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A Phosphorescent Ir(III) Complex for Selective Fluoride Ion Sensing with a High Signal-to-Noise Ratio**

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Among the anions, fluoride is attracting particular interest because of its detrimental effects on humans exposed to it in the course of their activities. Medical treatments, such as those for dental care and osteoporosis, as well as environmental treatments, such as the fluorination of drinking water, have resulted in increased human exposure to fluoride ions. This is of concern, given that overexposure to fluoride ions causes health hazards such as bone disease and inhibition of the immune system.[1] Consequently, various sensing techniques have been developed for the purpose of detecting fluoride ions, including fluoride-selective electrodes[2] or specific receptors involving hydrogen-bonding interactions[1a,3] and, more recently, Lewis acid–base interactions.[4] Recently, receptors based on a strong and selective boron–fluoride ion interaction have been found to achieve highly efficient fluoride ion detection.[5] In particular, sterically hindered boryl groups such as dimesitylboryl and tridurylboryl moieties showed enhanced size-selectivity toward fluoride ions.[5b–f,i,k–l,p,r,6] Moreover, some of them exhibited protic media tolerance, which is very advantageous compared with other receptors.[5a,c,6d,f] In this regard, pioneering efforts to develop fluoride ion sensors using boryl receptors have been accomplished based on absorption colorimetric changes,[5b–e] fluorescence changes,[5f–n] NMR spectral shifts,[5o] and electrochemical property changes.[5p–s] However, in terms of enhancing the signal-to-noise (S/N) ratio, less consideration has been given to signal-transmitting functionalities that are electronically conjugated with boryl receptors.

Among the approaches to using boryl receptors, fluorescence detection is considered the most effective to sensing applications because of the high sensitivity, easy visualization, and fast response time for detection.[5c,f,i,k,6b,e,7] However, fluorescence is prone to contamination by background emission resulting from scattering and chromophoric impurities (autofluorescence) when the technique is applied to real samples containing complex or inhomogeneous systems. Such signal contamination reduces the achievable S/N ratio, leading to poor sensitivity. A potential solution to overcome this problem is to utilize long-lived phosphorescence signals (on the order of microseconds) that are easily extracted from raw signals through time-gated acquisition, because most of the noise signals arise from either fluorescence or scattering and thus have much shorter (< several nanoseconds) lifetimes. To date, there have been few (to the best of our knowledge, two) reports on phosphorescent fluoride ion receptors. One type of phosphorescent receptor, platinum(II) terpyridine complexes, showed modulated phosphorescent intensity through interaction with fluoride ions.[8] However, the phosphorescent photoluminescence quantum yields (PLQYs) of these systems were too small (<0.011, $CHCl_3$) to achieve practical sensitivity. In another example, Melaimi et al. achieved phosphorescent fluoride ion detection by employing a heteronuclear boron/mercury bidentate Lewis acid in the frozen state at 77 K.[6d] However, although Melaimi et al. successfully demonstrated a fairly high binding constant ($K > 10^8\ M^{-1}$) as well as two-color phosphorescence detection, one basic requirement for practical luminescence sensing, that is, high-sensitivity room-temperature phosphorescence (RTP) detection, was not achieved. Therefore, the search for new RTP receptors with high phosphorescent PLQYs remains an important challenge.

Charge-neutral and air-stable cyclometalated Ir(III) complexes have been extensively studied because of their extremely high phosphorescent PLQY, even at room temperature.[9] In particular, we[10] and other groups[11] have developed Ir(III) complexes with very high phosphorescent PLQYs and devised methods to easily tune the phosphorescence colors. It has been observed that even the air-equilibrated solution state of these complexes showed acceptable RTP intensity. This favorable RTP property is attributed to the strong spin–orbit coupling provided by the core Ir atom, which facilitates an efficient and fast radiative decay from the triplet excited state of the complex. Although work on these Ir(III) complexes has been primarily focused on developing electrophosphorescent dopant materials for use in organic light-emitting devices (OLEDs), we hypothesized that the intense and stimuli-responsive phosphorescence emission of these complexes make them well suited to use as functional emitters. Hence, we conjectured that the incorporation of a sterically hindered boryl group into the ligand structure of an Ir(III) complex might enable the development of a fluoride ion-sensitive phosphorescence sensor capable of room temperature operation. In this Communication, we discuss the

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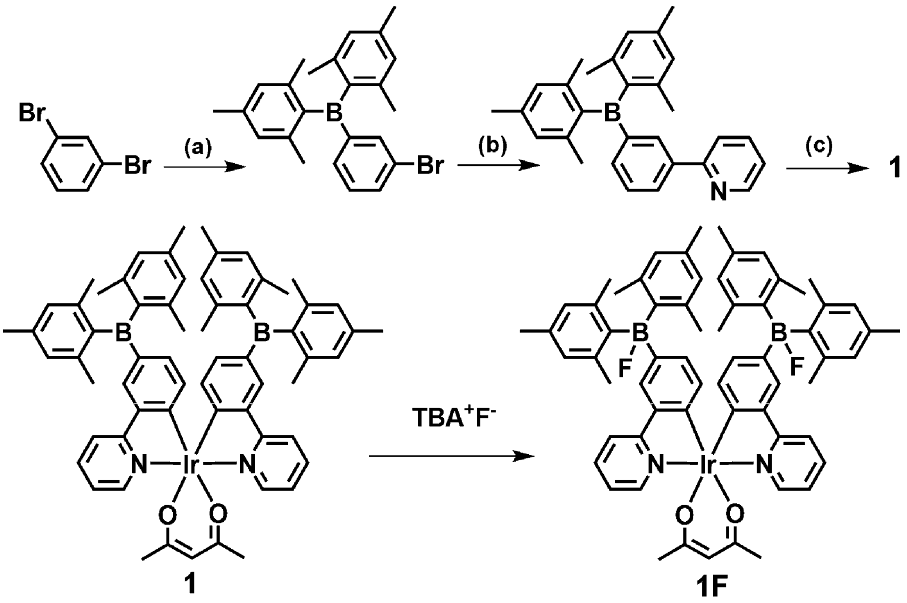

