Photoluminescent Metal-Organic Nanotubes via Hydrothermal in Situ Ligand Reactions

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Hydrothermal reactions of $CdCl_2$, oxalic acid, 1,3,5-benzenetricarboxylic acid and o-phenylene diamine (o-PD) yielded three novel coordination polymers $[NaCd_4(btc)_3(H_2bbim)_4(H_2O)_2]\cdot 2H_2O$ (**1**), $[KCd_4(btc)_3(H_2bbim)_4(H_2O)_2]\cdot 2H_2O$ (**2**) and $[Cd(H_2bbim)(H_2bimbdc)(HbimbdcH)]\cdot H_2O$ (**3**) [btc = 1,3,5-benzene tricarboxylate, H_2bbim = 2,2′-bisbenzimidazole, $HbimbdcH_2$ = 1-(2-Benzimidazolyl)-3,5-benzene dicarboxylic acid]. The benzimidazole derivatives were in situ gener-

ated via hydrothermal metal/ligand condensation of oxalic acid or 1,3,5-benzenetricarboxylic acid with o-phenylenediamine. Both **1** and **2** have novel single-walled nanotubular coordination structures and show strong red photoluminescence at room temperature.

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Introduction

Metal coordination polymers have been extensively investigated in the last decade due to their intriguing structural diversity and promising physical/chemical properties for potential applications including porosity, catalysis and photoluminescence properties.[1,2] In situ metal/ligand reactions are very important in both organic chemistry and coordination chemistry,[3–5] which suggests a feasible and efficient way to design and prepare new organic and inorganic/organic hybrid compounds. Many different types of in situ ligand reactions have been reported, including dehydrogenative carbon–carbon coupling and alkylation,[6,7] hydroxylation,[8] oxidation,[9] decarboxylation,[10] cycloaddition of organic nitrile and unsaturated nitrogen-containing heterocyclic compounds,[11] hydrolysis,[12] transformation between inorganic and organic sulfur,[13] acylation[14] and conformational isomerisation.[15] Hydrothermal in situ metal/ligand synthesis has attracted continuous interest though it is still a great challenge to predict and control the structures of final products. New ligands and novel coordination compounds, especially those difficult or inaccessible through direct reactions of organic and inorganic species, have been obtained from organic precursors in the presence of metal ions through in situ ligand reactions under hydrothermal conditions. In this communication, we report three photoluminescent cadmium benzimidazole coordination

compounds from hydrothermal metal/ligand reactions. Two benzimidazole derivatives in the coordination compounds, 2,2′-bisbenzimidazole (H_2bbim) and 1-(2-benzimidazolyl)-3,5-benzene dicarboxylic acid ($HbimbdcH_2$), were formed from in situ condensation between o-phenylenediamine (o-PD) and oxalic acid or 1,3,5-benzene tricarboxylic acid ($btcH_3$). Compounds **1** and **2**, $[MCd_4(btc)_3(H_2bbim)_4(H_2O)_2]\cdot 2H_2O$ (M = Na **1** and K **2**) are isomorphous to each other, which have metal-organic nanotubular structures consisting of $\{Cd_4(btc)_3(H_2bbim)_4\}$ units. Compound **3**, $[Cd(H_2bbim)(H_2bimbdc)(HbimbdcH)]\cdot H_2O$, is an infinite coordination chain assembly containing two in situ formed benzimidazole ligands. Though the condensation between o-PD and oxalic acid into 2,2′-bisbenzimidazole and many coordination complexes based on benzimidazole ligand have been reported,[16] it is the first observation of the in situ condensation between o-PD and 1,3,5-benzene tricarboxylic acid while in previous reported cases, they are likely to form mixed-ligand coordination compounds.

