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# New luminescent porous coordination polymers with acylamide-decorated linker for anions recognition and reversible I<sub>2</sub> accommodation

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A series of new luminescent porous coordination polymers (PCPs) with acylamide groups have been prepared. Single crystal X-ray analyses revealed that they gave isomorphous structures and displayed significant 1D quadrilateral channels. The luminescent properties of NTU-2 and NTU-3 in solid state have been studied in detail, and which demonstrated that both of them are an ideal luminescence sensor for selective probing Cu<sup>2+</sup> ions with high quenching effect coefficients (211.2 and 212.8 M<sup>-1</sup>). Meanwhile, NTU-2, NTU-3 and NTU-4 show rapid and reversible I<sub>2</sub> accommodation property.

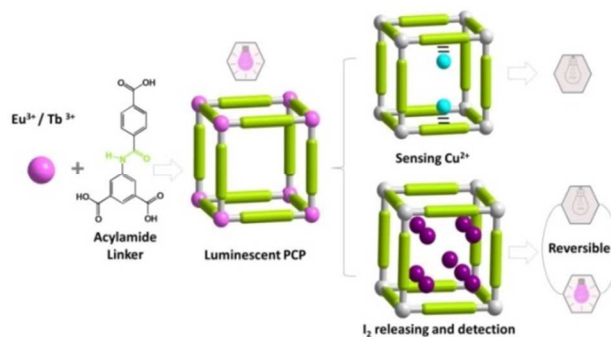
During the past few years, porous coordination polymers (PCPs) have attracted intensive attention for their promising applications in catalysis,<sup>1</sup> gas storage,<sup>2</sup> separation,<sup>3</sup> nonlinear optics,<sup>4</sup> magnetism,<sup>5</sup> and luminescence.<sup>6</sup> They can be readily assembled from the designed ligands and metal ions/clusters. In terms of their high porosity, PCP materials demonstrate incomparable advantages than that of their competitors, since their pore types and sizes can be easily and systematically adjusted through different coordination matrix of ligands and metal ions.<sup>7</sup> More importantly, their functional pore-surface can be tuned by changing different metal centers,<sup>8</sup> inserting functional groups on involved ligands,<sup>9</sup> and/or immobilizing well-selected moieties.<sup>10</sup>

With unique advantages of sharp, nonoverlapping, and easily identifiable emission bands of intra-4f transitions,<sup>11</sup> lanthanide-(III) ions, such as Eu<sup>3+</sup> and Tb<sup>3+</sup>, attracted a great deal of scientific interests for addressing the challenges in engineering of luminescent PCP materials.<sup>12</sup> Because, to certain extent, they can show long luminescence lifetimes, high luminescence quantum yield, notable fluorescence monochromaticity, characteristic sharp emission. More interestingly, the luminescence based recognition for small molecules or metal ions became a hot research topic in very recent. Thus, several methods have been pursued to achieve this goal, such as introducing hydrogen donor/accepters, decorating Lewis basic and acidic sites, and exposing open metal sites. However, among them, Lewis basic sites were usually chosen for sensing metal ions, since the reduced antenna efficiency of luminescent center by involving the binding of metal ions and open nitrogen atoms.<sup>6b,13</sup> However, it still remains a challenge for rational “design” and “control” of tailor-made Ln-PCPs with open nitrogen atoms, as the difficulty of getting open N sites after the coordination assembly, especially toward Ln(III) ions with high coordination number (usually 8 or 9 or 12).

