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Lone pair $-\pi$ interaction-induced generation of non-interpenetrated and photochromic cuboid 3-D naphthalene diimide coordination networks[†]

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Interpenetration is an intrinsic behaviour for the porous coordination networks. To prevent the interpenetration, a common strategy is the imposition of geometric or steric restrictions by incorporating bulky moieties into organic tectons. So far, most of the available incorporations have been achieved through a covalent connection, while few involved in the non-covalent weak interactions. In this paper, we have reported that such interpenetration can be prevented by the less common lone pair– π interactions. By imposing the lone pair– π interactions through the addition of lone-pair-bearing *N*-methylpyrrolidin-2one or iodine, combinations of rigid naphthalene diimide tectons bearing two divergently oriented pyridyl units at both imide extremities with ZnSiF₆ led to non-interpenetrated cuboid 3-D coordination networks that should have been interpenetrated. In addition, such close-contacting lone pair– π interactions between electron donors and acceptors have also been demonstrated to play a key role in their photochromic properties.

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Introduction

Porous coordination networks or metal–organic frameworks (MOFs) have attracted much interest because of their potential applications such as gas storage, catalysis and separation.¹ When dealing with porous frameworks, the primary focus has been on the pore size of the crystalline materials.² However, upon increasing the pore size, the system always undergoes interpenetration in order to increase the stability of the final architecture at the expense of free space.³ To prevent such interpenetration, a common strategy is the erection of geometric or steric restrictions by incorporating bulky substituents or moieties into organic tectons.⁴ So far, most of the available incorporations have been achieved through a covalent connection,⁵ while few involved in the non-covalent weak interactions.⁶

Non-covalent interactions related to the electron-deficient aromatic (π -acidic) systems have recently emerged as a new branch of supramolecular chemistry. For instance, Matile et al. reported that the π -acidic NDI derivatives could enable anion transport, recognition and catalysis *via* anion– π interactions.⁷ Lone pair- π interaction, which takes place between lone-pairbearing electronegative atoms of the neutral molecules and π -acidic aromatic systems, is a counterintuitive intermolecular force in supramolecular chemistry.8 Generally, it is too weak to be harnessed in the self-assembly. However, recently we have reported a series of detectable lone pair- π interactions in the electron-deficient naphthalene diimides (NDIs).9 Due to such lone pair- π interactions, the π - π interactions in the crystal of organic tecton, N,N'-di(4-pyridyl)-1,4,5,8-naphthalene diimide (DPNDI, Scheme 1), have been found to be seriously hindered and almost no π -stacks have been found. Based on this finding, there is every reason to believe that the lone pair- π interactions between DPNDIs and lone-pair-bearing small molecules can be used to prevent the interpenetrations in porous coordination networks. Herein, we have reported that this design concept is indeed viable.

For the realization of this concept, the porous cuboid 3-D architecture of the type ab2 (Fig. 1, left) was selected as a proof-of-concept target because it has been demonstrated to be facilely formed by the combination of bipyridyl organic tectons (*e.g.* T1–T3 in Scheme 1) and $ZnSiF_6$ behaving as an



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Fig. 1 Schematic representation of non-interpenetrated (left) and twofold interpenetrated (right) cuboid networks of the ab2 type based on the combination of bipyridyl organic tectons with $ZnSiF_{6}$.

infinite pillar, indicating that the same can also apply to the tecton DPNDI.¹⁰ A further reason is that the elongation of organic tectons (*e.g.* T4–T5 in Scheme 1) has been reported to generate a two-folded interpenetrated network (Fig. 1, right).¹¹ Compared with T4 (13.5 Å), DPNDI is much longer (15.4 Å, close to T5 of 15.6 Å), which implies that the combination of DPNDIs and ZnSiF₆ should have led to an interpenetrated cuboid 3-D network. However, as expected, such interpenetration is prevented in two obtained crystals 1 and 2 by imposing the lone pair– π interactions through the addition of lone-pairbearing *N*-methylpyrrolidin-2-one (NMP) or iodine as guest molecules.

Experiments

Materials and measurements

N-Methylpyrrolidin-2-one (NMP, 99%), ZnSiF₆·6H₂O (98%), ethanol (EtOH, 99%), and I₂ were obtained from commercial suppliers. All chemicals and reagents were used as received unless otherwise stated. The organic tecton DPNDI was synthesized following the reported process.¹² The infrared spectra have been measured in the range of 400–4000 cm⁻¹ using a Perkin-Elmer FT-IR spectrophotometer. Powder X-ray diffraction (PXRD) patterns have been recorded on a Rigaku Mini-Flex-II X-Ray diffractometer, while thermogravimetric analyses (TGA) of crystalline samples have been performed on a STA 449C simultaneous thermal analyser with a heating rate of 10 °C min⁻¹ under an N₂-atmosphere. UV-Vis diffuse reflectance spectra were recorded at room temperature on a Varian Cary 500 UV-Vis spectrophotometer equipped with an integrating sphere.

