Boron-dipyrromethene dyes for incorporation in synthetic multi-pigment light-harvesting arrays

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Abstract: The synthesis of light-harvesting arrays requires modular pigment building blocks. Boron-dipyrromethene dyes are well-suited for the photochemical sensitization of free base or metalloporphyrins. Direct access to boron-dipyrromethene dyes bearing reactive substituents is provided by a simple synthetic route involving two one-flask reactions. Reaction of pyrrole or 2-methylpyrrole with an aldehyde under gentle acid catalysis affords the corresponding dipyrromethane. Subsequent oxidation (DDQ or *p*-chloranil) and complexation affords the dye. Boron-dipyrromethene dyes bearing iodo- or ethynyl-phenyl substituents at the *meso*-position have been prepared as modular components for building block applications. These dyes are stable, accessible, and have suitable spectroscopic features for use as porphyrin accessory pigments in light-harvesting arrays.
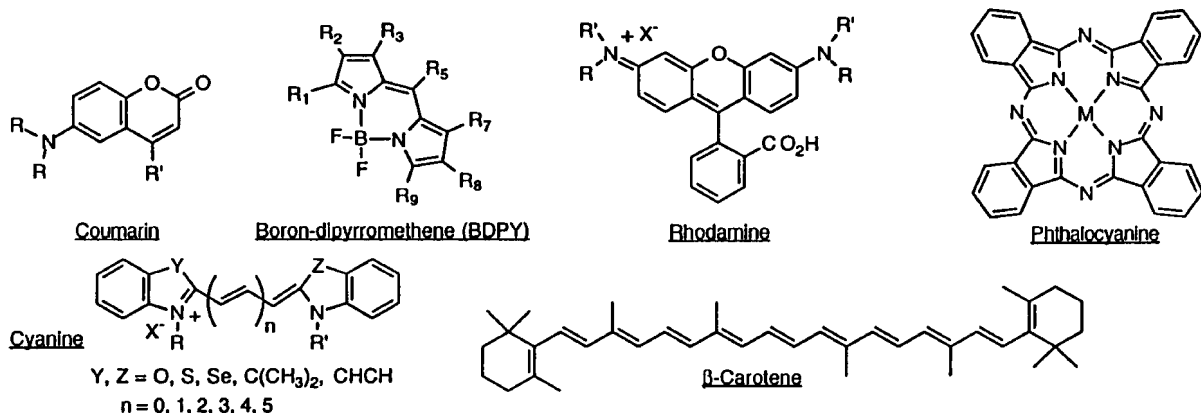
INTRODUCTION

Light-harvesting, the absorption of light and the efficient migration of the resulting excited singlet state among an array of pigments, constitutes the first step of photosynthesis (1,2). Synthetic light-harvesting systems are of great interest for probing mechanisms of electronic energy migration among pigments, and may provide the basis for new types of molecular photonic devices. The synthetic challenges in preparing light-harvesting systems are considerable, as a large number of pigments must be arranged in close proximity in a defined architecture. Among various pigments, members of the porphyrin family are attractive due to their strong absorption, their facile excited state energy and electron transfer reactions, and their close resemblance to the chlorophylls. The porphyrins absorb strongly in the blue but have rather weak absorptions across the remainder of the visible spectrum, including the red region. To effectively capture visible light, accessory pigments are necessary that absorb strongly in regions of the spectrum where porphyrins are relatively transparent. In addition, the appropriate choice of accessory pigments can provide an opportunity to introduce excitations selectively at particular sites in a multi-pigment array, assuming the absorption bands of the component chromophores are fairly well preserved upon formation of the array.

Recently we developed a building block approach for synthesizing light-harvesting arrays comprised of porphyrins (3-5). This synthetic approach uses porphyrin building blocks bearing peripheral functional groups that are joined covalently in a controlled manner during the construction of the array. To include pigments that will sensitize porphyrins in these arrays, a pigment must have appropriate synthetic and photophysical properties. The properties of an ideal porphyrin accessory pigment would include:

- intense absorption band in a region where the porphyrin absorbs weakly, i.e., to the blue (<400 nm) of the porphyrin Soret band, sensitizing S_2, or in the visible region (440 - 600 nm), sensitizing S_1.

