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Bis(diarylethenyl)thiophenes, -bithiophenes, and -terthiophenes: A New Series of Electrochromic Systems that Exhibit a Fluorescence Response

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Abstract: 2,5-Bis(diarylethenyl)thiophenes (**1**) and their bithiophene (**2**) and terthiophene (**3**) homologues were designed as a new series of viroline/cyanine-hybrid-type electrochromic materials. Alkoxyphenyl and dialkylaminophenyl groups are used, respectively, as the aryl group in the cyanine parts of **1/2/3O** and **1/2/3N**, which emit fluorescence in the neutral state but not in the oxidized state. Voltammetric analyses of 18 newly prepared electron donors show that they all undergo reversible two one-electron oxidations. Redox potentials, UV/Vis spectral features, and fluorescence quantum yields are important parameters for characterizing the present electrochromic behavior with a fluorescence response, and can be finely tuned by changing aryl groups in the cyanine part, the number of thiophene rings in the viroline part, and the alkyl-chain length of the alkoxyphenyl or dialkylaminophenyl groups ($R = CH_3$, C_8H_{17} , $C_{16}H_{33}$), which makes this a versatile platform for the design of novel electrochromic materials.

Keywords: Electrochromism, Redox System, Fluorescence, Molecular Response System, Dication

Introduction

Tetraaryl-substituted ethylenes **4**^{1,2} and butadienes **5**² are representative members of violene/cyanine-hybrid-type redox systems^{2,3} exhibiting electrochromic behavior⁴ (Scheme 1), the characteristics of which can be finely-tuned by changing the Ar₂C end-groups (cyanine-parts). π -Extension of the violene-part is another method for modifying these properties, but simply extended vinylogues⁵ are not suitable due to their instability in the presence of oxygen and proton. Thus, there is a growing need for methods to insert cyclic π -systems⁶ such as a *p*-phenylene unit as in 1,4-bis[2,2-(4-dimethylaminophenyl)]ethenylbenzene *p*-**6N-a**, which was prepared as a stable molecule.⁷ While it showed a reversible two-electron oxidation-wave in the voltammogram, the dicationic state was not stable enough for isolation and instead transformed into oligomeric polycations (Scheme 2) despite the stability of its *p*-quinod structure.⁸ Intermolecular C-C bond formation at the methine carbons⁹ also occurs upon oxidation of the corresponding *m*-isomer (*m*-**6N-a**), since effective conjugation does not occur between the two cyanine-dye parts.⁸

During the course of our continuing studies on novel redox-based response systems,^{10,11} a series of violene/cyanine-hybrids were designed, in which one (**1**), two (**2**), or three (**3**) thiophene-2,5-diyl units are inserted between the two Ar₂C=CH end-groups¹² based on the above results. Compared with the *p*-quinodimethane skeleton, thienoquinoid-type

π -systems are less labile¹³ due to the lower aromaticity of thiophene. Another advantage is the effective electronic communication between two terminal chromophores through the coplanar oligothiophene unit,^{14,15} which has been demonstrated by its use as a "molecular wire".¹⁶ To achieve strong absorption and thermodynamic stability of the Ar_2C^+ unit,¹⁷ 4- ROC_6H_4 (**O**) and 4- $\text{R}_2\text{NC}_6\text{H}_4$ (**N**) were chosen as aryl groups with some variation of the alkyl-chain length [$\text{R} = \text{CH}_3$ (**a**), C_8H_{17} (**b**), $\text{C}_{16}\text{H}_{33}$ (**c**)]. These are the central points in the design of 18 novel electrochromic systems presented here (Scheme 3). This report¹⁹ describes their preparation, redox properties, X-ray structures, and electrochromic behavior with a fluorescence response.^{11b,20}

