Inorganic Chemistry
Communication

Inorg. Chem. **2010**, *49*, 6775–6777 **6775**
DOI: 10.1021/ic100853h

Metal−Organic Frameworks Containing a Tetrapyridylcyclobutane Ligand Derived from Isomerization Reaction

Abdul Malik Puthan Peedikakkal, Charlene Shi Yun Peh, Lip Lin Koh, and Jagadese J. Vittal*

Department of Chemistry, National University of Singapore, 3 Science Drive, Singapore 117543, Singapore

Received April 30, 2010

The *rctt* isomer of tetrapyridylcyclobutane prepared from the solid-state [2 + 2] cycloaddition reaction of [bpeH$_2$]·2CF$_3$CO$_2$ [bpe = 1,2-bis(4-pyridyl)ethene] undergoes isomerization reaction to the *rtct* isomer in 100% yield, and this tetrahedral tetrapyridyl ligand forms two metal−organic frameworks having **ptt** and **pts** topology.

Cyclobutane derivatives are important starting materials for many cyclic and acyclic systems,[1,2] and the regio- and stereoselective synthesis of cyclobutane derivatives is one of the key issues in organic photochemistry.[2] Since the pioneering work of Schmidt,[3] many efforts were directed toward gaining control over the dimerization reaction of alkene derivatives in the solid state.[4] Such an assembly offers a unique possibility of regiocontrolled access to a single cyclobutane derivative in quantitative yield but limited applicability in the chiral synthesis of substituted cyclobutane products.[2,5]

Solid-state and solution photodimerization of azastilbene derivatives[6,7] has been found to be very useful in the synthesis of stereoselective cyclobutane rings. Recently, various efforts have been made to synthesize stereospecific cyclobutane derivatives from *trans*-1,2-bis(4-pyridyl)ethene (bpe) in the solid state via noncovalent interactions or metal-mediated assembly.[8,9] In particular, small organic molecules have been used as templates for the direct photoreaction of bpe to produce stereospecific *rctt*-tetrakis(4-pyridyl)cyclobutane (*rctt*-tpcb) in gram quantities.[8] Such photoreactions controlled by the packing of olefinic double bonds[3,4] in bpe result in the most favorable isomer *rctt*-tpcb, but other isomers such as *rtct*-tpcb are less available or inaccessible.[6,10,11] On the other hand, the *rtct*-tpcb isomer is formed in relatively higher yield by the isomerization of alkylated *rctt*-tpcb in solution.[7]

Organic spacers with pyridyl groups are attractive ligands in the construction of metallosupramolecular architectures[12] and metal−organic frameworks (MOFs).[13−20] Ligands acting as four connecting nodes bridging the metal secondary building units are used in the construction of MOFs,[14,15] and hence the tpcb ligands that can act as 4-connecting nodes are suitable for this purpose.[8,16] Although one-dimensional (1D), two-dimensional (2D), and capsule-like frameworks have

---

*To whom correspondence should be addressed. E-mail: chmjjv@nus.edu.sg.

(1) (a) Namyslo, J. C.; Kaufmann, D. E. *Chem. Rev.* **2003**, *103*, 1485–1537. (b) Lee-Ruff, E.; Mladenova, G. *Chem. Rev.* **2003**, *103*, 1449–1483.

(2) (a) Griesbeck, A. G.; Mattay, J. In *Synthetic Organic Photochemistry*; Marcel Dekker: New York, 2005. (b) Hoffmann, N. *Chem. Rev.* **2008**, *108*, 1052–1103.

(3) Schmidt, G. M. J. *Pure Appl. Chem.* **1971**, *27*, 467–678.

(4) (a) Ramamurthy, V.; Venkatesan, K. *Chem. Rev.* **1987**, *87*, 433–481. (b) Toda, F. *Acc. Chem. Res.* **1995**, *28*, 480–486. (c) Tanaka, K.; Toda, F. *Chem. Rev.* **2000**, *100*, 1025–1074.

(5) (a) Fagnoni, M.; Dondi, D.; Ravelli, D.; Albini, A. *Chem. Rev.* **2007**, *107*, 2725–2756. (b) Canales, E.; Corey, E. J. *J. Am. Chem. Soc.* **2007**, *129*, 12686–12687. (c) Ischay, M. A.; Anzovino, M. E.; Du, J.; Yoon, T. P. *J. Am. Chem. Soc.* **2008**, *130*, 12886–12887.

