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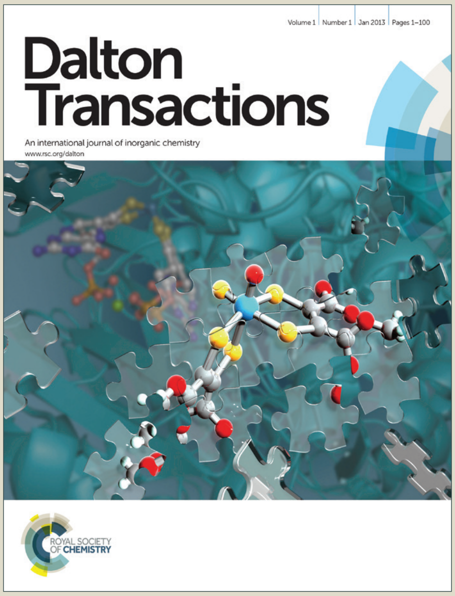

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Facile Synthesis of Highly Fluorescent BF_2 Complexes Bearing Isoindolin-1-one Ligand

Naixun Gao, Chi Cheng, Changjiang Yu, Erhong Hao, Shengyuan Wang, Jun Wang, Yun Wei, Xiaolong Mu and Lijuan Jiao**

Laboratory of Functional Molecular Solids, Ministry of Education; Anhui Laboratory of Molecule-Based Materials; School of Chemistry and Materials Science, Anhui Normal University, Wuhu, Anhui, China 241000.

*To whom correspondence should be addressed. E-mail: haoehong@mail.ahnu.edu.cn, jiao421@mail.ahnu.edu.cn

Abstract

Stable organoboron complexes as classic fluorescent molecules have found various applications in biotechnology and material science. A new class of isoindolin-1-one based BF_2 complexes containing pyridine or benzothiazole groups has been prepared from a facile “one-pot” reaction and was characterized structurally, spectroscopically and electrochemically. These novel dyes show broad and intense absorption and emission bands in solution with high fluorescence quantum yields. Significantly larger Stokes shifts and higher photostability were obtained for these dyes in comparison to those of classical BODIPYs.

Introduction

Boron complexation is a well-known method to rigidify molecules and thus generates or enhances fluorescence. Stable tetracoordinated organoboron complexes with high absorption coefficients and fluorescence quantum yields as potential functional luminophores have recently received much attention and have been used for an array of applications.[1-5] Among them, significant research efforts have been dedicated towards boron dipyrromethene (BODIPY, **A** in Figure 1) dyes.[6] BODIPY dyes enjoy their excellent photophysical properties and the easily tunable spectroscopic properties through structural modification of the chromophore. However, they often exhibit small Stokes shifts due to minimal reorganization of the molecules upon photoexcitation. Therefore, many research efforts have been devoted to the development of BODIPY analogues with larger Stokes shifts.[7] On the other hand, non-pyrrolic BODIPY analogues recently attracted much interest and possessed many advantages including the following: (1) readily available, cheaper and more stable starting materials; (2) easier synthesis, especially for the asymmetrical dyes and generally no oxidation step needed; (3) unparalleled diversity in structures; (4) larger Stokes shifts and better photostability of dyes. Thus, a variety of O,O-bi-,[8-10] N,N-bi-,[11-12] N,O-bi-,[13-15] O,N,O-tri-,[16,17] N,N,N-tri-,[17] and N,N,O,O-tetradentated[18] boron complexes have been efficiently synthesized and some show larger Stokes shifts with remarkable photostabilities.

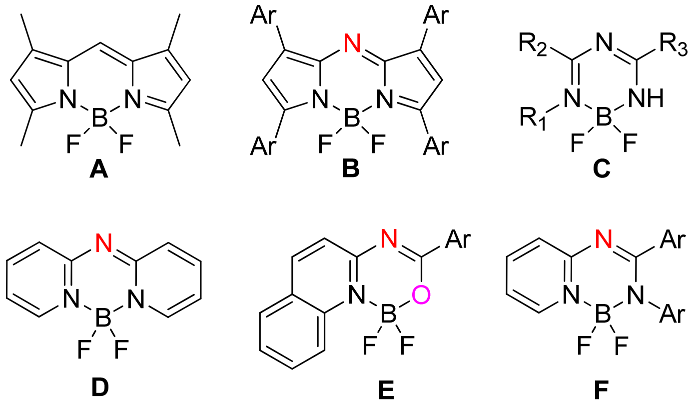


Fig. 1. Chemical structures of representative BF_2 complexes **A-F**.

