

# CO<sub>2</sub> regulates molecular rotor dynamics in porous materials

Silvia Bracco,<sup>†</sup> Tetsuya Miyano,<sup>‡</sup> Mattia Negroni,<sup>†</sup> Irene Bassanetti,<sup>†</sup> Luciano Marchio,<sup>§</sup> Piero Sozzani,<sup>†,\*</sup> Norimitsu Tohnai,<sup>‡,\*</sup> and Angiolina Comotti<sup>†,\*</sup>

<sup>†</sup> Department of Materials Science, University of Milano Bicocca, via R. Cozzi 55, 2015, Milano, Italy.

<sup>‡</sup> Department of Material and Life Science, Graduate School of Engineering, Osaka Univ. 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan.

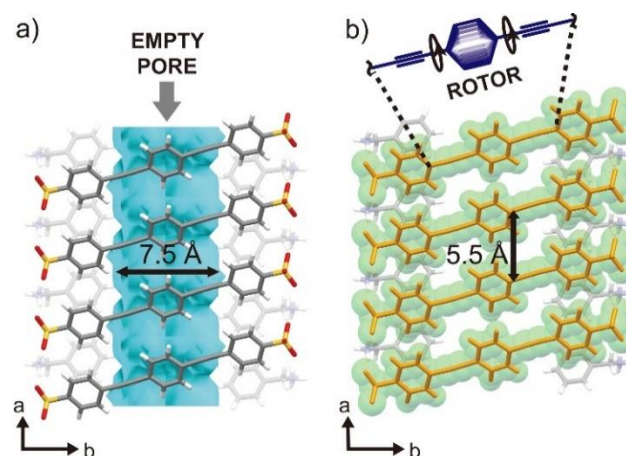
<sup>§</sup> Department of Chemistry, University of Parma, Parco Area delle Scienze 17/a, 43124 Parma, Italy.

**ABSTRACT:** A crystalline hydrogen-bonded framework with permanent porosity built by rod-like struts, that are engineered to bear ultra-fast molecular rotors between two triple bonds, offered the possibility to control rotational rates upon CO<sub>2</sub> adsorption. CO<sub>2</sub> entered the pores from the gas phase and reduced the rotational rates from the extremely fast regime of 10<sup>7</sup> Hz regime at 216 K, down to 10<sup>5</sup> Hz. CO<sub>2</sub>-rotor interaction was observed by <sup>2</sup>H NMR response to the dynamics of rotors in contact with CO<sub>2</sub> in the crystal structure and by 2D <sup>1</sup>H-<sup>13</sup>C NMR. This new approach reveals that rotor dynamics can be regulated by intermolecular interactions between molecular rotors and an adsorbed gas that has diffused into accessible crystal channels.

Carbon dioxide is perhaps the most important gas in nature because of its role in prominent biological mechanisms, such as carbon fixation in the vegetal world, and is emitted by animal combustion processes, thus it is a protagonist in the global energy cycle.<sup>1</sup> Both its interaction with much higher molar mass molecules and its reversible capture/release play a key role in such processes, therefore fine-modulation of the dynamics at interfaces is central to understanding and mimicking a vast anthology of chemical and biological phenomena.<sup>2</sup>

Porous materials offer a valid platform for observing gas-solid interfaces,<sup>3</sup> because of the high surface area that promotes gas interactions with molecular moieties facing the cavities. When molecular moieties exhibit fast rotary motion, they can be included in the challenging area of ‘molecular rotors and motors’.<sup>4</sup> If rotors are properly engineered in the walls of porous architectures<sup>5</sup> it is possible to follow the dynamics of the molecular entities as a function of host-guest interactions occurring at the interfaces.<sup>6</sup> Supramolecular chemistry<sup>7</sup> provides the principles for designing functional multidentate molecules that self-assemble into an architecture endowed with both dynamics and porosity. To date, only rare examples of Porous Molecular Materials (PMCs) with rotors in their main framework are found in the literature.<sup>6b</sup> Here we present a molecular crystal that shows extremely fast rotor dynamics and low-density architecture endowed with permanent porosity and capable of gas absorption. The porous and absorptive molecular structure was realized by the robustness of charge-assisted hydrogen bonds and the use of rigid molecular rods bearing the rotors. In fact, we designed a suitable strut that contains a central *p*-phenylene unit (the rotor) connected through ethynyl groups to other *p*-phenylenes and terminated by two sul-

