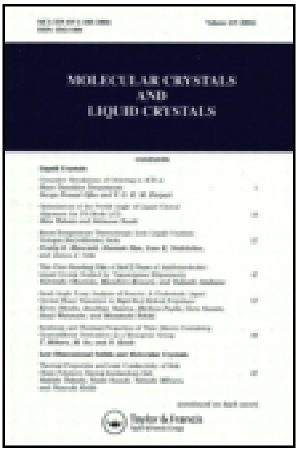

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# New TTP Donors Containing Chalcogenopyran-4-ylidene: Preparation, Structures, and Electrical Properties

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# New TTP Donors Containing Chalcogenopyran-4-ylidene: Preparation, Structures, and Electrical Properties

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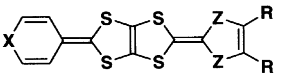
Abstract Several TM-PDT analogous donors, where TM-PDT is 2-[4,5-bis(thiomethyl)-1,3-dithiol-2-ylidene]-5-(pyran-4-ylidene)-1,3,4,6-tetrathiapentalene, have been prepared. Cyclic voltammetry demonstrated that chalcogen atom exchange at chalcogenopyran moiety in donors strongly influenced their redox potentials. Electrical conductivity of all their salts showed a semiconducting behavior with relatively small activation energy. Crystal structure of (SM-PDT)(TCNQ) , where TM-PDT is 2-[4,5-bis(selenomethyl)-1,3-dithiol-2-ylidene]-5-(pyran-4-ylidene)-1,3,4,6-tetrathiapentalene, has been revealed to compose of the D-A type mixed stacks.

Keywords π-electron donor; electrochemical property; cation radical salt; electrical conductivity; crystal structure

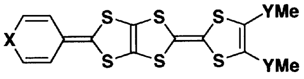
## INTRODUCTION

In most organic metals the intermolecular interactions between π-planes (“face-to-face”) and/or sulfur atoms (“side-by-side”) have played an important role. In order to extend the variations of intermolecular interactions, we have recently reported synthesis and electrical properties of the cation radical salts of PDT-TTP derivatives,[1,2] which have chalcogen atoms in their molecular-“edges”. Among them, (TM-TPDS)$_2$AsF$_6$[3] gave three-dimensional donor array based on the “edge-to-side” interaction, and its conductivity was metallic down to about

100 K. In order to stabilize a metallic state and enhance the intermolecular interactions between donor-edge and -side, displacement with larger chalcogen atoms in donor-edge is expected to be one of the useful methods. In this proceedings, we report synthesis and electrochemical properties of several chalcogen analogues of TM-PDT with substitution of larger chalcogen atoms in their terminals, and crystal structure and electrical properties of their conducting complexes.



PDT-TTP : X = O, Z = S, R = H
TM-PDT : X = O, Z = S, R = SMe
TM-TPDS : X = S, Z = Se, R = SMe



SM-SPDT (**1Aa**): X = Y = Se
TM-SPDT (**1Ab**): X = Se,Y = S
SM-TPDT (**1Ba**): X = S, Y = Se
SM-PDT (**1Ca**) : X = O, Y = Se

