Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Synthesis of stable monoporphyrinate lanthanide(III) complexes without ancillary ligand

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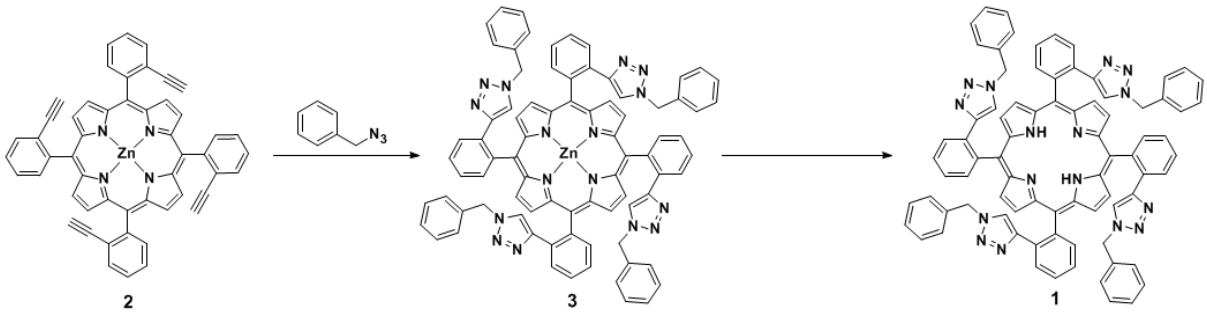
Experimental Section

Measurements. Absorption and FT-IR spectra were recorded on a JASCO V-660 and BrukerVertex70 spectrometer, respectively. For the observation of steady-state emission spectra in the near-infrared (NIR) region, a photomultiplier tube (Hamamatsu, H9170-75), a lock-in amplifier (EG&G, 7225 DSP) combined with a chopper, and a CW He-Cd laser (Melles Griot, Omnichrome 74) for the 442 nm excitation were used. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance DPX 400 spectrometer at 25°C in $CDCl_3$. MALDI-TOF-MS was performed on an Applied Biosystems 4700 proteomics analyzer with α-cyano-4-hydroxycinnamic acid as the matrix.

Time-Resolved Fluorescence Decay. A time-correlated single-photon-counting (TCSPC) system was used for measurements of spontaneous fluorescence decay and fluorescence anisotropy decay. As an excitation light source, we used a mode-locked Ti:sapphire laser (Spectra Physics, MaiTai BB) which provides ultrashort pulse (80 fs at full width half maximum, fwhm) with high repetition rate (80 MHz). This high repetition rate slows down to 1 M ~ 800 kHz by using homemade pulse-picker. The pulse-picked output pulse was frequency-doubled by a 1 mm thickness of a BBO crystal (EKSMA). The fluorescence was collected by a microchannel plate photomultiplier (MCP-PMT, Hamamatsu, R3809U-51) with a thermoelectric cooler (Hamamatsu, C4878) connected to a TCSPC board (Becker & Hickel SPC-130). The overall instrumental response function was about 25 ps (fwhm). A vertically polarized pump pulse by a Glan-laser polarizer was irradiated to samples, and a sheet polarizer, set at an angle complementary to the magic angle (54.7°), was placed in the fluorescence collection path to obtain polarization-independent fluorescence decays.

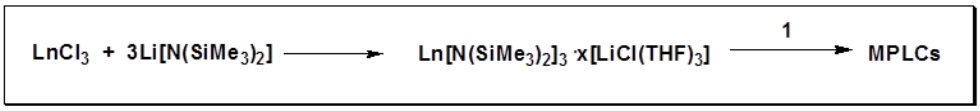
Synthesis.



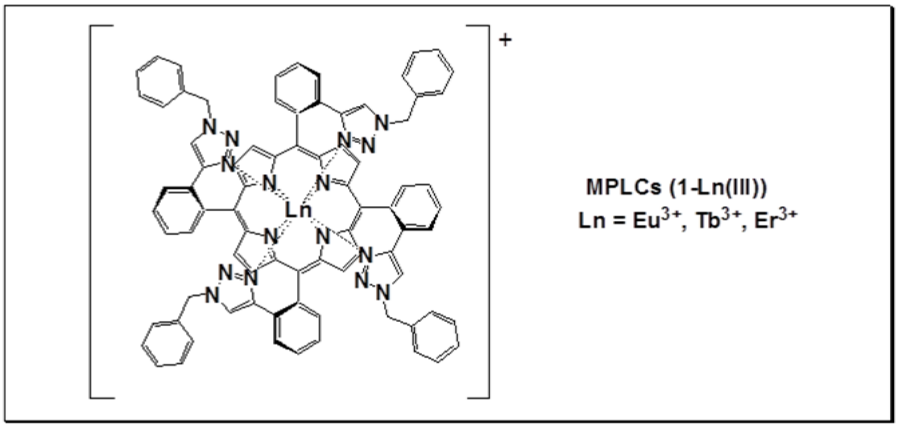
Synthesis of 2: Compound **2** was synthesized by the literature procedure[1].

