Improvement of Luminescence Quantum Efficiency by Intermolecular Interaction

Hwasoon Jung, Kyungwook Kim, Subin Lee, Hyesu Hwang, Kwangseo Park, Jinho Kim, Soon-Ki Kwon,[†,*] and Youngjin Kang[*]

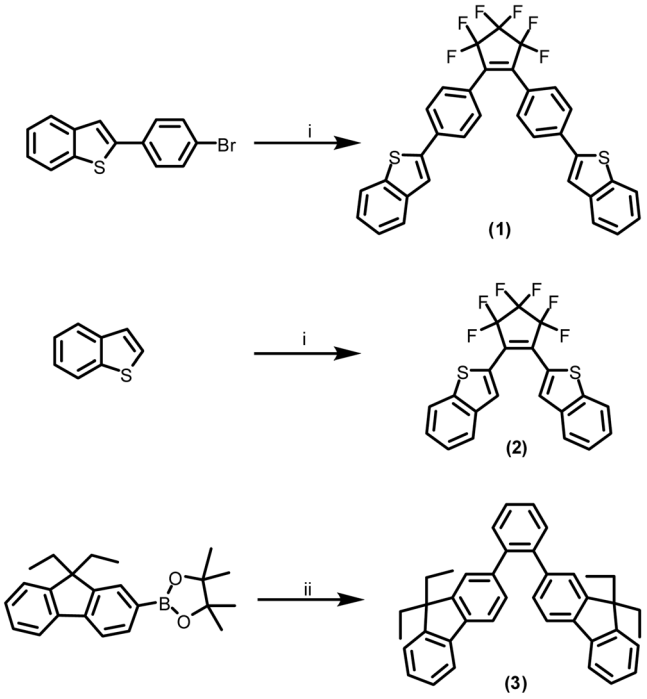
Division of Science Education & Department of Chemistry, Kangwon National University, Chuncheon 200-701, Korea
[*]E-mail: kangy@kangwon.ac.kr
[†]School of Nano & Advanced Materials Science and Engeering and ERI, Gyeongsang National University, Jinju 660-701, Korea
Received July 11, 2007

Key Words : Fluorescence, Quantum yields, Photoluminescent property, Crystal structure, Intermolecular interaction

Due to their unique photophysical properties, highly fluorescent compounds are currently of great interest for material science applications, such as photo-electronics, organic light-emitting diodes (OLEDs) and chemical sensors.[1] In particular, efforts have focused on the improvement of fluorescence quantum yields (Φ_F), since the Φ_F of emitting materials and the device efficiency in OLEDs are generally related.[2] For this purpose, several approaches have been suggested including the attachment of anthracene and/or pyrene units having high Φ_F to the molecular framework, the extension of π-conjugation and the introduction of electron-withdrawing groups (F, CN, etc) as substituents.[3] Among such approaches, the introduction of electron-withdrawing groups to the molecular backbone has received greater attention, because the molecules containing these groups have shown unusual and high fluorescence quantum efficiency through the intermolecular interactions. Such phenomenon is often called aggregation induced emission (AIE).[4] During our ongoing efforts on the development of luminescent materials, we have observed that fluorene- and anthracene-based compounds linked by a perfluorocyclopentene core unit have high fluorescence quantum efficiency as compared to 9,10-diphenylanthracene (DPA).[5] Our interest in the synthesis of highly fluorescent materials containing a perfluorocyclopentene core unit, which can provide binding sites for hydrogen atoms of adjacent molecules via intermolecular interactions, has prompted us to investigate the syntheses and photophysical properties of their derivatives. Here, we report on the syntheses, crystal structure and optical properties of a series of V-shaped molecules containing the linker of an electron-withdrawing moiety. In addition, the effect of electron-withdrawing substituents on fluorescence quantum efficiency has been systematically evaluated at the molecular level.

Scheme 1 outlines the synthesis of the series of benzothiophene derivatives. Compound **1** and **2** were prepared by the addition of octafluorocyclopentene to the corresponding lithiated compound, prepared from the reaction of a small excess of *n*-BuLi and the bromoarene at −78 °C. The standard work up and crystallization from CH_2Cl_2/hexane produces compounds as colorless or pale yellow solids in moderate yields (45-55%). In addition, to evaluate the effect of a perfluorocyclopentene ring on structural features and photoluminescence, we have synthesized an aromatic analogue of compound **3**, through Pd-mediated Suzuki coupling. The structures of **1-3** have been characterized by ^{1}H-NMR, ^{13}C-NMR and elemental analyses, including X-ray diffraction analysis of **2**.

