Synthesis, Characterization, and Optical and Electrochemical Properties of New 2,1,3-Benzoselenadiazole-Based CT-Type Copolymers

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ABSTRACT: New alternating donor−acceptor charge-transfer (CT)-type copolymers consisting of didodecyloxy-*p*-phenylene (**Ph**), *N*-(4-dodecyloxyphenyl)carbazole (**Cz**), or *N*-hexyldiphenylamine (**Da**) unit (π-electron donor) and 2,1,3-benzoselenadiazole (**BSe**) unit (π-electron acceptor) were prepared by palladium-catalyzed Suzuki coupling reaction in 85−96% yields. The copolymers with the **Ph** and **Cz** units were soluble in common organic solvents and gave number-average molecular weights of 8300 and 6600, respectively, in GPC analysis; the copolymer with the **Da** unit was partly soluble in the solvents. The UV−vis absorption peak of the polymers appeared in the range of 420−530 nm in solutions and films, and the optical transition is considered to be accompanied by CT from the donor unit to the **BSe** unit. Quantum-chemical calculations of a trimeric model compound (**Ph**−**BSe**−**Ph: 10**) supported the notion that the optical activation of the copolymer involved the CT process. Cyclic voltammetry revealed that the copolymers were susceptible to both electrochemical oxidation and reduction, and they had a LUMO level ranging from −3.08 to −2.91 eV and a HOMO level ranging from −5.56 to −5.12 eV. Comparison of the electronic effect of the **BSe** unit with that of a 2,1,3-benzothiadiazole unit is discussed.

Introduction

There is currently much attention focused on π-conjugated polymers due to their potential usability for polymer optoelectronic devices such as light-emitting diodes (OLEDs),[1] field-effect transistors (FETs),[2] and photovoltaic devices.[3] Electrically conducting polypyrrole and poly(ethylenedioxythiophene) are industrially used to prepare, for example, electric capacitors and PET-based conducting films. Among π-conjugated polymers, those containing benzene-fused heteroaromatic rings with nitrogen atom(s), so-called poly(benzazole)s, are a class of materials that has shown interesting electrical and optical properties. Poly(2,1,3-benzothiadiazole-4,7-diyl),[4] poly(2-alkyl-benzimidazole-4,7-diyl),[4,5] and poly(2-alkyl-1,2,3-benzotriazole-4,7-diyl)[6] were previously reported, and they showed n-type electronic properties.

2,1,3-Benzothiadiazole (Chart 1) is a well-known heteroaromatic compound with a high electron-accepting feature because of containing two electron-withdrawing imine (C=N) nitrogens. Various π-conjugated copolymers of 2,1,3-benzothiadiazole with thiophene,[7] pyrrole,[8] carbazole,[9] fluorene,[10] and dialkoxy-*p*-phenyleneethynylene units[11] have been developed to date. It was reported that introduction of the 2,1,3-benzothiadiazole (**BTd**) unit into the π-conjugated polyfluorene backbone improved the electron-transporting ability and the electroluminescence (EL) efficiency of the polymer.[9a] Applications of such donor−acceptor copolymers to OLEDs and to bulk heterojunction photovoltaic devices have recently been studied.[12,13]

We aim for replacement of sulfur atom in the **BTd** unit with selenium and design new donor−acceptor CT-type copolymers consisting of the 2,1,3-benzoselenadiazole (**BSe**) unit. Cao and co-workers reported synthesis of several π-conjugated polymers containing the **BSe** unit or a 2,1,3-naphthoselenadiazole unit; however, examples of π-conjugated polymers containing such units are still not many.[14] Because differences in chemical properties between selenium in the **BSe** unit and sulfur in the **BTd** unit may render interesting functionalities to the aimed π-conjugated polymer, expansion of the chemistry of π-conjugated polymers containing the **BSe** unit is considered to be needed. The replacement of sulfur of tetrathiafulvalene (TTF) with selenium is one of the promising modifications for extending the metallic state of a charge-transfer (CT) salt of TTF with tetracyano-*p*-quinodimethane (TCNQ).[15]

In this paper, we describe synthesis, characterization, and optical and electrochemical properties of new processable **BSe**-containing donor−acceptor π-conjugated polymers. As illustrated in Chart 2, dialkoxy-*p*-phenylene (**Ph**), carbazole (**Cz**), and diphenylamine (**Da**) units were chosen as the partner donor component. Such hybridization of the donor (D in Chart 2) and acceptor moieties will facilitate manipulation of the electronic structure of the polymer,[16] and various CT-type π-conjugated polymers have been prepared.[7,11,17]

For the copolymer with the **Ph** unit, it apparently forms a π-conjugated system along the polymer main chain. In cases of the copolymers with the **Cz** or **Da** unit, they do not have such a π-conjugated system formally due to the presence of consecutive C−N−C single bonds. However, the copolymers seem to be able to form an expanded electron system through the **Cz** and **Da** units because homopolymers constituted of the **Da** unit, $(\mathbf{Da})_n$, also seem to form such an expanded electron system as judged from their UV−vis peak position (λ_{max} = about 380 nm)[18] which is comparable to that of poly(*p*-phenylene) (λ_{max} = about 380 nm). Optical data of the copolymers with the **Cz** or **Da** unit also support formation of such an expanded electron system, as described below.

