Supramolecular Chemistry

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Discrete Double-to-Quadruple Aromatic Stacks: Stepwise Integration of Face-to-Face Geometries in Cocrystals Based on Indolocarbazole**

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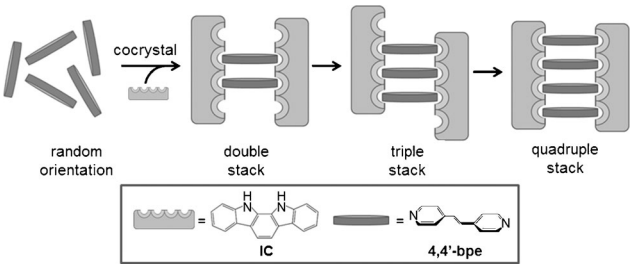
Stacks of aromatic molecules are of great importance in nature and chemistry.[1] The ability to engineer well-defined stacks is expected to foster expedited development of advanced supramolecular materials with unique properties.[2] Much effort has been placed on the development of reliable approaches to stack aromatic compounds based on covalent,[3] metal–ligand,[4] hydrogen-bonding,[5] arene–arene,[6] and electrostatic forces.[7] However, parallel face-to-face arrangements of aromatic units are energetically less favorable,[8] and, as addressed by Fujita et al., engineering discrete, moderate-sized aromatic stacks remains a challenge.[9] In fact, the formation of discrete stacks of more than three aromatic units that is mediated by multicomponent self-assembly has only been achieved with the assistance of either metal–ligand forces (for example, capsules)[9] or electrostatic forces (for example, molecular tweezers) thus far.[10] The ability to stack aromatic compounds in a modular fashion, particularly in the solid state, would grant access to tunable materials with targeted properties.[2]

Indolocarbazoles are molecules based on a conjugate aromatic system of two pyrrole and three benzene rings.[11] The pyrrole rings, which present two rigidly disposed hydrogen-bond-donor N–H groups, are known to bind strongly to negatively charged species. Thus, in supramolecular chemistry, indolocarbazoles are employed as potent anion receptors.[12] The N–H groups, however, have remained largely unexplored for applications in the solid state. In principle, the N–H groups can effectively equip indolocarbazoles to become novel molecular receptors in solids.

Herein, we report an integration of aromatic stacks into discrete assemblies that is based on hydrogen bonds in the solid state. We used indolo[2,3-*a*]carbazole (IC) to organize *trans*-1,2-bis(4-pyridyl)ethylene (4,4′-bpe) into double, triple, and quadruple stacks within cocrystals of $(IC)_2(4,4'\text{-bpe})_2{\cdot}2(MeCN)$, $(IC)_2(4,4'\text{-bpe})_3$, and $(IC)_2(4,4'\text{-bpe})_4$, respectively (Scheme 1). In each case, IC interacts with 4,4′-bpe through N–H···N hydrogen bonds that enforce aromatic stacking exclusively in a face-to-face manner. We also show that UV irradiation of $(IC)_2(4,4'\text{-bpe})_4$ induces the olefin to undergo a topochemical [2+2] photodimerization to afford



Scheme 1. Integration of 4,4′-bpe into double-to-quadruple discrete stacks enforced by IC.

rctt-tetrakis(4-pyridyl)cyclobutane (4,4′-tpcb) stereoselectively, owing to the enforced quadruple stacking.

Our interest in IC stems from the use of small molecules as templates to direct reactivity in solids.[13] We hypothesized that the N–H groups of IC form hydrogen bonds with a hydrogen bond acceptor such as the bipyridine 4,4′-bpe to enforce a stacking geometry suitable for photodimerization.[14] To better understand the binding motifs of IC in a solid, we first determined the crystal structure of IC.

