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Encapsulating Naphthalene in an Electron-Deficient MOF to Enhance Fluorescence for Organic Amines Sensing

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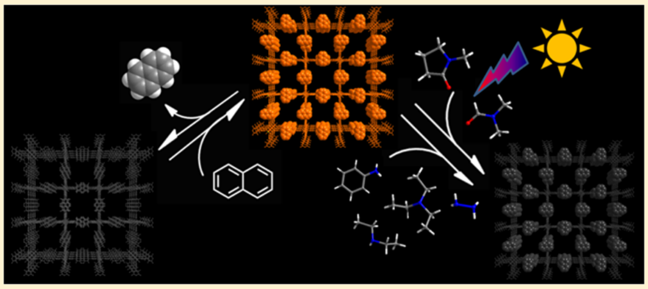
S *Supporting Information*

ABSTRACT: Host−guest encapsulation of electron-rich naphthalene molecules into a weakly emissive porous metal−organic framework based on π-electron-deficient (π-acidic) naphthalene diimide tectons leads to orange-emissive crystals, which can be used to sense strongly basic organic amines in a fast response, high photostability, and tunable sensitivity. Moreover, such host−guest inclusion crystals are also a good photochromic probe for the detection of weakly basic *N*-methyl-2-pyrrolidone and *N*,*N*-dimethylformamide molecules.



INTRODUCTION

Metal−organic frameworks (MOFs) as a new class of multifunctional materials have attracted considerable interest because of their fascinating structures[1−4] and potential applications such as gas storage, catalysis, photoluminescence, ion exchange, drug delivery, and sensing.[5−16] Some of these applications (e.g., gas sorption and chemical sensing) depend on the pore natures of MOFs.[17−24] Naphthalene diimide (NDI)-based MOFs are an attractive class of porous materials with an expanded π-electron-deficient (π-acidic) cavity,[25−28] which in principle are excellent candidates for chemical sensors to detect the electron-rich (basic) organic amines through charge-transfer-induced luminescent and colorimetric changes. However, this ideal desirability is hampered by the weak fluorescence of most reported porous MOFs based on NDIs.[29−31]

Because of the weakly emissive NDIs, the common strategy to enhance fluorescence is the incorporation of electron-donating moieties into NDIs core through covalent bond. However, this method is an elaborate strategy because the separation of byproduct is tedious.[32] Recently, Hisaeda's group has reported that the photoluminescence of NDIs can also be enhanced by the interplay with electron-rich π-systems through charge-transfer interactions.[33] Inspired by it, a luminescent NDI-based MOF is anticipated by encapsulated electron-rich guests into its electron-deficient pore spaces.[34−37] As expected, herein we reported that host−guest encapsulation of electron-rich naphthalene molecules into a weakly emissive porous MOF, $ZnSiF_6(DPNDI)_2$, (Figure 1, DPNDI = *N*,*N*′-di(4-pyridyl)-1,4,5,8-naphthalene diimide) resulted in orange-emissive crystals. As a result, the obtained host−guest crystals can serve as a luminescent and colorimetric probe for the detection of strongly basic organic amines, as well as a photochromic probe for weakly basic *N*-methyl-2-pyrrolidone (NMP) and *N*,*N*-dimethylformamide (DMF) molecules.

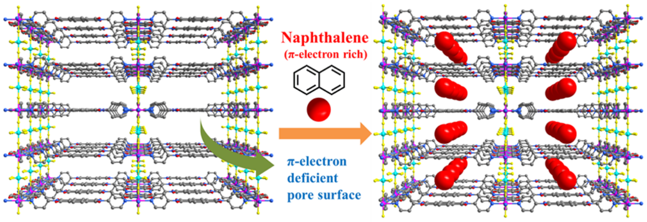


Figure 1. Enscapulation of naphthalene molecule into **1a**.

