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Synthesis and photoluminescence properties of BF_2 complexes with 1,3-diketone ligands

Katsuhiko Ono,[a,*] Kyohei Yoshikawa,[a] Yujiro Tsuji,[a] Hiroyuki Yamaguchi,[a] Rie Uozumi,[a] Masaaki Tomura,[b] Keijiro Taga[a] and Katsuhiro Saito[a]

[a] *Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso, Showa-ku, Nagoya 466-8555, Japan*
[b] *Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan*

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Abstract—BF_2 complexes with 1,3-diketone ligands were synthesized, and their optical and electrochemical properties were studied. The colors of the complexes varied depending on the structures of the 1,3-diketone ligands. The absorption and emission maxima of the complexes with 1,3-diaryl-1,3-diketone ligands were considerably red shifted as compared to those of the complexes with 1-aryl-3-trifluoromethyl-1,3-diketone ligands, suggesting an extended π-conjugation of the 1,3-diaryl-1,3-diketone moieties. The molar absorption coefficients and quantum yields of the complexes with 1,3-diaryl-1,3-diketone ligands were larger than those of the complexes with 1-aryl-3-trifluoromethyl-1,3-diketone ligands. Cyclic voltammetry measurements revealed that the reduction potentials of the BF_2 complexes were higher than those of the free ligands. These complexes exhibited various emission colors in the solid states due to the intermolecular interactions.

1. Introduction

Currently, organic electroluminescent (EL) devices are an active area of research because of their potential applications in flat-panel displays.[1] There has been considerable interest in new light-emitting materials for the research and development of organic EL devices. Synthetic studies have been conducted on various phosphorescent materials with heavy metals such as iridium[2] and platinum[3] and on fluorescent boron complexes.[4–13] These boron complexes have attracted considerable attention as fluorescent EL emitters. The boron complexes with 1,6-bis(2-hydroxyphenyl)pyridine ligands were synthesized and their EL properties were investigated.[9] Recently, the introduction of electron-rich triphenylamine into a boron complex led to the formation of a bipolar material, which was used as a yellow light emitter to fabricate an efficient single-layer EL device.[10] Furthermore, organoboron quinolates with various functional groups were synthesized,[11] and their photoluminescence properties were investigated in comparison to those of tris-8-hydroxyquinoline aluminum (Alq_3) analogues,[1,14] which are well known as EL emitters. The organoboron quinolate moiety was integrated into polymers to produce light-emitting polymer materials.[12] The BF_2 complexes with 1,3-diketones have also attracted attention as fluorophores due to their unique optical properties.[13] With regard to this, we synthesized BF_2 complexes with various 1,3-diketone ligands and studied their optical and electrochemical properties (Fig. 1). Their emission maxima and quantum yields depended on the structures of the 1,3-diketone ligands. The electron affinities of the BF_2-chelating moieties were investigated. In this paper, we report the synthesis of boron complexes **1** and **2** and their optical and electrochemical properties.

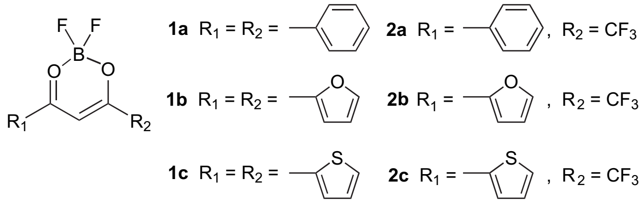

Figure 1. Structure of boron complexes **1** and **2**.

2. Results and discussion

Boron complexes **1** and **2** were obtained in yields of 50–85% by the reaction between boron trifluoride–diethyl etherate and the corresponding 1,3-diketones (Scheme 1). These complexes were purified by sublimation under reduced pressure and their structures were determined using spectral data and elemental analysis. The melting points and colors of

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Keywords: Boron complex; 1,3-Diketone; Photoluminescence; Electron affinity.

