

Supporting Information

Cationic coordination polymer with thirteen-fold interpenetrating dia network: selective coloration and ion-controlled photochromism

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1 EXPERIMENTAL SECTION

2 **Materials and Measurements.** 1,1'-bis(4-carboxyphenyl)-(4,4'-bipyridinium) dichloride was
3 prepared according to the literatures,^{S1} while other chemicals with reagent-grade quality were obtained
4 from commercial sources and used without further purification. The infrared spectra were recorded on a
5 Thermo Scientific Nicolet iS10 FT-IR spectrometer as KBr pellets in the range of 400-4000 cm⁻¹. The
6 solid UV-vis spectra were confirmed on a Perkin-Elmer Lambda 900 spectrometer. The powder X-ray
7 diffraction (PXRD) patterns were collected on a Bruker D8 Advance powder diffractometer with Cu
8 K α radiation ($\lambda = 1.5406 \text{ \AA}$) at a scanning rate of 2 $^\circ$ ·min⁻¹ for 2 θ ranging from 3 $^\circ$ to 50 $^\circ$.
9 Thermogravimetric analysis was carried out in the temperature range of 30-800 $^\circ$ C on a TA Q50
10 apparatus. Scanning electron microscopy (SEM) images were performed on a Hitachi SU8010
11 instrument equipped with an energy-dispersive spectroscopy (EDS) detector. EPR experiments were
12 recorded on a Bruker E-500 spectrometer working at X band (9.8 GHz). Raman spectra were carried
13 out on a B&W TEK BWS415-785S spectrometer, which was equipped with 100% laser power
14 irradiation in order to minimize the fluorescence interference. Laser: 785 nm, laser intensity: 10 mW.
15 Cyclic voltammetry (CV) was carried out on a CHI760E workstation (Shanghai CH Instrument Company,
16 China) with a three-electrode system, where the counter, reference and working electrodes are a platinum
17 wire, an Ag/AgCl electrode and a modified glassy carbon electrode (GCE), respectively. For preparation of
18 the modified GCE, a bare GCE ($\Phi = 3\text{mm}$) was polished with slurry alumina, sonicated and washed
19 thoroughly with ethanol and deionized water. 1 mg samples of **Cd-CCP** or **Cd-CCP-X** ($X = \text{F}^-$, Cl^- , Br^-
20 and I^-) were dispersed in the mixture of 0.1mL deionized water and 10 μL Nafion (5%) by sonication to
21 form a suspension. Then 2.5 μL suspension was drop-coated onto the modified GCE, and the electrode was
22 dried in air.

23 **Synthesis of Cd-CCP.** H₂bcbpCl₂ (19 mg, 0.04 mmol) and cadmium iodide (37 mg, 0.1 mmol) were
24 added to a mixed solution of deionized water and acetonitrile (3/3 mL). The resulting solution was
25 placed in a 23mL Teflon-lined stainless-steel autoclave and heated in an oven at 140 $^\circ$ C for five days.
26 After cooling to room temperature, red block crystals (15 mg) were obtained in 24% yield based on

1 H₂bcbpCl₂. FT-IR (KBr disk, ν cm⁻¹): 3116 (w), 3051 (w), 1633 (s), 1611 (s), 1574 (m), 1535 (m),
2 1486 (w), 1435 (m), 1389 (s), 1300 (w), 1248 (w), 1221 (w), 1039 (w), 1020 (w), 1006 (w), 852 (m),
3 830 (m), 784 (s), 755 (w), 700 (w), 666 (w), 577 (w), 471 (w).

4 **X-ray Data Collection and Structure Determination.** Data collection for **Cd-CCP** was performed
5 on a Bruker APEXII diffractometer equipped with graphite monochromated Mo-K α radiation ($\lambda =$
6 0.71073 Å) by using the ω -scan mode at 293(2) K. The structure was solved by direct methods, the
7 metal atoms were located from the E-maps, and other non-hydrogen atoms were derived from the
8 successive difference Fourier peaks. The structure was refined on F^2 by full-matrix least-squares using
9 the *SHELXTL*-2014 program package.^{S2} All non-hydrogen atoms were refined anisotropically.
10 Hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms and refined
11 with fixed thermal factors. Details of the structure solution and final refinement for **Cd-CCP** are given
12 in Table S1. CCDC-2040463 contains the supplementary crystallographic data.

1 **Table S1.** Crystal Data and Data Collection and Refinement Parameters for **Cd-CCP**.

Compound	Cd-CCP
formula	$C_{48}H_{38}N_4O_{11}I_4Cd_2$
formula weight	1579.22
temperature (K)	293 (2)
wavelength (Å)	0.71073
crystal system	monoclinic
space group	$P2_1/c$
a (Å)	10.9067(3)
b (Å)	33.3651(10)
c (Å)	14.2180(5)
α (°)	90
β (°)	96.6610(10)
γ (°)	90
volume (Å ³)	5139.0(3)
Z	4
D_c (Mg/m ³)	2.041
μ (mm ⁻¹)	3.292
data collected	79202
unique data (R_{int})	10508
parameters	626
GOF on F^2	1.059
R_1^a [$I > 2\sigma(I)$]	0.0742
wR_2^b	0.2197

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

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1 **Table S2.** The comparison of the structures and properties between **Cd-CCP** and the viologen-
 2 based CCPs reported in the literatures.

