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PYRAZINE-FUSED EXTENDED DONORS, BDTFP, EDT-BDTFP, AND BEDT-BDTFP: NOVEL DONORS AND THEIR CONDUCTING COMPLEXES

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Novel pyrazine-fused extended donors, BDTFP, EDT-BDTFP, and BEDT-BDTFP have been synthesized by convenient methods. [BDTFP]/[TCNQ] is metallic down to 150 K [BDTFP]₂[PF₆]/[PhCl]_{0.5} showed room temperature conductivity of 40 S cm⁻¹.

Keywords: pyrazine-fused donors; TCNQ complexes; cation radical salts

INTRODUCTION

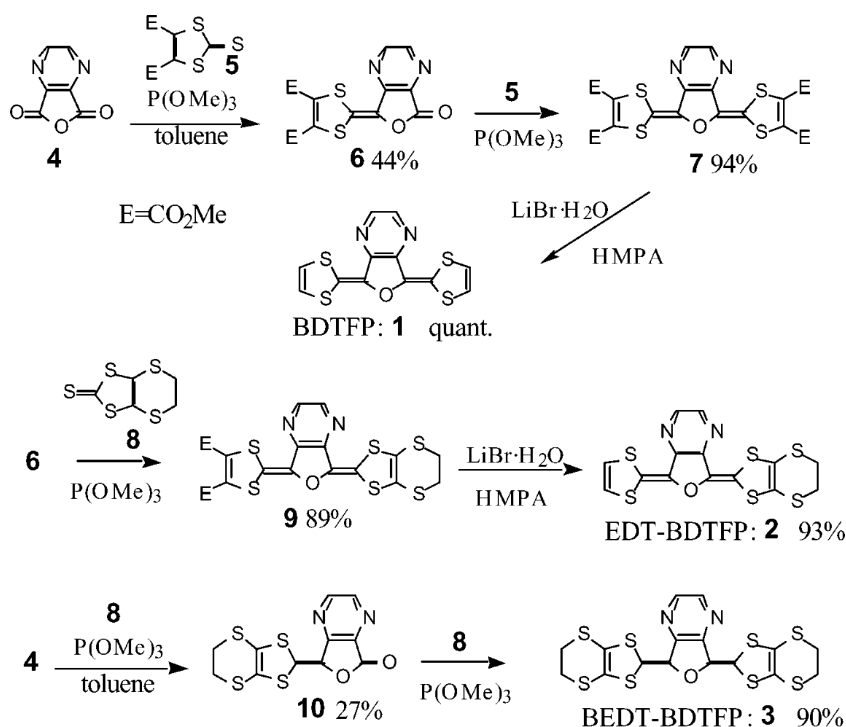
Elongation of donor π -systems is a prominent molecular design strategy to decrease Coulombic repulsive energy [1] which can participate in increasing the transfer integrals of electron wave functions and to increase in the thickness of the effective conducting layer which can contribute to produce high T_c organic superconductors [2]. We have so far synthesized thiopheno- or selenopheno-quinonoid-extended TTF type donors [1,3]. However, these extended donors have high electron donating abilities and air-sensitive in solution. To weaken the electron donating ability of the extended donors, we have now synthesized novel pyrazine-fused extended donors, BDTFP **1**, EDT-BDTFP **2**, and BEDT-BDTFP **3** in very convenient synthetic routes, and investigated electrical properties of their charge-transfer (CT) complexes and cation radical salts of **1**.

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RESULTS AND DISCUSSION

The synthetic routes of **1**, **2**, and **3** are outlined in Scheme 1.

Pyrazine-2,3-dicarboxylic anhydride (**4**), conveniently available by the dehydration of pyrazine-2,3-dicarboxylic acid, was allowed to react with 2 equiv. of 4,5-bis(methoxycarbonyl)-1,3-dithiole-2-thione (**5**) in the presence of excess amount of trimethyl phosphite in refluxing toluene to afford mono-capped intermediate **6** in 44% yield. Treatment of **6** with **5** in trimethyl phosphite at 90°C afforded tetrakis(methoxycarbonyl) derivative **7** in 94% yield. The tetraester **7** was easily demethoxy-carbonylated with lithium bromide monohydrate in hexamethylphosphoric triamide at 90°C and then at 155°C to give the novel pyrazine-fused donor, BDTFP **1** in quantitative yield. When **6** was allowed to react with 2 equiv. of 4,5-ethylenedithio-1,3-dithiole-2-thione (**8**) in trimethyl phosphite at 100°C, the unsymmetrically capped compound **9** was obtained in 89% yield. The ethylenedithio derivative, EDT-BDTFP **2**, was obtained in 93% yield by



