ORGANIC
LETTERS

2011
Vol. 13, No. 9
2260–2262

Resorcinol-Templated Synthesis of a Cofacial Terpyridine in Crystalline π-Stacked Columns

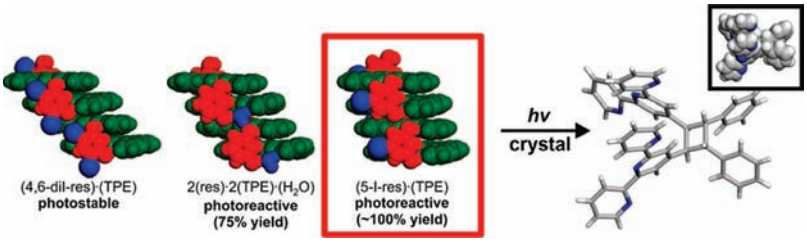
Saikat Dutta, Dejan-Krešimir Bučar, and Leonard R. MacGillivray*

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242-1294, United States

len-macgillivray@uiowa.edu

Received February 27, 2011

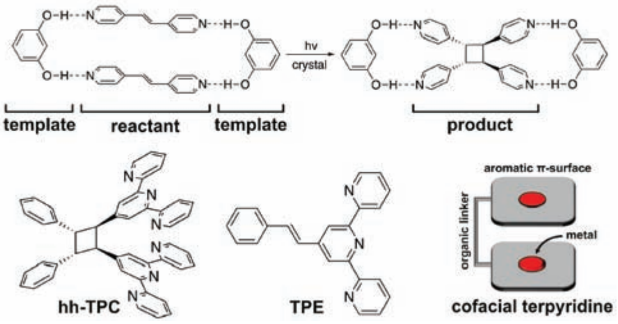
ABSTRACT



A resorcinol achieves a templated stereospecific and near-quantitative synthesis of a cofacial terpyridine in the solid state. The solid-state synthesis occurs in one-dimensional π-stacked columns with reactivities highly sensitive to peripheral groups attached to the template.

Small-molecule templates based on resorcinol (res)[1] can assemble olefins into discrete hydrogen-bonded assemblies in the solid state that become covalently fixed via [2 + 2] photodimerizations[2] to give architecturally rich molecules difficult to achieve in solution (e.g., [*n*]ladderanes) (Scheme 1). Here, we report the use of a res to construct the cofacial terpyridine (TPY) hh-TPC stereospecifically and in near quantitative yield in a solid. Cofacial molecules such as hh-TPC have been studied for over three decades as platforms to bind metal ions and recognize molecules with applications in catalysis, biomimicry, and self-assembly (e.g., porphyrins).[3] Despite significant advances, the solution-phase synthesis of cofacial molecules is often tedious, requiring multiple steps that proceed in low yields. Nguyen and Mirkin have shown how the synthetic problem can be addressed supramolecularly using a weak-link approach to coordination chemistry.[4] Since a cyclobutane ring from a [2 + 2] cycloaddition stacks two aromatics in close proximity, we endeavored to use a res to stack TPE noncovalently in a cocrystal[1] and then covalently fix the olefins to generate hh-TPC. Although TPY has widespread appeal

Scheme 1. Supramolecular Construction of hh-TPC



---

(1) 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.

(2) (a) Bhogala, B. R.; Captain, B.; Parthasarathy, A.; Ramamurthy, V. *J. Am. Chem. Soc.* **2010**, *132*, 13434–13442. (b) Grove, R. C.; Malehorn, S. H.; Breen, M. E.; Wheeler, K. A. *Chem. Commun.* **2010**, *46*, 7322–7324. (c) Kole, G. K.; Tan, G.-K.; Vittal, J. J. *Org. Lett.* **2010**, *12*, 128–131. (d) Amirakis, D. G.; Garcia-Garibay, M. A.; Rowan, S. J.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 4256–4261. (e) Tanaka, K.; Toda, F. *Chem. Rev.* **2000**, *100*, 1025–1074.

(3) (a) Collman, J. P.; Chong, A. O.; Jameson, G. B.; Oakley, R. T.; Rose, E.; Schmittou, E. R.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 516–533. (b) Chang, C. J.; Loh, Z. -H.; Shi, C.; Anson, F. C.; Nocera, D. G. *J. Am. Chem. Soc.* **2004**, *126*, 10013–10020.

