

## Unique crystal structures of donor–acceptor complexes: crossed arrangement of two charge-transfer columns

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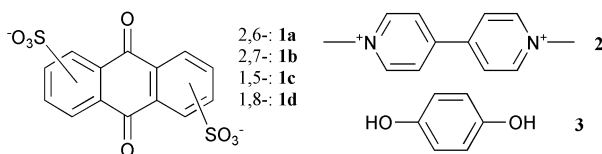
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Unique crystal structures containing two kinds of crossed charge-transfer (CT) columns are demonstrated by cocrystals consisting of ion pairs of acceptors of methyl viologen and anthraquinone disulfonate derivatives and a donor, hydroquinone, mediated by electrostatic and donor–acceptor (DA) interactions.

DA interactions in crystals leading to CT absorption in the visible region has been attracting intense interest in view of their photo and electronic properties.<sup>1–5</sup> In the field of supramolecular chemistry,<sup>6</sup> DA interactions have also received much attention as one of the intermolecular forces to control and predict the structure of complexes since the aromatic donor and acceptor molecules tend to form alternate stacks with  $\pi$ -planes approximately parallel with each other.<sup>7–9</sup> Although there have been extensive studies on DA complexes, the composition in almost all known crystals is 1:1 for the D:A molecular ratio.<sup>9</sup> We consider that complicated but highly organised CT complexes consisting of three or more molecular components can be synthesised by introducing electrostatic interaction between charged molecules in addition to DA interactions.

In this communication, we report the formation of novel molecular crystals consisting of three molecular components: anthraquinone disulfonate derivatives (**1a–d**), methylviologen (**2**) and hydroquinone (**3**) as a result of both DA and electrostatic interactions. Both methyl viologen and anthraquinone derivatives are electron acceptors, while hydroquinone is a typical donor. They form DA complexes with various donor or acceptor molecules and are used as supramolecular components.<sup>6</sup>

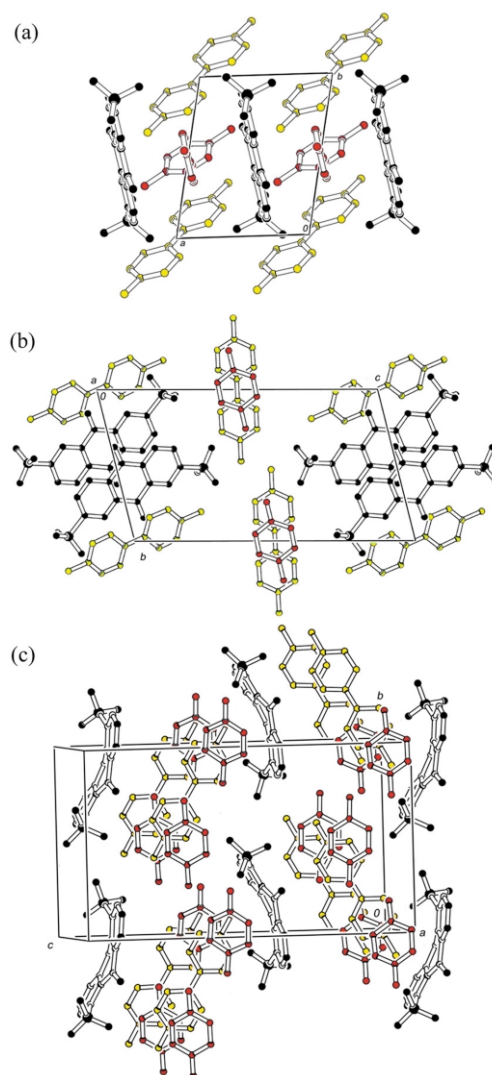


Reddish coloured crystals are precipitated from aqueous solutions containing mixtures of the chloride of **2** and alkali metal salts of **1a–c** and **3**. However the solution containing **1d**, **2** and **3** did not form crystals.† From the results of NMR and elemental analysis, the crystals consist of three components and water molecules. The ratio of **1a–c**:**2**:**3**:H<sub>2</sub>O are 1:1:2:2 (**C1**), 1:1:1:1 (**C2**) (2:2:1:0 (**C2'**))‡ and 1:1:2:2 (**C3**), respectively. These crystals are free from inorganic ions. The position of sulfonyl groups on the anthraquinone affects the composition of the complexes. The composition ratios of the precipitates do not match the ratios of reagents introduced to the solution.† In our preparative experiments, we were not successful in isolating pure complexes formed from aqueous solutions of two components of **1a–d**:**3**, **2**:**3** and **1b–d**:**2** and only the ion pair **1a**:**2** was isolated as pure crystals. These results suggest that all three components play an important role in the formation and isolation of complexes from solutions through electrostatic and DA interactions.

Diffuse reflectance spectra of **C1**, **C2** and **C3** dispersed in barium sulfate exhibit absorption bands having maximum wavelength absorption at 484, 529 and 466 nm, respectively.

The absorption bands are absent in the pure donor and acceptor molecules, and are therefore assigned to CT transitions.

