Supporting Information

A Giant Coordination Cage based on Sulfonylcalix[4]arenes

Shangchao Du, Chunhua Hu, Ji-Chang Xiao, Huaqiao Tan, and Wuping Liao*

Experimental Section

Materials and Measurements: *p-tert*-Butylsulfonylcalix[4]arene ($H_4SC4A\text{-}SO_2$)[1] and 4,4',4''-(benzene-1,3,5-triyl-tris(ethyne-2,1-diyl))tribenzoic acid (H_3BTE) [2] were synthesized by literature method and other reagents were purchased from commercial sources and used as received. Co 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-Kα radiation ($\lambda = 0.71073$ Å).

Synthesis of CIAC-105: Purple single crystals of **CIAC-105** were obtained from reaction of the mixture of *p-tert*-butylsulfonylcalix[4]arene (0.075 g, 0.09 mmol), $CoCl_2 \cdot 6H_2O$ (0.1 g, 0.4 mmol), 1,3,5-benzenetricarboxylic acid (H_3BTC) (0.02 g, 0.1 mmol), triethylamine (2 drops), CH_3OH (5 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: 0.14 g, ca. 70 % with respect to calixarene. The EDS analysis reveals that the molar ratio of Co : S : Cl = 49.45 : 49.27 : 1.28, comparable to the expected Co:S ratio (1:1). Elemental analysis: calculated (%) for $[(C_2H_5)_3NH]_6\ [Co_{24}(OH)_6(C_{40}H_{44}S_4O_{12})_6(C_9H_3O_6)_8] \cdot 72\ CH_3OH \cdot 48\ DMF$, C 45.40, H 7.67, N 5.81; found (%): C 43.36, H 5.96, N 6.28.

Synthesis of CIAC-106: Purple single crystals of **CIAC-106** were obtained by the analogous method with the mixture of *p-tert*-butylsulfonylcalix[4]arene (0.075 g, 0.09 mmol), $CoCl_2 \cdot 6H_2O$ (0.1 g, 0.4 mmol), 4,4',4''-benzene-1,3,5-triyl-tribenzoic acid (H_3BTB) (0.044 g, 0.1 mmol), triethylamine (2 drops) and N,N-dimethylacetamide (DMA) (3.0 ml). Yield: 0.16 g, ca. 50 % with respect to calixarene. The EDS analysis reveals that the molar ratio of Co : S : Cl = 44.01 : 52.67 :

3.33, comparable to the expected Co:S ratio (1:1). Elemental analysis: calculated (%) for $[(C_2H_5)_3NH]_6$ $[Co_{24}(OH)_6(C_{40}H_{44}S_4O_{12})_6(C_{27}H_{15}O_6)_8]$ · 178 DMA, C 55.21, H 8.04, N 9.84: found (%), C 45.75, H 6.96, N 9.13.

Synthesis of CIAC-107: Purple single crystals of **CIAC-107** were obtained by the analogous method with the mixture of *p-tert*-butylsulfonylcalix[4]arene (0.075 g, 0.09 mmol), $CoCl_2 \cdot 6H_2O$ (0.1 g, 0.4 mmol), 4,4*'*,4*"*-(benzene-1,3,5-triyl-tris(ethyne-2,1-diyl))tribenzoic acid (H_3BTE) (0.051 g, 0.1 mmol), triethylamine (2 drops) and N,N-dimethylacetamide (DMA) (3.0 ml). Yield: 0.12 g, ca. 30 % with respect to calixarene. The EDS analysis reveals that the molar ratio of Co : S : Cl = 47.37 : 52.13 : 0.50, comparable to the expected Co:S ratio (1:1). Elemental analysis: calculated (%) for $[(C_2H_5)_3NH]_6$ $[Co_{24}(OH)_6(C_{40}H_{44}S_4O_{12})_6(C_{33}H_{15}O_6)_8]$ · 128 DMA, C 56.38, H 7.34, N 8.37; found, C 47.79, H 6.48, N 9.76.

Crystallographic Analyses.

The intensity data were recorded on a Bruker APEX CCD system with Mo-Kα radiation (λ = 0.71073 Å). The crystal structures were solved by means of Direct Methods and refined employing full-matrix least squares on F^2 (SHELXTL-97).[3] The diffraction data were treated by the "SQUEEZE" method as implemented in PLATON.[4] All non-hydrogen atoms except the butyl group of **CIAC-106** were refined 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 six $(C_2H_5)_3NH^+$ cations were not included for all the three 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-869988 - 869990 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.

SQUEEZE results for these three compounds are as follows:

(1) CIAC-105

```
loop_
  _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   0.000   0.000   0.000       607       146 ' '
   2   0.399 -0.024   0.013     14154      6105 ' '
   3   0.000   0.000   0.330       165        61 ' '
   4   0.000   0.000   0.500       595       259 ' '
   5   0.000   0.000   0.671       165        59 ' '
   6   0.500   0.500   0.000       596       259 ' '
   7   0.500   0.500   0.500       607       146 ' '
   8   0.500   0.500   0.171       165        59 ' '
   9   0.500   0.500   0.829       164        61 ' '
```

SQUEEZE gives 7155 electrons/unit cell for the voids which are occupied by 12 $(C_2H_5)_3NH^+$ and solvents (DMF or CH_3OH). 12 $(C_2H_5)_3NH^+$ per unit cell give 696 e^-. It remains 7155 – 696 =

6459 e^-. So there are 174 DMF (40 e^-) molecules or 395 CH_3OH (18 e^-) molecules per unit cell and 87 DMF or 197 CH_3OH for each formula, respectively, since Z = 2. The suitable formula for this compound should be $[(C_2H_5)_3NH]_6\{[Co_4(SC4A)OH]_6(BTC)_8\}$ • 87 DMF or $[(C_2H_5)_3NH]_6\{[Co_4(SC4A)OH]_6(BTC)_8\}$ • 197 CH_3OH. It is difficult to determine the number of DMF or CH_3OH if there are mixed solvents in the structure.

(2) CIAC-106

```
loop_
   _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    0.000    0.000    0.000        1243          363 ' '
     2    0.449 -0.003 -0.002        45134        16433 ' '
     3    0.500    0.500    0.500        1242          363 ' '
```

That is SQUEEZE gives 17159 electrons/unit cell for the voids. The voids are occupied by 12 $(C_2H_5)_3NH^+$ and an amount of DMA molecules. Due to 12 $(C_2H_5)_3NH^+$ give 696 e^-, it remains 17159 – 696 = 16463 e^-. So there are 356 DMA molecules (48 e^-) per unit cell and 178 DMA for each formula, since Z = 2. The suitable formula for this compound should be $[(C_2H_5)_3NH]_6\{[Co_4(SC4A)OH]_6(BTB)_8\}$ • 178 DMA.

