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BIS(DIARYLETHENYL)THIOPHENE, -BITHIOPHENE, AND -TERTHIOPHENE: A NEW SERIES OF VIOLENE-CYANINE HYBRID-TYPE ELECTRON DONORS

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Dedicated to Professor Isao Kuwajima on the occasion of his 77th birthday

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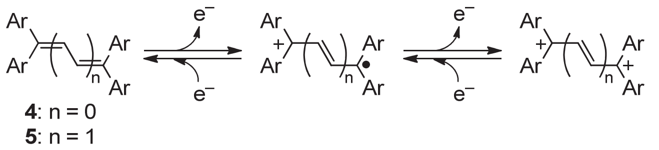
Abstract – The title fluorescent (oligo)thiophenes **1**-**3** were designed as new violene/cyanine-hybrid-type electron donors, which have two 4-methoxyphenyl groups each on the two cyanine parts. Voltammetric analyses showed that they all undergo reversible two-stage one-electron oxidation. The intramolecular short S(thiophene) -- C_{ipso}(Ar) contacts were commonly present in their X-ray structures, and the coplanarily extended geometries are suitable for π-delocalization. Electrochemical oxidation of **1**-**3** caused continuous changes in their UV-Vis-NIR and fluorescence spectra although the oxidized species are too labile to be isolated.

Tetraarylethylenes **4**[1,2] and their vinylogues such as 1,1,4,4-tetraarylbutadienes **5**[2] are important components of violene/cyanine-hybrid-type[2,3] electrochromic systems[4] (Scheme 1), the characteristics of which can be altered by changing the Ar_2C end-groups (cyanine-parts). π-Extension of the violene-part is another method for modifying the properties, but simple vinylogues[5] are less attractive due to their instability against oxygen and proton. Thus, there is a growing interest on the compounds, to which cyclic π-systems are inserted as the extended violene-part.[6]

Based on the above consideration and our recent success in constructing methyleneacridan-type redox systems with the (oligo)thiophene skeleton,[7] the title violene/cyanine-hybrids were newly designed, in which one (**1**), two (**2**), or three (**3**) thiophene-2,5-diyl units are inserted between the two Ar_2C=CH end-groups (Scheme 2). This report describes their preparation, X-ray structures, redox properties, and perturbation of the number of thiophene units on the physical/spectral properties of **1** - **3**.



Scheme 1. Redox scheme for the violene-cyanine hybrids
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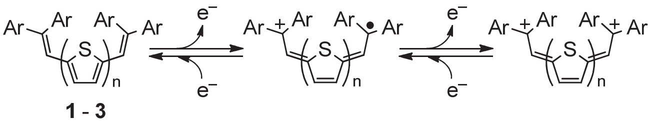
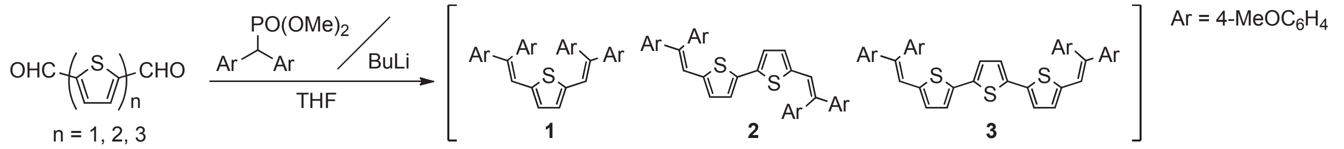


Scheme 2. Redox scheme for new donors **1-3**



Scheme 3. Preparation scheme of new donors

By the Wittig-Horner reaction of 2,5-diformylthiophene with $(4\text{-MeOC}_6\text{H}_4)_2\text{CHP(=O)(OMe)}_2$/BuLi in THF, the new donor **1** was obtained in 92% yield. Similarly, **2** and **3** were prepared from diformylbithiophene and diformylterthiophene in respective yields of 96% and 91%.[8] They were isolated as stable yellow-orange crystalline materials (Scheme 3).

