<Electronic Supplementary Information>

Indistinguishability and distinguishability between amide and ester moieties in the construction and properties of M_6L_8 octahedron nanocages

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Refinements of structures with the SQUEEZE routine in PLATON.

For the three $[Pd_6L_8]^{12+}$ cages, nitrate anions and solvent molecules in the voids were highly disordered and were impossible to refine using conventional discrete-atom models. Therefore, the residual electron density was treated as diffuse contributions using the SQUEEZE of the PLATON software and located a series of voids (see below).[1]

For **1**,

```
 _platon_squeeze_void_nr
 _platon_squeeze_void_average_x
 _platon_squeeze_void_average_y
 _platon_squeeze_void_average_z
 _platon_squeeze_void_volume
 _platon_squeeze_void_count_electrons
 _platon_squeeze_void_content
  1 –0.022 –0.035 –0.002     26035     10461 ' '
_platon_squeeze_details
;
```

For **2**,

```
  _platon_squeeze_void_nr
  _platon_squeeze_void_average_x
  _platon_squeeze_void_average_y
  _platon_squeeze_void_average_z
  _platon_squeeze_void_volume
  _platon_squeeze_void_count_electrons
  _platon_squeeze_void_content
   1 –0.011 –0.009 –0.002     30627     11432 ' '
   2  0.000  0.500  0.000        23        29 ' '
   3  0.167  0.333  0.333        23        29 ' '
   4  0.167  0.833  0.333        23        29 ' '
   5  0.333  0.167  0.667        23        30 ' '
   6  0.500  0.000  0.000        23        29 ' '
   7  0.500  0.500  0.000        23        29 ' '
   8  0.667  0.833  0.333        23        30 ' '
   9  0.833  0.167  0.667        23        29 ' '
  10  0.833  0.667  0.667        23        29 ' '
_platon_squeeze_details
;
```

For **3**,

```
  _platon_squeeze_void_nr
  _platon_squeeze_void_average_x
  _platon_squeeze_void_average_y
  _platon_squeeze_void_average_z
  _platon_squeeze_void_volume
  _platon_squeeze_void_count_electrons
  _platon_squeeze_void_content
   1 –0.012 –0.009 –0.001     31443     11817 ' '
_platon_squeeze_details
;
```

References for X-ray crystallography:

1 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7-13.

Table S1 Crystal data for **1**, **2**, and **3**

	1	**2**	**3**
Complex	$[Pd_6(C_{36}H_{21}N_3O_6)_8]$-$(NO_3)_{12}\cdot 11H_2O\cdot$-$10(CH_3)_2SO$	$[Pd_6(C_{36}H_{21}N_6O_3)_8]$-$(NO_3)_{12}\cdot 10H_2O\cdot$-$13(CH_3)_2SO$	$[Pd_6(C_{36}H_{21}N_3O_6)_4(C_{36}H_{21}N_6O_3)_4]$-$(NO_3)_{12}\cdot 13H_2O\cdot 14(CH_3)_2SO$
Formula*	$C_{300}H_{204}N_{24}O_{54}S_6Pd_6$	$C_{288}H_{192}N_{48}O_{24}Pd_6$	$C_{291}H_{183}N_{36}O_{36}Pd_6$
M_w* (g mol^{-1})	5839.63	5347.30	5398.13
Cryst. system	Rhombohedral	Rhombohedral	Rhombohedral
Space group	*R*-3	*R*-3	*R*-3
a (Å)	28.372(1)	45.1264(7)	45.5042(7)
c (Å)	59.480(2)	27.6353(4)	27.6805(4)
γ (°)	120	120	120
V (Å^3)	41466(3)	48736(1)	48984(1)
σ* (Mg m^{-3})	0.702	0.547	0.549
Z	3	3	3
μ (mm^{-1})	0.254	0.193	0.193
Data corrected	216733	268667	261632
Completeness	100 (θ = 26.5°)	100 (θ = 26.5°)	100 (θ = 26.0°)
R_{int}	0.1453	0.1219	0.1280
Parameters	586	874	874
GoF on F^2	0.944	1.036	0.852
R_1 [$I > 2\sigma(I)$][a]	0.0889	0.0549	0.0626
wR_2 (all data)[b]	0.2398	0.1348	0.1843

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, [b] $wR_2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}$

******The anions and solvent molecules are missing from this formula since they could not be located due to extensive disorder.*

