

Ancillary ligand-assisted assembly of C_3 -symmetric 4,4',4''-nitrilotribenzoic acid with divalent Zn^{2+} ions: Syntheses, topological structures, and photoluminescence properties

Li-Ting Cui^{a,1}, Yan-Fei Niu^{a,1}, Jie Han^b, Xiao-Li Zhao^{a,*}

^a Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, PR China

^b School of Science & Technology, The Open University of Hong Kong, Kowloon, Hong Kong SAR, PR China

ARTICLE INFO

Article history:

Received 30 December 2014

Received in revised form

16 March 2015

Accepted 31 March 2015

Available online 8 April 2015

Keywords:

4,4',4''-nitrilotribenzoic acid

Photoluminescence property

MOF

Crystal engineering

Self-assembly

Hydrogen bonds

ABSTRACT

4,4',4''-nitrilotribenzoic acid (H_3L), a C_3 -symmetric ligand, was found to self-assemble into two polymorphs driven by intermolecular hydrogen-bonding interactions. Reactions of this ligand with Zn^{2+} under solvothermal conditions resulted in four new coordination polymers bearing interesting structural motifs: $[Zn_2(L)_2(py)_2] \cdot 2(H_2NMe_2)^+ \cdot DMF \cdot 2H_2O$ (**1**), $[Zn_2(L)(H_2L)(bipy)] \cdot 1.5H_2O \cdot Guest$ (**2**), $[Zn_2(L)_2(bipy)] \cdot 2(H_2NMe_2)^+ \cdot 2DMF$ (**3**), and $[Zn_3(L)_2(bpa)] \cdot 2H_2O \cdot Guest$ (**4**) ($H_3L=4,4',4''$ -nitrilotribenzoic acid, DMF=dimethylformamide, py=pyridine, bipy=4,4'-bipyridine, bpa=1,2-bis(4-pyridyl)diazene). Single-crystal structural analysis revealed that compound **1** exhibits a rare example of twofold interpenetrating anionic 3D (3,3)-net framework containing helical channels, whereas in **2**, the 3D pillar-layer structure generated from bipy-pillared $Zn_2(L)(H_2L)$ layer is further reinforced by intermolecular hydrogen bonding among pairs of free $-COOH$ units. Compound **3** shows an interesting entangled architecture of 2D \rightarrow 3D parallel polycatenation consisting five-coordinated Zn^{2+} ions. Compound **4** displays a 3D pillar-layer framework with trimeric $Zn_3(CO_2)_6$ serving as secondary building unit (SBU). The syntheses, structures, thermal stabilities, powder X-ray diffractions and solid-state photoluminescence properties for these crystalline materials have been carried out. In addition, supramolecular assembly of H_3L under solvothermal conditions will also be addressed.

© 2015 Published by Elsevier Inc.

1. Introduction

Considerable efforts have been made in the rational design of functional metal–organic frameworks (MOFs) because of their diverse structural topologies and potential applications in gas storage and separation, drug delivery, catalysis and luminescence [1–4]. It has been well documented that the construction of MOFs is influenced by both structural components and synthetic conditions, including coordination nature of metal centers, organic linkers, pH values, temperature, and so on [5]. The rational design of MOFs is very challenging and there are as yet no established rules for the designed synthesis of target products.

As a continuation of our efforts toward the isolation of novel MOFs, in particular MOFs based on C_3 -symmetric ligands, we are interested in the use of bridging organic ligands endowed with

multicarboxylate groups and C_3 -symmetry. In this regard, rigid C_3 -symmetric ligand, 4,4',4''-nitrilotribenzoic acid (H_3L), was employed. There are multiple reasons for exploring H_3L . First, the combination of threefold symmetry and carboxylic acid makes it an ideal building block in the field of crystal engineering [6]; second, the tridentate bridging carboxylate ligands have exhibited potential applications in the generation of multi-dimensional porous MOFs with new topologies [7]; moreover, the triphenylamine core is well-known for its ease in oxidation of the nitrogen center and the ability to transport charge via the radical cation species with high stability. It is thus envisioned that the strong reductive excited state of the triphenylamine moiety in MOFs may initiate a photo-induced electron transfer, rendering their potential application in photocatalysis [8]. For example, Yaghi et al. have reported the first example of a fully catenated FeS_2 pyrite net generated from assembly of octahedral zinc acetate units and this triangular L^3- linker [7a]. Suh et al. have found that a porous H_3L -based MOF shows enhanced hydrogen storage by forming fabricated palladium nanoparticles in this redox-active MOF [8c]. However, in comparison with the large number of porous MOFs

* Corresponding author. Fax: +86 21 62233179.

