3,5-Diaryl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) Dyes: Synthesis, Spectroscopic, Electrochemical, and Structural Properties

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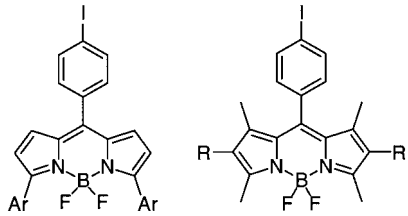
This research was undertaken to obtain new "BODIPY" dyes that fluoresce at relatively long wavelengths. The title compounds **1a**−**e** were prepared via a divergent route involving Suzuki couplings of arylboronic acids to *N*-*tert*-butoxycarbonyl-4-bromopyrrole **2**, condensation of the products with an acid chloride, and incorporation of the boron difluoride entity. Two alkyl-substituted systems **7a** and **7b** were also prepared for comparison; the critical difference between structures **1** and **7** is that the former have an aryl group attached to each pyrrole nucleus whereas the latter only have alkyl substituents on that same ring. UV absorption and fluorescence emission data were compared for compounds **1** and **7**. Absorption and fluorescence emission maxima for compounds **1** occur at higher wavelengths than for compounds **7**, and the Stokes shifts for the aryl-substituted compounds **1** are larger than for the alkyl-substituted compounds **7**. Fluorescence quantum yields measured for compounds **1** are less than for compounds **7**, and possible reasons for this are outlined. Other physical data for the compounds were also collected. Oxidation and reduction potentials of the systems were obtained from cyclic voltammetry experiments, and a single-crystal X-ray structure determination was performed for the bisnaphthyl-substituted compound **1b**.

Introduction

4,4-Difluoro-4-bora-3a,4a-diaza-s-indacene dyes[1] are extremely fluorescent materials[2] that have found numerous applications in biochemistry and molecular biology.[3] The trade name for these "BODIPY" dyes is associated with Molecular Probes (Eugene, OR),[4] and much of the literature on them is patent material designed to restrict unlicensed commercial uses. BODIPY dyes tend to be sold in small quantities for biochemical experiments, and amounts typically required for synthetic organic chemistry are prohibitively expensive. As part of an effort to make new fluorescent tags for DNA sequencing, we required a series of compounds for which the emission maxima would be higher than approximately 520 nm and easily varied via minor modifications in a synthetic pathway. It was reasoned that BODIPY dyes **1** with 3,5-diaryl substituents might have the desired characteristics. Synthetic schemes that allowed for incorporation of variable substitution on the 3,5-diaryl units could afford a series of dyes with tunable fluorescent characteristics, and the added conjugation should shift their absorption maxima to longer wavelengths than the corresponding alkyl-substituted materials (i.e., above ca. 520 nm). Computerized structure search routines indicated that molecules of type **1** had not been reported. Consequently, a project was initiated to synthesize these materials[5] and investigate their salient physical and spectroscopic properties. A full account of that work is given here.



Ar	
1a	Ph
1b	1-Naph
1c	4-MeOC$_6$H$_4$
1d	4-FC$_6$H$_4$
1e	2-MeOC$_6$H$_4$

R	
7a	H
7b	Et

Results and Discussion

Synthesis. Scheme 1 depicts the synthetic route that was used for preparation of compounds **1a**−**e**. Suzuki coupling[6,7] of *N*-*tert*-butoxycarbonyl-4-bromopyrrole **2**[8,9] with five different arylboronic acids[10] gave the protected 2-arylpyrroles **3a**−**e**. Removal of the BOC-protecting

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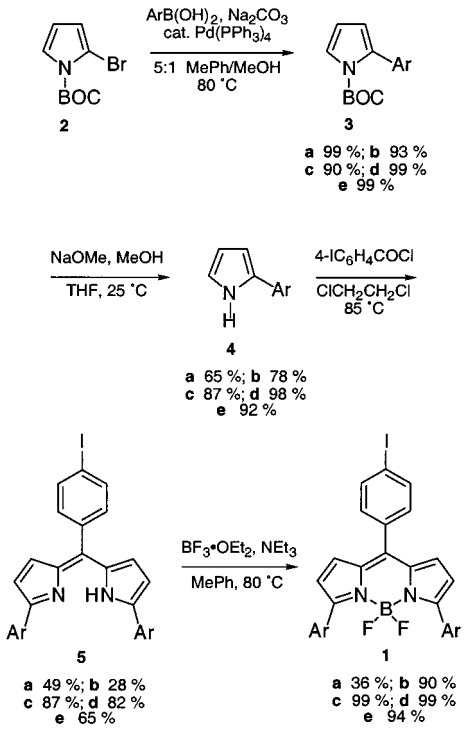
Scheme 1. Syntheses of Compounds 1a−e



group gave the derivatives **4**.[11] We favor this synthesis of arylpyrroles over some existing routes,[12−14] for reasons already outlined,[5] i.e., convenience and overall yields. Pyrroles **4** can be converted directly to the target materials **1** in a one-pot, two-step procedure, but superior overall yields were obtained when the intermediate dipyrromethenes **5** were isolated. That isolation process was best done using a deactivated alumina column; extensive decomposition occurred when silica gel was used as a support. In one particular experiment, a 10% yield was obtained on silica, but over 90% on alumina.

Some notable points concerning the syntheses of these compounds are as follows. The route is divergent from compound **2**. Attempts to couple 2-pyrroleboronic acid with aryl halides were explored, but gave much less satisfactory results. Yields of the dipyrromethenes **5a** and **5b** were the lowest in the series, presumably because of incomplete reactions. In fact, ketones **6a** and **6b** are intermediates in these transformations, and these were formed in significant quantities in those particular syntheses. The products **1a−e** were isolated as dark violet crystalline materials. In solution they are beautifully colored. For instance in chloroform **1a** is brick red, **1b** is red, **1c** is violet, **1d** is fuchsia, and **1e** is dark violet. Two alkyl-substituted systems **7** were also prepared[15] to provide closely related molecules without aryl pyrrole substituents for spectroscopic comparisons.

