

Dynamic Photo-Switching in Metal–Organic Frameworks as a Route to Low-Energy Carbon Dioxide Capture and Release**

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For post-combustion carbon dioxide capture technology to realize widespread viability, the energy costs must be drastically reduced. Current adsorbent technologies that rely on pressure, temperature, or vacuum swings consume as much as 40 % of the production capacity of a power plant, most of which is associated with the liberation of CO₂ from the capture medium.^[1] Ultimately this penalty, or parasitic energy load, must be brought closer to the thermodynamic minimum of about 4 % to avoid prohibitive cost increases.^[2] Given that the triggers for release of adsorbed carbon dioxide, such as vacuum and heating, are so energy intensive,^[1a,3] requiring energy from the power plant, there is strong motivation to develop new release triggers that do not require extra energy from the plant, using renewable energy sources such as the sun. In conjunction with this, adsorbents with maximum gas sorption efficiency can further reduce the costs compared to the conventional energy-intensive CO₂ gas separation process.

Light, and in particular concentrated sunlight, is an extremely attractive stimulus for triggering CO₂ release. If used with an adsorbent material that strongly absorbs sunlight concomitant with the desorption of large amounts of CO₂, it may be possible to drastically reduce the energy costs.

Perhaps the most attractive adsorbent candidates are metal–organic frameworks (MOFs), because of their large adsorption capacities,^[4] and the potential for incorporation of light-responsive organic groups within the pore structure.^[4c,5] MOFs are an important class of 3D crystalline porous

materials comprised of metal centers and organic ligands, joined periodically to establish a crystalline porous array.^[4d] The large internal surface areas can be used to adsorb unprecedented quantities of gases,^[4e,6] with particular interest in hydrogen,^[4e,7] methane,^[4e,7c,h,8] and carbon dioxide emergent.^[1a,c,4e,7b,h,9]

Methods for the incorporation of light-responsive groups within MOFs include the use of pendant groups pointing into the pores,^[10] and filling of pores with light-responsive guest molecules.^[11] The responsive groups within these materials may then alter their conformation when exposed to filtered light which results in a change in adsorption capacity, as reported thus far for static conditions.^[10,11]

The responsive groups within these MOFs can be statically set to one position or another. For use in photo-switching carbon dioxide capture, MOFs that can respond dynamically, or to the broadband radiation found in sunlight whilst loaded with adsorbed gas, are ideal. This will increase the speed of operation and lower the energy costs (see Figure 1)

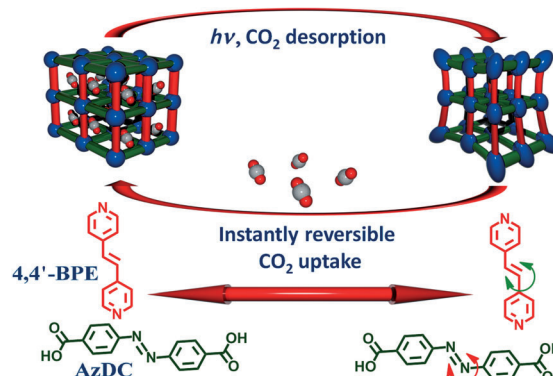


Figure 1. Dynamic photo-switching in the light-responsive MOF Zn(AzDC)(4,4'-BPE)_{0.5} leads to instantly reversible CO₂ uptake.

Azobenzene and its derivatives are well-known photochromic molecules that can undergo clean and efficient reversible photoisomerization about the azo bond to *cis* and *trans* states upon irradiation (coordinated *trans*: $\lambda_{\text{max}} \approx 370$ nm, *cis*: $\lambda_{\text{max}} \approx 460$ nm).^[12] Conversion of azobenzene to the 4,4'-dicarboxylate (AzDC) delivers a ligand that can be incorporated into MOF architectures. Furthermore, the pillar ligand *trans*-1,2-bis(4-pyridyl)ethylene (4,4'-BPE) has also been reported to demonstrate *cis*–*trans* photoisomerizability when coordinated to a metal complex.^[13] Combination of these two ligands within zinc-based MOFs generates the triply

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interpenetrated framework $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$, which exhibits an open topology amenable to high capacity and selective adsorption of hydrogen and carbon dioxide (see Figure SI-1).^[14]