SCHEME 1

heating **9** with 10 equiv. of lithium bromide monohydrate in hexamethylphosphoric triamide at 90°C and then 155°C. The cross-coupling reaction of the anhydride **4** with **8** in the presence of excess of trimethyl phosphite in toluene at 110°C afforded mono-capped compound **10** in 27% yield. The bis-capped new donor, BEDT-BDTPF **3** was synthesized in 90% yield by heating the mixture of **10** and **8** in trimethyl phosphite without solvent at 100°C.

Contribution of the polarized resonance structure **1B** in **1** is significant since **1** exhibits characteristic intramolecular charge transfer band at 500–620 nm which is not observed in the corresponding benzene-fused donor BDTBF as shown in Figure 1.

The pyrazine-fused donors, **1–3** exhibited two well-defined reversible one-electron oxidation waves in cyclic voltammograms. As shown in Table 1, E_1^{ox} values of BDTPF **1** and BEDT-BDTPF **3** are higher by 0.12 V than those of the corresponding benzene-fused donors BDTBF (+0.24 V) [4] and BEDT-BDTBF (+0.37 V) [5], which is ascribed to the stabilization of the energy levels of the HOMOs of **1** and **3** by the annelation of the electron-deficient pyrazine ring.

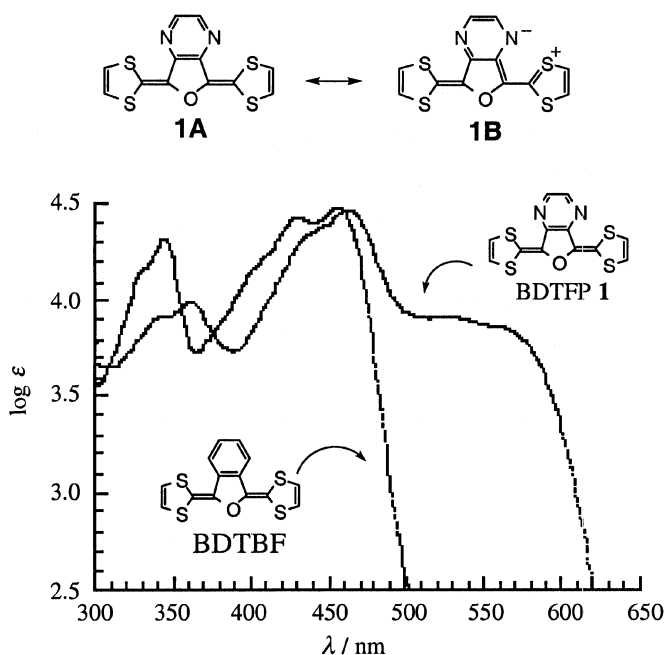


FIGURE 1 UV-Vis spectra of BDTPF **1** and BDTBF in THF.

TABLE 1 Oxidation Potentials^a of the Pyrazine-Fused Donors

Compound	E_1^{OX}	E_2^{OX}	ΔE^{OX}	$\log K_{\text{SEM}}$
BDTFP 1	+0.36	+0.62	0.26	4.41
EDT-BDTFP 2	+0.43	+0.67	0.24	4.07
BEDT-BDTFP 3	+0.49	+0.70	0.21	3.56

^a Potentials are given in V *vs* SCE, 1.0 mM PhCN soln with 0.1 M TBAP, 50 mVs⁻¹

BDTFP **1** formed 1:1 CT-complexes with TCNQ and TCNQF₄, whereas EDT-BDTFP **2** and BEDT-BDTFP **3** formed 1:1 CT-complexes only with stronger acceptor, TCNQF₄. The room temperature conductivities measured on a compressed pellet and ν_{CN} bands in IR spectra and activation energies determined from temperature dependencies of resistivities of the complexes are summarized in Table 2.

[BDTFP][TCNQ] showed fairly high room temperature electrical conductivity of 20 S cm⁻¹ even the measurement was carried out on a compressed pellet and exhibited semiconducting temperature dependence of the resistivity in the temperature region from 125 K to 80 K with $E_a = 0.049$ eV. However, Arrhenius plot of temperature dependence of the resistivity is not linear in the temperature region from room temperature down to 150 K (Figure 2).

