

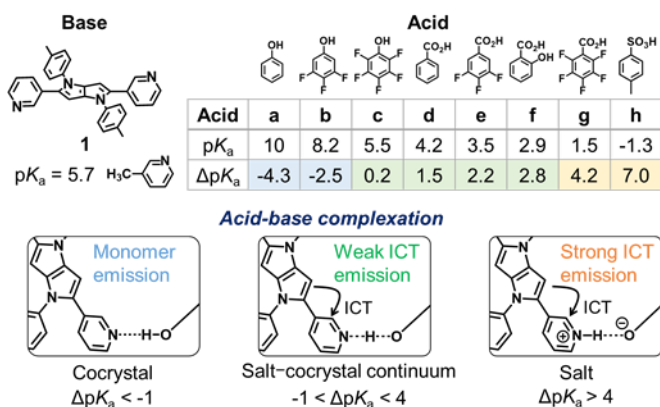
## Design of photo-functional soft crystals based on degree of protonation in the acid-base complexes

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In terms of crystal engineering, there has been significant interest in differentiating salts and cocrystals, and where appropriate position of the proton in the continuum in the systems. It is generally accepted that  $\Delta pK_a$  value ( $pK_a$  (protonated base) –  $pK_a$  (acid)) and the crystalline environment determine the extent of proton transfer. The  $pK_a$  value is greater than 4, a salt is expected to form and the  $pK_a$  value is less than -1 lead toward co-crystals forms. However, when  $\Delta pK_a$  is in the range of  $-1 < \Delta pK_a < 4$ , the crystals result in molecular salt, cocrystal or disordered solid with partial proton transfer forms, and the location of the acidic proton depends on the specific crystal packing environment.

Here we report that the three states (salts/cocrystals/salt-cocrystal continuum) can be distinguished by solid-state photoluminescent color changes based on acid-base complexes consisting of a pyridine-modified pyrrolo[3,2-*b*]pyrrole derivative (**1**)<sup>1)</sup> which shows intramolecular charge-transfer (ICT) character and organic acids such as phenol, carboxylic acid and sulfonic acid derivatives (**a-h**) (**Figure 1**). The results proved that the multicolor



**Figure 1.** Chemical structure of two-component crystal motifs and suggested mechanism for photofunction modulation by increasing the ICT strength.

photoluminescent properties were observed from blue, green, and yellow depends on the  $\Delta pK_a$  value between the **1** and the organic acids (**a-h**). In addition, the salt-cocrystal continuum ( $-1 < \Delta pK_a < 4$ ) showed vapochromism /vapofluorochromism against  $\text{CH}_2\text{Cl}_2$ <sup>2)</sup>. Single crystal neutron diffraction measurements supported that the optical property modulation resulted from difference of the extent of proton transfer to the pyridyl moiety of the dye by inclusion and desorption of  $\text{CH}_2\text{Cl}_2$ .

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