

## Metal–Organic Frameworks as Platforms for Functional Materials

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**CONSPECTUS:** Discoveries of novel functional materials have played very important roles to the development of science and technologies and thus to benefit our daily life. Among the diverse materials, metal–organic framework (MOF) materials are rapidly emerging as a unique type of porous and organic/ inorganic hybrid materials which can be simply self-assembled from their corresponding inorganic metal ions/clusters with organic linkers, and can be straightforwardly characterized by various analytical methods. In terms of porosity, they are superior to other well-known porous materials such as zeolites and carbon materials; exhibiting extremely high porosity with surface area up to 7000 m<sup>2</sup>/g, tunable pore sizes, and metrics through the interplay of both organic and inorganic components with the pore sizes ranging from 3 to 100 Å, and lowest framework density down to 0.13 g/cm<sup>3</sup>. Such unique features have enabled metal–organic frameworks to exhibit great potentials for a broad range of applications in gas storage, gas separations, enantioselective



separations, heterogeneous catalysis, chemical sensing and drug delivery. On the other hand, metal–organic frameworks can be also considered as organic/inorganic self-assembled hybrid materials, we can take advantages of the physical and chemical properties of both organic and inorganic components to develop their functional optical, photonic, and magnetic materials. Furthermore, the pores within MOFs can also be utilized to encapsulate a large number of different species of diverse functions, so a variety of functional MOF/composite materials can be readily synthesized.

In this Account, we describe our recent research progress on pore and function engineering to develop functional MOF materials. We have been able to tune and optimize pore spaces, immobilize specific functional groups, and introduce chiral pore environments to target MOF materials for methane storage, light hydrocarbon separations, enantioselective recognitions, carbon dioxide capture, and separations. The intrinsic optical and photonic properties of metal ions and organic ligands, and guest molecules and/or ions can be collaboratively assembled and/or encapsulated into their frameworks, so we have realized a series of novel MOF materials as ratiometric luminescent thermometers,  $O_2$  sensors, white-light-emitting materials, nonlinear optical materials, two-photon pumped lasing materials, and two-photon responsive materials for 3D patterning and data storage.

Thanks to the interplay of the dual functionalities of metal—organic frameworks (the inherent porosity, and the intrinsic physical and chemical properties of inorganic and organic building blocks and encapsulated guest species), our research efforts have led to the development of functional MOF materials beyond our initial imaginations.

### 1. INTRODUCTION

Research on metal–organic frameworks (MOFs) and/or coordination polymers is certainly one of the most active research fields among chemistry and materials community, as witnessed in a large number of publications.<sup>1,2</sup> MOFs now can be conventionally designed and constructed from a large number of metal ions and/or metal-containing clusters, and organic ligands through very straightforward solvothermal synthesis approach, and their structures can be routinely characterized by laboratory X-ray, synchrotron, and/or neutron diffraction studies.<sup>1–4</sup> Compared with traditional porous materials such as zeolites and carbon materials, MOFs are unique in terms of their extraordinarily high porosities, tunable pores, and diverse functional sites. Their extremely high porosities with surface area up to about 7000 m<sup>2</sup> g<sup>-1</sup> have made MOF materials

particularly useful for the storage of hydrogen, methane, and acetylene gases, and the capture of carbon dioxide; while their finely tuned pores with functional sites have enabled us to address those very challenging separations of small and large molecules, and to develop materials for sensing, drug delivery, and heterogeneous catalysis.<sup>5–7</sup>

MOFs can also be considered as organic/inorganic hybrid materials.<sup>8–27</sup> That has provided us the bright promise of making use of inherent porosities, and physical and chemical properties of inorganic metal nodes, organic building blocks and encapsulated species inside the pores to target a variety of functional MOF materials. As shown in Figure 1, we have been

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Figure 1. Graphic illustration of pore and function engineering to develop functional MOF materials.

able to engineer the pores through the tuning of pore sizes/ channels, surface areas and functional sites to develop MOF materials for gas storage, gas separations and enantioselective separations. We have also been able to engineer the functions through the incorporation of a number of photoactive components of metal ions/metal clusters, organic linkers and encapsulated species to target optical and photonic MOF materials.

This Account focuses on our recent research progress on pore and function engineering and thus developing functional MOF materials since 2011.<sup>28–45</sup> Specifically, we have realized several MOF materials of unique pores and functional sites for (a) methane storage,  $C_2H_2/C_2H_4$  separation, enantioselective separation of secondary alcohols, carbon dioxide capture, and separations. We have further made use of luminescent lanthanide ions, organic dyes, nonlinear optically active organic dyes, photoactive organic linkers as the components and/or the encapsulated guest species of MOFs to realize optical and photonic MOF materials and thus as (b) ratiometric luminescent thermometers,  $O_2$  sensors, white-light-emitting materials, nonlinear optical materials, two-photon pumped lasing materials, and two-photon responsive materials for 3D patterning and data storage.

## 2. PORE ENGINEERING OF METAL-ORGANIC FRAMEWORKS FOR GAS STORAGE, GAS SEPARATIONS, AND ENANTIOSELECTIVE SEPARATIONS

The key of developing MOF materials for gas storage and separations of small molecules is to engineer the pores, so the pore spaces can be efficiently utilized for gas storage while the pore sizes and functional sites can be collaboratively enforced for their differential recognitions and uptakes of small molecules.

