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# Fluorescent 3-Methylene-2,3-Dihydrochalcogenophenes Incorporated in a Rigid Dibenzobarrelene Skeleton

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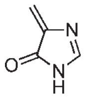
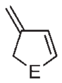
## ABSTRACT

**The fluorescent 3-methylene-2,3-dihydroselenophene derivative ($\Phi_F$ = 0.86 in $CH_2Cl_2$) incorporated in a dibenzobarrelene skeleton was synthesized by the reaction of a four-membered selenaplatinacycle with dimethyl acetylenedicarboxylate (DMAD) or reaction of bis(dibenzobarrelenyl) diselenide with DMAD in the presence of $Pd(PPh_3)_4$ and $PPh_3$. A fluorescent sulfur homologue ($\Phi_F$ = 1.0 in $CH_2Cl_2$) was also synthesized by the reaction of bis(dibenzobarrelenyl) disulfide with DMAD in the presence of $Pd(PPh_3)_4$. Selected chemical transformations of these diesters were also investigated.**

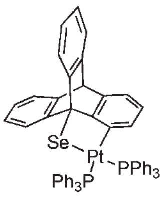
Luminescent compounds are attracting considerable attention in the fields of biochemistry[1] and materials science, as exemplified by organic light-emitting devices (OLED).[2] Olefins are potentially fluorescent due to the large energy difference between the first excited singlet state ($S_1$) and the first excited triplet state ($T_1$), but they are usually nonfluorescent due to *E*-*Z* isomerization or other photochemical reactions.[3] Fixing olefins into planar rigid scaffolds and introducing appropriate substituents can convert the non- or weak fluorescence systems to strong fluorescence systems, as reported for stilbenes.[4] Another example is the fluorophore in green fluorescent proteins (GFP), which has a 1-amino-2-aza-1,3-butadiene conjugate system with *s-trans* configuration in 3-methylene-2,5-diazacyclopenten-4-one **1**.[1,5] While **1** has an additional carbonyl group, those having simpler analogs of **1** are 3-methylene-2,3-dihydrochalcogenophenes **2**, reported in this communication, which include 1-chalcogeno-1,3-butadienes with *s-trans* configuration as fluorophores. Here we report on moderately to strongly fluorescent compounds bearing the fluorophores in a rigid dibenzobarrelene skeleton.



**1**



**2**
E = S, Se



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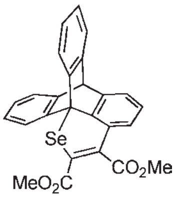

**4**

We previously reported the intramolecular cyclometalation of hydrido-selenolato $Pt^{II}$ complexes *cis*-[PtH(SeTrip)$L_2$] ($L_2$ = mono- or bidentate phosphine ligands;

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[1] (a) Shimonura, O. *Bioluminescence*; World Scientific: Hackensack, NJ, 2006. (b) Shimomura, O. *Angew. Chem., Int. Ed.* **2009**, *48*, 5590–5602. (c) Chalfie, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 5603–5611. (d) Tsien, R. Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 5612–5626 and references cited therein.

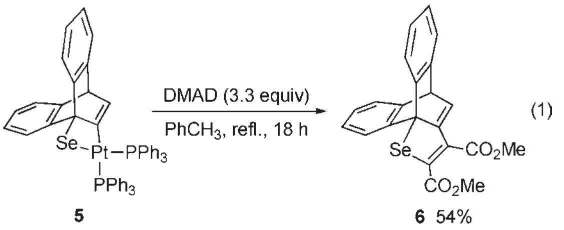
[2] *Organic Light-Emitting Devices*; Müllen, K., Scherf, U., Eds.; Wiley-VCH: Weinheim, 2006.

[3] Turro, N. J.; Ramamurthy, V.; Scaiano, J. C. *Modern Molecular Photochemistry of Organic Molecules*; University Science Books: Sausalito, CA, 2010; Chap. 10, pp 705–799.

