Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron Letters
Tetrahedron Letters 48 (2007) 7675–7679

Synthesis of a solvent-sensitive highly fluorescent derivative of perfluorocyclopentene

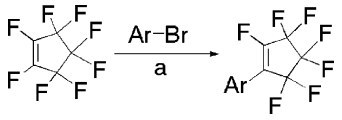
Zhan-Xian Li, Wei Sun, Yan-Feng Yue, Ming-Hua Zheng, Chun-Hu Xu, Jing-Yi Jin, Chen-Jie Fang and Chun-Hua Yan*

Beijing National Laboratory for Molecular Sciences, State Key Lab of Rare Earth Materials Chemistry and Applications, PKU-HKU Joint Lab in Rare Earth Materials and Bioinorganic Chemistry, Peking University, Beijing 100871, China

Received 18 June 2007; revised 21 August 2007; accepted 24 August 2007
Available online 30 August 2007

Abstract—A solvent-sensitive highly fluorescent compound, *N*-[2-(1′,3′,4′,4′,5′,5′-hexafluorocyclopentenyl)]-4-(5-methoxy-thiazolyl)pyridine (**1D**) was synthesized as an unexpected product of the reaction of 4-bromo-5-methoxy-2-(4-pyridyl)thiazole (**1B**) with perfluorocyclopentene in the presence of *n*-BuLi. Primary mechanism of this reaction was proposed, and the photophysical properties of **1D** in different solvents were studied.

Photo-switching systems are attracting more and more interest owing to their bistable states, which can be achieved under irradiation at particular wavelengths selectively and regularly. As thermally stable and high fatigue-resistant compounds, diarylethene derivatives with heterocyclic aryl groups have been explored extensively due to the remarkably different properties of open/closed isomers such as absorption spectra,[1] fluorescence spectra,[1b,2] refractive indices,[3] IR spectra,[4] oxidation/reduction potentials,[5] and so on. Particularly, the rational design and successful syntheses of asymmetric diarylethenes based on perfluorocyclopentene are important in modulating the properties of their bistable thermal states, which are crucial for realizing their practical applications in information storage, photo-switching devices, etc.[2c,d,5c,6] As a necessary step during the syntheses of these photoactive molecules, reactions between perfluorocyclopentene and bromine-substituted aromatic compounds play an important role, the general synthetic procedure of which is depicted in Scheme 1.[1b,7] In the present work, the reaction of 4-bromo-5-methoxy-2-(4-pyridyl)thiazole (**1B**) with perfluorocyclopentene in the condition as described afforded not only the desired compound 1-{4-[5-methoxy-2-(4-pyridyl)thiazolyl]}perfluorocyclopentene (**1C**), but also an unexpected product *N*-[2-(1′,3′,4′,4′,5′,5′-hexafluorocyclopentenyl)]-4-(5-methoxy-thiazolyl)pyridine(**1D**). With discussing the reactions of its analogs under the same conditions, a reasonable explanation is proposed for the formation of **1D**. Furthermore, **1D** is a strong fluorophore in solution and its fluorescent properties are dependent significantly on solvents.



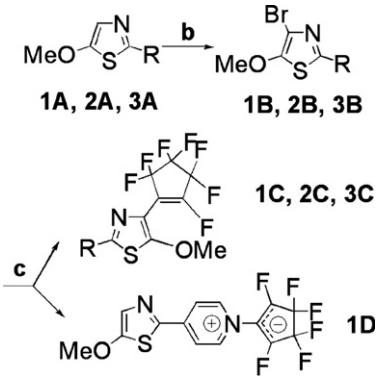
Scheme 1. General procedure for reaction of perfluorocyclopentene and bromine-substituted aromatic compounds. Reaction conditions: (a) *n*-BuLi, THF, −78 °C → rt.