#### 2.1. Methane Storage

Maximizing volumetric methane storage and delivery working capacities of MOF materials is the most challenging tasks. It requires very specific control of the porosities, pore sizes and functional sites of the MOFs. To make use of a moderately size of hexa-carboxylic acid, we realized a unique MOF [Cu<sub>3</sub>(BHB)]

 $(UTSA-20; H_6BHB = 3,3',3'',5,5',5''-benzene-1,3,5-triyl-hexa$ benzoic acid) of the augmented zyg net built based on the wellknown dicopper paddlewheel Cu<sub>2</sub>(COO)<sub>4</sub> SBUs.<sup>28</sup> There exist 1D rectangular pores of about  $3.4 \times 4.8$  Å<sup>2</sup> and 1D cylinders of 8.5 Å diameter along the *c* axis, with open metal sites pointing to the pores for binding guest molecules (Figure 2a). The porosity of this MOF is moderate of  $1620 \text{ m}^2/\text{g}$ . However, the pore spaces and the corner cages of suitable sizes within this MOF can be efficiently utilized for the capture of methane molecules. This MOF also has moderately high open copper sites for the binding of methane molecules. These two unique structure features have enabled UTSA-20 to take up methane efficiently. Its density of adsorbed methane in micropores is  $0.22 \text{ g/cm}^3$ , highest ever reported under room temperature and 35 bar. Overall, UTSA-20 has volumetric methane storage capacity of 195 cm<sup>3</sup> (STP) cm<sup>-3</sup> under 35 bar storage condition (Figure 2b).

The ideal MOFs should have not only balanced porosities and framework densities,<sup>29</sup> but also high densities of functional sites/ groups and pore cages for their efficient methane storage and thus to optimize the volumetric methane storage capacities. When we introduced pyrimidine groups into the well-known NOTT-101, the new MOF  $[Cu_2L(H_2O)_2]$ ·5DMF·3H<sub>2</sub>O (UTSA-76, Figure 3a) exhibits much higher methane storage capacity of 257 cm<sup>3</sup> (STP) cm<sup>-3</sup> at 298 K and 65 bar (Figure 3b).<sup>30</sup> More importantly, UTSA-76 shows the highest methane storage working capacity of 197 cm<sup>3</sup> (STP) cm<sup>-3</sup>. Systematical studies further confirmed that these nitrogen-containing groups do play certain roles for the enhanced methane storage and working capacities of the resulting MOFs.<sup>31</sup> These studies indicate the potential to further improve methane storage and working capacities of MOF materials through the immobilization of specific functional sites/groups into their pore surfaces.

### 2.2. Separations of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>

We have developed mixed-metal-organic frameworks (M'MOFs) from metalloligands to construct a series of isostructural MOF materials whose micropores have been systematically tuned.<sup>32,33</sup> To make use of the same metalloligand Cu(SalPycy), but to incorporate different secondary ligands of dicarboxyates, we have been able to finely tune the micropores of



Figure 2. (a) Two types of 1D channels in UTSA-20, with open metal sites pointing to the pores. (b) Temperature-dependent total high-pressure methane sorption isotherms of UTSA-20. Reproduced with permission from ref 28. Copyright 2011 Wiley-VCH.

the resulting two M'MOFs, Zn<sub>3</sub>(BDC)<sub>3</sub>[Cu(SalPycy)].  $(G)_x(M'MOF-2; BDC = 1,4-benzenedicarboxylate; G = guest$ molecules) and  $Zn_3(CDC)_3[Cu(SalPycy)] \cdot (G)_x(M'MOF-3)$ (CDC = 1,4-cyclohexanedicarboxylate).<sup>32</sup> M'MOF-3 has smaller pores than M'MOF-2, leading to its much higher selective separations of  $C_2H_2/C_2H_4$  because of the enhanced sieving effects. These are first examples of porous materials for adsorptive separations of  $C_2H_2/C_2H_4$ . The separation selectivities of these M'MOFs for  $C_2H_2/C_2H_4$  can be further improved by tuning their micropores through the introduction of different diamines (red), carboxylates (pink), and substituted alkane groups, as shown in Figure 4a, in their iso-structural M'MOFs.<sup>33</sup> M'MOF-3a displays the highest  $C_2H_2/C_2H_4$  separation selectivity of 24.03. Their potential for the practical separation of  $C_2H_2/C_2H_4$  at ambient conditions has been also examined by simulated breakthrough experiments, displaying that the



**Figure 3.** (a) Crystal structure of UTSA-76. (b) Temperature dependent high-pressure methane sorption isotherms of UTSA-76a (data of pure methane gas stored in a high pressure gas tank is represented as dash black curve). Reproduced with permission from ref 30. Copyright 2014 American Chemical Society.

activated M'MOF-4 has the best performance because of its balanced moderately high separation selectivity and acetylene uptake, which can produce high purity ethylene (>99.0%) from the  $C_2H_4/C_2H_2$  mixture for industrial usage (Figure 4d).

Although MOF-74 series are quite powerful for the separations of  $C_2H_2/C_2H_4$ ;<sup>11,34</sup> they suffer from their low separation selectivities because the open metal sites within these MOFs can interact with both  $C_2H_2$  and  $C_2H_4$ . The ideal MOFs for  $C_2H_2/C_2H_4$  separation should not only have high  $C_2H_2/C_2H_4$ sieving effects and separation selectivites but also display considerable acetylene uptakes. We recently realized a unique microporous MOF [Cu(ATBDC)]·G (UTSA-100; H<sub>2</sub>ATBDC = 5-(5-amino-1H-tetrazol-1-yl)-1,3-benzenedicarboxylic acid; G= guest molecules) which can indeed meet the above requirements.<sup>35</sup> As shown in Figure 5, UTSA-100a has opening windows of 3.3 Å and suitable pores and cages of 4.0 Å to enforce its highly selective  $C_2H_2/C_2H_4$  separations (a selectivity of 10.72). The moderately high porosity and the immobilized functional sites -NH<sub>2</sub> for their preferential interactions with  $C_2H_2$  also enable UTSA-100a to take up moderately amount of C<sub>2</sub>H<sub>2</sub>. Such a balanced moderately high separation selectivity and C<sub>2</sub>H<sub>2</sub> uptake has enabled UTSA-100 to be superior to other MOFs (M'MOF-3a, MgMOF-74, CoMOF-74, FeMOF-74, and NOTT-300), exhibiting highly efficient removal of acetylene from ethylene/acetylene mixtures containing 1% acetylene.

