Anthracene array-type porous coordination polymer with host–guest charge transfer interactions in excited states†

Daisuke Tanaka,[a] Satoshi Horike,‡[a] Susumu Kitagawa,*[a] Masaaki Ohba,[a] Miki Hasegawa,[b] Yoshiki Ozawa[c] and Koshiro Toriumi[c]

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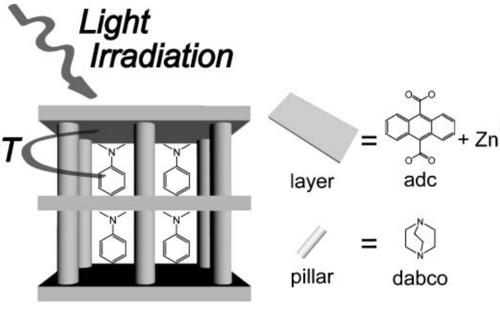
Confinement of electron donor guests affords an efficient, photo-induced charge transfer (CT) with the anthracene moieties of a porous coordination polymer.

Functionalization of porous coordination polymers (PCPs) is very topical in the area of materials chemistry because of their potential applications in various fields, including separation, ion exchange, catalysis, sensing and optoelectronics.[1] Especially, PCPs prepared from large π-conjugated molecules could be useful as optical materials. There are several reasons for this. (1) π-conjugated groups are frequently introduced into PCPs, resulting in π moieties being uniformly distributed, in a high content, throughout the crystal structure. The supramolecular organization of π-conjugated molecules plays an important role in facilitating energy, charge and electron transfer processes. (2) PCPs can serve as hosts for the incorporation of photoactive and/or redox active molecules into their nanosized spaces, therefore yielding a potentially useful new class of host–guest nanostructures. (3) The confinement of molecules into small nanosized spaces alters their properties and reactivity. For example, if one is able to optimize the assemblies that comprise a PCP–guest redox couple, then a photoinduced charge transfer (CT) between the host and confined guests in the nanosized space would occur, resulting in novel photoactive materials. However, such function-engineered PCPs with large π-conjugated systems are not popular,[2] although a few examples of photo-induced host–guest interactions in the nanosized pores of PCPs have been reported.[3]

In this paper, the authors describe the design of PCPs with a π-conjugated pore surface in order to achieve a CT interaction in the excited state between a host framework and guest molecules. The anthracene derivatives are suitable molecular units for PCPs because of their large interaction area and unique π–π* electron transitions, which provide useful chemical and physical properties. Zn^{II} complexes are also suitable candidates; they provide not only versatile structures but also photoluminescent properties. The authors therefore synthesized the PCP of $\{[Zn_2(adc)_2(dabco)]\}_n$ (**1**) (adc = 9,10-anthracenedicarboxylate,[4] dabco = 1,4-diazabicyclo-[2.2.2]octane) and demonstrated that its photoluminescent properties originated from the host–guest CT interaction (Scheme 1).

The solvothermal reaction of $Zn(NO_3)_2 \cdot 6H_2O$, adc and dabco in a mixture of *N*,*N*-diethylformamide (DMF) and MeOH afforded the solvated framework compounds $\{[Zn_2(adc)_2(dabco)](DMF)_{3.6}(MeOH)_{1.8}(H_2O)_{1.8}\}_n$ (**1** ⊃ Solvents). Single crystal X-ray analysis demonstrated that the 3D porous network of **1** ⊃ Solvents is based on 2D layers of $\{[Zn^{II}(adc)]\}_n$, constructed from paddle-wheel units, and pillars of dabco. This is similar to previously reported PCPs (Fig. 1).[5,6] The solvent in **1** ⊃ Solvents is not crystallographically well-defined, even at 150 K. The numbers of guest molecules are estimated from thermal gravimetric (TG) measurement and elemental analysis (EA) (see ESI†). The dihedral angle between the adc π plane and the (110) plane is 58.5°, although that of $\{[Zn_2(bdc)_2(dabco)]\}_n$ (bdc = 1,4-benzenedicarboxylate), similar to **1** ⊃ Solvents, is 0°.[5a] This large torsion angle gives a nonporous, undulated 2D sheet of $\{[Zn^{II}(adc)]\}_n$, where the anthracene units exist in a highly dense and uniform fashion. The distance between the adjacent anthracene π planes in the sheet is 3.75 Å, which is too large for π–π interactions. Therefore, there is no interaction between anthracene units in this crystal structure. The undulated 2D sheets are connected by dabco pillars, affording 2D channels with cross-sections of 5.6 Å × 5.8 Å along the [110] and [1–10] directions as shown in Fig. 1(b). An adsorbed guest molecule is expected to interact with the accessible anthracene π planes. The total solvent accessible volume in the crystal structure of **1** ⊃ Solvents is



Scheme 1 Schematic illustration of host–guest CT interaction in excited states.

