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Self-assembly of 1- and 2-Dimensional Multicompartmental Arrays via the 2-Aminopyrimidine H-Bonding Motif and Selective Guest Inclusion

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Abstract—The H-bond mediated self-assembly of aminopyrimidine substituted anthracene derivatives **4** and **5**, respectively, generate 1- and 2-dimensional multicompartmental arrays in the solid state as revealed by X-ray crystallographic analysis. The derived 'pigeon-hole' lattice is defined by *syn*-coplanar positioning of anthracene moieties at a distance of ca. 7 Å, allowing the formation of selective clathrate-type inclusion entities with guests of appropriate shape and size, in particular phenazine, which presents both structural and interactional complementarity. These data provide insight into the interplay of the different structural and interactional features of the molecular components to the controlled generation of electron donor–acceptor (EDA) and charge transfer arrays directed toward the design of functional supramolecular materials.

Introduction

Recognition processes occurring at the molecular level offer a powerful tool for the spontaneous but controlled generation of extended supramolecular arrays through self-assembly.[1] They provide strategies towards the design of nanostructured materials and solid state engineering[2] through 'bottom-up' pathways bypassing nanofabrication procedures. Their implementation requires, in particular, the identification of persistent and selective H-bonding arrays for deriving a library of modular recognition groups as scaffolds for the attachment of functional residues. Thus, recognition-directed self-assembly has led, for instance, to the formation of supramolecular discrete[3,4] and polymeric[3,5] liquid crystals, organic magnets[6] and electroactive materials.[7] Pursuing our exploration of the 2-aminopyrimidine H-bonding motif,[8–11] we report herein the H-bond mediated self-assembly of 1- and 2-dimensional multicompartmental arrays possessing π stacking features and capable of forming clathrate-type inclusion entities[8] with guest molecules of appropriate shape and size.

Design of the molecular components

As part of a general investigation into the self-assembly of H-bonded systems,[1,3,8] we have described previously the modular covalent combination of noncovalent synthons (also termed tectons[12]) encoding 1-dimensional H-bonding motifs toward the construction of noncovalent synthons expressing 2-dimensional motifs, or 'β-networks'. Thus, the combination of 2-aminopyrimidine residues as in **1**[9] and **2**[10] has allowed the generation of flat and pleated sheet architectures, respectively. In the case of chiral *bis*-2-aminopyrimidine **3**, folding of the 2-dimensional object results in the formation of a 3-dimensional array of parallel unoccupied helical channels.[11] Recognizing that the distance between alternate aminopyrimidines assembled in a H-bonded ribbon is ca. 7 Å (Fig. 1, bottom left), ideal for formation of π-molecular complexes via intercalation, inspired the design of tectons **4** and **5** where the anthracene residues provides a flat π-surface and the hydrogen bonding head groups are held perpendicular to the aromatic plane by steric interaction with the *peri* hydrogens. The anthracene unit was selected in view of its ability to form π-complexes with redoxactive electrodeficient compounds such as tetracyanoethylene[13] and *o*-chloranil[14] as well as exciplexes (Fig. 1) with electron rich partners (e.g. diethylaniline).[15]

