Supplementary Material (ESI) for Dalton Transactions

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An Unprecedented Densely Self-Catenated Metal−Organic Framework Containing Inclined Catenated Honeycomb-like Units with the Highest Topological Density among 4-Coordinated Nets

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Single-crystal X-ray diffraction

X-ray single-crystal diffraction data was collected on an Agilent SuperNova Dual diffractometer with Mo-Kα radiation (λ = 0.71073 Å) at 293 K with ω scan mode. CrysAlis PRO[1] software was used to collect, index, scale and apply analytical absorption correction based on faces of the crystal. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares technique using the SHELXL-97 program package[2]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of organic ligands were generated theoretically and refined isotropically with fixed thermal factors. The aqua hydrogen atoms in **1** were located from difference Fourier maps and refined with isotropic displacement parameters.

References

(1) Agilent Technologies, CrysAlis PRO Agilent Technologies, Yarnton, England, **2012**.

(2) Sheldrick, G. M. *A short history of SHELX*, *Acta Crystallogr.*, Sect. A, **2008**, 64, 112.

Electrochemical experiment

The electrochemical analysis was carried out using a CHI 660E electrochemical workstation. A conventional three-electrode system was used at room temperature. The title complex chemically bulk-modified carbon paste electrodes (CPE) were used as the working electrodes. A saturated calomel electrode and a platinum electrode were used as reference and auxiliary electrodes, respectively. The complex modified carbon paste electrode (**1**-CPE) was fabricated as follows: 0.5 g acetylene black powder and 0.03 g complex was mixed and grounded together by an agate mortar and pestle to achieve a uniform mixture, and then 0.2 ml of Nujol oil was added with stirring. The homogenized mixture was used to pack a 3 mm inner diameter glass tube to a length of 1 cm, and the tube surface was wiped with weighing paper. Electrical contact was established with a copper rod through the back of the electrode. The same procedure was used for the preparation of the bare CPE.

Catalysis Experiments

The photo-catalytic performance of complex **1** for the degradation of methyl orange was measured in typical processes: 0.01 mmol of solid catalysts (**1**) or $CoCl_2 \cdot 6H_2O$ and 0.04 mmol of sodium persulfate (the catalyst/persulfate molar ratio is 1:4) were mixed together with 100 mL of methyl orange solution (10 mg/L, pH = 3.0), which was magnetically stirred about 30 min in a dark environment to obtain the uniform working solution. Then the resulting solution was irradiated with UV light under stirring and the temperature of the reaction solution was maintained at 30 ºC by cooling water circulation. A sample (3.0 mL) was taken out at given time intervals and separated through centrifugation and then subsequently analyzed by using a UV-visible spectrometer at 506 nm. The photo-catalytic degradation of methyl orange was conducted on an XPA-7 type photochemical reactor (Xujiang Machine Factory, Nanjing, China) equipped with a 100 W mercury lamp (mean wavelength 365 nm) with light intensities at quartz tube positions of 12.7 mW/cm^2. In addition, the control experiment for degrading methyl orange was also performed under the same conditions without any catalysts. The stability of complex **1** after the photo-catalytic process was tested through XRPD.

The degradation efficiency of methyl orange is defined by considering the initial absorbance values of the dye solution (A_0) and the absorbance values (A_t) of the solution at reaction time:

$$\text{Degradation efficiency} = \frac{A_0 - A_t}{A_0} \times 100\% \qquad (1)$$

The 3D supramolecular topology of compound **1** performed by the ToposPro software

```
##################
1:C26 H28 Co N4 O6
##################
Topology for Co1
--------------------
Atom Co1 links by bridge ligands and has
Common vertex with                                        R(A-A)
Co 1      0.8070     0.2685     0.3511    ( 1 0 0)    10.891A          1
Co 1     -0.1930     0.7315    -0.1489    ( 0 1 0)    11.014A          1
Co 1     -0.1930    -0.2685     0.8511    ( 0 0 1)    17.692A          1
Co 1      0.3070    -0.7685    -0.1489    ( 0-1 0)    18.037A          1
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Structural group analysis
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Structural group No 1
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Structure consists of 3D framework with Co

Coordination sequences
----------------------
Co1:   1   2   3    4    5    6     7     8     9    10
Num    4  12  33   90  201  406   650   920  1198  1520
Cum    5  17  50  140  341  747  1397  2317  3515  5035
----------------------
TD10=5035

Vertex symbols for selected sublattice
--------------------------------------
Co1 Point symbol:{6^3.10^3}
Extended point symbol:[6.10(12).6.10(12).6.10(12)]
Rings coincide with circuits
--------------------------------------
Point symbol for net: {6^3.10^3}
4-c net; uninodal net

Topological type: cgh5 (personal.ttd) {6^3.10^3} - VS [6.10(12).6.10(12).6.10(12)] (103665 types in
11 databases)
Elapsed time: 14.42 sec.
```

Table S1. Selected bond lengths [Å] and angles [º] for complex **1**.

