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A guest-induced reversible switching of a self-assembled H-bonded supramolecular framework $\ensuremath{\dagger}$

Pierre Mobian,* Clarisse Huguenard and Marc Henry*

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A new class of organic crystalline 2,2'-biphenol-based H-bonded material displaying 1D-channels encapsulating solvent molecules is described. A reversible guest-induced crystal-to-crystal conversion between the solvated H-bonded phase and a compact H-bonded non-solvated phase was observed. The energy competition between intramolecular H-bonds formation and solvation of organic pores has been characterized using PACHA calculations.

Clathrates are a fascinating class of supramolecular crystalline solids that elicit major interest for fundamental purposes and practical issues.¹ A particular class of clathrates that attracts considerable attention are dynamic systems where reversible guest-induced crystal-to-crystal transformation occurs.² Many efforts have been made to characterize dynamic porous coordination polymers showing dynamic behaviours.³ However, focusing on crystalline materials formed by the self-assembly of organic building blocks, few examples of dynamic clathrates have been reported.⁴ For these particular systems, removing the guest molecules trapped in the porous frameworks usually led to the irreversible collapse of the structures into dense forms.^{5,6} A remarkable exception concerns organic hydrogenbonded networks which often exhibit flexibility.⁷

Herein, we report the dynamic behavior of a new class of organic crystalline materials based on the readily available 2,2'-biphenol derivative, *i.e.* 2',2''-dihydroxy-3,5,3''',5'''-tetra-methyl-1,1':3', 3'':1'',1'''-tetraphenyl (http).

(**Phase I**) (Fig. 1d) with 1D channels along the *a*-axis. A close observation of the structure indicated that each **http** unit interacts with two neighbours through intermolecular OH···O hydrogen bonds with an O···O distance of about 3 Å to form a 1D columnar assembly shown in Fig. 1b. It is also worth noting that in the solid state the two central crystal structure phenyl rings of the **http** unit adopts anticlinal conformation (measured torsion angle: 116°) that renders this molecule chiral. Consequently, in the crystal, these 1D columnar assemblies could also be regarded as an infinite self-association of **http** heterochiral dimers (Fig. 1a). Each column is then surrounded by four analogues through CH– π interactions (Fig. 1c). As shown in the ESI[†], the other OH moiety is not H-bonded but rather engaged in a O–H···pi bonding with an interaction energy very similar to the intermolecular H-bond.

The repetition of this latest supramolecular motif creates distorted hexagonal 1D channels with an inner diameter ranging from 4.4 Å to 5.3 Å (see ESI†). The solvent-accessible free volume of these channels is estimated to be 388 A^3 representing 14% of the total crystal volume.⁸

The presence of guest molecules trapped inside the channels was evidenced by thermogravimetric analysis (TGA), which showed a rapid weight loss (13%) upon heating from 75 °C to 95 °C. XRD analysis was not able to resolve the molecular disorder, but ¹H and ¹³C solid-state NMR analyses enabled us to identify the solvents trapped in the as-synthesized solid.



Crystals suitable for X-ray analysis (space group $Pna2_1$) were obtained by allowing *n*-pentane to diffuse into a dichloromethane solution of **http**. Structure analysis revealed that **http** solid-state organization led to a honeycomb-like structure

E-mail: mobian@unistra.fr, henry@unistra.fr



Fig. 1 X-Ray crystal structure of **http** (**Phase I**). (a) Capped sticks representation of a **http** heterochiral dimer, the blue dotted line represents the hydrogen bond existing between two http units. (b) View along the *b*-axis of a 1D columnar assembly. (c) View along the *a*-axis of the pentameric assembly of 1D columns. (d) Spacefill model of the resulting porous network (in all cases hydrogens are omitted for clarity).

Laboratoire de Chimie Moléculaire de l'Etat Solide, UMR 7140, Université de Strasbourg, 67070 Strasbourg, France.

[†] Electronic supplementary information (ESI) available: Synthetic pathway and characterization of **http**, X-ray diffraction data, NMR experimental, TGA, DSC thermograms and PACHA calculations. CCDC 817017, 817018. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc13124a

Reproducible NMR signals due to CH_2Cl_2 species were indeed observed on ¹H magic angle spinning (MAS) spectrum (4.9 ppm) as well as ¹³C cross-polarization (CP) MAS (54.2 ppm) spectrum. Signals from *n*-pentane were also observed at 0.75/1.2 ppm on ¹H MAS and at 14.3/22.2/34.2 ppm on ¹³C CPMAS spectra (Fig. 2a). See ESI† for ¹H spectra.