The triply interpenetrated framework $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ was prepared solvothermally using previously reported methods (see Supporting Information).^[14] The framework is assembled from paddle wheel dinuclear Zn_2 units, bridging AzDC dianions and 4,4'-BPE pillar ligands. Photoresponsive studies in solid state revealed a photoactive framework. *Trans*- and *cis*-AzDC $n\text{-}\pi^*$ (S1 state) and $\pi\text{-}\pi^*$ (S2 state) transitions can be detected at 455 and 380 nm in the excitation spectra, respectively (Figure SI-5). The coordination of 4,4'-BPE to Zn results in a photoactive species under light irradiation.^[13b] The *trans* isomer of the 4,4'-BPE ligand exhibits overlapping excitation bands of metal-to-ligand (MLCT) and ligand-to-ligand (LLCT) charge-transfers in the 310–375 nm region (Figure SI-6 in the Supporting Information).^[13b] Excitation in this region generates *trans*–*cis* isomerization as shown in the excitation spectra where the MLCT band maximum shift to 285 nm.^[13d] Both *cis*-AzDC and 4,4'-BPE can return to their *trans* state.

Herein we report the discovery of strong, low-energy photoresponse in $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ and find that the behavior is dynamic and localized, irrespective of the use of broadband or filtered light sources. Previous researches have not detected *cis*–*trans* changes where azo groups are part of the MOF wall and not as pendant groups in the pores.^[15] In the present article it is reported that bending about the azo group can be observed to occur on a local scale in a dynamic fashion, perfect for on-line adsorbent regeneration. The effect was directly observed in the UV/Vis emission profiles and time-resolved infrared spectra, and indirectly through gas adsorption experiments with careful controls in place, and pore analysis calculations. We found agreement with the literature in that the effects could not be observed over larger length scales; synchrotron X-ray diffraction did not reveal a structural change.^[16] This unusual property was exploited to trigger the uptake and release of carbon dioxide in real time, during adsorption experiments. Exposure to UV light resulted in an instantaneous release of up to 64% of the adsorbed CO_2 using broadband radiation, similar to concentrated solar sources. Furthermore, the response was found to be fully reversible. The dynamic, yet localized structural movements have been directly characterized spectroscopically, and isolated with several careful control experiments.

As shown in Figure 2, $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ exhibits unprecedented dynamic switching under CO_2 adsorption, with a 42% desorption capacity under static irradiation conditions (red and black curves), and as much as 64% during dynamic measurements (blue curve). Light irradiation increased the MOF surface energy, in which intermolecular interactions between CO_2 molecules and the surface weakened, and thus triggered instantaneous CO_2 release. Dynamic irradiation isotherms follow values obtained under continuous irradiation conditions, however the reversal in uptake was not entirely complete under the dynamic measurement conditions employed. Such dynamicity could not be triggered by free AzDC and 4,4'-BPE molecules because of the small

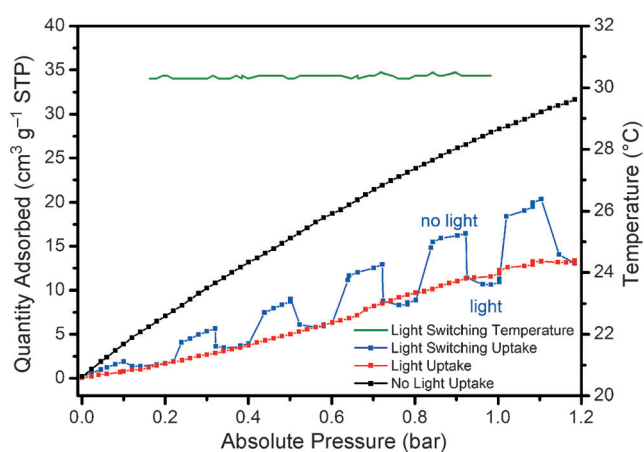


Figure 2. CO_2 adsorption isotherms of $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ at 303 K in the presence of light (red), absence of light (black), and unfiltered light switching environment (blue). Temperature fluctuations were not observed during the light switching experiment (green). The light intensity was fixed at 24.6 W cm^{-2} in the wavelength range of 200–500 nm (STP = standard temperature and pressure).

pores of the MOF ($3.4 \times 3.4 \text{ \AA}$).^[14] A series of careful control experiments were undertaken to ensure that this phenomenon was not an experimental or material artefact, but due solely to the dynamic photoresponse observed. Careful localized temperature monitoring showed that the temperature varied by less than 0.2°C , indicating that minor localized heating did occur, however it was not a significant factor in the uptake variation (Figure 2). Furthermore, experiments with control materials including SAPO-34 zeolite, and also a framework without known photoactive groups, Cu-BTC (Basolite C300), showed almost no CO_2 uptake variations upon UV irradiation (0.2 and 2% vs. 64% for $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$), see Figure SI-10. An isobar has been measured, where temperature was changed with constant pressure, and these show that the temperature needs to rise by 25 K for the same uptake variation to be observed (Figure SI-11). A degree of the release may be due to general sample heating, although this is likely to be small given the negligible change in control samples.