EXPERIMENTAL SECTION

Materials and measurements. All chemical materials were purchased from commercial sources and used without further purification. ^1H nuclear magnetic resonance (^1H NMR) spectra were recorded on Bruker Avance NMR spectrometer (400 MHz). Fourier transform infrared spectra were taken on a PerkinElmer 2000 spectrometer from KBr pellets in the range of 4000−400 cm^{-1}. Electron spin resonance (ESR) measurements were performed with a Bruker A300 instrument under ambient atmospheric condinion. Powder X-ray diffraction (PXRD) patterns were collected on Rigaku Mini Flex-II X-ray diffractometer with Cu Kα ($\lambda = 1.5418$ Å) radiation in the range of 5−50° at a rate of 10°/min. Thermogravimetric analyses (TGA) were performed on a TG-209 system analyzer under nitrogen atmosphere from room temperature to 800 °C at a ramp rate of 10 °C/min. Solid-

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state UV−vis absorbance studies were performed with a Varian Cary 500 UV−vis spectrophotometer at room temperature. Fluorescence spectra were recorded on an Edinburgh Instrument FLS 980 fluorescent spectrometer on powdered material of the compound. Elemental analyses of C, H, and N were performed on a Vario EL III elemental analyzer. The photoluminescence quantum yield was recorded on a Hamamatsu C11347−11 absolute luminescence quantum yield measurement system equipped with an integrating sphere apparatus and a 150 W CW Xenon light source.

Preparation of $ZnSiF_6(DPNDI)_2$ (1a). The complex **1a** was synthesized following the reported process.[38] In crystallization tubes, upon slow diffusion of an ethanol solution of $ZnSiF_6 \cdot 6H_2O$ (0.10 mmol, 0.021g) into an NMP (5 mL) solution of DPNDI (0.05 mmol, 0.021 g), light-yellow crystalline material was obtained after several days in the dark, which was washed with mother liquid and then immersed in EtOH to stand for 3 d. The resulting solids were filtered and dried in vacuum. Elemental analysis calcd (%) for $C_{48}H_{24}F_6N_8O_8SiZn$: C 55.61, H 2.29, N 10.69; found 55.93, H 2.33, N 10.99%. IR (KBr pellet, cm^{-1}): 3563 (w), 3066 (w), 1718 (s), 1671 (s), 1570 (s), 1449 (m), 1358 (s), 1253 (s), 1136 (m), 983 (s), 766 (m), 618 (s).

Preparation of 1a⊃Naphthalene. The freshly prepared dry samples (20 mg) of **1a** were immersed in EtOH solution of the different concentrations (5, 20, 40, 75, 100, 150 mM) of naphthalene, after which the mixture was allowed to stand for 3 d. The resulting solids were filtered and washed with EtOH several times to remove dye molecules on the crystal surface. The resulting solids were dried in vacuum. IR (KBr pellet, cm^{-1}): 3532 (w), 3077 (w), 3040 (w), 1713 (s), 1676 (s), 1581 (s), 1443 (m), 1343 (s), 1243 (s), 1120 (m), 988 (s), 819 (m), 761 (m), 618 (s).

Naphthalene Release. Dry samples of **1a**⊃naphthalene (2 mg) were immersed in respective deuterated solvents (0.6 mL) in sealed glass bottles, after which the mixture was allowed to stand for 12 h. The resulting supernatants were used for NMR measurements.

The Solvent-Sensing Experiment. The solvent-sensing experiment was performed as follows: finely ground samples of dired **1a**⊃naphthalene (2 mg) were immersed in different organic solvents (3 mL), treated by ultrasonication for 30 min, and then aged to form stable emulsions before fluorescence was measured.

■ RESULTS AND DISCUSSION

Millimeter-sized single crystals of **1** were synthesized via slow diffusion of zinc fluorosilicate hexahydrate into *N*-methylpyrrolidin-2-one solution of DPNDI as described in the literature.[38] **1** is a crystalline porous material exhibiting two types of one-dimensional channels along the *b* and *c* axes of ~7 × 20 and 20 × 20 Å, respectively (Figures 1, S1, and S2). Thermogravimetric analysis of **1** showed that the channels are occupied by solvent molecules, that the solvent molecules were evacuated at 200 °C, and that the resulting dried framework (hereafter named as **1a**) was stable up to 350 °C (Figure S3, Supporting Information). The PXRD patterns are not changed on the removal of solvent molecules.

