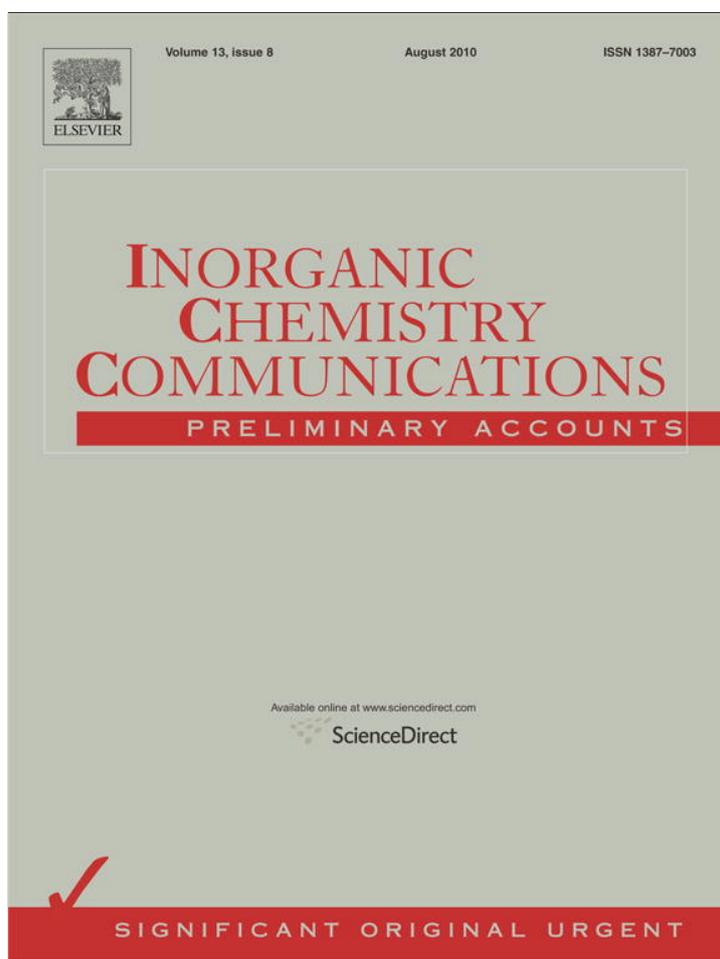


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Novel interpenetrating and non-interpenetrating structures based on semi-rigid 4,4'-biphenyl-based ligand

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ABSTRACT

The reactions of semi-rigid bidentate ligand 4,4'-bis(benzimidazol-1-ylmethyl)biphenyl (bbmb) with NiCl_2 and CuCl_2 and $\text{Cd}(\text{OAc})_2$ afford novel complexes $\{[\text{M}(\text{bbmb})_2(\text{Cl})(\text{OH})](\text{H}_2\text{O})_2\}_n$ ($\text{M} = \text{Ni}$ (**1**), Cu (**2**)) and $[\text{Cd}_2(\text{OAc})_4(\text{bbmb})_3]_2(\text{CH}_3\text{OH})_3(\text{H}_2\text{O})_2$ (**3**). Both complexes **1** and **2** feature parallel 2-fold interpenetrating (4,4)-windmill-like layer morphology. Complex **3** presents unique discrete quad-nuclear motif comprised by two couples of alternating single and double twisting chains. The three complexes exhibit active second-order NLO effects.

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Along with the development of crystal engineering, heterocyclic biphenyl compounds have been developed as functional ligands to construct metal–organic frameworks (MOFs) with complex and efficient functions [1]. Among various biphenyl derivatives, 4,4'-biphenyl-based ligands have received attention because of its internal rotation axis, which is possible to control the rotation about this position of the biphenyl backbone. Lately, many particular 4,4'-biphenyl-based metal complexes are reported featuring interesting topologies, including unique 4-connected 3D framework with $(6^2 \cdot 8^2 \cdot 10^2)(6^2 \cdot 8^3 \cdot 10)(6^2 \cdot 8^3 \cdot 9)$ topology, rare (3,5)-connected 3D framework with *gra* topology [2], 2D chiral structure [3], the first 3-fold interpenetrating network of β -Sn $4^{85}6^3$ topology [4] and interesting 3D Kagom lattice open framework [5], and so on [6–12]. These examples reveal that the choice of 4,4'-biphenyl-based ligands as a spacer is prone to result in fascinating skeleton structures. As far as nitrogenous heterocyclic 4,4'-biphenyl-based ligands, the donor N atoms usually have enough long spacers, which should be easy to feature interpenetrating morphology. However, to the best of our knowledge, 4,4'-biphenyl-based complexes seldom display interpenetrating motifs. The fewer examples include $\{[\text{Co}(\text{L})_3](\text{ClO}_4)_2\}_n$ [4] and $[\text{Cu}(\text{bdc})(\text{L})]_n$ [9] ($\text{H}_2\text{bdc} = 1,4$ -benzene-dicarboxylate; $\text{L} = 4,4'$ -bis(1-imidazolyl)biphenyl), both of which feature 3-fold interpenetrating motifs.