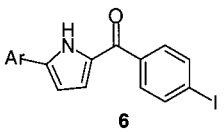


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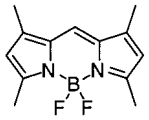
Table 1. Maximum Molar Absorptivities (ϵ_{max}), the Wavelength of ϵ_{max} ($\lambda_{abs.max}$), and the Stokes Shifts (the latter value reported is the difference between wavelengths for the maximum of absorption and corrected fluorescence spectra)

solvent	compound	$\epsilon_{max\ (abs)}$[a] ($M^{-1}\ cm^{-1}$)	$\lambda_{abs.max}$ (nm)	Stokes shift (nm)
EtOH	**1a**	53300	558	34
	1b	48300	550	63
	1c	54100	585	44
	1d	42100	559	33
	1e	30700	549	52
	7a	46300	504	10
	7b	75800	528	13
$CHCl_3$	**1a**	52400	555	33
	1b	49000	542	65
	1c	54100	582	44
	1d	42200	555	35
	1e	30500	545	53
	7a	47100	500	10
	7b	75900	524	13

[a] Estimated errors in ϵ_{max} are within 500 $M^{-1}\ cm^{-1}$.

Spectroscopic Properties. Absorption spectra of the aryl-BODIPY derivatives **1a−1e** have similar band shapes, but they are different to those observed for **7a** and **7b**. For **7a**, the absorption and fluorescence wavelength maxima are almost identical to the BODIPY **8**,[2,4] indicating that the 4-iodobenzene entity connected to carbon C-8 has little impact on the spectral band shapes of these compounds. Qualitatively, the fluorescence spectra of all the compounds **1**, **7**, and **8** (presumably a $S_1 \rightarrow S_0$ transition) show an approximate mirror symmetry with their absorption spectra. For compounds **7** and **8** the mirror symmetry is nearly perfect, but for compounds **1** it is less so.



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Compound **7b** had the highest molar absorptivity (ϵ_{max} = 75 000 $M^{-1}\ cm^{-1}$) of dyes **1** and **7**, being similar to that for the unsubstituted derivative **8** (ϵ_{max} = 80 000 $M^{-1}\ cm^{-1}$). For compounds **1** and **7a**, however, the maximum molar absorptivities are lower and range from 30 000 to 55 000 $M^{-1}\ cm^{-1}$ (Table 1). The Stokes shifts measured for compounds **1a−1e** were 3−6 times larger than for the compounds **7**. Moreover, these Stokes shifts do not vary much when the solvent is changed from ethanol to chloroform. These solvents have markedly different polarities hence this observation implies that the large Stokes shift observed are not caused by significantly different permanent dipole moments in the electronic ground and excited states.

Fluorescence quantum yields were calculated and determined experimentally for compounds **1** and **7**, and the data are given in Table 2. Radiative lifetimes (τ_0) were calculated from the absorption spectra using the modified Strickler−Berg equation.[16] The fact that the τ_0 values are similar for ethanol and chloroform reflects the fact that the molar absorptivities and refractive indices are very

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Table 2. Experimental and Calculated Fluorescence Quantum Yields (Φ_{exp} and Φ_{calc}) Obtained for Compounds 1 and 7. the Measured Fluorescence Lifetime (τ), the Calculated Radiative Lifetime (τ_0), and the Calculated Förster Radius (R_0) Are Presented

solvent	compound	Φ_{exp}	Φ_{calc}	τ (ns)[a]	τ_0 (ns)	R_0 (Å)
EtOH	**1a**	0.15 ± 0.01	0.15	1.1	6.9 ± 0.7	35.8 ± 0.9
	1b	0.20 ± 0.02	0.16	1.1	6.8 ± 0.1	31.5 ± 0.4
	1c	0.33 ± 0.01	0.35	2.4	6.8 ± 0.6	41.8 ± 0.8
	1d	0.15 ± 0.01	0.10	0.8	8.6 ± 0.5	34.5 ± 0.5
	1e	0.05 ± 0.01	0.03	0.3	10.5 ± 0.3	24.6 ± 0.3
	7a	0.55 ± 0.04	0.54	3.0	5.5 ± 0.4	46.3 ± 0.9
	7b	0.75 ± 0.03	0.57	5.0	8.7 ± 0.3	45.8 ± 0.9
$CHCl_3$	**1a**	0.20 ± 0.03	0.18	1.2	6.5 ± 0.1	38.2 ± 0.8
	1b	0.38 ± 0.03	0.30	2.1	7.1 ± 0.3	36.3 ± 0.6
	1c	0.42 ± 0.02	0.37	2.6	7.3 ± 0.4	43.8± 0.9
	1d	0.22 ± 0.01	0.13	1.1	8.6 ± 0.5	37.9 ± 0.8
	1e	0.08 ± 0.01	0.06	0.6	10.6 ± 0.7	28.4 ± 0.1
	7a	0.64 ± 0.02	0.53	3.0	5.7 ±0.6	47.7± 0.9
	7b	0.78 ± 0.03	0.52	4.8	9.1 ± 0.3	46.4 ± 0.9

[a] Errors in the measured fluorescence lifetimes are within 0.1 ns.

Table 3. Electrochemical Data for 1a−e in Acetonitrile (scan rate 100 mV s^{-1})

	Ar	$E_{ox,pa}$ (V) vs ferrocene	$E_{red,1/2}$ (V) vs ferrocene
1a	Ph	+0.91	−1.15
1b	1-Nap	+0.98	−1.15
1c	4-$MeOC_6H_4$	+0.68	−1.20
1d	4-FC_6H_4	+0.93	−1.11
1e	2-$MeOC_6H_4$	+0.84	−1.19

similar in the two solvents. Time-resolved fluorescence experiments were used to measure the actual fluorescence decay. The lifetimes τ recorded in this way were found to be monoexponential for all compounds studied. Comparison of the calculated and measured lifetimes shows that the experimental values recorded were always shorter. This implies that nonradiative relaxation processes that are not accommodated in the calculations were operative. Fluorescence quantum yield calculated according to $\Phi_{calcd} = \tau/\tau_0$ agreed well with the experimental fluorescence quantum yields, except for **1b**, **1d**, and **7b** in ethanol, and except for **1b**, **1d**, **7a**, and **7b** in chloroform.

