CrystEngComm

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/crystengcomm

Journal Name

ARTICLE

Design and Synthesis of Luminescent Porous Coordination Polymers for Chromaticity Modulation, Sensing Nitrobenzene and Iodine Encapsulation

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Haijun Wang,[a] Fujun Cheng,[a] Changchang Zou,[a] Qianqian Li,[a] Yinying Hua,[a] Jingui Duan,*[abc] and Wanqin Jin*[a]

We design and prepare a family of luminescent porous coordination polymers (PCPs) by three C_{2v} symmetry ligands with increased conjugation moieties. Single crystal X-ray analyses revealed that their pore types/sizes and volumes were systematically tuned. Eu-based NTU-5 and NTU-8 emit red light. However, in constrast with typical green emissions of Tb-based PCPs, the increased conjugation moieties in NTU-6 and NTU-9 with Tb center resulted in very unusual blue emissions. Those unique emissions from those iso-structures demonstrated the varied path ways of electronic transfer, and which were further confirmed by lifetime experiments. Encouraged by those observations, the chromaticity modulation from pink to blue has been well realized by a facile method of self assembly of the Te-H_3L ligand and varied molar ratio of Eu^{3+}/Tb^{3+} ions. Additionally, NTU-6 and NTU-9 showed the high potential for nitrobenzene sensing (quenching effect coefficients: 589.5 and 445.6 M^{-1}) and encapsulating I_2 molecules.

Introduction

Porous coordination polymers (PCPs), formed from organic linkers that are bridged together by metal ion or clusters, has witnessed rapid developments of applications in various disciplines, such as, gas storage and separation, setero-selectivity catalysis, proton conductivity and chemical sensing[1]. In contrast with zeolite and activated carbon[2], deliberate selection of inorganic clusters and organic linkers will bring more significant opportunities for constructing the structures with high surface area, high porosity and tuneable pore size/type[3].

With unique advantages of sharp, nonoverlapping, and easily identifiable emission bands of intra-*4f* transitions, lanthanides-based PCPs (Ln-PCPs) offer a unique platform for the development of solid state luminescent materials in crystalline form[4]. However, the defined electronic energy levels of lanthanides center, by the filled $5s^25p^6$ subshells, offer less sensitive to related chemical environment, and which enable them unlike some organic fluorophores that may change emission performance on the basis of conditions of different guests or solvents. According to some recent studies, efficient energy transferring from the antenna effect, excited of an adjacent strongly absorbing chromophore to the Ln^{3+} centers, could circumvent this problem[5]. Therefore, the selection of a suitable sensitizer is very important. Till now, several strategies, such as, encapsulating luminescent moiety within the pore[6], doping different lanthanide centers[7] and changing temperature[8], have been employed to tune the emission of Ln-PCPs. However, the systematic design and prepare Ln-PCPs with gradually increased conjugation moieties have not been reported before.

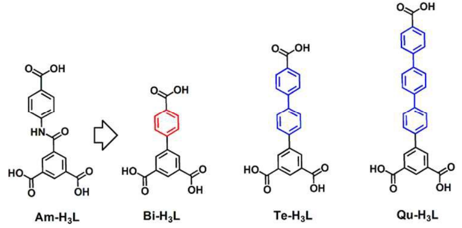
In our previous work, we investigated the structures and properties of some highly porous frameworks with low symmetry ligands (C_{2v})[3b, 9]. The related PCPs with functional amide moiety and fine-tuned pore systems demonstrated high storage/selectivity toward CO_2, as well as good selectivity for Cu^{2+} ions sensing. Here, in order to continue our work, we designed and prepared another two rigid C_{2v} ligands (Te-H_3L and Qu-H_3L), featuring increased conjugation moieties, for preparing high porous and functional PCPs (Scheme 1). This is because the increased- and uniform-distributed conjugation groups with different color zones to Ln^{3+} ions play an important role for assembling of porous structures, and also facilitating energy, charge and electron transfer for potential chromaticity modulation[10]. Based on this idea and combined with one reported ligand (Biphenyl-3,4',5-tricarboxylic acid: Bi-H_3L), seven Ln-based PCPs, $[Ln(L)(H_2O)_2]\cdot$*Guest*, named as NTU-5 to NTU-10, (Ln^{3+}: Eu^{3+}, Tb^{3+} and La^{3+}; H_3L: [1,1':4',1''-terphenyl]-3,4'',5-tricarboxylic acid (Te-H_3L) and [1,1';4',1'';4'',1''']-quaterphenyl -3,4''',5-tricarboxylic acid (Qu-H_3L); NTU: Nanjing Tech University) were prepared. NTU-5 and

---

[a] State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical engineering, Nanjing Tech University, Nanjing, 210009, China. Email: duanjingui@njtech.edu.cn; wqjin@njtech.edu.cn.
[b] State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210023, China
[c] Jiangsu National Synergetic Innovation Center for Advanced Materials, Nanjing Tech University, Nanjing, 210009, China

Electronic Supplementary Information (ESI) available: NMR spectra of ligands, IR, TG, PXRD of Crystals, emission spectra, and I_2 releasing. Crystallographic data (CIF). CCDC number of 7 PCPs: 1454151-1454157. See DOI: 10.1039/x0xx00000x

NTU-8 with Eu^{3+} center emit red light. However, unusual blue emissions, different with the typical green emission of Tb^- based PCPs, were found in NTU-6 and NTU-9. Thus, fine chromaticity modulations from blue to pink were successfully achieved by the facile method of self-assembly of Te-H_3L ligand and varied molar ratio of Eu^{3+}/Tb^{3+} ions. Additionally, in contrast with other benzene derivatives, NTU-6 and NTU-9 featuring quenching effect coefficients (589.5 M^{-1} and 445.6 M^{-1}) are highly sensitive for nitrobenzene detection only. Further, their porous natures were explored by the effective capturing and releasing of iodine.



Scheme 1 Molecular structure of designed Te-H_3L and Qu-H_3L ligands with increased conjugation system.

Experiments

General procedures of the experiment, ligand synthesis can be found in the Supporting Information.