(6) (a) Vansant, J.; Toppet, S.; Smets, G.; Declercq, J. P.; Germain, G.; Meerssche, M. V. *J. Org. Chem.* **1980**, *45*, 1565–1573. (b) Vansant, J.; Smets, G.; Declercq, J. P.; Germain, G.; Meerssche, M. V. *J. Org. Chem.* **1980**, *45*, 1557–1565.

(7) Horner, M.; Hünig, S. *Liebigs Ann. Chem.* **1982**, 1183–1210.

(8) MacGillivray, L. R.; Papaefstathiou, G. S.; Friščić, T.; Hamilton, T. D.; Bučar, D.-K.; Chu, Q.; Varshney, D. B.; Georgiev, I. G. *Acc. Chem. Res.* **2008**, *41*, 280–291.

(9) (a) Nagarathinam, M.; Peedikakkal, A. M. P.; Vittal, J. J. *Chem. Commun.* **2008**, 5277–5288. (b) Vittal, J. J. *Coord. Chem. Rev.* **2007**, *251*, 1781–1795. (c) Nagarathinam, M.; Vittal, J. J. *Macromol. Rapid Commun.* **2006**, *27*, 1091–1099. (d) Toh, N. L.; Nagarathinam, M.; Vittal, J. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 2237–2241.

(10) (a) Briceño, A.; Fulgence, A.; Hill, Y.; Atencio, R. *Dalton Trans.* **2008**, 3275–3278. (b) Bruciño, A.; Leal, D.; Atencio, R.; Delgado, G. D. *Chem. Commun.* **2006**, 3534–3526.

(11) Natarajan, A.; Kaliappan, R.; Mague, J. T.; Ramamurthy, V. *Chem. Commun.* **2005**, 4542–4544.

(12) Steel, P. J. *Acc. Chem. Res.* **2005**, *38*, 243–250.

(13) (a) Ockwig, N. W.; Delgado-Friedrichs, O.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2005**, *38*, 176–182. (b) Batten, S. R.; Neville, S. M.; Turner, D. R. In *Coordination polymers: Design, Analysis and Application*; Royal Society of Chemistry: Cambridge, U.K., 2009.

(14) Kim, J.; Chen, B.; Theresa, M. R.; Li, H.; Eddaoudi, M.; Moler, D. B.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2001**, *123*, 8239–8247.

(15) Nitrogen-based ligand in a tetrahedral orientation: Dincă, M.; Dailly, A.; Long, J. R. *Chem.*—*Eur. J.* **2008**, *14*, 10280–10285.

(16) Bučar, D.-K.; Papaefstathiou, G. S.; Hamilton, T. D.; Chu, Q. L.; Georgiev, I. G.; MacGillivray, L. R. *Eur. J. Inorg. Chem.* **2007**, 4559–4568.

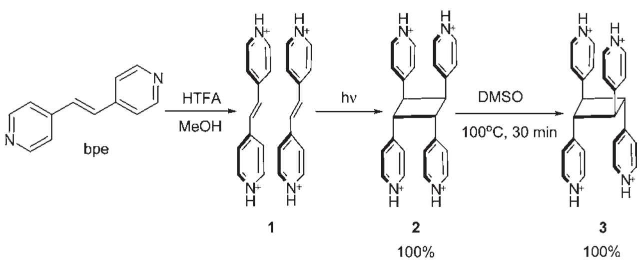
(17) Light-induced [2 + 2] dimerization resulting in 3D frameworks during crystallization: (a) Blake, A. J.; Champness, N. R.; Chung, S. S. M.; Li, W.-S.; Schröder, M. *Chem. Commun.* **1997**, 1675–1676. (b) Lee, J. Y.; Hong, S. J.; Kim, C.; Kim, Y. *Dalton Trans.* **2005**, 3716–3718.

(18) Mir, M. H.; Koh, L. L.; Tan, G. K.; Vittal, J. J. *Angew. Chem., Int. Ed.* **2010**, *49*, 390–393.

(19) Liu, D.; Li, H.-X.; Ren, Z.-G.; Chen, Y.; Zhang, Y.; Lang, J.-P. *Cryst. Growth Des.* **2009**, *9*, 4562–4566.

(20) **pts** and **ptt** nets: (a) Abrahams, B. F.; Hoskins, B. F.; Michail, D. M.; Robson, R. *Nature* **1994**, *369*, 727–729. (b) Park, K. M.; Iwamoto, T. *J. Chem. Soc., Chem. Commun.* **1992**, 72–74.