While polycyclic aromatic residues have been attached to

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† X-ray structural analysis

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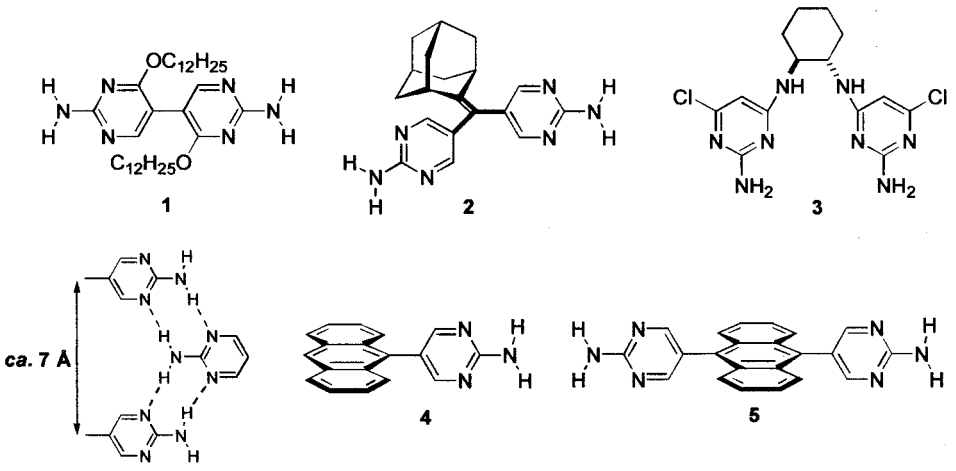


Figure 1. 2-Aminopyrimidine based molecular components for the generation of 1-, 2- and 3-dimensional supramolecular H-bonded networks.

covalent scaffolds to achieve a suitable distance for π complexation (ca. 7 Å), in 'molecular tweezers' possessing acridine backbones,[16] we herewith describe self-assembled *noncovalent* scaffolds of a geometry commensurate with intercalative binding. Furthermore, unlike systems incorporating covalent scaffolds, which thus far have been restricted to the formation of discrete complexes, related H-bonded assemblies are amenable toward the design of multi-dimensional substrate–receptor arrays. This capability offers design strategies for the controlled generation of 1- and 2-dimensional electron donor–acceptor (EDA)/charge transfer (CT)[17,18] arrays.

Synthesis and self-assembly of the molecular components

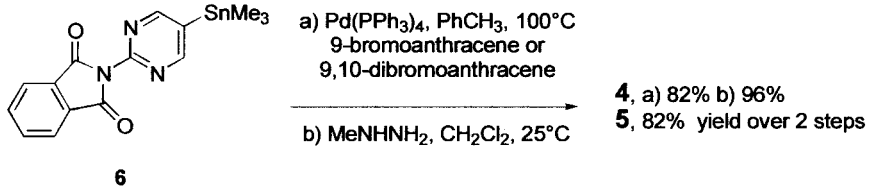
For the synthesis of **4** and **5**, we take advantage of our previously reported 2-phthalimido-5-(trimethylstannyl)-pyrimidine **6**.[10] Thus, Stille coupling of **6** with 9-bromoanthracene or 9,10-dibromoanthracene, followed by methylhydrazine mediated removal of the phthalimido protecting group, gives tectons **4** and **5** in high yields (Scheme 1).

The self-assembly of the molecular components **4** and **5** is expected to generate, respectively, one-dimensional and two-dimensial supramolecular arrays, based on the formation of hydrogen-bonded ribbons between the Janus-type 2-amino pyrimidine recognition groups (see Fig. 1, bottom left). No such interactions were detected in solution in the conditions employed; further studies are in progress. In the presence of guest molecules of suitable size, shape and chemical composition, cocrystals were obtained which were investigated by determination of their crystal structures.

Solid state structure of the self-assembled lattice generated by component 5 with selective guest inclusion

On the basis of geometrical considerations, phenazine appeared to be a guest particularly well suited for inclusion into the cavities that molecular component **4** was expected to generate by self-assembly. Furthermore, it was surmised that its central nitrogen sites would fit snuggly into the assembly at the level of the angle defined by the N···HNH···N H-bonding arrays and might provide additionally favorable electrostatic interactions with these hydrogen sites. Indeed, when a DMSO solution containing a *single* equivalent of phenazine and tecton **5** was cooled, cocrystals were formed. Their investigation by X-ray crystallography yielded a structure in which phenazine is inserted between two anthracene units in a 2-dimensional 'pigeon-hole' lattice maintained by the hydrogen-bonding arrays defined by the amino-pyrimidine groups. A view from above the surface defined by the 2-dimensional H-bonding motif, in which the phenazine guest is omitted, reveals the multi-compartmental array (Fig. 2). The distance between alternate anthracene residues in the H-bonded ribbon is 7.73 Å. An NH···N distance of 3.0 Å is observed. An image depicting the phenazine guest reveals that it completely fills the compartment with adjacent anthacenes moieties perfectly eclipsed (Fig. 3).