5-Methoxy-2-(4-pyridyl)thiazole (**1A**) and **1B** were synthesized according to the modified method reported in the literature.[8] The total synthetic process of **1C**[9] and **1D**[10] is shown in Scheme 2 and the synthetic approaches were completed according to the reported recipe.[7] The possible mechanism is presented in Scheme 3. The formation of **1D** might be ascribed to the enhanced nucleophilicity of the nitrogen atom in the pyridyl group after treatment of **1B** with *n*-BuLi.

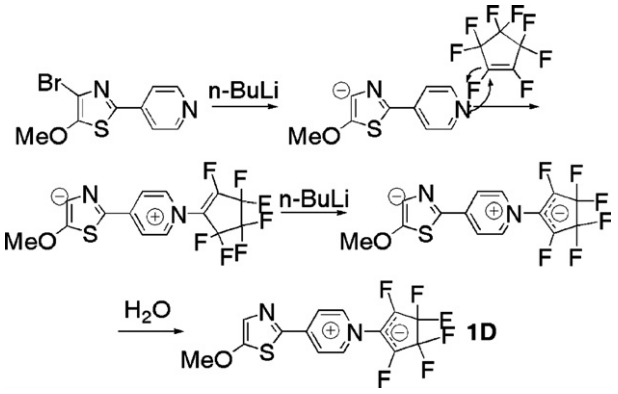
To study the formation mechanism of **1D**, 4-bromo-5-methoxy-2-(2-pyridyl)thiazole (**2B**)[8] and 4-bromo-5-methoxy-2-(3-pyridyl)thiazole (**3B**)[8] were treated with

Keywords: *N*-[2-(1′,3′,4′,4′,5′,5′-Hexafluorocyclopentenyl)]-4-(5-methoxy-thiazolyl)pyridine; 4-Bromo-5-methoxy-2-(4-pyridyl)thiazole; Perfluorocyclopentene; Solvent-sensitive; Highly fluorescent.
* Corresponding author. Tel./fax: +86 10 62754179; e-mail: yan@pku.edu.cn

0040-4039/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2007.08.086



Scheme 2. Synthetic procedure of compounds **1C**, **2C**, **3C**, and **1D**. Reaction conditions: (b) *N*-Bromosuccimide, $CHCl_3$, rt; (c) *n*-BuLi, perfluorocyclopentene, THF, −78 °C → rt. **1A**–**1D**: R = 4-pyridyl; **2A**–**2C**: R = 2-pyridyl; **3A**–**3C**: R = 3-pyridyl.



Scheme 3. Possible formation mechanism of **1D**.

n-BuLi and perfluorocyclopentene, respectively, (Scheme 2), with the product desired as 1-{4-(5-methoxy-2-(2-pyridyl)thiazolyl)}perfluorocyclopentene (**2C**[11]) and 1-{4-(5-methoxy-2-(3-pyridyl)thiazolyl)}perfluorocyclopentene (**3C**[12]), respectively. No analogs of **1D** were detected in the controlled experiments. The different results of three reactions can be explained as follows. Firstly, from the point of charge-delocalization, the influences of carbon anions of the thiazole rings on 4-pyridyl and 2-pyridyl groups are almost identical, both quite great, which increase the negative charges localized on the nitrogen atoms in the pyridine rings, hence improving their nucleophilicity. For **3B**, however, there is nearly no influence from the carbon anion of the thiazole ring on the nitrogen atom in 3-pyridyl group. As a consequence, it is more favorable for the nitrogen atom in 4-pyridyl and 2-pyridyl moiety to react with perfluorocyclopentene than that in 3-pyridyl moiety. Considering the steric effect, it is more favorable for the nitrogen atom in 4-pyridyl moiety than that in 2-pyridyl moiety to attack the double bond in perfluorocyclopentene. Thus it is more possible for the reaction of **4B** and perfluorocyclopentene to produce **1D**.