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Chart 1. Benzazoles Which Show Electron-Accepting Nature

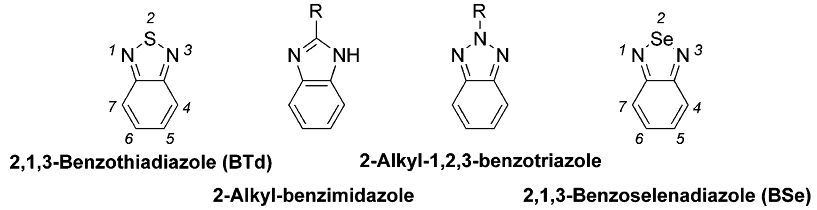


Chart 2. New CT-Type Polymers Consisting of the BSe Unit

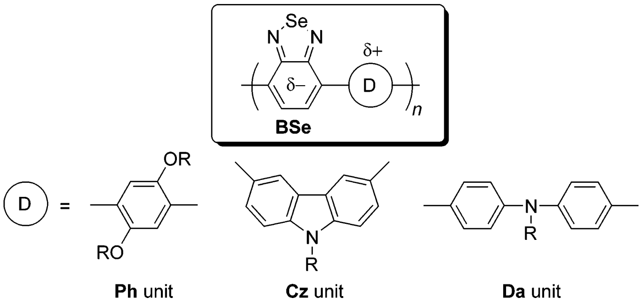
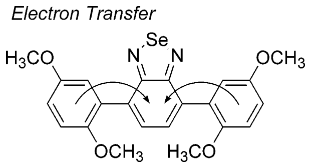


Chart 3. Charge Transfer Which Occurs during the Photoexcitation of 10



Results and Discussion

Synthesis. Synthetic routes of the monomers are outlined in Scheme 1. The X-ray crystal structure of **1** reveals a planar structure of the **BSe** ring in **1** with a Se−N bond length of ca. 1.79 Å and a N=C bond length of ca. 1.33 Å as shown in the Supporting Information (Figure S1); these observed bond lengths are consistent with the *ortho*-quinoid structure of **1**.[19]

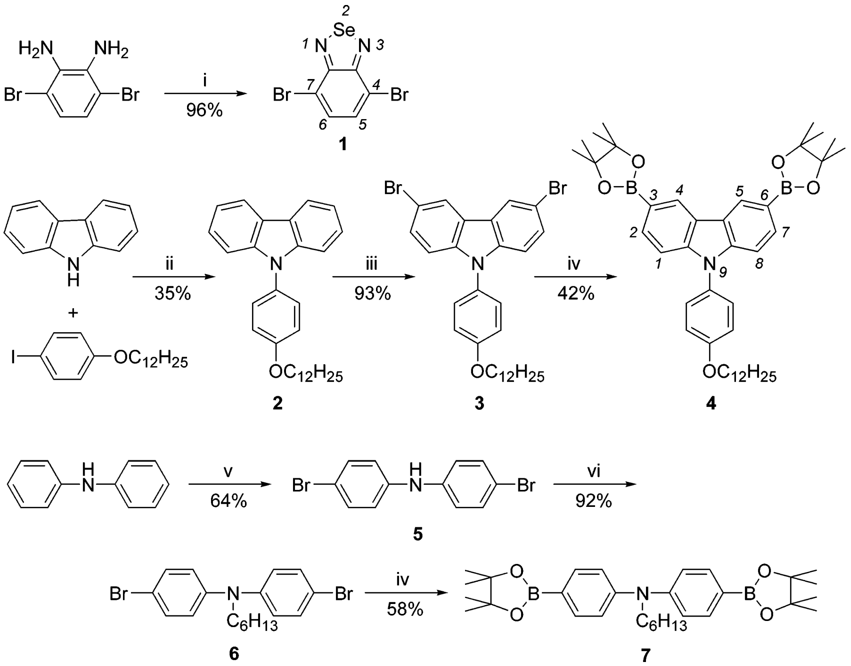
As described in Scheme 2, preparation of the **BSe**-containing copolymers, **P(BSe-Ph)**, **P(BSe-Cz)**, and **P(BSe-Da)**, was accomplished via polycondensation between **1** and the corresponding diboronic esters under Suzuki coupling conditions in the presence of $Pd(PPh_3)_4$, K_2CO_3, and Aliquat336.[20] A related trimeric model compound, **10**, and a **BTd**-containing polymer, **P(BTd-Da)**, were also prepared.

The polymerization results are summarized in Table 1. Yields of the polymers were higher than 85%. **P(BSe-Ph)** and **P(BSe-Cz)** were readily soluble in organic solvents such as $CHCl_3$, THF, toluene, and 1,2-dichlorobenzene, whereas **P(BSe-Da)** and **P(BTd-Da)** were only partially (ca. 50−70%) soluble in these solvents. The number-average molecular weights (M_n's) of the polymers estimated from GPC ranged from 6400 to 8300 vs polystyrene standards, with the polydispersity index (M_w/M_n) of 1.2−1.6. The M_n values corresponded to the degree of polymerization (n in Scheme 2) of 11−19. For **P(BSe-Da)** and **P(BTd-Da)**, the M_n values were obtained only for the $CHCl_3$-soluble part, and the insoluble part was considered to have a higher M_n.

Thermogravimetric analysis (TGA) revealed that the polymers were thermally stable up to 340 °C under N_2, and their 5% weight-loss temperatures (T_d's) ranged from 360 to 442 °C (cf. Table 1).

NMR and IR. Figure 1 depicts the ^1H NMR spectra of the polymers in $CDCl_3$. The NMR spectrum of **P(BSe-Ph)** (part a) gives two aromatic signals at about δ 7.7 and 7.4 in a 1:1 peak area ratio; they are assigned to

Scheme 1. Synthesis of the Monomers[a]