### 2.3. Carbon Dioxide Capture and Separation

Design of MOFs for carbon capture and separation at ambient conditions is very challenging; this is because the CO<sub>2</sub> storage capacities at room temperature and low pressure (1 bar) are determined by a number of factors such as pore volumes, pore sizes, open metal sites and functional groups. We targeted a very special MOF UTSA-16 [K(H<sub>2</sub>O)<sub>2</sub>Co<sub>3</sub>(cit) (Hcit)] from a very cheap chemical citric acid (Hcit).<sup>36</sup> The framework has a diamond topology (Figure 6a,b). The activated UTSA-16 can take up large amount of CO<sub>2</sub> (160 cm<sup>3</sup> cm<sup>-3</sup>) at ambient conditions. Neutron diffraction studies show that the suitable pore cages of about 4.5 Å can efficiently capture four molecules of CO<sub>2</sub> which are further enforced by the hydrogen bonding interactions with the terminal coordinated water molecules on the pore surfaces (Figure 6c,d).

### 2.4. Enantioselective Separation of Secondary Alcohols

The chiral pore environments in above-mentioned M'MOFs have also enabled them to be highly selective for the enantioselective separation of secondary alcohols (Figure



**Figure 4.** (a) Schematic diagram for the synthesis of four mixed-metal organic frameworks (M'MOFs) of tunable chiral pores. (b) Single crystal structure of M'MOF-6 viewed along *a* axis. (c)  $C_2H_2$  and  $C_2H_4$  adsorption isotherms of M'MOF-6a at 295 K. Ppm  $C_2H_2$  in outlet gas as a function of the dimensionless time for M'MOFs. (d) Plot of the number of millimoles of  $C_2H_2$  captured per liter of adsorbent material during the time interval  $0-\tau_{break}$  against the breakthrough time  $\tau_{break}$  for packed bed adsorber with step-input of a  $1/99 C_2H_2/C_2H_4$  mixture at 296 K and total pressures of 100 kPa. The breakthrough times,  $\tau_{break}$  correspond to those when the outlet gas contains 40 ppm of  $C_2H_2$ . Reproduced with permission from ref 33. Copyright 2012 American Chemical Society.



**Figure 5.** Pore structure of UTSA-100 and the  $C_2H_2$  binding site. (a) Pore structure showing the zigzag channels along the *c* axis and the cage with the diameter of about 4.0 Å in the pore wall with the window openings of 3.3 Å. (b) The acetylene sits right at the small cage connecting two adjacent channel pores. (multiple-point interactions of the acetylene molecule with framework:  $d[O(-CO_2)\cdots H(C_2H_2)] = 2.252$  Å,  $d[H(-NH_2)\cdots (C_2H_2)] = 2.856$  Å). (c) Pore size distribution (PSD) of UTSA-100a. (d) Acetylene (red) and ethylene (blue) sorption at 296 K. (e) Plot of  $C_2H_2$  captured per liter of adsorbent (<40 ppm of  $C_2H_2$  in outlet gas), during the time interval  $0-\tau_{break}$  plotted as a function of the time interval  $\tau_{break}$ . (f) Experimental column breakthrough curve for  $C_2H_2/C_2H_4$  mixed gas containing 1%  $C_2H_2$  over UTSA-100a. The experiment temperatures are 296 K except FeMOF-74 (318 K) and NOTT-300 (293 K). Reproduced with permission from ref 35. Copyright 2015 Nature Publishing Group.

7).<sup>32,33</sup> The chirality of the pore environment has been introduced by making use of different chiral diamines. Because

the chiral pores of these isostructural M'MOFs can be systematically tuned, these M'MOFs display enantioselective



**Figure 6.** (a) Structure of UTSA-16 and (b) its diamond framework topology. (c) Structure of  $CO_2$  loaded UTSA-16 indicating a couple of  $CO_2$  molecules loaded within the cage, and (d) the cooperative interactions between  $CO_2$  molecules and the framework. Reproduced with permission from ref 36. Copyright 2012 Nature Publishing Group.

separation for different alcohols.<sup>37</sup> The best one, M'MOF-7, can efficiently separate 1-phenylethanol up to ee of 82.4%.

### 3. FUNCTION ENGINEERING OF METAL-ORGANIC FRAMEWORKS TO DEVELOP OPTICAL AND PHOTONIC MATERIALS

The capacities to incorporate a number of photoactive lanthanide ions, encapsulated dye molecules, and organic linkers into the resulting MOFs have enabled us to readily construct a series of optical and photonic MOF materials.

# 3.1. Mixed-Lanthanide MOFs as Ratiometric Luminescent Thermometers

Isostructural lanthanide MOFs can be readily synthesized, so we can construct their mixed-lanthanide MOFs whose contents of

different lanthanide ions can be variably changed to tune their luminescence, and thus for their functional properties.<sup>37–39</sup> We have demonstrated the first ratiometric luminescent MOF thermometer based on a Eu<sup>3+</sup>/Tb<sup>3+</sup> mixed-MOF,  $Eu_{0.0069}Tb_{0.9931}$ -DMBDC (DMBDC = 2,5-dimethoxy-1,4-benzenedicarboxylate).<sup>38</sup> Upon excitation at 381 nm, Eu<sub>0.0069</sub>Tb<sub>0.9931</sub>-DMBDC exhibits simultaneously the  ${}^{5}D_{4} \rightarrow {}^{7}F_{I}$  (*J* = 6, 5, 4, and 3) transitions of the Tb<sup>3+</sup> and the  ${}^{5}D_{0} \rightarrow {}^{7}F_{I}$  (J = 1, 2, 3, and 4) transitions of Eu<sup>3+</sup> ions. Eu<sub>0.0069</sub>Tb<sub>0.9931</sub>-DMBDC exhibits a significantly different temperature-dependent luminescent behavior from those of Tb-DMBDC and Eu-DMBDC. The linear relationship of the emission intensity ratio  $(I_{\rm Tb}/I_{\rm Eu})$  of the  ${}^{5}\text{D}_{4} \rightarrow$  $^{7}F_{5}$  (Tb<sup>3+</sup>, 545 nm) to  $^{5}D_{0} \rightarrow ^{7}F_{2}$  (Eu<sup>3+</sup>, 613 nm) transition with the temperature provides the potential for the ratiometric luminescent thermometers. To incorporate a new organic ligand with a higher triplet state energy, we realized Tb<sub>0.9</sub>Eu<sub>0.1</sub>PIA  $(H_2 pia = 5 - (pyridin - 4 - yl) isophthalic acid)$  (Figure 8a-c) with a much higher relative sensitivity of 3.27%  $K^{-1}$  (Figure 8d).<sup>39</sup>