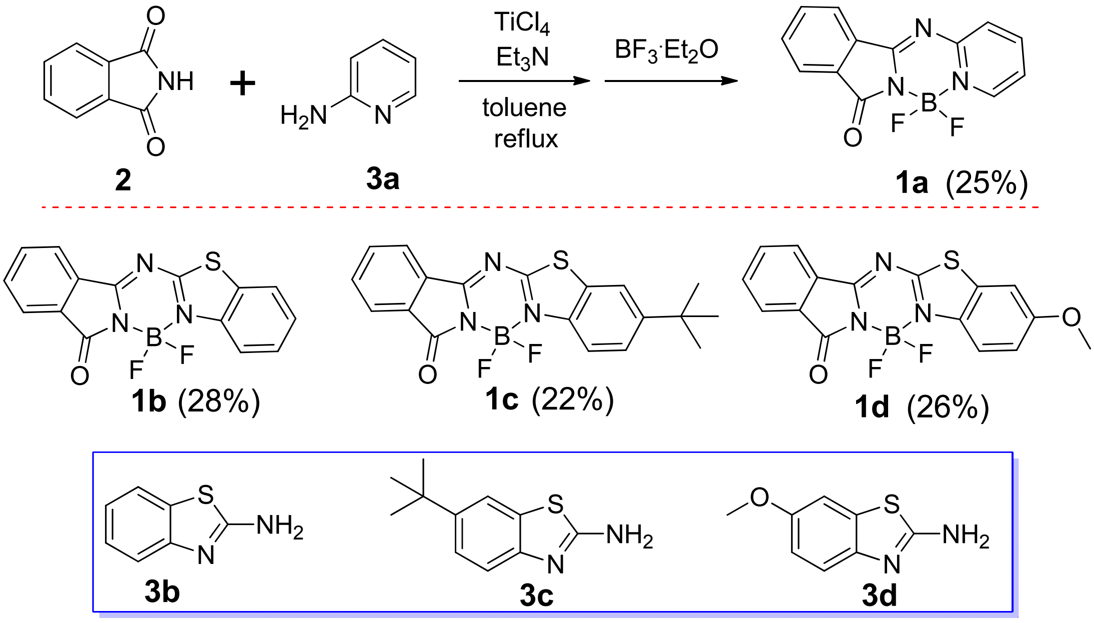
Aza-BODIPYs (**B** in Figure 1) generally have longer absorption and emission bands than those of BODIPYs due to the electron deficient nature of the *meso*-Nitrogen atom. So far, only limited BF_2

complexes of aza-BODIPY analogues have been reported. BF_2 complexes **C** and their π-extended boron complexes by Wüerthwein[17,19] and pyridine based dyes **D, E** and their derivatives by Fu,[20] and Zhu[21] all show high thermal, chemical stabilities and favorable photophysical properties. A class of BF_2 complexes **F** was recently synthesized by You and coworkers[22] through Pd catalyzed coupling reactions and showed mechanochromic luminescence.

Recently, we have reported a series of isoindole (from phthalimide) and pyrrole based BODIPY dyes which show tunable absorption/emission spectra from visible to NIR region.[23] Herein, by replacing pyrrole groups with pyridine or benzothiazole groups, we present the synthesis and properties of a small series of photostable nonpyrrolic BF_2 complexes **1a-d** bearing isoindolin-1-one ligand and pyridine[24] or benzothiazole groups.

Results and Discussion

Inspired by the above pyridine based BODIPY analogues, we decided to synthesize nonpyrrolic BF_2 complexes **1a** from phthalimide and 2-aminopyridine. However, there are few reports of phthalimide imines in the literature. Several phthalimide imines were reported from more reactive phthalonitrile.[25] However, we found that the protocols developed by Hall et al.[26] for imine condensation of relatively unactivated carbonyl groups could be adapted for the activation of phthalimide. Thus, in the presence of titanium tetrachloride and triethylamine, phthalimide **2** was reacted with equal amount of 2-aminopyridine **3a** in refluxing toluene, and the mixture was further reacted with $BF_3 \cdot OEt_2$ for complexation to provide **1a** in 25% yield (Scheme 1). The "one-pot" procedure was further successfully applied to synthesize **1b-d** in similar yields from various 2-benzothiazoleamine **3b-d** and phthalimide **2**. These dyes were characterized by high resolution mass spectrometry and the NMR analysis. The structures were further confirmed by single crystal analysis of **1a** and **1c**.