Co(1)-O(2)	2.016(4)	Co(1)-N(1)	2.050(4)
Co(1)-O(3)	1.990(4)	Co(1)-N(3)	2.018(4)
O(2)-Co(1)-O(3)	122.41(18)	O(2)-Co(1)-N(3)	104.18(19)
O(2)-Co(1)-N(1)	90.89(16)	O(3)-Co(1)-N(1)	107.04(17)
O(3)-Co(1)-N(3)	114.17(18)	N(1)-Co(1)-N(3)	116.58(17)

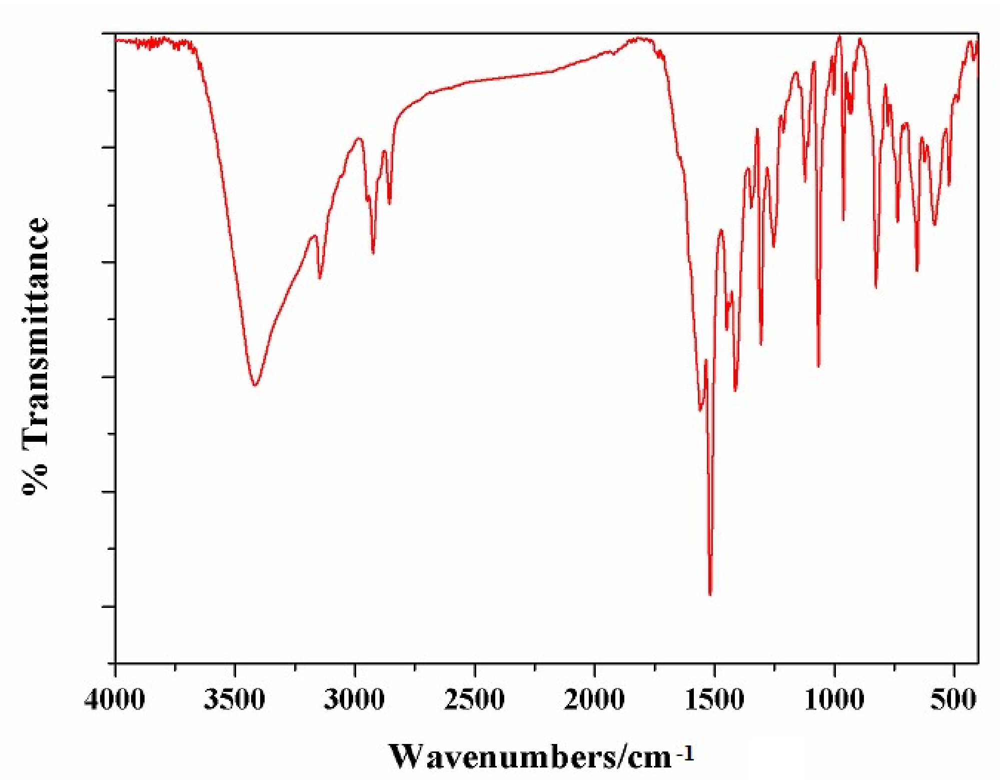