(3)CIAC-107

```
loop_
  _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    0.025 -0.012 -0.002        55011          12172 ' '
   2    0.001 -0.001    0.500          849            403 ' '
   3    0.500    0.500    0.000          883            423 ' '
```

SQUEEZE gives 12172 electrons/unit cell for the voids. 12 $(C_2H_5)_3NH^+$ per unit cell give 696 e^-. It remains 12996 – 696 = 12300 e^-. So there are 256 DMA molecules (48 e^-) per unit cell and 128 DMA for each formula, since Z = 2. The suitable formula for this compound should be $[(C_2H_5)_3NH]_6\{[Co_4(SC4A)OH]_6(BTE)_8\}$ • 128 DMA.

Gas Adsorption Analyses

Activation of Cages. As-synthesized samples of **CIAC-107** 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 CO_2. And then the chamber containing the sample and liquid CO_2 was heated up around 40 °C and kept under the supercritical condition (typically 11 MPa) for 1 h. CO_2 was slowly vented (ca. 1 h) from the chamber at around 40 °C, yielding activated nanocages.

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 and H_2 gases were used in all adsorption measurements. The N_2 and H_2 isotherms were measured using a liquid nitrogen bath (77 K).

Iodine Adsorption by sublimation. The uptake of iodine by sublimation at 25 °C was processed following the reported method.[5] The sample was desolvated under dynamic vacuum for 10 h before being placed in a sealed vessel in the presence of solid iodine. And then the vessel with the samples was kept at 25 ºC and weighed at various time intervals.

Mass spectrometry

ESI mass spectrum in negative-ion mode was acquired using an IonSpec HiRes Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR-MS) (Lake Forest, CA, USA) with a 7-T shielded superconducting magnet and a Micromass Z-spray electrospray source. The spray voltage, source, and probe temperature were set at 2400 V, 80 and 100 °C, respectively.

^{1}H-NMR measurement

^{1}H-NMR spectra were recorded on a Bruker AV 400 (DMF-d_7 as internal standard, chemical shifts in ppm).

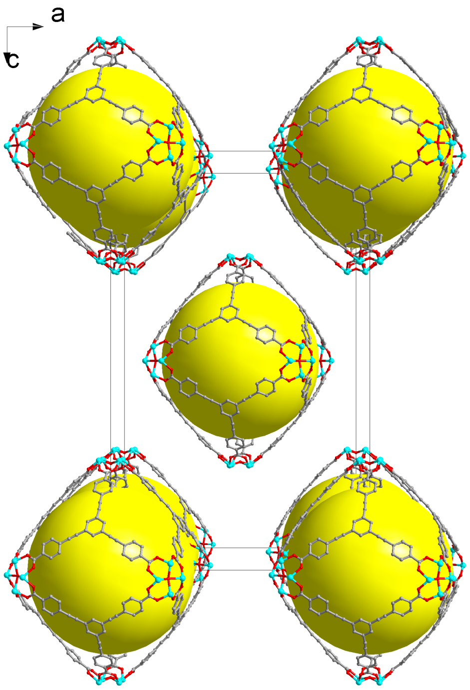
[1] N. Iki, H. Kumagai, N. Morohashi, K. Ejima, M. Hasegawa, S. Miyanari and S. Miyano, *Tetrahedron Lett*., 1998, **39**, 7559.

[2] H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. Özgür Yazaydin, R. Q. Snurr, M. O’Keeffe, J. Kim and O. M. Yaghi, *Science*, 2010, **329**, 424.

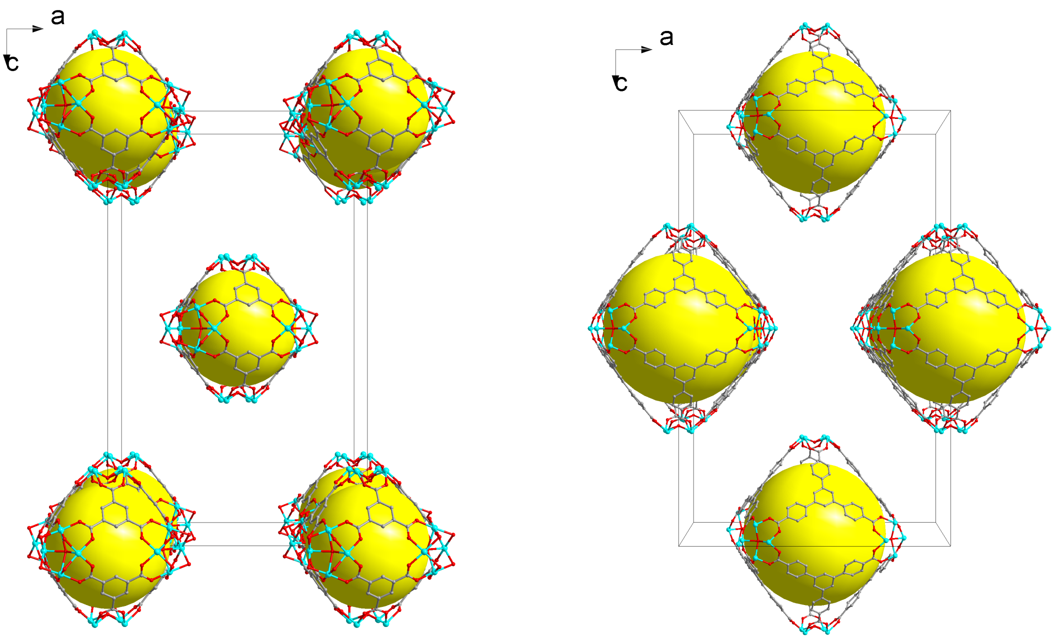
[3] G. M. Sheldrick, *Acta Crystallogr. Sect. A*: *Fundam. Crystallogr.*, 2008, **64**, 112.

[4] P. van der Sluis and A. L. Spek, *Acta Cryst. Sect. A.*, 1990, **46,** 194.

[5] T. Hasell, M. Schmidtmann and A. I. Cooper, *J. Am. Chem. Soc.*, 2011, **133**, 14920.



CIAC-107



CIAC-105 **CIAC-106**

Fig. S1 Packing diagram of the nanocages**.** The calixarene molecules are omitted for clarity.