[4] (a) DeBoer, C. D.; Schlessinger, R. H. *J. Am. Chem. Soc.* **1968**, *90*, 803–804. (b) Saltiel, J.; Zafiriou, O. C.; Megarity, E. D. *J. Am. Chem. Soc.* **1968**, *90*, 4759–4760. And for recent papers: (c) Yamaguchi, S.; Xu, C.; Tamao, K. *J. Am. Chem. Soc.* **2003**, *125*, 13662–13663. (d) Fukazawa, A.; Hara, M.; Okamoto, T.; Son, E.-C.; Xu, C.; Tamao, K.; Yamaguchi, S. *Org. Lett.* **2008**, *10*, 913–916. (e) Saito, M.; Nakamura, M.; Tajima, T. *Chem.—Eur. J.* **2008**, *14*, 6062–6068.

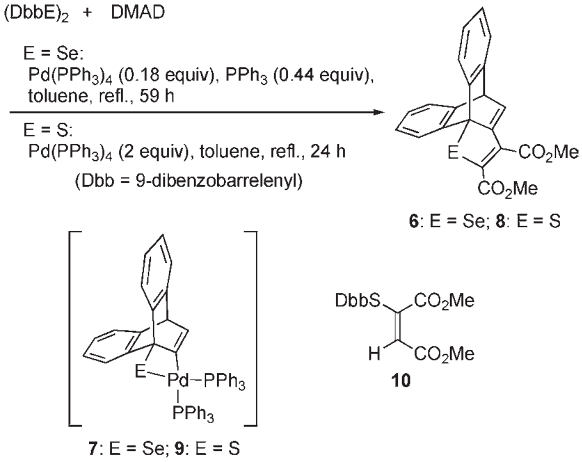
10.1021/ol2013523

Trip = 9-triptycyl) to give five-membered 1,2-selenaplatinacycles.[6] One of them, **3**, underwent carboselenation with dimethyl acetylenedicarboxylate (DMAD) to give the 1*H*-2-benzoselenin derivative **4**.[7] In the course of our study, we examined the cyclometalation of *cis*-[PtH(SeDbb)-$(PPh_3)_2$] (Dbb = 9-dibenzobarrelenyl) to furnish three types of selenaplatinacycles.[8] One of the three is the four-membered 1,2-selenaplatinacycle **5**, and we found that the reaction of **5** with DMAD yielded the carboselenation product **6** exhibiting blue fluorescence with a high quantum yield ($\Phi_F$ = 0.86) (eq 1).



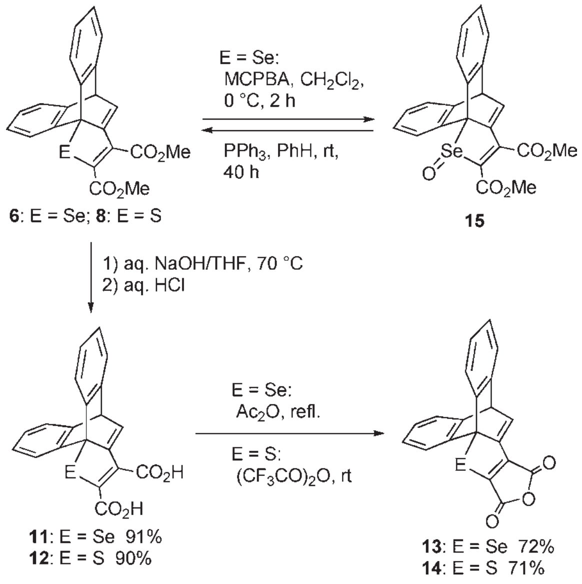
The parent 3-methylene-2,3-dihydroselenophene was reported by Brandsma as an unstable material for isomerization to 3-methylselenophene.[9] Compound **6** was also synthesized by the reaction of diselenide $(DbbSe)_2$ with DMAD (3.6 equiv) in the presence of a catalytic amount of $Pd(PPh_3)_4$ (0.18 equiv) and $PPh_3$ (0.44 equiv) at 0.39 mol equiv with respect to used $(DbbSe)_2$ together with recovered $(DbbSe)_2$ (63%) (Scheme 1). From our previous study,[10] the reaction of $(DbbSe)_2$ with $Pd(PPh_3)_4$ was expected to give 1,2-selenapalladacycle **7** as the key intermediate, and the subsequent reaction of **7** with DMAD would yield **6** and $Pd^0$ species. Although we planned a catalytic cycle of the regenerated $Pd^0$ species, this worked only a few times. In a similar way, the reaction of disulfide $(DbbS)_2$ with DMAD (3.2 equiv) in the presence of an excess amount of $Pd(PPh_3)_4$ (2 equiv) yielded **8** (0.50 mol equiv) together with (*E*)-(DbbS)($MeCO_2$)C=CH($CO_2Me$) (**10**) (0.42 mol equiv). Compound **8** would have been formed through 1,2-thiapalladacycle **9**, and vinyl sulfide **10** is equivalent to the *syn*-hydrothiolation product of thiol DbbSH with DMAD.

