Molecular Recognition

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Amine-Responsive Adaptable Nanospaces: Fluorescent Porous Coordination Polymer for Molecular Recognition**

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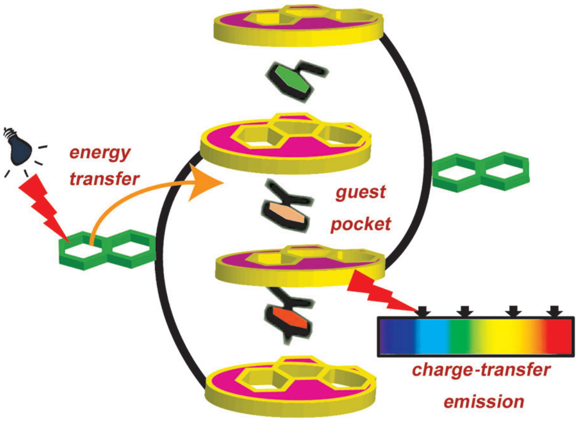
Abstract: *Flexible and dynamic porous coordination polymers (PCPs) with well-defined nanospaces composed of chromophoric organic linkers provide a scaffold for encapsulation of versatile guest molecules through noncovalent interactions. PCPs thus provide a potential platform for molecular recognition. Herein, we report a flexible 3D supramolecular framework* $\{[Zn(ndc)(o\text{-}phen)]\cdot DMF\}_n$ *(o-phen = 1,10-phenanthroline, ndc = 2,6-napthalenedicarboxylate) with confined nanospaces that can accommodate different electron-donating aromatic amine guests with selective turn-on emission signaling. This system serves as a molecular recognition platform through an emission-readout process. Such unprecedented tunable emission with different amines is attributed to its emissive charge-transfer (CT) complexation with o-phen linkers. In certain cases this CT emission is further amplified by energy transfer from the chromophoric linker unit ndc, as evidenced by single-crystal X-ray structural characterization.*

Porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) have emerged as an important class of materials with potential application in several diverse fields, because of their simple synthetic strategy and the possibility to introduce various functionalities by choosing different organic linkers and metal ions.[1] The introduction of flexibility into such materials can lead to adaptable behavior towards the encapsulation of guest molecules.[2] In this context, it can be imagined that the porosity introduced by the weak supramolecular interactions (π···π or C–H···π interactions) between 1D coordination polymers consisting of aromatic linkers would be dynamic, in contrast to their higher dimensional counterparts formed solely by metal–linker coordination bonds. The unique guest/stimuli-responsive behavior of PCPs compared to conventional porous materials are advantageous for applications such as selective adsorption/separation, molecular recognition, and sensing properties.[3–5] Such flexible nanospaces would allow the accommodation of various guest molecules through specific host–guest interactions.[6] However, the chemical affinity of the coordination spaces limit the inclusion of an appropriate guest molecule and thus pore structure functionalization is crucial. Flexible nanospaces constructed from chromophoric organic linkers should also provide a rapid fluorescence readout of the recognition processes leading to stimuli-responsive PCPs. This fluorescence transduction mechanism is highly sensitive to environment and thus accommodation of various guests in the nanospace can lead to either changes in the emission wavelength, an increased or decreased emission intensity, or may even give rise to a new emission band as a result of charge transfer (CT) or exciplex/excimer formation.[7]

Aromatic amines are very important in drug synthesis and in the field of polymers but have also been shown to be carcinogenic in humans.[8] Therefore, the simple detection and capture of aromatic amines is of paramount importance both for health and the environment. Herein, we envisioned the design of a flexible PCP that would show adaptive guest encapsulation through donor–acceptor interactions and that could be used for specific recognition of the guest, such as



Scheme 1. Representation of a fluorescent porous coordination polymer and its adaptable nanospace (guest pocket) suitable for the recognition of aromatic guest molecules through an emission-readout process.