Synthesis of Ln(Bi-L) (Ln^{3+} = Eu^{3+}, Tb^{3+} and La^{3+}): The same procedure was employed in the preparation of these three complexes with different metal salts. As an example, only Eu(Bi-L) complex was described in detail. A mixture of $Eu(NO_3)_3·6H_2O$ (12 mg), Bi-L (5 mg) and DMF/H_2O=1:1 (1 mL) was stirred for ca. 20 min in air, then transferred and sealed in a 4 mL Teflon-lined autoclave, which was heated at 80 °C for 48 h. After cooling to the room temperature, colorless crystals were obtained. Yield: 65% (based on Ligand). Elemental analysis calcd (%) for [$C_{15}H_{11}EuO_8$]: C, 38.23; H, 2.35; found: C, 37.96; H, 2.63; For Tb(Bi-L), yield: 61% (based on Ligand). Elemental analysis calcd (%) for [$C_{15}H_{11}TbO_8$]: C, 37.68; H, 2.32; found: C, 38.13; H, 2.68; For La(Bi-L), yield: 82% (based on Ligand). Elemental analysis calcd. (%) for [$C_{15}H_{11}LaO_8$]: C, 39.32; H, 2.42; found: C, 38.93; H, 2.55.

Synthesis of NTU-5: A mixture of $Eu(NO_3)_3·6H_2O$ (12 mg), Te-H_3L (5 mg), HNO_3 (10 µl, 16 mol/L) and DMF/H_2O=5:1 (1 mL) was stirred for ca. 20 min in air, then transferred and sealed in a 4 mL Teflon-lined autoclave, which was heated at 120 °C for 48 h. After cooling to the room temperature, colorless crystals were obtained. Yield: 45% (based on Ligand). Elemental analysis calcd. (%) for [$C_{21}H_{15}EuO_8$]: C, 46.09; H, 2.76; found: C, 46.38; H, 2.89.

Synthesis of NTU-6: A mixture of $Tb(NO_3)_3·6H_2O$ (12 mg), Te-H_3L (5 mg), HNO_3 (30 µl, 16 mol/L) and DMF/methanol /H_2O=4:2:0.5 (1 mL) was stirred for ca. 20 min in air, then transferred and sealed in a 4 ml Teflon-lined autoclave, which was heated at 80 °C for 48 h. After cooling to the room temperature, colorless crystals were obtained. Yield: 54% (based on Ligand). Elemental analysis calcd. (%) for [$C_{21}H_{15}TbO_8$]: C, 45.51; H, 2.73; found: C, 44.18; H, 2.87.

Synthesis of NTU-7: A mixture of $La(NO_3)_3·6H_2O$ (12 mg), Te-H_3L (5 mg) and DMF/methanol =1:3 (1 mL) was stirred for ca. 20 min in air, then transferred and sealed in a 4 ml Teflon-lined autoclave, which was heated at 80°C for 48 h. After cooling to the room temperature, colorless crystals were obtained. Yield: 38% (based on Ligand). Elemental analysis calcd. (%) for [$C_{21}H_{15}LaO_8$]: C, 47.21; H, 2.83; found: C, 47.68; H, 2.87.

Synthesis of NTU-8: A mixture of $Eu(NO_3)_3·6H_2O$ (12 mg), Qu-H_3L (6 mg) and DMF/H_2O=5:1 (1 mL) was stirred for ca. 20 min in air, then transferred and sealed in a 4 ml Teflon-lined autoclave, which was heated at 80 °C for 48 h. After cooling to the room temperature, colorless crystals were obtained. Yield: 46% (based on Ligand). Elemental analysis calcd. (%) for [$C_{27}H_{19}EuO_8$]: C, 52.02; H, 3.07; found: C, 52.43; H, 3.34.

Synthesis of NTU-9: A mixture of $Tb(NO_3)_3·6H_2O$ (12 mg), Qu-H_3L (6 mg) and DMF/methanol /H_2O=4:2:0.5 (1 mL) was stirred for ca. 20 min in air, then transferred and sealed in a 4 ml Teflon-lined autoclave, which was heated at 80 °C for 48 h. After cooling to the room temperature, colorless crystals were obtained. Yield: 39% (based on Ligand). Elemental analysis calcd. (%) for [$C_{27}H_{19}TbO_8$]: C, 51.45; H, 3.04; found: C, 51.82; H, 2.98.

Synthesis of NTU-10: A mixture of $La(NO_3)_3·6H_2O$ (12 mg), Qu-H_3L (6 mg) and DMF/methanol /H_2O=4:2:0.5 (1 mL) was stirred for ca. 20 min in air, then transferred and sealed in a 4 ml Teflon-lined autoclave, which was heated at 80 °C for 48 h. After cooling to the room temperature, colorless crystals were obtained. Yield: 39% (based on Ligand). Elemental analysis calcd. (%) for [$C_{27}H_{19}LaO_8$]: C, 53.13; H, 3.14; found: C, 52.82; H, 3.31.

Results and discussion

Solvothermal reactions of $Ln(NO_3)_3·6H_2O$ (Ln: Eu^{3+}, Tb^{3+} and La^{3+}) and three C_{2v} ligands (Bi-H_3L, Te-H_3L and Qu-H_3L) afforded seven block crystals of Ln(Bi-L), NTU-5 to NTU-10, respectively. Single-crystal X-ray diffraction analyses revealed that those series of PCPs can be formulated as [$Ln(L)(H_2O)_2$]·*Guest*. Six of them crystallize in the monoclinic $C_{2/c}$ space group and the other in $I_{2/a}$ space group (Table 1). All bond lengths and bond angles, especially for Ln-O and O-Ln-O, are within their rational range. The asymmetric units of them include one lanthanide atom, two coordinated H_2O molecules and one ligand, respectively. Each Ln^{3+} ion is coordinated in a dodecahedron geometry with four O atoms from two chelate ligands, three O atoms from bridged ligands and two water molecules. The ligands act as a μ^4-bridge link to four Ln^{3+} ions (Fig. S4), the Ln-Ln clusters are bridged together by six carboxylate groups to form a three-dimensional (3D) open framework with quadrilateral channels (Fig. 1). Since the systemically tuned length of involved ligands at 4’ position, the generated cages in those series PCPs increased gradually from 15 Å to 21 Å (Fig. 1d, 1e and 1f). However, the moiety of isophthalic acid restricted the pore sizes to be about 6.5 × 6.5 $Å^2$ along related direction of those series compounds (Figure 1g). Further, the increased conjugation systems in Te-H_3L and Qu-H_3L offer significant chance for π···π interaction of adjacent ligands in NTU-5 to NTU-10 (Fig. 2), indicating the potential for different electronic transitions[11]. In addition, the comprehension of underlying network topology is helpful in understanding the features of whole structures. Here, $Ln_2(ArCOO)_4$ clusters were simplified as 6-connected nodes, where, L^{3-} ligands is 3-connected linkers. Thus, all of them show 3-dimensional 3, 6-connected nets (Fig. 3) with mono-tile inside, as well as same Schläfli symbol of $\{4^2.6\}_2\{4^4.6^2.8^7.10^2\}$, which is rare in popular 3, 6-c frameworks[12]. The calculated solvent-accessible volumes of NTU-5 to NTU-10, using PLATON program, reached to 50.9% to 54.1%, highlighting their porous nature. The phase purities of them were confirmed by powder X-ray diffraction patterns, respectively (Fig. S11, S14 and S17). The thermal gravimetric analyses showed that thermal decomposition of those series structures are started around 450℃ under N_2 atmosphere. (Fig. S10, S13 and S16).