Yellow crystals of **2** that were suitable for X-ray analysis were obtained by the slow evaporation in CH_2Cl_2 and hexane. The crystal structures and selected bond lengths and angles of **1** are presented in Figure 1. As shown in the Figure, two benzothiophene groups connected by the hexafluorocyclopentene linker are twisted with respect to each other. Note that the hexafluorocyclopentene linker and one (S1 ring) of two benzothiophene rings are arranged a nearly coplanar manner with a dihedral angle of 5.44°, while the other (S2 ring) is highly tilted toward the hexafluorocyclopentene core with a dihedral angle of 71.96°. This observation is very uncommon in diarylethene derivatives



Scheme 1. Synthetic routes of **1**, **2** and **3**. (i) *n*-BuLi/THF, −78 °C, octafluorocyclopentene (0.5 eq); (ii) K_2CO_3, benzyltrimethylammoniumchloride, $Pd(PPh_3)_4$ (5 mol%), toluene, reflux.

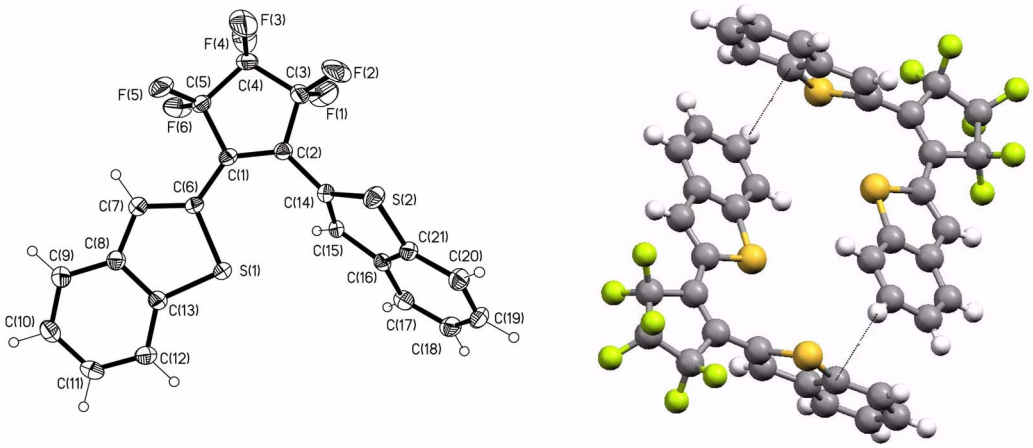


Figure 1. Molecular structure of **2** with 50% thermal ellipsoids and a labeling scheme (left); Diagram of two adjacent molecules in a unit cell packing showing macrocyclic structure through intermolecular C(π)···H interactions (right). Selected bond lengths (Å) and angles (deg): C1-C6 1.450(3), C2-C14 1.474(2), C1-C2-C14 128.77(17), C2-C1-C6 130.70(17).

and also indicates the lack of effective π-conjugation throughout the whole molecule. This unusual arrangement of two benzothiophene rings around the perfluorocyclopentene core can be due to the intermolecular interactions between two adjacent asymmetric units (See supporting information). There is an interesting spatial arrangement in the crystal lattice. Compound **2** exhibits face-to-edge C(π)···H interactions, as demonstrated by the distance of C21···H11(2.880 Å). As a consequence, **2** shows macrocyclic structure that has an approximately C2 symmetry. The separation distance between two mean planes (C14-C16, C21 and S2) is approximately 10.42 Å.

The bond lengths C1-C6 and C2-C14 are 1.450(3) Å and 1.474(2) Å, respectively. These are similar to those of previously reported diarylethene compounds.[5] Compound **2** has several intermolecular interactions that appear to direct the expanded packing of the solid-state structure. The packing diagram (See supporting information) displays a zigzag shape of molecules with slipped H···F and C(π)···H intermolecular interactions (F6···H9, 2.49 Å; C16···H7, 2.85 Å; C17···H7, 2.89 Å). However, additional intermolecular interactions, such as π–π stacking, were not found in the packing structure of **2**.

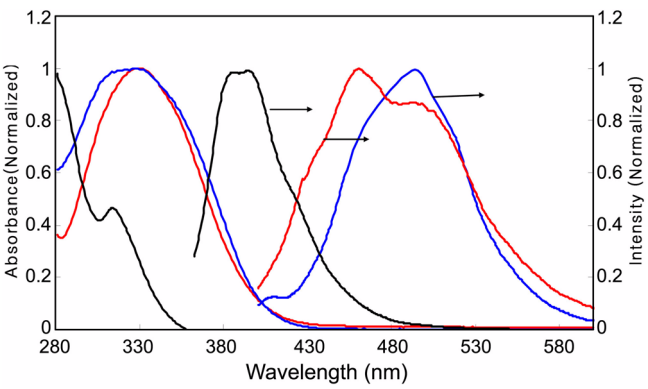


Figure 2. Absorption and emission spectra of **1** (red line), **2** (blue line) and **3** (black line).

