

Electronic Supplementary Material (ESI) for Dalton Transactions.

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SUPPLEMENTARY MATERIAL

**Syntheses and magnetic properties of high dimensional
cucurbit[6]uril-based metal organic rotaxane frameworks**

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Experimental Section

Materials and Physical Measurements.

[PR43]²⁺·2[NO₃]⁻ and CB[6] were synthesized according to the references.^{1,2} Other purchased chemicals reagents were used without any further purification. The IR spectra were recorded from KBr pellets in the range of 4000-400 cm⁻¹ on a Mattson Alpha-Centauri spectrometer. Elemental analyses (C, H, and N) were performed on a PerkinElmer 2400 elemental analyzer. Elemental Co contents of compounds **1-3** were determined using an ICP-9000 (N+M) (USA Thermo Jarrell-Ash Corp). Thermogravimetric analysis (TGA) was performed on a PerkinElmer TG-7 analyzer over the temperature 20-800 °C in a nitrogen-gas atmosphere with a heating rate of 10 °C min⁻¹. Variable temperature magnetic susceptibility data were obtained in the temperature range of 2-300 K using a SQUID magnetometer (Quantum Design, MPMS-5) with an applied field of 1000 Oe. X-ray photoelectron spectroscopy analyses were performed on a VG ESCALABMKII spectrometer with an Al-K α (1486.6 eV) achromatic X-ray source. Powder X-ray diffraction (XRD) measurements were recorded on a Rigaku Smart Lab with Cu-K α ($\lambda = 1.5418 \text{ \AA}$) radiation in the range 5-50°. X-ray diffraction data collection of the compounds was performed using a Bruker Smart Apex II CCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. All absorption corrections were performed by using the SADABS program. The formulas of compounds **1** and **2** were determined by the combination of elemental analysis, TGA data and the crystallographic data. The water is randomly disordered in compound **3** and the formula of compound **3** was determined by the combination of elemental analysis, TGA data and the SQUEEZE results. The crystallographic data of compound **1-3** have been deposited in the Cambridge Crystallographic Data Center as supplementary publication with CCDC: 1909151, 1909152, 1909153.

Preparation of [Co₂(PR43)(BDC)₂Cl₂] \cdot 4H₂O (**1**).

A mixture of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (19.0 mg, 0.08 mmol), $[\text{PR43}]^{2+} \cdot 2[\text{NO}_3]^-$ (55.7 mg, 0.04 mmol), H_2BDC (9.97 mg, 0.06 mmol), 3 drops of triethylamine (where a 1 ml injection syringe is used) and 4 mL of H_2O was stirred for 30 min, and then transferred and sealed in a 18 mL Teflon-lined stainless steel container, which is heated at 140 °C for 72h. Block purple crystals of **1** suitable for X-ray crystallography were obtained, washed with distilled water, and dried in air. Yield: 40.6% based on [PR43]. Elemental analysis calc. for $\text{C}_{68}\text{H}_{76}\text{Co}_2\text{Cl}_2\text{N}_{28}\text{O}_{24}$. (%): C 43.94, Co 6.34, H 4.12, N 21.10; Found: C 44.76, Co 6.21, H 3.94, N 21.62.

Preparation of $[\text{Co}_2(\text{PR43})(\text{BTC})_2] \cdot 6\text{H}_2\text{O}$ (2).

2 was synthesized by a procedure similar to that was used for **1** with H_3BTC (10.5 mg, 0.05 mmol) instead of H_2BDC . Yield: 36.4% based on [PR43]. Elemental analysis calc. for $\text{C}_{70}\text{H}_{80}\text{Co}_2\text{N}_{28}\text{O}_{31}$. (%): C 43.62, Co 6.12, H 4.18, N 20.35; Found: C 44.56, Co 5.98, H 4.06, N 20.54.

Preparation of $[\text{Co}_2(\text{PR43})(\text{BPT})_2] \cdot 20\text{H}_2\text{O}$ (3).

