922
C	-7.286826	-6.435511	-0.6592
H	-8.02904	-7.031469	-1.177938
C	-5.929129	-6.632722	-0.835739
H	-5.608152	-7.418506	-1.510504
C	-4.992691	-5.854416	-0.124655
C	-5.52173	-4.883359	0.754954
H	-4.866609	-4.226661	1.315733
C	-6.883765	-4.718372	0.885364
H	-7.324728	-3.962384	1.524473
C	-3.539216	-6.017219	-0.304412
C	-3.005501	-6.363623	-1.593135
H	-3.677565	-6.506261	-2.433922
C	-1.65465	-6.462634	-1.787839
H	-1.264263	-6.700037	-2.773844
C	-0.732928	-6.242421	-0.71506
C	0.654095	-6.291483	-0.897761
H	1.052912	-6.506949	-1.886524
C	1.539092	-6.057256	0.167929
C	2.952539	-6.048141	-0.01789
H	3.332904	-6.204038	-1.024222
C	3.817779	-5.779059	1.028955
C	3.278824	-5.551847	2.342894
H	3.951283	-5.4059	3.182719
C	1.929017	-5.568917	2.559715
H	1.537355	-5.416184	3.561924
C	1.008824	-5.79214	1.486076
C	-0.376896	-5.746893	1.669662
H	-0.776106	-5.544093	2.660986

C	-1.261492	-5.941942	0.595874
C	-2.672232	-5.827082	0.757629
H	-3.055417	-5.613706	1.752508
C	5.26744	-5.66643	0.794858
C	5.938812	-6.422146	-0.189082
H	5.415569	-7.167914	-0.776891
C	7.293634	-6.254126	-0.403752
H	7.836806	-6.82978	-1.144589
C	7.407809	-4.628836	1.283475
H	8.040203	-3.925207	1.812711
C	6.060847	-4.765799	1.54251
H	5.620872	-4.140568	2.310694
N	7.755071	5.48698	0.186598
N	-8.0151	5.362655	0.3182
C	9.486048	-5.181552	0.075979
H	9.745528	-5.863287	-0.738302
H	10.004921	-5.52694	0.974762
C	9.235419	5.255028	0.355653
H	9.452444	5.390672	1.41868
H	9.732809	6.058807	-0.191329
C	7.287135	6.436411	-0.657931
H	8.029453	7.03281	-1.176012
C	5.929469	6.633927	-0.834376
H	5.608614	7.420403	-1.508396
C	4.992906	5.854986	-0.124156
C	5.521786	4.882988	0.754503
H	4.866567	4.22577	1.314559
C	6.883792	4.717743	0.884854
H	7.324631	3.961042	1.5232
C	3.539451	6.018066	-0.303852
C	3.005822	6.365681	-1.592279
H	3.67794	6.509085	-2.432892
C	1.654979	6.464892	-1.786967
H	1.26464	6.703215	-2.772769
C	0.733195	6.243693	-0.714439
C	-0.653824	6.292887	-0.897183
H	-1.052586	6.509239	-1.885774
C	-1.538878	6.057674	0.168244
C	-2.952315	6.048629	-0.017667
H	-3.332631	6.205379	-1.023886
C	-3.817603	5.778575	1.028891
C	-3.278707	5.55028	2.342668
H	-3.951206	5.403572	3.182329
C	-1.928918	5.567234	2.559585
H	-1.537313	5.41366	3.561687
C	-1.008671	5.791419	1.486196
C	0.377032	5.746031	1.669815
H	0.776191	5.542371	2.660983
C	1.261685	5.942033	0.59625
C	2.672412	5.826988	0.757974
H	3.055541	5.612697	1.752677
C	-5.267235	5.665981	0.794629
C	-5.938662	6.422342	-0.188781
H	-5.41548	7.168572	-0.776059
C	-7.293467	6.254336	-0.403602
H	-7.836661	6.830464	-1.144055
C	-7.40752	4.627829	1.282454
H	-8.039856	3.923755	1.811165
C	-6.060576	4.764733	1.541607
H	-5.620549	4.138982	2.309337
C	-9.855327	3.753754	-0.260447
C	-10.901513	3.12466	0.422557
H	-11.406356	3.633838	1.240555
C	-11.346593	1.859938	0.02335
H	-12.195888	1.413017	0.534182
C	-10.748034	1.190014	-1.050727
C	-9.666139	1.809268	-1.699787
H	-9.191059	1.311402	-2.541849
C	-9.230578	3.076875	-1.319731
H	-8.421824	3.550961	-1.873006
C	-9.670835	-3.894952	-0.134057
C	-9.987677	-2.873751	0.772967
C	-9.811228	-3.64846	-1.506056
C	-10.45744	-1.640184	0.316477
H	-9.912235	-3.052622	1.844033
C	-10.282371	-2.415718	-1.956976
H	-9.58575	-4.429574	-2.229552
C	-10.63251	-1.399863	-1.053886
H	-10.725806	-0.872382	1.037472
H	-10.417592	-2.257292	-3.023851
C	-11.300231	-0.128797	-1.56251
H	-11.260278	-0.124741	-2.657356