In addition, recent studies showed that high porous PCPs

were believed as effective adsorbents for drug delivery and dyes encapsulating.<sup>14</sup> The research into iodine on porous materials also becomes an active field, since their high potential capabilities for enriching and releasing of gaseous and volatile radioactive nuclides.<sup>15</sup> Iodine, as a very important element, is primarily used in nutrition for human life, and industry for production of acetic acid and certain polymers. However, the natural source of iodine is scarce, and moreover, iodine is a bluish-black solid appearing to sublimate into a noxious gas. Therefore, highly efficient iodine storage and controllable releasing are urgently required.<sup>15a,16</sup>

We are interested in construction of porous coordination polymers with interesting properties based upon multidentate ligands.<sup>3d, 7b, 10a, 10b, 17</sup> Herein, taken the above consideration in mind, we believed that the coordination assembly of a ligand with Lewis basic site and luminescent node is a effective method to construct the PCPs with the above expected functions. We choose a relatively small multidentate ligand with inserted-acylamide group, 5-(4-carboxy-benzoylamino)-isophthalic acid (H<sub>3</sub>L), and Ln(NO<sub>3</sub>)<sub>3</sub> (Ln = Eu<sup>3+</sup>, Tb<sup>3+</sup> and Nd<sup>3+</sup>) to synthesize PCPs ([EuL(H<sub>2</sub>O)]-Guest (Nanjing Tech University: NTU-2), [TbL(H<sub>2</sub>O)]-Guest (NTU-3), [Nd<sub>4</sub>L<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>]-Guest (NTU-4) by solvothermal synthesis. The generated NTU-2 and NTU-3 are high sensitive to Cu<sup>2+</sup> ions, and a certain degree of luminescence quenching to Mn<sup>2+</sup>, Ni<sup>2+</sup> and Co<sup>2+</sup>, but not to Zn<sup>2+</sup>, Cd<sup>2+</sup>, and Na<sup>+</sup>. In addition, NTU-2, NTU-3 and NTU-4 show rapid and reversible I<sub>2</sub> accommodation property.



**Scheme 1** New route for design PCPs with multi-functions.

Hydrothermal reactions of tricarboxylate ligands (H<sub>3</sub>L) and Ln(NO<sub>3</sub>)<sub>3</sub> (Ln = Eu<sup>3+</sup>, Tb<sup>3+</sup> and Nd<sup>3+</sup>) at 110°C for two days afforded needle-like crystals of NTU-2, NTU-3 and NTU-4, respectively. Single crystal X-ray diffraction analyses reveal that NTU-2 and NTU-3, formulated as [LnL(H<sub>2</sub>O)]-Guest, crystallize in *F*<sub>ddd</sub> space group with two half Eu<sup>3+</sup> ions, two half coordinated water molecules and one L<sup>3-</sup> ligand in an

asymmetric unit. Each  $\text{Eu}^{3+}$  ion is coordinated in decahedral geometry with seven O atoms from six different ligands and a water molecule. The ligands act as  $\mu_6$ -bridge linking six  $\text{Eu}^{3+}$  ions (Fig. 1a). The adjacent  $\text{Eu}^{3+}$  ions are bridged by three carboxylate groups, leading to an inorganic helical chain with a 14.5 Å screw pitch along  $a$  axis (Fig. 2a). Each inorganic helical chain was linked by  $\text{L}^{3-}$  ligands to form the 3D framework with 1D quadrilateral channels ( $12 \times 13 \text{ \AA}^2$ ) (Fig. 2b and 2c).

NTU-4 crystallizes in space group  $P-1$  with the parameters of  $a = 14.331(2) \text{ \AA}$ ,  $b = 23.7137(15) \text{ \AA}$ ,  $c = 25.4868(14) \text{ \AA}$ ,  $\alpha = 86.039(2)^\circ$ ,  $\beta = 74.929(3)^\circ$  and  $\gamma = 74.441(2)^\circ$ . One asymmetric unit includes four  $\text{L}^{3-}$  ligands, four  $\text{Eu}^{3+}$  ions and four coordinated water molecules. In this structure, the coordination geometries of Nd1, Nd2 and Nd4 ions were also decahedra, but Nd3 possesses the dodecahedral geometry. Thus, the ligands act as  $\mu_6$ - and  $\mu_7$ -bridge linking six  $\text{Nd}^{3+}$  ions (Fig. 1c). The generated inorganic helical chain linked by  $\text{L}^{3-}$  ligands to form the 3D framework with very similar 1D channels as that of NTU-2 and NTU-3 (Fig. 2 and S8).