3 was synthesized by a procedure similar to that was used for **1** with H_3BPT (14.3 mg, 0.05 mmol) instead of H_2BDC . Yield: 43.6% based on [PR43]. Elemental analysis calc. for $\text{C}_{82}\text{H}_{114}\text{Co}_2\text{N}_{28}\text{O}_{44}$. (%): C 42.57, Co 5.09, H 4.97, N 16.95; Found: C 42.31, Co 5.21, H 5.08, N 16.73.

Table S1. Crystallographic data and structure refinements for compounds **1-3**.

	1	2	3
Empirical formula	[Co ₂ (PR43)(BDC) ₂ Cl ₂] ₂ ·4H ₂ O	[Co ₂ (PR43)(BTC) ₂] ₂ ·6H ₂ O	[Co ₂ (PR43)(BPT) ₂] ₂ ·20H ₂ O
Mr	1858.32	1927.48	2313.86
T/K	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P2₁/c</i>	<i>Pbca</i>	<i>P2₁/n</i>
<i>a</i> /Å	14.256(5)	19.034(5)	13.868(5)
<i>b</i> /Å	19.149(5)	14.409(5)	14.824(5)
<i>c</i> /Å	14.830(5)	27.801(5)	25.364(5)
<i>α</i> (°)	90.000(5)	90	90.000(5)
<i>β</i> (°)	110.087(5)	90	92.949(5)
<i>γ</i> (°)	90.000(5)	90	90.000(5)
<i>V</i> /Å ³	3802(2)	7625(4)	5207(3)
<i>Z</i>	2	4	2
<i>D_c</i> /mg m ⁻³	1.623	1.679	1.476
<i>μ</i> /mm ⁻¹	0.607	0.547	0.423
measured reflections	38328	16951	41404
Independent reflections	9304	6476	9162
data/restraints/parameters	9304/24/577	6476/21/595	9162/1/613
goodness-of-fit on F ²	1.043	1.138	1.086
<i>R</i> ₁ ^a [<i>I</i> > 2σ(<i>I</i>)]	0.0406	0.1019	0.0521
<i>wR</i> ₂ ^b (all data)	0.1137	0.2386	0.1716

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

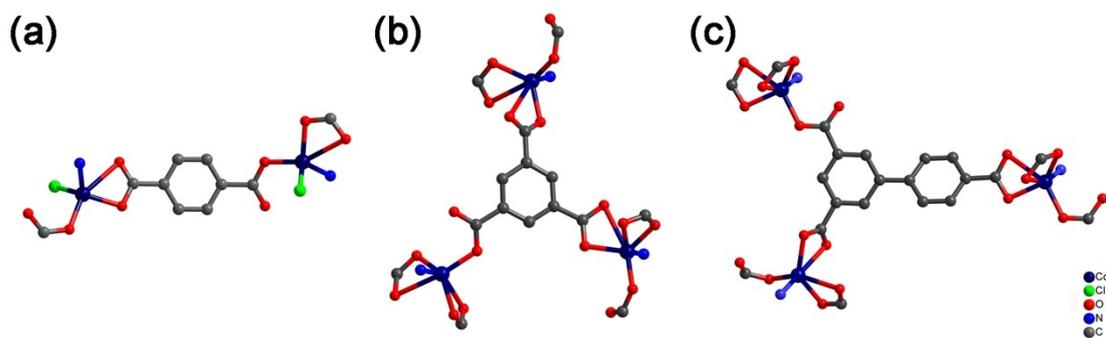


Fig. S1 The coordination environment of H₂BDC, H₃BTC and H₃BPT.

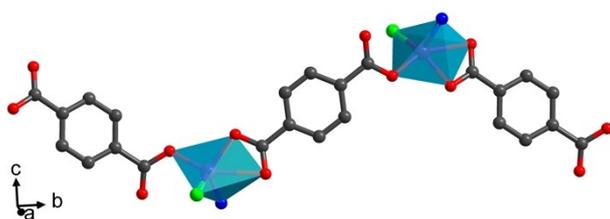


Fig. S2 The chemical views of the one dimensional chain in **1**.