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aromatic amines. Recognition of the guest molecule by the host framework can be detected by changes in the emission. This process requires a luminescent PCP with bright emission and the presence of a strong electron donor/acceptor in the framework backbone. Thus, we have picked a chelator (*o*-phen: 1,10-phenanthroline), linker (ndc: 2,6-naphthalenedicarboxylate) and connector ($\mathrm{Zn^{II}}$ ions) as the molecular components of our system (Scheme 1). The employment of these components leads to the formation of a 1D coordination polymer $\{[\mathrm{Zn(ndc)}(o\text{-phen})]\cdot\mathrm{DMF}\}_n$ (**1**), that further extends to form a 3D porous supramolecular structure through $\pi\cdots\pi$ and C−H$\cdots\pi$ interactions. The 3D structure shows structural flexibility as shown by in situ powder XRD (PXRD) measurements coupled with $\mathrm{CO_2}$ adsorption and solvent vapor adsorption studies. We have exploited the structural dynamics and π-electron-rich coordination nanospaces of **1** for the recognition of different aromatic amines, specifically aniline (AN), *N*-methyl aniline (NMA), *N*,*N*′-dimethyl aniline (DMA), and *N*,*N*′-dimethyl-*p*-toluidine (DMPT), using both visible color changes and changes in the emission color of the system (Scheme 1). This selective turn-on emission with aromatic amines is attributed to the charge-transfer complexation of *o*-phen ligands with aromatic amines, which in certain cases is further sensitized by energy transfer from the ndc chromophore, as evidenced by single-crystal X-ray structural characterization. This is the first time that such unprecedented turn-on aromatic amine recognition in a PCP has been reported.

Under solvothermal conditions,[9] ndc and *o*-phen were co-assembled with $\mathrm{Zn(NO_3)_2{\cdot}6\,H_2O}$ to form a 3D supramolecular structure. The hexacoordinated $\mathrm{Zn^{II}}$ metal centers (Zn1 and Zn2) are chelated to two carboxylate groups of two ndc subunits and the other two coordination sites on the $\mathrm{Zn^{II}}$ center are occupied by an *o*-phen unit.[9] The $\mathrm{Zn^{II}}$ centers are connected by ndc linkers along the (101) plane to form a 1D zigzag chain (Figure 1 a). These chains are aligned parallel to each other through C−H$\cdots$OCO (ca. 2.76 Å) interactions between ndc linkers. These interactions result in the formation of a 2D corrugated sheet lying in the crystallographic *ac* plane (Figure 1 b). These herringbone-type packed 2D sheets protrude into the groove of another similar 2D sheet through C−H(*o*-phen)$\cdots\pi$(ndc) (approximately 3.58–3.60 Å) and C−H(*o*-phen)$\cdots$O(ndc) interactions and result in the formation of a 3D supramolecular structure with distorted rectangular-shaped 1D channels along the *a*-axis (Figure 1 c). These channels are filled with guest DMF molecules. Upon removal of these guest molecules, a void space of 28 % of the total cell volume can be calculated.[10] Note, the *o*-phen from each 1D coordination chain is positioned in a periodic manner in a 2D sheet where DMF molecules are encapsulated, resulting in the formation of a column of coordinated *o*-phen subunits and DMF guest molecules along the *c*-axis (Figure 1 d). Removal of the guest solvent molecules from the pores at 170 °C under vacuum shows notable changes in the PXRD pattern compared to that of the as-synthesized framework **1**.[9] The Bragg diffractions for (101) and $(10\bar{1})$ planes, which pass through the ndc linker and the $\mathrm{Zn^{II}}$ metal center, shifts to higher angles after exclusion of the guest solvent molecules, implying shrinkage in the framework.[9] Upon indexing of the PXRD pattern of desolvated **1** (**1′**), a decreased cell volume (1990 $\mathrm{Å^3}$) can be calculated for **1′** compared to that of **1**.[9] These results show that this 3D supramolecular structure, built up by noncovalent interactions, is flexible, and that the structure can be modulated by removal or reintroduction of guest solvent molecules.