- sharp long-wavelength absorption band, so that all molecules of one type yield nearly the same excited state energy.
- wavelength of absorption tunable by synthetic design, so that the chemistry developed for one type of pigment can be extended to all members of the same class.
- excited state lifetime of sufficient duration for quantitative energy transfer to the porphyrin, though large lifetime differences among classes of pigments can be tolerated and still achieve efficient transfer by use of the appropriate molecular architecture.
- stability toward repetitive photochemical excitation.
- synthetic compatibility with a modular building block approach.
- high (organic) solubility to facilitate synthesis, characterization, and photochemical analysis.
- ease of purification by liquid chromatography (size exclusion or adsorption).

A selection of pigments absorbing in the visible region of the spectrum, and their typical spectral parameters, are shown in Table 1. These values are quite general and can vary for specific pigments in specific environments, as well as derivatives of these structures. Covalent model systems containing a porphyrin and one or more pigments have been prepared where the pigment is a carotene (6) or related polyene (7), cyanine (8), rhodamine (3), phthalocyanine (9), or boron-dipyrromethene (BDPY) dye (5). The fluorescence quantum yield (Φ_f) provides one measure of the properties of the excited singlet state, though a high fluorescence yield is not necessary for efficient energy transfer. Indeed, pigments with very low fluorescence yields can function as efficient accessory pigments (vide infra).

Coumarin   Boron-dipyrromethene (BDPY)   Rhodamine   Phthalocyanine

Cyanine

Y, Z = O, S, Se, C(CH₃)₂, CHCH
n = 0, 1, 2, 3, 4, 5

β-Carotene

Each class of pigment has pros and cons for incorporation into light-harvesting systems, as no one pigment class possesses all of the idealized properties enumerated above. Coumarins have high fluorescence yields but only modest absorption coefficients, and their absorption is in the blue where porphyrins absorb strongly. Carotenes are neutral and non-polar, have high absorption coefficients, some degree of wavelength tunability, but extremely low fluorescence yields. Nonetheless the carotenes undergo energy transfer to porphyrins with high efficiency when the appropriate distance and orientation criteria are satisfied (6). Cyanine dyes have wavelength tunability across the entire visible range and into the near-IR, high absorption coefficients, generally modest fluorescence yields, but can undergo thermal and photoinduced cis-trans isomerization (25). Rhodamines have little wavelength tunability, high absorption coefficients, and high fluorescence yields. Cyanine dyes and rhodamines each bear a permanent positive charge, and their ionic nature presents problems in most chromatographic methods of purification, especially when covalently attached to neutral non-polar porphyrins. Phthalocyanines absorb strongly in the red, have high fluorescence yields in the appropriate metalation state, but the long-wavelength absorption is at lower energies than that of the porphyrins, consequently the phthalocyanines cannot be used to sensitize porphyrins. The boron-dipyrromethene (BDPY) pigments have sharp absorption bands with modest

TABLE 1. Typical spectral parameters of some pigments.

Pigment	λ range (nm)	ε (M^{-1}cm^{-1})	Φ$_f$ range	polarity
coumarins	320-460[a]	15,000 - 50,000[a]	0.5 - 0.8[b]	neutral, non-polar
β-carotene	452[c]	139,000[c]	~0[d]	neutral, non-polar
cyanines	400 - 900[e]	100,000 - 250,000[f]	~0 - 0.5[f]	ionic
rhodamines	520 - 580[a]	70,000 - 140,000[a]	0.6 - 1.0[g]	ionic
phthalocyanines	665 - 700[h]	80,000 - 280,000[h]	~0 - 0.7[i]	neutral, non-polar
BDPY	480 - 550[j,k]	40,000 - 100,000[j,k]	0.02 - 1.0[k,l]	neutral, polar

a (10); b (11); c (12); d (13); e (14); f (15); g (16); h (17); i (18); j (19-23); k (this work); l (20-24).

extinction coefficients, modest fluorescence quantum yields, and are polar but non-ionic. Though boron-dipyrromethene dyes have lower extinction coefficients than rhodamines, cyanines, and carotenes, lower fluorescence quantum yields than rhodamines, and relatively little wavelength tunability compared with the cyanines, their sharp absorption band around 500 nm and their non-ionic nature make them especially attractive for incorporation into synthetic light-harvesting systems.

