Supporting Information for:

Halogen dependent symmetry change in two series of wheel cluster organic frameworks built by La_{18} tertiary building units

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Experimental Section:

Materials and physical measurements. All chemicals and solvents were commercially purchased and used without further purification. Elemental analysis was measured on a Vario MICRO Elemental Analyzer instrument. IR spectra (KBr pellets) were recorded on an ABB Bomem MB102 spectrometer over a range 400-4000 cm^{-1}. The thermogravimetric analyses (TGA) were performed on a Mettler Toledo TGA/SDTA 851^{e} analyzer in air atmosphere with a heating rate of 10 ºC/min from 30 ºC to 1000 ºC. Powder X-ray diffraction (PXRD) data were collected on a Rigaku Mini Flex II diffractometer using CuKα radiation (λ = 1.54056Å) under ambient conditions. The X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Scientific ESCALAB 250 instrument with a monochromatic Al Kα source. The UV diffuse reflection data were recorded at room temperature using a powder sample with $BaSO_4$ as a standard (100% reflectance) on a PerkinElmer Lamda-950 UV spectrophotometer and scanned at 200-800 nm. The absorption data are calculated from the Kubelka-Munk function, ($F(R)=(1-R)^2/2R=K/S$),[1] where R representing the reflectance, K the absorption, and S the scattering. The mixture of a single crystal and 50 mg dry KCl powder was well grounded and then pressed into a disk for the CD measurement with a MOS-450 spectropolarimeter.

X-Ray Crystallography. Crystallographic data of complexes **FJ-25**, **FJ-26**, **FJ-27** were collected on a Supernova single crystal diffractometer equipped with graphite-monochromatic CuKα radiation (λ = 1.54178 Å) at 298 K. The structure was solved with direct methods using SHELXS-97[2] and refined with the full-matrix least-squares technique based on F^2 using the SHELXL-97.[3] Non-hydrogen atoms were refined anisotropically, and all hydrogen atoms bond C were generated geometrically. Crystallographic diagrams were drawn using the DIAMOND software package.[4]

Supporting Figures:

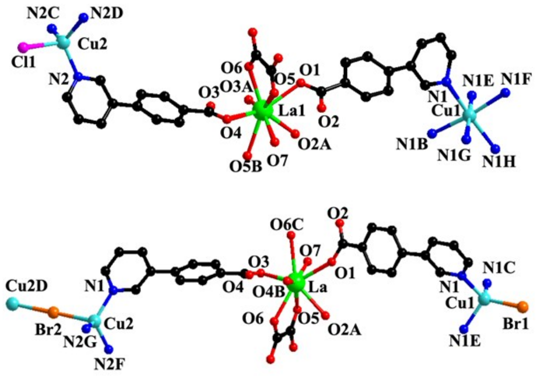


Fig. S1 The asymmetric unit of **FJ-25** (up) and **FJ-26** (down), showing the coordination environments of La and Cu atoms. Atoms with "A"~"H" in their labels are symmetry-generated. Symmetry code for **FJ-25** A: -*x*, -*x*+*y*, -*z*; B: -*y*, -1+*x*-*y*, *z*; C: -*x*+*y*, -*x*, *z*; D: -*y*, *x*-*y*, *z*; E: -*y*, -*x*, -0.5-*z*; F: 1-*x*+*y*, *y*, -0.5-*z*; G: 1-*x*+*y*, -*x*, *z*; H: *x*, -1+*x*-*y*, -0.5-*z*. Symmetry code for **FJ-26** A: 1-*x*+*y*, 1-*x*, *z*; B: *x*-*y*, -*y*, 0.5-*z*; C: 1-*y*, *x*-*y*, *z*; D: -*x*, -*y*, 1-*z*; E: 1-*x*+*y*, 1-*x*, *z*; F: -*y*, *x*-*y*, *z*; G: -*x*+*y*, -*x*, *z*.

