Electronic supplementary information (ESI)

Synthesis

The inorganic salt and acid were of commercial quality and were used without further purification. Q[8] was synthesized using published procedures.¹ Elemental analysis was carried out on a EURO EA-3000 element analyzer. Infrared spectra were recorded on a Bruker Vertex70 FT-IR spectrophotometer in the region 4000-400 cm⁻¹ using KBr pellets. Thermal analysis was performed on a Netzsch STA 409 PC thermal analyzer at a heating rate of 10°C/min in nitrogen.

Preparation of $\{Cs(H_2O)[(Hyb)_2@Q[8]]_2\}^+ 2Hyb \cdot CI \cdot 24H_2O.$

A mixture of Q[8]·18H₂O (250 mg, 166 mmol) and a 6-fold excess of **Hyb** (137 mg, 0.996 mmol) was dissolved in ~20 mL of 6 mol·L⁻¹ HCl at 50°C while being stirred until the Q[8] and **Hyq** dissolved completely. An 8-fold excess of CsCl (280 mg, 1.328 mmol) was added and the solution was again stirred for 5 min. The solution was allowed to stand to allow slow evaporation in air at room temperature. Colorless crystals were obtained from the solution over the course of two weeks. The yield in terms of Q[8] was 51%. Anal. Calcd for C₁₃₈H₁₈₄N₆₄O₇₆CsCl: C 40.37, H, 4.47, N, 21.83. Found: C, 41.07; H, 4.05; N, 21.91.

The resulted 3D framework composed of multifused one dimensional coordination polymers incorporating caesium cation ions which link the adjacent Q[8]-based one dimensional coordination polymers through coordination to their portal oxygens. ESI-1a-d show this 3D framework from different directions respectively.



ESI-1a-d 3D framework with different linear channels obseved from different directions respectively

Comparison of the FT-IR spectra reveals a obvious shift of the vibration of portal carbonyl of Q[8] in the crystals of the compound. The absorption band of portal carbonyl shifts down with ~9 cm⁻¹, further confirming that both of the included guest Hyb and the coordinated Cs⁺ ion in the compounds interact with portal carbonyls of Q[8]. Figure 3 shows Fourier transform infrared (FT-IR) spectra of the free Q[8], the free guest Hyb and the crystals of the compound.



ESI-2. Fourier transform infrared spectra of the free Q[8], the free guest **Hyb** and the crystals of the compound.

Thermal analysis reveal obviously difference of the above mentioned compound from the free Q[8] (ESI-3). Comparison of the DSCand TG curves indicates that the free Q[8] shows a relatively simple variation: an endothermic band around ~72°C with a weight loss of ~20% corresponding to a fast dehydration, then a large endothermic band starting at ~360°C with a weight loss of ~41% corresponding to a decomposition of Q[8]; the free guest **Hyb** shows two endothermic bands which correspond to melt and decomposition of **Hyb** with peak temperatures at ~215°C and ~242°C, respectively; the compound shows a similar fast dehydration endothermic band with a minor weight loss of ~13.5%, which corresponds to the partial latticed water molecules in the compound. A weight loss of ~7 % starting at ~260°C and ending at ~360°C indicates a flat and broad endothermic band which could correspond to the decomposition of the latticed and included **Hyb** in the compound, the host Q[8] shows a large endothermic band with a peak temperature at ~450°C which is delayed by about ~40°C compared to the free Q[8], suggesting that the coordination of the Cs metal ions to Q[8] leads to the stabilization of the Q[8].



ESI-3. Differential scanning calorimetry and theromgravimetry curves of the free Q[8], the free guest **Hyb**, and the crystals of the compound in N₂.

References

1 (a) J. Kim, I. S. Jung, S. Y. Kim, E. Lee, J. K. Kang, S. Sakamoto, K. Yamaguchi and K. Kim, *J. Am. Chem. Soc.*, 2000, **122**, 540; (b) patent: A. I. Day and A. P. Arnold, Method for synthesis cucurbiturils, WO 0068232, **2000**, 8.