Synthesis of 3: $CuSO_4 \cdot 5H_2O$ (0.32 g, 1.3 mmol) and sodium ascorbate (0.26 g, 1.3 mmol) were added to a mixture of **2** (0.2 g, 0.26 mmol) and benzyl azide (0.17 g, 1.3 mmol) in 20 mL THF/H_2O (1:1). The reaction mixture was stirred for 12 h at 50 °C, and then the organic layer was separated, dried over $MgSO_4$ and filtered. After evaporation of the solvent under reduced pressure, the residue was purified using column chromatography with 70% ethyl acetate/CH_2Cl_2, and the second fraction was collected and evaporated to dryness. The residue was recrystallized from CH_2Cl_2/Et_2O to afford αααα-atropisomer of **3** as a purple solid (0.25 g, 74 %): ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ = 8.68 (s, 8 H), 8.46 (d, J = 8 Hz, 4 H), 7,94-7.88 (m, 8 H), 7.69 (t, J = 7.6 Hz, 4 H), 5.61-5.51 (m, 20 H), 4.89 (s, 4 H), 4.06 ppm (s, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 167.76, 149.83, 147.23, 139.77, 134.64, 133.33, 133.17, 132.47, 131.95, 130.88, 128.85, 128.81, 127.72, 127.38, 126.99, 126.36, 126.32, 121.80, 119.44, 68.16, 52.27, 38.74, 31.94, 30.37, 29.71, 29.37, 28.93, 23.75, 22.99, 22.70, 14.13, 14.06, 10.97, 1.03 ppm; MALDI-TOF-MS:*m/z*:calcd. for $C_{80}H_{56}N_{16}Zn$: 1306.82 $[M]^+$; found 1306.60.

Synthesis of 1: To a CH_2Cl_2 solution (10 mL) of **3** (100 mg, 0.08 mmol), trifluoroacetic acid (1 mL) was added and stirred for 30 min. The reaction mixture was poured into water, and then extracted with CH_2Cl_2. After the evaporation of solvent, compound **1** was obtained as purple solid with quantitative yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ = 8.65 (s, 8 H), 8.52 (d, J = 8 Hz, 4 H), 7.96-7.90 (m, 8 H), 7.70 (t, J = 7.6 Hz, 4 H), 6.01 (t, J = 7.6 Hz, 4 H), 5.68 (t, J = 7.6 Hz, 8 H), 5.41 (d, J = 8 Hz, 8 H), 4.83 (s, *4* H), 3.98 (s, 8 H), - 2.73 ppm (s, 2H); MALDI-TOF-MS:*m/z*: calcd. for $C_{80}H_{58}N_{16}$: 1243.42 $[M]^+$; found 1242.51.



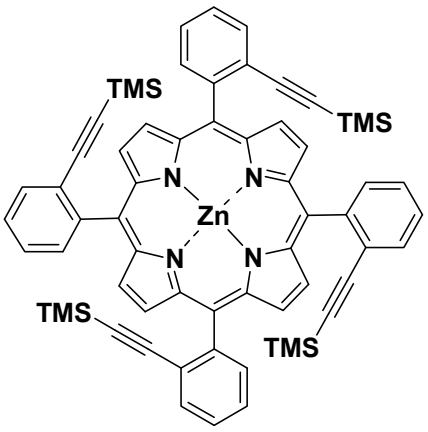
Synthesis of $Ln[N(SiMe_3)_2]_3$·x[$LiCl(THF)_3$]: $Ln[N(SiMe_3)_2]_3$·x[$LiCl(THF)_3$] was synthesized by the literature procedure[2].



