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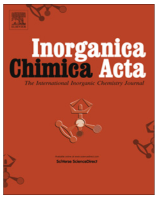

Three interdigitated metal–quinolone complexes from self-assembly of mixed ligands and cadmium salts

Xin Wang [a], Shi-Wei Yan [a], Juan Yang [a], Dong-Rong Xiao [a,*], Hua-Yi Zhang [a], Jin-Ling Zhang [a], Xiao-Lin Chi [a], En-Bo Wang [b]

[a] *College of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, PR China*
[b] *Key Laboratory of Polyoxometalate Science of Ministry of Education, Department of Chemistry, Northeast Normal University, Changchun 130024, PR China*

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ABSTRACT

Three interdigitated metal–quinolone complexes, $[Cd_2(cfH)_2(btec)(H_2O)_2]\cdot 6H_2O$ (**1**), $[Cd_2(ppaH)_2(1,3\text{-}bdc)_2]\cdot 4.25H_2O$ (**2**) and $[Cd_2(LevofH)(1,3\text{-}bdc)_2(H_2O)_2]$ (**3**) (cfH = ciprofloxacin, ppaH = pipemidic acid, LevofH = levofloxacin, btec = 1,2,4,5-benzenetetracarboxylate, 1,3-bdc = 1,3-benzenedicarboxylate) have been synthesized and characterized by elemental analyses, IR spectra, X-ray powder diffractions, TG analyses and single crystal X-ray diffraction. Compound **1** exhibits a (2D → 3D) interdigitated architecture that is first assembled from 2D wavelike (6,3) nets with side arms. Compound **2** is the first example of (2D → 3D) interdigitated metal–ppaH complex, which is constructed from sidearm-containing 2D layers of (4,4) topology. Compound **3** is built from 1D double chains with dangling levofloxacin ligands protruding from one side of the chain, and each pair of these double chains are interdigitated with each other to generate a perfect molecular zipper. By inspection of the structures of **1**–**3**, it is believed that the short aromatic polycarboxylate ligands are important for the construction of interdigitated metal–quinolone complexes. The photoluminescent properties of compounds **1**–**3** have also been investigated.

1. Introduction

Crystal engineering of metal–organic frameworks (MOFs) has attracted considerable interest, owing to their tremendous potential applications as functional materials, such as microelectronics, nonlinear optics, gas storage, molecular selection, ion exchange and catalysis, as well as their intriguing variety of topologies and entangled motifs [1,2]. Aided by the rapid growth of network-based crystal engineering, a variety of appealing interpenetrating nets have been designed [3] and reviewed by Robson, Batten, Ciani, Proserpio and their co-workers [1b,4a,b]. For interpenetrated networks, it is necessary to break internal connections in order to separate the individual nets [4,6b]. While some other types of entangled frames, such as interdigitated structures [6,7] and polythreaded networks with poly-pseudo-rotaxanes [8], can be disentangled without the need for breaking links. As these architectures are more flexible than the usual MOFs entirely based on coordination bonds [5a,b,f], they have the potential applications ranging from sensor devices to drug-delivery vehicles [5c–f]. Unfortunately, metal-drug complexes with interdigitated or polythreaded structures are extremely rare [10b,d,e], although many organic drugs have the potential to act as ligands, and the resulting metal-drug complexes are particularly important both in coordination chemistry and biochemistry [9,10].

Quinolones are a large family of synthetic antibacterial agents and widely used in clinical practice for the treatment of variety of infections. Ciprofloxacin (cfH), pipemidic acid (ppaH) and levofloxacin (LevofH) (Scheme 1), belonging to this family, are very active against aerobic Gram-negative microorganisms [11,12]. The mechanism of action of the quinolones is not completely understood at present, and there are two main explanations of the activity of quinolones proposed: one is their inhibition of the supercoiling of DNA catalyzed by the enzyme DNA gyrase; the other one is their interaction with the DNA molecule via a metal complex intermediate [10,12]. Recently, theoretical–experimental studies indicate that metal ions play an important role in the mechanism of action of these drugs [12,13]. Despite the key role that the metal ions may play in this system, the structurally characterized metal–quinolone complexes, especially entangled metal–quinolone complexes, are extremely rare [10]. Therefore, we sought to exploit viable routes to construct entangled metal–quinolone complexes.