Keeping in mind the aforementioned point, we start to employ semi-rigid 4,4'-biphenyl-based spacers as bidentate ligands together with metal ions, in the hope that interesting interpenetrating networks as well as the influence factors on interpenetrations could

be found. Herein, we report two interestingly dual-fold interpenetrated polymeric complexes $\{[\text{M}(\text{bbmb})_2(\text{Cl})(\text{OH})](\text{H}_2\text{O})_2\}_n$ ($\text{M} = \text{Ni}$ (**1**), Cu (**2**)) and one unique discrete quad-nuclear complex $[\text{Cd}_2(\text{OAc})_4(\text{bbmb})_3]_2(\text{CH}_3\text{OH})_3(\text{H}_2\text{O})_2$ (**3**) (bbmb = 4,4'-bis(benzimidazol-1-ylmethyl)biphenyl). Complexes **1** and **2** are the first examples of two-fold interpenetration in 4,4'-biphenyl-based coordination polymers, while complex **3** presents non-interpenetrated large molecular as a result of the terminal coordination of acetate. Besides, 4,4'-biphenyl and benzimidazole derivatives are well-known good nonlinear optical (NLO) chromophores since both classes have effective π -conjugated systems within biphenyl groups [13]. In order to further develop this promising field, the second-order nonlinear optical properties of the three complexes are investigated. The result reveals that the three complexes present strong SHG active.

Complex **1** was synthesized by the hydrothermal reactions of bbmb with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in a 25 mL Teflon-lined stainless steel vessel at 150 °C for 5 days [14]. bbmb was synthesized according to literature [15]. Single-crystal X-ray diffraction revealed that complex **1** crystallizes in the tetragonal system with space group $P4/nmc$ and exhibits 2-D twofold interpenetrating networks [16]. As shown in Fig. 1, the center Ni atom is in a slightly elongated octahedral environment: four N atoms from different bbmb are located in an equatorial plane (the mean deviation of the center Ni from the plane is 0.0706 Å); Cl^- and OH^- occupy the axial position with the Cl-Ni-O angle of 180°. Ni–Cl, Ni–O and four Ni–N bond lengths are 2.3963(11), 2.301(3) and 2.1006(16) Å, respectively. Each Ni atom is the tetragonal node, and four benzimidazoles from four bbmb spread out from the basal Ni atom as propeller. The four bbmb ligands also present an extended geometry with “Z” shape and resemble to spiral blades stretching in the same side of the basal Ni1 atom, resulting in a large cavity. In the cavity, all the adjacent Ni···Ni distances are 22.2073 Å, and the vertical distance