Since the discovery of carbon nanotubes (CNTs) in 1991,[17] nanotubular structures, including inorganic nanotubes[18] containing carbon and other elements such as nitrides, oxides and sulfides and metal-organic nanotubes,[19] have received much attention in the field of nanoscience and technology and materials science because of their novel structures and accordingly potential intriguing applications in ion, water and other small molecule channels, molecular electronics and devices, and photoelcetronics etc.[20] Notably although a large number of metal organic frameworks (MOFs) with one-dimensional molecular chain structures as well as with open one-dimensional tubular channels have been synthesized in the past decades,[21,22] only a few metal coordination polymers containing isolated infinite nanotubular structures have been reported. The difficulties may

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come from the interconnection or interweaving of the nanotubular subunits into higher-dimensional frameworks by the multidentate ligands.[23] A previous reported strategy to prepare metal-organic nanotubes was to generate a square subunit firstly and then to link them up through the second ligands from the four vertexes.[22] In compounds **1** and **2**, similar square metal-organic nanotubes were obtained yet from a different strategy that the versatile 1,3,5-benzene tricarboxylic acid (H_3btc) takes the responsibility of linking the infinite nanotubular skeleton while the in situ generated 2,2′-bisbenzimidazole (H_2bbim) is situated on the vertex as an ancillary ligand to block the further interconnection with adjacent molecular arrays.

Results and Discussion

Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in monoclinic space group $C2/m$. The asymmetric unit consists of two crystallographically unique Cd^{II} ions (Figure 1), half of sodium ion, two H_2bbim, one and a half btc and two disordered aqua molecules. Cd1 is in a distorted octahedral geometry chelated by one H_2bbim and one btc ligand [Cd1–N 2.299(4) to 2.340(4), Cd1–O 2.302(4) to 2.530(4) Å]. Its coordination sphere is further completed by two carboxylate oxygen atoms from two different btc [Cd1–O 2.302(4) to 2.530(4) Å]. Cd2 is also in a {CdN_2O_4} distorted octahedral geometry surrounded with one H_2bbim and three btc units [Cd2–N 2.299(4) to 2.340(4), Cd2–O 2.302(4) to 2.725(8) Å]. Na1 is situated in a special position with mirror plane symmetry and adopts a heavily distorted octahedral geometry coordinated by four oxygen atoms from three btc ligands and two disordered water molecules [Na1–O 2.122(2) to 2.325(2) Å, O–Na1–O 56.85(7) to 153.04(9)°]. The two 1,3,5-btc ligands have distinct coordination modes. One btc connects four cadmium and one sodium ions via the chelation (Cd1), *syn-anti* bridging (two Cd2) and μ_2:η^2 (Cd1 and Na1) modes while the other btc is situated across the mirror-symmetric plane along the 1,4-position on the benzene ring linking four cadmium and one sodium atoms via the chelation (two Cd2) and μ_3:η^2,η^2 (two Cd1 and Na1) fashions. Accordingly every four Cd1 and Cd2 atoms are bridged by three btc ligands to form an infinite 1-D elliptical tubular coordination assembly with the repeating unit of {Cd_4(btc)$_3$(H_2bbim)$_4$} (see parts a–d of Figure 2). The H_2bbim ligands are parallel to each other on the corners of the cadmium tube, rendering it like a pseudo square metallamacrocycle ring in the size of about 20×22 Å when viewed along the c-axis (Figure 2, b). With omitting the sodium atoms and H_2bbim ligands, the Cd_4(btc)$_3$ coordination framework is a (3,4)-connected net by simplifing the cadium centers and btc units as 3- and 4-connecting topological nodes, respectively. The tubular network could be viewed as the result from rolling up the planar (3,4)-connected layer (Figure 2, c, d). The tube runs parallel to the c-axis with two kinds of nodes composed of four Cd1 and four Cd2 atoms in the dimensions of about 6.51×7.74 Å and about 4.63×8.99 Å,

respectively. Inside the nanotubes lie the disordered bonded and free H_2O molecules. Each metal-organic nanotube has the intermolecular face-to-face π-π interactions with four adjacent nanotubes between H_2bbim ligands in the distance of 3.05–3.25 Å (calculated based on the least-square planes of the aromatic rings, Figure 3), into a 3D supramolecular architecture. **2** is isostructural to **1** except that the potassium ions take the place of sodium atoms.
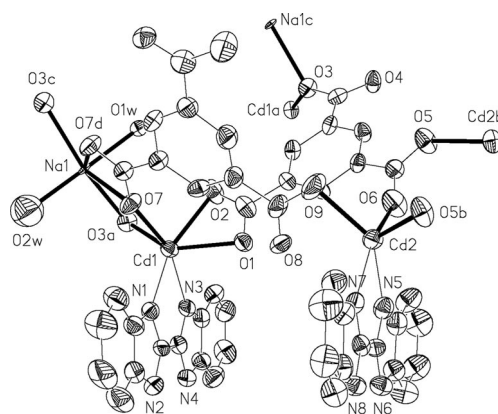

