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Introduction

Light-responsive coordination polymers (CPs) constructed from earth-abundant metal ions or metal clusters and chromophoric π -conjugated organic linkages have attracted significant interest due to their well-organized structures and

Tailoring the coordination microenvironment of Zn(II) in a light-responsive coordination polymer system for molecular sensing and photodegradation performance⁺

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The behaviour of photoexcited electrons in light-responsive coordination polymers (CPs) significantly determines their performance in fluorescence sensing, smart materials, photoelectric display and photocatalysis, and this behaviour can be skilfully manipulated by optimizing the geometric and electronic structures of the ligand field around the metal ion. To reveal the micro-environmental effect of the ligand field on the bandgap and photoexcited electrons, three semiconductive Cd(II)-based CPs have been achieved through coordination of π -conjugated 2,6-bis(2-pyrazin-2-yl)-4-(4-(tetrazol-5-yl)phenyl)pyridine (HL) and 1,3,5-benzenetricarboxylic acid (H₃BTC) with Cd(μ) ion. Possessing N₃O₄ and O₆ donors, complex 1 assumed an extended triple-decker sandwich structure with a central {Cd₂(BTC)} sheet terminated up and down by planar L⁻ spacers. Two quadrangular {Cd₂(L)₂} dimers with N_4O_3 and N_4O_2 donors were propagated by doubly deprotonated HBTC²⁻ connectors to the cationic (4 4) layer of 2. The reproducible $\{Cd_2(L)_2\}$ dimers with only N₄O₃ donors in **3** were extended by mirror-symmetric HBTC²⁻ linkers to a bent chain. The distinct donor combinations in the local ligand fields of Cd(II) ions dominated the bandgaps and movements of the charge-carriers. Emitting intense steel blue fluorescence, complex 1 served as a highly efficient bilirubin probe with a guenching constant up to 9.48×10^4 M⁻¹ driven by photo-induced electron charge and Förster resonance energy transfer. In contrast, complex 2, with excellent separation efficiency of charge carriers, acted as a photocatalyst to completely degrade methylene blue up to 97% within 90 minutes of UV irradiation. Apparently, slight modifications of the surroundings of the ligand field by a heterodonor strategy achieved a remarkable effect on the photophysical properties of the semiconductive CPs, providing valuable hints for the construction of photosensitive CPs.

> promising applications in fluorescence sensing, photocatalysis, energy transformation and photochromism.¹⁻⁵ Apart from their large surface area and highly robust framework, the inherent semiconductor motifs of these lightactive CPs (optical bandgap, energy band structure, and transportation resistance of the charge carrier) are highly important for their feasible applications.6-8 The potentials and bandgaps of the energy bands are skillfully regulated by geometric and electronic modifications on the local ligand field around the metal ion (field symmetry, coordination microenvironments, types and negativity of the donors).9,10 The valence band (VB) is significantly derived from the N, O and S atoms of the organic linkages. In contrast, the conductive band (CB) is essentially contributed from the split d orbits of the metal center induced by the ligand field.^{11,12} The subtle manipulations of the ligand field and coordination microenvironment around the metal ion of semi-conductive CPs are particularly important. Upon light irradiation, the

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^c Power Machinery Institute of Inner Mongolia, Hohhot 010010, P. R. China † Electronic supplementary information (ESI) available: Selected bond lengths and angles, hydrogen-bonding parameters, crystal-packing figures, TG curves, bandgaps for 1–3, binding modes for the both ligands, UV-vis absorbance spectra of MB in the presence of 2 and 3, and photocatalytic mechanism over 1–3. CCDC numbers 2053677–2053679 for 1–3. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d4ce00952e

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photogenerated electrons progressively jump from VB to CB, accompanied by remarkable changes in spin, charge and emission of the photoactive CPs. Good recombination of the electron-hole pair can emit intense fluorescence, acting as a characteristic signal to detect contaminants in environments and/or bio-markers of human disease through the intensity change of the CPs. For example, a well-designed fluorescent postsynthetically modified UIO-66-PSM have been effectively quenched by free bilirubin via a fluorescent resonant energy transfer process.¹³ A pillared paddle wheel Zn(II)-CP with complementary energy acceptors and donor units serves as a highly sensitive probe for toxic Hg(II) ion.¹⁴ Alternatively, poor recombination of the charge carriers endows the excellent photocatalytic activity of CPs to decompose organic dyes through the catalytically active holes attacking the reaction substrate or further oxidation of photogenerated electrons. Thus, skillful control of the photoinduced electrons is highly significant for the performance enhancement of target semiconductive CPs. То systematically investigate the effect of microenvironments on bandgap and photoexcited electrons,¹⁵ co-coordination of 2,6-bis(2-pyrazin-2-yl)-4-(4-(tetrazol-5-yl) light-harvesting phenyl)pyridine (HL) and 1,3,5-benzenetricarboxylic acid (H₃BTC) with inorganic Cd(II) ion was performed in wellcontrolled alkaline media. The comparable binding affinities of N- and O-donors towards Cd(II) ion is expected to construct adjustable coordination micro-environments for better elaboration of the ligand-field effect. Additionally, the stepwise deprotonation and flexible coordination modes of H₃BTC can well regulate the framework diversity of the target complexes. As expected, three semiconductive Cd(II)-CPs possessing the same ligand fields but different binding surroundings ($N_3O_4 \nu s$. N_4O_3 as well as $N_4O_2 \nu s$. O_6) have been solvothermally yielded. The three CPs exhibit distinct bandgaps and separation/recombination efficiency of the photogenerated electron-hole pair, responsible for the appealing functions either as a sensitive fluorescence probe for bilirubin or as a photocatalyst for the decomposition of methylene blue (MB). Herein, solvothermal syntheses, crystal structures, photophysical characterizations, bilirubin sensing and photodegrading MB of the semiconductive CPs are discussed to reveal the heterodonor effect of the ligand field.

