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Tuning the formations of metal-1,3,5-benzenetricarboxylate frameworks via the assistance of amino acids

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ABSTRACT

Seven new metal-1,3,5-benzenetricarboxylate coordination polymers have been synthesized by modification of auxiliary components during the assembly reactions. Their structures have been determined by single-crystal X-ray diffraction analyses and further characterized by XRD and TGA. Interestingly, they show fascinating topological structures. Compounds **1** and **2** possess the undulating layer structure with 3-connected **hcb** network and (3,6)-connected **kgd** network. Compound **3** possesses three-dimensional (3D) pillared-layer structure with 3-connected 2-fold interpenetrating **srs** net. Compound **4** also has the 3D 2-fold interpenetrating pillared-layer structure; however, it has (3,5)-connected **hms** topology because the Cd(II) center is 5-connected. Compound **5** possess 3D structure through hydrogen bonding interactions between ladder-like layers. Compounds **6** and **7** have the similar 3D frameworks with 4-connected **umc** net and (3,7)-connected $(3.4.5)(3^2.4^6.5^5.6^8)$ topology, respectively. The photoluminescent properties of compounds **2–7** were also investigated.

1. Introduction

Metal-organic frameworks (MOFs) have recently attracted much attention because of their intriguing structural topologies and potential applications as functional materials for catalysis, luminescence, nonlinear optics (NLO), conductivity, magnetism, gas sorption and separation [1–4]. However, it remains a challenge to design successful synthetic strategies for the preparation of the MOFs with the expected and intriguing structures [5–12]. It is generally known that the synthesis of the MOFs can be affected by several factors, such as the structural characteristic of the ligand, coordination nature of the metal ion, solvent system template, pH value of the solution, steric requirement of the counterion, reaction temperature, and the metal-to-ligand ratio [13–23]. Yaghi et al. employed different solvents and organic bases and successfully synthesized a series of Zn-BTC (BTC=1,3,5-benzenetricarboxylate) frameworks [24], finding that the dimensionality of the resulting Zn-BTC framework is mainly dependent on the solvent media and the strength of organic base. Basing on the previous studies, our attentions mainly concentrate on the effects of the pH value of the solution.

Amino acid and hydroxycarboxylic acid play different roles in the formation of various types of structures: firstly, they both can act as organic ligands owing to their coordination sites to the metal ion [25–29]. Secondly, they can be regarded as the templates to construct new framework architectures. Finally, they can be used to adjust the pH value of the solutions because of the existence of the carboxyl group and the amino group. Herein, we report a series of new metal-BTC coordination polymers which are synthesized by the modification of auxiliary components during the assembly reactions, namely $[Cd(BTC)(DMF)]^- \cdot TPA^+$ (**1**), $Cd(BTC)_{1/3}(HCOO)(DMF)$ (**2**), $Cd_3(BTC)_2(DBO)(DMF)_2$ (**3**), $Cd(BTC)(tmdpy) \cdot (CH_3)_2NH_2$ (**4**), $Cd(BTC)(PCD)(H_2O)_2$ (**5**), $Mn(BTC)(OH) \cdot (DBO)$ (**6**), $Mn_3(\mu_3\text{-}OH)(BTC)_2(DMF) \cdot (DBO)$ (**7**), (H_3BTC=1,3,5-benzenetricarboxylate, DBO=1,4-diazabicyclo-[2.2.2]octane, DMF=N, N-Dimethylformamide, tmdpy=1,3-Di(4-pyridyl)propane, PCD=2-pyrazinecarboxylic acid, TPA^+=tetrapropylammonium cation). Different amino acids and hydroxycarboxylic acids were used as buffering agents for the synthesis of these eight complexes. Interestingly, these complexes show fascinating topological structures.

2. Experimental details

2.1. Materials and instrumentation

All the syntheses were performed in 20 mL glass vial under autogenous pressure. Reagents were purchased commercially and used without further purification. Thermal analysis was carried out

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Table 1
A summary of crystal data of all compounds.

Compound	1	2	3	4	5	6	7
Chemical formula	$C_{24}H_{38}CdN_2O_7$	$C_7H_9CdNO_5$	$C_{27}H_{36}Cd_3N_3O_{23}$	$C_{26}H_{17}CdN_4O_6$	$C_{14}H_8Cd_2N_2O_{11}$	$C_{32}H_{32}Mn_2N_5O_{14}$	$C_{32}H_6Mn_3N_4O_{15}$
Formula mass	578.96	299.55	1107.79	593.84	605.02	820.51	851.23
Crystal system	Orthorhombic	Trigonal	Triclinic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
a (Å)	18.2988(6)	14.3563(3)	11.5178(5)	16.8094(7)	8.7154(2)	16.0445(9)	15.4035(9)
b (Å)	8.9290(3)	14.3563(3)	12.4126(5)	14.4553(7)	13.1045(5)	11.8985(6)	16.2311(10)
c (Å)	15.5317(8)	8.2827(4)	13.1708(5)	10.4397(3)	14.5010(3)	18.3896(10)	26.268(3)
α (°)	90.00	90.00	94.261(3)	90.00	90.00	90.00	90.00
β (°)	90.00	90.00	92.978(3)	90.00	90.00	104.452(5)	95.187(7)
γ (°)	90.00	120.00	93.134(3)	90.00	90.00	90.00	90.00
volume (Å^3)	2537.72(18)	1478.38(8)	1871.99(13)	2536.69(18)	1656.17(8)	3424.3(7)	6540.5(8)
Dc (g cm^{-3})	1.515	2.019	1.965	1.555	2.426	1.592	1.729
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Space group	*Pca*2(1)	$P\bar{3}$	$P\bar{1}$	*Pnma*	$P2_12_12_1$	*C*2/c	*C*2/c
Z	4	6	2	4	4	4	8
F(000)	1200	876	1094	1188	1160	1684	3368
Observed	6243/3086	3522/2632	12183/6597	8211/2330	5084/2765	6481/3010	11993/5775
GOF on F^2	1.038	1.088	1.106	1.206	1.034	1.066	1.074
Rint	0.0274	0.0272	0.0335	0.0424	0.0206	0.0196	0.0497
*R*1, wR2 ($I > 2\sigma(I)$)	0.0261, 0.0605	0.0299, 0.0742	0.0361, 0.0797	0.0436, 0.1333	0.0234, 0.0637	0.0520, 0.1619	0.0629, 0.1588
*R*1, wR2 (all data)	0.0323, 0.0635	0.0448, 0.1052	0.0485, 0.0881	0.0578, 0.1482	0.0241, 0.0641	0.0606, 0.1671	0.1020, 0.1906

