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Convenient Syntheses and Photophysical Properties of 1-Thio- and 1-Seleno-1,3-Butadiene Fluorophores in Rigid Dibenzobarrelene and Benzobarrelene Skeletons

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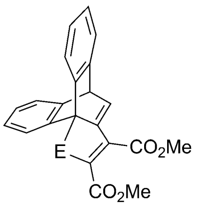
Luminescent compounds have attracted considerable attention in the fields of biochemistry[1] and materials science as exemplified by organic light-emitting devices (OLEDs).[2] In recent years, several types of fluorescent compounds with heteroatoms, such as boron, silicon, phosphorus, and sulfur, have been incorporated in conjugated systems,[3] in which these heteroatoms provide crucial perturbations to the electronic nature of the HOMO and/or the LUMO of the corresponding carbon counterparts. A significant characteristic of these compounds is the dramatic change in photophysical properties given by the chemical modification of heteroatoms. For example, oxides of fused thiophene derivatives exhibit a bathochromic shift in emissions and, in some cases, show larger quantum yields in the solid state than the corresponding unoxidized derivatives.[4] Chalcogenides or complexes with transition metals of phosphole derivatives exhibit similar properties.[5] In addition, some dendritic phosphole oxides[6] show aggregation-induced emission (AIE).[7] These outcomes provide useful chemistry for the heteroatom-containing luminescent compounds.

We recently reported fluorescent compounds **1** bearing a 3-methylene-2,3-dihydrochalcogenophene in a rigid dibenzobarrelene skeleton, in which 1-thio- and 1-seleno-1,3-butadienes behave as the main contributor to the fluorescence.[8] The fluorescence quantum yields (Φ_F) of **1** in dichloromethane were very high despite the presence of a heavy atom: 1.0 for **1** (E=S) and 0.86 for **1** (E=Se).



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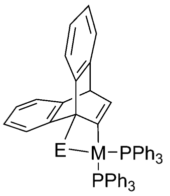

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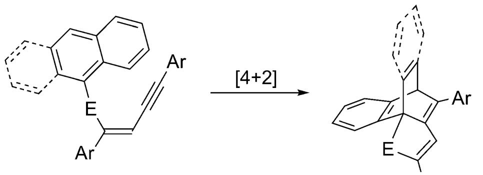
E = S, Se
M = Pd, Pt

The synthesis of **1** is based on the reaction of isolated or intermediately formed chalcogenametallacycles **2** with dimethyl acetylenedicarboxylate. In our studies, we have been seeking to expand the substitution patterns of the 1-chalcogeno-1,3-butadiene fluorophores to reveal the potential as functional materials. Thus, we worked out an alternative synthetic strategy, the intramolecular cycloaddition between a 9-anthryl moiety and an alkynyl moiety, in which it is straightforward to construct the dibenzobarrelene scaffold accompanying an additional ring system in one process [Eq. (1)].[9] Furthermore, this intramolecular cycloaddition has the potential to synthesize the corresponding benzobarrelene analogues by using 1-naphthyl as the ynophile,[10] which would provide insight into the electronic and steric roles of benzene rings fused on the barrelene core. In this communication, we present the intramolecular [4+2]-cycloadditions of 1-(anthrylchalcogeno)- or 1-(naphthylchalcogeno)enynes **I** (E=S, Se) to synthesize dibenzobarrelene or benzobarrelene derivatives **II**, respectively, which have a substitution pattern, which was hard to obtain by our previous method, and are all highly fluorescent in solution. In addition, some of the oxide properties of the sulfur derivatives are reported.