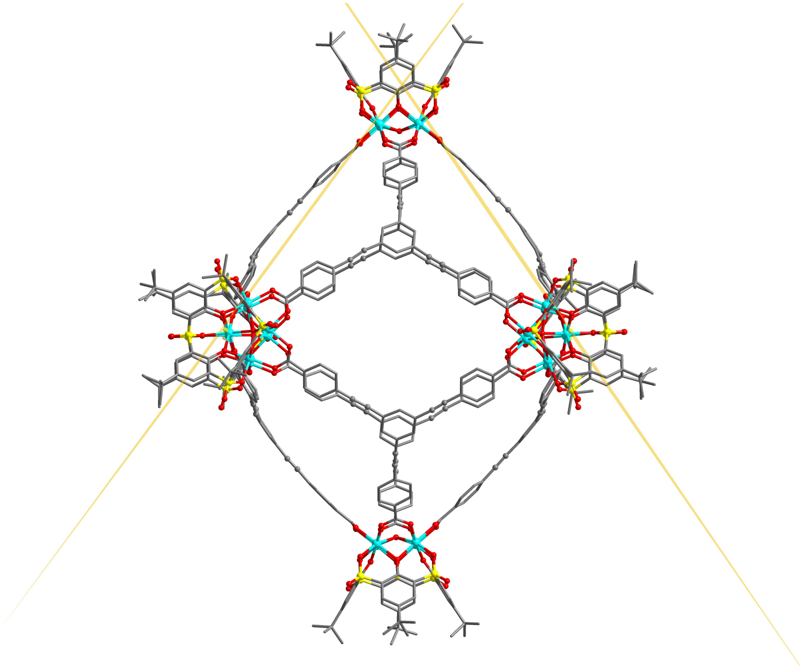


Fig. S2 Close observation of coordination cage of **CIAC-107**. A plane (in yellow) crosses through three carboxylate carbon atoms of one BTE molecule.

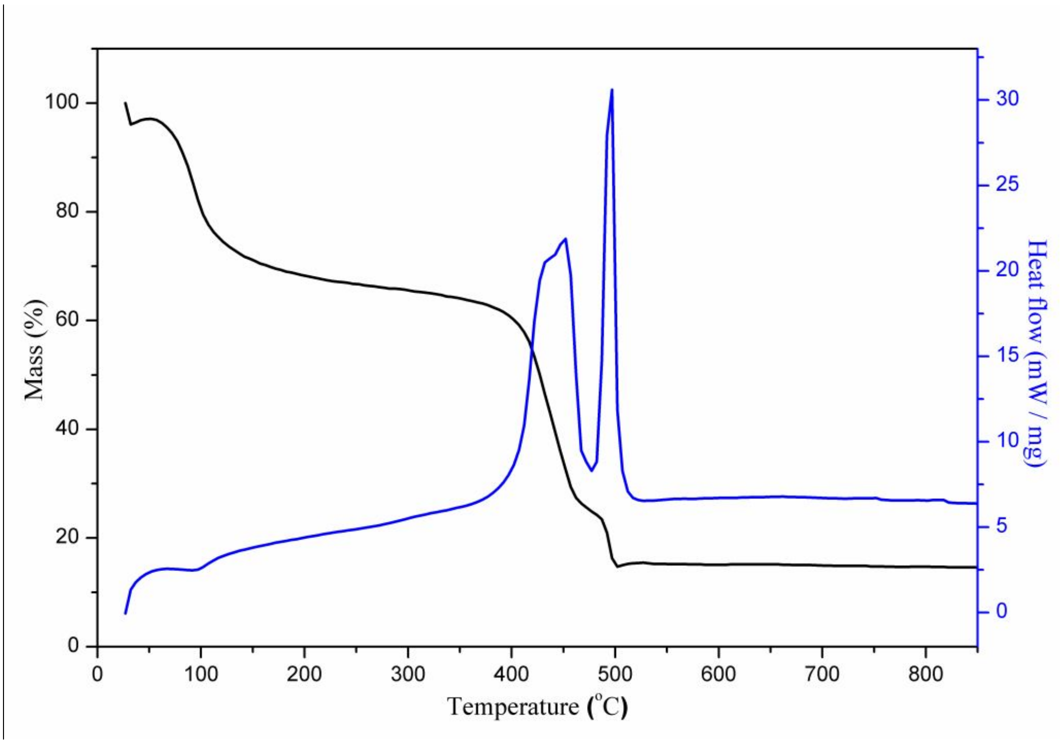


Fig. S3 TGA-DSC curves for **CIAC-105**.

