

Discrete versus Infinite Molecular Self-Assembly: Control in Crystalline Hydrogen-Bonded Assemblies Based on Resorcinol

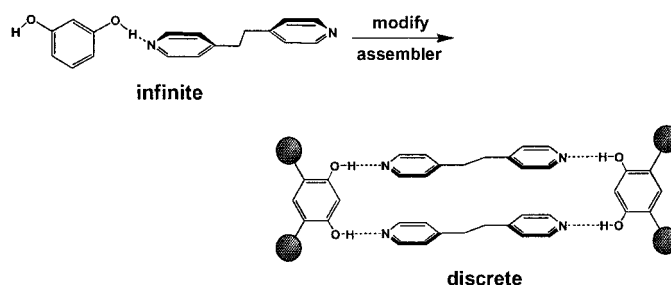
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ABSTRACT



Cocrystallization of 1,2-bis(4-pyridyl)ethane (4,4'-bipyeth) with resorcinol (res), 4-chlororesorcinol (4-Cl-res), and 4,6-dichlororesorcinol (4,6-di-Cl-res) yields molecular solids (4,4'-bipyeth)·(res) 1a, 2(4,4'-bipyeth)·2(4-Cl-res) 1b, and 2(4,4'-bipyeth)·2(4,6-di-Cl-res) 1c with components held together by O–H···N hydrogen bonds. In 1a the components form an infinite 1D polar array, whereas in 1b and 1c the components form 0D four-component complexes. Formation of the discrete assemblies is attributed to peripheral steric effects, which block the solid-state polymerization.

A major challenge facing chemists is an ability to control processes of molecular self-assembly.¹ Such processes involve designing molecules that organize by way of noncovalent forces (e.g., hydrogen bonds, π – π interactions) into molecular assemblies, typically of nanoscale dimensions,² that exhibit, in a way similar to that of biological systems (e.g., viruses), properties not provided by one of the constituent molecules (e.g., proteins). Although the process of molecular self-assembly may yield either zero- (0D), one- (1D), two- (2D), or three-dimensional (3D) frameworks, it remains difficult,^{3,4} owing to subtle structure

effects of molecular recognition,⁵ to preselect components that will assemble to form either a discrete (i.e., 0D) or infinite (i.e., 1D, 2D, or 3D) structure.^{3–5} An ability to establish such control of molecular structure promises to provide a route to molecules and materials with applications in catalysis, separations, and information storage, applications that may meet or surpass those of Nature.⁶

Our interests lie in using discrete hydrogen-bonded molecular assemblies, of nanoscale dimensions,² to control

(1) Fyfe, M. C. T.; Stoddart, J. F. *Acc. Chem. Res.* **1997**, *30*, 393.
(2) Drexler, K. E. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5275.
(3) Recent organic examples: (a) Zafar, A.; Geib, S. J.; Hamuro, Y.; Carr, A. J.; Hamilton, A. J. *Tetrahedron* **2000**, *56*, 8419. (b) MacGillivray, L. R.; Reid, J. L.; Ripmeester, J. A. *Chem. Commun.* **2001**, 1034. (c) Kolotuchin, S. V.; Zimmerman, S. C. *J. Am. Chem. Soc.* **1998**, *120*, 9092. (d) Jolliffe, K. A.; Timmerman, P.; Reinhoudt, D. N. *Angew. Chem., Int. Ed.* **1999**, *38*, 933.

(4) Recent inorganic examples: (a) Moulton, B.; Lu, J.; Mondal, A.; Zaworotko, M. J. *Chem. Commun.* **2001**, 863. (b) Eddaoudi, M.; Kim, J.; Wachter, J. B.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2001**, *123*, 4368. (c) Tabellion, F. M.; Seidel, S. R.; Arif, A. M.; Stang, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 7740. (d) Tabellion, F. M.; Seidel, S. R.; Arif, A. M.; Stang, P. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 1529.