Results and Discussion

Tetrakis(4-alkoxyphenyl)-substituted Donors 1/2/3O-a,b,c

Preparation and Molecular Structures of 1/2/3O

By Wittig-Horner reaction of 2,5-diformylthiophene with (4- $\text{CH}_3\text{OC}_6\text{H}_4$)₂CHP(=O)(OCH₃)₂ **7O-a**/*n*BuLi in THF, the new donor **1O-a** was obtained as yellow crystals in 92% yield. Similarly, **2O-a** (y. 96%) and **3O-a** (y. 91%) were prepared from diformylbithiophene and diformylterthiophene, respectively (Scheme 4). Wittig-Horner reagents with longer alkyl chains, (4- $\text{C}_8\text{H}_{17}\text{OC}_6\text{H}_4$)₂CHP(=O)(OC₂H₅)₂ **7O-b** and (4- $\text{C}_{16}\text{H}_{33}\text{OC}_6\text{H}_4$)₂CHP(=O)(OC₂H₅)₂ **7O-c**, were newly prepared from the

corresponding benzhydrols **8O-b,c** via chlorides **9O-b,c** (Scheme S1). By the reactions of **7O-b,c** with diformylthiophene, -bithiophene and -terthiophene, octyl derivatives **1O-b** (y. 81%), **2O-b** (y. 57%), **3O-b** (y. 95%) as well as hexadecyl derivatives **1O-c** (y. 85%), **2O-c** (y. 97%), and **3O-c** (y. 79%) were also obtained. These six compounds with long alkoxy chains were isolated as stable yellow-orange crystalline materials.

According to the results of X-ray analyses²¹ of the three methoxy derivatives **1/2/3O-a**, the violene π -system consisting of thiophene unit(s) and the ethenyl groups is nearly planar, in which two neighboring thiophenes in **2/3O-a** adopt either an anti or syn arrangement (Figs. 1a-c). For all of the diarylethenyl units in **2/3O-a**, while one of the 4-CH₃OC₆H₄ groups is nearly coplanar with the violene part [dihedral angle θ_2 : 19.4(1) for **2O-a**, 15.8(3)° for **3O-a**], the other is rather perpendicular to the ethenyl group unit [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) (Fig. 2 and 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 observed geometries. According to the theoretical calculation (B3LYP/6-31G*) for **2/3O-a**, a geometry similar to that found in the crystal was obtained by structural optimization (Table 1 and Figs. 1d-f),²² which supports the notion described above. In the solid-state geometry of **1O-a**, slight deformation of the

violene π -system is caused by steric repulsion between the two inner aryl groups, yet 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 any alkoxy group also adopts a geometry similar to **1O-a**.²³

Redox and Spectroscopic Properties of **1/2/3O**

Before we examined the electrochromic response, we considered the redox behavior and spectroscopic properties. According to voltammetric analyses of the methoxy derivatives (**1/2/3O-a**), they undergo reversible two one-electron oxidations (Figs. 3a, S1, and S3) as in tetrakis(4-methoxyphenyl)ethylene **4O-a**^{1a} and many other violene/cyanine-hybrids. The first (E_1^{ox}) and second (E_2^{ox}) oxidation potentials of **1O-a** are +0.86 and +1.00 V vs SCE in CH_2Cl_2 , respectively, and nearly identical values were obtained for bithiophene **2O-a** (E_1^{ox} +0.84 V, E_2^{ox} +0.99 V) and terthiophene **3O-a** (E_1^{ox} +0.84 V, E_2^{ox} +0.95 V). These behaviors are in accord with the theoretically calculated HOMO levels for **1/2/3O-a** shown in Fig. 4a. Different chain lengths (CH_3 vs C_8H_{17} , $C_{16}H_{33}$) of the alkoxy group in **1/2/3O-b,c** scarcely affected the oxidation potentials for this series of compounds (Table 2).

Comparisons of the UV/Vis spectra of methoxy derivatives **1/2/3O-a** show a considerable red shift for the first band with an increase in the number of thiophene units in the violene part [λ_{max} : 406 nm (log ϵ : 4.59) for **1O-a**, 435 (4.72) for **2O-a**, and 453 (4.76) for **3O-a**, respectively] (Table 3 and Fig. 5a). The same effects were observed in the cases of **1/2/3O-b,c**. If we consider the large MO coefficients on the thiophene rings in LUMOs of **1/2/3O-a** estimated by the DFT calculations (Fig. 4a), the observed red shift 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.²⁴

These electron donors **1/2/3O-a** are also fluorescent. Consistent with the absorption spectra, among these compounds, the fluorescence maximum of terthiophene **3O-a** occurs at the longest wavelength [λ_{em} : 527 nm (Φ_{f} : 0.14) in CH₂Cl₂] (Table 3). The emission maxima for **1O-a** [518 (0.01)] and **2O-a** [518 (0.09)] are the same, and the larger Stokes shift and lower quantum efficiency for **1O-a** can be accounted for by supposing larger conformational flexibility due to the lower planarity of the violene π -system as well as steric repulsion between the two inner aryl groups. The alkyl chain length has only small effects on the absorption and emission wavelengths (Figs. 5b-d).

