Angewandte
Communications

DOI: 10.1002/anie.201207218

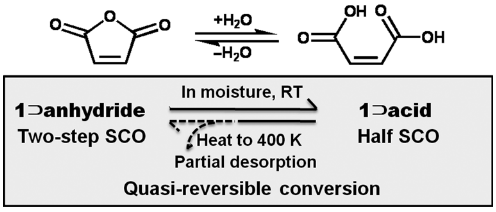
Spin Crossover

The Effect of an Active Guest on the Spin Crossover Phenomenon**

Xin Bao, Helena J. Shepherd, Lionel Salmon, Gábor Molnár, Ming-Liang Tong, and Azzedine Bousseksou**

A straightforward method for the reversible modification of solid-state properties is a goal being constantly pursued in the development of molecular switches, and molecular electronic and photonic devices. As one of the most attractive molecule-based switchable materials, spin crossover (SCO) complexes present different magnetic, optical, electrical and structural properties in response to external stimuli (such as temperature, pressure, light, or magnetic fields), driven by conversion of the electron configuration between high spin (HS) and low spin (LS) states.[1] However, the extreme sensitivity of SCO behavior to subtle effects, including humidity or solvent inclusion in the crystal lattice, often impedes the ability to regulate these switchable properties at will. On the other hand, this sensitivity may be exploited if the host-guest chemistry of the material can be controlled. A recent demonstration of this is the incorporation of SCO centers into porous coordination polymers (PCPs),[2] which allows the fine-tuning of SCO properties through the inclusion of guest molecules without disrupting the framework structure.[3] It has been suggested that guest molecules could be used as a new perturbation to switch spin state at constant (ideally ambient) temperature. A few encouraging results have already been reported, especially for the three-dimensional Hofmann-like SCO-PCP $\{Fe(pz)[M(CN)_4]\}$ (M = Ni, Pt, Pt; pz = pyrazine).[4] This includes the dynamic interplay between SCO and the host-guest function,[5] the precise control of transition temperature upon I_2 addition,[6] and a significant enhancement in cooperativity through the inclusion of thiourea.[7] Particularly, in the work of Kepert et al.[5] and Ohba et al.,[8] the spin state has been successfully switched at room temperature through the chemical response of the framework. However, the critical operating conditions are difficult to achieve in practical applications; in Ohba's study for example, several successive steps are required: the adsorption of one guest (benzene), desorption under vacuum, adsorption of another guest (CS_2), and a subsequent desorption under vacuum. It is necessary to develop a more efficient approach to regulate SCO properties. Ligand-driven light-induced spin change (LD-LISC) is a promising strategy; spin conversion could be triggered by *cis–trans* isomerization of the ligand by means of light over a broad range of temperatures.[9] However, the drastic structural rearrangement of the whole lattice that accompanies the isomerization makes it difficult to achieve in densely packed assemblies, and the current successful examples are limited to only a few mononuclear complexes.

As an alternative approach, we considered using an active guest to regulate and/or switch spin states in SCO-PCP materials, taking advantage of host-guest interactions. Theoretically, any suitably sized active molecule that can be readily modified in response to light, thermal, or chemical stimuli could become a suitable candidate, thus providing numerous appealing choices when coupled with different SCO-PCPs. As a proof of concept for this new approach, we have utilized a chemically active guest, maleic anhydride, which can be hydrolyzed into maleic acid and converted back by gentle heating, as shown in Scheme 1. $\{Fe(pz)[Pt(CN)_4]\}$ (**1**) was chosen as the SCO host, because of its robust framework, regular pores, and sensitivity to guest perturbations. A quasi-reversible modification of SCO properties between a two-step abrupt spin transition with hysteresis loops and a half spin transition at lower temperature was observed during the guest-conversion process.



Scheme 1. Interconversion between maleic anhydride and maleic acid (above) and the clathrates (below).

