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Cooperative Polar Ordering of Acentric Guest Molecules in Topologically Controlled Host Frameworks

Jennifer A. Swift[†] and Michael D. Ward*

Department of Chemical Engineering and
Materials Science, University of Minnesota,
421 Washington Avenue, SE,
Minneapolis, Minnesota 55455

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The achievement of polar order in molecular crystals consisting of achiral components is one of the more intriguing challenges in organic solid-state chemistry. Polar order has been realized in numerous organic inclusion compounds based on urea, thiourea, and perhydrotriphenylene hosts, which have one-dimensional channels that confine polar head-to-tail chains of guest molecules.[1−5] Although a structure-directing role has been ascribed to thiourea hosts,[6] models for bulk polar ordering in these one-dimensional inclusion compounds largely have been based on direct head-to-tail contacts between guests.[5] We describe here the discovery of inclusion compounds in which a lamellar molecular host framework promotes polar alignment of guest molecules, orthogonal to the lamellae, through readily identifiable host−guest interactions.

Recently we reported a series of crystalline inclusion compounds based on lamellar host frameworks constructed from guanidinium and various organodisulfonate ions.[7−9] The organic residues of the organodisulfonate ions serve as molecular “pillars” that connect opposing two-dimensional hydrogen-bonded sheets of topologically complementary guanidinium (**G**) ions and sulfonate (**S**) groups, creating inclusion cavities between the **GS** sheets. The **GS** host frameworks are inherently pliant; puckering of the **GS** sheets and rotation and conformational twisting of the pillars serve to optimize host−guest packing. The **GS** host can also adapt to differently sized guests by forming a discrete “bilayer” or a lower density continuous “brick” architecture, the latter templated by larger guests or guest aggregates. Both architectures can be described as lamellae of alternating **GS** sheets and pillar−guest ensembles, but the two frameworks are principally distinguished by the number of **GS** sheets separating the guest layers (two for the bilayer and one for the brick) and an enforced offset of the inclusion cavities in adjacent layers of the brick framework.

We have observed several bilayer inclusion compounds with the composition $(\mathbf{G})_2(\mathbf{BPDS})\cdot$guest ($\mathbf{BPDS}$ = 4,4′-biphenyldisulfonate) in which acentric meta-substituted aromatic guests form polar motifs

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* To whom correspondence should be addressed; email: wardx004@tc.umn.edu.

[†] Current address: Department of Chemistry, Georgetown University, Box 571227, Washington, DC 20057.

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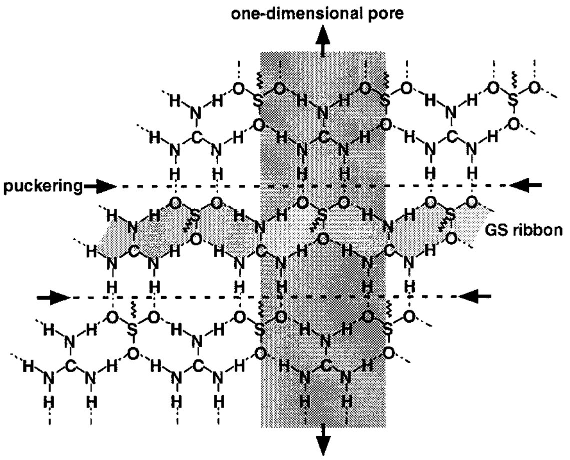
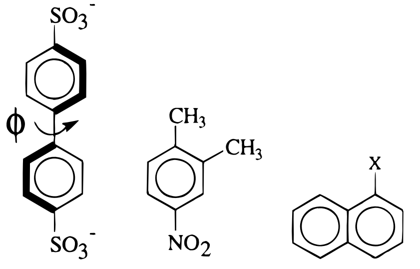


within the galleries.[7,10] However, antiparallel orientation of the guests in adjacent **GS** bilayers afforded bulk centrosymmetry. Despite numerous attempts using various pillars and guests, we have not observed bulk polar ordering in any bilayer framework. We have now discovered, however, that the $(\mathbf{G})_2(\mathbf{BPDS})$ *brick* framework supports polar ordering of the acentric guests nitro-*o*-xylene (NX), 1-nitronaphthalene (NN), 1-iodonaphthalene (IN), and 1-cyanonaphthalene (CN). These isomorphous inclusion compounds crystallize in the polar space group $Pna2_1$ with the compositions $(\mathbf{G})_2(\mathbf{BPDS})\cdot$NX (**I**), $(\mathbf{G})_2(\mathbf{BPDS})\cdot$NN (**II**), $(\mathbf{G})_2(\mathbf{BPDS})\cdot$IN (**III**), and $(\mathbf{G})_2(\mathbf{BPDS})\cdot$CN (**IV**).[11]