Coordination Polymers	Structure	Properties	References
$[\text{Cu}_2\text{L}(\text{H}_2\text{O})_2] \cdot (\text{NO}_3)_2 \cdot 5.5\text{H}_2\text{O}$	3D cationic framework; nbo-type topology	dye capture and $\text{Cr}_2\text{O}_7^{2-}$ removal	S3
$\{[\text{Cd}(\text{Bpybc})_2] \cdot 2\text{ClO}_4 \cdot 7\text{H}_2\text{O}\}_n$	1D double helical cationic chains	photochromism	S4
$\{[\text{Ln}_3(\text{bcbp})_3(\text{NO}_3)_7] \cdot \text{NO}_3 \cdot \text{ClO}_4\}_n$	3D cationic framework;	$\text{Cr}_2\text{O}_7^{2-}$ and ammonia sensing	S5
$\{[\text{Zn}_3(\text{L})_2(\text{H}_2\text{O})_8] \cdot 2(\text{SO}_4) \cdot 2(\text{H}_2\text{O})\}_n$	four-fold interpenetrating 2D cationic layer	photochromism	S6
$\{[\text{Zn}(\text{L})(\text{H}_2\text{O})_2] \cdot \text{NO}_3 \cdot \text{H}_2\text{O}\}_n$	3D cationic two-fold interpenetrating framework	photochromism	
$\{[\text{Eu}(\mu_2\text{-OH})(\text{L})(\text{H}_2\text{O})] \cdot \text{NO}_3 \cdot \text{H}_2\text{O}\}_n$	1D cationic rod-like infinite chain	photochromism, photo- modulated luminescence, photoswitchable NLO and piezoelectric properties	S7
$\{[\text{Tb}_4(\mu_3\text{-OH})_4\text{L}_3 \cdot (\text{H}_2\text{O})_7] \text{Cl}_{0.63} \cdot (\text{NO}_3)_{4.37} \cdot 3\text{H}_2\text{O}\}_n$	3D cationic framework;	photochromism, photomodulated fluorescence, and luminescent pH Sensing	S8
$[\text{Cd}_4(\text{pc}_1)_3\text{Cl}_6] \cdot \text{CdCl}_4 \cdot \text{guest}$	3D cationic framework;	ammonia uptake	S9
$\text{Zn}(\text{bcbp})(\text{PO}_3\text{F})$	2D cationic layer	photochromism	S10
$\{[\text{Cu}_2(\text{bdcbp})(\text{H}_2\text{O})_2] \cdot 2\text{NO}_3 \cdot 2\text{H}_2\text{O}\}_n$	3D cationic framework	$\text{Cr}_2\text{O}_7^{2-}$ adsorption and dye separation	S11
$\text{Eu}(\text{bc bpy})_3(\text{H}_2\text{O})_3 \cdot 3\text{NO}_3$	3D cationic framework;	colorimetric and thermochromic responses	S12
$\{[\text{Cd}(\text{bcbp})_2(\text{CdI}_4)] \cdot 3\text{H}_2\text{O}\}_n$	3D cationic framework; thirteen-fold interpenetrating dia network	selective coloration and ion- controlled photochromism	This work

1 **Table S3.** EDS results for **Cd-CCP-X**.^{S13}

Cd-CCP-F: $\{[\text{Cd}(\text{bcbp})_2(\text{CdI}_4)_{0.65}\text{F}_{0.70}] \cdot 3\text{H}_2\text{O}\}_n$							
Point 1		Point 2		Point 3		Average	
Element	Weight%	Element	Weight%	Element	Weight%	Element	Weight%
C	41.6	C	41.2	C	42.4	C	41.7
N	4.5	N	4.7	N	3.8	N	4.3
F	1.2	F	1.0	F	1.1	F	1.1
Cd-CCP-Cl: $\{[\text{Cd}(\text{bcbp})_2(\text{CdI}_4)_{0.54}\text{Cl}_{0.92}] \cdot 3\text{H}_2\text{O}\}_n$							
Point 1		Point 2		Point 3		Average	
Element	Weight%	Element	Weight%	Element	Weight%	Element	Weight%
C	44.2	C	43.4	C	43.1	C	43.6
N	4.3	N	4.0	N	4.3	N	4.2
Cl	2.8	Cl	2.3	Cl	3.0	Cl	2.7
Cd-CCP-Br: $\{[\text{Cd}(\text{bcbp})_2(\text{CdI}_4)_{0.39}\text{Br}_{1.23}] \cdot 3\text{H}_2\text{O}\}_n$							
Point 1		Point 2		Point 3		Average	
Element	Weight%	Element	Weight%	Element	Weight%	Element	Weight%
C	43.3	C	45.3	C	45.2	C	44.6
N	3.9	N	4.2	N	4.4	N	4.2
Br	7.7	Br	6.8	Br	7.8	Br	7.4
Cd-CCP-I: $\{[\text{Cd}(\text{bcbp})_2(\text{CdI}_4)_{0.34}\text{I}_{1.32}] \cdot 3\text{H}_2\text{O}\}_n$							
Point 1		Point 2		Point 3		Average	
Element	Weight%	Element	Weight%	Element	Weight%	Element	Weight%
C	42.8	C	42.7	C	43.4	C	43.0
N	4.6	N	3.8	N	3.6	N	4.0
I	25.7	I	26.0	I	256.2	I	25.6

1 **Table S4** Formal potentials, onset potentials of the first reduction peaks, HOMO and LUMO
 2 energies and band gaps of **Cd-CCP** and **Cd-CCP-X**.^a

	E_1 (V)	E_2 (V)	$E_{\text{Red}}^{\text{Onset}}$ (V)	E_g (eV) ^b	LUMO (eV) ^c	HOMO (eV) ^d
Cd-CCP	-0.242	-0.843	-0.202	2.000	-4.498	-6.498
Cd-CCP-F	-0.258	-0.849	-0.210	2.200	-4.490	-6.690
Cd-CCP-Cl	-0.262	-0.875	-0.218	2.175	-4.482	-6.657
Cd-CCP-Br	-0.282	-0.936	-0.239	1.990	-4.461	-6.451
Cd-CCP-I	-0.311	-0.967	-0.257	1.959	-4.443	-6.402

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5 ^aPotentials are reported vs Ag/AgCl. ^bBand gap calculated from the onset wavelength (λ_{onset} , nm) of
 6 the UV-vis spectrum using $E_g = 1240/\lambda_{\text{onset}}$. ^cCalculated using $E_{\text{LUMO}} = -(E_{\text{Red}}^{\text{onset}} + 4.70)$ (eV).^{S14}