The structural flexibility of **1′** was further investigated from a $\mathrm{CO_2}$ adsorption (195 K) measurement (Figure 2 a). The uptake of $\mathrm{CO_2}$ increases gradually (from point A) up to P/P_0 of approximately 0.18 (point B) followed by a sudden rise, and reaches a final uptake quantity of $48\,\mathrm{mL\,g^{-1}}$ ($\approx$0.9 molecules/formula unit; point C). The desorption pathway (black dot centered diamond symbols) does not retrace the adsorption pathway (half-black diamond symbols), instead showing a large hysteretic sorption profile. To understand this adsorption behavior, we have studied in situ PXRD measurements coupled with $\mathrm{CO_2}$ adsorption and recorded diffraction patterns of **1′** at each adsorption point. PXRD patterns recorded at points A–E in the isotherm (Figure 2 b < xfigr2) were indexed[9] and these show a continuous increase in the cell volume from points A to C (point A: 2143 $\mathrm{Å^3}$; point C: 2963 $\mathrm{Å^3}$), suggesting expansion of the framework structure to accommodate guest $\mathrm{CO_2}$ molecules. This rearrangement may be driven by interactions between $\mathrm{CO_2}$ and the aromatic π-electron cloud.[11] Finally, at the last

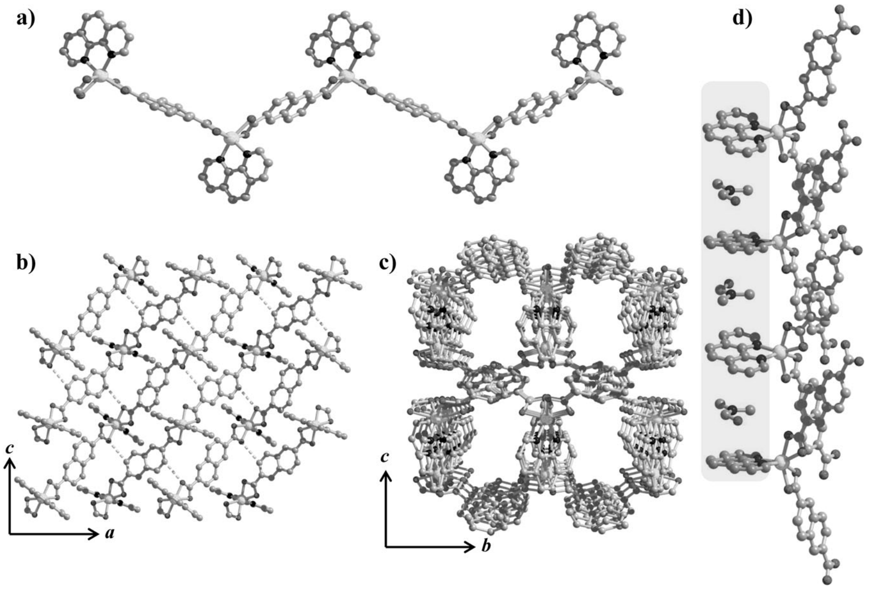

Figure 1. Crystal structure and packing diagrams of $\{[\mathrm{Zn(ndc)}(o\text{-phen})]\cdot\mathrm{DMF}\}_n$ (**1**). a) 1D zigzag chain of compound **1**, b) 2D corrugated sheet, c) view of the rectangular channels along the *a*-axis formed by the supramolecular organization of 1D chains, d) columnar stacking of the {Zn(*o*-phen)} subunit and the guest DMF molecules.

