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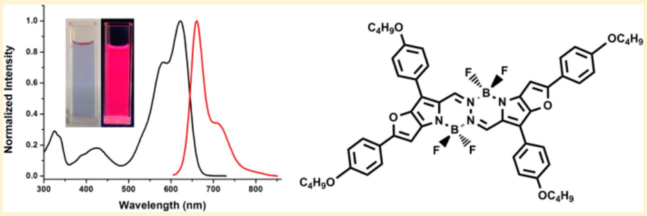
β-Furan-Fused bis(Difluoroboron)-1,2-bis((1H-pyrrol-2-yl)methylene)hydrazine Fluorescent Dyes in the Visible Deep-Red Region

Lin Zhou,[†,§] Defang Xu,[‡,§] Huaizhi Gao,[†] Chao Zhang,[†] Fangfang Ni,[†] Wenqi Zhao,[†] Dandan Cheng,[†] Xingliang Liu,[*,†] and Aixia Han[*,†]

[†]Chemical Engineering College, Qinghai University, Xining 810016, China

[‡]Key Lab of Comprehensive and Highly Efficient Utilization of Salt Lake Resources, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810008, China

Supporting Information



ABSTRACT: Novel β-furan-fused bis(difluoroboron)-1,2-bis-((1H-pyrrol-2-yl)methylene)hydrazine (BOPHY) fluorescent dyes (**F-BOPHY1−3**) were prepared through an efficient process, and their structures were confirmed by ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, MALDI-TOF HRMS, and element analysis. Their optical properties were then characterized by UV−vis absorption and photoluminescence (PL) spectroscopy. The UV−vis absorption and PL spectra of the dyes shifted to longer wavelengths relative to those of BOPHY because of the fusion of their furan rings, which extended π-conjugation of the molecules. All of the dyes exhibited large extinction coefficients (109700−12300 M^{-1} cm^{-1}), deep-red fluorescence emission (646−667 nm), moderate fluorescence quantum yields (0.30−0.45), as well as high chemical stability and photostability in solution. These advantageous properties show that these compounds are important to the design of efficient long-wavelength fluorescent dyes and are suitable for various applications in biotechnology and materials science.

INTRODUCTION

Organic fluorescent dyes have attracted much attention in the past decade because of their potential applications as biological probes,[1−5] molecular sensors,[6−11] and components of opto-electronic devices.[12−16] In particular, tetracoordinate organoboron complexes of π-conjugated chelates, such as boron dipyrromethene (BODIPY) and other N,N− and N,O−chelates, have been of widespread interest because of their favorable synthetic protocol, high chemical and environmental stability, and promising photophysical properties.[17−35] It is remarkable that Zissel and co-workers have carried out a great deal of work on the design and synthesis of boron complexes, including functional BODIPY derivatives,[21,22,36−39] Boranils,[40,41] 2-(2′-hydroxyphenyl)benzoxazole borate complexes,[42−44] and others.[35,45−47] Among the many diverse examples of recent fluorescent dyes based on boron complexes, bright and long-wavelength dyes with fluorescence emission in the low-energy red and near-infrared (NIR) spectral regions (650−900 nm) continues to attract a sustained research interest due to their material and biological applications, such as optical data storage,[48] electrochromic devices,[49] photoconductors,[50] chemosensors,[51−55] immunoassay labels and bioconjugated probes,[56−58] photodynamic therapy,[59−63] and in vitro and in vivo imaging agents.[64−67] Recent efforts have been focused on tuning the fluorescent emission to the red region and even to the NIR region by modifying the core of the dye,[68−75] in which extending conjugation of the system is an effective modification.[73] For example, Suzuki et al. synthesized high-performance β-furan-fused fluorophores based on BODIPY that cover a wide spectral range, from the yellow to the NIR region.[76] Jiao et al. reported a new class of NIR β-thiophene-fused boron difluoride azadipyrromethenes with sharp absorption and fluorescence emission bands at around 800 nm.[77] Therefore, extending the conjugation of the system through fusion of the aromatic ring is a suitable method for synthesis of long-wavelength fluorescent dyes. Despite many investigations on different aspects of organoboron complexes, the development of synthetic routes to important organic chromophores with spectral properties in the NIR and red spectral regions remains a challenge. In 2014, Ziegler et al. reported the first synthesis of the fluorophore based on pyrrole−boron difluoride, bis(difluoroboron)-1,2-bis((1H-pyrrol-2-yl)methylene)hydrazine (BOPHY, Scheme 1).[78] Almost simultaneously, Jiao et al. also synthesized a series of BOPHY compounds,[79] whose structures were identical to that reported by Ziegler and co-workers. Since then, several BOPHY molecules, which were functionalized with systems containing alkyl and aryl functional groups starting from substituted pyrroles or by single or double Knoevenagel condensation and by the palladium-catalyzed cross-coupling reactions, have been developed by Ziegler, Zissel, and their co-workers.[80−82]

