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Designed Cocrystals Based on the Pyridine–Iodoalkyne Halogen Bond

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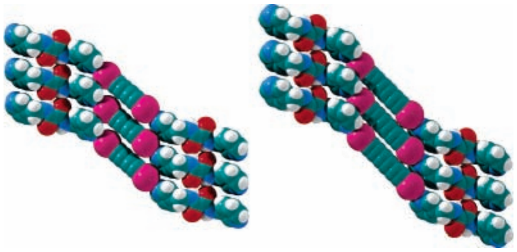
ABSTRACT



Diiodobutadiyne (1) and diiodohexatriyne (2) form cocrystals with bispyridyl oxalamides and ureas, based on the halogen bond between the alkynyl iodine and pyridine nitrogen. In each cocrystal, the oxalamide or urea host forms one-dimensional hydrogen-bonded networks, aligning the diiodopolyyne for potential topochemical polymerization with a repeat distance matching the host repeat.

Controlling the arrangement of small molecules in crystalline solids remains a challenge for materials chemistry. Chemists have demonstrated that both hydrogen bonding and π stacking can be used as noncovalent controls to prepare crystals with designed structures.[1] In contrast, halogen bonds, the noncovalent interactions between Lewis acidic halogen atoms and electron-pair-donating heteroatoms,[2] have been recognized as a significant force in crystal packing of many halogen-containing organic compounds[3,4] but have only recently attracted attention as potential guides for the formation of crystals of a specific desired structure. Reported examples have demonstrated that halogen bonding can provide local order.[3,5] We present here several examples of designed materials that combine halogen bonding of iodoalkynes with oxalamide or urea hydrogen bonding to create layered materials with predictable three-dimensional structures.

Iodoalkynes are good Lewis acids as a result of the polarizability of iodine and the higher electronegativity of sp-hybridized carbon.[6–8] Both diiodopolyynes **1** and **2** (Figure 1) form ordered crystals in the presence of Lewis bases.[9,10]

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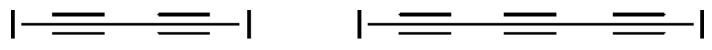
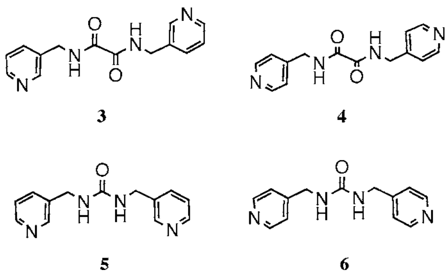


1 2

Figure 1. Diiodopolyynes **1** and **2**.

For example, we have used the Lewis acidity of **2** to prepare cocrystals with triphenylphosphine oxide, allowing for characterization of **2** by X-ray diffraction.[6] Yamamoto, Kato, and co-workers have built multicomponent solids containing iodoalkynes and organic radical cation salts, in which the molecular spacings are determined by halogen bonding between the iodoalkyne and the negative counterion of the salt.[4] In each of these examples, however, there were no expectations a priori for the overall organization of the crystal.

Bispyridyl oxalamides **3** and **4** and ureas **5** and **6** (Figure 2) are excellent cocrystallizing hosts to promote the ordered assembly of hydrogen-bond donors. The oxalamide or urea moieties are self-complementary hydrogen-bonding units that reliably form α networks,[11] leaving the pyridyl groups available for additional hydrogen bonding with the guest. In cocrystals of these hosts with diynyl carboxylic acids, hydrogen bonds between pyridine nitrogens and acid hydrogens align the diynes with appropriate orientation and repeat distance for topochemical 1,4-polymerization.[12]

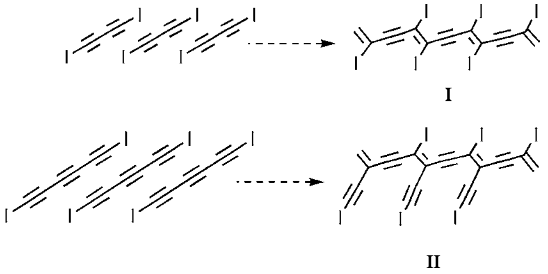


3 4 5 6

Figure 2. Bispyridyl compounds **3**−**6** act as Lewis basic hosts.

On the basis of the halogen bond that forms between pyridine and iodoalkynes,[8] we recognized that compounds **3**−**6** could also act as cocrystalizing hosts for compounds **1** and **2**, aligning the monomers for topochemical polymerization (Scheme 1). The resulting polymers **I** and **II** would be unique among polydiacetylenes in having iodine atom side groups. Polymer **I**, made up of only carbon and iodine, could be considered a precursor to iodine-doped carbyne.

Scheme 1. 1,4-Polymerization of **1** and **2** Would Give Polymers **I** and **II**

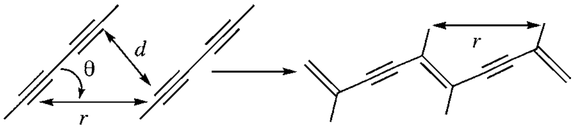


Compounds **3**−**6** each contain two pyridine rings that can form halogen bonds with **1** or **2**. To create cocrystals of these host molecules with each of the diiodopolyynes, a 1:1 mixture of the host and guest are dissolved in warm methanol. Slow evaporation of the solvent leads to X-ray quality crystals. Using this method, we have obtained cocrystals of **1** with each of the four host compounds and of **2** with hosts **3** and **4**.