Experimental

Materials and instruments

HL was purchased from Jinan Henghua Science & Technology Co. Ltd. All other raw chemicals were from Tianjin Chemical Reagent Factory and were used directly without further purification. Elemental analyses for C, H and N were carried out with a CE-440 (Leeman-Labs) analyzer. Fourier transform (FT) IR spectra (KBr pellets) were taken on an Avatar-370 (Nicolet) spectrometer in the range 4000–400 cm⁻¹. Powder X-ray diffraction (PXRD) patterns were obtained from a Bruker D8 Advance diffractometer at 40 kV and 40 mA for Cu K α radiation (λ = 1.5406 Å), with a scan speed of 0.1 s per step and a step size of 0.01° in 2θ . The simulated PXRD patterns were calculated based on the single-crystal X-ray diffraction data and processed with the free Mercury v1.4 program provided by the Cambridge Crystallographic Data Center. Thermogravimetric analysis (TGA) experiments were carried out on a simultaneous DTG-60A compositional analysis instrument (Shimadzu, Japan) from room temperature to 800 °C under N₂ atmosphere at a heating rate of 5 °C min⁻¹. UV-vis diffuse reflectance spectra (DRS) and absorption spectra were carried out on U-4100 UV-vis spectrophotometer (Hitachi, Japan) equipped with an sphere integrating assembly and UV-2700 а spectrophotometer (Shimadzu, Japan). The X-ray photoelectron spectroscopy (XPS) measurements were carried out on an AXIS Ultra DLD X-ray photoelectron spectroscope (Shimadzu, Japan). Photoluminescent spectra and emission lifetime were collected on an Edinburgh Instruments FLS1000 fluorescence spectrophotometer. Optical images of the samples were taken on a Leica DM6 B upright digital research microscope from Leica microsystems.

Synthesis of $[Cd_2(H_2O)(C_2H_5OH)(L)(BTC)]_n$ (1). $CdCl_2 \cdot 5H_2O$ (14.2 mg, 0.05 mmol), HL (19.0 mg, 0.05 mmol), triethylamine (30 µL), H₃BTC (10.6 mg, 0.05 mmol), doubly deionized water (3.0 mL) and ethanol (3.0 mL) are sealed in a Teflon-lined stainless-steel vessel (23.0 mL) and heated at 160 °C for 72 hours under the autogenic pressure. After the mixture is cooled to room temperature at a rate of 5.625 °C h⁻¹, brown block-shaped single crystals suitable for X-ray analysis are obtained directly, washed with cold water, and dried in air. Yield: 85% based on HL ligand. Calcd. for C₃₁H₂₃Cd₂N₉O₈: C, 42.58; H, 2.65; N, 14.42%. Found: C, 42.64; H, 2.72; N, 14.62% (Fig. S1†). FT-IR (KBr pellet, cm⁻¹): 3061 (s), 2973 (w), 1606 (s), 1533 (s), 1483 (w), 1444 (w), 1426 (w), 1374 (s), 1178 (w), 1152 (w), 1081 (w), 1033 (s), 1005 (w), 935 (w), 841 (m), 769 (m), 727 (m), 682 (w), 576 (w), 484 (w).

Synthesis of {[Cd₂(H₂O)(H_{0.5}L)(L)(HBTC)]·0.5Cl·4H₂O}_{*n*} (2). Yellow block-shaped single crystals of 2 are directly generated by adopting similar procedures to 1 in the absence of triethylamine. Yield: 72% based on H₃BTC ligand. Calcd. for C₄₉H_{38.5}Cd₂Cl_{0.5}N₁₈O₁₁: C, 45.34; H, 2.99; N, 19.42%. Found: C, 45.62; H, 2.75; N, 19.67% (Fig. S1†). FT-IR (KBr pellet, cm⁻¹): 3378 (s), 3096 (w), 1656 (s), 1608 (s), 1547 (s), 1461 (m), 1397 (w), 1370 (s), 1272 (m), 1149 (m), 1097 (w), 1080 (w), 1032 (s), 1005 (w), 934 (w), 846 (s), 758 (m), 730 (m), 684 (w), 535 (w), 487 (w).

Synthesis of {[Cd(H₂O)(L)(HBTC)_{0.5}]-1.5H₂O}_{*n***} (3). Yellow block-shaped single crystals of 3 suitable for X-ray diffraction analysis are obtained by adopting similar procedures to 1, with the amount of triethylamine decreased to 10 \muL. Yield: 63% based on HL ligand. Calcd. for C_{24.50}H₁₉CdN₉O_{5.50}: C, 45.99; H, 3.00; N, 19.70%. Found: C, 45.88; H, 2.82; N, 20.11% (Fig. S1). FT-IR (KBr pellet, cm⁻¹): 3389 (s), 3096 (w), 1661 (s), 1608 (s), 1548 (s), 1460 (w), 1434 (w), 1397 (w), 1372 (s), 1268 (m), 1172 (s), 1151 (m), 1083 (m), 1032 (s), 1006 (m), 846 (s), 732 (m), 681 (m), 488 (w).**

X-ray crystallography

Diffraction intensities for 1-3 are collected on a Bruker APEXdiffractometer equipped with graphite-Π CCD monochromated Mo K α radiation ($\lambda = 0.71073$ Å) using the $-\omega$ scan technique. There is no evidence of crystal decay during data collection. Semiempirical multi-scan absorption corrections are applied by SADABS,16 and the program SAINT is used for integration of the diffraction profiles.¹⁷ The structures are solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs.^{18,19} Anisotropic thermal parameters are assigned to all non-H atoms. The site occupancy of H6B attached to N6 of the tetrazolyl group in 2 is 50%. One lattice water molecule (O6) in 3 is disordered with a site occupancy of 0.5. The final crystallographic data are summarized in Table 1. Selected bond lengths and angles and hydrogenbonding parameters are provided in Tables S1-S4.†