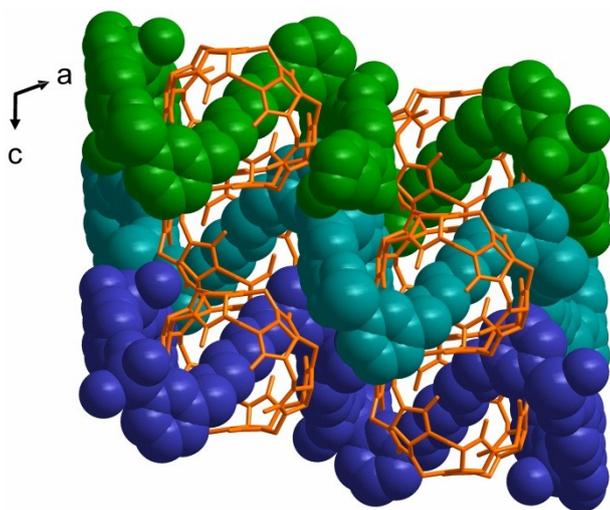


Fig. S3 The 3D supramolecular architectures as viewed along the *b* axis in **1**.

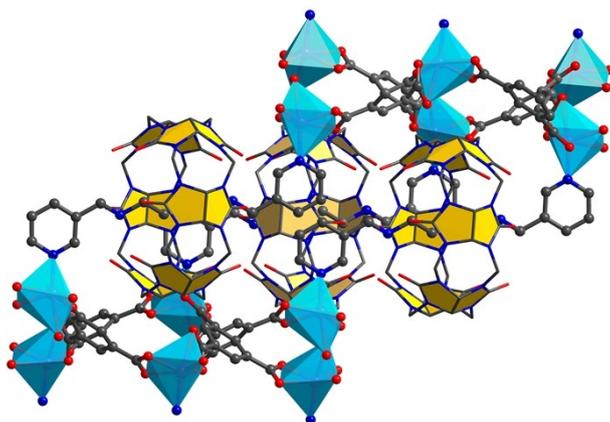


Fig. S4 The 3D frameworks as viewed along the *a* axis in **2**. Hydrogen atoms are omitted.

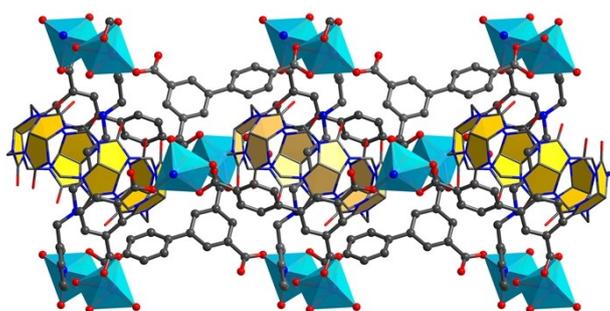


Fig. S5 The 3D frameworks as viewed along the *c* axis in **3**. Hydrogen atoms are omitted.

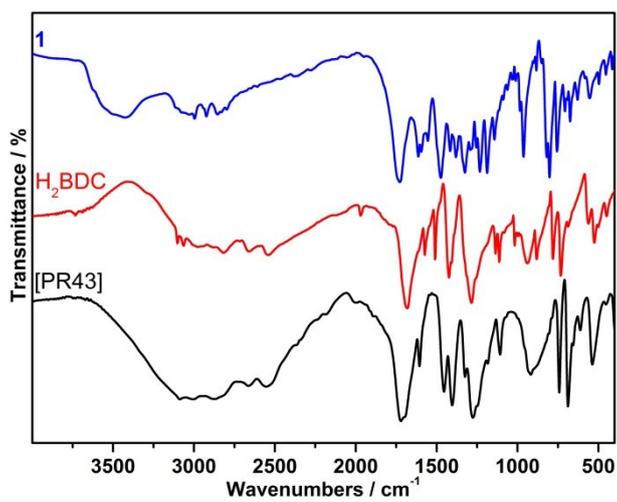


Fig. S6 The IR spectrum of compound **1**, H₂BDC and [PR43]²⁺·2[NO₃]⁻.