Scheme 1. TFA-Mediated Synthesis of *rctt*-tpcb Using the Photoreaction of **1** in the Solid State and the Selective Synthesis of *rtct*-tpcb via the Isomerization Reaction of **2** in the Solution Phase



been synthesized, three-dimensional (3D) frameworks using tpcb nodes remain a challenge,[16,17] the reason being that the stereochemistry of *rctt*-tpcb may not allow the formation of 3D frameworks easily. As a consequence, the 3D frameworks of tpcb have rarely been isolated during solution crystal growth in the presence of light[17] and single crystal-to-single crystal structural transformation.[18] On the other hand, the pyridyl groups in *rtct*-tpcb are oriented in a tetrahedral fashion, which makes it suitable for the fabrication of 3D frameworks.[19]

Our earlier work on the isomerization of cyclobutane derivatives in solution[21] prompted us to study the utility of trifluoroacetate (TFA) in the photoreactivity of bpe and trifluoroacetic acid (HTFA) in the isomerization of tpcb rings. Here we report the synthesis of *rctt*-tpcb and its isomerization to the *rtct* stereoisomer, as exemplified in Scheme 1. Further, *rtct*-tpcb has been employed to assemble MOFs having **ptt** and **pts** net topology.

The salt $[bpeH_2]\cdot 2TFA$ (**1**) was synthesized by the direct treatment of bpe with HTFA in methanol. The X-ray structure reveals an infinite hydrogen-bonded assembly of $[bpeH_2]^{2+}$ cations and $CF_3CO_2^-$ anions held together by N−H···O interactions [N1−H1···O7, 2.630(5) Å; N2−H2···O3, 2.623(5) Å; N3−H3···O2, 2.608(5) Å; N4−H4···O6, 2.620(5) Å] and further by very weak C−H···O and C−H···F interactions (Figure 1a), forming a 2D layer. Figure 1b shows three such adjacent but independent layers, namely, **A**···**B**···**C** running in the *b* direction. However, only the adjacent **C**···**C** layers are interacting through very weak F···F contacts[22,23] where the C=C bonds in the $[bpeH_2]^{2+}$ cations are oriented in a parallel fashion with a distance of 4.26 Å, which is somewhat longer to be photoreactive.[3] It may be noted that the distances between the olefinic double bonds of the nearest $[bpeH_2]^{2+}$ cations in the adjacent layers **A**···**A**, **A**···**B**, and **B**···**C** are 5.150−6.567 Å with a slip-stacked arrangement.

Interestingly, powdered **1** kept between the glass plates was irradiated under an UV lamp for a period of 24 h and produced $[rctt\text{-tpcb-}H_4]^{4+}$ (**2**) in 100% yield as determined by the ^{1}H NMR spectroscopy[24] in DMSO-d_6. Although the C=C bonds between **C**···**C** layers are likely to react under UV irradiation, the **A**···**B** and **B**···**C** layers are expected to be photostable because of the distance criterion. The quantitative dimerization of **2** can therefore be rationalized by the cooperative movements of layers during the photoreaction, and such cooperative molecular movements have been observed in the solid state before.[4,9]

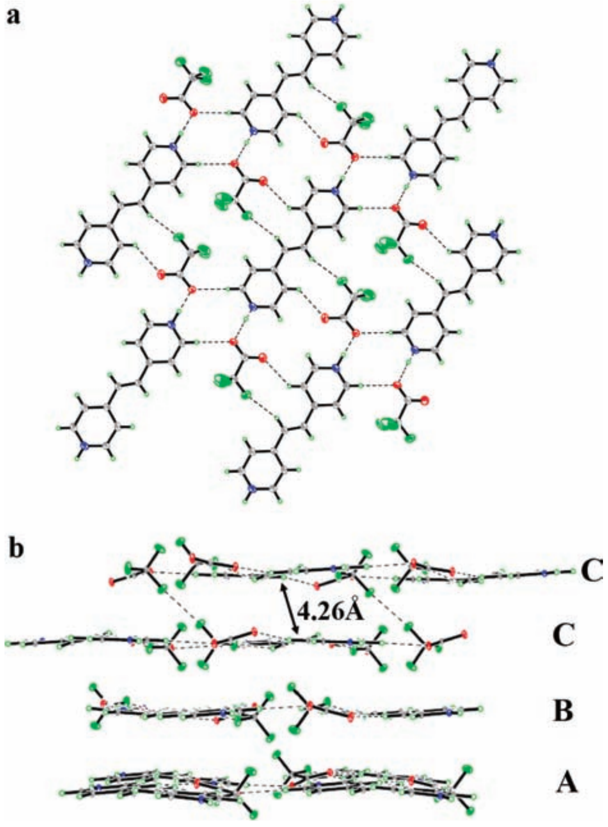


Figure 1. (a) Portion of the packing in **1**. The nitrogen (blue), oxygen (red), and fluorine (green) are as indicated. (b) Packing arrangement of 2D layers of **A**···**B**···**C**. The olefinic C=C bonds between the **C**···**C** layers are aligned in a parallel fashion with a distance of 4.26 Å.

