

## **A tetraphenylethene-based Pd<sub>2</sub>L<sub>4</sub> metallacage with aggregation-induced emission and stimuli-responsive behavior**

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Lin Cheng and Liping Cao

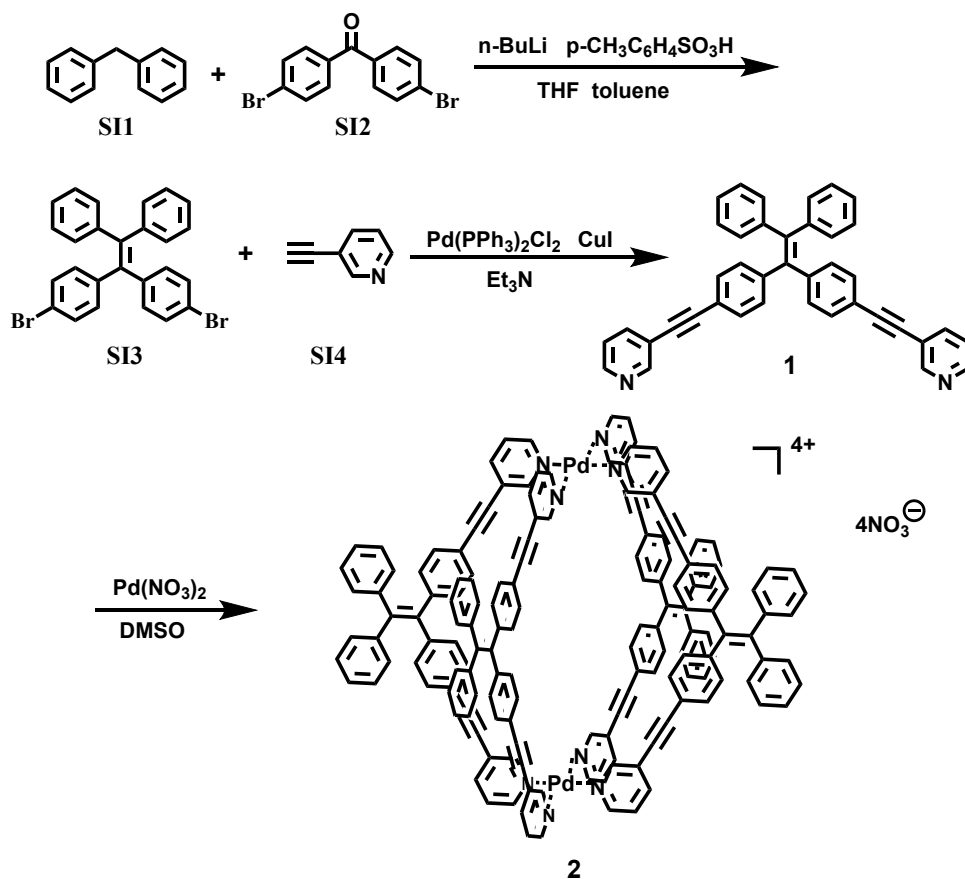
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**General Experimental Details.** Starting materials were purchased from commercial suppliers were used without further purification. Compound **SI3**<sup>1</sup> was prepared according to the literature procedures. Melting points were measured on a XT-4 apparatus in open capillary tubes and are uncorrected. TLC analysis was performed using pre-coated plastic plates from Merck. IR spectra were recorded on a JASCO FT/IR 4100 spectrometer and are reported in cm<sup>-1</sup>. UV-Vis spectra were recorded on a Agilent Cary-100 spectrometer. Fluorescence spectra were recorded on a Horiba Fluorolog-3 spectrometer equipped with a xenon discharge lamp using 1 cm quartz cells. NMR spectra were measured on a Bruker spectrometer operating at 400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C NMR spectra. Mass spectrometry was performed using an Electron Spray Ionization (ESI) on a Bruker MICROTOF-Q II electrospray instrument. SEM was carried out on a Hitachi SU8010 microscope. X-ray diffraction data collection of the compounds were recorded by Bruker D8 Venture photon II diffractometer.

