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Microwave-Assisted Solvothermal Synthesis and Optical Properties of Tagged MIL-140A Metal–Organic Frameworks

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Supporting Information

ABSTRACT: A series of tagged MIL-140A-R frameworks have been synthesized using a microwave-assisted solvothermal method. Compared with their UiO-66-R polymorphs, the absorption energies in the MIL-140A-R series (R = NH_2, NO_2, Br, Cl, and F) are extended toward the visible region because of the spatial arrangement of the linkers.

Metal–organic frameworks (MOFs) are a class of hybrid materials formed by the self-assembly of metal ions or clusters and polydentate bridging ligands.[1] Because of the virtually limitless combinations of metals and ligands, the physicochemical properties of MOFs can be judiciously tuned for specific applications. As a result, these materials have shown promise for a number of diverse applications in areas including molecular separation, gas sorption, catalysis, and luminescene.[2]

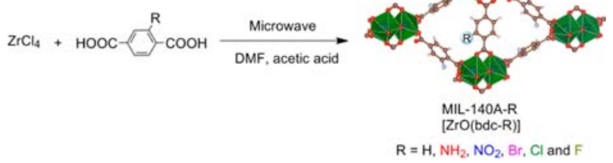
Recently, significant progress has been made in the UiO isoreticular MOF series.[3] This class of frameworks is characterized by octahedral Zr_6 secondary building units (SBUs) bound to 12 linear dicarboxylate ligands (1,4-benzenedicarboxylate in UiO-66, $[Zr_6O_4(OH)_4(O_2CC_6H_4CO_2)_{12}]$) to afford a three-dimensional periodic structure in which each centric octahedral cage is connected to eight corner tetrahedral cages through triangular windows.[3b] UiO-66 exhibits exceptional thermal, chemical, and mechanical stability;[4] however, its upper analogues (that is, frameworks with the same topology but longer organic linkers), such as UiO-67 ($[Zr_6O_4(OH)_4(O_2CC_{12}H_8CO_2)_{12}]$), exhibit comparatively low stability even under atmospheric conditions.[4,5]

Serre and co-workers recently reported another series of zirconium-based MOFs, which are polymorphs of the UiO series, denoted MIL-140, with the general formula [ZrO(L)] (L = linear dicarboxylate ligand).[6] In MIL-140, instead of Zr_6O clusters, zirconium oxide chains act as SBUs and are oriented along the *c* axis. Each cluster is connected to six other chains through the dicarboxylate linkers. This results in one-dimensional triangular channels rather than three-dimensional connecting pores in UiO.[6]

The chemical and mechanical stabilities of the MIL-140 frameworks exceed those of the UiO series, especially in the case of the analogues with longer linkers.[5,6] These improvements can be attributed to (i) the reduced flexibility of the infinite zirconium oxide chains in MIL-140 compared to the Zr_6O clusters in UiO and (ii) the presence of π-stacking of the aromatic linkers in MIL-140, which leads to short-range dispersive interactions that enhance the stability of the framework.[6]

In a previous study, we developed a microwave-assisted solvothermal synthesis method for MIL-140.[7] Our present goal is to assess how functionalization of 1,4-benzendicarboxylic acid (H_2bdc) contributes to and modifies the chemical and physical properties of MIL-140A ($[ZrO(O_2CC_6H_4CO_2)]$). Five analogues of H_2bdc with different functional groups (H_2bdc-R; R = NH_2, NO_2, Br, Cl, and F) were employed to produce a new series of tagged MIL-140A systems (see Scheme 1).

Scheme 1. Synthetic Routes to MIL-140A and MIL-140A-R (R = NH_2, NO_2, Br, Cl, and F)



The reaction conditions employed for synthesis of the MIL-140A-R series were analogous to those for MIL-140A reported previously in the literature.[7] The microwave synthesis protocol was selected for its distinct advantages in terms of reduction in the synthesis time and increase in the energy efficiency.[8] In addition, our previous study indicated that MIL-140A-NH_2 was unattainable using the conventional electric heating method.[7]

The powder X-ray diffraction (PXRD) patterns obtained for as-synthesized MIL-140A-R are presented in Figure 1a. The positions and relative intensities of the peaks for the MIL-140A-R frameworks were consistent with the as-synthesized MIL-140A parent material,[6] which demonstrates that the tagged MIL-140A-R frameworks are topologically equivalent to MIL-140A.

