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PAPER

Multifunctional amino-decorated metal–organic frameworks: nonlinear-optic, ferroelectric, fluorescence sensing and photocatalytic properties[†]

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Solvothermal reactions of 2-amino-1,4-benzene dicarboxylic acid (NH₂bdcH₂) and N-auxiliary ligands in the presence of manganese(II), zinc(II) and cobalt(II) salts have given rise to four new metal–organic frameworks, namely, [Mn₅(NH₂bdc)₅(bimb)₅·(H₂O)_{0.5}]_n (bimb = 4,4'-bis(1-imidazolyl)biphenyl) (1), [Zn(NH₂bdc)(bix)·(DMF)₂]_n (bix = 1,4-bis(imidazol-1-ylmethyl)benzene) (2), [Co(NH₂bdc)(bix)·(DMF)·(CH₃CH₂OH)]_n (3) and [Co(NH₂bdc)(bpp)]_n (4) (bpp = 1,3-bis(4-pyridyl) propane). Single-crystal X-ray diffraction analyses revealed that MOF 1 displays 5-fold interpenetrating 4-connected dia 3D net; MOFs 2 and 3 are isomorphic, which possess 3-fold interpenetrating dia 3D nets; MOF 4 exhibits 4-connected sql 2D net. Noncentrosymmetric structures and multifunctionality in 1–3 are established by varying ligands and metal centers. In the solid state, polar MOFs 1–3 exhibit nonlinear-optic (NLO) and MOF 1 demonstrates typical ferroelectric behaviour with a remnant electric polarization (P_r) of 1.2 µC cm⁻² and an electric coercive field (E_c) of 0.35 kV cm⁻¹. In addition, MOF 2 could be a potential luminescent probe for detecting nitrobenzene or 2-nitrotoluene *via* fluorescence enhancement and has been evaluated as a promising visible-light-driven photocatalyst for degradation of organic pollutants.

Introduction

Over the past few years, metal-organic frameworks (MOFs) have attracted tremendous attention owing to their intriguing structural topologies and wide potential applications including gas storage and separation, catalysis, enantioselective separation, luminescent sensing, and magnetic materials.¹⁻⁴ Even more remarkably, these applications can be combined and integrated into individual frameworks to form multifunctional MOFs.5 Despite impressive progress in the area of MOFs, currently, it remains a significant challenge to introduce, in a rational and systematic way, more complex functionality within the lattice. The strategy to incorporate "functional" metal centers or functional groups on the organic bridging ligands into specific MOFs has been proved to be very effective to address this challenge.⁶ In particular, employing some amine-derivatized MOFs to realize high storage and high selectivity toward CO_2 has recently been attempted.7 However, examples of this family from readily

accessible components with multifunctionality is seldom reported.⁸

For this purpose, we have chosen 2-amino-1,4-benzene dicarboxylic acid (NH_2bdcH_2) as a ligand, which is a particularly effective building block because (1) it has many potential coordination modes, allowing for the construction of a topologically diverse family of materials;⁹ (2) the polar NH_2bdcH_2 would be more effective in constructing the noncentrosymmetric framework, which is an essential requirement for nonlinear-optical (NLO) and ferroelectric behavior; (3) the amino substituent acting as an auxochromic and bathochromic group in the aromatic ring, may shift the absorption wavelength and promote charge transfer interactions of the resulting architecture, which is promising for the development of luminescent probes and visible-light photocatalysts.

Solvothermal reactions of NH₂bdcH₂ and N-auxiliary ligands with transition-metal centers $(Mn^{2+}/Zn^{2+}/Co^{2+})$ have yielded $[Mn_5(NH_2bdc)_5(bimb)_5 \cdot (H_2O)_{0.5}]_n$ (bimb = 4,4'-bis(1-imidazolyl)biphenyl) (1), $[Zn(NH_2bdc)(bix) \cdot (DMF)_2]_n$ (bix = 1,4bis(imidazol-1-ylmethyl)benzene) (2), $[Co(NH_2bdc)(bix) \cdot$ $(DMF) \cdot (CH_3CH_2OH)]_n$ (3) and $[Co(NH_2bdc)(bpp)]_n$ (4) (bpp = 1,3-bis(4-pyridyl)propane) based on single crystal X-ray structural, thermogravimetric (TG), and elemental analyses. MOF 1 displays a 5-fold interpenetrating 4-connected **dia** 3D net; MOFs 2 and 3 are isomorphic, and possess 3-fold interpenetrating **dia** 3D nets; MOF 4 exhibits a 4-connected **sql** 2D net. Noncentrosymmetric structures and multifunctionality in 1–3 are established by varying ligands and metal centers. In the solid

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state, polar MOFs 1–3 exhibit nonlinear-optic (NLO) properties and MOF 1 demonstrates typical ferroelectric behaviour with a remnant electric polarization (P_r) of 1.2 µC cm⁻² and an electric coercive field (E_c) of 0.35 kV cm⁻¹. More exciting, MOF 2 could be a potential luminescent probe for detecting nitrobenzene or 2nitrotoluene *via* fluorescence enhancement and has been evaluated as a promising visible-light-driven photocatalyst for the degradation of organic pollutants. To the best of our knowledge, this is the first example of MOFs exhibiting two interesting combined characteristics.