Slow evaporation of an acetonitrile (MeCN) solution of IC yielded colorless plate-like crystals that were suitable for single-crystal X-ray diffraction. IC crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit consists of two molecules of IC in a distorted edge-to-face, or T-shaped, arrangement with an angle between the planes of 64.2° (Figure 1a). The distances between the pyrrole N atoms

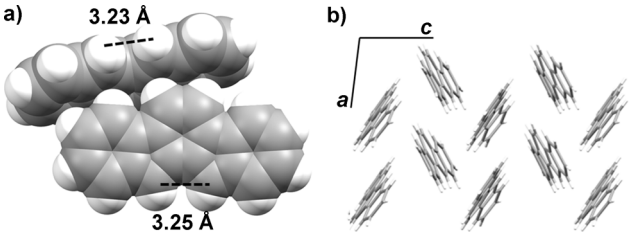


Figure 1. X-ray structure of IC: a) N···N distance and edge-to-face interaction in a space-filling model, and b) extended packing viewed along the *b* axis.

(3.23 Å and 3.25 Å) are comparable to the ones of the N–H groups involved in anion coordination (ca. 3.10–3.25 Å),[12] yet less than those of the hydroxy O atoms of resorcinol-based templates (ca. 4.8 Å).[15] When viewed along the *b* axis, the extended packing is of a herringbone pattern, similar to the one observed for high-pressure benzene[16] and naphtha-

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lene,[17] where each IC interacts with four neighbors through N–H···π and C–H···π forces (Figure 1b).

We next determined the ability of IC to act as a molecular receptor in a solid. Thus, IC and 4,4′-bpe were individually dissolved in a minimal amount of MeCN (1:1 molar ratio). Upon mixing, pale-yellow plate-like crystals grew in less than 1 h. ^{1}H NMR spectroscopy revealed the solid to consist of IC, 4,4′-bpe, and MeCN in a 1:1:1 ratio.

Crystal structure analysis confirmed IC to interact with 4,4′-bpe in the cocrystal solvate $(IC)_2(4,4'\text{-bpe})_2\cdot 2\,MeCN$. The components crystallize in the monoclinic space group $P2_1/n$ with an asymmetric unit that consists of one IC, one 4,4′-bpe, and one MeCN molecule. IC and 4,4′-bpe interact through a cyclic array of four N–H···N bonds (d(N···N) = 2.885(3) and 2.937(3) Å) to give a discrete four-component assembly (Figure 2a). The tilt angle between IC and 4,4′-bpe

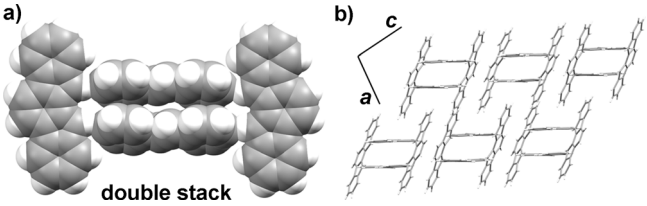

Figure 2. X-ray structure of $(IC)_2(4,4'\text{-bpe})_2\cdot 2\,MeCN$: a) space-filling model, and b) extended packing viewed along the *b* axis (solvent omitted for clarity).

is 66.3°. Moreover, two molecules of 4,4′-bpe lie stacked in a face-to-face geometry, and are offset by approximately 0.5 Å. The stacked C=C bonds of 4,4′-bpe lie parallel to each other, and are separated by 3.85 Å. The assemblies pack in an interdigitated fashion, with IC atop 4,4′-bpe (Figure 2b). The included MeCN interacts with IC through C–H···N(MeCN) forces. To our knowledge, $(IC)_2(4,4'\text{-bpe})_2\cdot 2(MeCN)$ is the first example of a cocrystal that is based on an indolocarbazole.[18]

During the course of our experiments, we also obtained crystals of a habit different to that of $(IC)_2(4,4'\text{-bpe})_2\cdot 2\,MeCN$. More specifically, when cocrystallization was performed using a 1:2 molar ratio of IC and 4,4′-bpe, rapid precipitation from MeCN afforded colorless needle-like crystals. ^{1}H NMR spectroscopy revealed the crystals to consist of IC and 4,4′-bpe in a 2:3 ratio.