### Synthetic Procedures and Characterization Data

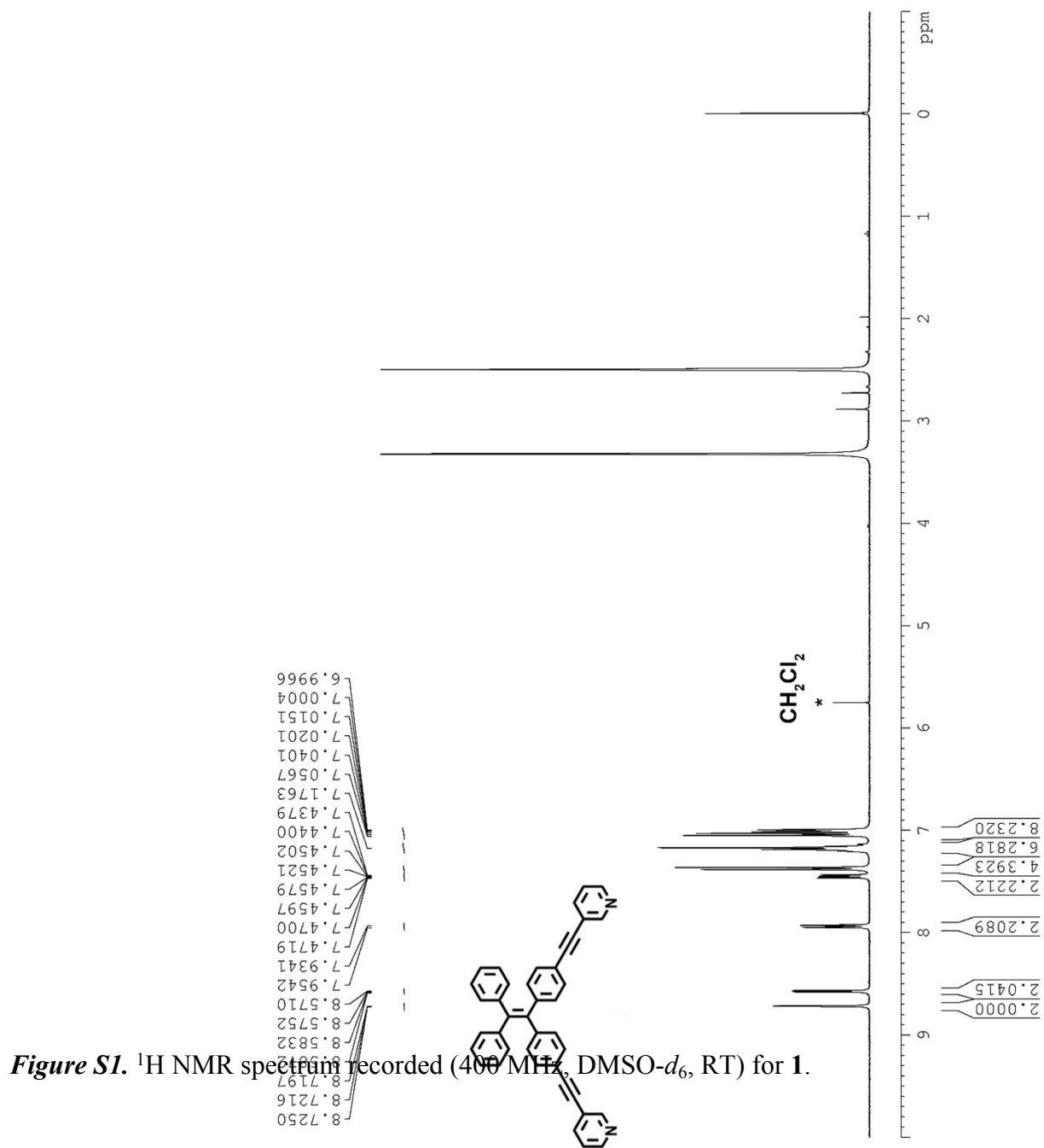


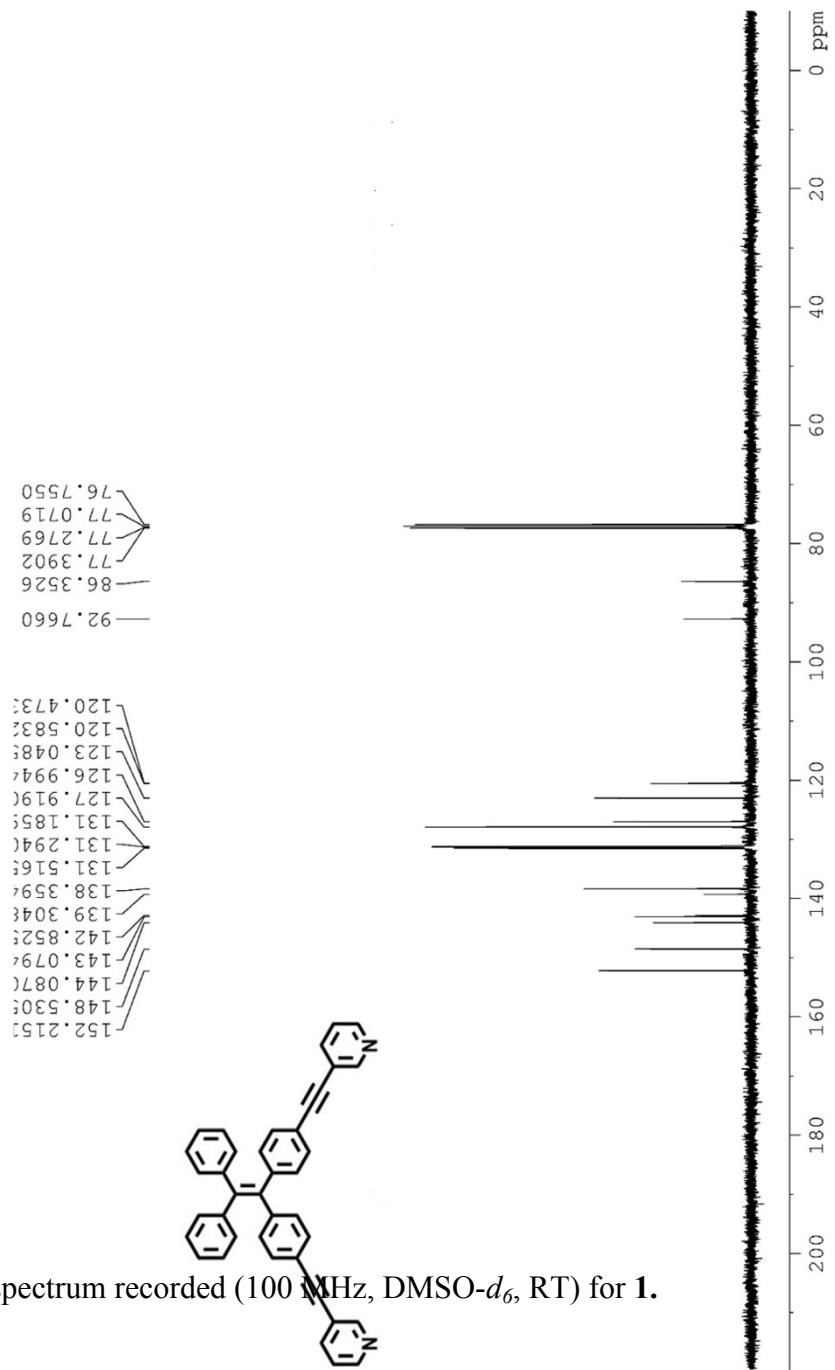
**Compound SI3.** Under a nitrogen atmosphere, a 2.5 M solution of n-butyllithium in hexane (12.0 mL, 25.0 mmol) was slowly added to a solution of diphenylmethane (2.2 g, 13.3 mmol) in anhydrous tetrahydrofuran (100 mL) by a syringe with the temperature kept under 0 °C. After stirring for 1 h, a solution of bis(4-bromophenyl)methanone (3.0 g, 8.8 mmol) in anhydrous THF, And the suspending mixture was warmed to room temperature and stirred for 24 h. After the reaction finished, the mixture was quenched with an aqueous solution of ammonium chloride and extracted with dichloromethane. The organic layer was combined and concentrated after drying with anhydrous sodium sulfate and the resulting crude hydroxy intermediate was dissolved in toluene (80 mL). p-toluenesulfonic acid (3.0 g, 17.6 mmol) was added to the solution, and the mixture was heated at reflux for 12 h and cooled down to room temperature. The mixture was evaporated and the crude product was purified by silica gel column chromatography using n-hexane as eluent to yield **SI3** as a white powder (2.56 g, 60%). The <sup>1</sup>H NMR matches that reported in the reported literature.<sup>1</sup>

**Compound 1.** In an oven-dried Schlenk flask equipped with a magnetic stirrer was added **SI3** (150 mg, 0.31 mmol), **SI4** (158 mg, 1.53 mmol), bis(triphenylphosphine)-palladium(II) dichloride (0.25 mg, 0.08 mmol), and CuI (29 mg, 0.15 mmol). The mixture was placed under nitrogen atmosphere, and anhydrous triethylamine (22 mL) was added by syringe. The reaction was heated at 90 °C for 48 h under nitrogen, then cooled down to room temperature and the solvents were removed under reduced pressure. The residue was dissolved in dichloromethane (200 mL) and washed successively by water (150 mL). After drying over Na<sub>2</sub>SO<sub>4</sub>, the organic solvent was evaporated to afford the crude product as brown solid, which was purified using column chromatography to yield **1** as a light-yellow powder (28%). M.p. = 240 -241 °C. IR (cm<sup>-1</sup>): 3435s, 3056m, 3028m, 2221m, 1634w, 1557m, 1499s, 1399s, 841s, 763s, 699s. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): 8.73 (dd, *J* = 0.8 and 2.5, 2H), 8.58 (dd, *J* = 1.8 and 4.6, 2H), 7.94 (dt, *J* = 1.8 and 4.6, 2H), 7.46 (ddd, *J* = 0.8, 2.5, and 4.6, 2H), 7.38 (d, *J* = 8.4, 4H), 7.25-7.10 (m, 6H), 7.05 (d, *J* = 8.4, 4H), 7.03-6.98 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 152.2, 148.5, 144.0, 143.1, 142.9, 139.3, 138.4, 131.5, 131.3, 131.2,