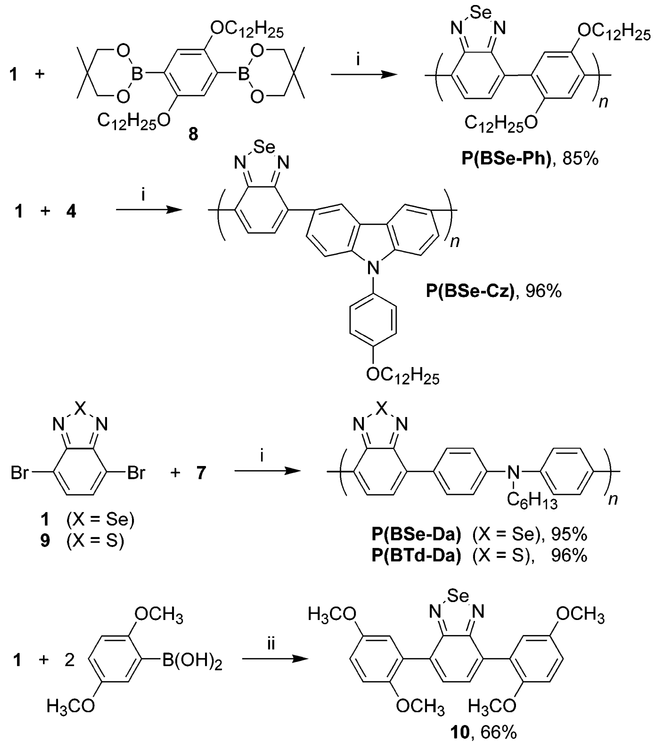
[a] Reagents and conditions: (i) SeO_2, $EtOH/H_2O$, reflux; (ii) Cu, K_2CO_3, DMSO, 180 °C; (iii) NBS, DMF, −10 °C to r.t.; (iv) (1) *n*-BuLi, THF, −78 °C; (2) 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, −78 °C to r.t.; (v) NBS, THF, −78 °C to r.t.; (vi) *n*-$C_6H_{13}Br$, *tert*-BuOK, THF, 60 °C. $C_{12}H_{25}$ and C_6H_{13} represent dodecyl and hexyl groups, respectively.

Table 1. Preparation of Donor−Acceptor Copolymers

polymer	yield (%)	color	M_n[a]	M_w/M_n[a]	P_n[b]	T_d[c] (°C)	T_g[d] (°C)
P(BSe-Ph)	85	bright-yellow	8300	1.6	13	384	92
P(BSe-Cz)	96	red	6600	1.2	11	360	141
P(BSe-Da)	95	red-purple	6400[e]	1.4	15	374	164
P(BTd-Da)	96	red	7500[e]	1.4	19	442	144

[a] Estimated from GPC (eluent = $CHCl_3$, polystyrene standards). [b] Degree of polymerization based on the repeating unit. [c] 5% weight-loss temperature measured by TGA under N_2. [d] Glass-transition temperature measured by DSC under He. [e] For the $CHCl_3$-soluble part.

Scheme 2. Synthesis of the Polymers and the Model Compound[a]



[a] Reagents and conditions: (i) $Pd(PPh_3)_4$, K_2CO_3, Aliquat336, toluene/H_2O, 85 °C. (ii) $Pd(PPh_3)_4$, K_2CO_3, THF/H_2O, 60 °C.

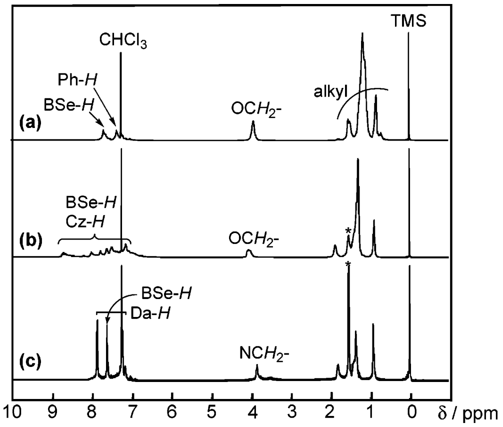


Figure 1. ^{1}H NMR spectra of (a) **P(BSe-Ph)**, (b) **P(BSe-Cz)**, and (c) **P(BSe-Da)** in $CDCl_3$. The asterisk denotes the peak due to H_2O.

aromatic protons in the **BSe** unit and the **Ph** unit, respectively. Peaks of the alkoxy side chains are observed in the range of δ 3.93−0.82. In the ^{1}H NMR spectrum of **P(BSe-Cz)** (part b), there are six broad aromatic peaks attributed to protons of the **BSe** and the **Cz** units. For **P(BSe-Da)** (part c), a singlet peak at δ 7.6 is assigned to protons of the **BSe** unit, and the **Da** unit affords two doublets at δ 7.9 and 7.2; the latter peak is overlapped with the $CDCl_3$ impurity peak.

IR spectra of the polymers show peaks originated from the monomeric units. However, the ν(C−Br) peak at about 920 cm^{-1} and the ν(O−B−O) peak at about 670 cm^{-1} of the monomers[21] become unobservable (cf. Figure S2).

UV−vis Absorption and Photoluminescence (PL). The UV−vis and PL spectra of the polymers are depicted in Figure 2. The spectroscopic data of the polymers and the model compound are summarized in Table 2. In solutions, the polymers gave two distinct absorption peaks (λ_{max}): one near 320 nm and another in a range of 420−500 nm. The former peak is assigned to a π−π* transition mainly occurred in the monomeric units, whereas the lower-energy peak is mainly associated with electronic transition occurred in the main chain. The appearance of the latter UV−vis peak of **P(BSe-Cz)** and **P(BSe-Da)** at the long wavelengths supports the notion that these polymers have the expanded conjugation system through the C−N−C bonds in the **Cz** and **Da** units. An n−π* transition in **P(BSe-Cz)** and **P(BSe-Da)** is considered to appear around 300 nm; however, it seems to be hidden under the strong π−π* transition band.[22a]

The lower energy UV−vis peak of the polymers is shifted by 5−30 nm to a longer wavelength when measured with cast films, presumably due to increase in coplanarity of the polymer and/or occurrence of intermolecular electronic interactions between the polymer molecules in the solid state.