Experimental

Materials and physical measurements

The reagents and solvents employed were commercially available and used as received. Ligand bimb was prepared by literature methods.¹⁰ C, H and N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. IR spectra were recorded on KBr pellets on a Bruker Vector 22 spectrophotometer in the 4000-400 cm⁻¹ region. Thermogravimetric analyses were performed on a simultaneous SDT 2960 thermal analyzer under flowing N2 with a heating rate of 10 °C min⁻¹ from ambient temperature to 700 °C. The powder XRD data were collected on a Siemens D5005 diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å) over the 2θ range 5–50° at room temperature. A pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm was used to generate an SHG signal from samples. The backward scattered SHG light was collected using a spherical concave mirror and passed through a filter which transmits only 532 nm radiation. The solid-state diffuse-reflectance UV/Vis spectra for powder samples were recorded on a Perkin-Elmer Lambda 35 UV/Vis spectrometer equipped with an integrating sphere by using BaSO₄ as a white standard.

P-E hysteresis loop and I-V curves

The single crystal with approximate size of $1.0 \times 0.13 \times 0.13$ mm³ for 1 was selected to measure the dielectric hysteresis loop on a ferroelectric tester (Radient Technology), with electrodes made of Cu wire with about 150 µm diameter covered by Agconducting glue on one relatively larger crystallographic face. When the applied electric field varied from positive to negative voltage, an electric hysteresis loop was observed.

Fluorescence measurements

Compound **2** was immersed in fresh distilled methanol for 4 days to remove the nonvolatile solvates (DMF), and the extract was decanted every day and fresh methanol was replaced. Then it was activated by drying under a dynamic vacuum at 80 °C overnight. The activated sample (30 mg) of **2** was immersed in methanol solvent (20 mL) with a different organic solvent (0.2 mL) to form solvent included compound **2**, which was collected by filtration and dried for 24 h at 20 °C. The sample was pressed on a glass slide for the photoluminescence studies. Fluorescence measurements were recorded with a Hitachi 850 fluorescence spectrophotometer.

Photocatalytic experiments

The visible light source was a 500 W halogen lamp with a UV cutoff filter (providing visible light with $\lambda > 400$ nm) and the UV light source was a 350 W xenon lamp. A suspension of powdered catalyst (50 mg) in a fresh aqueous solution of X3B (50 mL, 6 × 10^{-6} mol L⁻¹) at pH 6 was first sonicated for 5 min, and shaken at a constant rate in the dark overnight (to establish an adsorption–desorption equilibrium of X3B on the sample surface). At given irradiating intervals, a series of suspensions of a certain volume were collected and filtered through a membrane filter (pore size, 0.45 µm) to remove suspended catalyst particles, and the filtrate was analyzed on the UV/vis spectrometer. The organic dye concentration was estimated by the absorbance at 510 nm, which directly relates to the structure change of its chromophore. The UV/vis spectra for solution samples were obtained on a Shimadzu UV 2450 spectrometer.

Synthesis of $[Mn_5(NH_2bdc)_5(bimb)_5 \cdot (H_2O)_{0.5}]_n$ (1)

A mixture of $MnCl_2 \cdot 4H_2O$ (19.7 mg, 0.10 mmol), NH_2bdcH_2 (18.1 mg, 0.10 mmol), bimb (28.6 mg, 0.10 mmol) in DMA (1 mL) and H_2O (1 mL) was placed in a parr Teflon-lined stainless steel vessel (25 cm³), and then the vessel was sealed and heated at 140 °C for 2 days. After the mixture was slowly cooled to room temperature, yellow crystals of **1** were collected (yield: 75% based on Mn). Anal. Calcd. For $C_{26}H_{19,20}MnN_5O_{4,10}$: C, 59.80; H, 3.71; N, 13.41%; found: C, 59.82; H, 3.75; N, 13.46%. IR spectrum (cm⁻¹): 3446m, 3337m, 3134m, 2361w, 1621s, 1542s, 1517s, 1430s, 1383s, 1335m, 1309m, 1254m, 1119w, 1064m, 1005w, 962w, 897w, 841m, 819w, 779w, 739m, 655m, 624w, 575w, 526m.

Synthesis of $[Zn(NH_2bdc)(bix) \cdot (DMF)_2]_n$ (2)

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (29.7 mg, 0.10 mmol), NH_2bdcH_2 (18.1 mg, 0.10 mmol), bix (23.8 mg, 0.10 mmol), DMF(3 mL) was placed in a 5 mL glass vial, which was sealed and heated at 110 °C for 2 days. After the mixture was slowly cooled to room temperature, light yellow crystals of **2** were collected (yield: 55% based on Zn). Anal. Calcd. for $C_{28}H_{33}N_7O_6Zn$: C, 53.57; H, 5.30; N, 15.63; found: C, 53.63; H, 5.25; N, 15.66%. IR spectrum (cm⁻¹): 3428m, 3325m, 3130m, 2929w, 1670s, 1611s, 1576s, 1524m, 1438m, 1365s, 1251s, 1093s, 1030w, 952m, 831m, 772m, 720w, 656m, 624w, 579w.