H	-12.365533	-0.186408	-1.303052	C	9.811651	3.648841	-1.506111
C	9.855169	-3.753866	-0.260299	C	9.986972	2.873112	0.77265
C	10.901977	-3.124818	0.421806	C	10.282428	2.416092	-1.95737
H	11.407447	-3.633992	1.239416	H	9.58671	4.430344	-2.229351
C	11.346784	-1.860138	0.022191	C	10.456409	1.639534	0.315822
H	12.196505	-1.413209	0.532307	H	9.911216	3.051558	1.843764
C	10.747345	-1.190211	-1.051406	C	10.631824	1.399696	-1.05457
C	9.664879	-1.809422	-1.699539	H	10.417939	2.258041	-3.024264
H	9.189109	-1.311552	-2.541212	H	10.724179	0.871327	1.03661
C	9.229575	-3.077003	-1.319074	C	11.299159	0.128589	-1.563598
H	8.420337	-3.551066	-1.871662	H	12.364642	0.186225	-1.304871
C	9.670828	3.894809	-0.134047	H	11.258461	0.124521	-2.658419

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O	-0.374316	-5.147182	-0.538916	C	-1.735581	2.478255	-0.015883
O	-3.832586	-1.922429	-0.870037	C	-1.217908	1.152289	-0.027829
O	-3.971271	-0.714022	1.426332	C	-5.261279	-0.556171	2.013705
O	-3.61279	3.893435	0.351136	H	-5.997702	-0.252918	1.259277
O	-1.38973	4.804421	-0.484034	H	-5.23621	0.181003	2.825551
H	-2.35134	4.761766	-0.181449	H	-5.520738	-1.536401	2.415727
O	1.174063	4.322372	-1.3585	C	-0.925457	3.553212	-0.41935
O	5.085501	0.277622	1.712472	C	0.416444	3.310398	-0.835303
O	3.7808	-2.373595	0.190748	C	0.92963	2.01969	-0.833463
O	2.048771	-4.36417	-0.331573	C	0.14717	0.92274	-0.352768
H	1.254726	-4.973815	-0.430014	C	1.453025	5.452507	-0.511667
C	-0.767726	-3.952177	-0.477072	H	2.232386	6.016825	-1.028069
C	-2.163714	-3.621479	-0.617384	H	1.827856	5.114499	0.463287
H	-2.823281	-4.440789	-0.873461	H	0.564119	6.071391	-0.373905
C	-2.590725	-2.325915	-0.535098	C	2.306201	1.754034	-1.394749
C	-1.677161	-1.234848	-0.181678	H	2.651943	2.619255	-1.961211
C	-0.266493	-1.494471	-0.276964	H	2.255028	0.8968	-2.078176
C	0.183967	-2.843808	-0.346647	C	3.238722	1.452737	-0.240625
C	-4.820901	-2.902667	-1.179847	C	3.095104	0.264127	0.390627
H	-5.734793	-2.341667	-1.379775	C	2.063267	-0.730269	-0.023115
H	-4.975532	-3.581958	-0.332447	C	0.669721	-0.417522	-0.227654
H	-4.538724	-3.477933	-2.070175	C	4.183832	2.561648	0.129619
C	-2.104795	0.047196	0.189701	H	5.007368	2.596618	-0.597742
C	-3.399996	0.340045	0.810911	H	4.628843	2.448138	1.117206
C	-3.905345	1.609568	0.83825	H	3.663371	3.524839	0.061727
H	-4.865076	1.849036	1.278352	C	3.919085	-0.074696	1.608745
C	-3.128721	2.729776	0.364336	C	3.23057	-0.809204	2.748523