A guest-free sample of **1** was exposed to maleic anhydride vapor, forming **1⊃anhydride** clathrate with a formula of $\mathbf{1}\cdot 0.9(C_4H_2O_3)(H_2O)$, as evidenced by thermogravimetry (TG) and elementary analyses. Additionally, the species were analyzed by IR spectroscopy (Figure 1). The two characteristic bands at 1850 cm^{-1} and 1778 cm^{-1} are attributed to the symmetric and asymmetric C=O stretching modes in the anhydride, thus unambiguously confirming the pres-

---

[*] X. Bao, Prof. Dr. M.-L. Tong
Key Laboratory of Bioinorganic and Synthetic Chemistry of Ministry of Education; State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry & Chemical Engineering, Sun Yat-Sen University
Guangzhou 510275 (China)
E-mail: tongml@mail.sysu.edu.cn
X. Bao, Dr. H. J. Shepherd, Dr. L. Salmon, Dr. G. Molnár, Dr. A. Bousseksou
Laboratoire de Chimie de Coordination, CNRS and Université de Toulouse, UPS, 31077 Toulouse (France)
E-mail: azzedine.bousseksou@lcc-toulouse.fr

[**] This work was supported by the CHEMOSWITCH project (ANR 2010 BLAN-1018 01) and the NSFC (91122032, 21121061). X.B. thanks the China Scholarship Council for a scholarship.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201207218.

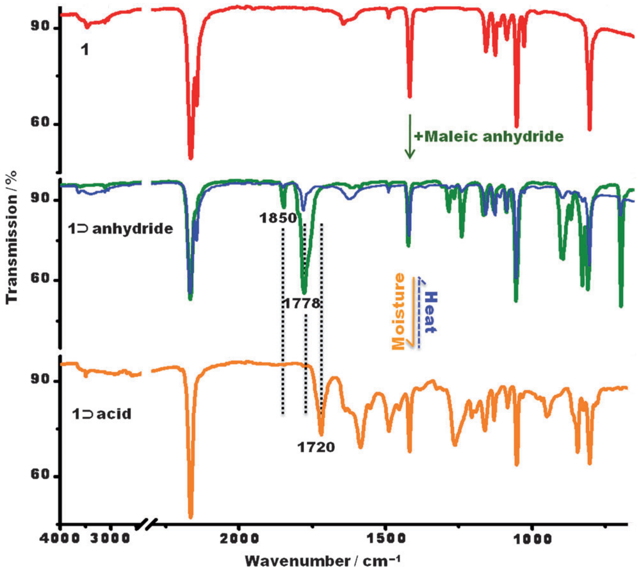


Figure 1. IR spectra of **1**, **1⊃anhydride**, and **1⊃acid**.

ence of maleic anhydride. Subsequently, the complete conversion of maleic anhydride into maleic acid within the framework is achieved by simply maintaining the sample in a humid environment at ambient temperature. Consequently, the IR bands at 1850 and 1778 cm^{-1} were replaced by the symmetric C=O stretching mode of carboxylic acid at 1720 cm^{-1} (Figure 1). This modified clathrate is denoted **1⊃acid** (**1**$\cdot$0.9($C_4H_4O_4$)(H_2O)). The reverse transformation is achieved by heating, such that maleic acid releases one water molecule and reverts to maleic anhydride. However, this step is accompanied by partial desorption of the guest, as demonstrated by the reappearance and reduction in intensity of the IR bands at 1850 and 1778 cm^{-1} respectively (Figure 1).

The drastic modification of SCO behavior upon guest transformation was verified by variable-temperature magnetic susceptibility measurements (Figure 2). **1⊃anhydride** displays a complete two-step SCO. The $\chi_M T$ value changes from 3.5 cm^{3}mol^{-1}K at 300 K to 0.5 cm^{3}mol^{-1}K at 50 K, via a 20 K wide plateau with a $\chi_M T$ value of 2.0 cm^{3}mol^{-1}K. The transitions are very sharp, and are centered at $T_{c1}{\downarrow}=200$ K, $T_{c2}{\downarrow}=170$ K in the cooling mode, and $T_{c1}{\uparrow}=209$ K, $T_{c2}{\uparrow}=186$ K in the warming mode, thus defining 9 K and 16 K wide hysteresis loops for the higher and lower temperature steps, respectively. After the in situ hydrolysis of maleic anhydride, the SCO behavior of the framework (**1⊃acid**) becomes a monotonically incomplete spin transition. The $\chi_M T$ value changes between 3.3 cm^{3}mol^{-1}K at 300 K and 2.0 cm^{3}mol^{-1}K at 50 K, which corresponds to a ca. 57% LS residual. The transition temperatures are $T_c{\downarrow}=155$ K and $T_c{\uparrow}=159$ K, thus defining a distorted 4 K wide hysteresis. If **1⊃acid** is heated to 400 K, the reverse transformation occurs and the two-step SCO behavior of **1⊃anhydride** reappears, superimposed with the room temperature SCO characteristic of the empty framework, which is caused by partial desorption of the guest (see magnetic (Figure S14) and DSC data (Figure S17) in the Supporting Information,).