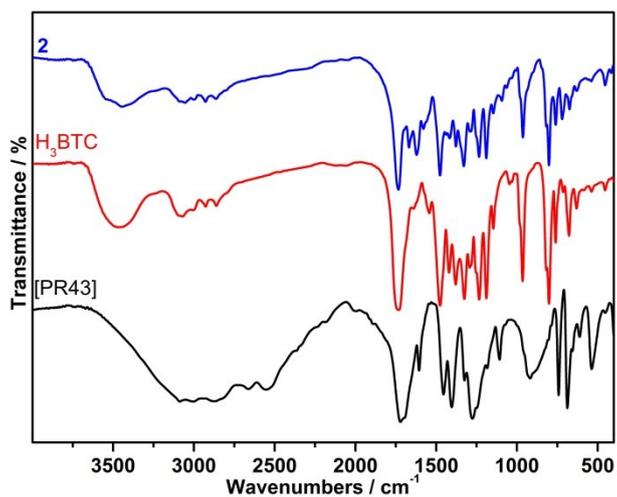


Fig. S7 The IR spectrum of compound **2**, H₃BTC and [PR43]²⁺·2[NO₃]⁻.

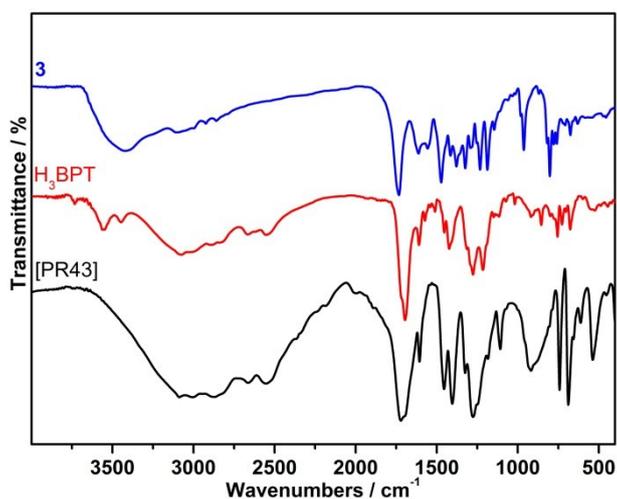


Fig. S8 The IR spectrum of compound **3**, H₃BPT and [PR43]²⁺·2[NO₃]⁻.

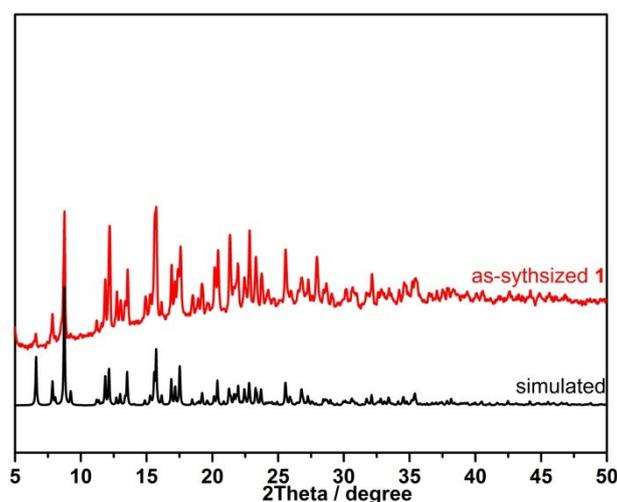


Fig. S9 PXRD patterns for compound **1** and simulated spectra of compound **1** from single crystal data.

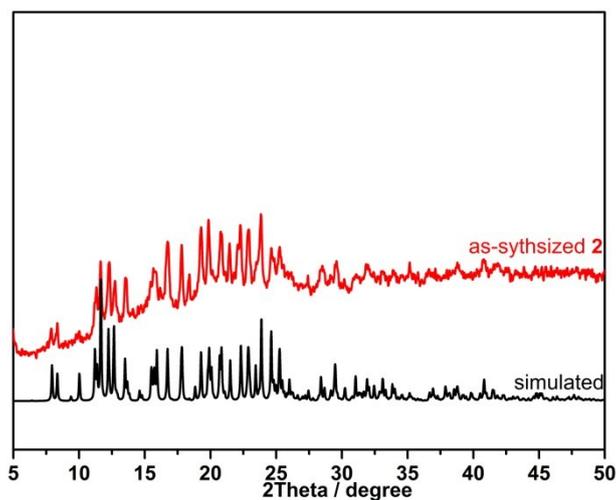


Fig. S10 PXRd patterns for compound **2** and simulated spectra of compound **2** from single crystal data.