To our surprise, crystal structure analysis revealed IC to interact with three molecules of 4,4′-bpe, thus enforcing triple stacking in cocrystals of the composition $(IC)_2(4,4'\text{-bpe})_3$. The components crystallize in the monoclinic space group $P2_1/c$, with an asymmetric unit that consists of two molecules of IC, and two full and two half molecules of 4,4′-bpe. As with $(IC)_2(4,4'\text{-bpe})_2\cdot 2(MeCN)$, the components are sustained by four N–H···N hydrogen bonds (d(N···N) = 2.903(3), 2.906(3), 2.988(3), and 2.991(3) Å; Figure 3a). In contrast to $(IC)_2(4,4'\text{-bpe})_2\cdot 2(MeCN)$, the IC molecules lie offset in such a way that only the central molecule of 4,4′-bpe (molecule **A**) is bridged by two N–H···N forces. Each remaining N–H group of IC participates in a single N–H···N hydrogen bond with 4,4′-bpe

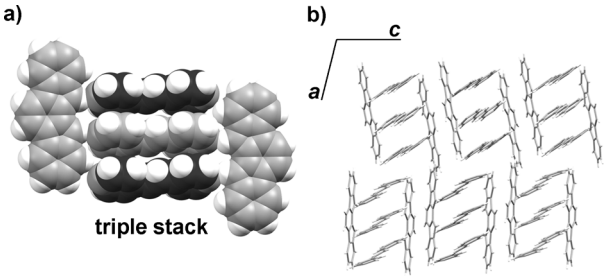

Figure 3. X-ray structure of $(IC)_2(4,4'\text{-bpe})_3$: a) space-filling model, and b) extended packing viewed along the *b* axis.

(molecule **B**). The remaining N atoms of 4,4′-bpe form C–H···N forces with IC (d(C···N) = 3.410(5) and 3.473(5) Å). As a consequence of the assembly process, the components form a discrete five-component assembly that is based on enforced triple stacking. The tilt angles between the planes of IC and 4,4′-bpe are 65.0° (**A**) and 67.7° (**B**). Thus, the stacking of the three 4,4′-bpe molecules is manifested in a face-to-face BAB manner. The C=C bonds of the stacked olefins lie parallel with the C atoms that are separated by 3.82 and 3.84 Å. Adjacent assemblies pack interdigitated and offset (Figure 2b). We are unaware of a report of enforced aromatic stacking of three molecules within a discrete, self-assembled, purely organic structure.[19] The work of Fujita et al. has described double-to-quintuple stacks hosted by metal–organic coordination cages.[10]

Remarkably, when the crystallization conditions to generate triple-stacked $(IC)_2(4,4'\text{-bpe})_3$ were extended to periods of days, slow precipitation of IC and 4,4′-bpe from a MeCN solution in 1:2 molar ratio afforded colorless plate-like crystals, with a composition of $(IC)_2(4,4'\text{-bpe})_4$, as determined by ^{1}H NMR spectroscopy.

Crystal structure analysis of $(IC)_2(4,4'\text{-bpe})_4$ revealed discrete six-component assemblies, which crystallize in the monoclinic space group $P2_1/c$, and feature quadruple stacking of 4,4′-bpe (Figure 4a). In this arrangement, which is analogous to the one of double-stacked $(IC)_2(4,4'\text{-bpe})_2\cdot 2\,MeCN$, the components are held together by a cyclic array of four N–H···N hydrogen bonds (d(N···N) = 2.982(7) and 2.928(6) Å). More specifically, the quadruple stacking is defined by two inner molecules of 4,4′-bpe (**A**), which

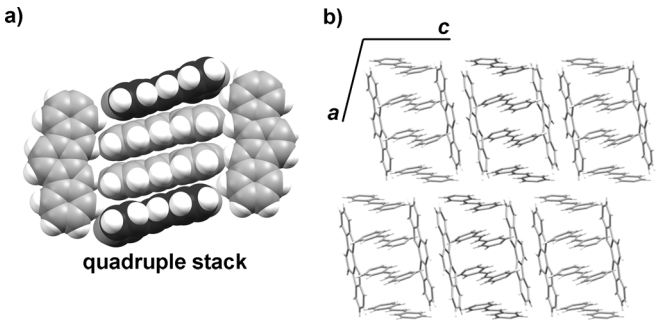

Figure 4. X-ray structure of $(IC)_2(4,4'\text{-bpe})_4$: a) space-filling model, and b) extended packing viewed along the *b* axis (disorder omitted for clarity).