* Corresponding author. Tel./fax: +81 52 735 5407; e-mail: ono.katsuhiko@nitech.ac.jp

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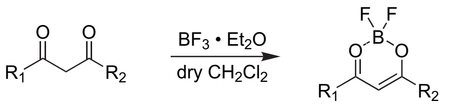
compounds **1** and **2** are summarized in Table 1. The melting point increases with an increase in the number of aryl groups because the boron complex of hexafluoroacetylacetone was obtained as an oil. The colors of these complexes varied depending on the structures of the 1,3-diketone ligands. The UV–vis spectra of **1** and **2** in dichloromethane are shown in Figure 2. The longest absorption maxima of **1** are red shifted as compared to those of **2** (Table 2) and the molar absorption coefficients of **1** are higher than those of **2**. These results suggested an effective π-conjugation between the two aryl groups via the BF_2-chelating moiety.



Scheme 1. Synthesis of boron complexes with 1,3-diketone ligands.

Table 1. Melting points and colors of boron complexes **1** and **2**

Compound	Mp/°C	Color	Compound	Mp/°C	Color
1a	195–196	Light yellow	**2a**	127–128	Colorless
1b	225–226	Orange	**2b**	90–91	Pale yellow
1c	267–269	Orange	**2c**	150–151	Light yellow

These boron complexes exhibited photoluminescence (PL) in solution and in the solid states. These PL data are listed in Table 2. The emission maxima of **1** in dichloromethane are red shifted as compared to those of **2**, suggesting an extended π-conjugation of the ligands of **1**. The quantum yields of **1** and **2** in dichloromethane were measured relative to 9,10-diphenylanthracene (Φ_{PL}=0.82).[15] The quantum yields of **1** are higher than those of **2** and these quantum yields are not greatly affected by the kind of aryl groups. In addition, the quantum yields of **1** in toluene are higher than those in dichloromethane,[13] and these values were affected by the kind of aryl groups (Table 2). Figure 3a shows the photograph of the PL emission of **1** and **2** in dichloromethane, indicating that the blue emission of **2a**–**c** is weaker than that of **1a**–**c**. These results are compatible with their quantum yields. The fluorescence spectra in the solid states were measured using cast films, which were prepared from the solutions of **1** and **2** in dichloromethane. The PL maxima are red shifted as compared to those in solution (Table 2). The red shifts of **1a**–**c** are larger than those of **2a**–**c**. This result is because of the intermolecular interactions in the solid states. Thus, compounds **1** and **2** exhibited various emission colors in the solid states, as shown in Figure 3b.

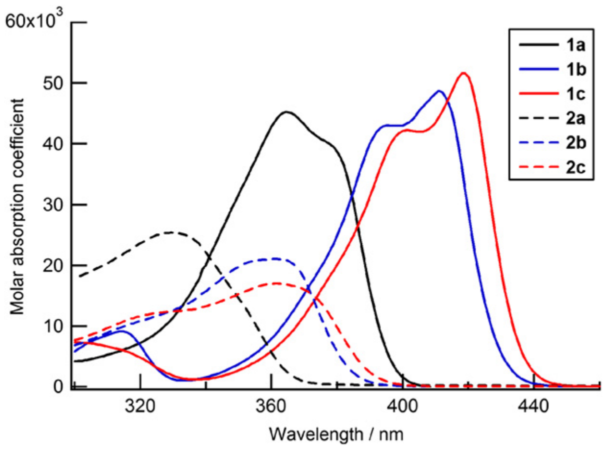


Figure 2. UV–vis spectra of boron complexes **1** and **2**.