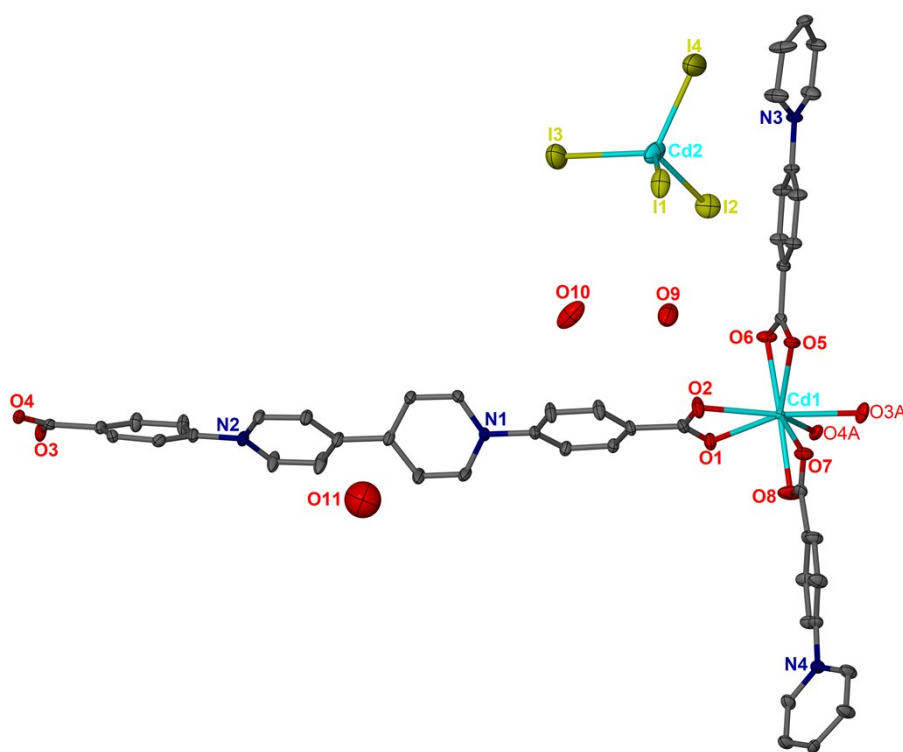
7 ^dHOMO = LUMO - E_g .

1 **Table S5.** FT-IR spectrum signals and assignment for Cd-CCP.^{S15}

Band (cm ⁻¹)	Assignment
3116 (w)	O–H stretching in water
3051 (w)	C–H stretching from pyridinium rings
1633 (s)	pyridinium ring stretching
1611 (s)	C=N/C=C stretching from pyridinium rings
1574 (m)	Asymmetric stretching vibration of the carboxylate group
1535 (m)	Aromatic C–C ring stretching
1486 (w)	Aromatic C–C ring stretching
1435 (m)	Aromatic C–C ring stretching
1389 (s)	Symmetric stretching vibration of the carboxylate group
1300 (w)	Aromatic ring stretching
1248 (w)	C–C stretching
1221 (w)	C–pyridinium ring breathing
1039 (w)	C–pyridinium ring breathing
1020 (w)	Aromatic C–H in plane bending
1006 (w)	Aromatic ring stretching
852 (m)	Aromatic ring stretching
830 (m)	Aromatic C–H pyridinium ring substitution bands
784 (s)	Aromatic ring stretching

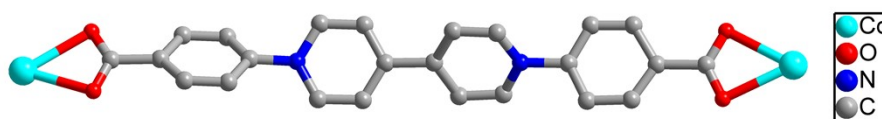
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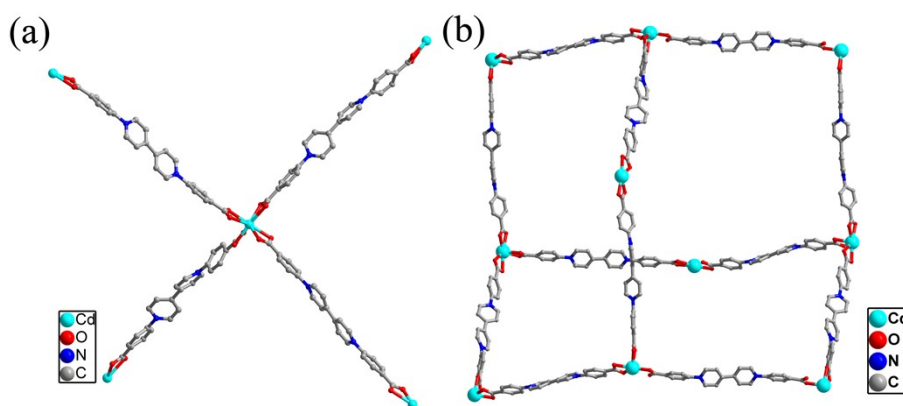
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2 **Figure S1** Asymmetric unit of **Cd-CCP** (all atoms with displacement ellipsoids at the 30% probability level;
 3 symmetry codes: A, $2+x$, $3/2-y$, $1/2+z$). Hydrogen atoms are omitted for clarity.