fonate anions. The strut was shown to spontaneously self-assemble with *n*-benzylammonium counterions (Figures 1 and S1). The *p*-phenylene rotor is inserted at the center of the rod, like a wheel mounted on an axle, and is pivoted in between two triple bonds, thus experiencing a virtually barrier-free rotation. The resulting molecular architecture shows low-density packing wherein empty crystalline channels are self-organized. The pores are open and easily accessible from the gas phase, as proven by reversible CO<sub>2</sub> adsorption. The rotor speed can be reduced by the gas molecules diffused in the open nanochannels, but the rotation was fully recovered again after guest removal under vacuum, thus realizing crystals that are switchable in their dynamics. This feature is relevant for the construction of switchable ferroelectric materials and gas sensors.<sup>4a</sup>

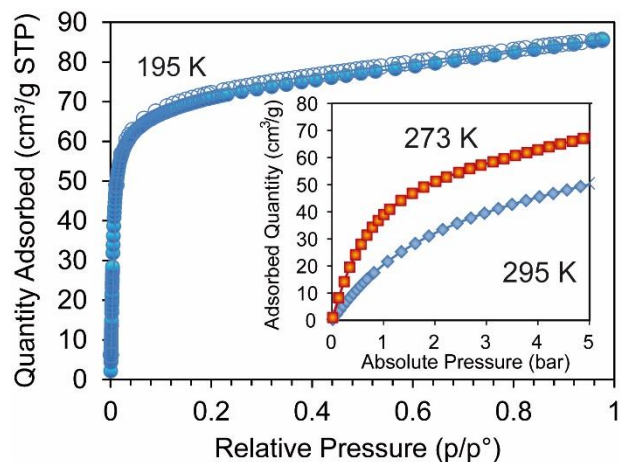


**Figure 1.** a) Crystal structure of the permanently porous compound **1** as viewed perpendicular to the channel axis. The empty channel is described by sky blue region calculated by a sphere of 1.0 Å. b) 4,4'-bis(sulfophenylethynyl)benzene moieties in the crystal structure showing the distance between the two central *p*-phenylene rings (above: chemical structure of the *p*-phenylene rotor attached to two ethynyl groups).

The molecular strut 4,4'-bis(sulfophenylethynyl)benzene (BSPEB) was crystallized with *n*-benzylamine (BA) from a mixture of methanol and 1,4-dioxane to yield the inclusion compound with 1,4-dioxane. The porous crystalline compound (**1**) was obtained by evacuation under mild conditions (10<sup>-2</sup> torr and 80 °C for 2h) and its crystal structure was resolved by single crystal X-ray diffraction (monoclinic space group P2<sub>1</sub>/c). It consists of non-

polar layers orderly alternated with polar double-layers, forming a 2D charge-assisted hydrogen-bond network (Figure S4). The crystal structure reveals an array of parallel and independent 1D channels, of rectangular cross-section of  $4.4 \times 7.5 \text{ \AA}^2$ , to which the *p*-phenylene moieties are exposed (Figures 1a). No substantial changes in the crystal structure were observed from 298K down to 130K, except for a slight contraction of the unit cell volume (SI, Table S4), indicating the full preservation of the empty porous architecture with temperature.  $^{13}\text{C}$  CP MAS NMR spectrum confirmed that no residual guest is included within the channels.