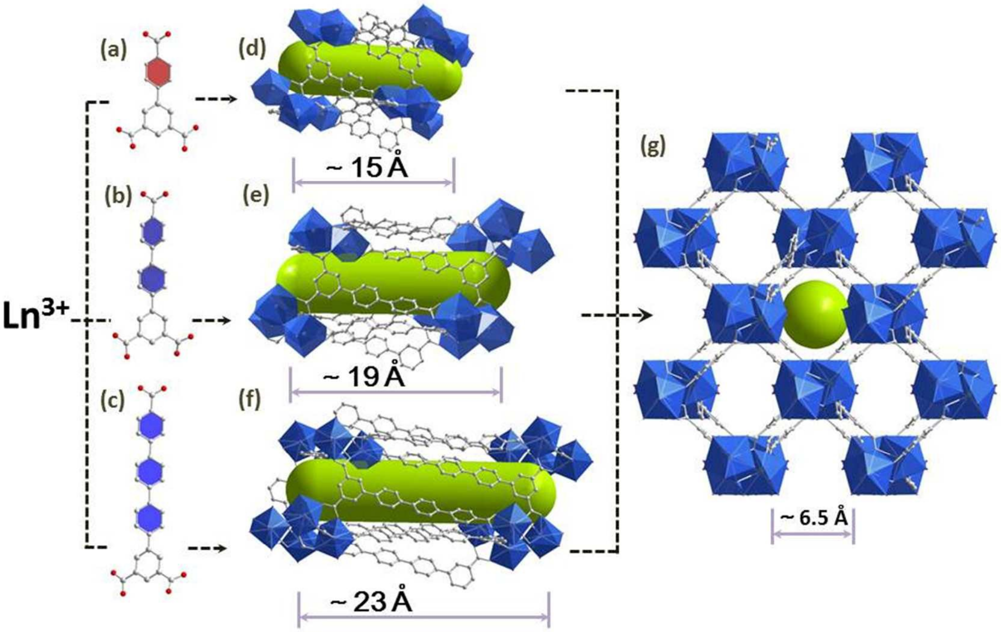


Fig. 1 View of the structures of series PCPs. The molecule structures of three C_{2v} ligands with different varied conjugation systems (a, b and c); Comparison of pore size in related PCPs (d, e and f); same window apertures (6.5 × 6.5 $Å^2$) regulated by isophthalic acid in those series PCPs (g).

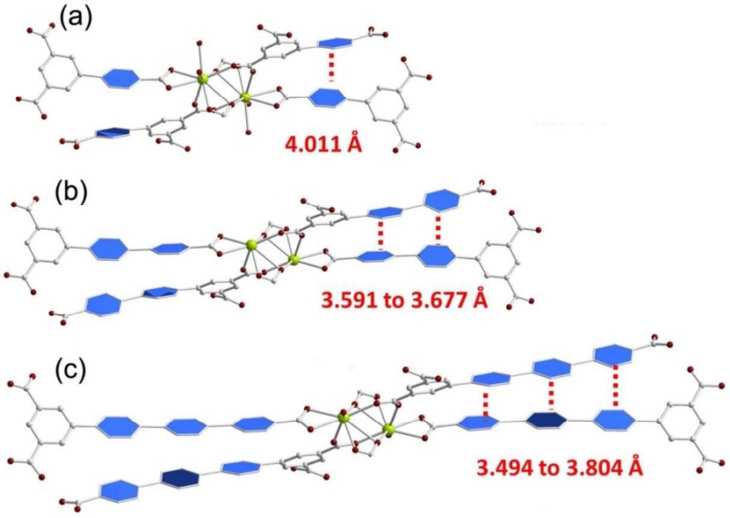


Fig. 2 The view of short π···π interactions in La(Bi-L) and NTU-5 to -10 systems.