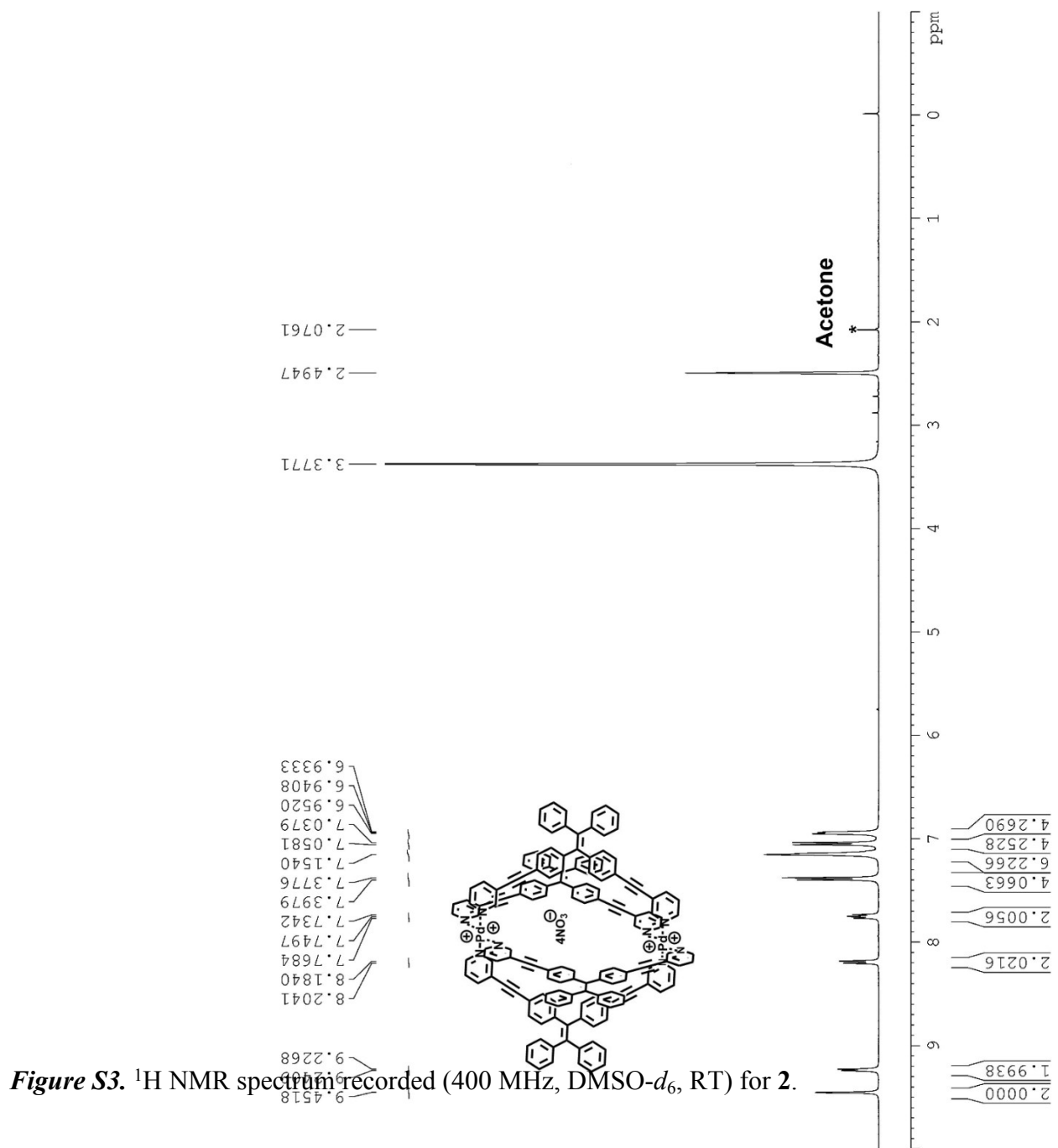
127.9, 127.0, 123.0, 120.5, 120.4, 92.7, 86.3. HR-MS:  $M/Z=535.2163$  ( $[C_{40}H_{26}N_2+H]^+$ , calcd. for  $[C_{40}H_{26}N_2+H]^+$ , 535.2169).

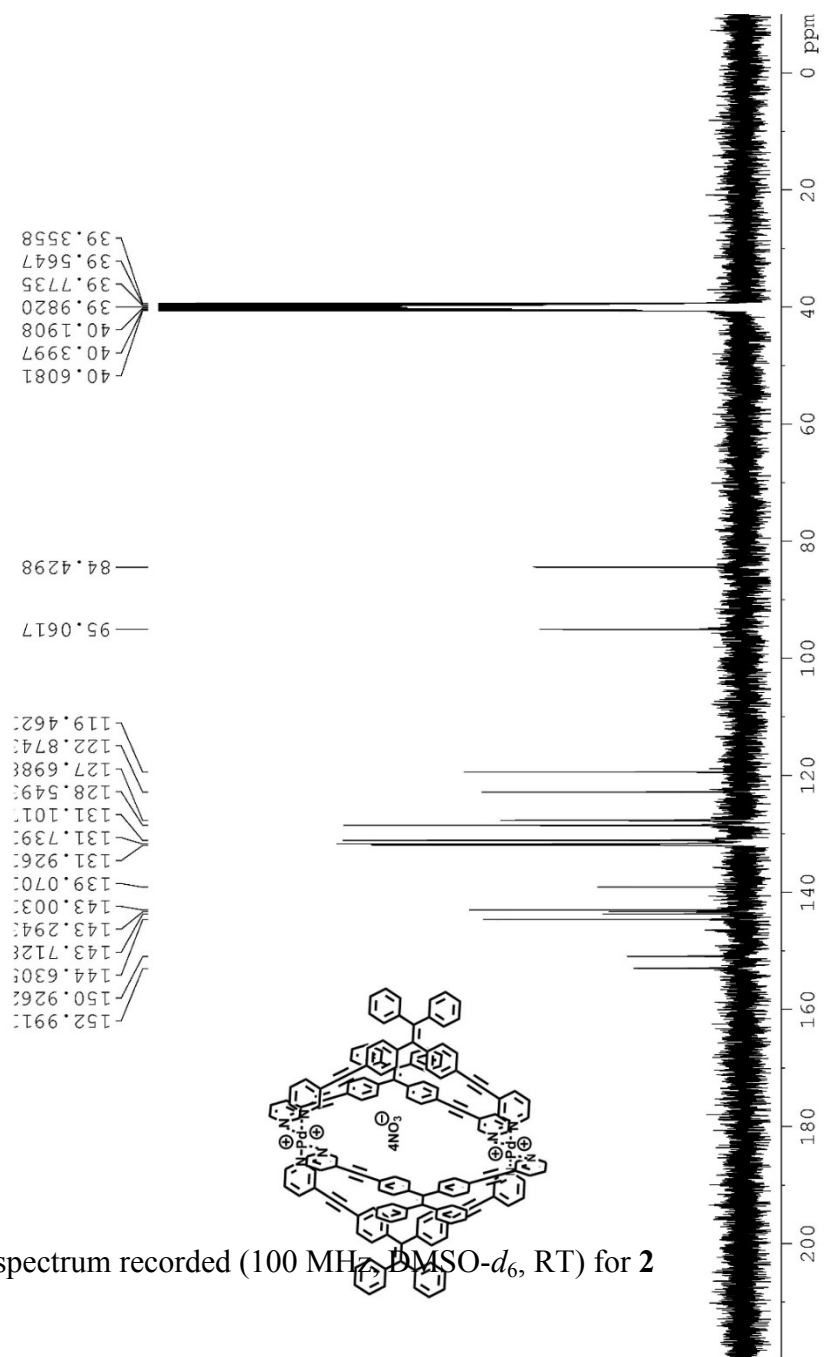
**Cage 2.** Compound **1** (10 mg, 0.02 mmol) and  $Pd(NO_3)_2$  (2.15 mg, 0.01 mmol) were mixed in DMSO (1 mL), and then precipitated and washed carefully with isopropyl acetate (50 mL) and dried under vacuum to yield the yellow solid product. M.p. > 300 °C. IR ( $cm^{-1}$ ): 3421m, 3056w, 2228m, 1635m, 1506m, 1385s, 813w, 699m.  $^1H$  NMR (400 MHz, DMSO- $d_6$ ): 9.45 (s, 8H), 9.23 (d,  $J = 6.0$  8H), 8.20 (d,  $J = 7.8$ , 8H), 7.76 (dd,  $J = 6.0$  and 7.8, 8H), 7.40 (d,  $J = 8.1$ , 16H), 7.25-7.10 (m, 24H), 7.06 (d,  $J = 8.1$ , 16H), 7.00-6.85 (m, 16H).  $^{13}C$  NMR (100 MHz, DMSO- $d_6$ ): 153.0, 150.9, 144.6, 143.7, 143.3, 143.0, 139.1, 131.9, 131.7, 131.1, 128.5, 127.7, 122.9, 119.5, 95.1, 84.4. HR-MS:  $M/z=587.6770$  ( $[C_{160}H_{104}N_8Pd_2]^{4+}$ , calcd. for  $[C_{160}H_{104}N_8Pd_2]^{4+}$ , 587.6624); 804.2287 ( $[C_{160}H_{104}N_9Pd_2O_3]^{3+}$ , calcd. for  $[C_{160}H_{104}N_9Pd_2O_3]^{3+}$ , 804.2126); 1237.3422 ( $[C_{160}H_{104}N_{10}Pd_2O_6]^{2+}$ , calcd. for  $[C_{160}H_{104}N_{10}Pd_2O_6]^{2+}$ , 1237.3131).