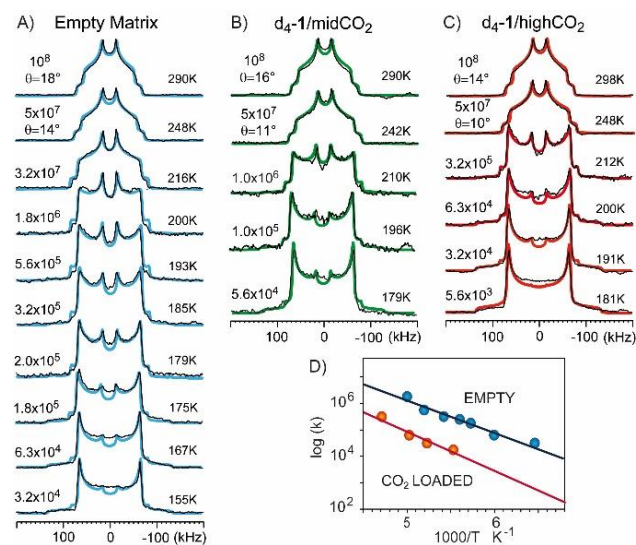
The permanent porosity with open channels in the crystalline material was demonstrated by a  $\text{CO}_2$  adsorption/desorption isotherm performed at 195 K (Figure 2). It showed a type-I Langmuir profile with an uptake of  $86 \text{ cm}^3(\text{STP})\text{g}^{-1}$  at  $p/p^\circ=0.97$  consistent with 2  $\text{CO}_2$  moles per mole of host and the complete filling of the available void in the crystal structure. The uptake is comparable to that of best-performing porous molecular crystals containing 1D channels with similar cross-section.<sup>8</sup> Moreover, the crystals absorb  $\text{CO}_2$  efficiently at 273K and 298K, reaching 80% pore-filling at 5 and 10 bar, respectively. The isosteric heat of adsorption, according to the Clausius-Clapeyron equation, was  $30 \text{ kJmol}^{-1}$  at low coverage ( $< 5 \text{ cm}^3 \text{ g}^{-1}$ ) and reached a plateau with  $27 \text{ kJmol}^{-1}$  at more than  $10 \text{ cm}^3 \text{ g}^{-1}$ ; these energy values are explained by the encapsulation of  $\text{CO}_2$  in the electron-rich environment of the  $\pi$ -system.<sup>3b</sup>



**Figure 2.**  $\text{CO}_2$  adsorption/desorption isotherms of porous compound **1** at 195 K, showing the permanent porosity of the crystalline material. The insert shows the  $\text{CO}_2$  adsorption isotherms at 298 K and 273 K and up to 5 bar.

The channel wall structure reveals that the separation between the axes of central *p*-phenylene rings on adjacent molecules is  $5.5 \text{ \AA}$  (Figure 1b). Considering that each aromatic ring possesses a lateral van der Waals hindrance of *ca.*  $1.7 \text{ \AA}$ , a space much larger than that of a face-to-face configuration is available, enforcing the expectation that such moieties could be efficient as fast molecular rotors. Robust evidences were provided by  $^2\text{H}$  solid-state NMR spectroscopy, which is a unique method to understand the motional trajectories and reveal the mechanism of the reorientation of the C-D vectors.<sup>9</sup> Thus, the porous compound selectively deuterated on the central *p*-phenylene moiety (*d*<sub>4</sub>-**1**) was prepared to investigate the dynamics of this rotor.  $^2\text{H}$  spin-echo NMR spectral profiles of *d*<sub>4</sub>-**1** vary progressively with increasing temperature from 155 to 290 K (Figure 3A) and were successfully simulated by considering reorientational rates spanning from  $10^4$  to  $10^8$  Hz, according to the timescale sensitivity of wide-line  $^2\text{H}$  NMR.

The line-shape analysis indicates that the mechanism of motion is consistent with a rapid two-site  $180^\circ$  flip reorientation of *p*-phenylene moieties about their para-axis. At a temperature of 216K, the spectrum exhibits a restricted profile with 30.8kHz separation between singularities, due to motional averaging. The profile is reduced to one fourth of the 'static' Pake spectrum, indicating an exchange rate  $k > 10^7 \text{ Hz}$ . At a temperature as low as 200K, the motional regime is still in the Megahertz domain. This unusually fast regime of motion at such temperatures overcomes the exchange rates of *p*-phenylene groups in most organic materials and solid polymers.<sup>4b,10</sup> More specifically, the extremely fast dynamics is a benchmark in this class of porous crystalline materials.<sup>5,11</sup> The motion in compound *d*<sub>4</sub>-**1** is still fast at 175K, with reorientation rates in the order of  $10^5 \text{ Hz}$ .



**Figure 3.** Experimental  $^2\text{H}$  spin-echo NMR spectra as function of temperature of A) porous compound *d*<sub>4</sub>-**1**; compound *d*<sub>4</sub>-**1** loaded with  $\text{CO}_2$  at 3.3. bar (B) and 5.4 bar (C) at room temperature. The  $^2\text{H}$  NMR spectral profiles were simulated considering a two-site  $180^\circ$  flip mechanism (blue, green and red, respectively). ( $\theta$ ) corresponds to libration semi-amplitude. The reorientation rates (*k*) in Hz are reported. D) Arrhenius plots of the  $\log(k)$  versus the inverse of temperature.