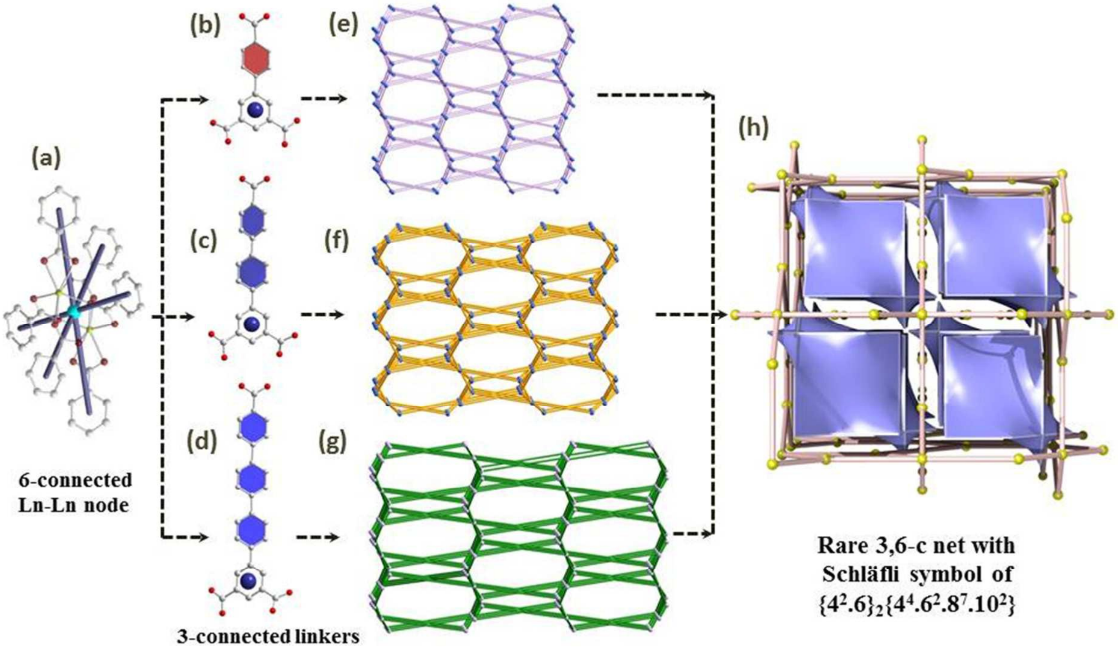


Fig. 3 Topology analysis of series of PCPs: the six connected Ln-Ln clusters (a); the 3-connected linkers (b, c and d); topological diagrams of La(Bi-L) (e), NTU-5, -6, -7 (f) and NTU-8, -9, -10 (g); All networks are two-nodal (3, 6)-c nets with one kind tile and share with same and rare Schläfli symbol of $\{4^2.6\}_2\{4^4.6^2.8^7.10^2\}$ (h).

Table 1 Crystal data and structure refinements for complexes

	NTU-5	NTU-6	NTU-7	NTU-8	NTU-9	NTU-10	La(Bi-L)
Empirical formula	$C_{21}H_{15}O_8Eu$	$C_{21}H_{15}O_8Tb$	$C_{21}H_{15}O_8La$	$C_{27}H_{19}O_8Eu$	$C_{27}H_{19}O_8Tb$	$C_{27}H_{19}O_8La$	$C_{15}H_{11}O_8La$
Formula weight	547.29	554.26	534.24	623.38	630.35	610.33	458.15
Space group	*C2/c*	*C2/c*	*C2/c*	*C2/c*	*C2/c*	*I2/a*	*C2/c*
a /Å	33.02(5)	33.13(2)	33.69(3)	42.142(15)	42.145(7)	13.999(10)	24.799(18)
b/Å	13.317(19)	13.572(8)	12.970(11)	14.065(5)	14.296(3)	17.647(11)	13.263(10)
c/Å	14.22(2)	14.049(9)	14.771(12)	13.870(5)	13.771(2)	42.040(3)	14.971(11)
β/°	101.739(15)	101.324(7)	101.572(9)	101.996(5)	101.683(2)	97.948(1)	96.635(8)
V/Å3	6122(15)	6194(7)	6323(9)	8042(5)	8125(2)	8537.8(11)	4891(6)
Z	8	8	8	8	8	8	8
Dcalc/gcm^{-3}	1.188	1.189	1.122	1.03	1.031	0.950	1.244
μ/mm^{-1}	2.079	2.313	1.380	1.590	1.771	1.029	1.773
Θ rangeº	1.3, 25.0	1.3, 25.0	1.2, 25.0	1.0, 25.0	1.0, 25.0	1.0, 25.0	1.7, 25.0
Index ranges	-33≤ h ≤39	-39≤ h ≤39	-40≤ h ≤39	-48≤ h ≤49	-50≤ h ≤50	-16≤ h ≤14	-29≤ h ≤29
	-15≤ k ≤15	-16≤ h ≤16	-15≤ k ≤15	-16≤ k ≤16	-15≤ k ≤17	-17≤ k ≤17	-15≤ k ≤15
	-16≤ l ≤16	-16≤ h ≤16	-17≤ l ≤15	-16≤ l ≤11	-16≤ l ≤16	-50≤ l ≤50	-17≤ l ≤17
R_1	0.0651	0.0375	0.0406	0.1014	0.0461	0.0521	0.0448
$wR_{2a}[I>2\sigma(I)]$	0.1891	0.0832	0.096	0.2824	0.1277	0.1363	0.1331
GOF	1.02	1.03	1.03	0.99	1.03	1.08	1.132

To determine whether the ligands provide efficient sensitization for the lanthanide ions, the solid state luminescent spectra of this series PCPs are recorded at room temperature (Fig. S19-20). The excitation spectra were obtained by monitoring the emission of Eu-complexes at 619 nm, and the results showed that the optimum excitation wavelengths for Eu(Bi-L) and NTU-5 are 396 nm, as well as blue shifted wavelength for NTU-8 (360 nm). The emission spectra of them revealed well-resolved magnified luminescence of *f–f* transitions, attributed to the energy transfer from ligands to

Eu^{3+}. Characteristic transitions of the Eu^{3+} ion are also evidents for them, at 594, 619, 651 and 702 nm, which are ascribed to the $^5D_0 \rightarrow {}^7F_J$ (J = 1, 2, 3, and 4) transitions, respectively. In contrast, Tb-based PCPs exhibit ligand related excitation spectra. The optimal excitation wavelengths gradually increased from 351 nm (Tb(Bi-L)) to 356 nm (NTU-6) and 368 nm (NTU-9). More surprisingly, NTU-6 and NTU-9 demonstrate significant blue shifted emissions around 400 nm, but not the typical characteristic emissions of Tb^{3+}, such as, the emission of Tb(Bi-L) at 490 nm, 546 nm, 586 nm and 623 nm. To understand these special emissions, we investigated the lifetimes of their as-synthesized phase at room temperature (Fig. 4). The luminescence lifetimes of three Eu-based PCPs and Tb(Bi-L) were determined to be 600-1100 μs, which are similar to the performances of Eu- and Tb-based PCPs with typical metal-centered emission (antenna effect)[9c]. However, as expected, NTU-6 (764 ps) and NTU-9 (1441 ps) displayed significant short lifetime, which arise from direct organic ligands excitation[4, 13].