To further explore the inclusion capabilities of **5**, crystallizations in the presence of other π-molecular guest were attempted. Nitrobenzene, perchloroethylene and



Scheme 1. Synthesis of **4** and **5**.

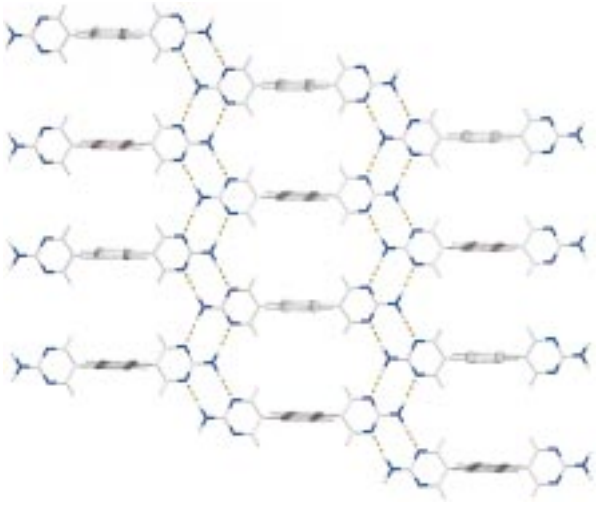


Figure 2. X-Ray structure of **5**·Phenazine cocrystal: a 2-dimensional multicompartmental array with phenazine omitted for clarity.

hexafluorobenzene all yielded cocrystals as evidenced by NMR analysis. Determination of the structure of the perchloroethylene cocrystal revealed a 2-dimensional H-bonded network identical to that obtained for the **5**·phenazine cocrystal. Both perchloroethylene and DMSO are included and share each compartment. The location of the two guests is such that their positions alternate in adjacent compartments of a given stack. This fact slightly perturbs the overall symmetry of the 2-dimensional array such that the two NH···N distances of the aminopyrimidine are no longer equivalent, i.e. 3.04 and 2.99 Å. Nevertheless, the average geometry of the compartment preserved an inter-anthracene distance of 7.65 Å (Fig. 4).

Solid state structure of the self-assembled lattice generated by component 4

For the self-assembly of **4**, which possesses only a single H-bonding unit, it was not clear whether the 2-aminopyrimidine H-bonding motif would be robust enough to persist. Additionally, with **4** the inclusion of guests could be precluded by interdigitation of the anthracene moieties. Slow evaporation of an ethyl acetate solution of **4** gave single crystals. X-Ray diffraction revealed a solid state structure analogous to that obtained for **5**, in which however a 1-dimensional multicompartmental array with an NH···N distance of 3.03 Å and an inter-anthracene distance of 7.51 Å is observed. Thus, in lieu of interdigitation, the anthracene-based compartments persist, each containing one molecule of ethyl acetate and the aminopyrimidine H-bonding motif persists (Fig. 5).

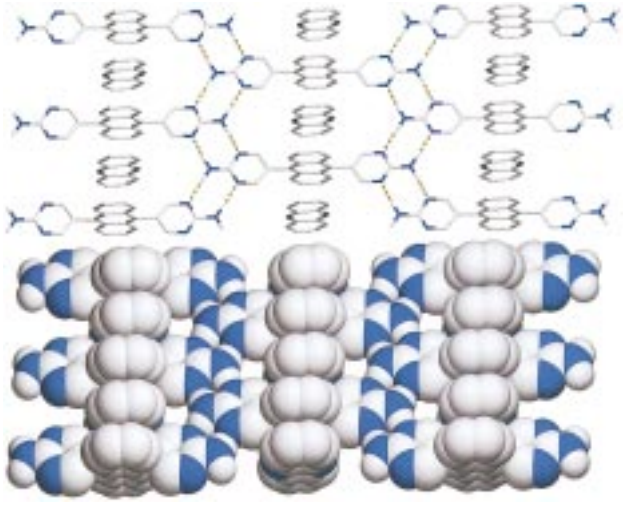


Figure 3. X-Ray structure of **5**·Phenazine cocrystal: ball and stick (top) and space filling (bottom) representations.