In order to find the reasons of changed coordinated geometries, we compared the Ln-O distances of those three structures. The Nd-O bond distances (Nd-O: 2.341-2.863 Å) are a little longer than that of Eu-O and Tb-O (Eu-O: 2.286-2.498 Å; Tb-O: 2.300-2.419 Å), since the factor of decreased ion radius in lanthanide elements. However, even the

coordination geometries of them changed, the potential solvent accessible volumes, calculated by PLATON<sup>18</sup>, of them are as high as 66% to 67% (NTU-2: 66.9%; NTU-3: 67.0% and NTU-4: 66.7%). In addition, the window apertures of the frameworks reached to  $12 \times 13 \text{ \AA}^2$  that are large enough for trapping metal ions or iodine species. Furthermore, enriched open acylamide units lined on the interior of channels in all of them, reflecting the potential sensing functions based on their luminescent metal centers.

The powder X-ray diffraction (PXRD) showed high phase purity and crystallinity of them. The thermal gravimetric analyses showed that the thermal decomposition of those three structures started around 450°C under  $\text{N}_2$  atmosphere.

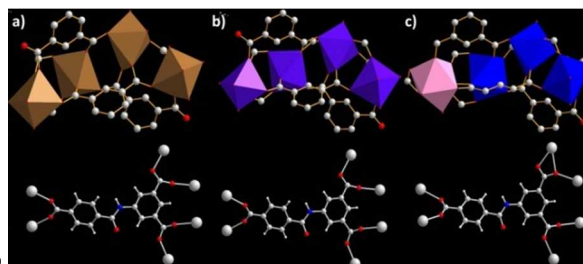


Fig. 1 The view of changed clusters and ligands coordination in NTU-2 (a), NTU-3 (b) and NTU-4 (c) (decahedra: brown, purple and blue; dodecahedra: pink).