Synthesis of MPLCs (1-Ln(III)), (Ln = Eu^{3+}, Tb^{3+}, Er^{3+}): **1** (0.50 g, 0.40 mmol) and $Ln[N(SiMe_3)_2]_3$·x[$LiCl(THF)_3$] (3 mL) were placed in a Schlenk flask. The flask was degassed under high vaccum and back-filled with nitrogen, and then TCB (50 mL) was added. The solution was stirred and refluxed for 12 h at 220 °C. The solution was filtered by column

chromatography with CH_2Cl_2, and then the residue was purified by column chromatography with 5 % MeOH/CH_2Cl_2 to give MPLCs (**1**-Ln(III)) in 10 % − 30 % yields. MALDI-TOF-MS:*m/z*: calcd. for $C_{80}H_{56}N_{16}Tb$: 1399.41 $[M]^+$; found 1401.15, calcd. for $C_{80}H_{56}N_{16}Eu$: 1393.41 $[M]^+$; found 1394.86, calcd. for $C_{80}H_{56}N_{16}Er$: 1408.42 $[M]^+$; found 1408.83.

Isolation of αααα-atropisomer of 3: The Cu^{I}-catalyzed alkyne-azide click reaction between benzyl azide and **2** resulted in **3** as a mixture of four different atropisomers (αααα, ααβ, ααββ, and αβαβ). Although the diffrences of Rf values were very small, TLC profile exhibited aviously four different spots. Because of the small diffrences in Rf values, the isolation of each atropiosmer using column chromatography was significantly difficult. Therefore, we have purified from the precursor of **2** (**2**-TMS).



2-TMS

From the reaction mixture of 2-TMS synthesis,[1] two set of porphyrin mixtures have been separated by silica column chromatography with eluent of CH_2Cl_2/Hexane (10/90). The first fraction was mixture of ααββ and αααα atropisomers, and the second fraction was mixture of αβαβ and αααβ atropisomers. The TMS groups in each mixture were deprotected using tetrabutylammonium fluoride to afford corresponding mixture of 2 with quantitative yields. Then, the each mixture of 2 was reacted with benzyl azide to afford corresponding mixture of 3 with over 90% of yields. Finally, αααα atropisomer was separated by recrystallization method in biphasic solvent (CH_2Cl_2/Et_2O). For αβαβ and αααβ atropisomers, careful column chromatography was utilized to separate each other.

Structural determination of atropisomers: The ^{1}H NMR spectra of each atropisomers were obviously different each other. The pyrrole β proton signals of αααβ and ααββ atropisomers should be more complicated than those of αααα and αβαβ atropisomers when consider the symmetry of molecules. In fact, αααα and αβαβ atropisomers exhibited single sharp peak of pyrrole β protons, whereas αααβ and ααββ atropisomers exhibited multiple peaks of pyrrole β proton. Therefore, the molecular structure of αααβ and ααββ atropisomers can be directly confirmed by the comparison of ^{1}H NMR spectra. However, because both αααα and αβαβ atropisomers has highly symmetric structure, we cannot directly determine the structure from the result of ^{1}H NMR experiment. In our previous report, we have examined that triazole-bearing zinc porphyrin exhibits significantly strong binding affinity to anionic guests according to the cooperative C-H hydrogen bonding by triazole groups. Because the maximum coordination number of zinc ion in porphyrin is five, the total numbers of C-H hydrogen bonding formation can be varied by the numbers of triazole groups in same direction. The maximum numbers of simultaneous C-H hydrogen bonding formation for αααα, αααβ, αβαβ and ααββ atropisomer is 4, 3, 2, and 2, respectively. Therefore, the order of binding affinities of porphyrins to anionic guest should be αααα > αααβ > αβαβ = ααββ atropisomers. Based on the above information, we have determined structures of each atropisomers in our previous investigation.[1]