# 3.2. MOF Dye Composites as Ratiometric Luminescent Thermometers

Because luminescence can be also introduced through the incorporation of luminescent species inside the pores, we developed the MOF⊃dye composite approach for ratiometric luminescent thermometers and realized the first dye-encapsulated MOF ZJU-88⊃perylene composite for this application. By adding the solution of perylene in DMF into the reaction mixture to construct lanthanide MOF [Eu<sub>2</sub>(QPTCA) (NO<sub>3</sub>)<sub>2</sub>(DMF)<sub>4</sub>]. (CH<sub>3</sub>CH<sub>2</sub>OH)<sub>3</sub> (ZJU-88), the dye-encapsulated MOF ZJU-88⊃perylene was synthesized (Figure 9a).<sup>40</sup> The MOF ZJU-88⊃perylene features a red-emitting of Eu<sup>3+</sup> at 615 nm and an appended blue emitting around 473 nm of perylene dyes. The luminescence intensity ratios between Eu<sup>3+</sup> ions and perylene dyes in ZJU-88⊃perylene correlate linearly very well to the temperature in the range of 20 to 80 °C, enabling it as a novel ratiometric thermometer at the physiological temperature with a maximum relativity sensitivity of 1.28% K<sup>-1</sup>.

#### 3.3. MOF > Lanthanide lons Thin Films as O<sub>2</sub> Sensors

For practical sensor applications, it is of interest to fabricate MOFs as thin films on different types of substrates to realize their



**Figure 7.** Three-dimensional (3D) pillared framework with chiral pore cavities for M'MOF-3 (left), and the 3D pillared framework exclusively encapsulating S-PEA molecules for M'MOF-3⊃S-PEA. (Zn, pink; Cu, cyan; O, red; C, gray; N, blue; H, white). Reproduced with permission from ref 32. Copyright 2011 Nature Publishing Group.



**Figure 8.** (a) Crystal structure of TbPIA showing coordination environments around  $Tb^{3+}$ . (b) Two-dimensional framework. (c) Emission spectra of  $Tb_{0.9}Eu_{0.1}PIA$  recorded between 14 and 300 K (excited at 360 nm). The insets are the optical photographs of luminescent  $Tb_{0.9}Eu_{0.1}PIA$  at 14 K (left) and 300 K (right) excited under 365 nm UV lamps. (d) Temperature-dependent intensity ratio of  $Tb^{3+}_{0.4}(546 \text{ nm})$  to  $Eu^{3+}_{0.4}(615 \text{ nm})$  and the fitted curve for  $Tb_{0.9}Eu_{0.1}PIA$  and  $Eu_{0.0069}Tb_{0.9931}$ -DMBDC. Reproduced with permission from ref 39. Copyright 2013 American Chemical Society.



**Figure 9.** (a) Schematic representation of dual-emitting ZJU-88⊃perylene (EnT, energy transfer; Em, emission). (b) Emission spectra of ZJU-88⊃perylene recorded from 20 to 80 °C, excited at 388 nm. Reproduced with permission from ref 40. Copyright 2015 WILEY-VCH.

optoelectronic integration circuits. We introduced the  $Tb^{3+}$  ions into the indium MOF films,  $[(CH_3)_2NH_2][In_3O-(BTC)_2(H_2O)_3]_2[In_3(BTC)_4]$  (CPM-5) and  $In_3O(OH)-(H_2O)_2[BTC]_2$  (MIL-100(In)) through the postfunctionalization (Figure 10a).<sup>41</sup> Both CPM-5 $\supset$ Tb<sup>3+</sup> and MIL-100(In) $\supset$ Tb<sup>3+</sup> thin films exhibit the characteristic emission bands of Tb<sup>3+</sup>, and the luminescence of these films can be gradually quenched by the increasing pressure of O<sub>2</sub> (Figure 10b). The quenching efficiencies of CPM-5 $\supset$ Tb<sup>3+</sup> and MIL-100(In) $\supset$ Tb<sup>3+</sup> films are about 47% and 88% at 1 atm of O<sub>2</sub>, respectively, suggesting that these two films are capable of sensing oxygen gas (Figure 10c).

## 3.4. MOF⊃Dye Composites as White-Light-Emitting Materials

Using the dye-encapsulated MOF, we also demonstrated its application in white-light-emitting phosphor. By encapsulating the red-light emitting dye 4-(*p*-dimethylaminostyryl)-1-methylpyridinium (DSM) and the green-light emitting dye acriflavine (AF) into a blue-emitting anionic MOF  $(Me_2NH_2)_3[In_3(BTB)_4]\cdot 12DMF\cdot 22H_2O$  (ZJU-28) through an ion-exchange process to yield the MOF $\supset$ dye composite ZJU-28 $\supset$ DSM/AF,<sup>42</sup> we achieved a single-phased white-light-emitting phosphor with ideal CIE coordinates of (0.34, 0.32), high CRI value of 91, and moderate CCT value of 5327 K (Figure 11). The MOF $\supset$ dye composite approach will offer a great flexibility and potential to rationally design white phosphors, and thus to develop high-performance white light-emitting diodes.

