A Supramolecular Ferroelectric Realized by Collective Proton Transfer

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Experimental

Commercially available 5,5’-dimethyl-2,2’-bipyridine (55DMBP) was purified by vacuum sublimation. Iodanilic acid (H2ia), which was prepared from p-iodanil according to the literature [1], was purified twice by gradient sublimation in vacuum after recrystallization (toluene or methanol). The purity was checked by elementary analysis and mass spectra. Analysis (% calcd, % found for C6H2O4I2): C (18.39, 18.36), H (0.51, 0.43). The intermediate substance p-iodanil, which was synthesized by the reactions of p-bromanil with KI and then with NaI [1], inevitably permits contamination of hardly separable 2-bromo-3,5,6-triiodo-p-benzoquinone. This impurity content was found to be a few to 10% by the mass spectra even after repeating the treatments with NaI, recrystallization (ethyl acetate or toluene), and gradient sublimation processes. However, the purified final product H2ia does not find any Br-substituted contaminants (if present, less than 1 %, the detection limit of the mass spectra).

Single crystals of the [H-55DMBP][Hia] co-crystals were grown by slow evaporation of the solvent at room temperature after stoichiometric amounts of the 55DMBP and H2ia were dissolved in methanol. The deuteration of the hydrogen bonds was achieved by employing 99.5%-deuterated CH3OD (Aldrich) as the solvent. The degree of deuteration was 0.93, which was determined by the infrared vibrational spectra on the KBr disk; amount of residual undeuterated species was estimated...
by diminishing band intensity of undeuterated acid at 959 cm$^{-1}$ by using the band at 1040 cm$^{-1}$ of 55DMBP as a relative standard.

The dielectric constant was measured with an LCR meter (HP 4284A) using the single crystal with gold paste as the electrodes. Hydrostatic pressure was generated in a clump-type high-pressure cell using pressure-transmitting oil (Idemitsu Kosan Daphne 7373). Thermal change of pressure due to the contraction of the medium was corrected according to the literature [2]. In the polarization hysteresis measurements, while the triangle waveform voltage was applied, the electric charge was measured by a current/charge-to-voltage converter and transformed to the polarization.

References