BPDS NX (I) X = NO_2 (II)
X = I (III),
X = CN (IV)

The biphenyl pillars[12] in these inclusion compounds define the walls of one-dimensional channels, oriented along the crystallographic *a* axis, that confine the guests within "pockets" between highly puckered (001) **GS** sheets (Figure 1). The puckering forces all the pillars in a given layer to tilt in the same direction, along the *a* axis, while reversing the tilt in the adjacent layers. The guest orientation along the *a* axis mimics this reversal within each layer. More important, the guest molecules exhibit polar alignment along the *c* axis such that the net orientation of their C−X dipoles is orthogonal to the (001) plane. The lamellar **GS** brick framework effectively isolates the guests in its puckered pockets so that direct guest−guest contacts are blocked within the layers by the pillars along *b* and between layers by the **GS** sheets along *c*. The brick framework enforces a pseudo-body-centered orthorhombic (pseudo-BCO) guest motif,[13] with the guests in adjacent layers offset along *a* and *b* such that direct head-to-tail alignment along the lamellar stacking direction, intervened by **GS** sheets, is impossible. The IN and CN guests of **III** and **IV** exhibit partial disorder about a noncrystallographic 2-fold axis along *a* and *b*, respectively.[14] This disorder and the observation of centrosymmetric $(\mathbf{G})_2(\mathbf{BPDS})$ brick framework inclusion compounds with centric guests[8] establish that the **GS** host framework itself is not intrinsically polar.

Four conceivable configurations of the guest dipoles in the pseudo-BCO lattice are depicted in Figure 2. Motif A represents the net polar ordering observed in **I**−**IV**. The hypothetical centrosymmetric motif B consists of polar layers aligned in opposite directions, whereas the hypothetical centrosymmetric motifs C and D have nonpolar layers. A rudimentary model demonstrates that guest−guest dipolar interactions would favor these motifs in the order C > D > A >B. However, dielectric screening by the ionic host[15] and the rather large distances between the dipoles in **I**−**IV**, enforced by the inclusion cavities of the host structure, conspire to reduce the structure-directing role of dipole−dipole interactions between guests. We note it has been argued that centric ordering in molecular crystals is not correlated with the dipole moments of the molecular constituents.[16]

The suppression of the dipolar contributions by the **GS** host provides an opportunity for other forces, including host−guest interactions, to direct guest ordering during formation of the inclusion compound. Indeed, short host−guest (**G**)N···O(nitro) contacts in **I** and **II** (2.978 and 2.967 Å, respectively) are less than the sum of the van der Waals radii[16] for these two heteroatoms (3.07 Å). The shortest (**G**)N···I and (**G**)N···N(cyano) contacts in **III** and **IV** (3.655 and 3.279 Å, respectively) slightly exceed the sum of their respective van der Waals radii (3.55 and 3.10 Å). The trend in these host−guest contacts and the observation of partial guest disorder in **III** and **IV** is consistent with the dipole moments of the guests (**I** > **II** ≥ **III** > **IV**),[17] supporting

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(10) Swift, J. A.; Reynolds, A. M.; Ward, M. D. *Chem. Mater.* **1998**, *10*, 4159.

(11) The inclusion compounds were crystallized in nearly quantitative yield at room temperature by slow evaporation of methanol solutions containing equimolar amounts of guanidine hydrochloride (Aldrich) and 4,4′-biphenyldisulfonic acid (TCI), in the presence of an excess of the appropriate guest. Lattice constants for the inclusion compounds: (**I**) $a = 15.5457(5)$, $b = 7.4379(2)$, $c = 23.7189(7)$, $R/R_w = 0.084/0.208$; (**II**) $a = 15.7309(8)$, $b = 7.3988(4)$, $c = 23.233(1)$, $R/R_w = 0.052/0.102$; (**III**) $a = 16.0943(3)$, $b = 7.4787(2)$, $c = 23.3874(5)$, $R/R_w = 0.049/0.132$; (**IV**) $a = 16.4448(4)$, $b = 7.3914(2)$, $c = 22.6154(2)$, $R/R_w = 0.047/0.107$. Presently, we have not observed any polymorphs of these materials.