Förster radii[17] for compounds **1** and **7** were calculated from absorption and corrected fluorescence spectra. The values obtained range between 25 and 48 Å and show a modest solvent dependence. These values are considerably lower than the Förster radius for **8**, i.e., less than 57 ± 1 Å.[2]

Finally, various NMR parameters were recorded for dyes **1** and **7**, but no striking differences were observed. For instance, chemical shifts in the ^{11}B NMR spectra reveal that the different aryl substituents do not impart any significant influences; the values obtained fall within the relatively narrow range of −1.26 to −1.92 ppm. Proton NMR signals for the naphthyl-substituted BODIPY **1b** were broad at ambient temperature, but sharpen when the sample is heated to 80 °C in toluene. This phenomenon is attributed to restricted motion of the naphthyl groups.

Electrochemical Properties. Cyclic voltammetry was used to probe the electronic effects of the various aryl substituents on the BODIPY electrophore. Table 3 shows salient details form this study. All new aryl-

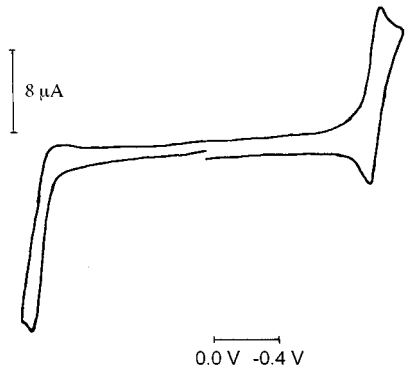
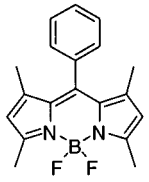


Figure 1. Cyclic voltammogram of **1b** in acetonitrile (at 100 mV s^{-1}).

substituted BODIPYs display irreversible oxidation waves and reversible reduction waves. The reduction and oxidation potentials are not large, so the compounds are quite easily reduced and also quite easily oxidized. Electrochemical data have been reported for compound **9**[18] and that data serves as a useful point of reference for the current study.



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oxidation potential +0.76 V
reduction potential -1.57 V
(versus ferrocene)

With the exception of compound **1c**, the compounds shown in Table 3 have higher oxidation potentials than **9**. This may be attributed to inductive destabilization of the cationic form by the 4-iodo substituents on the *meso* aromatic ring and/or to lowering of the oxidation potentials by the alkyl substituents of compound **9**. The fact that the oxidation waves for compounds **1** are irreversible implies that the radical cations generated on the anode react rapidly to form other products. Electrochemical polymerization of pyrroles (a well-known industrial process)[19,20] may be operative for the BODIPY systems. Reversible oxidation waves for compound **9** may reflect retardation of pyrrole−pyrrole coupling processes by the alkyl substituents. Peak potentials for compounds in the series **1a**−**e** vary over a 0.3 V range wherein the methoxy-substituted compounds **1c** and **1e** exhibit the lowest potentials. This is probably due to mesomeric stabilization of the charges by the methoxy substituents. The fact that the 2-methoxy compound has a higher oxidation potential than the 4-methoxy derivative indicates steric effects in the former case disfavor an ideal alignment of orbitals. Similar stereoelectronic effects may be operative for the naphthyl compound **1b**, which has a higher oxidation potential than the phenyl compound **1a**. Further evidence for congestion in the naphthyl compound is seen on the proton NMR of this compound (vide supra). In contrast to the oxidative processes, electrochemical reduction of compounds **1a**−**e** was shown to be

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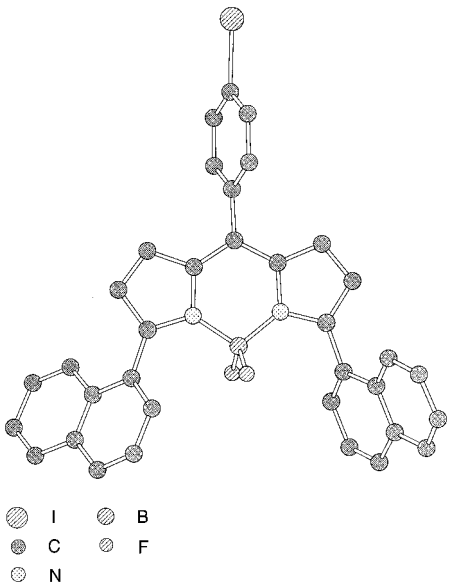

Figure 2. Chem3D representation of compound **1b** (data from solid-phase crystal structure determination).

reversible and to occur over a relatively small range (0.1 V). This may be due to reduction centered at the *meso* position and stabilized by the relatively electron poor aryl iodide. Aryl substituents at the 3- and 5-position have less pronounced effects although, predictably, the 3,5-di-(4-fluoroaryl) BODIPY has the least negative reduction potential in the series.

Solid State Structure of Compound 1b. A single-crystal X-ray analysis of compound **1b** (Figure 2) showed that the molecule is sterically congested. All three aryl substituents were shown to be twisted relative to the BODIPY plane. The torsional angle formed between the 8-*p*-iodophenyl group and the BODIPY core unit was measured as 71°; this is presumably due to interaction of the BODIPY 2- and 7-protons with the *ortho*-protons of the 8-*p*-iodophenyl group. Conversely, it appears to be that the fluorine atoms prevent the naphthyl groups from adopting orientations coplanar with the BODIPY core. The two naphthalene−BODIPY torsional angles measured were around 50° and 60°, respectively.