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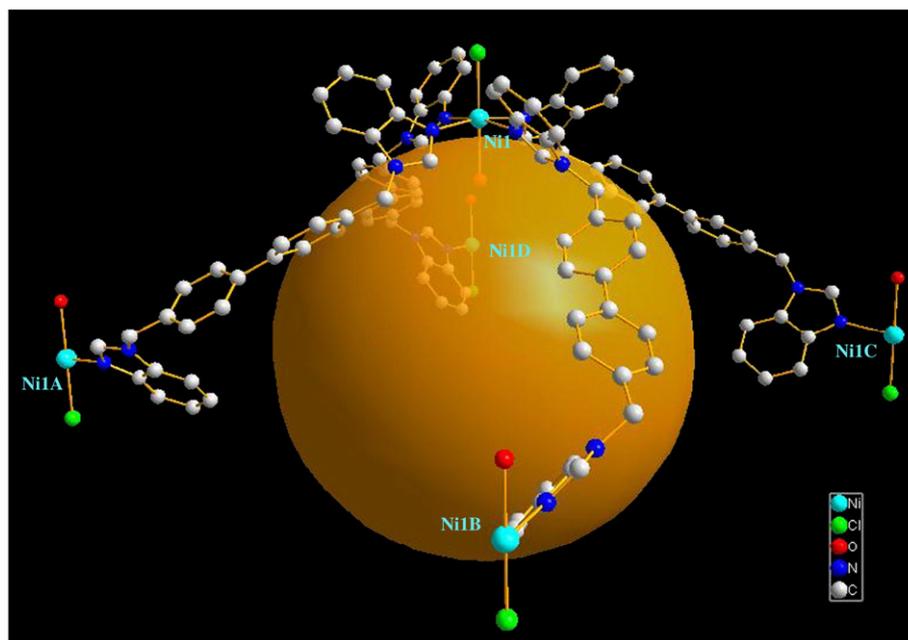


Fig. 1. A perspective view of $[\text{Ni}(\text{bbmb})_2(\text{Cl})(\text{OH})]$ units in complex **1** (lattice water molecules and hydrogen atoms are omitted for clarity).

from basal Ni1 atom to the plane (composed of Ni1A, Ni1B, Ni1C and Ni1D) is 8.8167 Å. As shown in Fig. 2, each bbmb as a bridging bidentate ligand links two metal nodes, leading to 2-D wrinkled

networks with (4,4) nets. Such two layers arrange in a parallel fashion and allow incorporation of each other giving rise to a twofold interpenetrating motif, as a schematic illustration in Fig. 3(a). The

