Supporting Information

Bridging calixarene-based {Co_4} units into a square or belt with aromatic dicarboxylic acids

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Experimental Section

Materials and Measurements: *p-tert*-Butylthiacalix[4]arene (H_4TC4A) was synthesized by literature method,[1] and other reagents were purchased from commercial sources and used as received. EDS analyses of Co, S and Cl were performed on a HITACHI S-4800 Scanning Electron Microscope. TGA measurement is performed on a PYRIS DIAMOND from room temperature to 900℃, with a heating rate of 10℃ min^{-1} under atmosphere. FT-IR spectra (KBr pellets) were taken on a Bruker Vertex 70 spectrometer. Powder X-ray diffraction (XRD) was determined by a Bruker D8 Advance diffractometer. N_2 adsorption measurement was performed on a Micromeritics ASAP 2020 machine.

Syntheses of CIAC-201: Purple block crystals of **CIAC-201** were obtained from reaction of the mixture of *p*-tert-butylthiacalix[4]arene (0.07g, 0.1 mmol), $CoCl_2 \cdot 6H_2O$ (0.1 g, 0.4 mmol), isophthalic acid (H_2L^1) (0.02g, 0.12mmol), DMF (6 ml), CH_3OH (2ml) and tetramethylammonium hydroxide solution (25%, several drops) in a 20 ml Teflon-lined autoclave which was kept at 130 °C for 3 days and then slowly cooled to 18 °C at about 2 °C/h. Elemental analysis (%): C45.13, H 5.30, N 2.61. IR (KBr, cm^{-1}): 3408 (m), 2962 (s), 1657(m),1560 (s), 1435 (s), 1391 (s), 1250 (w), 1082 (w), 838(s), 712 (s), 659(w), 539 (w). The EDS analysis reveals that the molar ratio of Co, S and Cl molar is 7.89: 7.62: 2.11, comparable to the expected value 4: 4: 1 (Fig. S1).

Syntheses of CIAC-202: Purple block crystals of **CIAC-202** were obtained from reaction of the mixture of *p*-tert-butylthiacalix[4]arene (0.07g, 0.1 mmol), $Co(Ac)_2 \cdot 4H_2O$ (0.1 g, 0.4 mmol), 2,6-pyridinedicarboxylic acid (H_2L^2) (0.02g, 0.12mmol), $CHCl_3$ (5 ml), CH_3OH (5ml) and tetramethylammonium hydroxide solution (25%, 0.5 ml) in a 20 ml Teflon-lined autoclave which was kept at 130 °C for 3 days and then slowly cooled to 18 °C at about 2 °C/h. Elemental analysis (%): C 44.66, H 4.24, N 1.72. The chloride anions in the compound would come from the decomposition of chloroform. IR (KBr, cm^{-1}): 3407 (m), 2961 (s), 1578(s),1393 (s), 1303 (w), 1256 (s), 1190 (w), 1081 (w), 843(s), 723 (s), 657(w), 531 (w). The EDS analysis of **1** reveals that the molar ratio of Co, S and Cl molar is 15.38: 13.41: 8, comparable to the expected value 4: 4: 1(Fig. S1).

Syntheses of CIAC-203: Purple block crystals of **CIAC-203** were obtained from reaction of the mixture of *p*-tert-butylthiacalix[4]arene (0.07g, 0.1 mmol), $CoCl_2 \cdot 6H_2O$ (0.1 g, 0.4 mmol), *p*-phthalic acid(H_2L^3)(0.02g, 0.12mmol), $CHCl_3$ (4 ml), CH_3OH (4ml) and tetramethylammonium hydroxide solution (25%, several drops) in a 20 ml Teflon-lined autoclave which was kept at 130 °C for 3 days and then slowly cooled to 18 °C at about 2 °C/h. Elemental analysis (%): C 42.19, H 4.93, N 0.02, indicating that there is no $(CH_3)_4N^+$ cations in the structure. IR (KBr, cm^{-1}): 3358 (m), 2963 (s), 2864(w),1561(s), 1460 (s), 1386 (s), 1258 (s), 1089 (w), 1006 (w), 892 (w), 826(m), 750 (s), 659(w), 545 (m). The EDS analysis reveals that the molar ratio of Co, S and Cl molar is 13.45: 11.53: 7.04, comparable to the expected value 8: 8: 5 (Fig. S1).