Table 2. Absorption and emission maxima and quantum yields of complexes **1** and **2**

Compound	λ_{abs}[a]/nm (log ε)	λ_{em}[a]/nm	$\lambda_{em,film}$/nm	$\Phi_{PL(CH_2Cl_2)}$[b]	$\Phi_{PL(toluene)}$[c]
1a	376 sh (4.61)	417	531	0.22	0.70
1b	411 (4.69)	454	562	0.27	0.42
1c	419 (4.71)	459	572	0.32	0.52
2a	329 (4.40)	397	454	0.01	<0.01
2b	361 (4.32)	410	483	0.01	<0.01
2c	361 (4.23)	417	505	0.01	<0.01

[a] In CH_2Cl_2.

[b] Measured relative to 9,10-diphenylanthracene (Φ_{PL}=0.82), λ_{ex}=350 nm.

[c] Measured relative to 9,10-diphenylanthracene (Φ_{PL}=0.82), λ_{ex}=375 nm.

In order to investigate the redox properties of boron complexes **1** and **2**, cyclic voltammetry (CV) in acetonitrile was performed. The voltammograms displayed reversible ($E_{1/2}$) and irreversible (E_p) reduction waves for **1** and **2**, respectively. No oxidation waves were observed up to +1.9 V versus Fc/Fc^+. The reduction potentials are listed in Table 3. These electron affinities increased on BF_2 chelation as compared to those of the 1,3-diketone ligands (e.g., 1,3-diphenyl-1,3-propanedione: E_p^{red}=−1.96 V, 4,4,4-trifluoro-1-phenyl-1,3-butanedione: E_p=−1.58 V). The electron affinities of **2** are stronger than those of **1** due to the electron-withdrawing trifluoromethyl groups of complexes **2**. In addition, the 1,3-diaryl-1,3-diketone ligands increased the stability of the anion radical states of complexes **1**. The electron-accepting units were determined to be the BF_2-chelating moieties because their electron affinities were not affected by the kind of aryl groups.

The B3LYP/6-31G(d) calculations[16] of complexes **1c** and **2c** were performed in order to estimate the influence of the 1,3-diketone ligands. The energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were higher in compound **1c** than in **2c** (HOMO/eV: **1c**, −6.47; **2c**, −7.27, LUMO/eV: **1c**, −2.80; **2c**, −3.22). The TD calculations indicated that the HOMO–LUMO gap of **1c** is smaller than that of **2c** (gap/eV: **1c**, 3.41; **2c**, 3.86). These results are consistent with those of the respective electron affinities and absorption edges. The HOMOs and LUMOs are shown in Figure 4. In the HOMO of **1c**, the atomic orbital coefficients delocalize on the whole of the 1,3-di(2-thienyl)-1,3-diketone ligand. The HOMO of **2c** has large coefficients on the 3-(2-thienyl)-3-buten-2-one moiety. The LUMOs of **1c** and **2c** have large coefficients on the BF_2-chelating moieties.

The molecular structure of **1c** was investigated by X-ray crystallographic analysis. A single crystal of **1c** was grown from chloroform. The molecule is disordered in the region of BF_2-chelating moiety and thienyl groups. Therefore, the structure was dissolved as a mixing model of stereoisomers.[17] The molecular structure is shown in Figure 5a. The B–O bonds in the BF_2-chelating moiety are equivalent and these bond lengths are 1.481 Å and 1.482 Å. The

