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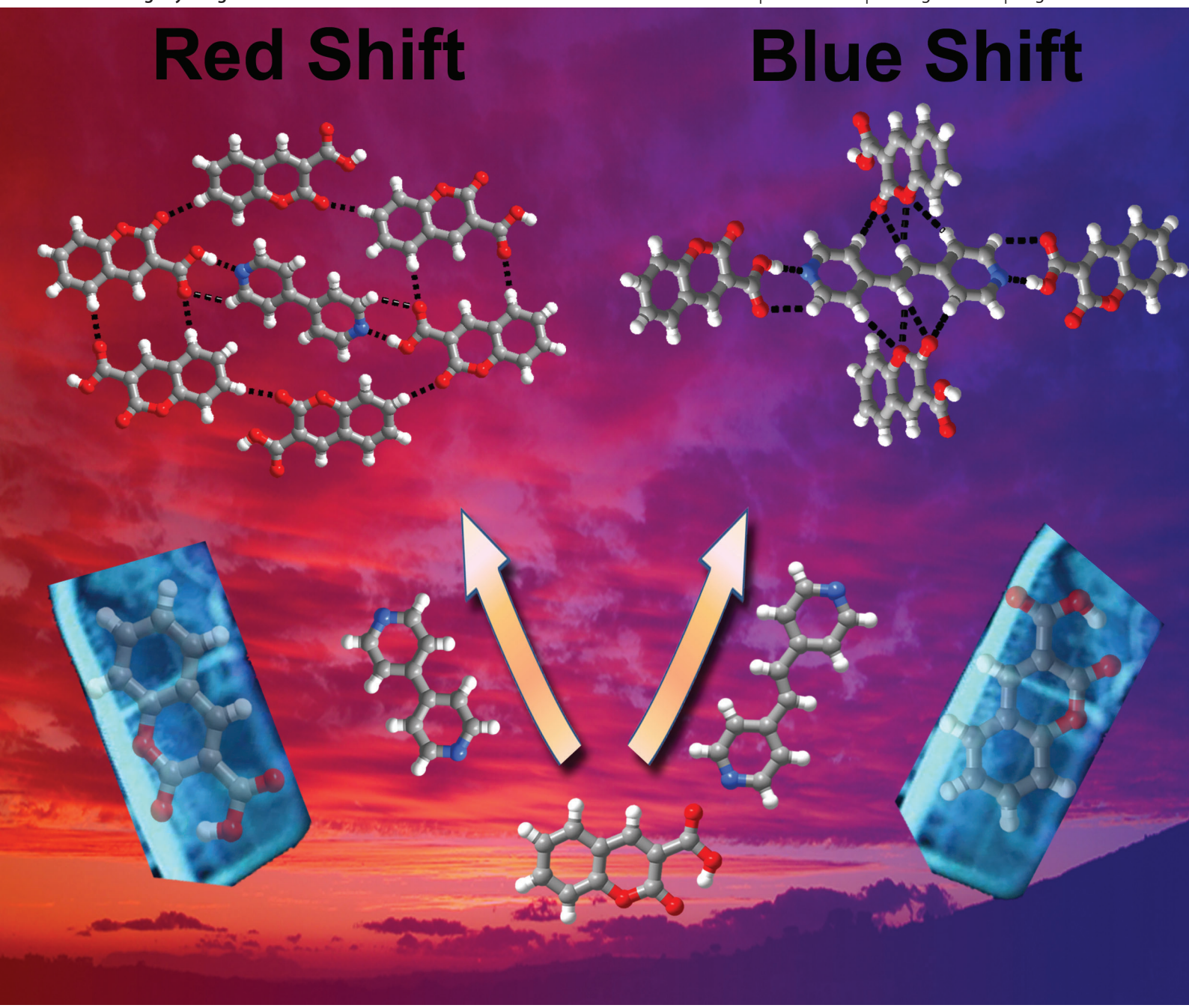

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Modification of luminescent properties of a coumarin derivative by formation of multi-component crystals†

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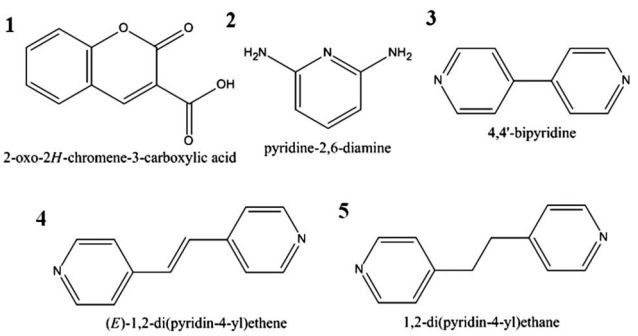
Four new multi-component crystals of a carboxylic acid derivative of coumarin have been synthesised based on a hydrogen bond synthon approach.