At high temperature, above 248K, the linewidth restriction together with the weakening of the spectral shoulders is apparent, demonstrating that the rapid libration of the central *p*-phenylene ring must be included. Rates in the fast exchange limit ( $10^8 \text{ Hz}$ ) and libration amplitudes up to  $\theta = \pm 18^\circ$  are achieved at room temperature. This result is consistent with the ( $^{13}\text{C}$ ) $T_1$  relaxation measurements in compound **1**. In fact, the signal at  $\delta = 131.2 \text{ ppm}$  assigned to CH carbons of the *p*-phenylene rotor exhibits a  $T_1$  relaxations as short as 515 ms at room temperature, falling close to the maximum relaxation rate and in nanosecond correlation times.

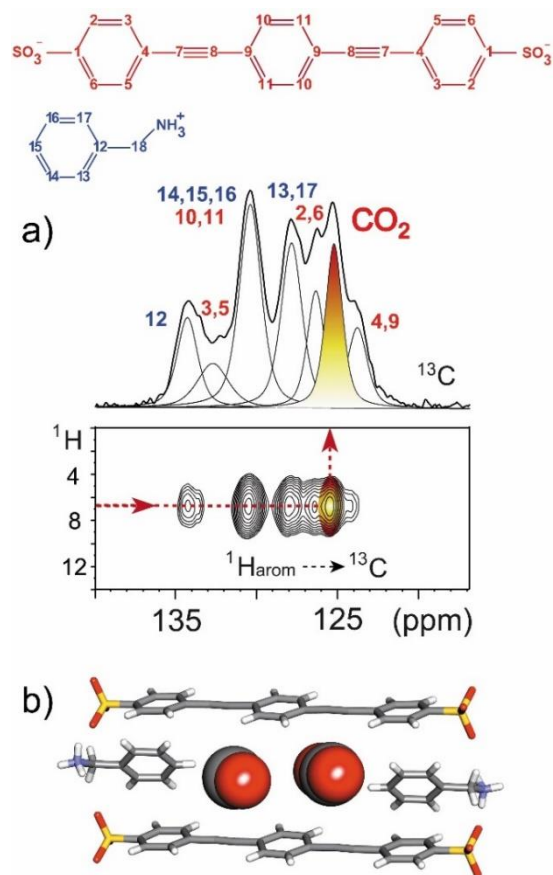
Moreover, as the rotors are easily accessible by the gas phase,  $\text{CO}_2$  can effectively regulate rotor dynamics. Thus, the crystalline powders were sealed under pressurized  $\text{CO}_2$  at 3.3 bar and 5.4 bar at room temperature (denoted as *d*<sub>4</sub>-**1**/mid $\text{CO}_2$  and *d*<sub>4</sub>-**1**/high $\text{CO}_2$ , respectively). The crystal structure of samples after  $\text{CO}_2$  loading at these pressures does not change, as shown by X-ray diffraction and  $^{13}\text{C}$  CP MAS NMR at room and low temperature (SI).

$^2\text{H}$  NMR spectra were collected at variable temperatures (Figure 3B and C): at room temperature and down to 240K, the spectral profiles remained unaltered with respect to those of the empty matrix, i.e. the fast rotational regime of  $5 \times 10^7 \text{ Hz}$  prevails and the loading of the channels remains moderate. On the contrary, at

200K, a clear reduction in the molecular rotor spinning-rate of two orders of magnitude was observed in the *d*<sub>4</sub>-**1**/highCO<sub>2</sub> sample with respect to the empty crystals; the same reduced spinning rate ( $k=6.3\times 10^4\text{Hz}$ ) was observed in the empty matrix at a much lower temperature, i.e. 167K, making it evident that the effect of CO<sub>2</sub> on rotor dynamics is comparable to a drop of 33K. Moreover, the spectrum at 181K showed a virtually static Pake spectrum ( $k=5.6\times 10^3\text{Hz}$ ), clearly showing that CO<sub>2</sub> molecules enter the crystal and diffuse into the open pores where they encounter rotors, hampering their facility to rotate. At lower loadings (*d*<sub>4</sub>-**1**/midCO<sub>2</sub>), intermediate dynamics were deduced by <sup>2</sup>H line shape analysis (Figure 3B).

