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From lamellar net to bilayered-lamella and to porous pillared-bilayer: reversible crystal-to-crystal transformation, CO₂ adsorption, and fluorescence detection of Fe³⁺, Al³⁺, Cr³⁺, MnO₄⁻, and Cr₂O₇²⁻ in water

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Abstract

DOI: 10.1039/D0DT02606A 5-NH₂-1,3-H₂bdc lamellar net $[Zn(5-NH_2-1,3-bdc)(H_2O)]$ An aqua-coordinated (1, 5-amino-1,3-benzenedicarboxylic acid) has been found to proceed a reversible stimuli-responsive 2D-to-2D crystal-to-crystal transformation with water-free bilayered-lamellar a net $[Zn(5-NH_2-1,3-bdc)]$ (1') upon removal and rebinding of aqua ligands, whereas a 2D porous pillared-bilayer [Zn₂(5-NH₂-1,3-bdc)₂(NI-bpy-44)]·DMF (2,NI-bpy-44 = N-(pyridin-4-yl)-4-(pyridin-4-yl)-1,8-naphthalimide) has been engineering tailored by introducing NI-bpy-44 to replace the coordinated aqua ligands. Pillared-bilayer 2 displayed moderate CO₂ uptakes of 79.1 cm³ g⁻¹ STP at $P/P_0 = 1$ and 195 K with an isosteric heat of CO₂ adsorption (Q_{st}) of 37.0 kJ mol⁻¹ at zero-loading. Noteworthy, the water suspensions of 1 and 2 both showed good fluorescence performances, which were effectively quenched by Fe³⁺, MnO₄⁻, and Cr₂O₇²⁻ ions and shifted to long wavelength by Fe³⁺, Al³⁺, and Cr³⁺, even with the coexistence of equal-amount of most other interfering ions. Taken Stern–Volmer quenching constant, limit of detection, quenching efficiency, anti-interference ability, and visual observation into consideration, it is clear that 1 and 2 both are promising excellent fluorescence sensors for highly sensitive detection of Fe³⁺, MnO₄⁻, and $Cr_2O_7^{2-}$.

1

Introduction

Over the past two decades, the explosive development of coordination polymers (CPs) and metalorganic frameworks (MOFs) have led to active discussion of not only structural and chemical diversity but also high prospects for practical applications. From a structural point of view, one particularly intriguing property in CPs/MOFs is solid-state structural transformation, especially single-crystal to single-crystal transition,¹⁻⁶ which represents one of the most fanscinating phenomenon that is the stimuli-responsive structural transformation between the solid phases with the retention of single crystallinity.⁷⁻¹⁰ Obviously, solid-state structural transformations are triggered by external stimulus, such as solvent,⁷⁻¹⁵ heat,¹⁵⁻¹⁷ counterion,¹⁸⁻²⁰ light,^{21,22} and mechanochemical force,²³ and thus can provide a means to regulate the structure and properties of the materials. So far, it is very familiar that the characteristic solid-state structural transformation induced by the removal/readsorption of guest molecules from/to the host framework itself,^{10–15,24–26} however, only a few of cases have shown the change in coordination environment of the metal centers arising from coordination bond cleavage and/or formation.^{7-9,27,28} Wu and coworkers, for example, have recently reported a one-dimensional (1D) zigzag chain structure $[Zn(L^{salpyca})(H_2O)]_n$ where $H_2L^{salpyca} = 4$ -hydroxy-3-(((pyridin-2-yl)methylimino)methyl)benzoic acid, which exhibited remarkably reversible 1D-to-2D framework flexibility upon removal and rebinding of coordination water molecules, accompanied changes in coordination sphere (structure) and in fluorescence wavelength (property).⁷

In recent times, significant attention has been paid to luminescent CPs and MOFs that can be used to perform the vapor-phase sensing and liquid-phase detection for hazardous chemicals including various harmful organic polluants and different toxic heavy metals in either typical cationic form, such as Hg^{2+} , Pb^{2+} , Cu^{2+} , Fe^{3+} , Al^{3+} , Cr^{3+} , or high valent oxo anionic form, such as CrO_4^{2-} , $Cr_2O_7^{2-}$, MnO_4^{-} .²⁹⁻⁴¹ This is because that the release of these hazardous chemicals would cause water contamination and thus adverse effect on humanity and other organisms as well as life environment and ecological system.⁴²⁻⁴⁴ For CP/MOF-based sensors, the fluorescence detection of metal ions and anions is mainly working in nonaqueous phases while not in water systems.^{45–50} View Article Online Such a limited detecting property is explained by the reason that most of CP/MOF materials show poor water stability.⁵¹ Therefore, it is agreeable to design highly stable CP/MOF materials as fluorescence sensors that work in aqueous media and show excellent sensing preformance.

Herein, we report our investigations on the reversible crystal-to-crystal transformations between an aqua-coordinated 2D lamellar net $[Zn(5-NH_2-1,3-bdc)(H_2O)]$ (1, 5-NH₂-1,3-H₂bdc = 5-amino-1,3-benzenedicarboxylic 2D acid) and water-free bilavered-lamellar а net [Zn(5-NH₂-1,3-bdc)] (1') upon dehydration/rehydration processes. Such a dynamic structural transformation gives an idea to tailor a covalently bonded pillared-bilayer structure [Zn₂(5-NH₂-1,3-bdc)₂(NI-bpy-44)]·DMF NI-bpy-44 (2,= N-(pyridin-4-yl)-4-(pyridin-4-yl)-1,8-naphthalimide) showing moderate CO₂ sorption capacity. Further, 1 and 2 both emit strong blue fluorescence emissions in water, and their water suspensions exhibit fluorescence detection of not only trivalent iron (Fe³⁺), aluminum (Al³⁺), and chromium (Cr^{3+}) cations but also permanganate (MnO_4^{-}) and dichromate $(Cr_2O_7^{2-})$ anions in excellent sensitivity, low limit of detection, and good anti-interference ability over most other perturbed ions.

Experimental section

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Materials and instruments

Chemicals were commercially obtained and used without further purification. Ligand NI-bpy-44 was prepared according to literature methods reported previously.³³ Room-temperature X-ray powder diffraction (XRPD) patterns were measured on a Shimadzu XRD-7000 diffractometer equipped with a graphite monochromatized Cu K α radiation ($\lambda = 1.5406$ Å) at 40 kV and 30 mA. Variable-temperature XRPD measurements were performed at the BL17A1 beamline of the synchrotron light source, Taiwan Light Source (TLS), with beam energy of 1.5 GeV situated at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The wavelength of the incident X-rays was 0.6889 Å, and the diffraction patterns were scanned with a Fuji Bas 2500 IP

scanner. Thermogravimetric (TG) analyses were performed under nitrogen with a Thermo Cahn View Article Online DOI: 10.1039/DODT02606A VersaTherm HS TG analyzer with a heating rate of 5 °C min⁻¹. Infrared (IR) spectra were recorded on a Perkin-Elmer Frontier Fourier transform infrared spectrometer using KBr discs or attenuated total reflection (ATR) technique; abbreviations used for the IR bands are s = strong, m = medium, w = weak, br = broad. Fluorescence spectra were recorded at ambient temperature on a Hitachi F7000 fluorescence spectrophotometer equipped with a 150 W xenon lamp as an excitation source. Elemental analyses (C, H, N) were measured on an Elementar Vario EL III analytical instrument.

