A tailor-made hexagonal system in a molecular conductor

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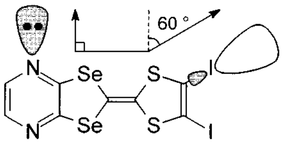
A unique hexagonal system based on an organic π-donor has been tailored by the *strong* and *directional* I···N intermolecular interaction, and its highly symmetrical structure including two types of channels and high conductivity are reported.

The development of highly symmetrical systems is always of interest in materials science as in the cases of molecular conductors based on fullerenes,[1,2] and the introduction of a characteristic intermolecular interaction is necessary to construct a unique molecular-based crystal system. One of the major techniques for controlling solid-state molecular assemblies is the use of the hydrogen bond,[3] however, it is not always enough to fix the direction of the interaction. Recently, we have found that the *strong* and *directional* I···X (X = CN, S or halogen atoms) type cation···anion interaction is useful to control the molecular arrangement of organic conductors.[4] An example of the above I···N interaction is the impressive one-dimensional chain structure in the crystal of *p*-iodobenzonitrile.[5] In the course of our study to extend and generalize the new I···N architecture for molecular-based materials, we have designed diiodo(pyrazino)diselenadithiafulvalene (DIPS, **1**; Scheme 1) which contains two interaction sites, the iodine atom and the nitrogen atom on the edges of the skeleton. Here we report the synthesis, structure and physical properties of a unique hexagonal system with high conductivity and two types of channels tailored by the strong and directional I···N intermolecular interactions.



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Scheme 1 Schematic view of molecular structure of a new iodine-bonded π-donor **1** and directions of lone pair on the pyrazine ring and σp LUMO on the C–I bond (see text)

Synthesis of **1**† was achieved by the cross-coupling reaction of 4,5-diiodo-1,3-dithiole-2-one[6] and pyrazine-fused 1,3-diselenole-2-one.[7] Long rod-like single crystals (average size 1 mm long, 0.1 mm diameter) of $(\mathbf{1})_3(PF_6)(solv.)_x$ [solv. = chlorobenzene, dichloromethane or trichloroethane] were obtained by the galvanostatic oxidation (1.0 μA) of a solution (20 ml) containing **1** (*ca.* 8 mg) and tetrabutylammonium hexafluorophosphate (*ca.* 20 mg) as a supporting electrolyte. Single crystals were grown on the anode within a few days and the hexagonal section of the rod is in accordance with the hexagonal crystal system (Fig. 1). Elemental analyses indicate that the donor-anion ratios of the salts are 3 : 1 and the solvent used in the crystallization is included in the crystal.‡

Temperature dependences of the conductivity for the salts were measured by the standard four-probe method. They are all semiconductive from room temperature, however, the room temperature conductivity is rather high ($\sigma_{rt} \approx 10$ S cm^{-1}) and the activation energy is small (*ca.* 50 meV).

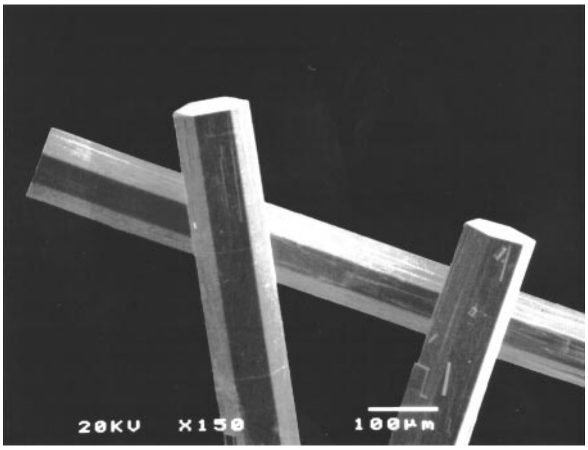

Fig. 1 Photographic SEM image of single crystals for $(\mathbf{1})_3(PF_6)$(chlorobenzene)$_{1.15}$

