

Table 1. Redox potentials of the new donors **5a–c**, **7** and **6a**.

Compound	E_1^* (V)	E_2^* (V)	$E_2 - E_1$ (V)
BEDT-TTF (6a)	0.48	0.89	0.41
7	0.55	0.96	0.41
5a	0.54	0.96	0.42
5b	0.47	0.89	0.42
5c	0.53	0.97	0.44

* vs SCE, 1.0 mM solutions in CH_2Cl_2 with 0.1 M Bu_4NPF_6 ; scan rate 100 mV/s.

The nucleophilic displacement reaction of **2** [8] with **1** in one step using dry THF as solvent gave thione **3** in a 88% yield. The same product was obtained by the reaction of $(\text{Bu}_4\text{N})_2[\text{Zn}(\text{dmit})_2]$ ($\text{dmit} = 1, 3\text{-dithiol-2-thione-4, 5-dithiolate}$) with **1** but the yield was lower than 50%.

Coupling reaction of thione **3** in dry benzene with an excess of triethyl phosphite gave alkene **7**. The product was purified by column chromatography on silica gel with CH_2Cl_2 as eluent. Coupling reactions of the thione **3** with ketones **4a**, **4b**, **4c** in benzene with an excess of triethyl phosphite gave a mixture of symmetrical and unsymmetrical π -donors. The mixture was separated by column chromatography. The donors can be obtained also by the use of the corresponding thiones instead of ketones but the yields are lower. By this method we can prepare many TTF derivatives with methoxy groups, using thiones or ketones similar to **4**.

As expected, the cyclic voltammograms of the new donors exhibit two $1e^-$ reversible oxidation peaks corresponding to the successive generation of the radical cation and the dication (Table 1). The MeO group increases the redox potentials, but they are comparable with those of BEDT-TTF indicating that the new donors are suitable for the preparation of conducting radical cation salts.

The electron donating properties of these new donors were tested by preparing conducting radical cation salts with I_3^- and PF_6^- . The properties of these salts and others with different anions will be reported elsewhere.

Experimental Section

Compound **2** was prepared by methods reported in [8].

Compound **1** was prepared by a method similar to that reported in [7], as follows: A mixture of 9.6 g (165 mmol) of glyoxal, 13 ml of anhydrous MeOH and 1 ml of SOCl_2 were introduced in a three-necked flask, equipped with a thermometer, a pressure equalizing dropping funnel and a condenser with a CaCl_2 tube. The mixture was heated to dissolve

the glyoxal, cooled with an ice-salt bath, and 24 ml of SOCl_2 was added dropwise so that the inside temperature did not exceed 5°C . After 50% of SOCl_2 had been added a vigorous gas evolution started and the reaction became endothermic. At this moment the cooling bath was replaced by a heating bath and the rest of SOCl_2 was added faster keeping the inside temperature at $20\text{--}30^\circ\text{C}$. The procedure took place in 3 h. The solution was stirred overnight. The excess of SOCl_2 and the solvent were evaporated under vacuum. Our product was purified by distillation under reduced pressure (19 Torr) at $78\text{--}80^\circ\text{C}$ (lit. 79°C [7]). The product, when placed in a refrigerator, crystallized as transparent crystals (18.0 g, yield 68%), m.p. 72°C . – $^1\text{H NMR}$ (300 MHz, CDCl_3): $\delta = 5.45$ (s, 1H, CHCl), 3.55 (s, 3H, OMe).

Compound **3** was prepared as follows: To a solution of 2.4 g (10 mmol) of **2** [8] in 50 ml of CH_3CN a solution of 1.58 g (10 mmol) of **1** in 10 ml of CH_3CN was added. The mixture was stirred for 15 min under N_2 at room temperature. During this time the color changed from red to orange-yellow. The mixture was filtered. The filtrate was evaporated *in vacuo* and the residue was purified by column chromatography on SiO_2 with CH_2Cl_2 as eluent to give **3** (2.2 g, yield 88%) as a yellow solid, m.p. 123°C . – UV/vis (CH_2Cl_2): $\lambda_{\text{max}1}(\text{lg } \epsilon) = 403 \text{ nm}$ (4.12), $\lambda_{\text{max}2}(\text{lg } \epsilon) = 273 \text{ nm}$ (3.88). – $^1\text{H NMR}$ (300 MHz, CDCl_3): $\delta = 3.58$ (s, 6H, 2 OMe) and 5.32 (s, 2H, 2 OCH). – $\text{C}_7\text{H}_8\text{O}_2\text{S}_5$ (284.3): calcd. C 29.56, H 2.83; found C 29.42, H 2.81.