Preparation of [Zn(5-NH₂-1,3-bdc)(H₂O)] (1)

The synthesis of **1** has been published in 2002.⁵² An alternative synthetic route is herein reported as follow. A DMF solution (2 mL) of Zn(NO₃)₂·6H₂O (14.9 mg, 0.050 mmol) was sealed in a Teflon-lined autoclave, followed by a DMF solution (2 mL) of 5-NH₂-1,3-H₂bdc (9.1 mg, 0.050 mmol) and then by neat DMF (1 mL) and H₂O (5 mL). The autoclave was heated to 80 °C, with a heating rate of about 8.3 °C h⁻¹, and held at that temperature for 36 h and then cooled to room temperature, with a cooling rate of about 1.0 °C h⁻¹. Plate-shaped orange crystals were collected in a yield of 88% based on Zn(NO₃)₂ (11.6 mg, 0.044 mmol). The bulk phase purity of **1** was confirmed by XRPD measurements, which shown well-matched diffraction patterns between the observed one and the simulated one calculated from the single-crystal structure data (Fig. 1). IR (KBr pellet, cm⁻¹): 3261m, 3000m, 1622m, 1577m, 1552s, 1482w, 1440w, 1410w, 1358s, 1320w, 1151s, 1114w, 1001w, 966w, 936w, 900w, 843w, 802w, 771m, 739m, 648w, 599w, 574w. Anal. Calcd for CsH7NO₅Zn: C, 36.60; H, 2.69; N, 5.34%. Found: C, 37.24; H, 2.94; N, 5.47%.

Preparation of anhydrous material $\{[Zn(5-NH_2-1,3-bdc)]\}_n$ (1')

An amount of crystalline samples of **1** was placed in a scintillation vial, which was then heated to 300 °C in an oven for 2 h to give the anhydrous material **1'**. IR (ATR, cm⁻¹): 3273w, 3101w, 1642m, 1550s, 1480w, 1410s, 1352w, 1330s, 1251m, 1158w, 1108s, 1002w, 962w, 930m, 892w, 846w,

807w, 774s, 730s, 681w, 659m, 580w, 561w. Anal. Calcd for C₈H₅NO₄Zn: C, 39.30; H, 2.06; N, View Article Online DOI: 10.1039/D0DT02606A

Preparation of rehydrated material {[Zn(5-NH₂-1,3-bdc)(H₂O)]}_n (1-R)

A sample of **1'** was immersed in water for 1 d, then the rehydrated material $\{[Zn(5-NH_2-1,3-bdc)(H_2O)]\}_n$ (**1-R**) was obtained. IR (ATR, cm⁻¹): 3379br, 3261w, 3000w, 1621m, 1574m, 1544s, 1481w, 1440m, 1410s, 1352s, 1322w, 1155s, 1117w, 1002w, 966w, 933w, 898w, 837m, 802m, 769m, 736s, 670w, 646w, 599w. Anal. Calcd for C₈H₇NO₅Zn: C, 36.60; H, 2.69; N, 5.34%. Found: C, 37.50; H, 2.90; N, 5.71%.

Preparation of $\{[Zn_2(5-NH_2-1,3-bdc)_2(NI-bpy-44)] \cdot DMF\}_n$ (2)

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A DMF solution (2 mL) of NI-bpy-44 (8.8 mg, 0.025 mmol), a DMF solution (1 mL) of $Zn(NO_3)_2$ ·6H₂O (14.9 mg, 0.050 mmol), and a DMF solution (2 mL) of 5-NH₂-1,3-H₂bdc (9.1 mg, 0.050 mmol) were separately prepared. The three DMF solutions were sealed in a Teflon-lined autoclave in sequence, followed by neat H₂O (1.25 mL). The autoclave was heated to 80 °C, with a heating rate of about 8.3 °C h⁻¹, and held at that temperature for 48 h and then cooled to room temperature, with a cooling rate of about 1.0 °C h⁻¹. Plate light-brown crystals were collected in a yield of 70% based on NI-bpy-44 (16.0 mg, 0.018 mmol). The bulk phase purity of **2** was confirmed by XRPD measurements, which shown well-matched diffraction patterns between the observed one and the simulated one calculated from the single-crystal structure data (Fig. S10). IR (KBr pellet, cm⁻¹): 3452br, 3260br, 3142br, 1715m, 1676m, 1624m, 1571s, 14841w, 1364s, 1238m, 1095m, 964w, 782m, 733m, 673m. Before elemental analysis, the sample was immersed in methanol for 72 h to remove nonvolatile solvates, and then drying under a dynamic vacuum at 50 °C for 24 h. Found: C, 50.61; H, 3.72; N, 7.55%. Anal. Calcd Required for C₄₁H₃₀N₆O₁₁Zn₂·3.5H₂O: C, 50.43; H, 3.82; N, 8.61%.

Single-crystal X-ray structure determinations

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The molecular structure of **1'** was solved by the DASH⁵⁰ program for the structure model searching through variable-temperature XRPD data using Taiwan Light souce wiggler Powder X-ray beamline BL17A1. The structural data were refined using the Jana2006 program.⁵⁴ Quality single crystals of 2 suitable for X-ray diffraction were selected for indexing. Intensity data were collected at 150(2) K by using a Bruker D8 Venture diffractometer equipped with graphite monochromatized Mo K α radiation ($\lambda = 0.71073$ Å). Starting models for structure refinement were found using direct methods with SIR92 program,⁵⁵ and the structural data were refined by full-matrix least-squares methods against F^2 using the SHELXL-2014/7,⁵⁶ incorporated in WINGX-v2014.1 crystallographic collective package.⁵⁷ On the basis of different Fourier maps, non-hydrogen atoms were positioned. and then refined anisotripically for most of them. The NI-bpy-44 ligand was disordered over a crystallographic inversion center, so the naphthalimide moiety was found to be occupied in two statistic positions, which together with the lattice DMF molecules were refinement isotropically. Hydrogen atoms bound on carbon atoms were placed in geometrically ideal positions and refined as riding mode, while that bound on nitrogen atoms were structurally evident in the difference Fourier map, and then fixed at calculated positions and included in the final refinement. All of the hydrogen atoms were refined isotropically. Experimental details for X-ray data collection and the refinements are summarized in Table 1. CCDC 1991622–1991623 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.

