Supporting Information

A supramoleculear self-assembled flexible open framework based on coordination honeycomb layers possessing octahedral and tetrahedral Co^{II} geometries

Yang Zou,*[a] Yuanyuan Li,[a] Chaoyong Yu,[a] Fei Yin[a] and Myoung Soo Lah *[b]

[a] *Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou, 310018, China*
E-mail: zouyang@zstu.edu.cn

[b] *Interdisciplinary School Green Energy, Ulsan National Institute Science & Technology, Ulsan 689798, South Korea. E-mail: mslah@unist.ac.kr*

Materials

The following chemicals were used as received with no further purification: *p*-phthaloyl chloride, 5-amino isophthalic acid, triethylamine, $CoCl_2 \cdot 6H_2O$, *N,N'*-dimethylformamide (DMF), *N,N'*-dimethylacetamide (DMA), methanol and acetone from Aladdin-reagent, Inc.

General procedures

All the reagents were purchased from commercial sources and were used without further purification. Infrared spectra were recorded using KBr pellets in the range 4000-400 cm^{-1} employing a Nicolet FT-IR 400 system. Thermogravimetric analysis (TGA) was performed in a nitrogen stream using an Pyris Diamond system with a heating rate of 10^oC min^{-1}. Powder X-ray diffraction (PXRD) data was recorded by a Bruker D8 ADVANCE automated diffractometer. The adsorption isotherms were measured at 273 K for MeOH and 77 K for N_2 using a Micrometric ASAP2020M system with ultra-pure N_2 (99.999%) and HPLC grade MeOH. The temperature-dependent magnetic susceptibility of **1** was measured with crystalline powder samples on a Quantum Design MPMS XL-7 Squid magnetometer in a magnetic field of 1000 Oe under the temperature range 2–300K.

Preparation of 4,4',4''-[1,3,5-benzenetriyltris(carbonylimino)]-trisbenzoic acid (H_3L): The synthesis of 4,4',4''-[1,3,5-benzenetriyltris(carbonylimino)]-trisbenzoic acid (H_3L) was achieved by using a previously reported procedure[1]:3.96g (15.00 mmol) sample of 1,3,5-benzenetricarboxylic acid chloride is added to a solution of 6.20g (45.1 mmol) of 4-amino benzoic acid and 4mL of triethylamine in 100 mL of DMA. The mixture is stirred for 16 hrs, and then 500 mL water was added. White precipitate formed was filtered and the solid was washed with acetone, water, methanol and finally ether and further dried in vacuum. Yield = 8.11 g (86.9%). IR (KBr): ν/cm^{-1}): 3320(b), 1695(vs), 1600(s), 1530(s), 1410(vs), 1320(s), 1250(s), 1178(s), 1118(m), 1010(m), 954(w), 858(m).

Preparation of $\{[Co_2(L)Cl(DMF)_2(H_2O)]\cdot S_x\}_n$ 1: A solvothermal reaction of $CoCl_2 \cdot 6H_2O$(0.0263 g, 0.11 mmol) and H_3L (0.0285 g, 0.05 mmol) in 6 mL DMF-H_2O (20 : 1 volume ratio) was performed at 85^oC for 1 week. The blue block crystals of **1** were obtained in 50% yield (based on ligand).The crystals were soaked in DMF overnight and in methanol for 3 days and filtered and dried in vacuum at 150^oC overnight to obtain **1a**. IR (KBr, cm^{-1}): 3400(b), 1660(vs), 1600(vs), 1531(vs), 1400 (vs), 1320(s), 1250(w), 1180(w), 1110(w), 1010(w), 860(m), 785(m),735(w) Elemental analysis: Calcd. for $[([Co_2(L)Cl(DMF)_2(H_2O)]\cdot 2DMF\cdot 5H_2O$. ($C_{42}H_{61}N_7O_{19}ClCo$, fw = 1062.3): C, 47.48; H, 5.79; N, 9.23%. Found: C, 47.1; H, 5.87; N, 9.15%.