Compounds **5a**, **5b**, **5c** were prepared as follows: A mixture of **3** (300 mg, 1.05 mmol), and **4a** or **4b** or **4c** (1.05 mmol) and triethyl phosphite (2 ml, 12 mmol) was refluxed in 10 ml of dry benzene for 4 h. The mixture was evaporated *in vacuo* and the residue was purified by column chromatography on SiO_2 with CH_2Cl_2 as eluent. The first fraction contained **6**, the second **5a** or **5b** or **5c**, and the third **7**. Physico-chemical data for **5a**: yellow-orange crystals, 13% yield, m.p. $180\text{--}181^\circ\text{C}$. – UV/vis (CH_2Cl_2): $\lambda_{\text{max}1}(\text{lg } \epsilon) = 346 \text{ nm}$ (4.05), $\lambda_{\text{max}2}(\text{lg } \epsilon) = 318 \text{ nm}$ (4.18). – $^1\text{H NMR}$ (300 MHz, CDCl_3): $\delta = 3.55$ (s, 6H, 2 OMe), 3.29 (s, 4H, 2 SCH_2) and 5.23 (s, 2H, 2 CH). – $\text{C}_{12}\text{H}_{12}\text{O}_2\text{S}_8$ (444.5): calcd. C 32.41, H 2.72; found C 32.22, H 2.92. Physico-chemical data for **5b**: orange crystals, 10% yield, m.p. 179°C . – UV/vis (CH_2Cl_2): $\lambda_{\text{max}1}(\text{lg } \epsilon) = 350 \text{ nm}$ (4.26), $\lambda_{\text{max}2}(\text{lg } \epsilon) = 323 \text{ nm}$ (4.51), $\lambda_{\text{max}3}(\text{lg } \epsilon) = 310 \text{ nm}$ (4.46). – $^1\text{H NMR}$ (300 MHz, CDCl_3): $\delta = 3.54$ (s, 6H, 2 OMe), 4.25 (s, 4H, 2 CH_2) and 5.22 (s, 2H, 2 CH). – $\text{C}_{12}\text{H}_{12}\text{O}_4\text{S}_6$ (412.6): calcd. C 34.93, H 2.93; found C 34.81, H 2.93. Physico-chemical data for **5c**: orange crystals, 21% yield, m.p. $187\text{--}188^\circ\text{C}$. – UV/vis (CH_2Cl_2): $\lambda_{\text{max}1}(\text{lg } \epsilon) = 346 \text{ nm}$ (3.93), $\lambda_{\text{max}2}(\text{lg } \epsilon) = 318 \text{ nm}$ (4.14). – $^1\text{H NMR}$ (300 MHz, CDCl_3): $\delta = 2.40$ (m, 2H, CH_2), 2.69 (m, 4H, 2 CH_2), 3.54 (s, 6H, 2 OMe), and 5.22 (s, 2H, 2 CH). – $\text{C}_{13}\text{H}_{14}\text{O}_2\text{S}_8$ (458.8): calcd. C 34.03, H 3.08; found C 34.11, H 2.99.

Compound **7** was prepared as follows: A mixture of **3** (300 mg, 1.05 mmol) and triethyl phosphite (2 ml, 12 mmol) was refluxed in 10 ml of dry benzene for 4 h. The mixture was evaporated *in vacuo* and the residue was purified by column chromatography on SiO₂ with CH₂Cl₂ as eluent to give **7** as orange-yellow crystals, 60% yield, m.p. 186–187 °C. – UV/vis (CH₂Cl₂): λ_{max1}(lg ε) = 339 nm (4.13), λ_{max2}(lg ε) = 311 nm (4.17). – ¹H NMR (300 MHz, CDCl₃): δ = 3.56 (s, 12H, 4 OMe) and 5.23 (s, 4H, 4 CH). –

C₁₄H₁₆O₄S₈ (504.8): calcd. C 33.31, H 3.19; found C 33.45, H 3.08.

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