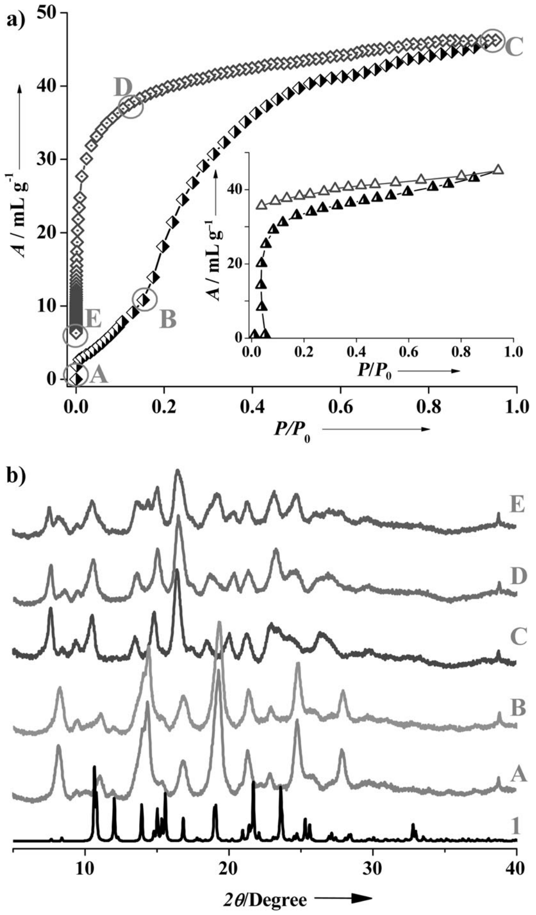

Figure 2. a) CO_2 adsorption (half-black diamonds) and desorption (black dot centered diamonds) isotherms of **1′** at 195 K. $P_0 = 760$ Torr (CO_2). Inset: C_6H_6 vapor adsorption (half-black triangles) and desorption (white triangles) isotherms of **1′** at 298 K. $P_0 = 12.601$ kPa (C_6H_6). b) PXRD patterns of **1′** at different stages of CO_2 adsorption as shown in (a).

desorption point (point E), which shows an approximate CO_2 retention of 6 mL g^{-1} in the pores, the structure does not revert back to contracted desolvated phase **1′**, as shown from the cell volume (2836 Å^3). However, after complete removal of CO_2 at room temperature, the desolvated structure is regenerated.[9] The high pressure adsorption profile at 273 K also shows a double-step uptake indicating similar CO_2-induced structural rearrangement.[9] On the other hand, N_2 gas is unable to diffuse into the pores at 77 K, possibly as a result of the high diffusion barrier which is unable to overcome the weak interaction between the framework and N_2 molecules or by the contracted pore size which is not sufficient to accommodate N_2 guest molecules.[12]

We next studied the vapor adsorption of benzene into desolvated **1′** to further examine the flexibility of the framework (Figure 2 a, inset). We observed a gated sorption profile (threshold pressure $P/P_0 \approx 0.1$) with benzene and the final uptake quantity indicates the adsorption of one molecule of benzene per formula unit of **1′**. This result suggests that structural rearrangement occurs during adsorption and such expansion of the framework is driven by specific π⋯π interactions between the host and the benzene guest molecules. The commensurate benzene adsorption led us to believe that similar aromatic molecules may be encapsulated in the coordination nanospace based on a charge-transfer interaction with electron-donating guest molecules. Compound **1** shows strong blue emission with a maximum at $\lambda = 427$ nm ($\lambda_{ex} = 330$ nm) as a result of the presence of the naphthalene chromophore (Figure 3 a).[9] The inclusion of a strong electron donor, such as an aromatic amine, may interfere with the emission properties of **1**. Four aromatic amines, AN, NMA, DMA, and DMPT, were selected, with different electron-donating abilities and variable sizes.[9] The postsynthetic guest-encapsulated compounds of **1′** (where the guest molecules were incorporated after the synthesis of **1′**) showed strong color differences, with AN@**1′** (**1a**), NMA@**1′** (**1b**), DMA@**1′** (**1c**), and DMPT@**1′** (**1d**) inclusion compounds appearing light brown, pale yellow, yellow, and orange in color, respectively. ^{1}H NMR spectroscopic studies suggest that 0.81, 0.99, 0.98, and 0.61 molecules of AN, NMA, DMA, and DMPT, respectively, were encapsulated within the framework (see Supporting Information).[9] PXRD patterns of the inclusion compounds are quite different to **1′** indicating that structural reorganization occurs after amine encapsulation.[9] The intense colors observed for **1a**–**1d** are clearly shown also in the UV/Vis absorption spectra, where strong charge-transfer (CT) bands are observed.[9] The emission properties were also interesting, with red shifted broad emission bands detected in the emission spectra of all four inclusion compounds. Compound **1a** shows a slightly shifted emission maximum at $\lambda = 450$ nm whereas **1b** exhibits dual emission with maxima at $\lambda = 425$ and 546 nm, respectively,