Synthesis

DPNDI. DPNDI (0.10 mmol, 42.0 mg) was added in NMP (5 mL) solution, and then the solution was stirred for 5 minutes at room temperature. The resulting brown solution was left standing for two days; light yellow block crystals were obtained from the filtrate. Yield: 82% based on DPNDI. IR data (KBr, cm^{-1}): 3038(w), 2969(w), 1715(m), 1695(s), 1617(m), 1508(s), 1422(m), 1303(m), 1225(m), 988(m), 806(m), 754(m).

Crystals 1 and 2. In crystallization tubes, a solution (0.5 mL) of NMP–EtOH (1:1, v/v) was carefully layered on an NMP (5 mL) solution of DPNDI (0.05 mmol, 0.021 g), and then the EtOH solution of $ZnSiF_{6}$ ·6H₂O (0.10 mmol, 0.021 g) (together with I₂ (0.05 mmol, 13 mg) for 2) in EtOH (5 mL) was carefully added as a second layer. Crystals suitable for X-ray analysis were obtained after several days in the dark.

1: light yellow crystal, yield: 25% based on DPNDI. IR data (KBr, cm⁻¹): 3548(w), 3067(w), 2957(w), 1695(m), 1645(s), 1608(s), 1537(m), 1352(m), 1243(m), 1089(s), 988(m), 806(s), 754(m), 618(w).

2: Reddish brown crystal, yield: 18% based on DPNDI. IR data (KBr, cm⁻¹): 3478(w), 3076(w), 2934(w), 1705(s), 1685(s), 1603(m), 1529(m), 1302(m), 1265(m), 1068(s), 958(m), 806(s), 759(m), 635(w).

X-ray diffraction analysis

Crystal data for organic tecton DPNDI were collected using a graphite monochromatic Mo-K α radiation ($\lambda = 0.71073$ Å) using a w scan mode on a RIGAKU RAXIS-RAPID IP diffractometer at 293 K, while complexes 1 and 2 were collected on a Rigaku Saturn 724 CCD diffractometer with Mo K α radiation (λ = 0.71073 Å) at 113 K. The structures were solved by direct methods and different Fourier syntheses. All calculations were performed by full-matrix least-squares methods on F^2 using the SHELXTL-97 program,¹³ all the non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms were fixed at calculated positions and refined using a riding model. For complexes 1 and 2, some of the included solvents were in disorder and thus their contributions were subtracted from the data using SQUEEZE from the PLATON package of crystallographic software.¹⁴ All the crystal data and the structure refinements are summarized in Table 1. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1028277, 1025385 and 1025386 for DPNDI, 1 and 2, respectively.

Results and discussion

As we have reported previously,⁹ due to the strong π - π interactions, the organic tecton DPNDI is almost insoluble in common organic solvents but is highly soluble in the electron-rich

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Table 1 Crystal data and structure refinement parameters for DPNDI, 1 and 2^{a,b}

Complexes	DPNDI	1	2
Crystal size (mm)	0.38 imes 0.32 imes 0.20	0.45 imes 0.28 imes 0.22	0.28 imes 0.22 imes 0.18
Empirical formula	$C_{34}H_{30}N_6O_6$	$C_6H_{1,45}F_{0,75}NOSi_{0,13}Zn_{0,13}$	$C_6H_3F_{0.75}I_{0.20}NOSi_{0.13}Zn_{0.13}$
Formula weight	618.64	129.47	157.04
Crystal system	Monoclinic	Tetragonal	Tetragonal
Space group	C2/c	P4/mmm	P4/mmm
a (Å)	21.341(5)	19.702(4)	19.739(3)
b (Å)	6.9041(14)	19.702(4)	19.739(3)
c (Å)	21.272(4)	7.4311(15)	7.4768(15)
α (°)	90	90	90
β (°)	103.30(3)	90	90
γ (°)	90	90	90
$V(Å^3)$	3050.2(11)	2884.6(10)	2913.2(9)
Z	4	8	8
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	1.347	0.596	0.716
μ (Mo K α) (mm ⁻¹)	0.095	0.258	0.691
F(000)	1296	518	617
Collected reflections	14 511	24 189	24 611
Independent reflections	3468 (0.0372)	1968 (0.0461)	1984(0.0550)
Goodness-of-fit on F^2	1.042	1.076	1.186
R_1 , ^{<i>a</i>} w R_2 ^{<i>b</i>} ($I > 2\sigma(I)$)	0.0603, 0.1600	0.0641, 0.2035	0.1088, 0.3423
R_1 , ^{<i>a</i>} w R_2 ^{<i>b</i>} (all data)	0.0943, 0.1797	0.0642, 0.2038	0.1100, 0.3465
${}^{a}R_{1} = \sum F_{0} - F_{0} / \sum F_{0} , {}^{b}WR_{2}$	$= \left[\sum w (F_0^2 - F_0^2)^2 / \sum w (F_0^2) \right]^{1/2}.$		