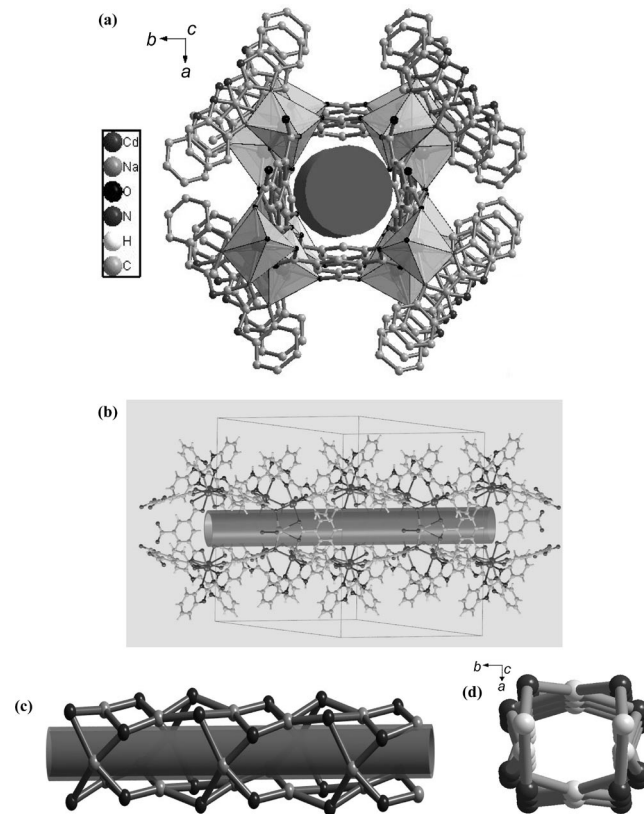Figure 1. ORTEP drawings of the coordination geometry on the cadmium ions in 1.

Figure 2. Top (a) and side (b) views of the nanotubular structure of compound **1** (tube interior, dark column). Side (c) and top (d) views of the simplified (3,4)-connected topological framework.
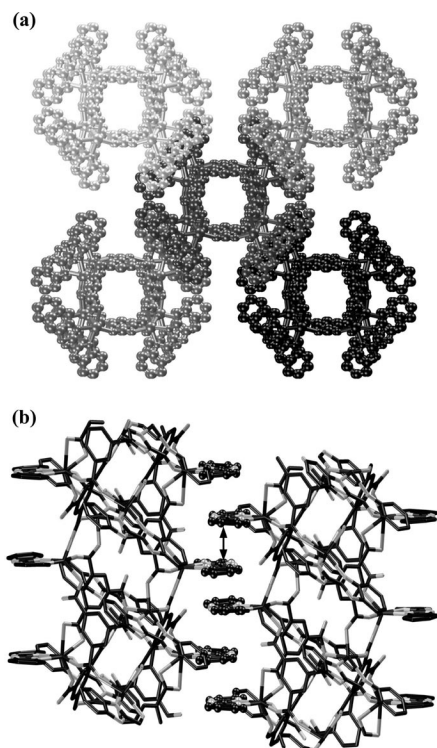
Figure 3. (a) The supramolecular packing of the nanotubular structures viewed along the *c*-axis of **1**. The H, Na and H₂O species are omitted for clarity. (b) The off-set face-to-face π-π interaction in the distance of ca. 3.05–3.25 Å between H₂bbim groups from the neighboring metal-organic nanotubes.