#### 3.5. MOF⊃Dye Composites as Second-Order Nonlinear Optical Materials

To make use of the pore confinement to align nonlinear optically active (the polarization P responds nonlinearly to the electric field E of the light) dye molecules into the pores, we developed a novel approach to construct NLO MOF materials. MOF ZJU-28, with 1D channels of about 7.1 × 8.5 A<sup>2</sup>, can encapsulate different types of cationic dye molecules (Figure 12a); however, their pore confinement effects for these dye cations are different, which have been clearly demonstrated in their NLO properties of the resulting MOF⊃dye composites.<sup>43</sup> Second harmonic generation (SHG) measurements indicate that the NLO intensities of the



**Figure 10.** (a) Energy transfer processes and O<sub>2</sub> quenching processes of CPM-5 $\supset$ Tb<sup>3+</sup> (up) and MIL-100(In) $\supset$ Tb<sup>3+</sup> (down). (b) Emission spectra of activatedMIL-100(In) $\supset$ Tb<sup>3+</sup> films under different oxygen partial pressure  $P_{O_2}$ . (c) Reversible luminescence quenching of MIL-100(In) $\supset$ Tb<sup>3+</sup> film upon alternating exposure to 1 atm of O<sub>2</sub> and N<sub>2</sub>. (d) Stern–Volmer plots showing  $I_0/I$  vs oxygen partial pressure  $P_{O_2}$  for the activated two MOF films. Reproduced with permission from ref 41. Copyright 2014 American Chemical Society.



Figure 11. (a) Schematic illustration of the encapsulation of cationic dyes into ZJU-28 via ion-exchange process. (b) Photographs of the 365 nm ultraviolet LED coated with ZJU-28 $\supset$ DSM/AF (0.02 wt % DSM, 0.06 wt % AF) phosphor when the LED is tuned off and tuned on. Reproduced with permission from ref 42. Copyright 2015 WILEY-VCH.

dye-encapsulated MOFs are heavily dependent on the included guest dyes: the longer the terminal alkyl chains of the included hemicyanine dyes, the stronger the NLO intensity of the resulting MOF material (Figure 12b,c). As a result, ZJU-28⊃DPASD (DPASD = 4-(4-(diphenylamino)styryl)-1-dodecylpyridinium) exhibits much higher NLO property (Figure 12d).

# 3.6. MOF>Dye Composites as Two-Photon Pumped Lasing Materials

We demonstrated a new two-photon-pumped microlaser by encapsulating the cationic pyridinium hemicyanine dye 4-[*p*- (dimethylamino)styryl]-1-methylpyridinium (DMASM) with a large two-photon absorption (TPA) cross section into an anionic MOF, bio-MOF-1 (Figure 13a). Because of the pore confinement of DMASM molecules within bio-MOF-1,<sup>44</sup> the dyeencapsulated MOF bio-MOF-1⊃DMASM exhibits a much stronger emission at 610 nm with a fluorescence quantum efficiency of 25.87% than that of the DMASM solution.

The high luminescent efficiency and the large TPA cross section of the DMASM dye enable the bio-MOF-1⊃DMASM to generate significant two-photon excited fluorescence and stimulated emission under excitation with a Nd:YAG laser at 1064 nm (Figure 13b and c). More importantly, because the opposing top and bottom faces of the MOF crystals indeed function as two reflectors of a Fabry–Perot cavity and provide strong self-cavity optical confinement and optical feedback, the TPP lasing is observed around 640 nm when pumped under a 1064 nm pulse laser with a threshold of 0.148 mJ (Figure 13d).

## 3.7. A Two-Photon Responsive Metal–Organic Framework for 3D Patterning

By utilizing a photoactive organic linker 2,5-bis(3,5-dicarboxyphenyl)-1-methylpyridinium hydroxide, a MOF with tunable two-photon pumped luminescence properties has been realized.<sup>45</sup> Under the UV light illumination, the MOF material exhibits a significant two-photon excited fluorescence change in response to infrared femtosecond laser of 900 nm. This unique two-photon response allows for two photon patterning and imaging in high-resolution ( $1 \times 1 \times 5 \mu m^3$ ) 3D structure (Figure 14). Because of the irreversible photochemical process, the fluorescent pattern is much more stable and does not show much decay even after 30 days. The incorporation of photoactive linkers to tune the luminescence of MOF materials for 3D patterning and two-photon imaging will enable MOFs to be useful materials for sensor arrays and data storage media.



**Figure 12.** (a) Schematic illustration of pyridinium hemicyanine chromophores incorporated into ZJU-28 via ion exchange. (b) SHG spectra of ZJU-28 $\supset$ DPASD. Inset: The SHG intensity of ZJU-28 $\supset$ DPASD as a function of the energy of fundamental frequency laser. (c) Confocal scanning microscopic images of a triangular prism crystal of ZJU-28 $\supset$ DPASD in a depth scanning mode imaged using SHG signals. (d) Comparison of the SHG intensities of  $\alpha$ -quartz, ZJU-28, and the chromophore included ZJU-28. Reproduced with permission from ref 43. Copyright 2012 WILEY-VCH.



**Figure 13.** (a) Enscapsulation of pyridinium hemicyanine cationic dye DMASM into bio-MOF-1. (b) Illustration of the two-photon pumped lasing. (c) Single-photon and two-photon excited emission spectra of bio-MOF-1⊃DMASM. (d) Two-photon pumped lasing spectra of bio-MOF-1⊃DMASM under different pumped pulse energy. Inset: microscopy image of a bio-MOF-1⊃DMASM single crystal excited at 1064 nm (left) and power dependence profile of the fluorescence intensity (right). Reproduced with permission from ref 44. Copyright 2013 Nature Publishing Group.

## 4. CONCLUSION AND OUTLOOK

In this Account, we have summarized our recent progresses on pore and function engineering to develop functional MOF materials for their broad applications in gas storage, gas separation, enantioselective separation, luminescence sensing, white-light emitting, nonlinear optics, lasing device, and 3D patterning and data storage. Because we can readily design and tune the porosities, pore sizes, and functional sites of MOFs, MOF materials are very promising for gas storage, gas separation and enantioselective separations. We can certainly target novel functional MOF materials beyond their porosities through the incorporation of a variety of metal ions/metal clusters, organic linkers and encapsulated species within pores of unique physical and chemical properties. Theoretically speaking, an infinite number of metal ions and organic linkers can be assembled into metal–organic frameworks to have variable framework struc-