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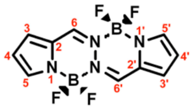
Scheme 1. Molecular Structure of BOPHY



BOPHY

$\lambda_{\text{abs max}}$ (CH_2Cl_2) = 424 nm; $\varepsilon_{\max}$ (CH_2Cl_2) = 4.09 X 10^4 M^{-1} cm^{-1};
$\lambda_{\text{em max}}$ (CH_2Cl_2) = 465 nm; Φ(CH_2Cl_2) = 0.95

Nevertheless, the limited amounts of functionalized dyes cannot meet the needs of materials science applications. Therefore, the design and synthesis of BOPHY dyes with easily tailored long-wavelength and intense fluorescence emission remains a challenge. Herein, we report a series of BOPHY fluorescent dyes (**F-BOPHY1−3**, Scheme 2) with novel molecular structures and good optical properties. They were prepared by fusing substituted furan rings to the 4,5- and 4′,5′-positions of the BOPHY core. We believe that our design can, in theory, increase the delocalization on the BOPHY core and thus move the absorption and emission bands to above 600 and 640 nm, respectively.

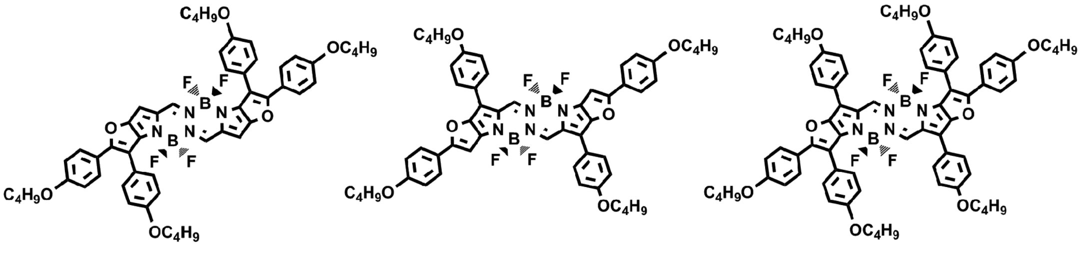
■ RESULTS AND DISCUSSION

Syntheses of Dyes F-BOPHY1−3. The synthetic routes for *β*-furan-fused dyes **F-BOPHY1−3** were shown in Scheme 3. Aryl substitutions were performed in the first step by Suzuki−Miyaura coupling to give **3** from 5-bromofuran-2-carbaldehyde **1** and (4-butoxyphenyl)boronic acid **2** with a high yield of 96%. Furopyrrole **4** was synthesized via Hemetsberge−Knittel reaction from **3** at 40% yield.[83] Regioselective and stepwise bromination of **4** with a suitable amount of bromine gave the corresponding monobromofuropyrrole **5a** (1 equiv of Br_2) and dibromofuropyrrole **5c** (2 equiv of Br_2) in 83% and 93% yields, respectively. Interestingly, monobromofuropyrrole **5b**, which is brominated at different positions from those in **5a**, was obtained in 89% yield by replacing the reagent bromine with NBS. Similar to **3**, **6** was obtained by Suzuki−Miyaura cross-coupling reactions of **5** and (4-butoxyphenyl)boronic acid **2** (>90% yield). Compound **7** was readily obtained by a decarboxylation reaction from **6** under basic conditions. The key synthetic precursors **8**, which could readily react with hydrazine to form dimeric Schiff base chelates **9**, were prepared from **7** through Vilsmeier reaction. The target molecules **F-BOPHY1−3** could be easily prepared through the complex reaction between chelates **9** and boron trifluoride diethyl ether complex in around 50% yields. **F-BOPHY1−3** are soluble in $CHCl_3$, CH_2Cl_2, benzene, toluene, and THF, and poorly soluble in alcohols (such as methanol and ethanol), DMSO, DMF, and aliphatic hydrocarbon solvents (such as cyclohexane and *n*-hexane) at room temperature. All intermediates and target molecules were purified by column chromatography on silica gel, and unambiguously characterized by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy, TOF high resolution mass spectrum (HRMS) (see Supporting Information).