Scheme 1. Synthesis of the Ir(III) complex. a) (i) *n*-Butyllithium, tetrahydrofuran (THF), −78 °C; (ii) dimesitylboron fluoride, THF, room temperature. b) 2-(Tributylstannyl)pyridine, Pd(PPh$_3$)$_4$, toluene, reflux. c) (i) IrCl$_3\cdot x$H$_2$O, 2-ethoxyethanol:H$_2$O, 140 °C, Ar saturation; (ii) 2,4-pentanedione, Na$_2$CO$_3$, 2-ethoxyethanol, 140 °C, Ar saturation.

outstanding fluoride ion-sensing behavior of a novel and strongly phosphorescent Ir(III) complex bearing boryl groups. By introducing dimesitylboryl groups into a phenylpyridine ligand, we accomplished highly fluoride ion-selective sensing in organic solution based on the phosphorescence color change of the resulting Ir(III) complex. In addition, we have demonstrated a method to significantly enhance the S/N ratio through time-gated signal purification by exploiting the long-lived phosphorescence emission of the Ir(III) complex, which could be separated from the noise emission resulting from an intended fluorescent impurity (fluorescein isothiocyanate, FITC). Most importantly, we were successful in detecting aqueous fluoride ions using polymer films (poly(methylmethacrylate), PMMA) doped with the Ir(III) complex.

As mentioned by Yamaguchi and Gabbaï, the high steric demand imposed on the dimesitylboryl group enables size-selective anion–boron binding interactions.[5a,b,6d] These two dimesitylboryl groups were introduced into the chelating ligand according to Scheme 1. Lithiation of 1,3-dibromobenzene followed by treatment with dimesitylboron fluoride produced the borylated phenyl bromide, which was subsequently transformed to the chelating ligand via the Pd- catalyzed Stille reaction. Then, a Nonoyama reaction of the ligands and IrCl$_3\cdot x$H$_2$O gave the corresponding μ-chloride-bridged Ir(III) dimer.[12] Finally, we obtained the boryl group-containing heteroleptic Ir(III) complex (**1**) by substituting a 2,4-pentanedione for the chloride ion with the assistance of sodium carbonate. Complex **1** was fully characterized using spectroscopic data, which were in full agreement with the structure presented in Scheme 1. Complex **1** exhibited high solubility in common organic solvents such as toluene, dichloromethane, dioxane, and acetonitrile, and also showed good physical compatibility with PMMA.

As expected, **1** displayed distinct optical changes on interaction with fluoride ions in UV–vis absorption titration experiments (0.2–5 equiv. of tetrabutylammonium fluoride, TBAF) (see also Table 1), as shown in Figure 1a. For the fluoride ion-free compound **1**, the UV–vis spectrum showed three distinct peaks (wavelength/nm (logarithm of molar absorption coefficient) = 267 (4.30), 309 (4.22), 374 (4.04)) related to the singlet ligand-centered transitions along with a rather broad band (454 (3.23)) arising from either the metal-to-ligand charge-transfer (MLCT) or triplet ligand-centered transition.[10f] Upon addition of TBAF solution (tetrahydrofuran, THF) to **1**, however, all these peak absorbances gradually decreased concomitant with the emergence and growth of red-shifted absorptions at 276 (4.36) nm and 486 (3.11) nm. In particular, the lowest-energy absorption band (486 nm) responsible for the red-shifted phosphorescence emission (Fig. 1b) appears with an appreciable absorption coefficient, which clearly suggests that a low-bandgap Ir(III) complex (**1F**) is formed by fluoride ion coordination. A probable mechanism of this bathochromic shift is a significant stabilization of frontier orbitals (preferentially the lowest unoccupied molecular orbital (LUMO), see SI1 in the Supporting Information for density functional theory (DFT) calculation results) of **1F** by complexation of electronegative fluoride ions.

Compound **1** was found to bind 2 eq. of fluoride ion (Job plot based on the absorption, SI2). Because the two dimesitylboryl

Table 1. Photophysical data for the Ir(III) complex.

	λ_{abs} [nm] (log ε)[a]	λ_{PL}[nm] [a]	PLQY [b]			
			degassed solution	air-equilibrated solution [c]	film [d]	$\tau_{phosphorescence}$[μs] [a]
1	267 (4.30), 309 (4.22), 374 (4.04), 454 (3.23)	512	0.57	0.09	0.17	0.56
1F	276 (4.36), 339 (3.76), 385 (3.48), 486 (3.11)	567	0.38	0.06	0.16	1.2

[a] 1.0 × 10^{-5} M, MeCN. [b] See Experimental Section for details. [c] Air equilibration for at least 6 h. [d] Absolute PLQY; spin-coated PMMA films (quartz substrate) doped with the Ir(III) complex (10 wt %).