The naphthalene molecules were encapsulated into the pores by adding sample of **1a** to the naphthalene ethanol solution with different concentrations (5, 20, 40, 75, 100, 150 mM), and then the mixture was allowed to stand for 3 d. The resulting solids were filtered and washed with ethanol several times to remove the residual naphthalene molecules on the crystal surface. It is interesting to find that the sample undergoes a color change from off-white to yellow (Figure 2a). The solid diffuse reflectance spectrum of **1a** after soaking in naphthalene solution shows a strong absorption in the region of 450−600 nm (Figure S7, Supporting Information), which can be attributed to the charge transition between the NDI and naphthalene molecules in the framework,[33,34] which suggests that the naphthalene molecules were successfully introduced into the framework to form a crystal accommodating naphthalene molecules (**1a**⊃naphthalene). It should be pointed out that the naphthalene molecules were encapsulated into **1a** through intermolecular interactions, which not only immobilize the naphthalene molecules in the pores but also facilitate the charge transfer between the naphthalene molecules and the electron-deficient **1a**. To confirm such encapsulation is attributed to the strong donor−acceptor interactions between naphthalene and MOF framework, a naphthalene releasing experiment was performed in several pure solvents (ethanol, chloroform, acetonitrile, and dimethyl sulfoxide) measured by ^1H NMR spectroscopy. Upon addition of the sample of **1a**⊃naphthalene to deuterated solvents for 12 h at room temperature, the signal of ^1H NMR at 7−8 ppm assigned to the released naphthalene molecules almost cannot be observed (Figure S8, Supporting Information), which indicates that the naphthalene molecules are hardly released in organic solvents. Hence, a conclusion that the enrichment is resulted from donor−acceptor interactions of naphthalene and MOF framework can be demonstrated. On the basis of the TGA, the naphthalene in **1a**⊃naphthalene composites were determined to be 0.12 wt % (150 mM). In addition, the PXRD also confirmed that the crystals are stable during the release experiment of naphthalene molecules from **1a** framework (Figure S15, Supporting Information).

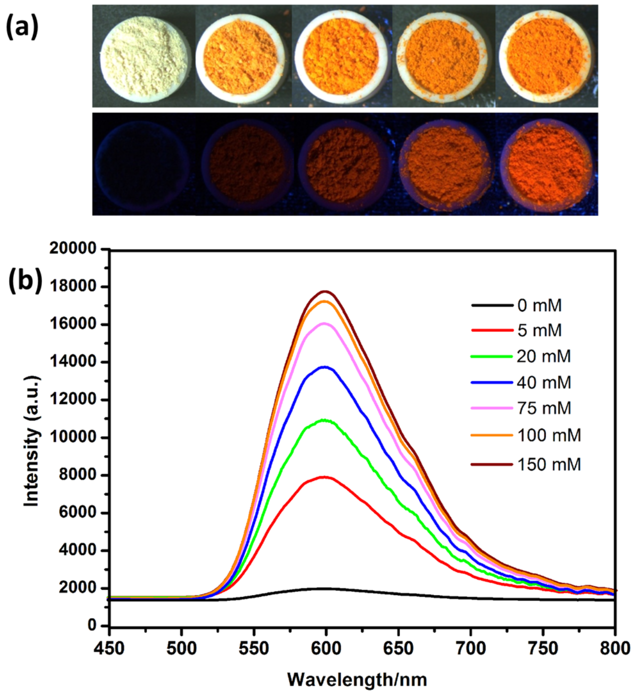

Figure 2. (a) Photographs showing photoluminescence enhancements of **1a**⊃naphthalene with different naphthalene concentrations (left to right) 0, 5, 20, 75, and 150 mM (top) under ambient light and (bottom) under 365 nm UV light. (b) The photoluminescence response of **1a**⊃naphthalene to different concentrations of naphthalene.