3 crystallizes in the space group of $P\bar{1}$ and displays a 1-D chain-like coordination structure. There are one cadmium atom, one H₂bbim, two 1-(2-Benzimidazolyl)-3,5-benzene dicarboxylate (HbimbdcH and H₂bimbdc) and one lattice aqua molecules in the asymmetric unit. The metal center is in a distorted octahedral geometry (Figure 4, a) surrounded by the chelated H₂bbim [Cd1–N 2.347(2) to 2.358(2) Å] and HbimbdcH [Cd1–O 2.382(2) to 2.388(2) Å] and two monodentate H₂bimbdc ligands [Cd1–O 2.223(2) to 2.355(2) Å]. Interestingly the protons on the two 1-(2-benzimidazolyl)-3,5-benzenedicarboxylates have different dispositions, HbimbdcH and H₂bimbdc. On HbimbdcH the imidazolyl ring is mono-protonated and the second proton is situated on the carboxylic group. The other carboxylate on HbimbdcH is chelated to the cadmium ion and the ligand, similar to H₂bbim, acts as a terminal component. Contrastively, two prontons on H₂bimbdc are attached to the nitrogen atoms on the imidazolyl ring and both carboxylate groups adopt the mono-dentate mode linking the cadmium nodes into an infinite chain along the *a*-axis. The two adjacent 1-D chains are joined together with the closest interchain Cd⋯Cd separation of 7.815 Å through bifurcate hydrogen bonds between the protonated imidazolyl rings on H₂bbim and the carboxylate from H₂bimbdc [N2*a*⋯O2 2.799(3), N4*a*⋯O2 2.763(3) Å] and π-π stacking interactions between the H₂bbim ligands with the face-to-face distance of 3.490 Å, generating 1-D hydrogen-bonded double-chain motifs (Figure 4, b). Neighboring double-chains are

linked into a 3-D supramolecular architecture via extensive hydrogen bonds (Figure 4, c) between intermolecular HbimbdcH ligands [O8*a*⋯N8 2.658(3) Å] and among the lattice water molecule, HbimbdcH and H₂bimbdc [O1w⋯O5 2.738(3), O1w⋯O4 2.866(3) Å, N5⋯O1w 2.708(3) Å].
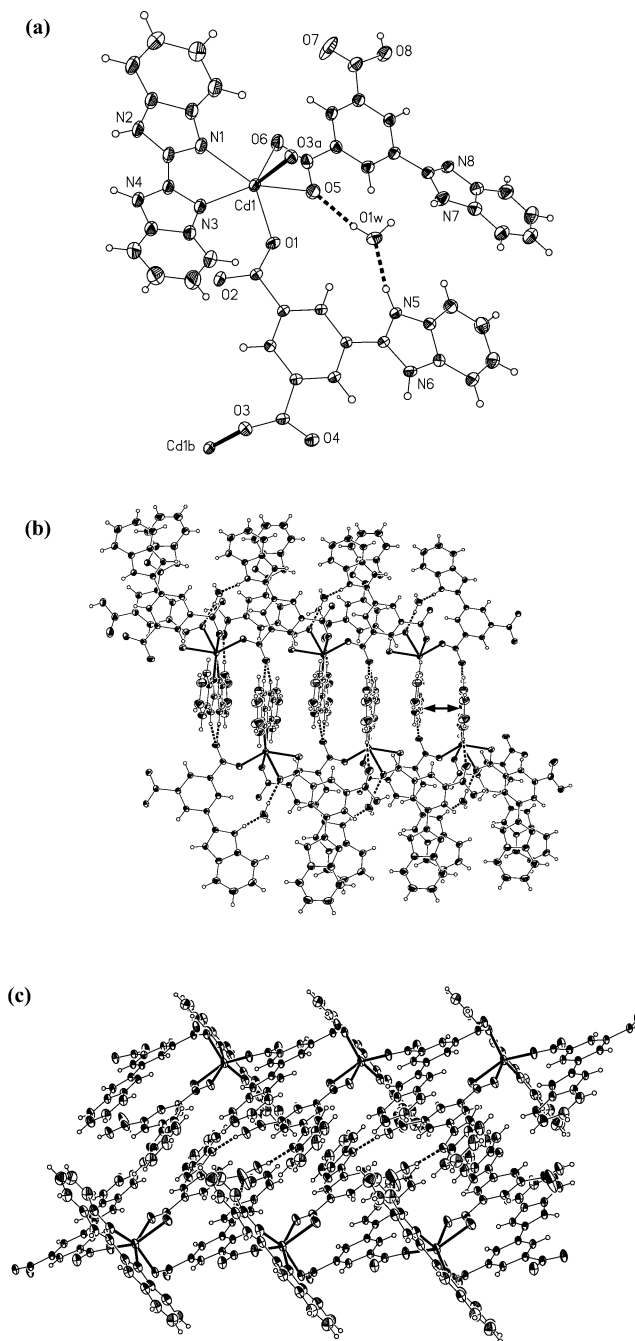

Figure 4. ORTEP drawing of the coordination geometry on the cadmium ion in **3** (a). The interchain π-π stacking interaction along the *a*-axis (b) and hydrogen-bonding interaction along the *b*-axis (c) interactions in 3-D supramolecular architecture of **3**.

