



Synthesis and photoluminescence properties of π -extended fluorene derivatives: the first example of a fluorescent solvatochromic nitro-group-containing dye with a high fluorescence quantum yield

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ABSTRACT

Functional π -extended fluorene derivatives, 2,7-di(*p*-substituted-phenyl)fluorenes containing different functional groups such as hydrogen, trimethylsilyl (TMS), methoxycarbonyl, cyano, and nitro groups, were synthesized. Except for the nitro group, the resulting compounds exhibited extremely high fluorescence quantum yields ($\Phi_F > 0.85$ in chloroform). The diphenylfluorene containing nitro groups have higher fluorescence quantum yield ($\Phi_F = 0.31$ in *N,N'*-dimethyl-formamide) than other nitro-group-containing fluorophores which were previously reported ($\Phi_F < 0.1$). Furthermore, this compound exhibited large Stokes' shift with green to orange emission and unique on–off behavior of the emission by solvents.

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Polyfluorene (PF) and its derivatives possess exceptional electro optical characteristics and are thus essential components of organic light-emitting diodes (OLEDs).^{1–4} PF and its derivatives have high solubility, good film-forming capability, and high luminescence quantum yields in the blue region. However, PF generally shows excimer emission (the formation of dimerized units in the excited state that emit at lower energies) in the solid state; this affects the bathochromic shift of the fluorescence wavelength and the lifetime of light-emitting devices.^{5–7} Bifluorene, in contrast, exhibits the same blue photoluminescence as that emitted by a PF chromophore, in solution as well as in the solid state, although it consists of only two fluorene moieties linked to each other.^{8–10} Therefore, in the case of bifluorene, high luminescence quantum yields can be obtained by a slight extension of π -conjugation. One method for obtaining fluorene derivatives with extended π -conjugation involves the introduction of two benzene rings into the 2,7-positions of the fluorene core. This is an extremely convenient method for obtaining π -extended fluorene derivatives. π -Extended fluorene derivatives containing different *p*-functionalized phenyl groups^{11–15} have already been synthesized according to this method. If carboxyl groups are present at the *p*-positions,¹¹ a π -extended fluorene system can be used to synthesize polyester or polyamide. However, the details of the photochemical behavior of π -extended fluorene derivatives, especially silyl and nitro

groups, remain relatively unknown. Moreover, to the best of our knowledge, there have been no reports on nitro-group-containing π -extended fluorophores exhibiting high fluorescence quantum yields. Nitro-group-containing polycyclic hydrocarbons such as fluorescein derivatives exhibit a maximum fluorescence quantum yield of 0.07.¹⁶ In general, the fluorescence quantum yield of a fluorophore containing nitro groups is extremely low because of the decrease in the radiative rate and the increase in the internal conversion rate of an excited state fluorophore.^{15–18} We observed that attaching a nitro group directly to the fluorophore skeleton resulted in a low fluorescence quantum yield. Therefore, fluorescent solvatochromism in the case of a nitro-group-containing dye has not been achieved. In order to obtain a fluorene derivative with high fluorescence quantum yield, we attempted to introduce a nitro group with a *p*-substituted phenyl group into the fluorophore core.

In this Letter, we report the synthesis of 2,7-diarylfluorenes containing different functional groups, such as methoxycarbonyl,



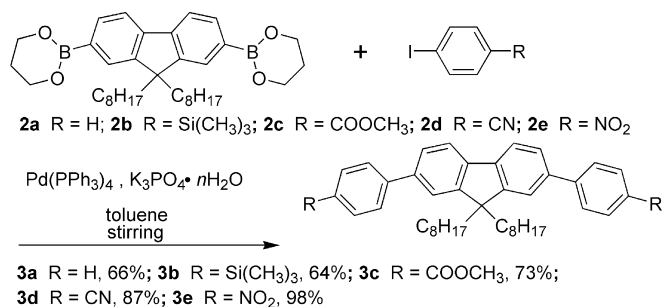
R = H, Si(CH₃)₃, COOCH₃, CN : High Fluorescence Quantum Yield