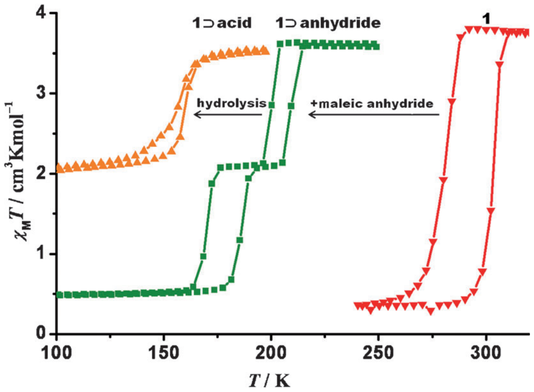


Figure 2. Variable-temperature magnetic susceptibility studies of **1**, **1⊃anhydride**, and **1⊃acid**.

The ^{57}Fe Mössbauer results agree well with the magnetic analyses (Figures S4 and S5, and Table S2). The spectrum of **1⊃anhydride** at 230 K consists of a unique quadrupole doublet with an isomer shift of $\delta=1.11$ mm s^{-1} and a quadrupole splitting of $\Delta E_Q=1.48$ mm s^{-1}, which is characteristic of HS Fe^{II}. Upon cooling to 182 K, a singlet with $\delta=0.37$ mm s^{-1} appears and accounts for 49% of the total area, which is consistent with a half spin transition within the plateau range. Upon further cooling to 80 K, only the singlet ($\delta=0.48$ mm s^{-1}) is preserved, owing to completion of the spin transition. The Mössbauer spectrum of **1⊃acid** at 300 K consists of one quadrupole doublet with $\delta=1.06$ mm s^{-1} and $\Delta E_Q=1.20$ mm s^{-1}, which confirms that all Fe^{II} ions are in the HS state. Upon cooling to 80 K, a singlet ($\delta=0.36$ mm s^{-1}) and a doublet ($\delta=1.31$ mm s^{-1} and $\Delta E_Q=1.38$ mm s^{-1}) coexist with an area ratio of 54:46, which is in accordance with incomplete SCO behavior.

The unit cell parameters as a function of temperature in the cooling mode were measured for a single crystal of **1⊃anhydride**. The cell parameters decrease in two well-defined steps (Figure S1), which is consistent with a contraction of the framework during the two-step spin-transition process. Careful analysis of the diffraction images revealed no supercell reflections or other evidence for a crystallographic phase transition at any investigated temperature. To follow the structural changes associated with SCO, full data collection was carried out at 250 K (HS), 200 K (intermediate phase (IP)) and 110 K (LS) for **1⊃anhydride** and at 180 K (HS) and 100 K (mixed spin state) for **1⊃acid**. All the structures are reported here in the tetragonal space group *P*4/*mmm* and have a three-dimensional porous framework similar to those previously described.[6–8,10] The network is composed of two-dimensional planes of $\{Fe[Pt(CN)_4]\}_\infty$ bridged by pyrazine ligands along the [001] direction. The three-dimensional channels accommodate highly disordered water molecules and the maleic anhydride or maleic acid guests. In both cases, the atomic positions of the guests have not been included in the structural model because of their random distribution and/or fast reorientation. However, it can be seen from contour maps of the residual electron density (see Figure 3 for **1⊃anhydride**) that these unmodeled molecules are located around the center of the pores, on planes parallel to the $\{Fe[Pt(CN)_4]\}_\infty$ sheets, sandwiched between two $[Pt(CN)_4]$