Crystallographic data collections and refinements of structure

A crystal was coated with paratone oil and the diffraction data were measured at 115 K on a Siemens SMART CCD diffractometer equipped with a graphite monochromatic Mo Ka (λ= 0.71073 Å). The data were corrected for Lorentz and polarization effects (SAINT), and multi-scan absorption corrections based on equivalent reflections were applied (SADABS).

Crystal structure of **1**: Light blue block shaped crystal, 0.25 x 0.20 x 0.10 mm^3, $C_{39}H_{20}N_6O_{19}ClCo_2$, fw = 1029.92 $g{\cdot}mol^{-1}$, monoclinic, space group *P21/c*, a = 11.015(6) Å, 17.421(9) Å, c = 29.938(17) Å, β = 93.99(1)°,V = 5731(5) $Å^3$, Z = 4, μ = 0.691mm^{-1}, 28467 reflections were collected, 10082 were unique [R_{int} = 0.175]. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 (SHELXTL)[2]. The contributions of the disordered solvent molecules were removed from the diffraction data using the SQUEEZE routine of PLATON software.[3] Since the DMF molecules are badly disordered, we cannot find all solvent molecules and their exact location and amount, as well as the anisotropic refinement for this badly disordered solvent molecules seems also impossible. Thereby, in '1.cif' file, we only defined partly solvent molecules that is refined by isotropic refinement, resulting in the high R1=0.1078 and *ωR2*=0.2810 values. Then, we carry out Platon Squeeze program towards these badly disordered solvent molecules, leading to the better R1=0.0797 and *ωR2*=0.1565 values, which is reported as '1squeeze.cif' file.

References

(1) X. Song, Y. Zou, X. Liu, M. Oh and M.S. Lah, New J. Chem., 2010, 34, 2396.

(2) G. M. Sheldrick, SHELXTL-Plus, Crystal Structure Analysis Package; Bruker Analytical X-Ray; Madison, WI, USA, 1997.

(3) A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2001.

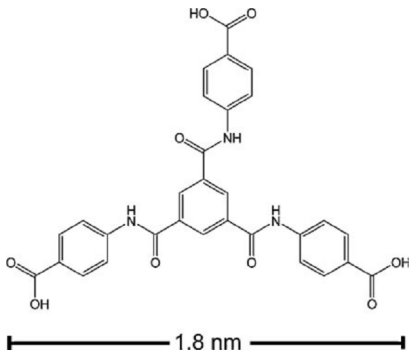
Table S1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{39}H_{20}N_6O_{19}ClCo_2$	
Formula weight	1029.92	
Temperature	115(2) K	
Crystal system	Monoclinic	
Space group	*P21/c*	
Unit cell dimensions	a = 11.015(6) Å	α = 90°.
	b = 17.421(9) Å	β = 93.99(1)°.
	c = 29.938(17) Å	γ = 90°.
Volume	5731(5) $Å^3$	
Z	4	
Density (calculated)	1.194 g/cm^3	
Absorption coefficient	0.691 mm^{-1}	
F(000)	2076	
Crystal size	0.25 x 0.20 x 0.10mm^3	
Theta range for data collection	2.3 to 25.00°.	
Index ranges	-13<=h<=8, -20<=k<=18, -33<=l<=35	
Reflections collected	28467	
Independent reflections	10082 [R(int) = 0.175]	
Completeness to theta = 25.00°	99.8%	
Absorption correction	Empirical	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10082 / 0 / 574	
Goodness-of-fit on F^2	0.95	
Final R indices [I>2sigma(I)]	R1 = 0.1078, wR2 = 0.2810	
R indices (all data)	R1 = 0.2272 , wR2 = 0.3267	
Largest diff. peak and hole	1.14 and -0.68 $e·Å^{-3}$	