Fig. 2 A Single crystal structure of cocrystal DPNDI with NMP highlighting the lone pair $-\pi$ and CH $-\pi$ interactions. For clarity, all the H atoms except for those present in methyl of NMP are omitted.

solvents, such as DMF, DMA, and NMP. The good solubility is mainly attributed to the formation of lone pair– π interaction between the solvents and NDI π -acceptors during the dissolution. This important design basis for this work is again confirmed by the cocrystal structure of DPNDI and NMP (Fig. 2), which revealed that each DPNDI molecule is stabilized by two recumbent NMP molecules—one above and another below the NDI plane—through lone pair– π and CH– π ($d_{C-\pi} = 3.53$ Å) interactions. The distances between the oxygen lone-pair electrons in both NMP molecules and the imide ring of DPNDI are around 3.26 Å, while the angles between NMP and NDI planes are around 3.62°.

In view of the fact that the height between the two neighbouring organic tectons for cuboid 3-D architectures from ZnSiF_6 is around 7.60 Å that can only fill one recumbent NMP but not the previously reported stand-up DMF molecule,⁹ NMP

was chosen as the lone-pair-bearing guest molecule. Lightvellow crystals of 1 were obtained in quantitative yields upon slow diffusion of ethanol solution of ZnSiF6.6H2O into NMP solution of DPNDI with a buffered layer of a mixed solution of ethanol and NMP (1:1 in volume) after several days. Indeed, the X-ray single-crystal diffraction analysis revealed that it is a non-interpenetrated cuboid 3-D framework (tetragonal, space group P4/mmm, for details, see ESI[†] and Fig. S1-S2) with the formed channels filled by a mixture of ethanol and NMP (Fig. 3). Due to the bad disorder, neither of them could be refined and thus both of them were subtracted from the data using SQUEEZE. The purity of the crystalline materials generated for 1 was investigated by X-ray diffraction on powder samples (PXRD), which reveals that almost only one phase was observed because of a good fit between their simulated and observed patterns (Fig. S4, ESI†). The slight discrepancies come from the trace collapsed crystalline materials upon removal of the guest molecules (particularly ethanol) during their separation and measurement.

For the cuboid 3-D framework, each Zn^{2+} cation adopts a hexacoordinated octahedral coordination geometry to contact with two F atoms (Zn–F distance in the 2.01–2.03 Å) and four N atoms belonging to four DPNDI tectons (Zn–N distance of 2.16 Å). As expected and previously observed with other bipyridyl tectons,^{10,11} such octahedral Zn^{2+} cations and SiF_6^{2-} anions are staggered with each other (*ca.* 45° for both the cases) and mutually bridged through the formation of Zn–F bonds to generate an infinite linear ZnSiF₆ pillar with a Zn–Zn distance of *ca.* 7.43 Å along the pillars (Fig. 3a), which is slightly shorter than those from the electron-rich organic tectons.^{10,11} The interconnection of consecutive ZnSiF₆ pillars by DPNDI tectons leads to the final 3-D cuboid architecture with a Zn–Zn distance of 19.70 Å perpendicular to the pillars Paper



Fig. 3 Portions of the X-ray crystal structures (ball-and-stick superimposed with space-filling model) of the cuboid 3-D framework **1** generated upon combining DPNDI tectons with $ZnSiF_6$ pillars showing the formation of pillars (a) as well as channels along *a* and *c* axis (b and c). H atoms and solvent molecules are omitted for clarity.

(Fig. 3b and c). For each DPNDI tecton in both the cases, the NDI core and the pyridine group are almost mutually perpendicular (a dihedral angle in free ligand of *ca.* 70.4°),⁹ which is mainly attributed to their good separations in cuboid 3-D architectures.