Synthesis of $[Co(NH_2bdc)(bix) \cdot (DMF) \cdot (CH_3CH_2OH)]_n$ (3)

Compound **3** was prepared in a similar way to **2**, using Co(NO₃)· 6H₂O (0.10 mmol) instead of Zn(NO₃)₂·6H₂O. Purple crystals of **3** were collected (yield: 70% based on Co). Anal. Calcd. for C₂₆H₃₀CoN₆O₆: C, 53.71; H, 5.20; N, 14.45%; found: C, 53.75; H, 5.26; N, 14.48%. IR spectrum (cm⁻¹): 3427m, 3326m, 3128m, 1661s, 1617s, 1556s, 1522s, 1425s, 1369w, 1283s, 1254m, 1236m, 1148w, 1106m, 1090m, 1030w, 944w, 828w, 773m, 749w, 725w, 660m,621s, 577s, 513s.

Synthesis of $[Co(NH_2bdc)(bpp)]_n$ (4)

A mixture of $Co(NO_3) \cdot 6H_2O$ (29.1 mg, 0.10 mmol), NH_2bdcH_2 (18.1 mg, 0.10 mmol) and bpp (19.8 mg, 0.10 mmol), DMF

(1 mL) and ethanol (1 mL) was placed in a 5 mL glass vial, which was sealed and heated at 110 °C for 2 days. After slowly cooled to room temperature, purple crystals of **4** were collected (yield: 29% based on Co). Anal. Calcd. for $C_{21}H_{19}CoN_3O_4$: C, 57.79; H, 4.39; N, 9.63%; found: C, 57.82; H, 4.44; N, 9.64%. IR spectrum (cm⁻¹): 3448m, 3345w, 2929w, 1619s, 1558s, 1497m, 1428s, 1385s, 1330w, 1257m, 1141s, 1069w, 1023w, 959w, 892w, 843m, 812m, 773m, 705w, 614w, 577w, 519w.

X-ray crystallography

Suitable single crystals of 1-4 were selected and mounted in air onto thin glass fibers. 1, 3, 4 were measured at room temperature on a Bruker SMART APEX CCD-based diffractometer with graphite-monochromatic Mo K α radiation ($\lambda = 0.71073$ Å). Data reductions and absorption corrections were performed with the SAINT and SADABS software packages, respectively.11 Xray intensity data for 2 were collected on a Rigaku Saturn 724 + CCD X-ray diffractometer with graphite monochromatic Mo K\alpha radiation ($\lambda = 0.71073$ Å) at 173 K. CrystalClear software (Rigaku Inc., 2007) was used for data reduction and empirical absorption correction. The structures of all the crystals were solved by direct method using SHELXS-97 (ref. 12) and developed by conventionally alternating cycles of least-squares refinement on F^2 (SHELXL-97)¹³ and different Fourier synthesis. All the non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were generated theoretically, allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters. To assist the refinement, several restraints were applied: for 3, the disordered C13/C14/C15/C16/C17/C18 atoms of benzene rings were restrained in order to obtain reasonable thermal parameters; the N1 atom of NH₂bdcH₂ ligand is disordered to three positions (N1/N1'/N1") in compound 4. Crystallographic data and other pertinent information for 1-4 are summarized in Table 1, while the selected bond lengths and angles are listed in Table S1.[†] More details on the crystallographic studies as well as atom displacement parameters are presented in the CIF.

 Table 1
 Crystal data and structure refinement for 1–4

Results and discussion

Description of the crystal structures

Interestingly, crystallographic analysis showed that 1 crystallizes in the acentric space group Cc. The asymmetric unit of 1 consists of five independent Mn(II) atoms, five individual NH₂bdc²⁻ anions and five distinct bix bridges, as well as two disordered free water molecules with occupancy of 0.2 and 0.3, respectively (Fig. S1a[†]). All Mn(II) centers adopt distorted octahedral coordination geometry defined by four oxygen atoms from two NH_2bdc^{2-} moieties and two nitrogen atoms from separate bimb bridges (Fig. 1a). The NH₂bdc²⁻ moieties connect Mn(II) atoms in bidentate-chelating mode to form onedimensional (1D) chains, which were pillared by the rigid bimb ligands to afford a three-dimensional (3D) porous structure with large channels of size ca. 20.5×19.4 , 17.9×10.9 and 34.6 \times 10.9 Å² (based on Mn····Mn separation) along the *a*-, *b*- and c-directions, respectively (Fig. S1b-d†). The channels nearly disappear with a free volume of only 5.6% upon interpenetration.¹⁴ Further examinations reveal that 1 adopts a five interpenetrating 4-connected dia net with a Schläfli symbol of 6⁶ (Fig. 1b).15

To investigate the influence of the N-auxiliary ligands and metal centers on the structure of the complexes, the reaction of flexible bix and NH₂bdcH₂ with Zn(NO₃)₂·6H₂O was carried out. A new complex 2 with acentric space group Cc was obtained. The Zn(II) centers adopt a distorted tetrahedral coordination geometry, composed of two oxygen atoms from two NH₂bdc²⁻ anions and two separate bix nitrogen atoms (Fig. 1c). For the bix ligand, two terminal imidazole groups assume a trans conformation, additionally, their planes are steeply titled 99.6 and 102.9° with respect to the average plane of the phenyl, respectively. In 2, each NH₂bdc²⁻ anion coordinates to two Zn atoms with monodentate coordination modes, generating a 1D chain along the c axis, which is further linked by bix to achieve a 3D porous structure. The individual 3D network is "open" with larger hexagonal channels of size ca. $23.9 \times 20.7 \text{ Å}^2$, smaller " π "shaped channels of size ca. 20.2 \times 14.2 Å² and rectangular channels of size *ca*. 13.9 \times 11.0 Å² (based on Zn–Zn distances)