Scheme 1 Syntheses of dyes **1a-d** and their yields.

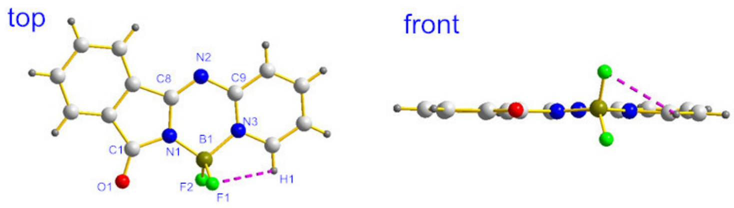


Fig. 2 Top view (left) and front view (right) of X-ray structures of compounds **1a**. C, light gray; H, gray; N, blue; B, dark yellow; O, red; F, green.

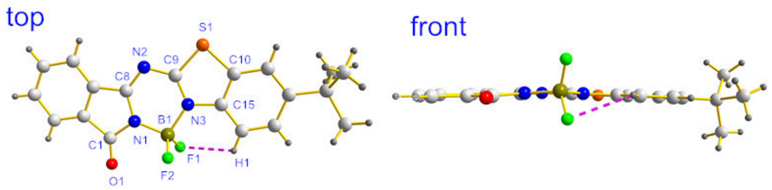


Fig. 3 Top view (left) and front view (right) of X-ray structures of compounds **1c**. C, light gray; H, gray; N, blue; B, dark yellow; O, red; S, orange; F, green.

Crystals of **1a** and **1c** suitable for X-ray analysis were obtained by slow diffusion of hexane into their dichoromethane solutions. Both dyes exhibit similar planar structures as shown in Figures 2 and 3. The boron atoms of **1a** and **1c** have a tetrahedral geometry and the plane defined by F-B-F atoms is perpendicular to that of the C_2N_3 core of the compounds. The C1-O1 bond lengths of **1a** (1.207(18) Å) and **1c** (1.204(57) Å) are typical C=O (ca. 1.22 Å) bond lengths. The B1-N3 bond distance of **1a**

(1.589(19) Å) are about 0.071 Å longer than the B1-N1 bond distance (1.518(17) Å) due to the asymmetry of these molecules, while the B1-N3 bond distance of **1c** (1.579(45) Å) are only about 0.033 Å longer than the B1-N1 bond distance (1.546(5) Å). Multiple intramolecular and intermolecular C-H···F hydrogen bonds between F atoms and various hydrogen atoms are formed due to the strong electron negativity of the F atom. These strong intermolecular hydrogen bondings also help the establishment of the crystal packing structure (Figures S1 and S2, Supporting Information) and make these dyes nearly parallel to each other in a head-to-tail orientation.

Dyes **1a-d** show relatively broad and intense absorption and emission bands in solution as shown in Figure 4. The maximum absorption wavelength of benzothiazole derived **1b** (371 nm) was slightly longer than that of pyridine derived **1a** (362 nm). The absorption maximum can be further red-shift through the variations of the electron-donating groups on 6-position of benzothiazole. **1c** containing *tert*-butyl group absorbs at 380 nm, while **1d** containing methoxyl group absorbs at 400 nm. Similar red-shifts on fluorescence were observed from **1a-1d** with the longest maximum emission wavelength at 541 nm for **1d** (Figure 4).

Benzothiazole derived **1b-d** show strong fluorescence in the range of 455-558 nm with fluorescence quantum yields range from 0.29 to 1.0 in different solvents as summarized in Table 1, while **1a** exhibits a weaker fluorescence in the range of 415-442 nm. The absorption bands of **1a-d** also show little solvatochromism but lose their vibronic structure in more polar solvents as shown in Figure 5a and Figures S3-S9 in Supporting Information. The emission bands of these dyes, especially for **1d**, can be further tuned through the variation of the polarity of solvents. For example, the emission maximum of **1d** is red-shifted from 500 to 524, 541, 542, and 558 nm by simply changing the solvent from hexane to toluene, tetrahedrofuran, dichloromethane and acetonitrile (Figure 5b and Table 1). The solvatochromic shifts of the fluorescence emission found here are similar to BODIPYs with electron donating groups at 3,5- positions as reported by Boens and coworkers.[27] The positive solvatochromic effect and the relative lower fluorescence quantum yields of **1d** (in comparison with those of **1b** and **1c**) indicate a possible intramolecular charge transfer process from electron rich benzothiazole to the C_2N_3 motif. More importantly, along with their high fluorescent quantum yields, dyes **1b-d** give Stokes shifts in the range of 5345-7341 cm^{-1}, which are much larger than that of classical BODIPY dyes like BODIPY **A** (495 cm^{-1} in dichloromethane).