R = NO₂ : Unique Fluorescence Solvatochromism

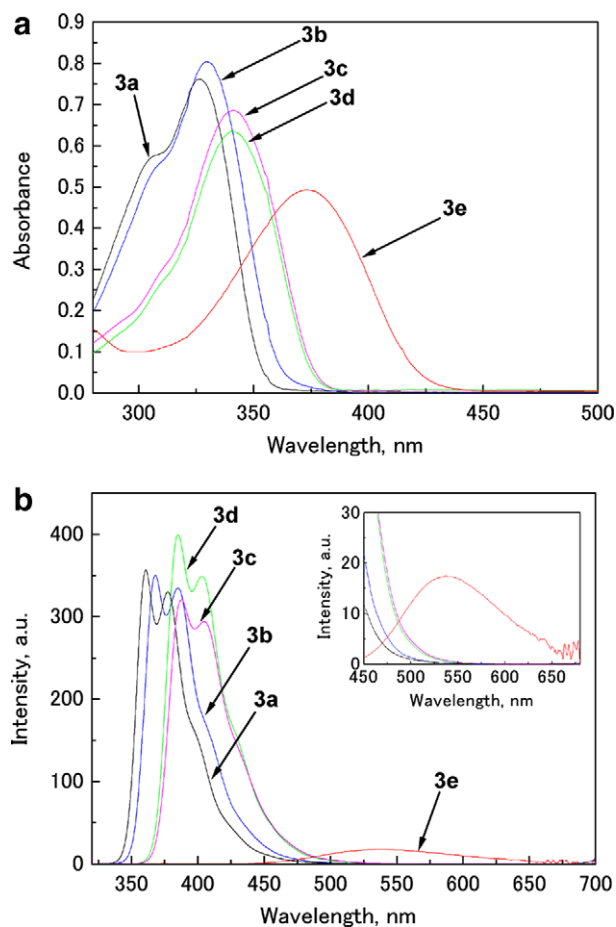
Chart 1.

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Scheme 1. Synthesis of π -extended fluorene derivatives (**3a–e**).**Table 1**
Spectroscopic parameters of fluorene derivatives at room temperature

Entry	Functional group	λ_A^a (nm)	ϵ^b (M ⁻¹ cm ⁻¹)	λ_F^c (nm)	Φ_F^d	τ_F^e (ns)
3a	H	327	76,100	361, 377	0.85	1.40
3b	TMS	330	80,400	368, 385	0.89	1.01
3c	COOCH ₃	341	68,600	388, 405	0.94	1.48
3d	CN	341	63,400	385, 403	0.95	0.95
3e	NO ₂	373	49,300	538	0.11	1.92

^a Absorption wavelengths taken at the maximum of the absorption band in chloroform.^b Absorption coefficient at the maximum of the absorption band in chloroform.^c Fluorescence wavelengths in chloroform.^d Absolute quantum yields of **3a–e** were measured in chloroform.^e Fluorescence lifetime in *N,N*-dimethyl formamide.**Figure 1.** (a) UV-vis absorption and (b) fluorescence spectra of **3a–e** (**3a–e**) = 1.0×10^{-5} M) in deaerated chloroform. Inset: detail of the longer-wavelength region.

trimethylsilyl, cyano, and nitro groups (Chart 1). Our objective was to investigate how the photoluminescence properties of a π -extended fluorene system are affected by the substituents on the fluorene core. Moreover, we report the first example of a fluorescent solvatochromic nitro-group-containing dye with high fluorescence quantum yield.

The π -extended fluorenes **3a–e** were successfully prepared by a palladium-catalyzed Suzuki–Miyaura reaction¹⁹ of fluorene bis boronic ester and iodobenzene derivatives (Scheme 1).^{20–23} The π -extended fluorenes were obtained in 64–98% yields. The structures of **3a–e** were confirmed by ¹H NMR spectra, FT-IR spectra, mass spectrometry, and elemental analysis.