The crystal structure of **1D** is illustrated in Figure 1 and the crystallographic data are collected in supplemental materials (Table S1). Bond lengths and angles are summarized in Table S2. The bond lengths of C10–C11 and C10–C14 are 1.391(4) and 1.375(5) Å, respectively, which are shorter than those of C11–C12 (1.507(5) Å), C12–C13 (1.510(5) Å), and C13–C14 (1.514(5) Å), indicating the formation of a π_3^4 bond within C11–C10–C14. The dihedral angle of the thiazolyl and pyridyl fragments is 5.1°, implying that the two fragments are nearly parallel. The small dihedral angle of the pyridyl and perfluorocyclopentene planes (16.7°) also suggests that these two planes are parallel to some extent. Therefore, an overall planarity within this compound excluding the methoxy group is suggested, which means that the molecule is a wonderful π-conjugative system, bearing both positive and negative charges within the molecule and exhibiting a fine planarity.

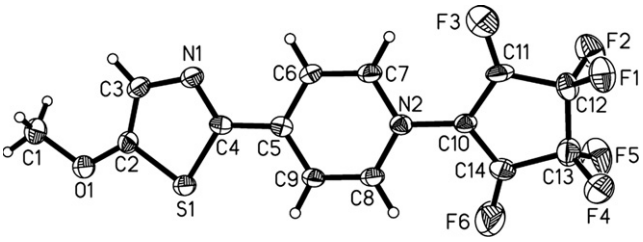


Figure 1. Crystal structure of **1D**.

Figure 2a shows the UV–vis absorption and fluorescence spectra of **1D** in dichloromethane. The detailed photophysical data in various solvents are collected in Table 1. In the same solvent, the shapes of absorption and emission spectra look quite like the mirror image of each other (Fig. 2a), implying no change in the configuration between the ground and excited states. With the increase of the polarity and the protonation ability of solvents, a hypsochromic shift of λ_{max} from 433 nm in dichloromethane to 407 nm in methanol is observed in the absorption spectra with the molar absorption coefficients of about 10^4 M^{-1} cm^{-1}, which is consistent with the reported results of pyridinium.[13] The fluorescence quantum yield is very high in aprotic solvents with weaker dipole–dipole interaction (Table 1). The simultaneous existence of positive and negative charges within the molecule benefits the charge transfer greatly. Besides, the fine planarity of the molecule suppresses nonradiative deactivation processes efficiently, mainly the internal conversion. However, the fluorescence quantum yield decreases severely from 0.76 to 0.02 with the increase of the protonation ability and dipole–dipole interaction of solvents, due to the intermolecular interactions between **1D** and the solvent molecules. The fluorescence decay curves are fitted as mono-exponential decays for **1D** in all the selected solvents (Fig. S1) and the fluorescence lifetime recorded for **1D** is shortened from 2.81 ns in dichloromethane to 0.22 ns in DMSO with the protonation capacity and dipole–dipole interaction of solvent increasing, which is consistent with the changing order of the fluorescence quantum yield. Compared with the photophysical properties of **1A** in different solvents,[8a] it is noted that a remarkable red-shift of λ_{max}^{abs} and λ_{max}^{em} of **1D** occurs in the selected solvents with higher fluorescence quantum yields, which are more