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).[2] The diffraction data were treated by the "SQUEEZE" method as implemented in PLATON.[3] All non-hydrogen atoms except the disordered butyl carbon atoms in CIAC-201 were refined anisotropically. Hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. four $(CH_3)_4N^+$ cations were included into the formula by charge balance for **CIAC-201** and **-202**. The unidentified solvent molecules were not included for all these 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 big, but typical in such system. CCDC-872774-872776 contain 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-201

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 -0.081 -0.072 -0.013 10847 3538 ' '

(2) CIAC-202

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 -0.098 -0.047 -0.055 10313 3526 ' '

(3) CIAC-203

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 -0.031 -0.034 -0.034 1513 480 ' '

1 N. Iki, C. Kabuto, T. Fukushima, H. Kumagai, H.Takeya, S. Miyanari, T. Miyashi and S. Miyano, *Tetrahedron.*, 2000, **56**, 1437–1443.

2 G. M. Sheldrick, *Acta Crystallogr. Sect. A*: *Fundam. Crystallogr.* **2008**, *64*, 112.

3 P. van der Sluis, A. L. Spek, *Acta Cryst. Sect. A.* **1990**, *46***,** 194.

Table S1. Selected bond lengths/distances (Å) and angles (º) for compound **CIAC-201**

Co(1)–O(2)	1.992(4)	Co(2)–O(1)	1.975(4)
Co(1)–O(2)[a]	1.992(4)	Co(2)–O(2)	1.999(5)
Co(1)–O(4)	2.019(4)	Co(2)–O(3)[a]	1.999 (5)
Co(1)–O(4)[a]	2.019(4)	Co(2)–O(5)	2.043(5)
Co(1)–S(3)	2.549(3)	Co(2)–S(1)	2.522(2)
Co(1)–Cl(1)	2.613(3)	Co(2)–Cl(1)	2.659(2)
Co(3)–O(1)	1.989(4)	Co(3)–O(1)[a]	1.989(4)
Co(3)–O(6)	2.021(5)	Co(3)–O(6)[a]	2.021(5)
Co(3)–Cl(1)	2.606(3)	Co(3)–S(2)	2.569(3)
Co(1)···Co(2)	3.2253(13)	Co(1)···Co(3)	4.5395(18)
Co(2)···Co(3)	3.2365(12)	Co(2)···Co(2)[a]	4.5976(12)
Co(1)–O(2)–Co(2)	107.8(2)	Co(2)–Cl(1)–Co(3)	75.86(6)
Co(2)–O(1)–Co(3)	109.4(2)	Co(1)–Cl(1)–Co(2)	75.42(6)
Co(1)–Cl(1)–Co(3)	120.9(1)	Co(2)–Cl(1)–Co(2)[a]	119.7(1)
Symmetry code: (a) -x, y, z			

Table S2. Selected bond lengths/distances (Å) and angles (º) for compound **CIAC-202**

Co(1)–O(1)	1.989(2)	Co(2)–O(1)	1.986(2)
Co(1)–O(1)[a]	1.989(2)	Co(2)–O(1)[b]	1.986(2)
Co(1)–O(3)	2.035(2)	Co(2)–O(2)	2.029(2)
Co(1)–O(3)[a]	2.035(2)	Co(2)–O(2)[b]	2.029(2)
Co(1)–S(2)	2.556(1)	Co(2)–S(1)	2.503(1)
Co(1)–Cl(1)	2.6103(9)	Co(2)–Cl(1)	2.658(1)
Co(1)···Co(2)	3.2269(7)	Co(1)···Co(1)[c]	4.5466(8)
		Co(2)···Co(2)[c]	4.5783(9)
Co(1)–O(1)–Co(2)	108.6(1)	Co(1)–Cl(1)–Co(2)[a]	75.53(3)
Co(1)–Cl(1)–Co(1)[c]	121.13(6)	Co(1)–Cl(1)–Co(2)	75.53(3)
		Co(2)–Cl(1)–Co(2)[a]	118.89(6)
Symmetry codes: (a) x, y, 1-z; (b) y, x, z; (c) y, x, 1-z			

Table S3. Selected bond lengths/distances (Å) and angles (º) for compound **CIAC-203**

