View Online / Journal Homepage / Table of Contents for this issue
Dynamic Article Links

CrystEngComm

Cite this: *CrystEngComm*, 2012, **14**, 4850–4856

www.rsc.org/crystengcomm

PAPER

Five porphyrin-core-dependent metal–organic frameworks and framework-dependent fluorescent properties†

Chao Zou, Ming-Hua Xie, Guo-Qiang Kong and Chuan-De Wu*

Received 13th March 2012, Accepted 2nd May 2012
DOI: 10.1039/c2ce25357g

The reaction of 5,10,15,20-tetra(carboxyphenyl)porphyrin (H_6**TCPP**) or metalated M-H_4**TCPP** (M = Co^{II}, Ni^{II}, Cu^{II} and $V^{IV}O$) with lead nitrate afforded five metal–organic frameworks (MOFs), [Pb_2(H_2**TCPP**)]·4DMF·H_2O (**1**), Pb_2(Co–**TCPP**)(H_2O)(DMF)]·1.5DMF (**2**), [Pb_2(Ni–**TCPP**)(DMF)(H_2O)]·1.5DMF·2H_2O (**3**), [Pb_2(Cu–**TCPP**)(DMF)(H_2O)]·1.5DMF·2H_2O (**4**) and [Pb_2(VO–**TCPP**)(H_2O)$_2$]·4DMF (**5**). Single crystal X-ray diffraction analysis revealed that the five MOFs based on the **TCPP** scaffolds differ in framework topologies and porphyrin configurations that are varied from flat to wavy to bowl-shaped. The porphyrin cores play a pivotal role in the formation of the distinct coordination frameworks by controlling the stacking fashion of the porphyrins, the coordination modes of **TCPP** and the coordination spheres of the Pb^{2+} cations. Solid-state photoluminescent experiments suggest that the emissions of these compounds are dependent on the framework structures, and are insensitive to the porphyrin cores.

Introduction

Metal–organic frameworks (MOFs) are a class of interesting materials which have been intensively investigated in the diverse application fields of luminescence, gas storage, sensing, magnetics and catalysis.[1–3] Because the properties of MOFs are dependent on their framework structures and functionalities of the building species, controlled synthesis of well-defined MOFs has been one of the most active areas by designing functional ligands and selecting metal nodes.[2,3]

Porphyrin and metalloporphyrin molecules have been used as active constituents to construct a variety of materials in the last few years because of their unique physical, biological and chemical functionalities.[4–9] MOFs constructed from the robust porphyrin building blocks often present interesting framework topologies and properties.[5–8] Moreover, the functionality of porphyrinic MOFs can be easily tailored to realize various applications by modifying porphyrin peripheries and varying porphyrin metals.[6,9,10]

It has been observed that the framework structures of porphyrinic MOFs are very sensitive to various factors of the reaction conditions, metal nodes and porphyrin peripheries.[6–8] However, little work has systematically studied the effect of the porphyrin metal on the controlled formation of distinct metal–organic coordination networks.[5] The unique nature of the heavy p-block lead(II) ion offers great opportunities in terms of assembling unusual network topologies with interesting properties due to its large radius, variable coordination number and flexible coordination geometries.[11] To understand the porphyrin core effect, we have used 5,10,15,20-tetra(carboxyphenyl)porphyrin (H_6**TCPP**) and metalated M–H_4**TCPP** (M = Co^{II}, Ni^{II}, Cu^{II} and $V^{IV}O$) as bridging ligands, and lead(II) cations as connecting nodes to construct five interesting porphyrinic MOFs (Scheme 1), [Pb_2(H_2**TCPP**)]·4DMF·H_2O (**1**), Pb_2(Co–**TCPP**)(H_2O)(DMF)]·1.5DMF (**2**), [Pb_2(Ni–**TCPP**)(DMF)(H_2O)]·1.5DMF·2H_2O (**3**), [Pb_2(Cu–**TCPP**)(DMF)(H_2O)]·1.5DMF·2H_2O (**4**) and [Pb_2(VO–**TCPP**)(H_2O)$_2$]·4DMF (**5**). Single crystal X-ray diffraction analysis revealed that the framework structures of these MOFs are dependent on the porphyrin cores with interesting framework-dependent luminescent properties.