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(6) (a) Whitesides, G. M.; Simanek, E. E.; Mathias, J. P.; Seto, C. T.; Chin, D. N.; Mammen, M.; Gordon, D. M. *Acc. Chem. Res.* **1995**, *28*, 37. (b) Lawrence, D. S.; Jiang, T.; Levett, M. *Chem. Rev.* **1995**, *95*, 2229.

chemical reactivity in organic solids.⁷ Specifically, we have shown that cocrystallization of resorcinol with the rigid, planar *trans*-1,2-bis(4-pyridyl)ethylene (4,4'-bpe) yields a discrete four-component assembly, 2(4,4'-bpe)·2(res) (where res = resorcinol) held together by four O–H···N hydrogen bonds, where two olefins of two bipyridines are preorganized in a stacked arrangement by the diol for [2 + 2] photo-reaction. By forcing the reaction to occur within a complex,⁸ this modular⁹ method eliminates vexatious problems of intermolecular forces that have made such topochemical designs unreliable,¹⁰ enabling, in a similar way as in solution, molecular synthesis by design.

During experiments aimed at extending this solid-state approach to alkyl functionality¹¹ using the flexible 1,2-bis-(4-pyridyl)ethane (4,4'-bipyeth) (Figure 1) as a model

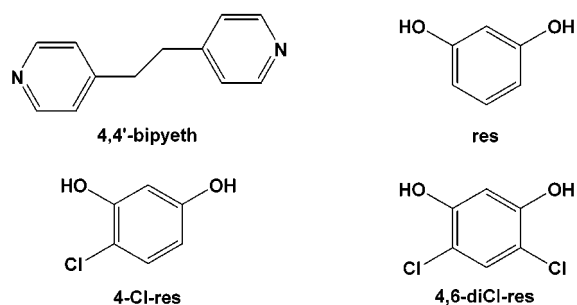


Figure 1.

substrate, we have discovered the ability of the parent resorcinol assembler,² in (4,4'-bipyeth)·(res) **1a**, to assemble with 4,4'-bipyeth to form an infinite 1D array where res adopts a divergent conformation¹² that precludes stacking of the bipyridine. Moreover, to achieve the targeted 0D assembly, we have discovered that it is necessary to derivatize the assembler,² in 2(4,4'-bipyeth)·2(4-Cl-res) **1b** and 2(4,4'-bipyeth)·2(4,6-diCl-res) **1c** (where 4-Cl-res = 4-chlororesorcinol and 4,6-diCl-res = 4,6-dichlororesorcinol), with substituents that possess an ability to block the solid-state polymerization and promote the diol to adopt a convergent conformation to give the 0D framework.⁶ In addition to facilitating enforced stacking of alkyl functionality in organic solids,¹¹ the application of the assembler derivative provides insight into factors that influence assembly processes that lead to either discrete or infinite molecular frameworks, which is of much current interest.^{3–5}

Single crystals of **1a** were grown by allowing a solution of 4,4'-bipyeth (0.012 g) and res (0.007 g) in acetonitrile (5

mL) to slowly evaporate to dryness during a period of 1 day. The composition of **1a** was confirmed by way of single-crystal¹³ X-ray diffraction and ¹H NMR spectroscopy.

An ORTEP perspective, as well a space-filling view, of **1a** is shown in Figure 2. In a similar way as for 2(4,4'-bpe)·

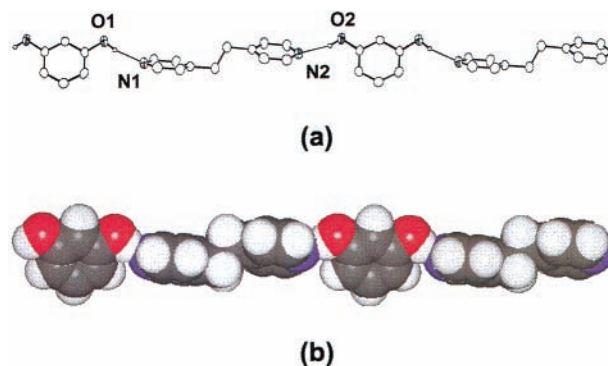


Figure 2. X-ray crystal structure of **1a**: (a) ORTEP perspective and (b) space-filling view. Selected interatomic distances (Å): O1···N1 2.729(2), O2···N2 2.700(3). Color scheme: red = oxygen, blue = nitrogen, gray = carbon, white = hydrogen.