H	3.332007	-1.889315	2.594911	C	4.599825	-2.611716	-0.965481
H	2.162928	-0.573089	2.810628	H	4.62296	-1.718062	-1.602304
H	3.732184	-0.547012	3.683593	H	4.22594	-3.474085	-1.528148
C	2.473786	-2.059901	-0.070605	H	5.601151	-2.817665	-0.58371
C	1.557629	-3.124558	-0.273015				

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N	7.478635	-3.051075	0.794536	H	-1.323044	-3.752941	2.960967
N	-7.922856	-3.210985	-0.042553	C	-1.69284	-4.485696	0.964463
C	9.005606	3.184465	-0.581462	C	-3.11073	-4.355543	1.020478
H	9.457086	3.715768	0.261168	H	-3.547069	-3.938236	1.924792
H	9.598609	3.418025	-1.469471	C	-3.905123	-4.646016	-0.075998
C	8.940071	1.687834	-0.326297	C	-3.30012	-5.193662	-1.257484
C	9.871784	0.825038	-0.918533	H	-3.925331	-5.478079	-2.097995
H	10.631765	1.214339	-1.591645	C	-1.946744	-5.37239	-1.32971
C	9.839359	-0.547742	-0.648457	H	-1.50272	-5.783838	-2.231691
H	10.572234	-1.198082	-1.119929	C	-1.090771	-4.977882	-0.252535
C	8.8759	-1.075331	0.220671	C	0.302978	-4.995206	-0.362694
C	7.943526	-0.210872	0.8051	H	0.757755	-5.355951	-1.281543
H	7.163567	-0.573067	1.465119	C	1.121993	-4.497174	0.663896
C	7.972083	1.153801	0.532601	C	2.528649	-4.370886	0.497171
H	7.213034	1.776282	0.99709	H	2.956705	-4.710037	-0.440519
C	8.865127	-2.5622	0.545212	C	-5.326531	-4.259045	-0.07416
H	9.288155	-3.155678	-0.270105	C	-6.135648	-4.322967	1.079522
H	9.449186	-2.781077	1.443762	H	-5.777127	-4.79202	1.989479
C	7.037711	-3.293767	2.053794	C	-7.413349	-3.795912	1.070844
H	7.777694	-3.24239	2.844469	H	-8.059232	-3.828157	1.940889
C	5.709386	-3.581678	2.303789	C	-7.191527	-3.187493	-1.187234
H	5.417328	-3.783355	3.32794	H	-7.652454	-2.703554	-2.040624
C	4.768312	-3.621145	1.252121	C	-5.916049	-3.707491	-1.233007
C	5.275321	-3.399887	-0.050541	H	-5.344871	-3.595635	-2.145883
H	4.612038	-3.383031	-0.907422	N	-7.769201	3.93826	-0.12386
C	6.60757	-3.119663	-0.246411	N	7.643527	3.7654	-0.779997
H	7.021649	-2.901856	-1.224053	C	-9.263102	-2.539186	-0.017197
C	3.331665	-3.827634	1.48616	H	-9.753307	-2.850857	0.908198
C	2.730196	-3.426455	2.729538	H	-9.84396	-2.94319	-0.849953
H	3.34059	-2.98319	3.509938	C	-9.153348	-1.027252	-0.101916
C	1.381112	-3.536022	2.924058	C	-9.662341	-0.341896	-1.209266
H	0.940495	-3.198523	3.858318	H	-10.122552	-0.887886	-2.029211
C	0.523154	-4.048177	1.898679	C	-9.621541	1.056902	-1.259879
C	-0.869055	-4.078841	2.02808	H	-10.050397	1.567826	-2.118412