The UV–vis absorption, fluorescence spectra, and absolute quantum yields (Φ_F)²⁴ of the π -extended fluorenes were obtained in deaerated chloroform solution. The fluorescence lifetimes (τ_F)²⁵ of **3a–e** were measured in deaerated *N,N*-dimethylformamide (DMF) because the highest fluorescence intensity of **3e** was obtained. The spectroscopic parameters of the fluorene derivatives **3a–e** are shown in Table 1. Figure 1 shows the UV–vis absorption and fluorescence spectra of compounds **3a–e**. As it can be observed in Figure 1a, the UV–vis absorption maxima of compounds **3a** and **3b** were almost the same. The UV–vis absorption maxima of **3c** and **3d**, which have electron-withdrawing groups, were red-shifted by ca. 10 nm relative to that of **3a** and the enormous red shift of 46 nm was observed in **3e**. The molar absorption coefficients (ϵ) at the maxima of the molar absorption bands of compounds **3a–d** were large. However, the molar absorption coefficient of **3e** was the lowest among the 2,7-diphenylfluorene derivatives. It is likely that the UV–vis absorption spectrum of **3e** was affected by spin-forbidden charge transfer. The fluorescence spectra of **3a**, excited at absorption maximum, showed two peaks at 361 and 371 nm (Fig. 1b). The fluorescence maxima of **3c** were red-shifted by ca. 20 nm relative to those of **3a**. Therefore, **3c** and **3d** fluoresced with a bright blue color in chloroform. These results suggest that the excited state energies of **3c** and **3d**, which have more polar structures than **3a**, might be lower than that of **3a** in a slightly polar solvent such as chloroform. The fluorescence quantum yield of **3a** was 0.85; therefore, a highly fluorescent fluorene chromophore can be designed by introducing two benzene rings into the fluorene core, as described in an earlier paper.¹² The fluorescence quantum yield of **3a** is higher than that of the other known π -conjugated PFs ($\Phi_F = 0.55–0.79$).^{26,27} The fluorescence quantum yield of **3b** containing TMS groups was high ($\Phi_F = 0.89$), which is corresponded to the fact that the TMS-group-containing fluorophore shows high fluorescence quantum yield.²⁸ Furthermore, the absolute fluorescence quantum yields of **3c** and **3d** were 0.94 and 0.95, respectively. Derivatives **3c**¹² and **3d**, which have electron-withdrawing groups, exhibited high fluorescence quantum yields. This implies that most of the photons absorbed by compounds **3c** and **3d** were emitted exclusively as fluorescence. The fluorescence maximum of **3e** was red-shifted by more than 100 nm relative to the fluorescence maxima of the other π -extended fluorenes, and the emission band of **3e** in the long-wavelength region was barely discernible as

Table 2
Spectroscopic parameters of **3e** in various solvents at room temperature

Solvent	λ_A (nm)	ϵ (M ⁻¹ cm ⁻¹)	λ_F (nm)	Φ_F	τ_F (ns)	Dielectric constant ^a
Cyclohexane	357	50,000	N.D. ^b	N.D. ^b	N.D. ^b	2.0
Toluene	365	48,200	N.D. ^b	N.D. ^b	N.D. ^b	2.4
Chloroform	373	49,300	538	0.11	1.18	4.8
EtOH	368	45,700	N.D. ^b	N.D. ^b	N.D. ^b	24.5
DMF	380	45,100	569	0.31	1.92	36.7
DMSO	382	42,100	589	0.28	1.82	46.7

^a Data from Ref. 10.^b N.D.: Not determined because of no emission.

compared to the emission bands of **3a–d**. The fluorescence lifetimes of these fluorene derivatives were approximately 1 ns; the short lifetime is responsible for the high fluorescence quantum yields in these molecules.^{12,28} Here, it should be noted that the fluorescence quantum yield of **3e** (0.11) is lower than the yields of the other π -extended fluorenes. However, this fluorescence quantum yield of **3e** is exceptionally higher than the yields of other general nitro-group-containing fluorophores ($\Phi_F < 0.01$).^{17,18}

In order to examine the solvent sensitivity of the unique UV–vis absorption and emission properties of nitro-group-containing π -extended fluorene, the UV–vis absorption and fluorescence spectra

were measured in several polar and non-polar media such as cyclohexane, toluene, chloroform, ethanol (EtOH), DMF, and dimethyl sulfoxide (DMSO). The photophysical properties of **3e** are listed in Table 2. Figure 2 shows the UV–vis absorption and fluorescence spectra of **3e** in various solvents. The UV–vis absorption intensities of **3e** in various solvents were almost the same. However, the UV–vis absorption maxima were distinctly red-shifted when solvents with high dielectric constants were used.²⁹ The UV–vis absorption maximum of compound **3e** in DMSO was red-shifted by 25 nm relative to that of **3e** in cyclohexane. These drastic shifts of the UV–vis absorption wavelengths might be affected due to the charge transfer molecule whose energy in ground state changes by solvents.