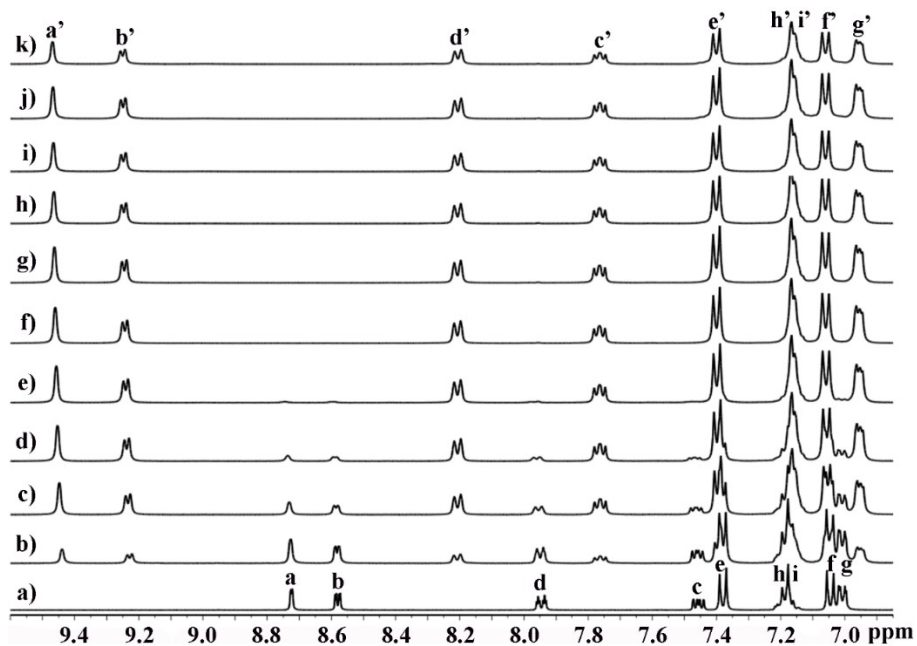
**Figure S2.** <sup>13</sup>C NMR spectrum recorded (100 MHz, DMSO-*d*<sub>6</sub>, RT) for **1**.



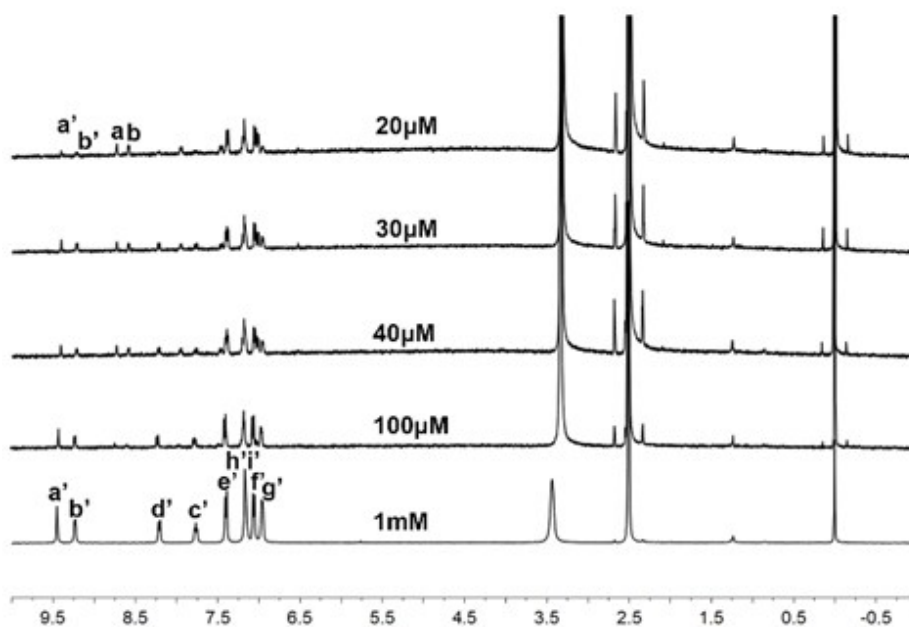


**Figure S4.**  $^{13}\text{C}$  NMR spectrum recorded (100 MHz,  $\text{DMSO-}d_6$ , RT) for **2**

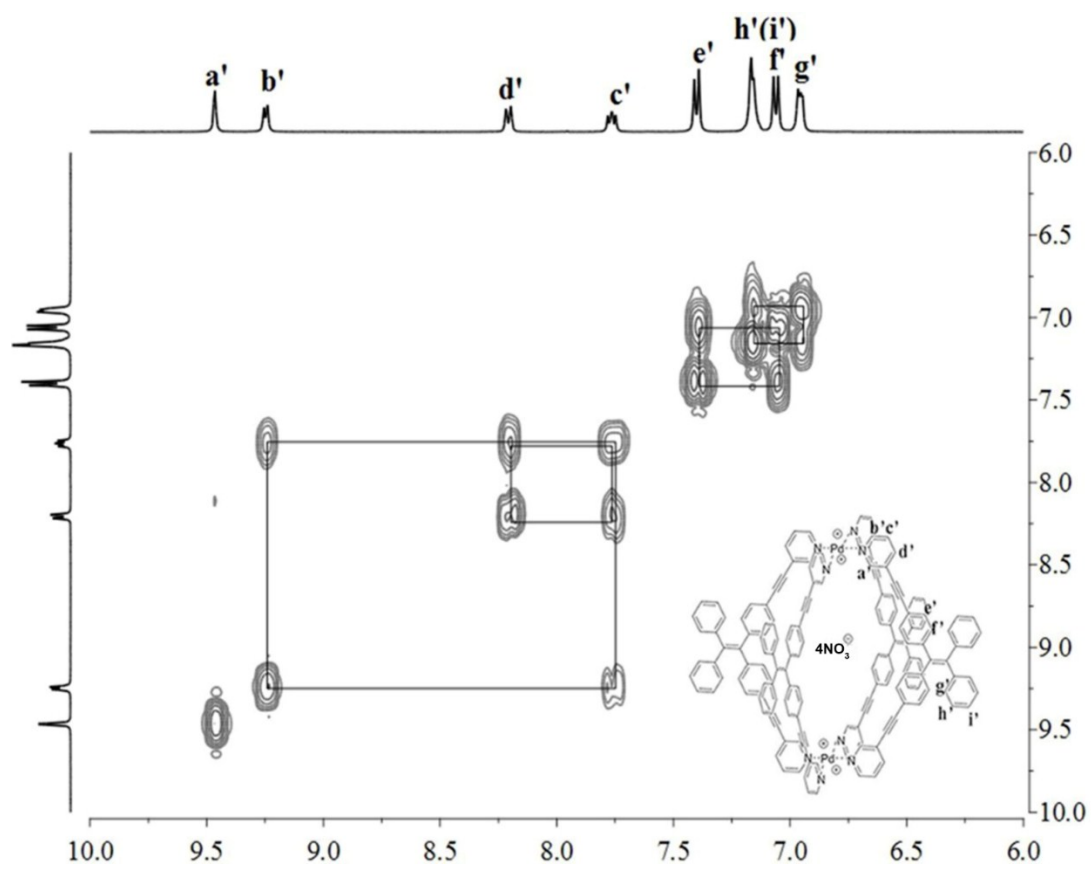




**Figure S5.** Partial  $^1\text{H}$  NMR spectra (400 MHz,  $\text{DMSO-}d_6$ , 298K) of the titration of **1** (16.0 mM) with  $\text{Pd}(\text{NO}_3)_2$ : a) 0; b) 0.1; c) 0.2; d) 0.3; e) 0.4; f) 0.5; g) 0.6; h) 0.7; i) 0.8; j) 0.9; k) 1.0 equiv.