C	-9.071395	1.79055	-0.20415	H	5.289526	5.460044	0.893512
C	-8.543303	1.101541	0.900325	C	7.027615	4.457762	0.211231
H	-8.119683	1.651786	1.737262	H	7.616067	4.655785	1.099954
C	-8.585968	-0.289788	0.950815	C	6.978554	3.515467	-1.936946
H	-8.202419	-0.800628	1.831329	H	7.52725	2.963896	-2.692121
C	-9.123002	3.308479	-0.222607	C	5.67629	3.926925	-2.117137
H	-9.587349	3.676952	-1.141056	H	5.189431	3.687248	-3.055328
H	-9.708976	3.690748	0.616939	O	-1.572569	-3.337661	-4.145504
C	-7.405517	4.654956	0.967909	O	2.899532	-3.113419	-2.604158
H	-8.165022	4.802272	1.727403	O	3.610464	-0.610112	-2.666611
C	-6.126955	5.164065	1.097469	O	5.091365	0.493543	1.705059
H	-5.894941	5.732236	1.990979	O	3.431536	0.490503	3.620685
C	-5.157934	4.940653	0.098123	H	4.294117	0.575568	3.108264
C	-5.601079	4.257776	-1.056771	O	0.839013	0.07532	4.508464
H	-4.923916	4.041917	-1.873278	O	-4.006573	2.25165	0.71511
C	-6.883409	3.766969	-1.139754	O	-4.226837	-0.898375	-0.695446
H	-7.235765	3.193095	-1.989038	O	-3.433693	-2.365942	-2.74161
C	-3.73404	5.270955	0.285348	H	-2.941002	-2.838368	-3.491702
C	-3.172322	5.227432	1.608103	C	-0.717374	-2.888513	-3.341896
H	-3.82288	5.092841	2.465599	C	0.685325	-3.179735	-3.510013
C	-1.819921	5.266355	1.799855	H	0.933878	-3.861171	-4.313844
H	-1.411286	5.195675	2.804437	C	1.613599	-2.695208	-2.633449
C	-0.918189	5.345639	0.691473	C	1.24739	-1.757877	-1.564708
C	0.466705	5.218597	0.84335	C	-0.145815	-1.645344	-1.235827
H	0.883008	5.08353	1.839351	C	-1.121885	-2.138225	-2.147716
C	1.326664	5.234076	-0.267871	C	3.383877	-3.937483	-3.677534
C	2.72668	5.005115	-0.135167	H	4.445882	-4.085766	-3.477466
H	3.112906	4.793483	0.858682	H	3.253197	-3.43404	-4.64098
C	3.563854	4.973546	-1.239232	H	2.875717	-4.907997	-3.688311
C	3.01142	5.234847	-2.541755	C	2.171844	-0.996307	-0.829601
H	3.666349	5.286632	-3.406087	C	3.48253	-0.574866	-1.329184
C	1.674409	5.474566	-2.702335	C	4.447246	-0.089173	-0.484255
H	1.276532	5.689744	-3.690471	H	5.426522	0.214006	-0.832439
C	0.776842	5.450229	-1.586843	C	4.178437	0.105927	0.915148
C	-0.606995	5.598611	-1.73609	C	2.80744	-0.08163	1.377499
H	-1.021837	5.749897	-2.730255	C	1.802997	-0.545691	0.481273
C	-1.472837	5.510558	-0.632453	C	4.849863	-0.233721	-3.267297
C	-2.889709	5.476869	-0.791688	H	5.665713	-0.88023	-2.921227
H	-3.28982	5.579726	-1.797317	H	5.089026	0.813035	-3.04235
C	4.981451	4.60858	-1.089365	H	4.706777	-0.358491	-4.340662
C	5.72092	4.886056	0.081408	C	2.496407	0.158244	2.729363

