COMMUNICATION www.rsc.org/chemcomm | ChemComm

Exploiting the use of hydrogen bonding and metal-coordination in the self-assembly of photoreactive multicomponent networks†

Yennifer Hill and Alexander Briceño*

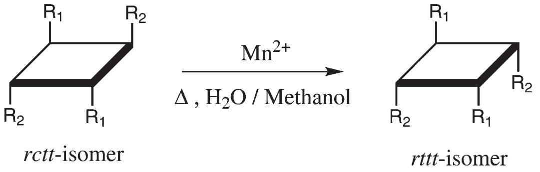
Received (in Austin, TX, USA) 8th May 2007, Accepted 2nd July 2007
First published as an Advance Article on the web 26th July 2007
DOI: 10.1039/b706936g

An unprecedented example of concomitant harmonisation of hydrogen bonding and metal-templating to direct a topochemical [2+2] cycloaddition with quantitative yield is reported.

Supramolecular assistance to covalent synthesis represents an important alternative to prepare stereocontrolled compounds either in solution or in the solid state.[1,2] In recent times, H-bonding[1] and metal-templated[3] have been successfully used to direct topochemical [2 + 2] cycloaddition of olefins. In particular, transition metal atoms display well-known coordination geometry preference, this structural feature provides single points to combine both crystal engineering tools to assembly metal–organic building blocks bearing distinctive ligands with variable multiple binding donor–acceptor sites.[4] Such binding capacity can be finely tuned to induce self-assembly of discrete metal motifs with encoded necessary information (*e.g.* O–H and pyridyl groups) into multi-component supramolecular aggregates. This approach has been employed in the assembly of supramolecular arrays based on both coordinated and H-bonded bridging bipyridines.[5] The structural similitude of these N-donor ligands with stilbene derivatives could be exploited for the rational design of novel materials with ideal geometrical parameters required for solid state photoreaction.[1f,6] In this context, we have recently described the use of multivalent templates based on aquo complex H-bonded multi-component networks as a strategy to direct reactivity of stilbenes.[7] Thus, we anticipated that a simple manner to module the number of multiple binding sites on the metal complex should be possible through the control of the coordinated water molecule content. In this report, we have explored this approach to drive topochemical formation of dimers of an asymmetrical stilbene [*trans*-1-(2-pyridyl)-2-(4-pyridyl)ethylene (2,4-bpe)] from multi-component metal assemblies: $[Mn(2,4\text{-bpe})_2(OH_2)_4](ClO_4)_2\cdot 2(2,4\text{-bpe})\cdot 2H_2O$ (**1**) and $[Mn(2,4\text{-bpe})_2(NCS)_2(OH_2)_2]$ (**2**).‡ These compounds represent unprecedented harmonisation examples, to the best our knowledge, of H-bonding and metal templates to mediate a [2 + 2] photodimerisation in the solid state. The UV-irradiation of both compounds lead to the regioselective formation of head to tail *rctt*-1,3-bis(2-pyridyl)-2,4-bis(4-pyridyl)cyclobutane (**3**) [*rctt*-2,4-tpcb-ht; tpcb = tetrapyridylcyclobutane] (Scheme 1). Compound **2** irradiated and after heating under reflux in a H_2O–MeOH mixture produces unexpected asymmetrical stereomutation of the *rctt*-dimer to the *rttt*-isomer (**4**). The crystal structures bearing these isomers (**3** and **4**), are also presented.‡

Crystals of **1** and **2** were prepared from H_2O–MeOH solutions of $Mn(ClO_4)_2\cdot 6H_2O$ with 2,4-bpe and $MnCl_2\cdot 2H_2O$, NaNCS and 2,4-bpe, respectively. Both compounds were obtained as single phases and were characterised by elemental analysis, IR and single-crystal X-ray studies (see ESI†).