The boron-dipyrromethene dyes were first prepared by Treibs and Kreuzer in 1968 (19). The complexation of dipyrromethenes with metals such as Zn, Co, Cu, Ni, Pt was known a generation earlier, but these metals give bis-dipyrromethene complexes and can undergo exchange (26). Treibs and Kreuzer described two synthetic routes to monomeric, stable boron-dipyrromethene (BDPY) complexes. First, the BF$_3$-catalyzed condensation of 2,5-dimethylpyrrole with acetic anhydride affords the corresponding pentamethyl, mono- or bis-acylated BDPY dyes in < 10% yield. Alternatively, treatment of a dipyrromethene with triethylamine and BF$_3$-etherate affords the BDPY dye in 55-80% yield. The former method affords symmetric dyes while the latter is applicable to any dipyrromethene regardless of the pyrrole substitution pattern, though the synthesis of asymmetric dipyrromethenes often requires syntheses of pyrroles and can be low-yielding. In applying the dipyrromethene-complexation procedure, Vos de Wael and co-workers found that dipyrromethenes with less than three alkyl substituents decomposed slightly and the parent unsubstituted dipyrromethene decomposed completely (20).

The BDPY dyes have been exploited as fluorescent probes in life sciences applications (21,22). Numerous BDPY dyes now are commercially available (27). Most of these have flexible tethers linking the pyrrole moiety of the BDPY to a reactive functional group for attachment to biomolecules. As part of our building block approach to multi-pigment light-harvesting arrays, we sought BDPY dyes bearing functional groups attached to a rigid linker so that the resulting structure would be well-defined. The best coupling strategy that we have found joins ethyne and iodo-substituted building blocks via neutral, copper-free Pd-mediated coupling reactions (1-2 h at 35 °C), and affords diphenylethyne linked arrays in 60-80% yields (28). In order to incorporate boron-dipyrromethene dyes into this modular approach, we have designed, synthesized, and characterized BDPY dyes bearing ethyne or iodo groups. The use of these dyes as porphyrin accessory pigments in multi-pigment arrays will be described elsewhere.

RESULTS AND DISCUSSION

We have developed two approaches for introducing functionality into BDPY dyes that avoid laborious syntheses of pyrrole derivatives. The first approach mirrors the two-step room temperature synthesis of *meso*-porphyrins (29). This porphyrin synthesis uses pyrrole and takes advantage of the wide assortment of available benzaldehyde building-blocks to introduce functionality at the porphyrin *meso*-position. Through the use of 2-methyl pyrrole rather than pyrrole, reaction with an aldehyde can occur at the one free α-position but cannot proceed beyond the dipyrromethane stage.

Thus 4-iodobenzaldehyde condensed readily with two equiv of 2-methylpyrrole under nearly the same conditions for pyrrole-aldehyde condensation in the porphyrin synthesis (10^{-2} M pyrrole and 10^{-3} M trifluoroacetic acid in CH_2Cl_2 at room temperature for 1.5 h). Consumption of the aldehyde was monitored by thin layer chromatography. A simple base wash followed by removal of the solvent and quick vacuum desiccation gave dipyrromethane 1a in 95% yield. Dipyrromethane 1a is a stable compound and could be stored in the freezer for 3 months before signs of discoloration developed. Subsequent treatment of 1a with 2,3,5,6-tetrachloro-1,4-benzoquinone (p-chloranil) afforded a black reaction mixture. When thin layer chromatography showed that all of the starting dipyrromethane had been consumed, triethylamine and BF₃-etherate were added in that sequence. Silica gel column chromatography gave the BDPY 1 in 15% yield (14% overall). These conditions for boron complexation are nearly identical to those of Treibs and Kreuzer (19). BDPY 2 was prepared in 8.2% overall yield via dipyrromethane 2a in identical manner. This route embodies several features of the two-step room temperature synthesis of meso-porphyrins, including pyrrole-aldehyde condensation conditions, subsequent oxidation with p-chloranil, and use of the aldehydic compound to introduce functionality into the target molecule.