X-Ray structural analyses were performed on the single crystals and all salts crystallize into a hexagonal $P6_3/mcm$ space group and are isostructural.§ Fig. 2 shows the unit cell of the PF_6–chlorobenzene salt and there are two types of triangular units of the donor molecules within the *ab* plane, ordered clockwise and anticlockwise, respectively. The hexagonal lattice is constructed by the alternating repetition of these triangular units. The shortest intermolecular I···N distance is 2.879(6) Å and it is almost 20% shorter than the sum of the van der Waals radii (3.53 Å; Bondi[8]). This characteristic I···N contact is much shorter than that of the above-mentioned *p*-iodobenzonitrile crystal (3.18 Å)[5a] and indicates the existence of a very strong intermolecular I···N interaction. The value of the C–I···N angle is almost linear [178.3(2)°] and it is in good agreement with the direction of the pσ LUMO along the carbon–iodine single bond and the lone pair on the pyrazine ring

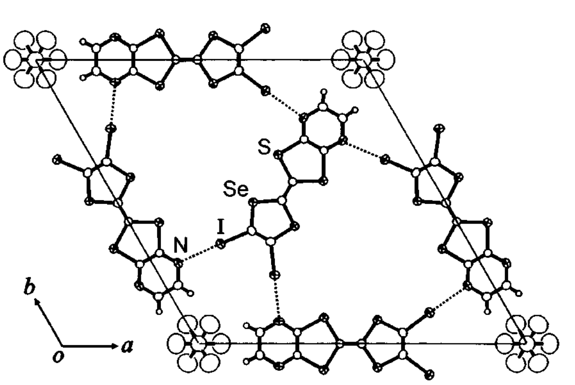

Fig. 2 Crystral structure of $(\mathbf{1})_3(PF_6)$(chlorobenzene)$_{1.15}$ viewed along the crystallographic *c* axis. Chlorobenzene molecules are omitted for clarity. The shortest I···N intermolecular distance (dotted line) is 2.879(6) Å.

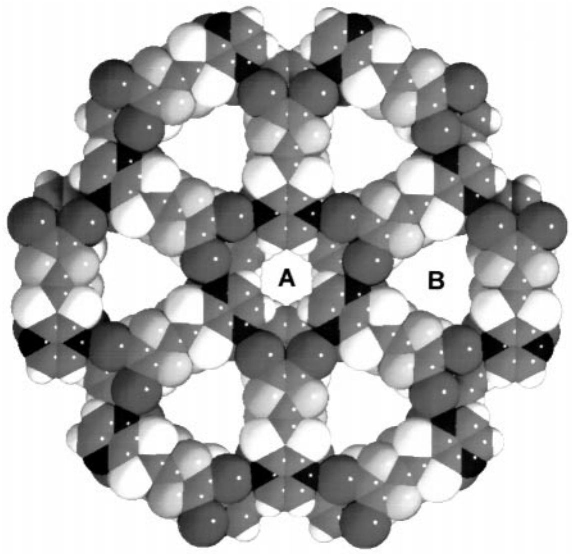

Fig. 3 Extended hexagonal donor-column arrangement of the $(\mathbf{1})_3$(anion)(solv.)$_x$ crystal system

(Scheme 1). The donor molecule also forms a one-dimensional column along the *c* axis within the head-to-tail mode, this is the regular manner for unsymmetrical π-donors. The topology of the donor network should be recognized as the combination of: (i) characteristic I···N intermolecular interaction parallel to the molecular plane, and (ii) columnar stack perpendicular to the molecular plane.