Table 1 Photophysical properties of dyes **1a-1d** in different solvents at room temperature

dyes	solvent	λ_{abs}^{max} (nm)	ε[b] (cm^{-1} M^{-1})	λ_{em}^{max} (nm)[d]	ϕ[e]	τ[f] (ns)	χ^2[g]	Stokes-shift (cm^{-1})
1a	hexane	359, 377(sh)[a]	25863	415	0.10	nd	nd	3759
	toluene	362, 380(sh)	24160	435	0.25	1.09	1.020	4636
	CH_2Cl_2	361, 379(sh)	24296	441	0.31	1.19	1.055	5025
	THF	360, 378(sh)	25256	443	0.20	0.88	1.047	5204
	CH_3CN	359, 377(sh)	23965	442	0.15	0.82	1.049	5231
1b	hexane	365, 383(sh)	nd[c]	455	0.89	2.90	1.079	5419
	toluene	370, 387(sh)	21187	475	0.93	3.38	1.036	5974
	CH_2Cl_2	371	21722	478	1.00	3.50	1.010	6034
	THF	369	22721	479	0.96	3.25	1.034	6223
	CH_3CN	368	22964	498	0.87	3.56	1.018	7094
1c	hexane	375, 393(sh)	25793	469	1.00	3.41	1.023	5345
	toluene	380, 396(sh)	18102	493	0.86	3.23	1.025	6032
	CH_2Cl_2	380	18702	504	1.00	3.25	1.050	6475
	THF	377	19250	502	0.73	3.16	1.023	6605
	CH_3CN	376	18458	512	0.96	3.14	1.019	7064
1d	hexane	390, 409(sh)	nd	500	0.40	3.10	1.028	6578
	toluene	396	15483	524	0.49	2.71	1.002	6169
	CH_2Cl_2	400	15270	541	0.47	2.69	1.011	6578
	THF	395	15530	542	0.35	2.39	1.090	6832
	CH_3CN	396	17034	558	0.29	2.31	1.007	7331
A	CH_2Cl_2	506	87096	519	0.95	nd	nd	495

[a] Shoulder. [b] The molar absorption coefficient at maximum absorption peak; measured in solution containing 1% dichloromethane as a co-solvent. [c] Not determined. [d] **1a** was excited at 360 nm, **1b** and **1c** were excited at 370 nm, **1d** was excited at 380 nm. [e] The absolute quantum yields; the standard errors are less than 5%. [f] Fluorescence lifetime; standard deviations are less than 0.1 ns. [g] χ^2 corresponding to the fitting of fluorescence lifetime curves.