I: E = S, Se   **II**   (1)

For the preparation of (9-anthrylthio)enyne **3** (Ar=Ph), 9-anthrylthiolate (AntS$^-$), generated by the reduction of di-9-anthryl disulfide with NaBH$_4$ in EtOH and THF, was allowed to react with 1,4-diphenyl-1,3-butadiyne (**4a**) at reflux.[11] Unexpectedly, the reaction proceeded directly to the desired final product **5a** with 73% yield, indicating that the enyne **3** (Ar=Ph) readily underwent an intramolecular cycloaddition under the stated conditions (Scheme 1). In a similar manner, dibenzobarrelenethio derivatives (hereafter, abbreviated as Dbb-S) **5** with aryl groups substituted by an MeO (**5b**), F (**5c**), or CF$_3$ (**5d**) group at the *para* position and the corresponding selenium analogues (similarly abbreviated as Dbb-Se) **6a–d** were synthesized in high

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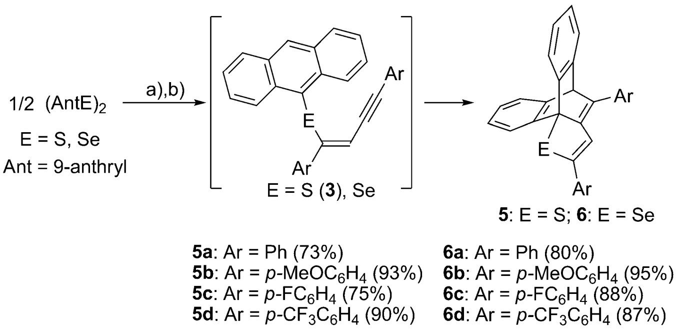
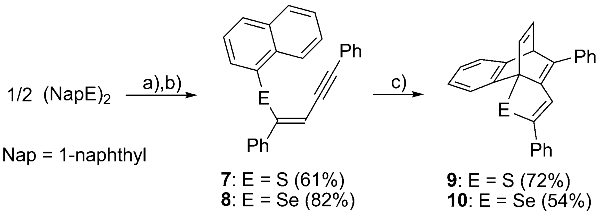


Scheme 1. Synthesis of dibenzobarrelene (Dbb) derivatives **5** and **6**. a) NaBH$_4$, THF, EtOH, RT (for **4b** (Ar = *p*-MeOC$_6$H$_4$): BuOH, DMF); b) ArC≡C–C≡CAr (**4**), THF, EtOH, reflux (for **4b**: BuOH, DMF).

yields. In the case of MeO derivatives **5b** and **6b**, the reactions were slow at reflux in EtOH/THF mixture due to the π-donating methoxy substituent, which lowered the reactivity of diyne **4b** toward nucleophile AntE$^-$, so the syntheses were performed at higher temperature at reflux in BuOH/DMF (DMF = dimethyl formamide).

This synthetic strategy was successfully applied for the synthesis of the benzobarrelene derivatives (monobenzobarrelenes, abbreviated as Mbb-S and Mbb-Se) by employing di-1-naphthyl dichalcogenides (Scheme 2). In this case, the enyne intermediates **7** and **8** were isolated, and the cyclization was performed by heating their xylene solutions at 160 °C in an autoclave to give Mbb-S **9** and Mbb-Se **10** with 72 and 54 % yields, respectively.



Scheme 2. Synthesis of benzobarrelene (Mbb) derivatives **9** and **10**. a) NaBH$_4$, THF, EtOH, RT; b) PhC≡C–C≡CPh (**4a**), THF, EtOH, reflux; c) xylene, 160 °C in an autoclave.

The structures of **5**–**10** were determined by spectroscopic methods and X-ray crystallography for **5** and **6**.[12] A representative ORTEP drawing of Dbb-Se **6d** is depicted in Figure 1. The bond lengths and angles of the 1-chalcogeno-1,4-diaryl-1,3-butadiene part in Dbb-S **5** and Dbb-Se **6** are in the normal ranges and almost independent of the substituents on the aryl groups. The five-membered rings with a sulfur or selenium atom were planar. The torsion angles of the aryl group attached at C2 to the planar five-membered ring were smaller than those at C5 (**5**: Ar-C2: 4.3(4)–17.4(4)°; Ar-C5: 25.9(3)–47.3(10)°; **6**: Ar-C2: 6.5(4)–33.9(3)°; Ar-C5: 38.5(3)–55.5(3)°).