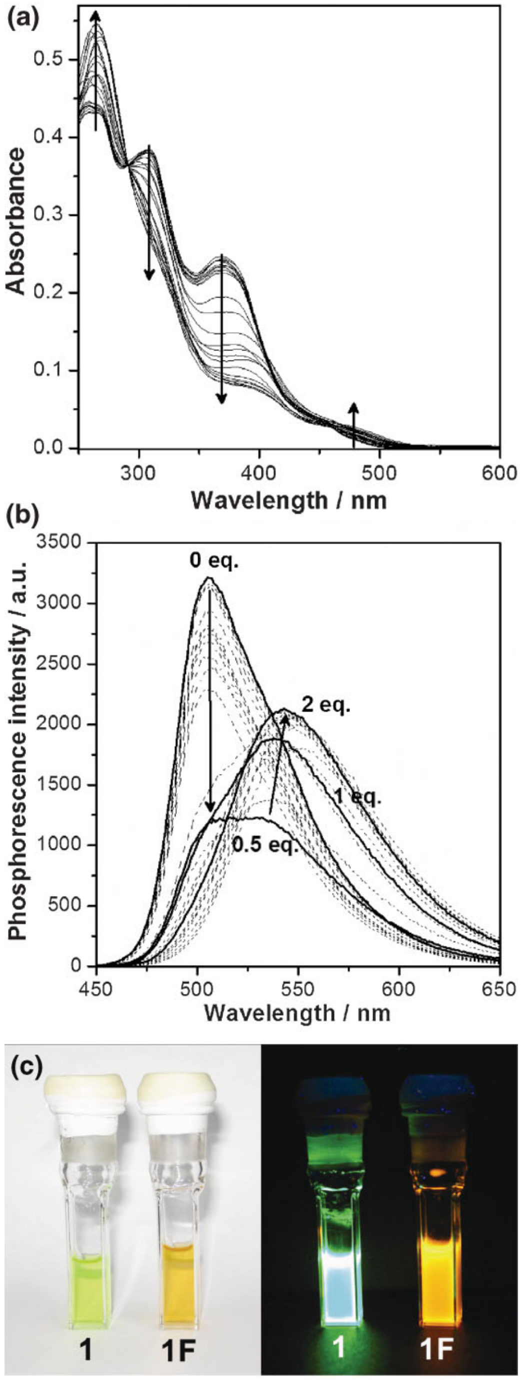

Figure 1. a) Absorption titration spectra, and b) change in phosphorescence spectra of **1** (1.0×10^{-5} M, MeCN) upon addition of tetrabutylammonium fluoride (0.2–5 equiv.). c) Changes in absorption color (left) and phosphorescence color (right) of **1** before (1) and after (1F) addition of tetrabutylammonium fluoride.

groups in **1** are electronically separated in the ground state and spatially distant from each other, the first (**1** + fluoride ion) and second ([**1** · fluoride ion] + fluoride ion) binding events result in identical spectral changes to give a linear dependency of the absorption change upon increase in fluoride ion concentration (SI2), thus potentially enabling an enlarged detection range compared with that of a receptor containing a single boryl group. The strength of **1** to coordinate with fluoride ions was investigated through Benesi–Hildebrand analysis (SI2) using the UV–vis absorption titration data to give a binding constant (K) of $(9.17 \pm 0.32) \times 10^4$ M^{-1},[1a] which is similar to the values reported previously for boryl group-based fluorescent receptors.[1a,5b,i,j] Coordination of a fluoride ion to the dimesitylboryl group was further demonstrated by ^{11}B NMR (193 MHz) experiments ($CDCl_3$, BF_3 standard, SI3). The chemical shift of the borons moved from 73.65 ppm (**1**) to 3.81 ppm (**1F**).[6f] Furthermore, we could find no unbound boron peak in the ^{11}B NMR spectra of a mixture of **1** and 2 eq. of fluoride ions, which indicates high binding affinity of **1** toward fluoride ions.

Both **1** and **1F** (1.0×10^{-5} M, acetonitrile (MeCN)) showed highly intense RTP with phosphorescence PLQYs of 0.57 and 0.38, respectively.[13] Also, we found that **1** and **1F** maintained PLQYs of 0.09 and 0.06, even after subsequent air equilibration (for 6 h). Furthermore, this decrease in PLQYs was much suppressed for PMMA films doped with **1** or **1F** (10 wt %, see below). Compound **1** enabled colorimetric and ratiometric phosphorescence sensing by displaying two different phosphorescence colors. As shown in Figure 1b and c, upon addition of fluoride ions, the bluish-green phosphorescence (512 nm) of **1** immediately changed to the orange phosphorescence (567 nm) of **1F**. This corresponds to the Commission Internationale de L'Eclairage (CIE) coordinates changing from (0.19, 0.56) to (0.46, 0.50) (SI4), which is sufficient for phosphorescence colorimetric and ratiometric sensing. Compared with luminescent receptors displaying a monotonic change only in intensity, this two-color phosphorescence behavior is particularly advantageous in terms of sensitivity, as described by Kubo et al.[5f] One interesting observation in Figure 1b is that the red-shifted peak (567 nm) has a prominent intensity upon addition of as little as 0.5 eq. of fluoride ion. We also found that this peak intensity reaches a saturated level faster than that observed in the absorption spectra (SI2, SI5). This is most likely attributed to the occurrence of an intramolecular interligand energy transfer from the green phosphorescent (unfluorinated) ligand to the orange phosphorescent (fluorinated) ligand, as was observed in other heteroleptic Ir(III) complex systems.[10a,d,g] Because a reference complex without the boryl groups did not show any observable phosphorescence change upon addition of fluoride ions (SI6), we are convinced that this phosphorescence behavior originated from the proposed boron–fluoride ion interaction. Very importantly, if we define the phosphorescent sensitivity (S) as

$$S = \frac{I_{567nm}}{I_{512nm} \cdot \mathrm{A}_{345\,\mathrm{nm}}} \tag{1}$$

where $I_{567\ \mathrm{nm}}$ and $I_{512\ \mathrm{nm}}$ are the intensities at 567 nm and 512 nm of the phosphorescence spectra from the Ir(III) complex after mixing with an anion, the fluoride ion-selectivity of **1** is determined to be unprecedentedly high as summarized

