Design of Organic Superstructure based on a Preorganised Donor–Acceptor Unit

Joe Otsuki,* Tsutomu Oya, Seung-Hwan Lee and Koji Araki

Institute of Industrial Science, University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106 Japan

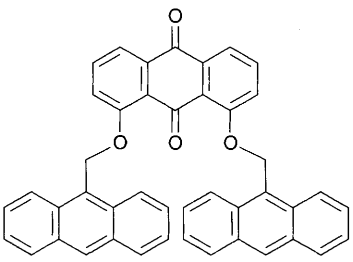
Use of preorganised donor–acceptor molecules for controlling and generating solid-state architecture is demonstrated by a molecule having donors and acceptors nearly orthogonal to each other which yields a superstructure composed of alternating layers of donor–acceptor columns of different orientations upon cocrystallisation with TCNQ.

Self-assembly of molecules possessing programmed structural information has recently been one of the central themes of supramolecular chemistry,[1] with hydrogen bonding being the most widely used intermolecular force.[2] Organic π–π donor–acceptor (DA) interactions[3] have advantages comparable to hydrogen-bonding interactions. Directionality is manifested by the fact that most crystals of DA complexes consist of stacks of alternate, near parallel donor and acceptor molecules[4] (with important exceptions including segregated stacks).† Interactions may be strengthened by increasing the size of the aromatic ring, while multipoint interactions are used for stronger hydrogen bond association. This interaction has the unique advantage that the resulting structure is directly associated to the way the π-orbitals interact and hence are the electronic properties.

Here we propose a new method of controlling three-dimensional molecular arrangement and producing more complex DA superstructures. It is based on using a unit molecule that has a preorganised set of donor(s) and acceptor(s). Especially interesting is when more than one donor and/or acceptor in the molecule are arranged in non-parallel orientations. If the DA columns develop along the directions in line with the molecular structure, more than one dimensional DA structure may be obtained.

We prepared a bis-anthracene host molecule, 1,8-bis[(9-anthryl)methoxy]-9,10-anthraquinone **1**, which was shown to sandwich nitrofluorenone derivatives between the two anthryl arms with DA interaction in solution.[9] In this molecular design, two donors (anthracenes) are connected by an acceptor (anthraquinone). From molecular mechanics, it was expected that the two anthryl moieties are held in face-to-face orientation by the nearly orthogonal anthraquinone spacer.

Single crystals suitable for the X-ray analysis were obtained by cocrystallising **1** with TCNQ.‡ The crystal consists of 1 : 1 complexes of **1** and TCNQ and a molecule of dichloromethane.§ The two anthryl groups lie in parallel planes and TCNQ is sandwiched in-between. This association motif is essentially the same as that in solution, which was deduced from ^{1}H NMR ring current calculations.[9] The distance from the plane of TCNQ and the anthryl group is 3.45 Å, which is slightly shorter than that in the anthracene–TCNQ complex (3.50 Å[10]). The centre of TCNQ is offset from the centre of the anthracene ring as opposed to the centre-on-centre geometry adopted by the anthracene–TCNQ complex[10] which has the maximum charge transfer stabilisation energy.[3] The dihedral angle between the anthraquinone plane and the anthryl group is 102°. This is probably to put the anthracene rings at optimal separation (3.9 Å) to accommodate TCNQ.[9,11]



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Inspection of the packing of the complex in the crystal reveals a superstructure composed of alternating layers with orthogonal extended DA columns. On the outside of the anthracene arm is the anthraquinone group of another **1**, separated by 3.6 Å, to form an extended column of DA stacks (Figs. 1 and 2). These columns pack in the same orientation to make a layer with