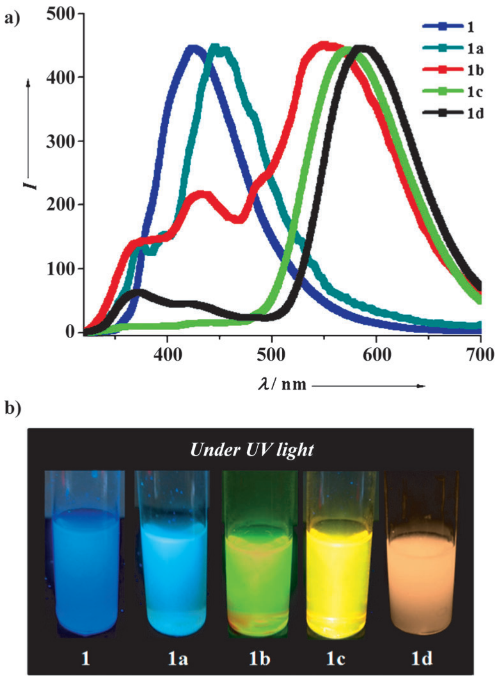

Figure 3. a) Emission spectra of compound **1** and inclusion compounds **1a**–**1d** upon excitation at $\lambda = 330$ nm. b) Photographs of compounds **1** and **1a**–**1d** after dispersion in methanol under irradiation with UV light ($\lambda_{exc} = 350$ nm).

when excited at $\lambda = 330$ nm (Figure 3a). For compounds **1c** and **1d**, the emission maxima are detected at $\lambda = 576$ and 595 nm, respectively. Note, as the electron-donor strength of the amine increases from AN < NMA < DMA < DMPT, the emission maxima also shift to higher wavelengths.

Thus, each aromatic amine can be easily and efficiently recognized through a characteristic visible color change and turn-on emission (Figure 3b). We propose that the featureless broad emission bands in **1b**–**1d** originate from the CT interaction between the guest and the host framework, as suggested from the excitation spectra.[7d] Excitation spectra showed the presence of ground-state interactions, thus ruling out the possibility of exclusive excited-state exciplex emission.

To fully explain these results, the precise molecular arrangements of the guests with the host framework and their interactions with ndc and *o*-phen subunits must be established. Therefore, single crystals of the guest-encapsulated framework were obtained by using the in situ method[9] and the X-ray crystal structures of {[Zn(ndc)(*o*-phen)]·NMA}$_n$ (**1b′**), {[Zn(ndc)(*o*-phen)]·DMA}$_n$ (**1c′**), and {[Zn(ndc)(*o*-phen)]·DMPT}$_n$ (**1d′**) were determined. It was not possible to obtain an X-ray crystal structure of **1a**, with encapsulated aniline, because of very poor single crystallinity.[9] All compounds showed a similar 1D coordination chain as that of **1**, where guest DMF molecules are replaced by the respective amines, and the molecular packing remains similar (Figure 4a–f).[9] In all three frameworks, guest molecules are arranged in a face-to-face fashion with *o*-phen, and the π···π distances indicate strong interactions (centroid–centroid distances: 3.56 Å (**1b′**), 3.55 Å (**1c′**), and 3.65 Å (**1d′**); Figure 4e–g). Interestingly, the naphthalene (ndc) chromophores do not interact with guest amine molecules strongly and instead remain tethered to the *o*-phen by similar C−H···π interactions, as observed in **1** (Figure 1). Furthermore, the structures show that to accommodate larger sized guests, the ndc linkers bend (forming a bow shape) and the orientation of the guest differs in each case. Therefore, to accommodate various sizes of guests, the supramolecular pores are modified and expanded accordingly, suggesting the highly dynamic and adaptive nature of the framework.[9]