(12) The values for the dihedral angle ϕ are as follows: **I**, 34.4°; **II**, 33.9°; **III**, 35.2°; and **IV**, 35.0°.

(13) This is described as a "pseudo" body-centered orthorhombic motif because the lattice representations in Figure 2 actually have dimensions corresponding to $a/2$, b, c due to the crystallographic inequivalence of adjacent guests in the *a*-axis channels.

(14) X-ray structure refinement suggested major:minor orientation ratios of 63:37 and 56:44 were measured for **III** and **IV**, respectively. The structure of **IV** was solved in the noncentrosymmetric $Pna2_1$ space group because the data supported an unequal population of the two guest orientations; however, the disorder closely approaches that expected for a centrosymmetric solution.

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(17) Reported dipole moments: μ(NX) = 4.82: Ivanov, M. G.; Zhuravlev, E. Z.; Dergunov, Yu. I.; Elizarova, T. P. *J. Gen. Chem. USSR* **1990**, *60*, 1078. μ(NN) = 4.00: Rampolla, R. W.; Smyth, C. P. *J. Am. Chem. Soc.* **1958**, *80*, 1057. μ(IN) = 3.99: Le Fevre, R. J.; Sundaram, W. A. *J. Chem. Soc.* **1962**, 4756. μ(CN) = 1.44: Jain, S. R.; Walker, S. *J. Phys. Chem.* **1971**, *75*, 2942.

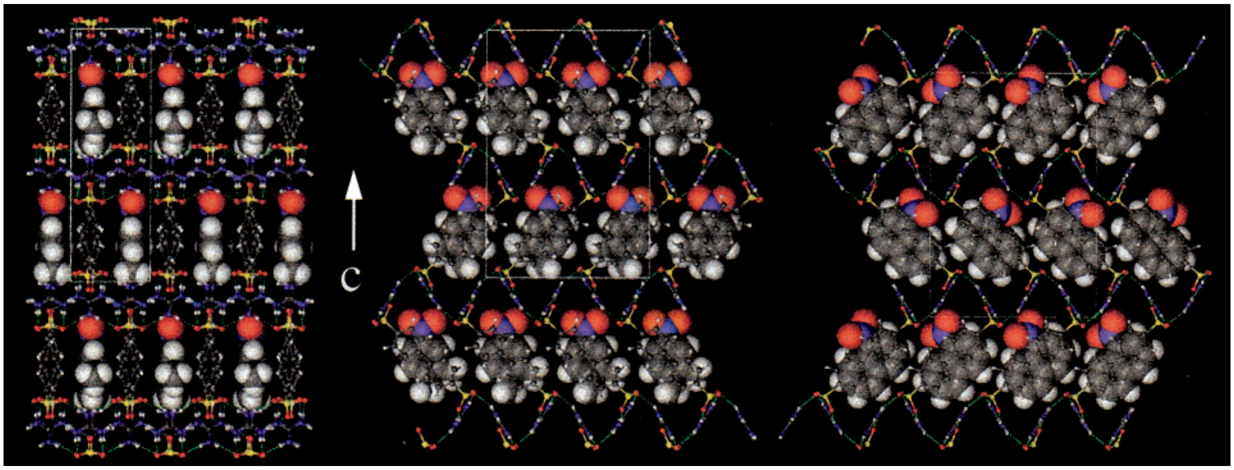

Figure 1. The molecular packing in crystals of $(\mathbf{G})_2(\mathbf{BPDS})$·(4-nitro-*o*-xylene) (**I**) (left, middle) and $(\mathbf{G})_2(\mathbf{BPDS})$·(1-nitronaphthalene) (**II**) (right). The left panel illustrates the guest organization in the channels of the brick framework of **I** as viewed down the *a* axis. The middle and right panels depict the guest organization in these channels, running left to right across the page. The **GS** ribbons, running along the *b* axis, are orthogonal to the page in the middle and right panels.