As a continuation of our work on entangled metal–quinolone complexes [10b–e], quinolones and short aromatic polycarboxylates were selected as mixed ligands in an attempt to construct interdigitated metal–quinolone complexes, based on the following considerations: (i) The bulky quinolones usually act as one-end coordinated ligands [10], which can be regarded as lateral arms,

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* Corresponding author. Tel.: +86 23 68252360; fax: +86 23 68254000.
E-mail address: xiaodr98@swu.edu.cn (D.-R. Xiao).

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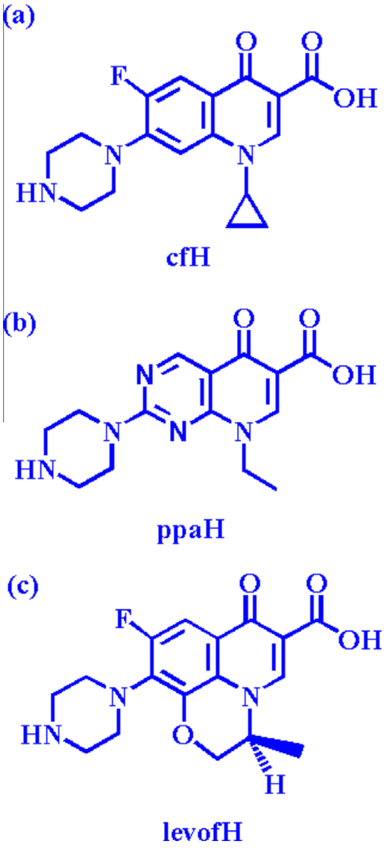

Scheme 1. Structures of cfH (a); ppaH (b); LevofH (c).

thus providing a necessary condition for the formation of interdigitation [7a–c]. (ii) The use of short aromatic polycarboxylate ligands like 1,3-benzenedicarboxylate (1,3-bdc) and 1,2,4,5-benzenetetracarboxylate (btec) could provide great possibilities for the construction of 1D double-chains or 2D layers of large windows [10b,14], thereby offering another necessary condition for the generation of interdigitation. (iii) Furthermore, when the aromatic polycarboxylate is shorter than the quinolone ligand, the distance between the adjacent quinolones in the complex is shorter than the length of quinolone ligand, which may lead to the quinolone ligands nearly perpendicularly protruding from two sides of the 1D double-chains or 2D layers (Fig. S1) [10e,12e] and thus favor the formation of interdigitated structures. In view of these points, we have performed many experiments. Fortunately, these efforts have led to the isolation of three interdigitated metal–quinolone complexes, namely, $[Cd_2(cfH)_2(betc)(H_2O)_2]{\cdot}6H_2O$ (**1**), $[Cd_2(ppaH)_2(1,3\text{-bdc})_2]{\cdot}4.25H_2O$ (**2**) and $[Cd_2(LevofH)(1,3\text{-bdc})_2(H_2O)_2]$ (**3**). The syntheses and crystal structures of these compounds will be represented and discussed. In addition, the photoluminescent properties for compounds **1**–**3** were investigated.

2. Experimental

2.1. Materials and methods

All chemicals were commercially purchased and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Cd atom was determined by a tps-7000 Plasma-Spec(I) inductively coupled plasma atomic emission spectrometer (ICP-AES). IR spectra were recorded in the range 400–4000 cm^{-1} on a Bio-Rad FTS-185FT/IR Spectrophotometer using KBr pellets. TG analyses were performed on a NETZSCH STA 449C instrument in flowing N_2 with a heating rate of 10 °C min^{-1}. Excitation and emission spectra were performed on an F-4500 fluorescence spectrophotometer equipped with a 150 W xenon lamp as the excitation source. XRPD data were recorded on a XD-3 diffractometer using Cu Kα (λ = 1.5406 Å) radiation.