UV/Vis absorption spectra of **1**, and **2** exhibit intense absorption bands between 280 nm and 400 nm, indicating that the electronic transitions are mostly benzothiophene-centered π-π^*. The optical band gaps of **1** and **2** were determined by their corresponding absorption threshold (2.86 eV for **1**, 2.91 eV for **2**, respectively). To examine the effect of the perfluorocyclopentene linkage on the electronic transition, we measured the absorption spectrum of **3**, which contains a benzene ring instead of perfluorocyclopentene, under the same conditions. Interestingly, the maximum peak observed for **3** exhibits a significant blue shift (λ_{max}= 280 nm) relative to those of **1**, and **2**. In addition, the UV edge in **3** appears at a much higher energy than those in **1** and **2**. From the point of those observations, when perfluorocyclopentene unit is employed as a core, more effective π-conjugation occurs between the core and side units. However, when the core unit of perfluorocyclopentene is replaced by benzene, effective π-conjugation throughout whole molecules does not occur. This might be due to the strong steric repulsion between the benzene core and the bulky 9,9-diethylfluorene. The emission spectra of compounds **1**, **2** and **5** in solution at room temperature are dominated by fluorescence in the region of 380-550 nm. The λ_{max} values in emission spectra are at 504 nm for **1**, 463 nm (495(sh)) for **2** and 396 nm for **3**, respectively. This result can also be explained by correlating the electronic and structural effects originating from the perfluorocyclopentene unit. The introduction of perfluorocyclopentene gives rise to an increase in the electron-withdrawing nature of molecules and effective π-conjugation between core and side units, leading to more red-shifts of **1** and **2** than in **3**. It is worth noting that the quantum yields of **1** is higher than that of 9,10-diphenylanthracene, which is a highly fluorescent molecule (Φ_F = 0.95) and often used as the blue standard in quantum yield measurement.[6] To investigate the effect of the core unit on the fluorescence quantum yield, we have synthesized two compounds, 1,2-bis(9,9'-diethylfluoren-2-yl)-3,3,4,4,5,5-hexafluorocyclopentene (**BFFC**) and 1,2-

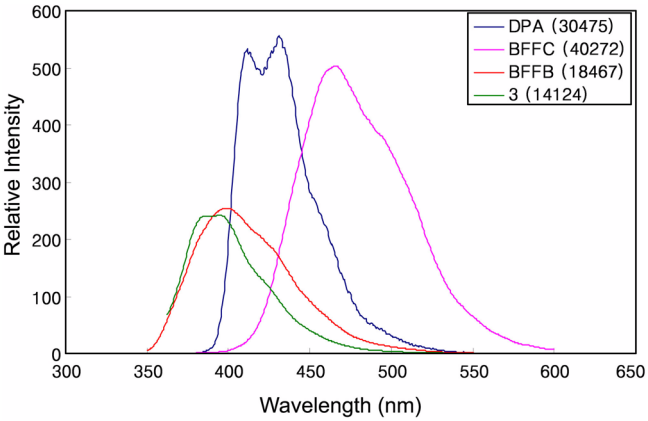


Figure 3. Comparison of fluorescence intensity for **DPA**, **BFFC**, **BFFB** and **3**. insect: integrated fluorescence intensity (excitation at 340 nm, slit width 3 nm).

difluoro-4,5-bis(9,9'-diethylfluoren-2-yl)benzene (**DFFB**) according to previous literature.[5] The determination of the quantum yield was performed by the comparative method, which was established by Williams *et al.*.[7] As shown in Figure 3, the integrated fluorescence intensity has the following order: **BFFC** > **DPA** > **DFFB** > **3**. Compound **3**, which is linked by a benzene ring and lacks a fluorine atom, shows the lowest quantum yield. The striking difference between **BFFC**, **DFFB** and **3** is the number of fluorine atoms in core unit. In general, the rigidity of molecular structure has an influence on the fluorescence quantum yields.[8] As reported previously, **BFFC** has a 2-D puckered sheet structure through a lot of intermolecular C(π)···H, C(π)···F and F···H in the crystal packing. However, **BFFB** has a 1-D column-like structure in the crystal packing.[5] The structural difference is clearly caused by the number of fluorine atoms (intermolecular interactions). Despite the lack of crystal structure for **3**, we believe that strong intermolecular interactions render molecules with rigidity and lead to high quantum efficiency.