Conclusion

The new aryl-substituted BODIPYs described here are accessible via a straightforward route. As expected, substitution of aryl groups onto the pyrrole rings of the BODIPY framework causes the corresponding wavelengths of the fluorescence emission maxima (denoted by $\lambda_{em.max}$) to be red-shifted relative to the corresponding alkyl-substituted compounds. The Stokes shifts for compounds **1** are also higher than their alkyl counterparts, a factor that also helps shift their fluorescence $\lambda_{em.max}$ values to higher wavelength. However, the fluorescence quantum yields for the aryl-substituted compounds tend to be lower than the corresponding alkyl-substituted ones. This may be attributed to nonradiative energy loss due to spinning motions about the *C*-aryl single bonds. Indeed, it may not be a coincidence that the second highest fluorescence quantum yield in the series **1a**−**e** was for the naphthyl derivative **1b** for which rotation of the aryl groups was slow enough to be observed on the NMR time scale. Molecular modifications that totally eliminate this degree of rotational freedom should increase the fluorescence quantum yields, but this point was not tested here. Such modifications could also be designed to hold the aryl substituents into the BODIPY plane. The electrochemical studies here demonstrate that electron-withdrawing and electron-releasing aryl substituents have less impact on the oxidation and reduction potentials than expected, consistent with twisting of the aryl substituents out of the BODIPY plane. Such deformations were observed in the solid-state structural analysis of compound **1b**.

There are several potential applications of the compounds reported in this study. They could aid the design of fluorescent chemosensors,[21] act as reporter molecules for dynamics, structure, and function of biomolecules,[2] provide light-harvesting systems for artificial photosynthesis,[22] and for multipigment arrays in molecular photonic devices.[23]

Experimental Section

General Experimental. Compounds **1c** and **3**−**5c** were prepared as previously described.[5] Procedures for the preparation of compounds **7a** and **7b** will be reported elsewhere.[15] All chemicals were obtained from commercial suppliers and used without further purification. THF and toluene were distilled from Na/benzophenone prior to use, acetonitrile used for the electrochemical studies was distilled from CaH_2, and 1,2-dichloroethane was distilled from CaH_2.

All NMR spectra were recorded on a Varian instrument at 200 and 300 MHz (^{1}H) as well as 75 MHz (^{13}C) and 64 MHz (^{11}B). NMR chemical shifts are expressed in ppm relative to internal solvent peaks, and coupling constants were measured in hertz. For ^{11}B-NMR, BF_3•Et_2O has been used as a reference. For recording the cyclic voltammograms, a BAS-100A electroanalyzer has been used.

***N-tert*-Butyloxycarbonyl-2-phenylpyrrole (3a).** *N-tert*-Butyloxycarbonyl-2-bromopyrrole[8,9] (4.61 g, 18.7 mmol), phenylboronic acid (2.28 g, 18.7 mmol), tetrakis(triphenylphosphine)-palladium (432 mg, 0.2 mmol), Na_2CO_3 (18.7 mL, 37.4 mmol, 2.0 M aqueous solution), PhMe (78 mL), and MeOH (16 mL) were added to a Schlenk tube and freeze-thaw-degassed three times and then heated to 80 °C for 14 h. The reaction mixture was filtered through a plug of silica gel on Celite using EtOAc as eluant. After concentration, the crude product was purified via flash chromatography using a gradient of 100% hexanes to 5% EtOAc/hexanes as eluant giving **3a** as a clear oil (4.49 g, 99% yield). R_f 0.25 (5% EtOAc in hexanes); MS (FAB$^+$, NBA = 4-nitrobenzoic acid) *m*/*z* (%) 243 (M^+); HRMS calcd [M + H$^+$] 243.1259, found [M + H$^+$] 243.1253;^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.42−7.32 (m, 6 H), 6.29−6.22 (m, 2 H), 1.39 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 149.3, 134.9, 134.4, 129.1, 127.4, 127.0, 122.4, 114.3, 110.4, 83.3, 27.5.

2-Phenylpyrrole (4a).[14] A suspension of sodium methoxide (594 mg, 11.0 mmol) in MeOH (3.0 mL) was added to a stirred solution of *N-tert*-butyloxycarbonyl-2-phenylpyrrole **3a** (895 mg, 3.67 mmol) in THF (10.5 mL) and stirred at 25 °C for 15 h. The reaction was diluted with Et_2O (150 mL) and extracted with H_2O (2 × 50 mL) and brine (2 × 50 mL), dried (Na_2SO_4), filtered, and concentrated. The crude reaction mixture was crystallized from hexanes, giving the **4a** as white plates (339 mg, 65% yield). R_f 0.20 (10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.42 (bs, 1 H), 7.46 (d, J = 7.5 Hz, 2 H), 7.35 (t, J = 7.5 Hz, 2 H), 7.18 (d, J = 7.2 Hz, 1 H), 6.85−6.82 (m, 1 H),

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6.52 (bs, 1 H), 6.29 (q, J = 2.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 132.7, 132.0, 128.8, 126.1, 123.8, 118.8, 110.0, 105.9.

6-(4″-Iodophenyl)-5,5′-diphenylpyrromethene (5a). 2-Phenylpyrrole **4a** (1.06 g, 7.4 mmol), 4-iodobenzoyl chloride (2.0 g, 7.4 mmol), and 1,2-dichloroethane (37 mL) were heated to reflux for 45 h, during which time the solution gradually acquired a purple hue. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and extracted with H_2O (50 mL), 1 M HCl (50 mL), 1 M NaOH (50 mL), and brine (50 mL), dried (Na_2SO_4), filtered, and concentrated. The crude product was purified via flash chromatography on alumina using 30% CH_2Cl_2/hexanes as eluant, giving the title compound **5a** as a dark purple solid (1.94 g, 49% yield). R_f 0.63 (10% EtOAc/hexanes); mp 177−9 °C;^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.90 (d, J = 7.2 Hz, 4 H), 7.79 (d, J = 8.1 Hz, 2 H), 7.48 (t, J = 6.9 Hz, 4 H), 7.39 (d, J = 7.2 Hz, 2 H), 7.26 (d, J = 8.4 Hz, 2 H), 6.82 (d, J = 4.5 Hz, 2 H), 6.65 (d, J = 4.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.3, 137.6, 136.9, 132.5, 131.7, 130.4, 129.1, 128.4, 126.2, 125.2, 121.3, 115.9, 109.0.