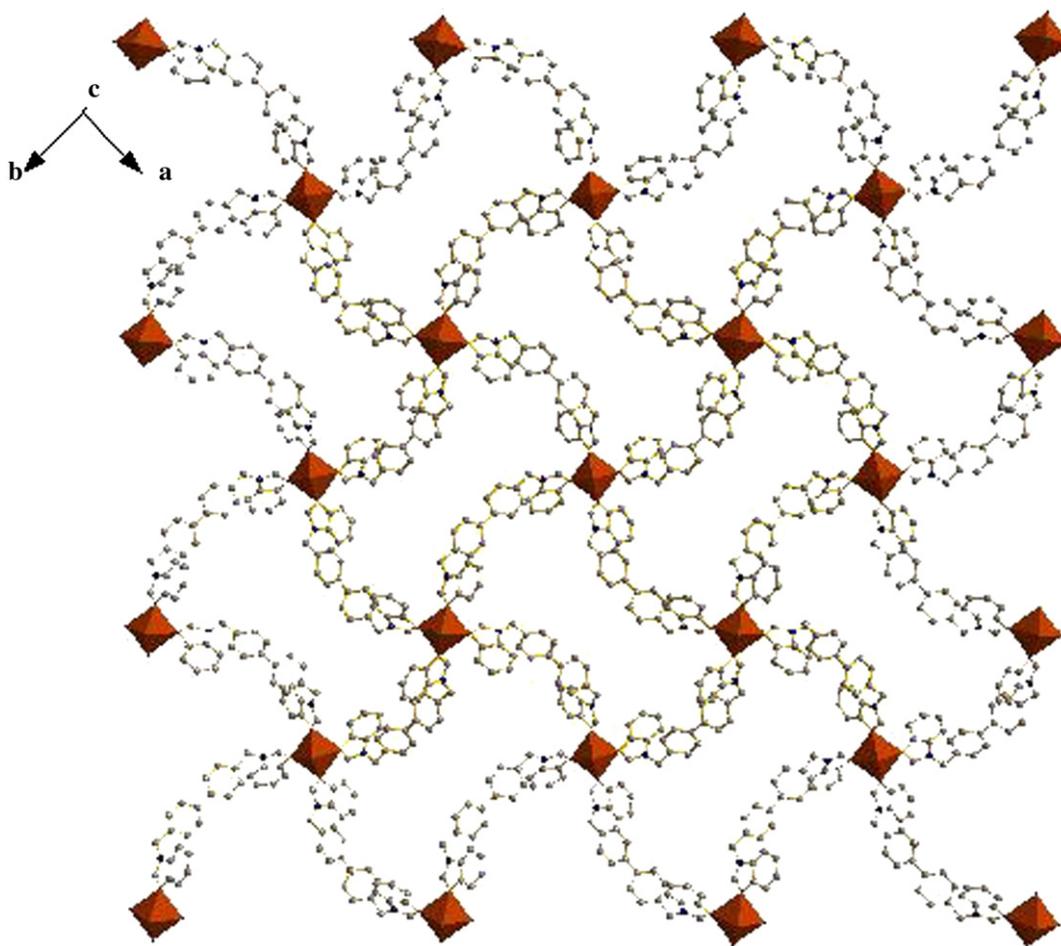


Fig. 2. The 2-D wrinkled networks of complex **1** viewed along the *c*-axis. Lattice H_2O molecules have been omitted for clarity.

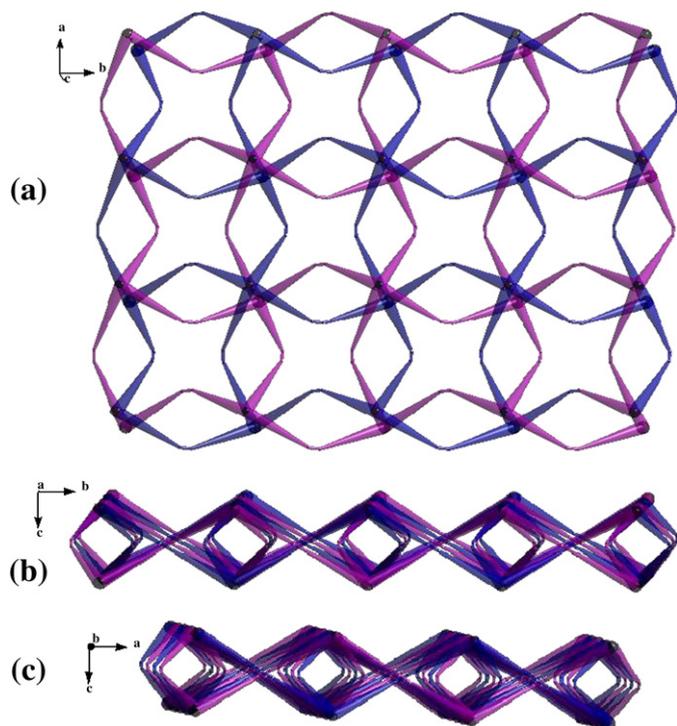


Fig. 3. The schematic representation of the twofold interpenetrating networks with (4,4) nets in complex **1**. Individual nets, shown in purple and blue, respectively, are idealized by representing the metal/metal connection via ligand bbmb as bent pipes. The dots represent metal ions.

twofold interpenetrating layers arrange in a parallel fashion and pack together along the *c*-axis, showing porous channels in *a* and *b* directions (Fig. 3(b) and (c)). The lattice water molecules are disordered in the channels.

The procedure of complex **2** is the same as that for **1**, except that $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ was used instead of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ [17]. Single-crystal analysis revealed that the crystal structure of **2** is analogous to that of **1** except that the center Cu atoms replace the Ni atoms [18]. Accordingly, no details about the structure of **2** are discussed here. When we compare the crystal structure of complex **2** with that of the reported 1-D chain complex $[\text{Cu}_2(\text{OAc})_4(\text{bbmb})_{1.5} \cdot \text{CH}_3\text{CN} \cdot 2\text{CH}_3\text{OH}]_n$ [15], and find that the terminal coordination of acetate seems to prevent the complex from forming interpenetrating architectures. Thus, in order to further understand and evaluate the influence of

acetate anions on the interpenetration frameworks, we further employ bbmb to reaction with metal acetates.