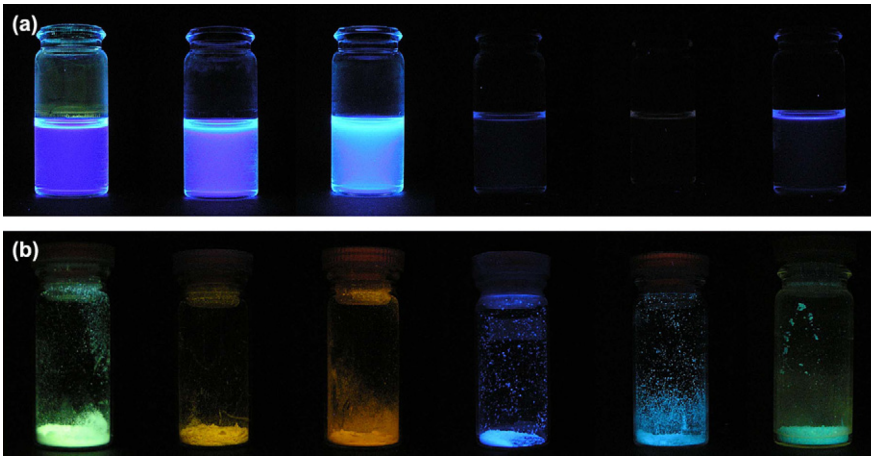


Figure 3. PL emission of **1** and **2** (a) in CH_2Cl_2 (1.0×10^{-4} M) and (b) in the solid states.

Table 3. Reduction potentials of boron complexes **1** and **2**[a]

Compound	$E_{1/2}^{red}$/V	Compound	E_p^{red}/V
1a	−1.26	**2a**	−0.96
1b	−1.24	**2b**	−0.96
1c	−1.24	**2c**	−0.94

[a] 0.1 M n-Bu_4NClO_4 in MeCN, in Pt electrode, scan rate 100 mV s^{-1}, V versus Fc/Fc^+.

1,3-diketone skeleton is almost planar. The molecules are stacked to form a columnar structure (Fig. 5b). In the column, two types of overlap mode were observed and their face-to-face distances are 3.42 Å and 3.48 Å, as shown in Figure 5c and d, respectively. These values are similar to the sum of the van der Waals radii of carbon atoms (3.40 Å). The molecules form a dimer by the overlap mode shown in Figure 5c with an intermolecular F···H–C(2) distance of 2.82 Å. Although the distance is slightly longer than the sum of their van der Waals radii (2.67 Å), the BF_2-chelating moiety plays a crucial role as the building block of the molecular assembly. The overlap mode in Figure 5d reveals the interactions between the BF_2-chelating moieties and the thienyl groups. Because the BF_2-chelating moiety is electron deficient and the thienyl groups are electron rich, the face-to-face stacking is attributed to an intermolecular charge-transfer (CT) interaction. These intermolecular interactions cause the red shift of the PL emission in the solid states more than in solution.

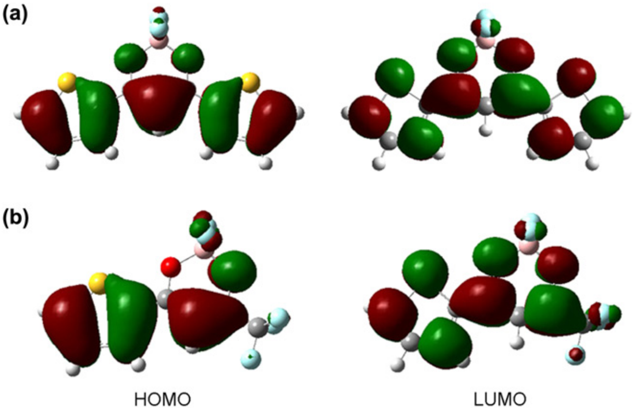


Figure 4. HOMOs and LUMOs of (a) **1c** and (b) **2c**.

3. Conclusions

In summary, we synthesized BF_2 complexes with 1,3-diketone ligands and investigated their optical and electrochemical properties as new light-emitting materials. The colors of their complexes varied depending on the structures of the 1,3-diketone moieties. The absorption and emission maxima of **1** were considerably red shifted as compared to those of **2**, suggesting an extended π-conjugation of the 1,3-diketone moieties. The molar absorption coefficients and quantum yields of **1** were larger than those of **2**. In the CV study of these boron complexes, the BF_2-chelating moieties behaved as electron-accepting units. The introduction of a trifluoromethyl group into the BF_2-chelating moiety increased the electron affinity. The anion radical states of these complexes were stabilized by 1,3-diaryl-1,3-diketone ligands. These complexes exhibited various emission colors in the solid states due to their intermolecular interactions. Because these are candidates for use as dopants in light-emitting layers in a study of EL devices, further investigation of their potential applications is in progress.