Fluorescence emission of **3e** was observed in chloroform, DMF, and DMSO. However, no emission was observed in cyclohexane, toluene, and EtOH. The fluorescence maximum of **3e** in DMSO was red-shifted by 51 nm relative to that of **3e** in chloroform. The emission wavelength range for this molecule range from yellow to orange region (Fig. 2b). The fluorescence quantum yield of **3e** in DMF (0.31) was the highest in three solvents, which is an extremely high value for a nitro-group-containing fluorophore. This high value is most certainly a result of the introduction of a phenyl group between the fluorescence core (fluorene skeleton) and the nitro groups. The fluorescence lifetimes of **3e** in three different solvents were correlated with its fluorescence quantum yields in each solvent. Thus, it can be inferred that the absorption and fluorescence maxima are controlled by the solvent. Further, the on–off behavior of the emission is controlled by the solvent. The on–off behavior of the emission of **3e** might be attributed to the reorganization of the fluorene and *p*-functionalized phenyl units into a highly twisted charge transfer excited state conformation (Chart 2), analogous to a twisted intramolecular charge transfer (TICT) model.^{30,31} Long-wavelength emission, which might be assigned to the emission from the charge transfer state, was observed in a polar solvent, as suggested by the TICT model. The detailed assignment of the on–off emission and the changes of fluorescence intensities or fluorescence lifetimes are now in progress.

In conclusion, π -extended fluorenes containing different functional groups were successfully synthesized by means of the Suzuki–Miyaura cross-coupling reaction. Except for the nitro-group-containing π -extended fluorene system, all other derivatives showed intense blue light emission. Fluorene derivatives containing cyano and methoxycarbonyl groups had high fluorescence quantum yields. π -Extended fluorene systems containing nitro groups exhibited unique on–off emission that was dependent on the solvent. Furthermore, the absolute fluorescence quantum yield of compound **3e** is extremely higher than that of the other well-known nitro-group-containing fluorophore. Owing to their excellent emission properties, π -conjugated donor–acceptor molecules can be used as luminescent sensor materials.

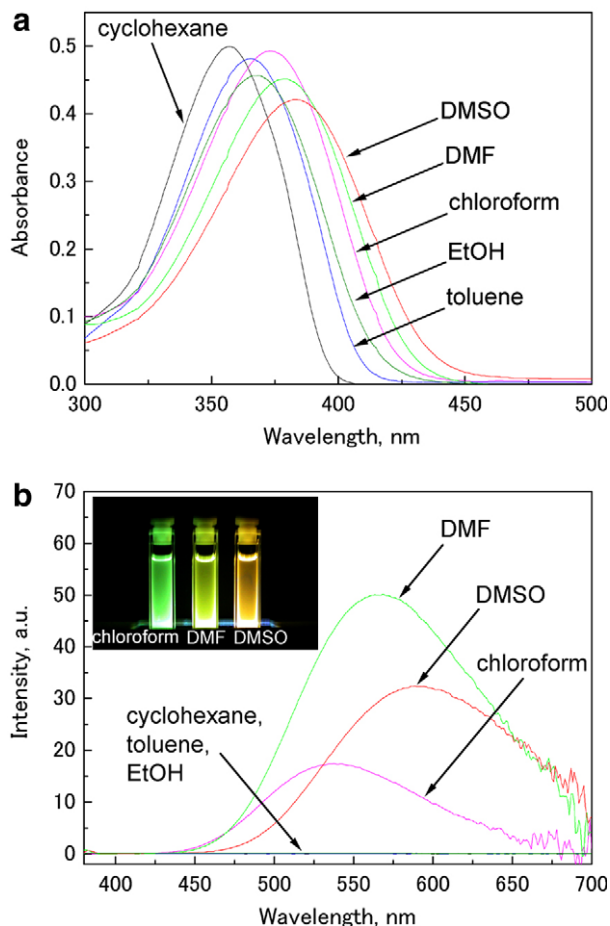


Figure 2. (a) UV–vis absorption and (b) fluorescence spectra of **3e** ($[3e] = 1.0 \times 10^{-5}$ M) in various solvents.

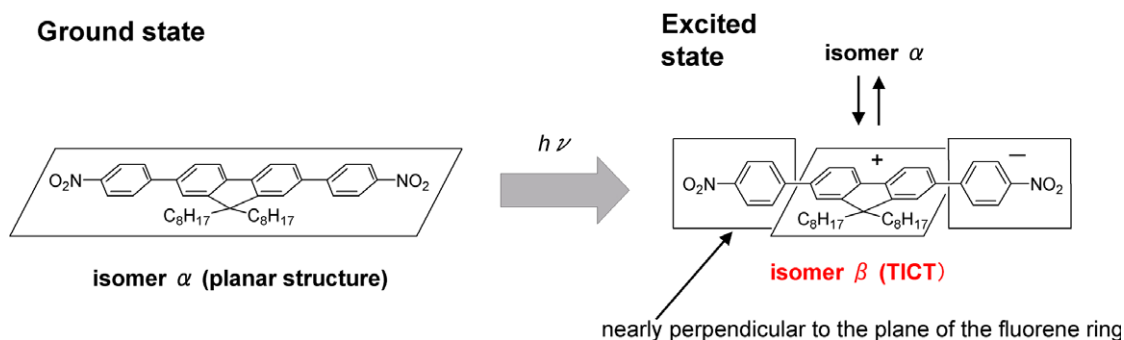


Chart 2.