(4) Oliveri, C. G.; Heo, J.; Nguyen, S. T.; Mirkin, C. A.; Wawrzak, Z. A. *Inorg. Chem.* **2007**, *46*, 7716–7718.

10.1021/ol200532t

as a building block in supramolecular chemistry,[5] only two cocrystals of a TPY had, to our surprise,[6] been reported while a photodimerization of a TPY had not been described in the solid state or solution. We show the assembly process of TPE and a series of res affords unexpected reactive hydrogen-bonded columns[7] that afford hh-TPC stereospecifically and in near-quantitative yield when a specific combination of template shape, hydrogen-bonding, and π-stacking of TPE is satisfied within the columnar structures. The ability of hh-TPC to form cofacial complexes with transition metals is also reported.

To determine the feasibility to construct hh-TPC in a solid, we first studied the photoreactivity of pure TPE.[8] Single crystals were obtained from hot hexane after cooling to room temperature in 1 day. The X-ray structure revealed the olefin to pack in a geometry expected to render TPE photostable (Figure 1).[9] The olefin adopted an *s-trans,s-trans* conformation[5] with nearest neighbor C=C bonds separated by 6.07 Å (centroid-to-centroid), well beyond the limit for photodimerization.[8] Upon exposure to medium-pressure Hg broadband UV radiation, TPE was photostable.

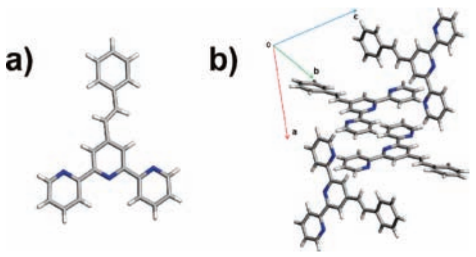


Figure 1. Structure of TPE: (a) *s-trans,s-trans* conformation and (b) packing.

Whereas pure TPE is photostable, TPE reacted in near-quantitative yield to give a cyclobutane product when 5-I-res was a template. Co-crystallization of TPE with 5-I-res from CH_3NO_2 afforded crystals of (5-I-res)·(TPE) upon evaporation. When powdered (5-I-res)·(TPE) was UV-irradiated for 3 days, TPE formed a cyclobutane in 98% yield, as evidenced by the disappearance of the olefinic protons (δ = 7.71, 7.55 ppm) and appearance of two cyclobutane protons (δ = 4.75, 5.00 ppm) (Supporting Information). The emergence of two peaks suggested that TPE reacted to give a head-to-head photoproduct.[1]

An X-ray structure analysis of (5-I-res)·(TPE) revealed the components to assemble, as expected, via O−H···N (O···N: 2.76 Å, 2.77 Å, 2.94 Å, 2.96 Å) hydrogen bonds (Figure 2). The assembly process, however, generated 1D columns[6] with adjacent olefins linked by offset 5-I-res molecules. Each TPE stacked head-to-head and adopted the *s-trans,s-trans* conformation, with the 2-pyridyl groups forming hydrogen bonds to the res. The C=C bonds were separated at 3.79 and 3.82 Å, which positioned TPE to react to give hh-TPC in the solid.

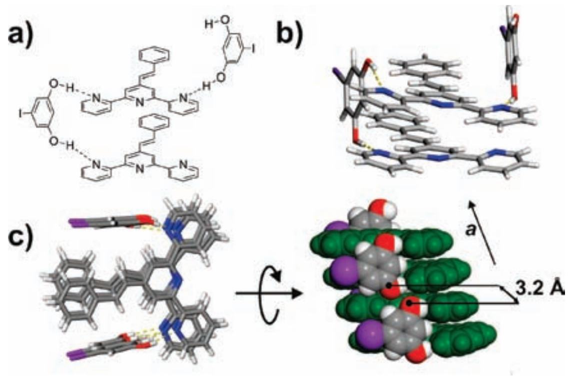


Figure 2. X-ray structure of (5-I-res)·(TPE): (a) schematic, (b) hydrogen bonding, and (c) overhead and side-on.