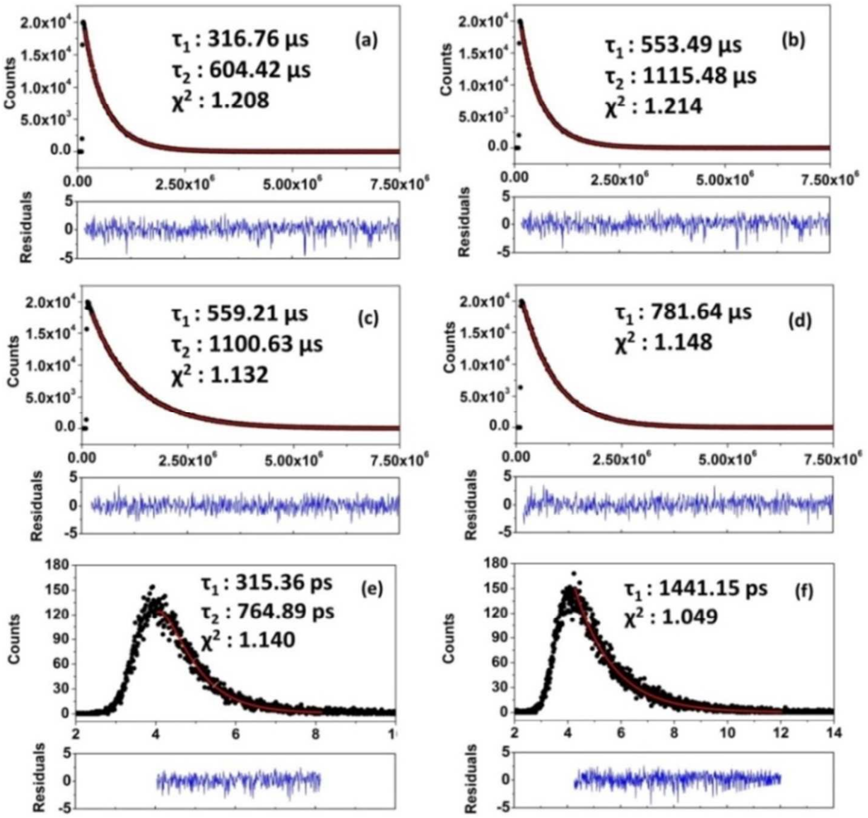


Fig. 4 The fitted decay curve monitored for Eu(Bi-L) (a), NTU-5 (b), NTU-8 (c), Tb(Bi-L) (d), NTU-6 (e) and NTU-9 (f) in the solid state at room temperature. Black line: experimental data; Red line: fitted by $Fit = A + B_1 \cdot e^{(-t/\tau_1)} + B_2 \cdot e^{(-t/\tau 2)} + B_3 \cdot e^{(-t/\tau_3)} + B_4 \cdot e^{(-t/\tau_4)}$.

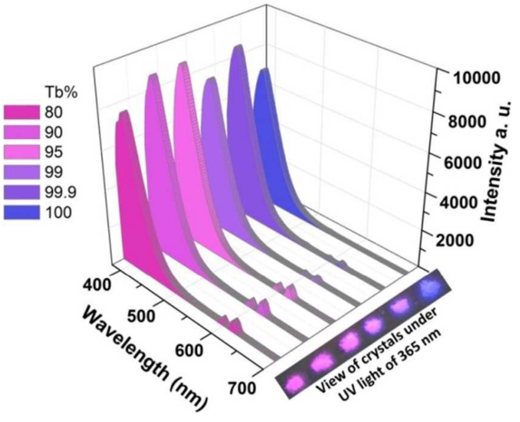


Fig. 5 Luminescent spectra of Eu/Tb(Te-L) and their photographs under UV light of 365 nm.

Bearing unique emissions and isostrutures of NTU-5 and NTU-6, we believed that the chromaticity modulation from pink to blue would be possible. Thus, we prepared a family of Eu_x/Tb_{1-x}(Te-L) in which mixed Eu^{3+}/Tb^{3+} ions with varied molar ratio can be systematically incorporated into the frameworks (mole ratio of Tb^{3+}: 80-100%). The PXRD patterns indicate that these series samples featuring same structure as NTU-5 and -6 (Fig. S21). With the increased ratio of Eu^{3+} ion, luminescent spectra of them showed that the peak around 592 nm and 616 nm gradually increased. Meanwhile, a strong and broad peak around 400 nm was found in all of them (Fig. 5). The systematic chromaticity modulation from pink to blue have been realized, which was confirmed by the photograph of these series samples under UV light (365 nm). Thus, the fine-tuned emissions would make the compounds of Eu_x/Tb_{1-x}(Te-L) as promising materials for desired light devices.

Recently, luminescent detection of small organic molecules has received a great deal of attention, and thus a large number of luminescent PCPs have been reported[14]. Although these luminescent PCPs display good sensing properties, the detection of benzene derivatives need to be further improved. Considering the unique blue emissions and high conjugated groups of Tb-based PCPs, it is necessary to explore their performances or sensing benzene derivatives. Hexane exchanged NTU-6 and NTU-9 were immersed in benzene, toluene, m-xylene, chlorobenzene and nitrobenzene to form aromatic molecules incorporated materials (A@NTU-6 and A@NTU-9) for their luminescence studies. As shown in Figure 6, the luminescent spectra are largely dependent on the guest molecules, particularly in case of nitrobenzene, which exhibit the most significant quenching effects in NTU-6 and also in NTU-9. The mechanism of molecules reorganization should be explained as the function of strongly electron-withdrawing -NO_2 group that offer the electron transition between the framework and nitrobenzene molecules[15]. For further understanding these observations, quenching effects of these two PCPs were calculated by Stern-Volmer equation ($I_0 / I = 1 + K_{sv} [M]$). By comparing the quenching effect coefficients (K_{sv}) in table 2, we found that the K_{sv} for nitrobenzene in NTU-6 and NTU-9 reached to 589.6 and 445.5 M^{-1}, revealing very high sensitivity for nitrobenzene detection. Thus, these results imply that both of NTU-6 and NTU-9 might be utilized as the novel functional sensing materials for benzene derivatives.