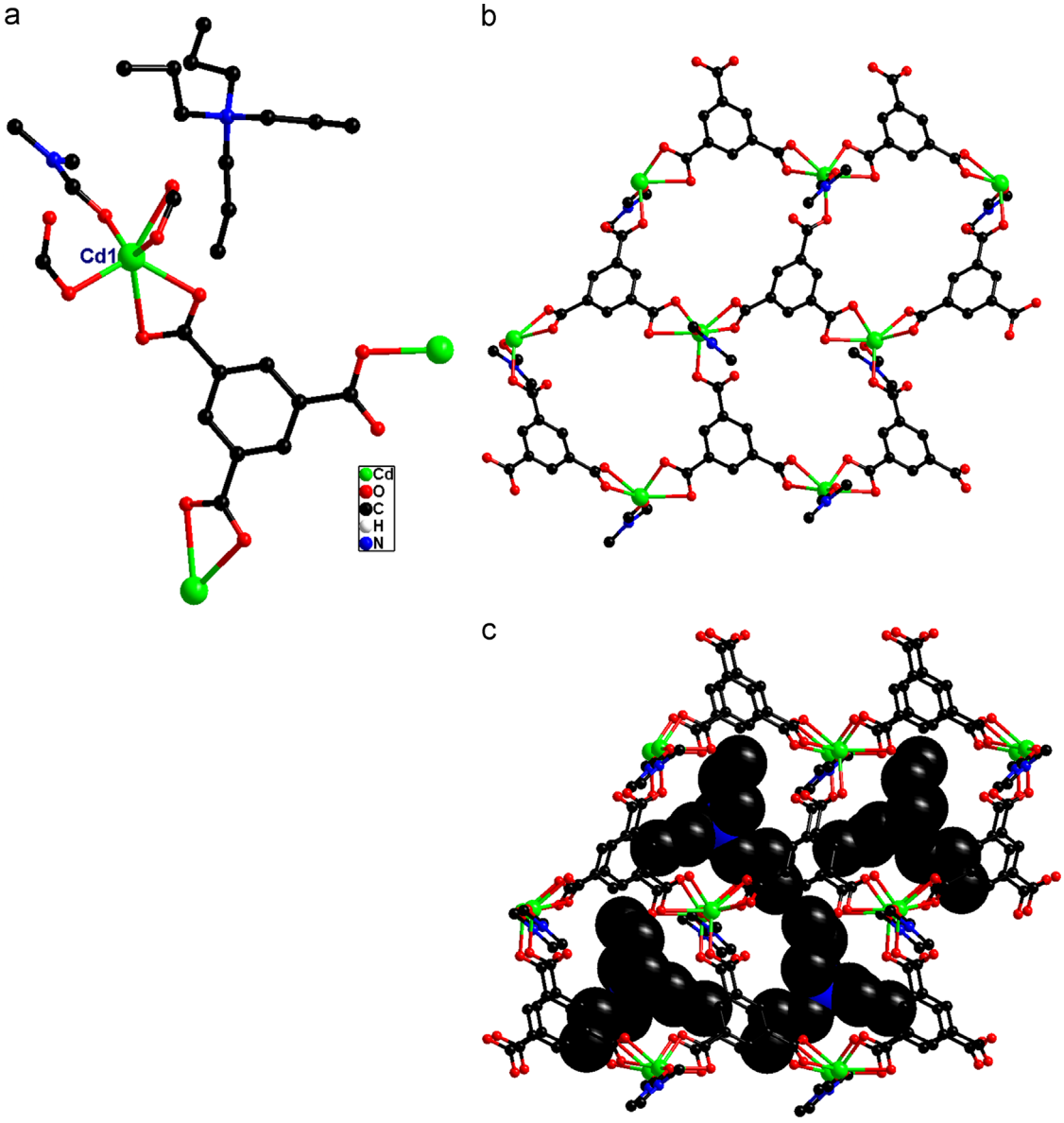

Fig. 1. (a) The coordination environment in **1**. (b) The 2D wave-like network of **1**. (c) The 3D packing diagram.