	1	2	3	4
Formula	C ₂₆ H _{19.2} MnN ₅ O _{4.1}	$C_{28}H_{33}N_7O_6Zn$	C ₂₆ H ₃₀ CoN ₆ O ₆	C ₂₁ H ₁₉ CoN ₃ O ₄
Formula weight	522.20	628.98	581.49	436.32
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	Сс	Cc	Сс	Pbca
alÅ	34.569(3)	20.661(4)	20.960(4)	11.7678(14)
b/Å	17.656(2)	11.567(2)	11.530(2)	17.166(2)
c/Å	20.504(2)	14.227(3)	14.211(3)	19.269(2)
$\alpha /^{\circ}$	90	90	90	90
βI°	108.326(3)	116.01(3)	116.24(3)	90
· γ/°	90	90	90	90
V/Å ³	11 880(2)	3055.7(13)	3080.4(13)	3892.5(8)
Ζ	20	4	4	8
$\rho_{\rm calcd} {\rm g}^{-1} {\rm cm}^{-3}$	1.460	1.367	1.254	1.489
μ/mm^{-1}	0.600	0.855	0.603	0.915
Collected reflections	48 525	8464	12 113	26 667
Unique reflections	22 713	4519	5741	3584
$R_1 [\hat{I} > 2\sigma(I)]$	0.0570	0.0587	0.0526	0.0395
wR_2 (all data)	0.1342	0.1331	0.1058	0.0942



Fig. 1 Coordination environments of central metal atoms and ligands in 1 (a), 2 (c), and 4 (e); schematic view of the 5-fold interpenetrating for 1 (b) and the 3-fold interpenetrating for 2 (d) as well as the 2D framework of 4 (f).

along the *c*-, *a*- and *b*-directions (Fig. S2†). Its structure can be simplified to a three interpenetrating 4-connected **dia** net (Fig. 1d). Despite the framework interpenetration, the structure retains a 39.8% solvent accessible void volume (1215.0 out of the 3055.7 Å³ unit cell volume), where DMF molecules reside as labile ligands.

When $Zn(NO_3)_2 \cdot 6H_2O$ was replaced by $Co(NO_3) \cdot 6H_2O$, complex 3 was obtained. Because the structure is very similar to that of compound 2, we do not describe it any further. Changing the N-auxiliary ligand from bix to more flexible bpp leads to a change in the final architecture from noncentrosymmetric for 3 to symmetric for 4. Compound 4 crystallizes in the centric space group Pbca. All Co atoms situated in a tetragonal pyramid arrangement, are coordinated by three oxygen atoms from two NH₂bdc²⁻ fragments and two bpp nitrogen atoms (Fig. 1e). For the bpp ligand, two terminal pyridine groups assume a cis conformation and are steeply titled at 103.4°. Each NH₂bdc²⁻ anion links two Co atoms by adopting bidentate-chelating and monodentate coordination modes. The extension of the structure into a 2D sheet is accomplished by NH₂bdc²⁻ and bpp linking the metal centers (Fig. S4[†]). Topologically, the 2D network can be seen as a 4connected sql net with Schläfli symbol (4⁴6²) (Fig. 1f).¹⁶

Obviously, from the crystal structures described above, the metal centers and dissimilar bridging backbones (rigid or flexible) have great impacts on the structures of the complexes. The phase purity of the bulk material was independently confirmed by powder X-ray diffraction (PXRD). The PXRD patterns of all as-synthesized products closely match the simulated ones from the single-crystal data, indicating that products are in a pure phase (Fig. S5–S8†).

NLO and ferroelectric properties

1–3 crystallize in a noncentrosymmetric space group Cc that belongs to a polar point group (C_s) , which is associated with a second harmonic generation (SHG) response and ferroelectric behavior. Our preliminary measurements on powdered samples of 1-3 suggest that, at ambient temperature, 1 and 2 are approximately 0.5 times as SHG active as urea, 3 is 0.4 times as active. Additionally, the ferroelectric properties were examined. Because the crystal sizes of 2 and 3 are relatively small, only the single crystal of 1 was selected to measure the dielectric hysteresis loop on a ferroelectric tester. An electric hysteresis loop is clearly observed for the single crystal of 1 at room temperature (Fig. 2); further, the extremely low leakage currents demonstrate that the observed hysteresis loops are clearly due to ferroelectricity (Fig. S9[†]). Experimental results indicate the presence of electric hysteresis loops with a remnant electric polarization (P_r) of 1.2 μ C cm⁻² and an electric coercive field (E_c) of 0.35 kV cm⁻¹; the spontaneous saturation polarization (P_s) of complex 1 is *ca*. 2.556 μ C cm⁻², which is obviously significantly higher than those found in a typical ferroelectric compound (e.g., NaK- $C_4H_4O_6 \cdot 4H_2O$ (Rochelle salt), $P_s \approx 0.25 \,\mu\text{C cm}^{-2}$), a MOF with tetrazole Cd(TBP)(Cl) (TBP = N-(4'-tetrazoyl-benzyl)proline) $(P_{\rm s} \approx 0.50 \ \mu \text{C cm}^{-2})$, and polythreading MOFs containing opposite charged motifs ($P_s \approx 0.57 - 0.81 \ \mu C \ cm^{-2}$) as well as inorganic-organic hybrids (TAMS) Bi_2Cl_8 (TAMS²⁺ = trimethylamino-N-methyl stilbazolium, $P_s \approx 0.08 \ \mu C \ cm^{-2}$), but smaller than that found in a typical ferroelectric BaTiO₃ synthesized by the peptide-assisted synthesis method $(P_{\rm s} \approx 6.5 \,\mu{\rm C \, cm^{-2}})^{.17}$ More importantly, a low applied electric field can polarize this sample to be ferroelectric, meaning practical utilization, compared to BaTiO₃ where its E_c is about 7–8 kV cm⁻¹, much larger than that of compound 1. Such properties probably originate from the permanent dipoles of nonsymmetric NH₂bdcH₂ (1.9880 Debye) and the ionic displacement polarizations.¹⁸ Notably, compound 1 is a 5-fold interpenetrating architecture, the charge centers for a single net do not easily coincide with each other in the crystal state, which would be more effective in increasing the polarity than common neutral complexes and therefore exhibit NLO and ferroelectric properties.