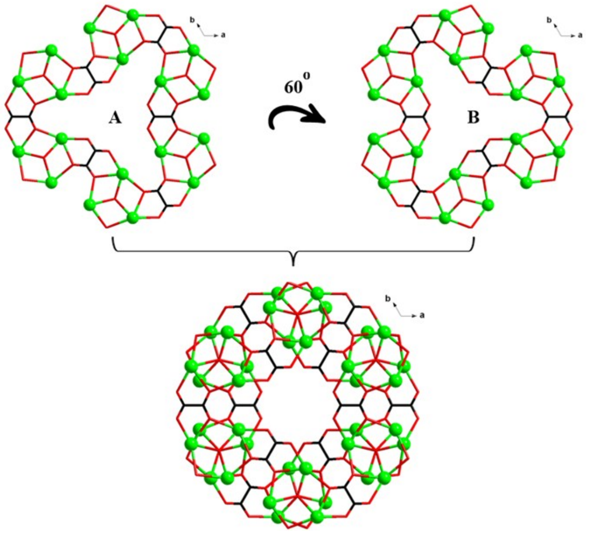
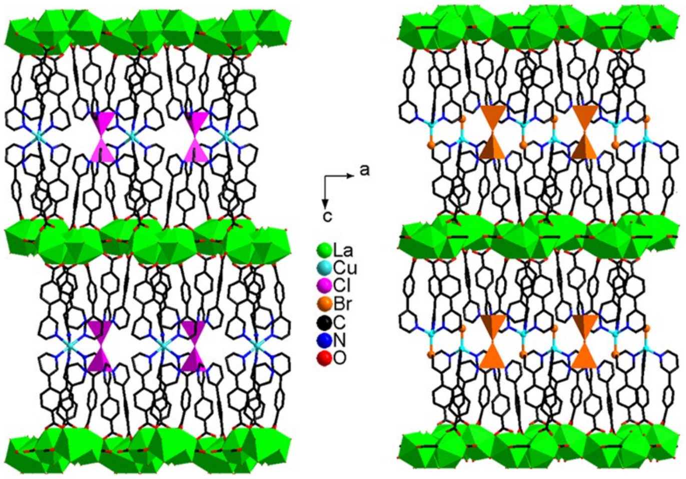


Fig. S2 The stacking of the La_{18} wheels in **FJ-25**.



FJ-25 **FJ-26/27**

Fig. S3 The side view of the overall WCOFs.

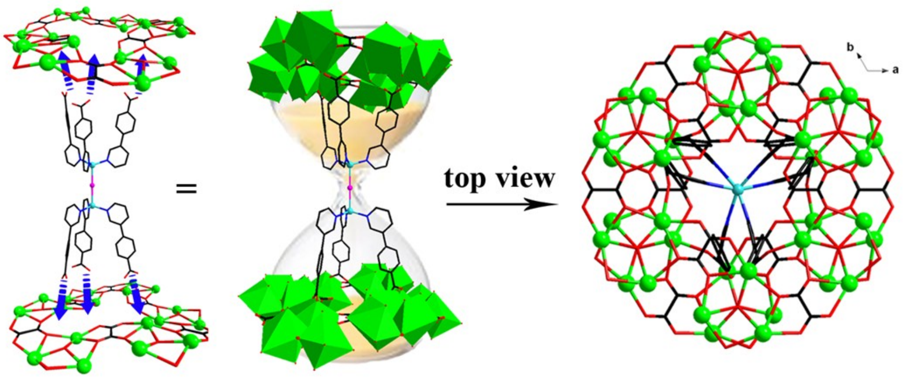


Fig. S4 The assembly of the hourglass.

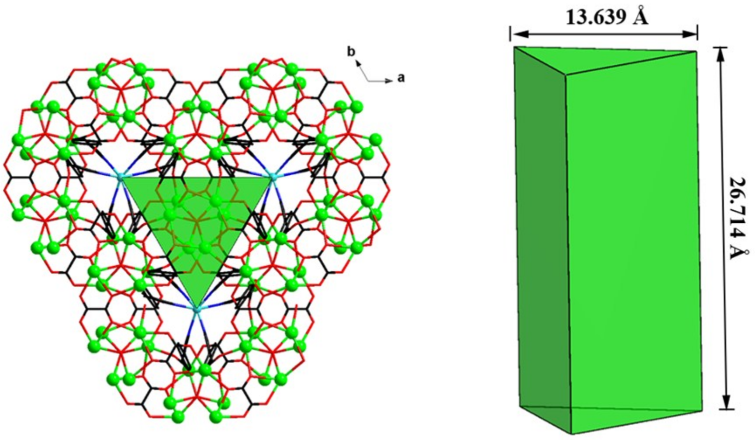


Fig. S5 The top (left) and side (right) view of the trigonal prism cage.

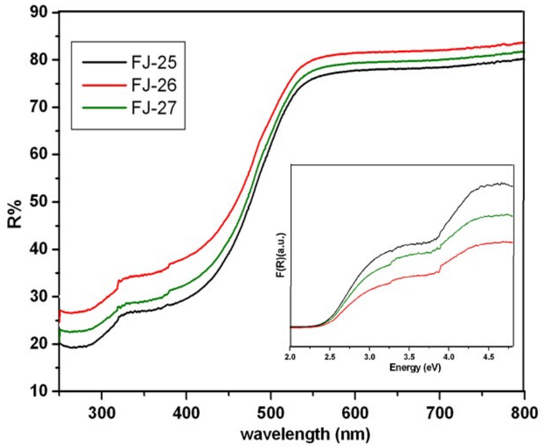


Fig. S6 Plots of UV-vis absorption spectra of **FJ-25**, **FJ-26** and **FJ-27**. Insert are their corresponding bands gaps.