Electrochromic Properties of **1/2/3O**

An electrochromic response from yellow to green was observed upon the electrochemical oxidation of **1O-a** in CH_2Cl_2 . At the expense of the absorption at 406 nm in the UV/Vis/NIR spectrum, new bands gradually appeared at 714 and 1072 nm (Fig. 6a). The latter band in the NIR region is characteristic of the HOMO-SOMO transition of **1O-a**^{•+}. Association of **1O-a**^{•+} is unlikely under the experimental conditions by considering the use of highly diluted solution. The presence of isosbestic points at 360 and 470 nm indicates the clean conversion of **1O-a** to **1O-a**^{•+}, although attempts to isolate the cation radical salts through the use of preparative-scale experiments with several oxidants have thus far failed. When the same electrolysis was followed by fluorescence spectroscopy, a continuous decrease in emission was observed (Fig. 6b), since the oxidized state is non-fluorescent. Such behavior is characteristic of a two-way-output system in response to electrochemical input.

Similar electrochromism accompanied by fluorescence ON/OFF switching²⁰ was observed upon the electrochemical oxidation of **2/3O-a** (Figs. 6c-f), where the newly appearing band at 714 in **1O-a** was red-shifted to 766 and 816 in the cases of **2O-a** and **3O-a**, 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 complete reversibility of the chromic behavior, the oxidized state should be stabilized, which

prompted us to replace the CAr_2^+ unit with one with a greater pK_R^+ value,¹⁷ e.g., dialkylaminophenyl derivatives.

Tetrakis(4-dialkylaminophenyl)-substituted Donors 1/2/3N-a,b,c

Preparation and Molecular Structures of 1/2/3N

By Witting-Horner reactions using $[4-(\text{CH}_3)_2\text{NC}_6\text{H}_4]_2\text{CHP(=O)(OCH}_3)_2$ **7N-a**,^{9a} dimethylaniline-based donors with one (**1N-a**, y. 89%), two (**2N-a**, y. 77%), and three (**3N-a**, y. 60%) thiophene units were obtained from the corresponding dialdehydes as orange-red crystals (Scheme 4). The octyl derivatives, **1N-b** (y. 82%), **2N-b** (y. 60%), and **3N-b** (y. 91%), were obtained as orange-red oils with the use of $[4-(\text{C}_8\text{H}_{17})_2\text{NC}_6\text{H}_4]_2\text{CHP(=O)(OC}_2\text{H}_5)_2$ **7N-b**, whereas the hexadecyl derivatives, **1N-c** (y. 55%), **2N-c** (y. 53%), and **3N-c** (y. 78%), were obtained as orange-red solids with the use of $[4-(\text{C}_{16}\text{H}_{33})_2\text{NC}_6\text{H}_4]_2\text{CHP(=O)(OC}_2\text{H}_5)_2$ **7N-c**. Phosphonates **7N-b,c** were newly prepared from the corresponding diarylketones **10N-b,c** via benzhydrols **8N-b,c** (Scheme S2).