4,4-Difluoro-8-(4′-iodophenyl)-3,5-diphenyl-4-bora-3a,4a-diaza-s-indancene (1a). Boron trifluoride etherate (3.4 g, 24 mmol) was added to a mixture of compound **5a** (1.94 g, 3.6 mmol), NEt_3 (1.8 g, 18 mmol), and PhMe (36 mL). The resulting solution was stirred at 25 °C for 10 min and then heated to 80 °C for 20 min. Fluorescence appeared 2 min after addition of BF_3 at 25 °C. The crude reaction mixture was filtered through a plug of SiO_2 on Celite and then concentrated. Purification via chromatography on basic alumina and a gradient of 10 to 20% $CHCl_3$/hexanes as eluant gave the title compound **1a** as a dark purple solid (750 mg, 36% yield). R_f 0.27 (40% $CHCl_3$/hexanes); mp 157−158 °C; MS (FAB$^+$, NBA) m/z (%) 546 (M^+); HRMS calculated [M + Na$^+$] 546.0580, found [M + Na$^+$] 546.0619; IR (neat) ν (cm^{-1}) 1560, 1542, 1284, 1144; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.88−7.82 (m, 6 H), 7.41−7.38 (m, 6 H), 7.30 (d, J = 8.4 Hz, 2 H), 6.83 (d, J = 4.2 Hz, 2 H), 6.60 (d, J = 4.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$ 75 MHz) δ 159.3, 137.6, 136.0, 133.8, 132.5, 132.1, 130.5, 129.6, 129.4, 128.2, 121.1, 96.6; ^{11}B NMR ($CDCl_3$, 64 MHz) δ −1.58 (t, J = 31 Hz).

***N-tert*-Butyloxycarbonyl-2-(1′-naphthyl)pyrrole (3b).** *N-tert*-Butyloxycarbonyl-2-bromopyrrole (4.00 g, 16.3 mmol), 1-naphthylboronic acid (2.80 g, 16.3 mmol), tetrakis(triphenylphosphine)palladium (370 mg, 0.33 mmol), Na_2CO_3 (16.3 mL, 32.5 mmol, 2.0 M aqueous solution), PhMe (88 mL), and MeOH (12 mL) were added to a Schlenk tube and heated to 80 °C for 18 h. The two layers were then separated, and the aqueous layer was back-extracted with ethyl ether (2 × 40−50 mL). The combined organic layers were washed with water (70 mL) and dried over $MgSO_4$. After concentration, the crude product was purified via flash chromatography using 1:7 EtOAc/hexanes as eluant giving the title compound **3b** (R_f 0.75) as colorless crystals (4.45 g, 93% yield). mp 78−79 °C; MS (FAB$^+$, NBA) m/z (%) 293 (M^+); HRMS calculated [M^+] 293.1416, found [M^+] 293.1418; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.92−7.84 (m, 2 H), 7.62−7.41 (m, 6 H), 6.39 (t, J = 3.8 Hz, 1 H), 6.31 (dd, J = 3.8, 2.2 Hz, 1 H), 0.88 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.9, 129.4, 128.7, 128.6, 127.9, 123.5, 122.9, 121.6, 121.4, 121.2, 120.6, 117.4, 110.6, 106.2, 78.5, 22.5.

2-(1′-Naphthyl)pyrrole (4b). A suspension of sodium methoxide (0.59 g, 10.8 mmol) in MeOH (3.0 mL) was added to a stirred solution of *N-tert*-butyloxycarbonyl-2-(1′-naphthyl)-pyrrole **3b** (1.05 g, 3.6 mmol) in THF (11 mL) and stirred at 25 °C for 12 h. The reaction was diluted with Et_2O (150 mL) and washed with H_2O (2 × 50 mL), dried ($MgSO_4$), filtered, and concentrated. The product was purified by flash chromatography using 1:4 EtOAc/hexanes as eluant (R_f 0.55) giving the title compound **4b** as a colorless oil which crystallizes on standing (550 mg, 78% yield). mp 172−173 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.10−8.15 (m, 1 H), 7.60−7.75 (m, 2 H), 7.35−7.14 (m, 4 H), 6.65−6.68 (m, 1 H), 6.35−6.39 (m, 1 H), 6.23−6.26 (m, 1 H). The analytical data are in accord with those reported.[14]

6-(4″-Iodophenyl)-5,5′-bis(1-naphthyl)pyrromethene (5b). 2-(1′-Naphthyl)pyrrole **4b** (153 mg, 0.79 mmol), 4-iodobenzoyl chloride (422 mg, 1.58 mmol), and 1,2-dichloroethane (4 mL) were heated to reflux for 19 h, during which time the solution gradually acquired a purple hue. Without workup the crude product was purified via chromatography on basic alumina using 20% ethyl ether/hexanes (R_f 0.45) as eluant giving the title compound **5b** as a dark purple solid (70 mg, 29% yield). mp 177−178 °C; MS (FAB$^+$, NBA) m/z (%) 599 (M^+), HRMS calculated [M^+] 599.0984, found [M^+] 599.1039; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.75 (d, J = 7.2 Hz, 2 H), 7.94−7.82 (m, 8 H), 7.54−7.31 (m, 8 H), 6.89 (d, J = 4.2 Hz, 2 H), 6.80 (d, J = 4.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.7, 141.5, 138.3, 137.0, 134.1, 132.6, 131.3, 130.9, 129.3, 128.9, 128.5, 127.4, 126.9, 126.7, 126.0, 125.2, 119.6, 95.0.

4,4-Difluoro-8-(4′-iodophenyl)-1,7-bis(1′-naphthyl)-4-bora-3a,4a-diaza-s-indancene (1b). Compound **5b** (30 mg, 0.05 mmol), boron trifluoride etherate (36 mg, 0.25 mmol), NEt_3 (15 mg, 0.15 mmol), and anhydrous PhMe (3 mL) were heated to 80 °C for 20 min. The crude reaction mixture was subjected to flash chromatography (R_f 0.38) on silica using 50% $CHCl_3$/hexanes as eluant, giving the title compound **1b** as a dark purple solid (29 mg, 90% yield). mp 165−166 °C (dec); MS (FAB$^+$, NBA) m/z (%) 646 (M^+); HRMS calculated [M^+] 646.0895, found [M^+] 646.0910; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.99 (d, J = 7.2 Hz, 2 H), 7.89−7.76 (m, broadened by coalescence, 8 H), 7.50 (d, J = 7.2 Hz, 2 H), 7.54−7.38 (m, broadened by coalescence, 6 H), 7.02 (d, J = 4.2 Hz, 2 H), 6.65 (d, J = 4.2 Hz, 2 H); in d_8-toluene at 80 °C, the broad naphthyl signals are sharp multiplets. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 157.78, 143.1, 137.7, 135.3, 133.8, 133.3, 132.1, 131.9, 130.0, 129.7, 129.6, 128.4, 128.4 (br), 126.3, 125.9, 124.9 (br), 122.8, 96.8; ^{11}B NMR ($CDCl_3$, 64 MHz) δ −1.92 (t, J = 30.3 Hz).