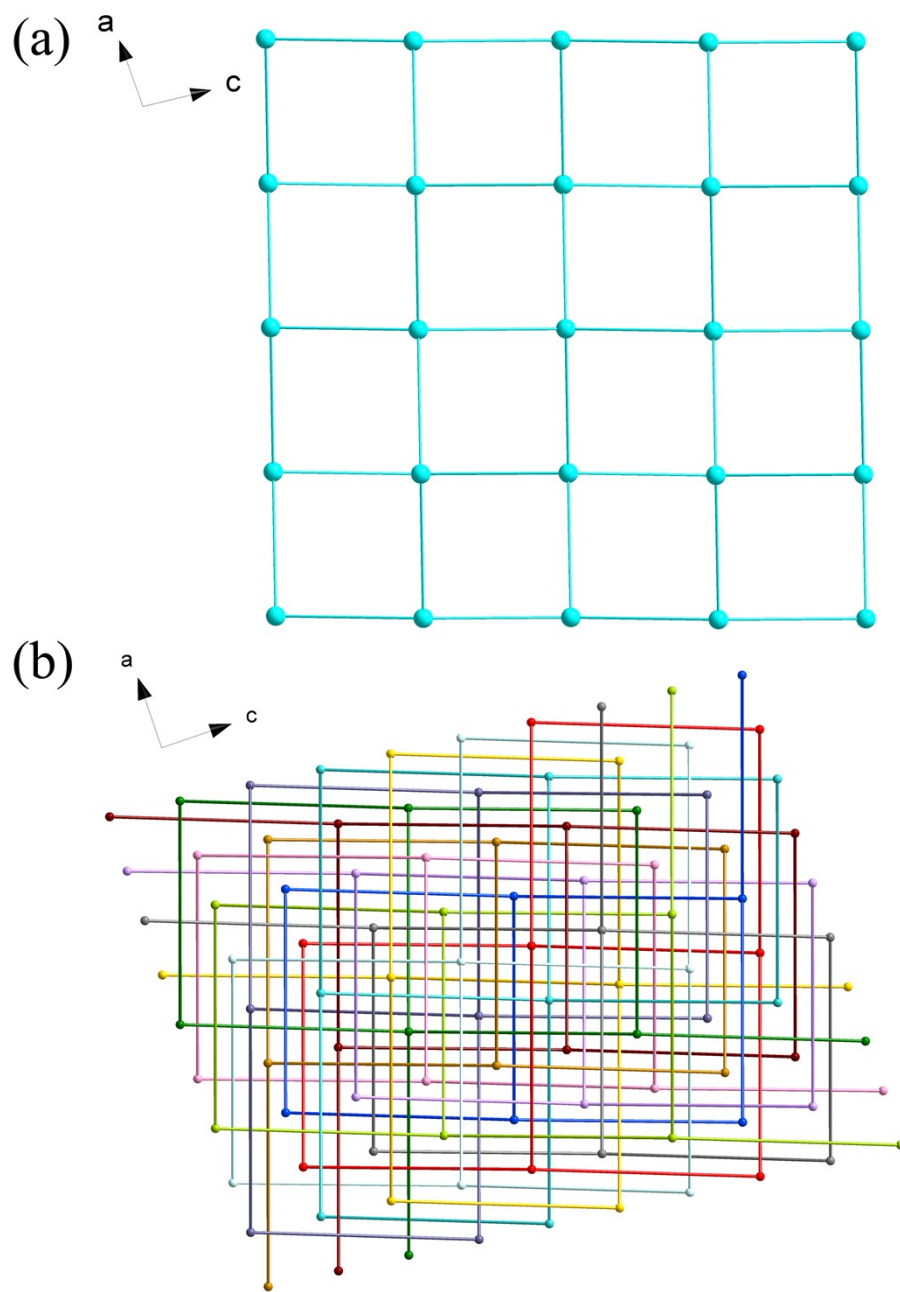
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5 **Figure S2** Coordination mode of Harris notation $[2.1_11_1_21_2]$ for the deprotonated bcbp ligand in **Cd-CCP**.

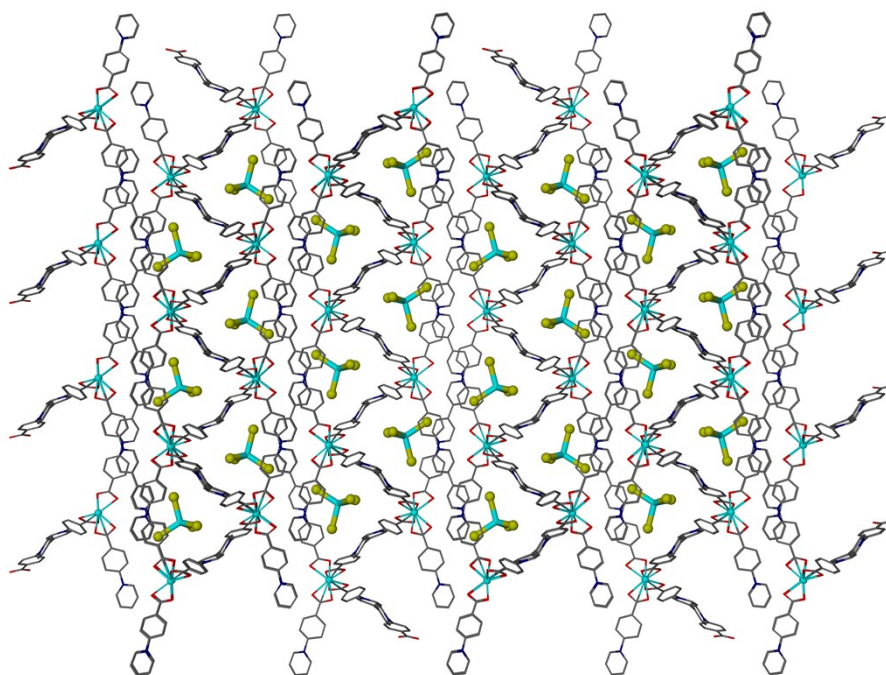


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7 **Figure S3** (a) View of the coordination mode of Cd(II) ion in **Cd-CCP**. (b) Representation of the diamondoid cage in
 8 **Cd-CCP**.



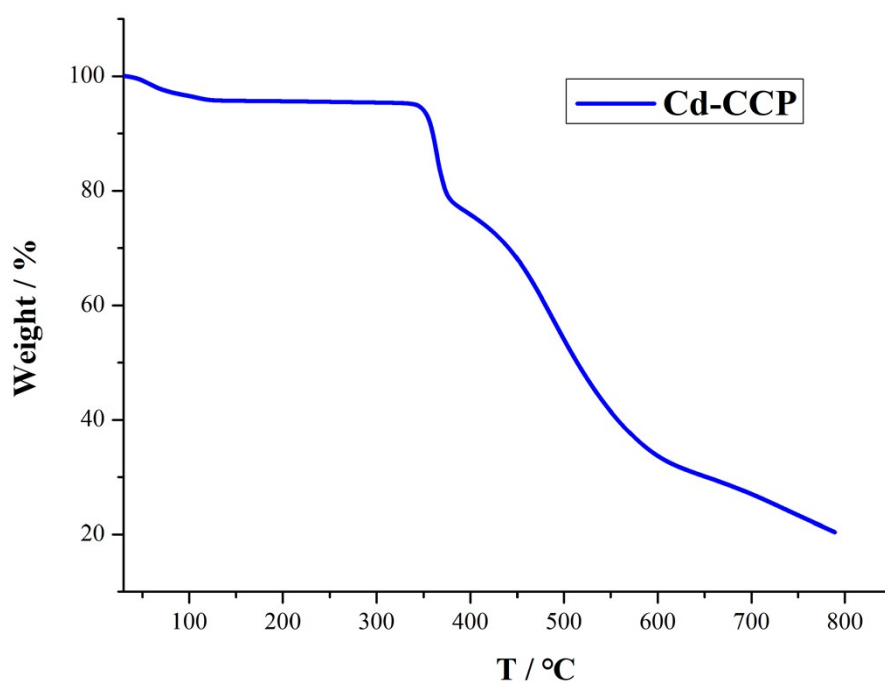
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2 **Figure S4** (a) Single topological 3D **dia** net of **Cd-CCP** viewed from b axis; (b) Thirteen-fold interpenetrated
3 network of **Cd-CCP** viewed from b axis.