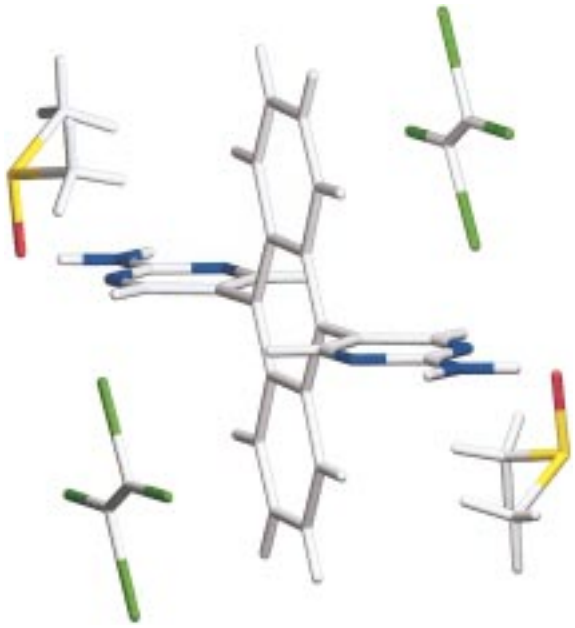


Figure 4. X-Ray structure of **5**·C_2Cl_4·DMSO cocrystal revealing the positioning of the guests.

It is noteworthy that while the H-bonding motif of **4** and **5** is

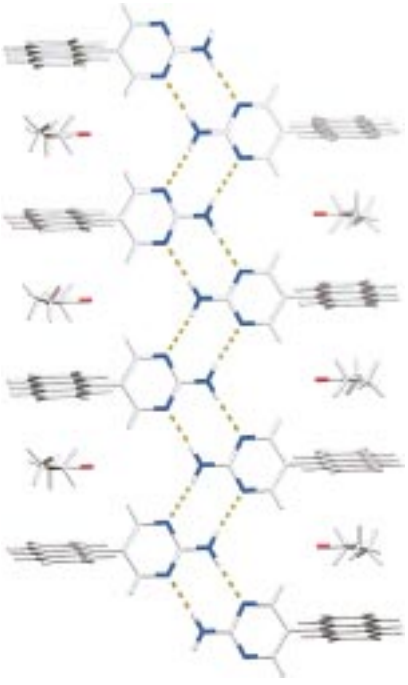


Figure 5. X-Ray structure of **4**·ethyl acetate cocrystal.

guest independent, related anthracenes incorporating resorcinol H-bonding recognition groups[19] do not express persistent H-bonding motifs, and inter-anthracene distances ranging between ca. 3.5–14 Å in a given stack are observed depending upon the particular attributes of the guest. It is plausible that the enhanced integrity of the aminopyrimidine hydrogen-bonding array for both π-molecular and saturated guests is a consequence of the 2-point H-bond contacts between each Janus face of the heterocyclic recognition groups.

Conclusion

That molecules possess information manifested in their geometric (shape, size) and interactional features, which is expressed through their intermolecular interaction with other molecules, is a fundamental precept of supramolecular chemistry, and hence, of molecular recognition directed self-assembly.[1] In order to quantify this principle it is desirable to identify the dominant supramolecular interactions, assess their relative importance and implement the dominant supramolecular interactions (steric, van der Waals, π-molecular interactions, H-bonding and solid state packing) such that all operate in consonance. The viability of the self-assembly paradigm that evolves, in turn, is defined by the extent to which the molecular building blocks assemble in a predictable manner. Ideally, for suitably designed noncovalent synthons, the information embodied by the molecular components should be readout following a well-defined interactional algorithm to selectively and persistently yield one of many possible non-covalent objects.