The asymmetric unit of **1** contains one half of cationic complex $[Mn(2,4\text{-bpe})_2(OH)_4]^{2+}$, one free 2,4-bpe molecule and one water of crystallisation. The metal centre is placed on an inversion centre and showed a slightly distorted octahedral environment, in which four water molecules are located in the equatorial plane [Mn–Ow range: 2.161(3)–2.211(3) Å], and two pyridine nitrogen atoms in the axial sites [Mn–N 2.282(3) Å]. Both bipyridines are coordinated by 4-pyridyl nitrogen in a monodentate fashion. In the crystal structure this metal complex participates as donor of eight hydrogen bonds through the coordinated water molecules (see Fig. S2, ESI†). Each metallic motif is linked to four 2,4-bpe molecules *via* O–H···N hydrogen bonds involving both coordinated and free bipyridines [O···N range: 2.745(4)–2.877(5) Å]. Coordinated 2,4-bpe of adjacent metal complexes are connected through the remaining 2-pyridyl unit, whereas free 2,4-bpe are bonded by 4-pyridyl site. Additional O–H···O interactions are observed between coordinated water molecules, crystallisation water and perchlorate anions [O···O range: 2.696(3)–2.943(6) Å]). These interactions generate a hydrogen bonded layer extended in the $(11\bar{1})$ plane, as depicted in Fig. 1(a). This 2D array displays rhomboidal grids defined by four Mn centres [Mn···Mn distances: 14.47 × 18.01 Å]. Within this cavities are located the perchlorate anions and water molecules of crystallisation, allowing the assembly of the layers through H-bonding interactions. In this layer either coordinated or free 2,4-bpe molecules are arranged in a parallel manner, allowing π–π interaction between pairs of molecules. Similar sheet-like networks, bearing 4,4-bipy and 4,4-bpe ligands have been previously reported.[3d,5] A remarkable feature of this organisation is the presence of two types of intermolecular contacts between double bonds of neighbouring 2,4-bpe molecules, where concomitant H-bonding and metal–template interactions participate in the orientation of the molecules in a head-to-tail fashion (ht). Both contacts display C=C···C=C



Scheme 1 R_1 = 2-pyridyl; R_2 = 4-pyridyl.

Laboratorio de Síntesis y Caracterización de Nuevos Materiales, Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 21827, Caracas, 1020-A, Venezuela. E-mail: abriceno@ivic.ve; Fax: +58-212-5041350; Tel: +58-212-5041320

† Electronic supplementary information (ESI) available: Experimental details. Fig. S1–S7. XRD patterns, Views of the structures **1–4**, ^1H NMR and UV-vis spectra. See DOI: 10.1039/b706936g

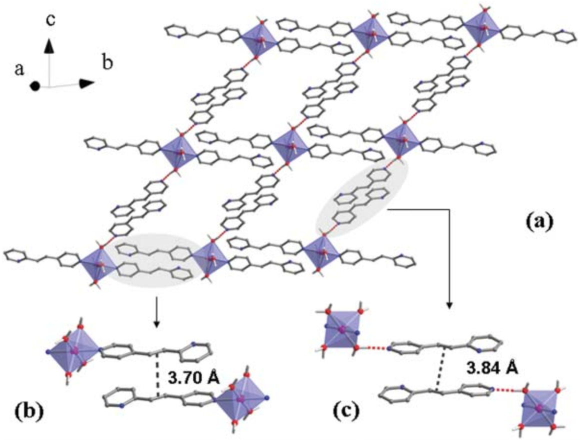


Fig. 1 (a) View of the layers found in the crystal structure of **1**. Transparent gray ovals show the two types of contacts between 2,4-bpe molecules: centrosymmetrically related pairs of molecules oriented by metal coordination (symmetry: $2 - x$, $-y$, $-z$) (b), and sustained by hydrogen bonds (symmetry: $1 - x$, $2 - y$, $1 - z$) (c).

(centroid-to-centroid: <3.85 Å) distances suitable for topochemical [2 + 2] cycloaddition, according to the limiting value proposed by Schmidt (<4.2 Å).[6] These pairs of molecules are related by a centre of symmetry and the relative orientation and close contact between the molecules anticipate the formation of the ht-isomer (Fig. 1(b) and (c)).