Sensing experiment

Well-crushed crystalline **1** (10 mg) is immersed into doubly distilled water (100 mL). The resulting mixture is ultrasonicated for 10 minutes and aged for one hour to obtain uniform dispersion (0.1 mg mL⁻¹). The stock solutions of analytes (1.0×10^{-3} mol L⁻¹) are prepared by dissolving appropriate amounts of MCl_x (M = K⁺, Na⁺, Ca²⁺, Fe³⁺, Fe²⁺ and Zn²⁺, x = 1-3), uric acid (UA), creatinine (Cre), creatine, glucose (Glu), ascorbic acid (AA) and bilirubin in doubly distilled water (100 mL). For the luminescent sensing experiments, 200 µL freshly prepared stock solution of analyte is added to the dispersion of **1** (3 mL). The emission spectra of **1** are recorded in the absence and presence of

Table 1 Crystal data and structure refinement for 1–3^a

different analytes. For fluorescence titration measurements, freshly prepared aqueous solution of bilirubin $(1.0 \times 10^{-3} \text{ mol L}^{-1})$ is gradually introduced to the suspension of 1 (3 mL), and the emission spectrum of the resultant mixture is recorded. The interference experiments are carried out by monitoring the emission intensity of 1 at 490 nm upon stepwise introducing bilirubin and one of the interfering substances. The reusability of the probe is evaluated by recycling the powder by centrifugal separation after the sensing experiment. The regenerated powder is washed with deionized water and dried for the next round of the sensing experiment.

Photodegradation of MB

Well-ground photocatalyst (10 mg) is dispersed in the MB stock solution in water (4.0 mg L⁻¹, 30 mL). The resultant mixture is continuously agitated in the dark for four hours to ensure the adsorption-desorption equilibrium. The mixture is then illuminated by a 300 W Hg lamp with a cut-off filter of 420 nm ($\lambda \ge 420$ -780 nm) at 25 °C prior to MB photodegradation. During the photocatalytic process, a portion of the suspension (3 mL) is removed successively from the reaction system at fixed time intervals, and the dispersed solid is isolated by centrifugation. The absorption intensity of the clarified solution at 664 nm is measured by UV-vis spectrophotometer to calculate the degradation efficiency of the MB.

Computational details

The Vienna *ab initio* simulation package $(VASP)^{20}$ is used to perform the first-principles calculations of **1** and bilirubin.

	1	2	3				
Empirical formula	$C_{31}H_{23}Cd_2N_9O_8$	$C_{49} H_{38.50} Cd_2 Cl_{0.50} N_{18} O_{11}$	C24.50H19CdN9O5.50				
F_{w}	875.39	1298.00	639.89				
Crystal size (mm)	$0.25 \times 0.24 \times 0.22$	0.22 imes 0.21 imes 0.18	$0.22 \times 0.21 \times 0.18$				
Crystal system	Triclinic	Triclinic	Monoclinic				
Space group	$P\bar{1}$	$P\bar{1}$	C2/c				
<i>a</i> (Å)	7.6589(3)	12.7084(18)	28.303(4)				
b (Å)	8.3363(3)	14.097(2)	11.5779(17)				
c (Å)	22.8520(13)	14.426(2)	18.807(3)				
α (°)	96.080(4)	82.747(3)	90				
β(°)	94.163(4)	83.256(3)	128.062(2)				
γ (°)	97.240(3)	75.061(2)	90				
$V(Å^3)$	1433.77(12)	2467.4(6)	4852.2(12)				
$Z, D_{\rm c} ({\rm g \ cm^{-3}})$	2, 2.028	2, 1.747	8, 1.752				
h/k/l	-9, 9/-9, 9/-27, 27	-15, 15/-12, 17/-18, 17	-35, 35/-14, 13/-21, 23				
F(000)	866.0	1302	2568				
μ (mm ⁻¹), $R_{\rm int}$	1.558, 0.0340	0.972, 0.0213	0.961, 0.0384				
Reflections collected/unique	10 479/5026	16 008/10153	15 611/5036				
Data/restraints/params	5026/6/463	10 153/0/727	5036/0/367				
R_1 , ^{<i>a</i>} w R_2 ^{<i>b</i>} ($I > 2\sigma(I)$)	0.0323, 0.0634	0.0397, 0.1090	0.0288, 0.0638				
R_1 , w R_2 (all data)	0.0410, 0.0690	0.0478, 0.1122	0.0407, 0.0674				
GOF on F^2	1.031	1.067	1.031				
$\Delta ho_{ m max}$, $\Delta ho_{ m min}$ (e Å ⁻³)	0.64/-0.54	0.975/-0.954	0.532 / -0.574				

^{*a*} $R_1 = \sum (||F_0| - |F_c||) / \sum |F_0|$. ^{*b*} $wR_2 = [\sum w(|F_0|^2 - |F_c|^2)^2) / \sum w(F_0^2)^2]^{1/2}$.

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For the modeling of core electrons, pseudopotentials implemented in the projector augmented wave method²¹ are used. Based on the Perdew-Burke-Ernzerhof (PBE) functional, a generalized gradient approximation is used for structural optimizations and electronic properties.²² The momentum space integration is conducted using $4 \times 4 \times 4$ Monkhorst-Pack *k*-point meshes. The cut-off energy of plane wave expansion is set to 500 eV. All atoms are allowed to relax until the forces are less than 0.01 eV Å⁻¹ and total energies are converged to 10^{-5} eV.