Fig. 3 shows the extended donor network projected onto the *ab* plane and we can see that there are two types of channels along the *c* axis. One is hexagonal and surrounded by the edges of donor molecules (channel site A, *ca.* 4 Å diameter) and the other is an equilateral triangle surrounded by the sides of donor molecules (channel site B, side length *ca.* 7.5 Å). The PF_6 anion is in channel site A and the phosphorus atom is on the crystallographic special position. The included solvent is in channel site B and is highly disordered due to the low symmetry of the molecule compared with the crystallographic symmetry. Comparing the structures of the salts including different solvent molecules, the whole crystal system is not affected by changing of the solvent and the hexagonal arrangement is identical. The guest-independent channel structure is similar to those of the inorganic ‘zeolite’ systems[9] and it would be promising to introduce functionalized guest molecules to obtain multi-functionalized materials. Preliminary thermogravimetric experiments indicated that the PF_6–dichloromethane single crystals began to release the included solvent around 80 °C. The decrease in the sample weight had stopped after annealing at 110 °C for 5 days in the case of the powdered sample and the amount of weight loss (*ca.* 6% *vs.* initial weight) is in accordance with the calculated weight percent of dichloromethane included in the crystal.

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Notes and References

† Selected data for **1**: orange–red wool; mp > 250 °C (decomp.); ^{1}H NMR ($CDCl_3$, 500 MHz); δ 8.12 (s, 2H); MS (EI, 70 eV): 602 ($C_8H_2N_2I_2S_2{}^{80}Se_2$, M^+), 475 ($M^+ - I$), 348 ($M^+ - I_2$); Calc. for $C_8H_2N_2I_2S_2Se_2$: C, 15.96; H, 0.33; N, 4.65. Found: C, 16.05; H, 0.48; N, 4.66%.

‡ Contents of the solvent molecules based on elemental analyses are: chlorobenzene *ca.* 1.15, dichloromethane *ca.* 1.66, trichloroethane *ca.* 1.30.

§ X-Ray diffraction data were collected on a Mac Science four-circle diffractometer (solv. = chlorobenzene) or a Rigaku AFC6S automatic four-circle diffractometer (solv. = dichloromethane, trichloroethane) with monochromated Mo-Kα(λ = 0.71069 Å) radiation up to $2\theta = 60°$ at 293 K. The structures were solved by direct methods and refined with full-matrix least-squares methods using reflections with $I \geqslant 3\sigma(I)$. The data were corrected for Lorentz and polarization effects. Anisotropic thermal parameters were used for non-hydrogen atoms except disordered solvent molecules. All calculations were performed with use of the ‘teXsan’ program package of MSC. *Crystal data* for $(\mathbf{1})_3(PF_6)(\text{chlorobenzene})_{1.15}$: $(C_{24}H_6N_6I_6S_6Se_6)(PF_6)(C_6H_5Cl)_{1.15}$, M = 2080.30, hexagonal, space group $P6_3/mcm$ (no. 193), a = 20.242(2), c = 7.274(2) Å, V = 2581.2(6) Å^3, μ = 82.32 cm^{-1}, D_c = 2.676 g cm^{-3}, $F(000)$ = 1891.40, Z = 2, R = 0.031, R_w = 0.021, GOF = 1.70 for 912 observed reflections out of 2647 unique reflections. $(\mathbf{1})_3(PF_6)(\text{dichloromethane})_{1.66}$: $(C_{24}H_6N_6I_6S_6Se_6)(PF_6)(CH_2Cl_2)_{1.66}$, M = 2091.85, hexagonal, space group $P6_3/mcm$ (no. 193), a = 20.165(5), c = 7.28(1) Å, V = 2562(2) Å^3, μ = 84.02 cm^{-1}, D_c = 2.711 g cm^{-3}, $F(000)$ = 1897.44, Z = 2, R = 0.050, R_w = 0.036, GOF = 2.28 for 721 observed reflections out of 1513 unique reflections. $(\mathbf{1})_3(PF_6)(\text{trichloroethane})_{1.30}$: $(C_{24}H_6N_6I_6S_6Se_6)(PF_6)(C_2H_3Cl_3)_{1.30}$, M = 2124.29, hexagonal, space group $P6_3/mcm$ (no. 193), a = 20.20(2), c = 7.263(8) Å, V = 2565(3) Å^3, μ = 84.23 cm^{-1}, D_c = 2.750 g cm^{-3}, $F(000)$ = 1929.60, Z = 2, R = 0.044, R_w = 0.023, GOF = 1.33 for 547 observed reflections out of 1512 unique reflections. CCDC 182/978.

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