Fluorescence sensing experiments

The fluorescence sensing experiments were evaluated in H₂O suspensions. A crystalline sample (3 mg) was ground and added into 3 mL water, which was then ultrasonicated with pulsed ultrasound for 10 min and agitated for further 30 min to result in a stable H₂O suspension. Aqueous solutions of the nitrate salt of each of the metal cations Na⁺, K⁺, Mg²⁺, Ca²⁺, Al³⁺, Pb²⁺, Cr³⁺, Mn²⁺, Fe³⁺, Co^{2+} , Ni^{2+} , Cu^{2+} , Ag^+ , and Cd^{2+} and the potassium or sodium salt of each of the anions F⁻, Cl^- , Br⁻, View Article Online Γ^- , NO_3^- , ClO_4^- , CO_3^{2-} , MnO_4^- , SO_4^{2-} , CrO_4^{2-} , $Cr_2O_7^{2-}$, and PO_4^{3-} were prepared at a concentration of 0.10 M for qualitative and anti-interference studies and 0.010 M for quantitative titration studies (0.0010 M for MnO_4^- sensing of **2**). The luminescence titration experiments were carried out by adding aqueous solution of metal cations and anions step by step, and the luminescence emission spectra were monitored.

	I' (from XRPD data)	2
empirical formula	$C_8H_5NO_4Zn$	$C_{41}H_{30}N_6O_{11}Zn$
$M_{ m w}$	244.5	913.45
crystal system	monoclinic	monoclinic
space group	$P2_{1}/n$	P2/c
<i>a</i> (Å)	7.39374(17)	19.898(5)
<i>b</i> (Å)	8.1713(2)	7.618(5)
<i>c</i> (Å)	13.3835(3)	16.128(5)
$\beta(^{\circ})$	96.8777(17)	101.547(5)
$V(Å^3)$	802.76(4)	2395.3(18)
Ζ	4	2
<i>T</i> (K)	540	150(2)
λ (Å)	0.6889	0.71073
D_{calc} (g cm ⁻³)	2.0231	1.267
F_{000}	488	932
$\mu (\mathrm{mm}^{-1})$	2.87	1.059
$\theta_{min}, \theta_{max}$ (°)	1.000, 20.945	2.968, 26.394
$R_1^a (I > 2\sigma(I))$	0.0267	0.0911
$wR_2^b (I > 2\sigma(I))$	0.0305	0.2483
R_1^a (all data)	0.0267	0.1095
wR_2^b (all data)	0.0305	0.2654
GOF on F^2	1.10	1.113
${}^{a}R_{1} = \sum F_{o} - F_{c} /$	$\sum F_o _{.b} WR_2 = \{\sum [W(F_o)]$	$\left[2 - F_c^2\right]^2 \left[w(F_o^2)^2 \right]^{1/2}$

Table 1. Crystallographic data for 1' (from XRPD data) and 2

Results and discussion

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Structure and phase transformation of [Zn(5-NH₂-1,3-bdc)(H₂O)] (1)

The molecular structure of **1** has already been published in 2002,⁵² which displays a two-dimensional (2D) lamellar net suiting the binodal (6,3) honeycomb (**hcb**) topology by

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considering the Zn centers and the 5-NH₂-1,3-bdc^{2–} ligands both as 3-connected nodes (Fig. S1). Of View Article Online DOI: 10.1039/DODT02606A particular note, all of the aqua ligands are oriented toward the same side of the lamellar net whereas all of the amino groups are oriented to the opposite side. Two such lamellae, where the aqua ligands are oriented face-to-face, are linked together in pair through hydrogen bonding interactions between the coordinated aqua ligands and the uncoordinated carboxylate oxygen atoms of the 5-NH₂-1,3-bdc^{2–} ligands (O···O, 2.629(4) and 2.648(3) Å) to form a 2D hydrogen-bonded bilayer structure (Fig. S2). Such a packing manner in **1** might result in an anhydrous sample upon thermal dehydration.

The thermogravimetric (TG) curve of 1 suggested the removal of coordinated aqua ligands between 187–327 °C and confirmed the high thermal stability up to about 485 °C (Fig. S3). When the aqua-coordinated (hydrated) 1 was heating to 300 °C for 2 h, an anhydrous compound $[Zn(5-NH_2-1,3-bdc)]$ (1') was actually obtained, confirmed by elementary analysis. An obvious change in the XRPD patterns is that the peak (202) at $2\theta = 27.68^{\circ}$ in **1** is largely shifted to $2\theta =$ 29.70° in 1' (Fig. 1); this clearly results in conversion to a new solid-state phase. Variable-temperature XRPD studies indicate that phase transformation of 1 taken place at about 250 °C and this structure remained intact till to 280 °C (Fig. S4). Noteworthy, after immersing anhydrous phase 1' in H_2O for 24 h, the so-obtained solid samples, termed as 1-R, show XRPD patterns very similar to that of as-synthesized 1 (Fig. 1), implying regeneration of hydrated phase 1. In other words, such crystal-to-crystal phase transformations are reversible. Other than XRPD patterns, TG analysis and IR spectra provide further supports for the reversible crystal-to-crystal transformations between hydrated phase 1 and anhydrous phase 1'. As observation, TG curve of anhydrous 1' shows no weight lose before framework collapse upon heating to about 460 °C while the TG trace of 1-R is almost consistent with that of as-synthesized 1 (Fig. S3). In terms of IR spectra, the band at 1622 cm⁻¹ for **1** is blue-shifted to 1642 cm⁻¹ for **1'** after dehydration whereas the bands at 1577 and 1440 cm⁻¹ are disappeared and a new band is appeared at 1251 cm⁻¹ for 1' (Fig. S5). In addition, the bands at 1358 and 1151 cm⁻¹ are largely weakened while those at 1320

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and 1114 cm⁻¹ are strengthened, all of which are associated with slight shift in band position. These View Article Online Changes, however, would be returned back after rehydration of **1'**. Therefore rehydrated **1'** (i.e. **1-R**) has the IR spectrum very similar to that of as-synthesized **1**. As a consequence, the IR spectra prove that phase transformation is reversible between hydrated phase **1** and anhydrous phase **1'**.



Fig. 1 XRPD patterns of simulated, as-synthesized, and dehydrated 1 (1'), and rehydrated 1' (1-R) as well as simulated 1'.

Molecular structure of [Zn(5-NH₂-1,3-bdc)] (1')

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After thermal dehydration of **1**, it is noted that the crystal morphology remained but, unfortunately, the crystal transparency became poor, thus the single-crystal X-ray diffraction analysis for the dehydrated crystal of **1'** could not be conducted. Fortunately, the molecular structure of **1'** was well determined by the DASH⁵³ and the Jana2006⁵⁴ programs based on the proper high-quality XRPD patterns obtained at high temperature (540 K). As a representative, the solid-state structure of **1'** belongs to monoclinic space group $P2_1/n$, and the asymmetric unit consists of one Zn(II) center and one 5-NH₂-1,3-bdc²⁻ dianion. The 5-NH₂-1,3-bdc²⁻ dianion bridges four Zn(II) centers through its one monodentely-carboxylate, one bidentely-carboxylate and one amino groups (Fig. 2a). In turn, the Zn(II) center adopts a 4-coordinate tetrahedral geometry defined by three carboxylate oxygen atoms from three 5-NH₂-1,3-bdc²⁻ ligands and one amino nitrogen atom from forth 5-NH₂-1,3-bdc²⁻ ligand (Fig. 2b). Connection of Zn(II) centers and 5-NH₂-1,3-bdc²⁻ dianions forms an expanded 2D

bilayered-lamella net (Fig. 2c). When the 5-NH₂-1,3-bdc^{2–} ligand and the Zn center both are View Article Onlineconsidered as 4-connected nodes (Fig. 2a), the bilayered-lamella net can be topologically simplified as a (4,4)-connected net with the point symbol of (4²6⁴)(4²6⁴) (Fig. 2d). These bilayered-lamella nets are stacked in parallel fashion along the crystallographic *a*-axis, and hydrogen-bonding interactions between the amino groups and the oxygen atoms of carboxylate groups of two neighboring nets (N···O, 2.991 and 3.221 Å) are formed (Fig. 2e).