References and notes

- Fukuda, M.; Sawada, K.; Yoshino, K. *Jpn. J. Appl. Phys.* **1989**, *28*, 1433–1435.
- Leclerc, M. J. *Polym. Sci., Polym. Chem. Ed.* **2001**, *39*, 2867–2873.
- Jo, J.; Chi, C.; Höger, S.; Wegner, G.; Yoon, D. Y. *Chem. Eur. J.* **2004**, *10*, 2681–2688.
- Morisaki, Y.; Chujo, Y. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 288–293.
- Pei, Q.; Yang, Y. J. *Am. Chem. Soc.* **1996**, *118*, 7416–7417.
- Grice, A. W.; Bradley, D. D. C.; Bernius, M. T.; Inbasekaran, M.; Wu, W. W.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 629–631.
- Sainova, D.; Miteva, T.; Nothofer, H. G.; Scherf, U.; Glowacki, I.; Ulanski, J.; Fujikawa, H.; Neher, D. *Appl. Phys. Lett.* **2000**, *76*, 1810–1812.
- Grisorio, R.; Dell'Aquila, A.; Romanazzi, G.; Suranna, G. P.; Mastroianni, P.; Cosma, P.; Acerno, D.; Amendola, E.; Ciccarella, G.; Nobile, C. F. *Tetrahedron* **2006**, *62*, 627–634.
- Grisorio, R.; Piliago, C.; Fini, P.; Cosma, P.; Mastroianni, P.; Gigli, G.; Suranna, G. P.; Nobile, C. F. *J. Phys. Chem. C* **2008**, *112*, 7005–7014.
- Wang, I.; Botzung-Appert, E.; Stéphan, O.; Ibanez, A.; Baldeck, P. L. *J. Opt. A: Pure Appl. Opt.* **2002**, *4*, 258–260.
- Ergen, E.; Weber, M.; Jacob, J.; Herrmann, A.; Müllen, K. *Chem. Eur. J.* **2006**, *12*, 3707.
- Belletete, M.; Morin, J. F.; Beaupre, S.; Leclerc, M.; Durocher, G. *Synth. Metall.* **2002**, *126*, 43–51.
- Wu, R.; Schumm, J. S.; Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1996**, *61*, 6906.
- Destri, S.; Pasini, M.; Botta, C.; Porzio, W.; Bertini, F.; Marchiò, L. *J. Mater. Chem.* **2002**, *12*, 924.
- Neeraj, A.; Pabitra, K. N.; Periasamy, N. *J. Chem. Sci.* **2008**, *120*, 355.
- Rtishchev, N. I.; Samoilov, D. V.; Martynova, V. P.; El'tsov, A. V. *Russ. J. Gen. Chem.* **2001**, *71*, 1467–1478.
- Samori, S.; Tojo, S.; Fujitsuka, M.; Spitler, E. L.; Haley, M. M.; Majima, T. *J. Org. Chem.* **2007**, *72*, 2785–2793.
- Beinhoff, M.; Weigel, W.; Jurczok, M.; Rettig, W.; Modrakowski, C.; Brüdgam, I.; Hartl, H.; Schlüter, A. D. *Eur. J. Org. Chem.* **2001**, *20*, 3819–3829.
- Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483.
- Typical procedure: 3a** (–H): The toluene solution of 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) **1** (0.56 g, 1.00 mmol), iodobenzene **2a** (0.45 g, 2.20 mmol), $K_3PO_4 \cdot nH_2O$ (1.92 g, 6.69 mmol), and $Pd(PPh_3)_4$ (0.10 g, 0.089 mmol) was heated under argon atmosphere for 24 h. After cooling to room temperature, the resulting mixtures were concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using toluene as an eluent: yield 66%; colorless oil.