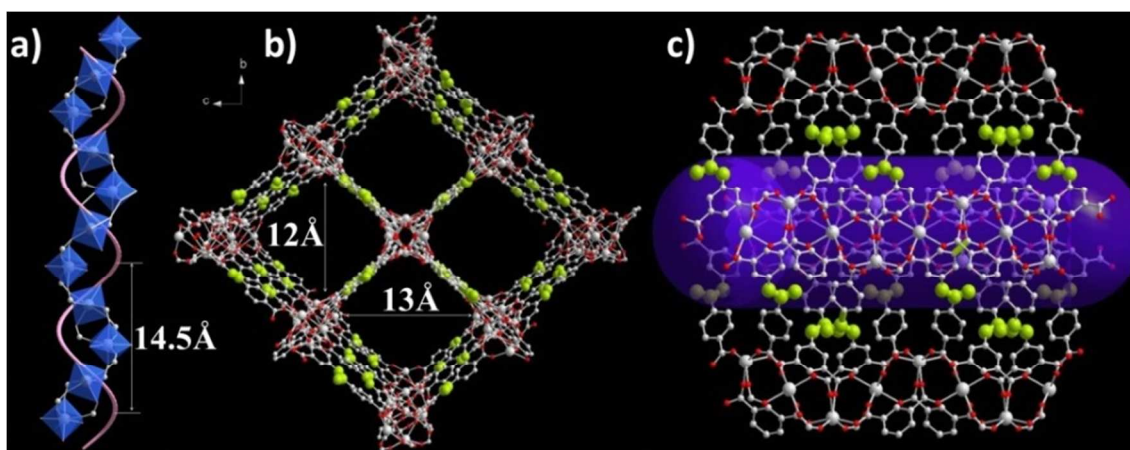


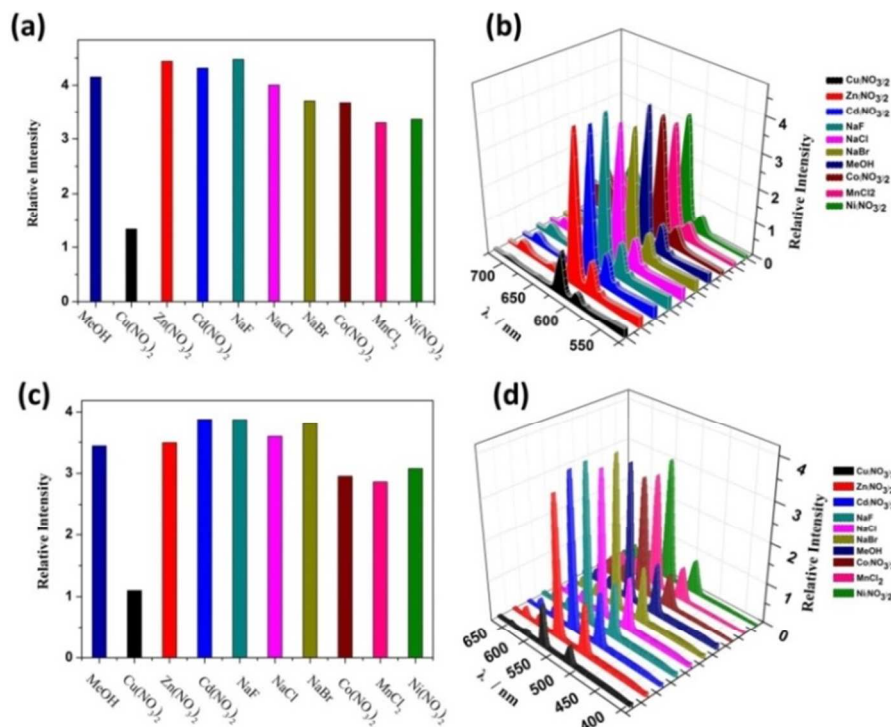
Fig. 2 The structure of NTU-2: the inorganic helical chain (a); packing view of 1D quadrilateral nanotube along  $a$  axis (b), packing view of 1D quadrilateral nanotube along  $b$  axis. The modified acylamide groups were highlighted by green color.

Due to the high porosities, luminescent nodes and enriched Lewis basic sites, NTU-2 and NTU-3 demonstrate the possibility for metal ions sensing. The methanol-exchanged NTU-2 and NTU-3 were immersed in the methanol solution that containing different metal salts ( $\text{M}(\text{NO}_3)_2$ ;  $\text{M} = \text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ;  $\text{MnCl}_2$ ;  $\text{NaX}$ ;  $\text{X} = \text{F}^{-1}$ ,  $\text{Cl}^{-1}$ ,  $\text{Br}^{-1}$ ) to form metal ion incorporated  $\text{M@NTU-2}$  and  $\text{M@NTU-3}$  for their luminescence studies. The PXRD patterns showed that both of them kept the integrity of their frameworks, even after loading different metal salts. The excitation and photoluminescence (PL) spectra of these series of samples are shown in Figure S9. Comparing these spectra, the adsorption of  $\text{L}^{3-}$  ligand should be ascribed as the excitation peak around 349 nm, and additionally, the  $f-f$  transitions of  $\text{Eu}^{3+}$  ion were

