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Outer surface interaction to drive cucurbit[8]uril-based supramolecular frameworks: possible application in gold recovery

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Experimental Section

Reagents. Q[8] was prepared and purified according to the method developed in our laboratory.^{S1} All chemicals {HAuCl4·3H₂O, ZnCl₂, CdCl₂·2.5H₂O, NiCl₂·6H₂O, CoCl₂·6H₂O, MnCl₂·4H₂O, FeCl₃·6H₂O, CuCl₂·2H₂O, H₂PtCl₆·xH₂O and N₂H₄·H₂O (80%, wt%)} and solvents (HCl, HNO₃) are analytical reagent and used as received.

Preparation of 1.

Method 1: Au(III) (2.50 mM HAuCl4, 1.0 ml) was mixed with Q[8] (1.25 mM, 1.0 ml) in an aqueous HCl solution (6 M) at room temperature within a few days. Yellow single crystals were obtained.

Method 2: Au(III) (2.06 mM HAuCl4, 1.0 ml) was added into Q[8] (1.03 mM, 1.0 ml) in aqueous HNO3 solution (3.5 M) at 70 $^{\circ}$ C, then cooled it to room temperature for a few days. Yellow single crystals were obtained.

Method 3: A mixture of Q[8] (5.00 mM, 5.0 mL) and HAuCl₄ (10.00 mM 5.0 mL) in aqueous HCl solution (6 M) was placed at room temperature, the yellow precipitate occurred immediately. Then the precipitate was collected, washed three times with aqueous HCl solution (6 M), dried in air (yield 80%, based on Q[8]·10H₂O). The yellow precipitate was obtained and verified by the PXRD. The pattern of the yellow precipitate is consistent with the simulated one (see Figure S1).

Method 4: HAuCl₄ (6.18 mM 5.0 mL) was mixed with Q[8] (3.09 mM, 5.0 mL) in aqueous HNO₃ solution (3.5 M) at at 70 °C, which was cooled to room temperature, the yellow precipitate occurred immediately. The precipitate was collected, washed three times with aqueous HNO₃ solution, dried in air (yield 90%, based on Q[8]·10H₂O). The yellow precipitate was obtained and verified by the PXRD. The pattern of the yellow precipitate is consistent with the simulated one (see Figure S1).

Preparation of 2.

 $Q[8]\cdot 10H_2O$ (100 mg) dissolved in hot HNO_3 (3.5 M, 20 mL) with stirring, then cooled the solution to room temperature and placed in a dark place for a few days. Colorless crystals were obtained in 50% yield based on $Q[8]\cdot 10H_2O$ (see Figure S2).

Preparation of 3.

 $Q[8] \cdot 10H_2O$ (100 mg) dissolved in hot HCl (6 M, 20 mL) at stirring, then cooled the solution to room temperature and placed in a dark place for a few days. Colorless crystals were obtained in 50% yield based on $Q[8] \cdot 10H_2O$ (see Figure S3).

Preparation of 4.

Q[8] (10 mg, 0.007 mmol) and H₂PtCl₆ (1.5 mg, 0.014 mmol) were dissolved in 6.0 M HCl (3

mL). The solutions were left to stand, allowing the volatiles to slowly evaporate in air at room temperature. Light-orange crystals were obtained from the solution within a few days.

Co-precipitation experiments: Q[8] (5.00 mM, 5.0 mL) with HAuCl₄ (20.00 mM, 2.5 mL) and chloride metal salts (20.00 mM, 2.5 mL) in aqueous HCl solution (6 M) have been performed, and the chloride metal salts were ZnCl₂, CdCl₂, NiCl₂, CoCl₂, MnCl₂, FeCl₃, and CuCl₂, in addition of H₂PtCl₆, respectively. A yellow precipitate formed immediately. The yellow precipitate was filtered, washed three times with aqueous HCl solution, and then dried to yield the samples for EDS and PXRD (see Figure S4, S6).

Similarly, a mixture of HAuCl₄ (6.18 mM, 5.0 mL) and chloride metal salts (30.90 mM, 1.0 mL) was added into Q[8] (3.09 mM, 5.0 mL) in aqueous HNO₃ solution (3.5 M) at 70 °C. The chloride metal salts were ZnCl₂, CdCl₂, NiCl₂, CoCl₂, MnCl₂, FeCl₃, and CuCl₂, in addition of H₂PtCl₆, respectively. A yellow precipitate formed immediately. The yellow precipitate was filtered, washed three times with aqueous HNO₃ solution, and dried to yield the samples for EDS and PXRD (see Figure S5, S7).

Reduction experiments of [AuCl₄]⁻: A (0.1069 g) dispersed in water (30.0 mL) and heated to 50 °C with stirring, then dropped 3.0 mL 80% N_2H_4 · H_2O in the suspension liquid, black precipitate occurred immediately. Centrifuged the reaction solution at 10,000 rpm for 5 min after 2 hours. Removed supernatant and washed the precipitate with 30 mL 6 M HCl for three times to dissolve Q[8], and collected the metallic luster Au powder (0.0103 g) (see Figure S11, S12).

Movie 1: Dropping 1 mL HAuCl₄ (ca: 13.26 mM in 6 M aqueous HCl solution) into 1 mL Q[8] in aqueous hydrochloric acid (ca: 6.63 mM in 6 M aqueous HCl solution), the yellow precipitation was formed immediately. The photo inserted into the movie is the SEM of the precipitation.

Energy dispersive spectrometry (EDS): EDS was measured on a field emission scanning electron micro-analyser (Hitachi SU-8010).

Powder X-ray diffraction (PXRD): PXRD data of representative samples were collected on a PANalytical B. V. EmpyreanX X-ray diffractometer using Cu radiation (Ka1/Ka2 ½ 1.540598 Å, 45 kV, 40 mA) at room temperature.