Results and discussion

Syntheses

Acting as a functional building block, phenyl-based polycarboxylate ligand has strong coordination ability to transition metal ions through stepwise deprotonation and diverse binding modes.^{23,24} Moreover, the binding affinity of carboxylate O competes well with heterocyclic N donors in the conjugated skeleton, which offers a good opportunity for manipulations of the coordination micro-environment of the metal ion. Indeed, self-assembly of the ternary system has been achieved by controlling the basicity and temperature of the reactant medium. As a weak organic base, triethylamine is used to adjust the deprotonation of H₃BTC. The number of the deprotonation sites of H₃BTC is found to be closely related with the amount of triethylamine. The deprotonation extent and binding modes of tri-carboxylate significantly dominate the structural diversity of the system. Strong characteristic bands at 1656 and 1661 cm⁻¹ in the FT-IR spectra of 2 and 3 confirm the incomplete deprotonation of the H₃BTC ligand.

Crystal structures

 $[Cd_2(H_2O)(C_2H_5OH)(L)(BTC)]_n$ (1). 1 crystallizes in the triclinic P1 space group (Table 1), exhibiting an infinite triple-decker sandwich structure with the middle $\{Cd_2(BTC)\}$ layer terminated up and down by bulky conjugated L spacers. The asymmetric unit of 1 contains two $Cd(\pi)$ ions, one fully deprotonated BTC3-, one monodeprotonated Lanion, one ethanol and one water molecule. As shown in Fig. 1a, the Cd1 is seven-coordinated by three N and four O donors from L⁻, BTC³⁻, ethanol and water molecules, adopting a distorted pentagonal bipyramidal configuration. The Cd2 is surrounded by six carboxylate O donors from five BTC³⁻ anions, demonstrating irregular octahedral coordination geometry. The bond lengths of Cd-N and Cd-O vary between 2.185(3) and 2.639(3) Å (Table S1[†]), comparable to previously reported Cd(II)-based CPs with carboxylate, pyridyl and pyrazinyl moieties.²⁵ Notably, the Cd-O_{aqua} bond is the shortest of all the seven bond lengths around Cd1, implying the remarkable stability of the coordinated water molecule. The triply deprotonated BTC³⁻ anion adopts a μ_6 - k^6 O1:O2:O3:O4:O5:O6-mode, and the mono-deprotonated L⁻ ligand represents a tridentate



Fig. 1 (a) Local coordination surroundings of Cd^{II} ions in **1** (H atoms were omitted for clarity, symmetry codes: A = x, 1 + y, z; B = -x, 3 - y, -z, C = -1 - x, 2 - y, -z; D = -x, 2 - y, -z), (b) connections of Cd^{II} ion with BTC³⁻ in **1**, (c) three-layer sandwich structure of **1** with the central {Cd(BDC)} layer terminated by L⁻ terminus.

chelating mode through one central pyridyl and two bilateral pyrazinyl groups (N1, N2, N3-L⁻, Fig. S2⁺).

A pair of μ_3 - η^1 : η^2 -COO⁻ groups from two BTC³⁻ ligands aggregate two crystallographically identical Cd2 ions into a {Cd₂(COO)₂} dimer. These dimers are further extended by four-connected BTC³⁻ linkages, leading to a {Cd₂(BTC)₂} corederived sheet with intra- and inter-core intermetallic distances of 3.8820(4) and 4.7105(7) Å, respectively (Fig. 1b). The central sheet is encapsulated on the both sides by chromophoric L⁻ spacers, resulting in an extended tripledecker sandwich layer (Fig. 1c). Furthermore, the repeated sandwiches are tightly aligned through the interlayer O_{aqua}-H···N_L hydrogen-bonding interactions between the coordinated water molecule and the tetrazolyl or pyrazinyl moieties of L⁻ ligand, giving rise to a dense supramolecular network with an interlayer Cd2··· separation of 23.57 Å (Table S2† and Fig. S3†).

 $\{ [Cd_2(H_2O)(H_{0.5}L)(L)(HBTC)] \cdot 0.5Cl \cdot 4H_2O \}_n$ (2). 2 crystallizes from the triclinic crystal system with $P\bar{1}$ space group (Table 1), assuming a cationic grid-layer with two unique $\{Cd_2(L)_2\}$ dimers alternately extended by threeconnected HBTC²⁻ connectors. The asymmetric unit includes two Cd(II) ions, a doubly deprotonated HBTC²⁻, two deprotonated L⁻, half a free Cl⁻, one coordinated and four free water molecules. As demonstrated in Fig. 2a, the Cd1 is in a pseudo-pentagonal bipyramid constructed by four N and three O_{carboxylate} donors from two L⁻ and two HBTC²⁻ ligands. The unique Cd2 is in the N₄O₂ donors furnished by L⁻, HBTC²⁻ and aqua ligands. The Cd-O and Cd-N bonds vary between 2.183(3) and 2.593(3) Å (Table S3⁺), comparable to known Cd(II)-CPs with carboxylate, pyridyl and pyrazinyl segments.²⁵ Although the ligand fields of the Cd(II) ions are the same in 1 and 2, their donor environments are quite

different. The doubly deprotonated HBTC²⁻ adopts a μ_3 - k^4 O1: O1,O2:O3-mode (Fig. S2†), behaving as a three-connected node. By contrast, both unique L⁻ anions represent a μ_2 - k^4 N1,N2,N3:N7-bridging manner through the dipyrazinylpyridyl and tetrazolyl moieties (Fig. S2†), different from the tridentate-chelating manner of L⁻ pincer in **1**.

