SUPPORTING INFORMATION

Coordination polymers constructed from tetrahedral shaped adamantane tectons

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Experimental Section

Materials

All reagents and solvents, purchased from commercial sources, were used as received, without any further purification.

1. Experimental procedures

Synthesis of 1,3,5,7- tetrakis{4-(4-pyridyl)phenyl}adamantane (L^1)
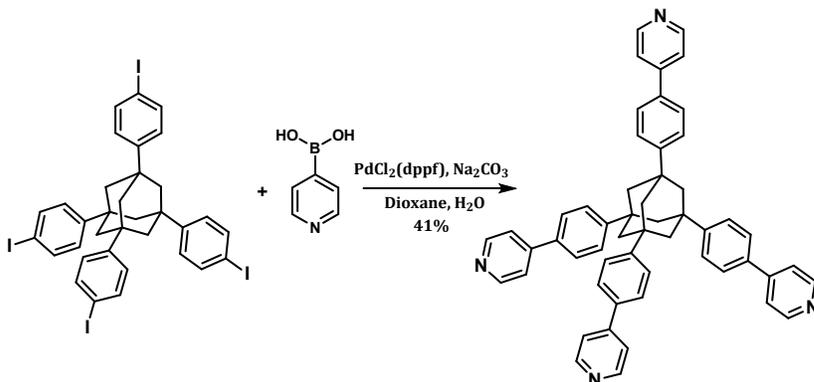
Scheme S1

Synthesis of 1,3,5,7- tetrakis(4-cyano-phenyl)adamantane (L^2)
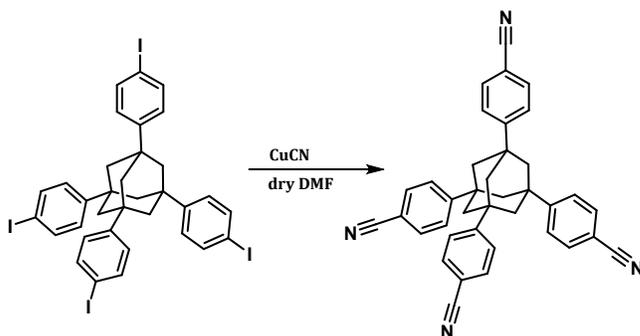
Scheme S2

2. Physical measurements

2.1. Crystallographic data collection and structure determination

The X-ray diffraction measurements were performed on Oxford Diffraction SuperNova diffractometer using hi-flux micro-focus Nova Cu Ka radiation (for compound **1**) and on a STOE IPDS II single crystal diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) (for compound **2**). The structures were solved by direct methods and refined by full-matrix least-squares techniques based on F^2 using the SHELXL-2013 program package.[S1] The non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in fixed, idealized positions and refined as rigidly bonded to the corresponding carbon atoms. Since attempts to locate and refine the positional parameters for disordered entities in the crystal structure of **1** were not fully successful, the "solvent mask routine" available in the

Olex2[S2] program was used to account for the scattering from the voids accommodating out-of-sphere BF_4^- anions and H_2O molecules. As the result, the value of R_1obs has been reduced from 0.1033 to 0.0750. Crystallographic data and structure refinement parameters for **1** and **2** are presented in Table **S1**. Selected bond distances and angles are collected in Table **S2**.

CCDC reference number: 1508551-1508552

Table S1. Crystallographic data, details of data collection and structure refinement parameters for **1** and **2**.