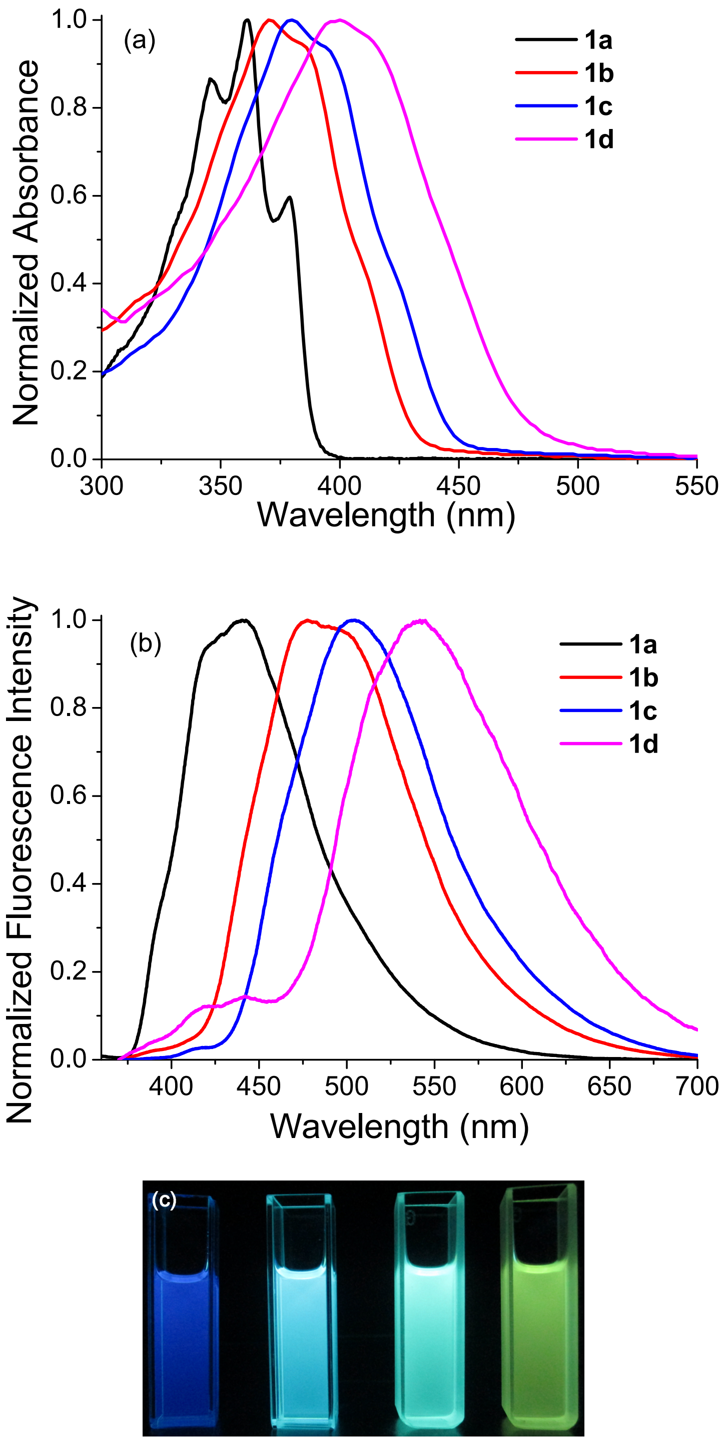


Fig. 4 Normalized absorption (a) and emission (b) spectra of dyes **1a** (black), **1b** (red), **1c** (blue) and **1d** (magenta) in dichloromethane. Photo (c) of fluorescence of **1a-d** (from left to right) in dichloromethane taken under a handheld UV (365 nm) lamp.

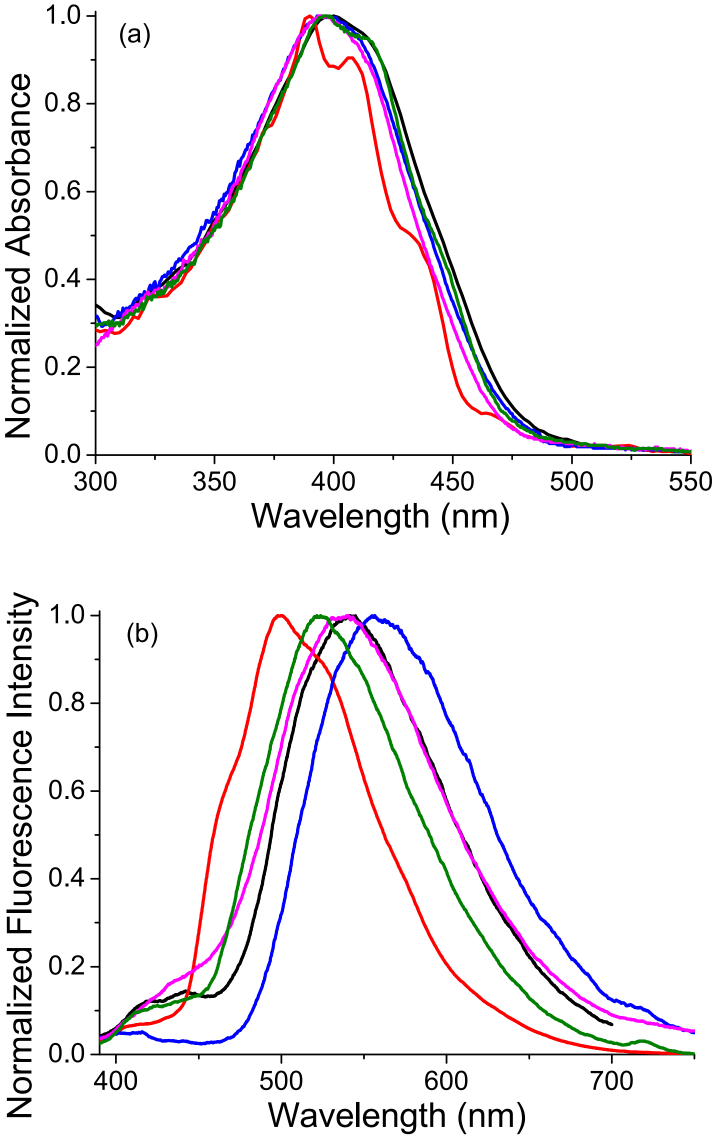


Fig. 5 Normalized absorption (a) and emission (b) spectra of dye **1d** recorded in five different solvents. hexane (red), toluene (green), THF (magenta), dichloromethane (black), acetonitrile (blue).