Each of the cocrystals contains the two predicted structural motifs of the initial design: the oxalamide or urea units form hydrogen-bonding networks in one dimension, while the iodine atoms are in close contact with the pyridine nitrogens, controlling the alignment in the second dimension and leading to a layered material. The crystals each have the expected 1:1 stoichiometry. Figure 3 shows the structures of the cocrystals of diyne **1** with hosts **3** and **5** and of triyne **2** with host **3**, as determined by X-ray diffractometry.

Achieving topochemical polymerization to make a polydiacetylene requires that the monomer diyne units be arranged with a repeat distance (r) of $\sim$5 Å and an orientation angle (θ) of $\sim$45 ° relative to the translation axis, as shown in Scheme 2.[13] These structural guidelines bring C1 of one diyne into van der Waals contact with C4 of the next diyne, ($d \approx$3.5 Å), favoring 1,4-polymerization. Table 1 gives the values of these parameters for each of the prepared cocrystals.

Scheme 2. Structural Parameters that Control the Topochemical Polymerization of Diynes[a]



[a] Optimal values for 1,4-polymerization are $r = 4.9$ Å, $\theta = 45°$, and $d = 3.5$ Å.[13]

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(9) Rod-shaped molecules **1** and **2** each form disordered needle-shaped crystals on their own. For synthetic procedure for **1**, see ref 9; for **2**, see ref 7.

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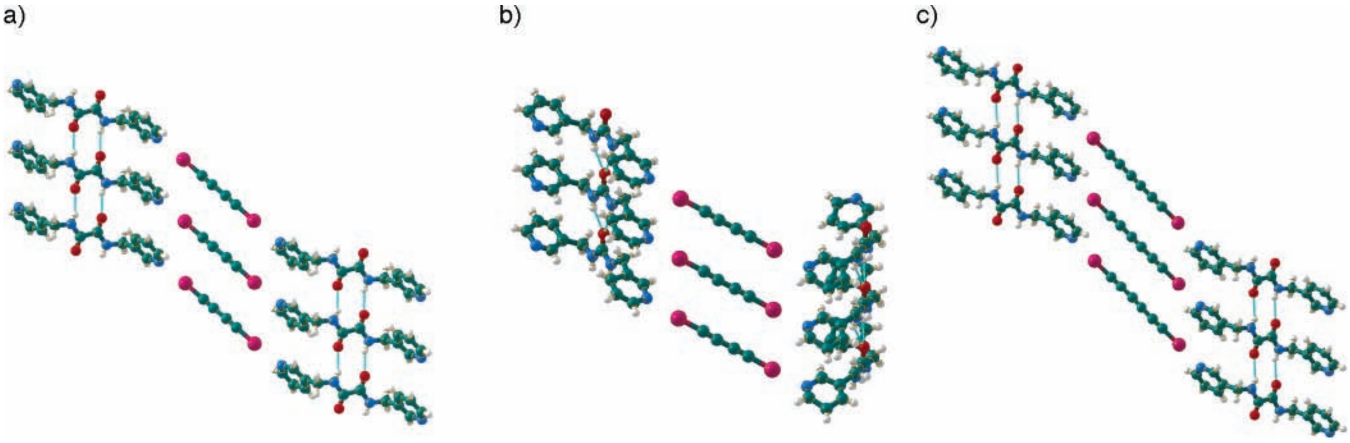

Figure 3. Cocrystals of (a) diyne **1** with oxalamide **3**, (b) diyne **1** with urea **5**, and (c) triyne **2** and oxalamide **3**.

Although each crystal displays the desired halogen and hydrogen bonding patterns, they show significant variation in repeat distance (r) and tilt angle (θ), and therefore in the C1−C4 distance (d). Oxalamide **3**, with 3-pyridyl ends, provides the most favorable geometric parameters. In the **1·3** cocrystal, $d = 3.90$ Å, smaller than the intermolecular close contacts in other successful topochemical polymerizations.[14] In the **2·3** cocrystal, d is even smaller, at 3.67 Å, but the repeat distance ($r = 5.28$ Å) is longer than the desired value for the target polymer. Cocrystals **1·3** and **2·3** undergo a visible color change, from colorless or pale yellow to shiny gray, over a few days at room temperature or several weeks at −15 °C. However, X-ray diffraction studies on the darkened **1·3** cocrystals indicate no change in overall structure and no significant polymerization. Likewise, the crystals turn dark under heat, UV irradiation, or γ-rays, but none of these treatments leads to an observable difference in the crystal structure. The color changes may indicate initial reaction, but the relatively long repeat distances in cocrystals **1·3** and **2·3** disfavor propagation of reaction along the chain of monomers.

Table 1. Structural Parameters of the Cocrystals

cocrystal	r	θ (deg)	d^a (Å)
1·3	5.11	51	3.90
1·4	5.02	65	4.89 (4.65)
1·5	4.53	63	4.36
1·6	4.52	68	4.74 (4.24)
2·3	5.28	44	3.67
2·4	4.97	63	4.67 (4.53)

[a] Intramolecular C1−C4 distance. (The intramolecular C1−C2 distance is given in parentheses where this distance is smaller.)

In contrast, cocrystals **1·4** and **2·4** have promising repeat distances, but steric repulsion leads to large tilt angles in each, so that the C1−C4 intermolecular contacts are longer than the C1−C2 contacts for these crystals. Both **1·4** and **2·4** are stable at room temperature for weeks and at −15 °C indefinitely.

The cocrystals presented here demonstrate that halogen bonding can control ordered assembly of diiodopolyynes such as **1** and **2**. However, the greater steric requirement of the halogen atom in these compounds presents an additional challenge for achieving a suitable supramolecular structure for topochemical polymerization. We are currently addressing this issue by using high pressure and by altering the host structure to accommodate the greater size of the iodine atom.

Supporting Information Available: Structural images and data for all cocrystals in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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