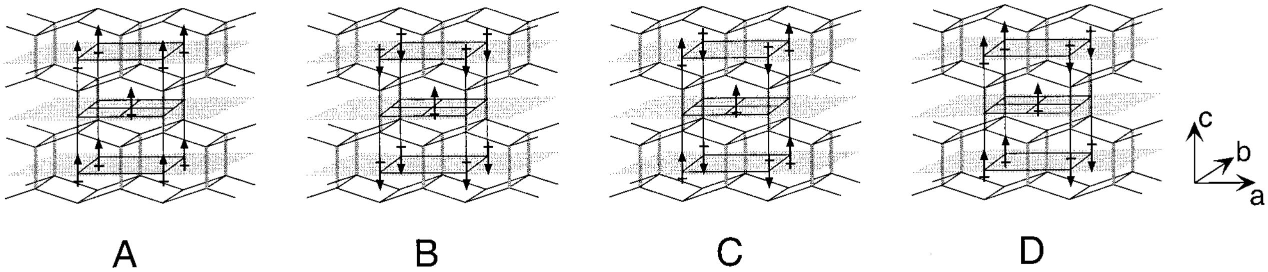

Figure 2. Schematic of four possible guest dipole motifs in the puckered pseudo body-centered orthorhombic $(\mathbf{G})_2(\mathbf{BPDS})$ brick framework: (A) observed polar ordering in which all dipoles are parallel; (B) a hypothetical nonpolar, centrosymmetric motif in which the orientation of polar guest layers is inverted in adjacent layers; (C and D) two hypothetical nonpolar centrosymmetric motifs in which the orientations of the guest dipoles alternate within each layer. The gray-shaded planes represent the infinite (001) lamallae of guests.

a structure-directing role for ion−dipole interactions resulting from these specific contacts. Although the contacts in **III** and **IV** exceed the van der Waals limit, ion−dipole interactions are long range ($1/r^2$).[18]

We anticipate that growth of **I**−**IV** occurs layer-by-layer[19,20] via simultaneous assembly of pillared lamellae and guest inclusion. Guest ordering will be influenced by the local environment during assembly of the inclusion cavities on the crystal surface. Figure 3 illustrates an edge-on view of the puckered host−guest lamellae corresponding to motifs A−D during stepwise crystal growth. Using **I** as a working example, inclusion of the NX guest in a puckered pocket brings its $C-NO_2$ substituent into near-equal proximity with *two* **G** ions (the next closest contact in **I** is 3.09 Å) at either the top or bottom of the pocket (Figure 3 is depicted as involving identical contact with two **G** ions, but the following arguments are valid for two inequivalent contacts in the puckered pocket). The path to the observed motif A involves ion−dipole interactions between $C-NO_2$ dipoles on every guest and all **G** sites at the bottom surface of a given **GS** sheet. Inductive effects would reduce the strength of ion−dipole interactions between these **G** sites and the $C-NO_2$ dipoles on guests approaching from above, in the antiparallel direction, during assembly of the next layer. This would prompt the guests in this emerging layer to orient parallel, as in path A, so that the same number of ion−dipole interactions can be achieved with the next **GS** sheet. Consequently, the contacts between the **G** ion and the $C-NO_2$ guest dipoles are uniform throughout the crystal, generating a continuous polar domain. In contrast, the path motifs B, C, and D produces **G** sites that *share* dipole contacts or are *devoid* of ion−dipole contacts. These sites would render motifs B−D, during crystallization and in the bulk crystal, energetically less

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[18] The crystal structures reveal N−H···heteroatom distances that are larger than conventionally accepted values for hydrogen bond distances, assuming ideal positions for the hydrogen atoms. [See: Taylor, R.; Kennard, O. *Acc. Chem. Res.* **1984**, *17*, 320; Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120.]

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[20] Real-time, in-situ atomic force microscopy performed in our laboratory has demonstrated that the growth of molecular crystals typically proceeds via layer-by-layer growth. (a) Carter, P. W.; Hillier, A. C.; Ward, M. D. *J. Am. Chem. Soc.* **1994**, *116*, 944−953. (b) Mao, G. Z.; Lobo, L.; Scaringe, R.; Ward, M. D. *Chem. Mater.* **1997**, *9*, 773. Compounds **I**−**IV** each exhibit a blocklike morphology, signifying roughly equal growth rates in the three principal lattice directions. We surmise this is a consequence of the favorable growth parallel to the GS sheet because of hydrogen bonding, and growth normal to the sheet promoted by the protruding pillars. (Crystals with the brick architecture as in **I**−**IV** cannot terminate with a molecularly smooth surface.) AFM investigations of the crystallization of these inclusion compounds are in progress.