NMR spectra of 3

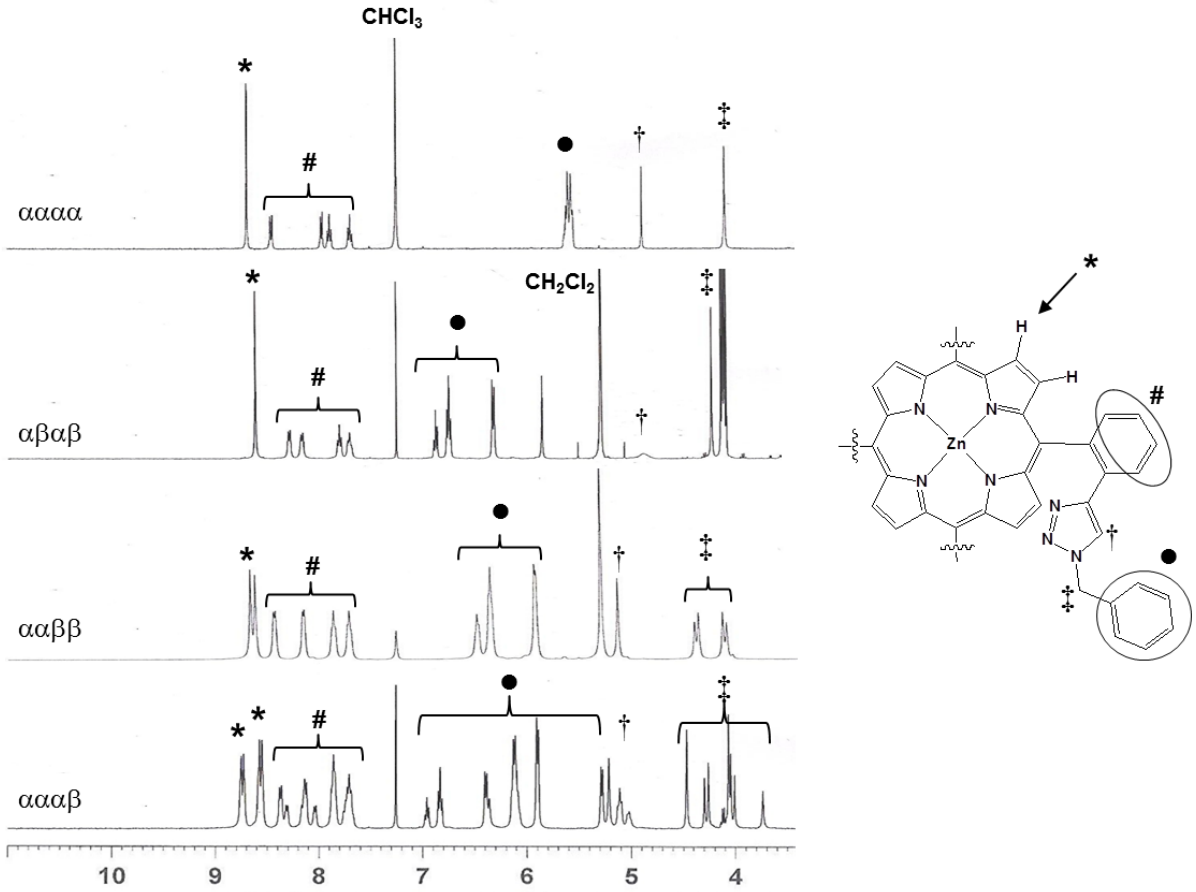


Figure S1. NMR spectra of 4 different atropisomers of **3.**

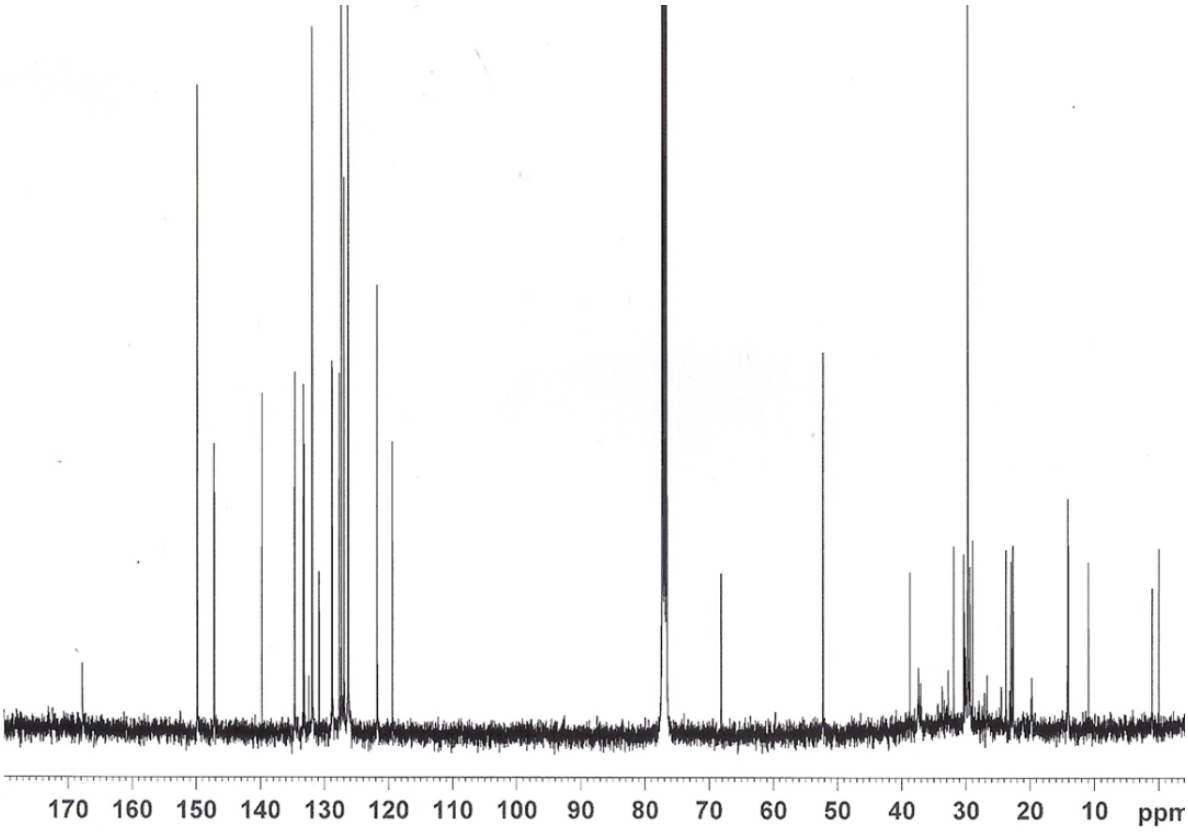


Figure S2. ^{13}C NMR spectrum of αααα atropisomer of **3.**