Table S2 Distances [Å]and angles [°] of selected hydrogen bonding for **1**

D-H…A	d(D-H)	d(H..A)	d(D…A)	<D-H…A
N3- H3A…O2[a]	0.8600	2.1300	2.942(9)	157.00
N1- H1A…Cl1[b]	0.8600	2.7600	3.491(9)	143.00
C6- H6…Cl1[b]	0.9300	2.7200	3.643(9)	173.00
C17- H17…Cl1[c]	0.9300	2.7900	3.646(9)	154.00
C13- H13…O1	0.9300	2.3800	2.894(14)	115.00
C17- H17…O2	0.9300	2.3500	2.835(11)	112.00
C25- H25…O3	0.9300	2.3200	2.900(13)	120.00

Symmetry operators:(a) -*x*+1, -*y*+2, -*z*+1; (b) -*x*+1, *y*+1/2, -*z*+1/2; (c) *x*, -*y*+3/2, *z* +1/2.



Scheme S1 Nano-sized tricarboxylic ligand: 4,4',4''-[1,3,5-benzenetriyltris(carbonylimino)]-trisbenzoic acid.

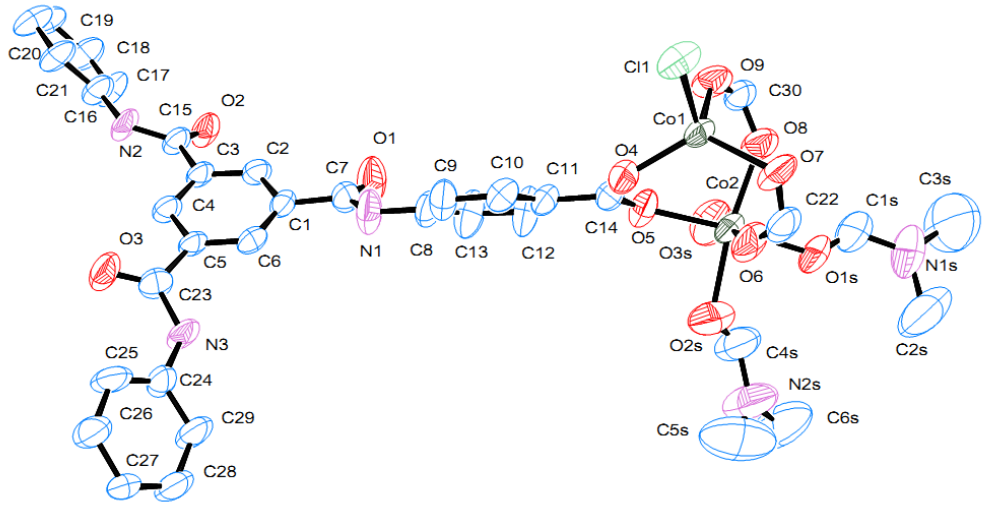


Figure S1. ORTEP picture of the asymmetric unit in crystal structure of **1** with 50% of thermal ellipsoid probability displacement. Hydrogen atoms and uncoordinated solvent molecules are omitted for clarity. Atom colours shown as carbon - blue, nitrogen - violet, oxygen – red, chloride – green and cobalt- dark green.

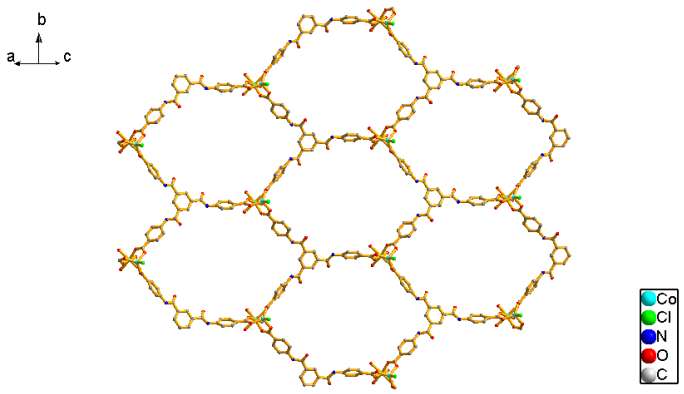


Figure S2. The honeycomb-like 2D structure of **1**.