That TPE in (5-I-res)·(TPE) reacted to give hh-TPC was confirmed by X-ray diffraction. Single crystals of 2(5-I-res)·(hh-TPC) formed by allowing a CH_3NO_2 solution of the reacted solid to evaporate over 1 day. An X-ray analysis confirmed hh-TPC with TP groups stacked at 5.21 Å and twisted by 1.8° (Figure 3a), a geometry comparable to cofacial TP frameworks.[10] Remarkably, the components form a discrete six-component assembly sustained by eight O−H···N hydrogen bonds (O···N 2.73, 2.77, 2.77, 2.85 Å), with two 5-I-res that link two molecules of hh-TPC (Figure 3b). The generation of hh-TPC represents the first synthesis of a cofacial molecule in a solid.

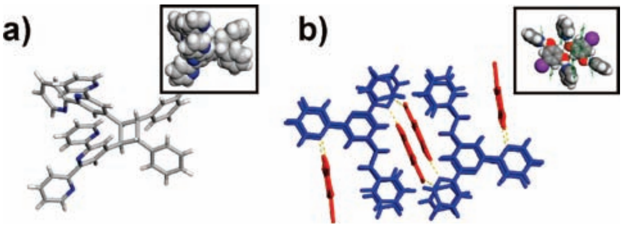


Figure 3. X-ray structure of 2(5-I-res)·(hh-TPC): (a) hh-TPC and (b) wireframe of six-component assembly (space-fillings insets).

---

(5) (a) Constable, E. C. *Chem. Soc. Rev.* **2007**, *36*, 246–253. (b) Flamigni, L.; Collin, J.-P.; Sauvage, J.-P. *Acc. Chem. Res.* **2008**, *41*, 857–871.

(6) (a) Messina, M. T.; Metrangolo, P.; Resnati, G.; Quici, S.; Pilati, T. *Supramol. Chem.* **2001**, *12*, 405–410. (b) Liantonio, R.; Logothetis, T. A.; Messina, M. T.; Metrangolo, P.; De Santis, A.; Pilati, T.; Resnati, G. *Collect. Czech. Chem. Commun.* **2002**, *67*, 1373–1382.

(7) Friščić, T.; MacGillivray, L. R. *Mol. Cryst. Liq. Cryst.* **2006**, *456*, 155–162.

(8) Novel synthesis based on: Kadjane, P.; Charbonnière, L.; Camerel, F.; Lainé, P. P.; Ziessel, R. *J. Fluoresc.* **2008**, *18*, 119–129.

(9) Schmidt, G. M. J. *Pure Appl. Chem.* **1971**, *27*, 647–678.

(10) (a) Crowley, J. D.; Bosnich, B. *Eur. J. Inorg. Chem.* **2005**, 2015–2025. (b) Betley, T. A.; Wu, Q.; Van Voorhis, T.; Nocera, D. G. *Inorg. Chem.* **2008**, *47*, 1849–1861.

To gain insight into the assembly and reactivity of TPE, the olefin was cocrystallized with the parent res and 4,6-di-I-res. X-ray analyses revealed columns, demonstrating robustness of the π-stacked structure. For res, a H_2O molecule assembled in 2(res)·2(TPE)·(H_2O), participating in hydrogen bonds that bridge adjacent res (O···O: 2.67 Å, 2.80 Å) and TPE molecules (O···N: 2.83 Å; O···O: 2.67) (Figure 4a). The C=C bonds were parallel and separated by 3.84 and 4.46 Å. UV-irradiation produced hh-TPC in 75% yield. For 4,6-diI-res, the res interacted, similar to (5-I-res)·(TPE), directly with each TPE via the O–H groups in (4,6-di-I-res)·(TPE) (O···N: 2.83 Å; 2.67) (Figure 4b). In contrast to (5-I-res)·(TPE), however, the C=C bonds adopted a *slipped and antiparallel* geometry, being separated by 4.63 Å. TPE was photostable in (4,6-di-I-res)·(TPE).

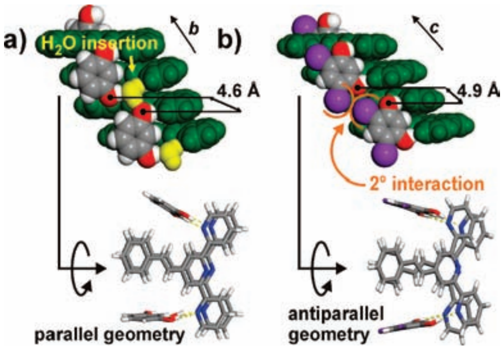


Figure 4. X-ray structures of stacked columns and olefin geometries: (a) 2(res)·2(TPE)·(H_2O) and (b) (4,6-diI-res)·(TPE).