Fig. 2 Views of (a) the coordination mode of $5-NH_2-1,3-bdc^{2-}$ ligand and (b) the coordination sphere of the Zn(II) center in 1', both of which are regarded as 4-connected nodes. (c) Side- and top-vies of the 2D bilayered-lamella net in 1'. (d) Topological view of the 2D bilayered-lamella net in 1', where pink and dark-gray balls represent Zn(II) centers and $5-NH_2-1,3-bdc^{2-}$ dianions, respectively. (e) Packing diagram of the bilayered-lamella nets in 1', showing inter-lamella N–H…O hydrogen-bonding interactions (dashed lines). Carbon-bound hydrogen atoms are omitted for clarity.

When comparing the molecular structures of **1** and **1'**, it is clear that they show a close relationship that both of them belong to the same crystal system (monoclinic) and space group $(P2_1/n)$. From a structural point of view, there are two kinds of uncoordination carboxylate oxygen

atoms which are hydrogen-bonded with the aqua ligands in 1 (Fig. S2c), one of which would DOI: 10.1039/D0DT02606A minorly shift toward the Zn(II) centers in neighboring lamellar net to form new Zn-Ocarboxylate covalent bonds after thermal removal of aqua liagnds (Fig. 3 and Fig. S6). This means that the carboxylate oxygen atom is the key atom not only in the structural stransformation from the 2D lamella to the 2D bilayered-lamella, but also in the topochemical conversion of a hydrogen-bonded network into a covalently bonded framework and vice versa.^{7,58–60} In other words, such reversible structural transformations between the lamella in aqua-coordinated 1 and the bilayered-lamella in anhydrous 1' upon dehydration/rehydration involve coordination bond "cleavage-repair" phenomenon. Such a change makes the adjustments of cell parameters from a = 9.044(1) Å, b =8.264(1) Å, c = 11.646(1) Å, and $\beta = 100.77(1)^{\circ}$ for $\mathbf{1}^{52}$ to a = 7.39374(17) Å, b = 8.1713(2) Å, $c = 100.77(1)^{\circ}$ 13.3835(3) Å, and $\beta = 96.8777(17)^{\circ}$ for 1', and thus the reduction of cell volume by 6.1% (855.0(2)) Å³ for 1 and 802.76(4) Å³ for 1'). Noteworthy, the changes in the lengths of a- and c-axis are relative large, with differences of about -1.65 Å and +1.73 Å, respectively, while the change in the length of *b*-axis is relative small, with a difference of only about -0.09 Å. Further, the difference in β angle is about -3.89°. Such changes indicate that after aqua removal the lamellar nets in 1 is shifted mainly along both a and c vectors rather than b vector to be coverted to the bilayered-lamella in 1' without change the space group.



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Fig. 3 Reversible structural transformations between the lamella in aqua-coordinated **1** and the bilayered-lamella in anhydrous **1'** through coordination bond "cleavage–repair" phenomenon dehydration/rehydration. The arrows indicate how the two face-to-face oriented lamellar nets slide after dehydration to form the single bilayered-lamellar net through the newly formed Zn–O_{carboxylate} covalent bonds and vice versa.

Crystal structure and thermal properties of [Zn₂(5-NH₂-1,3-bdc)₂(NI-bpy-44)]·DMF (2)

The packing feature of **1** and the formation of **1'** make it possible that a covalently bonded pillared-bilayer structure may be engineering tailored if a bridging bispyridyl ligand is introduced to replace the coordinated aqua ligands. This assumption is well supported by the formation of $[Zn_2(5-NH_2-1,3-bdc)_2(NI-bpy-44)]$ ·DMF (**2**), which as orange crystals was obtained from the hydro(solvo)thermal reactions of $Zn(NO_3)_2$ ·6H₂O and 5-NH₂-1,3-H₂bdc together with a well-defined bispyridyl pillar ligand, *N*-(pyridin-4-yl)-4-(pyridin-4-yl)-1,8-naphthalimide (NI-bpy-44),³³ in DMF/H₂O media.

Complex **2** crystallizes in monoclinic space group $P2_1/c$, and its asymmetric unit contains one Zn(II) center, one 5-NH₂-1,3-bdc²⁻ dianion, one-half of a NI-bpy-44 ligand disordered over a crystallographic inversion center, and one-half of a lattice DMF molecule. The Zn(II) center adopts a 4-coordinate tetrahedral geometry defined by two carboxylate oxygen atoms from two 5-NH₂-1,3-bdc²⁻ ligands, one amino nitrogen atom from third 5-NH₂-1,3-bdc²⁻ ligand, and one 4-pyridyl nitrogen atom from one NI-bpy-44 ligand (either imide end or naphthalene end, Fig. 4a). In turn, the 5-NH₂-1,3-bdc²⁻ dianion bridges three Zn(II) centers through its two monodentely-carboxylate and one amino groups (Fig. S7a). Connection of Zn(II) centers and 5-NH₂-1,3-bdc²⁻ dianions expands to be a 2D zinc–dicarboxylate layer laid on the crystallographic *bc* plane, which can be simplified into a honeycomb (**hcb**) 6³-topology by considering the Zn(II) centers and the 5-NH₂-1,3-bdc²⁻ ligands both as 3-connected nodes (Fig. S7). A pair of zinc–dicarboxylate honeycomb layers is connected by NI-bpy-44 ligands to afford an overall pillared-bilayer net with 1D rhombic-shaped channels running along the crystallographic *b*-axis (Fig. 4b). These channels have open pore sizes of 8.98×17.53 Å², defined by Zn…Zn separation in