well revealed by the peak at 395 nm. Similarly, NTU-2 exhibits the characteristic transitions of the frameworks with  $\text{Eu}^{3+}$  ions at 590, 616, 652 and 702 nm, which are ascribed to the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$ ,  $^5\text{D}_0 \rightarrow ^7\text{F}_2$ ,  $^5\text{D}_0 \rightarrow ^7\text{F}_3$  and  $^5\text{D}_0 \rightarrow ^7\text{F}_4$  transitions. Meanwhile, NTU-3 shows the typical luminescent transitions of  $\text{Tb}^{3+}$  ion at 488, 543, 582 and 619 nm. More interestingly, their luminescent intensities can be influenced by different incorporated metal salts. The  $\text{Cu}^{2+}$  ion shows a significant quenching effect on the luminescence intensity of NTU-2 and NTU-3, meanwhile, the  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  ions with different electron configurations imposed a certain degree of luminescence quenching.<sup>19</sup> In contrast, other metal ions show a negligible effect on luminescence intensity. This quenching effect of  $\text{Cu}^{2+}$  ions in NTU-2 and NTU-3 result from the

affinity of acylamide toward  $\text{Cu}^{2+}$ , and as a result, decreases the efficiency of energy transfer from acylamide-decorated linker to  $f-f$  transitions of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  centers.<sup>6b, 13</sup> To further examine the sensing sensitivity for  $\text{Cu}^{2+}$  ion, NTU-2 and NTU-3 were immersed in methanol solution with gradually decreased  $\text{Cu}^{2+}$  concentration from  $10^{-1}$  to  $10^{-3}$  mol·L<sup>-1</sup>. Noteworthy, the luminescence intensity of

$\text{Cu}@\text{NTU-2}$  and  $\text{Cu}@\text{NTU-3}$  are heavily relied on the concentration of  $\text{Cu}^{2+}$  ion.<sup>20</sup> As shown in Fig. S16 and S17, nearly 30% of the emission intensity was decreased when  $\text{Cu}^{2+}$  ion concentration was  $10^{-3}$  mol·L<sup>-1</sup> and ~85% was quenched when the concentration increased to  $10^{-1}$  mol·L<sup>-1</sup>. This observation was confirmed by N1s X-ray photoelectron spectroscopy (XPS) studies (Fig. S18).



**Fig. 3** PL spectra of M@NTU-2 and M@NTU-3: comparison of the luminescence intensity of the peak at 616 nm for M@NTU-2 (a) and 546 nm for M@NTU-3 (c), the full PL spectra of M@NTU-2 (b) and M@NTU-3 (d).

For further understanding these observations, quenching effects of these two PCPs were calculated by the Stern-Volmer equation ( $I_0 / I = 1 + K_{sv} [M]$ ). By comparing the quenching effect coefficients ( $K_{sv}$ ) in table 1, we found that the  $K_{sv}$  for  $\text{Cu}^{2+}$  in NTU-2 and NTU-3 reached to 211.2 and 212.8 M<sup>-1</sup>, revealing high sensitive for  $\text{Cu}^{2+}$  sensing. More over, those values are larger than that of quenching effect coefficients of the structure of [Eu(pdc)<sub>1.5</sub>] with lewis basic pyridyl sites (89.4 M<sup>-1</sup>).<sup>6b</sup>

Table 1 Quenching effect coefficients ( $K_{sv}$ ) of different metal salt on the luminescence intensity of M@PCPs.