The crystal structure of **2** is built up from a neutral discrete metal complex, in contrast to the crystal structure of **1**. The Mn centre displays similar octahedral coordination geometry as that observed for **1**, with four N-atoms from two thiocyanate ligands and two 4-pyridyl nitrogens [Mn–N range: 2.169(4)–2.316(3) Å]). The remaining coordination sites are occupied by two coordinated water molecules (Mn–Ow range: 2.183(3)–2.193(3) Å). All pairs of ligands adopt a *trans* configuration around the metal (Fig. 2). In this metal complex the H-bonding capacity has been reduced due to the replacement of two coordinated water molecules by two NCS^- anions in comparison with that to **1** (donor of four hydrogen bonds, Fig. S3, ESI†). Crystal packing of **2** forms an H-bonded 2-D-network from self-assembly of metal complex units *via* hydrogen bonds, in which each complex is linked to four adjacent complexes through the coordinated water molecules. Each water molecule interacts with one SCN^- and one 2-pyridyl unit to form layers parallel to *ab*-plane [O···S average: 3.234(4) Å; O···N range: 2.702(8)–2.799(5) Å]. This complex is isomorphous with Fe-derivative recently reported.[8] A detailed description of this 2-D array and its H-bonding interactions is given in this article. Another view related with the potential reactivity in the solid state of this compound is shown here. Neighbouring H-bonded layers are assembled through π–π intercalations between pyridine rings in a zipper-like fashion to afford a 3-D network (Fig. 2).

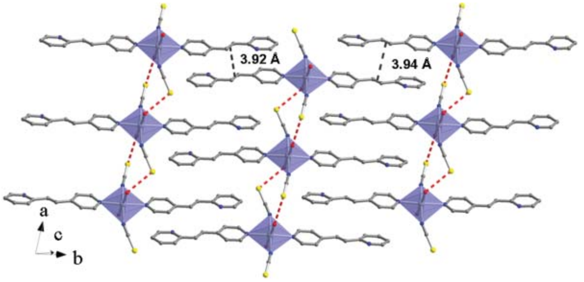


Fig. 2 View of the crystal structure of **2** in the *ab* plane, showing the pyridine ring π–π intercalations and short contacts between double bonds along the *a*-axis.

This interaction mode determines the presence of face-to-face contacts between coordinated 2,4-bpe molecules [average distance: 3.93 Å] and provides a head-to-tail orientation between them (Fig. 2). This array also exhibits two types of contacts between double bonds with adequate distances (centroid to centroid <3.95 Å) to favour the cycloaddition reaction,[6] similarly to those observed for **1**.

As anticipated, the ^1H NMR characterisation of the compounds obtained after UV irradiation of **1** and **2** for 2 days confirms photocycloaddition in both cases. The spectrum of the crude dimer (**3**) obtained from **1** reveals that this conversion is quantitative (yield: 100%), showing the total disappearance of the signals corresponding to the starting pyridine and the presence of two signals at 4.70 and 4.86 ppm characteristic signals of the C–H protons of the *rctt*-2,4-tpcb-ht[9] (Fig. S4(a), ESI†). This result suggests an efficient photoreaction in both pairs of 2,4-bpe contacts previously mentioned.

On the other hand, after irradiation, the product of **2** became insoluble in H_2O–MeOH at room temperature, in contrast to the solubility showed by the starting complex. This low solubility is associated with the possible formation of metal-oligomers as consequence of an apparent cross-linking *via* multiple [2 + 2] cycloaddition into the layers. The photoproduct of **2** was only soluble under reflux or in DMSO, and was later extracted with H_2O–CH_2Cl_2. Surprisingly, the spectrum of the solid isolated from the photoreaction of **2** showed the presence of the same signals observed for **3**, together with an additional complex set of signals, in particular in the region of the aliphatic methine protons (see Fig. S4, ESI†). These signals are consistent with the formation of a *rctt* and *rttt*-stereoisomeric mixture, in a ratio *ca.* 1 : 1 with a total conversion of 91%. (Fig. S4(b), ESI†). It is important to note that the rare *rttt*-configuration is not observed, to our knowledge, from direct photoirradiation of stilbenes in solution.[1c,10] In general, such processes with asymmetrical stilbenes are quite inefficient in solution, generating a complex mixture of side products in low yields. A rational explanation to the formation of the *rttt*-isomer in the solid state would imply the participation of a pedal-like change conformation mechanism[11] accompanied by a concomitant *trans*–*cis* isomerisation mechanism.[1g] This behaviour could be in agreement with the static disorder observed on the double bonds of one of the coordinated pyridines in **2** (Fig. S3(b), ESI†). Nevertheless, in order to gain a better insight about this process, further studies demonstrated that such result was not reproducible in the solid state. In all cases where the solid **2** was dissolved in DMSO at room temperature only the formation of the *rctt*-isomer was observed, which was always obtained in *ca.* 88–92%. Therefore, the formation of the *rttt*-isomer from the solid state was discarded due to the possibility of a rearrangement *ex-situ* (in solution) of the *rctt*-dimer. This change occurs *via* thermal stereomutation,[12] during the dissolution of **2** (irradiated) upon reflux in a H_2O–CH_3OH mixture. Such behaviour was confirmed by ^1H NMR spectroscopy, observing the formation of the *rttt*-isomer once again. Interestingly, this stereomutation does not