C	1.157845	-0.00692	3.19127	H	-3.092499	1.402405	3.950123
C	0.1584	-0.381417	2.299176	H	-2.74331	2.607387	2.698592
C	0.452452	-0.621546	0.918079	H	-1.443547	1.975476	3.750661
C	1.299911	1.183899	5.317395	C	-3.082717	1.619854	0.212521
H	0.593714	1.243306	6.147029	C	-2.604183	1.936514	-1.193827
H	1.276525	2.113641	4.737971	H	-3.215186	1.380299	-1.915186
H	2.30857	1.002361	5.688195	H	-1.558547	1.661291	-1.354901
C	-1.252394	-0.557294	2.813253	H	-2.73473	3.003044	-1.379876
H	-1.260609	-0.56422	3.903122	C	-2.888595	-1.160865	-0.778758
H	-1.651475	-1.512367	2.455018	C	-2.487798	-1.92561	-1.911442
C	-2.076422	0.584779	2.260462	C	-4.888548	-0.972849	0.580132
C	-2.38836	0.513542	0.946803	H	-4.897331	-0.006491	1.087657
C	-1.944864	-0.616811	0.086913	H	-4.409594	-1.724351	1.21464
C	-0.556002	-0.966959	-0.051939	H	-5.914606	-1.267774	0.358461
C	-2.356927	1.720252	3.197889				

HB ⊂ ExAnBox^{4+}

N	-6.871551	-5.6087	0.245946	H	1.632487	-3.473893	-2.15149
N	8.863892	-4.762406	-1.1125	C	2.364457	-4.720806	-0.549597
C	-9.521795	4.651822	0.355991	C	3.745913	-4.57074	-0.867445
H	-9.734409	5.282857	-0.509767	H	4.011926	-3.945212	-1.716394
H	-10.040466	5.079763	1.2179	C	4.730915	-5.169932	-0.102626
C	-8.356185	-5.714023	0.471191	C	4.356563	-5.958379	1.038647
H	-8.490739	-6.004929	1.51508	H	5.123974	-6.453359	1.626014
H	-8.715293	-6.535349	-0.154233	C	3.038763	-6.149618	1.352907
C	-6.405763	-5.446949	-1.017402	H	2.766446	-6.776896	2.197589
H	-7.144406	-5.487676	-1.80935	C	1.99859	-5.548154	0.577086
C	-5.06729	-5.222116	-1.260793	C	0.645298	-5.738971	0.874889
H	-4.741999	-5.114169	-2.28939	H	0.368381	-6.369233	1.716647
C	-4.145163	-5.149094	-0.193118	C	-0.361257	-5.14093	0.101824
C	-4.656817	-5.37125	1.102678	C	-1.740259	-5.379415	0.365657
H	-4.019507	-5.285497	1.976753	H	-1.994775	-6.046458	1.184249
C	-6.007007	-5.592486	1.290998	C	6.15552	-5.016785	-0.451827
H	-6.436504	-5.733381	2.276268	C	6.590876	-4.990116	-1.791794
C	-2.729016	-4.83162	-0.429392	H	5.888687	-5.109027	-2.609429
C	-2.358479	-3.954505	-1.507007	C	7.935224	-4.869414	-2.091183
H	-3.132938	-3.468878	-2.09317	H	8.30446	-4.873171	-3.110336
C	-1.045125	-3.684891	-1.772796	C	8.481819	-4.777368	0.188131
H	-0.781054	-3.007986	-2.581268	H	9.274868	-4.663334	0.91855
C	0.0029	-4.28721	-1.005616	C	7.154505	-4.912894	0.540498
C	1.356209	-4.096866	-1.303453	H	6.89827	-4.914051	1.594096