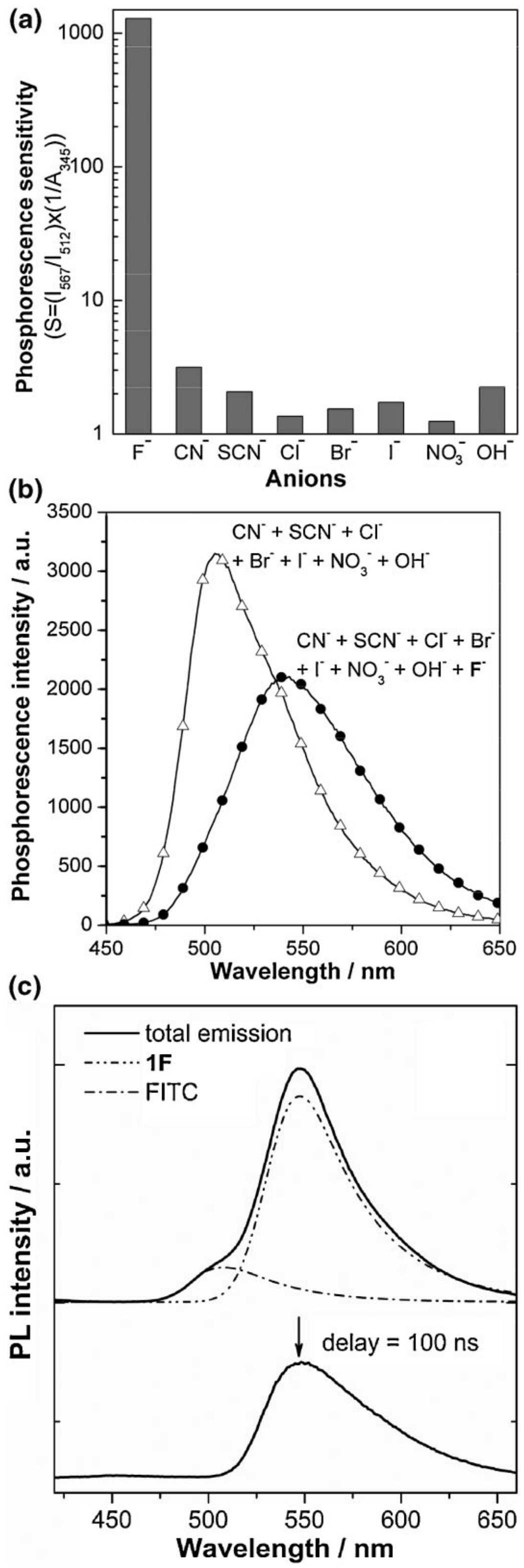

Figure 2. a) Phosphorescence sensitivity ($S = (I_{567}/I_{512}) \times (1/A_{345})$: I_{567} and I_{512} are the intensities at 567 nm and 512 nm, respectively, of the phosphorescence spectra after addition of anions; A_{345} is the absorbance at the excitation wavelength of 345 nm) toward anions. Note that the vertical axis is a log scale. b) Phosphorescence spectra showing the high fluoride ion selectivity of **1**; empty triangles: phosphorescence spectra of **1** (1.0×10^{-5} M, MeCN) upon addition of cyanide ion, thiocyanide ion, chloride ion, bromide ion, iodide ion, nitrate ion, and hydroxide ion (5 eq. each); filled circles: phosphorescence spectra after subsequent addition of fluoride ion (5 eq.). c) Time-gated acquisition of phosphorescence signals: total spectrum (upper curve) and the discriminated spectrum acquired after a 100 ns delay (lower curve) of **1F** (1.0×10^{-5} M, MeCN) containing a green-fluorescent impurity (FITC). Broken lines in the upper total spectrum indicate the spectral portion of **1F** and FITC.

in Figure 2a; **1** almost exclusively reacts with fluoride ions over other halide ions (chloride ion, bromide ion, and iodide ion) and multi-atomic anions (cyanide ion, thiocyanide ion, hydroxide ion, and nitrate ion), resulting in ca. 1000 times greater selectivity. In fact, the admixture of **1** and seven test anions (fluoride ion, chloride ion, bromide ion, iodide ion, cyanide ion, thiocyanide ion, hydroxide ion, and nitrate ion; 5 eq. each; 1.0×10^{-5} M, MeCN) shows characteristic **1F** phosphorescence, whereas a control sample, the fluoride ion-absent admixture, exhibits unperturbed **1** phosphorescence (Fig. 2b). To our knowledge, this is the highest value in phosphorescent fluoride ion-sensing ever reported. This can be attributed to the significantly improved phosphorescence change provided by the high phosphorescent PLQY of both **1** and **1F**.

As mentioned above, one of the prime benefits of using phosphorescent receptors is the possibility of facile signal purification through time-gated acquisition. It was found that the phosphorescence lifetimes (τ) of **1** and **1F** (1.0×10^{-5} M) were 0.56 μs and 1.2 μs, respectively, enabling facile elimination of background emissions. This "signal purification" is successfully demonstrated in Figure 2c; an air-equilibrated solution containing both **1F** and an intentionally added fluorescent impurity, FITC (1.0×10^{-5} M each, MeCN),[14] exhibits a total spectrum (upper curve) that is contaminated by the green fluorescence of FITC. However, acquisition after a delay time of 100 ns for the sample effectively eliminates the green fluorescent noise, and thus gives the clean phosphorescent signal (lower curve) of **1F**. It should be noted that this improves S from 280 (upper curve) to 1214 (lower curve), a factor of about 4.3 times, which emphasizes the effectiveness of using our phosphorescent receptor.

An important issue associated with fluoride ion sensing is the applicability of receptors in aqueous media. In particular, much effort has been expended for borylated receptors targeting water tolerance, but successful demonstrations are rare.[5a,c,6d,f] In our attempt to produce water tolerance, it turned out that **1** unfortunately exhibited almost no fluoride ion-binding-induced optical changes either in the aqueous or mixed aqueous solutions (such as aqueous 6 mM 4-(2-hydroxyethyl)-1-piperazine ethane sulfonic acid sodium salt (HEPES). buffer solution,[6f] water/THF 9:1 or water/MeCN 4:1, v/v); even when a large excess of fluoride ions (100 eq.) was applied, the inherent bluish-green phosphorescence of **1** showed no distinguishable change in aqueous media (SI7). This lack of response probably originates from either a competitive interaction of fluoride ions and water