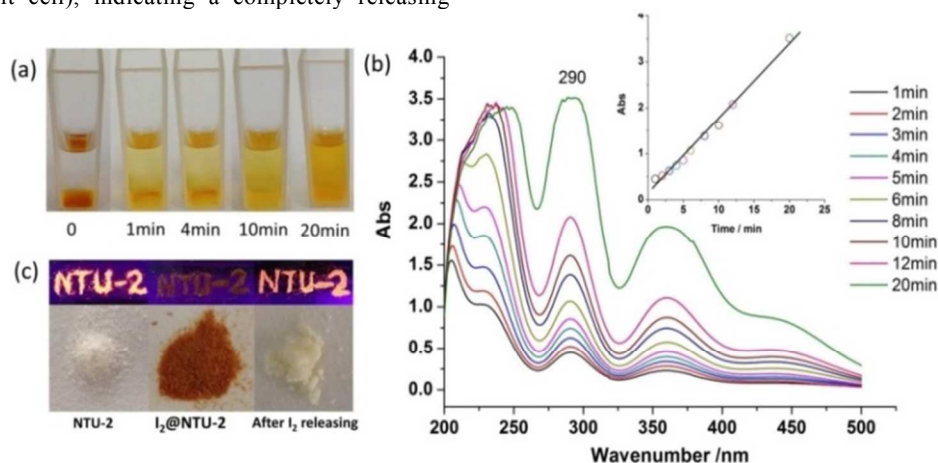
Metal ion	$K_{sv}$ [M <sup>-1</sup> ]	$K_{sv}$ [M <sup>-1</sup> ]
	M@NTU-2	M@NTU-3
$\text{Cu}^{2+} / \text{NO}_3^-$	211.2	212.8
$\text{Zn}^{2+} / \text{NO}_3^-$	-6.5	-1.5
$\text{Cd}^{2+} / \text{NO}_3^-$	-3.8	-11.3
$\text{Na}^+ / \text{F}^-$	-7.2	-11.2
$\text{Na}^+ / \text{Cl}^-$	3.7	-4.3
$\text{Na}^+ / \text{Br}^-$	11.8	-9.7
$\text{Co}^{2+} / \text{NO}_3^-$	12.9	16.4
$\text{Ni}^{2+} / \text{NO}_3^-$	26.1	11.8
$\text{Mn}^{2+} / \text{Cl}^-$	23.7	20.1

Bearing the unique structure characteristics, we then

investigated the accommodation property of iodine ( $\text{I}_2$ ) on NTU-2, NTU-3 and NTU-4.  $\text{I}_2$  is known as an electron acceptor and its kinetic diameter is 5.2 Å, which is smaller than the window aperture of the frameworks. After soaking the hexane-exchanged PCPs in  $\text{I}_2$  solution of hexane for 24 h. we got the samples of  $\text{I}_2@\text{PCPs}$ . For NTU-2, the color of it changed from white to deep yellow, and while the luminescence of it was quenched. This is because iodine as heavy atom is well known to quench the fluorescence emission. In addition, the ESR spectra of  $\text{I}_2@\text{NTU-2}$  at ambient and UV light demonstrated that the luminescence quenching is clearly caused by  $\text{I}_2$ , but not by the radical species (Fig. S23).<sup>21</sup> Thus, all of the above observations suggested that  $\text{I}_2$  was captured by the framework successfully. The sample of  $\text{I}_2@\text{NTU-2}$  was evacuated at room temperature to remove  $\text{I}_2$  attached on the crystal surfaces. Then, the TGA profile of  $\text{I}_2@\text{NTU-2}$  shows a 21% weight loss in the temperature range of 50 - 160 °C and each unit cell in NTU-2 can accommodate about 16.6  $\text{I}_2$  molecules (Fig. S19). In order to confirm this behavior, the air dried  $\text{I}_2@\text{NTU-2}$  was soaked into dry ethanol, the color of the crystals changed gradually from deep yellow to colorless, and the color of the ethanol solution gradually changed to yellow from colorless within 20 mins (Fig. 4a). To further study the process of  $\text{I}_2$  releasing, the

*in-situ* UV-spectra were collected at room temperature (Fig. 4b). The releasing rate of I<sub>2</sub> kept as a constant, thus, the intensity of the absorbance increased linearly with time, especially for the peaks at 290 and 360 nm. Compared with the standard line of I<sub>2</sub> solution at 290 nm, we found that the concentration of I<sub>2</sub> solution reached to 1042 mg·L<sup>-1</sup> (14.6 I<sub>2</sub> molecules per unit cell), indicating a completely releasing

during 20 mins. Therefore, I<sub>2</sub> sorption process is reversible in NTU-2, and which was clearly confirmed again by the photos of excited samples of NTU-2 (Fig. 4c). In addition, the I<sub>2</sub> accommodation behaviors of NTU-3 and NTU-4 are almost same as that of NTU-2 (Fig S21 and 22). Briefly, all of those three PCPs have potential for enriching and releasing I<sub>2</sub>.