N	7.720096	4.96922	0.985944	H	-5.255074	6.000397	-0.759216
N	-8.047236	4.775845	0.622458	C	-7.224944	5.418491	-0.243771
C	10.32415	-4.603212	-1.447782	H	-7.696721	5.901732	-1.09185
H	10.401674	-4.730086	-2.530262	C	-7.526029	4.178073	1.722872
H	10.850581	-5.436569	-0.975046	H	-8.233053	3.671588	2.369451
C	9.171069	5.104579	1.372725	C	-6.172184	4.189278	1.970333
H	9.183497	5.30734	2.447007	H	-5.813629	3.665358	2.847713
H	9.539585	5.996458	0.862067	C	-9.926035	3.214111	0.117645
C	7.190569	5.734948	0.003036	C	-10.646856	2.505953	1.085804
H	7.862547	6.432052	-0.484148	H	-10.929471	2.988031	2.019429
C	5.851829	5.644615	-0.33106	C	-11.066635	1.194763	0.83845
H	5.467373	6.303342	-1.101945	H	-11.672172	0.683178	1.582582
C	4.999862	4.765188	0.366604	C	-10.77298	0.559452	-0.375351
C	5.591875	3.957338	1.363311	C	-10.020539	1.266122	-1.329501
H	5.013008	3.212275	1.900624	H	-9.801716	0.803292	-2.289198
C	6.93685	4.078545	1.644925	C	-9.608845	2.576365	-1.091679
H	7.431697	3.470966	2.393431	H	-9.071763	3.117279	-1.868772
C	3.552724	4.71871	0.090686	C	-9.06312	-4.41711	0.148669
C	3.048197	4.899024	-1.242371	C	-9.042207	-3.342271	1.05057
H	3.743896	4.985939	-2.071972	C	-9.765284	-4.273379	-1.053662
C	1.701677	4.916367	-1.487725	C	-9.722258	-2.158821	0.760584
H	1.330952	5.02284	-2.503527	H	-8.519986	-3.438462	2.001033
C	0.756751	4.796437	-0.418558	C	-10.446641	-3.087846	-1.339386
C	-0.624802	4.885139	-0.626101	H	-9.818593	-5.099673	-1.759699
H	-1.003633	5.049001	-1.631327	C	-10.451031	-2.019134	-0.432214
C	-1.529093	4.791544	0.445654	H	-9.71754	-1.348606	1.485604
C	-2.935047	4.894249	0.247852	H	-11.013472	-3.012659	-2.263904
H	-3.28935	5.020007	-0.770462	C	-11.339795	-0.811013	-0.700102
C	-3.824747	4.787737	1.305909	H	-11.642541	-0.82546	-1.752909
C	-3.308906	4.600898	2.636229	H	-12.264844	-0.950586	-0.124743
H	-3.987339	4.574925	3.482591	C	10.864508	-3.269872	-0.993144
C	-1.964718	4.515082	2.863227	C	11.848724	-3.203348	-0.001973
H	-1.589992	4.402599	3.877223	H	12.22666	-4.113795	0.458453
C	-1.026823	4.594314	1.785834	C	12.384115	-1.968931	0.378755
C	0.351699	4.508667	1.992739	H	13.167653	-1.940295	1.131487
H	0.731676	4.380958	3.003112	C	11.947614	-0.779847	-0.217175
C	1.255976	4.604042	0.923422	C	10.939288	-0.853011	-1.193403
C	2.662621	4.550264	1.134301	H	10.586216	0.058008	-1.669243
H	3.023648	4.429302	2.151868	C	10.409366	-2.079944	-1.582574
C	-5.274277	4.819924	1.076468	H	9.653591	-2.11207	-2.365704
C	-5.858717	5.454608	-0.043086	C	9.994579	3.888058	1.028565