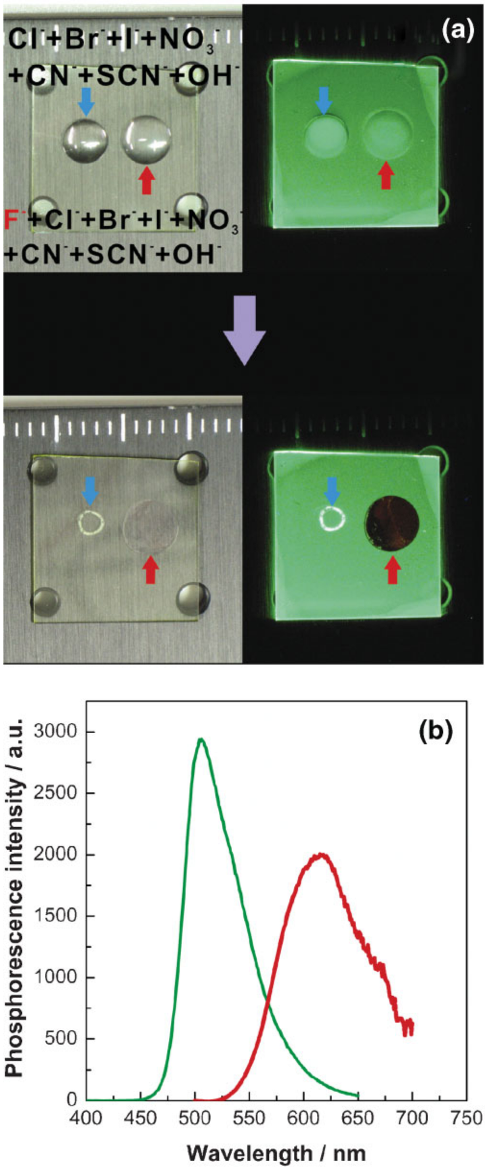

Figure 3. a) Photos showing phosphorescence color changes of the PMMA film doped with **1** (10 wt %) upon placing a droplet of the aqueous (6 mM HEPES buffer) solution containing anions (5×10^{-5} M for each, left: a control droplet without fluoride ions; right: a target droplet containing fluoride ions); Top: just after placing the droplets; Below: after evaporating the solvent at room temperature; Left: under room light; Right: under UV light (365 nm). b) Phosphorescence spectra of the treated spot (red) and the untreated surroundings (green) of the film.

toward the boron center or the highly exothermic hydration of fluoride ions in aqueous media.[6f] Whatever the reason, this problem can be circumvented if we use a doped polymer system of **1**. We found that if we removed an aliquot of an aqueous solution containing fluoride ions (5.0×10^{-5} M) and placed it onto the top of PMMA films doped with **1** (10 wt %), subsequent evaporation of the water solvent at room temperature or 50–70 °C gave a pale red spot, as shown in Figure 3a. Under 365 nm irradiation, we could observe intense reddish-orange phosphorescence from this spot while the untreated surroundings showed the initial green phosphorescence of **1**. We found that the absolute PLQYs of the film (after air equilibration for 3 days) were 0.17 (before fluoride ion treatment, **1**) and 0.16 (after fluoride ion treatment, **1F**) which are high enough to be adopted for a practical sensing system. Notably, S for this film calculated from the spectrum of Figure 3b is as high ($S > 1700$) as that of the solution experiment, thus demonstrating the high potential of this method. Interestingly, we additionally observed that the phosphorescence PLQY ratio of **1F** to **1** is improved (94%) in this film state compared with that (64%) of solution states, which might be attributed to the intermolecular energy transfer from **1** (interior of the film) to **1F** (surface of the film) in the concentrated film state. We also found that the phosphorescent intensity of the doped film did not show a temperature-dependent decrease over the tested temperature range. This film-based sensing exhibited robustness against aqueous hydroxide and cyanide ions and also high fluoride ion selectivity (SI9). However, it should be mentioned that **1**, both in the solution (MeCN or aqueous HEPES buffer solution) state and in the film (PMMA) state, did not respond to NaF or KF (SI7–SI9) due to the absence of phase transfer activity in these analytes. Use of a separate phase transfer cation such as tetrabutylammonium ion is probably demanded to overcome this limitation.

To summarize, we have synthesized a highly phosphorescent Ir(III) complex bearing fluoride ion-sensitive dimesitylboryl groups (**1**). This complex exhibited both extremely high selectivity toward fluoride ions ($S > 1000$) and high-efficiency two-color phosphorescence behavior at room temperature, enabling colorimetric as well as ratiometric fluoride ion sensing. More importantly, highly effective signal purification was demonstrated using time-gated acquisition of the phosphorescent signals to enhance the S/N ratio. Finally, aqueous fluoride ions could be successfully detected by applying the solution to the PMMA films doped with **1**, thus enabling the realization of a practical sensing system.

Experimental

Material Syntheses: 2-Dimesitylborylbromobenzene: A THF solution (80 mL) of 1,3-dibromobenzene (2.07 g, 8.76 mmol) was stirred under an Ar atmosphere and cooled to −78 °C. n-BuLi (1.6 M in hexane, 5.48 mL, 9.03 mmol) was added to this solution dropwise, and the temperature of the reaction mixture was maintained at −78 °C for 30 min. Then dimesitylboron fluoride (2.47 g, 9.20 mmol) in THF (20 mL) was added to the reaction vessel via a syringe. After 30 min, the temperature was raised to room temperature and the reaction mixture was stirred overnight. Concentration and subsequent silica gel column purification (n-hexane/ethyl acetate (EtOAc) = 49:1) gave a white powder (2.53 g, 6.24 mmol) in 71% yield. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 2.01 (s, 12H), 2.30 (s, 6H), 6.82 (s, 4H), 7.21 (t, $J = 7.6$ Hz, 1H), 7.41 (d, $J = 7.4$ Hz, 1H), 7.58 (d, $J = 7.9$ Hz, 1H), 7.61 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 21.39, 21.45, 22.51, 22.63, 23.66, 123.14, 128.32, 128.55, 128.59, 130.04, 134.68, 134.79, 138.48, 138.66, 139.14, 139.32, 141.04, 141.08. HRMS (EI) m/z: calcd for $C_{24}H_{26}BBr$: 404.1311; found: 404.1313. Anal. calcd for $C_{24}H_{26}BBr$: C 71.14, H 6.47; found: C 70.97, H 6.45.