Table 2 Quenching effect coefficients (K_{sv}) of different benzene derivatives on the luminescence intensity of A@PCPs.

	K_{sv} [M^{-1}] A@NTU-6	K_{sv} [M^{-1}] A@NTU-9
nitrobenzene	589.6	445.5
benzene	9.3	8.6
toulene	10.6	6.0
m-xylene	4.9	7.6
chlorobenze	11.7	19.5

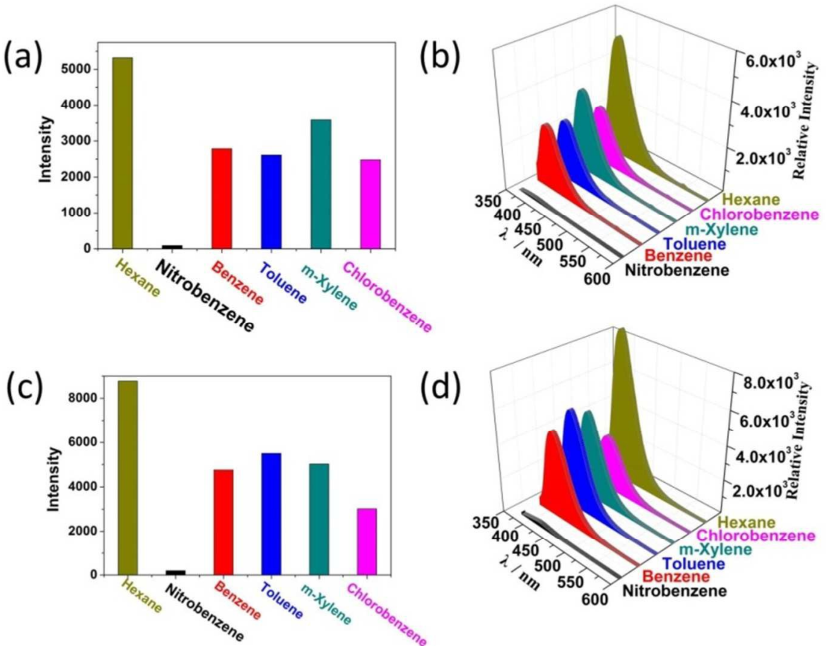


Fig. 6 Luminescent spectra of NTU-6 and NTU-9 with different benzene derivatives: comparison of the luminescence intensity of the peak at 397 nm (a) and 408 nm (c), the full luminescent spectra of NTU-6 (b) and NTU-9 (d) with different guest.

Generally, iodine was primarily used in human nutrition and in 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 that visibly sublimates into a noxious gas. Thus, it is necessary to find the material with high efficient iodine enriching and releasing[16]. Bearing the high porosity of those series PCPs, their accommodation properties of iodine (I_2) were investigated (Fig. 7 and S22-25). Here, we discuss the results of NTU-6 and NTU-9 in detail.

After soaking the hexane-exchanged PCPs (~30 mg) in high concentrated I_2 solution (hexane) for 24 h, we found that the color of PCPs changed from white to deep yellow, while the luminescence was quenched (Fig. S25-27). This is because iodine as a heavy atom is well known for quenching the fluorescence emission, reflecting successful iodine absorption. To determine the possible interactions of host and iodine species, X-ray photoelectron spectroscopy (XPS) of NTU-6, NTU-9, and their I_2 encapsulated phases were performed, respectively. Comparing the binding energies, no special interactions of I_2…O and I_2…Tb were found (Fig. S29). However, considering their structures, the encapsulation should be assigned as the I_2…π interaction from introduced conjugation moieties[17]. Additionally, XPS results of I3d scan showed that the valence of encapsulated iodine species is zero[16b], and which indicate that only the physical absorption occur (Fig. S30).

TG experiments showed that ~14% weight loss in the temperature range of 65 - 200℃ were found about air dried I_2@NTU-6 and I_2@NTU-9. Those values indicate that each unit cell of NTU-6 and NTU-9 can accommodate about 2.8 and 3.2 I_2 molecules, respectively (Fig. S31-32). In order to confirm this behavior, another partial of air dried I_2@NTU-6 was soaked into dry ethanol, with its color changed gradually from deep yellow to colorless. Meanwhile, the colorless ethanol solution gradually changed to yellow. To further study the process of I_2 releasing, the *in-situ* UV-spectra were collected at room temperature. The intensity of the absorbance increased with time, especially for the peaks at 290 and 360 nm. Compared with the standard curve of I_2 solution at 290 nm, we found that the concentration of I_2 solution reached to 1455 mg·L^{-1} and 779 mg·L^{-1} for I_2@NTU-6 (20 mg in 2 mL EtOH) and I_2@NTU-9 (14 mg in 2.5 mL EtOH) releasing. Further calculation show that 2.95 and 3.21 I_2 molecules were released for each corresponding unit cell, reflecting completely release. Therefore, I_2 sorption process is reversible in NTU-6 and NTU-9, and which were clearly confirmed by their luminescent spectra and photographs (Fig. S26). In addition, the I_2 accommodation behaviors of other four PCPs have also been examined. Thus, the porosity of those PCPs has been identified, as well as their potential for efficient enriching and releasing I_2 molecules.

Conclusions

In summary, by using rational-designed C_{2v} symmetry ligands, we have constructed seven new luminescent PCPs with systematically tuned pore parameters. The luminescent experiments showed that the high conjugated moieties resulted in unusual blue emissions from Tb-based NTU-6 and NTU-9, but typical red light from Eu-based NTU-5 and NTU-8. Those unique emissions from these iso-structures demonstrated the varied path ways of electronic transfer, and which were further confirmed by lifetime experiments. Bearing the iso-structure of NTU-5 and NTU-6, the fine-tuned chromaticity from pink to blue has been realized by a facile method of self-assembly of the Te-H_3L ligand and varied molar ratio of Eu^{3+}/Tb^{3+} ions. Further, the sensing experiments and quenching effect coefficients (589.6 and 445.5 M^{-1}) showed that both NTU-6 and NTU-9 are ideal luminescence sensors for selective probing nitrobenzene. Meanwhile, their porous natures have been identified, as well as the potential for efficient enriching and releasing I_2. Thus, our strategy for PCPs tuning will offer the significant possibility to create new luminescent systems and devices.

