Electronic Supplementary Information (ESI)

Ionic semiconductor: DC and AC conductivity of anilinium tetrathiafulvalene-2-carboxylate

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1. General

^{1}H nuclear magnetic resonance (NMR) spectrum was recorded on Bruker AVANCE system (600 MHz). Infrared (IR) spectrum was measured with a Perkin Elmer SPECTRUM GX-Raman.

Ammonium hydroxide solution, 28%, dimethyl sulfoxide-d_6, 99.96 atom% D, were purchased from Sigma-Aldrich Japan. Diethyl ether, toluene, hexane, and ethyl acetate were purchased from KANTO CHEMICAL. Aniline was purchased from TOKYO CHEMICAL INDUSTRY and distilled before use.

2. Dc conductivity of a compressed pellet sample

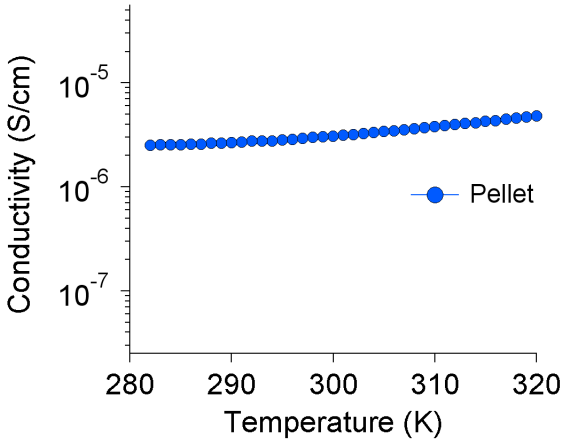

Figure S1. Dc conductivity of a compressed pellet, which was measured by four-probe method from 280 to 320 K.

3. X-ray powder diffraction pattern

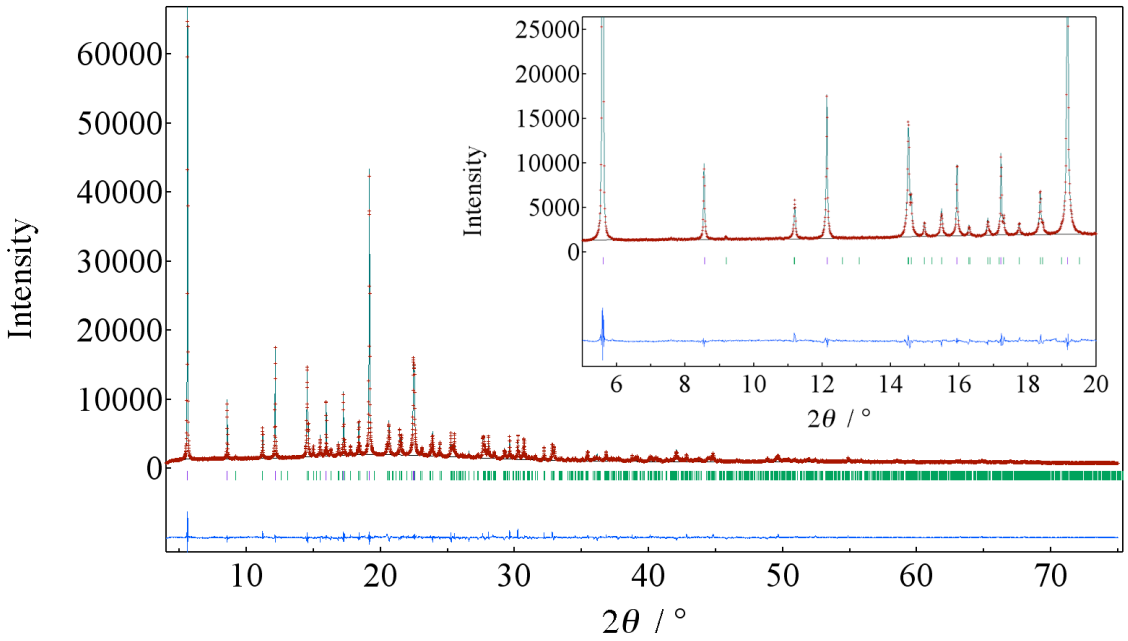

Figure S2. X-ray diffraction pattern of the powder crystals. Inset figure shows zoomed peaks from 5 to 20 degree of 2θ. Red plots show experimental data, green line indicates fitted function by Reitveld method[9a], and blue line shows the residue, indicating good agreement with each other.