2-(2′-(Dimesitylboryl)phenyl)pyridine: 2-Dimesitylborylbromobenzene (2.40 g, 5.92 mmol), tetrakis(triphenylphosphine)palladium(0)

(0.90 g, 0.77 mmol), and tri-*n*-butylstannylpyridine (4.36 g, 11.9 mmol) were dissolved in toluene (60 mL). The reaction mixture was refluxed for two days under an Ar atmosphere. Concentration and subsequent silica gel column purification (*n*-hexane/EtOAc = 30:1) gave a yellowish-white powder (0.75 g, 1.86 mmol) in 31% yield. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 2.02 (s, 12H), 2.30 (s, 6H), 6.82 (s, 4H), 7.17 (t, $J = 5.0$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 1H), 7.56 (d, $J = 7.3$ Hz, 1H), 7.60 (d, $J = 7.9$ Hz, 1H), 7.66 (td, $J = 5.6, 0.3$ Hz, 1H), 8.05 (s, 1H), 8.17 (d, $J = 7.7$ Hz, 1H), 8.64 (d, $J = 3.6$ Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 13.78, 17.48, 21.35, 23.70, 26.96, 28.44, 121.05, 122.16, 128.44, 128.49, 128.77, 129.24, 130.95, 134.49, 136.83, 137.12, 138.90, 138.32, 141.06, 141.87, 146.54, 149.80, 157.88. HRMS (EI) *m*/*z*: calcd for $C_{29}H_{30}BN$: 430.2471; found: 430.2470. Anal. calcd for $C_{29}H_{30}BN$: C 86.35, H 7.50, N 3.47; found: C 86.21, H 7.44, N 3.51.

*Iridium(III) bis[2-(2′-(dimesitylboryl)phenyl)pyridinato-N,C$^{2'}$]-acetylacetonato (**1**)*: **1** was synthesized through a standard two-step procedure according to the literature method [11e]. 2-(2′-(Dimesitylboryl)phenyl)pyridine (530 mg, 1.31 mmol) and iridium(III) chloride hydrate (Aldrich, 131 mg, 0.438 mmol) were dispersed in a binary solvent system of 2-ethoxyethanol (32 mL) and water (11 mL). The reaction mixture was stirred at 145 °C for 12 h under an Ar atmosphere. After cooling to room temperature, the yellow precipitate was filtered and thoroughly washed with water (100 mL), ethanol (60 mL), and finally cool acetone (20 mL). The precipitate was dissolved in CH_2Cl_2 and recrystallized from a mixed solution of hexane/toluene (10 mL:25 mL) to give a μ-chloride-bridged iridium(III) dimer (fine yellow crystals, 318 mg, 0.154 mmol) in 35% yield. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 1.22 (t, $J = 7.0$, 2H), 1.26 (s, 3H), 1.89 (s, 48H), 2.26 (s, 24H), 3.54 (m, 2H), 3.74 (m, 1H), 5.88 (t, $J = 7.8$ Hz, 2H), 5.92 (d, $J = 8.0$ Hz, 1H), 6.64 (m, 3H), 6.73 (s, 16H), 6.80 (m, 2H), 7.59 (s, 3H), 7.65 (m, 3H), 7.73 (m, 3H), 9.20 (d, $J = 5.4$ Hz, 2H), 9.44 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 15.37, 21.39, 23.61, 29.59, 29.92, 62.14, 66.80, 71.69, 118.95, 119.05, 122.47, 122.55, 122.81, 128.12, 130.10, 130.20, 130.47, 130.59, 131.82, 131.88, 131.98, 136.59, 136.65, 138.04, 138.05, 138.56, 138.68, 140.94, 142.17, 143.87, 143.96, 144.01, 144.10, 152.08, 153.74, 155.89, 156.33, 156.87, 168.11, 168.22, 168.29, 168.39. MALDI-TOF-MS *m*/*z* 2102.88 ($M + K^+$), calcd for $C_{116}H_{116}B_4Cl_2Ir_2N_4 =$ 2064.77. Anal. calcd for $C_{116}H_{116}B_4Cl_2Ir_2N_4$: C 67.48, H 5.66, N 2.71; found: C 67.40, H 5.77, N 2.84.

The well-dried μ-chloride-bridged iridium(III) dimer (100 mg, 0.0484 mmol), sodium carbonate (51.3 mg, 0.484 mmol), and 2,4-pentanedione (24.2 mg, 0.242 mmol) were dissolved in 2-ethoxyethanol (20 mL). After degassing, the reaction vessel was maintained under an Ar atmosphere. The temperature was raised to 140 °C and the reaction mixture was stirred for 3 h. The cooled crude mixture was poured into EtOAc (150 mL), and extracted with water (100 mL, three times) to remove 2-ethoxyethanol. Silica gel column purification with *n*-hexane/EtOAc = 4:1 and reprecipitation in ether/*n*-hexane = 10 mL:40 mL gave a yellow powder (79.4 mg, 0.0724 mmol) in 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 1.82 (s, 3H), 1.93 (br m, 27H), 2.27 (s, 12H), 5.26 (s, 1H), 6.21 (d, $J = 7.7$ Hz, 2H), 6.74 (s, 8H), 7.10 (t, $J = 6.0$ Hz, 2H), 7.65 (m, 6H), 7.71 (d, $J = 7.9$ Hz, 2H), 8.48 (d, $J = 5.5$ Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 21.39, 23.61, 28.95, 29.92, 100.68, 119.05, 121.68, 128.10, 132.06, 132.90, 137.20, 137.90, 137.99, 140.93, 142.34, 145.07, 148.46, 158.74, 168.52, 185.08. FAB-MS (DIP) *m*/*z* 1096 (M^+), 997, 595, 403, 154, 136. Anal. calcd for $C_{63}H_{65}B_2IrN_2O_2$: C 69.04, H 5.98, N 2.56; found: C 68.95, H 6.12, N 2.56.

Characterization: Absorption spectra of the solution state were recorded with a Shimadzu UV-1650-PC from 280 to 700 nm. Photoluminescence (PL) spectra were obtained with a Shimadzu RF-5301-PC spectrophotometer in the range of 400–700 nm. Typically, Ar-saturated 10 μmol solutions were prepared for measuring absorption and PL spectra. For the transient PL measurements, a quartz cuvette containing an Ar-saturated solution of the Ir(III) complex was tightly sealed under an Ar atmosphere. An excitation pulse at 355 nm was generated from the third harmonic output of a Q-switched Nd:YAG laser (Continuum, Surelite). The time duration of the excitation pulse was ca. 6 ns. The emission light was collimated before entering the monochromator slit and then spectrally resolved using a 15 cm monochromator (Acton Research, SP150) equipped with a 600 grooves/mm grating after passing the sample. The spectral resolution was about 3 nm for the transient PL experiment. The light signal was detected via a photomultiplier tube (PMT) (Hamamatsu, R928). The output signal from the PMT was recorded with a 500 MHz digital storage oscilloscope (Tektronix, TDS3052) for the temporal profile measurement. $Ir(ppy)_3$ [13] and quinine sulfate [15] were used as reference materials for the solution phosphorescence PLQY. For the measurements of absolute PLQY of polymer films, a system consisting of a 6 inch integrated sphere was used: an excitation beam of 345 nm radiation from a high power xenon lamp and a monochromator was loosely focused on the sample, and the emission light was spectrally resolved using a 30 cm monochromator (Acton) after passing through the sample. The light signal was detected via a PMT.