**Figure 14.** (a) Zwitterionic and neutral tetracarboxylate linkers for the construction of two-photon responsive MOFs. (b) Fluorescence spectra evolution of  $H_4L1$ ·OH upon exposure to UV light at 365 nm. (c) Schematic illustration of the assembly of L1 incorporated MOF ZJU-56-0.20 via a multivariate approach and femtosecond laser writing inside the MOF single crystal through a two-photon process. (d) Top view of two-photon excited fluorescent image of a 2D code stack. Scale bar, 25  $\mu$ m. (e) Reconstructed lateral image along the indicated line in panel a (left), and lateral view imaged by using one photon fluorescence (right). (f) Three-dimensional reconstructed image of the stacked 2D code pattern. (g) Intensity profiles of the fluorescent codes along lines 1 and 2 in panels (b) and (c), respectively. Reproduced with permission from ref 45. Copyright 2015 American Chemical Society.

tures and porosities and to introduce physical and chemical functionalities. In fact, the first protein based metal-organic framework has been recently realized.<sup>46</sup> Furthermore, the pore spaces within metal-organic frameworks can encapsulate a number of species ranging from metal nanoparticles, metal complexes, organic compounds, and biological molecules.<sup>47-</sup> These unique features of metal-organic frameworks have enabled MOFs to be one of the most promising and variable platforms to develop functional materials. Commercialization of some prototype metal-organic framework materials by multinational companies has certainly facilitated the ongoing active research endeavor on functional MOF materials.<sup>50</sup> Close collaboration with chemists, physicists, biologists, and engineering scientists of different expertise and industrial partners will not only initiate novel ideas on the exploration of functional MOF materials, but will also eventually lead to some practically useful materials for our daily life in the future.

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#### Notes

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(2) Zhou, H.-C.; Kitagawa, S. Introduction. Metal–Organic Frameworks (MOFs). *Chem. Soc. Rev.* 2014, 43, 5415–5418.

(3) Chen, B.; Xiang, S.; Qian, G. Metal–Organic Frameworks with Functional Pores for Recognition of Small Molecules. *Acc. Chem. Res.* **2010**, 43, 1115–1124.

(4) Zhou, H.-L.; Zhang, Y.-B.; Zhang, J.-P.; Chen, X.-M. Supramolecular-jack-like Guest in Ultramicroporous Crystal for Exceptional Thermal Expansion Behaviour. *Nat. Commun.* **2015**, *6*, 6917.

(5) Wang, C.; Liu, D.; Lin, W. Metal–Organic Frameworks as A Tunable Platform for Designing Functional Molecular Materials. *J. Am. Chem. Soc.* **2013**, *135*, 13222–13234.

(6) Czaja, A. U.; Trukhan, N.; Müller, U. Industrial Applications of Metal–Organic Frameworks. *Chem. Soc. Rev.* **2009**, *38*, 1284–1293.

(7) Sun, C.-Y.; Wang, X.-L.; Zhang, X.; Qin, C.; Li, P.; Su, Z.-M.; Zhu, D.-X.; Shan, G.-G.; Shao, K.-Z.; Wu, H.; Li, J. Efficient and Tunable White-Light Emission of Metal–Organic Frameworks by Iridium-Complex Encapsulation. *Nat. Commun.* **2013**, *4*, 2717.

(8) Horcajada, P.; Chalati, T.; Serre, C.; Gillet, B.; Sebrie, C.; Baati, T.; Eubank, J. F.; Heurtaux, D.; Clayette, P.; Kreuz, C.; Chang, J.-S.; Hwang, Y. K.; Marsaud, V.; Bories, P.-N.; Cynober, L.; Gil, S.; Férey, G.; Couvreur, P.; Gref, R. Porous Metal–Organic-Framework Nanoscale Carriers as a Potential Platform for Drug Delivery and Imaging. *Nat. Mater.* **2010**, *9*, 172–178.

(9) Talin, A. A.; Centrone, A.; Ford, A. C.; Foster, M. E.; Stavila, V.; Haney, P.; Kinney, R. A.; Szalai, V.; Gabaly, F. E.; Yoon, H. P.; Léonard, F.; Allendorf, M. D. Tunable Electrical Conductivity in Metal–Organic Framework Thin-Film Devices. *Science* **2014**, *343*, 66–69.

(10) Feng, D.; Gu, Z.-Y.; Chen, Y.-P.; Park, J.; Wei, Z.; Sun, Y.; Bosch, M.; Yuan, S.; Zhou, H.-C. A Highly Stable Porphyrinic Zirconium Metal–Organic Framework with shp-a Topology. I. J. Am. Chem. Soc. **2014**, 136, 17714–17717.

(11) Bloch, E. D.; Queen, W. L.; Krishna, R.; Zadrozny, J. M.; Brown, C. M.; Long, J. R. Hydrocarbon Separations in a Metal–Organic Framework with Open Iron(II) Coordination Sites. *Science* **2012**, *335*, 1606–1610.

(12) Fei, H.; Shin, J. W.; Meng, Y. S.; Adelhardt, M.; Sutter, J.; Meyer, K.; Cohen, S. M. Reusable Oxidation Catalysis Using Metal-Monocatecholato Species in a Robust Metal–Organic Framework. *J. Am. Chem. Soc.* **2014**, *136*, 4965–4973.

(13) Li, B.; Leng, K.; Zhang, Y.; Dynes, J. J.; Wang, J.; Hu, Y.; Ma, D.; Shi, Z.; Zhu, L.; Zhang, D.; Sun, Y.; Chrzanowski, M.; Ma, S. Metal– Organic Framework Based upon the Synergy of a Brønsted Acid Framework and Lewis Acid Centers as a Highly Efficient Heterogeneous Catalyst for Fixed-Bed Reactions. *J. Am. Chem. Soc.* **2015**, *137*, 4243– 4248.

(14) Nugent, P.; Belmabkhout, Y.; Burd, S. D.; Cairns, A. J.; Luebke, R.; Forrest, K.; Pham, T.; Ma, S.; Space, B.; Wojtas, L.; Eddaoudi, M.; Zaworotko, M. J. Porous Materials with Optimal Adsorption Thermodynamics and Kinetics for  $CO_2$  Separation. *Nature* **2013**, 495, 80–84.