2.2. Synthesis of $Cd_2(cfH)_2(btec)(H_2O)_2]{\cdot}6H_2O$ (**1**)

A mixture of $Cd(OAc)_2{\cdot}2H_2O$ (0.30 mmol), cfH (0.15 mmol), H_4-btec (0.15 mmol), and distilled water (8 mL) was stirred for 30 min in air, then sealed in an 18 mL Teflon-lined autoclave, which was heated at 120 °C for 96 h under autogenous pressure. After slow cooling to room temperature, yellow block crystals of **1** were filtered off, washed with distilled water and dried at ambient temperature (53 mg, yield: 55% based on cfH). *Anal.* Calc. for $C_{44}H_{54}Cd_2F_2N_6O_{14}$ (**1**): C, 45.80; H, 4.72; N, 7.28; Cd, 19.49. Found: C, 45.92; H, 4.93; N, 7.49; Cd, 19.67%. FT/IR data (cm^{-1}): 3501(m), 3401(m), 3233(w), 3047(w), 2958(w), 2854(m), 2484(w), 1904(w), 1813(w), 1629(s), 1557(s), 1517(w), 1488(m), 1383(s), 1327(w), 1304(s), 1268(s), 1196(w), 1179(m), 1149(w), 1133(w), 1110(w), 1090(w), 1063(w), 1035(s), 948(s), 909(s), 876(s), 833(w), 815(s), 789(w), 769(w), 747(m), 704(m), 685(w), 663(w), 642(w), 627(m), 567(m), 535(s), 507(m), 478(w), 445(w), 421(w).

2.3. Synthesis of $[Cd_2(ppaH)_2(1,3\text{-bdc})_2]{\cdot}4.25H_2O$ (**2**)

A mixture of $Cd(OAc)_2{\cdot}2H_2O$ (0.40 mmol), ppaH (0.20 mmol), 1,3-bdc (0.20 mmol), KOH (0.5 mmol), and distilled water (8 mL) was stirred for 30 min in air, then sealed in an 18 mL Teflon-lined autoclave, which was heated at 120 °C for 96 h under autogenous pressure. After slow cooling to room temperature, colorless block crystals of **2** were filtered off, washed with distilled water and dried at ambient temperature (70 mg, yield: 57% based on 1,3-bdc). *Anal.* Calc. for $C_{44}H_{50.5}Cd_2F_2N_{10}O_{18.25}$ (**2**): C, 42.75; H, 4.12; N, 11.33; Cd, 18.19. Found: C, 43.90; H, 4.30; N, 11.48; Cd, 18.07%. FT/IR data (cm^{-1}): 3419 (br), 3061(w), 2823(w), 2485(w), 1615(s), 1552(s), 1505(w), 1477(m), 1444(m), 1364(s), 1309(w), 1274(w), 1254(m), 1189(w), 1153(w), 1125(w), 1075(s), 1032(w), 981(w), 953(s), 919(w), 868(s), 821(w), 780(w), 751(s), 718(s), 658(w), 613(m), 535(m), 492(w), 440(w).

2.4. Synthesis of $[Cd_2(LevofH)(1,3\text{-bdc})_2(H_2O)_2]{\cdot}4.25H_2O$ (**3**)

A mixture of $Cd(OAc)_2{\cdot}2H_2O$ (0.5 mmol), LevofH (0.25 mmol), 1,3-bdc (0.25 mmol), adipic acid (0.25 mmol), Et_3N (0.5 mL), and distilled water (8 mL) was stirred for 30 min in air, then sealed in an 18 mL Teflon-lined autoclave, which was heated at 150 °C for 48 h and then heated at 160 °C for 80 h under autogenous pressure. After slow cooling to room temperature, yellow block crystals of **3** were filtered off, washed with distilled water and dried at ambient temperature (55 mg, yield: 46% based on 1,3-bdc). *Anal.* Calc. for $C_{34}H_{32}Cd_2F_2N_3O_{14}$ (**3**): C, 42.97; H, 3.39; N, 4.42; Cd, 23.65. Found: C, 42.77; H, 3.54; N, 4.62; Cd, 23.49%. FT/IR data (cm^{-1}): 3386 (br), 2860(w), 2658(w), 2523(w), 2483(w), 1902(w), 1630(s), 1606(s), 1582(w), 1561(w), 1474(m), 1456(w), 1442(w), 1425(w), 1384(s), 1347(w), 1268(m), 1185(w), 1151(w), 1126(s), 1092(w), 1051(m), 1023(m), 977(m), 951(s), 914(w), 875(w), 838(w), 819(s), 755(m), 737(w), 724(s), 690(w), 657(w), 631(w), 594(w), 497(w), 464(m), 434(w), 413(w).

2.5. X-ray crystallography

Suitable single crystals were selected for single-crystal X-ray diffraction analyses (diffractometer device type: Bruker Smart-Apex CCD for **1**–**2**; Rigaku R-AXIS RAPID IP for **3**). Absorption