Fig. 2 Dielectric hysteresis loops for single crystal 1 at room temperature.

Fluorescence sensing

The emission spectra for 2 exhibit a broad peak at 426 nm when excited at 380 nm, which is more likely to be due to ligand-tometal charge transfer (LMCT) than to intraligand transitions, since a broad emission ($\lambda_{max} = 551$ nm) is observed for NH₂bdcH₂ (Fig. S10[†]). Motivated by pioneering works to make use of microporous MOFs for detecting aromatic compounds,¹⁹ the potential of complex 2 for sensing aromatic compounds was explored. The addition of a small amount of different aromatic compounds to methanol differentially affects the luminescence intensities (Fig. 3). Of particular importance is the significant enhancing effect of nitrobenzene and 2-nitrotoluene on the luminescence emission of complex 2. Upon irradiation at 380 nm, complex 2 gives two new emission bands at 443 and 480 nm in the presence of either nitrobenzene or 2-nitrotoluene addition to the original peak at 426 nm. This is very different from the behaviors of luminescent MOFs reported earlier, for which nitro-containing aromatics gave similar quenching profiles. The work represents the very first example of the MOF family that exhibits such phenomena.

Photocatalytic activities

To elucidate the photoresponse wavelength region, the solid state diffuse-reflectance UV/vis spectra for the as-synthesized compounds were recorded (Fig. 4). Compounds 2-4 consist of absorption components both in the UV and visible region whereas compound 1 only exhibits UV absorptions. The absorption bands are around 380, 390, 380 and 390 for 1-4, respectively, which could be attributed to ligand-to-metal charge transfer (LMCT). It should be noted that the absorption band occurring in the visible region at 550 nm for 2 could also be assigned to LMCT. In the case of 3 and 4, additional clear peaks in the visible region were observed at 548(586) and 534(583) nm, which probably respectively originate from the dd spin-allowed transition of the Co^{2+} (d⁷) ions. The absorption of 1 in the visible region is not as distinct as that of other samples, which may result from the spin-forbidden d-d of the Mn^{2+} (d⁵) ion.

The presence of visible region transitions motivated us to explore applications of **2–4** in heterogeneous photocatalysis.²⁰ The photodegradation experiment under visible irradiation was



Fig. 3 Comparison of the solid state luminescence intensity of **2** introduced into different analytes (0.2 mL) in CH₃OH solutions (20 mL).



Fig. 4 UV/Vis diffuse-reflectance spectra of compounds **1–4** with BaSO₄ as the background.

carried out after the dark adsorption-desorption equilibrium was achieved. The distinctly shortened degradation time compared with the control experiments underlines that catalyst 2 is active for the decomposition of X3B (Scheme 1) under visible-light irradiation (Fig. 5). The kinetic data for the degradation of X3B can be well fitted by the apparent first-order rate equation, the rate constant under visible-light irradiation was found to be 0.33 h^{-1} for that of **2**. In contrast, compounds 3 and 4 are unable to degrade X3B efficiently under the same conditions (Fig. S12[†]). By careful comparison, it could be noted that the LMCT of 2 could occur in the visible region (550 nm), whereas that of other samples lie in the UV region, which may be the reason for the higher visible-light responsive catalytic activities for compound 2. After photocatalysis, compound 2 was recycled by filtration and powder XRD demonstrates that complex 2 is rather stable during photocatalysis. In addition, the presence of tert-butyl alcohol (TBA, a widely used OH scavenger) greatly depressed the photodegradation rate of X3B on catalyst 2, that is, the relevant rate constant for 2 sharply decreased to 0.027 h⁻¹ under visible light. The OH quenching experiment result suggests that the photodegradation of X3B on catalyst 2 is predominately through attack of OH radicals. A simplified model of the possible photocatalytic reaction mechanism is proposed, see Scheme S1.[†] To exclude the possibility that the photocatalytic properties of 2 result from dissolved molecular or oligomeric fragments of solid catalysts in the photocatalytic process, other control experiments were conducted. The reaction suspensions after 10 h of irradiation were filtered to remove the solid catalyst particles, and fresh X3B was added into the respective filtrates for catalysis testing. Without solid catalyst in the reaction system, the fresh X3B was not degraded during another 10 h of irradiation under halogen lamp, which indicates that the solution contains no photocatalytically active fragments. Clearly the photocatalytic activities arise solely from solid 2.