A pair of crystallographically identical μ_2 - k^4 N1,N2,N3:N7-L⁻ hold two pairs of centrosymmetric Cd(II) ions into two unique {Cd₂(L)₂} dimers with intermetallic distances of 11.7524(14) for Cd1…Cd1A and 11.2711(16) Å for Cd2…Cd2A (Fig. 2b). These {Cd₂(L)₂} dimers are alternately bridged by HBTC²⁻ connectors into a grid-layer with interdimer separations of 3.9733(6) and 19.2469(21) Å. The adjacent layers interact with each other through weak π … π interactions between HBTC²⁻ and the pyrazinyl/pyridyl segment of the L⁻ ligand as well as O_{aqua}-H…O_{carboxylate} hydrogen-bonding interactions between the coordinated water and carboxylate group of HBTC²⁻, resulting in a non-covalent supramolecular architecture (Table S2[†] and Fig. S4[†]).

{[Cd(H₂O)(L)(HBTC)_{0.5}]·1.5H₂O_{*l*n} (3). Complex 3 belongs to the monoclinic *C*2/*c* space group (Table 1), featuring a bent chain with {Cd₂(L)₂} dimers bridged by mirror-symmetric HBTC²⁻ connectors. The asymmetric unit includes one Cd(II) ion, half a doubly deprotonated HBTC²⁻, one monodeprotonated L⁻, and one aqua as well as one and a half free water molecules. The sole Cd(II) is in the N₄O₃ surroundings completed by two L⁻, one HBTC²⁻ and one aqua (Fig. 3a), also adopting a pseudo-pentagonal bipyramid configuration. The Cd–O and Cd–O separations are between 2.309(2) and 2.4726(18) Å (Table S4†), falling in the normal range of reported Cd(II)-CPs with carboxylate, pyridyl and pyrazinyl moieties.²⁵ Compared with 1 and 2, there is no



Fig. 2 (a) Local coordination environments of Cd^{II} ions in 2 (H atoms were omitted for clarity, symmetry codes: A = 1 - x, 2 - y, -z; B = 1 - x, 1 - y, -z; C = 2 - x, -1 - y, 1 - z), (b) cationic sheet of **2** with dimeric {Cd₂L₂} subunits extended by three-connected HBDC²⁻ connectors.



Fig. 3 (a) Local coordination surroundings of Cd^{II} ion in **3** (H atoms were omitted for clarity, symmetry codes: A = 0.5 - x, 1.5 - y, -z; B = -x, y, 0.5 - z), (b) zig zag chain of **3** with dimeric {Cd₂L₂} subunits extended by ditopic HBDC²⁻ connectors.

hexa-coordinate Cd(II) ion in **3**. The L⁻ ligand represents a μ_2 - k^4 N1,N2,N3:N7 mode, and the doubly deprotonated HBTC²⁻ anion is mirror-symmetric, behaving as a bis-bidentate chelating mode (μ_2 - k^4 O1,O2:O3,O4-HBDC²⁻, Fig. S2†).

A pair of L⁻ ligands hold two Cd(II) ions together in a head-to-tail manner (Fig. 3b), generating a reappearing {Cd₂(L)₂} subunit with a long intermetallic distance of 11.5181(15) Å. These separate subunits are aggregated by mirror-symmetric μ_2 - k^4 O1,O2:O3,O4-HBDC²⁻ linkages, resulting in a bent chain with an inter-subunit Cd(II)…Cd(II) distance of 10.0171(14) Å. The neighboring chains are packed into the architecture through interchain O_{aqua} -H… $O_{carboxylate}$ and O_{aqua} -H… $N_{pyridyl}$ hydrogen-bonds between the coordinated water and the carboxylate of HBTC²⁻ or pyridyl groups of L⁻ anions (Table S2† and Fig. S5†).

Structural comparisons of 2 and 3 reveal that the crystallographic symmetry and binding mode of $HBTC^{2-}$ significantly regulate the $\{Cd_2(L)_2\}$ -based overall structures. The $HBTC^{2-}$ in 2 is crystallographic non-symmetric, behaving as a three-connected linkage to aggregate three separate $\{Cd_2(L)_2\}$ dimers. In 3, it is mirror-symmetric and adopts a bis-bidentate chelating mode to hold two $\{Cd_2(L)_2\}$ together. Additionally, the coordination micro-environments for the octahedral Cd(n) ions are changed from O_6 in 1 to N_4O_2 in 2.

PXRD and thermal stability

Each PXRD pattern of the as-prepared samples 1–3 is in good agreement with the simulated one extracted from the singlecrystal diffraction data (Fig. 4 and S6†). These findings suggest that the bulk-prepared product possesses the same phase structure and has high phase-purity.

As a representative sample, the environmental robustness of **1** is assessed by soaking it in aqueous solutions with varying pH values (pH = 2-12) for half a day at room temperature. The PXRD pattern of the recovered powder changes insignificantly (Fig. 4), exhibiting the excellent water stability in a relatively wide pH range. The water robustness of **1** is more favorable due to the hydrophobic effect of the conjugated L⁻ component and strong metal binding ability to N and O donors judging from their comparable bond-lengths. The phase structure of **1** is well retained below 200 °C as evidenced from the well-matched PXRD profiles. Once the surrounding temperature is higher than 300 °C, crystalline **1** becomes an amorphous powder, accompanied by the absence of characteristic diffraction peaks.

The composition thermal stability of **1–3** is evaluated by TGA analyses between 25 °C and 800 °C. No obvious weightloss stage is observed for **1** between ambient temperature and 120 °C, suggesting that the coordinated water molecules



Fig. 4 PXRD patterns of 1 upon different external stimuli.

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of 1 are easily released in air. Coordinated ethanol and mixed organic ligands are consequently decomposed beyond 230 °C and are responsible for the broken of layered framework of 1 (Fig. S7†). The water molecule and counter Cl^- anion of 2 as well as the water molecules of 3 are released between 25 °C and 127 °C, resulting in weight losses of 7.6% and 7.0% (calcd. 8.3% and 7.0%). When heated beyond 303 °C, the skeletons of 2 and 3 start to collapse due to the partial decomposition of the organic ligands. Therefore, it can be concluded that 1–3 have good composition thermal stability and can be widely used in mild environments.