**Scheme 1.** Synthesis of **6** and **8** by the Reaction of $(DbbE)_2$ (E = S, Se) with DMAD



Selected chemical transformations of **6** and **8** are summarized in Scheme 2. Hydrolysis of **6** and **8** by heating under alkaline conditions gave dicarboxylic acids **11** and **12**, respectively, in high yields, which were dehydrated with acetic or trifluoroacetic anhydride to give anhydrides **13** and **14** with yields of 72% and 71%, respectively. Oxidation of **6** with *m*-chloroperoxybenzoic acid (MCPBA) in dichloromethane at 0 °C gave selenoxide **15** with an isolated yield of 21%. **8** was not oxidized under similar conditions, probably due to the low reactivity of the sulfur atom bound to the vinyl group bearing two electron-withdrawing ester groups. Selenoxide **15** was readily reduced to **6** quantitatively by treatment with triphenylphosphine at room temperature.

**Scheme 2.** Selected Chemical Transformations of **6** and **8**



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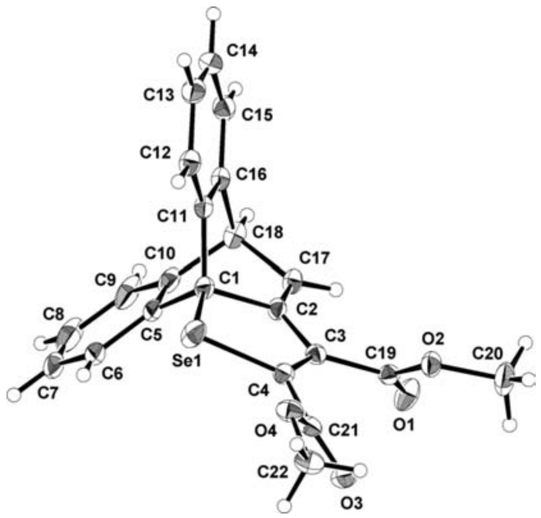
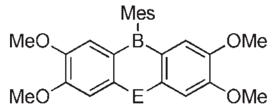


**Figure 1.** ORTEP drawing of **6** with 30% probability ellipsoids. Selected bond length (Å), bind angle (deg), and dihedral angle (deg) data: Se1−C1 1.962(2); C1−C2 1.540(2); C2−C3 1.440(3); C3−C4 1.341(3); C4−Se1 1.899(2); C2−C17 1.335(3); C17−C18 1.520(3); C3−C19 1.491(3); C4−C21 1.483(3); Se1−C1−C2 106.4(1); C1−C2−C3 114.3(2); C2−C3−C4 116.5(2); C4−Se1−C1 89.97(9); C1−C2−C17 113.5(2); C2−C17−C18 113.9(2); C17−C2−C3 132.2(2); C2−C3−C19 119.6(2); C19−C3−C4 123.9(2); C3−C4−C21 125.4(2); C21−C4−Se1 119.7(1); C4−C3−C19−O1 135.9(2); C3−C4−C21−O3 −32.8(3).

The structures of **6**, **8**, and **11**−**15** were identified by spectroscopic methods and, for **6** and **8**, by X-ray crystallography as well.[11] The structures of **6** and **8** were very similar on the whole, and an ORTEP drawing of **6** is depicted in Figure 1. The five-membered rings in **6** and **8** are planar, and the ester parts [C(=O)O] are distorted by 32−44° from the planes. The geometries of the 3-methylene-2,3-dihydrochalcogenophene parts are in the range of normal values. Although there is no significant intermolecular chalcogen-chalcogen interaction or $\pi-\pi$ stacking, there is weak intermolecular head-to-tail interaction between O3−C21 carbonyl groups (3.087 Å for **6** and 3.067 Å for **8**) and hydrogen bonding between O1 and H−C22 (2.469 Å for **6** and 2.405 Å for **8**).