The hydrothermal in situ condensations between *o*-phenylenediamine (*o*-PD) and oxalic acid into benzimidazolyl derivatives in the presence of different metal ions have been reported recently.[24] It was reported that the condensation

reactions involving H_2bbim ligand were pH dependent, which is similar to our results for the formation of H_2bbim and HbimbdcH$_2$ in **1**–**3** (Scheme 1). In our study, complexes **1**, **2** and **3** could be obtained when the pH values of the reaction systems were adjusted in the range of 2–4. Only compound **3** could be yielded from a slightly more basic solution with the pH value of 5. No crystalline solids of **1**–**3** were obtained when the pH values of the reaction solutions were adjusted to above 6. The optimum pH value for the condensation of o-PD and 1,3,5-benzene tricarboxylic acid to HbimbdcH$_2$ was 5 in the formation of **3** while a pH value of 4 was the optimum value for preparing complexes **1** and **2** since the highest yields could be obtained. No benzimidazole analogues could have been obtained in the previous report[24] when using 1,4-benzene dicarboxylic acid as an ancillary ligand or using other simple dicarboxylic acids taking the place of oxalic acid. Interestingly in our study, condensation can also be found between o-PD and 1,3,5-benzene tricarboxylic acid and a new multidentate ligand, HbimbdcH$_2$, was yielded. The presence of the cadmium ions in weakly acidic solution may play some critical catalytic role in the condensation.
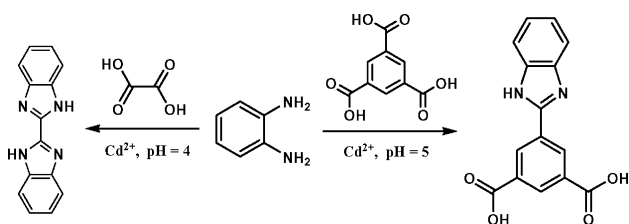
Scheme 1. The in situ reactions involving H_2bbim and HbimbdcH$_2$.

The photoluminescent (PL) spectra of **1**–**3** and the free H_2bimbdcH in the solid state were investigated at room temperature (Figure 5). Upon excitation at 593 nm, both **1** and **2** have very similar PL properties exhibiting sharp red emission with peak maximum at around 675 and 673 nm, respectively. At present, only two transition types of emission mechanisms-ligand-to-ligand charge transfer (LLCT)[16d,25] or ligand-to-metal charge-transfer (LMCT),[26] depending on natures of the metal and ligands, have been proposed in the Zn^{II}/Cd^{II}-based d^{10} metal coordination compounds. Since the free H_2bbim has a blue emission with a peak maximum at around 414 nm (λ_{ex} at 340 nm)[27] and the free H_3btc shows the emission bands at 323 and 358 nm (λ_{ex} at 300 nm),[25] such large bathochromic shifts for **1** and **2** may suggest that the aromatic rings of the ligands interact effectively with the metal ions and/or with each other through π-stacking interactions.[28] It is noteworthy that while most of coordination compounds display blue emission, the low energy luminescence for **1** and **2** are rather rare,[29] which are among the lowest energy emission or the longest emission wavelength in the luminescent d^{10} transition metal coordination polymers reported.[26] The free H_2bimbdcH displays a PL emission at 432 nm upon excitation at 322 nm in DMSO solution (Figure S1). **3** exhibits an intense blue–green emission peak at 416 nm and a shoulder at 464 nm upon excitation at 372 nm at room tem-

perature. The emission band of 416 nm for **3** is probably due to the π*-π transition of the ligands. While a bathochromic shift observed from the ligand, the shoulder peak of the emission spectrum at 464 nm for **3** can tentatively be assigned to ligand-to-metal charge transfer (LMCT).
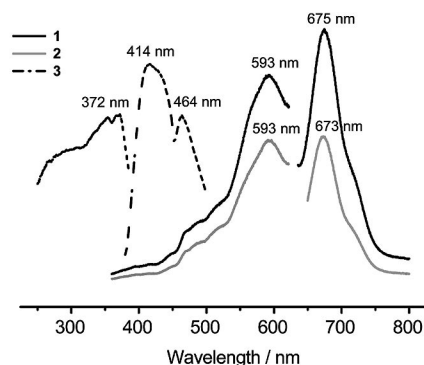

Figure 5. Room-temperature excitation (left) and emission spectra (right) of **1** (dark grey lines), **2** (grey lines) and **3** (dash lines).