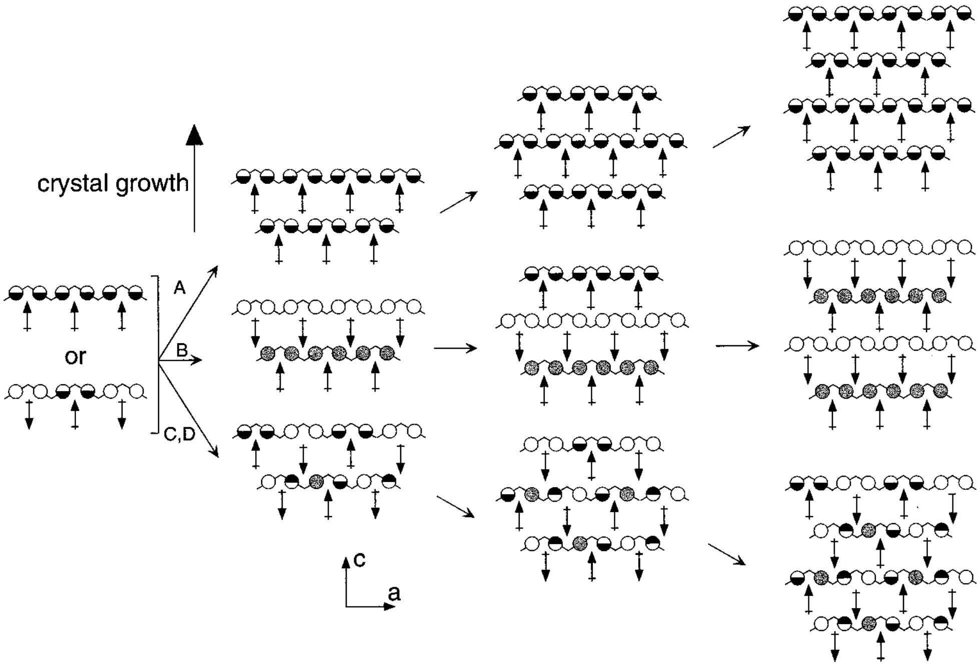

Figure 3. Schematic illustration of the layer-by-layer assembly of (A) polar and (B, C, and D) centrosymmetric domains formed during crystallization of the **GS** inclusion compounds, as viewed normal to the (010) plane (same view as the middle panel of Figure 1). The circles represent the **G** ions in the puckered pocket of the **GS** sheet. The contacts between the C−X guest dipoles (arrow end) and the two **G** ions in each pocket are depicted as either half-filled circles (one contact with the **G** ion from one side only, denoted by the black shading) or gray-shaded circles (shared contacts with the **G** ion by two antiparallel guests approaching from opposite sides of a sheet). **G** ions without C−X contacts are depicted as white circles.

favorable with respect to ion−dipole interactions.[21]

These inclusion compounds suggest that polar ordering can be achieved in lamellar host lattices that prohibit direct guest−guest dipolar contacts but allow cooperative host−guest interaction during crystal growth. We note that molecular modeling does not reveal any obvious directing influence on ordering along the *c* axis by the shape of the inclusion cavities. Polar guest alignment along the lamellar stacking direction is realized *even though the **GS** host framework itself is not intrinsically polar*, a phenomenon that can only be explained by cooperative effects during crystallization. It is interesting to note that these materials crystallize in the $Pna2_1$ space group, which belongs to the $mm2$ point group that is considered desirable for second-harmonic generation.[22] We anticipate that the ability to adjust the size and character of the inclusion cavities in **GS** frameworks through introduction of different organodisulfonate pillars will enable the inclusion of larger and more highly polarizable guests.

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Supporting Information Available: Tables of atomic coordinates and thermal parameters for compounds **I**−**IV** (also to be deposited in the Cambridge Crystallographic Database) and the calculations of the dipole−dipole energies of motifs A−D. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Interestingly, the dipole motifs in C and D closely resemble that in “spin frustrated” triangular Ising spin lattices, in which optimal antiferromagnetic alignment of neighboring spins is not achievable, making conditions for a ferromagnetic state more favorable. [Wannier, G. H. *Phys. Rev.* **1950**, *79*, 357. Bruinsma, R.; Aeppli, G. *Phys. Rev. B* **1984**, *29*, 2644.] Similarly, “dipole frustration” in motifs C and D would make motif A more favorable if dipole−dipole terms contribute to guest ordering.

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