Compounds **6**, **8**, and **11**−**14** showed blue to yellow-green emissions ($\lambda_{em}$ = 488−517 nm) in dichloromethane under argon with moderate to quantitative fluorescence quantum yields ($\Phi_F$ = 0.38−1.0) as summarized in Table 1. Selenoxide **15** largely diminished the fluorescent property ($\Phi_F$ = 0.034). Dicarboxylic acids **11** and **12** and acid anhydrides **13** and **14** showed bathochromic shifts in absorption ($\Delta\lambda_{abs}$ = 51−62 nm) compared to the respective diesters **6** and **8**, which are explained in terms of the extended conjugation led by the increase in the coplanarity between carbonyl groups and the 1-chalcogeno-1,3-butadiene conjugate system. The bathochromic shifts in absorption are larger than those of emission ($\Delta\lambda_{em}$ = 13−26 nm), so diesters **6** and **8** have larger Stokes shifts (7360 and 6780 cm$^{-1}$, respectively) than **11**−**14** (4030−4510 cm$^{-1}$). **8** has the largest $\Phi_F$ (1.00) in dichloromethane ($\lambda_{em}$ = 488 nm). In addition, **8** showed $\lambda_{em}$ at 443 nm in the solid state with $\Phi_F$ of 0.30, while **6** showed very weak emission in the solid state ($\Phi_F$ = 0.03). An obvious heavy atom effect of chalcogen atoms was reported on dibenzochalcogenoborines **16** ($\Phi_F$ = 0.30 for O, 0.08 for S, and 0.0007 for Se in cyclohexane at 298 K).[12] In the present case, although the heavy atom effect was conspicuous in the solid state, the difference was small in solution. It is worth noting that even **6**, **11**, and **13** bearing a selenium atom have rather large fluorescence quantum yields.



**16** E = O, S, Se

**Table 1.** Photophysical Properties of **6**, **8**, and **11**−**15**[a]

| | $\lambda_{abs}$ ($\varepsilon$)[b] /nm (/M$^{-1}$cm$^{-1}$) | $\lambda_{em}$[b] /nm | $\Phi_F$[c,d] | Stokes shift/cm$^{-1}$ (nm) |
|---|---|---|---|---|
| **6** | 370 (4700) | 494 | 0.86<br>0.03[b,e] | 6780 (124) |
| **11** | 421 (4200) | 507 | 0.38 | 4030 (86) |
| **13** | 421 (2100) | 517 | 0.62 | 4410 (96) |
| **8** | 359 (7400) | 488<br>443[e] | 1.00<br>0.30[b,e] | 7360 (129) |
| **12** | 410 (4100) | 503 | 0.72 | 4510 (93) |
| **14** | 421 (2600) | 514 | 0.95 | 4300 (93) |
| **15** | 341 (1600)<br>271 (3500) | 495 | 0.03 | 9120 (154) |

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

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(11) Crystallographic data for **6** and **8**. **6**: ($C_{22}H_{16}O_4Se$); yellow prism, Mo-Kα radiation ($\lambda$ = 0.71073), 103 K, $M_r$ = 423.31, monoclinic, $P2_1/c$, $a$ = 10.3327(6), $b$ = 15.1209(8), $c$ = 11.5507(6) Å, $\beta$ = 93.507(1)°, $V$ = 1801.30(17) Å$^3$, $Z$ = 4, $\mu$ = 2.110 mm$^{-1}$, $d_{calcd}$ = 1.561 g cm$^{-3}$, $R_1$ ($I > 2\sigma(I)$) = 0.0307, w$R_2$ = 0.0832 (all data) for 3354 reflections, 246 parameters, GOF 1.051. **8**: ($C_{22}H_{16}O_4S$); yellow prism, Mo-Kα radiation ($\lambda$ = 0.71073), 103 K, $M_r$ = 376.41, monoclinic, $P2_1/c$, $a$ = 10.2288(6), $b$ = 14.8538(8), $c$ = 11.6838(6) Å, $\beta$ = 93.302(1)°, $V$ = 1772.25(17) Å$^3$, $Z$ = 4, $\mu$ = 0.209 mm$^{-1}$, $d_{calcd}$ = 1.411 g cm$^{-3}$, $R_1$ ($I > 2\sigma(I)$) = 0.0432, $wR_2$ = 0.1056 (all data) for 3296 reflections, 246 parameters, GOF = 1.041.