The polymers show a yellow to deep-red PL emission with the peak (λ_{em}) in a range of 554−685 nm in THF (cf. Figure 2B) when irradiated with light at the lower energy absorption peak. Photoexcitation of the polymers with a shorter wavelength light at 300−335 nm gives essentially the same PL spectra, revealing that the photoenergy captured by the monomeric unit is transferred to the main chain.[22b]

Charge-Transfer (CT) Electronic State of the Polymer. The alternating donor−acceptor structure of the polymers seems to bring about a CT electronic character both in the ground state and in the excited state. The PL spectra of **P(BSe-Cz)** in various solvents (toluene, THF, CH_2Cl_2, and NMP) are exhibited in Figure 3A. When the polarity of the solvent increases from less polar toluene to highly polar NMP, the λ_{em} position of **P(BSe-Cz)** is red-shifted by 44 nm, showing a positive solvatochromism.[23] The PL intensity of the solution gradually decreased with increase in the polarity of the solvent and the Stokes shift. The degree of the shift in PL is much larger than that (ca. 5 nm) observed in the UV−vis spectrum, implying that the excited state is highly polarized and stabilized by solvation with the polar solvent after the photoexcitation.[23,24] Similar bathochromic shifts in PL were also observed in **P(BSe-Ph)** and **P(BSe-Da)** as depicted in Figure 3B. As demonstrated in Figure 3B, the PL peak

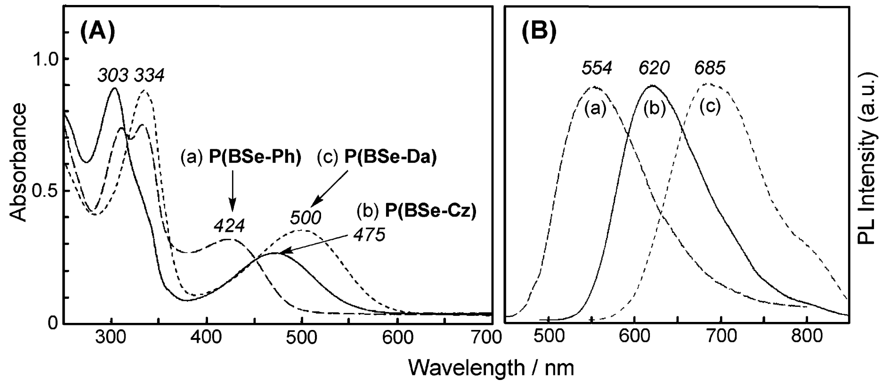


Figure 2. (A) UV–vis and (B) PL spectra of (a) **P(BSe-Ph)** (- - -), (b) **P(BSe-Cz)** (—), and (c) **P(BSe-Da)** (· · ·) in THF at room temperature. The PL spectra were recorded with excitation at the lower energy λ_{max} wavelength.

Table 2. Optical Data of the Polymers and the Model Compound[a]

polymer	THF solution λ_{max} (nm)	THF solution λ_{em} (nm)	THF solution Stokes shift (eV)	THF solution Φ^b (%)	film[c] λ_{max} (nm)	film[c] λ_{em} (nm)
10	301, 334, 403	571	0.91	9	305, 343, 410	557
P(BSe-Ph)	310, 334, 424	554	0.69	11	309, 342, 429	538
P(BSe-Cz)	303, 475	620	0.61	17	306, 486	633
P(BSe-Da)	334, 500	685	0.67	14	343, 527	666
P(BTd-Da)	321, 482	640	0.64	40	327, 501	635

[a] Measured at room temperature. [b] PL quantum yield calculated by comparing with the standard of quinine sulfate (ca. 10^{-5} M solution in 0.5 M H_2SO_4 having a quantum yield of 54.6%). [c] Cast from a $CHCl_3$ solution on a quartz plate.

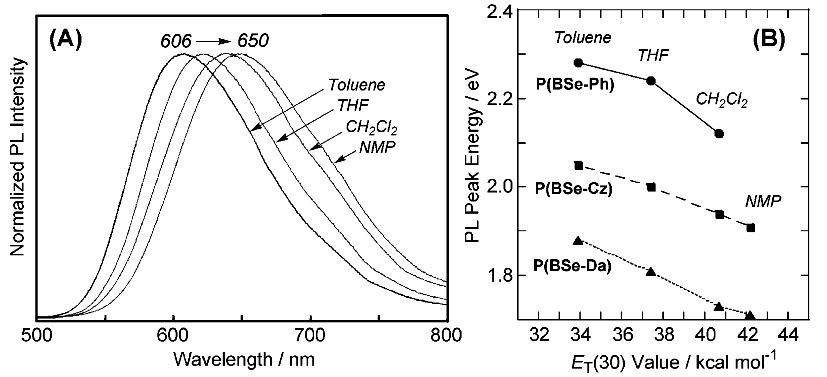


Figure 3. (A) Normalized PL spectra of **P(BSe-Cz)** in solvents. (B) Plots of the PL peak (λ_{em}) energy of the three kinds of polymers against the E_T(30) value of the solvent.

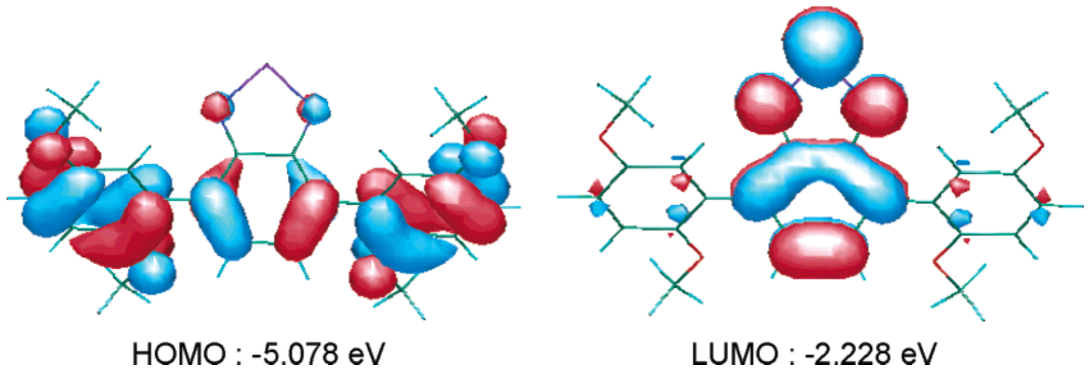


Figure 4. Representation of HOMO and LUMO of **10** based on the B3LYP/6-31G* calculation.

shifts to a longer wavelength with increase in the E_T(30) value,[23a] which is a measure of polarity of solvents.