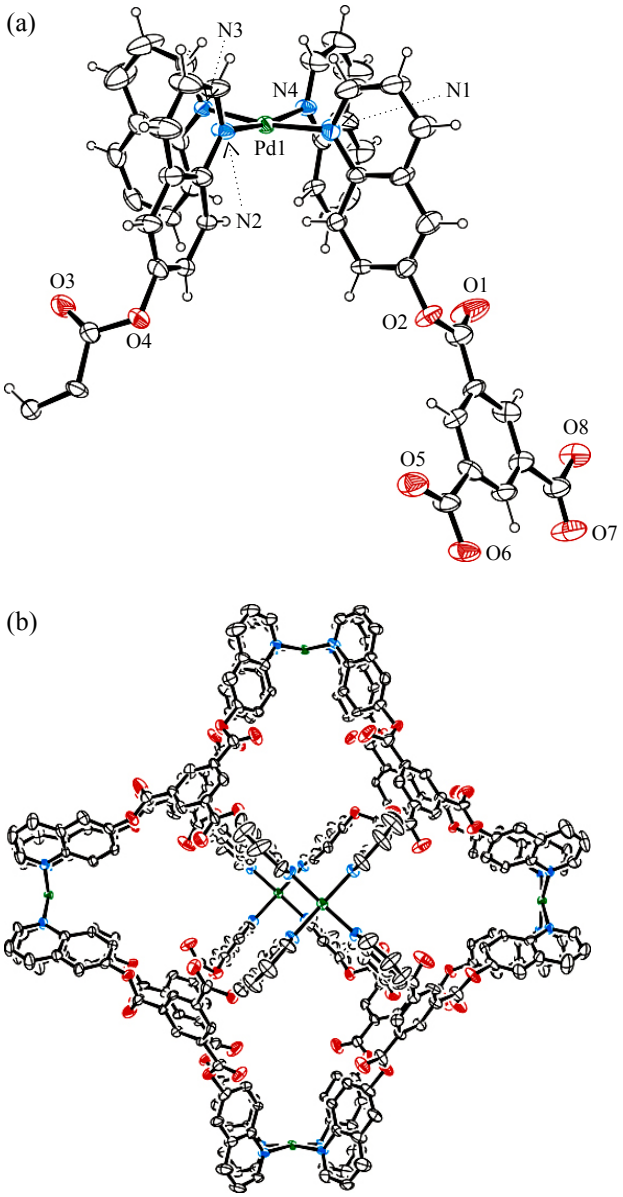

Fig. S1 ORTEP drawings of **1** showing the asymmetric unit (a) and the cage (b).

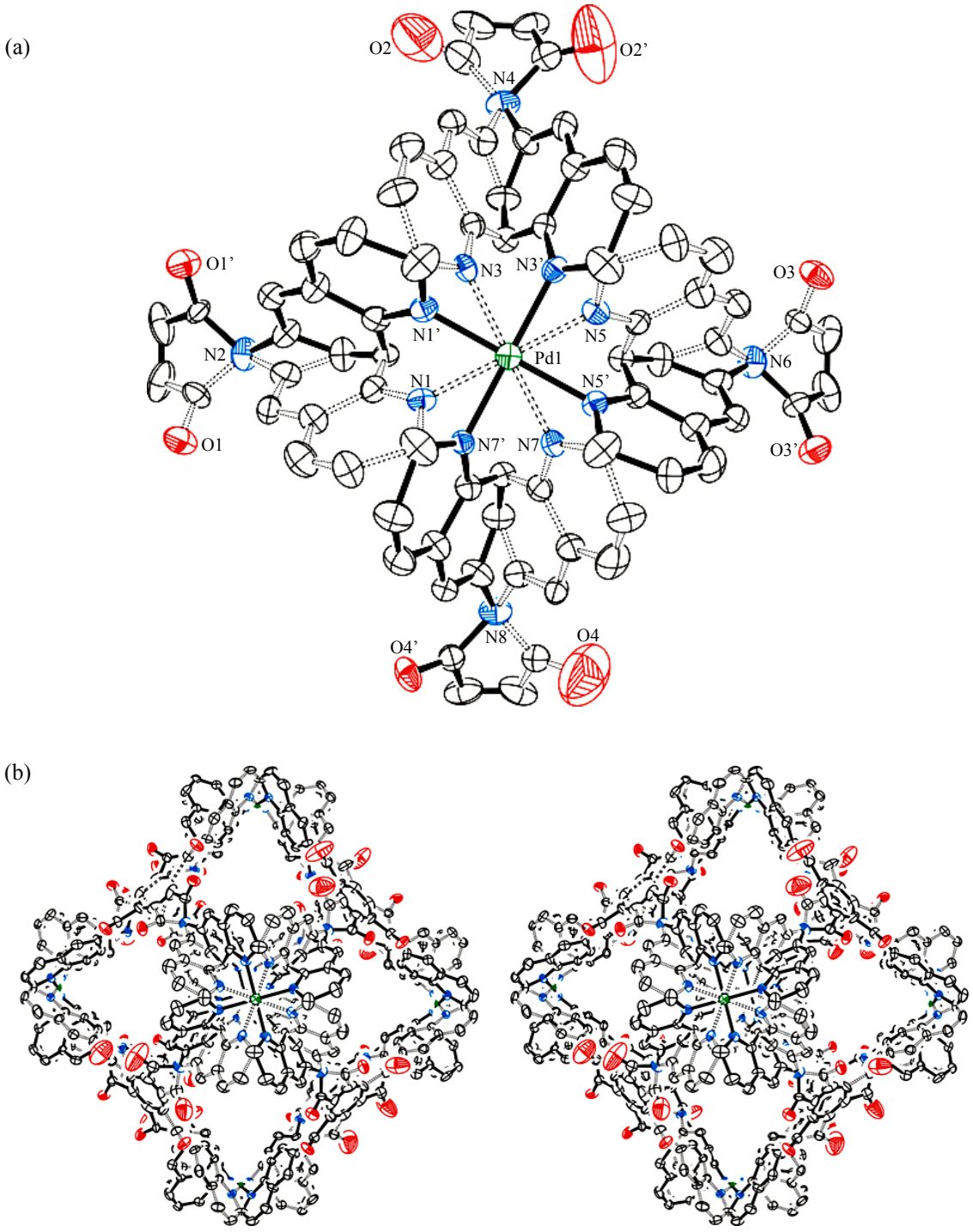

Fig. S2 Asymmetric unit (a) and stereo projection (b) of X-ray crystal structure for **2**. Hydrogen atoms, nitrate anions, and solvate molecules were omitted for clarity. Occupancies of each disorder are 50 : 50.