Thermogravimetric analysis revealed that all frameworks, except MIL-140A-NO_2, exhibited thermal stabilities up to ca. 450 °C. In addition, the theoretical and experimental weight loss profiles for MIL-140A and MIL-140A-R (calculated from their chemical formulas) were in good agreement, except for MIL-140A-NO_2. The relatively low thermal stability (ca. 300 °C) and disparity in the weight loss profile for MIL-140A-NO_2 (54% in the experiment compared with 61% in theory) are likely to result from the low crystallinity of the material (broad and low-intensity

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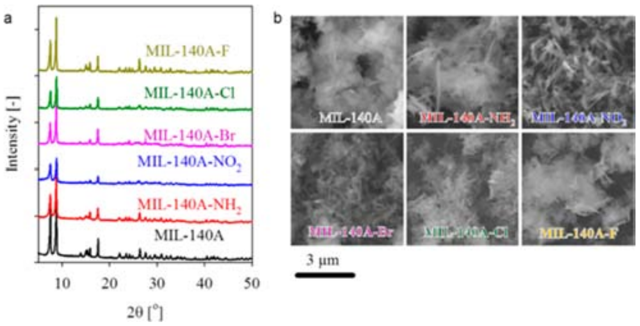

Figure 1. PXRD spectra (a) and SEM images (b) of as-synthesized MIL-140A (black) and MIL-140A-R [R = NH_2 (red), NO_2 (blue), Br (purple), Cl (green), and F (yellow)].

peaks as evidenced by the PXRD spectra; Figure 1a). A hydrothermal stability test confirmed that this class of materials is stable in liquid water at room temperature.

Prior to examining the porosities of the materials, a Soxhlet washing procedure was performed (*N*,*N*′-dimethylformamide exchange with methanol), followed by pore activation at moderate temperature (120 °C) in vacuo. All materials were found to retain moderate porosity (Brunauer−Emmett−Teller surface areas ranged from 150 to 335 $m^2 \cdot g^{-1}$) despite the presence of different functional groups on the bridging ligands. The decreases in the surface area (223, 120, 150, 213, and 283 $m^2 \cdot g^{-1}$ for R = NH_2, NO_2, Br, Cl, and F versus 335 $m^2 \cdot g^{-1}$ for MIL-140A) are largely attributed to the reduced free space available and the increased molecular weights of the functionalized MOFs.[3c]

Scanning electron microscopy (SEM) images show that the functionalized materials appear as platelike crystallites (Figure 1b), consistent with previous results for MIL-140A and MIL-140A-NH_2.[7] Interestingly, the resulting crystalline powders exhibit different colors depending on the functionalization of the linker (Figure 2). MIL-140A and MIL-140A-NH_2 exhibited the same color as their constituent dicarboxylic ligand (white for H_2bdc and MIL-140A and yellow for H_2bdc-NH_2 and MIL-140A-NH_2). However, MIL-140A-R (R = NO_2, Br, Cl, and F) appeared yellow, in contrast to the white color of their corresponding ligands. The color changes were quantified by diffuse-reflectance UV−vis analysis (Figure 2). For comparison, the UiO-66-R analogues were also synthesized according to the reported methods.[9]

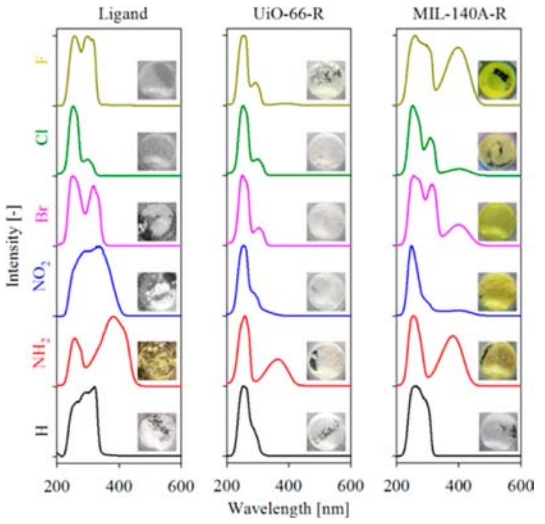

Figure 2. Diffuse-reflectance UV−vis spectra and digital images (insets) of MIL-140A-R and UiO-66-R with their respective tagged ligands H_2bdc-R (R = H, NH_2, NO_2, Br, Cl, and F).

The UV−vis spectrum of MIL-140A exhibits absorption bands below 350 nm, similar to the ligand H_2bdc itself and its UiO-66 analogue, whereas absorption bands are observed in the spectra of MIL-140A-NH_2 and UiO-66-NH_2 up to ~500 nm (Figure 2). Garcia et al. reported that electron transfer takes place from the photoexcited organic linker to the metal oxo cluster within MOF-5, a phenomenon termed linker-to-cluster charge transfer.[10] Herein, the visible-light absorption for MIL-140A-NH_2 is likely to be attributed to the electronic transition from the amine-containing chromophore to the Zr centers.[11]