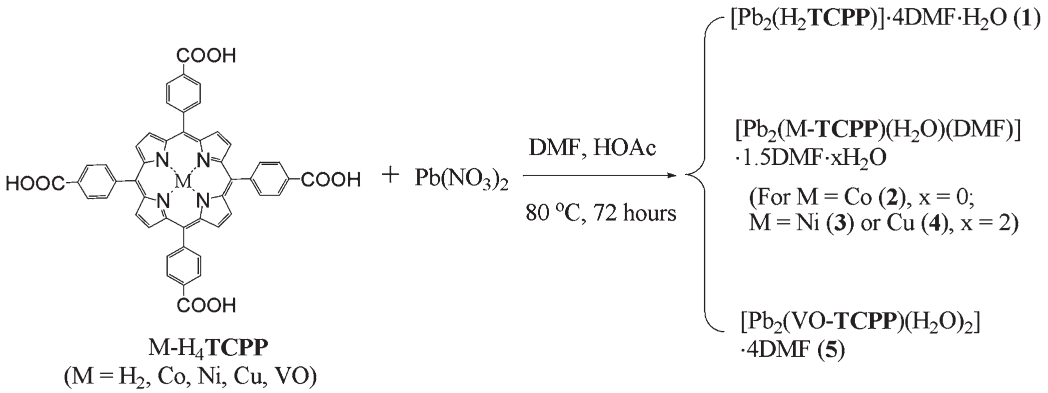
Experimental section

Materials and methods

All of the chemicals were obtained from commercial sources and were used without further purification, except 5,10,15,20-tetra(carboxyphenyl)porphyrin (H_6**TCPP**) and M–H_4**TCPP** (M = Co^{II}, Ni^{II}, Cu^{II} and $V^{IV}O$), which were synthesized according to the literature.[12] IR spectra were recorded from KBr pellets on a FTS-40 spectrophotometer. Powder X-ray diffraction (PXRD) data were recorded on a RIGAKU D/MAX 2550/PC using Cu-Kα radiation (λ = 1.5406 Å). Thermogravimetric analysis (TGA) was carried out under N_2 atmosphere on a NETZSCH STA 409 PC/PG instrument at a heating rate of 10 °C min^{-1}. The solid-state fluorescent spectra were recorded on a HITACHI F-2500 fluorescence spectrophotometer at room temperature. The photomultiplier tube voltage was 700 V and the scan speed was 300 nm min^{-1}, while the slit widths of the excitation and emission spectra were both 10 nm.

Department of Chemistry, Zhejiang University, Hangzhou, 310027, P. R. China. E-mail: cdwu@zju.edu.cn

† Electronic supplementary information (ESI) available. CCDC reference numbers 871466–871470. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ce25357g



Scheme 1 Schematic illustration of the synthesis procedures for compounds **1–5**.

Elemental analysis was performed on a ThermoFinnigan Flash EA 1112 element analyzer.

Synthesis of $[Pb_2(H_2TCPP)]\cdot4DMF\cdot H_2O$ (1)

A mixture of H_6**TCPP** (20 mg, 0.025 mmol) and $Pb(NO_3)_2$ (20 mg, 0.06 mmol) in a mixed solvent of DMF (15 mL) and acetic acid (1 mL) was heated to 80 °C for 3 days. Deep brownish crystals of **1** were filtered, washed with EtOH and ethyl ether, and dried at room temperature. Yield: 19 mg (50%, based on H_6**TCPP**). IR (KBr pellet): ν/cm^{-1} = 1654(s), 1603(w), 1577(w), 1528(w), 1491(w), 1387(s), 1247(w), 1219(w), 1177(w), 1096(m), 1017(w), 965(m), 845(m), 799(m), 774(m), 484(m), 445(w). Anal. Calcd. for **1** (%): C, 47.74; H, 3.61; N, 7.42. Found (%): C, 47.52; H, 3.65; N, 7.38.

Synthesis of $[Pb_2(Co–TCPP)(H_2O)(DMF)]\cdot1.5DMF$ (2)

The synthesis procedure of **2** is similar to that of **1**, except Co–H_4**TCPP** (22 mg, 0.025 mmol) was used instead of H_6**TCPP**. Yield: 16 mg (45%). IR (KBr pellet): ν/cm^{-1} = 1654(m), 1604(m), 1581(m), 1529(m), 1389(s), 1348(m), 1277(w), 1253(w), 1201(w), 1173(w), 1134(w), 1098(w), 1002(s), 870(m), 845(m), 798(m), 774(m), 715(m), 497(w), 421(w). Anal. Calcd. for **2** (%): C, 45.70; H, 3.01; N, 6.24. Found (%): C, 45.54; H, 3.04; N, 6.11.