4. Experimental

4.1. General

Melting points were measured with a Yanaco micro melting point apparatus and are uncorrected. IR, UV–vis, and PL spectra were obtained with Jasco FT/IR-5300, Hitachi U-3500, and Otsuka Electronics PTI-5100S spectrometers, respectively. Mass spectra (EI) were determined with a Hitachi M-2000S mass spectrometer operating at 70 eV by a direct inlet system. Elemental analyses were performed with a Perkin–Elmer 2400II analyzer. ^1H and ^{13}C NMR spectra were recorded with Varian Gemini (300 MHz) and Bruker Avance600 (150 MHz) spectrometers, respectively. Tetramethylsilane was used for these spectra as an internal standard.

4.2. Synthesis of boron complexes (1–2)

Boron trifluoride–diethyl etherate (0.38 mL, 2.94 mmol) was added to a solution of 1,3-diphenyl-1,3-propanedione

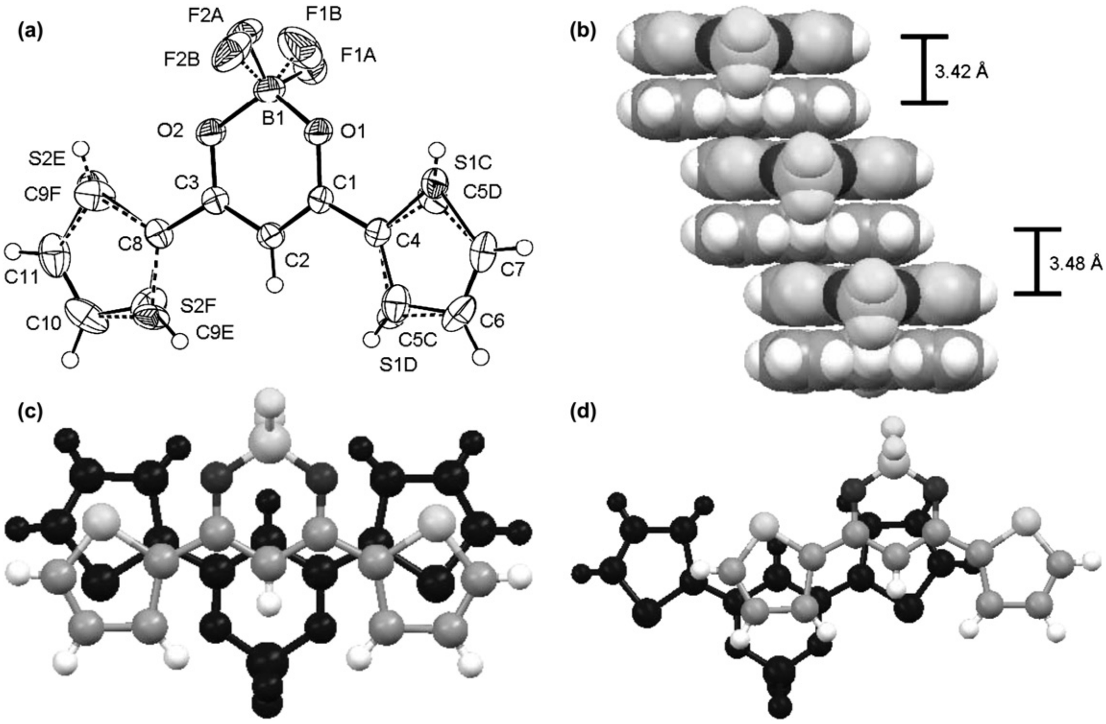


Figure 5. Crystal structure of **1c**: (a) molecular structure (ORTEP), (b) stacking, (c) overlap mode, (d) overlap mode.