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2 **Figure S5** Presentation of 3D cationic framework of **Cd-CCP** viewing along *a* axis, with triangular channels
3 occupied with [CdI₄]²⁻ anions.

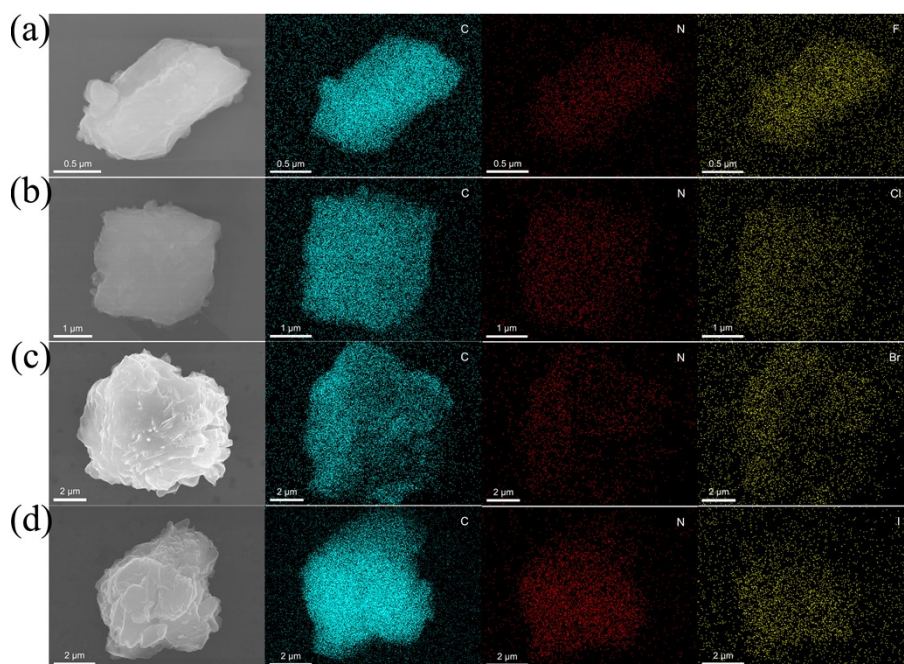
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6 **Figure S6** TGA curve of **Cd-CCP**. The thermogravimetric analysis indicates three lattice water molecules were
7 gradually released during 30-105 °C with 3.64% weight loss (calcd 3.42%). And its framework is stable up to 348 °C,
8 after which the framework begins to collapse.

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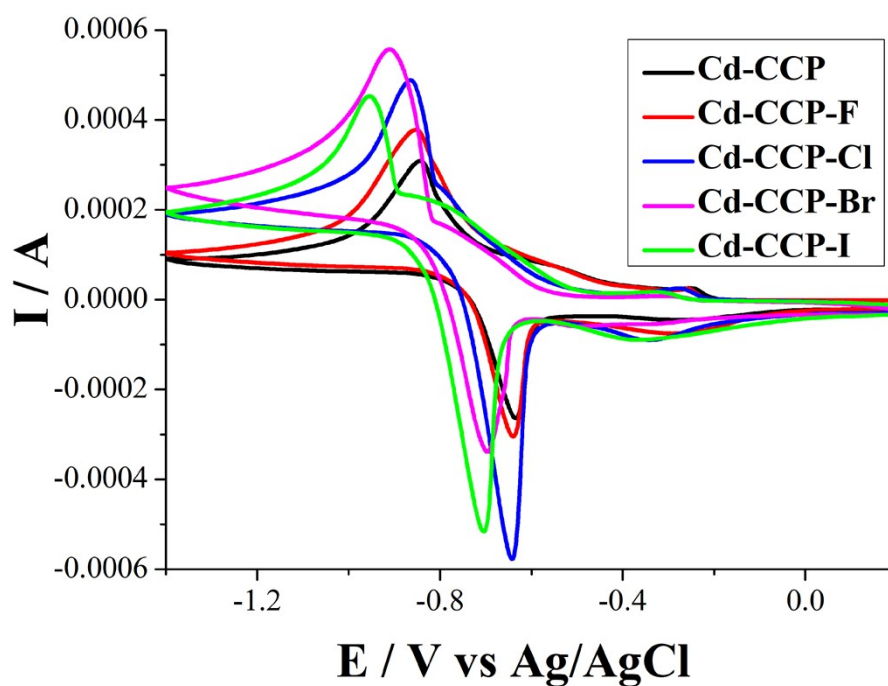
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2 **Figure S7** SEM images and EDS mappings of Cd-CCP-F (a), Cd-CCP-Cl (b), Cd-CCP-Br (c), and Cd-CCP-I (d).