4. Molecular orbital calculation

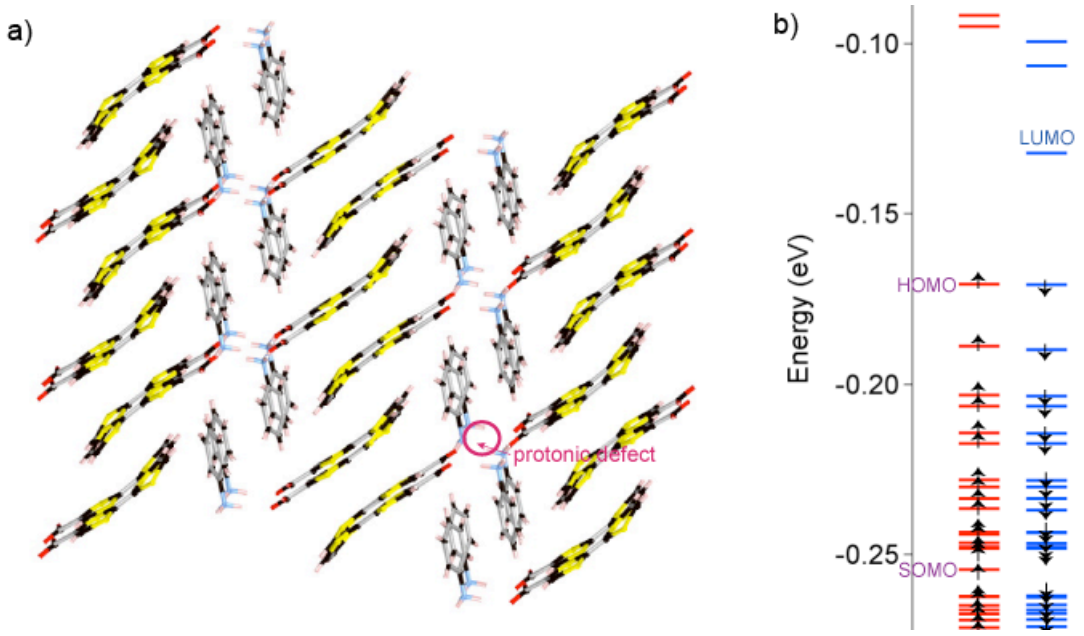

Figure S3. Molecular orbital calculation carried out with UHF/3-21G* using Gaussian 03 code.[S1] a) Molecular cluster composed of twenty-four molecular pair including one protonic defect. b) Molecular orbital for alpha spin (red) and for beta spin (blue).

The molecular coordinates were extracted from the X-ray structure in the text. The singly occupied molecular orbital (SOMO) is lowered than that of the highest occupied molecular orbital (HOMO), showing quasi-closed shell electron configuration as well as the ammonium salt[5a]. The lowest unoccupied molecular orbital (LUMO) of the beta spin is lower than that of the alpha spin, which provides acceptor (impurity) level.

5. Reference

S1. Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Montgomery Jr., J. A., Vreven, T., Kudin, K. N., Burant, J. C., Millam, J. M., Iyengar, S. S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G. A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J. E., Hratchian, H. P., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Ayala, P. Y., Morokuma, K., Voth, G. A., Salvador, P., Dannenberg, J. J., Zakrzewski, V. G., Dapprich, S., Daniels, A. D., Strain, M. C., Farkas, O., Malick, D. K., Rabuck, A. D., Raghavachari, K., Foresman, J. B., Ortiz, J. V., Cui, Q., Baboul, A. G., Clifford, S., Cioslowski, J., Stefanov, B. B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R. L., Fox, D. J., Keith, T., Al-Laham, M. A., Peng, C. Y., Nanayakkara, A., Challacombe, M., Gill, P. M. W., Johnson, B., Chen, W., Wong, M. W., Gonzalez, C. & Pople, J. A. Gaussian 03, Revision E.01, Gaussian Inc., Wallingford CT (2004).