To directly observe the structural oscillations, time-resolved FTIR spectroscopy under UV irradiation was performed, (Figure 3a,b). Significant changes in peak intensity for the region of $540\text{--}700 \text{ cm}^{-1}$ were observed under irradiation, whereas the remaining spectrum was unchanged. The peak intensity increase at 550 cm^{-1} can be attributed to C–C–C and C–C–N bending modes with AzDC,^[17] indicating low-energy structural variations about the azo group, which occurred due to the suppression of *cis*–*trans* isomerization.^[18] These bending modes are likely to be responsible for the spontaneous release of adsorbed CO_2 upon irradiation, in which the pore surface was activated and the surface energy was increased (Figure 3b). Similar experiments on the free ligand AzDC confirmed this effect (Figure 3a). An increase in intensity at 537 cm^{-1} indicated the activation of bending modes about the C–C–N bonds within the ligand. Furthermore, very minor peak increases in the free ligand at

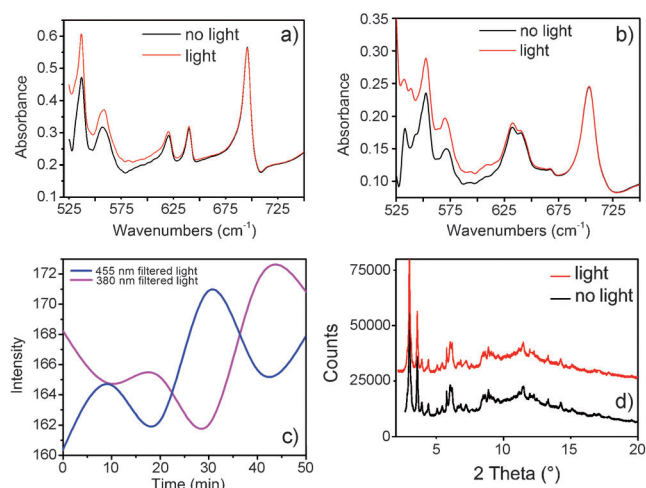


Figure 3. C–C–C and C–C–N low-energy FTIR bending modes in AzDC were found to be excited by UV light in both a) the ligand and b) the framework. c) Continual irradiation led to oscillations between native and excited states witnessed with UV/Vis absorption. d) It was confirmed that the transitions were local and dynamic, as synchrotron XRD experiments did not reveal any periodic changes.

1516 cm^{-1} were observed, assigned to higher energy *cis*-N=N stretching modes forming as the native *trans* material was excited.^[19] These modes were not seen to change within the framework, highlighting the restricted AzDC in this structure, which could not undertake these transitions. This also explains why no changes were seen in the X-ray diffractogram (Figure 3d). This result was also replicated with similar UV/Vis experiments, where only a small fraction of *cis* isomers were detected (Figure 3c). The framework was continuously exposed to either 365 or 460 nm light and the intensity of the absorption peak is monitored. Absorption related to *trans*-AzDC and *cis*-AzDC moieties was found to be complementary and also periodically changing, regardless of whether the excitation wavelength promoted formation of either *cis* or *trans* structures. Under continuous irradiation from either 370 nm (promote *cis*-AzDC) or 460 nm light (promote *trans*-AzDC), small fractions of the structure were found to periodically oscillate between both isomeric conformations in a complementary fashion given the additive nature of *cis* and *trans* peaks across the two separate experiments. Similar additive effects were less clear from 4,4'-BPE excitation profiles where there was considerable overlap, although this ligand also clearly underwent transitions whilst coordinated within the framework (Figure SI-7). Most likely, this continual reversion to native states even under irradiation that promotes an isomeric transformation stems from the structural stresses induced within the interpenetrated framework, due to the components also being critical to the topology, and not pendant to it. Furthermore, rapid changes predominantly through bending motions must occur throughout the framework to maintain the original triply interpenetrated framework and accommodate the constraints.^[20] The changes could not be observed on a periodic scale however, with synchrotron X-ray diffraction experiments revealing no changes (Figure 3d).