Time-resolved emissions of these dyes were studied and the fluorescence lifetimes (τ) via TCSPC (Time-Correlated-Single-Photon-Counting) were determined (Table 1). Most of these dyes gave a monoexponential decay function with lifetimes in the range of 0.82-3.50 ns (Figures S10-S28 in Supporting Information). Dyes **1b-d** have longer lifetimes than those of **1a** in the five different solvents studied. Solvents did not give significant difference in lifetimes of those dyes.

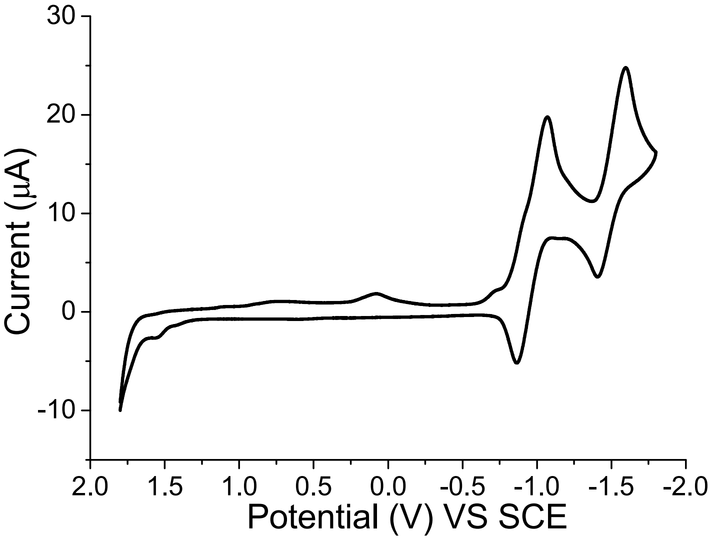


Fig. 6 Cyclic voltammograms of 1 mM **1d** measured in dichloromethane solution, containing 0.1 M TBAPF$_6$ as the supporting electrolyte at room temperature. Glassy carbon electrode as a working electrode, and the scan rate at 50 mV s^{-1}.

Table 2 Electrochemical data acquired at 50 mV/s, and HOMO-LUMO Gaps determined from spectroscopy of dyes **1a-1d**.[a]

dyes	$E_2{}^{o}{}_{B/B}$(V)	$E_1{}^{o}{}_{B/B^-}$(V)	LUMO (eV)	HOMO (eV)	E_g (eV)
1a	-1.56	-1.10	-3.43	-6.62	3.19
1b	-1.46	-0.89	-3.63	-6.50	2.87
1c	-1.42	-0.92	-3.61	-6.37	2.76
1d	-1.51	-0.97	-3.60	-6.17	2.57

[a] $E^{o}{}_{B/B}$ = reversible reduction potential; $E_{red}{}^{onset}$ = the onset reduction potentials; $E_{LUMO} = -e(E_{red}{}^{onset} + 4.4)$; E_g = bandgap, obtained from the intercept of the absorption spectra; $E_{HOMO} = E_{LUMO} - Eg$.

The electrochemical properties of the compound **1a-d** were studied by cyclic voltammetry. The data is summarized in Table 2. Dyes **1a-d** all exhibited two reversible reduction waves (Figure 6 and Figures S29-S31 in Supporting Information). The estimated LUMO values were -3.43 eV for **1a**, -3.63 eV for **1b**, -3.61 eV for **1c** and -3.60 eV for **1d**. Those LUMO values were significantly lower than the widely used electron-transport material Alq_3 which has LUMO value of -3.0 eV.[28] The HOMO values which were calculated from the optical bandgaps and the LUMO values are ranging from -6.17 eV to -6.62 eV for **1a-d**. These HOMO values are also lower than that of Alq_3 (-5.7 eV).