Notably, the spectra of the *d*<sub>4</sub>-**1**/highCO<sub>2</sub> sample below 212K fall in a range of constant CO<sub>2</sub> loading of 1.8 mole/mole, indicative of virtually complete filling of the channels (Table S7). This ensured that the loading parameter played no role in evaluating the activation energy, derived from an Arrhenius plot. The activation energy increased to 7.0 kcalmol<sup>-1</sup> in the fully loaded sample, compared to 5.7 kcalmol<sup>-1</sup> in the empty matrix, indicating that more energy is required for the 180° flip reorientation of the rotors when CO<sub>2</sub> is loaded. Thus, the exchange process between the stable arrangements of the two-site 180° flip mechanism is governed by an activation energy increased by 1.3 kcal mol<sup>-1</sup>, which may be accounted for by the stabilization of the ground state because of the favorable interactions between CO<sub>2</sub> and rotors. The steric hindrance generated by CO<sub>2</sub> in the channels hardly affects rotor trajectories, because the favorable interactions of CO<sub>2</sub> carbon with electron-rich ethynyl units observed in the crystal structure kept CO<sub>2</sub> molecules aside from the rotor.<sup>11a</sup> In fact, we have observed from the crystallographic structure with CO<sub>2</sub> and the Hirshfeld surfaces (SI) that the CO<sub>2</sub> oxygen interacts with the *p*-phenylene hydrogen ( $d_{\text{O-H}}=3.4\text{\AA}$ ). Although small, the amount of energy determined here accounts for a substantial 20% of the total energy involved in the *p*-phenylene flip, and this energy is sufficient to modulate the dynamical properties of the host. Treatment of the crystals under vacuum resulted in the reverse phenomenon, and the regaining of pristine fast rotor-dynamics.

The direct detection of CO<sub>2</sub> and its location in close contact with the rotors along the crystalline channels was achieved by 2D <sup>1</sup>H-<sup>13</sup>C HETCOR NMR of CO<sub>2</sub>-loaded compound **1** at low temperature (Figure 4). In fact CO<sub>2</sub> molecules, although depleted of hydrogens, can receive magnetization from the aromatic hydrogens of the struts through nuclear dipolar interactions and under cross-polarization conditions and produce a correlation signal.<sup>12</sup> Signal intensity decays rapidly with internuclear distance ( $\propto r^{-6}$ ) and requires relatively long residence times of the gas molecule on the site. Specifically, the notable intensity of CO<sub>2</sub> cross-peak demonstrates the occurrence of short internuclear distances of about 4 Å. 2D heteronuclear NMR correlations and cross-polarization from a solid to a gaseous molecule are rare,<sup>13</sup> providing clear evidence of gas associated with interaction sites. Moreover, the location of CO<sub>2</sub> molecules along the channels could be determined by synchrotron radiation XRD experiments on single-crystals sealed at 20 bar. The channel architecture was retained with respect to the empty structure and the distance of the adjacent rod-like molecules was unaltered (Figure 4b). Two CO<sub>2</sub> molecules are located per each host: they are aligned parallel to the channel axis and arranged in close association with the rod-like struts, which bear the rotors, in agreement with NMR results.



**Figure 4.** a) 2D <sup>1</sup>H-<sup>13</sup>C Hetero-correlated NMR spectrum of CO<sub>2</sub>-loaded compound **1** at 220 K. b) Crystal structure of compound **1** sealed at 20 bar under CO<sub>2</sub> atmosphere. CO<sub>2</sub> molecules diffused into the channel are depicted by a space-filling model.

In conclusion, the present work successfully shows that molecular rotors built in porous materials can be actively manipulated from the gas phase by simple exposure to gaseous CO<sub>2</sub>. This challenging phenomenon was enabled by engineering porous molecular crystals, which were endowed with extremely fast dynamics of their rotors and low energy barriers for rotation. The CO<sub>2</sub> molecules diffuse easily into the crystalline channels and interact individually with rotors, thus increasing by 1.3 kcalmol<sup>-1</sup> the activation energy for rotation and by braking the dynamics in the entire crystal. This measurement was realized by a newly designed experiment through <sup>2</sup>H NMR and 2D <sup>1</sup>H-<sup>13</sup>C NMR detection of the CO<sub>2</sub>-host interface. Motional behavior on solid surfaces in the presence of interacting gases takes on a fundamental and applicative relevance, since it addresses a crucial issue in catalysis and materials chemistry.