The X-ray analyses[9] on **1-3** revealed that the violene π−system consisting of thiophene unit(s) and the ethenyl groups is nearly planar, in which two neighboring thiophenes in **2,3** adopt either an *anti* or *syn* arrangement (Figure 1). For all of the diarylethenyl units in **2,3,** while one of the $4\text{-MeOC}_6\text{H}_4$ groups is more or less coplanar with the violene part [dihedral angle θ_2: 19.4(1)-48.8(1)°], the other is rather perpendicular to the ethenyl group [θ_1: 73.8(1) - 88.2(3)°] and shows a short interatomic contact [*d*: 2.94(1) - 3.12(1) Å] between the thiophene sulfur atom (S) and the ipso carbon (C_{ipso}) of the aryl group (sum of the van der Waals radii: 3.50 Å) (Table 1). The observed short contacts are highly likely to be associated with electronic interaction between σ^* (C-S) and π (C_{ipso}), resulting in conformational stability for the coplanarily extended geometries, which are suitable for electronic delocalization over the extended π-systems.

According to the theoretical calculation (B3LYP/6-31G*) for **1-3**, the geometry around the diarylethenyl units are similar to that found in the crystal (Table 1),[10] which supports the notion described above. In the solid-state geometry of **1**, slight deformation of the violene π−system is caused by steric repulsion between the two inner aryl groups, although the above-mentioned structural motif suitable for σ^* (C-S) and π (C_{ipso}) interaction still exists, which suggests that the S -- C_{ipso} contacts are attractive in nature. The electron donating group on the benzene nucleus is not necessary for this interaction since 2,5-bis(2,2-diphenylethenyl)thiophene without methoxy substituents also adopts a geometry similar to **1**.[11]

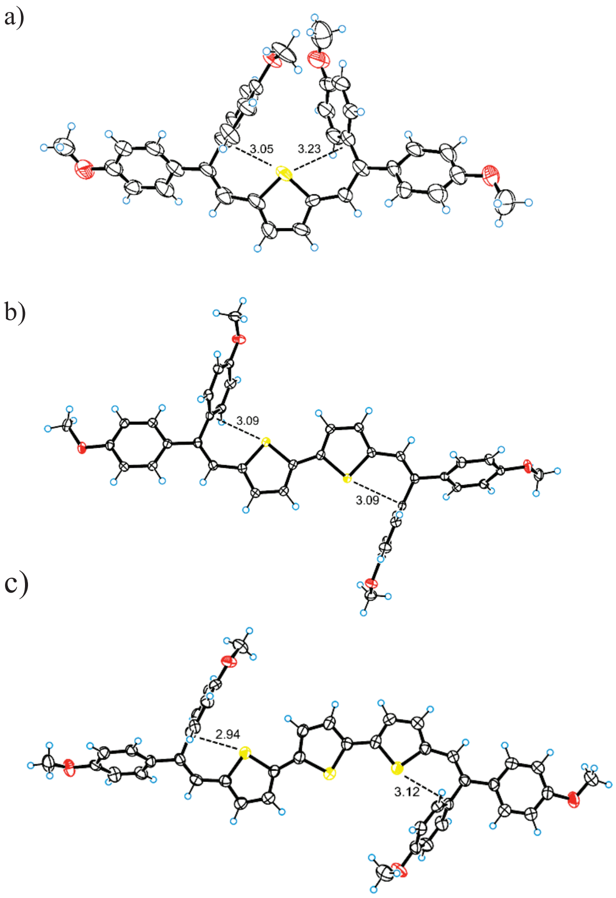
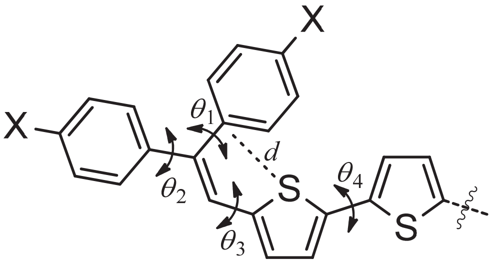


Figure 1. X-Ray structures of a) **1**, b) **2**, and c) **3** measured at 123 K. Thermal ellipsoids are shown at 50% probability level. The S--C_{ipso} contacts were shown by broken lines.