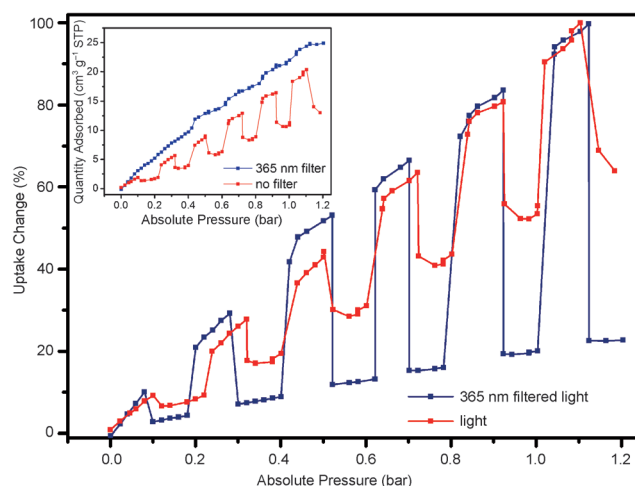


Figure 4. Performance of photo-switching according to light wavelength, normalized for flux. Filtered light of 365 nm is optimal for *cis*–*trans* photoisomerization of both AzDC and 4,4'-BPE ligands. Inset: original data without normalization.

Figure 4 (inset) shows that the absolute CO_2 uptake is increased and the amount released upon light exposure lessened when a filtered light source, which has a lower flux, is used. Filtering the light to 365 nm promotes photoisomerization in both the AzDC (Figure 3b) and 4,4'-BPE ligands (Figure SI-6). Accounting for variations in raw uptake amounts, and changing flux gives Figure 4. Here it is shown that the efficiency of CO_2 release is greatly enhanced by the use of 365 nm filtered light. In both cases the adsorption amounts in the absence of light irradiation are similar, yet CO_2 desorption is found to be more efficient with use of filtered 365 nm radiation. This effect is most pronounced at high partial pressures, yet it is notable that at partial pressures similar to those encountered in post-combustion capture gas streams (ca. 0.15 bar) that unfiltered light gives a very comparable response. The results imply that in cases where the light intensity is not a limiting factor, that filtration to 365 nm is preferable, but in other instances, unfiltered, concentrated sunlight will also perform almost as well, especially in post-combustion capture streams. Illuminations up to 20 W cm^{-2} (200 solar equivalents) can be achieved using concentrated sunlight.^[21] These remarkable results stem from the fact that the photoinduced structural changes in $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ are dynamic as witnessed both directly with UV/Vis and FTIR experiments, and indirectly driving photoresponsive gas adsorption.

The foregoing results demonstrate that the interpenetrated framework $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$ can undergo dynamic light-induced structural flexibility, which results in large variations in CO_2 uptakes. For the first time an experimental protocol was established to exploit this remarkable property for low-energy CO_2 capture and release. The variation in CO_2 capture performance was found to be exceptionally strong, as much as 64% under dynamic measurements and 42% under static conditions. Characterization of the framework showed that the light-induced structural flexibility is due to both the AzDC and 4,4'-BPE

ligands, occurring reversibly and on a local scale, even under irradiation that would promote formation on just one conformer. Detailed characterization showed that the transitions occurred only on a short range scale, and in a dynamic fashion, accounting for a lack of detection on longer length scales, in line with previous studies.

This approach represents a potential route to renewable energy CO₂ capture and release, and was found to remain effective under broadband irradiation. This means that unfiltered sunlight may be used instead of the energy-intensive temperature and pressure swings to release trapped gases.

Further developments in this area include other mechanistic investigations, in further increasing the already strong response, developing similar responses in the visible region, and taking advantage of the performance within industrially relevant mixed gas streams.