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[a] Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Kyoto, 615-8510, Japan. E-mail: kitagawa@sbchem.kyoto-u.ac.jp; Fax: +81-75-383-2732; Tel: +81-75-383-2733
[b] College of Science and Engineering, Aoyama Gakuin University, Sagamihara, Kanagawa, 229-8558, Japan. E-mail: hasemiki@chem.aoyama.ac.jp; Fax: +81-42-759-6221; Tel: +81-42-759-6221
[c] Department of Material Science, Graduate School of Material Science, University of Hyogo, 3-2-1 Kouto, Kamigori-cho, Ako-gun, Hyogo, 678-1297, Japan. E-mail: toriumi@sci.u-hyogo.ac.jp; Fax: +81-791-58-0154; Tel: +81-791-58-0155

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‡ Current address: Department of Chemistry, University of California, Berkeley, CA 94720-1460, USA. E-mail: horike@berkeley.edu

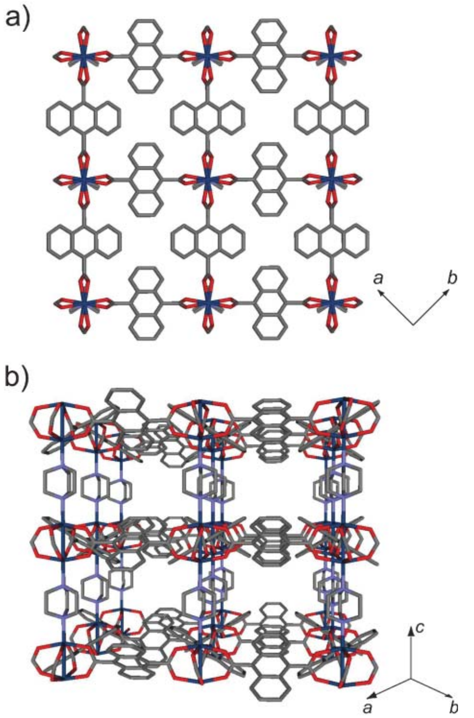

Fig. 1 Crystal structures of **1** $\supset$ Solvents (a) drawn from c axis, and (b) drawn from the [110] direction. The gray, purple, red and dark blue colors represent C, N, O and Zn, respectively. Disordered dabco and H atoms are omitted.§[1]

200.4 Å^3 per one anthracene molecule, and the void volume V_{void} is 35.9% of the total crystal volume, as calculated using the PLATON program.[7]

In order to examine the thermal stability of the porous networks, TG and X-ray powder diffraction (XRPD) measurements were carried out.¶ The stepwise TG curve of **1** $\supset$ Solvents indicates the formation of a dehydrated form by the removal of the solvent guest, **1**, which is stable up to 350 °C. Fig. 2(a) shows the XRPD patterns simulated from X-ray single-crystal data of **1** $\supset$ Solvents, raw experimental data of powder **1** $\supset$ Solvents and the dehydrated form of **1**. The good agreement of the peaks in these diagrams demonstrates that the porous network is retained without guest molecules. The nitrogen adsorption isotherm at 77 K, in Fig. 2(b), shows a type I behavior, which confirms the presence of micropores in **1**.

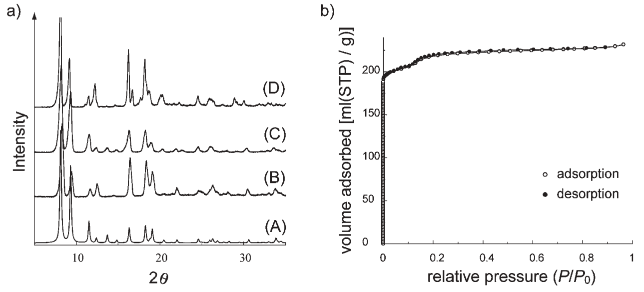

Fig. 2 (a) XRPD patterns of (A) simulated from a single crystal of **1** $\supset$ Solvents, (B) raw experimental **1** $\supset$ Solvents, (C) dried form, **1**, (D) DMA-adsorbed form, **1** $\supset$ DMA. (b) Adsorption isotherm of N_2 for **1** at 77 K.

The stable porous framework of **1** prompted the examination of photoinduced CT interactions between the host anthracene π wall and adsorbed guests. Among the many CT interactions of excited molecules, the pair of anthracene/*N,N*-dimethylaniline (DMA) has drawn considerable attention. Its reaction process is well known,[8] and hence this case was applied to the above mentioned porous framework. DMA was fully adsorbed in the pores by the immersion of **1** in liquid DMA, and the excess DMA outside the host crystals was removed under reduced pressure. This resulted in the DMA-adsorbed form, **1** $\supset$ DMA. The number of DMA molecules per one adc unit in **1** $\supset$ DMA is 1.0, as determined by TG analysis (see ESI†). Comparison of the XRPD pattern of **1** $\supset$ DMA with that of **1** reveals that small shifts and new peaks appeared (Fig. 2(a)), indicating the effective inclusion of DMA, as with benzene adsorption on $\{[Zn_2(bdc)_2(dabco)]\}_n$.[5a] After heating **1** $\supset$ DMA to 350 °C, the XRPD pattern was the same as that of the dried material **1**; therefore, the host framework shrinks back upon DMA desorption.