2(res),^{7a} the components of **1a** assemble in the solid state by way of O–H···N hydrogen bonds [O···N separations (Å), O1···N1 2.729(2), O2···N2 2.700(3)] where two pyridyl units of 4,4'-bipyeth are twisted with respect to the benzene ring of the diol (twist angles (deg), N1 58.0, N2 45.8). In contrast to 2(4,4'-bpe)·2(res), however, the components of **1a** form an infinite 1D polar array where the hydroxyl groups of the resorcinol unit adopt a divergent conformation along the periphery of the molecule.^{12,14} In this arrangement, the bipyridines assume a conformation virtually identical to that of pure 4,4'-bipyeth¹⁵ where the ethane moiety and pyridyl units lie approximately orthogonal (dihedral angles (deg), C9–C10–C12–C13 84.3, C12–C13–C14–C17 81.5). As a consequence of these forces, the bipyridines have assembled such that the closest N(bipyridine)···C–H(resorcinol) separations involve the 4- and 6-positions of the diol. Adjacent 1D assemblies of **1a** pack, antiparallel, to give a 2D layered structure where the bipyridine and resorcinol components are organized in an offset manner.

The observation that 4,4'-bipyeth assembles with res to form an infinite 1D array prompted us to develop an alternative strategy to produce the targeted four-component complex. Indeed, that alkyl groups, in the form of hydrocarbon chains, may stack in organic solids is established,¹¹ and the known flexibility of 4,4'-bipyeth¹⁶ suggested that the molecule could be forced to adopt a planar conformation

(7) (a) MacGillivray, L. R.; Reid, J. L.; Ripmeester, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 7817. (b) MacGillivray, L. R.; Siebke, M. M.; Reid, J. L. *Org. Lett.* **2001**, *3*, 1257.

(8) Feldman, K. S.; Campbell, R. F. *J. Org. Chem.* **1995**, *60*, 1924.

(9) A modular approach involves two or more different components.

(10) Coates, G. W.; Dunn, A. R.; Henling, L. M.; Ziller, J. W.; Lobkovsky, E. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 3641.

(11) Hydrocarbon chain packing gives rise to laminated solids: (a) Menger, F. M.; Lee, J.-J.; Hagen, K. S. *J. Am. Chem. Soc.* **1991**, *113*, 4017. (b) Hitchcock, P. B.; Mason, R.; Thomas, K. M.; Shipley, G. G. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 3036.

(12) Bacon, G. E.; Jude, R. J. *Z. Kristallogr.* **1973**, *138*, 19.

(13) Crystal data for **1a**: crystal size 0.30 × 0.30 × 0.35 mm³, triclinic, space group *P* $\bar{1}$, *a* = 7.707(2) Å, *b* = 9.1462(2) Å, *c* = 11.804(2) Å, α = 87.94(3)°, β = 86.55(3)°, γ = 71.33(3)°, *U* = 786.8(3) Å³, 2θ = 45°, Mo K α radiation (λ = 0.71070 Å) for *Z* = 2 and *R* = 0.046.

(14) For a similar assembly involving benzoquinone, see: Ito, T.; Minobe, M.; Sakurai, T. *Acta Crystallogr., Sect. B* **1970**, *26*, 1145.