Complex **3** was synthesized by the reaction of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ with bbmb in MeOH solution at room temperature [19]. As expected, complex **3** crystallizes as discrete double-metallogage structure with space group $P\bar{1}$ [20]. In the structure, there are four Cd^{II} ions bound by four ligands in the available coordination polyhedron, as illustrated in Fig. 4. These four cadmium atoms show two different kinds of coordination environments: the six-coordinated Cd1 and Cd1A atoms and the seven-coordinated Cd2 and Cd2A atoms. Cd1 or Cd1A is coordinated with three N atoms and three O atoms from three bbmb ligands and two terminal acetates, respectively. Cd2 or Cd2A atom adopts a seven-coordinate geometry made up of three nitrogen atoms and four O atoms. The Cd1–N(O) bond lengths lie in a narrow range [2.322(4)–2.439(5)Å] and the angles around Cd1 vary from 53.16 (15)° to 163.55(15)°. The corresponding bond lengths and angles around Cd2 are slightly different from those of Cd1, in the range of 2.328(6)–2.605(6)Å and 51.1(2)–175.88(17)°, respectively. Each bbmb ligand has an extended geometry with “Z” shape since the two terminal benzimidazole groups are at in opposite direction with reference to the average biphenyl plane and serve to link two adjacent Cd. Two bbmb ligands adopt double twisting chain structural motif linking Cd1 and Cd2, or Cd1A and Cd2A (Fig. 5). The double twisting chain can be regarded as a cage on account of the benzimidazole groups. Cd1 and Cd2A, Cd1A and Cd2 are further bridged by one bbmb ligand, respectively, resulting in a novel quad-nuclear architecture.

The UV–Vis spectra for the presented complexes and purely bbmb were obtained in the diffuse reflectance mode at room temperature. The results are shown in Fig. S1. For complex **1**, the twin absorptions at 247 and 287 nm have origins in the $\pi \rightarrow \pi^*$ absorption of bbmb [21]. The band assignments for the visible region are: 640 nm, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$, and 396 nm, ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$. The green colour of the Ni(II) complex is caused by the absorption at 396 nm due to a charge transfer (MLCT). For complex **2**, there is a shoulder absorption band between 300 and 330 nm, but the intensity is relatively weak and wears off rapidly. The broad band due to the ${}^2E_g \rightarrow {}^2T_{2g}(F)$ transition, which gives rise to the characteristic blue colour to copper(II) compounds, is centered at 657 nm, which is possibly associated with the different vibronic transitions [22]. Complex **3** shows the same absorption band as bbmb at around 270 nm, which can be ascribed to $\pi \rightarrow \pi^*$ intraligand transitions of bbmb.

We investigate the second-order nonlinear optical effects for the powder sample of complexes **1**, **2** and **3** via optical second-harmonic generation (SHG) at room temperature. The intensity of the green light (frequency-doubled output: $\lambda = 532$ nm) produced by the powder sample of the compound about 2.9, 2.9 and 3.6 times that

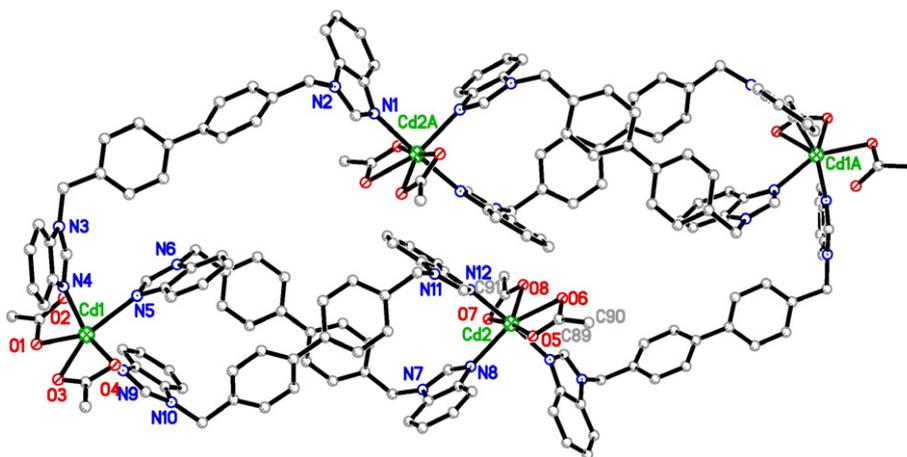


Fig. 4. The quad-nuclear backbone and atom numbering of complex **3**.