Table 1. Geometrical parameters of **1-3** determined by X-ray analyses at 123 K and by calculation (B3LYP/6-31G*)[a]

	d / Å	θ_1 / °	θ_2 / °	θ_3 / °	θ_4 / °
1	3.05(1)	82.0(4)	30.5(4)	9.7(4)	——
	3.23(1)	53.9(3)	32.7(4)	23.2(4)	——
	3.27	*61.9*	*32.3*	*8.7*	——
	3.31		*31.3*	*10.9*	——
2	3.09(1)	73.8(1)	19.4(1)	5.5(1)	9.7(1)
	3.09(1)	79.7(1)	48.8(1)	7.4(1)	——
	3.22	*63.4*	*29.8*	*15.0*	*14.1*
	3.23	*61.9*	*30.3*	*14.7*	——
3	2.94(1)	88.2(3)	44.9(3)	14.2(3)	2.1(2)
	3.12(1)	74.3(3)	15.8(3)	6.2(3)	15.1(2)
	3.19	*66.6*	*28.1*	*14.7*	*7.0*
	3.19	*66.3*	*28.1*	*15.0*	*7.1*

a) Values in italics are the calculated values.



According to the voltammetric analyses of **1-3**, they undergo reversible two-stage one-electron oxidation (Figure 2) as in tetrakis(4-methoxyphenyl)ethylene **4** (Scheme 1, n = 0, Ar = 4-$MeOC_6H_4$)[1] and many other violene/cyanine-hybrids. The first (E_1^{ox}) and second (E_2^{ox}) oxidation potentials of **1** are +0.86 and +1.00 V vs SCE in CH_2Cl_2, respectively. Nearly identical values were obtained for bithiophene **2** (E_1^{ox} +0.84 V, E_2^{ox} +0.99 V) and terthiophene **3** (E_1^{ox} +0.84 V, E_2^{ox} +0.95 V). These behaviors are in accord with the theoretical calculation, which predicts that the HOMO levels for **1-3** are nearly the same (Figure 3).

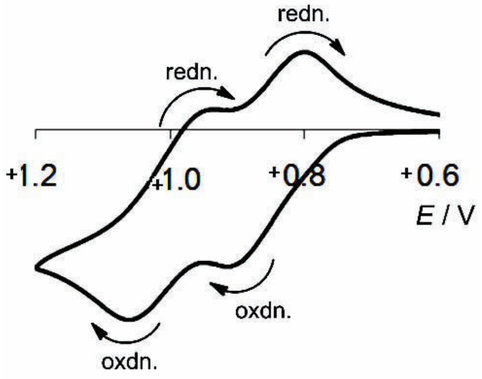


Figure 2. Cyclic voltammogram of **1** measured in CH_2Cl_2 containing 0.1 M Bu_4NBF_4 as a supporting electrolyte (E/V vs SCE, scan rate 100 mV s^{-1}, Pt electrode)

Comparisons of the UV-Vis spectra of **1-3** show a considerable redshift for the first band with an increase in the number of thiophene units in the violene part [λ_{max}/nm (log ε): 406 (4.59) for **1**, 435 (4.72) for **2**, and 453 (4.76) for **3**, respectively, in CH_2Cl_2] (Figure 4). If we consider the large MO coefficients on the thiophene rings in LUMOs of **1-3** estimated by the DFT calculations (Figure 3), the observed redshift can be accounted for by a lowering of the LUMO level with an increase in the number of thiophene units in the violene part, which reflects the electron-accepting properties of longer oligothiophenes.[12]