(15) Dihedral angle in pure 4,4'-bpe, 99.5°. See: Ide, S.; Karacan, N.; Tufan, Y. *Acta Crystallogr., Sect. C* **1995**, *C51*, 2304.

suitable for discrete assembly formation. Moreover, we reasoned that placement of single or multiple substituents in the 4- and/or 6-positions of res would enable the diol to direct stacking of 4,4'-bipeth within the targeted discrete structure (Figure 3).⁶ In addition to making the 1D hydrogen-

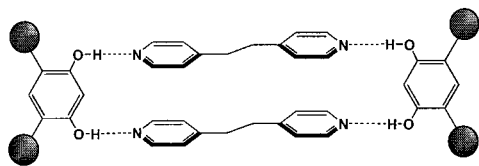


Figure 3.

bonded assembly energetically unfavorable by sterically protecting each "side" of the molecule,¹⁷ we anticipated that the positioning of the substituents near the hydroxyl groups would promote the hydrogen-bond donor functionality, by steric effects, to adopt a convergent conformation, the H-atoms being organized in a parallel fashion.¹⁸ Such substituents would, in effect, largely serve to preorganize¹⁹ the resorcinol derivative to form the targeted 0D array.

Crystals of **1b** and **1c** were grown by allowing a solution of 4,4'-bipyeth (0.012 g) and 4-Cl-res (0.009 g) or 4,6-di-Cl-res (0.011 g), respectively, in acetonitrile (5 mL) to slowly evaporate to dryness during a period of 1 day. The formulations of **1b** and **1c** were confirmed by way of single-crystal²⁰ X-ray diffraction and ¹H NMR spectroscopy.

ORTEP perspectives and space-filling views of **1b** and **1c** are shown in Figure 4. As anticipated, the components of **1b** and **1c** have assembled in the solid state to form discrete four-component complexes (assembly dimensions, $\sim 5 \times 22 \text{ \AA}$) held together by way four O—H \cdots N hydrogen bonds (O \cdots N separations (Å), O1 \cdots N1 2.727(4), O2 \cdots N2 2.706(4) for **1b**; O1 \cdots N1 2.677(3), O2 \cdots N2 2.679(3) for **1c**). In a similar way as for **1a**, the pyridine units are twisted with respect to the benzene ring of each diol (twist angles (deg), N1 61.1, N2 52.7 for **1b**; N1 86.3, N2 109.7 for **1c**). In this arrangement, the bipyridines lie stacked alongside each resorcinol unit where the methylene groups are aligned and separated by 4.13 Å in each solid. In contrast to **1a**, the

(16) Hennigar, T. L.; MacQuarrie, D. C.; Losier, P.; Rogers, R. D.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 972.

(17) We note other infinite assemblies may form.

(18) A search of the Cambridge Structure Database (Release 5.19, 2000, CCDC, Cambridge, U.K.) reveals 27 cocrystals involving resorcinol functionality with substituents located in the 4- and/or 6-position that are unable to form an intramolecular hydrogen bond with the adjacent hydroxyl group. In 26 cases, the hydroxyl moiety is directed away from the substituent.

(19) Cram, D. J. *Science* **1988**, *240*, 760.

(20) Crystal data for **1b**: crystal size $0.25 \times 0.28 \times 0.30 \text{ mm}^3$, monoclinic, space group $P2_1/n$, $a = 9.512(2) \text{ \AA}$, $b = 10.731(2) \text{ \AA}$, $c = 16.012(4) \text{ \AA}$, $\beta = 99.92(1)^\circ$, $U = 1609.9(7) \text{ \AA}^3$, $2\theta = 45^\circ$, Mo K α radiation ($\lambda = 0.71070 \text{ \AA}$) for $Z = 4$ and $R = 0.060$. Crystal data for **1c**: crystal size $0.20 \times 0.20 \times 0.25 \text{ mm}^3$, monoclinic, space group $P2_1/n$, $a = 9.254(2) \text{ \AA}$, $b = 11.684(2) \text{ \AA}$, $c = 15.949(3) \text{ \AA}$, $\beta = 97.13(3)^\circ$, $U = 1711.2(6) \text{ \AA}^3$, $2\theta = 45^\circ$, Mo K α radiation ($\lambda = 0.71070 \text{ \AA}$) for $Z = 4$ and $R = 0.036$.