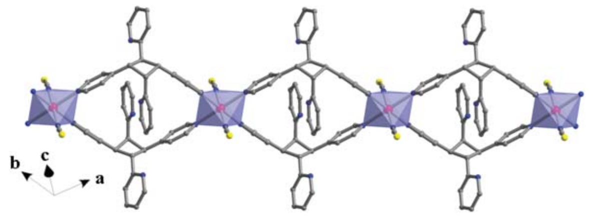


Fig. 3 Ball-and-stick representation of the 1D polymer observed in the crystal structure of **4**.

occur when the isolated dimer **3** is heated under reflux; this suggests that the molecular rearrangement is metal-assisted.

The stereochemistry of both isomers was confirmed by single-crystal X-ray diffraction analysis. Crystals of **3** were obtained by recrystallisation from a chloroform–DMSO mixture at 35 °C. The structure of the *rctt*-2,4-tpcb-ht isomer consists of 2D supramolecular sheets parallel to the *ac*-plane connected by weak van der Waals interactions (Fig. S5, ESI†). On the other hand, optical microscopy analysis of irradiated crystals of **1** and **2** reveals evident changes in their coloration and shapes. During the exposure both crystals became opaque with a colour change from dark brown to pale brown. Likewise, both compounds show evident signs of deformation and large internal fractures. These macroscopic features suggest that neither photoreaction proceeds *via* single crystal to single crystal.[13]

The *rttt*-isomer was isolated as part of a coordination polymer [Mn(*rttt*-2,4-tpcb-ht)$_4$(NCS)$_2$]$_n$ (**4**) obtained from the recrystallisation of **2** after irradiation and heating. The crystal structure of **4** consists of a 1-D coordination polymer built up from Mn-nodes linked by bridging *rttt*-isomers. The Mn atom lies on an inversion centre and displays a $\{MnN_6\}$ environment coordination sphere [Mn–N range: 2.172(4)–2.327(3) Å], in which four *rttt*-2,4-tpcb-ht molecules are located in the equatorial plane, and two N-atoms from NCS$^-$ ligands in the axial sites. The metal centres are connected exclusively by coordination of both 4-pyridyl units, the groups being oriented in a *cis* configuration on the cyclobutane ring, yielding a 1-D polymer along the [110]-direction (Fig. 3). The 2-pyridyl motifs do not exhibit metal-coordination modes, but are involved in the formation of self-complementary intramolecular hydrogen bonds between pairs of molecules along the chain [C24$\cdots$N4 3.359(6) Å]. These chains are organised in parallel and assembled in a criss-cross-like fashion through multiple interactions between the pyridyl rings (Fig. S6, ESI†).

In conclusion, we report two unprecedented examples of concomitant H-bonding and metal-templated approaches in multi-component metal assemblies to direct [2 + 2] photocycloaddition of an asymmetrical stilbene in the solid state. Non-photochemical formation of the isomer *rttt*-2,4-tpcb-ht is the first example, to the best of our knowledge, of an asymmetrical thermal stereomutation of a homodimer assisted by a metal centre. Further studies on thermal rearrangements in other cyclobutane derivatives promoted by transition metals are in progress.