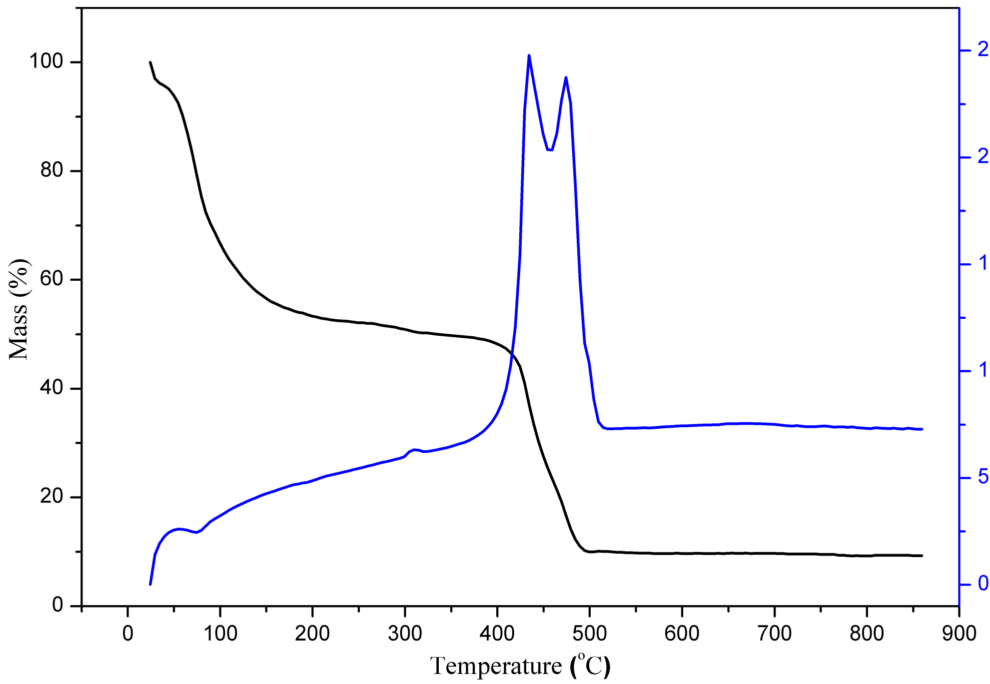


Fig. S4 TGA-DSC curves for **CIAC-106.**

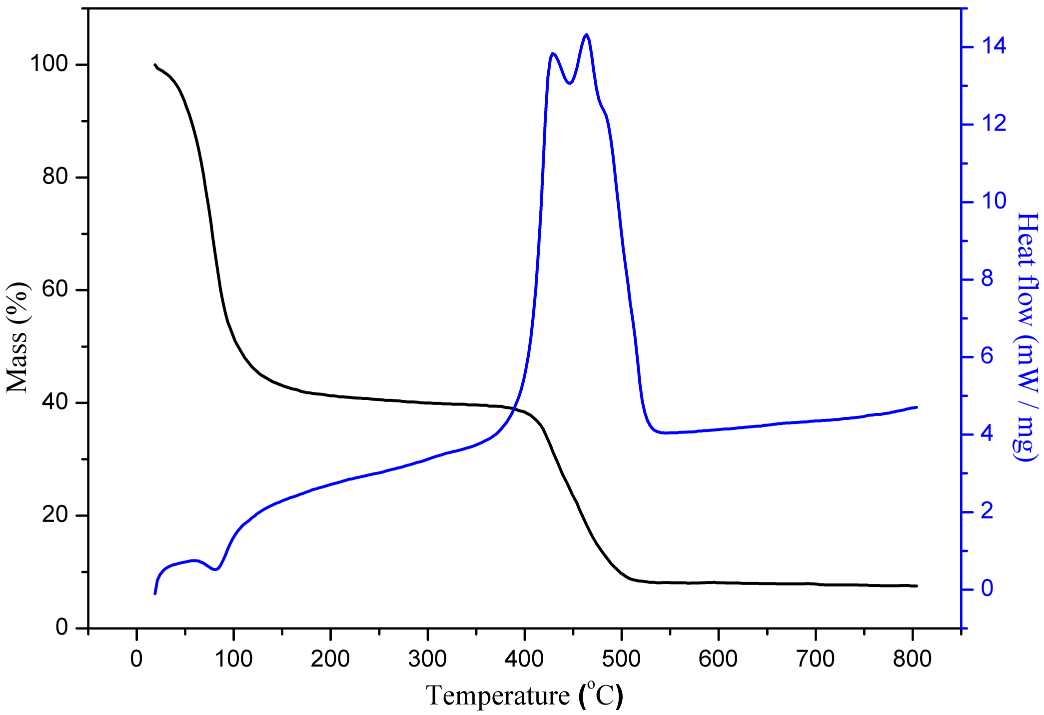


Fig. S5 TGA-DSC curves for **CIAC-107.**

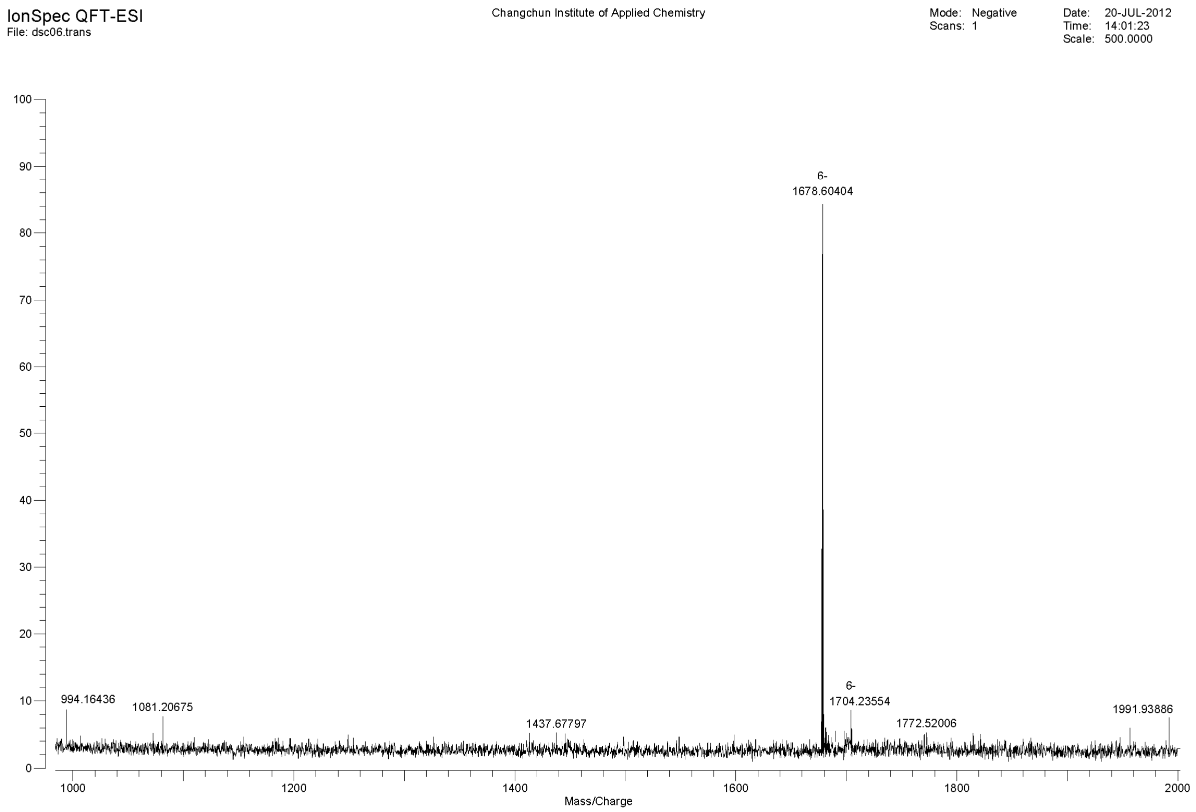


Fig. S6 ESI spectrum of **CIAC-106** in a DMF-methanol mixture (1678.60: $\{[Co_4(SC4A)OH]_6(BTB)_8\}^{6-}$).