Photophysical behavior of 1-3

The successful incorporations of the d^{10} -configured Cd(II) ion and π -conjugated HL component have endowed interesting photophysical properties to the resulting CPs. Thus, both the absorption and emission spectra of 1-3 are recorded in the solid-state at room temperature. 1-3 exhibit a broad absorption centered at 360 nm in the UV region, together with a weak shoulder band around 495 nm in the visible region (Fig. 5a). As compared with the HL ligand, the highenergy absorbance of 1-3 originates from the chromophoric L⁻-based n- π^* transition, and the latter is due to metal-toligand charge transfer (MLCT). Moreover, the binding of Cd(II) and HL in 1-3 inhibits the π - π * transition of HL, judging from the absence of a broad absorption at 600 nm. The optical bandgaps of these CPs are extracted with the available UV-vis DSR data through Tauc plots.^{26,27} By measuring the x-axis intercept of an extrapolated tangential line from the linear regime of the curve, the bandgap energies (E_{σ}) are estimated to be 2.07 eV, 1.50 eV and 1.82 eV for 1-3, respectively (Fig. S8[†]). Thus, 1-3 are semiconductors,²⁸ and the varied E_{g} values confirm the decisive roles of the ligand field through adjusting donor types and polyhedra geometry. The smallest E_{g} of 2 suggests the easiest separation of the photogenerated electron-hole pairs among 1-3.

Upon excitation at 395 nm, one broad and strong emission centered at 537 nm is observed for **1** with a bright

steel blue light (Fig. 5b). Due to the MLCT, the emission of 1 red-shifts away from that of the HL ligand by *ca.* 30 nm, suggesting good recombination of the photogenerated holeelectron pair. Under the same excitation as 1, both 2 and 3 display only a weak emission at 455 \pm 3 nm because of the intraligand charge transfer. The weak intensity implies poor recombination efficiency of the charge carriers, favorable for photocatalysis, especially in organic dye decomposition.²

Bilirubin sensing by 1

The intense emission in the eye-observable visible-region enables 1 to be a fluorescence probe. The uniform dispersion of 1 in water exhibits a broad emission at 490 nm upon excitation at 350 nm (Fig. 6a), an obvious blue-shift by 47 nm from that in the solid-state (Fig. S9[†]). The involvement of MCl_x (M = K⁺, Na⁺, Ca²⁺, Fe³⁺, Fe²⁺, and Zn²⁺), UA, Cre, creatine, glucose and AA in 1 causes no apparent change in the emission spectrum. The addition of bilirubin produces a severe decrease in the emission intensity of 1 at 490 nm (I_{490}) , accompanied by a new moderate band at 655 nm (I_{655}) . The spectral changes of 1 in the presence of different analytes are estimated by monitoring I_{490} (Fig. 6b). The quenching efficiency of **1** by bilirubin $((I_0 - I)/I_0 \times 100\%)$ is up to 82.5%, much higher than those of the other components examined herein (0.5-21.9%, Fig. 6b). Thus, 1 can selectively identify bilirubin in water systems through luminescent quenching.

The quenching constant (K_{sv}) of 1 by bilirubin was quantitatively evaluated by luminescence titration experiments. As illustrated in Fig. 6c, I490 and I655 undergo opposite changes with the gradually increasing bilirubin. When bilirubin is 3.33, 10.0 and 30.0 μ M, the I_{490} are 34.0%, 67.0% and 89.0% of the initial intensity and the I_{655} increase by 4.0, 6.3 and 7.7 times. Moreover, the color change of the system is naked-eye observed to be from blue-green to orange-red (Fig. 6c inset). The plot of I_0/I vs. [bilirubin] is linear with [bilirubin] $<30.0 \mu$ M, suggesting a static quenching mechanism. The best fit of the plot to the Stern-Volmer equation $(I_0/I) = K_{sv}[M] + 1$ (ref. 29 affords $K_{sv} = 9.48 \times$



Fig. 5 (a) UV-vis diffuse reflectance spectra for 1–3 and free HL ligand, (b) solid photoluminescence of 1–3 and free HL ligand measured at room temperature.



Fig. 6 (a) Emissions of 1 dispersed in water in the absence and presence of various substances, (b) emission intensity of 1 at 490 nm in the absence and presence of various substances, (c) luminescence of 1 with and without bilirubin dispersed in water, (d) Stern-Volmer equation of bilirubin at room temperature (inset: luminescence change after adding bilirubin under UV light irradiation of 365 nm), (e) fluorescence responses of 1 towards bilirubin in the presence of one of the other competing substances, (f) recyclability of 1 incorporated with bilirubin.

 10^4 M⁻¹ and R^2 (correlation coefficient) = 0.9925 (Fig. 6d). Compared with reported luminescence probes for bilirubin, the K_{sv} of 2 is bigger than those of sole MOF UIO-66-PSM and $\{[Eu(H_2O)(HCOO)(bpydb)]\cdot$ solvent $\}_n$,^{13,30} but moderately lower than those of the post-synthetically classical 1-NH₂@THB (ref. 31) and Zr-MOF:Eu³⁺ (ref. 32) as well as the fluorescent