Organic solid-state fluorescent dyes continue to receive considerable attention as a result of their advantageous properties such as ease of processing, low cost and high quantum yield resulting in the ability to construct well-defined self-emission materials and optoelectronic devices.[1] Obtaining controllable fluorescence with different emission wavelengths based on a particular dye molecule is critical to the development of new multi-colour luminescent materials,[2] such as the tunable solid-state dye laser. However, an effective strategy and methodology for tuning the luminescent characteristics of an organic solid is a long-standing problem. Recent developments in the area of organic luminescent materials suggest that the photophysical properties of the solid are largely determined by the molecular packing and accompanying intermolecular interactions.[3] As a result, an important step will be an ability to engineer and adjust the arrangement of the molecules within the solid. A strategy towards this objective is the use of multi-component crystals (including cocrystals and salts) where the active molecule is crystallised with a second (or more) component(s) (the co-former(s)).[3d,e,4d] Such an approach has been very effective in controlling the solid state properties of pharmaceutical compounds where hydrogen bonding and π–π interactions have been used as part of the design strategy.[4] It is to be expected, therefore, that the formation of multi-component crystals will allow—*via* the varying arrangements of the chromophore in the crystals—the luminescent properties of the selected chromophore to be varied. In addition, based on the relationship between the relative electronic energy levels of the components of the crystal, cocrystallisation may also result in novel energy/charge transfer effects.[4c]

Coumarin and its derivatives are an important family of fluorescent dyes with high luminescence quantum yield and are widely used in dye lasers,[5a] in electroluminescent devices,[5b] and as polarised luminescent materials.[5c] In the work described here, coumarin-3-carboxylic acid (**1** – see Scheme 1) was chosen as a model system to develop multi-component crystals with four pyridine-based molecules **2–5** as the co-formers, utilising the potential hydrogen bonding between the carboxylic acid function in **1** and the pyridine or aminopyridine functional group in the co-formers.[4,6] The detailed crystal structures, thermal measurements and fluorescence properties of the resulting multi-component crystals (one salt and three cocrystals) have been studied. Spectral data show that the luminescence of the crystals varies over a range of 400–460 nm. Additionally, periodic density functional theoretical (DFT) calculations suggest that two of the systems feature intermolecular energy transfer between the crystal building blocks, indicating that the as-prepared organic crystalline solids have potential applications in the field of energy conversion/storage or light-harvesting materials.

The coumarin-3-carboxylic acid-based multi-component crystals (**A**: **1** + **2**; **B**: **1** + **3**; **C**: **1** + **4**; **D**: **1** + **5**) were formed by the slow evaporation of a methanol solution containing **1** and the appropriate co-former with a 1 : 1 stoichiometry for **A** and 2 : 1 for **B**, **C** and **D**. Powder X-ray diffraction (PXRD) patterns, DSC and TG profiles of the resulting solids are shown in Fig. S1–S3 in the ESI† and differ from those of **1** and the



Scheme 1 Chemical structures of coumarin-3-carboxylic acid (**1**) and the co-former compounds (**2**. pyridine-2,6-diamine; **3**. 4,4′-bipyridine; **4**. (*E*)-1,2-di(pyridin-4-yl)ethene); **5**. 1,2-di(pyridin-4-yl)ethane).

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† Electronic supplementary information (ESI) available: Experimental, computational, crystallographic and thermal characterisation details of **A–D**. CCDC reference numbers 851664–851667. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ce25217a

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co-formers, demonstrating the formation of a new crystalline solid in each case. Single-crystal X-ray diffraction measurements (CCDC 851664–851667) show that the crystals are assembled *via* the expected hydrogen bonding between the carboxylic acid in **1** and the pyridine groups in the co-formers. The simulated PXRD patterns based on obtained single crystal structures are also in agreement with the powder data (Fig. S1†).