edge, within which lattice DMF molecules occupied. PLATON calculation⁶¹ suggests solvent DOI: 10 accessible void spaces of approximately 34.4% of the unit cell volume (824.4 Å³ to 2395.3 Å³). Topologically, the pillared-bilayer net, if each 5-NH₂-1,3-bdc²⁻ ligand is treated as a 3-connected node and each Zn center is treated as a 4-connected node, can be regarded as a (3,4)-connected net with the point symbol of $(6^3)(6^58)$ (Fig. 4c). These pillared-bilayer nets are stacked in the same manner (AAA sequence) very well along the crystallographic a-axis with strong hydrogen-bonding interactions between the amino groups and the oxygen atoms of carboxylate groups of two neighboring layers (N···O, 2.947(7) and 3.007(7) Å, Fig. 4d and Fig. S8). The structure topology of **2** is similar to that of $\{[Zn_2(5-NH_2-1,3-bdc)_2(bpy)]\cdot 6H_2O)\}_n$ (bpy = 4,4'-bipyridine),⁶² =1,2-di-4-pyridylethylene),⁶² $\{[Zn_2(5-NH_2-1,3-bdc)_2(dpe)]\cdot 5H_2O)\}_n$ (dpe 1,2-di-4-pyridylethane),62 $\{[Zn_2(5-NH_2-1,3-bdc)_2(dpa)]\cdot 5H_2O)\}_n$ (dpa 1,3-di-4-pyridylpropane),⁶² $\{[Zn_2(5-NH_2-1,3-bdc)_2(dpp)]\cdot 6H_2O)\}_n$ (dpp tetrakis(4-pyridyl)cyclobutane),⁶³ ${[Zn_2(5-NH_2-1,3-bdc)_2(tpcb) \cdot H_2O]}_n$ (tpcb = 4,4'-azobipyridine),⁶⁴ $\{[Zn_2(5-NH_2-1,3-bdc)_2(azpy)] \cdot 2DMF\}n$ (azpy = $\{[Zn_2(5-NH_2-1,3-bdc)_2(dipytz)] \cdot 1.15DMF \cdot 0.85MeOH\}_n$ (dipytz =di-3,6-(4-pyridyl)-1,2,4,5-tetrazine),⁶⁴ and $\{[Zn_2(5-NH_2-1,3-bdc)_2(tpim)] \cdot 2.5DMF \cdot 2H_2O\}_n$ (tpim = 2,4,5-tri(4-pyridyl)imidazole).⁶⁴

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TG curve of **2** reveals a gradual weight loss of 7.4% from room temperature to about 155 °C (Fig. S3), which is in good agreement with the escape of lattice DMF molecules (calcd. 7.8%). The framework is then thermally stable upon heating to about 380 °C and, subsequently, starts to collapse rapidly up till 490 °C due to the decomposition of organic ligands. The remaining residue of 19.7% corresponds to ZnO component (calcd. 17.8%).



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Fig. 4 (a) View of the coordination sphere of the Zn(II) center in **2**. Symmetry codes: A, 1 - x, 1 - y, 1 - z; B, x, -y - 1/2, z + 1/2; C, x, -y + 1/2, z + 1/2. (b) Perspective and (c) topologic views of the 2D pillared-bilayer net in **2**. Pink and dark-gray balls represent Zn(II) centers and 5-NH₂-1,3-bdc²⁻ dianions, respectively. (d) Packing diagram of the pillared-bilayer nets in **2**, showing 1D channels along the crystallographic *b*-axis where accommodated lattice DMF molecules (space-filling model). Dashed lines represent N–H…O hydrogen-bonding interactions. Carbon-bound hydrogen atoms are omitted for clarity.

Gas adsorption properties of activated 2

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Gas adsorption properties of activated 2 were carried out to study its porous property. Prior to gas adsorption experiments, 2 was activated by heating at 100 °C under a reduced pressure. N₂ adsorption analysis on the activated 2 performed at 77 K exhibits no appreciable adsorption (Fig. 5a). Comparison, the sorption of CO_2 on the activated 2 follows only a type I isotherm, but unsaturated yet, with a maximum sorption capacity of 79.1, 38.8, and 21.0 cm³ g⁻¹ STP at $P/P_0 = 1$ and 195, 273, and 298 K, respectively (Fig. 5a). Such results might be attributed to that CO₂ has a small kinetic diameter of 3.3 Å while N₂ has a large kinetic diameter of 3.64 Å,⁶⁵ which enable the access of CO₂ but not N₂ into the 1D rhombic-shaped channels of the activated 2 in the narrow-pore phase.^{66,67} As activated 2 did not adsorb N₂ at 77 K, its surface area was calculated by CO₂ adsorption at 195 K using the Brunauer-Emmett-Teller (BET) model to give a surface area of 225 $m^2 g^{-1}$. The two-temperature isosteric heat of CO₂ adsorption (Q_{st}) of activated 2 calculated from the adsorption at 273 and 298 K is 37.0 kJ mol⁻¹ at zero-loading (Fig. 5b), which is comparable to some well-known MOFs such as MOF-5,68 HKUST-1,69 MIL-53(Al),70 and bio-MOF-1.71 Of particular interest, as increasing CO_2 uptakes, the Q_{st} values reveal an uncommon increasing trace, which reach 58.6 kJ mol⁻¹ at adsorbed amount of 1.67 mmol g⁻¹. The high Q_{st} indicates strong adsorbent-adsorbate interactions between the framework and CO₂ guests that might take place on amine functions. Further, the unusual sharp rise in the Q_{st} curve is tentatively attributed to the framework–CO₂:CO₂ cooperation effect.⁷²



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Fig. 5 (a) N_2 (77 K) and CO₂ (195, 273, 298 K) adsorption isotherms of activated **2**. (b) The isosteric heat of CO₂ adsorption (Q_{st}) of activated **2**.

Stability and luminescence properties

XRPD patterns of **1** after immersing in H₂O, methanol (MeOH), dichloromethane (DCM), N,N'-dimethylformamide (DMF), N,N'-dimethylacetamide (DMAc), and toluene for 24 h clearly show that the checked XRPD profiles are closely matching to that of as-synthesized crystalline samples (Fig. 6a), implying the maintenance of the framework integrity and crystallinity and thus confirming the high stability of **1**. In addition, the IR spectra and TG traces of the recovered solid samples are very similar to that of as-synthesized **1** (Fig. S11), indicating that solvent exchange did not take place during the immersion. This makes sense owing to coordination of aqua ligands in **1**.

On the other hand, when 2 was soaked in different solvents mentioned above, the checked XRPD profiles are similar to that of as-synthesized crystalline samples (Fig. 6b), with slight difference in peak intensity, especially in H₂O, MeOH, and DCM. Such observations are tentatively attributed to either the orientation effect or the solvent-induced distortion of the 2D porous

pillared-bilayer net, and thus indicate that **2** is stable in DMF, DMAc, and toluene but less stable in View Article Online DOI: 10.1039/D0DT02606A H₂O, MeOH, and DCM. In terms of IR spectra and TG analyses, the recovered samples showed that their IR profiles are almost identical to that of as-synthesized **2** (Fig. S12a and Fig. 12b) but their TG curves are somewhat different from that of as-synthesized **2** (Fig. S12c). Taken both into consideration, partial solvent exchange or further solvent inclusion in the crystal lattices might take place during the immersion. In some cases, for example H₂O, MeOH, and DCM, such alternations might cause framework distortion of the 2D pillared-bilayer nets in **2**.



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Fig. 6 XRPD patterns of (a) 1 and (b) 2: simulated, as-synthesized, and treated with H_2O , MeOH, DCM, DMF, DMAc, and toluene for 24 h.