Scheme 1 Molecular structure of X3B.



Fig. 5 Control experiments on the photodegradation of X3B. (I) X3B/ visible light (without catalyst); (II) X3B/compound 2/TBA/visible light; (III) X3B/compound 2/dark; (IV) X3B/compound 2/visible light.

Conclusion

In conclusion, a series of diverse 4-connected amino-decorated MOFs based on mixed-ligand systems are prepared, which reveal interesting multiple physical properties. Single-crystal X-ray diffraction analyses revealed that MOF 1 displays a 5-fold interpenetrating 4-connected dia 3D net; MOFs 2 and 3 are isomorphic, and possess 3-fold interpenetrating dia 3D nets; MOF 4 exhibits a 4-connected sql 2D net. Noncentrosymmetric structures and multifunctionality in 1-3 are established by varying ligands and metal centers. In the solid state, polar MOFs 1-3 exhibit nonlinear-optic (NLO) properties and MOF 1 demonstrates typical ferroelectric behavior with a remnant electric polarization (P_r) of 1.2 μ C cm⁻² and an electric coercive field (E_c) of 0.35 kV cm⁻¹, which features MOF 1 as a potential material in microelectronics (e.g. tunable capacitors), computing (non-volatile memory devices) and transducers. In addition, MOF 2 could be a potential luminescent probe for detecting nitrobenzene or 2-nitrotoluene via fluorescence enhancement and has been evaluated as a promising visible-light-driven photocatalyst for degradation of organic pollutants. To the best of our knowledge, this is the first example that exhibits the combination of two interesting characters in MOFs, indicative of the very promise of such MOF material for homeland security, environmental and humanitarian implications. A comprehensive study of complex 2 is currently underway to fully understand the mechanism of the fluorescent enhancing effect on nitrobenzene or 2-nitrotoluene.

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Notes and references

1 (a) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, *Nature*, 2000, **404**, 982; (b) C. D. Wu, A. G. Hu, L. Zhang and W. B. Lin, J. Am. Chem. Soc., 2005, 127, 8940; (c) U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt and J. Pastre, J. Mater. Chem., 2006, 16, 626; (d) J. Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. B. T. Nguyen and J. T. Hupp, Chem. Soc. Rev., 2009, 38, 1450; (e) A. C. McKinlay, R. E. Morris, P. Horcajada, G. Ferey, R. Gref, P. Couvreur and C. Serre, Angew. Chem., Int. Ed., 2010, 49, 6260; (f) Z. B. Ma and B. Moulton, Coord. Chem. Rev., 2011, 255, 1623; (g) M. Dinca and J. R. Long, Am. Chem. Soc., 2005, 127, 9376; (h) D. Dubbeldam, C. J. Galvin, K. S. Walton, D. E. Ellis and R. O. Snurr, J. Am. Chem. Soc., 2008, 130, 10884; (i) J. R. Li, R. J. Kuppler and H. C. Zhou, Chem. Soc. Rev., 2009, 38, 1477; (j) S. K. Henninger, H. A. Habib and C. Janiak, J. Am. Chem. Soc., 2009, 131, 2776; (k) 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; (1) X. Bao, P. H. Guo, J. L. Liu, J. D. Leng and M. L. Tong, Chem.-Eur. J., 2011, 17, 2335; (m) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, Science, 2002, 295, 469; (n) T. Ahnfeldt, N. Guillou, D. Gunzelmann, I. Margiolaki, T. Loiseau, G. Férey, J. Senker and N. Stock, Angew. Chem., Int. Ed., 2009, 48, 5163; (o) M. D. Allendorf, C. A. Bauer, R. K. Bhakta and R. J. T. Houk, Chem. Soc. Rev., 2009, 38, 1330; (p) J. Zhang, S. M. Chen, H. Valle, M. Wong, C. Austria, M. Cruz and X. H. Bu, J. Am. Chem. Soc., 2007, 129, 14168; (q) J. J. Perry, J. A. Perman and M. J. Zaworotko, Chem. Soc. Rev., 2009, 38, 1400; (r) S. Horike, Y. Inubushi, T. Hori, T. Fukushima and S. Kitagawa, Chem. Sci., 2012, 3, 116.