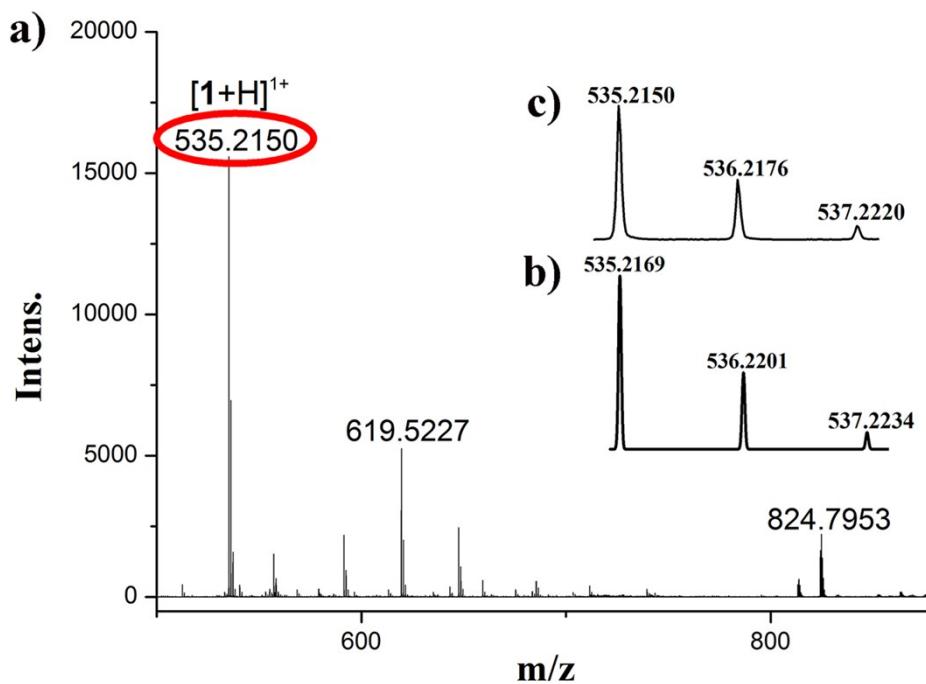


**Figure S6.**  $^1\text{H}$  NMR spectra (400 MHz,  $\text{DMSO-}d_6$ , 298K) of the cage **2** (20  $\mu\text{M}$ , 30  $\mu\text{M}$ , 40  $\mu\text{M}$ , 100  $\mu\text{M}$ , 1.0 mM)

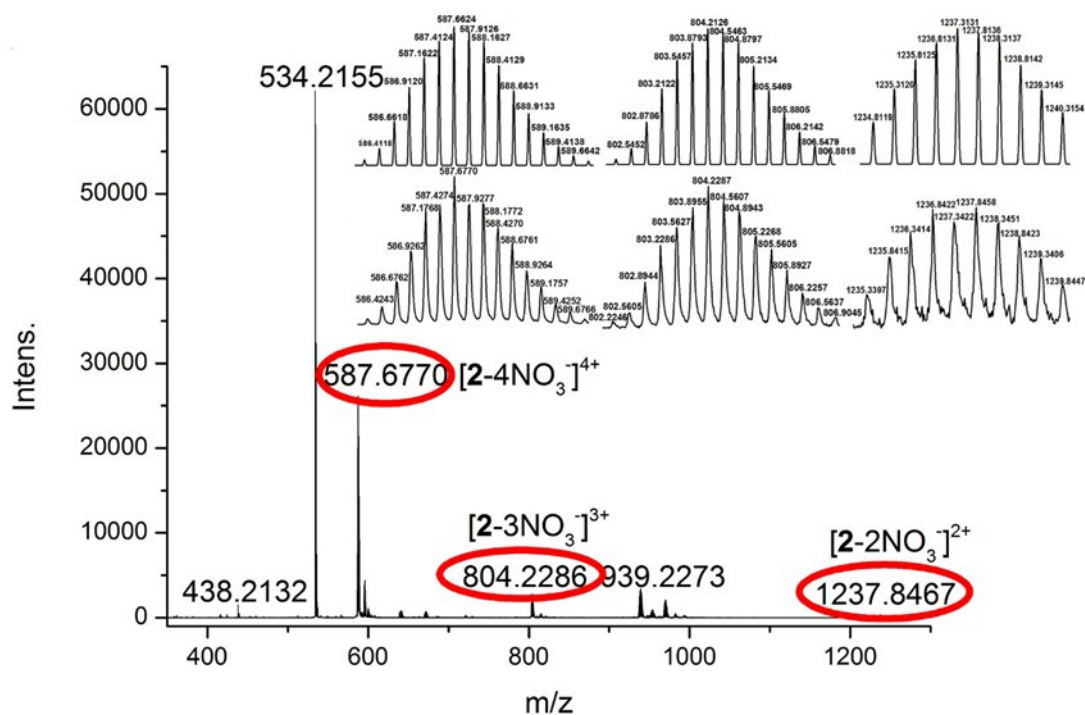


**Figure S7.** COSY NMR spectrum recorded (400 MHz, DMSO- $d_6$ , 298 K) for **2**.





**Figure S10.** High-resolution ESI-MS spectrum of **1**. b) simulated peak of  $[1+H]^{1+}$ , c) measured peak of  $[1+H]^{1+}$ .



**Figure S11.** High-resolution ESI-MS spectrum of **2**. Insert picture: simulated peak of  $[2-4NO_3]^{4+}$ ,  $[2-3NO_3]^{3+}$ ,  $[2-2NO_3]^{2+}$ , measured peak of  $[2-4NO_3]^{4+}$ ,  $[2-3NO_3]^{3+}$  and  $[2-2NO_3]^{2+}$ .

### **X-ray Structure determination.**

Data collections was performed on Bruker D8 Venture photon II diffractometer and graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The data was collected at 153 K crystal temperature (Oxford Cryosystems CRYOSTREAM 700), 50 kV and 30 mA with an appropriate  $0.5^\circ \omega$  scan strategy. Data reduction and integration were performed with SAINT (version 8.38A). All data was corrected for absorption effects using the empirical methods as implemented in SADABS (version 2016/2). The structures of **1** and **2** were solved by SHELXT (version 2018/2) and refined by full-matrix least-squares procedures using the SHELXL program (version 2018/3) through the OLEX2 graphical interface. All non-hydrogen atoms, including those in disordered parts, were refined anisotropically. All H-atoms were included at calculated positions and refined as riders, with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ . Further crystal and data collection details are listed in Table S1 and S2.

The crystal of **1**: Compound **1** (4.2 mg, 78.0  $\mu\text{mol}$ ) was dissolved in DMSO (1 mL) and the solution was passed through a  $0.45 \mu\text{m}$  filter into a 10 mL tube, which was placed inside a 500 mL wild-mouth bottle containing diethyl ether (20 mL). The bottle was capped, after slow evaporation of diethyl ether at room temperature into the DMSO solution for 2 days, and light-yellow single crystals of **1** were obtained.