The thermal stability of **1** was examined in air by thermogravimetric analysis (TGA). The TG curve exhibits three significant mass changes over the temperature range of 35–600 °C (Figure S2). A first weight loss of 2.98% (calcd. 3.0%) occurs between 35 and 250 °C corresponding to the loss of water molecules. The second weight loss of 28.9% at 250–425 °C is attributed to the partly decomposition of the organic ligands. The bulky compound decomposed between 425 and 525 °C with weight loss of 44.7%. Temperature dependent powder XRD of **1** showed that there was no significant structural change at 400 °C, indicating that the framework structures of **1** could be maintained upon the complete removal of the water molecules (Figure S3).

Experimental Section

General Remarks: All chemicals were purchased commercially and used without further purication. Powder X-ray Diffraction patterns were carried out with an X-ray Diffractometer [D8 ADVANCE]. Fluorescent spectra were measured at room temperature with a Spectrofluorophotometer [RF-5301PC system]. TG curve were measured with a Thermogravimetry [TG 209 F3 Tarsus]. All complexes were synthesized by a hydrothermal method under autogenous pressure.

Synthesis of 1 and 2: The hydrothermal reaction of CdCl$_2$·2.5H$_2$O, o-PD, oxalic acid, 1,3,5-benzenetricarboxylic acid, NaOH and H$_2$O in the molar ratio of 1:2:1:1:2:667 was performed (the pH value of the reaction system was 4) at 180 °C for 3 d, and then was cooled to a rate of ca. 5 °Ch^{-1} to give block crystals of 1 (yield 165 mg, 32%, based on CdCl$_2$·2.5H$_2$O). They were isolated by filtration, and washed with water. 2 was prepared in the same way as 1 but using KOH instead of NaOH (yield 180 mg, 34%, based on CdCl$_2$·2.5H$_2$O). 1: C$_{83}$H$_{57}$Cd$_4$N$_{16}$NaO$_{22}$ (2103.05): calcd. C 47.40, H 2.73, N 10.66; found C 47.96, H 3.00, N 11.28. IR data (KBr) for 1: ṽ = 3430 (br), 1611 (s), 1543 (s), 1424 (s), 1374 (vs), 1108 (m), 1031 (m), 736 (s) cm^{-1}. 2: C$_{83}$H$_{57}$Cd$_4$KN$_{16}$O$_{22}$ (2119.16): calcd. C 47.04, H 2.71, N 10.58; found C 47.57, H 2.94, N 11.12. IR data (KBr) for 2: ṽ = 3431 (br), 1612 (s), 1546 (s), 1424 (s), 1376 (vs), 1108 (m), 1031 (m), 736 (s) cm^{-1}. The phase purity of 1 and 2 has

been confirmed by PXRD experiments (see Supporting Information).

Synthesis of 3: The mixture of $CdCl_2$, *o*-PD, oxalic acid 1,3,5-benzene tricarboxylic acid and H_2O in the molar ratio of 1:2:1:1:667 was placed in a Parr Teflon-lined stainless steel vessel with vigorous magnetic stirring, the pH value of the reaction system was adjusted to ca. 5 with dilute NaOH solution. The mixture was heated at 180 °C for 3 d and was cooled to a rate of ca. 5 °C h^{-1} to room temperature, block crystals of **3** in pure phase (yield 80 mg, 17.4%, based on *o*-PD) were obtained as well as the crystals of HbimbdcH$_2$. They were both isolated by filtration, and washed with water. **3**: $C_{44}H_{30}CdN_8O_9$ (927.17): calcd. C 57.00, H 3.26, N 12.09; found C 56.42, H 3.40, N 11.98. IR data (KBr) for **3**: $\tilde{v}$ = 3375 (br), 1161 (m), 1551 (s), 1360 (s), 1269 (m), 1231 (m), 743 (s) cm^{-1}. HbimbdcH$_2$: $C_{15}H_{10}N_2O_4$ (282.25): calcd. C 63.83, H 3.57, N 9.93; found C 62.53, H 3.42, N 9.90. IR date (KBr): $\tilde{v}$ = 3429 (br), 3076 (m), 1696 (m), 1635 (s), 1430 (s), 1380 (s), 1230 (s), 1177 (m), 1118 (m), 1025 (m), 770 (s), 623 (m) cm^{-1}. The phase purity of **3** has been confirmed by PXRD experiments (see Supporting Information).