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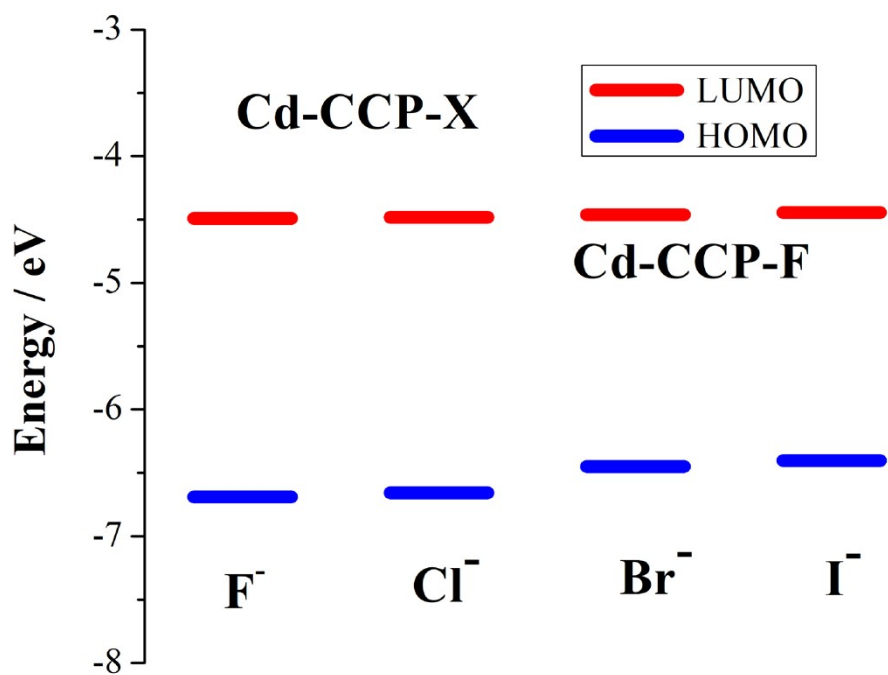
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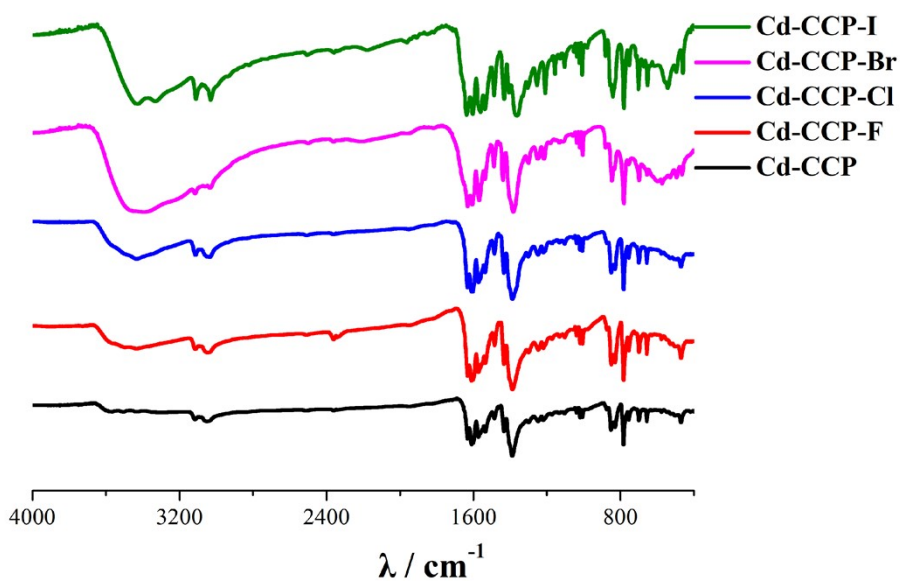
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7 **Figure S8** Cyclic voltammograms of Cd-CCP and Cd-CCP-X with the corresponding sodium salts as supporting
8 electrolytes (1 M, NaF, NaF, NaCl, NaBr, and NaI). Scan rate $\nu = 50 \text{ mV s}^{-1}$.



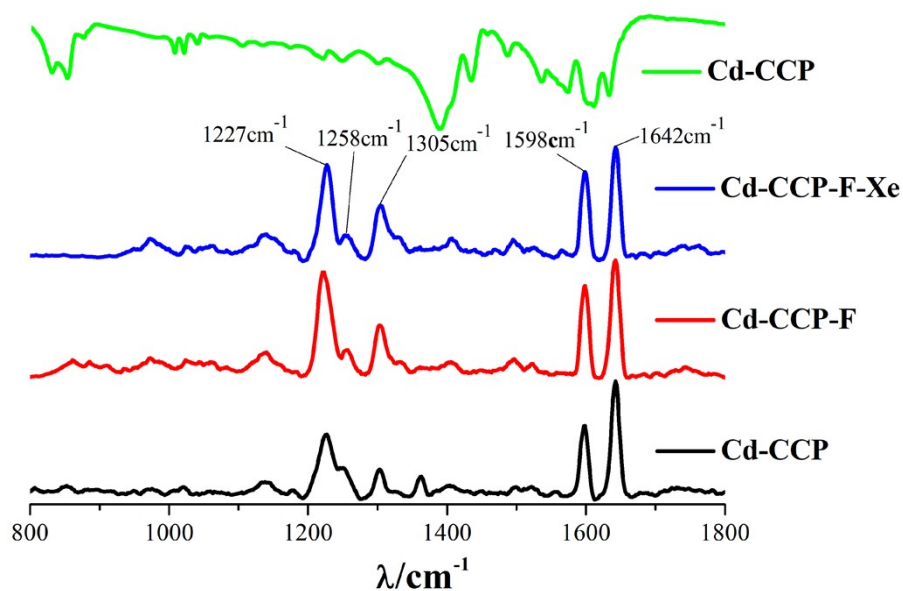
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2 **Figure S9** HOMO-LUMO energy levels for Cd-CCP-X.

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8 **Figure S10** FT-IR spectra of Cd-CCP, Cd-CCP-F, Cd-CCP-Cl, Cd-CCP-Br, and Cd-CCP-I.

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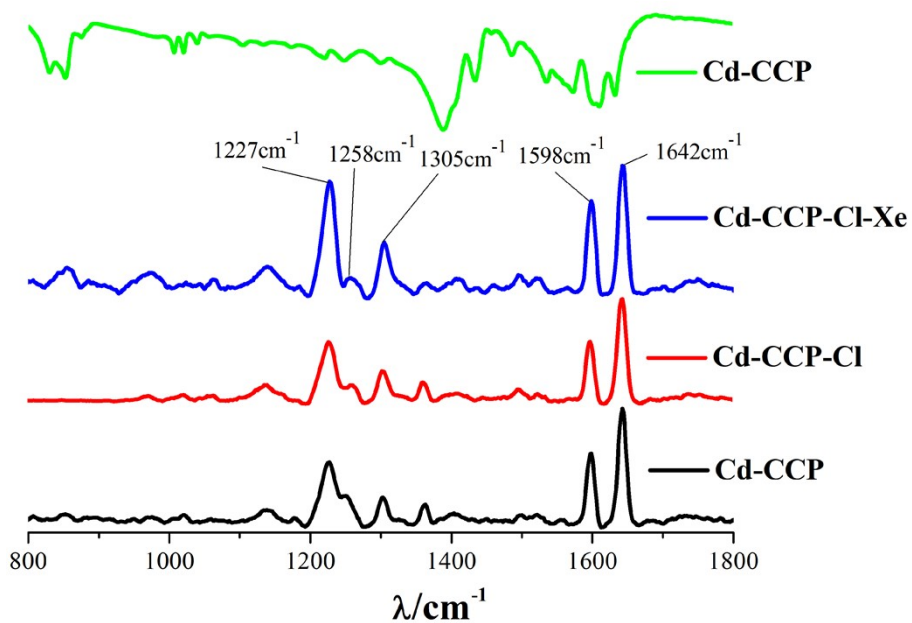
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2 **Figure S11** FT-IR spectrum of Cd-CCP (green), Raman spectra of Cd-CCP (black), Cd-CCP-F (red) and Cd-CCP-
 3 F-Xe (blue).