participate in the N–H···N forces, and two outer molecules (**B**), which form single C–H···N forces (d(C···N) = 3.493(9) Å). The C=C bonds of the stacked **A** molecules lie in a disordered fashion (occupancies: 0.63/0.37) over two sites. Consequently, the molecules that define the quadruple stacks pack in a face-to-face **BAAB** manner. The planes between IC and 4,4′-bpe are tilted at 79.4° and 89.1° for the **A** and **B** molecules, respectively, and are therefore closer to orthogonality than for $(IC)_2(4,4'\text{-bpe})_2{\cdot}2(MeCN)$ and $(IC)_2(4,4'\text{-bpe})_3$. The C=C bonds between stacked **A**–**A** and **A**–**B** pairs are separated by 3.91 Å and 3.94 Å, respectively. Similar to $(IC)_2(4,4'\text{-bpe})_3$, the assemblies lie in an interdigitated fashion (Figure 4).

The face-to-face stacking of 4,4′-bpe, and the proximity of the C=C bonds in each cocrystal, prompted us to study a possible [2+2] photodimerization in each solid.[14] In a typical experiment, a cocrystal (50 mg) was placed between two glass plates as a thin film, and exposed to broadband UV irradiation. Whereas $(IC)_2(4,4'\text{-bpe})_2{\cdot}2$ MeCN and $(IC)_2(4,4'\text{-bpe})_3$ were photostable,[20] the olefins of $(IC)_2(4,4'\text{-bpe})_4$ underwent a photodimerization to generate 4,4′-tpcb in ca. 40% yield after 60 h. The yield is consistent with a reaction of $(IC)_2(4,4'\text{-bpe})_4$ that involves the two inner disordered **A** molecules of 4,4′-bpe of the quadruple stack.[21] Thus, IC serves as a template to direct the [2+2] photodimerization in a solid.

Cocrystallization experiments confirmed the stereochemistry of 4,4′-tpcb and revealed IC and 4,4′-tpcb to interact through hydrogen bonds, similar to a resorcinol-based template.[13] Thus, when hot MeCN and chloroform solutions of IC and 4,4′-tpcb were combined, plate-like and pale-orange single crystals of (IC)(4,4′-tpcb) formed after a period of approximately one day. The components crystallize in the monoclinic space group $P2_1/c$, with a full molecule of IC and 4,4′-tpcb in the asymmetric unit (Figure 5). The components,

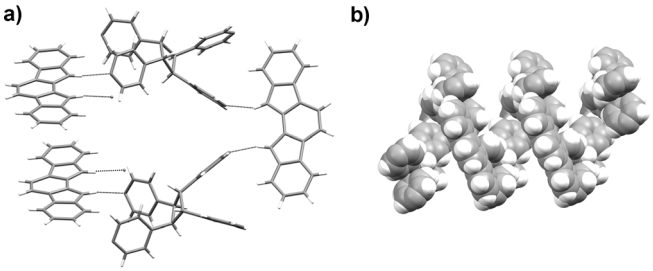

Figure 5. X-ray structure of (IC)(4,4′-tpcb): a) N–H···N forces between 4,4′-tpcb and IC, and b) space-filling model of the 1D structure.

as for the face-to-face stacked cocrystals, interact through N–H···N hydrogen bonds (d(N···N) = 2.912(2) and 2.880(2) Å). In contrast to a resorcinol-based template, the two hydrogen-bond-donor groups of an IC interact with two different molecules of 4,4′-tpcb. This observation can be attributed to the rigidity of the N–H groups, which may also account for the lack of reactivity in the double- and triple-stacked solids, $(IC)_2(4,4'\text{-bpe})_2{\cdot}2(MeCN)$ and $(IC)_2(4,4'\text{-bpe})_3$, respectively.

In conclusion, we have described double-to-quadruple stacks of aromatic compounds in cocrystals that are based on IC and sustained by N–H···N hydrogen bonds. Aside from exploring opportunities to engineer more complex self-assembled stacks based on IC and its derivatives, we are now investigating the scope of indolocarbazoles as templates to direct solid-state reactivity of higher-order assemblies and structures.

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[21] Given the photostabilities of the double and triple stacks, it is likely that the disordered atoms of the inner olefins of the quadruple stacks are able to undergo movement to form the cyclobutane rings. Given that only the two inner molecules lie in a disordered fashion, the maximum theoretical yield for the solid is expected to be approximately 50%.