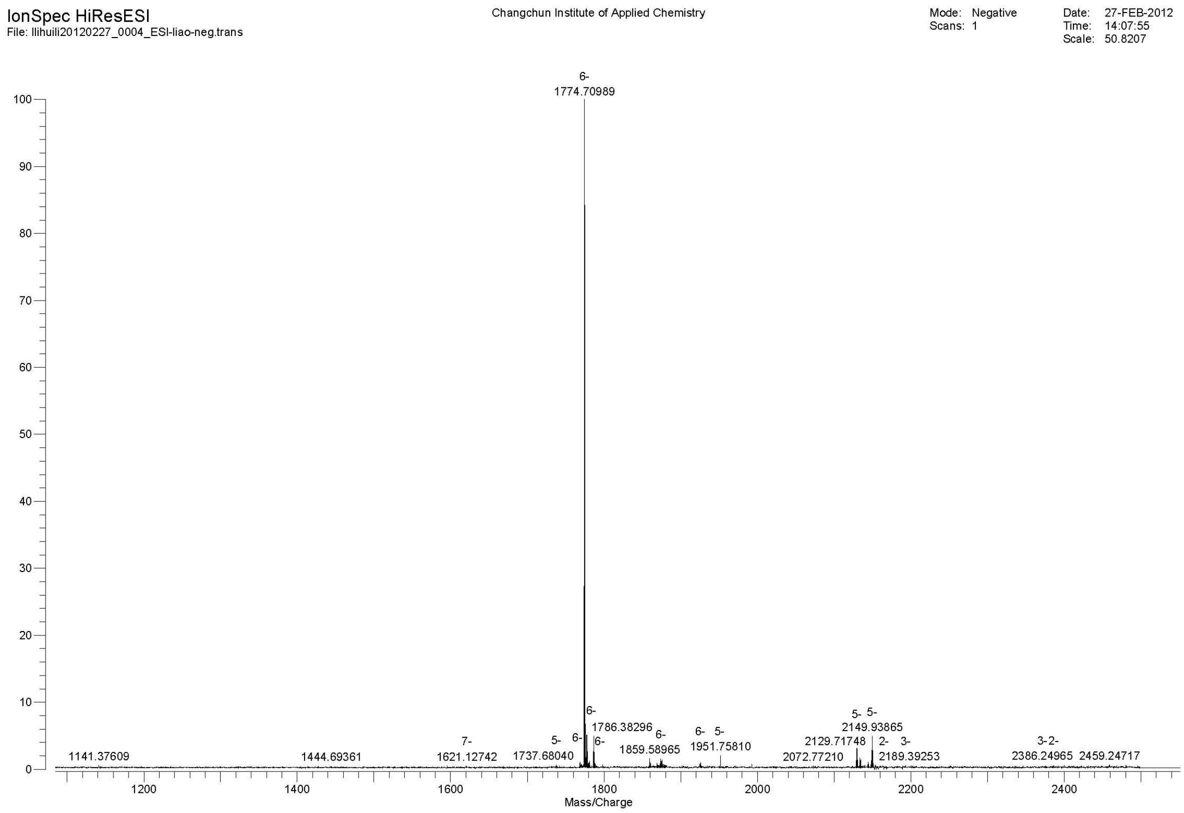


Fig. S7 ESI spectrum of **CIAC-107** in a DMF-methanol mixture (1774.71: $\{[Co_4(SC4A)OH]_6(BTE)_8\}^{6-}$).

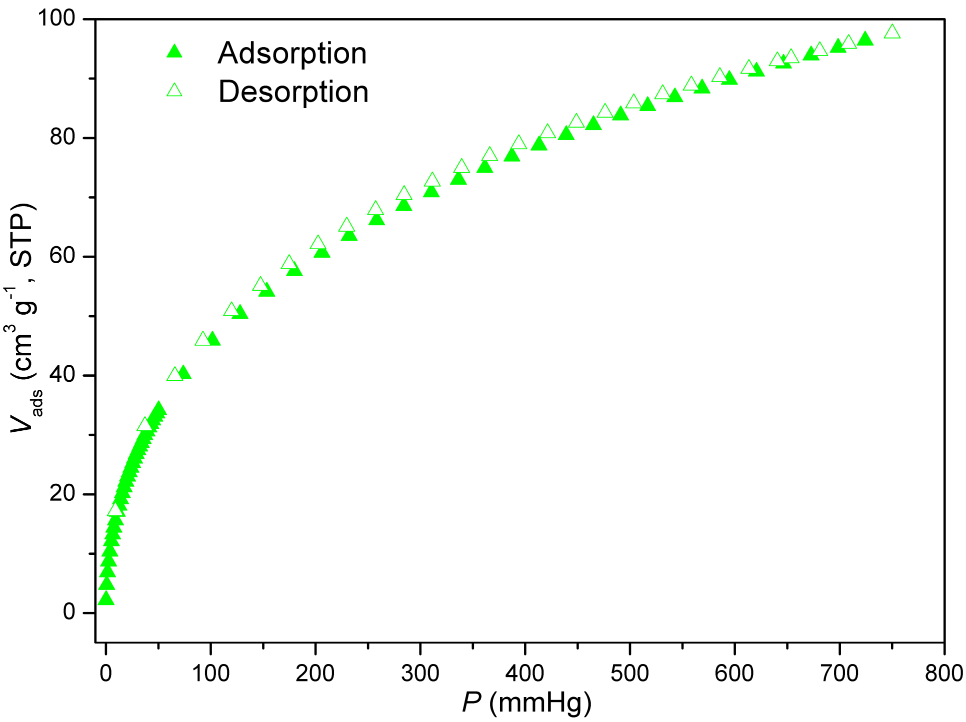


Fig. S8 Adsorption (solid) and desorption (hollow) isotherms of H_2 on **CIAC-107**.

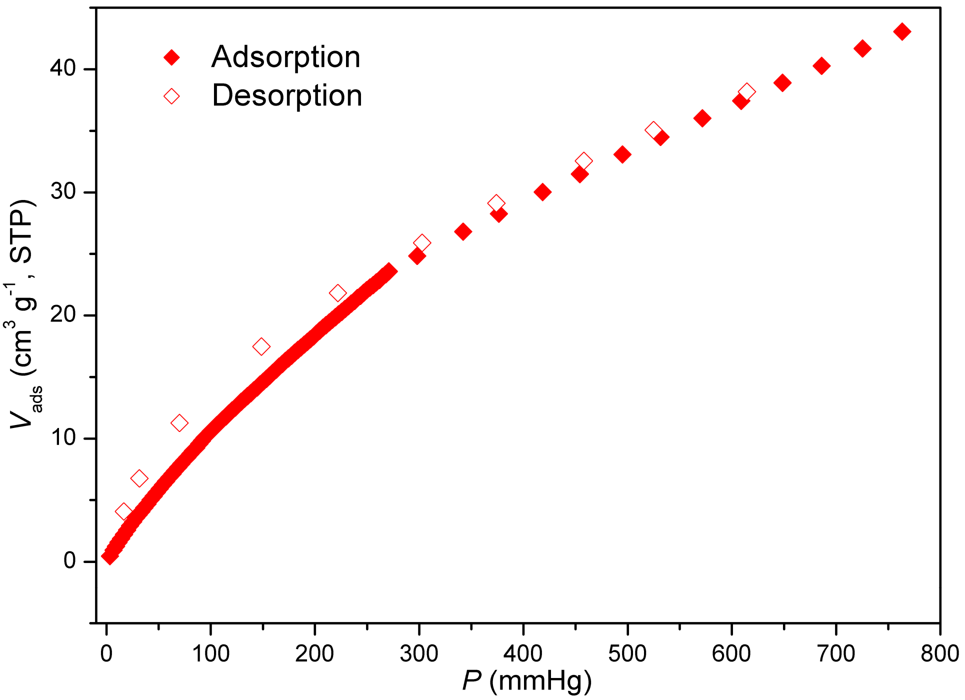


Fig. S9 Adsorption (solid) and desorption (hollow) isotherms of CO_2 on **CIAC-107**.

