Supporting Information

Proton-transfer salts between an EDT-TTF derivative having imidazole-ring and anilic acids: Multi-dimensional networks by acid-base hydrogen-bonds, π-stacks and chalcogen atom interactions

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General Information.

EDT-TTF-Im was prepared in our laboratory.[S1] $H_2CNA•6H_2O$ was prepared according to the procedure reported in the literatures[S2] from 2,5-dibromo-3,6-dicyano-1,4-benzoquinone which is readily accessible by our improved method.[S3] Infra-red (IR) spectra were measured using a Perkin-Elmer Paragon 1000 FT-IR spectrometer in KBr pellets (resolution of 4 cm^{-1}). Electronic spectra were measured on a Shimadzu UV-3100 spectrometer in KBr pellets. Elemental analyses were performed at the Center for Organic Elemental Microanalysis, Kyoto University.

X-ray crystallographic measurements were made on a MacScience DIP-2020K oscillator type X-ray imaging plate for **1** or on a Rigaku Raxis-Rapid imaging plate for **2** with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Structures were determined by a direct method using SHELXS-97.[S4] Least-squares refinement was performed on F^2 with SHELXL-97.[S5] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. An empirical absorption correction was applied.

[S1] T. Murata, Y. Morita, Y. Yakiyama, Y. Nishimura, T. Ise, D. Shiomi, K. Sato, T. Takui and K. Nakasuji, *Chem. Commun.*, **2007**, 4009.

[S2] (a) K. Wallenfels, G. Bachmann, D. Hofmann and R. Kern, *Tetrahedron*, 1965, **21**, 2239; (b) E. K. Andersen and I. G. K. Andersen, *Acta Crystallogr., Sect. B*, 1975, **31**, 379.

[S3] Md. B. Zaman, Y. Morita, J. Toyoda, H. Yamochi, S. Sekizaki and K. Nakasuji, *Mol. Cryst. Liq. Cryst.*, 1996, **287**, 249.

[S4] G. M. Sheldrick, *Program for the Solution of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1997.

[S5] G. M. Sheldrick, *Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1997.

Procedure for preparation

(EDT-TTF-Im•H^+)$_2$(ClA^{2-}) (1)

EDT-TTF-Im (21.0 mg, 6.4 μmol) and H_2ClA (13.8 mg, 6.4 μmol) were placed at the bottom of each side of an H-shaped tube. Diffusion of them in MeCN (60 mL) at room temperature for 2 months afforded dark red crystals (21.6 mg) suitable for X-ray analysis.

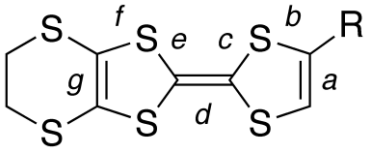
mp. 239–241 °C (dec.); IR (KBr) 3150–2500, 1624, 1465 cm^{-1}; UV (KBr) 318, 462 nm; Anal. Calcd for $C_{28}H_{18}Cl_2N_4S_{12}$: C, 36.16; H, 1.95; Cl, 7.62; N, 6.02; O, 6.88; S, 41.37%. Found: C, 36.38; H, 2.11; Cl, 7.39; N, 6.32; O, 6.68; S, 41.13%.

(EDT-TTF-Im•H^+)$_2$(CNA^{2-}) (2)

EDT-TTF-Im (3.6 mg, 1.1 μmol) and H_2CNA•$6H_2O$ (3.2 mg, 0.9 μmol) were placed at the bottom of each side of an H-shaped tube. Diffusion of them in MeCN (10 mL) at room temperature for 2 months afforded dark red crystals (1.7 mg) suitable for X-ray analysis. Due to too small amount of the sample, elemental analysis could not be performed.

IR (KBr) 3150–2500, 2196, 1625, 1517 cm^{-1}; UV (KBr) 278, 312, 444, 830 nm.