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The solid-state emission spectra of 1, 2, 5-NH₂-1,3-H₂bdc, and NI-bpy-44 were measured at DOI: 10.1039/D0DT02606A room temperature (Fig. S13). Upon excitation, 5-NH₂-1,3-H₂bdc exhibits an emission band with a maximum lying at 430 nm (λ_{ex} = 330 nm) while NI-bpy-44 shows an emission band centered at 434 nm ($\lambda_{ex} = 290$ nm). By exciting at 330 nm, lamella **1** displays a blue-light emission band centered at 434 nm, which mainly originates from ligand-centered charge transfer of the 5-NH₂-1,3-bdc²⁻ ligand modified by metal coordination due to the great resemblances in position and band shape between both. Pillared-bilayer 2 exhibits an emission bands centered at 432 nm upon excitation at 290 nm, which can tentatively be ascribed to the intraligand (IL) transitions of 5-NH₂-1,3-bdc²⁻ and/or NI-bpy-44 ligands admixed with the ligand-to-metal charge-transfer (LMCT) from the carboxylate groups to the Zn(II) centers.³² The emission spectra of uniform suspensions of 1 and 2 in H₂O, MeOH, DCM, DMF, DMAc, and toluene were also recorded (Fig. 7), upon excitation at 315 and 320 nm, respectively. It was found that their luminescent properties are varied as change of different solvents. The fluorescence intensity follows the trend H_2O (406 nm) > DMAc (406 nm) > DMF (386 nm) > MeOH (414 nm) > toluene (348 nm) > DCM (416 nm) for 1 and H_2O (406 nm) > MeOH (410 nm) > DCM (366 nm) > toluene (356 nm) > DMF (404 nm) ~ DMAc (406 nm) for 2. This is attributed to different collision interactions between the solvent molecules and the surface of the homogeneously dispersible fine particles of 1 and $2^{.73,74}$ Further, the emission maxima of these suspensions are varied from 348 to 416 nm for 1 and from 356 to 406 nm for 2.

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Fig. 7 Emission spectra of (a) **1** and (b) **2** dispersed in different solvents when excited at 315 and 320 nm, respectively.

Fluorescent sensing of metal cations and anions

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The good fluorescence performance of **1** and **2** prompt us to explore their fluorescent sensing properties toward metal cations in water (Fig. 8). Among the selected metal cations for sensing studies, alkali (Na⁺, K⁺) and alkali-earth cations (Mg²⁺, Ca²⁺) as well as Cd²⁺ show negligible fluorescence change (< 5% intensity change); Al³⁺, Mn²⁺, Co²⁺, and Ni²⁺ display weak degrees of fluorescence quenching efficiency of ca. 10–20% (quenching efficiency (%) = $(I_0 - I)/I_0 \times 100\%$, where I_0 and I are the maximum fluorescence intensity of **1** and **2** dispersed in water before and after addition of metal ions); Cu²⁺ and Ag⁺ cause moderate degrees of fluorescence quenching efficiency of 75.9% for **1** and 74.6% for **2**; Pb²⁺ (quenching efficiency = 88.4% for **1** and 83.8% for **2**) and Fe³⁺ (quenching efficiency = 99.0% for **1** and 95.6% for **2**) are the two most highest efficient quenchers. Noteworthy,

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trivalent cations (Fe^{3+} , Al^{3+} , Cr^{3+}) not only quench the fluorescence of 1 and 2 in water suspensions but also cause red-shift of 30 ± 4 and 20 ± 2 nm for 1 and 2, respectively, in emission maximum. These sensing behaviors are further examined by naked eyes. Under the irradiation of UV light of 365 nm, the bright blue light of the water suspensions of 1 and 2 turns to dark after the addition of Fe^{3+} and becomes pale with color change and slight dark after the addition of Al^{3+} and Cr^{3+} . respectively (Fig. S14). Meanwhile, both the water suspensions of 1 and 2 appear an obvious color Published on 21 September 2020. Downloaded by LA TROBE UNIVERSITY on 9/21/2020 4:18:06 PM. change from colorless to light-yellow under sunlight after Fe³⁺ incorporation (Fig. S14). As a result, direct visual observation in fluorescence sensing suggests quite straightforward sensing performance in detecting Fe^{3+} over Al^{3+} and Cr^{3+} , making 1 and 2 to be promising sensing materials for detection of Fe³⁺ ions. In this study, the unique fluorescence responses to trivalent Fe³⁺, Al³⁺, and Cr³⁺ ions have been

studied in details. In the above-mentioned fluorescence sensing experiments, Fe³⁺, Pb²⁺, and Cr³⁺ have exhibited significant quenching effects, making poor selectivity for fluorescence sensors 1 and 2. However, the anti-interference abilities in sensing Fe^{3+} , Al^{3+} , and Cr^{3+} were still explored on a series of competition experiments with the coexistence of equal-amount of perturbed metal cations (1 mM) in the water suspensions of 1 and 2 (Fig. 9). Experimental results clearly indicated that all of the selected perturbed metal cations did not influence the quenching ability in sensing Fe^{3+} by both 1 and 2, suggesting the excellent anti-interference ability towards Fe^{3+} . In cases of Al^{3+} and Cr³⁺, red-shift in emission maximum still taken place after adding both metal cations. In term of emission intensity, it is clear that Fe³⁺ and Pb²⁺ caused strong interference in sensing both metal cations. Further, Al³⁺ and Cr³⁺ would slightly interfere the sensing for each other. Other selected perturbed metal cations did not show significant competition. These observations imply good competitive sensing ability towards Al^{3+} and Cr^{3+} over most other perturbed metal cations.

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Fig. 8 Emission spectra of (a) **1** and (b) **2** dispersed in water upon addition of different cations of 1.0 mM when excited at 315 and 320 nm, respectively. (c) Bar diagram to show fluorescence quenching efficiency of **1** and **2** dispersed in water for different cations at 1.0 mM.



Fig. 9 Bar diagrams to show fluorescence quenching efficiency of (a) **1** and (b) **2** dispersed in water for Fe^{3+} ions with different perturbed anions in equal concentration (1.0 mM).

To explore the ability of sensing a trace quantity of Fe^{3+} , Al^{3+} , and Cr^{3+} ions in water, titration experiments were performed with varying concentrations (Fig. 10). In cases of detection of Fe^{3+} by 1 and 2 and Cr^{3+} by 2, the fluorescence of 1 and 2 continuously decreased in emission intensity along with gradually red-shift in emission position as the increase of concentration of Fe^{3+} and Cr^{3+} ions. In cases of detection of Al^{3+} and Cr^{3+} by 1, upon the addition of Al^{3+} ions from 0 to 0.06 mM and Cr^{3+} ions from 0 to 0.40 mM, the fluorescence intensity was continuously reduced and the fluorescence position was gradually red-shifted. Notably, when the concentrations of Al^{3+} and Cr^{3+} ions both were further increased to 1.00 mM, a clear fluorescence enhancement associated with

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slight red-shift was observed. The changes in detection of Al³⁺ and Cr³⁺ by **1** with analyte View Article Online Concentrations exhibited interesting turn-off-on fluorescence sensing performance.⁵ In case of detection of Al³⁺ by **2**, as incremental addition of Al³⁺ concentrations up to 0.16 mM, the fluorescence of **2** gradually decreased in intensity and was slightly red-shifted by 12 nm in position. When the Al³⁺ concentrations varied from 0.16 to 1.00 mM, the fluorescence position and intensity both were unstable.