Scheme 1. Synthesis of 1,9-dimethyl-boron dipyrromethene dyes.
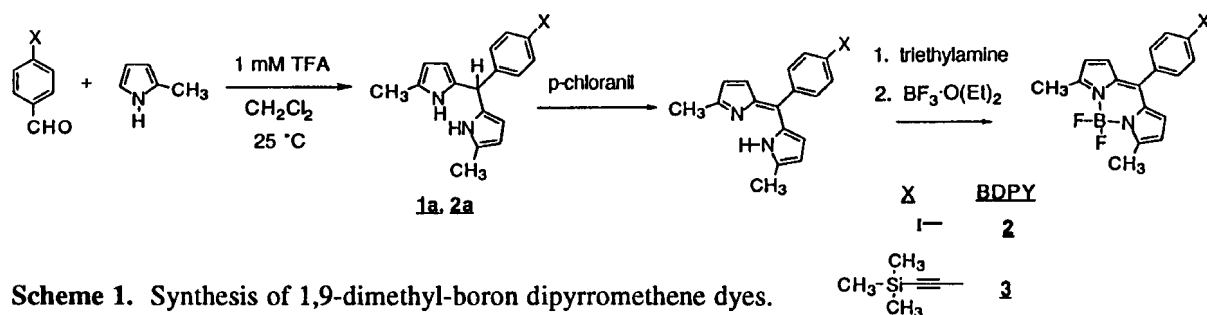
The first route employed 2-methyl pyrrole to cause pyrrole-aldehyde condensation to stop at the dipyrromethane stage. Recently we discovered a one-flask "solventless" method for preparing dipyrromethanes lacking any α- or β-substituents (30). In this method an aldehyde is dissolved in excess pyrrole at room temperature, and upon adding acid the dipyrromethane is formed selectively. The dipyrromethanes are stable to routine handling, can be chromatographed under neutral or slightly basic conditions, and are isolated in 45-80% yield. Taking advantage of this route, 5-phenyldipyrromethane was prepared and treated successively with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), triethylamine, and BF₃-etherate (Scheme 2). In contrast to the syntheses of 1 and 2, the dipyrromethane was not completely oxidized with p-chloranil, thus the more potent oxidant DDQ was employed. DDQ instantaneously gave complete oxidation and 3 was obtained easily by chromatography in 22% yield from the dipyrromethane. These data show that a boron-dipyrromethene dye lacking any α- or β-substituents can be prepared in a straightforward manner.

Scheme 2. Synthesis of a boron dipyrromethene dye lacking α- and β-substituents.
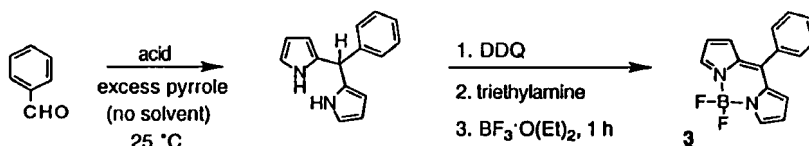
The BDPY dyes 1 and 2 are equipped for incorporation in multi-pigment arrays. The iodo and ethyne groups provide useful handles that can be joined via Pd-mediated coupling reactions. BDPY 2 has been incorporated as the input chromophore in a molecular photonic wire (5). Attempts to deprotect 3 using tetrabutylammonium fluoride in tetrahydrofuran led to decomposition of the dye. This perhaps is not
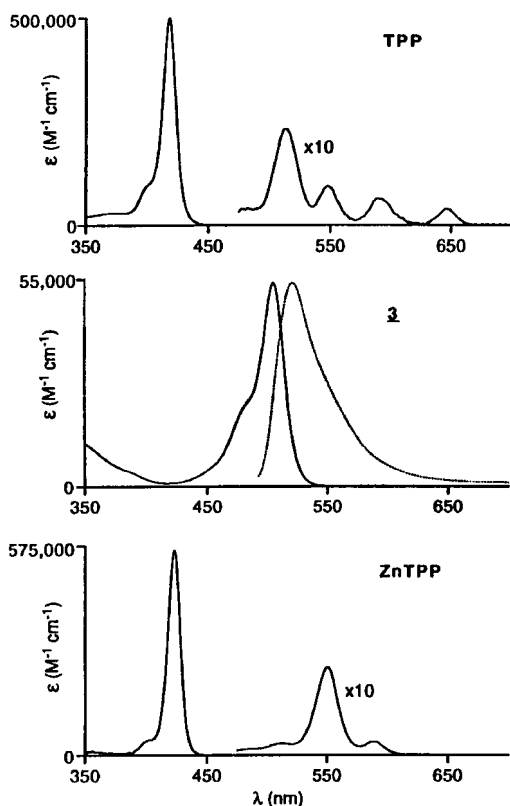
TABLE 2. Spectroscopic properties of boron-dipyrromethene dyes **1-3** at room temperature.

