

## Crystal Structure Consisting Both of Segregated and Mixed Donor–Acceptor Columns

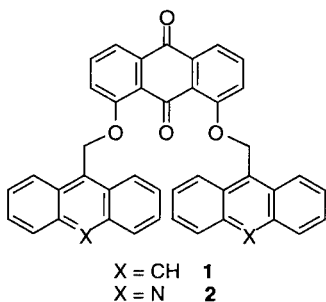
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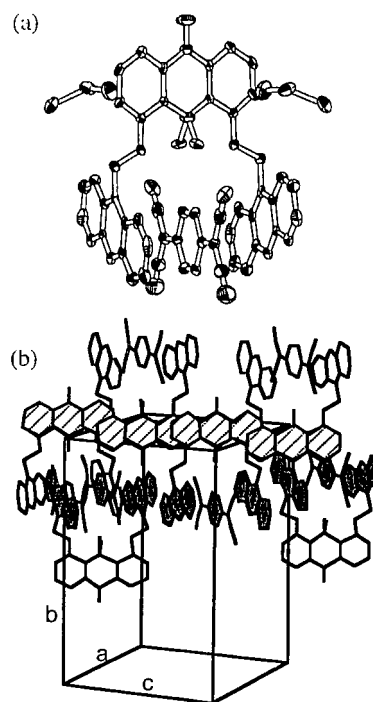
A host molecule in which two acridine arms are held by an anthraquinone spacer cocrystallizes with TCNQ into a new type of organic donor–acceptor structure consisting both of segregated acceptor (anthraquinone) columns and mixed donor–acceptor columns (acridine–TCNQ) extending in different directions.

Control over the solid-state structure in a predictable way is a topical subject in supramolecular chemistry and crystal engineering.<sup>1</sup> Structures comprising donor (D) and acceptor (A) molecules are especially interesting in view of their electronic properties. Organic  $\pi$ -donors and  $\pi$ -acceptors tend to crystallize into either segregated stacks<sup>2</sup> (i.e., ...AAA... and ...DDD...) or mixed stacks, in which donors and acceptors alternate (i.e., ...DADA...) in most cases.<sup>3</sup> Here we report a crystal structure consisting both of segregated and mixed stacks of organic donors and acceptors.

We have previously demonstrated a method of creating organic superstructures via  $\pi$ – $\pi$  interactions among  $\pi$ -donors and  $\pi$ -acceptors by using supramolecular building blocks.<sup>4</sup> In solution, an aromatic acceptor, such as TCNQ, is preferentially sandwiched by the bis-anthracene host compound **1** between its two donor arms appropriately deposited by the orthogonal aromatic spacer.<sup>5</sup> The binding is enhanced by a few orders of magnitude compared with simple mono-donors. This DA units accumulate to form a higher-order structure composed of layers of alternately stacked DA columns of different orientations.<sup>6</sup>



We have examined the effect of a dipole introduced in the arms with the use of 1,8-bis(acridin-9-ylmethoxy)anthracene-9,10-dione (**2**),<sup>7</sup> in which the anthracene arms in **1** are replaced by acridine arms while keeping structural modification minimum. A mixed chloroform solution of **2** and TCNQ shows a broad charge-transfer absorption band at 570 nm due to the interaction between the acridine arms and TCNQ. Much enhanced binding of TCNQ ( $K = 520 \text{ M}^{-1}$  at 25°C) by **2** compared to that by 9-methylacridine ( $K = 25 \text{ M}^{-1}$ ) suggests sandwich complex formation. The crystal consists of 1:1 complex of **2** and TCNQ and two molecules of  $\text{CH}_2\text{Cl}_2$ .<sup>8,9</sup> The two



**Figure 1.** The crystal structure of the complex **2**/TCNQ. (a) The ORTEP view (thermal ellipsoids for 50% probability) of the unit structure. Hydrogens are omitted for clarity. (b) The superstructure assembled from the units. The acceptor (i.e. anthraquinone) column along the  $c$ -axis is striped, whereas the DA (i.e. acridine and TCNQ) column along the diagonal line of  $ac$  plane is shaded.

acridyl groups lie in parallel planes and TCNQ is sandwiched in-between (Figure 1a). This association motif is essentially the same as that in the cocrystal of **1** and TCNQ. The distance from the plane of TCNQ and the acridyl group is 3.4 Å, which is within the range of  $\pi$ – $\pi$  interactions, evidenced by the deep green color of the crystal. A distortion of the anthraquinone occurs in order to give sufficient distance between the ether oxygen atoms and the quinoid oxygen atom.<sup>10</sup> Due to the  $C_2$  symmetry around the axis passing through the two quinoid groups, the two possible distortions are isoenergetic and consequently disorder is observed in the position of quinoid oxygen.