The absorption spectra of **1** and **1** $\supset$ DMA are shown in Fig. 3(a). The absorption maxima of **1** appear at 385, 367, 350, and 333 nm, close to those of monomeric anthracene, and are attributed to the π–π* transitions of the anthracene unit.[8e] There is no evidence of strong interactions between the anthracene π plane and the zinc paddle-wheel units. In the absorption spectra of **1** $\supset$ DMA, on the other hand, a pronounced change is observed. The absorption bands become broader and are shifted to longer wavelength, by about 15 nm, compared to those of **1**. As can be seen from the vinyl polymer with pendant anthracene DMA moieties, the change in the spectrum indicates that the anthracene units interact with DMA in the ground state to form a 1 : 1 weak CT complex in **1** $\supset$ DMA.[8h]

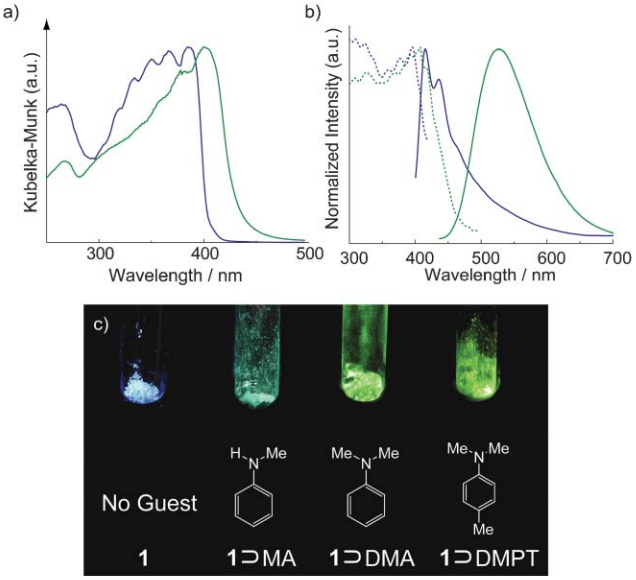

Fig. 3 (a) Diffuse reflectance UV-vis spectra and (b) excitation (dashed line) and emission (solid line) spectra of **1** (blue) and **1** $\supset$ DMA (green). The excitation wavelengths are 376 nm and 410 nm, respectively. (c) A snapshot of **1**, **1** $\supset$ MA, **1** $\supset$ DMA and **1** $\supset$ DMPT. The samples were subjected to UV irradiation.

The solid-state emission spectra of **1** and **1** $\supset$ DMA are shown in Fig. 3(b). A spectrum curve of **1** displays an emission maximum at 415 nm, with a vibrational band at 436 nm. Using published data,[8e,9] the spectrum can be assigned to an emission from the monomeric anthracene. This is in good agreement with the crystal structure, in which the anthracene π planes do not interact with each other. The luminescence quantum efficiency (Φ_F) of **1**, measured in air at room temperature, is below 0.01. This is very low compared to previously reported values of solid-state anthracene derivatives.[10] It is ascribed to quenching by the adsorbed oxygen or water on the pore walls, as well as concentration quenching.

The **1** $\supset$ DMA emission spectrum is quite different from that of **1**. Highly efficient quenching occurs in the excited-state fluorescence of monomeric anthracene, and a new broad emission band appears from 400 to 700 nm. The emission with large Stokes shift represents a photoinduced CT complex, an exciplex between the host anthracene unit (electron accepter) and the guest DMA molecules (electron donor). The absolute value of Φ_F is 0.13, which is more than 10 times larger than the value for **1**. In general, the exciplex emission is inefficient since its transition dipole moment is lower than that of fluorescence; that is, for transition from the singlet excited state to the ground state of the individual components. The complete quenching of monomeric anthracene emission and highly efficient exciplex emission of **1** $\supset$ DMA originate from the confined configuration of DMA in the nanopores, as previous studies have revealed the importance of donor–acceptor configuration.[8f,g,h] Strong exciplex emissions of solid-state materials are attractive targets for organic optical devices because exciplex emission provides an alternative mechanism to tune the color, as the emission wavelength depends on the ionization potential and the electron affinity of the donor and acceptor molecules, respectively.[11] In fact, **1**-adsorbed *N*-methylaniline (**1**-$\supset$MA) or *N*,*N*-dimethyl-*p*-toluidine (**1**-DMPT) provide blue-shifted or red-shifted exciplex emissions, relative to **1**, respectively (Fig. 3(c) and Fig. S9†). Their exciplex wavelengths are related to the ionization potentials of the guest molecules.‖ In addition, the electron donor guests and electron acceptor 2D sheets in **1** $\supset$ DMA define an alternating layered structure, as shown in Scheme 1. Because of its regularity and the close contact in the micropore, an efficient interaction can be obtained. The results provide us with a pore design strategy for the efficient conversion of light energy into electrical energy.[12]

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Notes and references

¶ CCDC 649114. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b707947h

‖ The ionization energies of MA, DMA and DMPT are 7.33, 7.12 and 6.95 eV, respectively.[13]

§ The dabco molecule lies at a site with imposed 4/*m* symmetry and is thus disordered. The Zn^{II} atom lies at a site with fourfold symmetry.

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