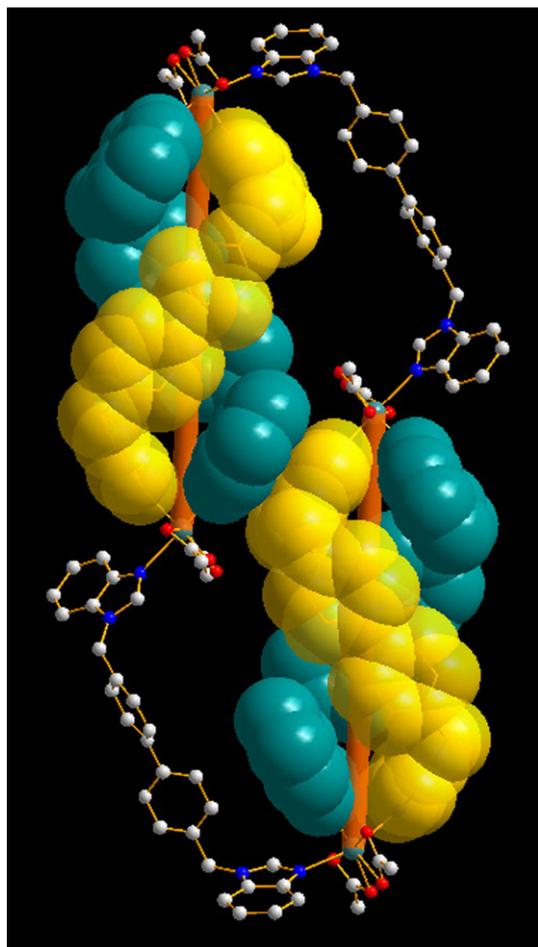


Fig. 5. The two couples of single chains and double twisting chains in complex **3**.

produced by a KDP powder for **1**, **2** and **3**, respectively. The results indicate that these complexes are all SHG active and have stronger SHG effects than KDP. In recent years, some centrosymmetric chromophores were reported exhibiting second-harmonic generation [23]. It is documented that the orientation and distances of molecules in cocrystalline are changed with the need of supermolecular system architecture, in which the change of the orientation can result in the change of the symmetry of the crystal. Thus, the variation of the distances leads to the change of nonlinear optical property of chromophore with centrosymmetry [23]. Furthermore, the crystals of **3** are unstable in air. The crystals lose guest solvent molecules and transform into opaque slowly upon removal from the mother liquor, possibly accompanying the loss of the centrosymmetry and resulting in the SHG active new crystalline phase. The SHG effects of these samples can be attributed to the extensive π -conjugated systems in biphenyl rings and benzimidazole, and the incorporation of metal ions, which introduce more sublevels into the energy hierarchy [24].

In summary, using halide anions in the synthesized systems of the semi-rigid ligand 4,4'-bis(benzimidazol-1-ylmethyl)biphenyl (bbmb) and Ni(II) or Cu(II) salts under hydrothermal conditions, we successfully prepared the novel two-fold interpenetrated polymeric complexes **1** and **2** based on semi-rigid spacers. Meanwhile, we found that the terminal coordination of acetate could prevent 4,4'-biphenyl-based complexes from building interpenetrating architectures, and thus result in low-dimension or none-interpenetration structures, namely, the discrete quad-nuclear motif of complex **3** and the 1-D chain complex $[\text{Cu}_2(\text{OAc})_4(\text{bbmb})_{1.5} \cdot \text{CH}_3\text{CN} \cdot 2\text{CH}_3\text{OH}]_n$ [15]. Besides, complexes **1**, **2** and **3** exhibit active second-order NLO effects,

suggesting that 4,4'-biphenyl-based metal complexes may have potential applications in NLO domain.

Acknowledgement

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Appendix A. Supplementary material

CCDC number: 757917 for **1**, 765776 for **2** and 757916 for **3**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (44) 1223-336-033; or deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi: 10.1016/j.inoche.2010.05.006.