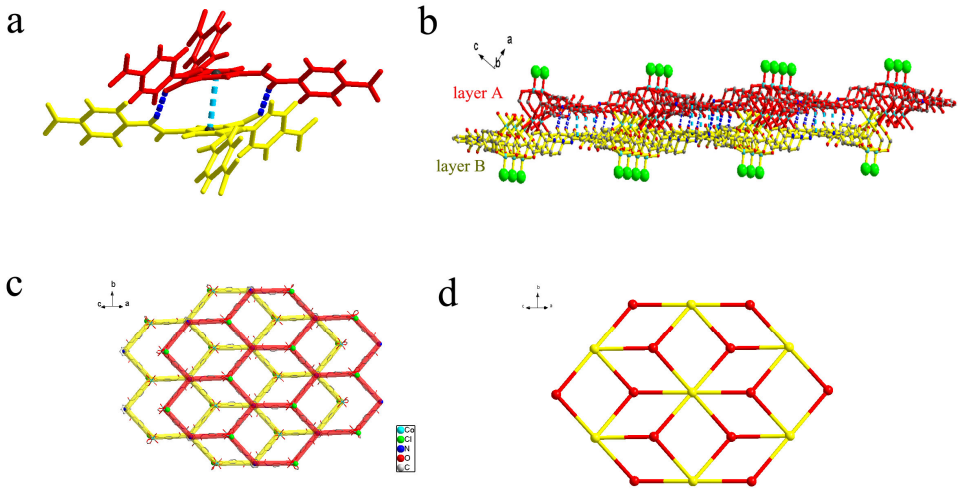


Figure S3. (a) Intermolecular N-H···O hydrogen bond (blue dash line) and π-π interaction between the central benzene moieties of the ligands (cyan dash line) to form a ligand pair Piedford unit among the two honeycomb-like layers (indicated by different color: red and yellow). Side (b) and top (c) views of the hydrogen bonded bilayer structure (green balls denote the chloride). (d) 2D bilayer structure with **kgd** topology.

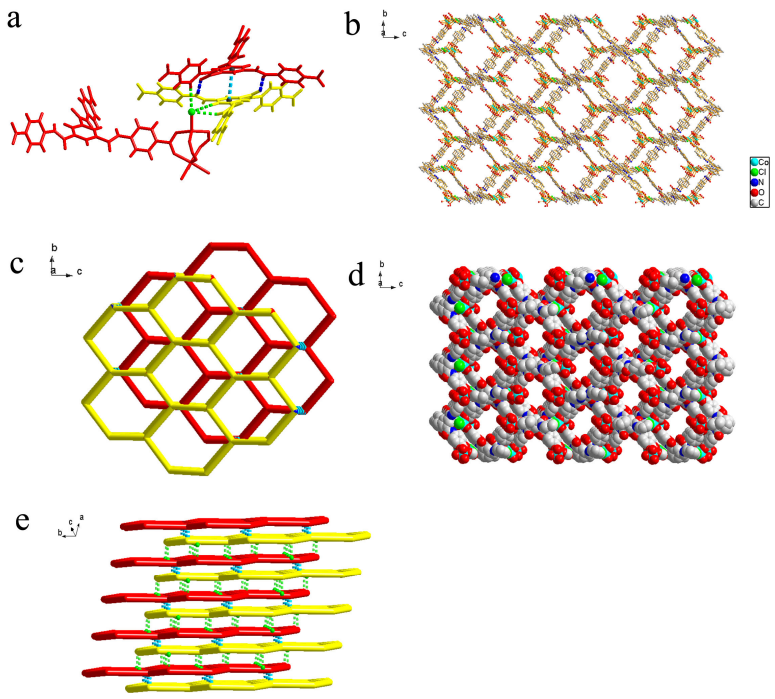


Figure S4. (a) N-H···Cl and C-H···Cl hydrogen bond (green dash line) between the adjacent bilayers (b) X-ray crystal structures of **1** showing channels along the *a* axis. (c)Top view of 3D packing of the simplfied honeycomb layers along *a* axis showing rhombic windows. (d) CPK model picture of the **1** illustrating the dimensions of the channel windows along the *a* axis. and side view (e) Side view of the simplfied honeycomb layers showing hydrogen bonding and π-π interaction (cyan dash line).Guest molecules are omitted for clarity.