The oxidation of Dbb-S **6a** with *meta*-chloroperoxybenzoic acid (MCPBA, 1 equiv) or MCPBA (2 equiv) in dichloromethane at room temperature gave the sulfoxide **11** (89 %) or the sulfone **12** (99 %), respectively. Similarly, oxidation of Mbb-S **9** with MCPBA (1 equiv) in dichloromethane at room temperature gave the sulfoxide **13** with quantitative yield and that with MCPBA (2 equiv) at reflux in dichloromethane yielded the sulfone **14** (66 %). The structures of **11**–**14** were determined by spectroscopic methods and confirmed by X-ray crystallography for **11**–**13**. Figure 2 presents

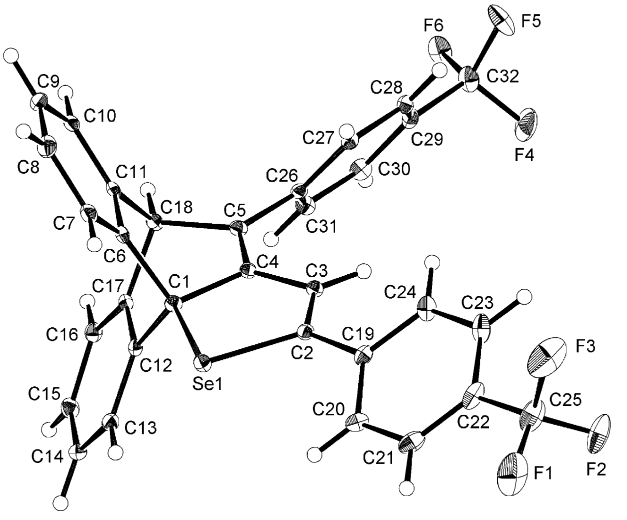


Figure 1. ORTEP drawing of Dbb-Se **6d** (Ar = *p*-CF$_3$C$_6$H$_4$) with 30 % probability ellipsoids. Selected bond lengths (Å) and torsion angles (°): C1–Se1: 1.960(2), Se1–C2: 1.915(2), C2–C3: 1.344(3), C3–C4: 1.432(3), C1–C4: 1.546(3), C4–C5: 1.348(3); C3-C2-C19-C24: 29.2(3), C4-C5-C26-C27: −55.5(3).

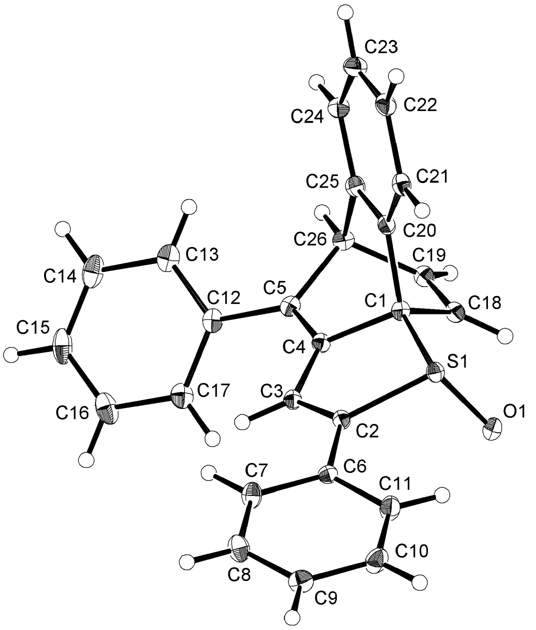
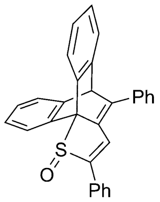


Figure 2. ORTEP drawing of Mbb-SO **13** with 30 % probability ellipsoids. Selected bond lengths (Å) and torsion angles (°): C1–S1: 1.8365(19), S1–C2: 1.8046(18), C2–C3: 1.358(2), C3–C4: 1.426(3), C1–C4: 1.537(2), C4–C5: 1.350(3), S1–O1: 1.5033(14); C3-C2-C6-C7: −20.4(3), C4-C5-C12-C13: −37.3(3).

an ORTEP drawing of Mbb-SO **13**. In the oxidation of Mbb-S **9**, the formation of two diastereomeric sulfoxides may be expected due to the presence of two chiral centers at the bridgeheads [(R_C*,R_C*)]. In our study, we obtained only one diastereomer (R_S*,R_C*,R_C*)-**13**. In the recrystallization of **13**, spontaneous crystallization occurred (the space group of the single crystal is chiral $P2_1$).