These unit DA complexes assemble themselves into a higher-order structure (Figure 1b). An acridine of one unit stacks with an acridine of the adjacent unit with a center-on-center geometry and in the antiparallel orientation so as to maximize the dipole–dipole interaction between them.<sup>11</sup> It is also likely that less electron rich acridine can stack with each other due to a smaller  $\pi$ – $\pi$  repulsion than in the case of the bis-

anthracene **1**,<sup>6,12</sup> where no anthracene–anthracene stack is involved. The separation between the two acridinyl groups is 3.5 Å. This [acridine–TCNQ–acridine] column runs along the shorter diagonal line of the *ac* plane. These columns pack in the same orientation to form a layer. On the other hand, the anthraquinone spacers stack with themselves to form a column along the *c* axis. The anthraquinone stagger with each other; only one benzo-ring is involved in the each stacking. The distance between the two quinone planes is 3.6 Å. There are cavities occupied by CH<sub>2</sub>Cl<sub>2</sub> between the anthraquinone columns which are separated by 16.6 Å.<sup>13</sup> One of the hydrogen atoms of CH<sub>2</sub>Cl<sub>2</sub> are in van der Waals contact with the nitrogen of acridinyl group.

The complex in the solid state exhibits a broad charge-transfer absorption band around 600 nm but not at 840 nm characteristic to TCNQ<sup>•-</sup>.<sup>14</sup> In addition, the complex shows a sharp absorption at 2222 cm<sup>-1</sup> in its IR spectrum diagnostic of the CN groups in neutral TCNQ.<sup>14</sup> Thus, the complex has the nature of weak charge-transfer complex in which charge-transfer in the ground state is minimum.

To summarize the structure of **2** and TCNQ in the DA representation, the crystal is composed of alternating layers of [D–A–D] columns and [A'] columns of different orientations. This is in contrast with the structure of **1**/TCNQ which consists of a [D–A–D–A'] pattern.<sup>8</sup> This crystal thus contains both acceptor columns and stacked DA columns alternating at the molecular level. As such, interaction between these columns might lead to new solid-state electronic properties yet to be explored. These crystal structures imply the power of supramolecular building block approach in creating interesting and complex DA arrays.

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- In the cocrystal of bis-anthracene **1** and TCNQ, the anthraquinone spacer comes next to an anthracene arm of a different molecule, generating stacked columns consisting of the repetition of [anthracene–TCNQ–anthracene–anthraquinone]. In terms of a DA viewpoint, it may be represented as [D–A–D–A'].
- The bis-acridine (**2**) was prepared as follows. 9-Bromomethylacridine (0.48 g, 1.8 mmol) and 1,8-dihydroxy-9,10-anthraquinone (0.144 g, 0.6 mmol) were stirred in CH<sub>2</sub>Cl<sub>2</sub> / H<sub>2</sub>O (20 mL / 60 mL) in the presence of NaOH (0.24 g, 6 mmol) and Bu<sub>4</sub>NCl (1.39 g, 5 mmol) at room temperature for 24 hours to yield precipitation, which was crystallized from CHCl<sub>3</sub> / hexane to afford **2** (0.21 g, 56 %); m.p. = 194 °C (decomposition); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 6.12 (s, 4H), 7.29 (m, 4H), 7.65 (m, 4H), 7.75 (4H), 7.80 (2H), 8.08 (d, *J* = 9 Hz, 4H), 8.41 (d, *J* = 9 Hz, 4H); IR (KBr): ν = 745, 754, 968, 1024, 1061, 1237, 1267, 1317, 1439, 1458, 1520, 1588, 1673 cm<sup>-1</sup>; FBMS: *m/z*: 623 [MH<sup>+</sup>].
- The crystal was obtained from CH<sub>2</sub>Cl<sub>2</sub> in an H-shaped glass vessel. The TCNQ was placed in one of the legs of the vessel and **2** in the other.
- Crystal data: C<sub>42</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>·C<sub>12</sub>H<sub>4</sub>N<sub>4</sub>·2CH<sub>2</sub>Cl<sub>2</sub>. *M* = 996.73. A deep green crystal, dimensions 0.5 × 0.5 × 0.8 mm, monoclinic, *C*2/*c*, *a* = 16.6390(19) Å, *b* = 21.011(3) Å, *c* = 13.3780(16) Å, β = 92.477(9)°, *V* = 4672.6(11) Å<sup>3</sup>, *Z* = 4, ρ<sub>calcd</sub> = 1.42 g cm<sup>-3</sup>; 2025 reflections measured on a Mac Science MXC18 diffractometer, all of which were used in the refinement, 2θ<sub>max</sub> = 120°, Cu Kα radiation (1.54178 Å) at *T* = 200 K. The structure was solved and refined on 337 variables (6.0 reflections parameter ratio) using the SHELXL-97. Disorder was observed at one of the quinoid oxygens, which was modeled at 50% site occupancy. All non-hydrogen atoms refined anisotropically. *R* = 0.083, *wR* = 0.217 (*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)).
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- MOPAC calculations (Sony Tektronix, CAChe) with PM3 parameters show that the acridine arm has a dipole moment of 2.1 debye, directing from the nitrogen atom to C-9. The anthraquinone spacer also has a dipole moment of 2.0 debye. However, its orientation is not optimum for the stacking due to the distortion; the dipole roughly directs from quinoid C-10 to one of ether oxygens, depending on the distortion.
- The ionization potentials are 7.45 and 7.8 eV for anthracene and acridine, respectively: "Kagaku Binran Kisoheii II," 4th ed., ed. by Chemical Society of Japan., Maruzen, Tokyo (1993).
- Thermogravimetry analysis showed that all CH<sub>2</sub>Cl<sub>2</sub> molecules dissociate from the crystal at 123–134 °C.
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