The UV-Vis diffuse reflectance spectra of **FJ-25-FJ-27** in the region 800-250 nm are shown in Fig. 5. It is clear that the three compounds have no obvious absorption from 800 nm to 550 nm, but the absorption sharply increases below 550 nm. The strong absorption bands at about 275 nm are ascribed to the ligand-centered transitions of L ligands. The optical absorption spectra for the three compounds were converted from the diffuse reflectance data by using the Kubelka-Munk function. From the given absorption edges, the band gaps can be estimated to be 2.32 eV for **FJ-25**, 2.30 eV for **FJ-26**, 2.28 eV for **FJ-27**, respectively, which are consistent with their colours. The band gaps of them are comparable with that of the reported wheel clusters.[5-6]

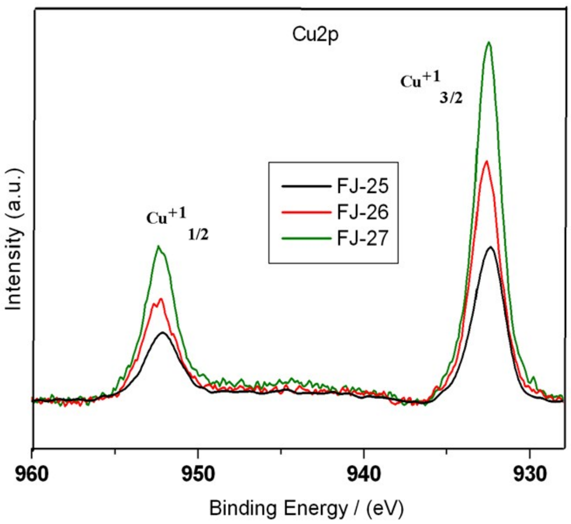


Fig. S7 The XPS spectrum of the three wheel cluster compounds.

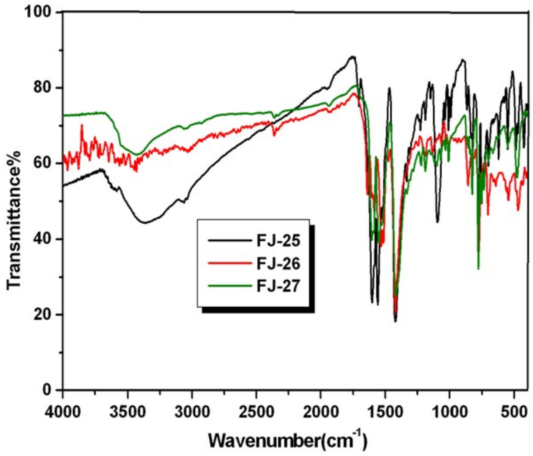


Fig. S8 The IR spectra of the wheel cluster compounds.

The IR Spectroscopy spectra of crystalline **FJ-25** to **FJ-27** were similar. The absorption band around 3400 cm^{-1} was assigned as the characteristic peaks of -OH vibration. The infrared spectra showed that the carboxylic acid units had been deprotonated as indicated by a shifted of stretching vibrations from 1700 cm^{-1} in the free carboxylic acid to 1600 cm^{-1}. The middle and narrow bands in the range of 1000-1470 cm^{-1} are attributed to C-N and C-C vibrations. It validates the existence of the COO^{-}, and OH groups in the crystal structure.

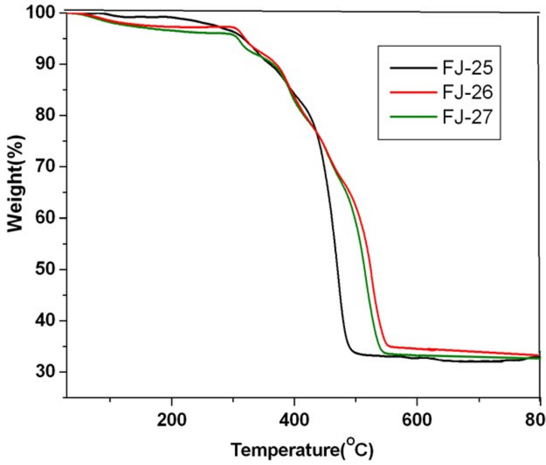


Fig. S9 The TGA plots of the wheel cluster compounds.