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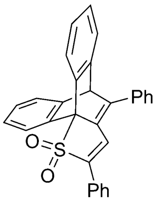

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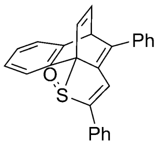

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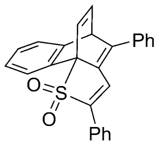

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Photophysical properties of **5**, **6**, **9**, and **10** are listed in Table 1. Figure 3 shows UV/Vis and emission spectra of **5a**, **6a**, **9**, and **10**. Dbb-S **5** and Mbb-S **9** in dichloromethane showed the longest absorption maxima (λ_{abs}) in the range of 378–398 nm with a molar extinction coefficient (ε) of 17000–23000 and the emission maxima (λ_{em}) in the range of 491–505 nm. Dbb-Se **6** and Mbb-Se **10** in dichloromethane exhibited λ_{abs} in a similar region [381–399 nm (ε=16000–23000)] and blueshifted λ_{em} (479–490 nm). Thus, Dbb-S **5** and Mbb-S **9** have larger Stokes shifts (5300–6100 cm^{-1}) than Dbb-Se **6** and Mbb-Se **10** (4700–5200 cm^{-1}). In comparison with diesters **1** and **2**, Dbb-E and Mbb-E (E=S, Se) have longer λ_{abs} with larger ε values and similar λ_{em} [**1**: λ_{abs}=359 nm (ε=7400) and λ_{em}=488 nm; **2**: λ_{abs}=370 nm (ε=4700) and λ_{em}=494 nm, in dichloromethane], indicating that the two aryl substituents in Dbb-E and Mbb-E have a substantial effect on λ_{abs} and ε values by the extension of conjugation. Stokes shifts of **1** and **2** are larger than Dbb-E and Mbb-E (**1**: 7360 cm^{-1}; **2**: 6780 cm^{-1}). Concerning the substituent effect in Dbb-S **5** and Dbb-Se **6**, **5b**, and **6b** with electron-donating *p*-MeO and **5d** and **6d** with electron-withdrawing *p*-CF_3 showed small bathochromic shifts in both λ_{abs} and λ_{em} compared with those of **5a** and **6a** (Ar=Ph). *para*-Fluorine groups in **5c** and **6c** revealed slight hypsochromic shifts.

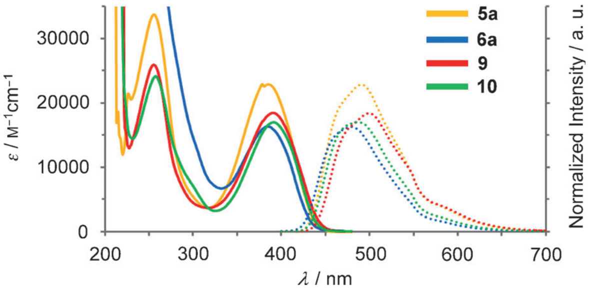

Figure 3. UV/Vis (——) and emission (•••••) spectra of **5a**, **6a**, **9**, and **10**.

In solution, compounds **5**, **6**, **9**, and **10** showed blue (λ_{em} 479 nm for **6a**) to green (λ_{em} 505 nm for **5d**) fluorescence in a relatively narrow region with almost quantitative quantum yields (Φ_F=0.97–1.0). It is clear that the free rotation of aryl substituents has no influence on the quantum yield. Because these compounds involve *cis*,*trans*-1,4-diaryl-1,3-butadienes in their fluorophores, their photophysical properties were compared with those of 1,4-diphenyl-1,3-butadienes (DPB). Although *trans*,*trans*-DPB is moderately fluorescent (λ_{abs}=332 nm, λ_{em}=373 nm, Φ_F=0.42 in hexane), *cis*,*trans*-DPB (λ_{abs}=313 nm, $\Phi_F<10^{-3}$ in hexane) and *cis*,*cis*-DPB (λ_{abs}=299 nm, $\Phi_F<10^{-3}$ in hexane) are substantially nonfluorescent by decay due to *cis*/*trans* isomerization and internal conversion.[13] In the DPBs, intersystem crossing is not efficient and isomerization takes place through twisted intermediates.[13] Thus, the present compounds demonstrate that anchoring a flexible fluorophore in a rigid scaffold is quite effective for emitting fluorescence, as has been seen in stilbenes incorporated in rigid ladder-type structures.[3]