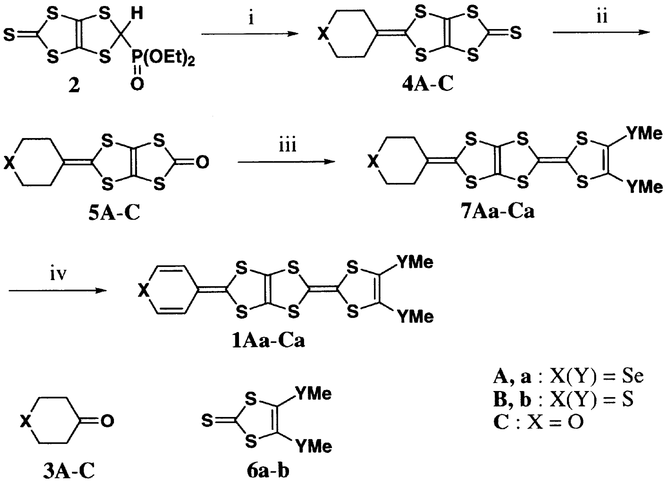
## RESULTS AND DISCUSSION

### Synthesis and Electrochemical Properties

Novel TM-PDT analogous donors were prepared according to similar procedure to synthesis of PDT-TTP derivatives[2] (Scheme 1). The Wittig-Horner reaction of phosphonate ester **2**[4] with tetrahydrochalcogenopyran-4-ones **3A**-**C**[5] gave thiones **4A**-**C** in 68-85% yields. Thiones **4A**-**C** were converted to corresponding ketones **5A**-**C** by treatment with mercury (II) acetate (44-60%). Cross-coupling reaction between **5A**-**C** and thione **6a**[6] or **6b** with neat triethylphosphite at 80 °C afforded tetrahydro compounds **7Aa**-**Ca** in 24-42% yields. The target donors were obtained by dehydrogenation of **1Aa**-**Ca** with DDQ in refluxing xylene (31-75%).

Cyclic voltammetry revealed that the new donors except SM-PDT exhibited three reversible one-electron oxidation waves and successively one irreversible one-electron wave. On the other hand, both SM-PDT and TM-PDT showed two reversible one-electron oxidation waves and one irreversible two-electron wave. Most TTP derivatives containing the pyran ring have demonstrated such a different redox behavior. Compared with the first oxidation potentials of new donors, no significant effect was observed by substitution at the thiomethyl groups. However, the oxidation potentials were largely shifted by displacement of chalcogen atom at the pyran moieties.

SCHEME 1



i) **3**, LDA, THF, −78 °C; ii) $Hg(OAc)_2$, $CHCl_3$-AcOH, room temp.; iii) **6**, $P(OEt)_3$, 80 °C; iv) DDQ, xylene, reflux.

TABLE 1. Redox Potentials of New Donors with Related Donor in Benzonitrile (V vs. $Fc/Fc^+$, 25 °C)

| Donor | $E_1$ | $E_2$ | $E_3$ | $E_4$ |
|---|---|---|---|---|
| SM-SPDT (**1Aa**) | −0.06 | +0.20 | +0.52 | +0.76[a] |
| TM-SPDT (**1Ab**) | −0.07 | +0.21 | +0.51 | +0.73[a] |
| SM-TPDT (**1Ba**) | −0.09 | +0.19 | +0.52 | +0.76[a] |
| SM-PDT (**1Ca**) | −0.05 | +0.22 | +0.68[b] | |
| TM-PDT | −0.04 | +0.24 | +0.66[b] | |

[a] Irreversible step. Anodic peak potentials. [b] Irreversible two-electron oxidation wave.

## Electrical Conductivity of Conducting Complexes

Cation radical salts were obtained by electrochemical oxidation in the presence of corresponding tetrabutylammonium salts in chlorobenzene containing 5%(v/v) ethanol at room temperature. TCNQ complexes were prepared by mixing the chlorobenzene solution of donor and TCNQ. Although TM-PDT mainly formed the 2:1 salts,[2] the compositions of the SM-PDT and TM-SPDT salts were 1:1 in most case. Unfortunately, no complex of the other new donors have been obtained. The electrical conductivities of the SM-PDT and TM-SPDT salts are relatively high ($\sigma_{rt}$ = $10^0$ $Scm^{-1}$) at room temperature except the $ClO_4$ salt of TM-SPDT. However, all of them showed a semiconducting behavior with small activation energy (~0.05 eV). On the other hand, the TCNQ complex of TM-SPDT is a semiconductor indicating moderate conductivity.