Anion Sensing Test: Widely used tetrabutylammonium salts were used for the anion sensing tests [5b,f,g]: tetrabutylammonium fluoride (1 M in THF, Aldrich), tetrabutylammonium chloride (Fluka), tetrabutylammonium bromide (Fluka), tetrabutylammonium iodide (Fluka), tetrabutylammonium cyanide (Aldrich), tetrabutylammonium thiocyanide (Aldrich), tetrabutylammonium hydroxide (Aldrich), and tetrabutylammonium nitrate (Aldrich). Other fluoride ion sources such as NaF (Aldrich) and KF (Aldrich) were also tested. Typically, 5 mL of a 20 μmol solution containing **1** and 5 mL of analyte solution was placed in a vial and transferred to a cuvette after 30 min. Coordination reactions were performed under ambient conditions.

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[1] a) C. B. Black, B. Andrioletti, A. C. Try, C. Ruiperez, J. L. Sessler, *J. Am. Chem. Soc.* **1999**, *121*, 10438. b) K. Kono, T. Dote, K. Usuda, M. Shimahara, in *Fluoride in Medicine, Biology and Toxicology*, Pomeranian Medical University, Warsaw **2003**, pp. 90–100. c) *National Primary Drinking Water Regulations: Public Notification Rule*, Vol. 65, US Environmental Protection Agency **2000**, pp. 25981– 26049.

[2] a) M. S. Frant, J. W. Ross, *Science* **1966**, *154*, 1533. b) M. Akhond, M. B. Najafi, J. Tashkhourian, *Sens. Actuators B* **2004**, *99*, 410.

[3] a) E. J. Cho, J. W. Moon, S. W. Ko, J. Y. Lee, S. K. Kim, J. Yoon, K. C. Nam, *J. Am. Chem. Soc.* **2003**, *125*, 12376. b) M. Boiocchi, L. Del Boca, D. E. Gomez, L. Fabbrizzi, M. Licchelli, E. Monzani, *J. Am. Chem. Soc.* **2004**, *126*, 16507. c) P. A. Gale, *Chem. Commun.* **2005**, 3761. d) D. H. Lee, H. Y. Lee, K. H. Lee, J. I. Hong, *Chem. Commun.* **2001**, 1188. e) K. Chellappan, N. J. Singh, I. C. Hwang, J. W. Lee, K. S. Kim, *Angew. Chem. Int. Ed.* **2005**, *44*, 2899.

[4] N. A. Chaniotakis, K. Jurkschat, D. Müller, K. Perdikaki, G. Reeske, *Eur. J. Inorg. Chem.* **2004**, 2283.

[5] a) C.-W. Chiu, F. P. Gabbaï, *J. Am. Chem. Soc.* **2006**, *128*, 14248. b) S. Yamaguchi, S. Akiyama, K. Tamao, *J. Am. Chem. Soc.* **2001**, *123*, 11372. c) M. H. Lee, T. Agou, J. Kobayashi, T. Kawashima, F. P. Gabbaï, *Chem. Commun.* **2007**, 1133. d) S. Solé, F. P. Gabbaï, *Chem. Commun.* **2004**, 1284. e) Y. Sun, N. Ross, S.-B. Zhao, K. Huszarik, W.-L. Jia, R.-Y. Wang, S. Macartney, S. Wang, *J. Am. Chem. Soc.* **2007**, *129*, 7510. f) Y. Kubo, M. Yamamoto, M. Ikeda, M. Takeuchi, S. Shinkai, S. Yamaguchi, K. Tamao, *Angew. Chem. Int. Ed.* **2003**, *42*, 2036. g) K. M. K. Swamy, J. Y. Lee, H. N. Lee, J. Chun, Y. Kim, S.-J. Kim, J. Yoon, *J. Org. Chem.* **2006**, *71*, 8626. h) S. Arimori, M. G. Davidson, T. M. Fyles, T. G. Hibbert, T. D. James, G. I. Kociok-Köhn, *Chem. Commun.* **2004**, 1640. i) Z.-Q. Liu, M. Shi, F.-Y. Li, Q. Fang, Z.-H. Chen, T. Yi, C.-H. Huang, *Org. Lett.* **2005**, *7*, 5481. j) C. R. Cooper, N. Spencer, T. D. James, *Chem. Commun.* **1998**, 1365. k) X. Y. Liu, D. R. Bai, S. Wang, *Angew. Chem. Int. Ed.* **2006**, *45*, 5475. l) D.-R.

Bai, X.-Y. Liu, S. Wang, *Chem. Eur. J.* **2007**, *13*, 5713. m) Y. Cui, F. Li, Z.-H. Lu, S. Wang, *Dalton Trans.* **2007**, 2634. n) W. Tan, D. Zhang, Z. Wang, C. Liu, D. Zhu, *J. Mater. Chem.* **2007**, *17*, 1964. o) M. T. Reetz, C. M. Niemeyer, K. Harms, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1472. p) C. Dusemund, K. R. A. S. Sandanayake, S. Shinkai, *J. Chem. Soc. Chem. Commun.* **1995**, 333. q) M. Melaïmi, S. Solé, C.-W. Chiu, H. Wang, F. P. Gabbaï, *Inorg. Chem.* **2006**, *45*, 8136. r) C. Bresner, S. Aldridge, I. A. Fallis, C. Jones, L.-L. Ooi, *Angew. Chem. Int. Ed.* **2005**, *44*, 3606. s) A. Sundararaman, M. Victor, R. Varughese, F. Jäkle, *J. Am. Chem. Soc.* **2005**, *127*, 13748.