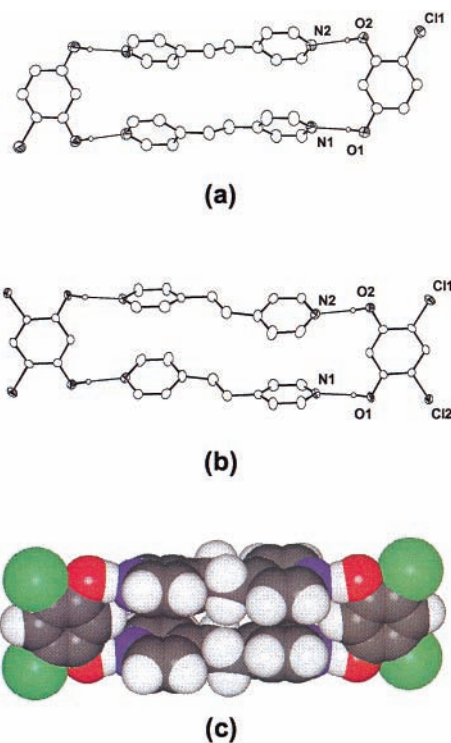


Figure 4. X-ray crystal structures of **1b** and **1c**: ORTEP perspectives of (a) **1b** and (b) **1c** and (c) space-filling view of **1c**. Selected interatomic distances (Å): O1 \cdots N1 2.727(4), O2 \cdots N2 2.706(4) for **1b**, O1 \cdots N1 2.677(3), O2 \cdots N2 2.679(3) for **1c**. Color scheme: green = chlorine.

bipyridines adopt an approximate planar conformation where the ethane moiety and pyridyl units are twisted toward coplanarity (dihedral angles (deg), C12—C13—C14—C17 46.0, C13—C12—C9—C10 144.7 for **1b**; C12—C13A—C14—C15 173.1, C13A—C12—C9—C10 165.9 for **1c**).²¹ Nearest-neighbor complexes of **1b** and **1c** assemble to form a 2D herringbone motif.²² Thus, in addition to promoting the formation of the 0D assembly, the substituents along the backbone of the resorcinol unit have enabled each derivative to effect the conformation of the bipyridine. Such supramolecular control of molecular conformation in an organic solid using a bifunctional molecule such as a resorcinol has, to our knowledge, not been demonstrated.²³

In this report, we have demonstrated control of a molecular assembly process that leads to either a discrete or infinite framework. By modifying a resorcinol assembler² with appropriately positioned functionality, we have shown that an infinite array may be converted to a discrete complex that is of nanoscale dimensions,² where enforced stacking of alkyl groups and control of molecular conformation has

(21) C13 of the ethane moiety in **1c** displays disorder across two sites [occupancies, 60 (C13A)/40 (C13B)].

(22) Desiraju, G. R.; Gavezzotti, A. *Acta Crystallogr., Sect. B* **1989**, *45*, 473.

(23) For a study involving a molecular capsule that facilitates supramolecular control of molecular conformation in solution, see: O'Leary, B. M.; Grotzfeld, R. M.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1997**, *119*, 11701.

been realized. Experiments are underway to extend the approach to substrates that combine alkyl groups and olefins where the targeted solid-state synthesis of products of diverse functionality may be achieved. Our observations augur well for an ability of this approach to enable such reliable engineering of reactivity in organic solids since a similar change to a linear template should provide access to a targeted reactive assembly.

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Supporting Information Available: Crystallographic reports and tables of positional and thermal parameters, bond lengths and angles, and NMR data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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