C	10.526174	3.731913	-0.258198
C	10.290068	2.928009	2.006756
C	11.350549	2.6455	-0.554081
H	10.334125	4.480275	-1.024509
C	11.106708	1.838382	1.70331
H	9.922373	3.051885	3.02365
C	11.660835	1.688725	0.423739
H	11.791494	2.565925	-1.544752
H	11.350325	1.1193	2.481631
C	12.613169	0.54511	0.126794
H	13.277196	0.398084	0.985532
H	13.262541	0.828674	-0.711837
O	-2.748105	-3.41765	2.908932
O	-5.055897	-1.147996	-0.515158
O	-5.129479	1.347346	-0.035235
O	-3.068232	3.929951	-3.396305
O	-0.609996	3.576402	-3.960878
H	-1.544745	3.955424	-3.980907
O	1.690969	2.049975	-3.649305
O	3.827555	1.289258	1.987576
O	1.968456	-1.565434	2.615392
O	-0.230651	-3.066674	3.172612
H	-1.157319	-3.425086	3.325588
C	-2.775793	-2.499936	2.04045
C	-4.005562	-2.153686	1.380848
H	-4.873708	-2.737732	1.650618
C	-4.027304	-1.255245	0.350198
C	-2.865968	-0.4193	0.045088
C	-1.596406	-0.844186	0.56879
C	-1.552133	-1.836687	1.589934
C	-6.313921	-1.732622	-0.169967
H	-7.004208	-1.45692	-0.966768
H	-6.674147	-1.339839	0.786474
H	-6.244212	-2.822687	-0.115448
C	-2.925578	0.753462	-0.730863
C	-4.132906	1.558861	-0.925668
C	-4.193728	2.536967	-1.876867
H	-5.078856	3.143452	-2.022773
C	-3.026591	2.935237	-2.62272
C	-1.779283	2.220368	-2.3655
C	-1.725572	1.207286	-1.368341
C	-6.468255	1.644812	-0.438453
H	-6.701361	1.144361	-1.38394
H	-6.626157	2.720197	-0.549918
H	-7.116121	1.266807	0.352134
C	-0.624881	2.564795	-3.090697
C	0.572119	1.806128	-2.916876
C	0.631107	0.833542	-1.926239
C	-0.475764	0.608754	-1.052482
C	1.588748	2.182077	-5.090407
H	2.586063	1.953454	-5.469572
H	1.295894	3.195022	-5.367324
H	0.865261	1.463045	-5.488481
C	1.868195	-0.015037	-1.759785
H	2.478719	0.026894	-2.66311
H	1.572783	-1.056113	-1.581922
C	2.620033	0.536528	-0.56815
C	2.082004	0.328774	0.660208
C	0.835244	-0.48325	0.832512
C	-0.388272	-0.243122	0.104643
C	3.825428	1.355729	-0.926595
H	4.615126	0.683684	-1.29332
H	4.230838	1.920095	-0.093226
H	3.571389	2.026036	-1.756055
C	2.637407	1.00425	1.884568
C	1.665499	1.406181	2.978181
H	1.523379	0.563328	3.663018
H	0.687883	1.690558	2.577479
H	2.098452	2.232785	3.546143
C	0.846359	-1.434835	1.849133
C	-0.329886	-2.155732	2.205399
C	2.702895	-2.800461	2.539431
H	3.097608	-2.937183	1.526105
H	2.073085	-3.646531	2.819617
H	3.524178	-2.693418	3.249262

References

[S1] Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.

[S2] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J. ; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L. ; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, revision E.01, Gaussian, Inc.: Wallingford CT, **2013**.