The solid-state emission spectra of DPNDI, **1a**, and naphthalene were investigated at room temperature. The DPNDI in state solid shows two broad bands with maximum absorption at 430 and 579 nm in the emission spectrum when excited at 300 nm (Φ_f < 0.1%), which arise from the intramolecular and intermolecular electron transitions. The sample of **1a** also exhibits two broad bands at the same position of DPNDI ligand in a very low quantum yield ($\Phi_f < 0.1\%$) and short average lifetime ($\tau \approx 6.3$ ns). However, the intensity of the emission of **1a** at 579 nm is much lower than the emission at 430 nm, which is because the intermolecular electron transition was suppressed by framework (Figure S9, Supporting Information). Surprisingly, as the naphthalene molecules are gradually encapsulated into the pore matrix, the resulting **1a**⊃naphthalene host−guest crystals display strong fluorescence in the orange region (Figure 2). With the naphthalene concentration increasing, the emission is gradually enhanced dramatically. When the concentration of the naphthalene was 150 mM, the emission intensity reached a maximum value at 600 nm in orange colors with a high fluorescent quantum yield of 15.6% and a long average lifetime ($\tau \approx 27.7$ ns; Figure 2b, Figure S14, Supporting Information). Such photoluminescence enhancements can be attributed to the exciplex electronic charge transfer state formed by the framework and naphthalene guest molecules.[33] To determine whether such enhanced fluorescence properties are originated from host−guest interactions, we recorded the emission spectra of naphthalene and a physical grounded mixture of naphthalene and **1a** under the same concentrations. Naphthalene displays a sharp emission at 337 nm in solid state, different from those in **1a**⊃naphthalene. In addition, the mechanically grounded mixture presents both emission bands of **1a** and naphthalene when excited at 275 nm in the solid state (Figures S11 and S12, Supporting Information), which is also different from those of **1a**⊃naphthalene (Figure S12, Supporting Information). These results indicate that the naphthalene is uniformly encapsulated in the pores of **1a**⊃naphthalene as isolated molecules but not aggregates in host−guest crystals.

So far, there have been several examples involving NDI-based MOFs reported; the photophysical properties of these MOFs have not yet been studied because of the very weak fluorescent properties of NDI.[39−42] As a result, their potential application as a fluorescent sensor is hampered. For the luminescent **1a**⊃naphthalene, although encapsulated by naphthalene molecules, it still possesses an electron-deficient square channel of ca. 20 Å × 20 Å along the direction of $ZnSiF_6$ (c axis, Figure S1, Supporting Information) and is capable to sense organic amines. To explore the ability of **1a**⊃naphthalene to sense a trace quantity of organic amines, its fluorescence spectra were measured upon addition of analytes, which showed that, with increasing concentrations of aniline solution added to the fixed amount **1a**⊃naphthalene, rapid and strong fluorescence quenching was observed (Figure S18, Supporting Information). However, other functionalized analytes, such as benzene, toluene, chlorobenzene, and nitrobenzene, exhibited a negligible fluorescence quenching when encapsulated in **1a**⊃naphthalene. Moreover, the universality of this host−guest MOF toward a wide range of organic amines, such as triethylamine, diethylamine, and hydrazine was also tested (Figures 3b and S19), which showed that all of them can quench the photoluminescence of **1a**⊃naphthalene. Among them, the quenching by trimethylamine is most slow due to its bulky size. Accompanied with the fluorescence quenching, the color of host−guest crystals are also changed upon addition of the above amines (Figures 3a and S21), which may be attributed to the electron transfer from strongly basic amines to π-acidic NDI moieties.[43−45] To improve applicability, the sensing ability of **1a**⊃naphthalene toward the vapors of organic amines was also studied. In a typical experiment, **1a**⊃naphthalene was exposed to the above organic amine vapors for a period of time (∼2 h) at room temperature, and then we measured their fluorescence changes. Similar to the phenomena observed by adding the amine solutions, the fluorescence of **1a**⊃naphthalene was also completely quenched when exposed to the amine vapors (Figure S22, Supporting Information).

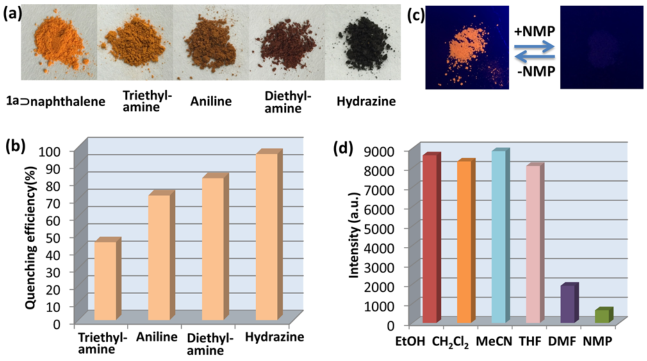

Figure 3. (a) Photograph showing the color changes of **1a**⊃naphthalene samples in the presence of the different amines; (b) bar chart representation for quenching efficiency of **1a**⊃naphthalene in the presence of different organic amines (10 mM) in EtOH; (c) photograph showing fluorescence quenching of **1a**⊃naphthalene toward NMP solvent (under 365 nm UV light); (d) emission intensities (600 nm) of **1a**⊃naphthalene in various solvents.