X-ray crystallographic analysis of 2 and 3. Crystallographic data collections for 2 and 3 were carried out on a Bruker Smart Apex II CCD area detector diffractometer with graphite-monochromated Mo K α radiation (λ = 0.71073 Å) at about 293(2) K using ω -scan technique. The diffraction data were integrated by using the SAINT program,^{S2} which was also used for

the intensity corrections for the Lorentz and polarization effects. Semiempirical absorption corrections were applied using SADABS program.^{S3} The structures were solved by direct methods, and all of the non-hydrogen atoms were refined anisotropically on F² by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package.^{S4, S5} All the non-hydrogen atoms were refined anisotropically, and the carbon-bound hydrogen atoms were introduced at calculated positions, and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. The details of the crystal parameters, data collection and refinements for the complexes are summarized in Table S1. CCDC numbers of 1953105 for **2** and 1953100 for **3**, containing the supplementary crystallographic data for this paper can be obtained free of charge from the Cambridge Crystallographic Data Centre via ww.ccdc.cam.ac.uk/data_request/cif.

Compound	1	2	3	4
Empirical formula	$C_{48}H_{48}N_{32}O_{16}Au_2Cl_8$	$C_{48}H_{48}N_{32}O_{16}$	$C_{48}H_{118}N_{32}O_{51}$	C ₉₆ H ₂₅₀ Cl ₆ N ₆₄ O ₁₀₈ Pt
Formula weight	2006.72	1329.18	1959.74	4437.39
Crystal system	trigonal	trigonal	tetragonal	tetragonal
Space group	R -3 (148)	R -3 (148)	I 41/a (88)	I 41/a (88)
a (Å)	29.869(3)	29.828(3)	28.225(5)	28.5200(19)
c (Å)	24.766(4)	24.556(3)	22.062(4)	21.998(3)
γ (°)	120.00	120.00	90.00	90.00
T (K)	93(2)	293(2)	296(2)	293(2)
$V(Å^3)$	19135(4)	18920(4)	17575(7)	17892.96(297)
Ζ	9	9	8	4
$Dc (g \cdot cm^{-3})$	1.9346	1.050	1.481	1.64713
μ (mm ⁻¹)	3.811	0.082	0.132	1.004
<i>F</i> (000)	11196	6192	8304	9272
Data collected	7757	7497	11024	7870
Independent data	6331	4933	6833	5807
$R_{ m int}$	0.0520	0.0518	0.0794	0.0662
Goodness-of-fit	1.002	1.081	1.256	1.093
$R_1 \left[I \ge 2\sigma \left(I\right)\right]$	0.0415	0.0516	0.0742	0.0682
$wR_2 [I \ge 2\sigma (I)]$	0.1200	0.1351	0.1711	0.2003
R_1 (all data) ^a	0.0484	0.0822	0.1255	0.0845
wR_2 (all data) ^b	0.1219	0.1456	0.1941	0.2121
CCDC number	1816481	1953105	1953100	1434827

 Table S1.
 The details of the crystal parameters, data collection and refinements of 1 to 4.

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|. \ {}^{b}wR_{2} = |\Sigma w(|F_{o}|^{2} - |F_{c}|^{2})| / \Sigma |w(F_{o})^{2}|^{1/2}, \text{ where } w = 1 / [\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP]. \qquad P = (F_{o}^{2} + 2F_{c}^{2}) / 3.$



Figure S1. The crystal structure (top) and PXRD patterns (bottom) of the as-synthsized sample of **3**.



Figure S2. The PXRD patterns of as-synthsized samples of 1 in the aqueous solution of HCl and HNO₃.



Figure S3. The PXRD patterns of as-synthsized sample of **2**.



Figure S4. The EDS patterns of the co-precipitation of as-synthesided 1 in the present of (a) $ZnCl_2$, (b) $CdCl_2$, (c) $NiCl_2$, (d) $CoCl_2$, (e) $MnCl_2$, (f) $FeCl_3$, (g) $CuCl_2$ and (h) H_2PtCl_6 , respectively in HCl aqueous solution.



Figure S5. The PXRDs of all co-precipitation of as-synthesided 1 in HCl aqueous solution.



Figure S6. The EDS patterns of the co-precipitation of as-synthesided **1** in the absent (a) and present of (b) $ZnCl_2$, (c) $CdCl_2$, (d) $NiCl_2$, (e) $CoCl_2$, (f) $MnCl_2$, (g) $FeCl_3$, (h) $CuCl_2$ and (i) H_2PtCl_6 , respectively in HNO₃ aqueous solution.



Figure S7. The PXRDs of all co-precipitation of as-synthesided 1 in HNO₃ aqueous solution.



Figure S8. The crystal structure of 4.



Figure S9. The PXRDs of co-precipitation as-synthesided 1 in the abesent (black) and present (red) of of H_2PtCl_6 in HCl aqueous solution.



Figure S10. The EDS patterns of co-precipitation of as-synthesided 1 in the absent (top, red) and present (bottom, black) of H_2PtCl_6 in HCl aqueous solution.



Figure S11. The photographs of as-synthesized sample 1 before (a) and after (b, c) reduction by hydrazine hydrate, wherein (b) was unwashed, and (c) was washed with hydrochloric acid.



Figure S12. The PXRD patterns of as-synthsized sample 1 before (a) and after (b, c) reduction by hydrazine hydrate, wherein (b) was unwashed, and (c) was washed with hydrochloric acid.



Figure S13. The EDS of as-synthsized sample **1** before (black) and after (red) reduction by hydrazine hydrate, which was washed with hydrochloric acid .

Reference:

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