While each of the MIL-140A-R analogues displayed an absorption band edge at ca. 475 nm, which could be fitted with a Gaussian peak with a maximum at ~400 nm, the UiO-66-R frameworks functionalized with electron-withdrawing groups (NO_2, Br, Cl, and F) and their corresponding dicarboxylate ligands are transparent between 400 and 600 nm. Considering the similarity in the chemical compositions of UiO-66-R and MIL-140A-R (ZrO clusters linked by H_2bdc with pendent functional groups),[3b,6] such changes in the optical properties between these two polymorphs may be rationalized on the basis of differences in their ligand arrangements. It is well-known that the optical properties of materials are not only related to the identities of the component metal centers and ligands but that they are also dependent on the structural features of the multidimensional system, which may give rise to intermolecular energy transfer.[2a]

In UiO-66-R, the dicarboxylate ligands are spatially separated in the three-dimensional coordination space. However, in MIL-140A-R, 50% of the aromatic linkers are aligned by π stacking,[6] which results in short-range interactions between the ligands. Indeed, previous density functional theory (DFT) calculations have indicated that the stacking interaction in MIL-140A is comparable to that present in H_2bdc crystals.[6] In an independent study, Brédas et al. reported that strong face-to-face interactions are predicted when the distance between two stilbene dimers is less than ~5 Å, resulting in modification of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbital levels of the dimer and a corresponding red shift in absorption.[12] Considering that the minimum C−C distance of a bdc π-dimer in MIL-140A is ~3.8 Å, there is a strong probability for the occurrence of such a phenomenon in this system.

Photoluminescence (PL) analysis was performed to gain insight into the origin of the absorption bands in MIL-140A-R. Several types of PL in MOFs have been classified, including (i) ligand-based luminescence (particularly from highly conjugated ligands), (ii) metal-centered emission (widely observed in lanthanide MOFs), and (iii) charge-transfer luminescence. Under 405 nm laser excitation at room temperature (at the maximum of the lowest-energy absorption band in Figure 2), the MIL-140A-R frameworks (R = NH_2, NO_2, Br, Cl, and F) exhibit similar PL spectra (see the SI), which are characterized by emission peaks at 470 and 503 nm. In general, ligand-based luminescence is dependent on the chemical nature of the linkers.[13] Given the variety of funtionalized ligands examined in this study, the fluorescence observed in the MIL-140A-R series is more likely attributed to linker-to-cluster charge transfer rather than ligand-based luminescence.

Considering the differences in the structures of the UiO-66-R and MIL-140A-R polymorphs provides some insight into the origins of their differing optical properties. In UiO-66-R, the bdc-R linkers are spatially isolated, and the LUMO of the bdc-R ligands (R = NO_2, Br, Cl, and F) lies relatively lower in energy than the Zr_6O cluster SBUs. Thus, the energy-transfer pathway from the ligand to the zirconium-based cluster (either $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$) is relatively inefficient. Because of π-stacking interactions between the aromatic linkers in MIL-140A-R, the HOMO and LUMO levels of the bdc-R ligands are likely to be modified such that the efficiency of the energy migration from the lowest excited singlet state of the π-stacked bdc-R linkers to the zirconium oxide chains is enhanced.

In summary, spectral analysis of a series of tagged MIL-140A-R frameworks, which have been synthesized using a microwave-assisted solvothermal method, reveals that the optical response of MIL-140A-R (R = NO_2, Br, Cl, and F) can be tailored toward absorption in the visible region. In view of the extensive interest in the photochemical properties of UiO-66-R (R = H, NH_2) and related MIL frameworks, which have been shown to act as photocatalysts for hydrogen generation and the selective oxidation of alcohols,[14] it is of interest to compare the optical properties of the less widely studied MIL-140A-R polymorph with a view toward its potential applications. This study demonstrates that it is possible to engineer the physical and chemical properties of frameworks by varying the spatial arrangement of the ligands. High-level DFT calculations are currently underway to elucidate the origin of variations in the optical band gaps of these materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) O'Keeffe, M.; Yaghi, O. M. *Chem. Rev.* **2012**, *112* (2), 675−702.

(2) (a) Allendorf, M. D.; Bauer, C. A.; Bhakta, R. K.; Houk, R. J. T. *Chem. Soc. Rev.* **2009**, *38* (5), 1330−1352. (b) D'Alessandro, D. M.; Smit, B.; Long, J. R. *Angew. Chem., Int. Ed.* **2010**, *49* (35), 6058−6082. (c) Corma, A.; García, H.; Llabrés I Xamena, F. X. *Chem. Rev.* **2010**, *110* (8), 4606−4655.