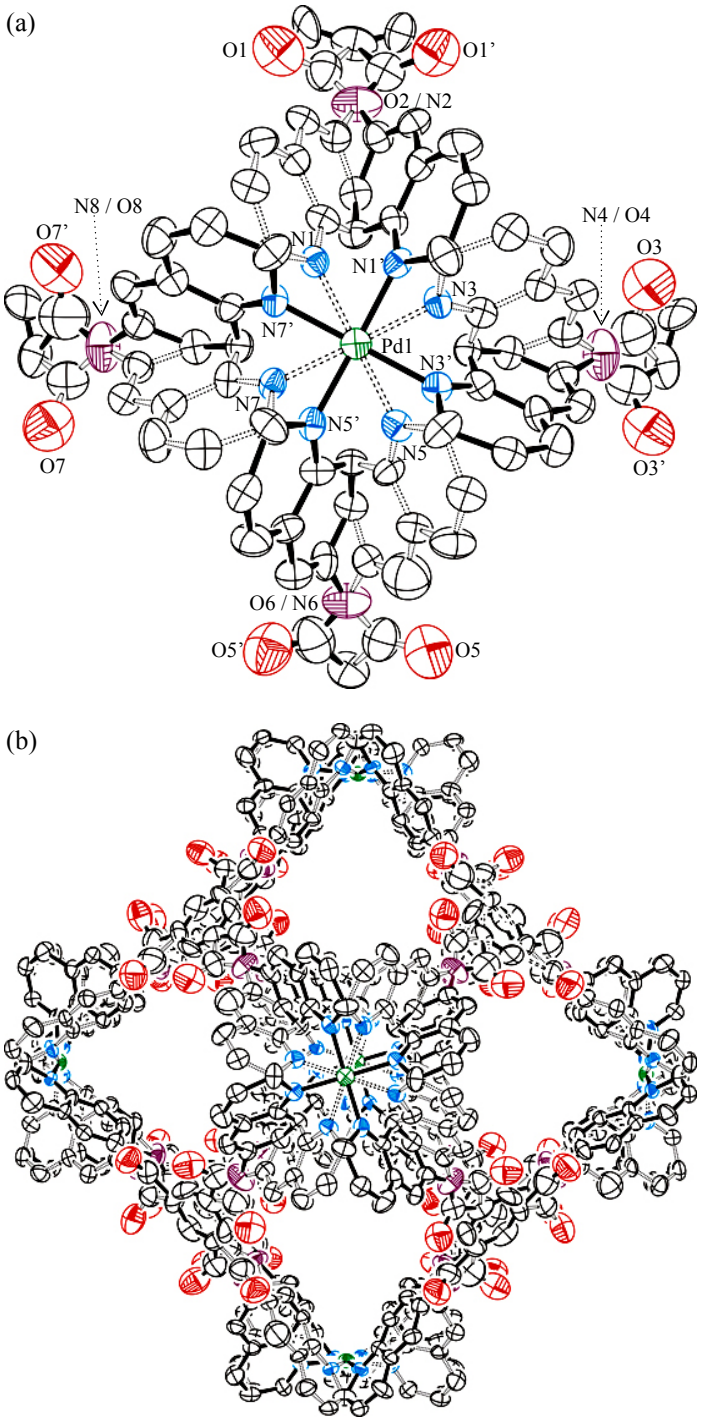

Fig. S3 ORTEP drawings of **3** showing the asymmetric unit (a) and the cage (b). Substitutional disorder between oxygen and nitrogen atoms was introduced. Hydrogen atoms, nitrate anions, and solvate molecules were omitted for clarity. Occupancies of each disorder are 50 : 50.