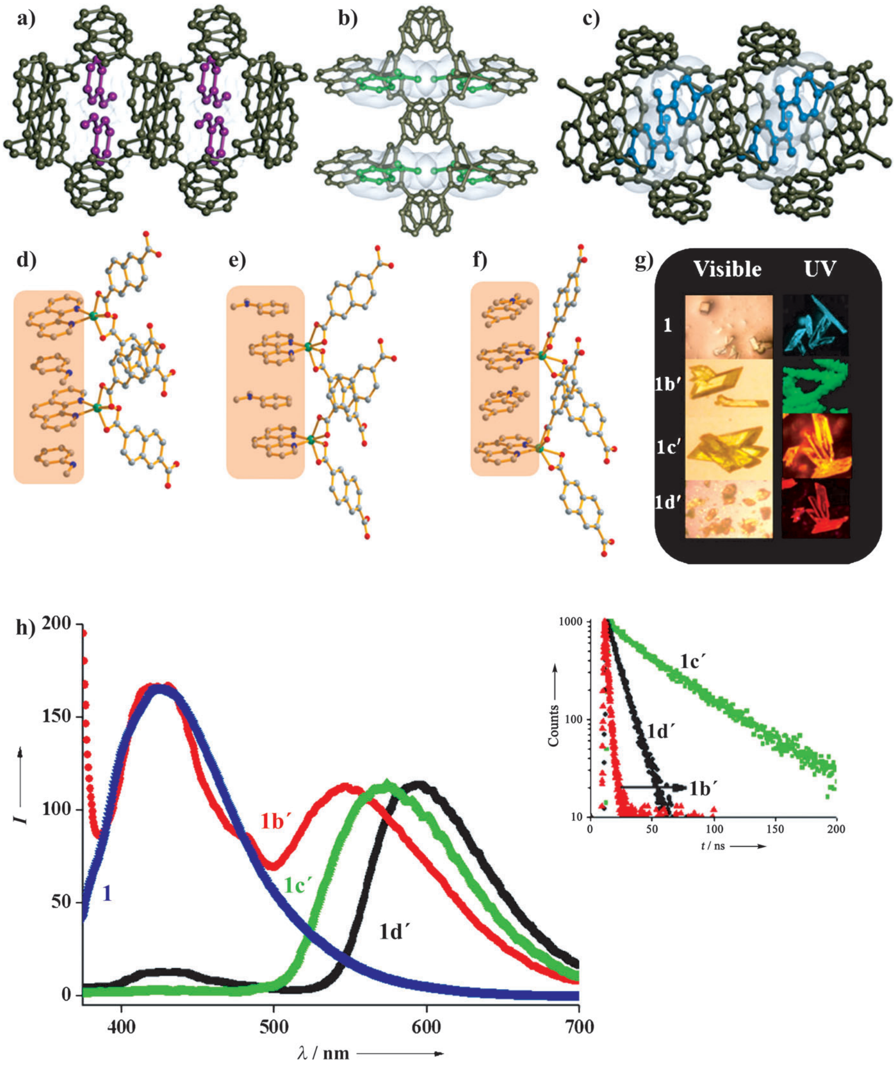

Figure 4. a)–c) Single-crystal X-ray structural characterization showing the location of guest molecules in the coordination nanospaces of **1b′**–**1d′**. d)–f) Face-to-face interactions between stacked aromatic amines and the *o*-phen subunit in **1b′**–**1d′**. g) Images of crystals of **1** and **1b′**-**1d′** under visible light and UV light irradiation. h) Emission spectra of **1** and **1b′**–**1d′** upon excitation at $\lambda = 350$ nm. Inset: fluorescence lifetime profiles of **1b′** (recorded at $\lambda_{em} = 545$ nm), **1c′** ($\lambda_{em} = 575$ nm), and **1d′** ($\lambda_{em} = 595$ nm).

Compounds **1b′**–**d′** are light yellow, yellow, and orange in color, respectively, quite similar to compounds **1b**–**d** (Figure 4g). The emission spectra obtained for **1b′**–**d′** were very similar to those recorded for **1b**–**d**. This similarity suggests that the postsynthetic inclusion compounds (**1b**–**d**) have similar molecular arrangements to that of the in situ synthesized **1b′**–**d′** (Figure 4h). From the X-ray single-crystal structures, it is evident that a CT *o*-phen:amine complexation occurs, which is reflected in the featureless broad red-shifted emission bands and broad absorbance bands in the visible region of the UV/Vis absorption spectrum.[9] We expect that the structurally similar guest molecule aniline should assemble in a similar fashion inside the nanopores.

Interestingly, no naphthalene monomeric emission for **1c′** and negligible monomeric emission for **1d′** were measured. However, for **1b′**, monomeric emission of naphthalene ($\lambda_{em} = 425$ nm) and also CT emission ($\lambda_{em} = 546$ nm) were detected