To obtain further information about the CT electronic structure of the polymers, density-functional theory (DFT)[25] calculations for the model compound **10** were performed at the B3LYP/6-31G* level. Figure 4 reproduces the calculated molecular orbitals of **10**. Although the HOMO is delocalized over the π-conjugation systems, the LUMO is highly localized on the **BSe** unit. This indicates that the HOMO–LUMO UV–vis transition is accompanied by CT from the dimethoxyphenyl units to the central **BSe** unit (cf. Chart 3). The calculated HOMO–LUMO energy gap of **10** (2.85 eV) is in good agreement with the optical energy gap (2.53 eV) of **10** determined by the onset position of the UV–vis peak.

Because the photoexcitation of the **BSe**-D (donor) copolymer is also considered to be accompanied by

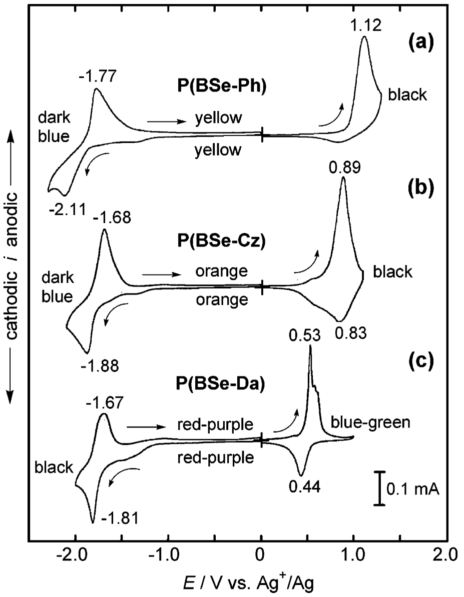
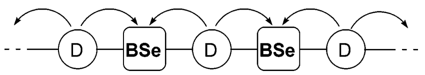


Figure 5. Cyclic voltammograms of films of (a) **P(BSe-Ph)**, (b) **P(BSe-Cz)**, and (c) **P(BSe-Da)** on a Pt plate in an acetonitrile solution of $[(C_2H_5)_4N]BF_4$ (0.10 M) under N_2. Sweep rate is 30 mV s^{-1}.

electron transfer from the donor unit to the **BSe** unit, the increase in the electron-donating ability of the donor unit is expected to make the photoexcitation of the copolymer easier and give the UV−vis peak at a longer wavelength:



The order of the UV−vis absorption peak, λ_{max}(**P(BSe-Da)**) = 500 nm > λ_{max}(**P(BSe-Cz)**) = 475 nm > λ_{max}(**P(BSe-Ph)**) = 424 nm, agrees with the order of the ionization potential (IP) of the donor unit, IP(diphenylamine)[26] = 7.36 eV < IP(carbazole)[26] = 7.57 eV < IP(dialkoxybenzene)[27] = ca. 8.6 eV. These results clearly indicate that the photoexcited polymer molecule has the charge-transferred polar structure. The ground state of the polymer is also considered to have a partly charge-transferred and polar structure due to the difference in electronegativity between the **BSe** unit and the donor unit. However, the degree of the CT in the ground state is considered not to be so large as in the photoexcited state because the UV−vis peak does not show such a large solvatochromism as that observed with PL. The appearance of the λ_{max} of **P(BSe-Da)** at a longer wavelength than that of **P(BTd-Da)** (cf. Table 2) indicates that the photoexcitation in **P(BSe-Da)** is a easier process because of a higher electron-accepting ability of the **BSe** unit than that of the **BTd** unit.

Electrochemical Response. The electrochemical redox behavior of the polymers was investigated by cyclic voltammetry (CV). As shown in Figure 5, all the polymers exhibit both p-doping (oxidation) and n-doping (reduction) peaks, and the CV data are listed in Table 3. The reduction peak appeared at −2.11 V vs Ag^+/Ag for **P(BSe-Ph)**, −1.88 V for **P(BSe-Cz)**, and −1.81 V for **P(BSe-Da)**. The n-doping in the polymer is considered to occur dominantly at the **BSe** moiety. The film was stable in repeated scans, and the same CV chart was obtained after 10 cycles when scanned in the negative potential region. The n-doping of **P(BSe-Da)** takes place at a negatively lower potential by about 0.1 V than that (−1.91 V vs Ag^+/Ag) of **P(BTd-Da)**. This suggests that the **BSe** unit has a stronger electron-accepting ability than the **BTd** unit, as discussed above.

In an oxidative potential region, a p-doping peak was observed at 1.12 V vs Ag^+/Ag for **P(BSe-Ph)**, 0.89 V for **P(BSe-Cz)**, and 0.53 V for **P(BSe-Da)**. The p-doping is considered to occur mainly at the donor unit, and the order of the p-doping potential is considered to reflect electron-donating ability (or IP) of the **Ph**, **Cz**, and **Da** units.

For p-doping of **P(BSe-Ph)**, it was almost irreversible, and only a weak cathodic (or p-dedoping) peak appeared at around 0.8 V vs Ag^+/Ag (cf. Figure 5a). π-Conjugated polymers with the dialkoxy-*p*-phenylene unit often give such an irreversible p-doping peak,[11b,24] which is considered to be due to a strong interaction of the anion dopant (BF_4^- in this case) with the OR group(s). **P(BSe-Cz)** and **P(BSe-Da)** clearly give the p-dedoping peak at 0.83 and 0.44 V vs Ag^+/Ag, respectively. The electrochemical reduction and oxidation are accompanied by color changes (electrochromism) of the polymer film, as shown in Figure 5.

The LUMO and the HOMO energy levels (E_{LUMO} and E_{HOMO}) of the copolymers can be deduced from the onset potentials of n- and p-doping waves, respectively, with the assumption that the energy level of ferrocene (Fc) is 4.8 eV below vacuum level.[28] The E_{LUMO} and the E_{HOMO} values of the polymers are included in Table 3. The E_{LUMO} ranges from −2.91 to −3.08 eV and is much lower than that (−2.4 eV) of 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD),[29] one of the most widely used electron-injecting/transporting materials in OLEDs, and is comparable to that of cyano-substituted poly(*p*-phenylenevinylene) (CN-PPV; ca. −3.0 eV).[1b] These low-lying E_{LUMO} values of the polymers are considered to originate from the strong electron-accepting property of the **BSe** unit.