Using a 10 kHz MAS speed, the overlap of the numerous ¹H signals of **http** gives rise to a broad pattern but signals of CH₂Cl₂ and *n*-pentane appear well separated and thin enough (150 Hz linewidth) to allow an estimation of the trapped solvents molar proportion. The as-synthesized product includes about 70% of *n*-pentane and 30% of CH₂Cl₂ molecules. Taking into account the TGA-weight loss, a host : guest ratio of 1:0.8 is inferred for **Phase I**. After twenty days storage in air, 80% of CH₂Cl₂ was spontaneously lost whereas less than 10% of *n*-pentane had left the solid, illustrating the predominant role of this hydrocarbon in **Phase I** stability. DSC traces displayed two intense endotherms, the first one at 90 °C and a second one at 155 °C which were attributed, respectively, to removal of solvent molecules and to the melting temperature of the product (mp: 156 °C) (see ESI†).

The characterization of the apohost phase (**Phase II**) thermally synthesized from **Phase I** was then performed. Despite the *a priori* amorphous aspect, X-ray powder diffraction (XRPD) (see Fig. S5, ESI†) and ¹³C CPMAS solid-state NMR analysis showed the apohost material to be crystalline. The X-ray diffraction pattern and the ¹³C CPMAS spectrum are strongly different from those obtained for the starting porous material



Fig. 2 ¹³C CPMAS NMR spectra of **http** powder (a) as-synthesized by diffusion of *n*-pentane into CH_2Cl_2 solution (**Phase I**), (b) after one night at 100 °C (**Phase II**), and (c) after further exposure to $CH_2Cl_2/$ *n*-pentane vapors for 36 h. Top: **http** methyl and trapped solvents signals range; bottom: **http** C, CH and CO signals range, see the text for details. Note: in (a) and (c) cases, CH₃ sites of **http** are identified at 20.2, 22.2 and 23.1 ppm (1:2:1) and one of the resonance coming from *n*-pentane overlap with the central signal.

(Fig. 2b). XRPD and ¹³C CPMAS systematic investigations allowed us to establish some other features of the system described below. Phase II may also be obtained as the direct product of *n*-pentane diffusion into a http CH₂Cl₂ solution if the temperature of the medium is not controlled. However, for a constant temperature (4 °C), Phase I is most frequently obtained. Similarly, using n-hexane or cyclohexane instead of *n*-pentane also led to solvated phases analogous to Phase I including hydrocarbon molecules. It was also observed that Phase II crystallized from a *n*-hexane/CH₂Cl₂/http system. The structure of Phase II was in fact resolved from this latter system that provided crystals suitable for X-ray analysis $(P2_1/n \text{ space group})$. In this case, the three-dimensional arrangement of the http units was shown to be compact. Fig. 3 presents the supramolecular organization of the http molecules in the crystal. First, two http molecules interact via an intermolecular $OH \cdots O$ hydrogen bond $(O \cdots O = 3.1 \text{ Å})$. Interestingly enough, such a dimer is built from two different http conformers. The first http conformer presents a synclinal arrangement of the two central phenyl rings, whereas the second http conformer displays an anticlinal conformation. The measured torsion angles between the two central phenol rings were, respectively, found to be 52° due to an intramolecular hydrogen bond (http1) and 116° (http2). The repetition of this dimeric motif (Fig. 3b) along the *b*-axis leads to an infinite 1D columnar assembly that is self-associated through van der Waals interactions to form the compact network (Fig. 3c).

To investigate the reversibility of the formation of the compact structure *i.e.* **Phase II**-to-**Phase I** conversion, a sample of **Phase II** prepared by heating **Phase I** at 120 °C was exposed to an atmosphere saturated with dichloromethane and pentane vapours at room temperature. TGA analysis of the resulting solid indicated a weight loss of 12%. Furthermore, it was evident from infrared spectroscopy, XRPD and ¹³C CPMAS solid-state NMR analysis that the starting **Phase II** was converted to **Phase I**. This taking-up of solvent molecules affected only very partially the infrared spectrum of **Phase II**. The hydrogen-bonded O–H stretch region (v = 3489-3473 cm⁻¹) became slightly sharper which might indicate a perturbation of the columnar hydrogen networks, and a new band at v = 2953 cm⁻¹ was observed that



Fig. 3 X-Ray crystal structure of **http** (**Phase II**). (a) Capped sticks representation of a **http** dimer formed by two different conformers interacting through an intermolecular hydrogen bond, the blue dotted line represents the hydrogen bond existing between two **http** units. (b) View along the *b*-axis of a 1D columnar assembly. (c) View along the *a*-axis of the resulting compact network (in all cases hydrogens are omitted for clarity).