Considering that the **1a**⊃naphthalene can sense strongly basic organic amines, we also explored its sensing capability toward common organic solvents (CH_2Cl_2, MeCN, tetrahydrofuran, EtOH, DMF, and NMP) with a lower basicity. When **1**⊃naphthalene (2 mg) was immersed in 3 mL of the above organic solvents for 30 min, the photoluminescence intensities were observed to be independent of the solvent except NMP and DMF (Figure 3d), which indicates that **1a**⊃naphthalene can be considered to be a probe to detect NMP and DMF solvent (Figure S16, Supporting Information). Importantly, the contaminative powder of **1a**⊃naphthalene can be regenerated by soaking in pure ethanol and reused in the aforementioned experiments without notable loss of the selectivity (Figure S17, Supporting Information). Thus, **1a**⊃naphthalene is a fluorescent sensor for the detection of NMP molecules in a high sensitivity, selectivity, and recyclability.

However, different from **1a**⊃naphthalene soaked by organic amines, the colors of those soaked from NMP and DMF solutions are not changed. It is known that NMP (or DMF) is a kind of electron-donating (weakly basic) solvent, which can give electrons to acceptors upon irradiation. As expected, the **1a**⊃naphthalene is photosensitive, giving a color change from yellow to brown upon exposure to UV−vis light when it soaks NMP molecules (Figure 4a). This characteristic phenomenon is similar to that observed for NDI derivatives,[46−49] suggesting that the color change of **1a**⊃naphthalene arises from the formation of the radical NDI species. To confirm the generation of the NDI radical, the ESR spectra of **1a**⊃naphthalene was studied before and after irradiation (Figure 4b). The wet sample of **1a**⊃naphthalene (soaking in NMP) exhibits no ESR signal before irradiation, but after irradiation it shows a single-peak radical signal with a g value of 2.0024. This indicates that the NDI radical should originate from NMP molecules to NDI moieties electron transfer, because no photochromic phenomenon or ESR signal was observed in the dry sample of **1a**⊃naphthalene (Figures S24 and S25, Supporting Information). In other words, due to the presence of electron-donating NMP, the DPNDI units can

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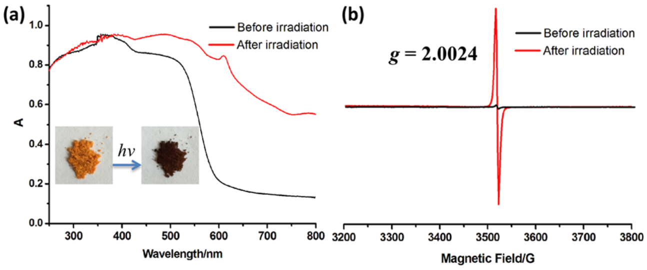

Figure 4. (a) UV−vis spectra showing the photochromic behavious of **1a**⊃naphthalene after soaking NMP solvent. (inset) The photochromic behaviors from photographic images. (b) ESR spectra of **1a**⊃naphthalene soaking NMP solvent.

accept electrons from NMP first to form the NDI radicals upon excitation but not generate the excited electronic charge-transfer state between naphthalene and DPNDI units. For organic amines, due to the stronger electron-donating ability (strongly basic) than NMP (weakly basic), each amine molecule can donate one electron to DPNDI units spontaneously under thermal stimulus and eventually lead to the color change and fluorescence quenching of the NDI radicals (Figure S26, Supporting Information).

CONCLUSION

In summary, we have employed host−guest interactions to prepare strongly luminescent crystals from a weakly emissive porous MOF based on electron-deficient NDI tectons. The high quantum yield of these crystals is attributed from an excited-state charge transfer between the electron-deficient NDI tectons in MOF hosts and naphthalene guests. More interestingly, such host−guest crystals are demonstrated to be a good luminescent and colorimetric probe for the detection of strongly basic organic amines, as well as a photochromic probe for weakly basic NMP and DMF molecules.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b00252.

> TGA, PXRD plots, photographs, ^{1}H NMR spectroscopy, UV−vis spectra, IR, ESR, fluorescence spectra, perspective view of three-dimensional framework of **1**. (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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