According to X-ray analyses of the three dimethylamino derivatives **1/2/3N-a** (Figs. 7a-c), a structural motif similar to that found in **1/2/3O-a** is present in the crystals of **2/3N-a** [θ_1 : 79.3(1) - 85.4(1)°] despite the adoption of packing arrangements different from those in **2/3O-a**. Thus, the electronic interaction through the short S--C_{ipso} contact [d :

2.94(1) - 3.01(1) Å] also determines the preferred conformation in dimethylamino derivatives **2/3N-a** (Fig. 2 and Table 1). Those geometries are again reproduced by DFT calculations (Figs. 7d-f). In the case of **1N-a**, however, only one of the two diarylethenyl units is involved in the S--C_{ipso} interaction. This difference can be accounted for by considering large steric repulsion between the two inner-directing 4-(CH₃)₂NC₆H₄ groups if **1N-a** adopts a structure similar to that in **1O-a**. In fact, according to the DFT calculation, the optimized S--C_{ipso} distance is much longer than in other cases. This could also explain why **1N-a** has a less coplanar arrangement of ethenyl units with a central thiophene ring [θ_3 : 44.9(2)°] than **2/3N-a** or **1/2/3O-a**.

Redox and Spectroscopic Properties of **1/2/3N**

Voltammetric analyses showed that **1/2/3N-a,b,c** undergo reversible two-electron oxidation. In contrast to the cases of alkoxy derivatives **1/2/3O-a,b,c**, however, E_1^{ox} and E_2^{ox} of the dialkylamino derivatives are very close to each other ($\Delta E \sim 0$), and thus only one pair of redox peaks was observed in each case (Table 2 and Figs. 3b, S2). This one-wave-two-electron oxidation process (Fig. S3) resembles that observed in tetrakis(4-dimethylaminophenyl)ethylene **4N-a**,² which can be accounted for by the smaller on-site Coulombic repulsion in its dication due to the reduced positive charge on the methylium carbon, thanks to the stronger donating ability of dialkylamino groups

compared to alkoxy groups. The longer alkyl-chains in the octyl (**b**) and hexadecyl (**c**) series are slightly more electron-donating than a methyl group (**a**), and thus marginally enhance the donating properties of **1/2/3N-b,c** compared to those of **1/2/3N-a**.

A greater difference was found between the E^{ox} values of **1N**, **2N**, and **3N**. Their donating properties are weakened by an increase in the number of thiophene units in the violene part (Table 2). This finding is in line with the HOMO levels of **1/2/3N-a** estimated theoretically (Fig. 4b). The DFT calculations also indicate that the LUMO levels of **1/2/3N-a** lower more prominently in the order **1N**, **2N**, and **3N** (lowest).

The UV/Vis spectra of dimethylamino derivatives **1/2/3N-a** exhibit strong absorptions in the longer-wavelength region compared to those for methoxy derivatives **1/2/3O-a** due to the higher HOMO level. Again, a considerable red shift of the first band is observed with an increase in the number of thiophene units in the violene part [λ_{max} : 440 nm ($\log \varepsilon$ 4.65) for **1N-a**, 462 (4.68) for **2N-a**, and 476 (4.80) for **3N-a**, respectively] (Table 3 and Fig. 8a). The observed red shift of absorption maxima by an increase in the number of thiophene units for **1/2/3N-a** can be accounted for the calculated HOMO-LUMO gap, which is reduced in the same order (Fig. 4b). Slight red shifts of the first bands for the octyl (**b**) and hexadecyl (**c**) derivatives relative to the corresponding dimethylamino compounds (**a**) can be accounted for by considering the slightly higher donating properties of the dialkylaminophenyl groups in **1/2/3N-b,c** compared to those of the dimethylamino

groups in **1/2/3N-a** (Figs. 8b-d).

Donors **1/2/3N-a,b,c** are weakly fluorescent (Table 3). Their quantum yields are much lower than those of **1/2/3O-a,b,c**. Among dimethylamino derivatives **1/2/3N-a**, **1N-a** with the strongest donating properties is least fluorescent (Φ_f : <0.005, λ_{em} : 540 nm), and the quantum yield increases with an increase in the number of thiophene units [Φ_f and λ_{em} : <0.005 and 557 nm for **2N-a**; 0.006 and 573 nm for **3N-a**]. The alkyl-chain length has been shown to significantly affect the fluorescence quantum yield in some polyalkylated fluorophores, and this is also the case for **1/2/3N-a,b,c**. Enhanced emission efficiency was observed for the hexadecyl series of compounds, and the quantum yields of **1/2/3N-c** [Φ_f : <0.005 for **1N-c**; 0.013 for **2N-c**; 0.016 for **3N-c**] are almost three times greater than those of the respective dimethylamino derivatives **1/2/3N-a**.