## ASSOCIATED CONTENT

### Supporting Information

Synthesis, crystallographic data, calorimetric analysis, NMR spectroscopy (PDF). Crystal structures (cif). The Supporting Information is available free of charge on the ACS Publications website.

## AUTHOR INFORMATION

### Corresponding author

Email: \*piero.sozzani@mater.unimib.it,

Email: \*tohnai@mls.eng.osaka-u.ac.jp,

## ACKNOWLEDGMENT

Cariplo Foundation 2016, PRIN 2015-CTEBBA and IN-RL14-2016 are acknowledged for financial support. The authors would like to thank Dr. Nicola Demitri of the Elettra synchrotron facility for technical advice during data collection and data treatment. JSPS KAKENHI Grant Number JP16H01027 in Precisely Designed Catalysts with Customized Scaffolding.

## REFERENCES

- (1) (a) Lorimer, G. *Annu.Rev.PlantPhysiol.* **1981**, *32*, 349-382. (b) Seneviratne, S. I.; Donat, M. G.; Pitman, A. J.; Knutti, R.; Wilby, R. L. *Nature* **2016**, *529*, 477-483. (c) Williamson, P. *Nature* **2016**, *530*, 153-155.
- (2) (a) Taylor, T. C.; Andersson, I. *Nature Struct. Biol.* **1996**, *3*, 95-101. (b) Assche, F.; Clijsters, H. *PlantCellEnviron.* **1990**, *13*, 195-206.
- (3) (a) Lu, A. H.; Dai, S. *Porous materials for carbon dioxide capture*; Springer: London, 2014. (b) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. *Chem. Rev.* **2012**, *112*, 724-781. (c) Nugent, P.; Belmabkhout, Y.; Burd, S. D.; Cairns, A. J.; Luebke, R.; Forrest, K.; Pharm, T.; Ma, S.; Space, B.; Woitas, L.; Eddaoudi, M.; Zaworotko, M. J. *Nature* **2013**, *495*, 80-84. (d) Yanai, N.; Kitayama, K.; Hijikata, Y.; Sato, H.; Matsuda, R.; Kubota, Y.; Takata, M.; Mizuno, M.; Kitagawa, S. *Nature Mater.* **2011**, *10*, 787-793. (e) Li, J.-R.; Yu, J.; Lu, W.; Sun, L.-B.; Sculley, J.; Balbuena, P. B.; Zhou, H.-C. *Nature Comm.* **2013**, *4*, 1-8. (f) Vaidhyanathan, R.; Iremonger, S. S.; Shimizu, G. K. H.; Boyd, P. G.; Alavi, S.; Woo, T. K. *Science* **2010**, *330*, 650-653. (g) Yang, S.; Sun, J.; Ramirex-Cuesta, A. J.; Callear, S. K.; David, W. I. F.; Anderson, D. P.; Newby, R.; Blake, A. J.; Parker, J. E.; Tang, C. C.; Schoeder, M. *Nature Chem.* **2012**, *4*, 887-894. (h) Sozzani, P.; Bracco, S.; Comotti, A.; Ferretti, L.; Simonutti, R. *Angew.Chem.Int.Ed.* **2005**, *44*, 1816-1820. (i) Yadav, V. N.; Comotti, A.; Sozzani, P.; Bracco, S.; Bonge-Hansen, T.; Hennum, M.; Gorbitz, C. H. *Angew.Chem.Int.Ed.* **2015**, *54*, 15684-15688.