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- [14] Preparation of **1**: Well-shaped light-green crystals suitable for X-ray diffraction were obtained from a mixture of bbmb [15] (41.4 mg, 0.1 mmol), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (47.4 mg, 0.2 mmol) and H_2O (8 ml) in a 25 ml Teflon-lined stainless steel vessel at 150°C for 5 days followed by slow cooling to room temperature at a rate of 20°C h^{-1} . Yield: 73.8 mg (46%). IR(KBr pellets)/ cm^{-1} : 3346 m, 3102 m, 1640 m, 1613 m, 1512 s, 1461 s, 1446w, 1389 s, 1342w, 1293 m, 1264 m, 1195 m, 1150 m, 1007 m, 949w, 893w, 751 s, 622w. Calc. For $\text{C}_{56}\text{H}_{49}\text{N}_8\text{O}_3\text{ClNi}$ (%): C, 68.90; H, 5.06; N, 11.48. Found: C, 68.82; H, 5.02; N, 11.52.
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- [16] Crystallographic data for **1** ($\text{C}_{56}\text{H}_{49}\text{N}_8\text{O}_3\text{ClNi}$): $M_r = 976.19$, space group $P4/mnc$, $a = 15.703(7) \text{ \AA}$, $b = 15.703(7) \text{ \AA}$, $c = 20.4699(9) \text{ \AA}$, $V = 5047.4(3) \text{ \AA}^3$, $Z = 4$, $\rho = 1.285 \text{ g cm}^{-3}$, $\mu = 0.490 \text{ mm}^{-1}$, $T = 293(2) \text{ K}$, reflections collected: 3165, independent reflections: 2421, $S = 1.063$, $R_1 = 0.0456$, $wR_2 = 0.1422$.
- [17] The procedure of **2** was the same as that for **1**, except that $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ (34.0 mg, 0.2 mmol) was used instead of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. Yield: 61.2 mg (43%). IR(KBr pellets)/ cm^{-1} : 3343 m, 3104 m, 1640 m, 1614 m, 1514 s, 1461 s, 1443w, 1390 s, 1350w, 1290 m, 1261 m, 1187 m, 1152 m, 1010 m, 943w, 892w, 752 s, 627w. Calc. For $\text{C}_{56}\text{H}_{49}\text{N}_8\text{O}_3\text{ClCu}$ (%): C, 68.56; H, 5.03; N, 11.42. Found: C, 68.52; H, 5.06; N, 11.37.
- [18] Crystallographic data for **2** ($\text{C}_{56}\text{H}_{49}\text{N}_8\text{O}_3\text{ClCu}$): $M_r = 981.0$, space group $P4/mnc$, $a = 15.7078(14) \text{ \AA}$, $b = 15.7078(14) \text{ \AA}$, $c = 20.465(3) \text{ \AA}$, $V = 5049.4(10) \text{ \AA}^3$, $Z = 4$, $\rho = 1.290 \text{ g cm}^{-3}$, $\mu = 0.538 \text{ mm}^{-1}$, $T = 293(2) \text{ K}$, reflections collected: 2239, independent reflections: 1176, $S = 0.990$, $R_1 = 0.0638$, $wR_2 = 0.1611$.
- [19] Preparation of **3**: a solution of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.2 mmol, 53.6 mg) in 4 ml MeOH was slowly added into a 4 ml MeOH solution of bbmb (41.4 mg, 0.1 mmol). Well-shaped colorless crystals suitable for X-ray diffraction were deposited within two weeks. Yield: 68.1 mg (38%). Crystals of **3** are unstable in air, and upon removal

- from the mother liquor, they lose guest solvent molecules and transform into opaque slowly. IR(KBr pellets)/ cm^{-1} : 3422w, 1563 s, 1502 s, 1408 s, 1289w, 1262 m, 1193 m, 1121w, 1009w, 937w, 909w, 808w, 747 s, 674w. $\text{C}_{92}\text{H}_{78}\text{N}_{12}\text{O}_8\text{Cd}_2$ (desolvated **3**) (%): C, 64.83; H, 4.61; N, 9.86. Found for **3** after heating to 150°C to remove solvent molecules (%): C, 64.91; H, 4.65; N, 9.89.
- [20] Crystallographic data for **3** ($\text{C}_{95}\text{H}_{94}\text{N}_{12}\text{O}_{13}\text{Cd}_2$): $M_r = 1834.61$, space group $P1$, $a = 14.8147(17)\text{\AA}$, $b = 17.055(2)\text{\AA}$, $c = 21.370(3)\text{\AA}$, $V = 4831.4(10)\text{\AA}^3$, $Z = 2$, $\rho = 1.261\text{ g cm}^{-3}$, $\mu = 0.504\text{ mm}^{-1}$, $T = 293(2)\text{ K}$, reflections collected: 21318, independent reflections: 12306, $S = 1.056$, $R1 = 0.0709$, $wR2 = 0.2103$.
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