**Fig. 4** Photographs showing the colour change of I<sub>2</sub> releasing in ethanol (a); the UV spectra of I<sub>2</sub>@NTU-2 releasing (b); The photographs showing the colour change of NTU-2 before and after I<sub>2</sub> accommodating and releasing.

In summary, by employing a well-designed ligand with acylamide groups, we have constructed three new frameworks with significant 1D quadrilateral channels. Ions sensing experiments and quenching effect coefficients (211.2 and 212.8 M<sup>-1</sup>) showed that NTU-2 and NTU-3 are ideal luminescence platforms for selective probing Cu<sup>2+</sup> ions. Meanwhile, NTU-2, NTU-3 and NTU-4 demonstrated rapid and reversible I<sub>2</sub> accommodation property. Thus, we have found a new system based on acylamide sites and luminescent nodes for metal ions recognition, and also for iodine accommodation and sensing. Our further efforts will be focused on the optimization of the structure of porous luminescent PCPs for achieving better property, and we also expect that luminescent PCP-based device will be constructed for many practical applications.

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## Notes and references

State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical engineering, Nanjing Tech University, Nanjing, 210009, China E-mail: duanjingui@njtech.edu.cn †Electronic Supplementary Information (ESI) available: PXRD, TGA, IR, XPS and lifetimes for NTU-2, NTU-3 and NTU-4. See DOI: 10.1039/b000000x/

‡ Fluorescence Measurements: the anion incorporated PCPs were prepared by introducing ~20 mg of methanol-exchanged samples into 10 ml of methanol solution (10<sup>-2</sup> mol·L<sup>-1</sup>) with different metal salts (M(NO<sub>3</sub>)<sub>2</sub>; M = Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>; MnCl<sub>2</sub>; NaX; X = F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>). Then the samples were collected by filtration and dried for 2 h at 100 °C. The PL properties were investigated in the solid state at room temperature. PL spectra were recorded on a Hitachi 850 fluorescence spectrophotometer.

The photomultiplier tube (PMT) voltage was 425 V, the scan speed was 480 nm/min. Stern-Volmer equation:  $I_0/I = 1 + K_{SV}[M]$ : The values  $I_0$  and  $I$  are the luminescence intensity of metal-ion-free PCP and metal-ion-incorporated PCP, respectively,  $[M]$  is the molar concentration of the metal ion, and  $K_{SV}$  is the quenching effect coefficient of the metal ion.

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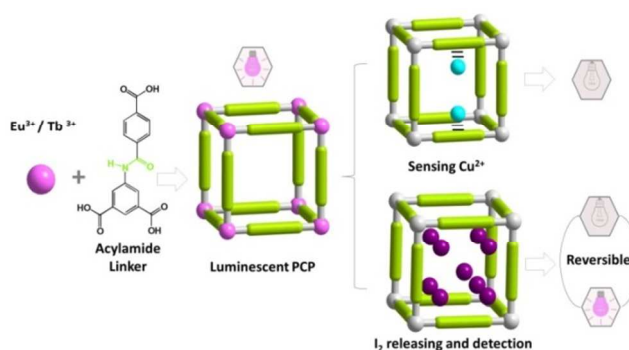
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# New luminescent porous coordination polymers with acylamide-decorated linker for anions recognition and reversible I<sub>2</sub> accommodation

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A new series of porous coordination polymers with significant 1D quadrilateral channels and open acylamide groups demonstrate good potential for selective probing Cu<sup>2+</sup> ions (quenching effect coefficients, NTU-2: 211.2 M<sup>-1</sup> and NTU-3, 212.8 M<sup>-1</sup>). Meanwhile, all of them show rapid and reversible I<sub>2</sub> accommodation property.