	1	2
Formula sum	$C_{54}H_{48}CuB_2F_8N_4O_2\cdot8H_2O$	$C_{29}H_{16}MnF_{12}N_2O_4$
Formula weight	1166.26	739.38
Crystal system	tetragonal	tetragonal
Space group	$I422$	$I\,4_1/a$
a/Å	12.8199(9)	11.645(5)
b/Å	12.8199(9)	11.645(5)
c/Å	32.617(4)	52.700(5)
α/°	90.000	90.000(5)
β/°	90.000	90.000(5)
γ/°	90.000	90.000(5)
V/Å^3	5360.5(1)	7146(6)
Z	4	8
D_c/g cm^{-3}	1.310	1.374
T/K	293	293
μ/mm^{-1}	1.218	0.465
Reflections collected	6049	32305
Independent reflection	1932[R_{int} = 0.0566]	3122 [R_{int} = 0.2541]
R_1^a [$I > 2\sigma(I)$]	0.0750	0.0604
wR_2^b (all data)	0.2671	0.1807
GOF	1.086	0.885
$\Delta\rho_{min}/\Delta\rho_{max}$ (e Å^{-3})	-0.24/1.26	-0.25/0.53
Flack parameter	0.42(7)	

$^a R_1 = \sum||F_o|-|F_c||/\sum|F_o|$. $^b wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_0^2)+(aP)^2+bP]$ where P= [max(F_0^2, 0) + 2F_c^2]/3.

Tables S2. Bond lengths (Å) and angles (deg) for **1** and **2**

1		2	
Cu1–N1	2.026(8)	Mn1 – O1	2.128(4)
Cu1–O1W	2.626(16)	Mn1– O2	2.156(5)
		Mn1 – N1	2.241(7)
O1W Cu1 O1W^A	180.0	O1 Mn1 O2	83.2(2)
O1W Cu1 N1	90.0(5)	O1 Mn1 O2^A	94.8(2)
O1W Cu1 N1^A	90.0(5)	O1 Mn1 O1^A	177.3(3)
O1W Cu1 N1^B	90.0(5)	O1 Mn1 N1	94.1(2)
O1W Cu1 N1^C	90.0(5)	O1 Mn1 N1^A	87.8(2)
N1 Cu1 N1^A	89.5(4)	O2 Mn1 O1^A	94.8(2)
N1 Cu1 N1^B	180.0(1)	O2 Mn1 O2^A	88.7(3)
N1 Cu1 N1^c	90.5(4)	O2 Mn1 N1	176.9(2)
N1^A Cu1 N1^B	90.5(4)	O2 Mn1 N1^A	90.0(2)
N1^A Cu1 N1^C	180.0(1)	O1^A Mn1 O2^A	83.2(2)
N1^B Cu1 N1^C	89.5(4)	O1^A Mn1 N1	87.8(2)
		O1^A Mn1 N1^A	94.1(2)
		O2^A Mn1 N1	90.0(2)
		O2^A Mn1 N1^A	176.9(2)
		N1 Mn1 N1^A	91.4(4)

^{A} = 1-*x*, 2-*y*, *z* ^{A} = 1-*x*, 0.5-*y*, *z*
^{B} =1.5-*x*, 1.5-*y*, 0.5-*z*
^{C} = 0.5+*x*, -0.5+*y*, 0.5-*z*
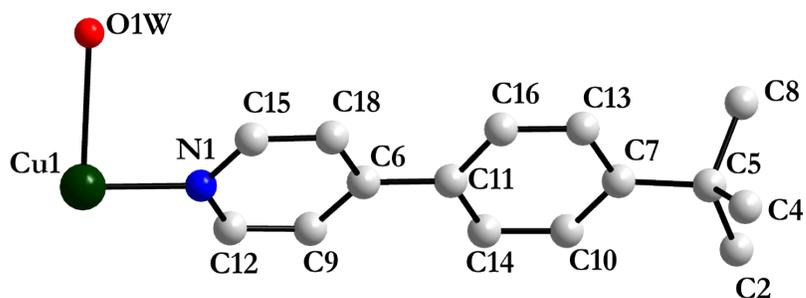
Figure S1. The asymmetric unit of compound **1.**
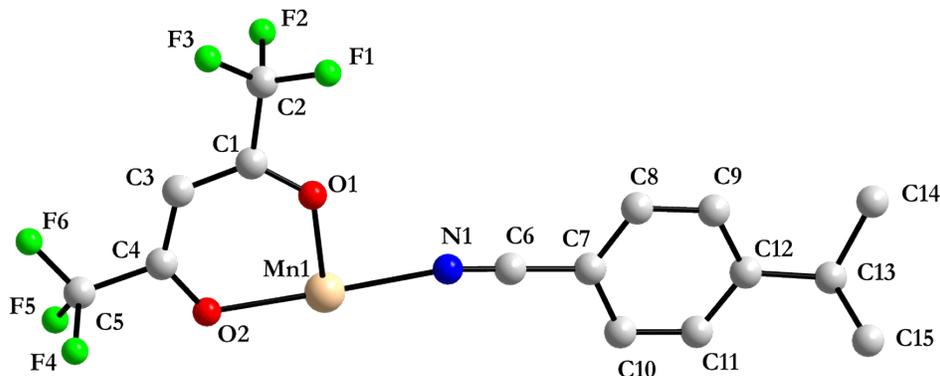
Figure S2. The asymmetric unit of compound **2**.