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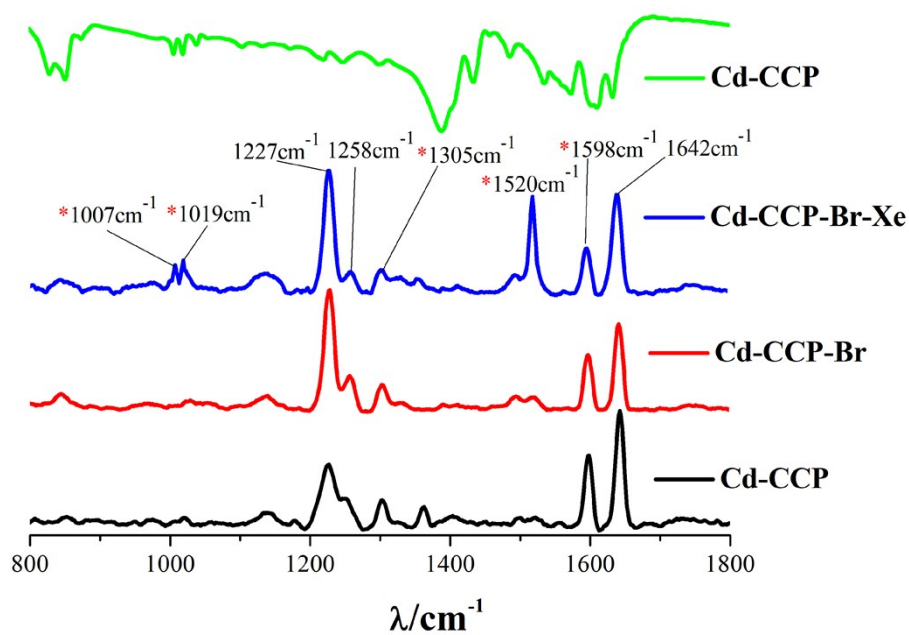
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8 **Figure S12** FT-IR spectrum of Cd-CCP (green), Raman spectra of Cd-CCP (black), Cd-CCP-Cl (red) and Cd-
 9 CCP-Cl-Xe (blue).

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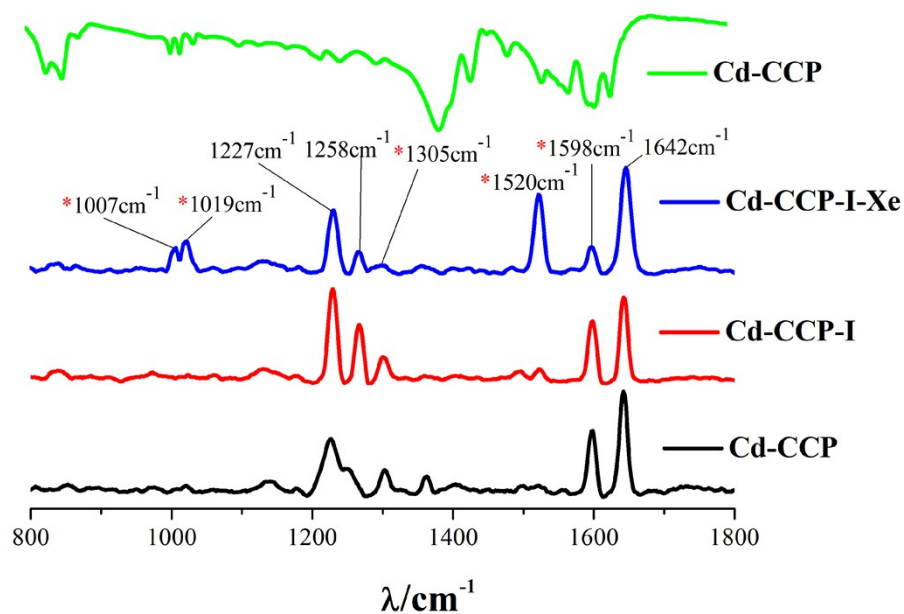
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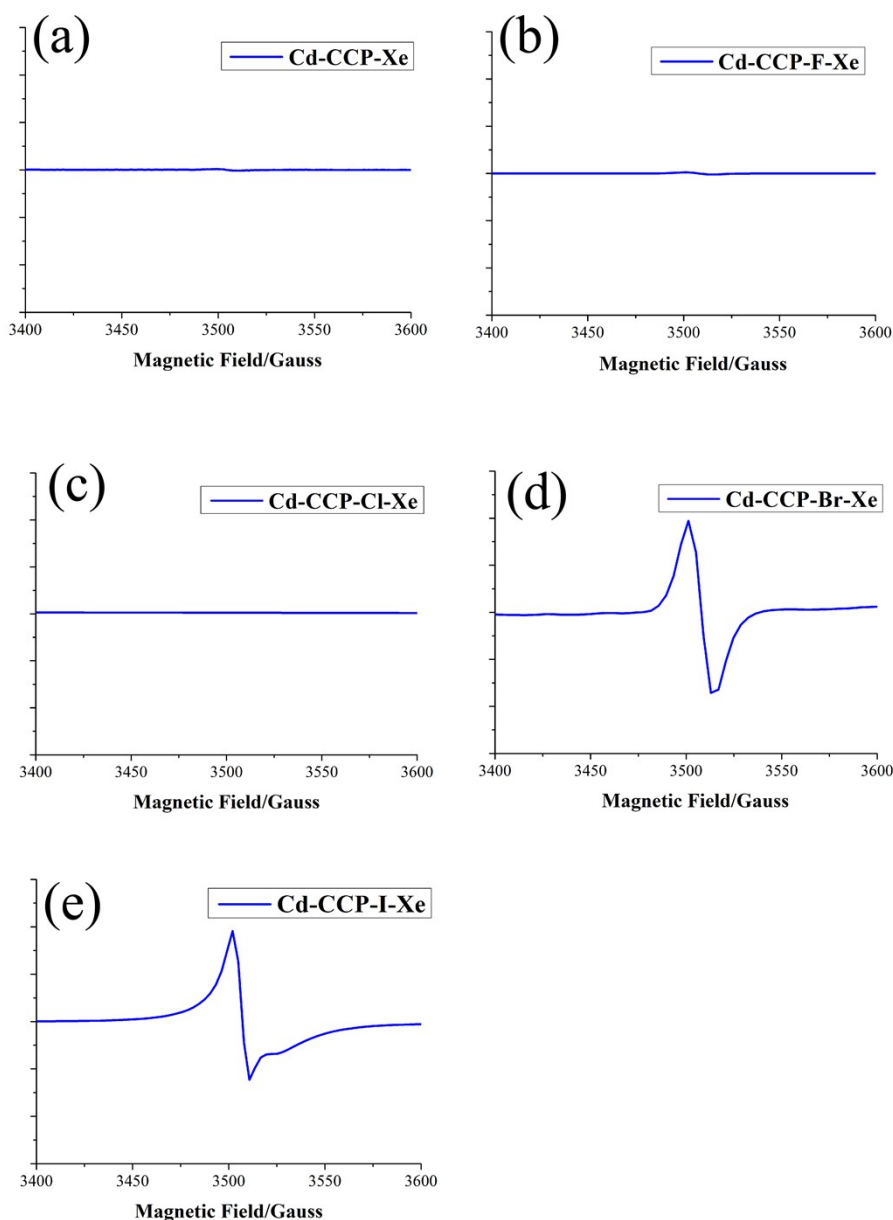
2 **Figure S13** FT-IR spectrum of **Cd-CCP** (green), Raman spectra of **Cd-CCP** (black), **Cd-CCP-Br** (red) and **Cd-**
 3 **CCP-Br-Xe** (blue).