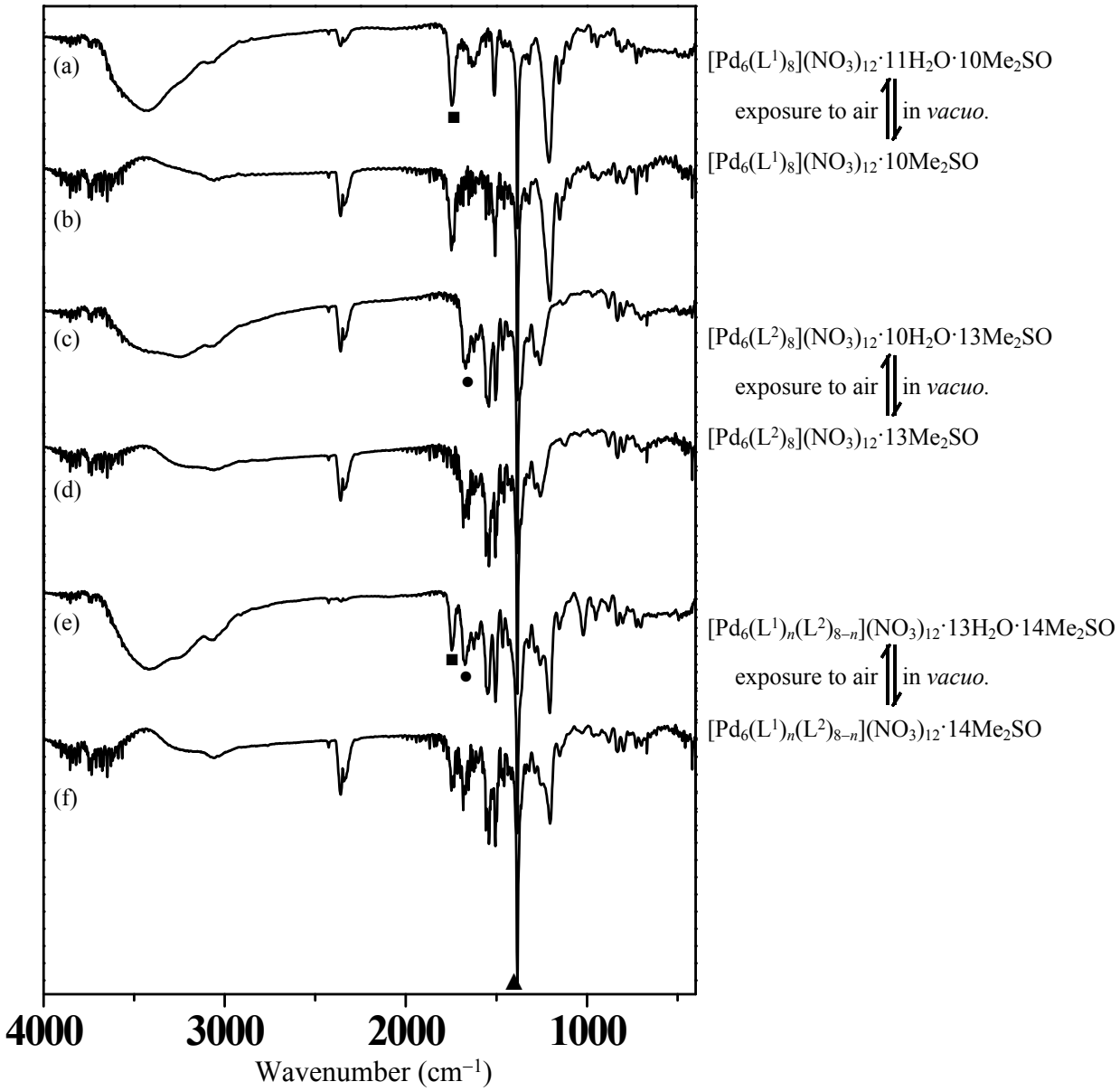

Fig. S4 IR spectra for **1** (a), **2** (c), and **3** (e). (b), (d), and (f) show the IR spectra of the dried samples of **1**, **2**, and **3**, respectively. Squares, circles, and triangle denote the stretching frequencies for carbonyl moieties of ester groups, carbonyl moieties of amide groups, and nitrate anions, respectively. The IR band around 2400 cm^{-1} comes from CO_2 in air.

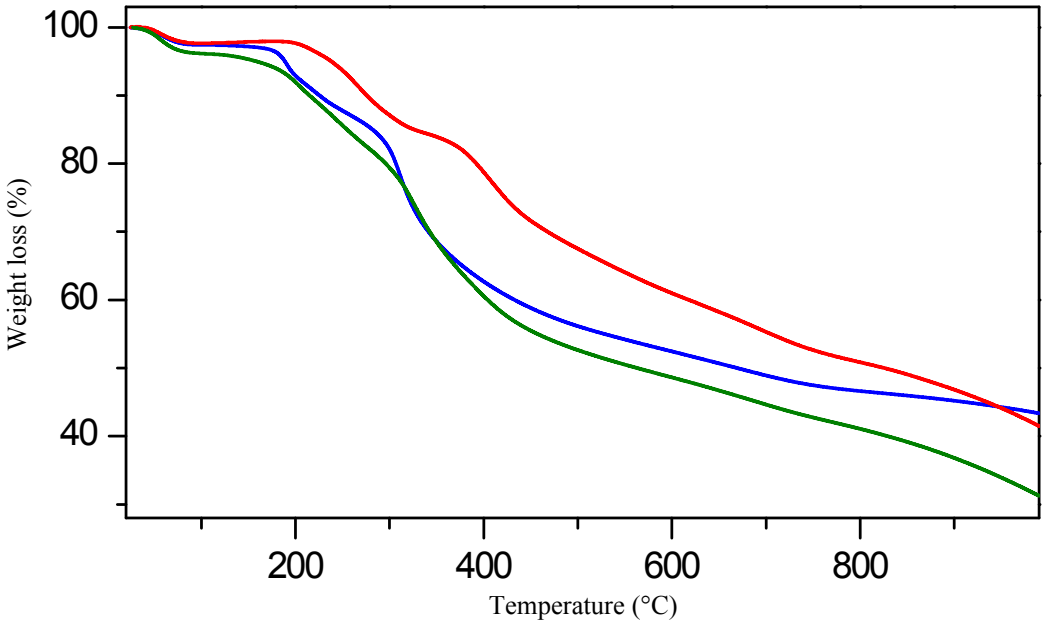

Fig. S5 TGA curves for **1** (blue), **2** (red), and **3** (green).