In the specific case of H-bond mediated self-assembly,[20] synergy among the various noncovalent interactions becomes especially important, for even when the cooperative action of numerous H-bonds is brought into play, the stability of a given superstructure may nevertheless be nominal. While the use of weak interactions is advantageous owing to their reversible formation and, hence, the capacity of supramolecular systems to correct errors that may occur in the course of their self-assembly, the outcome may be difficult to control. Reduced predictability becomes especially evident in the solid state, where crystal packing forces may be of the same order of magnitude as the predesigned interactions of the component molecules.[2,21] Even for very simple systems, kinetic effects or energetically similar crystal packing modes may exist resulting in the formation of crystalline polymorphs.[22] Indeed, the interplay of symmetry constraints and the many attractive and repulsive interactions in the solid state is sufficiently complex that a priori prediction of crystal packing motifs is viable only for rather simple systems and remains a worthy endeavor.[23] The importance of controlled crystal engineering[2] is, nevertheless, underscored by the fact that nonlinear optical properties,[24] ferromagnetic behavior,[25] electrical conductivity,[26] solid state reactivity[27] and ferromagnetic properties all critically depend on the relative orientation of the composite molecules in the solid state. The work described herein contributes to the search for reliable approaches to the controlled self-assembly of molecular components into extended supramolecular lattices and thus to the engineering of the organic solid state.

Furthermore, by means of more soluble derivatives of the parent structure **5**,[28] it may be possible to generate in solution, extended hydrogen-bonded arrays, that would reversibly assemble and dissociate and be able to select a given inclusion guest from a collection of substrates in a dynamic combinatorial fashion.[29]

Experimental

^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker SY 200 spectrometer at 200 MHz. ^{13}C NMR spectra were recorded on a Bruker SY 200 or on a Bruker ARX 500 MHz spectrometer at 50.3 and 125.72 MHz, respectively. Solvent was used as an internal reference for both ^{1}H and ^{13}C NMR spectra. Infrared spectra (IR) were obtained on a Perkin–Elmer 1600 Series FTIR instrument. Melting points (mp) were measured on an electrothermal Digital Melting Point Apparatus and are uncorrected. Electron impact (EI) and Fast Atom Bombardment (FAB) mass spectra were performed by the Service de Spectrometrie de Masse, Institut de Chimie, Université Louis Pasteur. Purchased reagents were used without purification. Toluene was distilled from sodium metal and dichloromethane from calcium hydride under a dry nitrogen atmosphere.

2-Phthalimido-5-bromopyrimidine—an improved procedure

A 100 mL round bottom flask containing 2-amino-5-bromopyrimidine (9.0 g, 51.7 mmol, 100 mol%) and phthaloyl dichloride (7.44 mL, 51.7 mmol, 100 mol%) was heated to 180°C for 40 min with stirring under a stream of nitrogen. After cooling to room temperature, the residue was dissolved in chloroform and evaporated onto silica gel. Chromatography (SiO_2; 4% ethyl acetate in dichloromethane) provided the title compound as a white powder (13.9 g, 88% yield) identical in all respects to material obtained by our previously reported procedure[10] and is readily crystallized from toluene.