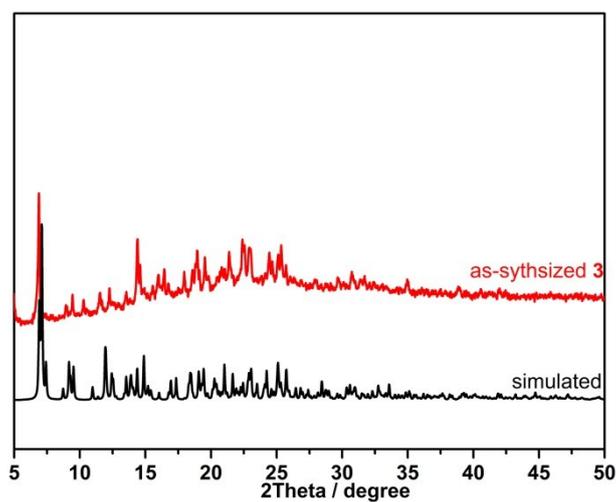


Fig. S11 PXRd patterns for compound **3** and simulated spectra of compound **3** from single crystal data.

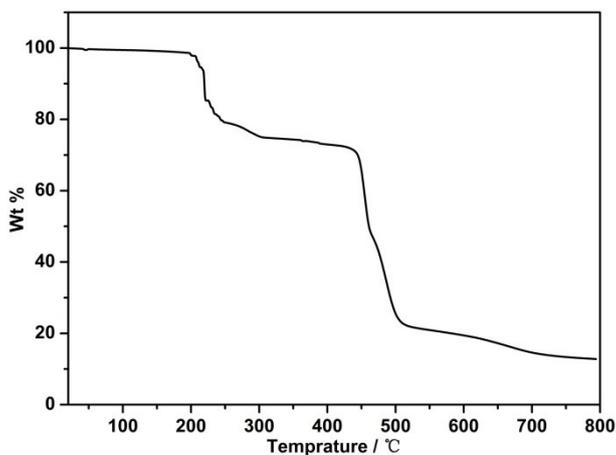


Fig. S12 Thermal gravimetric analysis (TGA) curves for as-synthesized compound **1**.

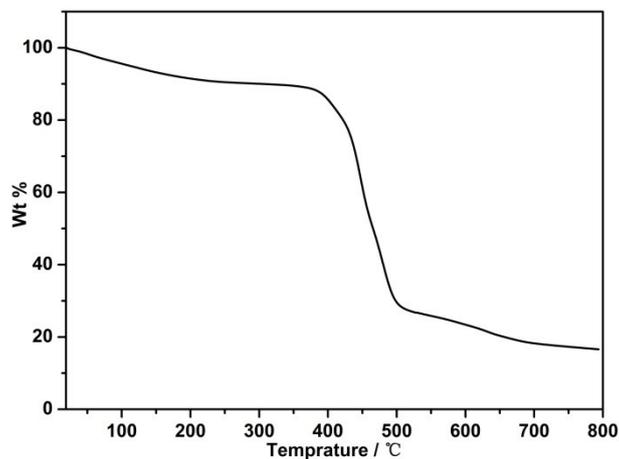


Fig. S13 Thermal gravimetric analysis (TGA) curves for as-synthesized compound 2.

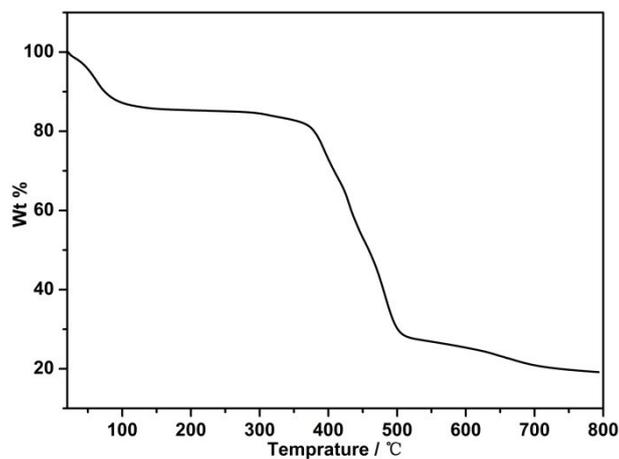


Fig. S14 Thermal gravimetric analysis (TGA) curves for as-synthesized compound 3.