Co(1)–O(1)	2.016(3)	Co(2)–O(1)	2.001(3)
Co(1)–O(4)	1.977(3)	Co(2)–O(2)	2.004(3)
Co(1)–O(5)	1.999(3)	Co(2)–O(6)	2.023(3)
Co(1)–S(1)	2.4722(13)	Co(2)–O(9)	2.156(3)
Co(1)–Cl(1)	2.7391(13)	Co(2)–S(2)	2.5214(12)
Co(1)–Cl(2)	2.4791(6)	Co(2)–Cl(1)	2.6259(12)
Co(3)–O(2)	2.014(3)	Co(4)–O(3)	2.001(3)
Co(3)–O(3)	2.012(3)	Co(4)–O(4)	1.998(3)
Co(3)–O(7)	2.028(3)	Co(4) –O(8)	2.004(3)
Co(3)–S(3)	2.5035(14)	Co(4)–O(10)	2.115(3)
Co(3)–Cl(1)	2.786(1)	Co(4)–S(4)	2.4891(14)
Co(3)–Cl(3)	2.3959(18)	Co(4)–Cl(1)	2.6161(13)
Co(1)···Co(2)	3.2556(7)	Co(2)···Co(3)	3.395(1)
Co(3)···Co(4)	3.2756(7)	Co(4)···Co(1)	3.366(1)
Co(1)···Co(3)	4.8565(9)	Co(2)···Co(4)	4.5384(9)
Co(1)–O(1)–Co(2)	108.25(13)	Co(2)–O(2)–Co(3)	115.31(13)
Co(1)–O(4)–Co(4)	115.76(14)	Co(3)–O(3)–Co(4)	109.42(14)
Co(1)–Cl(2)–Co(1)[a]	179.998(16)		
Symmetry code: (a)2-x, 2-y, 1-z			