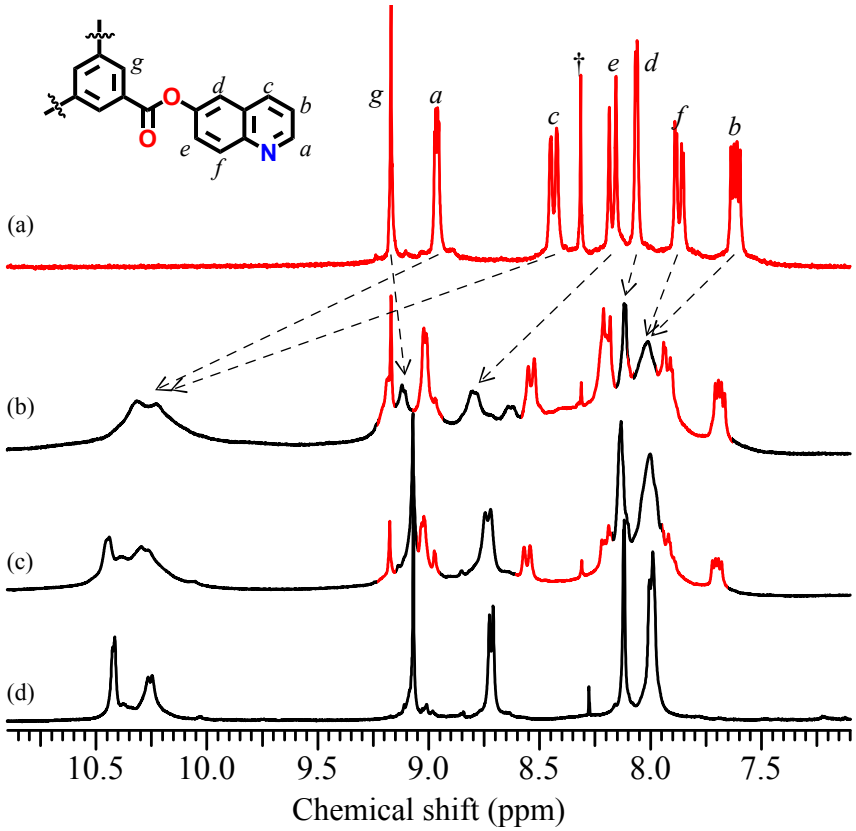

Fig. S6 ^{1}H NMR (Me_2SO-d_6) spectra for the self-assembly process of **1** from the components $Pd(NO_3)_2$ and L^1 in 3 : 4 mole ratio at 80 °C for 5 min (b), 3 h (c), and 7 h (d). (a) represents the resonance of L^1. Asterisk denotes $CHCl_3$.

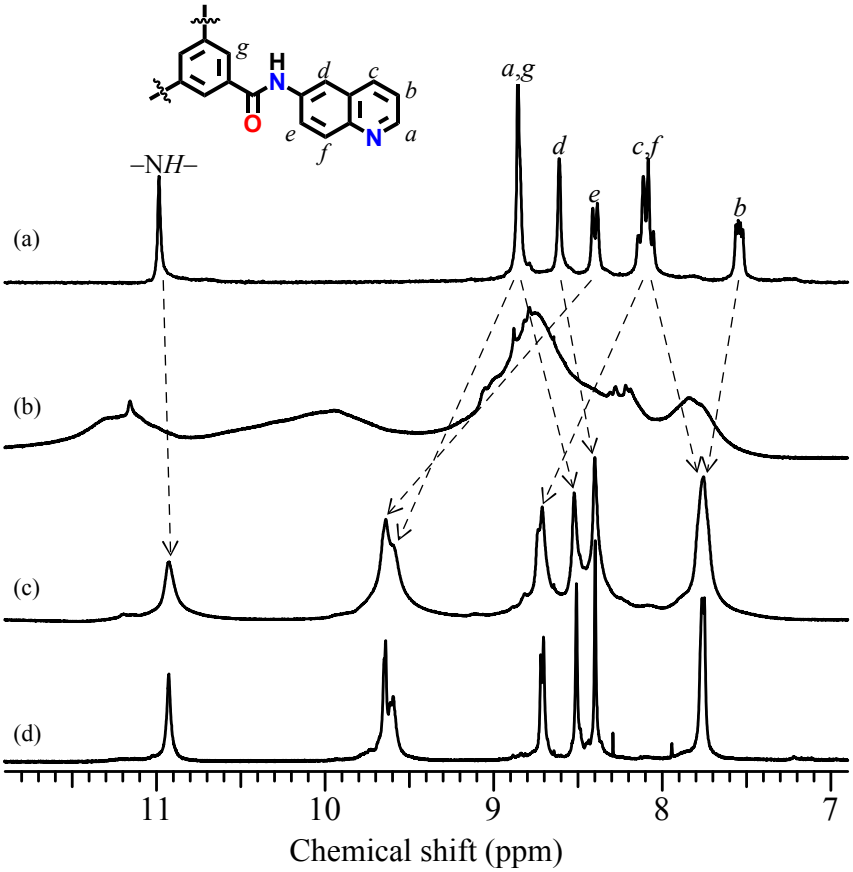

Fig. S7 ^{1}H NMR (Me_2SO-d_6) spectra for the self-assembly process of **2** from the components $Pd(NO_3)_2$ and L^2 in 3 : 4 mole ratio at 80 °C for 5 min (b), 3 h (c), and 7 h (d). (a) represents the resonance of L^2.