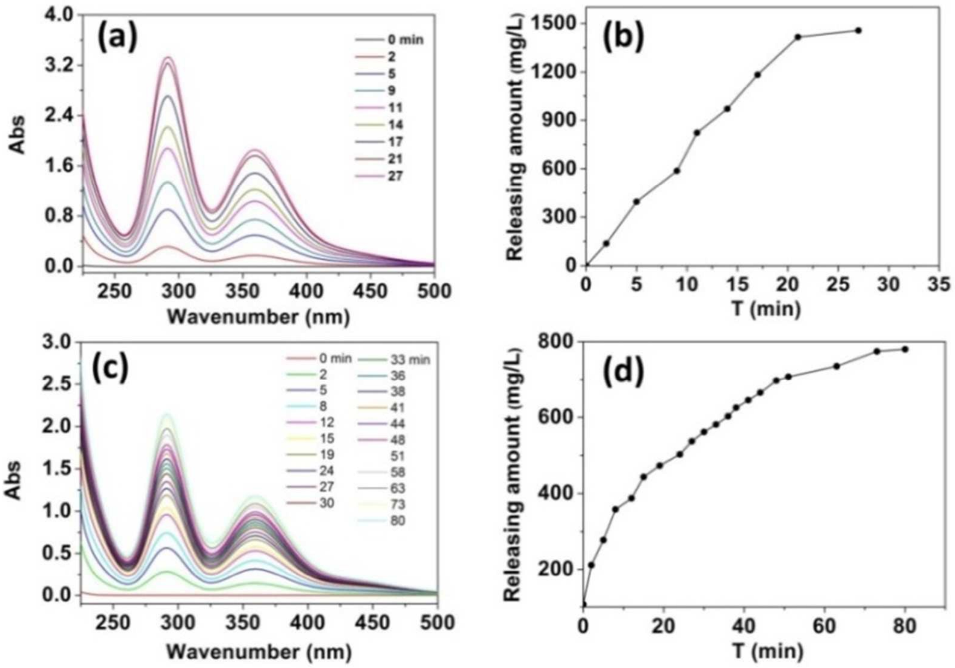


Figure 7. UV spectra of I_2 releasing from I_2@NTU-6 (a: 20 mg in 2 ml EtOH) and I_2@NTU-9 (c: 14 mg in 2.5 ml EtOH); the time course of I_2 releasing of I_2@NTU-6 (b) and I_2@NTU-9 (d), generated from the peak intensity at 290 nm, respectively.

Acknowledgements

The authors gratefully acknowledge financial support from NSFC (21301148) Innovative Research Team Program by the Ministry of Education of China (No. IRT13070), Talent Development Program of Nanjing Tech University (39801116), State Key Laboratory of Coordination Chemistry (SKLCC1616), and State Key Laboratory of Materials-Oriented Chemical Engineering (ZK201406). We also thank the valuable discussions from Prof. Lin Li and Prof. Zhen Yang.