In the solid state, Dbb-S **5** and Dbb-Se **6** have low (Φ_F=0.215 for **6a**) to high (Φ_F=0.812 for **5d**) fluorescence quantum yields. Compounds with an electron-donating MeO (**5b** and **6b**) and electron-withdrawing F and CF_3 (**5d**, **6c**, and **6d**) substituents have relatively large quantum yields. In a comparison between **5** and **6** with identical substituents, the values are larger for Dbb-S **5** than those for Dbb-Se **6**. However, this is not the case for Mbb-S **9** (Φ_F=0.090) and Mbb-Se **10** (Φ_F=0.200). In the crystals, no significant intermolecular interactions were observed except for **6d**, in

Table 1. Photophysical properties of **5**, **6**, **9**, and **10**.[a,b]

	λ_{abs} (ε) [nm (M^{-1}cm^{-1})]	λ_{em} [nm]	Φ_F[c]	Stokes shift [cm^{-1}]		λ_{abs} (ε) [nm (M^{-1}cm^{-1})]	λ_{em} [nm]	Φ_F[c]	Stokes shift [cm^{-1}]
5a (H)	378 (23000)	491 483[e]	0.996[d] 0.471[e]	6100	**6a** (H)	384 (16000)	479 472[e]	0.978[d] 0.215[e]	5200
5b (OMe)	388 (23000)	497 494[e]	1.0[d] 0.690[e]	5700	**6b** (OMe)	389 (23000)	487 481[e]	0.992[d] 0.604[e]	5200
5c (F)	378 (17000)	486 469[e]	1.0[d] 0.687[e]	5900	**6c** (F)	381 (17000)	476 466[e]	1.0[d] 0.252[e]	5200
5d (CF_3)	398 (18000)	505 514[e]	0.994[d] 0.812[e]	5300	**6d** (CF_3)	399 (17000)	490 511[e]	1.0[d] 0.465[e]	4700
9 (H)	391 (19000)	499 508[e]	0.970[d] 0.090[e]	5500	**10** (H)	391 (17000)	488 486[e]	0.982[d] 0.200[e]	5100

[a] The substituents at the *para* position of Ar groups are shown in parentheses. [b] In dichloromethane, unless otherwise noted. [c] Absolute fluorescence quantum yields were determined by using a calibrated integrating sphere system. [d] Under argon. [e] In the solid state.

which an aromatic CH–π interaction (edge-to-face aromatic interaction)[14] was observed between a hydrogen atom on a benzene ring (C9-*H*, see Figure 1) and *p*-$CF_3C_6H_4$ group attached to the C2 carbon in a neighboring molecule (CH···π: 2.511 Å), which might contribute to the large bathochromic shift (21 nm) from 490 nm in solution to 511 nm in the solid state.

Mbb-S **9** and Mbb-Se **10** exhibited both λ_{abs} and λ_{em} at somewhat longer wavelengths, by 13 and 7 nm and 8 and 9 nm, respectively, than the corresponding Dbb-S **5a** and Dbb-Se **6a**. Time-dependent (TD)-DFT calculations[15] were carried out on the unsubstituted model compounds **15** and **16** with barrelene derivative **17** as the reference to consider the excitation energies and the shapes of HOMO and LUMO. The calculated excitation energy of **16** (3.81 eV) was smaller than that of **15** (3.88 eV), reproducing the bathochromic shift of Mbb-S **9** ($\lambda_{abs}=391$ nm) compared with Dbb-S **5a** ($\lambda_{abs}=378$ nm). Figure 4 depicts the shapes of HOMO and LUMO of **15**–**17**, which indicate that their fluorescence is based mainly on 1-thiobutadiene moieties with some contribution from benzene rings and vinylene bridges. In the HOMO of **15**, orbital interactions exist between the 1-thiobutadiene conjugate system and benzene rings in a mutual counterphase manner. This is the case for **16**, in which a vinylene π orbital takes part. As the number of benzene rings decreases from **15** to **17**, both the HOMO and LUMO levels rise to a larger extent by the former, leading to a decrease in the excitation energies. A plausible explanation for the perturbation on energy levels of the 1-thiobutadiene conjugate systems in **15**–**17** is a larger through-space interaction of (1-thiobutadiene)-vinylene than that of (1-thiobutadiene)-benzene, providing a larger contribution of the vinylene bridge in HOMO than that of the benzene ring, which is assumed from the larger through-space interaction among three vinylene groups in barrelene than that among three benzene rings in triptycene.[16] Another factor of the decrease in HOMO levels of **15** and **16** compared with **17** is presumably the electron-withdrawing effect of the benzene ring(s).