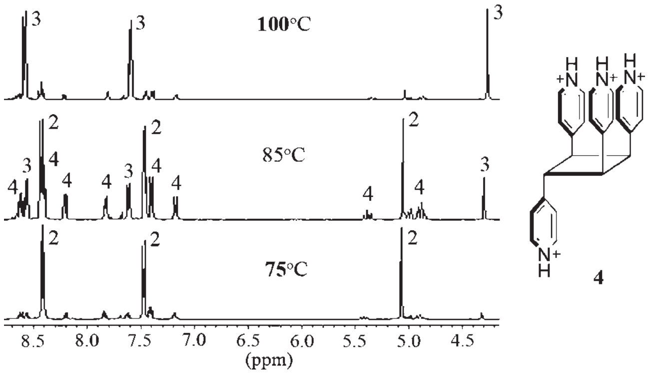


Figure 2. VT ^{1}H NMR spectra of photodimerized product **2** in DMSO-d_6. The spectra show the formation of protonated cyclobutane isomers *rctt*-tpcb, *rtct*-tpcb, and *rcct*-tpcb. The inset shows the structure of protonated *rcct*-tpcb.

Compound **2** undergoes an acid-catalyzed isomerization reaction in a DMSO-d_6 solution to give $[rtct\text{-tpcb-}H_4]^{4+}$ (**3**) and $[rcct\text{-tpcb-}H_4]^{4+}$ (**4**) in 4−5 days. Variable-temperature (VT) ^{1}H NMR studies[24] (from 25 to 100 °C at 10 °C intervals) show that the isomerization reaction becomes faster when the temperature is increased (Figure 2). Further, **3** turns out to be the major product at 100 °C (product distribution: **2**, 7.76%; **3**, 78.02%; **4**, 14.22%), and the isomerization is found to be irreversible. The neutral isomer *rtct*-tpcb can be conveniently

---

(21) Peedikakkal, A. M. P.; Vittal, J. J. *Chem. Commun.* **2008**, 441–443.
(22) Liu, J.; Wendt, N. L.; Boarman, K. J. *Org. Lett.* **2006**, 7, 1007–1010.
(23) Metrangolo, P.; Resnati, G. *Chem.—Eur. J.* **2001**, 7, 2511–2519.
(24) For details, see the Supporting Information.

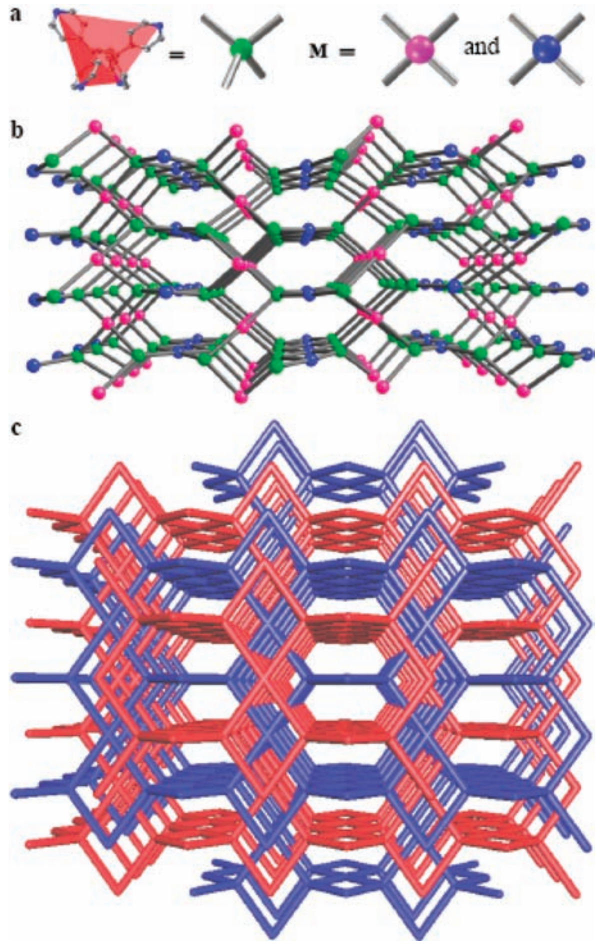


Figure 3. (a) Tetrahedral orientation of *rtct*-tpcb and a square-planar connector (M) = Zn^{II} and Co^{II}. Perspective views of (b) the **ptt** net in **5** and (c) two interpenetrated **pts** nets in **6**.

synthesized in 100% yield by heating photodimerized salts at 100 °C for 30 min and through further workup of **3**.