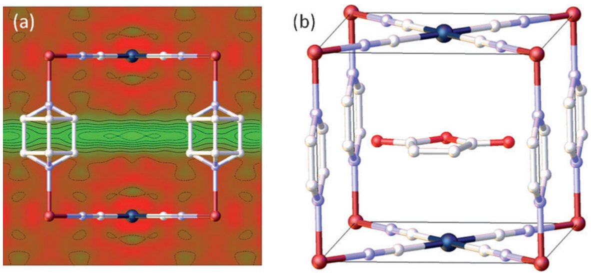


Figure 3. a) Difference electron density contour map for **1⊃anhydride** at 250 K in the *ac* plane at $^1/_2b$. Areas of positive residual electron density are shown in green. b) Illustration of the probable location of the maleic anhydride molecule within the unit cell. C white, N pale blue, Fe dark red, O red, Pt dark blue. H atoms are omitted for clarity.

units. Considering the planar structure of maleic anhydride and maleic acid, it is reasonable to infer that those guests lie parallel to [Pt(CN)$_4$] and are perpendicular to the pyrazine ligands. A more detailed description of the crystallographic treatment and a discussion of structural details are provided in the Supporting Information. The equatorial and axial Fe–N bond lengths of **1⊃anhydride** are 2.127(19) and 2.21(2) Å at 250 K, 2.033(17) and 2.09(3) Å at 200 K, and 1.95(2) and 2.02(2) Å at 110 K, which is consistent with iron(II) in the HS, IP, and LS states. Whereas for **1⊃acid**, the equatorial and axial Fe–N bond lengths are 2.108(16) and 2.13(2) Å at 180 K, and 2.041(15) and 2.09(2) Å at 100 K, which indicates an incomplete spin transition of the iron(II) ions.

A complimentary IR study was performed at variable temperature for **1⊃anhydride** and **1⊃acid**. Selected spectra in different spin states are given in Figure 4. For **1⊃anhydride**, drastic upward shifts (ca. 10 cm^{-1} for each step) were observed for the bands at 1167, 1087, and 802 cm^{-1} when going from the HS to the LS state. These shifts were previously assigned to the ring stretching, and the C–H in-plane and out-of-plane bending modes of pyrazine, respectively.[11] Moreover, another band shifts noticeably from 901 (HS) to 913 (LS) via 906 cm^{-1} (IP). We have tentatively assigned it to the C–H bending mode of maleic anhydride. In contrast, the C=O (1850 and 1778 cm^{-1}) and C–O (1300–1200 cm^{-1}) stretching modes of maleic anhydride, and the C≡N stretching mode (2174 cm^{-1}) in the host are barely shifted. For **1⊃acid**, the modification of the pyrazine vibrations at 1167 and 1087 cm^{-1} is not obvious, whereas the shift of the C–H out-of-plane bending mode is still significant (from 806 cm^{-1} in the HS state to 821 cm^{-1} below the temperature of the approximately half transition). The bands at 1274 and 969 cm^{-1}, which are attributed to C–O stretching and O–H bending modes of maleic acid, are shifted to 1286 and 990 cm^{-1} respectively, whereas the C=O stretch at 1720 cm^{-1} remains unchanged. The SCO behavior of **1⊃anhydride** and **1⊃acid** could be reproduced well by plotting the band position versus temperature. For example, Figure 4 shows the representative curve using ring stretching mode (pyrazine) for **1⊃anhydride** and C–H out-of-plane bending mode (pyrazine) for **1⊃acid**. The different IR responses of the two clathrates towards SCO clearly demonstrate the different effects of the guests. The modification of some specific vibrational modes of the guest, that is, the C–H vibration of maleic anhydride and the O–H and C–O vibrations of maleic acid indicates the coupling of those modes with the vibration of the framework. This coupling may be derived from short interactions of the C–H (**1⊃anhydride**) and carboxylic groups (**1⊃acid**) with the pyrazine ligand. The C=O vibration in both complexes is unaffected, which implies a lack of coupling to Fe–N and pyrazine vibrations within the framework.