Compound	λ_{abs} (nm)	fwhm (nm)	ε ($M^{-1}cm^{-1}$)	λ_{em} (nm)	Φ_f[a]
In toluene:					
1	515	25	59,000	532	0.22
2	516	25	48,800	535	0.078
3	503	25	54,000	521	0.053
In ethanol:					
1	511	23		526	0.14
2	512	24		529	0.047
3	499	25		514	0.025

[a]Quantum yields were determined by ratioing integrated corrected emission spectra to Rhodamine 123 (16); see Experimental section.

Figure 1. Absorption and fluorescence spectra of BDPY **3**, and the absorption spectra of two porphyrins. For comparison, tetraphenylporphyrin (TPP) has $\varepsilon_{514\ nm} = 23,000$ $M^{-1}cm^{-1}$, and its zinc chelate ZnTPP has $\varepsilon_{550\ nm} = 24,000\ M^{-1}cm^{-1}$ (32).

surprising, given the known sensitivity of the less substituted dipyrromethenes to nucleophiles (31). However, the trimethylsilyl group was removed cleanly (80% isolated yield) upon treating **3** with two equiv of K_2CO_3 in a solution of tetrahydrofuran/methanol (3:1) for 30 min at room temperature.

The absorption spectra of dyes **1-3** complement the absorption spectra of tetraphenylporphyrin (TPP) and its zinc chelate, ZnTPP (Figure 1). The absorption spectra of **1-3** are relatively sharp with a full width at half maximum (fwhm) of ~25 nm, and are relatively insensitive to changes in solvent polarity. The spectroscopic properties are summarized in Table 2.

The fluorescence quantum yields of dyes **1-3** are low compared with those of many other dipyrromethene dyes. Comparison of a family of BDPY dyes showed that the quantum yields of fluorescence were between 0.33 and 0.81 depending on the alkyl substitution pattern about the BDPY nucleus (20), while the unsubstituted parent BDPY has a fluorescence quantum yield of ~0.9 (24). The commercially available BDPY dyes generally have quantum yields greater than 0.5 (27). None of these compounds has the same substitution pattern as is present with **1-3**, nor do any have a phenyl group at the *meso*-position. Further studies are required to identify the source of the low fluorescence yields in **1-3**.

High fluorescence efficiency is of paramount importance if the BDPY is to serve as a fluorescent probe, as is the case in many biological applications, but a relatively low fluorescence yield is tolerable for dyes that serve as sensitizers. Efficient energy transfer (>80%) has been shown to occur in covalent sensitizer-porphyrin conjugates, where the sensitizer is a carotene ($\Phi_f < 10^{-4}$, ref 6), cyanine dye ($\Phi_f \leq 0.05$, ref 8), or zinc-porphyrin ($\Phi_f = 0.03$, ref 4). Efficient energy transfer also occurs from a BDPY (resembling **2**, Φ_f ~0.1) to a zinc porphyrin attached via a diphenylethyne linker (5). The ability to achieve efficient energy transfer with these BDPY dyes, in conjunction with their sharp absorption bands, facile syntheses via two simple routes to dipyrromethanes, and modular building block features should lead to wide applications in light-harvesting studies.

