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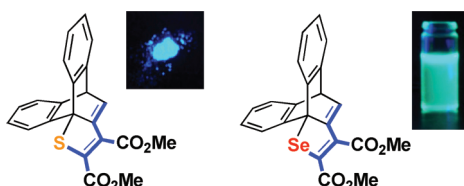
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ABSTRACT

The fluorescent 3-methylene-2,3-dihydroselenophene derivative (Φ_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 (Φ_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) (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.
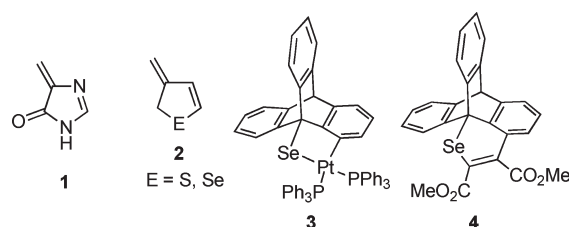
We previously reported the intramolecular cyclometalation of hydrido-selenolato Pt^{II} complexes *cis*-[PtH-(SeTrip)L$_2$] (L$_2$ = mono- or bidentate phosphine ligands;

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).
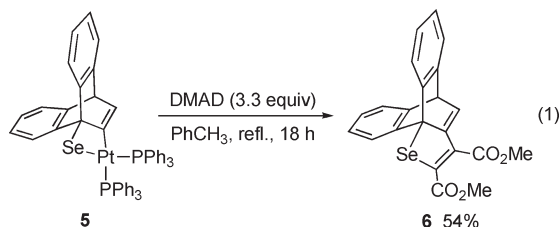
The parent 3-methylene-2,3-dihydroselenophene was reported by Brandsma as an unstable material for isomerization to 3-methylselenophene.[9] Compound **6** was also synthesized by the reaction of diselenide (DbbSe)$_2$ with DMAD (3.6 equiv) in the presence of a catalytic amount of Pd(PPh$_3$)$_4$ (0.18 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$_2$Me) (**10**) (0.42 mol equiv). Compound **8** would have been formed through 1,2-thiapalladacyle **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
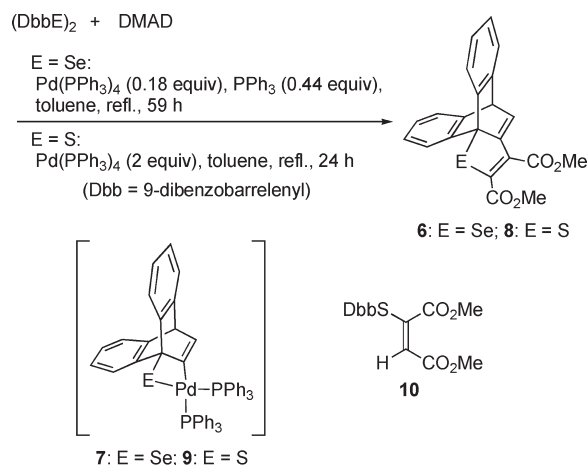
Selected chemical transformations of **6** and **8** are summarized in Scheme 2. Hydrolysis of **6** and **8** by heating under alkaline conditions gave dicarboxylic acids **11** and **12**, respectively, in high yields, which were dehydrated with acetic or trifluoroacetic anhydride to give anhydrides **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**
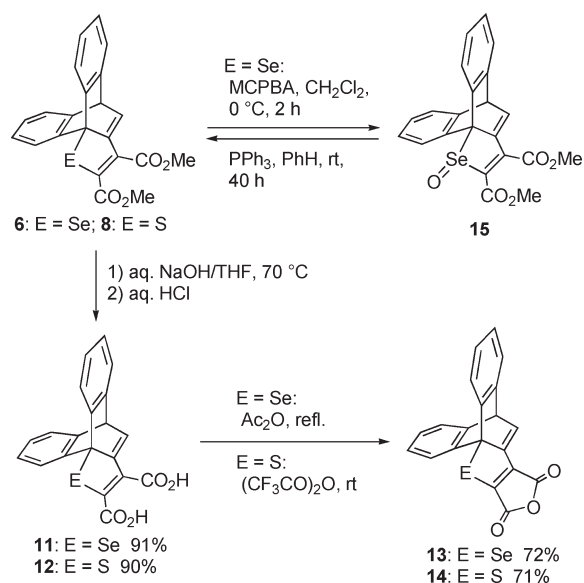
(5) (a) Shimomura, O. *FEBS Lett.* **1979**, *104*, 220–222. (b) Cody, C. W.; Prasher, D. C.; Westler, W. M.; Prendergast, F. G.; Ward, W. W. *Biochemistry* **1993**, *32*, 1212–1218. (c) Follenius-Wund, A.; Bourotte, M.; Schmitt, M.; Iyice, F.; Lami, H.; Bourguignon, J.-J.; Haiech, J.; Pigault, C. *Biophys. J.* **2003**, *85*, 1839–1850. (d) Bourotte, M.; Schmitt, M.; Follenius-Wund, A.; Pigault, C.; Haiech, J.; Bourguignon, J.-J. *Tetrahedron Lett.* **2004**, *45*, 6343–6348. (e) Barondeau, D. P.; Tainer, J. A.; Getzoff, E. D. *J. Am. Chem. Soc.* **2006**, *128*, 3166–3168. (f) Chen, K.-Y.; Cheng, Y.-M.; Lai, C.-H.; Hsu, C.-C.; Ho, M.-L.; Lee, G.-H.; Chou, P.-T. *J. Am. Chem. Soc.* **2007**, *129*, 4534–4535. (g) Dong, J.; Solntsev, K. M.; Poizat, O.; Tolbert, L. M. *J. Am. Chem. Soc.* **2007**, *129*, 10084–10085. (h) Wang, S.; Smith, S. C. *Phys. Chem. Chem. Phys.* **2007**, *9*, 452–458. (i) Forbes, M. W.; Jockusch, R. A. *J. Am. Chem. Soc.* **2009**, *131*, 17038–17039.