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- [1] a) D. M. D'Alessandro, B. Smit, J. R. Long, *Angew. Chem.* **2010**, *122*, 6194–6219; *Angew. Chem. Int. Ed.* **2010**, *49*, 6058–6082; b) J. Bao, P. M. Weber, *J. Am. Chem. Soc.* **2011**, *133*, 4164–4167; c) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae, J. R. Long, *Chem. Rev.* **2012**, *112*, 724–781.
- [2] a) P. H. M. Feron, *Int. J. Greenhouse Gas Control* **2010**, *4*, 152–160; b) A. S. Bhowan, B. C. Freeman, *Environ. Sci. Technol.* **2011**, *45*, 8624–8632.
- [3] a) G. T. Rochelle, *Science* **2009**, *325*, 1652–1654; b) J. A. Mason, K. Sumida, Z. R. Herm, R. Krishna, J. R. Long, *Energy Environ. Sci.* **2011**, *4*, 3030–3040; c) J. M. Simmons, H. Wu, W. Zhou, T. Yildirim, *Energy Environ. Sci.* **2011**, *4*, 2177–2185.
- [4] a) O. M. Yaghi, Q. Li, *MRS Bull.* **2009**, *34*, 682–690; b) D. Zacher, R. Schmid, C. Wöll, R. A. Fischer, *Angew. Chem.* **2011**, *123*, 184–208; *Angew. Chem. Int. Ed.* **2011**, *50*, 176–199; c) F. A. Almeida Paz, J. Klinowski, S. M. F. Vilela, J. P. C. Tome, J. A. S. Cavaleiro, J. Rocha, *Chem. Soc. Rev.* **2012**, *41*, 1088–1110; d) S. Horike, S. Kitagawa in *Metal–Organic Frameworks*, Wiley-VCH, Weinheim, **2011**, pp. 1–21; e) H.-C. Zhou, J. R. Long, O. M. Yaghi, *Chem. Rev.* **2012**, *112*, 673–674.
- [5] M. D. Allendorf, C. A. Bauer, R. K. Bhakta, R. J. T. Houk, *Chem. Soc. Rev.* **2009**, *38*, 1330–1352.
- [6] a) J.-R. Li, R. J. Kuppler, H.-C. Zhou, *Chem. Soc. Rev.* **2009**, *38*, 1477–1504; b) S. Ma, H.-C. Zhou, *Chem. Commun.* **2010**, *46*, 44–53.
- [7] a) L. J. Murray, M. Dinca, J. R. Long, *Chem. Soc. Rev.* **2009**, *38*, 1294–1314; b) F. Debatin, A. Thomas, A. Kelling, N. Hedin, Z. Bacsik, I. Senkovska, S. Kaskel, M. Junginger, H. Müller, U. Schilde, C. Jäger, A. Friedrich, H.-J. Holdt, *Angew. Chem.* **2010**, *122*, 1280–1284; *Angew. Chem. Int. Ed.* **2010**, *49*, 1258–1262; c) B. Kesanli, Y. Cui, M. R. Smith, E. W. Bittner, B. C. Bockrath, W. Lin, *Angew. Chem.* **2005**, *117*, 74–77; *Angew. Chem. Int. Ed.* **2005**, *44*, 72–75; d) X. Lin, J. Jia, X. Zhao, K. M. Thomas, A. J. Blake, G. S. Walker, N. R. Champness, P. Hubberstey, M. Schröder, *Angew. Chem.* **2006**, *118*, 7518–7524; *Angew. Chem. Int. Ed.* **2006**, *45*, 7358–7364; e) R. B. Getman, Y.-S. Bae, C. E. Wilmer, R. Q. Snurr, *Chem. Rev.* **2012**, *112*, 703–723; f) M. P. Suh, H. J. Park, T. K. Prasad, D.-W. Lim, *Chem. Rev.* **2012**, *112*, 782–835; g) K. Sumida, M. R. Hill, S. Horike, A. Dailly, J. R. Long, *J. Am. Chem. Soc.* **2009**, *131*, 15120–15121; h) X. Lin, N. Champness, M. Schröder, in *Functional Metal–Organic Frameworks: Gas Storage, Separation and Catalysis*, Vol. 293 (Ed.: M. Schröder), Springer, Berlin, **2010**, pp. 35–76.