The thermogravimetric analysis (TGA) carried out in air atmosphere from 30 to 800 °C showed two steps of weight loss. The first step weight loss corresponds to their dehydration. And then ejection of the organic components ensued. The final mass remnant matches reasonably well with a deposition of CuO and La_2O_3 (**FJ-25**: calcd. 31.2%, found 30.9%; **FJ-26**: calcd. 32.3%, found 32.5%; **FJ-27**: calcd. 31.2%, found 30.8%).

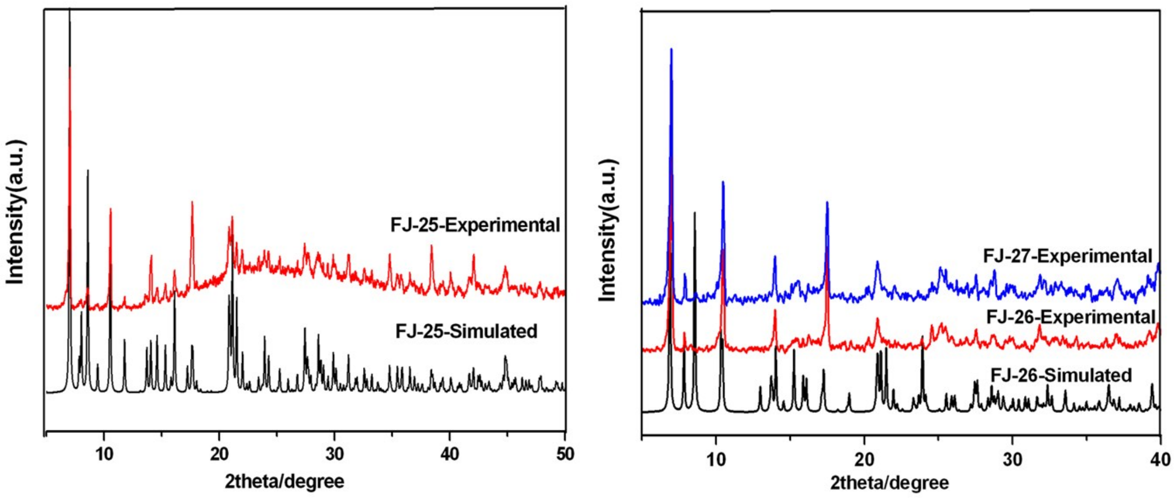


Fig. S10 PXRD patterns of the two series of the wheel cluster compounds.

Table S1 Crystal data and structure refinement for a pair of enantiomers, **FJ-25-1a** and **FJ-25-1b**.

Compound	**FJ-25-1a**	**FJ-25-1b**
Formula	$C_{150}H_{116}Cu_3La_6ClN_{12}O_{47}$	$C_{150}H_{116}Cu_3La_6ClN_{12}O_{47}$
Mr	3979.54	3979.54
Crystal system	hexagonal	hexagonal
Space group	$P6_322$	$P6_322$
a (Å)	13.0080(2)	13.0231(2)
c (Å)	50.2913(12)	50.5065(12)
V (Å^3)	7369.6(2)	7418.3(2)
Z	2	2
ρ(g cm^{-3})	1.793	1.782
μ(mm^{-1})	14.696	14.600
F(000)	3921	3921
Flack	0.011(13)	0.092(19)
GOF on F^2	1.080	1.059
Collected reflns	18430	17258
Unique reflns (R_{int})	4953	4849
Obsd reflns[I>2(I)]	4678	4501
Refined parameters	343	326
R_1[a]/wR_2[b][$I>2(I)$]	0.0687/0.1662	0.0875/0.2280
R_1[a]/wR_2[b](all data)	0.0729/0.1668	0.0921/0.2327

[a] $R_1 = \Sigma||F_o|-|F_c|| /\Sigma|F_o|$. [b] $wR_2 = \Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

References

1. W. W. Wendlandt and H. G. Hecht, *Reflectance Spectroscopy*, Interscience Publishers, New York, 1966.
2. G. M. Sheldrick, *SHELXS97, Program for Crystal Structure Solution (University of Göttingen, Göttingen, Germany, 1997).*
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5. J. W. Cheng, J. Zhang, S. T. Zheng and G. Y. Yang, *Chem.-Eur. J.*, 2008, **14**, 88.
6. W. H. Fang, J. W. Cheng and G. Y. Yang, *Chem.-Eur. J.*, 2014, **20**, 2704.