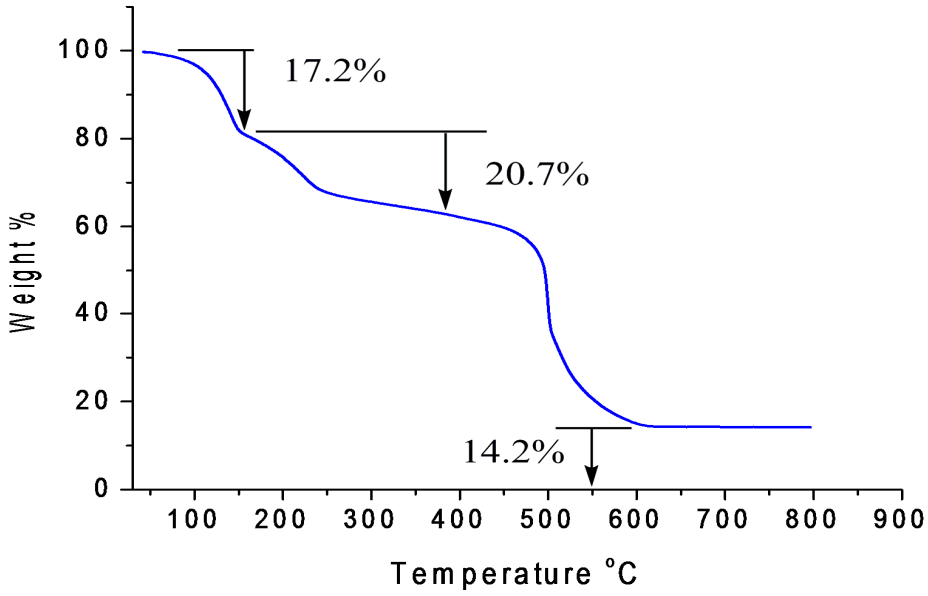


Figure S5. TGA curve of complexes **1**.

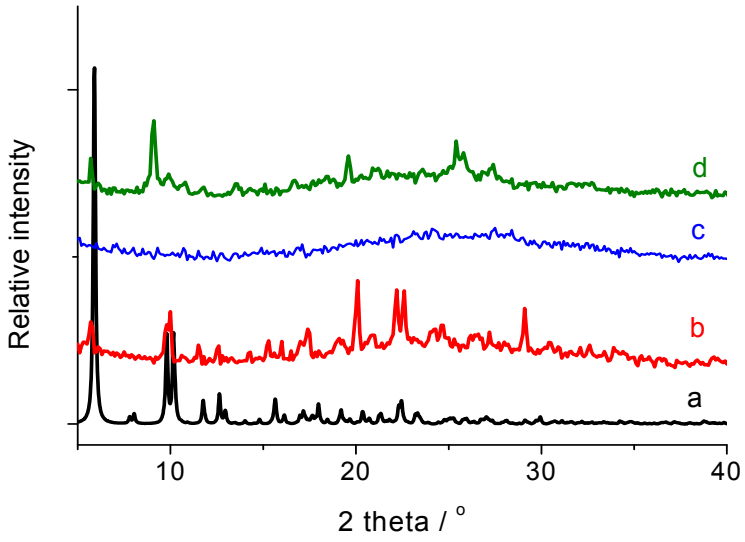


Figure S6. PXRD patterns of **1** and **1a**. (a) Simulated PXRD pattern from the single crystal structure of **1**, (b) as synthesized **1,** (c) actived, **1a** and (d) **1b** (**1a** immersed in a few drops of methanol).