The single crystal data allow us to compare the differences between the molecular arrangements in the products. Pure **1** exhibits a centrosymmetric structure with intermolecular hydrogen bonds between adjacent **1** molecules as well as an intramolecular hydrogen bond.[7] In **A**, proton transfer has taken place from the carboxylic acid group to the pyridine nitrogen atom, resulting in the formation of a salt. In the case of **B**, two $R_2^2(7)$ dimeric motifs, involving the carboxylic acid groups in **1** and the pyridine moieties at the two ends of the co-former **3**, result in a one-dimensional chain unit which further assembles into a zig-zag arrangement. Similar interactions are also observed in **C** and **D** (Fig. 1); no proton transfer occurs in these crystals.[4a]

To study the luminescence properties of **1** and its multi-component crystals, fluorescence measurements were performed and the resulting spectra are shown in Fig. 2. **1** has a maximum luminescence emission (λ^{em}_{max}) at *ca.* 417 nm (CIE 1931 colour coordinates: (0.1538, 0.1288)) with full width at half-maximum (fwhm) of 78 nm. For salt **A**, the λ^{em}_{max} remains essentially unchanged, although the emission broadens towards higher wavelength, increasing the fwhm to 90 nm. Cocrystal **B**, however, shows a significant red shift with λ^{em}_{max} at 456 nm, which may be attributed to a more planar stacking within this cocrystal; whilst cocrystals **C** and **D** show a blue shift compared with **1**, with λ^{em}_{max} at 399 and 404 nm, respectively. All of the luminescent emissive colour coordinates for these samples are populated in the blue region (Table S1†). UV fluorescence microscopy indicates that the transparent single crystals of **1** and **A–D** (top photographs in Fig. 3) show blue emission (bottom photographs in Fig. 3), consistent with the fluorescence spectroscopy results. These observations demonstrate that tunable blue luminescence of the fluorescent dye molecule can be achieved by the formation of multi-component crystals, and can be associated with the change

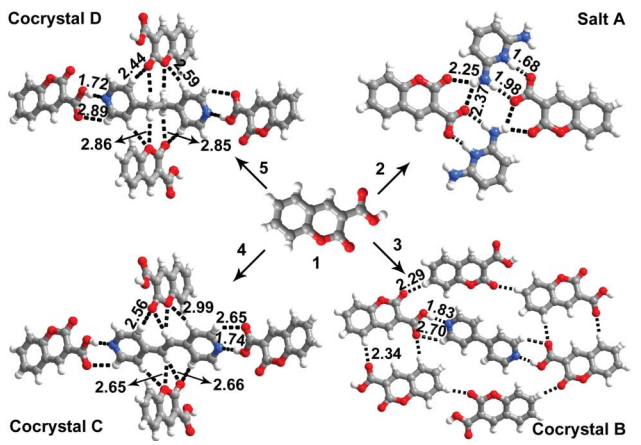

Fig. 1 The crystal structures of multi-component adducts **A–D** (**A** is a salt and **B–D** are cocrystals). Intermolecular hydrogen bonds and C–H···O contacts are indicated by dashed lines: H···X distances are given in Angstrom units.

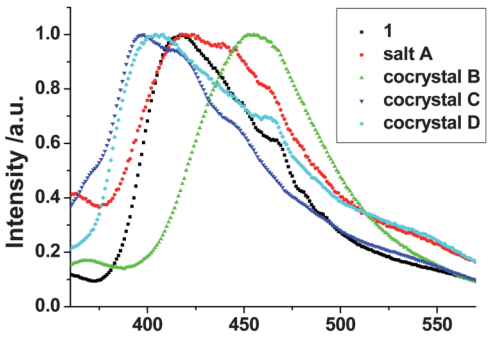

Fig. 2 The normalised fluorescence spectra of **1** and its multi-component crystal products (**A–D**).

in the molecular stacking and geometric arrangement of **1** within the different single crystals.

To better understand the electronic structure of the multi-component crystals and the interaction modes between **1** and its co-formers within the crystals, periodic DFT calculations were performed on the single crystal structural models of **1** and the multi-component crystals **A–D**. For the crystal of **1**, a frontier orbital analysis (Figs. S4, S5 and S6†) shows that the electron densities of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) are distributed over the whole π-system in the **1** molecule, suggesting that little intramolecular energy transfer occurs during the photoexcitation process. Upon formation of the salt **A**, analysis of the total electronic densities of states (TDOS) and partial electronic densities of states (PDOS) (Fig. 4a and Fig. S7†) reveals that HOMO-1 and HOMO are mainly populated on the C and N atoms in co-former **2**, whereas the LUMO and LUMO + 1 are mainly distributed on C and O atoms in the **1** molecule (see Fig. 4b) illustrating that intermolecular energy transfer occurs from co-former **2** to **1**. A similar energy transfer behavior can also be observed from **1** to co-former **3** in cocrystal **B**, where the HOMO-1 and HOMO are populated on **1** and the LUMO and LUMO + 1 are mainly distributed on co-former **3** (Fig. S8, S9 and S10†). This energy transfer between the supramolecular building blocks may contribute to the red shift of the luminescence of the cocrystal **B**. For cocrystals **C** and **D**, TDOS and PDOS analysis (Fig. S12, S13, S15 and S16†) show that the frontier orbitals (HOMO-1, HOMO, LUMO and LUMO + 1) are fairly localised on **1** (Fig. S11 and S14†), indicating that the co-formers **4** and **5** have little or no role in the photophysical process. The localised nature of the frontier orbitals on **1** and minor role of the co-former may explain the similar fluorescence spectra seen for cocrystals **C** and **D** (Fig. 2).