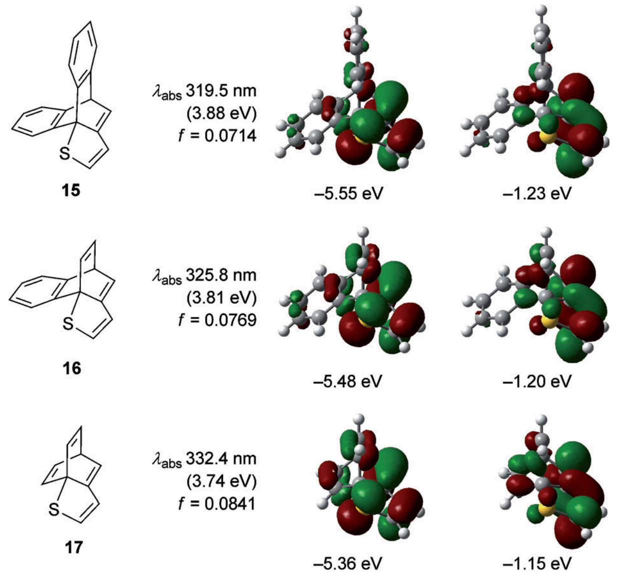

Figure 4. Calculated λ_{abs}, oscillator strength (*f*), HOMO (middle), and LUMO (right) of model compounds **15**–**17** obtained by TD-DFT calculations at the B3LYP/6-31+G(d,p) level.

Table 2 summarizes the photophysical data of oxides **11**–**14**. Compared with Dbb-S **5a** and Mbb-S **9**, large hypsochromic shifts were observed (17–37 nm for λ_{abs} and 29–46 nm for λ_{em}), which is in contrast with the case of the oxides of fused thiophene derivatives exhibiting a bathochromic shift.[4] These blueshifts are straightforwardly ascribed to shortening of the conjugate system from C=C–CH=C–S in **5a** and **9** to C=C–CH=C in **11**–**14** along with the electronic effect of electron-withdrawing sulfoxide or sulfone groups. The difference between Dbb-SO **11** and DbbSO$_2$ **12** is small in λ_{abs} (11 nm) or negligible in λ_{em} (only 3 nm). This is also true for Mbb-SO **13** and Mbb-SO$_2$ **14**. However, there are stark contrasts in their Φ_F values. Although the Φ_F values of Dbb-SO **11** and DbbSO$_2$ **12** in solution remain high (0.807 and 0.792, respectively) and are larger than those in the solid state (0.388 and 0.672, respectively), those of Mbb-SO **13** and Mbb-SO$_2$ **14** are quite low in solution (both $\Phi_F=0.020$ in dichloromethane) but, in the solid state, are enhanced to 0.597 and 0.144, respectively. This is attributed to the crystallization-induced emission (CIE) as observed in poly(phenyl)-substituted conjugate systems.[7] AIE was also observed for **13** and **14**. In 100% THF, Φ_F of **13** and **14** is 0.02, and in THF/H_2O 5:95, the values rose up to 0.07 and 0.19, respectively, in which the emission wavelengths were redshifted ($\lambda_{em}=474$ nm for **13** and 483 nm for **14**).