5-(9-Anthracenyl)-2-phthalimidopyrimidine. To a 50 mL round bottom flask charged with 2-phthalimido-5-(trimethylstannyl)pyrimidine (860 mg, 2.22 mmol, 100 mol%) and 9-bromoanthracene (856 mg, 3.33 mmol, 150 mol%) was added toluene (11 mL). Argon was bubbled through the resulting suspension for approximately 5 min at which point tetrakis(triphenylphosphine)palladium (33 mg, 0.032 mmol, 2.0 mol%) was added. Argon was bubbled through the suspension for an additional minute and the reaction vessel was placed in 100°C oil bath and stirred for 14 h. The reaction mixture was evaporated onto silica gel. Chromatography (SiO_2; 3% ethyl acetate in dichloromethane) provided the title compound (730 mg, 1.82 mmol) in 82% yield; ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.01 (s, 2H), 8.58 (s, 1H), 8.04 (m, 4H), 7.83 (dd, J=2.4, 3.1 Hz, 2H), 7.4–7.7 (m, 6H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 165.7, 160.7, 157.4, 152.7, 134.7, 131.5, 131.0, 130.5, 128.7, 127.1, 126.7, 125.4, 125.1, 124.1; IR (film):

1786, 1760, 1725, 1542, 1433, 1406, 1375, 718 cm^{-1}; EI-MS: Calculated for $C_{26}H_{15}N_3O_2$: $[M^+]$=401.1164; Found: 401.0.

5-(9-Anthracenyl)-2-aminopyrimidine, 4. To a dichloromethane solution (12 mL) of 5-(9-anthracenyl)-2-phthalimidopyrimidine (240 mg, 0.597 mmol, 100 mol%) was added methylhydrazine (159 μL, 2.98 mmol, 500 mol%). The reaction mixture was stirred at room temperature for 30 min and then evaporated onto silica gel. Chromatography (SiO_2; 40% ethyl acetate in dichloromethane) provided the title compound (155 mg, 0.57 mmol) in 96% yield; MP=178–179°C; ^1H NMR (200 MHz, $CDCl_3$): δ 8.51 (s, 1H), 8.41 (s, 2H), 8.05 (d, J=7.5 Hz, 2H), 7.77 (d, J=8.4 Hz, 2H), 7.45 (m, 4H), 5.91 (s, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 162.5, 159.9, 131.2, 130.9, 129.5, 128.5, 127.6, 126.0, 125.7, 125.2, 121.7; IR (film): 3332, 1590, 1479 cm^{-1}; EI-MS: Calculated for $C_{18}H_{13}N_3$: $[M^+]$=271.1109; Found: 271.3.

5,5′-(9,10-Anthracenyl)-2,2′-diaminobipyrimidine, 5. To a 50 mL round bottom flask charged with 2-phthalimido-5-(trimethylstannyl)pyrimidine (1.53 g, 3.94 mmol, 250 mol%) and 9,10-dibromoanthracene (530 mg, 1.57 mmol, 100 mol%) was added toluene (15 mL). Argon was bubbled through the resulting suspension for approximately 5 min at which point tetrakis(triphenylphosphine)palladium (91 mg, 0.078 mmol, 5.0 mol%) was added. Argon was bubbled through the suspension for an additional minute and the reaction vessel was placed in 100°C oil bath and stirred for 20 h. The reaction mixture was filtered and the solid was washed with chloroform and suspended in dichloromethane (500 mL). Methylhydrazine (10 mL) was added and the suspension was allowed to stir for 2 h at which point the reaction mixture was evaporated onto silica gel. Chromatography (SiO_2; 20% ethanol in chloroform) provided the title compound as a yellow powder (470 mg) in 82% yield over the two step sequence; MP>360°C decomposition (yellow needles from DMSO–nitrobenzene); ^1H NMR (200 MHz, d^6-DMSO): δ 8.31 (s, 4H), 7.75 (dd, J=6.9, 3.3 Hz, 4H), 7.53 (dd, J=6.9, 3.3 Hz, 4H), 6.95 (s, 4H); ^{13}C NMR (125.7 MHz, d^6-DMSO): δ 167.0, 163.2, 135.3, 134.2, 130.1, 129.9, 123.4; IR (film): 3332, 1593, 1490 cm^{-1}; EI-MS: Calculated for $C_{22}H_{16}N_6$: $[M^+]$=364.1436; Found: 364.3.

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