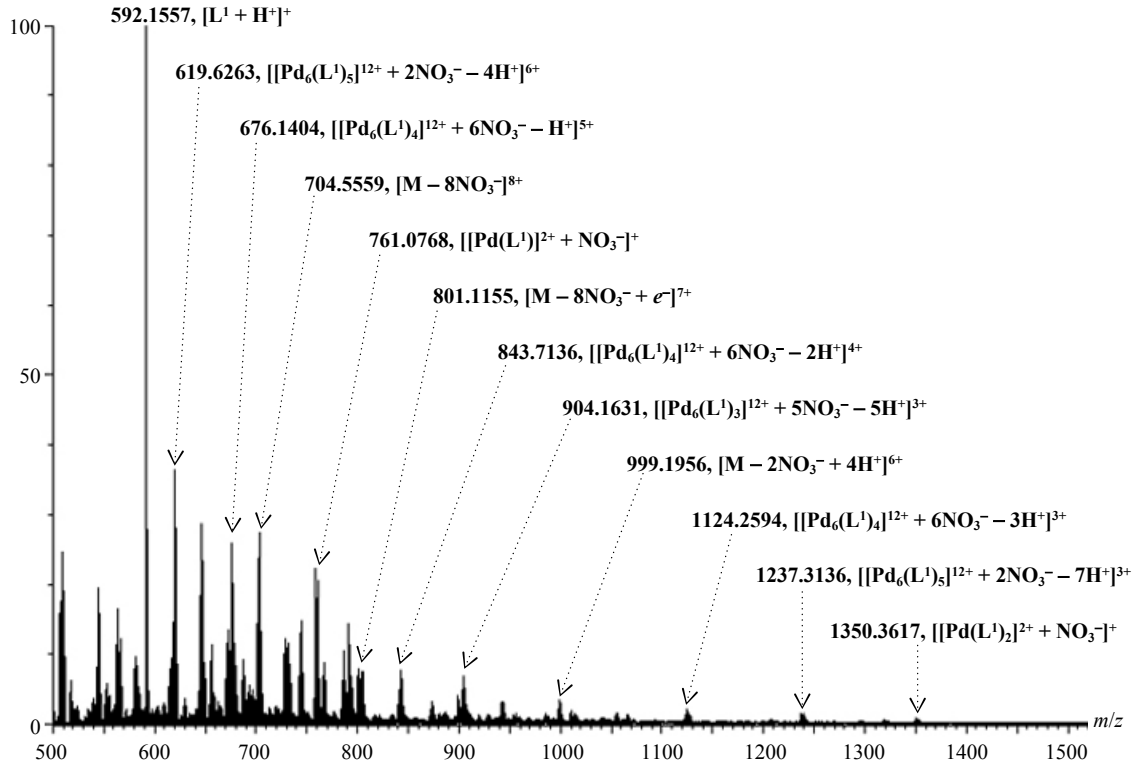

Fig. S8 ESI-MS data of **1**.

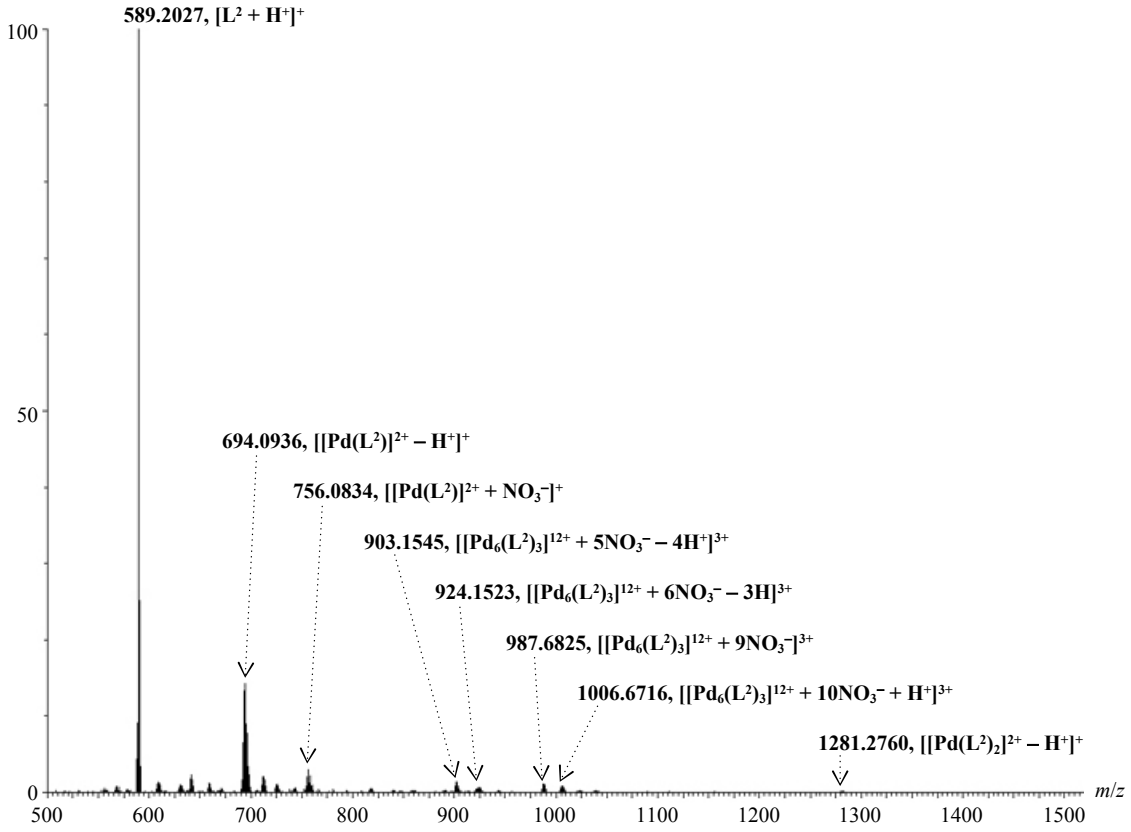

Fig. S9 ESI-MS data of **2**.