References

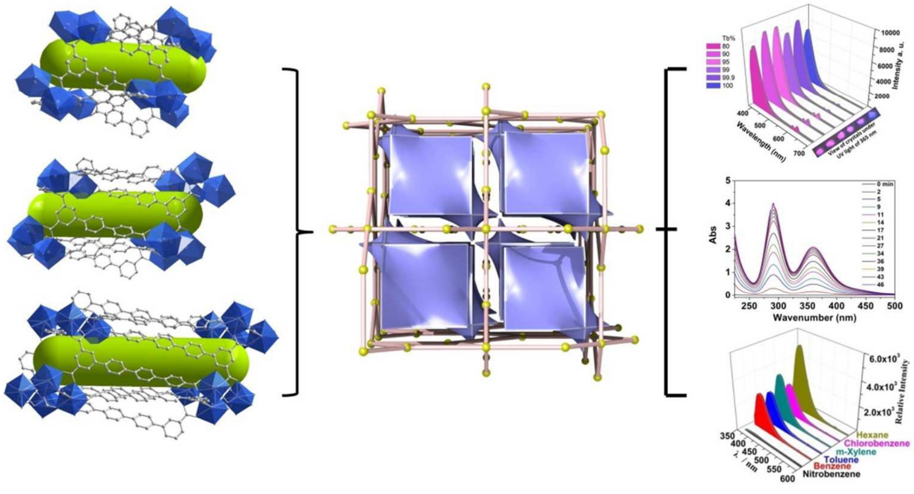
1. (a)H. Sato, W. Kosaka, R. Matsuda, A. Hori, Y. Hijikata, R. V. Belosludov, S. Sakaki, M. Takata and S. Kitagawa, *Science*, 2014, 343, 167-170; (b)P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Q. Ma, B. Space, L. Wojtas, M. Eddaoudi and M. J. Zaworotko, *Nature*, 2013, 495, 80-84; (c)H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, *Science*, 2013, 341, 974-986.
2. (a)D. Peralta, G. Chaplais, A. Simon-Masseron, K. Barthelet, C. Chizallet, A. A. Quoineaud and G. D. Pirngruber, *J. Am. Chem. Soc.*, 2012, 134, 8115-8126; (b)L. Borchardt, M. Oschatz, M. Lohe, V. Presser, Y. Gogotsi and S. Kaskel, *Carbon*, 2012, 50, 3987-3994.
3. (a)M. Li, D. Li, M. O'Keeffe and O. M. Yaghi, *Chem. Rev.*, 2014, 114, 1343-1370; (b)J. G. Duan, M. Higuchi and S. Kitagawa, *Inorg. Chem.*, 2015, 54, 1645-1649; (c)Y. B. Zhang, H. L. Zhou, R. B. Lin, C. Zhang, J. B. Lin, J. P. Zhang and X. M. Chen, *Nat. Commun.*, 2012, 3, 642-651; (d)B. S. Zheng, J. F. Bai, J. G. Duan, L. Wojtas and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2011, 133, 748-751; (e)B. L. Chen, M. Eddaoudi, S. T. Hyde, M. O'Keeffe and O. M. Yaghi, *Science* 2001, 291, 1021-1023; (f)M. Dinca and J. R. Long, *J. Am. Chem. Soc.,* 2007, 129, 11172-11176; (g)J. G. Duan, M. Higuchi, S. Horike, M. L. Foo, K. P. Rao, Y. Inubushi, T. Fukushima and S. Kitagawa, *Adv. Funct. Mater.*, 2013, 23, 3525-3530; (h) Q. K. Liu, J. P. Ma and Y. B. Dong, *J. Am. Chem. Soc.*, 2010, 132, 7005-7017.
4. Y. J. Cui, Y. F. Yue, G. D. Qian and B. L. Chen, *Chem. Rev.*, 2012, 112, 1126-1162.
5. Z. Q. Xia, Q. Wei, Q. Yang, C. F. Qiao, S. P. Chen, G. Xie, G. C. Zhang, C. S. Zhou and S. L. Gao, *CrystEngComm*, 2013, 15, 86-99.
6. C. A. Kent, D. M. Liu, L. Q. Ma, J. M. Papanikolas, T. J. Meyer and W. B. Lin, *J. Am. Chem. Soc.*, 2011, 133, 12940-12943.
7. K. A. White, D. A. Chengelis, K. A. Gogick, J. Stehman, N. L. Rosi and S. Petoud, *J. Am. Chem. Soc.*, 2009, 131, 18069-18071.
8. Y. J. Cui, H. Xu, Y. F. Yue, Z. Y. Guo, J. C. Yu, Z. X. Chen, J. K. Gao, Y. Yang, G. D. Qian and B. L. Chen, *J. Am. Chem. Soc.*, 2012, 134, 3979-3982.
9. (a)J. G. Duan, Z. Yang, J. F. Bai, B. S. Zheng, Y. Z. Li and S. H. Li, *Chem. Commun.*, 2012, 48, 3058-3060; (b)J. G. Duan, W. Q. Jin and R. Krishna, *Inorg. Chem.*, 2015, 54, 4279-4284; (c)J. G. Duan, C. C. Zou, Q. Q. Li and W. Q. Jin, *CrystEngComm*, 2015, 17, 8226-8230.
10. Y. Tong, X. Han, C. Huang, Z. Shao, L. Guo, Y. Wang, J. Ding and H. Hou, *Dalton Trans.*, 2016, 45, 3702-3707.
11. D. Tanaka, S. Horike, S. Kitagawa, M. Ohba, M. Hasegawa, Y. Ozawa and K. Toriumi, *Chem. Commun.,* 2007, 3142-3144.
12. Z. M. Hao, X. Z. Song, M. Zhu, X. Meng, S. N. Zhao, S. Q. Su, W. T. Yang, S. Y. Song and H. J. Zhang, *J. Mater. Chem. A*, 2013, 1, 11043-11050.
13. Q. R. Fang, G. S. Zhu, M. Xue, J. Y. Sun, F. X. Sun and S. L. Qiu, *Inorg. Chem.*, 2006, 45, 3582-3587.
14. (a)X. Q. Wang, L. L. Zhang, J. Yang, F. L. Liu, F. N. Dai, R. M. Wang and D. F. Sun, *J. Mater. Chem. A*, 2015, 3, 12777-12785; (b)F. H. Liu, C. Qin, Y. Ding, H. Wu, K. Z. Shao and Z. M. Su, *Dalton Trans.*, 2015, 44, 1754-1760; (c)Z. Y. Guo, X. Z. Song, H. P. Lei, H. L. Wang, S. Q. Su, H. Xu, G. D. Qian, H. J. Zhang and B. L. Chen, *Chem. Commun.*, 2015, 51, 376-379; (d) J. Y. Cheng, P. Wang, J. P. Ma, Q. K. Liu and Y. B. Dong, *Chem. Commun.*, 2014, 50, 13672-13675.
15. (a)Z. C. Hu, S. Pramanik, K. Tan, C. Zheng, W. Liu, X. Zhang, Y. J. Chabal and J. Li, *Cryst. Growth Des.*, 2013, 13, 4204-4207; (b)A. J. Lan, K. H. Li, H. H. Wu, D. H. Olson, T. J. Emge, W. Ki, M. C. Hong and J. Li, *Angew. Chem. Int. Ed.*, 2009, 48, 2334-2338.
16. (a)Q. K. Liu, J. P. Ma and Y. B. Dong, *Chem. Commun.*, 2011, 47, 7185-7187; (b)X. M. Zhang, C. W. Zhao, J. P. Ma, Y. Yu, Q. K. Liu and Y. B. Dong, *Chem. Commun.*, 2015, 51, 839-842; (c)D. F. Sava, M. A. Rodriguez, K. W. Chapman, P. J. Chupas, J. A. Greathouse, P. S. Crozier and T. M. Nenoff, *J. Am. Chem. Soc.*, 2011, 133, 12398-12401; (d)M. H. Zeng, Q. X. Wang, Y. X. Tan, S. Hu, H. X. Zhao, L. S. Long and M. Kurmoo, *J. Am. Chem. Soc.*, 2010, 132, 2561-2563.
17. C. Y. Pei, T. Ben, S. X. Xu and S. L. Qiu, *J. Mater. Chem. A*, 2014, 2, 7179-7187.

Design and Synthesis of Luminescent Porous Coordination Polymers for Chromaticity Modulation, Sensing Nitrobenzene and Iodine Encapsulation

Haijun Wang,[a] Fujun Cheng,[a] Changchang Zou,[a] Qianqian Li,[a] Yinying Hua,[a] Jingui Duan,*[abc] and Wanqin Jin*[a]

[a] State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical engineering, Nanjing Tech University, Nanjing, 210009, China. [b] State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210023, China. [c] Jiangsu National Synergetic Innovation Center for Advanced Materials, Nanjing Tech University, Nanjing, 210009, China

Received xx x xxxx; **Email:** duanjingui@njtech.edu.cn; wqjin@njtech.edu.cn



A family of porous coordination polymers from C_{2v} symmetry ligands with increased conjugation moieties were systematically designed and prepared, and which demonstrate the high promising for chromaticity modulation, sensing nitrobenzene, and I_2 encapsulation,