Electrochromic Properties of **1/2/3N**

The electrochromism of **1/2/3N** with a color change from orange-red to violet exhibits high reversibility thanks to the stability of their cationic species. Their reversible two-electron oxidation is favored^{3,25} by reducing the steady-state concentration of reactive open-shell species during the chromic response.

Under the constant-current electrochemical oxidation of **1N-c** in CH_2Cl_2 , new absorptions (λ_{max} : 802 nm) assignable to dicationic species²⁶ appeared at the expense of

the original band at 450 nm (Fig. 9a). The presence of several isosbestic points indicates that the steady-state concentration of the intermediary cation radical $1\text{N-c}^{+\bullet}$ is negligible. Redox conversion of $1\text{N-c}/1\text{N-c}^{2+}$ was found to be reversible. When the polarity of the electrodes was reversed, the original spectrum of 1N-c was completely recovered. Due to the very small value of Φ_f , 1N-c is not suitable as a multi-output response system (Fig. 9b), in contrast to $2/3\text{N-c}$, which have larger Φ_f values.

The electrochemical oxidation of 3N-c (Φ_f : 0.016) induced changes in the UV/Vis/NIR spectra, as shown in Fig. 9e, which were accompanied by changes in fluorescence (Fig. 9f), and thus represents a successful example of a two-way-output system. Notably, absorption in the NIR region (λ_{max} : 1200 nm) appeared upon electrochemical oxidation. A similar response was also observed with the use of 2N-c (Φ_f : 0.013)/ 2N-c^{2+} (λ_{max} : 954 nm) (Figs. 9c, d), which demonstrates the validity of using the present dialkylamino derivatives to develop two-way-output response systems with high reversibility.

Conclusion

The present results demonstrate that bis(diarylethenyl)-type electron donors with an (oligo)thiophene unit are feasible and easily-accessible platforms for constructing violene/cyanine-hybrid-type electrochromic systems that exhibit a fluorescent response as well as NIR absorption. The organic electrochromic systems that exhibit drastic changes

in the NIR absorption are rare but attracting increasing recent attention.²⁷ The substituents on the aryl groups and the number of thiophene units can be used as variables to systematically modify and tune the spectral (UV/Vis/NIR, fluorescent) and redox properties (E^{ox} , ΔE), thus making it possible to vary the electrochromic response. Long alkyl chains were found to increase the fluorescence efficiency of **1/2/3N**. In general, long chains are often seen in molecules that are used in liquid crystalline devices. Thus, with a proper molecular design based on the present platform, it may be possible to develop a novel mesophase with a phase transition that could be achieved not only by changes in temperature but also by changes in electrochemical input.²⁸ Studies along these lines are now in progress.

Supplementary material

Supplementary information including experimental procedure and characterization data of new compounds are available with the article through the journal Web site at <http://nrcresearchpress.com/doi/####>.

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independent reflections ($R_{\text{int}} = 0.063$), $R = 7.4\%$ (5193 data with $F > 2\sigma F$), CCDC 800034.

Crystal data of **3N-a**: MF $\text{C}_{48}\text{H}_{48}\text{N}_4\text{S}_3$, FW 777.11, monoclinic $P2_1/c$, $a = 15.616(8)$, $b = 7.476(4)$, $c = 36.27(2)$ Å, $\beta = 97.725(3)^\circ$, $V = 4196.1(3)$ Å³, $\rho = (Z = 4)$ 1.230 g cm⁻³, $T = 153$ K, 8663 independent reflections ($R_{\text{int}} = 0.104$), $R = 9.6\%$ (1225 data with $F > 2\sigma F$), CCDC 800036.

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Scheme 1. Redox scheme for the violene-cyanine hybrids.

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Scheme 2. Intermolecular C-C bond formation of *p*-quinoid dication *p*-6N-a²⁺.

Scheme 3. Redox scheme for novel electrochromic systems.

Scheme 4. Preparation scheme of new donors.

Table 1. Geometrical parameters of **1/2/3O-a** and **1/2/3N-a** determined by X-ray analyses at 123 K and by calculation (B3LYP/6-31G*)^{a,b}.