The photostability of TPE in (4,6-di-I-res)·(TPE) can be attributed to van der Waals interactions of the *ortho* I-atoms along the exterior of each column. The interactions impart a larger separation distance, as revealed by separations of adjacent res molecules [O···O (Å) 5-I-res 3.2 (98% yield), res 4.6 (75% yield), 4,6-diI-res 4.9 (0% yield)] and, thus, disrupt stacking of TPE in each column (Figure 4b). For 2(res)·2(TPE)·(H_2O), such "secondary" interactions are absent (Figure 4a), with the "smaller" res allowing the H_2O molecule to fill space in the column. Indeed, the ability of hh-TPC to form in near-quantitative yield in (5-I-res)·(TPE) appears to be akin to hitting a "supramolecular sweet spot"[11] where template shape, hydrogen bonds, and π-stacking of TPE are satisfied to allow the C-atoms to move[12] and fully react in the solid. These observations are important since they suggest that a res can covalently fix olefins in infinite, as well as discrete, self-assembled structures.[1]

Preliminary studies demonstrate that the TPY units that span the cyclobutane ring of hh-TPC support cofacial complexes with transition-metal ions (Figure 5). When hh-TPC was reacted with either $ZnCl_2$ or $Cu(NO_3)_2$ from CH_3OH solutions of DMF and H_2O, colorless and green crystals of $[Zn_2(hh\text{-}TPC)_2Cl_4]$ and $[Cu_4(hh\text{-}TPC)_2(NO_3)_8]$ formed after slow evaporation in 5 days, respectively. In $[Zn_2(hh\text{-}TPC)_2Cl_4]$, each TPY group chelates, in the *s-cis, s-cis* conformation,[2,3] a $ZnCl_2$ moiety with the Zn(II) ions in distorted trigonal bipyramidal geometries and separated by 7.65 Å (Figure 5a). In $[Cu_4(hh\text{-}TPC)_2(NO_3)_8]$, each cofacial complex forms a U-shaped tetranuclear assembly with metal ions, which sit in an octahedral geometry, separated by 6.76 Å (Cu1····Cu2) and 6.69 Å (Cu1····Cu1) (Figure 5b). Studies are underway to further elucidate the coordination behavior of hh-TPC.

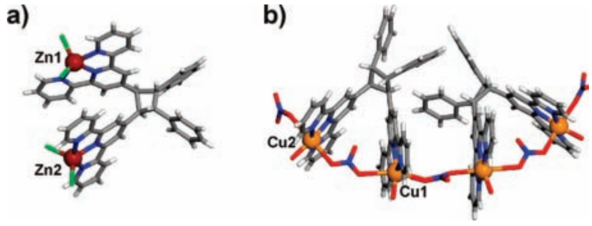


Figure 5. X-ray structures: (a) $[Zn_2(hh\text{-}TPC)_2Cl_4]$ and (b) $[Cu_4(hh\text{-}TPC)_2(NO_3)_8]$ (color code: Cl, green; Zn, brown; Cu, orange; O, red).

In this paper, the first synthesis of a cofacial molecule has been achieved in the solid state. hh-TPC has been generated 1D columns stereospecifically and in near-quantitative yield. The reactivity depends on secondary interactions of the template while the cofacial TP supports metal complexes. Our results add to a limited, yet growing, list of unusual molecules (i.e., ladderanes) constructed by fixing olefins in solids using templates.[1] We continue to identify targets of increasing complexity.

Acknowledgment. We thank the National Science Foundation (L.R.M., DMR-0133138) for support. We thank Elizabeth Elacqua for collection of spectral data.

Supporting Information Available. Details of syntheses, ^{1}H NMR spectra, and X-ray structure determinations. This material is available free of charge via the Internet at http://pubs.acs.org

---

(11) Gibb, B. C. *Angew. Chem., Int. Ed.* **2003**, *42*, 1686–1687.
(12) Garcia-Garibay, M. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 8945–8947.