- Compound 3b** (–Si(CH₃)₃) yield 64%; pale yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, J = 7.8 Hz, 2H), 7.68–7.56 (m, 12H), 2.04–2.00 (m, 4H), 1.19–1.05 (m, 20H), 0.77 (t, J = 7.1 Hz, 6H), 0.74–0.72 (m, 4H), 0.32 (s, 18H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 151.7, 142.1, 140.2, 140.0, 139.0, 133.8, 126.5, 126.0, 121.6, 120.0, 55.2, 40.4, 31.8, 30.0, 29.1, 23.8, 22.6, 14.1, –1.1 ppm; FT-IR (NaCl) 2926, 2854, 1598, 1465 cm^{–1}; MS (EI) calcd for C₄₇H₆₆Si₂ 686.4703, found 686.4696 (M⁺).
- Compound 3d** (–CN) yield 87%; colorless crystal; mp 106.9–107.2 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, J = 11.5 Hz, 2H), 7.78–7.76 (m, 8H), 7.60 (d, J = 11.5 Hz, 2H), 7.56 (s, 2H), 2.08–2.02 (m, 4H), 1.18–1.06 (m, 20H), 0.78 (t, J = 10.0 Hz, 6H), 0.71–0.68 (m, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 152.1, 145.9, 140.9, 138.4, 132.6, 127.7, 126.4, 121.5, 120.6, 119.0, 110.7, 55.5, 40.3, 31.7, 29.9, 29.1, 23.3, 22.6, 14.0 ppm; FT-IR (KBr) 2925, 2851, 2225, 1603, 1509, 1465 cm^{–1}; MS (FAB) calcd for C₄₃H₄₈N₂ 593.3896, found 593.3855 (M⁺); Anal. Calcd for C₄₃H₄₈N₂: C, 87.11; H, 8.16; N, 4.73. Found: C, 87.17; H, 8.41; N, 4.69.
- Compound 3e** (–NO₂) yield 98%; yellow crystal; mp 135.0–135.4 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, J = 12.9 Hz, 4H), 7.87–7.80 (m, 6H), 7.65 (d, J = 11.7 Hz, 2H), 7.60 (s, 2H), 2.10–2.04 (m, 4H), 1.20–1.07 (m, 20H), 0.78 (t, J = 9.9 Hz, 6H), 0.74–0.65 (m, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 152.2, 147.9, 147.0, 141.2, 138.1, 127.8, 126.7, 124.1, 121.7, 120.7, 55.6, 40.3, 31.7, 29.9, 29.1, 23.8, 22.5, 14.0 ppm; FT-IR (KBr) 2923, 2851, 1594, 1464, 1515, 1344 cm^{–1}; MS (FAB) calcd for C₄₁H₄₈N₂O₄ 633.3701, found: 633.3692 (M⁺); Anal. Calcd for C₄₁H₄₈N₂O₄: C, 77.82; H, 7.65; N, 4.43. Found: C, 77.73; H, 7.81; N, 4.39.
- Absolute fluorescence quantum yields were determined by the photoluminescence (PL) method using a Hamamatsu DynaSpec C 9920-02 absolute PL quantum yield measurement system.
- Time-resolved emission was measured on a Hamamatsu OB920 by time-correlated single-photon counting using a hydrogen flash lamp. Fluorescence lifetimes were determined by a single exponential curve fit.
- Chou, C.-H.; Hsu, S.-L.; Dinakaran, K.; Chiu, M.-Y.; Wei, K.-H. *Macromolecules* **2005**, *38*, 745–751.
- Burrows, H. D.; Melo, J. S.; Serpa, C.; Arnaut, L. G.; Monkman, A. P.; Hamblett, I.; Navaratnam, S. *J. Chem. Phys.* **2001**, *115*, 9601–9606.
- Maeda, H.; Maeda, T.; Mizuno, K.; Fujimoto, K.; Shimizu, H.; Inouye, M. *Chem. Eur. J.* **2006**, *12*, 824–831.
- Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. *Handbook of Photochemistry*, 3rd ed.; CRC Press, 2006.
- Grabowski, Z. R.; Rotkiewicz, K.; Rettig, W. *Chem. Rev.* **2003**, *103*, 3899–4031.
- Dias, F. B.; Pollock, S.; Hedley, G.; Pålsson, L.-O.; Monkman, A.; Perepichka, I. I.; Perepichka, I. F.; Tavasli, M.; Bryce, M. R. *J. Phys. Chem. B* **2006**, *110*, 19329–19339.