Comments on checkcif report

Compound **1**

All tested crystals were small and of poor quality. They exhibit extremely weak diffraction and the resolution of the collected X-ray data (for the best crystal) has been estimated to be 0.9 Å. Nevertheless the structure could be solved and successfully refined.

The A type alerts pointed out by the IUCr's *checkCIF* service are reported and commented:

Compound **2**

1) RINTA01_ALERT_3_A The value of Rint is greater than 0.25   Rint given 0.254

The crystals diffracted poorly, due to the small size. Several data collections were performed on different single crystals and the best one is reported herein.

2) PLAT601_ALERT_2_A Structure Contains Solvent Accessible VOIDS of   449 Ang^3

*Compound **2** crystallizes from a mixture of dichloromethane and n-heptane. When removed from the mother liquor the crystals remain clear in the air for several days. The solvent molecules must have left the crystals leaving the voids.*

S1. (a) G.M. Sheldrick, *Acta Cryst*., 2015, **A71**, 3; (b) G.M. Sheldrick, *Acta Cryst*., 2015, **C71**, 3;

S2. O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339.

2.2. Diffuse reflectance spectra

Diffuse reflectance spectra were performed on a JASCO V-670 spectrophotometer, using MgO as standards (Figure S3). **1**: 281, 321, 604 nm
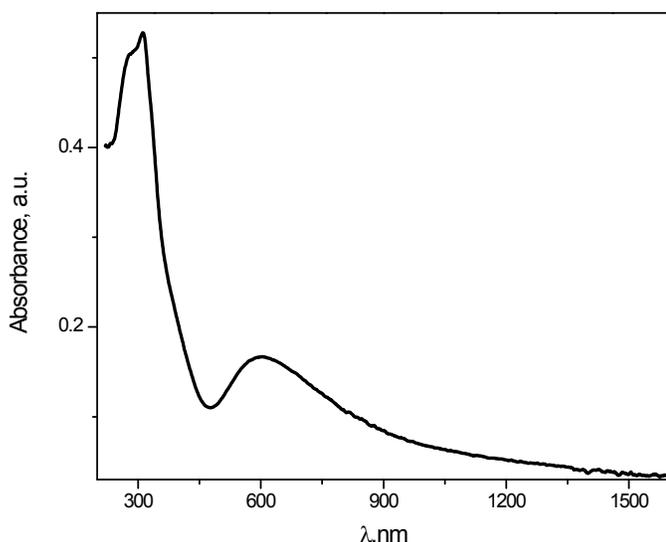
Figure S3. Diffuse reflectance spectrum of compound **1.**

2.3. Elemental and thermogravimetric analyses

Elemental analysis was carried out on a EuroEa Elemental Analyser.

1 $C_{54}H_{64}CuB_2F_8N_4O_{10}$: C, 55.61; H, 5.53; N, 4.80 % (calcd.); C, 54.93; H, 5.40; N, 4.90 %. (found)

2 $C_{29}H_{16}MnF_{12}N_2O_4$: C, 47.11; H, 2.18; N, 3.79 % (calcd.); C, 48.01; H, 2.07; N, 3.26 % (found).