This work presents a rare example of two-step spin transition behavior for a {Fe(pz)[Pt(CN)4]} framework. This feature has previously been observed in related framework materials with different bridging ligands.[3i,j] One of the most common reasons for such stepwise behavior is the presence of crystallographically inequivalent SCO centers, which is not the case for **1⊃anhydride**. Only one iron center was observed for both HS and LS structures by single crystal X-ray analysis. Moreover, the Mössbauer spectrum indicates a single Fe site in the pure HS/LS state. The other possibility is an overall structural rearrangement, for example, symmetry breaking, in the IP phase.[12] Although no crystallographic evidence for such an event was observed, it should be remembered that these experiments measure the structure averaged over both

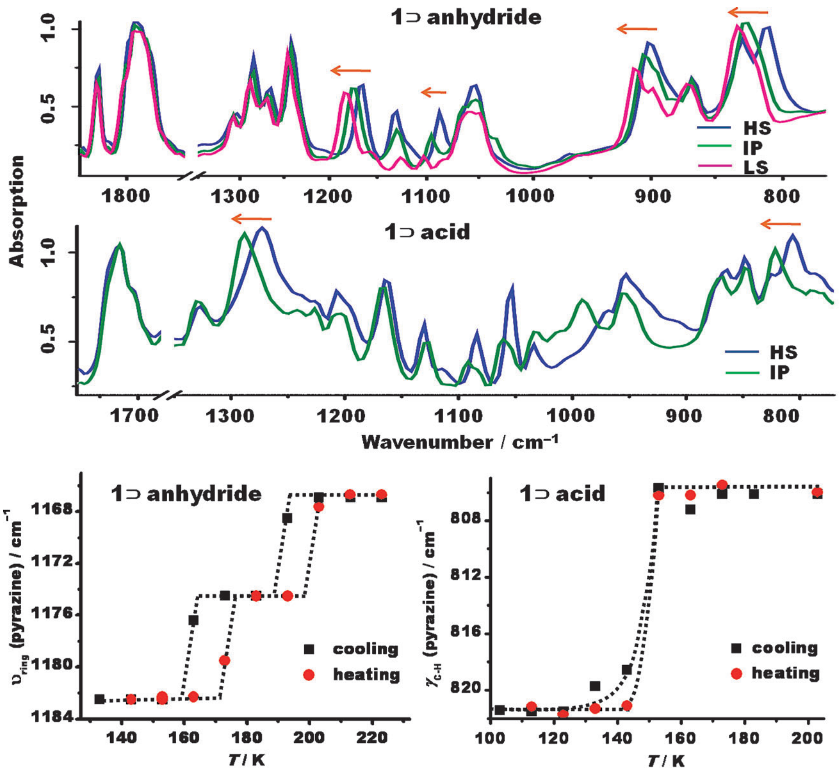


Figure 4. Selected IR spectra in different spin states, and temperature-dependent IR frequencies of **1⊃anhydride** and **1⊃acid**.

the time of the experiment and the volume of the crystal. Furthermore, the evidence for symmetry breaking can be very subtle, reflecting the often minor structural differentiation of active centers during the process. Hence, it is not always possible to detect a symmetry breaking phase transition using a standard laboratory X-ray diffraction setup;[12a] thus, this type of transition cannot be eliminated here. A variable temperature IR experiment was undertaken to shed some light on the possibility of local structural rearrangement. The IR spectra of **1⊃anhydride** at different temperatures can be classified into three distinct phases based on band position and intensity, which correspond to the HS, IP, and LS phases. The modification of the IR spectrum is attributed to the SCO, as obvious discontinuities are observed at the appropriate temperatures, which produces a much more significant effect than that produced by thermal expansion alone (Figures 4, S7 and S8). In addition, the spectra of the IP phase are not a superposition of the ones of the HS and LS states, which implies a synergetic structural rearrangement of the whole lattice rather than the formation of a mixed structure of separate HS and LS domains.

The in situ conversion of the guest has a drastic effect on the SCO behavior of the framework. The transition steps, transition temperature, and the completeness are all noticeably modified upon switching the guest through a chemical stimulus (water). There is a clear trend that the transition temperature decreases in the order of **1** > **1⊃anhydride** > **1⊃acid**. Moreover, **1⊃anhydride** undergoes a complete SCO whereas the transition of **1⊃acid** is incomplete. These phenomena could be explained by steric effects within the pores of the network. The hydrolysis of maleic anhydride to maleic acid is a ring-opening reaction; the inclusion of this larger acid guest hinders the contraction of the framework and stabilizes the HS state.