***N-tert*-Butoxycarbonyl-2-(4′-fluorophenyl)pyrrole (3d).** A Schlenk tube was charged with *N-tert*-butyloxycarbonyl-2-bromopyrrole (2.00 g, 8.13 mmol), 4-fluorophenylboronic acid (1.14 g, 8.13 mmol), and tetrakis(triphenylphosphine)palladium (190 mg, 0.16 mmol). The vessel was evacuated and then refilled with nitrogen three times. Freshly distilled toluene (44 mL) and degassed methanol (6 mL) were added via syringe. Degassed 2 M Na_2CO_3(aq) (8.13 mL, 16.26 mmol) was added, and then the mixture was stirred under a nitrogen atmosphere at 80 °C for 20h. Two layers formed. These were separated, and the organic layer was dried (Na_2SO_4) and then evaporated. The resulting oil was purified by flash chromatography eluting with 5% EtOAc/hexanes to yield 2.1 g of the compound **3d** (99% yield) as a clear oil. MS (FAB+, NBA) m/z (%) 261 (M^+); HRMS calculated [M^+] 261.1165, found [M^+] 261.1190; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.37 (dd, J = 3.3 Hz, 1.8 Hz, 1 H), 7.32 (dd, J = 8.9 Hz, 5.4 Hz, 1 H), 7.05 (t, J = 8.9 Hz, 1 H), 6.23 (t, J = 3.3 Hz, 1 H), 6.17 (dd, J = 3.3, 1.8 Hz, 1 H), 1.40 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.1 (d, J = 245 Hz, CF), 149.2, 133.8, 130.8 (d, J = 8.0 Hz, CH), 122.4, 114.5 (d, J = 4.5 Hz, CH), 114.2, 110.4, 83.6, 27.5.

2-(4′-Fluorophenyl)pyrrole (4d). A suspension of sodium methoxide (1.11 mg, 6.50 mmol) in MeOH (5 mL) was added to a stirred solution of *N-tert*-butyloxycarbonyl-2-(4′-fluorophenyl)pyrrole **3d** (1.11 g, 19.51 mmol) in THF (25 mL) and stirred at 25 °C for 2 h. The reaction was diluted with Et_2O (30 mL) and extracted with H_2O (2 × 20 mL) and brine (2 × 20 mL), dried (Na_2SO_4), filtered, and concentrated. The crude reaction mixture was purified on silica gel via flash chromatography using 10% EtOAc/hexanes as eluant. Compound **4d** was isolated as white plates (940 mg, 98% yield). mp 119−120 °C; R_f 0.38 (10% EtOAc/hexanes);^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.39 (m, 2 H), 7.02−7.08 (m, 2 H), 6.83−6.85 (m, 1 H), 6.43−6.46 (m, 1 H), 6.27−6.30 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 161.5 (d J = 244 Hz), 130.3 (d, J = 155 Hz), 125.5 (d, J = 8 Hz), 121.2, 118.8, 115.8 (d, J = 21 Hz), 110.1, 105.8.

6-(4″-Iodophenyl)-5,5′-bis(4-fluorophenyl)pyrromethene (5d). 2-(4′-Fluorophenyl)pyrrole **4d** (1.00 g, 6.17 mmol), 4-iodobenzoyl chloride (3.78 g, 14.2 mmol), and 1,2-dichloroethane (20 mL) were heated to reflux for 2 d, during which time the solution gradually changed to purple. The reaction mixture was diluted with CH_2Cl_2 (50 mL), extracted with H_2O (50 mL), dried (Na_2SO_4), filtered, and concentrated. The crude product was purified via flash chromatography using 20% EtOAc/hexanes as eluant giving **5d** as a dark purple

solid (1.35 g, 82% yield). mp 168−179 °C (dec); R_f 0.71 (10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.79−7.87 (m, 4 H), 7.26 (d, J = 8.4 Hz, 4 H), 7.17 (t, J = 8.7 Hz, 4 H), 6.77 (d, J = 4.2 Hz, 2 H), 6.65 (d, J = 4.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 185.6, 164.9, 153.4, 141.6, 137.0, 132.5, 129.8, 129.5, 127.9, 127.8, 116.3, 116.0, 115.7.

4,4-Difluoro-8-(4′-iodophenyl)-3,5-bis-(4′-fluorophenyl)-4-bora-3a,4a-diaza-s-indancene (1d). Compound **5d** (590 mg, 1.1 mmol), NEt_3 (0.462 mL, 3.3 mmol), and PhMe (30 mL) were stirred at 25 °C for 10 min. Boron trifluoride etherate (0.696 mL, 5.5 mmol) was added, and the reaction mixture was heated to 80 °C for 20 min and then cooled to 25 °C. The crude mixture was purified on basic alumina using 10% EtOAc/hexanes as eluant to yield **1d** as a dark purple solid (634 mg, 99%). R_f 0.2 (10% EtOAc/hexanes); mp 88−90 °C; MS (FAB$^+$, NBA) *m/z* (%) 582(M^+); HRMS calculated [M^+] 582.0389, found [M^+] 582.0460; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.83 (m, 6 H), 7.30 (d, J = 8.1 Hz, 2 H), 7.1 (t, J = 8.6 Hz, 4 H), 6.85 (d, J = 4.2 Hz, 2 H), 6.59 (d, J = 4.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 163.6 (d, J = 251 Hz, CF), 158.1, 142.7, 137.6, 136.0, 133.6, 132.0, 131.5 (d, J = 4 Hz, CH), 130.7, 128.5 (d, J = 3 Hz, C), 121.0, 115.5 (d, J = 22 Hz, CH), 96.8; ^{11}B NMR ($CDCl_3$, 64 MHz) δ −1.64 (t, J = 31.7 Hz).