X-Ray Crystallographic Study: Diffraction intensities of **1** and **3** were collected on a Bruker Apex CCD area-detector diffractometer (Mo-K_α, λ = 0.71073 Å). Diffraction data were recorded on an Oxford Diffraction Gemini R CCD diffractometer with Cu-K_α radiation (λ = 1.54178 Å) for **2** and HbimbdcH$_2$ at 150 K. The crystal temperature was controlled using an Oxford Cryosystems Cryostream cooling apparatus. The intensities of **1** and **3** were integrated with SAINT$^+$, which also applied corrections for Lorentz and polarization effects. Absorption corrections were applied by using multiscan program SADABS.[30] The structures were solved with direct methods and refined with a full-matrix least-squares technique with the SHELXTL program package.[31]

Compound 1: $C_{83}H_{57}Cd_4N_{16}NaO_{22}$, M = 2103.04, monoclinic, space group $C2/m$ (No. 15), a = 24.086(5), b = 24.388(5), c = 17.190(2) Å, β = 113.721(4)°, V = 9244(3) Å^3, Z = 4, T = 293(2) K, $F(000)$ = 4184, D_c = 1.511 g cm^{-3}, $\mu_{(Mo-K\alpha)}$ = 0.989 mm^{-1}; R_1 = 0.0899, wR_2 = 0.2333 and GOF = 0.988 for 582 parameters, 5046 reflections with $|F_o| \geq 4\sigma(F_o)$.

Compound 2: $C_{83}H_{57}Cd_4N_{16}KO_{22}$, M = 2119.15, monoclinic, space group $C2/m$ (No. 15), a = 24.0350(9), b = 24.3531(6), c = 17.1217(6) Å, β = 113.921(4)°, V = 9161.0(5) Å^3, Z = 4, T = 150(2) K, $F(000)$ = 4216, D_c = 1.536 g cm^{-3}, $\mu_{(Mo-K\alpha)}$ = 8.399 mm^{-1}; R_1 = 0.0579, wR_2 = 0.1802 and GOF = 1.074 for 586 parameters, 5999 reflections with $|F_o| \geq 4\sigma(F_o)$. Compound **3**: $C_{44}H_{30}CdN_8O_9$, M = 927.16, triclinic, space group $P\bar{1}$ (No. 2), a = 8.9977(7), b = 12.483(1), c = 17.1670(14) Å, α = 85.748(1), β = 76.909(1), γ = 85.070(1)°, V = 1868.1(3) Å^3, Z = 2, T = 293(2) K, $F(000)$ = 940, D_c = 1.648 g cm^{-3}, $\mu_{(Mo-K\alpha)}$ = 0.659 mm^{-1}; R_1 = 0.0391, wR_2 = 0.0942 and GOF = 0.981 for 560 parameters, 6230 reflections with $|F_o| \geq 4\sigma(F_o)$. HbimbdcH$_2$: $C_{15}H_{10}N_2O_4$, M = 282.25, triclinic, space group $P2_1/m$ (NO. 11), a = 5.9540(3) Å, b = 14.2039(4) Å, c = 7.3287(4) Å, β = 100.822(5)°, V = 608.77(5) Å^3, Z = 2, T = 150(2) K, $\rho_{calcd.}$ = 1.540 g cm^{-3}, $\lambda(Mo-K_\alpha)$ = 0.958 mm^{-1}. R_1 = 0.0365 $[I > 2\sigma(I)]$, wR_2 = 0.0988 (for all data).

CCDC-736573 (for **1**), -736574 (for **2**), -736575 (for **3**) and -736576 (for HbimbdcH$_2$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Excitation and emmission spectra of H$_2$bimbtcH, TGA curve of **1** and XRPD patterns for **1**–**3**.

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