Finally, the photostabilities of dyes **1a-d** were studied by continuous irradiation with a Xe lamp (500 W) in toluene and were compared with that of the known BODIPY **A** (Figure 1). Our dyes **1a-d** show better photostabilities than that of BODIPY **A** (Figure 7). No absorption intensity changes were observed for dyes **1a-d** during the period of strong irradiation (12 min), while absorption intensity of BODIPY **A** continuously decreased.

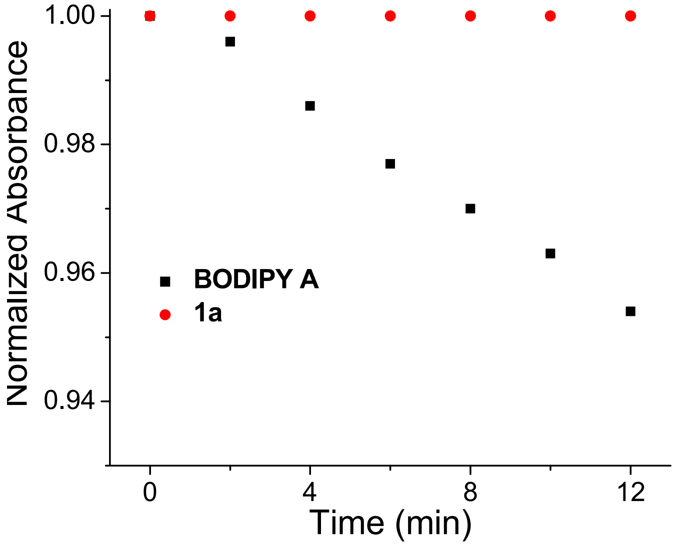


Fig. 7 Comparison of the photostability of dyes **1a-d** (2×10^{-5} M) and BODIPY **A** (1×10^{-5} M) in toluene under continuous irradiation with a 500 W Xe lamp; 35 mW cm^{-2}; 20 ^{0}C. Dyes **1b-d** exhibited almost the same unchanged intensity to that of **1a** and thus not included in figure for clarity.

Conclusions

In summary, we have designed and synthesized a small series of novel highly photostable isoindolin-1-one based BF_2 complexes containing pyridine or benzothiazole groups with strong absorption and fluorescence ranged from 415 to 558 nm. The tuning of their spectroscopic properties was achieved through the structural variations (e.g. the variation of the electron donating abilities on the starting 2-benzothiazoleamines) and the polarities of solvents. The well-ordered molecular packing, strong luminescence, large Stokes shifts, low LUMO values and high photostabilities indicate their potential applications in biotechnology and material science.

Experimental Section

General: Reagents and solvents were used as received from commercial suppliers unless noted otherwise. Anhydrous toluene was obtained by distillation of commercial analytical grade toluene over sodium. All reactions were performed in oven-dried or flame-dried glassware, and were monitored by TLC using 0.25 mm silica gel plates with UV indicator (60F-254). ^{1}H and ^{13}C NMR were recorded on a 300 MHz NMR spectrometer at room temperature. Chemical shifts (δ) are given in ppm relative to $CDCl_3$ (7.26 ppm for ^{1}H and 77 ppm for ^{13}C) or to internal TMS. High-resolution mass spectra (HRMS) were obtained using APCI-TOF in positive mode. Electrochemical studies made use of cyclic voltammetry with a conventional 3-electrode system using a 100W electrochemical analyzer in deoxygenated and anhydrous dichloromethane at room temperature. Glassy carbon working electrode, the saturated calomel electrode (SCE) reference electrode, platinum auxiliary electrode, and the sample solutions contained 1 mM sample and 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte were used. Argon was bubbled for 10min before each measurement.

Fluorometric analysis: UV-visible absorption and fluorescence emission spectra were recorded on commercial spectrophotometers (Shimadzu UV-2450 and Edinburgh Photonics FLS920 spectrometers). The absolute quantum yields of the samples in solutions were measured with calibrated integrating sphere. Fluorescence lifetimes were measured on a combined steady-state lifetime fluorescence spectrometer and the fluorescence lifetimes were obtained from deconvolution and distribution lifetime analysis. Details of the instrumentation and experimental procedures used have been described elsewhere.[29]

X-ray crystallography for 1a and 1c: Crystals of dyes **1a** (CCDC 981350) and **1c** (CCDC 981351) suitable for X-ray analysis were obtained by slow diffusion of hexane into their dichloromethane solutions. Data were collected using a diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at room temperature. Cell parameters were retrieved using SMART[30] software and refined using SAINT on all observed reflections. The determination of unit cell parameters and data collections were performed with Mo Kα radiation (λ) at 0.71073 Å. Data reduction was performed using the SAINT software,[31] which corrects for Lp and decay. The structure was solved by the direct method using the SHELXS-974 program and refined by least squares method on F2, SHELXL-97, incorporated in SHELXTL V5.10.