E-mail addresses: chan@ouhk.edu.hk (J. Han), xlzhao@chem.ecnu.edu.cn (X.-L. Zhao).

¹ Contributed equally to this work.

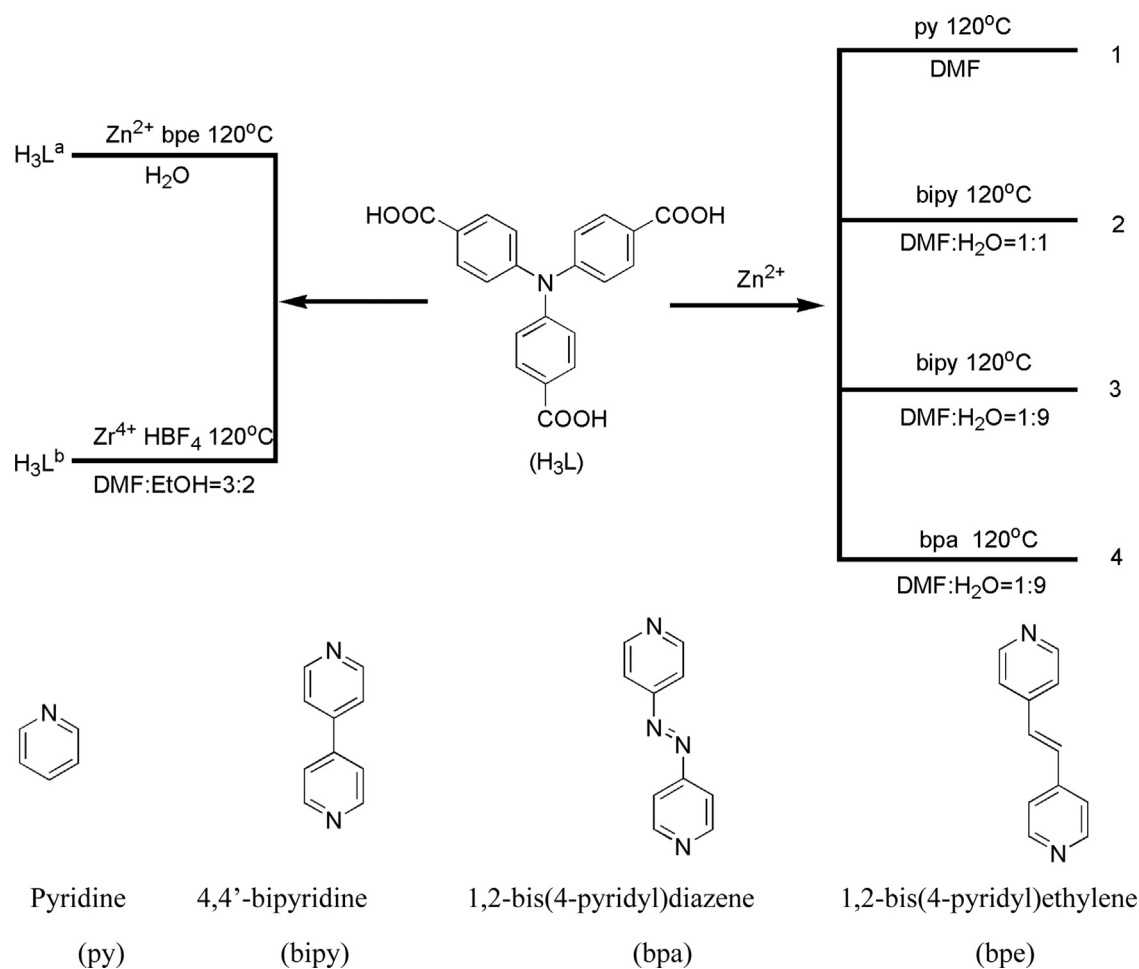


Table 1
Crystal data and structure refinements for H_3L^a , H_3L^b and compounds **1–4**.