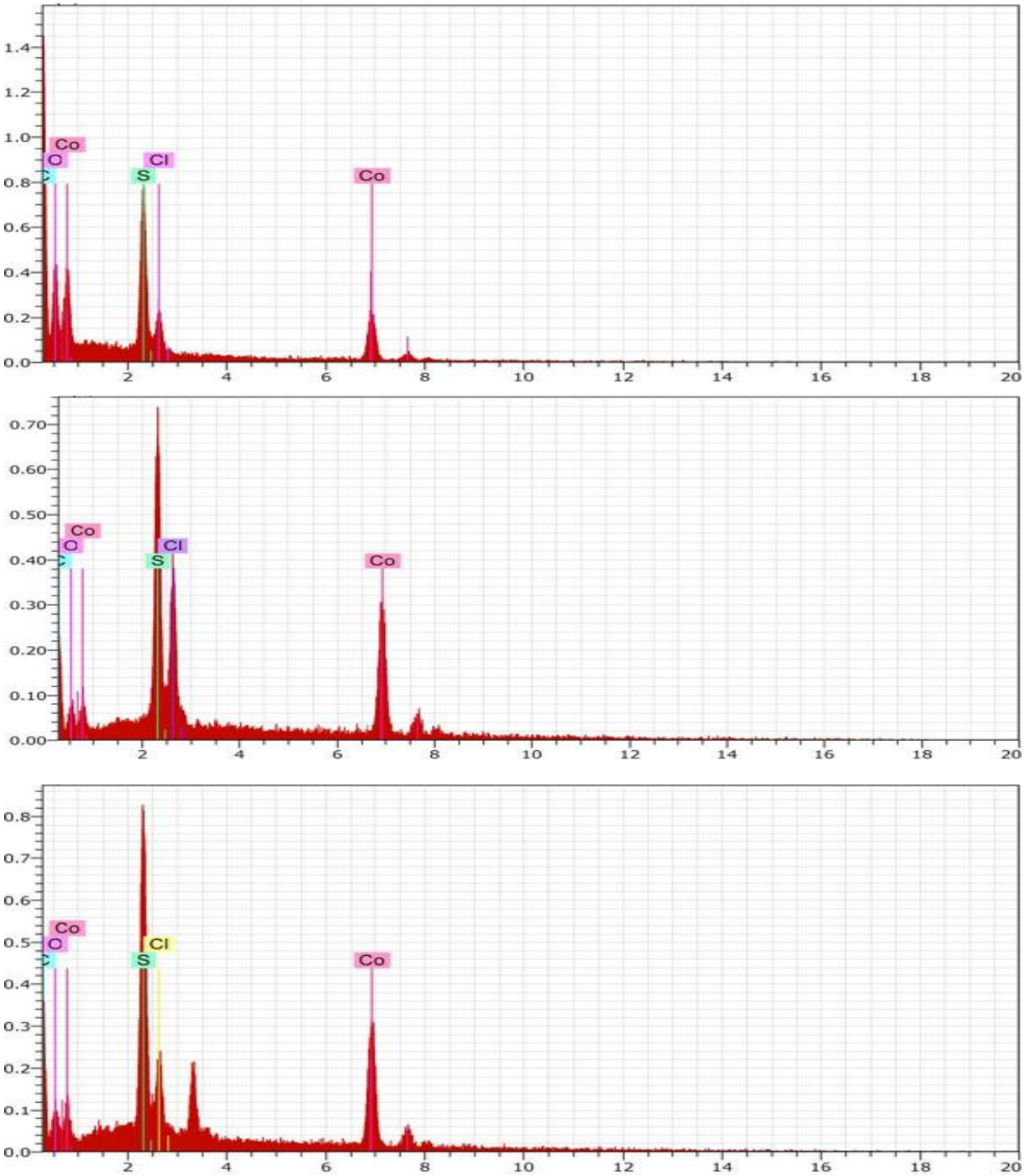

Fig. S1. EDS plots of **CIAC-201** (upper)，**-202** (middle) and **-203** (bottom).

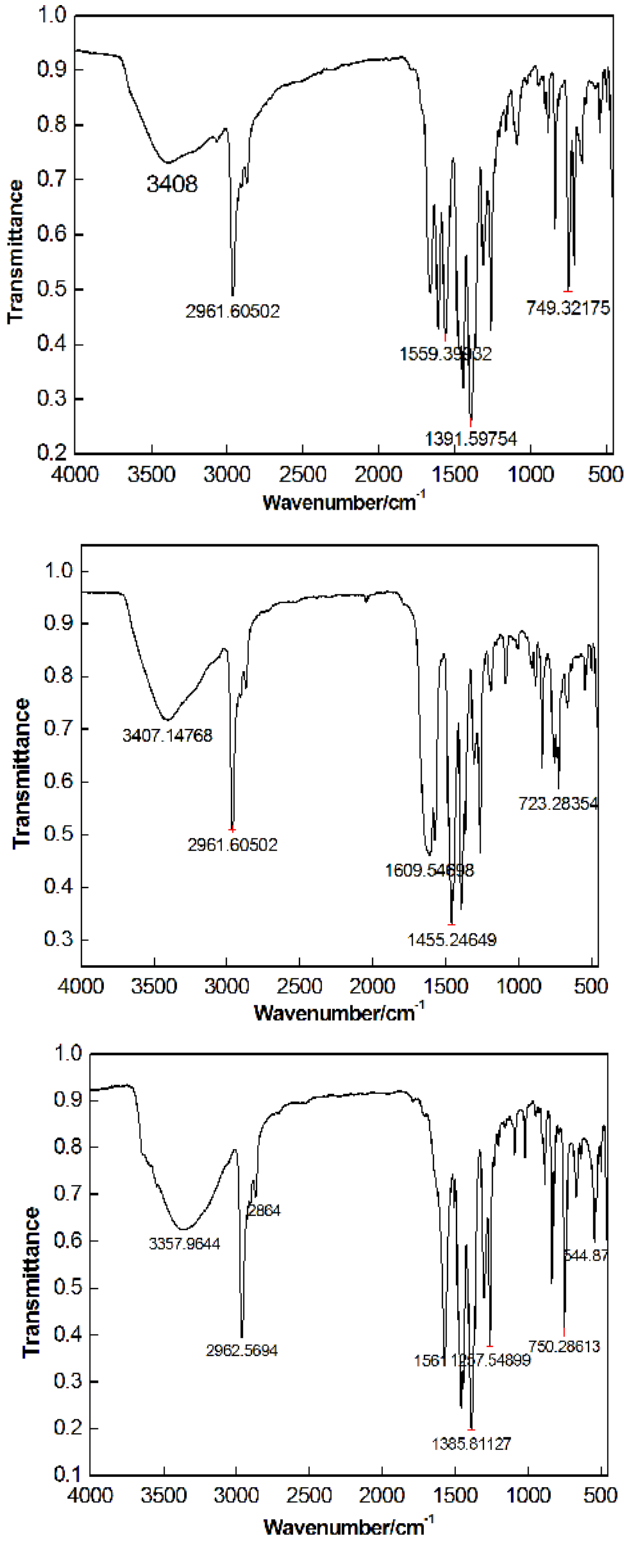

Fig. S2. IR-spectra of compound **CIAC-201** (upper)，**-202** (middle) and **-203** (bottom).