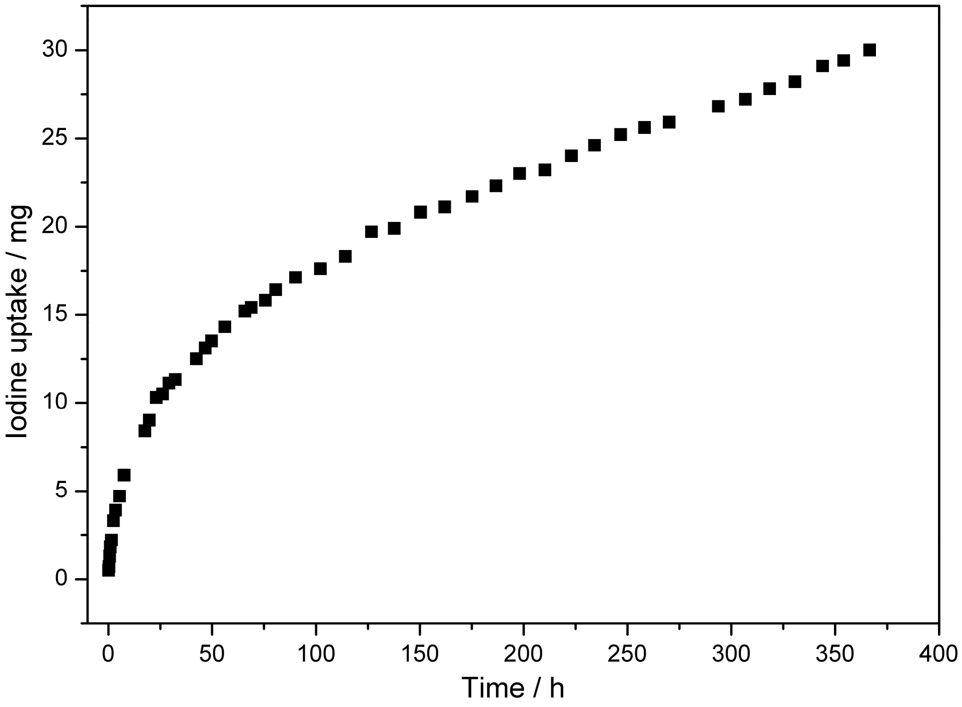
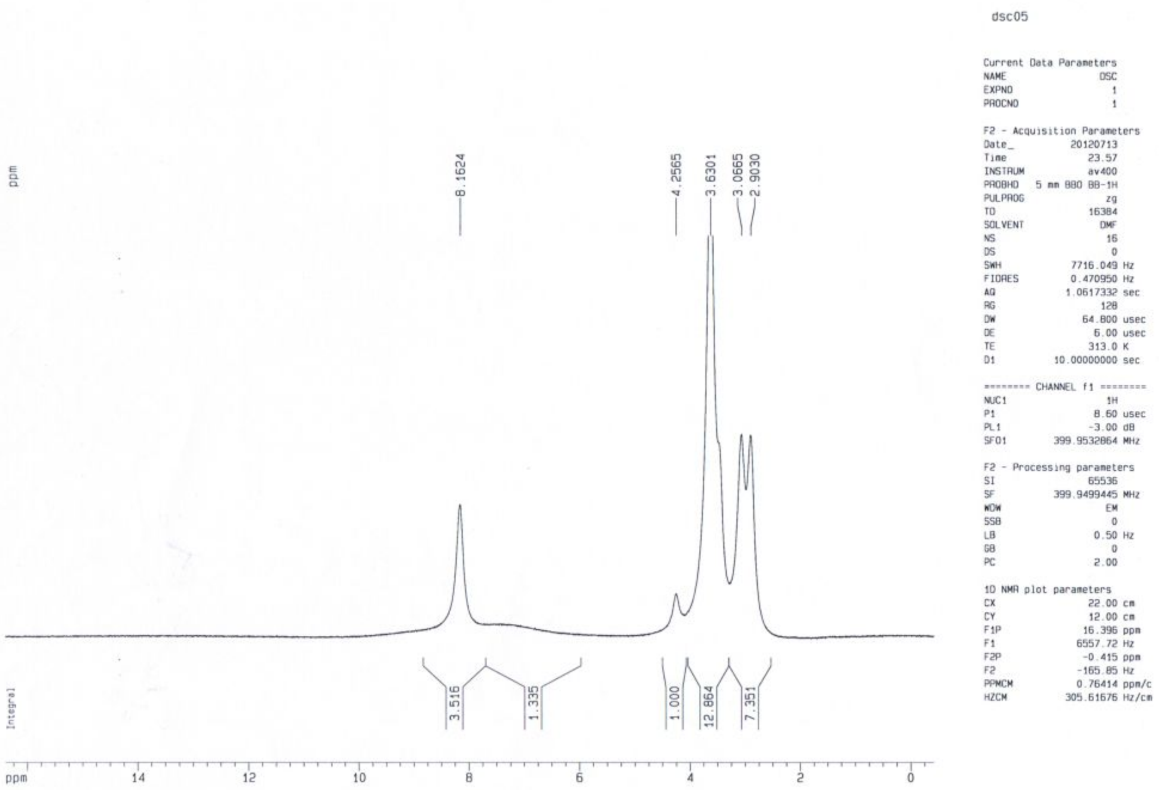
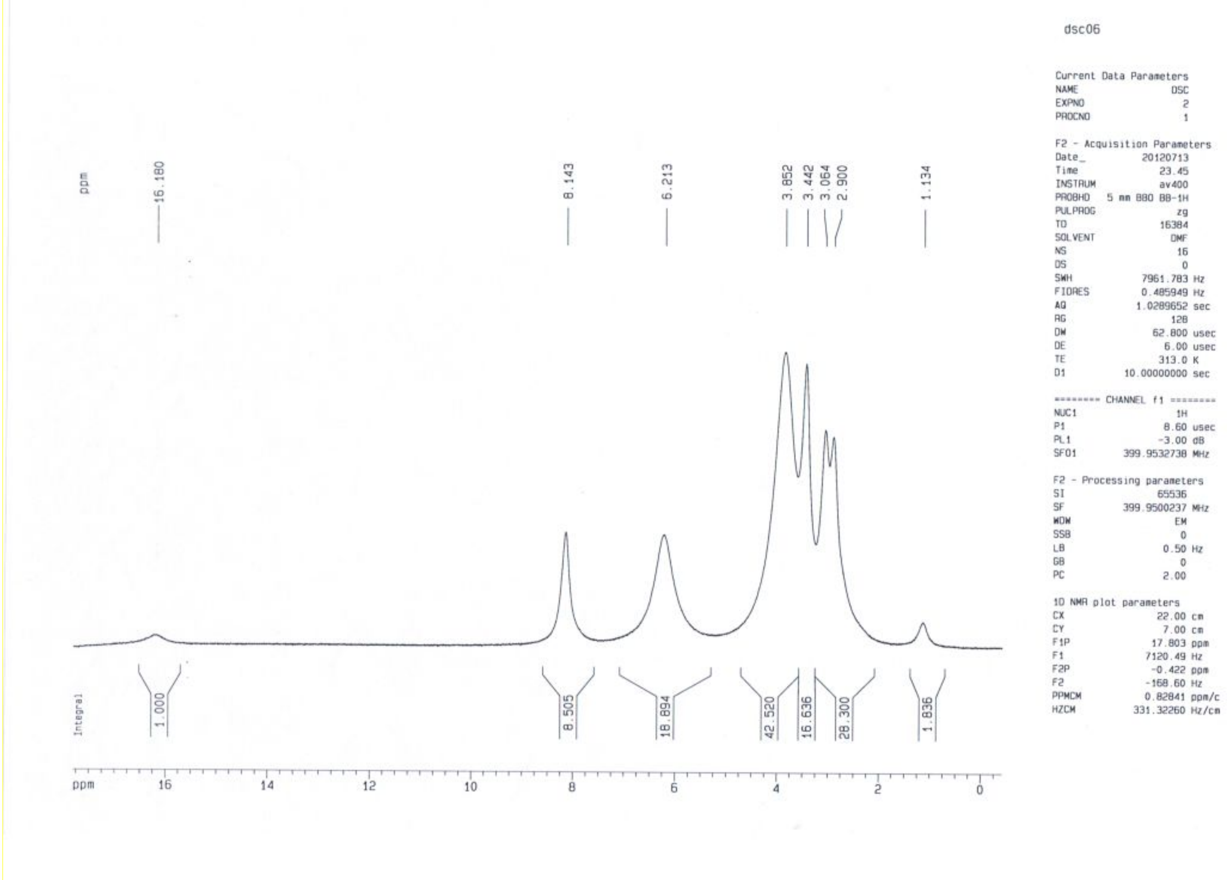