Figure S1. IR spectrums of complex **1**

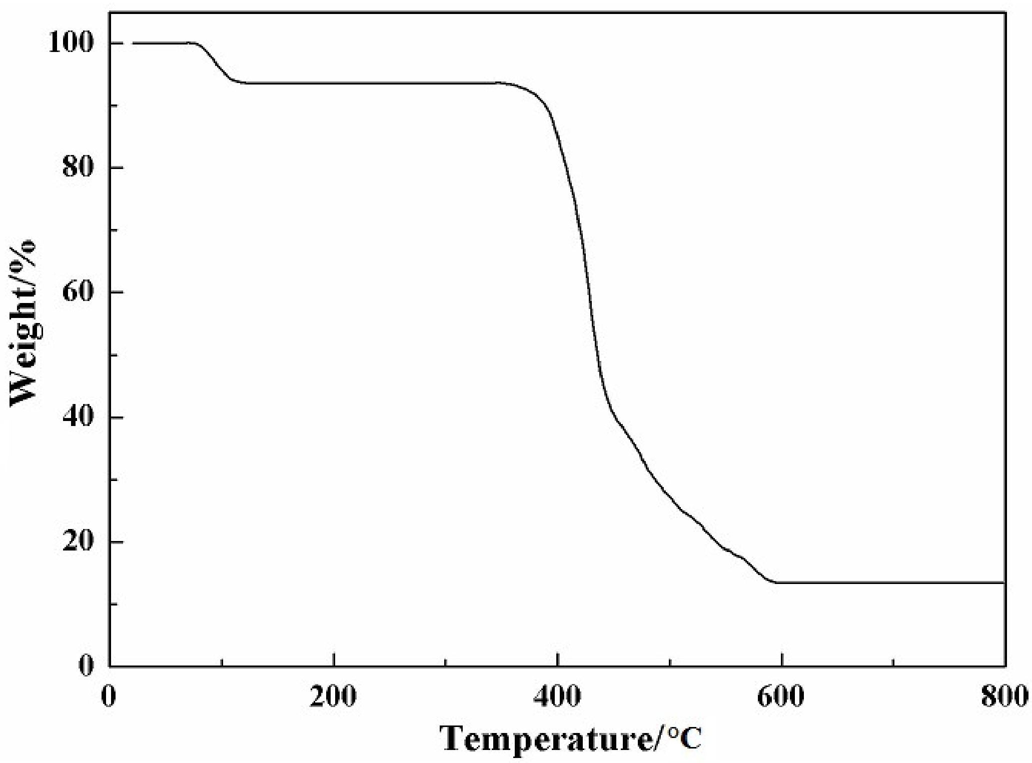

Figure S2. TGA curve of **1**.

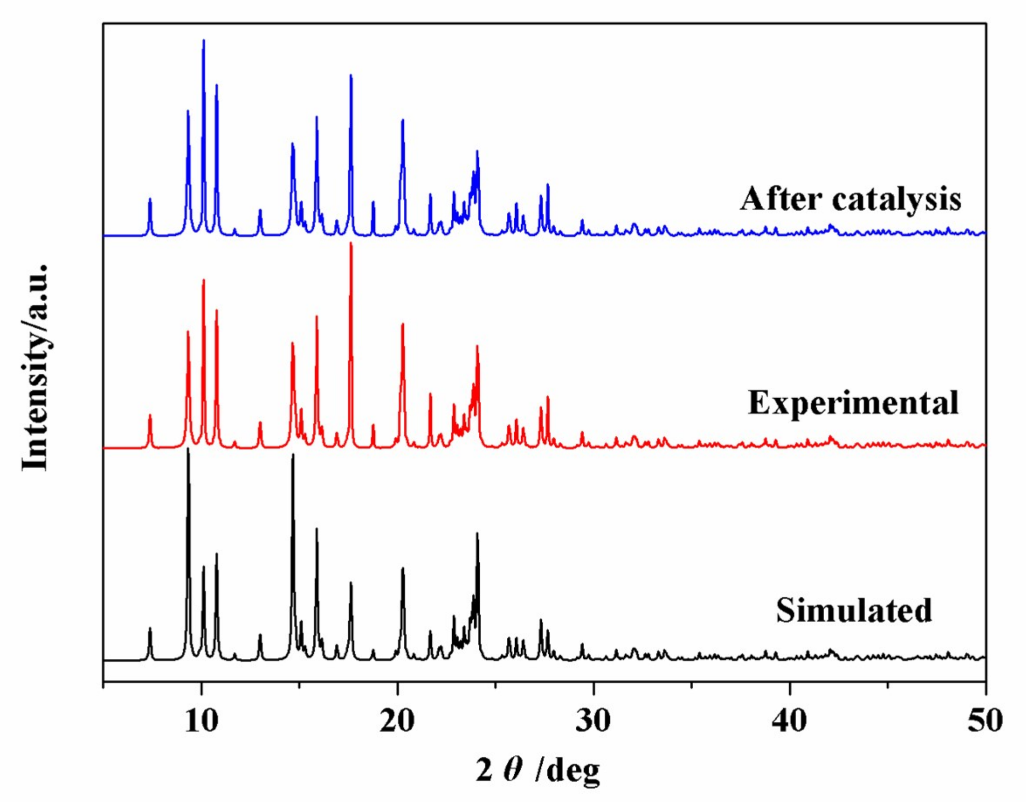

Figure S3. The simulated from single-crystal data, obtained from the experiment and after catalytic experiments X-ray powder diffraction patterns of complex **1**.