In summary, highly fluorescent compounds containing a perfluorocyclopentene core have been synthesized and the effect on fluorescence quantum efficiency of their derivatives has been systematically evaluated. The fluorescence quantum efficiency depends on the number of fluorine atoms. As intermolecular interactions increase, molecules become rigid, leading to higher fluorescence quantum efficiency.

Experimental Section

General Methods. All experiments were performed under dry N_2 atmospheres using standard Schlenk techniques. All solvents were freshly distilled over appropriate drying reagents prior to use. The starting materials 2-bromo-9,9'-diethylfluorene, 2-bromo-9,9'-dihexylfluorene, and 2-bromo-9,9'-spirobifluorene were prepared according to literature procedures.[9] For general experimental details, see supporting information.

Synthesis of 1,2-Bis{4-(2-benzo[b]thiophenyl)phenyl}-3,3,4,4,5,5-hexafluorocyc lopentene (1). Yields: 45%; m.p. 249-250 °C. MS (EI): m/z = 592 $[M]^+$. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 7.84 (d, J = 1.5 Hz, 1H), 7.75 (d, J = 1.6 Hz, 1H), 7.72 (AB, J = 8.4 Hz, 2H), 7.60 (s, 1H), 7.46 (AB, J = 9 Hz, 2H), 7.35 (m, 2H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 142.9, 140.8, 140.1, 136.7, 130.3, 127.7, 127.2, 125.3, 125.1 124.3, 122.7, 121.1, 30.1. Anal. Calcd for $C_{33}H_{18}F_6S_2$: C, 66.88; H, 3.06. Found: C, 66.79; H, 2.98.

Synthesis of 1,2-Bis(2-benzo[b]thiophenyl)-3,3,4,4,5,5-hexafluorocyclope ntene (2).[10] Yields: 51%; m.p. 132-134 °C. MS (EI): m/z = 440 $[M]^+$. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 7.86-7.83 (m, 2H), 7.76-8.11 (m, 4H), 7.38-7.43 (m, 4H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 130.7, 130.0, 129.6, 128.95, 128.4, 126.1, 125.2. Anal. Calcd for $C_{21}H_{10}F_6S_2$: C, 57.27; H, 2.29. Found: C, 57.10; H, 2.31.

Synthesis of 1,2-Bis(9,9-diethylfluoren-2-yl)benzene (3). Yields: 55% MS (EI): m/z = 518 $[M^+]$. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 7.16-7.71 (18H, m), 1.95 (8H, q), 0.29 (12H, t, J = 7.23 Hz). Anal. Calcd for $C_{40}H_{38}$: C, 92.62; H, 7.38. Found: C, 96.55; H, 7.29.

Fluorescence Measurement. UV/Vis and photoluminescent spectra were obtained with UV/Vis spectrometer Lambda 900 and a Perkin Elmer Luminescence spectrometer LS 50B, respectively. All solutions for photophysical experiments were degassed with more than three repeated freeze-pump-thaw cycles in a vacuum line. The emission slit width was at 3-5 nm. The relative quantum yields of PL (Φ_{PL}) for all compounds were determined relative to 9,10-diphenylanthracene (Φ_{PL} = 0.95) as the standard. A range of concentrations of solution of all compounds and standard were measured such that absorbance were less than 0.10 at the excitation wavelength (λ_{ex} = 340 nm). The quantum yield was then measured by the previously known process.[7]

X-ray Crystallography. All data were collected on a Bruker SMART diffractometer equipped with a graphite monochromated Mo Kα (λ = 0.71073 Å) radiation, and a CCD detector; 50 frames of two-dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. All data collections were performed at 173 K. Decay was monitored by 50 standard data frames measured at the beginning and end of data collection. The program SAINTPLUS[11] was used for integration of the diffraction profiles. The structures were solved by direct methods using the SHELXS program of the SHELXTL package[12] and refined by full matrix least squares against F^2 for all data using SHELXL. All non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions [U_{iso} = 1.2U_{eq} (parent atom)] and refined using a riding model with the exception of the hydrogen atoms of the coordinated water molecule. The initial positions of the hydrogen atoms of water molecule were obtained from difference electron density maps. Their positional parameters were then refined using a riding model. The summary of the crystal data, experimental details and refinement results for **2** is listed in Table 1. Crystallographic data for the structure