Table 2	Comparison	of the	reported	luminescence	probes t	for	bilirubin ^a
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Sensor	Linear range/µM	LOD/nM	$K_{\rm sv}/{ m M}^{-1}$
BAMD (ref. 33)	1×10^{-6} -500	0.0028	3.3×10^{10}
HSA-AuNCs (ref. 34)	1-50	248 ± 12	$5.5 imes 10^5$
BSA-CuNCs/Fe ³⁺ (ref. 11)	$0.1 imes 10^{-6}$ – 0.1	6.62	_
UIO-66-PSM (ref. 13)	0-500	0.00059	$8.95 imes 10^4$
$\{[Eu(H_2O)(HCOO)(bpydb)] \cdot solvent\}_n \text{ (ref. 30)}$	0-56.6	1750	$6.40 imes 10^4$
1-NH ₂ (a)THB (ref. 31)	10^{-12} -1.2 × 10^{-5}	0.00126	4.18×10^{6}
$Zr-MOF:Eu^{3+}$ (ref. 32)	0-15	450	$1.01 imes 10^5$
$[Cd_2(H_2O)(C_2H_5OH)(L)(BTC)]_n^{\text{this work}}$	0-30	1750	9.48×10^{4}
$ \begin{array}{l} \text{Infractors} & \text{Infractors} \\ \text{BSA-CuNCs/Fe}^{3+} (\text{ref. 11}) \\ \text{UIO-66-PSM} (\text{ref. 13}) \\ \{ [\text{Eu}(\text{H}_2\text{O})(\text{HCOO})(\text{bpydb})] \cdot \text{solvent} \}_n (\text{ref. 30}) \\ 1 \cdot \text{NH}_2 (\text{@THB} (\text{ref. 31}) \\ \text{Zr-MOF:Eu}^{3+} (\text{ref. 32}) \\ [\text{Cd}_2(\text{H}_2\text{O})(\text{C}_2\text{H}_5\text{OH})(\text{L})(\text{BTC})]_n^{\text{this work}} \end{array} $	$\begin{array}{c} 0.1 \times 10^{-6} - 0.1 \\ 0 - 500 \\ 0 - 56.6 \\ 10^{-12} - 1.2 \times 10^{-5} \\ 0 - 15 \\ 0 - 30 \end{array}$	6.62 0.00059 1750 0.00126 450 1750	

^{*a*} BAMD = 2,2'-((1E,1'E)-((6-bromopyridine-2,3-diyl)bis(azanylylidene))bis(methanylylidene)) diphenol, HSA = human serum albumin, BSA = bovine serum albumin, bydb = 4,4'-(4,4'-bipyridine-2,6-diyl) dibenzoate, NCs = nanoclusters.

molecule based biosensor of BAMD,³³ human serum albumin (HSA) stabilized gold nanoclusters (AuNCs),³⁴ and Fe(m) modulated BSA stabilized AuNCs (Table 2).¹¹ The ratio of I_{655}/I_{490} exhibits a concentration-dependent S-shaped curve. When [bilirubin] is beyond 60 μ M, the I_{655}/I_{490} value is constant (Fig. 6d inset).

The specificity and reusability are evidenced by continuously importing bilirubin and one interfering substance into **1**. The quenching extent of the system is approximately comparable to those caused by bilirubin and one of the interfering substances including UA, Cre, AA, Creatine, Glu, Na⁺, Fe²⁺, Zn²⁺, K⁺, Ca²⁺ and Fe³⁺ (Fig. 6e). After six continuous sensing recycles, both the luminescence

intensity and PXRD pattern of the recovered **1** are almost the same as those of the original sample (Fig. 6f). Thus, **1** can repeatedly and quickly discriminate bilirubin selectively and sensitively in urine.

The quenching mechanism of **1** was investigated by various structural characterizations. The PXRD pattern of **1** after distinguishing bilirubin is the same as that of the pristine one (Fig. S10†), ruling out structural collapse during the sensing process. The aqueous bilirubin solution demonstrates a wide absorption centered at 432 nm among the twelve analytes (Fig. S11†), showing a good overlap with the emission of **1** (Fig. 7a). Thus, the Förster resonance energy transfer (FRET) occurs non-radiatively from **1** (energy



Fig. 7 (a) UV-vis absorbance spectra of bilirubin, together with the excitation and emission spectra of **1**, (b) lifetime of **1** at 490 and 655 nm before and after injecting aqueous bilirubin solution, (c) time-dependent emission spectra of **1** and absorbance at 490 and 655 nm upon injecting aqueous bilirubin solution (30.0 uM), (d) electron density distributions for the LUMOs of **1** and bilirubin from DFT calculations, (e) high-resolution XPS spectra of **1** for Cd 3d, N 1s and O 1s regions before (blue line) and after bilirubin sensing (purple line).

donor) to bilirubin (energy acceptor) via weak dipole-dipole coupling, 3^{5-42} leading to the fluorescence quenching of 1. The fluorescence lifetime of 490 nm (τ_{490}) decreased from 6149.5 to 2857.9 ns upon introducing bilirubin (200 μ L, 1.0 × 10^{-3} mol L⁻¹). Correspondingly, the τ_{655} is 4751.8 ns (Fig. 7b). The lifetime change confirms the dynamic energy transfer process, which is further validated by the time-dependent fluorescence spectra of the mixture (Fig. 7c). After interacting with bilirubin, the characteristic peak of 1 at 490 nm decreases slightly and blue shifts, accompanied by a gradual and obvious increase centered at 655 nm within 40 minutes. These observations strongly suggest FRET between 1 and bilirubin. Density functional theory (DFT) calculations^{43,44} reveal that the HOMO and LUMO levels of 1 and bilirubin are -0.0259 and 1.9756 eV as well as 0.0376 eV and 1.4906 eV. The energy gap is 2.0015 eV, close to the bandgap derived from the DRS result. The LUMO energy is higher by 0.4850 eV than that of bilirubin, suggesting photo-induced electron transfer (PET) from the π -conjugated L⁻ moiety of 1 to bilirubin (Fig. 7d). X-ray photoelectron spectroscopy (XPS) measurements indicate that the binding energies for both the 1 s and 3d regions of the N and Cd(II) species remain almost unchanged before and after bilirubin sensing (Fig. 7e). In contrast, the binding energy for the 1s region of O shifts from 530.95 and 532.69 eV to 531.52 and 533.25 eV, indicating strong electron transfer interactions between 1 and bilirubin. Therefore, synergistic FRET and PET pathways are responsible for the sensing performance of 1.