(3) (a) Kim, M.; Cohen, S. M. *CrystEngComm* **2012**, *14* (12), 4096−4104. (b) Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. *J. Am. Chem. Soc.* **2008**, *130* (42), 13850−13851. (c) Kandiah, M.; Nilsen, M. H.; Usseglio, S.; Jakobsen, S.; Olsbye, U.; Tilset, M.; Larabi, C.; Quadrelli, E. A.; Bonino, F.; Lillerud, K. P. *Chem. Mater.* **2010**, *22* (24), 6632−6640. (d) Chavan, S.; Vitillo, J. G.; Gianolio, D.; Zavorotynska, O.; Civalleri, B.; Jakobsen, S.; Nilsen, M. H.; Valenzano, L.; Lamberti, C.; Lillerud, K. P.; Bordiga, S. *Phys. Chem. Chem. Phys.* **2012**, *14* (5), 1614−1626. (e) Vermoortele, F.; Bueken, B.; Le Bars, G.; Van de Voorde, B.; Vandichel, M.; Houthoofd, K.; Vimont, A.; Daturi, M.; Waroquier, M.; Van Speybroeck, V.; Kirschhock, C.; De Vos, D. E. *J. Am. Chem. Soc.* **2013**, *135* (31), 11465−11468. (f) Wu, H.; Chua, Y. S.; Krungleviciute, V.; Tyagi, M.; Chen, P.; Yildirim, T.; Zhou, W. *J. Am. Chem. Soc.* **2013**, *135* (28), 10525−10532.

(4) Schaate, A.; Roy, P.; Godt, A.; Lippke, J.; Waltz, F.; Wiebcke, M.; Behrens, P. *Chem.—Eur. J.* **2011**, *17* (24), 6643−6651.

(5) DeCoste, J. B.; Peterson, G. W.; Jasuja, H.; Glover, T. G.; Huang, Y.-g.; Walton, K. S. *J. Mater. Chem. A* **2013**, *1* (18), 5642−5650.

(6) Guillerm, V.; Ragon, F.; Dan-Hardi, M.; Devic, T.; Vishnuvarthan, M.; Campo, B.; Vimont, A.; Clet, G.; Yang, Q.; Maurin, G.; Ferey, G.; Vittadini, A.; Gross, S.; Serre, C. *Angew. Chem., Int. Ed.* **2012**, *51*, 9188.

(7) Liang, W.; D'Alessandro, D. M. *Chem. Commun.* **2013**, *49* (35), 3706−3708.

(8) (a) Liang, W.; Harris, A. T. *Mater. Lett.* **2011**, *65* (14), 2307−2310. (b) Klinowski, J.; Almeida Paz, F. A.; Silva, P.; Rocha, J. *Dalton Trans.* **2011**, *40* (2), 321−330.

(9) Vermoortele, F.; Vandichel, M.; Van de Voorde, B.; Ameloot, R.; Waroquier, M.; Van Speybroeck, V.; De Vos, D. E. *Angew. Chem., Int. Ed.* **2012**, *51* (20), 4887−4890.

(10) Alvaro, M.; Carbonell, E.; Ferrer, B.; Llabrés i Xamena, F. X.; Garcia, H. *Chem.—Eur. J.* **2007**, *13* (18), 5106−5112.

(11) Long, J.; Wang, S.; Ding, Z.; Wang, S.; Zhou, Y.; Huang, L.; Wang, X. *Chem. Commun.* **2012**, *48* (95), 11656−11658.

(12) Cornil, J.; dos Santos, D. A.; Crispin, X.; Silbey, R.; Brédas, J. L. *J. Am. Chem. Soc.* **1998**, *120* (6), 1289−1299.

(13) (a) Takashima, Y.; Martínez, V. M.; Furukawa, S.; Kondo, M.; Shimomura, S.; Uehara, H.; Nakahama, M.; Sugimoto, K.; Kitagawa, S. *Nat. Commun.* **2011**, *2*, 1−8. (b) Jiang, H.-L.; Feng, D.; Wang, K.; Gu, Z.-Y.; Wei, Z.; Chen, Y.-P.; Zhou, H.-C. *J. Am. Chem. Soc.* **2013**, *135* (37), 13934−13938. (c) Son, H.-J.; Jin, S.; Patwardhan, S.; Wezenberg, S. J.; Jeong, N. C.; So, M.; Wilmer, C. E.; Sarjeant, A. A.; Schatz, G. C.; Snurr, R. Q.; Farha, O. K.; Wiederrecht, G. P.; Hupp, J. T. *J. Am. Chem. Soc.* **2012**, *135*, 862−869.

(14) (a) Gomes Silva, C.; Luz, I.; Llabrés i Xamera, F. X.; Corma, A.; García, H. *Chem.—Eur. J.* **2010**, *16*, 11133−11138. (b) Shen, L.; Liang, S.; Wu, W.; Liang, R.; Wu, L. *Dalton Trans.* **2013**, *42*, 13649−13657. (c) Nasalevich, M. A.; Goesten, M. G.; Savenije, T. J.; Kapteijn, F.; Gascon, J. *Chem. Commun.* **2013**, *49*, 10575−10577.