The crystal of **2** $\cdot$ 4NO<sub>3</sub><sup>-</sup>: **2** $\cdot$ 4NO<sub>3</sub><sup>-</sup> (5.3 mg, 10  $\mu\text{mol}$ ) were dissolved in the mixture solution of DMSO and DMF(1:1, 1 mL) and the solution was passed through a  $0.45 \mu\text{m}$  filter into a 10 mL tube, which was placed inside a 500 mL wild-mouth bottle containing diethyl ether (20 mL). The bottle was capped, after slow evaporation of diethyl ether at room temperature into the DMSO and DMF solution for 7 days, and light-yellow single crystals of **2** $\cdot$ 4NO<sub>3</sub><sup>-</sup> were obtained.

**Table S1.** Data and structure refinement parameters for **1**

Chemical formula	C <sub>40</sub> H <sub>26</sub> N <sub>2</sub>
$M_r$	534.63
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	153
$a, b, c$ (Å)	17.1299 (8), 10.2595 (4), 17.7663 (11)
$\beta$ (°)	113.637 (1)
$V$ (Å <sup>3</sup> )	2860.4 (2)
$Z$	4
$F(000)$	1120
$D_x$ (Mg m <sup>-3</sup> )	1.241
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.07
Crystal size (mm)	0.12 × 0.07 × 0.04
Radiation source	fine-focus sealed tube
Absorption correction	Semi-empirical from equivalents
$T_{\min}, T_{\max}$	0.573, 0.745
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	16618, 2623, 2105
$R_{\text{int}}$	0.041
$\theta$ values (°)	$\theta_{\max} = 25.4, \theta_{\min} = 2.4$
$(\sin \theta/\lambda)_{\max}$ (Å <sup>-1</sup> )	0.603
Range of $h, k, l$	$h = -20 \rightarrow 20, k = -12 \rightarrow 12, l = -21 \rightarrow 20$
$R[F^2 > 2\sigma(F^2)]^a, wR(F^2)^b, S^c$	0.040, 0.105, 1.06
No. of reflections	2623
No. of parameters	191
$\Delta_{\max}, \Delta_{\min}$ (e Å <sup>-3</sup> )	0.14, -0.19

$$^a R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|. \quad ^b wR2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]].$$

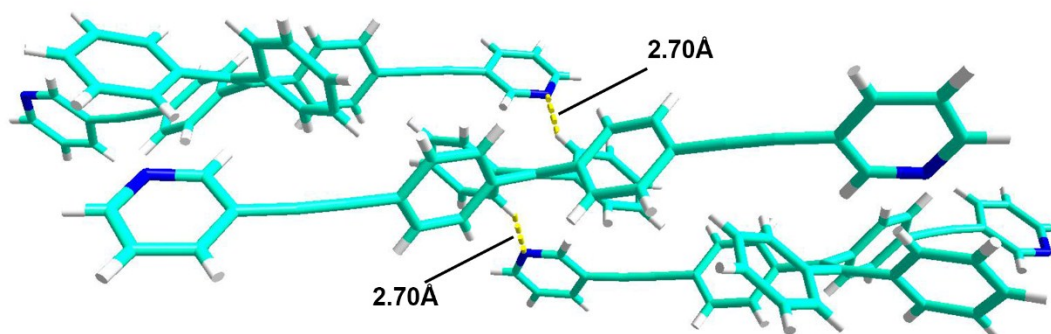
$$^c \text{Quality-of-fit} = [\Sigma [w(F_o^2 - F_c^2)^2] / (N_{\text{obs}} - N_{\text{params}})]^{1/2}, \text{ based on all data.}$$

**Table S2.** Data and Structure Refinement Parameters for **2•4NO<sub>3</sub><sup>-</sup>**

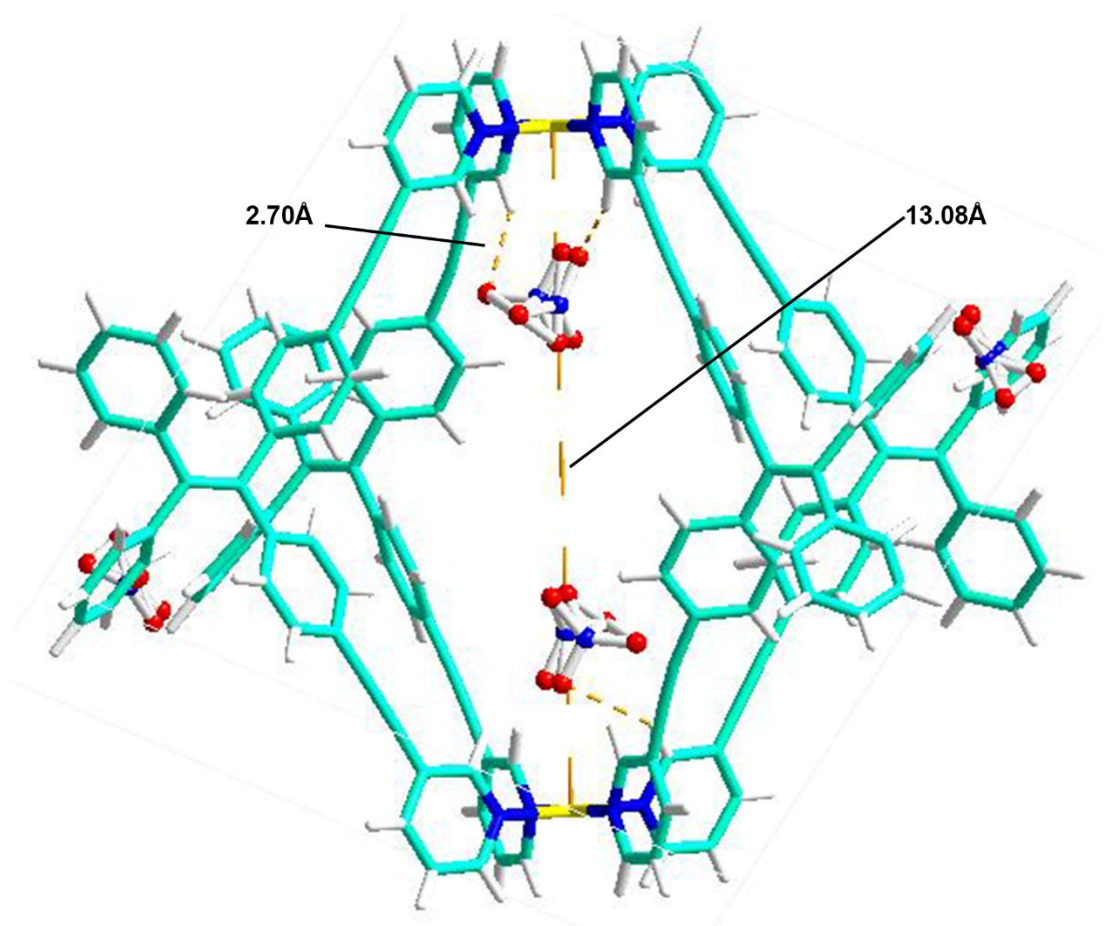
Chemical formula	C <sub>286</sub> H <sub>398</sub> N <sub>54</sub> O <sub>54</sub> Pd <sub>2</sub>
$M_r$	5669.36
Crystal system, space group	Triclinic, <i>P</i> -1
Temperature (K)	100
$a, b, c$ (Å)	15.7174 (6), 18.1192 (6), 18.6203 (7)
$\alpha, \beta, \gamma$ (°)	97.658 (1), 95.100 (1), 110.333 (1)
$V$ (Å <sup>3</sup> )	4875.6 (3)
$Z$	1
$F(000)$	3016
$D_x$ (Mg m <sup>-3</sup> )	1.931
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.31
Crystal size (mm)	0.12 × 0.06 × 0.05
Radiation source	fine-focus sealed tube
Absorption correction	Semi-empirical from equivalents <i>SADABS2016/2</i> (Bruker, 2016/2) was used for absorption correction. $wR2(\text{int})$ was 0.0742 before and 0.0642 after correction. The Ratio of minimum to maximum transmission is 0.8707. The $\lambda/2$ correction factor is Not present.
$T_{\text{min}}, T_{\text{max}}$	0.612, 0.703
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	128455, 17799, 15713
$R_{\text{int}}$	0.032
$\theta$ values (°)	$\theta_{\text{max}} = 25.4, \theta_{\text{min}} = 1.9$
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.603
Range of $h, k, l$	$h = -18 \rightarrow 18, k = -21 \rightarrow 21, l = -22 \rightarrow 22$
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.045, 0.138, 1.10
No. of reflections	17799
No. of parameters	947
No. of restraints	938
$\Delta_{\text{max}}, \Delta_{\text{min}}$ (e Å <sup>-3</sup> )	0.71, -0.41