NOMENCLATURE

Several different nomenclatures have been employed over the years for dipyrromethanes, their oxidized counterparts (dipyrromethenes, also known as dipyrrins), and the coordination compounds of the dipyrromethenes. We have followed IUPAC nomenclature for dipyrromethanes (33) and have extended this to the boron dipyrromethene complexes. In effect this updates the simple nomenclature originally employed by Treibs (19) and has the advantage that the numbering schemes for dipyrromethenes and the boron complexes are identical. The trivial names dipyrromethene and dipyrrin (33) have been used here interchangeably.
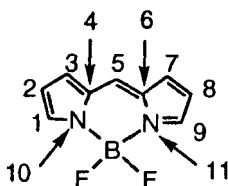
EXPERIMENTAL

4-Iodobenzaldehyde (Karl Industries, Inc.), BF_3-etherate (Aldrich), triethylamine (Fisher), and Rhodamine 123 (Kodak) was used as received. Toluene was distilled from $LiAlH_4$. ^1H NMR spectra were collected at 300 MHz (IBM FT-300). Mass spectra were obtained by laser desorption mass spectrometry. Flash chromatography was performed on Baker flash silica. Absorption spectra were collected using a Varian Cary 3 with 1 mm slit widths and 0.25 nm data intervals. Fluorescence spectra were collected using a Spex Fluoromax with 1 mm slit widths (4.25 nm) and 1 nm data intervals. Emission spectra were obtained with $A\lambda_{max} < 0.1$. Quantum yields were determined by ratioing integrated corrected emission spectra of the BDPY dyes in ethanol to Rhodamine 123 in ethanol, which has $\Phi_f = 0.9$ (16). Yields determined in toluene were ratioed to Rhodamine 123 in ethanol with correction for the differences in refractive index (34).

5-(4-Iodophenyl)-1,9-dimethyldipyrromethane (1a). This condensation follows nearly the same conditions employed for forming *meso*-porphyrins (29). In a 1 L one-neck round bottom flask with a stir bar was placed 2-methylpyrrole (35) (648 mg, 8 mmol), 4-iodobenzaldehyde (928 mg, 4 mmol), and 800 mL CH_2Cl_2. The clear solution was purged with Ar for 30 min. Trifluoroacetic acid (62 μL, 0.8 mmol, 10^{-3} M) was added to initiate the condensation. After 1.5 h TLC (silica, CH_2Cl_2) showed that all of the aldehyde had been consumed. The light yellow reaction mixture was then washed with 100 mL of 0.1 N NaOH, 200 mL of H_2O, dried (Na_2SO_4), filtered, and rotary evaporated to a viscous green oil. The oil was quickly placed on a vacuum line to remove residual solvent and prevent decomposition. A light green solid (1.44 g) was immediately obtained (95% yield). ^1H NMR ($CDCl_3$) δ 2.20 (s, 6 H, CH_3), 5.28 (s, 1 H, CH), 5.76 (d, 4 H, β-pyrrole), 7.00 (AA'BB', 2 H, ArH), 7.60 (AA'BB', 2 H, ArH).

N,N'-difluoroboryl-1,9-dimethyl-5-(4-iodophenyl)-dipyrrin (1). This oxidation follows the same conditions employed for forming *meso*-porphyrins (29). A 500 mg sample (1.33 mmol) of 1,9-dimethyl-5-(4-iodophenyl)dipyrromethane was dissolved in 10 mL toluene at room temperature in a 25 mL one-neck round bottom flask. *p*-Chloranil (327 mg, 1.33 mmol) was added at once and the reaction mixture was stirred at room temperature. After 5 min TLC (silica, CH_2Cl_2) showed that all of the dipyrromethane had been consumed. The dipyrromethene was visible as were several other components. Then triethylamine (1.30 mL, 9.31 mmol) was added to the black reaction mixture followed immediately by BF_3-etherate (2.66 mL of 2.5 M solution in toluene). After 1 h TLC (silica, $CHCl_3$) showed that product formation had leveled off. The reaction mixture was rotary evaporated to a black viscous material. Column chromatography (silica, $CHCl_3$) gave the desired product, which eluted as the third component. Removal of the solvent gave 85 mg (15%) of the title compound as an orange solid. mp 215-216 °C; ^1H NMR

(CDCl$_3$) δ 2.64 (s, 6 H, CH$_3$), 6.27 (d, 2 H, J = 3.9 Hz, β-pyrrole), 6.67 (d, 2 H, J = 3.9 Hz, β-pyrrole), 7.22 (AA'BB', 2 H, ArH), 7.81 (AA'BB', 2 H, ArH); C$_{17}$H$_{14}$BF$_2$IN$_2$ calcd mass 422.0, obsd 422.1; λ$_{abs}$ (toluene) 514 nm (fwhm = 25 nm, ε = 59,000 M^{-1}cm^{-1}); λ$_{em}$ (toluene) 532 nm.