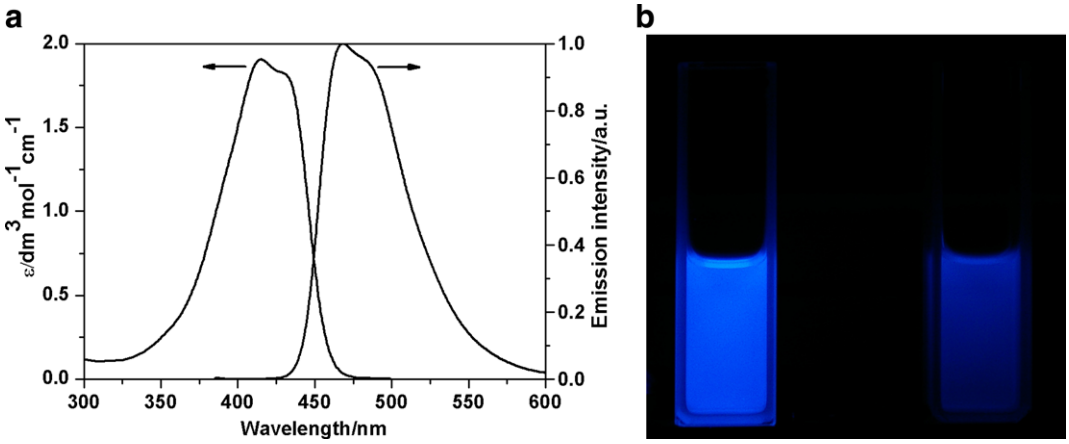


Figure 2. (a) Absorption (left) and fluorescence (right) spectra of **1D** in dichloromethane at rt; (b) Photograph of dichloromethane (left) and methanol (right) solution (ca. 4.4×10^{-5} M) of **1D** under the irradiation at 365 nm.

Table 1. Photophysical data of **1D** in different solvents

Medium (T/K)	λ_{max}^{abs}/nm (ε/10^4 M^{-1} cm^{-1})	λ_{max}^{em}/nm	Φ	τ/ns
CH_2Cl_2 (298)	415 (1.91)	466	0.76	2.81
	430 (1.82)	482		
$CHCl_3$ (298)	416 (2.00)	462	0.73	2.85
	433 (1.18)	481		
CH_3CN (298)	407 (1.87)	474	0.64	2.30
Acetone (298)	408 (1.85)	474	0.44	2.30
C_2H_5OH (298)	409 (1.87)	474	0.21	1.04
CH_3OH (298)	407 (1.89)	472	0.08	0.54
DMF (298)	410 (1.92)	485	0.04	0.41
DMSO (298)	410 (1.97)	490	0.02	0.22

influenced by solvents and the difference can be ascribed to the structural characteristics of the molecule **1D**. Irradiating ($\lambda = 365$ nm) **1D** in dichloromethane (Fig. 2b, left) at room temperature with a portable UV lamp (8 W) led to a strong blue fluorescence, while very weak fluorescence was detected in the methanol solution of **1D** (Fig. 2b, right). Due to its solvent-sensitive fluorescence, **1D** may have a potential application as a probe of the solvent polarity.[14]

Figure 3 describes the HOMO and LUMO of **1D** at the B3LYP/6-31G(d, p) level of theory calculated by GAUSSIAN 03 (see Ref. S1 in Supplementary data) and the resonance structures of **1D**. The HOMO and LUMO are mainly located in the perfluorocyclopentene moiety and the pyridyl ring, respectively, which stabilizes the resonance structure 'a' more remarkably than the other resonance structures.

Time-dependent density functional (TD-DFT) calculations are performed on **1D** to clarify the observed electronic transition behaviors, which proves that intramolecular charge transfer processes exist in the excited states. The transition energies calculated are highlighted in Figure 4. The calculated absorption-peak positions are in good agreement with the experimental results. The calculations provide not only a list of the electronic transitions that contribute to each of the excited states, but also the expansion coefficients that

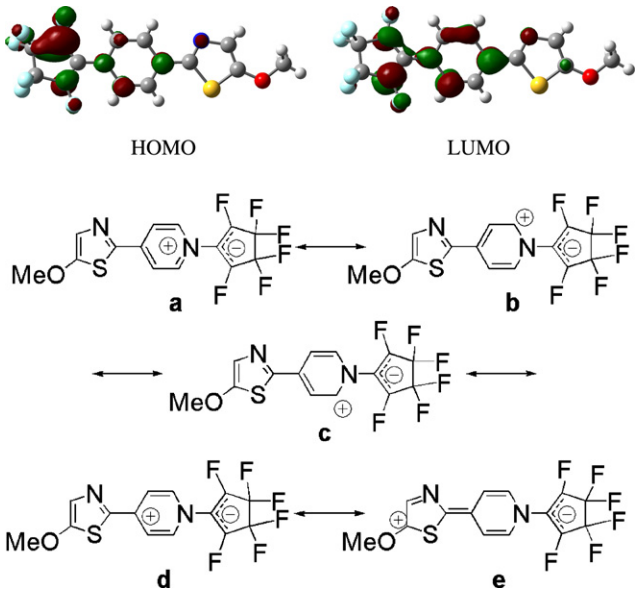


Figure 3. HOMO and LUMO of **1D** at the B3LYP/6-31G (d, p) level of theory calculated by GAUSSIAN 03 (top) and the resonance structures of **1D** (bottom).