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6 **Figure S14** FT-IR spectrum of **Cd-CCP** (green), Raman spectra of **Cd-CCP** (black), **Cd-CCP-I** (red) and **Cd-CCP-**
 7 **I-Xe** (blue).



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 2 **Figure S15** EPR spectra of Cd-CCP-Xe (a), Cd-CCP-F-Xe (b), Cd-CCP-Cl-Xe (c), Cd-CCP-Br-Xe (d) and Cd-
 3 CCP-I-Xe (e).

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5 References:

- 6 S1. (a) M. Leroux, N. Mercier, M. Allain, M. C. Dul, J. Dittmer, A. H. Kassiba, J. P. Bellat, G. Weber and I.
 7 Bezverkhyy, *Inorg. Chem.*, 2016, **55**, 8587; (b) Z. Y. Li, W. Y. Cai, X. M. Yang, A. L. Zhou, Y. Zhu, H. Wang, X.
 8 Zhou, K. C. Xiong, Q. F. Zhang and Y. L. Gai, *Cryst. Growth Des.*, 2020, **20**, 3466.
 9 S2. G. M. Sheldrick, *Acta Crystallogr. Sect. C-Struct. Chem.*, 2015, **71**, 3.
 10 S3 C. Zhang, Y. Liu, L. Sun, H. Shi, C. Shi, Z. Liang and J. Li, *Chem. - Eur. J.*, 2018, **24**, 2718.
 11 S4 J. K. Sun, P. Wang, Q. X. Yao, Y. J. Chen, Z. H. Li, Y. F. Zhang, L. M. Wu and J. Zhang, *J. Mater. Chem.*,
 12 2012, **22**, 12212.

- 1 S5 Z. Li, W. Cai, X. Yang, A. Zhou, Y. Zhu, H. Wang, X. Zhou, K. Xiong, Q. Zhang and Y. Gai, *Cryst. Growth*
2 *Des.*, 2020, **20**, 3466.
- 3 S6 H. Y. Li, J. Xu, L. K. Li, X. S. Du, F. A. Li, H. Xu and S. Q. Zang, *Cryst. Growth Des.*, 2017, **17**, 6311.
- 4 S7 H. Y. Li, H. Xu, S. Q. Zang and T. C. W. Mak, *Chem. Commun.*, 2016, **52**, 525.
- 5 S8 H. Y. Li, Y. L. Wei, X. Y. Dong, S. Q. Zang and T. C. W. Mak, *Chem. Mater.*, 2015, **27**, 1327.
- 6 S9 M. Leroux, N. Mercier, M. Allain, M. C. Dul, J. Dittmer, A. H. Kassiba, J. P. Bellat, G. Weber and I.
7 Bezverkhyy, *Inorg. Chem.*, 2016, **55**, 8587.
- 8 S10 J. J. Liu, Y. F. Guan, M. J. Lin, C. C. Huang and W. X. Dai, *Cryst. Growth Des.*, 2016, **16**, 2836.
- 9 S11 X. Yang, C. Yan, Z. Li, X. Li, Q. Yu, T. Sang, Y. Gai, Q. Zhang and K. Xiong, *Inorg. Chem.*, 2021, **60**, 5988.
- 10 S12 Y. Q. Sun, F. Wan, X. X. Li, J. Lin, T. Wu, S. T. Zheng and X. Bu, *Chem. Commun.*, 2016, **52**, 10125.
- 11 S13 (a) P. Yu, L. M. Wu, L. J. Zhou and L. Chen, *J. Am. Chem. Soc.*, 2014, **136**, 480; (b) P. Yu, L. J. Zhou and L.
12 Chen, *J. Am. Chem. Soc.*, 2012, **134**, 2227.
- 13 S14 C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale and G. C. Bazan, *Adv. Mater.*, 2011, **23**, 2367.
- 14 S15 H. L. Nguyen, F. Gandara, H. Furukawa, T. L. H. Doan, K. E. Cordova and O. M. Yaghi, *J. Am. Chem. Soc.*,
15 2016, **138**, 4330.