Supporting Information

Two 2D Metal-Calixarene Aggregates Incorporating Pre-designed Coordination Nanocages

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Experimental Section.

Materials and Measurements: p-tert-Butylthiacalix[4]arene (H4TC4A)¹ was synthesized by literature method and other reagents were purchased from commercial sources and used as received. Co, Fe and S analyses were determined by a HITACHI S-4800 Scanning Electron Microscope. TGA measurement is performed on a NETZSCH STA 449F3. Single crystal diffraction measurements were performed on a Bruker APEX CCD system with Mo-K α radiation ($\lambda = 0.71073$ Å).

Synthesis of CIAC-109: Yellow single crystals of CIAC-109 were obtained from the reaction of the mixture of *p*-tert-butylthiacalix[4]arene (0.0904 g, 0.125 mmol), FeCl₂·4H₂O (0.1010 g, 0.5 mmol), isonicotinic acid (INA) (0.06 g, 0.5 mmol), triethylamine (several drops), CH₃OH (3 ml) and N,N-dimethylformamide (DMF) (3 ml) in a 20 ml Teflon-lined autoclave which was kept at 130 °C for 3 days and then slowly cooled to 20 °C at about 4 °C / h. The crystals were isolated by filtration and then washed with methanol. Yield: 0.08 g, ca. 40 % with respect to calixarene. Elemental analysis: calculated (%) for $(C_2H_5)_3NH[Fe_4Cl(C_{40}H_{44}S_4O_4)(C_6H_4NO_2)_4(FeCl_2)] \cdot 4DMF$, C 49.55, H 5.24, N 6.34; found (%): C 47.61, H 5.23, N 6.22.

Synthesis of CIAC-110: Purple single crystals of CIAC-110 were obtained by the analogous method with $CoCl_2 \cdot 6H_2O$ replacing $FeCl_2 \cdot 4H_2O$. Yield: 0.12 g, ca. 45 % with respect to calixarene. Elemental analysis: calculated (%) for $(C_2H_5)_3NH[Co_4Cl (C_{40}H_{44}S_4O_4)(C_6H_4NO_2)_4(CoCl_2)] \cdot 4DMF$, C 49.17, H 5.19, N 6.29; found (%): C 46.89, H 5.20, N 6.05.

Crystallographic Analyses

The intensity data were recorded on a Bruker APEX CCD system with Mo-Ka radiation ($\lambda = 0.71073$ Å). The crystal structures were solved by means of Direct F^2 employing on Methods and refined full-matrix least squares (SHELXTL-97).² The diffraction data were treated by the SQUEEZE method as PLATON.³ All non-hydrogen implemented in atoms refined were anisotropically, and hydrogen atoms of the organic ligands and the hydroxide anion were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The unidentified solvent molecules and $(C_2H_5)_3NH^+$ cations were not included for all the two structures. Since the crystals do not diffract very well due to the structure disorder, the R factors in the final structure refinement are relatively large, but typical in such system. CCDC-927410-927411 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Gas Adsorption Analyses

Activation of the compounds. As-synthesized samples of **CIAC-109** were immersed in the methanol solution for 3 days, during which the solution/solvent was decanted and freshly replenished three times. Obtained samples were immersed in acetone for 12 h, during which the activation solvent was replenished more than four times. The sample was extracted by supercritical

S3

CO₂. Typically, the chamber containing the sample and liquid CO₂ was heated up around 40 °C and kept under the supercritical condition (~11 MPa) for 1 h. CO₂ was slowly vented (ca. 1 h) from the chamber at around 40 °C, yielding activated compounds.

Low-pressure gas sorption measurements

Low-pressure gas sorption experiments were carried out on a Micromeritics ASAP-2020M automatic volumetric instrument. Ultrahigh-purity-grade N_2 , H_2 and CO_2 gases were used in the sorption measurements. The N_2 and H_2 isotherms were recorded in a liquid nitrogen bath (77 K) while that of CO_2 in a mixed ice-water system.

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Fig. S1 Molecular structure of nanocage CIAC-109.



Fig. S2 Staggering layers and their stacking (a) and the extended supramolecular structure viewed along the c axis (b).



Fig. S3 Alternate stacking of the staggered layers and the formed axiolitic supramolecular void being of approximately $10.6 \times 24.9 \text{ Å}^2$.



Fig. S4 IR spectrum for compound **CIAC-109.** IR (KBr pellets): 3400 (m): v_{OH} ; 2957 (s): v_{CH3}^{as} ; 2867(m): v_{CH3}^{s} ; 1664 (s): $v_{C=O}$ (DMF); 1602 (s): v_{COO-}^{as} ; 1463 (m): δ_{CH3} ; 1401 (s): $v_{COO-}^{as} + \delta_{CH3}$.



Fig. S5 IR spectrum for compound **CIAC-110.** IR (KBr pellets): 3400 (m): v_{OH} ; 2957 (s): v_{CH3}^{as} ; 2867(m): v_{CH3}^{s} ; 1660 (s): $v_{C=0}$ (DMF); 1604 (s): v_{COO-}^{as} ; 1465 (m): δ_{CH3} ; 1404 (s): $v_{COO-}^{as} + \delta_{CH3}$.







Fig. S7 TGA-DSC curves for CIAC-110.



Fig. S8 Powder XRD patterns of compound CIAC-109.



Fig. S9 Powder XRD patterns CIAC-110.



Fig. S10 Photographs showing the adsorption of I₂ from the cyclohexane solution by activated CIAC-109 after 12 h. (left: blank; middle: 3 mg CIAC-109; right: 5 mg *p*-tert-butylthiacalix[4]arene)

After the activated samples were immersed in a cyclohexane solution of I_2 (0.5 ml containing 0.1 mg I_2 and one drop of ethanol) for 12 hours, the color of the solution became lighter obviously, which indicates that I_2 is adsorbed by the porous compound. After washing the adsorbed samples, the washing cyclohexane kept colorless, which means that I_2 diffused into the cavities of the compound but not adsorbed on the surfaces. For comparison, the cyclohexane solution of I_2 without the samples or with 5 mg of *p*-tert-butylthiacalix[4]arene was kept unchanged.

It is also found that the unactivated samples hardly adsorbed I_2 from the solution. That means, it is necessary to remove the solvent molecules in the structure to activate the porous compound, and the activation did not damage the structure because the calixarene molecules can not adsorb iodine from the cyclohexane solution and cyclohexane cannot wash the iodine adsorbed off.



Fig. S11 SEM images of the reddish brown product of **CIAC-109** after calcination in air (a and b) and its EDS (c) and XRD (d) patterns. The crystalline size calculated from XRD using Scherrer equation yields the average particle





Fig. S12 High magnification SEM images of the reddish brown residue α -Fe₂O₃, which shows that the grain sizes of these nanoparticles are of 30-40 nm.