Control of stacking patterns of two-dimensional molecular layers in hydrogen-bonded cocrystals composed of 2-pyrrolidone and anilic acids

([1]*Graduate School of Science, Kyoto University*, [2]*JASRI/SPring-8*, [3]*Department of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba*)
○Masaki Donoshita,[1] Yukihiro Yoshida,[1] Mikihiro Hayashi,[1] Ryuichi Ikeda,[1] Kunihisa Sugimoto,[2] Shogo Kawaguchi,[2] Yasuhisa Yamamura,[3] Kazuya Saito,[3] Hiroshi Kitagawa[1]
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In two-dimensional (2D) layered compounds, the stacking pattern of layers plays an important role in determining the chemical and physical properties. Therefore, it is desired to establish the methodology of controlling the stacking patterns. Assemblies of organic molecules can be an ideal platform for such a study because of tunable intermolecular interactions with diverse directionalities and strengths. We have investigated the structural phase transitions of a cocrystal PyCA (**Fig. 1**) composed of 2-pyrrolidone (Py) and chloranilic acid (CA)[1]. The cocrystal consists of molecular layers (**Fig. 1b,c**) involving one-dimensional (1D) hydrogen-bonded (HB) tapes (**Fig. 1a**). In PyCA, the competition of various interlayer interactions such as π···π and lone pair···π as well as the out-of-plane molecular motion of Py plays a crucial role in structural phase transitions resulting in four kinds of different stacking patterns including metastable ones. In this study, we prepared halogen-substituted cocrystals (PyFA, PyBA, and PyIA) using appropriate anilic acids (FA, BA, and IA, **Fig. 1a**) and investigated the substitution effect on the stacking pattern of the 2D layers. Single-crystal X-ray diffraction (SCXRD) revealed that all the halogen-substituted cocrystals adopt the 2D layers identical to PyCA, although they showed no structural phase transition in 100-298 K. Based on the results of ^{35}Cl nuclear quadrupole resonance experiments and the calculation of intermolecular interactions in addition to the SCXRD results, the effect of halogen substitution is discussed in terms of changes in atomic polarizability and bulkiness of halogens as well as the motion of Py, and the phase transition behavior characteristic of PyCA is attributed to the balance of these factors.

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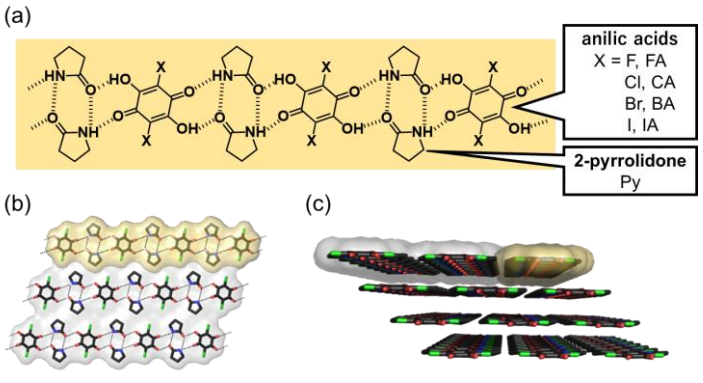

Figure 1. (a) 1D HB tape of cocrystals and (b) 2D assembly and (c) crystal structure of PyCA.