The spatial origin of the CT transition was established by X-ray crystallographic studies of single crystals of **C1**, **C2'** and **C3**.§ The crystal structure of **C1** was solved in the triclinic space group  $P\bar{1}$  (no. 2). Fig. 1(a) shows a packing diagram of the crystal viewed along the *c* axis. Interestingly, the structure consists of two alternately stacked DA columns arranged across each other. One column is formed from **3** and **2** along the *b* axis, the other is formed from **3** and **1a** along the *a* axis. The methylated pyridinium and the hydroquinone rings are almost parallel with an interplanar angle of 3.7° and a mean separation of 3.46 Å. In the columns consisting of anthraquinone and



**Fig. 1** Crystal packing of (a) **C1**, (b) **C2'** and (c) **C3**. Black, yellow and red indicate **1a–c**, **2** and **3**, respectively. Hydrogens and water molecules have been omitted for clarity.

hydroquinone components, **1a** and **3** are stacked face-to-face, also approximately parallel to each other, where the interplanar angle and distance are 6.9° and 3.57 Å, respectively. Hydroquinones are placed at the centre of anthraquinones. These arrangements and separations of the molecules in two columns are typical for the alternation of donors and acceptors in DA complexes.<sup>1,10,11</sup> The CT absorption band observed by diffuse reflection spectroscopy of **C1** is considered to arise from two DA columns.

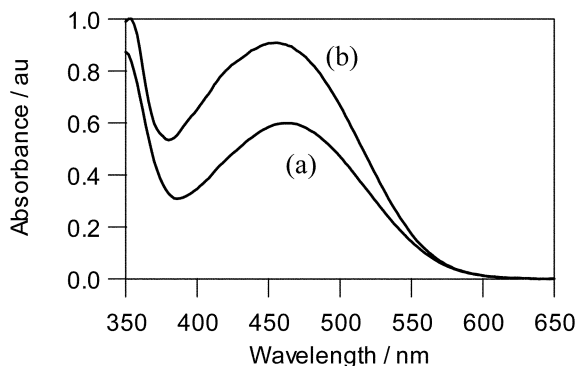
In the case of **C3** which has the same composition as **C1**, hydroquinones are alternately stacked only with methylviologen along the *a* axis, where the average angle and distance between the least square planes are 5.4° and 3.66 Å (Fig. 1(c)). This overlapping arrangement is typical for CT complexes.<sup>1,10,11</sup> The non-planar anthraquinone **1c** components are arranged between DA columns like partition plates. Differently from **1a**, **1c** does not act as a  $\pi$ -acceptor but simply as a counter anion for **2**.

**C2'** consists of two columns formed by **2:1b** and **2:3**, respectively (Fig. 1(b)). **2** and **3** show an alternately stacked arrangement as for typical CT complexes. The interplanar angle and the mean separation between the molecules are 5.5° and 3.52 Å, respectively. **2** and **1b** also form a stacking arrangement of the type **2:1b:1b:2**. In this case, CT interactions do not play a crucial role to form the column structure, since both **2** and **1b** have acceptor nature. It should be noted that **1b** is not reduced to the hydroquinone form, since the C–O distance of 1.22 Å is typical for double bonds.

OH groups of **3** in **C2'** participate in hydrogen bonding with oxygen atoms of sulfonyl groups. However it was impossible to assign the position of the H atoms of OH groups of **3** in **C1** and **C3**. Though it is well known that **3** is easily converted to the quinone through oxidation under various conditions, it is clear that **3** is present in the reduced state, since the C–O bond distances of **3** in **C1**, **C2'** and **C3** are 1.38, 1.37 and 1.37 Å, respectively, which are significantly longer than 1.23 Å for the C=O bond of quinones.<sup>12</sup> Water molecules in both **C1** and **C3** crystals form 1D hydrogen-bonding networks with oxygen atoms of sulfonyl groups. These bonds stabilize water molecules in the crystals.

A microspectrophotometer, with light polarised parallel to the *a* and *b* axes, was used to measure the electronic absorption spectra perpendicular to the *ab* face of a single crystal of **C1**, giving CT absorption maxima at 462 and 456 nm, respectively (Fig. 2). Since the transition moments of CT bands are strongly polarised along the DA stack axis,<sup>1,13,14</sup> these correspond to transitions between **1a** and **3**, and **2** and **3**, respectively.

Both electrostatic and CT interactions seem to play important roles in the formation of cocrystals from aqueous solution. This



**Fig. 2** Polarised absorption spectra of a crystal of **C1** measured from the direction normal to the *ab* face (see Fig. 1(a)). The polarisation plane of probe light is parallel with (a) *a* axis and (b) *b* axis, respectively.

result illustrates the possibility of forming new structure types by such novel molecular combinations.