This work was supported in part by FONACIT, grant LAB-97000821 and G-2005000433.

Notes and references

‡ *Crystal data*: for **1**: $C_{48}H_{52}Cl_2MnN_8O_{14}$, M = 1090.82, triclinic, space group $P\bar{1}$, a = 9.821(2), b = 10.751(2), c = 12.742(3) Å, α = 80.17(1), β = 78.99(1), γ = 89.30(2)°, U = 1300.7(4) Å^3, Z = 1, μ(Mo-Kα) = 0.43 mm^{-1}, D_c = 1.393 g cm^{-3}; R_{int} = 0.031, $R1(F^2)$ = 0.069, $wR(F^2)$ = 0.213, S = 1.05 for 4903 independent reflections ($I > 2\sigma(I)$). CCDC 644639. For **2**: $C_{26}H_{24}MnN_6O_2S_2$, M = 571.57, triclinic, space group $P\bar{1}$, a = 7.875(9), b = 10.3195(11), c = 17.814(2) Å, α = 78.178(8), β = 82.985(9), γ = 78.844(7)°, U = 1385.1(3) Å^3, Z = 2, μ(Mo-Kα) = 0.66 mm^{-1}, D_c = 1.371 g cm^{-3}; R_{int} = 0.038, $R1(F^2)$ = 0.071, $wR(F^2)$ = 0.20, S = 1.09 for 5261 independent reflections ($I > 2\sigma(I)$). CCDC 644640. For **3**: $C_{24}H_{20}N_4$, M = 364.44, monoclinic, space group $P2/c$, a = 16.307(3), b = 5.7271(7), c = 24.026(3) Å, β = 118.525(3)°, U = 1971.5(5) Å^3, Z = 4, μ(Mo-Kα) = 0.07 mm^{-1}, D_c = 1.228 g cm^{-3}; R_{int} = 0.073, $R1(F^2)$ = 0.069, $wR(F^2)$ = 0.173, S = 1.14 for 3777 independent reflections ($I > 2\sigma(I)$). CCDC 644641. For **4**: $C_{50}H_{40}MnN_{10}S_2$, M = 899.98, monoclinic, space group $C2/c$, a = 21.104(3), b = 14.0400(16), c = 17.205(2) Å, β = 111.224(2)°, U = 4751.4(10) Å^3, Z = 4, μ(Mo-Kα) = 0.41 mm^{-1}, D_c = 1.258 g cm^{-3}; R_{int} = 0.065, $R1(F^2)$ = 0.071, $wR(F^2)$ = 0.218, S = 1.04 for 4615 independent reflections ($I > 2\sigma(I)$). CCDC 644642. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b706936g

1 (*a*) *Top. Curr. Chem.*, 2005, **254**, 1–305 (Organic Solid Sate Chemistry special issue, ed. F. Toda); (*b*) L. R. MacGillivray, G. S. Papaefstathiou, T. Friščić, D. B. Varshney and T. D. Hamilton, *Top. Curr. Chem.*, 2004, **248**, 201; (*c*) M. Pattabiraman, A. Natarajan, R. Kaliappan, J. T. Mague and V. Ramamurthy, *Chem. Commun.*, 2005, 4542; (*d*) T. Caronna, R. Liantonio, T. A. Logothetis, P. Metrangolo, T. Pilati and G. Resnati, *J. Am. Chem. Soc.*, 2004, **126**, 4500; (*e*) D. G. Amirsakis, M. A. Garcia-Garibay, S. J. Rowan, J. F. Stoddart, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed.*, 2001, **40**, 4256; (*f*) N. Shan and W. Jones, *Tetrahedron Lett.*, 2003, **44**, 3687; (*g*) Y. Ito, T. Kitada and M. Horiguchi, *Tetrahedron*, 2003, **59**, 7323; (*h*) K. Takaoka, M. Kawamo, T. Ozeki and M. Fujita, *Chem. Commun.*, 2006, 1625; (*i*) S. Hirano, S. Toyota, F. Toda, K. Fujii and H. Uekuasa, *Angew. Chem., Int. Ed.*, 2006, **45**, 6013; (*j*) A. E. Keating and M. A. Garcia-Garibay, in *Organic and Inorganic Photochemistry*, ed. V. Ramamurthy and K. S. Schanze, Marcel Dekker, New York, 1998, **p. 195**.