MALDI-TOF-MS spectra

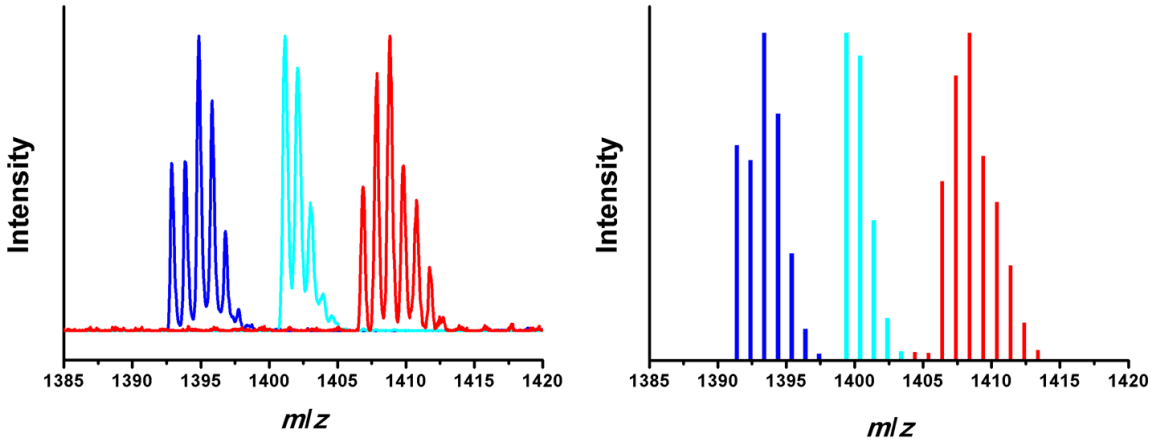


Figure S3. MALDI-TOF-MS spectra (left) of MPLCs with the result of molecular weight simulation (right).