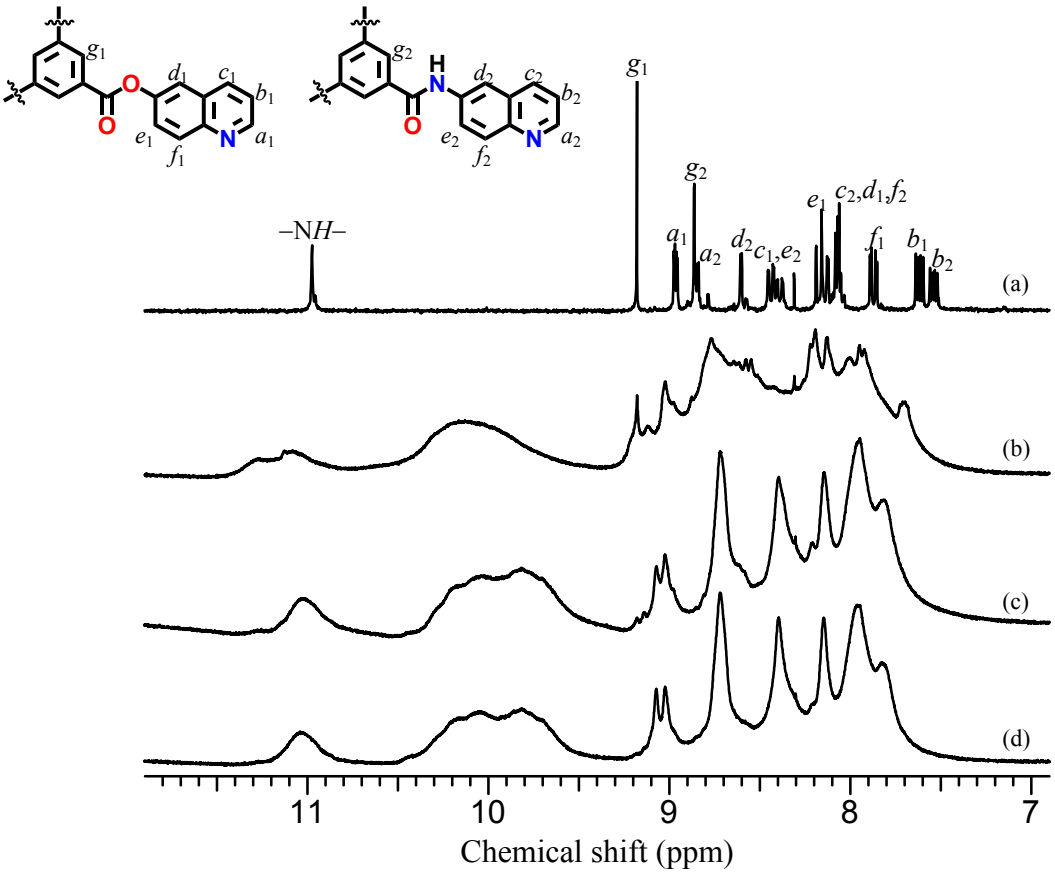

Fig. S10 ^{1}H NMR spectra (Me_2SO-d_6) for the self-assembly process of **3** from the components $Pd(NO_3)_2$, L^1, and L^2 in 3 : 2 : 2 mole ratio at 80 °C for 5 min (b), 3 h (c), and 7 h (d). (a) represents the resonance of a mixture of L^1 and L^2.