Table 3. Electrochemical Data and Energy Levels of the Copolymers

	redox potential[a] (V vs Ag^+/Ag)							
polymer	n-doping	n-dedoping	p-doping	p-dedoping	E_{LUMO}[b] (eV)	E_{HOMO}[c] (eV)	E_g^{ele}[d] (eV)	E_g^{opt}[e] (eV)
P(BSe-Ph)	−2.11 (−1.80)	−1.77	1.12 (0.85)	0.83	−2.91	−5.56	2.65	2.41
P(BSe-Cz)	−1.88 (−1.67)	−1.68	0.89 (0.52)	0.83	−3.04	−5.23	2.19	2.05
P(BSe-Da)	−1.81 (−1.63)	−1.67	0.53 (0.41)	0.44	−3.08	−5.12	2.04	1.95
P(BTd-Da)	−1.91 (−1.72)	−1.83	0.57 (0.44)	0.49	−2.99	−5.15	2.16	2.04

[a] Measured by cyclic voltammetry in an acetonitrile solution of $[(C_2H_5)_4N]BF_4$ (0.10 M). The values in parentheses are onset potentials of reduction and oxidation waves. [b] Calculated from the onset reduction potentials ($E_{onset(red)}$ vs Ag^+/Ag) by assuming that the absolute energy level of Fc^+/Fc is 4.8 eV below vacuum level: $E_{LUMO} = -(E_{onset(red)} - 0.09) - 4.8$ V. The value of 0.09 V is added to adjust the E value obtained vs Ag^+/Ag to Fc^+/Fc. The value of 0.09 V was obtained experimentally for the used electrochemical measuring system, and similar adjusting values have been reported.[28b−d] [c] Calculated from the onset oxidation potentials ($E_{onset(ox)}$ vs Ag^+/Ag) by assuming that the absolute energy level of Fc^+/Fc is 4.8 eV below vacuum level: $E_{HOMO} = -(E_{onset(ox)} - 0.09) - 4.8$ eV. [d] Calculated by the equation: $E_g^{ele} = E_{LUMO} - E_{HOMO}$. [e] Estimated from the onset position of the UV−vis absorption spectrum of the thin film.

The electrochemical band gap, E_g^{ele} (= $E_{LUMO} - E_{HOMO}$), is somewhat larger than the optically determined one (E_g^{opt}), presumably due to an interface barrier for charge injection.[30] These electrochemical data suggest that the electron-deficient **BSe** unit and the electron-rich **Ph**, **Cz**, and **Da** units lead to an increase in both electron and hole affinities, and the obtained polymers are expected to improve charge-transporting balance in electronic devices.

Conclusions

A series of donor−acceptor arranged polymers consisting of the electron-accepting **BSe** unit were synthesized via Suzuki coupling reaction. The UV−vis data and the solvent-dependent PL of the polymers support the presence of the CT electronic state, especially in the excited state. The p−n alternating copolymers were electrochemically active in both oxidation and reduction regions, as revealed by cyclic voltammetry. The obtained results are expected to contribute for designing electronic and optical devices by using such ambipolar charge-transporting materials.

Experimental Section

Materials and Syntheses. 3,6-Dibromo-1,2-phenylenediamine, carbazole, diphenylamine, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 2,5-dimethoxyphenylboronic acid, and Aliquat336 were purchased and used without further purification. 1-Dodecyloxy-4-iodobenzene,[31] 4,7-dibromo-2,1,3-benzoselenadiazole (**1**),[32] 4,4′-dibromodiphenylamine (**5**),[18] 1,4-bis(5,5-dimethyl-1,3,2-dioxaborinane-2-yl)-2,5-didodecyloxybenzene (**8**),[24a] 4,7-dibromo-2,1,3-benzothiadiazole (**9**),[4] and $Pd(PPh_3)_4$[33] were prepared according to the literature.

9-(4-Dodecyloxyphenyl)carbazole (2). A mixture of carbazole (6.69 g, 40.0 mmol), 1-dodecyloxy-4-iodobenzene (17.09 g, 44.0 mmol), activated copper[34] (4.07 g, 64.0 mmol), potassium carbonate (11.06 g, 80.0 mmol), and dry DMSO (20 mL) was stirred for 42 h at 180 °C under N_2. The reaction mixture was cooled, diluted with acetone, and filtered. The filtrate was added into water to form a white precipitate, which was collected by filtration, washed with water and methanol, and recrystallized from acetone/methanol to give **2** as a white solid (yield = 6.05 g, 35%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, J = 8.0 Hz, 2H), 7.43−7.24 (m, 8H), 7.09 (d, J = 8.8 Hz, 2H), 4.05 (t, J = 6.4 Hz, 2H), 1.85 (m, 2H), 1.53−1.27 (m, 18H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.34, 141.28, 129.95, 128.43, 125.72, 122.99, 120.15, 119.51, 115.49, 109.64, 68.40, 31.98, 29.74, 29.71, 29.68, 29.66, 29.48, 29.42, 29.36, 26.15, 22.76, 14.21. Anal. Calcd for $C_{30}H_{37}NO$: C, 84.26; H, 8.72; N, 3.28. Found: C, 83.53; H, 8.41; N, 3.23.