- 2 (a) S. Kaskel and R. Fischer, J. Mater. Chem., 2012, 22, 10093; (b) D. K. Cao, M. J. Liu, J. Huang, S. S. Bao and L. M. Zheng, Inorg. Chem., 2011, 50, 2278; (c) X. M. Zhang, T. Jiang, H. S. Wu and M. H. Zeng, Inorg. Chem., 2009, 48, 4536; (d) D. Liu, Z. G. Ren, H. X. Li, J. P. Lang, N. Y. Li and B. F. Abrahams, Angew. Chem., Int. Ed., 2010, 49, 4767; (e) X. Q. Zhao, B. Zhao, S. Wei and P. Cheng, Inorg. Chem., 2009, 48, 11048; (f) Z. M. Zhang, S. Yao, Y. G. Li, R. Clerac, Y. Lu, Z. M. Su and E. B. Wang, J. Am. Chem. Soc., 2009, 131, 14600; (g) S. M. Zhang, Z. Chang, T. L. Hu and X. H. Bu, Inorg. Chem., 2010, 49, 11581; (h) P. Yang, X. He, M. X. Li, Q. Ye, J. Z. Ge, Z. X. Wang, S. R. Zhu, M. Shao and H. L. Cai, J. Mater. Chem., 2012, 22, 2398; (i) D. B. Dang, P. Y. Wu, C. He, Z. Xie and C. Y. Duan, J. Am. Chem. Soc., 2010, 132, 14321.
- 3 (a) M. K. Sharma and P. K. Bharadwaj, *Inorg. Chem.*, 2011, **50**, 1889;
 (b) M. C. Das and P. K. Bharadwaj, *J. Am. Chem. Soc.*, 2009, **131**, 10942;
 (c) P. Mahata and S. Natarajan, *Inorg. Chem.*, 2007, **46**, 1250;
 (d) J. A. Zhao, L. W. Mi, J. Y. Hu, H. W. Hou and Y. T. Fan, *J. Am. Chem. Soc.*, 2008, **130**, 15222;
 (e) Y. S. Xue, Y. B. He, S. B. Ren, Y. F. Yue, L. Zhou, Y. Z. Li, H. B. Du, X. Z. You and B. L. Chen, *J. Mater. Chem.*, 2012, **22**, 10195;
 (f) Y. G. Huang, F. L. Jiang and M. C. Hong, *Coord. Chem. Rev.*, 2009, **253**, 2814;
 (g) F. Wang, Z. S. Liu, H. Yang, Y. X. Tan and J. Zhang, *Angew. Chem., Int. Ed.*, 2011, **50**, 450;
 (h) X. L. Zhou, M. Yu, Y. Liu, J. Y. Zhang, C. Y. Zhao, Y. X. Tong and C. Y. Su, *Angew. Chem., Int. Ed.*, 2007, **46**, 7399;
 (i) Y. Gong, Y. C. Zhou, T. F. Liu, J. Lu, D. M. Proserpio and R. Cao, *Chem. Commun.*, 2011, **47**, 5982.
- 4 (a) S. S. Chen, M. Chen, S. Takamizawa, M. S. Chen, Z. Su and W. Y. Sun, *Chem. Commun.*, 2011, **47**, 752; (b) H. D. Guo, X. M. Guo, S. R. Batten, J. F. Song, S. Y. Song, S. Dang, G. L. Zheng, J. K. Tang and H. J. Zhang, *Cryst. Growth Des.*, 2009, **9**, 1394; (c) H. Wu, H. Y. Liu, Y. Y. Liu, J. Yang, B. Liu and J. F. Ma, *Chem. Commun.*, 2011, **47**, 1818; (d) J. Q. Liu, B. Liu, Y. Y. Wang, P. Liu, G. P. Yang, R. T. Liu, Q. Z. Shi and S. R. Batten, *Inorg. Chem.*, 2010, **49**, 10422; (e) Q. Yue, L. Yan, J. Y. Zhang and E. Q. Gao, *Inorg. Chem.*, 2010, **49**, 8647; (f) H. Y. He, D. Q. Yuan, H. Q. Ma, D. F. Sun, G. Q. Zhang and H. C. Zhou, *Inorg. Chem.*, 2010, **49**, 7605.
- S. J. Garibay, Z. Q. Wang, K. K. Tanabe and S. M. Cohen, *Inorg. Chem.*, 2009, **48**, 7341; (b) K. H. Li, D. H. Olson, J. Y. Lee, W. H. Bi, K. Wu, T. Yuen, Q. Xu and J. Li, *Adv. Funct. Mater.*, 2008, **18**, 2205; (c) S. L. Qiu and G. S. Zhu, *Coord. Chem. Rev.*, 2009, **253**, 2891; (d) J. S. Hu, L. F. Huang, X. Q. Yao, L. Qin, Y. Z. Li, Z. J. Guo, H. G. Zheng and Z. L. Xue, *Inorg. Chem.*, 2011, **50**, 2404.
- 6 (a) J. W. Yoon, S. H. Jhung, J.-S. Chang and A. K. Cheetham, J. Am. Chem. Soc., 2006, **128**, 16846; (b) J. An, S. J. Geib and N. L. Rosi, J. Am. Chem. Soc., 2010, **132**, 38; (c) J. B. Lin, J. P. Zhang and

X. M. Chen, J. Am. Chem. Soc., 2010, **132**, 6654; (d) F. Debatin, A. Thomas, A. N. Kelling, B. Z. Hedin, I. Senkovska, S. Kaskel, M. Junginger, H. Müller, U. Schilde, C. Jäger, A. Friedrich and H.-J. Holdt, Angew. Chem., Int. Ed., 2010, **49**, 1258.