may correspond to absorption arising from asymmetrical C-H stretching of methyl groups in pentane (see ESI⁺). Fig. 2 shows a series of ¹³C CPMAS solid-state NMR spectra corresponding to Phase I, Phase II and the re-solvated Phase I. The symmetry changes caused by solvent removal and uptake are clearly demonstrated as two (150.0 and 150.5 ppm) and four (148.4, 150.3, 151.1 and 152.0 ppm) inequivalent CO sites are observed for Phase I and Phase II, respectively, in agreement with single-crystal XRD. Chemical shifts for CO sites are slightly different (150.2 and 150.5 ppm) in the re-solvated phase compared to the starting material and some other slight chemical shift differences are observed, but the re-solvated phase exhibits essentially the same spectrum as Phase I. These shifts are certainly induced by a different pore occupation due to a higher CH₂Cl₂ proportion in the re-solvated phase than in the starting material as evidenced in the top part of Fig. 2 and in ¹H MAS spectra (see ESI[†]).

In order to better characterize the role of solvent molecules in the formation of Phase I and Phase II, we have used the PACHA (Partial Atomic Charges Analysis) approach that allows us to compute reliable interaction energies from the sole knowledge of crystalline structures (see ESI[†] for computational details).^{9,10} Concerning Phase I, the intermolecular H-bond energy responsible for H-bonded chains of http molecules was found to be -22 kJ mol^{-1} , a value that may be compared to the energy associated by the stacking of these chains into a 3D structure of about -1 kJ mol^{-1} . The 1D nature of **Phase I** is thus clearly established. Concerning Phase II. molecular interactions between http1 molecules in the absence of http2 were found to be slightly destabilizing $(+1 \text{ kJ mol}^{-1})$ whereas molecular interactions between http2 molecules in the absence of http1 molecules were found to be slightly stabilizing (-3 kJ mol^{-1}) . Interweaving these two sub-networks was neatly stabilizing with an interaction energy of -12 kJ mol^{-1} . The intermolecular H-bond energy for H-bonded chains of http molecules was found to be -26 kJ mol^{-1} , whereas the energy associated with the intramolecular H-bonds was about twice this value at -50 kJ mol^{-1} .

In order to get a good understanding of the role played by solvent molecules, atomic coordinates were computed for dichloromethane and pentane molecules encapsulated within the network channel after minimization of steric energy using Gordin–Kim potentials.¹¹ Assuming a 1:1 host : guest ratio (1:0.8 measured) and channels entirely filled with dichloromethane, 1D chains of dichloromethane molecules (halogen bond energy of -18 kJ mol⁻¹) were obtained with an encapsulating energy of -26 kJ mol^{-1} . By contrast, for channels entirely filled with pentane, interactions between pentane molecules or with channels walls were found to be both rather weak $(-0.3 \text{ kJ mol}^{-1})$ and -1 kJ mol^{-1} respectively). In both cases there is clearly not enough energy to overcome the strong intramolecular H-bond observed in Phase II. Consequently, a network with channels filled with a 50:50 dichloromethane: pentane ratio (measured 70:30) was generated. The average interaction energy between the solvent molecules was found to be very stabilizing at -32 kJ mol⁻¹ while the average interaction energy with channels walls was found to be less stabilizing at -11 kJ mol^{-1} . The sum of both interactions (-43 kJ mol⁻¹) being still lower than the intramolecular H-bond energy, the interaction energy involving pentane molecules and channels half-filled with dichloromethane was computed and found to be strongly stabilizing $(-40 \text{ kJ mol}^{-1})$. Finally, the interaction energy involving dichloromethane molecules and channels half-filled with pentane was also computed and found to be less stabilizing $(-14 \text{ kJ mol}^{-1})$. It follows from this energy analysis that the only way to be competitive with the strong intramolecular H-bond $(-50 \text{ kJ mol}^{-1})$ in **Phase II** is to fill the channels first with dichloromethane and then encapsulate pentane molecules $(-40 - 32 = -72 \text{ kJ mol}^{-1})$ while filling first with pentane and then encapsulate dichloromethane is much less favorable $(-14 - 32 = -46 \text{ kJ mol}^{-1})$.

These oligophenylene structures being light emitters,¹² solidstate fluorescent measurements were also performed both on the solvated and compact state of the material. It was thus found that upon excitation at 340 nm, both phases exhibited luminescence centered at $\lambda_{max} = 400$ nm.

In conclusion, we were able to characterize a dynamic behavior of an organic crystalline solid. This dynamic phenomenon corresponds to the reversible guest-induced crystal-to-crystal conversion of a solvated to a compact phase. From a quantitative energy analysis it was found that the presence of both dichloromethane and pentane molecules within the channels was necessary for the occurrence of the reversible **Phase II** to **Phase I** transition.

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