MS33 Supramolecular recognition

MS33-02
Prevalent Polymorphism in Ternary Complexes using Robust Supramolecular Synthons
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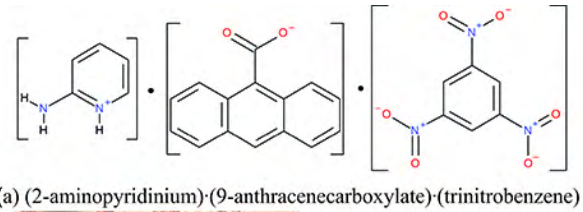
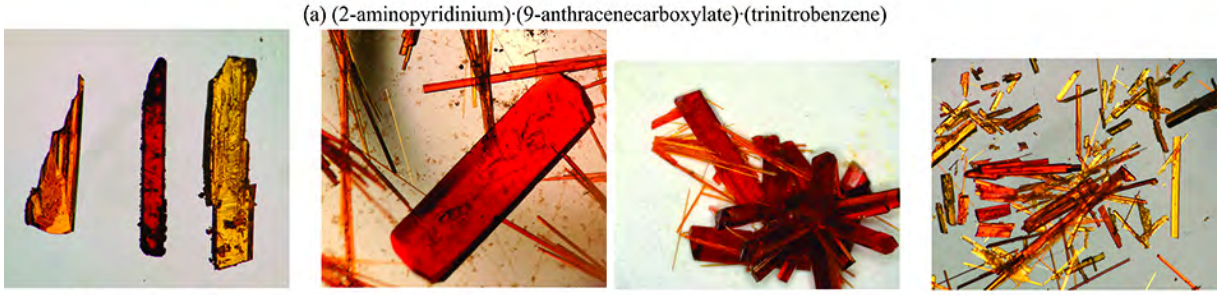
Abstract
Crystal engineering pertains to the control of the assembly of organic and inorganic components to a desired structure or a desired property. Organic components can be either one-component molecular solids, two-component, three-component, and higher with a predictable and stoichiometric combination of different molecules. Complexes between two or more organic compounds (in any physical state at room temperature) that remain neutral can result in a multi-component molecular complex. This scenario is often referred to colloquially as a co-crystal (or cocrystal). An additional scenario is for two (or more) components to undergo an intermolecular proton transfer with complimentary acid and basic functional groups. Such complexes are known as molecular salts as they do not contain inorganic acids or bases. We have found that we can easily make ternary complexes, consisting of a charge transfer binary complex hydrogen bonded to a third component using neutral and charge-assisted hydrogen bonding.[1] The colours of the ternary complexes change from yellow to orange to red depending on the identity of the third component, being a number of pyridines with nitro, amino or halogen atom substituents. Additionally, we have found that members of this series show colour polymorphism, whereby the different polymorphs can show the same range of colours. So far, we have systems that are dimorphic[2] and trimorphic.[3]

References
[1] Tania Hill, Rudolph M. Erasmus, Demetrius C. Levendis and Andreas Lemmerer. Combining two distinctive intermolecular forces in designing ternary co-crystals and molecular salts of 1,3,5-trinitrobenzene, 9-anthracenecarboxylic acid and ten substituted pyridines. CrystEngComm, 2019, 21, 5206–5210.
[2] Atiyyah Salajee, Caitlin Morrison and Andreas Lemmerer. Polymorphism of the ternary complex (2-amino-5-chloropyridine)·(9-anthracenecarboxylic acid)·(trinitrobenzene). An example of salt/cocrystal polymorphism. CrystEngComm, 2022, submitted.
[3] Andreas Lemmerer. All good things come in threes: first example of a trimorphic, ternary molecular salt complex. CrystEngComm, 2020, 22, 6091–6095.

Figure 1. (a) The three components of the ternary molecular salt. (b) A comparison of the colours of the three polymorphs (form **I** is usually needle-like). (c) Forms **I** (orange needle) and **II** (red block) isolated concomitantly from acetonitrile. (d) Forms **I** and **II** isolated from vapour diffusion (acetone/hexane). (e) Forms **I** (orange) and **III** (yellow) isolated concomitantly from vapour diffusion, showing the difference in colour (ethylacetate/hexane).



(a) (2-aminopyridinium)·(9-anthracenecarboxylate)·(trinitrobenzene)



(b) Forms **I**, **II** & **III** (c) Forms **I** & **II** (d) Forms **I** & **II** (e) Forms **I** & **III**