Compound	H_3L^a	H_3L^b	1	2	3	4
Empirical formula	$C_{84}H_{60}N_4O_{24}$	$C_{21}H_{15}NO_6$	$C_{59}H_{61}N_7O_{15}Zn_2$	$C_{52}H_{37}N_4O_{13.5}Zn_2$	$C_62H_{62}N_8O_{14}Zn_2$	$C_{52}H_{36}N_6O_{14}Zn_3$
M [g mol $^{-1}$]	1508.36	377.35	1238.93	1064.65	1273.98	1165.04
Crystal system	Trigonal	Trigonal	Monoclinic	Triclinic	Triclinic	Trigonal
Space group	$R\bar{3}$	$R\bar{3}c$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P3_12_1$
a [Å]	33.0454(14)	27.9421(11)	26.0328(6)	10.2824(3)	9.3189(3)	13.9538(2)
b [Å]	33.0454(14)	27.9421(11)	9.1655(2)	14.3227(4)	13.4985(4)	13.9538(2)
c [Å]	12.5494(7)	14.7900(7)	27.4382(6)	17.9095(5)	14.3207(4)	24.9246(7)
α [°]	90	90	90	67.600(1)	116.117(1)	90
β [°]	90	90	117.814(1)	84.589(1)	92.393(1)	90
γ [°]	120	120	90	73.704(1)	109.754(1)	120
V [Å 3]	11867.9(10)	10000.4(7)	5790.5(2)	2340.3(1)	1483.10(8)	4202.9(2)
Z	24	18	8	2	2	3
$\rho_{\text{calcd.}}$ [g cm $^{-3}$]	1.267	1.128	1.294	1.506	1.424	1.376
μ (MoK α) [mm $^{-1}$]	0.094	0.084	0.891	1.099	0.882	1.340
$F(000)$	4704	3528	2328	1084	660	1764
θ range (deg)	2.47–25.00	1.46–25.01	1.78–25.01	1.61–25.01	1.63–25.01	1.69–25.01
R_{int}	0.0406	0.0369	0.0424	0.0385	0.0312	0.0475
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0504$, $wR_2 = 0.1375$	$R_1 = 0.0403$, $wR_2 = 0.1080$	$R_1 = 0.0395$, $wR_2 = 0.1057$	$R_1 = 0.0367$, $wR_2 = 0.0897$	$R_1 = 0.0472$, $wR_2 = 0.1303$	$R_1 = 0.0341$, $wR_2 = 0.0891$
R indices (all data)	$R_1 = 0.0694$, $wR_2 = 0.1471$	$R_1 = 0.0473$, $wR_2 = 0.1122$	$R_1 = 0.0455$, $wR_2 = 0.1094$	$R_1 = 0.0553$, $wR_2 = 0.1039$	$R_1 = 0.0567$, $wR_2 = 0.1385$	$R_1 = 0.0364$, $wR_2 = 0.0903$

constructed with other multi-carboxylate ligands, systematic investigation of H_3L -based porous MOFs remains still rare. Here we wish to describe solvothermal syntheses of a family of MOFs based on H_3L : $[Zn_2(L)_2(py)_2] \cdot 2(H_2NMe_2)^+ \cdot DMF \cdot 2H_2O$ (**1**), $[Zn_2(L)$

$(H_2L)(bipy)] \cdot 1.5H_2O \cdot \text{Guest}$ (**2**), $[Zn_2(L)_2(bipy)] \cdot 2(H_2NMe_2)^+ \cdot 2DMF$ (**3**), $[Zn_3(L)_2(bpa)] \cdot 2H_2O \cdot \text{Guest}$ (**4**) (Scheme 1). The investigations of the thermal stability, powder X-ray diffraction (PXRD) and solid-state photoluminescence properties for these crystalline materials were also

Download English Version:

<https://daneshyari.com/en/article/7758746>

Download Persian Version:

<https://daneshyari.com/article/7758746>

[Daneshyari.com](https://daneshyari.com)