(6) (a) Ishii, A.; Nakata, N.; Uchiumi, R.; Murakami, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 2661–2664. (b) Nakata, N.; Yamaguchi, Y.; Ishii, A. *J. Organomet. Chem.* **2010**, *695*, 970–973. (c) Nakata, N.; Yoshino, T.; Ishii, A. *Phosphorus Sulfur Silicon* **2010**, *185*, 992–999.

(7) Ishii, A.; Kamon, H.; Murakami, K.; Nakata, N. *Eur. J. Org. Chem.* **2010**, 1653–1659.

(8) Ishii, A.; Yamaguchi, Y.; Nakata, N. *Dalton Trans.* **2010**, *39*, 6181–6183.

(9) Kulik, W.; Verkruijsse, H. D.; de Jong, R. L. P.; Hommes, H.; Brandsma, L. *Tetrahedron Lett.* **1983**, *24*, 2203–2204.

(10) Nakata, N.; Uchiumi, R.; Yoshino, T.; Ikeda, T.; Kamon, H.; Ishii, A. *Organometallics* **2009**, *28*, 1981–1984.
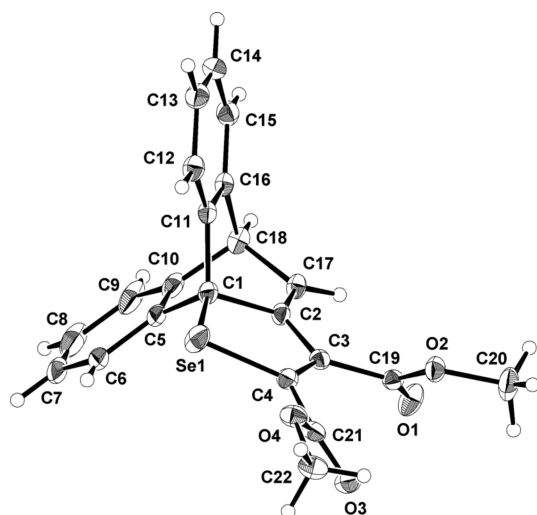
Figure 1. ORTEP drawing of **6** with 30% probability ellipsoids. Selected bond length (Å), bind angle (deg), and dihedral angle (deg) data: Se1−C1 1.962(2); C1−C2 1.540(2); C2−C3 1.440(3); C3−C4 1.341(3); C4−Se1 1.899(2); C2−C17 1.335(3); C17−C18 1.520(3); C3−C19 1.491(3); C4−C21 1.483(3); Se1−C1−C2 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 π−π 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 (λ_{em} = 488−517 nm) in dichloromethane under argon with moderate to quantitative fluorescence quantum yields (Φ_F = 0.38−1.0) as summarized in Table 1. Selenoxide **15** largely diminished the fluorescent property (Φ_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 Φ_F (1.00) in dichloromethane (λ_{em} = 488 nm). In addition, **8** showed λ_{em} at 443 nm in the solid state with Φ_F of 0.30, while **6** showed very weak emission in the solid state (Φ_F = 0.03). An obvious heavy atom effect of chalcogen atoms was reported on dibenzochalcogenoborines **16** (Φ_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.
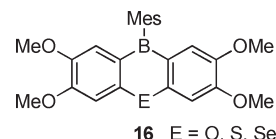

16 E = O, S, Se

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

	λ_{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 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)	488 443[e]	1.00 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) 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.

(11) Crystallographic data for **6** and **8**. **6**: ($C_{22}H_{16}O_4Se$); yellow prism, Mo-Kα radiation (λ = 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, β = 93.507(1)°, V = 1801.30(17) Å^3, Z = 4, μ = 2.110 mm^{-1}, d_{calcd} = 1.561 g cm^{-3}, R_1 (I > 2σ(I)) = 0.0307, wR_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 (λ = 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, β = 93.302(1)°, V = 1772.25(17) Å^3, Z = 4, μ = 0.209 mm^{-1}, d_{calcd} = 1.411 g cm^{-3}, R_1 (I > 2σ(I)) = 0.0432, wR_2 = 0.1056 (all data) for 3296 reflections, 246 parameters, GOF = 1.041.

(12) Kobayashi, J.; Kato, K.; Agou, T.; Kawashima, T. *Chem. Asian. J.* **2009**, *4*, 42−49.

(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.

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, λ_{abs} and λ_{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$_2$O (v/v = 3/7). While the Stokes shifts become larger as the E_T^N values increased, the Φ_F values of **6** and **8** measured in MeOH decreased somewhat to 0.54 and 0.89, respectively,

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

HOMO (−5.79 eV)   LUMO (−2.37 eV)

probably as a result of quenching by hydrogen bonding with the solvent.

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.

Supporting Information Available. Synthetic procedures and spectral characterization of **6**, **8**, and **11**−**15**, ORTEP drawing of **8**, Table of solvent effects on λ_{abs} and λ_{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.

(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.

(15) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, Third, Updated and Enlarged ed.; Wiley-VCH: Weinheim, 2003; pp 352−359.

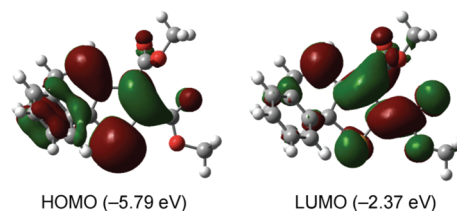(16) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319–2358.