For fluorescence quenching sensors, the fluorescence titration results and the quenching effects could be quantitatively interpreted using the Stern–Volmer (S–V) equation: $I_0/I = K_{sv} \times [Q] + 1$, where I_0 and I are the fluorescence intensities of **1** or **2** dispersed in water without and with analytes (quenchers), respectively, K_{sv} is the quenching constant of analyte, and [Q] is the molar concentration of analyte (quencher). The full S–V plots in the stage of fluorescence quenching for sensing Fe³⁺, Al³⁺, and Cr³⁺ by **1** and **2** in water are shown in Fig. S15. From the linear S–V plot of I_0/I against analyte concentration (Fig. 10, insets), the quenching constants, K_{sv} , were obtained that showed values of 9.80×10^4 M⁻¹ ($R^2 = 0.99077$ in 0–0.30 mM) and 1.71×10^4 M⁻¹ ($R^2 = 0.99629$ in 0–0.10 mM) for sensing Fe³⁺ by **1** and **2**, respectively, 2.47×10^4 M⁻¹ ($R^2 = 0.99889$ in 0–0.05 mM) and 3.92×10^3 M⁻¹ ($R^2 = 0.99952$ in 0–0.16 mM) for sensing Al³⁺ by **1** and **2**, respectively, and 5.99×10^3 M⁻¹ ($R^2 = 0.99963$ in 0–0.12 mM) and 3.05×10^3 M⁻¹ ($R^2 = 0.99967$ in 0–0.70 mM) for sensing Cr³⁺ by **1** and **2**, respectively.



Fig. 10 Fluorescence emission spectra of (a–c) **1** and (d–f) **2** dispersed in water (3 mg/3 mL) with incremental addition of Fe³⁺, Al³⁺, and Cr³⁺ concentrations. Inset: Linear Stern–Volmer plot of I_0/I against analyte concentration.

To estimate the detection sensitivity, the limit of detection (LOD) of **1** and **2** toward Fe³⁺, Al³⁺, and Cr³⁺ was calculated using the equation: LOD = $3\sigma/k$, where σ is the standard deviation from blank measurements and *k* is the absolute value of the slope of the linear calibration plot. ^{50,76,77} The LOD values were determined to be 0.317 μ M (corresponding to 18 ppb) and 0.709 μ M (corresponding to 40 ppb) for detection of Fe³⁺ by **1** for **2**, respectively, 2.44 μ M (corresponding to 66 ppb) and 5.59 μ M (corresponding to 151 ppb) for detection of Al³⁺ by **1** for **2**, respectively, and 13.9 μ M (corresponding to 724 ppb) and 7.87 μ M (corresponding to 410 ppb) for detection of Cr³⁺ by **1** for **2**, respectively (Fig. S16). As a result, detection of Fe³⁺ by **1** and **2** in water is obviously more sensitive compared to detection of Al³⁺ and Cr³⁺. These data are at a relatively high level when compared to those of the work reported for other MOF/CP-based sensors (Table S1).^{64,68–74,76–91} In short summary, the large *K*_{sv} values and the small LOD values as well as the detection stability and direct visual observation make **1** and **2** being excellent fluorescence-based chemical sensors for the selective detection of Fe³⁺ in the water system.

On the other hand, the fluorescence sensing tests for 1 and 2 dispersed in water towards anions

were further carried out (Fig. 11). As a representative, the luminescence of **1** and **2** are almost View Article Orime completely quenched by MnO₄⁻ (quenching efficiency = 99.1% for **1** and 99.7% for **2**) and Cr₂O₇²⁻ (quenching efficiency = 99.1% for **1** and 98.5% for **2**), and significantly partially quenched by CrO₄²⁻ (quenching efficiency = 92.9% for **1** and 86.9% for **2**). Comparably, other anions (F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, ClO₄⁻, CO₃²⁻, SO₄²⁻, and PO₄³⁻) show negligible or small change in intensity of **1** and **2**, either quenching or enhancement (< 13% intensity change). After MnO₄⁻ and Cr₂O₇²⁻ incorporation, the water suspensions of **1** and **2** both appear an obvious color change from colorless to red and yellow, respectively, under sunlight, whereas their bright blue lights turn off under the irradiation of UV light of 365 nm (Fig. S14). As CrO₄²⁻ also significantly quenched the fluorescence intensity of **1** and **2** dispersed in water in the fluorescence sensing experiments, it is concluded that the selectivity of fluorescence sensor **1** and **2** is not very good. However, in the coexistence of equal amount of other perturbed anions, the quenching efficiencies caused by MnO₄⁻ and Cr₂O₇²⁻ were not affected significantly, even in the presence of CrO₄²⁻ (Fig. 12), confirming the high anti-interference sensing ability towards MnO₄⁻ and Cr₂O₇²⁻, especially the former.



Fig. 11 Emission spectra of (a) **1** and (b) **2** dispersed in water upon addition of different anions of 1.0 mM when excited at 315 and 320 nm, respectively. (c) Bar diagram to show fluorescence quenching efficiency of **1** and **2** dispersed in water for different anions at 1.0 mM.



Fig. 12 Bar diagrams to show fluorescence quenching efficiency of (a) 1 and (b) 2 dispersed in water for MnO_4^- and $Cr_2O_7^{2-}$ ions with different perturbed anions in equal concentration (1.0 mM).

Titration experiments were investigated in water suspensions of **1** and **2** with gradually increased concentrations of MnO₄⁻ and Cr₂O₇²⁻ at room temperature (Fig. 13), which give linear S–V plots in the concentration range 0–0.10 mM for MnO₄⁻ and 0–0.26 mM for Cr₂O₇²⁻ for **1** and 0–0.30 mM for MnO₄⁻ and 0–0.30 mM for Cr₂O₇²⁻ for **2** (Fig. S17). From the linear S–V plots, the K_{sv} values of **1** for MnO₄⁻ and Cr₂O₇²⁻ were calculated to be 3.55 × 10⁴ M⁻¹ ($R^2 = 0.99353$) and 8.47 × 10³ M⁻¹ ($R^2 = 0.99891$), respectively, whereas that of **2** for MnO₄⁻ and Cr₂O₇²⁻ were calculated to be 3.05 × 10⁴ M⁻¹ ($R^2 = 0.99894$) and 9.01 × 10³ M⁻¹ ($R^2 = 0.99836$), respectively. Moreover, the LOD values of **1** for MnO₄⁻ and Cr₂O₇²⁻ were calculated to be 1.28 and 1.74 µM (corresponding to 152 and 376 ppb), respectively, whereas that of **2** for MnO₄⁻ and Cr₂O₇²⁻ were calculated to be 1.05 and 2.93 µM (corresponding to 125 and 633 ppb), respectively (Fig. S18). The large K_{sv} values and the small LOD values as well as the detection stability and direct visual observation make **1** and **2** being good fluorescence sensors for sensitive detection of MnO₄⁻ and Cr₂O₇²⁻ in the water system, which are well compared to those of the work reported for other MOF/CP-based sensors (Table S1).^{40,41,81–85,89,91–102}

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Finally, with the aim of practical application, we have tried to examine the real-time detection $V_{\text{iew Article Online}}$ performance like paper-strip based monitoring under UV-light toward Fe³⁺, Al³⁺, Cr³⁺, MnO₄⁻, and Cr₂O₇²⁻. Unfortunately, this is unsuccessful because **1** and **2** both emit solid-state fluorescence that is not intense enough to be applied in luminescent test paper.