FT-IR spectra

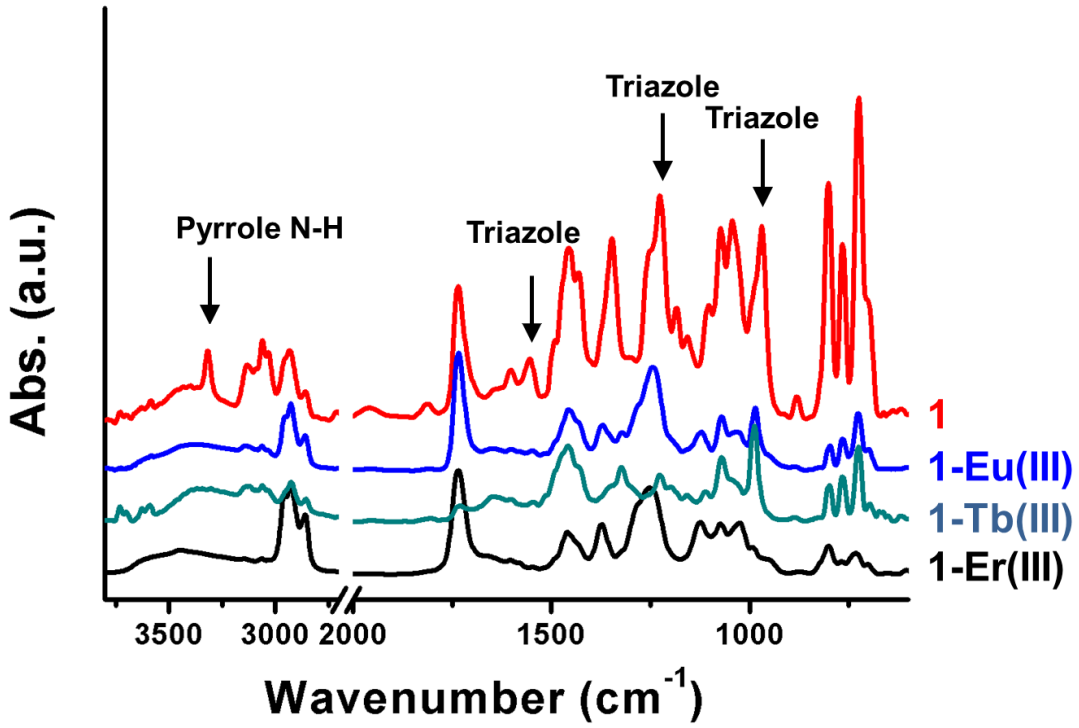


Figure S4. FT-IR spectra of **1** and MPLCs.

Molecular Mechanical Calculation

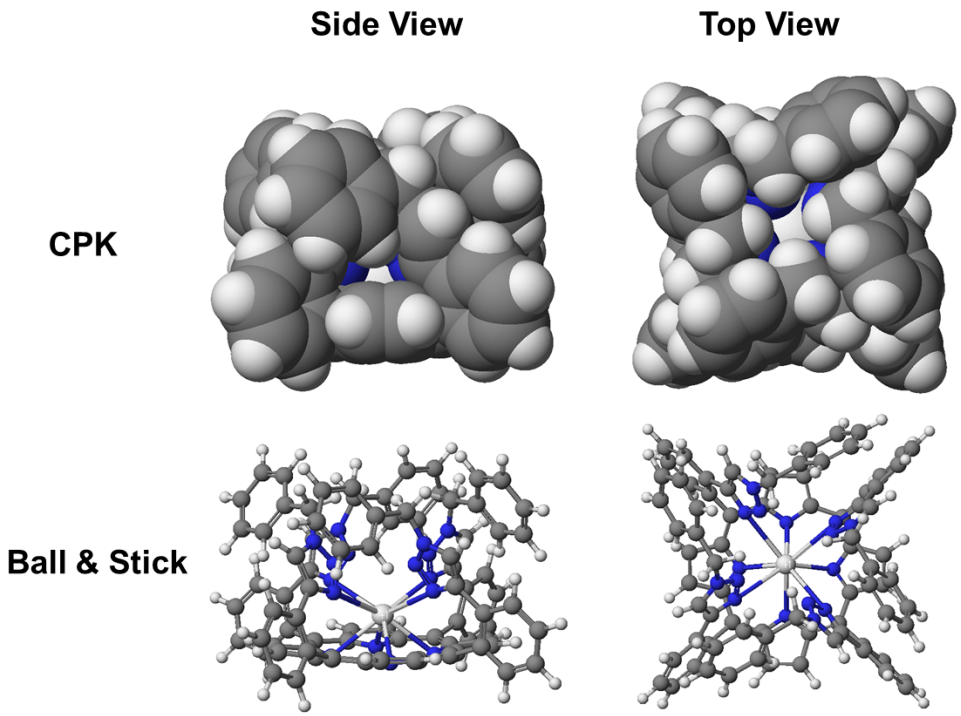


Figure S5. Structural optimization of **1-Eu(III)** by MM2 force field.

Reference

1. C.-H. Lee, S. Lee, H. Yoon, and W.-D. Jang, *Chem .Eur. J.*, **2011**, 17, 13898-13903.

2. W.-K. Wong, L. Zhang, W.-T. Wong, F. Xue and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.,* **1999**, 615-622.