(15) Shekhah, O.; Belmabkhout, Y.; Chen, Z.; Guillerm, V.; Cairns, A.; Adil, K.; Eddaoudi, M. Made-to-Order Metal–Organic Frameworks for Trace Carbon Dioxide Removal and Air Capture. *Nat. Commun.* **2014**, *5*, 4228.

(16) Yang, S.; Ramirez-Cuesta, A. J.; Newby, R.; Garcia-Sakai, V.; Manuel, P.; Callear, S. K.; Campbell, S. I.; Tang, C. C.; Schröder, M. Supramolecular Binding and Separation of Hydrocarbons within a Functionalized Porous Metal–Organic Framework. *Nat. Chem.* **2015**, *7*, 121–129.

(17) An, J.; Shade, C. M.; Chengelis-Czegan, D. A.; Petoud, S.; Rosi, N. L. Zinc-Adeninate Metal–Organic Framework for Aqueous Encapsulation and Sensitization of Near-infrared and Visible Emitting Lanthanide Cations. J. Am. Chem. Soc. 2011, 133, 1220–1223.

(18) Nguyen, N. T. T.; Furukawa, H.; Gándara, F.; Nguyen, H. T.; Cordova, K. E.; Yaghi, O. M. Selective Capture of Carbon Dioxide under Humid Conditions by Hydrophobic Chabazite-Type Zeolitic Imidazolate Frameworks. *Angew. Chem., Int. Ed.* **2014**, *53*, 10645–10648.

(19) Mondloch, J. E.; Katz, M. J.; Isley, W. C., III; Ghosh, P.; Liao, P.; Bury, W.; Wagner, G. W.; Hall, M. G.; DeCoste, J. B.; Peterson, G. W.; Snurr, R. Q.; Cramer, C. J.; Hupp, J. T.; Farha, O. K. Destruction of Chemical Warfare Agents Using Metal–Organic Frameworks. *Nat. Mater.* **2015**, *14*, 512–516.

(20) Zhu, Q.-L.; Li, J.; Xu, Q. Immobilizing Metal Nanoparticles to Metal–Organic Frameworks with Size and Location Control for Optimizing Catalytic Performance. *J. Am. Chem. Soc.* **2013**, *135*, 10210–10213.

(21) Gong, Q.; Hu, Z.; Deibert, B. J.; Emge, T. J.; Teat, S. J.; Banerjee, D.; Mussman, B.; Rudd, N. D.; Li, J. Solution Processable MOF Yellow Phosphor with Exceptionally High Quantum Efficiency. *J. Am. Chem. Soc.* **2014**, *136*, 16724–16727.

(22) Sun, L.; Hendon, C. H.; Minier, M. A.; Walsh, A.; Dincă, M. Million-Fold Electrical Conductivity Enhancement in  $Fe_2(DEBDC)$  versus  $Mn_2(DEBDC)$  (E = S, O). J. Am. Chem. Soc. **2015**, 137, 6164–6167.

(23) Harbuzaru, B. V.; Corma, A.; Rey, F.; Jordá, J. L.; Ananias, D.; Carlos, L. D.; Rocha, J. A Miniaturized Linear pH Sensor Based on a Highly Photoluminescent Self-Assembled Europium(III) Metal– Organic Framework. *Angew. Chem., Int. Ed.* **2009**, *48*, 6476–6479.

(24) Vaidhyanathan, R.; Iremonger, S. S.; Shimizu, G. K. H.; Boyd, P. G.; Alavi, S.; Woo, T. K. Direct Observation and Quantification of  $CO_2$ Binding Within an Amine-Functionalized Nanoporous Solid. *Science* **2010**, 330, 650–653.

(25) Zheng, S. T.; Wu, T.; Chou, C.; Fuhr, A.; Feng, P.; Bu, X. Development of Composite Inorganic Building Blocks for MOFs. *J. Am. Chem. Soc.* **2012**, *134*, 4517–4520.

(26) Sato, H.; Matsuda, R.; Sugimoto, K.; Takata, M.; Kitagawa, S. Photoactivation of a Nanoporous Crystal for On-Demand Guest Trapping and Conversion. *Nat. Mater.* **2010**, *9*, 661–666.

(27) Takashima, Y.; Martinez, V. M.; Furukawa, S.; Kondo, M.; Shimomura, S.; Uehara, H.; Nakahama, M.; Sugimoto, K.; Kitagawa, S. Molecular Decoding Using Luminescence from an Entangled Porous Framework. *Nat. Commun.* **2011**, *2*, 168.

(28) Guo, Z.; Wu, H.; Srinivas, G.; Zhou, Y.; Xiang, S.; Chen, Z.; Yang, Y.; Zhou, W.; O'Keeffe, M.; Chen, B. A Metal–Organic Framework with Optimized Open Metal Sites and Pore Spaces for High Methane Storage at Room Temperature. *Angew. Chem., Int. Ed.* **2011**, *50*, 3178–3181.

(29) He, Y.; Zhou, W.; Yildirim, T.; Chen, B. A Series of Metal– Organic Frameworks with High Methane Uptake and an Empirical Equation for Predicting Methane Storage Capacity. *Energy Environ. Sci.* **2013**, *6*, 2735–2744.

(30) Li, B.; Wen, H. M.; Wang, H.; Wu, H.; Tyagi, M.; Yildirim, T.; Zhou, W.; Chen, B. A Porous Metal–Organic Framework with Dynamic Pyrimidine Groups Exhibiting Record High Methane Storage Working Capacity. J. Am. Chem. Soc. **2014**, *136*, 6207–6210.

(31) Li, B.; Wen, H.-M.; Wang, H.; Wu, H.; Yildirim, T.; Zhou, W.; Chen, B. Porous Metal–Organic Frameworks with Lewis Basic Nitrogen Sites for High-Capacity Methane Storage. *Energy Environ. Sci.* **2015**, *8*, 2504–2511.

(32) Xiang, S. C.; Zhang, Z.; Zhao, C. G.; Hong, K.; Zhao, X.; Ding, D. R.; Xie, M. H.; Wu, C. D.; Das, M. C.; Gill, R.; Thomas, K. M.; Chen, B. Rationally Tuned Micropores within Enantiopure Metal–Organic Frameworks for Highly Selective Separation of Acetylene and Ethylene. *Nat. Commun.* **2011**, *2*, 204.