TABLE 2. Electrical Conductivity of Conducting Complexes (Donor)(Aceeptor)$_X$

| Donor | Acceptor | X[a] | $\sigma/Scm^{-1}$ [b] | Conducting Behavior |
|---|---|---|---|---|
| SM-PDT | $BF_4$ | – | 4.9 | *E*a = 40 meV |
| | $ClO_4$ | 1.1(Cl)[c] | 2.9 | *E*a = 48 meV |
| | $PF_6$ | 1.0 | 4.8 | *E*a = 50 meV |
| | $AsF_6$ | 1.0 | 8.3 | *E*a = 45 meV |
| | TCNQ | 1.0 | $3.9\times10^{-3}$ | – |
| TM-SPDT | $Au(CN)_2$ | 1.2(Au)[c] | 1.0 | *E*a = 40 meV |
| | $ClO_4$ | 1.6(Cl)[c] | $2.6\times10^{-3}$ | – |

[a] Determined by an X-ray analysis. [b] Measured on a single crystal by four-probe technique. [c] Determined based on energy dispersion spectroscopy from ratio of sulfur and the elements designated in parenthesis.

## Crystal Structure of (SM-PDT)(TCNQ)

Single crystal of (SM-PDT)(TCNQ) was determined by an X-ray analysis.[7] Donor and acceptor molecules are alternately stacked along the *c* axis. The donor plane is not parallel to the acceptor one in mixed

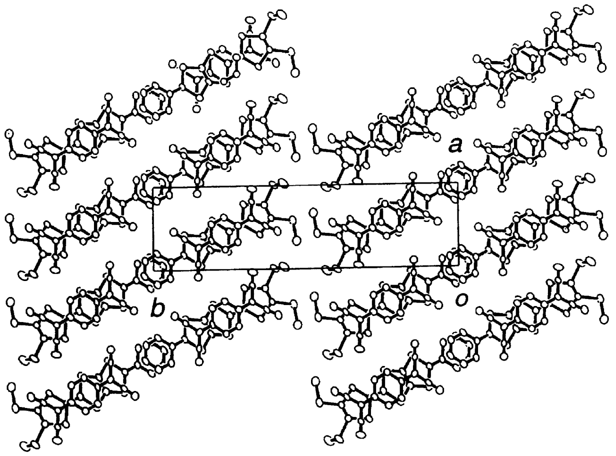


FIGURE 1. Crystal structure of (SM-PDT)(TCNQ) viewed along the *c* axis

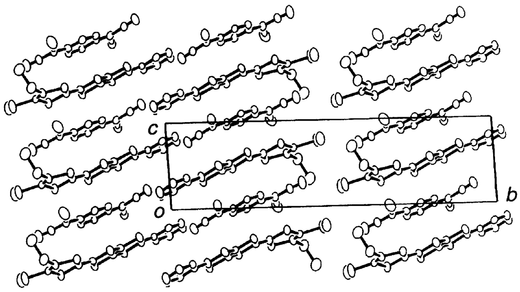


FIGURE 2. Crystal structure of (SM-PDT)(TCNQ) viewed along the *a* axis

stacks, and the dihedral angle between the tetrathiaethylene moiety in donor and the central six-membered ring in acceptor is 6.9°. Remarkable short contact (3.29 Å) between selenium atom in donor and nitrogen in acceptor along the transverse direction is observed.[8] Since the molecular length of TCNQ is shorter than that of donor, the pyran moiety in donor is stuck out from a mixed column. The pyran ring overlaps the other ones in the neighboring stacks along the molecular long axis, constructing one-dimensional column-like structure along the *c* axis (Figure 2). The mean distances between their planes are 3.25 and 3.53 Å. The C≡N stretching bands in this complex are 2197 and 2183 $cm^{-1}$. According to Chappel's equation,[9] the high degree of charge transfer is estimated. In spite of a D-A type mixed stack, it is not an insulator but a semiconductor with the normal order of conductivity, which suggests that coexistence of the overlap of the pyran moiety with a partial charge transfer state plays an important role.

Acknowledgements

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