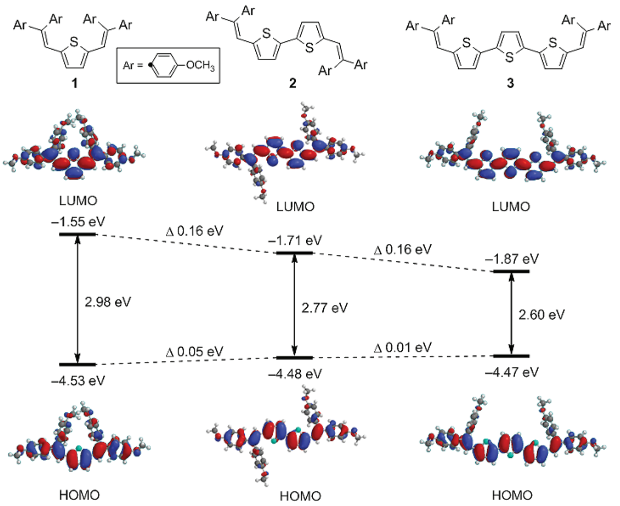


Figure 3. HOMO and LUMO levels of **1-3** calculated by B3LYP/6-31G*

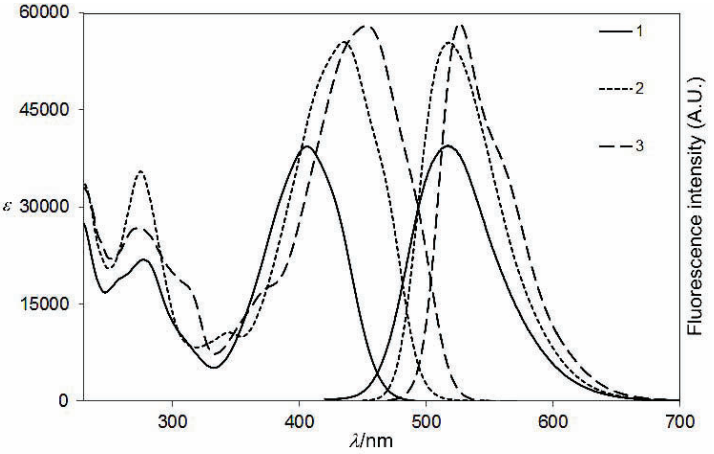


Figure 4. UV-Vis and FL spectra of **1-3** in CH_2Cl_2

These electron donors **1-3** are also fluorescent. Consistent with the absorption spectra, the fluorescence (FL) maximum of terthiophene **3** occurs at the longest wavelength [λ_{em}: 527 nm (Φ_f: 0.14) in CH_2Cl_2] among **1-3**. The FL maxima for **1** [518 (0.01)] and **2** [518 (0.09)] are the same, and the larger Stokes shift and lower quantum efficiency for **1** can be accounted for by supposing larger conformational flexibility of the violene π−system due to the steric repulsion between the two inner aryl groups, which would consume the excitation energy through the motion of the subunits in the excited state.

A drastic change in color from yellow to green was observed upon the electrochemical oxidation of **1** in CH_2Cl_2. At the expense of the absorption at 406 nm, new bands gradually appeared at 714 and 1072 nm in the UV-Vis-NIR spectrum (Figure 5a). The presence of isosbestic points at 360 and 470 nm indicates the clean conversion of **1** to the oxidized species,[13] although attempts to isolate the labile cationic state as a salt have thus far failed. When the same electrolysis was followed by FL spectroscopy, a continuous decrease in intensity was also observed (Figure 5b), suggesting that the oxidized state is non-fluorescent.