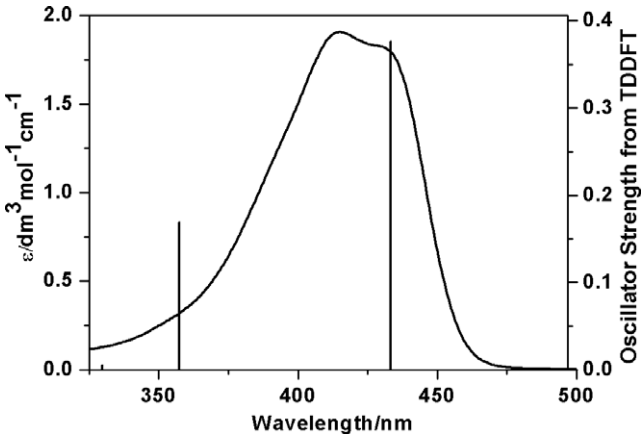


Figure 4. Electronic spectra of **1D** measured in dichloromethane at rt (left) and the calculated transition energies (from TD-DFT) are shown as bars (right).

Table 2. Excitations in **1D** that contribute to the transitions in the 300–500 nm range along with their relative contributions given by the expansion coefficients

λ_{ex} (nm)	E_{ex} (eV)	* f	Excited state	Expansion coefficient
332.97	3.7236	0.0049	HOMO→ LUMO + 4	0.67993
360.56	3.4386	0.1688	HOMO→ LUMO + 3	0.57905
436.30	2.8417	0.3761	HOMO→ LUMO + 2	0.63703

* f: Oscillator strength, which indicates the strength of absorption at that wavelength.

relate to the percent effects of the different excitations on the particular excited states (Table 2). The results demonstrate that the excitations in the range from 330 to 500 nm come from the HOMO to LUMO+4, LUMO+3 and LUMO+2 of **1D**.

In conclusion, we have obtained an unexpected compound **1D** from the reaction of perfluorocyclopentene and **1B** after treatment with *n*-BuLi. With comparative studies of the reactions between perfluorocyclopentene and **2B** or **3B,** a plausible explanation of the formation of **1D** is proposed. Investigation of its photophysical properties in various solvents illuminates that it is a solvent-sensitive highly fluorescent molecule, which implies its potential application as a probe. Further research of **1D** is in progress.

Acknowledgments

The authors thank the NSFC (20221101, 20490213 and 20423005) and PKU for the financial supports.

Supplementary data

Supplementary data associated with this Letter can be found, in the online version, at doi:10.1016/j.tetlet.2007.08.086.