Table 1. Crystallographic data and structure refinement for **2**

Chemical formula	$C_{21}H_{10}F_6S_2$
Formula weight	440.41
T (K)	173(2)
Crystal system	Monoclinic
Space group	$P2(1)/_C$
a (Å)	12.6272(6)
b (Å)	6.0836(3)
c (Å)	23.9412(12)
β (°)	103.6890(10)
V (Å^3)	1786.89(15)
Z	4
Absorption coefficient (mm^{-1})	0.363
F(000)	888
Crystal size (mm^3)	0.80 × 0.80 × 0.30
θ range (°)	1.66 to 28.30
Reflections collected / Unique	10613 / 4145
Data / restraints / parameters	4145 / 0 / 262
Goodness-of-fit on F^2	1.069
Final R indices	R_1 = 0.0446, wR_2 = 0.1137

reported here have been deposited at the Cambridge Crystallographic Data Center, CCDC No. 653537. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk), or electronically *via* www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information. General syntheses, crystal data, bond lengths, bond angles and packing diagram are available on the request from the corresponding author. (Fax: +82-33-242-9598, E-mail: kangy@kangwon.ac.kr)

Acknowledgement. This research was supported by a grant (F0004021) from Information Display R&D Center, one of the 21st Century Frontier R&D Program funded by the Ministry of Commerce, Industry and Energy of Korean government. This work was partially supported by KOSEF R&E (2006).

References

1. (a) Wei, Y.; Chen, C.-T. *J. Am. Chem. Soc.* **2007**, *129*, 7478. (b) Balan, B.; Gopidas, K. R. *Chem. Eur. J.* **2007**, *13*, 5173. (c) Hauser, P. C.; Liang, C. L. C.; Mueller, B. *Meas. Sci. Technol.* **1995**, *6*, 1081. (d) Kang, Y.; Moon, S.-T.; Park, S.; Kim, J.; Lee, S. S.; Park, K.-M. *Bull. Kor. Chem. Soc.* **2007**, *28*, 873. (e) An, B.-K.; Kwon, S.-K.; Park, S. Y. *Bull. Korean Chem. Soc.* **2005**, *26*, 1555.
2. (a) Mattoussi, H.; Murata, H.; Merritt, C. D.; Iizumi, Y.; Kido, J.; Kafafi, Z. H. *J. Appl. Phys.* **1999**, *86*, 2642. (b) Choi, K.; Lee, C.; Lee, K. H.; Park, S. J.; Son, S. U.; Chung, Y. K.; Hong, J.-I. *Bull. Korean Chem. Soc.* **2006**, *27*, 1549.
3. (a) Tao, S.; Peng, Z.; Zhang, X.; Wang, P.; Lee, C.-S.; Lee, S.-T. *Adv. Funct. Mater.* **2005**, *15*, 1716. (b) Lim, S.-J.; An, B.-K.; Jung, S. D.; Chung, M.-A.; Park, S. Y. *Angew. Chem. Int. Ed.* **2004**, *43*, 6346. (c) Lee, J. H.; Hwang, D. H. *Chem. Commun.* **2003**, 2836.
4. Zeng, Q.; Li, Z.; Dong, Y.; Di, C.; Qin, A.; Hong, Y.; Ji, L.; Zhu, Z.; Jim, C. K. W.; Yu, G.; Li, Q.; Li, Z.; Liu, Y.; Qin, J.; Tang, B. Z. *Chem. Commun.* **2007**, *1*, 70.
5. Han, M.; Lee, S.; Jung, J.; Park, K.-M.; Kwon, S.-K.; Ko, J.; Lee, P. H.; Kang, Y. *Tetrahedron* **2006**, *62*, 9769.
6. Lakowicz, J. R. *Principles of Fluorescence Spcetroscopy*; Kluwer Academic: New York, 1996.
7. Williams, A. T. R.; Winfield, S. A.; Miller, J. N. *Analyst* **1983**, *108*, 1067.
8. Morrison, D. J.; Trefz, T. K.; Piers, W. E.; McDonald, R.; Parvez, M. *J. Org. Chem.* **2005**, *70*, 5309.
9. Liu, X.-M.; He, C.; Huang, J.; Xu, J. *Chem. Mater.* **2005**, *17*, 434. (references cited therein)
10. Yamada, S.; Ishii, E.; Konno, T.; Ishihara, T. *Org. Biomol. Chem.* **2007**, *5*, 1442.
11. Bruker, *SAINTPLUS NT Version 6.22. Software Reference Manual*; Bruker AXS: Madison, Wisconsin, 2000.
12. Bruker, *SHELXTL NT Version 6.10. Program for Solution and Refinement of Crystal Structures*; Bruker AXS: Madison, Wisconsin, 2000.