In conclusion, an active guest was exploited for the first time to modify SCO behavior in a microporous framework. A drastic modification between two-step complete transition and monotonically varying, half spin transition was readily achieved by the chemical interconversion of maleic anhydride and maleic acid. Although the reversibility is hampered by the partial desorption of the guest in the current system, we believe that the idea of the incorporation of an active guest will open up new avenues in the development of smart switchable materials. There is great potential for exploitation in this area through the combination of abundant stimuli-responsive molecules with a wide variety of porous SCO hosts.

Experimental Section

Single crystal X-ray diffraction data for **1⊃anhydride** and **1⊃acid** were collected on a Bruker APEXII or Oxford Diffraction CCD diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Further details are given in the supporting information. CCDC 898529, 898530, 898531, 898532, 898533 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Magnetic measurements were recorded using a Quantum Design MPMS2 SQUID susceptometer with an applied field of 1 T and in the temperature range of 300–10–400–10–350 K. Experimental susceptibilities were corrected for diamagnetism. Room-temperature IR spectra were recorded on a PerkinElmer GX FT-IR 2000 spectrometer. Variable-temperature IR spectra were recorded using an IR microscope in reflection mode and a Linkam THMS-600 cryostage.

Received: September 6, 2012

Keywords: active guests · coordination polymers · host-guest systems · molecular devices · spin crossover

---

[1] a) O. Kahn, C. J. Martinez, *Science* **1998**, *279*, 44–48; b) P. Gütlich, Y. Garcia, T. Woike, *Coord. Chem. Rev.* **2001**, *219*, 839–879; c) P. Gütlich, H. A. Goodwin, *Topics in Current Chemistry*, *Vol. 233*, Springer, New York, **2004**; d) J. F. Létard, P. Guionneau, L. Goux-Capes, *Topics in Current Chemistry*, *Vol. 235*, Springer, New York, **2004**; e) A. Bousseksou, G. Molnár, L. Salmon, W. Nicolazzi, *Chem. Soc. Rev.* **2011**, *40*, 3313–3335.

[2] S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem.* **2004**, *116*, 2388–2430; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334–2375.

[3] a) J. A. Real, E. Andrés, M. C. Muñoz, M. Julve, T. Granier, A. Bousseksou, F. Varret, *Science* **1995**, *268*, 265–267; b) G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray, J. D. Cashion, *Science* **2002**, *298*, 1762–1765; c) G. J. Halder, K. W. Chapman, S. M. Neville, B. Moubaraki, K. S. Murray, J.-F. Létard, C. J. Kepert, *J. Am. Chem. Soc.* **2008**, *130*, 17552–17562; d) S. M. Neville, G. J. Halder, K. W. Chapman, M. B. Duriska, P. D. Southon, J. D. Cashion, J.-F. Létard, B. Moubaraki, K. S. Murray, C. J. Kepert, *J. Am. Chem. Soc.* **2008**, *130*, 2869–2876; e) S. M. Neville, G. J. Halder, K. W. Chapman, M. B. Duriska, B. Moubaraki, K. S. Murray, C. J. Kepert, *J. Am. Chem. Soc.* **2009**, *131*, 12106–12108; f) C. Bartual-Murgui, N. A. Ortega-Villar, H. J. Shepherd, M. C. Muñoz, L. Salmon, G. Molnár, A. Bousseksou, J. A. Real, *J. Mater. Chem.* **2011**, *21*, 7217–7222; g) C. Bartual-Murgui, A. Akou, L. Salmon, G. Molnár, C. Thibault, J. A. Real, A. Bousseksou, *Small* **2011**, *7*, 3385–3391; h) C. Bartual-Murgui, L. Salmon, A. Akou, C. Thibault, G. Molnár, T. Mahfoud, Z. Sekkat, J. A. Real, A. Bousseksou, *New J. Chem.* **2011**, *35*, 2089–2094; i) C. Bartual-Murgui, L. Salmon, A. Akou, N. A. Ortega-Villar, H. J. Shepherd, M. Carmen Muñoz, G. Molnár, J. A. Real, A. Bousseksou, *Chem. Eur. J.* **2012**, *18*, 507–516; j) F. J. Muñoz-Lara, A. B. Gaspar, M. C. Muñoz, M. Arai, S. Kitagawa, M. Ohba, J. A. Real, *Chem. Eur. J.* **2012**, *18*, 8013–8018.