***N-tert*-Butoxycarbonyl-2-(2′-methoxyphenyl)pyrrole (3e).** A Schlenk tube was charged with *N-tert*-butyloxycarbonyl-2-bromopyrrole (1.50 g, 6.10 mmol), 2-methoxyphenylboronic acid (0.93 g, 6.10 mmol), and tetrakis(triphenylphosphine)-palladium (0.35 g, 0.31 mmol). The vessel was evacuated and then refilled with nitrogen three times. Freshly distilled toluene (32 mL) and degassed methanol (4 mL) were added via syringe. Degassed 2 M Na_2CO_3 (aq) (6.1 mL, 12.196 mmol) was added. The mixture was stirred under a nitrogen atmosphere at 80 °C (oil bath) for 20 h. The layers were separated, and the organic layer was dried (Na_2SO_4) and then evaporated. The resulting oil was purified by flash chromatography, eluting with 5% EtOAc/hexanes to yield 1.65 g of the desired compound **3e** (99% yield) as a clear oil. R_f 0.25 (5% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.4 (dd, J = 3.3, 1.8 Hz, 1 H), 7.32 (tdd, J = 3.0, 1.8 Hz, 2 H), 7.00 (td, J = 7.4, 0.9 Hz, 1 H), 6.90 (dd, J = 8.0, 0.9 Hz, 1 H), 6.28 (t, J = 3.3 Hz, 1 H), 6.18 (dd, J = 3.3, 1.8 Hz, 1 H), 3.79 (s, 3 H), 1.36 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 157.3, 149.4, 130.2, 128.9, 124.2, 121.8, 124.2, 121.8, 120.2, 113.8, 110.3, 109.9, 82.7, 27.5.

2-(2′-Methoxyphenyl)pyrrole (4e).[14] A suspension of sodium methoxide (625 mg, 11.0 mmol) in MeOH (3.0 mL) was added to a stirred solution of *N-tert*-butyloxycarbonyl-2-(2′-methoxyphenyl)pyrrole **3e** (1.0 g, 3.66 mmol) in THF (15 mL) and stirred at 25 °C for 6 h. The reaction was diluted with Et_2O (30 mL), extracted with H_2O (2 × 20 mL) and brine (2 × 20 mL), dried (Na_2SO_4), filtered, and concentrated. The crude reaction mixture was purified on silica gel via flash chromatography using 10% EtOAc/hexanes, giving **4e** as white plates (580 mg, 91.5% yield). R_f 0.37 (10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.72 (d, J = 7.5 Hz 1 H), 7.21 (t, J = 7.5 Hz, 1 H), 7.00−7.06 (m, 2 H), 6.90−6.93 (m, 1 H), 6.67−6.69 (m, 1 H), 6.31−6.35 (m, 1 H), 4.0 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.7, 129.8, 126.7, 126.6, 121.4, 121.1, 117.8, 111.7, 108.9, 106.1, 55.6.

6-(4″-Iodophenyl)-5,5′-bis(2-methoxyphenyl)pyrromethene (5e). 2-(2′-Methoxyphenyl)pyrrole **4e** (430 mg, 2.48 mmol), 4-iodobenzoyl chloride (1.12 g, 4.97 mmol), and 1,2-dichloroethane (10 mL) were heated to reflux for 3 d, during which time the solution gradually turned deep green. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and extracted with H_2O (50 mL), dried (Na_2SO_4), filtered, and concentrated. The crude product was purified via flash chromatography using 20% EtOAc/hexanes as eluant, giving **5e** as a dark purple solid (450 mg, 65% yield). R_f 0.43 (20% EtOAc/hexanes); mp 177−178 °C; MS (FAB$^+$, NBA) *m/z* (%) 599 (M^+); HRMS calculated [M^+] 599.0906, found [M^+] 599.0883; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.07 (dd, J = 1.8, 7.8 Hz, 2 H), 7.83 (d, J = 8.4 Hz, 2 H), 7.34−7.40 (m, 2 H), 7.30 (d, J = 5.7 Hz, 2 H), 7.09 (d, J = 7.5 Hz, 2 H), 7.04 (d, J = 8.1 Hz, 2 H), 6.97 (d, J = 4.5 Hz, 2 H), 6.42 (d, J = 4.5 Hz, 2 H), 3.89 (s, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 157.3, 152.6, 140.6, 137.5, 136.7, 132.7, 129.8, 129.0, 128.3, 122.4, 120.9, 118.6, 111.6, 95.6, 55.9.

4,4-Difluoro-8-(4′-iodophenyl)-3,5-bis-(2-methoxyphenyl)-4-bora-3a,4a-diaza-s-indancene (1e). Compound **5e** (100 mg, 0.179 mmol), NEt_3 (0.075 mL, 0.537 mmol), and PhMe (5 mL) were stirred at 25 °C for 10 min. Boron trifluoride etherate (0.113 mL, 0.896 mmol) was added, and the reaction mixture was heated to 80 °C for 20 min. The crude mixture was purified on basic alumina using 10% EtOAc/hexanes to yield **1e** as a dark purple solid (102 mg, 93.9%). R_f 0.2 (10% EtOAc/hexanes); mp 109−110 °C; MS (FAB$^+$, NBA) *m/z* (%) 606 (M^+); HRMS calculated [M^+] 606.0883, found [M^+] 606.0901; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.91 (d, J = 8.1 Hz, 2 H), 7.75 (dd, J = 7.6, 1.2 Hz, 2 H), 7.38 (d, J = 8.4 Hz, 2 H), 7.34−7.39 (m, 2 H), 7.02 (td, J = 7.6, 1.2 Hz, 2 H), 6.95 (d, J = 8.4 Hz, 2 H), 6.85 (d, J = 4.2 Hz, 2 H), 6.63 (d, J = 4.2 Hz, 2 H), 3.80 (s, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 157.5, 155.7, 143.2, 137.4, 135.1, 134.0, 132.0, 131.8, 130.6, 129.3, 122.5, 121.8, 120.2, 110.9, 96.3, 55.7; ^{11}B NMR ($CDCl_3$, 64 MHz) δ −1.26 (t, J = 30.6 Hz).