	<i>d / Å</i>	<i>θ₁ / °</i>	<i>θ₂ / °</i>	<i>θ₃ / °</i>	<i>θ₄ / °</i>
1O-a	3.23(1)	53.9(3)	32.7(4)	23.2(4)	—
	3.05(1)	82.0(4)	30.5(4)	9.7(4)	—
	3.31	57.8	31.3	10.9	—
	3.27	61.9	32.3	8.7	—
2O-a	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	—
3O-a	3.12(1)	74.3(3)	15.8(3)	6.2(3)	15.1(2)
	2.94(1)	88.2(3)	44.9(3)	14.2(3)	2.1(2)
	3.19	66.6	28.1	14.7	7.0
	3.19	66.3	28.1	15.0	7.1
1N-a	3.14(1)	64.4(1)	14.5(2)	19.2(2)	—
	—	56.1(1)	23.5(2)	44.9(2)	—
	3.38	55.6	32.1	7.9	—
	3.38	56.0	32.0	7.5	—
2N-a	2.95(1)	80.5(1)	8.0(1)	10.3(2)	6.3(1)
	2.97(1)	79.3(1)	5.1(1)	11.9(2)	—
	3.23	60.0	29.2	16.7	12.0
	3.23	61.6	29.5	14.7	—
3N-a	2.94(1)	85.4(3)	3.9(3)	11.2(3)	14.4(2)
	3.01(1)	81.2(3)	12.1(3)	14.0(3)	13.1(2)
	3.21	62.1	30.2	15.2	12.5
	3.22	62.6	30.4	15.4	12.2

^a Values in italics are the calculated values.

^b Annotation is shown in Fig. 2.

Table 2. Redox potentials of **1/2/3O-a,b,c** and **1/2/3N-a** measured by cyclic voltammetry^a.

	a: R = CH₃		b: R = C₈H₁₇		c: R = C₁₆H₃₃	
	E_1^{ox}	E_2^{ox}	E_1^{ox}	E_2^{ox}	E_1^{ox}	E_2^{ox}
1O	+0.86	+1.00	+0.84	+0.97	+0.84	+0.97
2O	+0.84	+0.99	+0.84	+0.99	+0.83	+0.97
3O	+0.84	+0.95	+0.83	+0.94	+0.83	+0.94
	$E_1^{\text{ox}} = E_2^{\text{ox}}$		$E_1^{\text{ox}} = E_2^{\text{ox}}$		$E_1^{\text{ox}} = E_2^{\text{ox}}$	
1N	+0.40		+0.35		+0.36	
2N	+0.48		+0.43		+0.44	
3N	+0.54		+0.49		+0.50	

^a E/V vs SCE, scan rate 100 mV s⁻¹, Pt electrode, 0.1 mol dm⁻³ Bu₄NBF₄ as a supporting electrolyte in CH₂Cl₂.

Table 3. UV/Vis and fluorescence spectra of **1/2/3O-a,b,c** and **1/2/3N-a** measured in CH_2Cl_2 .

		$\lambda_{\text{max}} (\log \varepsilon)^{\text{a}}$	$\lambda_{\text{em}} (\Phi_{\text{f}})^{\text{b}}$
1O	a: R = CH_3	406 (4.59)	518 (0.01)
	b: R = C_8H_{17}	407 (4.64)	518 (0.02)
	c: R = $\text{C}_{16}\text{H}_{33}$	407 (4.56)	518 (0.02)
2O	a: R = CH_3	435 (4.72)	518 (0.09)
	b: R = C_8H_{17}	436 (4.72)	519 (0.10)
	c: R = $\text{C}_{16}\text{H}_{33}$	437 (4.71)	519 (0.11)
3O	a: R = CH_3	453 (4.76)	527 (0.14)
	b: R = C_8H_{17}	454 (4.82)	528 (0.15)
	c: R = $\text{C}_{16}\text{H}_{33}$	454 (4.78)	528 (0.15)
1N	a: R = CH_3	440 (4.65)	541 (<0.005)
	b: R = C_8H_{17}	450 (4.71)	544 (<0.005)
	c: R = $\text{C}_{16}\text{H}_{33}$	450 (4.74)	546 (<0.005)
2N	a: R = CH_3	462 (4.68)	557 (<0.005)
	b: R = C_8H_{17}	473 (4.75)	565 (0.010)
	c: R = $\text{C}_{16}\text{H}_{33}$	474 (4.81)	566 (0.013)
3N	a: R = CH_3	476 (4.80)	573 (0.006)
	b: R = C_8H_{17}	486 (4.82)	578 (0.012)
	c: R = $\text{C}_{16}\text{H}_{33}$	486 (4.87)	578 (0.016)