Fig. 13 Fluorescence emission spectra of (a,b) **1** and (c,d) **2** dispersed in water (3 mg/3 mL) with incremental addition of MnO_4^- and $Cr_2O_7^{2-}$ concentrations. Inset: Linear Stern–Volmer plot of I_0/I against concentration of MnO_4^- and $Cr_2O_7^{2-}$.

Proposed detection mechanisms

According to the literature reports, collapse of main framework, ion exchange with the targeted ions, the framework–ion interactions, and the excited-state processes including the resonance energy transfer and/or the competition absorption caused by the ions are the most possible mechanisms for ion analytes to quench fluorescence of MOFs.^{82–86} Herein, the recovered solid samples of **1** after treated with Fe³⁺, Al³⁺, Cr³⁺, MnO₄⁻, and Cr₂O₇²⁻ showed XRPD patterns that are almost identical with that of the as-synthesized (Fig. S19a), indicating that the fluorescence quenching or change of **1** caused by Fe³⁺, Al³⁺, Cr³⁺, MnO₄⁻, and Cr₂O₇²⁻ does not originated from the destruction of main

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In cases of sensing trivalent Fe³⁺, Al³⁺, Cr³⁺ ions, the red-shift in emission positions of **1** and **2**, especially the unique turn-off–on fluorescence responses for Al³⁺ and Cr³⁺ sensing by **1**, imply the occurrence of framework–ion interactions.⁷⁵ The IR spectra provide further supports. As a representative, the IR spectrum of **1** after treated with Fe(NO₃)₃ in water for 24 h is obviously different from that of the pristine **1** (Fig. S20a). In terms of Al(NO₃)₃ and Cr(NO₃)₃, the corresponding IR spectra are somewhat different from that of the pristine **1**. For the three cases, vibration at around 1354 cm⁻¹ in **1** becomes broadened, suggesting the existence of NO₃⁻ species. On the other hand, the IR spectra of **2** after treated with M(NO₃)₃ (M = Fe, Al, Cr) in water for 24 h show a high degree of similarity, which are obviously different from that of the pristine **2** (Fig. S20b). The characteristic C=O stretching vibration is shifted to 1665 cm⁻¹ from 1654 cm⁻¹ whereas the characteristic NO₃⁻ vibration appears at around 1360 cm⁻¹ for charge neutralization. In addition, vibration bands at ca. 1718 and 1570 cm⁻¹ in **2** are shifted to 1708 and 1585 cm⁻¹, respectively, associated with changes in transmittance after treated with M(NO₃)₃ (M = Fe, Al, Cr) in water for 24 h.

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recognition of 1 and 2 towards Fe^{3+} , Al^{3+} , Cr^{3+} , we have further checked the EDX data for the solid

DOI: 10.1039/D0DT02606A samples of 1 and 2 after treated with $Fe(NO_3)_3$ in water for 24 h. The EDX analyses for so-obtained samples show the existence of trace amounts of Fe^{3+} (Fig. S21), suggesting that cation exchange between trivalent Fe³⁺ ions and framework Zn²⁺ ions is less appropriate, probably due to charge difference. In consideration of these pieces of evidences from IR and EDX data and structural features, there might be weak interactions between Fe³⁺ ions and the carboxylate oxygen atoms of the 5-NH₂-1,3-bdc^{2–} ligands in the frameworks of 1 and 2, resulted in (slight) structure alternation.

On the other hand, the UV-vis absorption spectra of Fe³⁺ and Al³⁺ in aqueous solutions display obvious absorptions in the range 250–400 nm (centered at 294 nm for Fe³⁺ and 300 nm for Al³⁺), which are negligibly overlapping with the emission spectra of 1 and 2 (Fig. S22), excluding the possibility of energy transfer as a way to reduce the fluorescence intensity. Comparably, the UV-vis absorption spectrum of Cr^{3+} in aqueous solution shows three absorption bands centered at 298, 424. and 576 nm, which is greatly overlapping with the emission spectra of 1 and 2 (Fig. S22), implying energy transfer might be a way to quench the fluorescence. On the other hand, the UV-vis absorption spectra of Fe³⁺, Al³⁺, and Cr³⁺ ions all show a great deal of overlap with the excitation wavelength at 315 nm for 1 and 320 nm for 2, suggesting that the competitive absorption of excitation energy by the Fe³⁺, Al³⁺, and Cr³⁺ ions could play a key role to significantly decrease the transfer efficiency of the excitation energy and thus ultimately result in luminescence quenching.^{82,85} In short conclusion, fluorescence quenching of 1 and 2 by Fe^{3+} and Al^{3+} could be mainly attributed to competitive absorption of excitation energy while that caused by Cr^{3+} might be chiefly resulted from the collaboration of resonance energy transfer and competitive absorption of excitation energy; all these mechanisms might be facilitated by framework-ion interactions.

In case of MnO₄⁻, its UV-vis absorption spectrum shows a bit of overlap with the emission spectra of 1 and 2 but strong overlap with the excitation wavelength (Fig. S23a), suggesting that the competitive absorption of excitation energy by MnO₄⁻ displays the major contribution whereas the energy transfer process might contribute a minor effort in quenching fluorescence. In comparison,

 $Cr_2O_7^{2-}$ shows that its UV-vis absorption bands are greatly overlapped with the emission bands of 1 DOI: 10.1039/D0DT02606A and 2 but poorly overlapped with the excitation wavelength (Fig. S23b). This implies that the fluorescence quenching of 1 and 2 dispersed in water caused by $Cr_2O_7^{2-}$ is tentatively originated from the efficient resonance energy transfer.

Conclusion

In summary, we have demonstrated reversible crystal-to-crystal transformations between an aqua-incorporated lamellar net 1 and a water-free bilayered-lamellar net 1', whose solid-state structure was determined using the XRPD patterns, upon removal and rebinding of coordination aqua ligands. Further, a porous pillared-bilayer 2 with moderate CO_2 uptakes and high CO_2 binding energy has also been engineering tailored by the introduction of an N-tethering NI-bpy-44 ligand to replace the coordinated aqua ligands. The two CPs, i.e., the lamellar net 1 and the pillared-bilayer 2, both emit strong blue fluorescence emissions in water, making them to be promising multifunctional fluorescence sensing platforms in detection of Fe³⁺, MnO₄⁻, and Cr₂O₇²⁻ with high sensitivity, low limit of detection, and good anti-interference ability over other interfering metal cations and anions that are visually observed. Further, the lamellar net 1 exhibits interesting turn-off-on fluorescence sensing for detection of Al^{3+} and Cr^{3+} ions in water.

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Graphical Abstract

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Reversible structural transformations between an aqua-coordinated lamella 1 and an anhydrous bilayered-lamella 1' were achieved and a pillared-bilayer 2 was tailored; 1 and 2 both showed fluorescence detection performances toward Fe³⁺, Al³⁺, Cr³⁺, MnO₄⁻, and Cr₂O₇²⁻ in water.

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