Photodegradation of MB over 1-3

MB is chosen as a representative contaminant to estimate the catalytic activity of 1–3 under UV light irradiation. Prior to photodegradation, the absorption percentage of MB on the surface of the photocatalyst is 10.0%, 17.5% and 12.0%, respectively, for 1–3. The highest absorption of 2 results from its cationic nature. Upon UV illumination, the adsorptions of MB at 664 nm decrease at once (Fig. 8a and S12†), indicating that 1–3 have degraded MB efficiently under the assistance of UV light. The concentration of MB (C) is quantitatively calculated *via* the characteristic absorbance at 664 nm, and

 C/C_0 is plotted as a function of irradiation time. After 90 minutes of photo-irradiation, the C/C_0 values drop from 1.0 to 0.20 over 1, from 1.0 to 0.03 over 2 and from 1.0 to 0.30 over 3 (Fig. 8b), meaning the degradation percentages are 80%, 97% and 70%, respectively. Without photocatalyst, the degradation percentages are only 9.6%. To realize the same photodegradation percentage of 97%, the illumination times of 1 and 3 must be 170 and 150 minutes. Apparently, due to the largest absorption amount and inherent high photocatalytic activity, 2 exhibits the best photocatalytic performance of 1-3. Moreover, the photodegradation activity of 2 is better than that of neutral Cu(II)-derived CPs with 30membered ring-based layers and porous Co(II)-based framework.45 Compared with the porous Cu-MOF constructed by two kinds of planes from the orthogonal direction interpenetrating each other's pores,⁴⁶ the photocatalytic activity of MB degradation by 2 is comparable without the addition of co-catalyst H₂O₂, revealing the inherently high activity of 2.

To check the sustainability and reusability of the photocatalysts, three successive photocatalytic cycles were carried out with 2 as an example. The degradation percentage drops from 97% to 80% after three irradiations (Fig. 8c). The PXRD patterns and FT-IR spectra after three repeated photocatalytic cycles are almost the same as those of the pristine samples (Fig. S13 and S14⁺), suggesting the high stability of 1-3 as photocatalysts. The unsatisfactory recyclability of 2 with good thermal stability and phase structure is due to catalyst poisoning by the irreversible adsorption of MB molecule. The photocatalytic mechanism of MB degradation over 2 was checked by adding methanol, tert-butyl alcohol, and benzoquinone to catch the possible active species of hole (h⁺), hydroxyl radical (·OH), and/or superoxide radical (·O₂⁻).²³ The involvement of benzoquinone in the 2-assisted MB photodegradation greatly weakened the degradation efficiency by 46% (Fig. S15^{\dagger}), manifesting that $\cdot O_2^$ contributes more significantly than the other active substances (h^+ and $\cdot OH$). According to the reported model of the photocatalytic mechanism (Fig. S16[†]),¹⁵ the active $\cdot O_2^-$ is generated from the oxidation of oxygen by the



Fig. 8 (a) Time-dependent UV-vis absorbance spectra of MB aqueous solution over 2 under UV light irradiation (inset: color change of MB solution before and after photocatalysis), (b) time-dependent degradation percentage of MB over 1–3. (c) Recycling tests for MB degradation in the presence of 2.



Fig. 9 EIS (left) and transient photocurrent responses (right) of 1-3.

photogenerated electron of 2, highlighting the importance of the separation of charge carriers.

The charge-transfer resistance at the semiconductorelectrolyte interface is obtained from the radius of the arc in the Nyquist plot. The smallest radius of 2 compared to 1 and 3 indicates the fastest interfacial charge transfer (Fig. 9). Under UV-light irradiation, 1-3 present transient photocurrent responses, in which the photocurrent signals quickly switch through four on-off cycles. The photocurrent of 2 (0.73 μ A cm⁻²) is 1.66 and 2.43 times stronger than those of 1 and 3, suggesting the best electron-hole separation efficiency directed by the smallest bandgap (Fig. 9).47,48 All these results prove that 2 is more suitable as a photocatalyst for the photodegradation of MB.

Conclusions

Co-coordination and selective deprotonation of a phenylbased tricarboxylate and N-heterocyclic chromophore with $Cd(\pi)$ ion in well-tunable alkaline media afforded a neutral triple-decker sandwich layer with N₃O₄ and O₆ donor sets, a cationic {Cd₂(L)₂}-derived (4 4) layer with N_4O_3 and N_4O_2 donors, and a bent $\{Cd_2(L)_2\}$ -based chain with only N_4O_3 surroundings. The comparable micro-environments around the $Cd(\pi)$ ions preferentially dominated the bandgaps and the separation/recombination ability of the photoexcited electron-hole pair. The sandwich-layer with intense steel blue emission distinguishes bilirubin with high efficiency by PET and FRET. The positively charged grid-layer with the best electron-hole separation degraded methylene blue up to 97% after 90-minute UV lamp irradiation. Obviously, the heterodonor coordination strategy is effective in modulating the photophysical behavior of semi-conductive CPs, which affords fundamental insights on the structure-function relationships and opens a design concept for photoactive CPs on the atomic scale.

Data availability

Additional data are provided in the ESI[†] file. Crystallographic information files (CIF) can be obtained from the Cambridge

Structural Database *via* CCDC numbers 2053677–2053679 for 1–3.

Conflicts of interest

The authors declare no competing financial interest.

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