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## Notes and references

† *Preparation*: a molecular crystal (**C1**) consisting of **1a**, **2** and **3**: 41.2 mg (0.100 mmol) of sodium salt of **1a** and 31.1 mg (0.100 mmol) of trihydrated chloride salts of **2** and 44.0 mg (0.400 mmol) of **3** were dissolved in 10 g of hot water and left at rt for 1 day, giving deep red plate crystals of **C1** (**1a:2:3:H<sub>2</sub>O** = 1:1:2:2) in 30.6 mg (38%) yield (Found: C, 56.37; H, 4.35; N, 3.48; S, 7.83. Calc. for C<sub>38</sub>H<sub>36</sub>N<sub>2</sub>O<sub>14</sub>S<sub>2</sub>: C, 56.43; H, 4.49; N, 3.46; S, 7.93%). A similar method was used to prepare **C2** and **C3**. **C2** (**1b:2:3:H<sub>2</sub>O** = 1:1:1:1) was obtained as a brown powder in 40% yield (Found: C, 56.88; H, 3.81; N, 4.12; S, 9.43. Calc. for C<sub>32</sub>H<sub>28</sub>N<sub>2</sub>O<sub>11</sub>S<sub>2</sub>: C, 56.46; H, 4.15; N, 4.12; S, 9.42%). **C3** (**1c:2:3:H<sub>2</sub>O** = 1:1:2:2) was obtained as red needles in 37% yield (Found: C, 56.80; H, 4.10; N, 3.46; S, 7.93. Calc. for C<sub>38</sub>H<sub>36</sub>N<sub>2</sub>O<sub>14</sub>S<sub>2</sub>: C, 56.43; H, 4.49; N, 3.46; S, 7.93%).

‡ The composition of **C2** was changed after recrystallization from water to obtain dark-red crystals **C2'** which were subjected to X-ray analysis (**1b:2:3** = 2:2:1) (Found: C, 57.08; H, 3.75; N, 4.56; S, 10.35. Calc. for C<sub>58</sub>H<sub>46</sub>N<sub>4</sub>O<sub>18</sub>S<sub>4</sub>: C, 57.32; H, 3.82; N, 4.61; S, 10.55%).

§ *Crystal analysis*: **C1**: C<sub>38</sub>H<sub>36</sub>N<sub>2</sub>O<sub>14</sub>S<sub>2</sub>, *M* = 808.83, triclinic, space group *P* $\bar{1}$ (no.2), *a* = 7.129(4), *b* = 8.636(5), *c* = 15.185(8) Å,  $\alpha$  = 96.15(2),  $\beta$  = 102.40(2),  $\gamma$  = 98.27(1)°, *U* = 894.3(9) Å<sup>3</sup>, *Z* = 1, *D<sub>c</sub>* = 1.502 g cm<sup>-3</sup>, Cu-K $\alpha$  radiation (1.5418 Å); 3471 reflections measured (3341 unique: *R*<sub>int</sub> = 0.013); *R*<sub>1</sub>(*F*) = 0.0524 [for 2810 reflections with *I* > 2.0 $\sigma$ (*I*)], 2 $\theta$  < 139.73°, *wR*<sub>2</sub> = 0.1694 (*F*<sup>2</sup>); *T* = 296 K. CCDC 191675.

**C2'**: C<sub>58</sub>H<sub>46</sub>N<sub>4</sub>O<sub>18</sub>S<sub>4</sub>, *M* = 1215.26, triclinic, space group *P* $\bar{1}$ (no.2), *a* = 6.866(1), *b* = 10.475(2), *c* = 18.808(4) Å,  $\alpha$  = 75.84(1),  $\beta$  = 84.34(1),  $\gamma$  = 86.28(1)°, *U* = 1304.2(5) Å<sup>3</sup>, *Z* = 1, *D<sub>c</sub>* = 1.548 g cm<sup>-3</sup>, Cu-K $\alpha$  radiation (1.5418 Å); 5044 reflections measured (4895 unique: *R*<sub>int</sub> = 0.008); *R*<sub>1</sub>(*F*) = 0.0588 [for 4547 reflections with *I* > 2.0 $\sigma$ (*I*)], 2 $\theta$  < 139.85°, *wR*<sub>2</sub> = 0.1742 (*F*<sup>2</sup>); *T* = 296 K. CCDC 191674.

**C3**: C<sub>38</sub>H<sub>36</sub>N<sub>2</sub>O<sub>14</sub>S<sub>2</sub>, *M* = 808.83, monoclinic, space group *P1c1*(no.7), *a* = 7.830(2), *b* = 11.920(3), *c* = 20.356(3) Å,  $\beta$  = 101.77(2)°, *U* = 1859.9(8) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.444 g cm<sup>-3</sup>, Mo-K $\alpha$  radiation (0.7107 Å); 5232 reflections measured (4592 unique: *R*<sub>int</sub> = 0.0505); *R*<sub>1</sub>(*F*) = 0.0537 [for 1752 reflections with *I* > 2.0 $\sigma$ (*I*)], 2 $\theta$  < 55.00°, *wR*<sub>2</sub>(*F*<sup>2</sup>) = 0.2019; *T* = 223 K. CCDC 191673.

$$R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)]} \right\}^{0.5}$$

See <http://www.rsc.org/suppdata/cc/b2/b207809k/> for crystallographic files in CIF or other electronic format.

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