2 (*a*) M. J. Vela, V. Buchholz, V. Enkelmann, B. B. Snider and B. M. Foxman, *Chem. Commun.*, 2000, 2225; (*b*) M. J. Vela, B. B. Snider and B. M. Foxman, *Chem. Mater.*, 1998, **10**, 3167; (*c*) G. Díaz de Delgado, K. A. Wheeler, B. B. Snider and B. M. Foxman, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 420; (*d*) A. Sun, J. W. Lauher and N. S. Goroff, *Science*, 2006, **312**, 1030; (*e*) T. Hoang, J. W. Lauher and F. W. Fowler, *J. Am. Chem. Soc.*, 2002, **124**, 10656.

3 (*a*) I. G. Georgiev and L. R. MacGillivray, *Chem. Soc. Rev.*, 2007, **36**, 1239–1248; (*b*) J. F. Eubank, V. C. Kravtsov and M. Eddaoudi, *J. Am. Chem. Soc.*, 2007, **129**, 5820; (*c*) X.-Y. Wang, Z.-M. Wang and S. Gao, *Chem. Commun.*, 2007, 1127; (*d*) J. Y. Lee, S. J. Hong, C. Kim and Y. Kim, *Dalton Trans.*, 2005, 3716; (*e*) A. Michaelides, S. Shoulika and M. G. Siskos, *Chem. Commun.*, 2004, 2418; (*f*) M. Nagarathinam and J. J. Vittal, *Angew. Chem., Int. Ed.*, 2006, **45**, 4337.

4 (*a*) J. D. Badjić, A. Nelson, S. J. Cantrill, W. B. Turnbull and J. F. Stoddart, *Acc. Chem. Res.*, 2005, **38**, 723; (*b*) L. Baldini, A. Casnati, F. Sansone and R. Ungaro, *Chem. Soc. Rev.*, 2007, **36**, 254.

5 (*a*) G. De Munno, F. Cipriani, D. Armentano, M. Julve and J. A. Real, *New J. Chem.*, 2001, **25**, 1031; (*b*) G. De Munno, D. Armentano, T. Poerio, M. Julve and J. A. Real, *J. Chem. Soc., Dalton Trans.*, 1999, 1813; (*c*) J. Lu, T. Paliwala, S. C. Lim, C. Yu, T. Nju and A. J. Jacobson, *Inorg. Chem.*, 1997, **36**, 923; (*d*) L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Chem. Soc., Dalton Trans.*, 1997, 1801.

6 G. M. J. Schmidt, *Pure Appl. Chem.*, 1971, **27**, 647.

7 A. Briceño, D. Leal, R. Atencio and G. Díaz de Delgado, *Chem. Commun.*, 2006, 3534.

8 M. Du, C.-P. Li and X.-J. Zhao, *CrystEngComm*, 2006, **8**, 552.

9 G. S. Papaefstathiou, T. Friščić and L. R. MacGillivray, *J. Supramol. Chem.*, 2002, **2**, 227.

10 J. Vansant, S. Toppet, G. Smets, J. P. Declercq, G. Germain and M. V. Meerssche, *J. Org. Chem.*, 1980, **45**, 1565.

11 (*a*) L. R. MacGillivray, J. L. Reid, J. A. Ripmeester and G. S. Papaefstathiou, *Ind. Eng. Chem. Res.*, 2002, **41**, 4494; (*b*) S. Ohba, H. Hosomi and Y. Ito, *J. Am. Chem. Soc.*, 2001, **123**, 6349; (*c*) J. Harada, H. Uekusa and Y. Ohashi, *J. Am. Chem. Soc.*, 1999, **121**, 5809; (*d*) J. Harad, K. Ogawa and S. Tomoda, *Acta Crystallogr., Sect. B*, 1997, **53**, 662.

12 J. E. Baldwin, *Chem. Rev.*, 2003, **103**, 1197, and references therein.

13 T. Friščič and L. R. MacGillivray, *Z. Kristallogr.*, 2005, **220**, 351, and references therein.