(0.54 g, 2.42 mmol) in dry dichloromethane (10 mL) under nitrogen. The reaction mixture was stirred for 1.5 h. After removal of the solvent, the residue was filtered and washed with hexane. The solid was purified by sublimation at 200 °C under 10^{-3} Torr to provide boron complex **1a**[13] as light yellow needles with a yield of 0.33 g (50% yield). IR (KBr): 1543, 1489, 1375, 1047 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.20 (s, 1H), 7.54 (t, J=7.5 Hz, 4H), 7.68 (t, J=7.5 Hz, 2H), 8.13 (d, J=7.5 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 93.4, 128.9, 129.2, 131.9, 135.3, 183.2. Mass: m/z (%) 272 (96) [M^+], 271 (100), 253 (22), 195 (32), 105 (76). UV–vis (CH_2Cl_2): λ_{max} (log ε) 376 sh (4.61), 365 (4.66) nm. Anal. Calcd for $C_{15}H_{11}BF_2O_2$: C, 66.22; H, 4.08. Found: C, 66.32; H, 4.11.

Similar reaction conditions were applied to the synthesis of boron complexes **1b–c** and **2a–c**.

4.2.1. Compound 1b. Yield 75%. IR (KBr): 1586, 1518, 1362, 1022 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.73 (dd, J=3.7, 1.7 Hz, 2H), 6.98 (s, 1H), 7.59 (d, J=3.7 Hz, 2H), 7.79 (d, J=1.7 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 91.8, 114.2, 121.5, 148.4, 149.6, 171.1. Mass: m/z (%) 252 (100) [M^+], 233 (28), 187 (32). UV–vis (CH_2Cl_2): λ_{max} (log ε) 411 (4.69), 395 (4.63), 313 (3.98) nm. Anal. Calcd for $C_{11}H_7BF_2O_4$: C, 52.43; H, 2.80. Found: C, 52.30; H, 2.73.

4.2.2. Compound 1c. Yield 64%. IR (KBr): 1549, 1319, 1049 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.78 (s, 1H), 7.27 (dd, J=4.9, 3.9 Hz, 2H), 7.86 (dd, J=4.9, 1.1 Hz, 2H), 8.06 (dd, J=3.9, 1.1 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 92.6, 129.4, 134.5, 136.8, 137.1, 175.6. Mass: m/z (%) 284 (100) [M^+], 111 (67). UV–vis (CH_2Cl_2): λ_{max} (log ε) 419 (4.71), 401 (4.63) nm. Anal. Calcd for $C_{11}H_7BF_2O_2S_2$: C, 46.50; H, 2.48. Found: C, 46.23; H, 2.44.

4.2.3. Compound 2a. Yield 79%. IR (KBr): 1611, 1352, 1215, 1055, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.04 (s, 1H), 7.65 (t, J=7.8 Hz, 2H), 7.87 (t, J=7.8 Hz, 1H), 8.21 (d, J=7.8 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 94.4, 117.4 (q, J=277.4 Hz), 129.9, 130.3, 130.6, 138.5, 170.8 (q, J=38.9 Hz), 190.4. Mass: m/z (%) 264 (64) [M^+], 245 (18), 195 (58), 105 (100). UV–vis (CH_2Cl_2): λ_{max} (log ε) 329 (4.40) nm. Anal. Calcd for $C_{10}H_6BF_5O_2$: C, 45.50; H, 2.29. Found: C, 45.79; H, 2.14.

4.2.4. Compound 2b. Yield 85%. IR (KBr): 1618, 1472, 1343, 1273, 1204, 1051, 1022, 961, 677 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.90–6.91 (m, 2H), 7.92 (dd, J=3.8, 0.6 Hz, 1H), 8.01 (d, J=1.6, 0.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 94.1, 116.4, 117.6 (q, J=276.7 Hz), 128.0, 147.7, 154.4, 169.2 (q, J=37.4 Hz), 176.2. Mass: m/z (%) 254 (100) [M^+], 235 (94), 185 (100). UV–vis (CH_2Cl_2): λ_{max} (log ε) 361 (4.32) nm. Anal. Calcd for $C_8H_4BF_5O_3$: C, 37.84; H, 1.59. Found: C, 37.96; H, 1.36.