The isomer *rtct*-tpcb with a tetrahedral node has been used for the construction of two MOFs, namely, [Zn(*rtct*-tpcb)(H_2O)$_2$](ClO_4)$_2$·6.5H_2O (**5**) and [Co(*rtct*-tpcb)(F)$_2$]·5H_2O (**6**) (Figure 3). Colorless block crystals of **5** were obtained by layering a methanolic solution of *rtct*-tpcb on an aqueous solution of $Zn(ClO_4)_2 \cdot 6H_2O$. X-ray structure reveals that **5** forms 3D nets having **ptt** (twisted **pts**) topology[13,20] [Schläfli symbol is $(4.6^3.8^2)_2(4^2.6^2.8^2)$ $(6^2.8^4)$] (Figure 3b). There are two crystallographically independent Zn^{II} centers in **5** with octahedral geometry; each metal center is coordinated to four nitrogen atoms of the tetrahedrally disposed tpcb rings in a square plane, and two aqua ligands occupy the trans positions. The combination of a tetrahedral spacer and a square-planar metal connector yields **ptt** nets, which contain open pores in all three crystallographic directions. Especially, there are two kinds of pores along the *b* axis, having large honeycomb channels with opening dimensions of 9 × 19 Å and comparatively small rhombic channels with opening dimensions of 9 × 9 Å. The channels are loosely occupied with water molecules and disordered ClO_4^- anions. The empty space without the counterions and solvents in the cationic MOF **5** will account for ~61.7% of the unit cell volume.

Golden-yellow crystals of **6** were obtained by a solvothermal reaction of *rtct*-tpcb with $Co(OAc)_2.4H_2O$ and NaF. X-ray crystallography shows that the coordination environment in Co^{II} is very similar to that in **5** except that the F^- ions occupy the trans positions instead of the aqua ligands. The connectivity in **6** can be described as having **pts** topology if we consider that the Co^{II} center decorates the Pt position and the center of the cyclobutane ring of tpcb occupies the S position (Figure 3c). In the doubly interpenetrated **pts** net, five water molecules per formula unit fill up the pores present (17% solvent cavity).

Three topological nets commonly known by linking tetrahedral and square-planar units are **ptt**, **pts**, and **mog** (moganite).[13,20] Here, both **ptt** and **pts** nets look similar in their arrangement but differ in connectivity. The presence of ClO_4^- anions appears to prevent interpenetration by occupying the void space, thus influencing the formation of the **ptt** network in **5**. On the other hand, **6** forms doubly interpenetrated 3D networks with **pts** topology in the absence of any counterion. They can be considered as topological isomers.[25]

In summary, we report the stereospecific synthesis of *rtct*-tpcb, otherwise photochemically inaccessible in the solid state. This study shows that TFA plays a major role in the alignment of the C═C double bonds in bpe by weak F···F contacts, which undergoes a photochemical [2 + 2] cycloaddition reaction to furnish *rctt*-tpcb and further catalysis of the isomerization reaction to *rtct*-tpcb quantitatively in solution. This HTFA-catalyzed isomerization seems to be the easy way to access this isomer *rtct*-tpcb, which has tetrahedrally disposed pyridyl groups. Remarkably, *rctt*-tpcb displayed the ability to form MOFs with interesting topologies. Ongoing work is focused on the use of this ligand in constructing various supramolecular architectures.

Acknowledgment. Dr. Mangayarkarasi Nagarathinam is sincerely thanked for her help with powder X-ray diffraction and thermogravimetric analysis data and Geok Kheng Tan for X-ray data collection. We acknowledge the Ministry of Education for funding this project through NUS FRC Grant R-143-000-371-112.

Supporting Information Available: Experimental details, crystal data in CIF format, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

---

(25) Du, M.; Zhao, X. J.; Guo, J.-H.; Batten, S. R. *Chem. Commun.* **2005**, 4836–4838.