Spectroscopic Measurements. Absorption spectra were recorded on a GBC 912 (GBC Scientific Equipment Pty, Ltd, Australia) absorption spectrometer. The steady-state fluorescence emission and excitation spectra were obtained by using a SPEX Fluorolog 112 instrument (SPEX Industries, Metuchen NJ). The fluorimeter was calibrated by using a standard lamp from the Swedish National Testing and Research Institute (Borås, Sweden). All fluorescence spectra were corrected. The fluorescence quantum yield (Φ_{exp}) was calculated from eq 1.[24]

$$\Phi_{exp} = \Phi_{ref} \frac{F\{1 - \exp(-A_{ref} \ln 10)\} n^2}{F_{ref}\{1 - \exp(-A \ln 10)\} n_{ref}^2} \quad (1)$$

Here, F denotes the integral of the corrected fluorescence spectrum, A is the absorbance at the excitation wavelength, and n is the refractive index of the medium. The reference systems used were fluorescein (Φ_{ref} = 0.92[25] and 0.93[26]), rhodamine 101 methyl ester (Φ_{ref} = 1.0),[27] and *N,N′*-bis(1-hexylheptyl)-3,4:9,10-perylenebis(dicarboxyimide) (Φ_{ref} = 1.0).[28]

Radiative lifetimes (τ_0 in ns) were calculated from the modified Strickler−Berg (eq 2).[16]

$$\frac{1}{\tau_0} = 2.88 \times 10^{-9}\, n^2 \frac{\int_{fl.spec.} F(\tilde{\nu}) d\tilde{\nu}}{\int_{fl.spec.} F(\tilde{\nu}) \tilde{\nu}^{-3} d\tilde{\nu}} \int_{abs.spec.} \epsilon(\tilde{\nu}) \tilde{\nu}^{-1} d\tilde{\nu} \quad (2)$$

Here $F(\tilde{\nu})$, $\tilde{\nu}$, and $\epsilon(\tilde{\nu})$ denote the corrected fluorescence spectrum, the wavenumber of light (cm^{-1}), and the molar absorptivity, respectively. The refractive indices were measured and found to be n = 1.33 for buffer solution (pH = 9), n = 1.36 in ethanol, n = 1.42 for methylene chloride, and n = 1.45 for chloroform.

Förster radii (R_0)[17] were determined as follows. The corrected fluorescence spectrum and the measured molar absorptivity (in units of M^{-1} cm^{-1}) were used to calculate the Förster radius from:

$$R_{of} = \left\{ \frac{9000 \ln 10 \langle \kappa^2 \rangle \Phi J}{128 \pi^5 n^4 N_A} \right\}^{1/6} \quad (3a)$$

where

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$$J = \int \epsilon(\tilde{\nu}) f(\tilde{\nu}) \tilde{\nu}^{-4} \mathrm{d}\tilde{\nu} \tag{3b}$$

and

$$f(\tilde{\nu}) = \frac{F(\tilde{\nu})}{\int F(\tilde{\nu}) \mathrm{d}\tilde{\nu}} \tag{3c}$$

Here, N_A is the Avogadro constant, and the mean value of the orientational part of a dipole−dipole interaction is denoted by $\langle \kappa^2 \rangle$. In the calculation of the Förster radius, it is convenient to choose $\langle \kappa^2 \rangle = {}^2/_3$ as a reference state. The Förster radius using this reference value is denoted by R_0.

The time-correlated single-photon-counting experiments were performed on a PRA 3000 system (Photophysical Research Assoc. Inc., Ontario, Canada). The excitation source was a thyratron-gated flash lamp (Model 510C, PRA) filled with deuterium gas and operated at ca. 30 kHz. Excitation wavelengths were selected by interference filters (Omega/Saven AB, Sweden) centered at 500 nm (HBW = 12.1 nm) and 550 nm (HBW = 40 nm). The emission wavelengths were selected by an interference filter centered at 550 nm (HBW = 40 nm) and a long-pass filter of $\lambda > 610$ nm (Schott, Germany). The instrument response function was determined by using a light-scattering solution (LUDOX).

Cyclic Voltammetry. These experiments were conducted in anhydrous acetonitrile at room temperature. The potentials are reported vs ferrocene as internal standard using a scan rate of 100 mV s^{-1}, glassy carbon working electrode, $Ag/AgNO_3$ reference electrode, platinum counterelectrode, and a supporting electrolyte 0.1 M tetrabutylammonium hexafluorophosphate.

Crystal data (1b): $C_{35}H_{22}BF_2IN_2$, $M = 646.26$, monoclinic, $a = 12.278(3)$, $b = 14.203(3)$, $c = 16.332(3)$ Å, $\alpha = 90°$, $\beta = 109.20(3)°$, $\gamma = 90°$, $V = 2689.6(9)$ Å^3, space group $P2(1)/n$, $Z = 4$, $D_{calcd} = 1.596$ g cm^{-3}, abs coeff = 1.234 mm^{-1}, $F(000) = 1288$, Mo Kα $\lambda = 0.71073$ Å. The data were collected by ω scanning techniques, at 298 K on a Siemens R3 X-ray diffractometer in the range $2.64 < \Theta < 25.08°$; 9702 reflections were collected, corrected for Lorentzian polarization and absorption effects, of which 4740 were independent reflections [R(int) = 0.1196]. The structure solution was made using Direct Methods[29] and L.S. refinement of 370 parameters[30] on F^2 yielded final R indices [$I > 2\sigma(I)$]: $R(F) = 0.0676$ $wR(F^2) = 0.1291$; R indices (all data): $R(F) = 0.1776$; $wR(F^2) = 0.1638$. Hydrogens were placed on ideal positions, and the structural factors used were taken from The Tables for X-ray Crystallography (Vol. A).

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Supporting Information Available: Crystallographic data for compound **1b**; absorption and fluorescence emission spectra for compounds **1a**−**e**, **7a** and **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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