- 7 (a) R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, P. G. Boyd, S. Alavi and T. K. Woo, *Science*, 2010, **330**, 650; (b) R. Vaidhyanathan, S. S. Iremonger, K. W. Dawson and G. K. H. Shimizu, *Chem. Commun.*, 2009, 5230; (c) B. S. Zheng, J. F. Bai, J. G. Duan, L. Wojtas and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2011, **133**, 748; (d) S. Couck, J. F. M. Denayer, G. V. Baron, T. Rémy, J. Gascon and F. Kapteijn, *J. Am. Chem. Soc.*, 2009, **131**, 6326; (e) Y. Zou, S. Hong, M. Park, H. Chun and M. S. Lah, *Chem. Commun.*, 2007, 5182.
- 8 H. L. Jiang, Y. Tatsu, Z. H. Lu and Q. Xu, J. Am. Chem. Soc., 2010, 132, 5586.
- 9 (a) C. A. Black, J. S. Costa, W. T. Fu, C. Massera, O. Roubeau, S. J. Teat, G. Aromí, P. Gamez and J. Reedijk, *Inorg. Chem.*, 2009, 48, 1062; (b) C. P. Li, J. Chen, Q. Yu and M. Du, *Cryst. Growth Des.*, 2010, 10, 1623; (c) X. Y. Chen, B. Zhao, W. Shi, J. Xia, P. Cheng, D. Z. Liao, S. P. Yan and Z. H. Jiang, *Chem. Mater.*, 2005, 17, 2866; (d) Z. Y. Fu, J. L. Yi, Y. Chen, S. J. Liao, N. Guo, G. D. Yang, Y. X. Lian and X. T. Wu, *Eur. J. Inorg. Chem.*, 2008, 628.
- 10 J. Fan and B. E. Hanson, Chem. Commun., 2005, 2327.
- 11 Bruker Analytical X-Ray, Madison, WI, 2008.
- 12 G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112.
- 13 G. M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.
 14 A. L. Sach, L. And Countelling, 2002, 26, 7
- 14 A. L. Spek, J. Appl. Crystallogr., 2003, 36, 7.
- 15 (a) X. L. Wang, C. Qin, E. B. Wang and Z. M. Su, *Chem. Commun.*, 2007, 4245; (b) A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117; (c) S. R. Batten, *CrystEngComm*, 2001, **18**, 1; (d)

V. A. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio, CrystEngComm, 2004, 6, 377.

- 16 (a) J. F. Eubank, H. Mouttaki, A. J. Cairns, Y. Belmabkhout, L. Wojtas, R. Luebke, M. Alkordi and M. Eddaoudi, *J. Am. Chem. Soc.*, 2011, **133**, 14204; (b) C. Ren, Y. N. Zhang, W. J. Shi, B. Liu, Y. Y. Wang and Q. Z. Shi, *CrystEngComm*, 2011, **13**, 5179.
- 17 (a) H. Zhao, Z. R. Qu, Q. Ye, B. F. Abrahams, Y. P. Wang, Z. G. Liu, Z. L. Xue, R. G. Xiong and X. Z. You, Chem. Mater., 2003, 15, 4166;
 (b) Q. Ye, Y. M. Song, G. X. Wang, D. W. Fu, K. Chen, P. W. H. Chan, J. S. Zhu, D. S. Huang and R. G. Xiong, J. Am. Chem. Soc., 2006, 128, 6554; (c) X. Y. Duan, Q. J. Meng, Y. Su, Y. Z. Li, C. Y. Duan, X. M. Ren and C. S. Lu, Chem.-Eur. J., 2011, 17, 9936; (d) G. Xu, Y. Li, W. W. Zhou, G. J. Wang, X. F. Long, L. Z. Cai, M. S. Wang, G. C. Guo, J. S. Huang, G. Bator and R. Jakubas, J. Mater. Chem., 2009, 19, 2179; (e) G. Ahmad, M. B. Dickerson, Y. Cai, S. E. Jones, E. M. Ernst, J. P. Vernon, M. S. Haluska, Y. Fang, J. Wang, G. Subramanyam, R. R. Naik and K. H. Sandhage, J. Am. Chem. Soc., 2008, 130, 4.
- 18 H. R. Zhao, D. P. Li, X. M. Ren, Y. Song and W. Q. Jin, J. Am. Chem. Soc., 2010, 132, 18.
- (a) S. Pramanik, C. Zheng, X. Zhang, T. J. Emge and J. Li, J. Am. Chem. Soc., 2011, 133, 4153; (b) D. Tanaka, S. Horike, S. Kitagawa, M. Ohba, M. Hasegawa, Y. Ozawac and K. Toriumi, Chem. Commun., 2007, 3142; (c) H. Xu, F. Liu, Y. J. Cui, B. L. Chen and G. D. Qian, Chem. Commun., 2011, 47, 3153; (d) Y. J. Cui, Y. F. Yue, G. D. Qian and B. L. Chen, Chem. Rev., 2012, 112, 1126.
- 20 (a) C. G. Silva, I. Luz, F. X. L. Xamena, A. Corma and H. García, *Chem.-Eur. J.*, 2010, **16**, 11133; (b) M. C. Das, H. Xu, Z. Y. Wang, G. Srinivas, W. Zhou, Y. F. Yue, V. N. Nesterov, G. D. Qian and B. L. Chen, *Chem. Commun.*, 2011, **47**, 11715; (c) Y. H. Fu, D. R. Sun, Y. J. Chen, R. K. Huang, Z. X. Ding, X. Z. Fu and Z. H. Li, *Angew. Chem., Int. Ed.*, 2012, **51**, 3364.