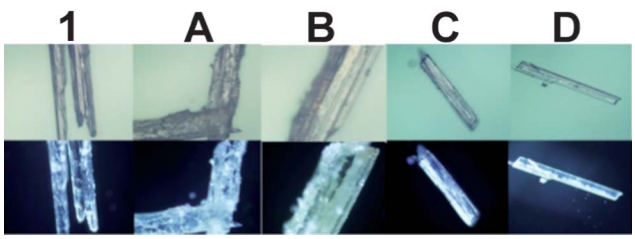

Fig. 3 Photographs of the single crystal samples for **1** and **A–D** under daylight (top) and UV irradiation (bottom) observed using a fluorescence microscope (at 50x magnification).

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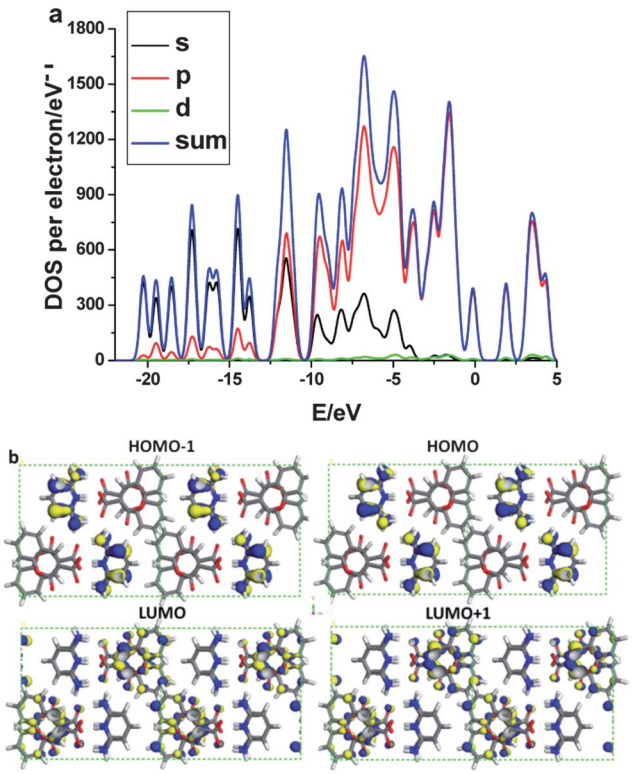

Fig. 4 a). Total and partial electronic densities of state (TDOS and PDOS) and b) frontier orbital profiles (HOMO–1, HOMO, LUMO, LUMO + 1) of crystal **A** (blue/yellow colours denote ± electronic wavefunction). The Fermi energy level E_F was set to zero.

We conclude that the energy transfer processes of the luminescent dye can be engineered by choosing appropriate co-former species with appropriate energy levels compared to **1**.

In summary, we have prepared four fluorescent multi-component crystals based on the coumarin derivative **1** using four pyridine-based co-formers. The resulting crystals exhibit luminescent emission in the range 400–460 nm suggesting they are potential candidates for blue light-emitting laser dye and solid-state luminescent materials. DFT calculations show that crystals **A** and **B** involve intermolecular energy transfer from the donor to the acceptor (**1** to co-former **2** in salt **A** or from co-former **3** to **1** in cocrystal **B**). Therefore, the tunable luminescent emission of the multi-component crystals can be attributed to the combined effect of changes in both the geometric arrangement and the electronic structures of the luminescent molecules incorporated in the different solids. It can be expected that such multi-component crystals may have potential applications in the fields of energy conversion and light-harvesting.[8] Moreover, as shown by our initial results, by appropriate choice of co-formers, tuning desirable luminescent properties, or even multi-colour organic-based material luminescence, will be possible.

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