3,6-Dibromo-9-(4-dodecyloxyphenyl)carbazole (3). To a solution of **2** (5.56 g, 13.0 mmol) in dry DMF (120 mL) was slowly added NBS (4.63 g, 26.0 mmol) −10 °C, and the mixture was stirred for 10 h at room temperature. The mixture was poured into a large amount of water to form a precipitate. The precipitate was separated by filtration, washed with water and methanol, and purified by column chromatography (silica, chloroform/hexane = 1:1, v/v). After evaporation, the product was recrystallized from acetone/methanol and dried under vacuum to give **3** as a white solid (yield = 7.07 g, 93%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 2.0 Hz, 2H), 7.48 (dd, J = 8.8 and 2.0 Hz, 2H), 7.35 (d, J = 8.8 Hz, 2H), 7.16 (d, J = 8.8 Hz, 2H), 7.08 (d, J = 8.8 Hz, 2H), 4.04 (t, J = 6.4 Hz, 2H), 1.85 (m, 2H), 1.55−1.27 (m, 18H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.79, 140.26, 129.19, 128.91, 128.25, 123.58, 123.05, 115.69, 112.70, 111.41, 68.45, 31.97, 29.73, 29.71, 29.67, 29.66, 29.47, 29.42, 29.30, 26.13, 22.76, 14.21. Anal. Calcd for $C_{30}H_{35}Br_2NO$: C, 61.55; H, 6.03; Br, 27.30; N, 2.39. Found: C, 61.50; H, 5.99; Br, 27.05; N, 2.39.

3,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-9-(4-dodecyloxyphenyl)carbazole (4). To a solution of **3** (4.68 g, 8.0 mmol) in dry THF (70 mL) at −78 °C was added dropwise 11.4 mL (18.0 mmol) of butyllithium (1.58 M in hexane), and the mixture was allowed to react for 2 h at −78 °C under N_2. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5.95 g, 32.0 mmol) was added to the solution, and the mixture was stirred overnight at room temperature. The resulting mixture was poured into water and was extracted with ether. The organic layer was washed with water and dried over anhydrous sodium sulfate. After filtration and evaporation, the residue was purified by column chromatography (silica, hexane/ethyl acetate = 9:1, v/v) and dried under vacuum to provide **4** as a pale-yellow solid (yield = 2.27 g, 42%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.69 (s, 2H), 7.82 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.8 Hz, 2H), 4.05 (t, J = 6.4 Hz, 2H), 1.85 (m, 2H), 1.55−1.27 (m, 18H), 1.39 (s, 24H), 0.89 (t, J = 6.8 Hz, 3H). Anal. Calcd for $C_{42}H_{59}B_2NO_5$: C, 74.23; H, 8.75; N, 2.06. Found: C, 74.08; H, 8.46; N, 2.11.

***N*-Hexyl-4,4′-dibromodiphenylamine (6).** A mixture of **5** (9.81 g, 30.0 mmol), potassium *tert*-butoxide (4.04 g, 36.0 mmol), and 150 mL of dry THF was stirred for 0.5 h at room temperature under N_2. 1-Bromohexane (5.94 g, 36.0 mL) was added to the solution, and the mixture was stirred for 24 h at 60 °C. After cooling to room temperature, the reaction mixture was poured into water and then extracted with chloroform. The combined organic layers were washed with water and dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated. The crude product was purified by column chromatography (silica, hexane/chloroform = 2:1, v/v) and dried under vacuum to give **6** as a colorless oil (11.38 g, 92%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, J = 9.2 Hz, 4H), 6.83 (d, J = 9.2 Hz, 4H), 3.60 (t, J = 7.8 Hz, 2H), 1.60 (m, 2H), 1.32−1.27 (m, 6H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.64, 132.16, 122.48, 113.78, 52.47, 31.61, 27.28, 26.73, 22.67, 14.06. Anal. Calcd for $C_{18}H_{21}Br_2N$: C, 52.58; H, 5.15; Br, 38.86; N, 3.41. Found: C, 52.71; H, 5.08; Br, 39.14; N, 3.43.

4,4′-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-*N*-hexyldiphenylamine (7). To a solution of **6** (10.28 g, 25.0 mmol) in dry THF (180 mL) at −78 °C was added dropwise 38.5 mL (60.0 mmol) of butyllithium (1.56 M in hexane) under N_2. After the mixture was stirred for 2 h at −78 °C, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18.61 g, 100 mmol) was added to the solution, and the mixture was warmed to room temperature and stirred overnight. The resulting mixture was poured into water, extracted with ether, and then dried over anhydrous magnesium sulfate. After evaporation, the crude product was recrystallized from hexane and dried under vacuum to provide **7** as bluish-white crystals (yield = 7.29 g, 58%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8.8 Hz, 4H), 7.00 (d, J = 8.8 Hz, 4H), 3.72 (t, J = 7.6 Hz, 2H), 1.64 (m, 2H), 1.33 (s, 24H), 1.27 (m, 6H), 0.86 (t, J = 6.8 Hz, 3H). FT-IR (KBr, cm^{-1}): 2979, 2930, 1610, 1594, 1397, 1357, 1320, 1274, 1145, 1093, 963, 859, 658. Anal. Calcd for $C_{30}H_{45}B_2NO_4$: C, 71.31; H, 8.98; N, 2.77. Found: C, 71.12; H, 8.60; N, 2.88.

P(BSe-Ph). **1** (1.02 g, 3.0 mmol) and **8** (2.01 g, 3.0 mmol) were dissolved in 30 mL of dry toluene under N_2. To the solution were added K_2CO_3(aq) (2.0 M, 15 mL; N_2 bubbled before use), $Pd(PPh_3)_4$ (0.17 g, 0.15 mmol), and a phase transfer catalyst, Aliquat336 (0.10 g, 0.24 mmol). After the mixture was stirred for 72 h at 85 °C, it was added into methanol to obtain a precipitate. The crude product was separated by filtration and washed with water, methanol, and acetone. The obtained polymer was dissolved in chloroform and reprecipitated in methanol. **P(BSe-Ph)** was collected by filtration, dried under vacuum, and obtained as a bright-yellow powder (yield = 1.60 g, 85%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (br, 2H), 7.37 (br, 2H), 3.93 (br, 4H), 1.49 (br, 4H), 1.16 (br, 36H), 0.82 (br, 6H). FT-IR (KBr, cm^{-1}): 2924, 2853, 1505, 1467, 1416, 1377, 1211, 1033, 846, 761. Anal. Calcd for $Br-(C_{36}H_{54}N_2O_2Se)_{13}-B(OH)_2$ (M_n = 8260): C, 68.05; H, 8.59; N, 4.41; O, 5.42; Br, 0.97. Found: C, 68.48; H, 8.34; N, 4.41; O, 5.37; Br, 0.77.