Thermogravimetric analysis was performed on a TA Q500 TGA instrument using platinum pan in nitrogen atmosphere. The heating rate was 5°C min^{-1} from room temperature (25°C) to 100°C and 10°C min^{-1} from 100 to 600°C.

The final formula of compound **1**, $[CuL^1(H_2O)_2](BF_4)_2 \cdot 8H_2O$, was established using the TGA and elemental analysis data. The TGA curve reveals that the dehydration of compound **1** starts at temperatures below 50˚C and it continues in multiple stages until the complete dehydration is reached around 245˚C. The weight loss of 15.5% at 245˚C can be assigned to ten water

molecules per formula unit, meaning eight crystallization water molecules. These values are in good agreement with the elemental analysis data.
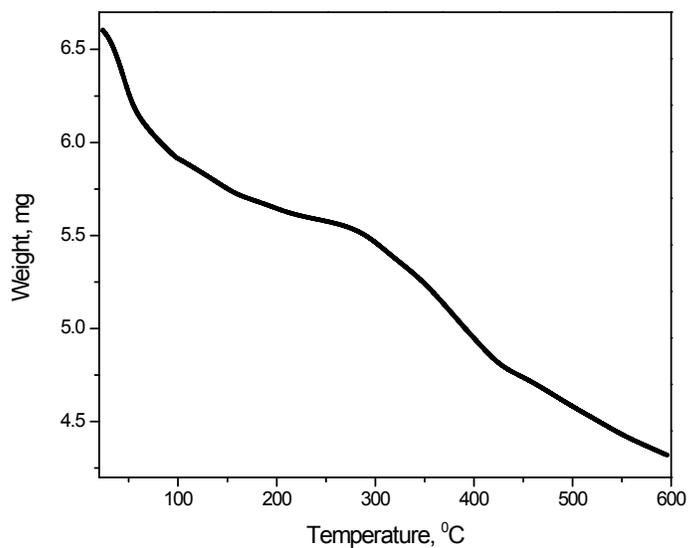
Figure S4. Thermogravimetric analysis for compound **1.**

2.4. X-ray powder diffraction

X-ray powder diffraction data were recorded on Proto diffractometer at 298 K.
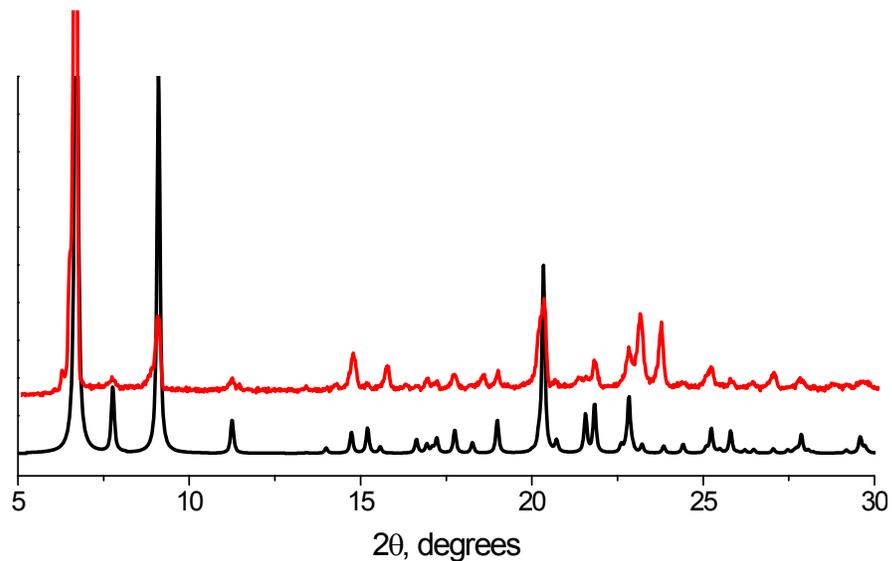
Figure S5. Simulated (black) and experimental (red) PXRD pattern for compound **2.**