(Figure 4 h).[9] This quenching of naphthalene emission in **1c′** and **1d′** was surprising as the ndc chromophore remains intact in the framework without undergoing any strong interaction with the encapsulated guest. The most reasonable explanation of such a quenching effect would be energy transfer from the excited ndc monomer to the guest:*o*-phen CT complex (in **1b′** and **1c′**), in line with the previous result.[13] The distances between the ndc and CT complex are in the range of 3.58–3.60 Å, which is suitable for such an energy-transfer process to occur. Further confirmation of the proposed energy-transfer process came from the time-resolved single photon counting experiments of **1c′** and **1d′** upon excitation at $\lambda = 370$ nm and monitoring the emission at $\lambda = 576$ and 595 nm, respectively (Figure 4 h, inset). In both cases, a biexponential decay was detected and the excited-state lifetimes are quite high, that is, 48.5 and 18.5 ns for **1c′** and **1d′**, respectively. Furthermore, the excitation spectra of **1c′–d′** (monitoring the emission at $\lambda = 650$ nm) show maxima at around $\lambda = 330$ nm. This maximum in the excitation spectrum corresponds to the absorption of naphthalene within the framework, revealing an energy transfer from ndc to the CT complex. Excited state lifetimes recorded at $\lambda = 410$ nm (that is, the wavelength of ndc donor emission) for **1c′** and **1d′** are found to be negligible, suggesting efficient energy transfer. Note, the lifetime for the as-synthesized framework **1** monitored at $\lambda = 420$ nm is 2.36 ns.[9] In the case of **1b′**, this energy-transfer process is not efficient, as can be realized from the dual emission and the fluorescence lifetime profile (Figure 4 h).[9] By excitation of **1b′** at $\lambda = 370$ nm and monitoring the emission at $\lambda = 420$ and 546 nm, excited-state lifetimes of 1.98 and 9 ns, respectively, are measured. The lifetime recorded at $\lambda = 420$ nm is for the monomeric ndc emission and this data is in good agreement with the as-synthesized framework **1**. For **1a**, the lifetime detected at emission wavelengths of $\lambda = 470$ and 400 nm are approximately 3 and 2 ns, respectively. This indicates the absence of an energy-transfer process and an efficient charge-transfer interaction in **1a**. As the orientation of guest amines within the host framework is not the same in all cases, the energy-transfer efficiency is different in **1b′–1d′**. The amplification of CT emission with longer excited-state lifetimes, caused by energy transfer between organic chromophores without metal-ion contributions (i.e. in the absence of metal-to-ligand or ligand-to-metal charge transfer), in PCPs (herein for **1c′** and **1d′**) is unprecedented. Furthermore, we have found that the amine is recognized (i.e. uptaken) by the framework within 5–10 seconds as a result of the rapid diffusion process.[9]

As alternative guest molecules, we have encapsulated various other aromatic guests, such as toluene (**1e**), nitrobenzene (**1f**), cyanobenzene (**1g**), and iodobenzene (**1h**).[9] These molecules all have a higher ionization potential compared to AN and thus have weaker electron-donating capabilities. Despite this, X-ray crystal structure determination of the toluene-included framework (**1e**) shows a similar molecular arrangement to that of **1b′–1d′**. In **1e**, toluene is stacked in a face-to-face arrangement with *o*-phen, with a π⋯π stacking distance 3.556 Å.[9] Interestingly, toluene (and the other guests nitrobenzene, cyanobenzene, and iodobenzene) does not form any CT complex. Instead, solvatochromic shifts of emission bands were measured in the emission spectra of these inclusion complexes. Time-resolved single photon counting experiments show lifetimes in the range of 2 ns which originate from ndc monomeric emission.[9]

In conclusion, we have synthesized a 3D supramolecular framework $\{[\mathrm{Zn(ndc)}(o\text{-phen})]\cdot\mathrm{DMF}\}_n$ featuring 1D nano-coordination spaces for molecular recognition. In situ PXRD-adsorption experiments reveal the structural flexibility of the framework upon CO_2 diffusion into the pores. This framework also adsorbs benzene commensurately. This feature is exploited herein for aromatic amine recognition through characteristic turn-on emission. Both aniline and each of the aniline derivatives (NMA, DMA, and DMPT) show characteristic red-shifted charge-transfer emission bands, which indicate their encapsulation. Furthermore, in some cases the sensitization of CT emission through energy transfer from the ndc chromophore results in a tunable emission profile and is unprecedented in PCP systems. These results demonstrate a simple and elegant design strategy that should pave the way for the design of novel porous luminescent platforms for molecular recognition.

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