General procedure for the synthesis: Phthalimide **2** (0.72 mmol) and compound **3** (0.72 mmol) were refluxed in toluene (20 ml) under Argon. To the solution, distilled triethylamine (1.0 ml) and titanium tetrachloride (0.3 ml, 2.7 mmol) were added. When the phthalimide spot on TLC disappeared, boron trifluoride etherate (1.5 ml) was added, and the reaction mixture was refluxed for 4 h. Then the solution was cooled and poured into water. The organic phase was extracted with dichloromethane (50 mL × 3). The organic layer was dried over anhydrous sodium sulfate and the solvent was removed under vacuum. The crude product was purified by silica gel column chromatography and the pure compound was obtained by recrystallization from chloroform and hexane.

Compound 1a: 1a was obtained using **2** (106 mg, 0.72 mmol) and **3a** (68 mg, 0.72 mmol), and was purified by silica gel column (dichloromethane/ethyl acetate=40:1, v/v), giving a yellow crystals in 25% yield (29 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 (d, *J* = 5.7 Hz, 1H), 8.13-8.19 (m, 1H), 8.00-8.05 (m, 1H), 7.92-7.97 (m, 1H), 7.70-7.76 (m, 3H), 7.46-7.51 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) 170.9, 160.7, 154.2, 144.0, 140.6, 136.0, 133.7, 131.7, 125.2, 124.3, 123.2, 121.4. HRMS (APCI) Calcd. for $C_{13}H_9BF_2N_3O$ $[M + H]^+$ 272.0801, found 272.0801.

Compound 1b: 1b was obtained using **2** (106 mg, 0.72 mmol) and **3b** (108 mg, 0.72 mmol), and was purified by silica gel column (dichloromethane/hexane=3:1, v/v), giving an orange solid in 28% yield (66 mg) ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.1 Hz, 1H), 7.96-8.03 (m, 2H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.75-7.78 (m, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H). HRMS (APCI) Calcd. for $C_{15}H_9BF_2N_3OS$ $[M + H]^+$ 328.0522, found 328.0522.

Compound 1c: **1c** was obtained using **2** (106 mg, 0.72 mmol) and **3c** (148 mg, 0.72 mmol), and was purified by silica gel column (dichloromethane/hexane=2:1, v/v), giving an orange solid in 22% yield (61 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15-8.19 (m, 1H), 7.95-8.02 (m, 2H), 7.80-7.82 (m, 1H), 7.70-7.76 (m, 3H), 1.40 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 172.8, 170.6, 163.8, 150.9, 138.7, 135.2, 134.5, 134.1, 131.6, 128.3, 127.1, 124.8, 123.7, 119.1, 118.3, 35.3, 31.3. HRMS (APCI) Calcd. for $C_{19}H_{17}BF_2N_3OS$ $[M + H]^+$ 384.1148, found 384.1149.

Compound 1d: **1d** was obtained using **2** (106 mg, 0.72 mmol) and **3d** (130 mg, 0.72 mmol), and was purified by silica gel column (dichloromethane/hexane =5:1, v/v), giving a red solid in 26% yield (67 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, J = 8.7 Hz, 1H), 7.95-8.01 (m, 2H), 7.74-7.76 (m, 2H), 7.22-7.26 (m, 2H), 3.91 (s, 3H). HRMS (APCI) Calcd. for $C_{16}H_{11}BF_2N_3O_2S$ $[M + H]^+$ 358.0628, found 358.0624.

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Electronic Supplementary Information (ESI) available: Additional UV-vis, fluorescence spectra, cyclic voltammograms, copies of NMR spectra and high resolution mass spectra for all new compounds, crystallographic information files (CIFs) for compounds **1a** and **1c** are available, See DOI:

Reference:

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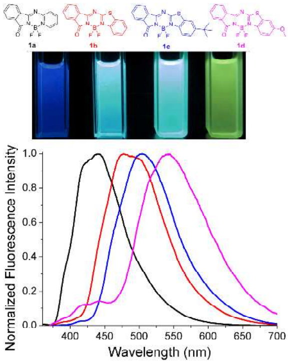
Table of Content



A new class of isoindolin-1-one based BF_2 complexes containing pyridine or benzothiazole groups has been prepared from a “one-pot” reaction.