$${}^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad {}^b wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]].$$

$${}^c \text{Quality-of-fit} = [\sum [w(F_o^2 - F_c^2)^2] / (N_{\text{obs}} - N_{\text{params}})]^{1/2}, \text{ based on all data.}$$

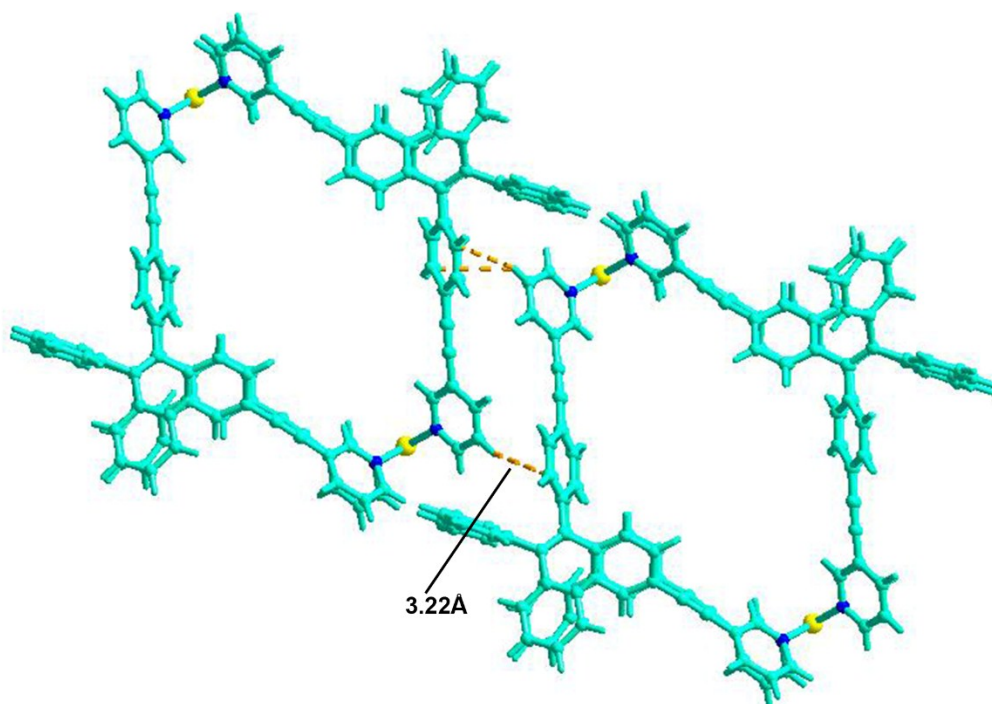


**Figure S12.** X-ray crystal structures of Ligand 1. Color scheme: C, green blue; N, dark blue; H, white; hydrogen bonds, yellow dashes.

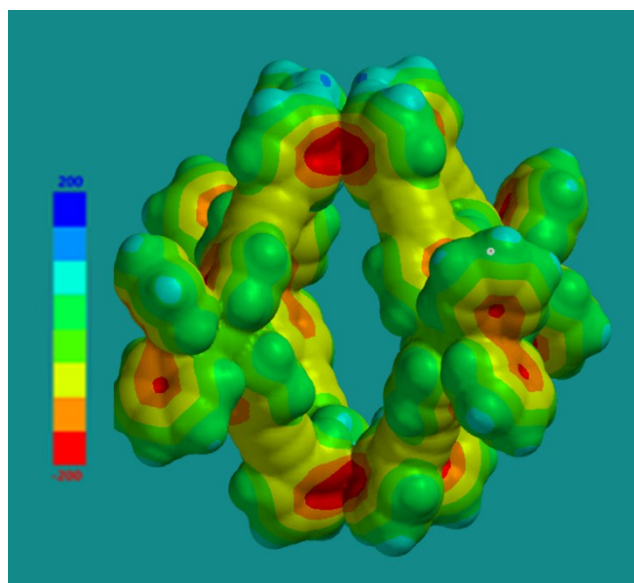


**Figure S13.** X-ray crystal structures of capsule 2•4NO<sub>3</sub><sup>-</sup>. Color scheme: Pd, yellow; C, green blue; N, dark blue; H, white; hydrogen bonds, yellow dashes;





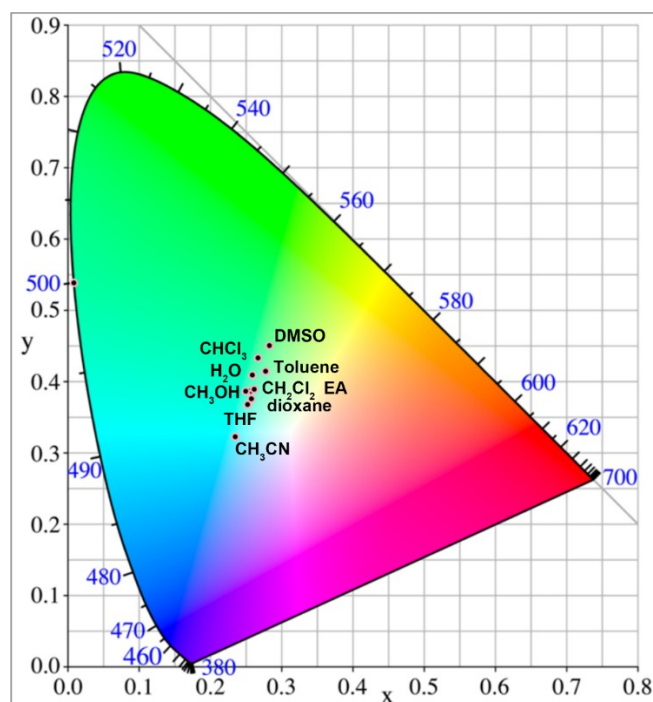
**Figure S14.** X-ray crystal structures of capsule **2**•4NO<sub>3</sub><sup>-</sup> Color scheme: Pd, yellow; C, green blue; N, dark blue; H, white; CH...π interactions, yellow dashes.