4.2.5. Compound 2c. Yield 67%. IR (KBr): 1615, 1408, 1364, 1273, 1206, 1082, 1049 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.80 (s, 1H), 7.41 (dd, J=4.9, 4.1 Hz, 1H), 8.22 (dd, J=4.9, 1.1 Hz, 1H), 8.26 (dd, J=4.1, 1.1 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 94.4, 117.5 (q, J=276.8 Hz), 130.9, 135.9, 139.5, 143.5, 168.8 (q, J=38.9 Hz), 181.9. Mass: m/z (%) 270 (64) [M^+], 251 (20), 201 (67), 111 (100). UV–vis (CH_2Cl_2): λ_{max} (log ε) 361 (4.23). Anal. Calcd for $C_8H_4BF_5O_2S$: C, 35.59; H, 1.49. Found: C, 35.65; H, 1.40.

4.3. Electrochemical measurements

CV was performed with a Toho Technical Research polarization unit PS-07 potentiostat/galvanostat. The CV studies of compounds **1** and **2** were carried out in acetonitrile with 0.1 M *n*-Bu_4NClO_4 at a scanning rate of 100 mV s^{-1} using Pt and Ag/Ag^+ electrodes. The values are expressed in potentials versus Fc/Fc^+.

4.4. X-ray crystallographic analysis of 1c

A single crystal of **1c** was obtained by recrystallization from chloroform. Crystal data for **1c**: 0.25×0.25×0.15 mm, $C_{11}H_7BF_2O_2S_2$, M=284.10, orange prism, triclinic, space group $P\bar{1}$, a=7.786(4), b=8.664(4), c=9.388(4) Å, α=91.780(10)°, β=101.128(9)°, γ=110.790(8)°, V=577.5 (5) $Å^3$, Z=2, D_c=1.634 g cm^{-3}, μ=0.474 mm^{-1}, F(000)=288. Reflection data were collected with a Rigaku MSC Mercury CCD diffractometer using graphite-monochromated Mo Kα radiation (λ=0.71070 Å) at 173 K. No absorption correction was applied. The structure was solved as a disordered model using the direct method (SHELXS-97).[18] All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares (SHELXL-97)[19] and all hydrogen atoms were placed in geometrically calculated positions and refined by using a rigid model. The final values of R_1=0.0550, GOF=1.629, and max./min. residual electron density 0.475/−0.230 e $Å^{-3}$ were obtained for 2458 unique reflections ($I>2\sigma(I)$). CCDC-648258 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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References and notes