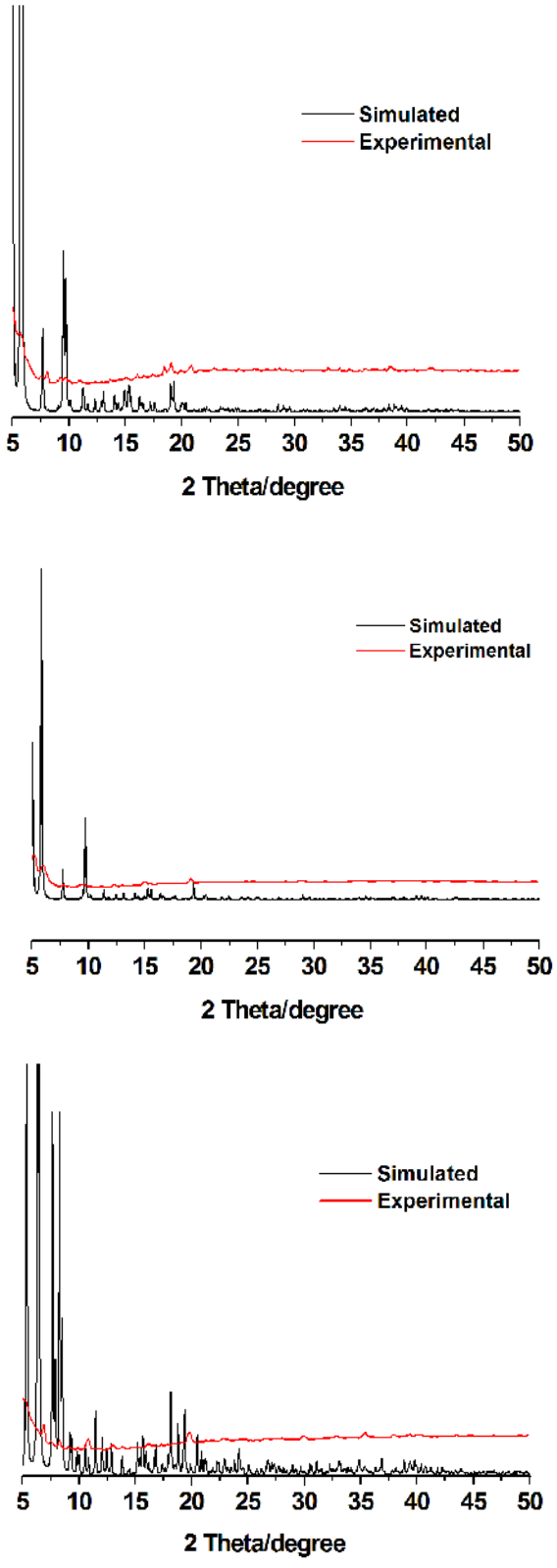

Fig. S3. Powder XRD plots of **CIAC-201** (upper)，**-202** (middle) and **-203** (bottom).

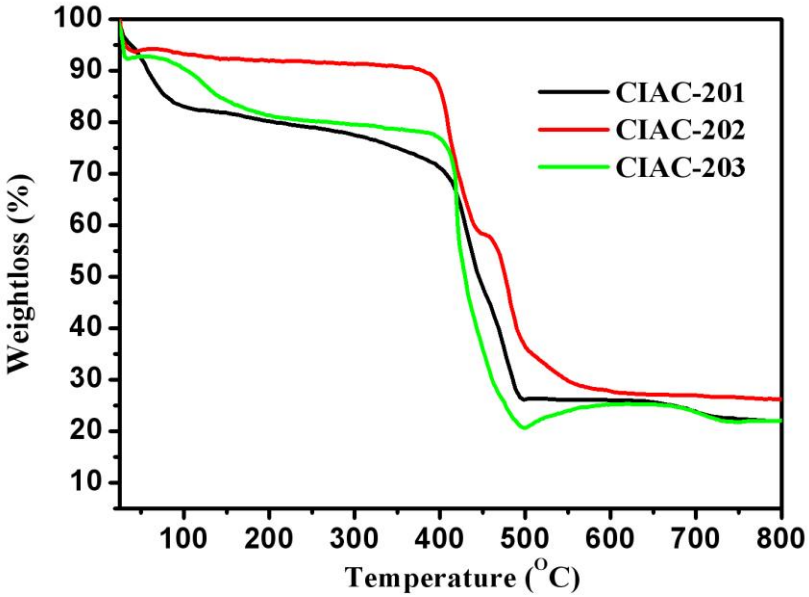

Fig. S4. TG curves of **CIAC-201** and **-203.**