Table 2. Photophysical properties of oxides **11**–**14**.[a]

	λ_{abs} (ε) [nm ($M^{-1}cm^{-1}$)]	λ_{em} [nm]	Φ_F[b]	Stokes shift [cm^{-1}]
11	361 (14000)	459 464[d]	0.807[c] 0.388[d]	5900
12	350 (17000)	462 449[d]	0.792[c] 0.672[d]	6900
13	365 (20000)	453 456[d]	0.019[c] 0.597[d]	5300
14	354 (19000)	453 466[d]	0.020[c] 0.144[d]	6200

[a] In dichloromethane, unless otherwise noted. [b] Absolute fluorescence quantum yields determined by using a calibrated integrating sphere system. [c] Under argon. [d] In the solid state.

In summary, we have demonstrated the short-step and high-yield syntheses of fluorescent compounds with 1,4-diaryl-1-thio- or 1-seleno-1,3-butadienes as the fluorophores in dibenzobarrelene (**5** and **6**) or benzobarrelene (**9** and **10**) scaffolds by the intramolecular [4+2]-cycloaddition between 9-anthryl or 1-naphthyl and alkynyl moieties. These compounds feature the fluorophores immobilized in a rigid skeleton and, at the same time, protected, in general, from intermolecular interaction by the nonplanar structures. Compounds **5**, **6**, **9**, and **10** are intrinsically fluorescent in solution and hardly undergo the quenching by intersystem crossing, despite the presence of heavy atoms, nor non-irradiative relaxation resulting from intermolecular interactions. Although their fluorescence quantum yields decrease in the solid state, some still remain high ($\Phi_F = 0.812$ for **5d** and 0.690 for **5b** and **5c**). With respect to their oxides, some characteristic properties were observed for benzobarrelene derivatives **13** and **14**. Their Φ_F values in the solid state are larger than those in solution (CIE), and AIE is observed. Studies on their physical properties, such as electrochemistry, and the synthesis of derivatives with a wider range of emission wavelengths are currently under investigation in our laboratory.

Experimental Section

Synthesis of Dbb-S 5a (Ar = Ph): A solution of di(9-anthryl) disulfide (350 mg, 0.84 mmol) in THF (16 mL) was added slowly to a solution of $NaBH_4$ (170 mg, 4.49 mmol) in EtOH (15 mL) at 0 °C under argon. After stirring for 30 min at 0 °C, a solution of 1,4-diphenyl-1,3-butadiyne (365 mg, 0.176 mmol) in EtOH (20 mL) was added to the mixture at 0 °C. The mixture was heated at reflux for 12 h, and then the reaction was quenched by addition of dilute hydrochloric acid. The mixture was extracted with dichloromethane, and the extract was washed with water, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was subjected to column chromatography (hexane/CH_2Cl_2 4:1) to give **5a** (506 mg, 73 %).

Keywords: cycloaddition · fluorescence · naphthalene · selenium · sulfur

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Intramolecular Cycloaddition

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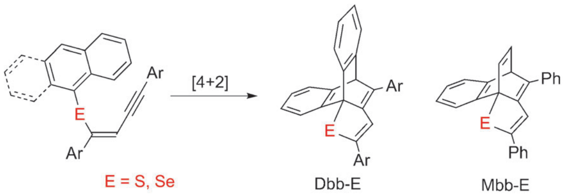
Convenient Syntheses and Photophysical Properties of 1-Thio- and 1-Seleno-1,3-Butadiene Fluorophores in Rigid Dibenzobarrelene and Benzobarrelene Skeletons



λ_{em} = 479–505 nm
Φ_F = 0.97–1.0
in CH_2Cl_2

λ_{em} = 466–514 nm
Φ_F = 0.09–0.81
in the solid state

No heavy-atom effect: Highly fluorescent, sulfur- or selenium-containing compounds were synthesized by intramolecular [4+2]-cycloadditions between 9-anthryl or 1-naphthyl and alkynyl moieties (see scheme). Their fluorescence is based on 1-chalcogeno-1,3-butadiene-conjugated system in a rigid skeleton. Some of them are also highly fluorescent in the solid state. The monoxide of Mbb-S is more fluorescent in the solid state ($\Phi_F = 0.6$) than in solution ($\Phi_F < 0.02$).