References and notes

1. (a) Irie, M. *Chem. Rev.* **2000**, *100*, 1685; (b) Frigoli, M.; Mehl, G. H. *Chem. Eur. J.* **2004**, *10*, 5243; (c) Hanazawa, M.; Sumiya, R.; Horikawa, Y.; Irie, M. *J. Chem. Soc., Chem. Commun.* **1992**, 206; (d) Irie, M.; Mohri, M. *J. Org. Chem.* **1988**, *53*, 803; (e) Pu, S.; Zhang, F.; Xu, J.; Shen, L.; Xiao, Q.; Chen, B. *Mater. Lett.* **2006**, *60*, 485.
2. (a) Tsivgoulis, G. M.; Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1119; (b) Jeong, Y.-C.; Yang, S. I.; Ahn, K.-H.; Kim, E. *Chem. Commun.* **2005**, 2503; (c) Kawai, T.; Kim, M.-S.; Sasaki, T.; Irie, M. *Opt. Lett.* **2002**, *21*, 275; (d) Fukaminato, T.; Sasaki, T.; Kawai, T.; Tamai, N.; Irie, M. *J. Am. Chem. Soc.* **2004**, *126*, 14843; (e) Wang, S.; Shen, W.; Feng, Y.; Tian, H. *Chem. Commun.* **2006**, 1497.
3. (a) Kim, M.-S.; Maruyama, H.; Kawai, T.; Irie, M. *Chem. Mater.* **2003**, *15*, 4539; (b) Myles, A. J.; Branda, N. R. *Adv. Funct. Mater.* **2002**, *12*, 167.
4. (a) Uchida, K.; Saito, M.; Murakami, A.; Nakamura, S.; Irie, M. *Adv. Mater.* **2003**, *15*, 121; (b) Uchida, K.; Saito, M.; Murakami, A.; Kobayashi, T.; Nakamura, S.; Irie, M. *Chem. Eur. J.* **2005**, *11*, 534; (c) Okubo, M.; Enomoto, M.; Kojima, N. *Solid State Commun.* **2005**, *134*, 777.
5. (a) Stellacci, F.; Bertarelli, C.; Toscano, F.; Gallazzi, M. C.; Zotti, G.; Zerbi, G. *Adv. Mater.* **1999**, *11*, 292; (b) Gorodetsky, B.; Samachetty, H. D.; Donkers, R. L.; Workentin, M. S.; Branda, N. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 2812; (c) Browne, W. R.; de Jong, J. J. D.; Kudernac, T.; Walko, M.; Lucas, L. N.; Uchida, K.; van Esch, J. H.; Feringa, B. L. *Chem. Eur. J* **2005**, *11*, 6414; (d) Baron, R.; Onopriyenko, A.; Katz, E.; Lioubashevski, O.; Willner, I.; Wang, S.; Tian, H. *Chem. Commun.* **2006**, 2147.
6. (a) Endtner, J. M.; Effenberger, F.; Hartschuh, A.; Port, H. *J. Am. Chem. Soc.* **2000**, *122*, 3037; (b) Raymo, F. M.; Tomasulo, M. *Chem. Soc. Rev.* **2005**, *34*, 327.
7. (a) Fernández-Acebes, A.; Lehn, J.-M. *Chem. Eur. J.* **1999**, *5*, 3285; (b) Odo, Y.; Matsuda, K.; Irie, M. *Chem. Eur. J.* **2006**, *12*, 4283; (c) Takami, S.; Kawai, T.; Irie, M. *Eur. J. Org. Chem.* **2002**, 3796; (d) Yokoyama, Y.; Shiraishi, H.; Tani, Y.; Yokoyama, Y.; Yamaguchi, Y. *J. Am. Chem. Soc.* **2003**, *125*, 7194; (e) Yamaguchi, T.; Irie, M. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1100; (f) Yamaguchi, T.; Fujita, Y.; Irie, M. *Chem. Commun.* **2004**, 1010; (g) Osuka, A.; Fujikane, D.; Shinmori, H.; Kobatake, S.; Irie, M. *J. Org. Chem.* **2001**, *66*, 3913; (h) Peters, A.; Vitols, C.; McDonald, R.; Branda, N. R. *Org. Lett.* **2003**, *5*, 1183.
8. (a) Zheng, M. H.; Jin, J. Y.; Sun, W.; Yan, C. H. *New J. Chem.* **2006**, *30*, 1192; (b) Takami, S.; Irie, M. *Tetrahedron* **2004**, *60*, 6155.