Fig. S10 Gravimetric uptake of iodine by **CIAC-107** as a function of time at 25 °C. (CIAC-107: 104.7 mg)



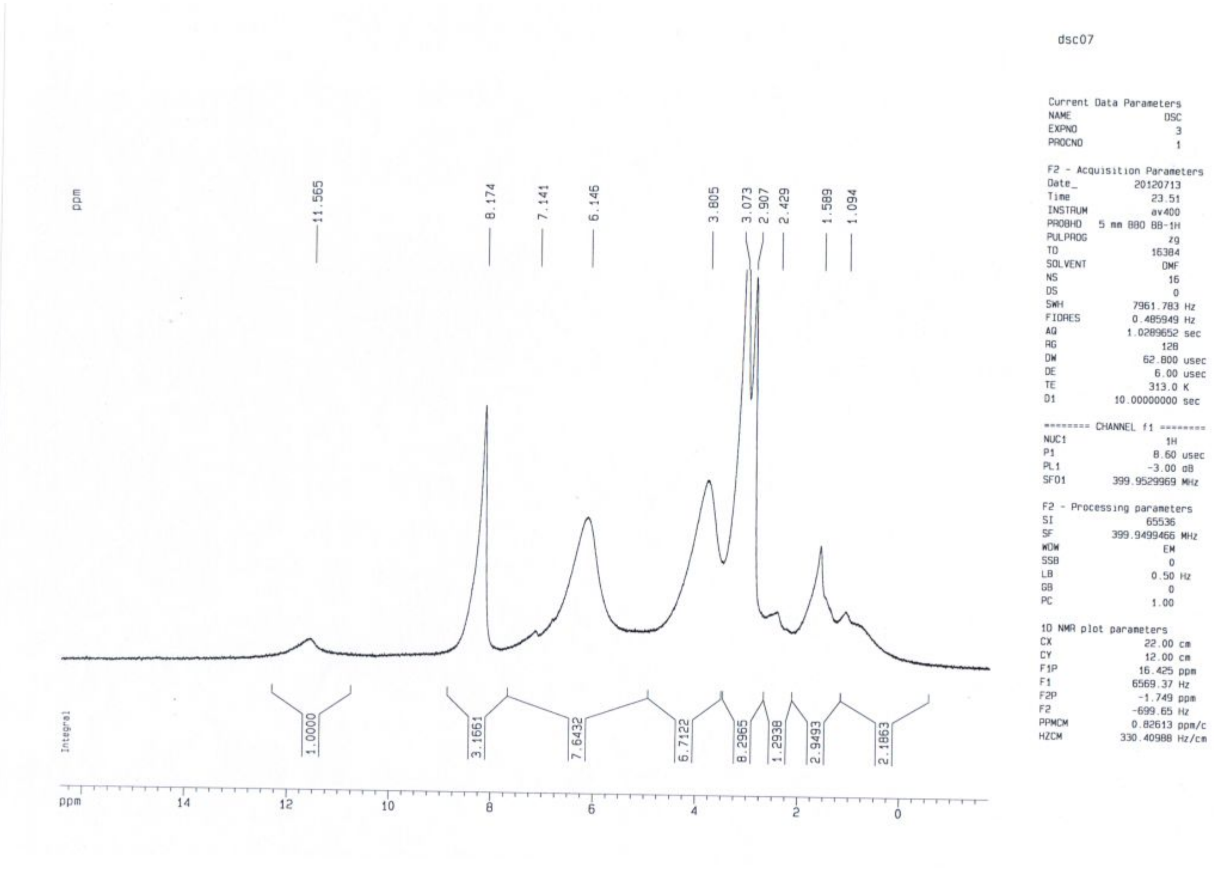
```
dsc05

Current Data Parameters
NAME                  DSC
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120713
Time                23.57
INSTRUM             av400
PROBHD   5 mm BBO BB-1H
PULPROG                zg
TD                  16384
SOLVENT               DMF
NS                     16
DS                      0
SWH              7716.049 Hz
FIDRES           0.470950 Hz
AQ              1.0617332 sec
RG                    128
DW                 64.800 usec
DE                   6.00 usec
TE                  313.0 K
D1            10.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.60 usec
PL1                 -3.00 dB
SFO1          399.9532864 MHz

F2 - Processing parameters
SI                  65536
SF            399.9499445 MHz
WDW                    EM
SSB                     0
LB                   0.50 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.00 cm
CY                  12.00 cm
F1P                16.396 ppm
F1                6557.72 Hz
F2P                -0.415 ppm
F2                -165.85 Hz
PPMCM             0.76414 ppm/c
HZCM            305.61676 Hz/cm
```