- (4) (a) Kottas, G. S.; Clarke, L. I.; Horinek, D.; Michl, J. *Chem.Rev.* **2005**, *105*, 1281-1376. (b) Collins, B.S.L.; Kistemaker, J.C.M.; Otten, E.; Feringa, B.L. *Nature Chem.* **2016**, *8*, 860-866. (c) Vogelsberg, C.S.; Garcia-Garibay, M.A. *Chem.Soc.Rev.* **2012**, *41*, 1892-1910. (d) Tabe, Y.; Yokoyama, H. *Nature Mater.* **2004**, *2*, 806-809. (e) Kobr, L.; Zhao, K.; Shen, Y.Q.; Comotti, A.; Bracco, S.; Shoemaker, R. K.; Sozzani, P.; Clark, N. A.; Price, J.C.; Rogers, C. T.; Michl, J. *J.Am.Chem.Soc.* **2012**, *134*, 10122-10131. (f) Brustolon, M.; Barbon, A.; Bortolus, M.; Maniero, A. L.; Sozzani, P.; Comotti, A.; Simonutti, R. *J.Am.Chem.Soc.* **2004**, *126*, 15512-15519. (g) Setaka, W.; Yamaguchi, K. *Proc.Nat.Acad.Sci.* **2011**, *109*, 9271-9275.
- (5) (a) Comotti, A.; Bracco, S.; Sozzani, P. *Acc.Chem.Res.* **2016**, *49*, 1701-1710. (b) Bracco, S.; Beretta, M.; Cattaneo, A.; Comotti, A.; Falqui, A.; Zhao, K.; Rogers, C.; Sozzani, P. *Angew.Chem.Int.Ed.* **2015**, *54*, 4773-4777. (c) Shustova, N. B.; Ong, T.-C.; Cozzolino, A.F.; Michaelis, V.K.; Griffin, R.G.; Dinca, M. *J.Am.Chem.Soc.* **2012**, *134*, 15601-15070. (d) Devautour-Vinot, S.; Maurin, G.; Serre, C.; Horcajada, P.; Paula da Cunha, P.; Guillerm, V.; de Souza Costa, E.; Taulelle, F.; Martineau, C. *Chem.Mater.* **2012**, *24*, 2168-2177. (e) Vogelsberg, C. S.; Bracco, S.; Beretta, M.; Comotti, A.; Sozzani, P.; Garcia-Garibay, M. *J.Phys.Chem.B* **2012**, *116*, 1623-1632. (f) Gould, S.L.; Tranchemontagne, D.; Yaghi, O.M.; Garcia-Garibay, M.A. *J. Am.Chem.Soc.* **2008**, *130*, 3246-3247. (g) Vukotic, V. N.; Harris, K. J.; Zhu, K.; Schurko, R. W.; Loeb, S. J. *Nature Chem.* **2012**, *4*, 456-460. (h) Bracco, S.; Comotti, A.; Valsesia, P.; Chmelka, B.F.; Sozzani, P. *Chem.Commun.* **2008**, *39*, 4798-4800.
- (6) (a) Inukai, M.; Fukushima, T.; Hijikata, Y.; Ogiwara, N.; Horike, S.; Kitagawa, S. *J.Am.Chem.Soc.* **2015**, *137*, 12183-12186. (b) Comotti, A.; Bracco, S.; Yamamoto, A.; Beretta, M.; Hirukawa, T.; Tohnai, N.; Miyata, M.; Sozzani, P. *J.Am.Chem.Soc.* **2014**, *136*, 618-621. (c) Comotti, A.; Bracco, S.; Ben, T.; Qiu, S.; Sozzani, P. *Angew. Chem. Int. Ed.* **2014**, *53*, 1043-1047. (d) Comotti, A.; Bracco, S.; Valsesia, P.; Beretta, M.; Sozzani, P. *Angew.Chem.Int.Ed.* **2010**, *49*, 1760-1764. (e) Jiang, X.; Duan, H.-B.; Khan, S.I.; Garcia-Garibay, M.A. *ACSCent.Sci.* **2016**, *2*, 608-613. (f) Yang, W.; Davies, A.J.; Lin, X.; Suyetin, M.; Matsuda, R.; Blake, A.J.; Wilson, C.; Lewis, W.; Parker, J.E.; Tang, C.C.; George, M.W.; Hubberstey, P.; Kitagawa, S.; Sakamoto, H.; Bichoutskaia, E.; Champness, N.R.; Yang, S.; Schroeder, M. *Chem.Sci.* **2012**, *3*, 2993-2999. (g) Elsaidi, S. K.; Mohamed, M.H.; Simon, C. M.; Braun, E.; Pham, T.; Forrest, K.A.; Xu, W.; Banerjee, D.; Space, B.; Zaworotko, M.J.; Thallapally, P.K. *Chem. Sci.* **2017**, DOI: 10.1039/c6sc05012c.