(33) Das, M. C.; Guo, Q.; He, Y.; Kim, J.; Zhao, C. G.; Hong, K.; Xiang, S.; Zhang, Z.; Thomas, K. M.; Krishna, R.; Chen, B. Interplay of Metalloligand and Organic Ligand to Tune Micropores within Isostructural Mixed-Metal Organic Frameworks (M'MOFs) for Their Highly Selective Separation of Chiral and Achiral Small Molecules. J. Am. Chem. Soc. 2012, 134, 8703–8710.

(34) He, Y.; Krishna, R.; Chen, B. Metal–Organic Frameworks with Potential for Energy-Efficient Adsorptive Separation of Light Hydrocarbons. *Energy Environ. Sci.* **2012**, *5*, 9107–9120.

(35) Hu, T. L.; Wang, H.; Li, B.; Krishna, R.; Wu, H.; Zhou, W.; Zhao, Y.; Han, Y.; Wang, X.; Zhu, W.; Yao, Z.; Xiang, S.; Chen, B. Microporous

#### **Accounts of Chemical Research**

Metal–Organic Framework with Dual Functionalities for Highly Efficient Removal of Acetylene from Ethylene/Acetylene Mixtures. *Nat. Commun.* **2015**, *6*, 7328.

(36) Xiang, S.; He, Y.; Zhang, Z.; Wu, H.; Zhou, W.; Krishna, R.; Chen, B. Microporous Metal–Organic Framework with Potential for Carbon Dioxide Capture at Ambient Conditions. *Nat. Commun.* **2012**, *3*, 954.

(37) Rao, X.; Huang, Q.; Yang, X.; Cui, Y.; Yang, Y.; Wu, C.; Chen, B.; Qian, G. Color Tunable and White Light Emitting Tb<sup>3+</sup> and Eu<sup>3+</sup> Doped Lanthanide Metal–Organic Framework Materials. *J. Mater. Chem.* **2012**, 22, 3210–3214.

(38) Cui, Y.; Xu, H.; Yue, Y.; Guo, Z.; Yu, J.; Chen, Z.; Gao, J.; Yang, Y.; Qian, G.; Chen, B. A Luminescent Mixed-Lanthanide Metal–Organic Framework Thermometer. J. Am. Chem. Soc. **2012**, *134*, 3979–3982.

(39) Rao, X.; Song, T.; Gao, J.; Cui, Y.; Yang, Y.; Wu, C.; Chen, B.; Qian, G. A Highly Sensitive Mixed Lanthanide Metal–Organic Framework Self-calibrated Luminescent Thermometer. J. Am. Chem. Soc. 2013, 135, 15559–15564.

(40) Cui, Y.; Song, T.; Yu, J.; Yang, Y.; Wang, Z.; Qian, G. Dye Encapsulated Metal–Organic Framework for Warm-White LED with High Color-Rendering Index. *Adv. Funct. Mater.* **2015**, *25*, 4796–4802.

(41) Dou, Z.; Yu, J.; Cui, Y.; Yang, Y.; Wang, Z.; Yang, D.; Qian, G. Luminescent Metal–Organic Framework Films as Highly Sensitive and Fast-Response Oxygen Sensors. *J. Am. Chem. Soc.* **2014**, *136*, 5527–5530.

(42) Cui, Y.; Song, R.; Yu, J.; Liu, M.; Wang, Z.; Wu, C.; Yang, Y.; Chen, B.; Qian, G. Dual-Emitting MOF Supersetdye Composite for Ratiometric Temperature Sensing. *Adv. Mater.* **2015**, *27*, 1420–1425.

(43) Yu, J.; Cui, Y.; Wu, C.; Yang, Y.; Wang, Z.; O'Keeffe, M.; Chen, B.; Qian, G. Second-Order Nonlinear Optical Activity Induced by Ordered Dipolar Chromophores Confined in the Pores of an Anionic Metal– Organic Framework. *Angew. Chem., Int. Ed.* **2012**, *51*, 10542–10545.

(44) Yu, J.; Cui, Y.; Xu, H.; Yang, Y.; Wang, Z.; Chen, B.; Qian, G. Confinement of Pyridinium Hemicyanine Dye within an Anionic Metal–Organic Framework for Two-Photon-Pumped Lasing. *Nat. Commun.* **2013**, *4*, 2719.

(45) Yu, J.; Cui, Y.; Wu, C. D.; Yang, Y.; Chen, B.; Qian, G. Two-Photon Responsive Metal–Organic Framework. J. Am. Chem. Soc. 2015, 137, 4026–4029.

(46) Sontz, P. A.; Bailey, J. B.; Ahn, S.; Tezcan, F. A. A Metal Organic Framework with Spherical Protein Nodes: Rational Chemical Design of 3D Protein Crystals. J. Am. Chem. Soc. **2015**, 137, 11598–11601.

(47) Falcaro, P.; Ricco, R.; Doherty, C. M.; Liang, K.; Hill, A. J.; Styles, M. J. MOF positioning technology and device fabrication. *Chem. Soc. Rev.* **2014**, *43*, 5513–5560.

(48) Tang, Y.-J.; Gao, M.-R.; Liu, C.-H.; Li, S.-L.; Jiang, H.-L.; Lan, Y.-Q.; Han, M.; Yu, S.-H. Porous Molybdenum-Based Hybrid Catalysts for Highly Efficient Hydrogen Evolution. *Angew. Chem., Int. Ed.* **2015**, *54*, 12928–12932.

(49) Aulakh, D.; Pyser, J. B.; Zhang, X.; Yakovenko, A. A.; Dunbar, K. R.; Wriedt, M. Metal–Organic Frameworks as Platforms for the Controlled Nanostructuring of Single-Molecule Magnets. *J. Am. Chem. Soc.* **2015**, *137*, 9254–9257.

(50) Jacoby, M. Materials Chemistry: Metal–Organic Frameworks Go Commercial. *Chem. Eng. News* **2013**, *91*, 34–35.