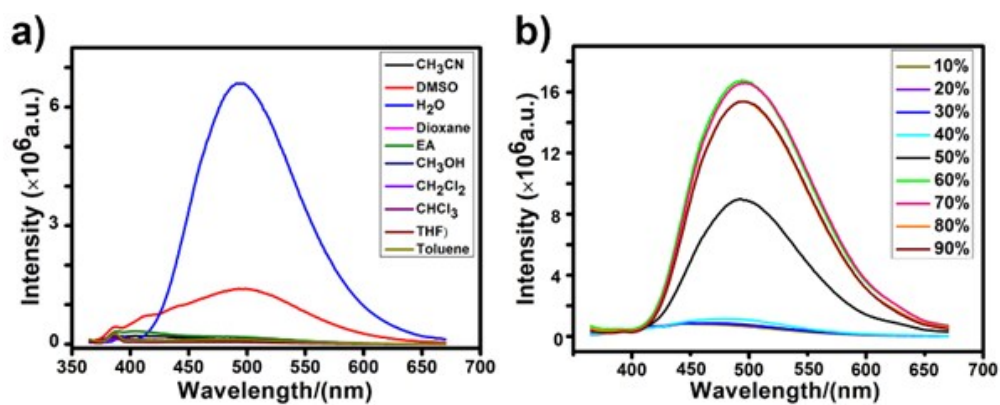
**Figure S15.** potential diagram of a cage **2**.

**Table S3.** The optical properties of **1** (20 μmol) and **2** (5 μmol)

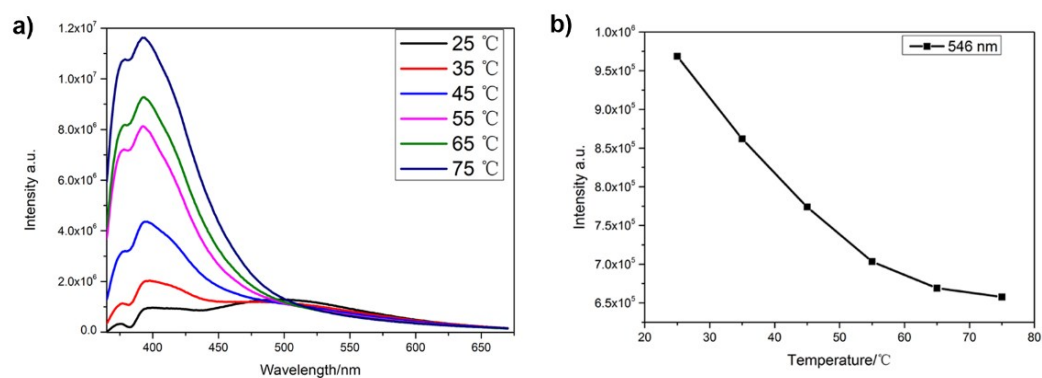
Sample	$\lambda_{\text{abs}}$	Em	$\Phi(\%)$
<b>1</b>	318nm	498	1.67
<b>2</b>	318nm	514nm	1.13



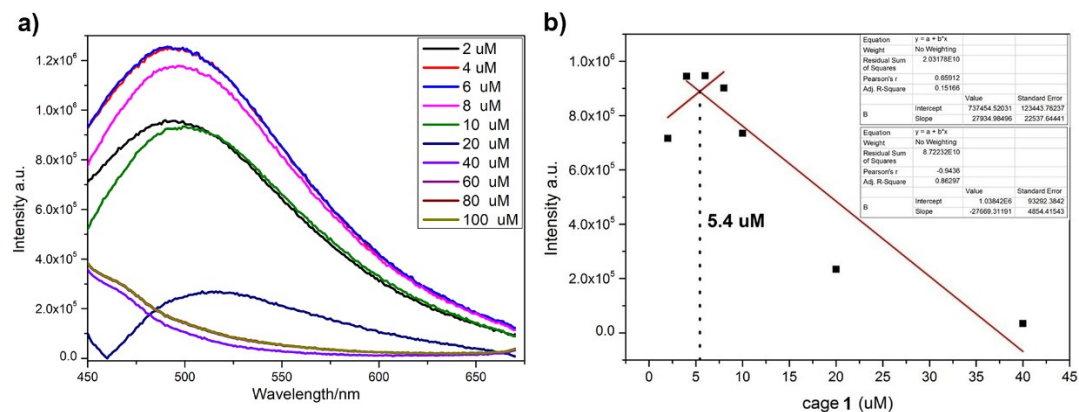
**Figure S16.** CIE spectra of **2** in different solvents ( $\lambda_{\text{ex}} = 345 \text{ nm}$ ), Ex/Em slit = 5 nm.



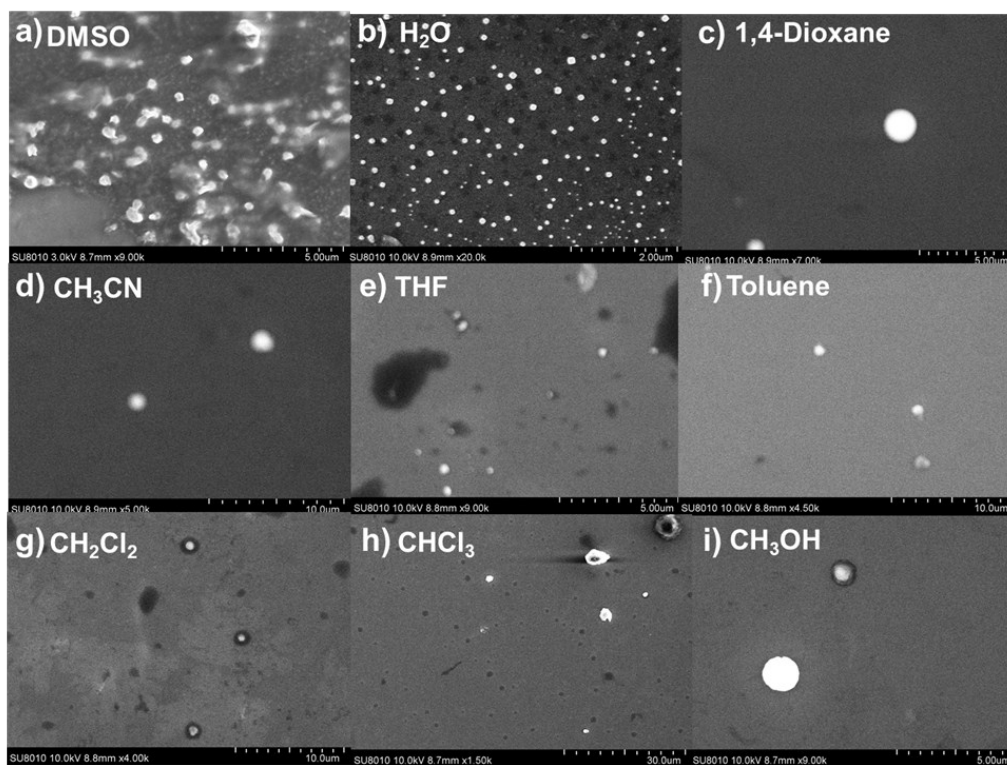
**Figure S17.** (a) Fluorescence spectra of **1** in different solvents. (b) Fluorescence spectra of **1** in H<sub>2</sub>O/DMSO (V:V)  $\lambda_{\text{ex}} = 345 \text{ nm}$ , Ex/Em slit = 5 nm.



**Figure S18.** Fluorescence spectra of **2** ( $5.0 \times 10^{-5}$  M) in DMSO ( $\lambda_{\text{ex}} = 345$  nm) at different temperature from 25 to 75 °C, Ex/Em slit = 5 nm.



**Figure S19.** Fluorescence emission spectra of **2** plot of maximum emission intensity at 545nm in DMSO.  $\lambda_{\text{ex}} = 345$  nm, Ex/Em slit = 5 nm.



**Figure S20.** SEM images of the **2** in different solvents.

## References

1. X. Zhou, H. Li, Z. Chi, Xi. Zhang, J. Zhang, B. Xu, Y. Zhang, S. Liu and J. Xu, *New J. Chem.* 2012, **36**, 685–693