- [8] a) Z. Guo, H. Wu, G. Srinivas, Y. Zhou, S. Xiang, Z. Chen, Y. Yang, W. Zhou, M. O'Keeffe, B. Chen, *Angew. Chem.* **2011**, *123*, 3236–3239; *Angew. Chem. Int. Ed.* **2011**, *50*, 3178–3181; b) H. Wu, W. Zhou, T. Yildirim, *J. Am. Chem. Soc.* **2009**, *131*, 4995–5000; c) A. W. Thornton, K. M. Nairn, J. M. Hill, A. J. Hill, M. R. Hill, *J. Am. Chem. Soc.* **2009**, *131*, 10662–10669; d) S. Ma, D. Sun, J. M. Simmons, C. D. Collier, D. Yuan, H.-C. Zhou, *J. Am. Chem. Soc.* **2008**, *130*, 1012–1016.
- [9] a) P. K. Thallapally, J. Tian, M. Radha Kishan, C. A. Fernandez, S. J. Dalgarno, P. B. McGrail, J. E. Warren, J. L. Atwood, *J. Am. Chem. Soc.* **2008**, *130*, 16842–16843; b) J. Liu, P. K. Thallapally, B. P. McGrail, D. R. Brown, J. Liu, *Chem. Soc. Rev.* **2012**, *41*, 2308–2322; c) G. D. Pirngruber, P. L. Llewellyn in *Metal–Organic Frameworks*, Wiley-VCH, Weinheim, **2011**, pp. 99–119.
- [10] J. Park, D. Yuan, K. T. Pham, J.-R. Li, A. Yakovenko, H.-C. Zhou, *J. Am. Chem. Soc.* **2012**, *134*, 99–102.
- [11] N. Yanai, T. Uemura, M. Inoue, R. Matsuda, T. Fukushima, M. Tsujimoto, S. Isoda, S. Kitagawa, *J. Am. Chem. Soc.* **2012**, *134*, 4501–4504.
- [12] a) J. Griffiths, *Chem. Soc. Rev.* **1972**, *1*, 481–493; b) M. Han, T. Honda, D. Ishikawa, E. Ito, M. Hara, Y. Norikane, *J. Mater. Chem.* **2011**, *21*, 4696–4702.
- [13] a) M. K. Itokazu, A. S. Polo, N. Y. M. Iha, *Int. J. Photoenergy* **2001**, *3*, 143–146; b) D. M. Dattelbaum, M. K. Itokazu, N. Y. Murakami Iha, T. J. Meyer, *J. Phys. Chem. A* **2003**, *107*, 4092–4095; c) J. M. Knaust, S. W. Keller, *Inorg. Chem.* **2002**, *41*, 5650–5652; d) S.-S. Sun, J. A. Anspach, A. J. Lees, *Inorg. Chem.* **2002**, *41*, 1862–1869; e) A. O. T. Patrocínio, M. K. Brennaman, T. J. Meyer, N. Y. Murakami Iha, *J. Phys. Chem. A* **2010**, *114*, 12129–12137.
- [14] B. Chen, S. Ma, E. J. Hurtado, E. B. Lobkovsky, H.-C. Zhou, *Inorg. Chem.* **2007**, *46*, 8490–8492.
- [15] a) A. Schaate, S. Dühren, G. Platz, S. Lilienthal, A. M. Schneider, P. Behrens, *Eur. J. Inorg. Chem.* **2012**, 790–796; b) A. Modrow, D. Zargarani, R. Herges, N. Stock, *Dalton Trans.* **2011**, *40*, 4217–4222.
- [16] a) S. Bureekaew, S. Shimomura, S. Kitagawa, *Sci. Technol. Adv. Mater.* **2008**, *9*, 014108; b) S. Horike, R. Matsuda, D. Tanaka, S. Matsubara, M. Mizuno, K. Endo, S. Kitagawa, *Angew. Chem.* **2006**, *118*, 7384–7388; *Angew. Chem. Int. Ed.* **2006**, *45*, 7226–7230.
- [17] M. I. Klima, A. V. Kotov, L. A. Gribov, *Zh. Strukt. Khim.* **1972**, *13*, 1060–1064.
- [18] C. A. Bauer, T. V. Timofeeva, T. B. Settersten, B. D. Patterson, V. H. Liu, B. A. Simmons, M. D. Allendorf, *J. Am. Chem. Soc.* **2007**, *129*, 7136–7144.
- [19] G. Socrates, *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, Wiley, Chichester, **2001**.
- [20] E. Y. Lee, S. Y. Jang, M. P. Suh, *J. Am. Chem. Soc.* **2005**, *127*, 6374–6381.
- [21] a) A. Manor, E. A. Katz, T. Tromholt, F. C. Krebs, *Adv. Energy Mater.* **2011**, *1*, 836–843; b) T. Tromholt, M. Manceau, M. Helgesen, J. E. Carlé, F. C. Krebs, *Sol. Energy Mater. Sol. Cells* **2011**, *95*, 1308–1314.