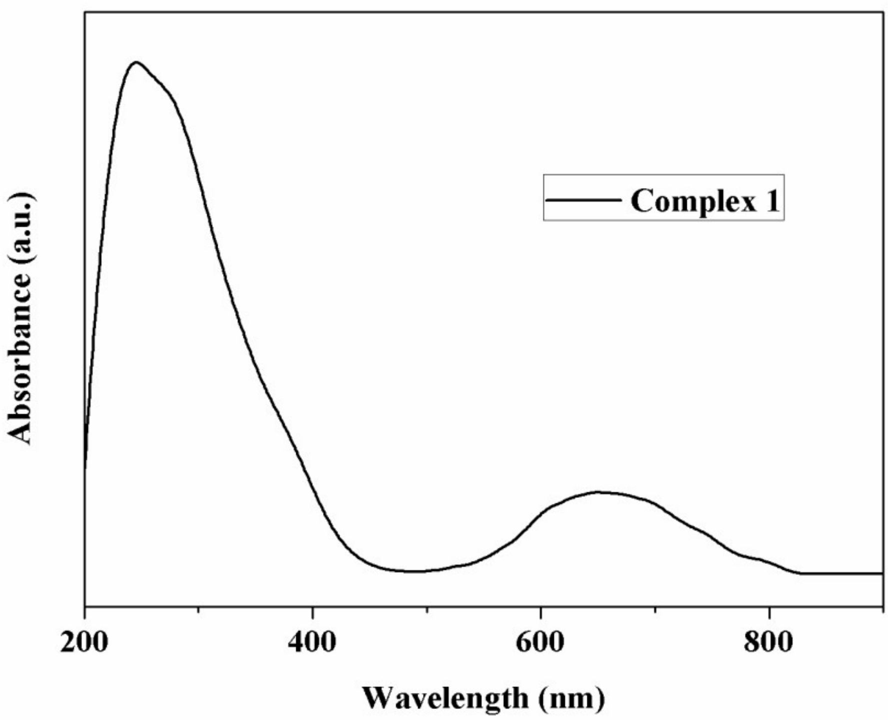

Figure S4. UV/Vis absorption spectrum of **1** with $BaSO_4$ as background.

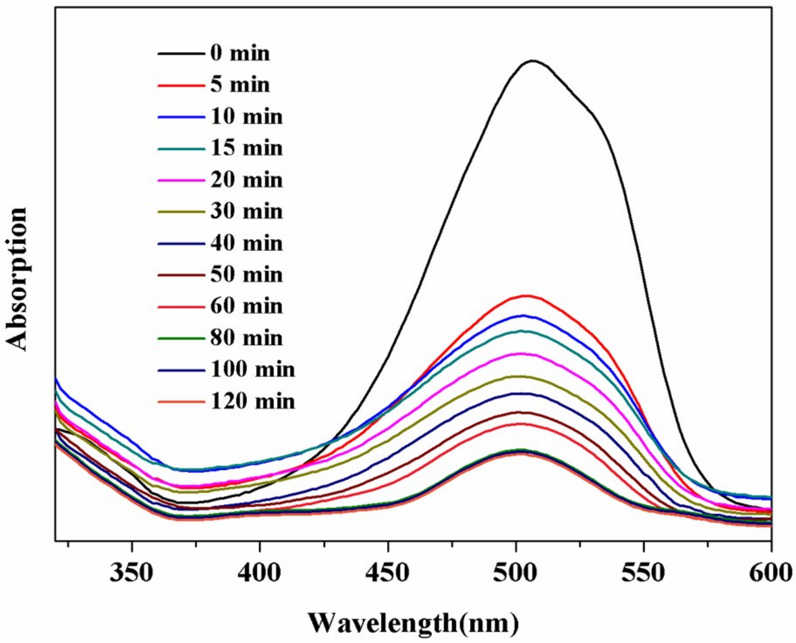

Figure S5. Absorption spectra of the MO solution during the decomposition reaction under UV irradiation in the presence of complex **1**.