^a Data of absorption maxima (λ_{max}) for the first band.

^b Excitation at absorption maxima (λ_{max}).

Fig. 1. X-ray structures of methoxyphenyl donors, a) **1O-a**, b) **2O-a**, and c) **3O-a**, measured at 123 K. Thermal ellipsoids are shown at 50% probability level. The S $\cdots$ C_{ipso} contacts were shown by broken lines. Optimized structures of d) **1O-a**, e) **2O-a**, and f) **3O-a** calculated by B3LYP/6-31G*.

Fig. 2. Structural annotation of **1/2/3O-a** and **1/2/3N-a** for the parameters determined by

X-ray analyses and calculation shown in Table 1.

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Fig. 3. Cyclic voltammograms of a) **1O-a** and b) **1N-a** measured in CH_2Cl_2 containing $0.1 \text{ mol dm}^{-3} \text{ Bu}_4\text{NBF}_4$ as a supporting electrolyte (E/V vs SCE, scan rate 100 mV s^{-1} , Pt electrode).

Fig. 4. HOMO and LUMO levels of a) **1/2/3O-a** and b) **1/2/3N-a** calculated by B3LYP/6-31G*.

Fig. 5. UV/Vis and Fluorescence spectra of a) **1/2/3O-a**, b) **1O**, c) **2O**, and d) **3O** measured in CH_2Cl_2 .

Fig. 6. Changes in a), c), e) UV/Vis/NIR and b), d), f) fluorescence spectra upon constant current electrolysis of **1O-a** (26 microA, 4.6×10^{-6} M), **2O-a** (28 microA, 3.5×10^{-6} M), and **3O-a** (28 microA, 3.5×10^{-6} M), respectively, in CH_2Cl_2 containing 0.05 M Bu_4NBF_4 as a supporting electrolyte (every 10 min).

Fig. 7. X-ray structures of dimethylaminophenyl donors, a) **1N-a**, b) **2N-a**, and c) **3N-a**, measured at 123 K. Thermal ellipsoids are shown at 50% probability level. The S--C_{ipso} contacts were shown by broken lines. Optimized structures of d) **1N-a**, e) **2N-a**, and f) **3N-a** calculated by B3LYP/6-31G*.

Fig. 8. UV/Vis and Fluorescence spectra of a) **1/2/3N-a**, b) **1N**, c) **2N**, and d) **3N** measured in CH_2Cl_2 .

Fig. 9. Changes in a), c), e) UV/Vis/NIR and b), d), f) fluorescence spectra upon constant current (10 microA) electrolysis of **1N-c** (9.0×10^{-6} M, every 1 min), **2N-c** (8.9×10^{-6} M, every 1.5 min), and **3N-c** (9.0×10^{-6} M, every 1.5 min), respectively, in CH_2Cl_2 containing 0.05 M Bu_4NBF_4 as a supporting electrolyte.

Electrochemical Two-way Switching

"Bis(diarylethenyl)thiophenes, -bithiophenes, and -terthiophenes: A New Series of Electrochromic Systems that Exhibit a Fluorescence Response"

Yusuke Ishigaki, Hidetoshi Kawai, Ryo Katoono, Kenshu Fujiwara, Hiroki Higuchi, Hirotsugu Kikuchi, and Takanori Suzuki*

(Text for Table of Contents)

The UV/Vis/NIR and fluorescence spectral properties can be finely-tuned by the number of thiophene unit, electron-donating heteroatom, and the alkyl chain length, thus endowing the title electron donors with redox-triggered two-way switching properties.