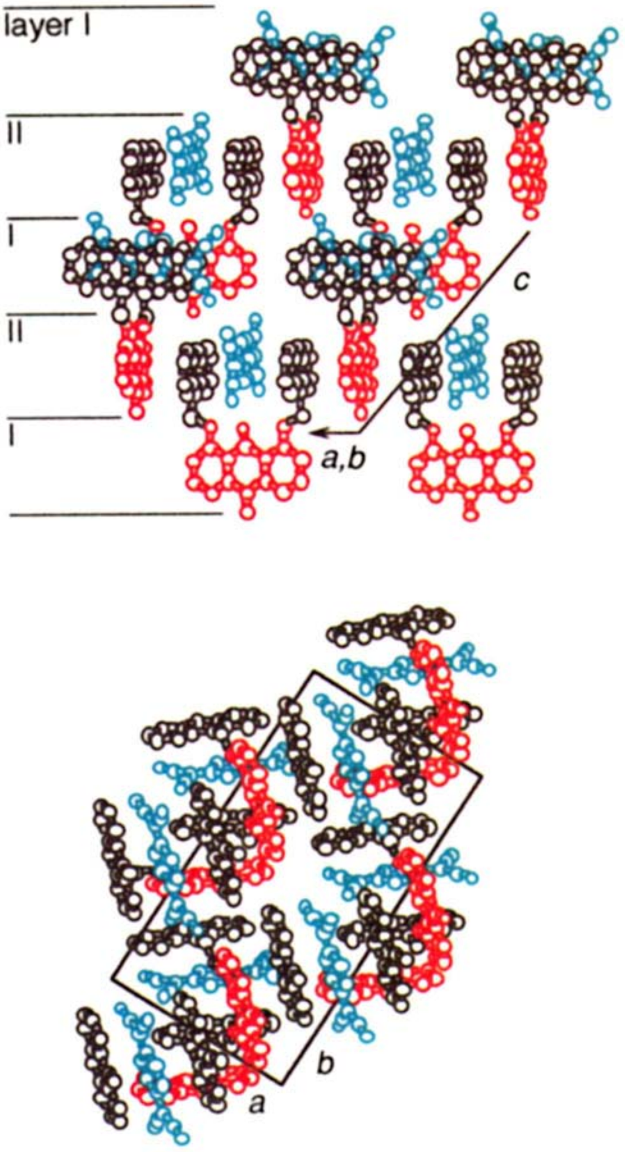

Fig. 1 The crystal packing of the complex. Hydrogens and dichloromethanes are omitted for clarity (black: anthrylmethyl moiety; red: anthraquinone spacer; blue: TCNQ). Top: The donor–acceptor columns run horizontally in the second and fourth layers (layer II) from the top and nearly perpendicular to the paper in the other layers (layer I). Bottom: Two layers are shown, as viewed from below of the top figure. The columns extend along one diagonal line of the *ab* plane of the unit cell in a layer and along the other diagonal line in the next layer.

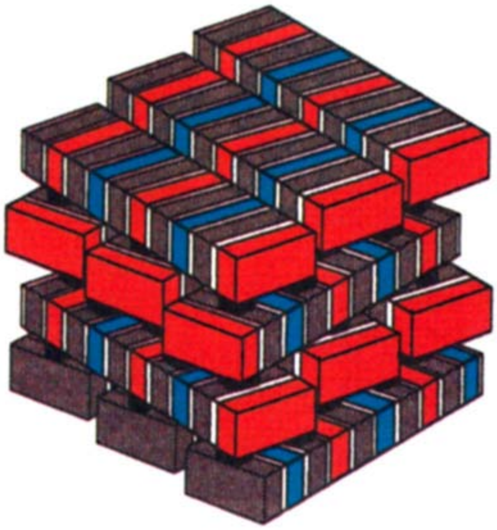

Fig. 2 Schematic representation of the superstructure [gray: anthracene; blue: TCNQ; red: anthraquinone; black: covalent linkage (–OCH_2–)]

intercolumn separation of 12.5 Å. The anthraquinone of **1** in the layer has two anthracene groups projecting from the layer on the same side. These anthracene groups in turn make another layer of DA columns with TCNQ and the anthraquinone with interlayer separation of 6.3 Å. Layers are related by the covalent linkage of anthracenes and anthraquinone in **1**. Hence the angle between the axis of the columns in adjacent layers is 102°. The molecular shape is thus directly reflected in the macroscopic relative orientation of the layers.

TCNQ is a stronger acceptor than anthraquinone and so the stack may be represented as:

$$\ldots\text{-D-A}_s\text{-D-A}_w\text{-D-A}_s\text{-D-A}_w\text{-}\ldots,$$

in which the different acceptors (D: donor; A_s: strong acceptor; A_w: weak acceptor) alternate. Therefore the HOMO and LUMO levels, or the potential surface, should have a unique double-well profile, which may not be accessible by conventional planar donors and acceptors. The bis-donor **1** is symmetrical but need not be, since the anthraquinone spacer can carry different donors. Therefore, more complex profiles may be constructed. All of the two-fold axes of symmetry of **1** direct in the same way (perpendicular to the *ab* plane). Hence the crystal is non-centrosymmetric, which is an important feature of non-linear properties.

In summary, the bis-donors connected by the acceptor spacer **1** have been shown to sandwich aromatic acceptors and form a two-dimensional DA superstructure¶ which reflects the pre-organized shape of the unit molecule. We have thus demonstrated the use of DA interaction as a programming element in generating the solid-state architecture. Unit molecules of similar structures but having other combinations of donors and acceptors are being made to confirm the generality of this approach.

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Footnotes

† Although crystals of the latter motif constitute a family of DA complexes which are expected to be (super)conductive and are attracting more attention,[5] the former type of DA packing is also interesting, *e.g.* for magnetic materials,[6] for exciton behaviour studies[7] and in electronic phase transition.[8]

‡ The crystals were obtained by the diffusion method by using an H-shaped glass tube. In one leg of the tube was put **1** and TCNQ in the other, and dichloromethane was slowly poured in so as not to disturb the solid. This was kept at a constant temp. for a few days. The black crystals grew to greater than 1 mm in 1 week.

§ *Crystal data* for $C_{44}H_{28}O_4{\cdot}C_{12}H_4N_4{\cdot}CH_2Cl_2$, black crystals, $M_r = 909.83$; monoclinic, space group *Cc*; $a = 1463.4(2)$, $b = 2393.7(3)$, $c = 1451.9(2)$ pm, $\beta = 119.23(1)°$, $V = 4438(1) \times 10^6$ pm^3, $Z = 4$; $D_c = 1.36$ g cm^{-3}; Cu-Kα ($\lambda = 1.54178$ Å); 1.655 mm^{-1}; $F(000) = 1880$; crystal dimensions: 0.50 × 0.50 × 0.30 mm; Mac Science MXC18 diffractometer; 4073 reflections measured, 3331 used. The structure was solved using CRYSTAN and SHELXS76. $R = 0.0637$, $R_w = 0.0775$, all non-hydrogen atoms refined anisotropically, H atoms calculated.

Atomic coordinates, bond length and angles, and thermal parameters have been deposited at The Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

¶ This organic crystal is structurally reminiscent of the superlattice of inorganic semiconductors: the inorganic superlattice is made up from alternating layers of different compositions, while in this case layers of different orientations alternate.

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