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TD-DFT calculations were carried out for **6** and **8** at the B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d) level,[13] where structure optimization was started from the geometries obtained by X-ray crystallography.[14] The calculated smallest excitation energies were 2.99 eV for **6** and 3.09 eV for **8** with oscillator strength (*f*) of 0.0864 and 0.1011, respectively. The largest contributor to excitation was the HOMO−LOMO transition. The respective shapes of the HOMO and LUMO of **6** and **8** are very similar to each other, and the HOMO and LUMO of **6** are shown in Figure 2, which indicates that excitation takes place mainly on the part of 1-seleno-*s*-*trans*-1,3-butadienes with some contribution from the benzene rings in HOMO and the ester groups in LUMO. Since the benzene rings and ester groups are on either side of the 1-chalcogeno-*s*-*trans*-1,3-butadiene moiety, we anticipated solvatochromism due to the excited state having a more polarized structure than the ground state by an intramolecular charge transfer.[15] Thus, solvent effects on absorption and emission were examined for **8**. As a result, increasing bathochromic shifts were observed with an increase in normalized solvent polarity parameters ($E_T^N$),[16] and the solvent effect was larger on emission than on absorption. For example, $\lambda_{abs}$ and $\lambda_{em}$ (Stokes shift/cm$^{-1}$) were 353 and 465 nm (6820) in hexane ($E_T^N$ = 0.009), 355 and 489 nm (7400) in acetonitrile ($E_T^N$ = 0.460), 357 and 500 nm (8010) in methanol ($E_T^N$ = 0.762), and 364 and 515 nm (8060) in MeOH−$H_2O$ (v/v = 3/7). While the Stokes shifts become larger as the $E_T^N$ values increased, the $\Phi_F$ values of **6** and **8** measured in MeOH decreased somewhat to 0.54 and 0.89, respectively, probably as a result of quenching by hydrogen bonding with the solvent.

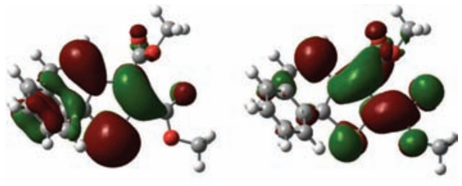
HOMO (−5.79 eV) LUMO (−2.37 eV)

**Figure 2.** Drawings of HOMO and LUMO of **6** calculated at the B3LYP/6-31+G(d,p)//B3LYP/6-31+(d) level.

In summary, we revealed 3-methylene-2,3-dihydrothiophenes and -selenophenes incorporated in a rigid dibenzobarrelene skeleton to be moderately to strongly fluorescent despite the presence of heavy main-group elements. The fluorescence is mainly based on 1-thio- and 1-seleno-1,3-butadiene systems with *s*-*trans* configuration. Chalcogen atoms and two ester groups in **6** and **8** may be chemically transformed, which would lead to their acquisition of functionality.

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**Supporting Information Available.** Synthetic procedures and spectral characterization of **6**, **8**, and **11**−**15**, ORTEP drawing of **8**, Table of solvent effects on $\lambda_{abs}$ and $\lambda_{em}$ for **8**, optimized coordinates of **6** and **8**, and CIF files of **6** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] Torsion angles of ester groups in the optimized structures. **6**: C4−C3−C19−O1 115.4°; C3−C4−C21−O3 −6.9°; **8**: C4−C3−C19−O1 127.1°; C3−C4−C21−O3 −15.5°, where atom numbers correspond to those in Figure 1.

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