From the standpoint of the tectonic length, the porous cuboid 3-D framework 1 should have been interpenetrated. However, the reality is just the opposite, which is supposed to be prevented by the interplays between the including NMP molecules and DPNDI units through lone pair– π interactions. As mentioned above, NMP molecules in the channels of 1 could not be refined and thus no lone pair– π interactions have been observed in crystallography. However, the clues of the close contacts between NMP molecules and DPNDI units can be found from the cocrystal structure of DPNDI and NMP (Fig. 2), as well as the thermogravimetric analysis (TGA) and photochromic studies (see below). As shown in Fig. S6,† around 40% sharp weight loss is observed for 1 at less than 150 °C, which may be due to the loss of crystalline solvents (ethanol and NMP) without strong interplay with the

framework. In the temperature range of 150–200 °C, *ca.* a 5% slower weight loss may be attributed to the loss of NMP molecules in the mezzanines between the consecutive DPNDI units through lone pair- π interactions.

It is known that the iodine atoms bear much looser lone pairs than O atoms, which suggests that iodine should have stronger lone pair- π interactions with DPNDI tectons than NMP molecules. As expected, the addition of iodine into the reaction mixtures of 1 led to reddish-brown crystals of 2. The single crystal structural analysis of the latter revealed that it is an isostructure of 1 (tetragonal, space group P4/mmm, see ESI[†]). The remarkable difference is included guest molecules in the mezzanines between consecutive DPNDI units (NMP for 1, but I_2 for 2, see Fig. S3[†]). Indeed, along the ZnSiF₆ pillars, each mezzanine between the consecutive DPNDI units in crystal 2 is observed to be occupied by I2 molecules with respective *ca.* 40% occupancies through the lone pair- π interactions. The distances between I atoms and imide rings are in the range of 3.74–3.76 Å (Fig. 4), which is slightly shorter than those found in the free ligand (3.26 Å between the O atoms of the NMP molecules and the imide rings in the cocrystals of DPNDI and NMP, wherein the atomic radius is 0.66 Å for O, while it is 1.95 Å for the I atom). The purity of the crystalline materials generated for 2 has been checked by PXRD (Fig. S5[†]), and their TGA has also been investigated (Fig. S7[†]). Compared with the TGA pattern of 1, the relatively slower weight loss in the temperature range of 150-200 °C disappeared in 2, which is somewhat confirmed by the lone pair- π interactions between NMP molecules and DPNDI units.

Recently Han and co-workers have reported a photochromic NDI coordination network due to the photo-induced NDI radical generation in the presence of the close-contracting and electron-donating amide molecules (*e.g.* DMF).¹⁵ Similarly, crystal **1** is sensitive to light and can undergo a photochromic transformation from yellow to dark green upon irradiation by a 365 nm UV light within 10 minutes, indicating the existence of the close contacts between the electron-donating NMP



Fig. 4 Portions of the X-ray structures (ball-and-stick model) of the cuboid 3-D frameworks **2** showing lone pair $-\pi$ interactions between I₂ (*ca.* 40% occupancies) and π -acceptors. H atoms, solvent molecules and another statistical I₂ (*ca.* 40% occupancies) towards antipodal imide units are omitted for clarity.



Fig. 5 The spectral changes of the cuboid 3-D frameworks 1 (a) and 2 (b) upon irradiation by a 365 nm UV light (11 W).

molecules and DPNDI units in crystal 1. In consistence with the decoloration, the solid-state UV/Vis diffuse reflectance spectra show that the appearance of an expected broad band with a maximum absorption of ca. 630 nm is assigned to the NDI radicals upon irradiation, whose intensity increases with the prolongation of irradiation time (Fig. 5a). However, the replacement of the NMP molecules in the mezzanines between the consecutive DPNDI units of the cuboid 3-D frameworks (crystal 1) by I_2 (crystal 2) with weaker electron-donating ability leads to reduction in the sensitivity towards light (Fig. 5b). In the process of photo-induced NDI radical generation, the NMP molecules have been reported to act as electron donors and could transfer electrons to DPNDI units upon irradiation.¹⁶ When the partial NMP molecules in the mezzanines have been replaced by poor electron-donating I₂, the number of closecontacting NMP molecules decreases. Undoubtedly, the sensitivity towards light is weakened, which again corroborates our deduction on the existence of lone pair- π interactions between NMP and DPNDI units in crystal 1.

Conclusions

In summary, we have reported a simple but efficient approach to prevent the interpenetration of cuboid 3-D coordination networks by imposing the lone pair– π interactions. In the presence of NMP or iodine as guest molecules, the combinations of naphthalene diimide tectons bearing two divergently oriented pyridyl units at both imide extremities with ZnSiF₆ behaving as infinite pillars lead to two non-interpenetrated and photochromic cuboid 3-D coordination networks that should have been interpenetrated. In addition, such close-contacting lone pair– π interactions between electron donors and acceptors have also been demonstrated to play a key role in their photochromic properties. Other application studies on these porous networks are in progress, which will be published in due course.

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