Table S1. Selected intramolecular bond lengths of EDT-TTF-Im.



	a/Å	*b*/Å	*c*/Å	*d*/Å	*e*/Å	*f*/Å	*g*/Å
EDT-TTF-Im[S1)]	1.338(3)	1.767(2) 1.731(2)	1.765(2) 1.764(2)	1.347(3)	1.751(2) 1.763(2)	1.767(2) 1.765(2)	1.341(3)
EDT-TTF-Im-F_4TCNQ[S1)]	1.349(5)	1.739(3) 1.724(4)	1.718(3) 1.721(3)	1.405(5)	1.708(3) 1.715(3)	1.729(4) 1.724(3)	1.359(5)
1	1.340(4)	1.751(3) 1.733(3)	1.755(3) 1.757(3)	1.344(4)	1.758(3) 1.754(3)	1.755(3) 1.752(3)	1.343(4)
2	1.353(3)	1.755(2) 1.732(2)	1.761(2) 1.762(2)	1.351(3)	1.754(2) 1.756(2)	1.758(2) 1.766(2)	1.352(3)

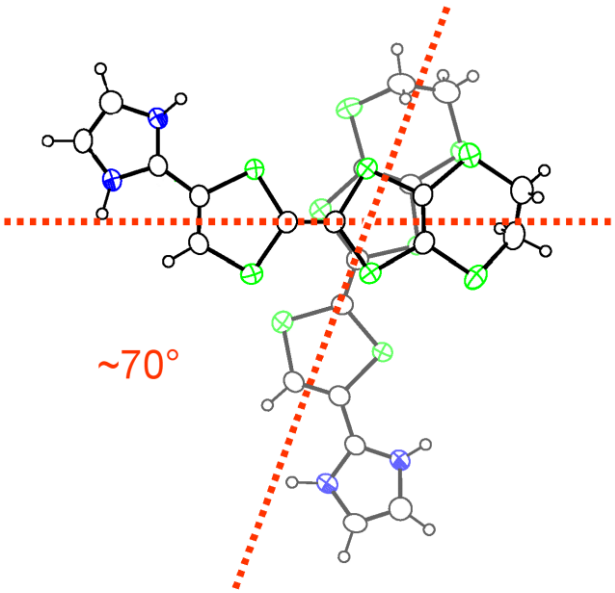


Figure S1. Overlap pattern of the interlayer stack in the crystal structure of **1**. Orange dotted lines indicate the twist angle of EDT-TTF-Im•H^+ molecules.

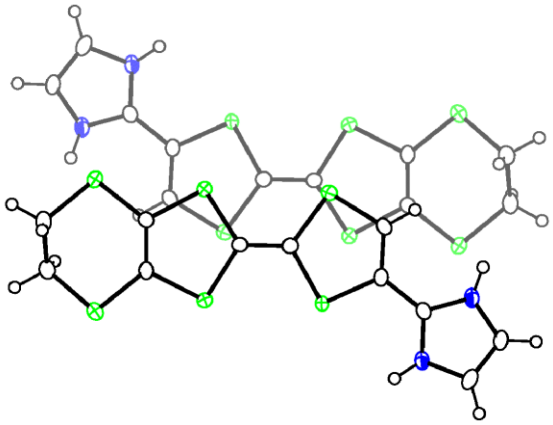


Figure S2. Overlap pattern of the interlayer stack in the crystal structure of **2**.

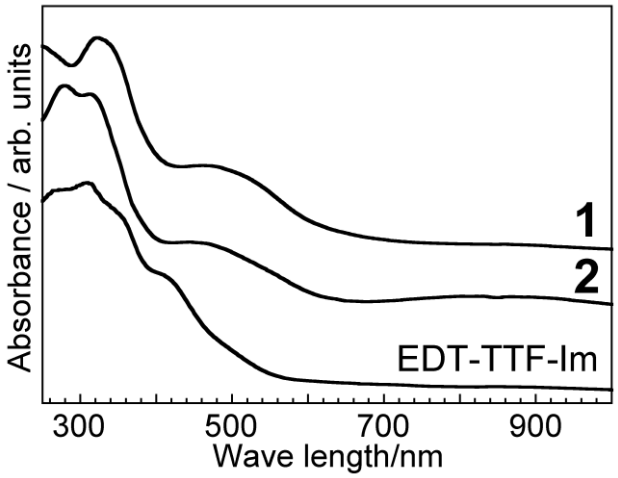


Figure S3. Electronic spectra of **1** and **2** in KBr pellets.