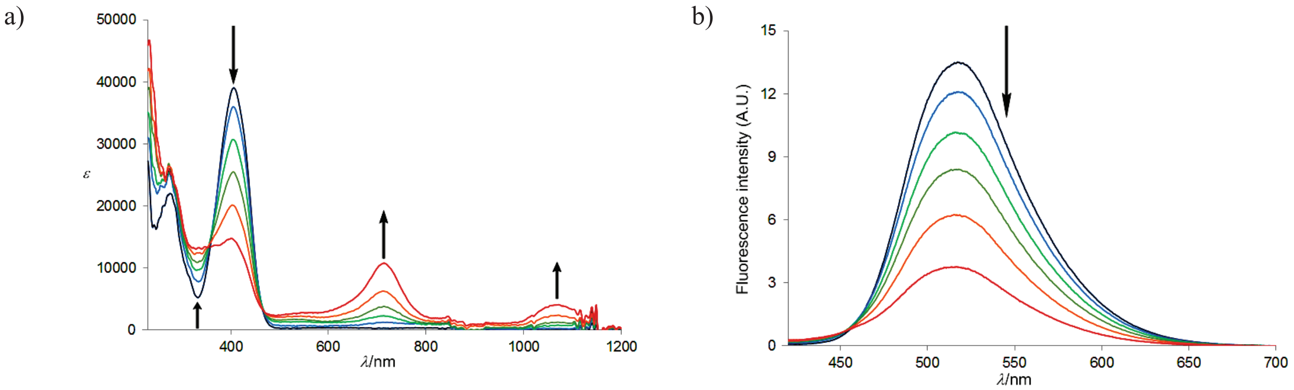


Figure 5. Changes in a) UV-Vis-NIR and b) FL spectra upon constant current (26 microA) electrolysis of **1** in CH_2Cl_2 (4.6 x 10^{-6} M) containing 0.05 M Bu_4NBF_4 as a supporting electrolyte (every 10 min)

Similar color change accompanied by decrease in FL intensity[14] was observed upon the electrochemical oxidation of **2,3,** where the newly appearing band at 714 in **1** was redshifted to 766 and 816 in the cases of **2** and **3**, respectively. When the electrode polarity was reversed, these bands in the long-wavelength region disappeared, but electrochemical reduction did not completely reproduce the full intensity of the starting UV-Vis spectrum. To achieve reversibility of the electrochromic behavior, the oxidized state should be more stabilized, namely, by replacing the CAr_2^+ unit with one with a greater pK_R+ value.

The present results showed that bis(diarylethenyl)-type electron donors with an (oligo)thiophene unit could be a feasible and easily-accessible platform for constructing violene/cyanine-hybrid-type electron donors. The number of thiophene units can be used as a variable to modify and tune the spectral properites (UV-Vis-NIR, FL) as well as the LUMO-level without changing the HOMO-level. Thus, with a proper molecular design stabilizig the cationic states, it would be possible to develop a novel dual electrochromic systems, by which not only UV-Vis-NIR but also FL spectral changes are reversibly induced. Studies along these lines are now in progress.

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8 Typical procedure: To a solution of dimethyl bis(4-methoxyphenyl)methylphosphonate (840 mg, 2.50 mmol) in 10 mL of dry THF was added BuLi in hexane (1.65 M, 1.50 mL, 2.48 mmol) dropwise over 5 min at –78 °C under Ar, and the mixture was stirred for 2 h. To the solution was added 2,5-thiophenedicarboxaldehyde (145 mg, 1.03 mmol) at –78 °C, and the mixture was gradually warmed up to 23 °C and stirred for 14 h. After diluted with water, the whole mixture was extracted with CH_2Cl_2. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. After filtration, solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (toluene/hexane = 3) to give **1** (535 mg) as a yellow solid in 92% yield. Data for **1**: mp 135-137 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm 7.17 (4H, brd, J = 9.0 Hz), 7.06 (4H, brd, J = 8.8 Hz), 6.92 (2H, s), 6.89 (4H, brd, J = 8.8 Hz), 6.79 (4H, brd, J = 9.0 Hz), 6.56 (2H, s), 3.90 (6H, s), 3.78 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 159.32, 159.02, 141.57, 139.16, 135.23, 131.61, 131.36, 128.09, 127.71, 119.22, 114.38, 113.56, 55.28, 55.13; IR (KBr): ν/cm^{-1} 3000, 2962, 2932, 2903, 2834, 1606, 1571, 1510, 1460, 1438, 1416, 1376, 1294, 1247, 1173, 1109, 1033, 884, 830, 808, 791, 738, 590, 569, 545, 520; LR-MS (FD): m/z (%) 562 (15), 561 (41), 560 (M^+, bp).