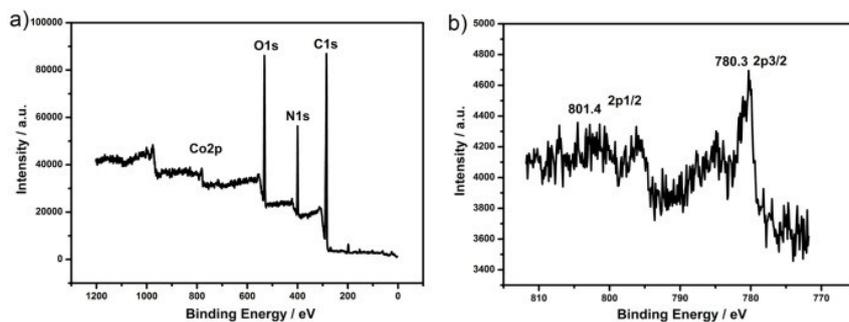


Fig. S15 XPS spectra of compound 1 give one peak at 780.3 eV, which can be ascribed to $\text{Co}^{\text{II}} 2p_{3/2}$.³

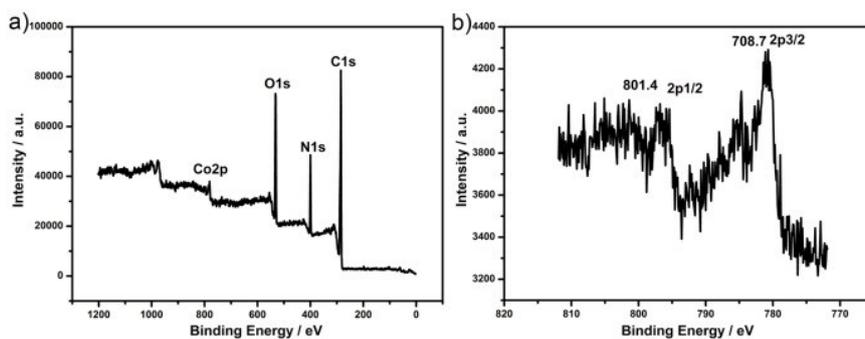


Fig. S16 XPS spectra of compound **2** give one peak at 780.7 eV, which can be ascribed to $\text{Co}^{\text{II}} 2p_{3/2}$.³

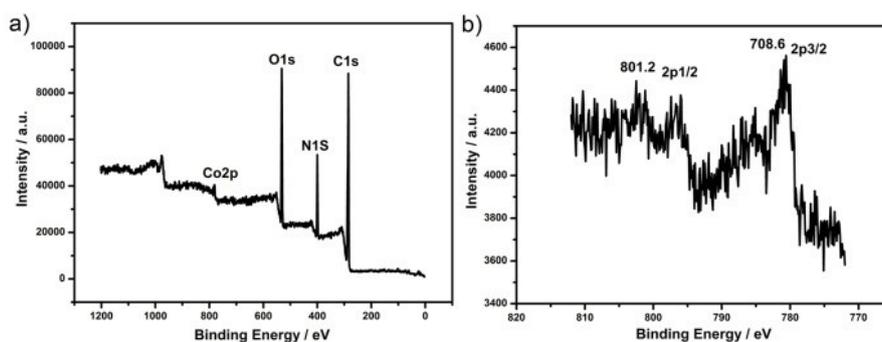


Fig. S17 XPS spectra of compound **3** give one peak at 780.6 eV, which can be ascribed to $\text{Co}^{\text{II}} 2p_{3/2}$.³

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2 D. Bardelang, K. A. Udachin, D. M. Leek, J. C. Margeson, G. Chan, C. I. Ratcliffe and J. A. Ripmeester, *Cryst. Growth Des.*, 2011, **11**, 5598-5614.

3 K Yu, B.-B. Zhou, Y. Yu, Z.-H. Su and G.-Y. Yang, *Inorg. Chem.*, 2011, **50**, 1862-1867.