Fig. S11 ^{1}H NMR spectra of **CIAC-105** (DMF-d_7, 400 MHz, 313 K).



```
dsc06

Current Data Parameters
NAME                DSC
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20120713
Time              23.45
INSTRUM           av400
PROBHD   5 mm BBO BB-1H
PULPROG              zg
TD                16384
SOLVENT             DMF
NS                   16
DS                    0
SWH            7961.783 Hz
FIDRES         0.485949 Hz
AQ            1.0289652 sec
RG                  128
DW               62.800 usec
DE                 6.00 usec
TE                313.0 K
D1          10.00000000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 8.60 usec
PL1               -3.00 dB
SFO1        399.9532738 MHz

F2 - Processing parameters
SI                65536
SF          399.9500237 MHz
WDW                  EM
SSB                   0
LB                 0.50 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.00 cm
CY                 7.00 cm
F1P              17.803 ppm
F1              7120.49 Hz
F2P              -0.422 ppm
F2              -168.60 Hz
PPMCM           0.82841 ppm/c
HZCM          331.32260 Hz/cm
```

Fig. S12 ^{1}H NMR spectra of **CIAC-106** (DMF-d_7, 400 MHz, 313 K).



```
dsc07

Current Data Parameters
NAME                 DSC
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120713
Time               23.51
INSTRUM            av400
PROBHD   5 mm 880 BB-1H
PULPROG               zg
TD                 16384
SOLVENT              DMF
NS                    16
DS                     0
SWH           7961.783 Hz
FIDRES        0.485949 Hz
AQ           1.0289652 sec
RG                   128
DW              62.800 usec
DE                6.00 usec
TE               313.0 K
D1         10.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                8.60 usec
PL1              -3.00 dB
SFO1       399.9529969 MHz

F2 - Processing parameters
SI                 65536
SF         399.9499466 MHz
WDW                   EM
SSB                    0
LB                  0.50 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.00 cm
CY                 12.00 cm
F1P               16.425 ppm
F1               6569.37 Hz
F2P               -1.749 ppm
F2               -699.65 Hz
PPMCM            0.82613 ppm/c
HZCM           330.40988 Hz/cm
```

Fig. S13 ^{1}H NMR spectra of **CIAC-107** (DMF-d_7, 400 MHz, 313 K).

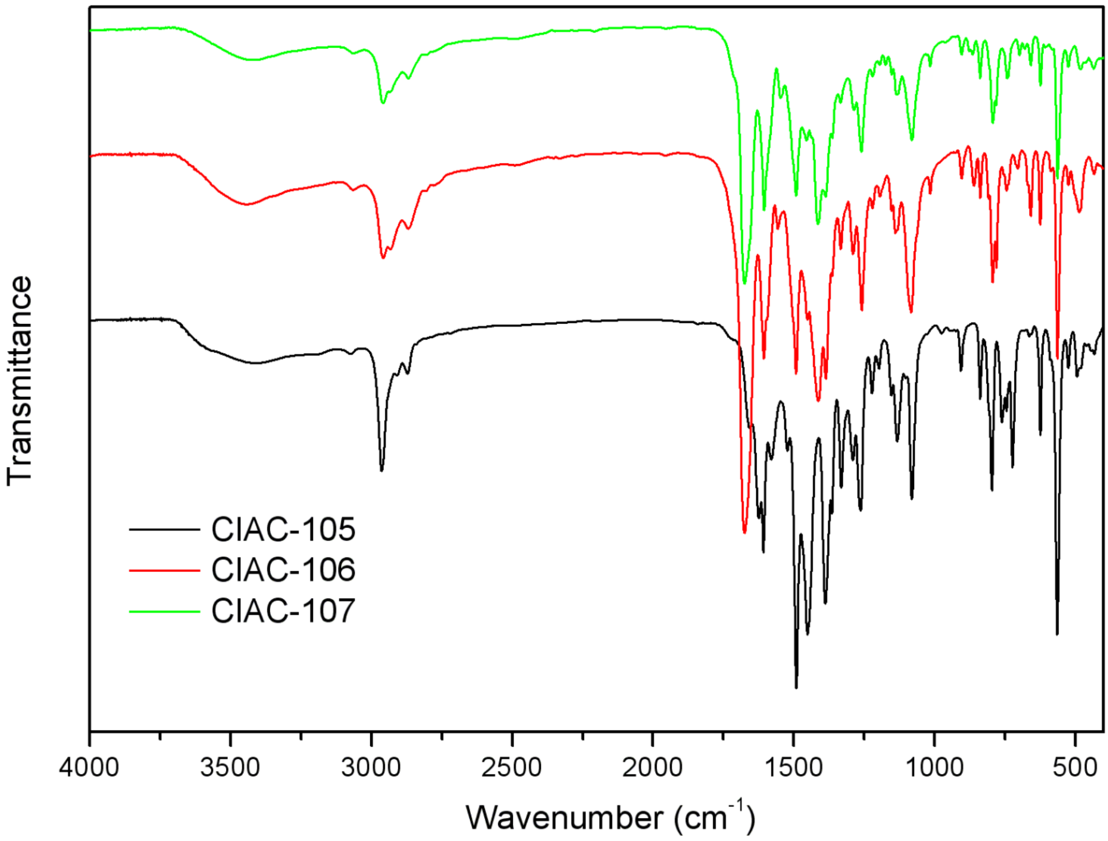


Fig. S14 IR spectrum of **CIAC-105, -106** and **-107**.