Other copolymers were prepared analogously. Spectroscopic and analytical data of the polymers are shown below.

P(BSe-Cz). Red powder (yield = 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70−6.98 (m, 12H), 4.07 (br, 2H), 1.87 (br, 2H), 1.29 (br, 18H), 0.88 (br, 3H). FT-IR (KBr, cm^{-1}): 2923, 2852, 1602, 1513, 1471, 1362, 1285, 1243, 1181, 809. Anal. Calcd for $Br-(C_{36}H_{37}N_3OSe)_{11}-B(OH)_2$ ($M_n = 6798$): C, 69.97; H, 6.06; N, 6.80; O, 3.06; Br, 1.18. Found: C, 70.55; H, 5.97; N, 6.27; O, 3.19; Br, 1.19.

P(BSe-Da). Red-purple powder (yield = 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, 4H), 7.62 (s, 2H), 7.24 (d, 4H), 3.85 (br, 2H), 1.81 (br, 2H), 1.35 (br, 6H), 0.91 (br, 3H). FT-IR (KBr, cm^{-1}): 3132, 2924, 2852, 1597, 1509, 1468, 1362, 1251, 1188, 818, 767. Anal. Calcd for $Br-(C_{24}H_{23}N_3Se)_{15}-B(OH)_2$ ($M_n = 6611$): C, 65.40; H, 5.29; N, 9.53; Br, 1.21. Found: C, 65.79; H, 5.27; N, 9.19; Br, 0.

P(BTd-Da). Red powder (yield = 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, 4H), 7.78 (s, 2H), 7.27 (d, 4H), 3.87 (br, 2H), 1.82 (br, 2H), 1.36 (br, 6H), 0.91 (br, 3H). FT-IR (KBr, cm^{-1}): 2924, 2853, 1598, 1515, 1477, 1362, 1252, 1189, 1116, 888, 818. Anal. Calcd for $Br-(C_{24}H_{23}N_3S)_{19}-B(OH)_2$ ($M_n = 7450$): C, 73.52; H, 5.94; N, 10.72; S, 8.18; Br, 1.07. Found: C, 73.94; H, 6.07; N, 10.70; S, 7.90; Br, 0.

4,7-Bis(2,5-dimethoxyphenyl)-2,1,3-benzoselenadiazole (10). Reaction of **1** (0.41 g, 1.2 mmol), 2,5-dimethoxyphenylboronic acid (0.55 g, 3.0 mmol), and $Pd(PPh_3)_4$ (0.06 g, 0.05 mmol) was carried out under similar conditions; THF was used as a solvent, instead of toluene. **10** was obtained as a yellow powder after purification by column chromatography (silica, chloroform as an eluent) and recrystallization form acetone/methanol (yield = 0.52 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (s, 2H), 7.09 (d, J = 3.2 Hz, 2H), 7.01 (d, J = 9.2 Hz, 2H), 6.96 (dd, J = 9.2 and 3.2 Hz, 2H), 3.81 (s, 6H), 3.74 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.59, 153.38, 151.34, 132.45, 129.67, 127.96, 117.44, 114.26, 112.75, 56.50, 55.80. FT-IR (KBr, cm^{-1}): 2996, 2951, 2832, 1582, 1498, 1464, 1422, 1298, 1267, 1217, 1180, 1093, 1047, 1023, 968, 852, 806, 766, 736. Anal. Calcd for $C_{22}H_{20}N_2O_4Se$: C, 58.03; H, 4.43; N, 6.15. Found: C, 57.39; H, 4.41; N, 6.18.

Instruments and Methods. NMR and FT-IR spectra were recorded on a JEOL EX-400 spectrometer and a JASCO FT/IR-460 Plus spectrometer, respectively. Elemental analyses were carried out with a LECO CHNS-932 analyzer and a Yanaco YS-10 SX-Elements microanalyzer. GPC traces were obtained with a Shimadzu LC-9A chromatograph equipped with a UV detector and Shodex 80M columns (eluent = $CHCl_3$; polystyrene standards). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a Shimadzu TGA-50 and a DSC-50 analyzer, respectively. The cast film was prepared from a dilute chloroform solution. UV−vis absorption and PL spectra were measured with a Shimadzu UV-3100 spectrometer and a Hitachi F-4010 spectrophotometer, respectively. Cyclic voltammetry of cast films of the polymers on a Pt plate was performed in an acetonitrile solution of $[(C_2H_5)_4N]BF_4$ (0.10 M) with a Pt counter electrode and an Ag^+/Ag reference electrode with a Toyo Technica Solartron SI 1287 electrochemical interface. Single crystals of **1** were grown from a chloroform solution. X-ray crystallographic analysis was made on a Rigaku Saturn CCD diffractmeter with graphite monochromated Mo Kα radiation. Data were processed using the Rigaku CrystalClear software package. The structure was solved by direct methods (SIR-92),[35] and structural parameters of non-hydrogen atoms were refined anisotropically according to a full-matrix least-squares technique.

The quantum-chemical calculations of the trimeric model compound **10** were performed using the Gaussian 03 series of programs[36] on a SGI Origin2000/128 at the Global Scientific Information and Computing Center of Tokyo Institute of Technology. Ground-state geometries were optimized at the Becke's three-parameter hybrid functional using the Lee−Yang−Parr correlation functional (B3LYP) level with the 6-31G* basis set. Vibrational analysis was carried at the same levels of the theory to optimize the structure as equilibrium structures.

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Supporting Information Available: X-ray crystal structure of **1**, FT-IR spectra and TGA thermograms of the polymers, and HOMO and LUMO representations for trimeric model compounds containing a **Cz** or **Da** unit. This material is available free of charge via the Internet at http://pubs.acs.org.

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