- (7) (a) Varshnev, C.B.; Sander, J.R.G.; Friscic, T.; MacGillivray, L.R. *Supramolecular Interactions. In Supramolecular Chemistry: From Molecules to Nanomaterials*, Steed, J.W.; Gale, P.A., Eds.; Wiley-VCH: New York, 2012; pp 9-24. (b) Desiraju, G.R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press: Oxford, UK, 1999. (c) Bishop, R. *Chem.Soc.Rev.* **1996**, *25*, 311-319. (d) Hosseini, M.W. *Chem.Commun.* **2005**, 5825-5829. (e) Ward, M.D. *Chem.Commun.* **2005**, 5838-5842.
- (8) (a) Breck, D. W. *Zeolite Molecular Sieves. Structure, Chemistry and Use*, Wiley: New York, 1974; pp 593-699. (b) Choudhary, V.R.; Mayadevi, S. *Zeolites* **1996**, *17*, 501-507. (c) Comotti, A.; Bracco, S.; Distefano, G.; Sozzani, P. *Chem.Commun.* **2009**, 284-286. (d) Comotti, A.; Fraccarollo, A.; Bracco, S.; Beretta, M.; Distefano, G.; Cossi, M.; Marchese, L.; Riccardi, C.; Sozzani, P. *Cryst.Eng.Comm.* **2013**, *15*, 1503-1507.
- (9) (a) Hoatson, G.L.; Vold, R.L. *NMR Basic Principles Prog.* **1994**, *7*, 1-67. (b) Spiess, H.W. *ColloidPolym.Sci.* **1983**, *261*, 193-209. (c) Simpson, J.H.; Rice, D.M.; Karasz, F.E. *J.Polym.Sci.PartB* **1992**, *30*, 11-16. (d) Aliev, A.E.; Mann, S.E.; Iuga, D.; Hughes, C.E.; Harris, K.D.M. *J.Phys.Chem.A* **2011**, *115*, 5568-5578.
- (10) (a) Kawaguchi, T.; Mamada, A.; Hosokawa, Y.; Horii, F. *Polymer* **1998**, *39*, 2725-2732. (b) Calucci, L.; Zamir, S.; Singer, D.; Zimmermann, H.; Wachtel, E.J.; Poupko, R.; Luz, Z. *Liq.Cryst.* **1997**, *22*, 1-9. (c) Cholli, A.L.; Dumais, J.J.; Engel, A.K.; Jelinski, J. W. *Macromolecules* **1984**, *17*, 2399-2404.
- (11) (a) Winston, E.B.; Lowell, P.J.; Vacek, J.; Chocholousova, J.; Michl, J.; Price, J.C. *Phys.Chem.Chem.Phys.* **2008**, *10*, 5188-5191. (b) Morris, W.; Taylor, R.E.; Dybowski, C.; Yaghi, O.M.; Garcia-Garibay, M.A. *J.Mol.Struct.* **2011**, *1004*, 94-101.
- (12) (a) Vega, A.J. *J. Am. Chem. Soc.* **1988**, *110*, 1049-1054. (b) Sozzani, P.; Comotti, A.; Bracco, S.; Simonutti, R. *Angew.Chem.Int.Ed.* **2004**, *43*, 2792-2797. (c) Bracco, S.; Comotti, A.; Ferretti, L.; Sozzani, P. *J.Am.Chem.Soc.* **2011**, *133*, 8982-8994. (d) van Rossum, B.-J.; de Groot, C.P.; Ladizhansky, V.; Vega, S.; de Groot, H.J. *J.Am.Chem.Soc.* **2000**, *122*, 3465-3472. (e) Sozzani, P.; Bracco, S.; Comotti, A.; Simonutti, R.; Camurati, I. *J.Am.Chem.Soc.* **2003**, *125*, 12881-12893. (f) Comotti, A.; Bracco, S.; Sozzani, P.; Hawxwell, S.M.; Hu, C.; Ward, M.D. *Cryst.Grow.Des.* **2009**, *9*, 3000-3002. (g) Kitao, T.; Bracco, S.; Comotti, A.; Sozzani, P.; Naito, M.; Seki, S.; Uemura, T.; Kitagawa, S. *J.Am.Chem.Soc.* **2015**, *137*, 5231-5238.
- (13) Bassanetti, I.; Comotti, A.; Sozzani, P.; Bracco, S.; Calestani, G.; Mezzadri, F.; Marchio, L. *J.Am.Chem.Soc.* **2014**, *136*, 14883-14895.

## Table of Contents