1. (a) Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913; (b) Adachi, C.; Tokito, S.; Tsutsui, T.; Saito, S. *Jpn. J. Appl. Phys.* **1988**, *27*, L713.
2. For examples, see: (a) Baldo, M. A.; Lamansky, S.; Burrows, P. E.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* **1999**, *75*, 4; (b) Adachi, C.; Baldo, M. A.; Forrest, S. R.; Thompson, M. E. *Appl. Phys. Lett.* **2000**, *77*, 904; (c) Ikai, M.; Tokito, S.; Sakamoto, Y.; Suzuki, T.; Taga, Y. *Appl. Phys. Lett.* **2001**, *79*, 156; (d) Tsuboyama, A.; Iwawaki, H.; Furugori, M.; Mukaide, T.; Kamatani, J.; Igawa, S.; Moriyama, T.; Miura, S.; Takiguchi, T.; Okada, S.; Hoshino, M.; Ueno, K. *J. Am. Chem. Soc.* **2003**, *125*, 12971; (e) Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Lee, H.-E.; Adachi, C.; Burrows, P. E.; Forrest, S. R.; Thompson, M. E. *J. Am. Chem. Soc.* **2001**, *123*, 4304; (f) Ono, K.; Joho, M.; Saito, K.; Tomura, M.; Matsushita, Y.; Naka, S.; Okada, H.; Onnagawa, H. *Eur. J. Inorg. Chem.* **2006**, 3676.
3. For examples, see: (a) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature* **1998**, *395*, 151; (b) O'Brien, D. F.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* **1999**, *74*, 442; (c) Adachi, C.; Baldo, M. A.; Forrest, S. R.; Lamansky, S.; Thompson, M. E.; Kwong, R. C. *Appl. Phys. Lett.* **2001**, *78*, 1622; (d) Kavitha, J.; Chang, S.-Y.; Chi, Y.; Yu, J.-K.; Hu, Y.-H.; Chou, P.-T.; Peng, S.-M.; Lee, G.-H.; Tao, Y.-T.; Chien, C.-H.; Carty, A. J. *Adv. Funct. Mater.* **2005**, *15*, 223; (e) Lu, W.; Mi, B.-X.; Chan, M. C. W.; Hui, Z.; Zhu, N.; Lee, S.-T.; Che, C.-M. *Chem. Commun.* **2002**, 206.
4. Jaska, C. A.; Emslie, D. J. H.; Bosdet, M. J. D.; Piers, W. E.; Sorensen, T. S.; Parvez, M. *J. Am. Chem. Soc.* **2006**, *128*, 10885.
5. Bosdet, M. J. D.; Jaska, C. A.; Piers, W. E.; Sorensen, T. S.; Parvez, M. *Org. Lett.* **2007**, *9*, 1395.
6. Inokuma, Y.; Yoon, Z. S.; Kim, D.; Osuka, A. *J. Am. Chem. Soc.* **2007**, *129*, 4747.
7. Wakamiya, A.; Taniguchi, T.; Yamaguchi, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 3170.
8. (a) Goze, C.; Ulrich, G.; Mallon, L. J.; Allen, B. D.; Harriman, A.; Ziessel, R. *J. Am. Chem. Soc.* **2006**, *128*, 10231; (b) Goze, C.; Ulrich, G.; Ziessel, R. *J. Org. Chem.* **2007**, *72*, 313.
9. Liu, Y.; Guo, J.; Zhang, H.; Wang, Y. *Angew. Chem., Int. Ed.* **2002**, *41*, 182.
10. Zhang, H.; Huo, C.; Zhang, J.; Zhang, P.; Tian, W.; Wang, Y. *Chem. Commun.* **2006**, 281.
11. Qin, Y.; Kiburu, I.; Shah, S.; Jäkle, F. *Org. Lett.* **2006**, *8*, 5227.
12. Nagata, Y.; Chujo, Y. *Macromolecules* **2007**, *40*, 6.
13. Cogné-Laage, E.; Allemand, J.-F.; Ruel, O.; Baudin, J.-B.; Croquette, V.; Blanchard-Desce, M.; Jullien, L. *Chem.—Eur. J.* **2004**, *10*, 1445.
14. (a) Montes, V. A.; Pohl, R.; Shinar, J.; Anzenbacher, P., Jr. *Chem.—Eur. J.* **2006**, *12*, 4523; (b) Montes, V. A.; Li, G.; Pohl, R.; Shinar, J.; Anzenbacher, P., Jr. *Adv. Mater.* **2004**, *16*, 2001.
15. Morris, J. V.; Mahaney, M. A.; Huber, J. R. *J. Phys. Chem.* **1976**, *80*, 969.
16. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; 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 C.02*; Gaussian: Wallingford, CT, 2004.
17. Chaloner, P. A.; Gunatunga, S. R.; Hitchcock, P. B. *Acta Crystallogr.* **1994**, *C50*, 1941.
18. Sheldrick, G. M. *SHELXS-97: Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.
19. Sheldrick, G. M. *SHELXL-97: Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.