N,N'-difluoroboryl-1,9-dimethyl-5-[4-(2-trimethylsilylethynyl)phenyl]dipyrrin (**2**). Following the procedure for **1**, condensation of 2-methylpyrrole (648 mg, 8 mmol) and 4-(2-trimethylsilylethynyl)benzaldehyde (3) (808 mg, 4 mmol) afforded dipyrromethane **2a** as a waxy white solid, which upon treatment with *p*-chloranil, triethylamine, and BF$_3$-etherate yielded 240 mg (8.2%) of the title compound. mp 230-231 °C; ^{1}H NMR (CDCl$_3$) δ 0.28 (s, 9 H, SiCH$_3$), 2.65 (s, 6 H, CH$_3$), 6.27 (d, 2 H, J = 3.6 Hz, β-pyrrole), 6.67 (d, 2 H, J = 3.6 Hz, β-pyrrole), 7.43 (AA'BB', 2 H, ArH), 7.57 (AA'BB', 2 H, ArH); C$_{22}$H$_{23}$BF$_2$SiN$_2$ calcd mass 392.2, obsd 392.2; λ$_{abs}$ (toluene) 516 nm (fwhm = 25 nm, ε = 48,800 M^{-1}cm^{-1}); λ$_{em}$ (toluene) 535 nm.

N,N'-difluoroboryl-5-phenyldipyrrin (**3**). A sample of 500 mg (2.25 mmol) of 5-phenyldipyrromethane (30) was dissolved in 20 mL toluene at room temperature in a 50 mL one-neck round bottom flask. DDQ (510 mg, 2.25 mmol) was added and the reaction mixture was stirred at room temperature. After 5 min TLC (silica, toluene) showed the dipyrromethene, several other components, and no unreacted dipyrromethane. Then triethylamine (2.20 mL, 15.75 mmol) was added to the black reaction mixture followed immediately by BF$_3$-etherate (1.94 mL of neat BF$_3$-etherate, 15.75 mmol). After 30 min TLC (silica, CH$_2$Cl$_2$) showed that product formation had leveled off. The reaction mixture was decanted from the black sludge and washed twice with H$_2$O, dried (Na$_2$SO$_4$), and evaporated to a black viscous material. Column chromatography (silica, CH$_2$Cl$_2$/hexanes 2:1) gave the desired product, which eluted as the second component. Removal of the solvent gave a viscous orange oil. Trituration of the orange oil with hexanes followed by vacuum filtration gave 130 mg (22%) of the title compound as an orange solid. mp 99-100°C; ^{1}H NMR (CDCl$_3$) δ 6.55 (d, 2 H, J = 3.6 Hz, pyrrole-H), 6.94 (d, 2 H, J = 3.6 Hz, pyrrole-H), 7.54, 7.58 (m, 5 H, ArH), 7.95 (s, 2 H, pyrrole-H); C$_{14}$H$_{11}$BF$_2$N$_2$ calcd mass 268.1, obsd 268.4; λ$_{abs}$ (toluene) 502 nm (fwhm = 25 nm, ε = 54,000 M^{-1}cm^{-1}); λ$_{em}$ (toluene) 521 nm.

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Corrigenda

Plenary and invited lecturs presented at the 3rd International Symposium on Functional Dyes (Functional Dye '95) held in Santa Cruz, California, USA, 16–21 July 1995

Boron-dipyrromethene dyes for incorporation in synthetic multi-pigment light-harvesting arrays. R. W. Wagner and J. S. Lindsey*. *Pure Appl. Chem.* 1996, **68**, 1373–1380.

The compound labels **2** and **3** in Scheme 1 should be **1** and **2**, respectively. Thus dipyrromethanes **1a** and **2a** afford BDPY dyes **1** and **2**, respectively. All other labels, including those in Scheme 2 and Table 2, are correct as shown.

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