Synthesis of $[Pb_2(Ni–TCPP)(DMF)(H_2O)]\cdot1.5DMF\cdot2H_2O$ (3)

The synthesis procedure of **3** is similar to that of **1**, except Ni–H_4**TCPP** (22 mg, 0.025 mmol) was used instead of H_6**TCPP**. Yield: 16 mg (43%). IR (KBr pellet): ν/cm^{-1} = 1654(m), 1604(m), 1578(m), 1529(m), 1387(s), 1350(m), 1284(w), 1247(w), 1206(w), 1173(w), 1140(w), 1097(w), 1003(s), 870(m), 845(m), 798(m), 774(m), 727(w), 714(m), 493(w), 432(w). Anal. Calcd. for **3** (%): C, 44.60; H, 3.20; N, 6.09. Found (%): C, 44.65; H, 3.12; N, 6.22.

Synthesis of $[Pb_2(Cu–TCPP)(DMF)(H_2O)]\cdot1.5DMF\cdot2H_2O$ (4)

The synthesis procedure of **4** is similar to that of **1**, except Cu–H_4**TCPP** (22 mg, 0.025 mmol) was used instead of H_6**TCPP**. Yield: 18 mg (47%). IR (KBr pellet): ν/cm^{-1} = 1654(m), 1604(m), 1581(m), 1529(m), 1389(s), 1342(w), 1280(w), 1247(w), 1206(w), 1173(w), 1134(w), 1098(w), 1000(s), 870(m), 846(m), 797(m), 774(m), 718(m), 564(w), 488(w). Anal. Calcd. for **4** (%): C, 44.46; H, 3.19; N, 6.07. Found (%): C, 44.32; H, 3.10; N, 6.15.

Synthesis of $[Pb_2(VO–TCPP)(H_2O)_2]\cdot4DMF$ (5)

The synthesis procedure of **5** is similar to that of **1**, except VO–H_4**TCPP** (22 mg, 0.025 mmol) was used instead of H_6**TCPP**. Yield: 21 mg (53%). IR (KBr pellet): ν/cm^{-1} = 1653(m), 1637(m), 1603(m), 1581(m), 1534(m), 1389(s), 1277(w), 1250(w), 1226(w), 1206(w), 1176(w), 1134(w), 1101(w), 1006(m), 982(w), 965(w), 871(w), 846(m), 801(m), 775(m), 723(m), 558 (w), 484 (m). Anal. Calcd. for **5** (%): C, 45.20; H, 3.54; N, 7.03. Found (%): C, 45.60; H, 3.58; N, 6.77.

Single crystal X-ray diffraction data collection and structure determination

The unit cell determination and data collection for the crystals of compounds **1–5** were performed on an Oxford Xcalibur Gemini Ultra diffractometer with an Atlas detector. The data were collected using graphite-monochromatic Mo-Kα radiation (λ = 0.71073 Å) at 293 K for compounds **1–4**, while the data of compound **5** were collected using graphite-monochromatic enhanced ultra Cu radiation (λ = 1.54178 Å) at 293 K. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm.[13] The structures of all compounds were solved by direct methods and refined by full-matrix least-square methods with the SHELX-97 program package.[14] As the solvent molecules in these compounds are highly disordered, the SQUEEZE subroutine of the PLATON software suite was used to remove the scattering from the highly disordered guest molecules. The resulting new files were used to further refine the structures.[15] H atoms on C atoms were generated geometrically. The data collection parameters, crystallographic data, and final agreement factors are collected in Table 1.

Results and discussion

The reaction of H_6**TCPP** with $Pb(NO_3)_2$ in a mixed solvent of DMF and acetic acid at 80 °C afforded deep brownish crystals of $[Pb_2(H_2$**TCPP**$)]\cdot4DMF\cdot H_2O$ (**1**). Single crystal X-ray diffraction analysis revealed that compound **1** crystallizes in the monoclinic $P2_1/c$ space group. The Pb^{2+} ion is chelated by two carboxylate groups of two H_2**TCPP**, and further coordinates to three carboxyl oxygen atoms of three H_2**TCPP** (Fig. 1). The three carboxyl oxygen atoms triply bridge two hepta-coordinated Pb^{2+}