Moreover, the temperature dependence of the static magnetic susceptibility of [BDTFP][TCNQ] measured by SQUID method on a powder sample is almost flat in the temperature region of 300 K–100 K, although the magnetic susceptibility slightly decreases with decreasing the temperature (Figure 3). Thus, Pauli-like paramagnetic behavior is realized in this temperature region. These facts indicate that [BDTFP][TCNQ] is essentially metallic down to ca. 150 K and undergoes a metal to insulator phase transition at around 100 K.

TABLE 2 Conductivities and IR Data of CT-Complexes of **1**, **2**, and **3**

Donor	Acceptor	(D:A) ^a	ν_{CN} ^b /cm ⁻¹	$\sigma_{\text{r.t.}}$ ^c /S cm ⁻¹	E_a ^d /eV
BDTFP 1	TCNQ	1:1	2195	20	0.049
BDTFP 1	TCNQF ₄	1:1	2193, 2173	0.1	—
EDT-BDTFP 2	TCNQF ₄	1:1	2191, 2171	9.5×10^{-4}	—
BEDT-BDTFP 3	TCNQF ₄	1:1	2189, 2169	0.18	0.111

^a Determined by elemental analysis. ^b Measured by FTIR (KBr disk). Neutral TCNQ: $\nu_{\text{CN}} = 2220$ cm⁻¹. Neutral TCNQF₄: $\nu_{\text{CN}} = 2222$ cm⁻¹. ^c Measured by four-probe method on a compressed pellet. ^d Determined by temperature dependence of resistivity.

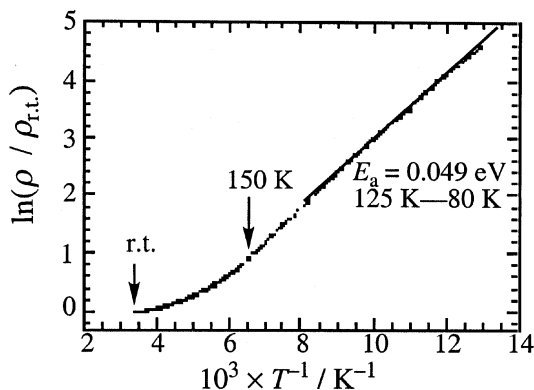


FIGURE 2 Temperature dependence of the normalized resistivity for [BDTFP][TCNQ] on a compaction pellet (Arrhenius plot).

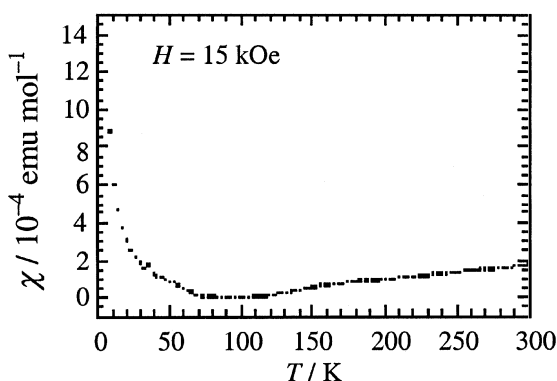


FIGURE 3 Temperature dependence of the static magnetic susceptibility of [BDTFP][TCNQ] measured by SQUID method on a powdered sample.

TABLE 3 Properties of Cation Radical Salts of BDTFP **1**

Anion	Appearance	(D:A:S) ^a	mp/°C	$\sigma_{r.t.}^b / \text{Scm}^{-1}$	E_a^c / eV
ReO ₄	brown scales	1:1	> 300	—	—
PF ₆	brown plates	2:1:0.5	213	40	0.076
AsF ₆	brown plates	2:1:0.5	213	4.0	0.078

^a Determined by elemental analysis.

^b Measured by four-probe method on a single crystal.

^c Determine by temperature dependence of resistivity.

Several cation radical salts of BDTFP listed in Table 3 were prepared by electrochemical oxidation using the corresponding tetra-*n*-butylammonium salts as the electrolytes in chlorobenzene. Of these [BDTFP]₂[PF₆][PhCl]_{0.5} and [BDTFP]₂[AsF₆][PhCl]_{0.5} are single crystals in good quality and showed fairly high conductivities of 40 and 4.0 S cm⁻¹, respectively, both of which showed semiconductive behavior. We are currently undergoing X-ray diffractive analysis of these salts.

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