[4] V. Niel, J. M. Martinez-Agudo, M. C. Muñoz, A. B. Gaspar, J. A. Real, *Inorg. Chem.* **2001**, *40*, 3838–3839.

[5] P. D. Southon, L. Liu, E. A. Fellows, D. J. Price, G. J. Halder, K. W. Chapman, B. Moubaraki, K. S. Murray, J.-F. Létard, C. J. Kepert, *J. Am. Chem. Soc.* **2009**, *131*, 10998–11009.

[6] a) R. Ohtani, K. Yoneda, S. Furukawa, N. Horike, S. Kitagawa, A. B. Gaspar, M. C. Muñoz, J. A. Real, M. Ohba, *J. Am. Chem. Soc.* **2011**, *133*, 8600–8605; b) G. Agustí, R. Ohtani, K. Yoneda, A. B. Gaspar, M. Ohba, J. F. Sánchez-Royo, M. C. Muñoz, S. Kitagawa, J. A. Real, *Angew. Chem.* **2009**, *121*, 9106–9109; *Angew. Chem. Int. Ed.* **2009**, *48*, 8944–8947.

[7] F. J. Muñoz-Lara, A. B. Gaspar, D. Aravena, E. Ruiz, M. C. Muñoz, M. Ohba, R. Ohtani, S. Kitagawa, J. A. Real, *Chem. Commun.* **2012**, *48*, 4686–4688.

[8] M. Ohba, K. Yoneda, G. Agustí, M. C. Muñoz, A. B. Gaspar, J. A. Real, M. Yamasaki, H. Ando, Y. Nakao, S. Sakaki, S. Kitagawa, *Angew. Chem.* **2009**, *121*, 4861–4865; *Angew. Chem. Int. Ed.* **2009**, *48*, 4767–4771.

[9] M. L. Boillot, J. Zarembowitch, A. Sour, *Topics in Current Chemistry*, *Vol. 234*, Springer, New York, **2004**, pp. 261–276.

[10] S. Cobo, D. Ostrovskii, S. Bonhommeau, L. Vendier, G. Molnár, L. Salmon, K. Tanaka, A. Bousseksou, *J. Am. Chem. Soc.* **2008**, *130*, 9019–9024.

[11] G. Molnár, V. Niel, A. B. Gaspar, J. A. Real, A. Zwick, A. Bousseksou, J. J. McGarvey, *J. Phys. Chem. B* **2002**, *106*, 9701–9707.

[12] For example, see: a) D. Chernyshov, M. Hostettler, K. W. Törnroos, H.-B. Bürgi, *Angew. Chem.* **2003**, *115*, 3955–3960; *Angew. Chem. Int. Ed.* **2003**, *42*, 3825–3830; b) S. Bonnet, M. A. Siegler, J. Sánchez Costa, G. Molnár, A. Bousseksou, A. L. Spek, P. Gamez, J. Reedijk, *Chem. Commun.* **2008**, 5619–5621; c) N. Bréfuel, H. Watanabe, L. Toupet, J. Come, N. Matsumoto, E. Collet, K. Tanaka, J.-P. Tuchagues, *Angew. Chem.* **2009**, *121*, 9468–9471; *Angew. Chem. Int. Ed.* **2009**, *48*, 9304–9307; d) M. Griffin, S. Shakespeare, H. J. Shepherd, C. J. Harding, J.-F. Létard, C. Desplanches, A. E. Goeta, J. A. K. Howard, A. K. Powell, V. Mereacre, Y. Garcia, A. D. Naik, H. Müller-Bunz, G. G. Morgan, *Angew. Chem.* **2011**, *123*, 926–930; *Angew. Chem. Int. Ed.* **2011**, *50*, 896–900.