From the corresponding dialdehydes, new donors **2** and **3** were similarly prepared. Data for **2**: mp 209-211 °C; ^{1}H NMR (300 MHz, $CDCl_3$): *δ*/ppm 7.23 (4H, brd, *J* = 9.0 Hz), 7.16 (4H, brd, *J* = 8.8 Hz), 7.04 (2H, s), 6.98 (4H, brd, *J* = 8.8 Hz), 6.82 (4H, brd, *J* = 9.0 Hz), 6.71 (4H, s), 3.89 (6H, s), 3.80 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): *δ*/ppm 159.67, 159.14, 140.91, 139.26, 137.11, 134.89, 131.48, 129.04, 128.04, 122.79, 119.09, 114.68, 113.66, 55.30; IR (KBr): ν/cm^{-1} 3003, 2953, 2931, 2908, 2835, 1604, 1571, 1509, 1460, 1439, 1418, 1409, 1367, 1285, 1248, 1178, 1171, 1106, 1031, 1011, 902, 877, 841, 835, 817, 786, 573, 537, 525; LR-MS (FD): *m*/*z* (%) 645 (8), 644 (21), 643 (45), 642 (M^+, bp). Data for **3**: m.p. 143-146 °C; ^{1}H NMR (300 MHz, $CDCl_3$): *δ*/ppm 7.24 (4H, brd, *J* = 8.9 Hz), 7.18 (4H, brd, *J* = 8.7 Hz), 7.07 (2H, s), 7.00 (4H, brd, *J* = 8.7 Hz), 6.88 (2H, d, *J* = 3.8 Hz), 6.82 (4H, brd, *J* = 8.9 Hz), 6.79 (2H, d, *J* = 3.8 Hz), 6.78 (2H, s), 3.89 (6H, s), 3.80 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): *δ*/ppm 159.73, 159.17, 141.14, 139.48, 136.61, 136.17, 134.82, 131.50, 131.38, 129.21, 128.07, 123.96, 122.84, 119.06, 114.73, 113.66, 55.33, 55.30; IR (KBr): ν/cm^{-1} 3063, 2994, 2954, 2929, 2903, 2833, 1605, 1571, 1509, 1462, 1439, 1416, 1373, 1286, 1245, 1178, 1173, 1107, 1062, 1032, 836, 831, 799, 786, 584; LR-MS (FD): *m*/*z* (%) 727 (12), 726 (38), 725 (60), 724 (M^+, bp).

9 Crystal data of **1**: MF $C_{36}H_{32}O_4S$, FW 560.71, monoclinic *C*2/*c*, a = 29.71(3), b = 12.58(1), c = 19.55(2) Å, β = 124.702(5)°, *V* = 6007.4(8) Å^3, ρ = (Z = 8) 1.240 g cm^{-3}, *T* = 153 K, 6280 independent reflections (*R*int = 0.075), *R* = 11.2% (1148 data with F > 2σF), CCDC 800033. Due to the small size of crystal available, quality of the the structural analysis is not high but just enough for comparing the structural features to those of **2,3**. Crystal data of **2**: MF $C_{40}H_{34}O_4S_2$, FW 642.83, monoclinic $P2_1/c$, a = 15.799(5), b = 9.795(3), c = 20.756(7) Å, β = 96.229(1)°, *V* = 3193.0(1) Å^3, ρ = (Z = 4) 1.337 g cm^{-3}, *T* = 153 K, 7199 independent reflections (*R*int = 0.023), *R* = 3.2% (4955 data with F > 2σF), CCDC 800035. Crystal data of **3**: MF $C_{44}H_{36}O_4S_3$, FW 724.95, orthorhombic $P2_12_12_1$, a = 9.741(3), b = 15.251(4), c = 24.139(7) Å, *V* = 3585.9(1) Å^3, ρ = (Z = 4) 1.343 g cm^{-3}, *T* = 153 K, 4510 independent reflections (*R*int = 0.074), *R* = 5.9% (1824 data with F > 2σF), CCDC 800037.

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