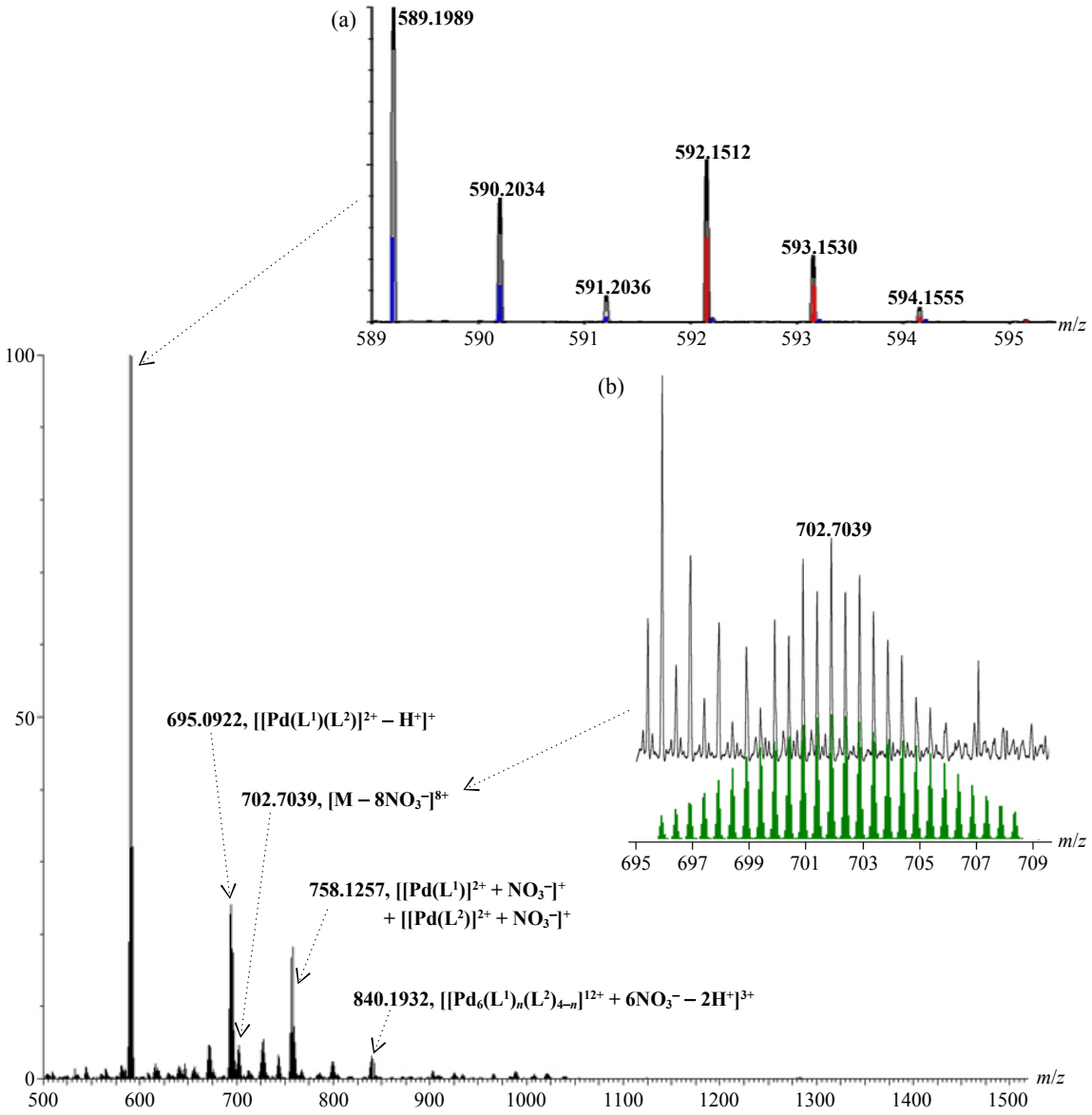

Fig. S11 ESI-MS data of **3**. (a) Calculated (L^1, red; L^2, blue) and experimental mass data (black) of $[L^1 + H^+]^+$ and $[L^2 + H^+]^+$. (b) Calculated (green) and experimental mass peaks (black) of $[M - 8NO_3]^{8+}$.

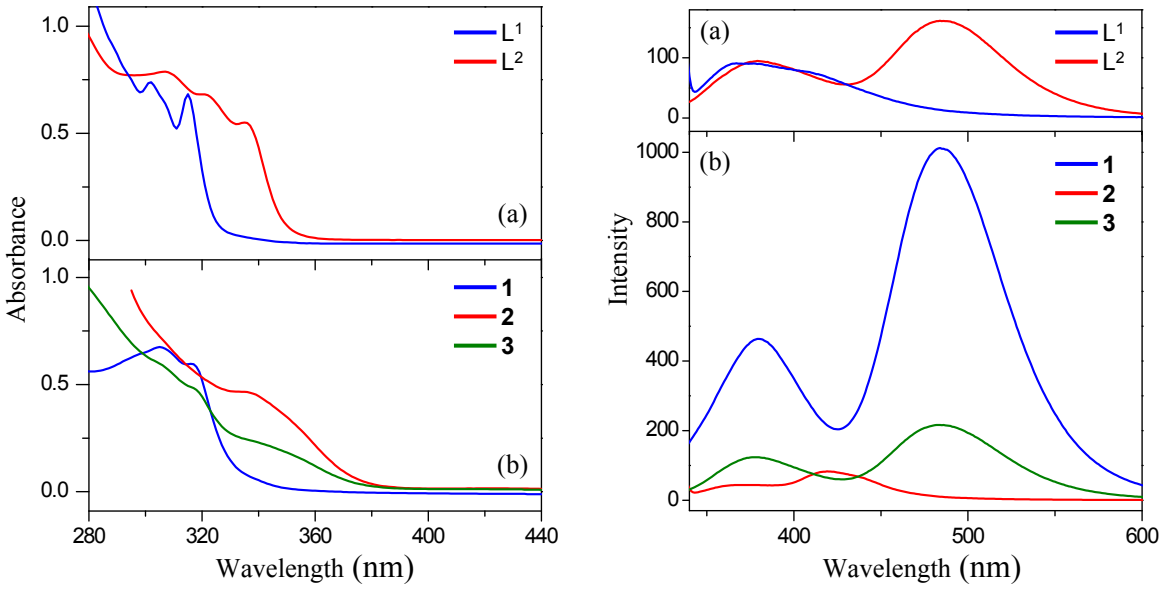

Fig. S12 UV-vis (left) and PL (right) spectra in a mixed DMF and water solution (*v*/*v* = 4:1) of the ligands (a) and cage complexes (b).