9. Compound **1C** (10.3%). IR (KBr, cm^{-1}): 1619, 1508, 1386, 1333, 1297, 1245, 1187, 1152, 1085, 1003, 979, 908, 852, 733. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.70 (d, $J = 4.5$ Hz, 2H), 7.70 (d, $J = 4.5$ Hz, 2H), 4.17 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 166.2, 151.5, 150.6, 139.8, 121.4, 119.4, 64.9. ^{19}F NMR ($CDCl_3$, 470 MHz): δ −36.87 (2F), −46.43 (2F), −51.82 (1F), −58.59 (2F). HRMS Calcd for $C_{14}H_7N_2OSF_7$ (*m*/*z*): 384.0167; found: 384.0173. Anal. Calcd for $C_{14}H_7N_2OSF_7$: C, 43.76; H, 1.84; N, 7.29. Found: C, 44.09; H, 1.91; N, 7.16.
10. Compound **1D** (Yield: 12.6%). ^1H NMR (DMSO-d_6, 400 MHz): δ 9.28 (d, $J = 7.3$ Hz 2H), 8.43 (d, $J = 7.3$ Hz 2H), 7.78 (s, 1H), 4.12 (s, 3H). Anal. Calcd for $C_{14}H_8F_6N_2OS$: C, 45.91; H, 2.20; N, 7.65. Found: C, 45.91; H, 2.63; N, 7.54. The detailed parameters for crystal structure are summarized in Table S1.
11. Compound **2C** (Yield: 33.5%). Mp: 119–120 °C. IR (KBr, cm^{-1}): 1695, 1585, 1525, 1510, 1436, 1392, 1345, 1332, 1296, 1282, 1193, 1144, 1117, 994, 977, 949, 786. ^1H NMR ($CDCl_3$, 200 MHz): δ 8.55–8.57 (m, 1H), 8.11–8.15 (m, 1H), 7.76–7.84 (m, 1H), 7.29–7.35 (m, 1H), 4.15 (s, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 167.6, 155.8, 150.7, 149.2, 137.1, 124.6, 120.9, 119.0, 116.4, 110.9, 64.4. ^{19}F NMR ($CDCl_3$, 314 MHz): δ −36.90 (2F), −46.32 (2F), −53.06 (1F), −58.56 (2F). HRMS Calcd for $C_{14}H_7N_2OSF_7$ (*m*/*z*): 384.0167; found: 384.0170. Anal. Calcd for $C_{14}H_7N_2OSF_7$: C, 43.76; H, 1.84; N, 7.29. Found: C, 43.68; H, 1.70; N, 7.17.
12. Compound **3C** (Yield: 55.6%). Mp: 90–92 °C. IR (KBr, cm^{-1}): 1679, 1526, 1510, 1404, 1348, 1330, 1284, 1194, 1139, 1112, 1075, 991, 978, 941, 810, 750. ^1H NMR ($CDCl_3$, 300 MHz): δ 9.01–9.02 (m, 1H), 8.64–8.65 (m, 1H), 8.16–8.20 (m, 1H), 7.37–7.41 (m, 1H), 4.15 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 165.5, 155.7, 151.3, 150.9, 146.9, 132.9, 129.2, 123.8, 115.8, 110.8, 64.8. ^{19}F NMR ($CDCl_3$, 470 MHz): δ −36.87 (2F), −46.43 (2F), −52.22 (1F), −58.56 (2F). HRMS Calcd for $C_{14}H_7N_2OSF_7$ (*m*/*z*):

384.0167; found: 384.0168. Anal. Calcd for $C_{14}H_7N_2OSF_7$: C, 43.76; H, 1.84; N, 7.29. Found: C, 43.80; H, 1.84; N, 7.26.

13. (a) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319; (b) Reichardt, C.; Che, D.; Heckenkemper, G.; Schäfer, G. *Eur. J. Org. Chem.* **2001**, 2343.
14. (a) Lu, Y.; Yang, Y.; Sellinger, A.; Lu, M.; Huang, J.; Fan, H.; Haddad, R.; Lopez, G.; Burns, A. R.; Sasaki, D. Y.; Shelnutt, J.; Brinker, C. J. *Nature* **2001**, *410*, 913; (b) Zhang, G.; Yang, G.; Wang, S.; Chen, Q.; Ma, J. S. *Chem. Eur. J.* **2007**, *13*, 3630; (c) Wu, Z.; Zhang, Y.; Ma, J. S.; Yang, G. *Inorg. Chem.* **2006**, *45*, 3140.