[6] a) T. Agou, J. Kobayashi, T. Kawashima, *Inorg. Chem.* **2006**, *45*, 9137. b) K. Parab, K. Venkatasubbaiah, F. Jäkle, *J. Am. Chem. Soc.* **2006**, *128*, 12879. c) C. D. Entwistle, T. B. Marder, *Angew. Chem. Int. Ed.* **2002**, *41*, 2927. d) M. Melaimi, F. P. Gabbaï, *J. Am. Chem. Soc.* **2005**, *127*, 9680. e) T. Agou, J. Kobayashi, T. Kawashima, *Org. Lett.* **2005**, *7*, 4373. f) T. W. Hudnall, F. P. Gabbaï, *J. Am. Chem. Soc.* **2007**, *129*, 11978.

[7] S. Yamaguchi, T. Shirasaka, S. Akiyama, K. Tamao, *J. Am. Chem. Soc.* **2002**, *124*, 8816.

[8] E. Sakuda, A. Funahashi, N. Kitamura, *Inorg. Chem.* **2006**, *45*, 10670.

[9] For recent reviews: a) M. S. Lowry, S. Bernhard, *Chem. Eur. J.* **2006**, *12*, 7970. b) V. Marin, E. Holder, R. Hoogenboom, U. S. Schubert, *Chem. Soc. Rev.* **2007**, *36*, 618. c) P.-T. Chou, Y. Chi, *Chem. Eur. J.* **2007**, *13*, 380.

[10] a) Y. You, S. Y. Park, *J. Am. Chem. Soc.* **2005**, *127*, 12438. b) Y. You, S. H. Kim, H. K. Jung, S. Y. Park, *Macromolecules* **2006**, *39*, 349. c) Y. You, C.-G. An, D.-S. Lee, J.-J. Kim, S. Y. Park, *J. Mater. Chem.* **2006**, *16*, 4706. d) Y. You, K. S. Kim, T. K. Ahn, D. Kim, S. Y. Park, *J. Phys. Chem. C* **2007**, *111*, 4052. e) Y. You, C.-G. An, J.-J. Kim, S. Y. Park, *J. Org. Chem.* **2007**, *72*, 6241. f) I. Lee, Y. You, S.-J. Lim, S. Y. Park, *Chem. Lett.* **2007**, 888. g) Y. You, J. Seo, S. H. Kim, K. S. Kim, T. K. Ahn, D. Kim, S. Y. Park, *Inorg. Chem.* **2008**, *47*, 1476.

[11] For selected references: a) X. Gong, M. R. Robinson, J. C. Ostrowski, D. Moses, G. C. Bazan, A. J. Heeger, *Adv. Mater.* **2002**, *14*, 581. b) C. Jiang, W. Yang, J. Peng, S. Xiao, Y. Cao, *Adv. Mater.* **2004**, *16*, 537. c) P. Coppo, M. Duati, V. N. Kozhevnikov, J. W. Hofstraat, L. De Cola, *Angew. Chem. Int. Ed.* **2005**, *44*, 1806. d) E. A. Plummer, A. van Diken, H. W. Hofstraat, L. De Cola, K. Brunner, *Adv. Funct. Mater.* **2005**, *15*, 281. e) S. Lamansky, P. Djurovich, D. Murphy, F. Adbel-Razzaq, H.-E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest, M. E. Thompson, *J. Am. Chem. Soc.* **2001**, *123*, 4304. f) A. B. Tamayo, B. D. Alleyne, P. I. Djurovich, S. Lamansky, I. Tsyba, N. N. Ho, R. Bau, M. E. Thompson, *J. Am. Chem. Soc.* **2003**, *125*, 7377. g) M. K. Nazeeruddin, R. Humphry-Baker, D. Berner, S. Rivier, L. Zuppiroli, M. Grätzel, *J. Am. Chem. Soc.* **2003**, *125*, 8790. h) A. Tsuboyama, H. Iwasaki, M. Furugori, T. Mukaide, J. Kamatani, S. Igawa, T. Moriyama, S. Miura, T. Takiguchi, S. Okada, M. Hoshino, K. Ueno, *J. Am. Chem. Soc.* **2003**, *125*, 12971. i) T. Tsuzuki, N. Shirasawa, T. Suzuki, S. Tokito, *Adv. Mater.* **2003**, *15*, 1455. j) C.-H. Yang, Y.-M. Cheng, Y. Chi, C.-J. Hsu, F.-C. Fang, K.-T. Wong, P.-T. Chou, C.-H. Chang, M.-H. Tsai, C.-C. Wu, *Angew. Chem. Int. Ed.* **2007**, *46*, 2418. k) W.-Y. Wong, C.-L. Ho, Z.-Q. Gao, B.-X. Mi, C.-H. Chen, K.-W. Cheah, Z. Lin, *Angew. Chem. Int. Ed.* **2006**, *45*, 7800. l) J. Huang, T. Watanabe, K. Ueno, Y. Yang, *Adv. Mater.* **2007**, *19*, 739. m) S. Kappaun, S. Sax, S. Eder, K. C. Möller, K. Waich, F. Niedermaier, R. Saf, K. Mereiter, J. Jacob, K. Müllen, E. J. W. List, C. Slugovc, *Chem. Mater.* **2007**, *19*, 1209.

[12] M. Nonoyama, *Bull. Chem. Soc. Jpn.* **1974**, *47*, 767.

[13] a) S. Sprouse, K. A. King, P. J. Spellane, R. J. Watts, *J. Am. Chem. Soc.* **1984**, *106*, 6647. b) K. R. J. Thomas, M. Velusamy, J. T. Lin, C.-H. Chien, Y.-T. Tao, Y. S. Wen, P.-T. Chou, *Inorg. Chem.* **2005**, *44*, 5677.

[14] 2 wt % of ethanol was added to solvate FITC.

[15] J. N. Demas, G. A. Crosby, *J. Phys. Chem.* **1971**, *75*, 991.