Photophysical Properties of F-BOPHY1−3. Dyes **F-BOPHY1−3** exhibited excellent optical properties with strong absorption and emission in solutions. As summarized in Figure 1 and Table 1, in dichloromethane, **F-BOPHY1** has a strong absorption at 606 nm with a large absorption coefficient (ε = 123 000 cm^{-1} M^{-1}). It had a fluorescence emission maximum at 646 nm (Figure 1b) and a moderate fluorescence quantum yield (Φ_f = 0.43), which was measured using cresyl violet (Φ_f = 0.54 in methanol) as the standard.[83] Maximum absorption and emission bands show 182 and 181 nm bathochromic shifts relative to those of unmodified BOPHY, respectively, and a nearly 3-fold increase in the absorption coefficient. Similar tetraphenyl-substituted **F-BOPHY2** exhibited absorption and emission at 622 nm (ε = 121 300 M^{-1} cm^{-1}) and 661 nm, respectively, red-shifted by 16 and 15 nm relative to those of **F-BOPHY1**. **F-BOPHY3**, which is substituted with six phenyls, showed absorption and emission maxima at 624 (ε = 109 700 M^{-1} cm^{-1}) and 667 nm, respectively, corresponding to 2 and 6 nm red shifts of the respective bands relative to those of **F-BOPHY2**. This difference is attributed to the structures of **F-BOPHY1** and **F-BOPHY3**: introduction of the phenyls B (Figure 2) increased the dihedral angles defined by the phenyl group A and the furan ring, thereby reducing the conjugated length of the molecules. This change can be verified from the optimized molecular structures of **F-BOPHY1−3** from density functional theory (DFT) calculations (Figure 2, Table S1) at the B3LYP/6-31G(d) level using the Gaussian 09W program.[84,85] The above spectral results show that the dihedral angle between the phenyl groups (A, B, and C) and the furan-fused BOPHY core, as well as the number of phenyl groups, affects the conjugation length of the molecules, thus determining the wavelengths of molecular absorption and emission.

The solvent effect on the absorption and fluorescence properties of **F-BOPHY1−3** was examined (Figures S1−S6) and the corresponding photophysical data are summarized in Table S3. The absorption and emission maxima of dyes **F-BOPHY1−3** were only slightly solvent-dependent. For example, the absorption maximum of **F-BOPHY1** in toluene emerged at 608 nm and blue-shifted to 594 nm in DMSO. This shift may be due to the lower degree of conjugation of **F-BOPHY1** resulting from its larger dihedral angle in more polar solvents.[86] In toluene, **F-BOPHY1** gave a strong emission at 641 nm, but with the increasing solvent polarity, its emission displayed a small red shift of 647 nm in DMSO. We also

Scheme 2. Molecular Structures of dyes F-BOPHY1−3



F-BOPHY1 **F-BOPHY2** **F-BOPHY3**

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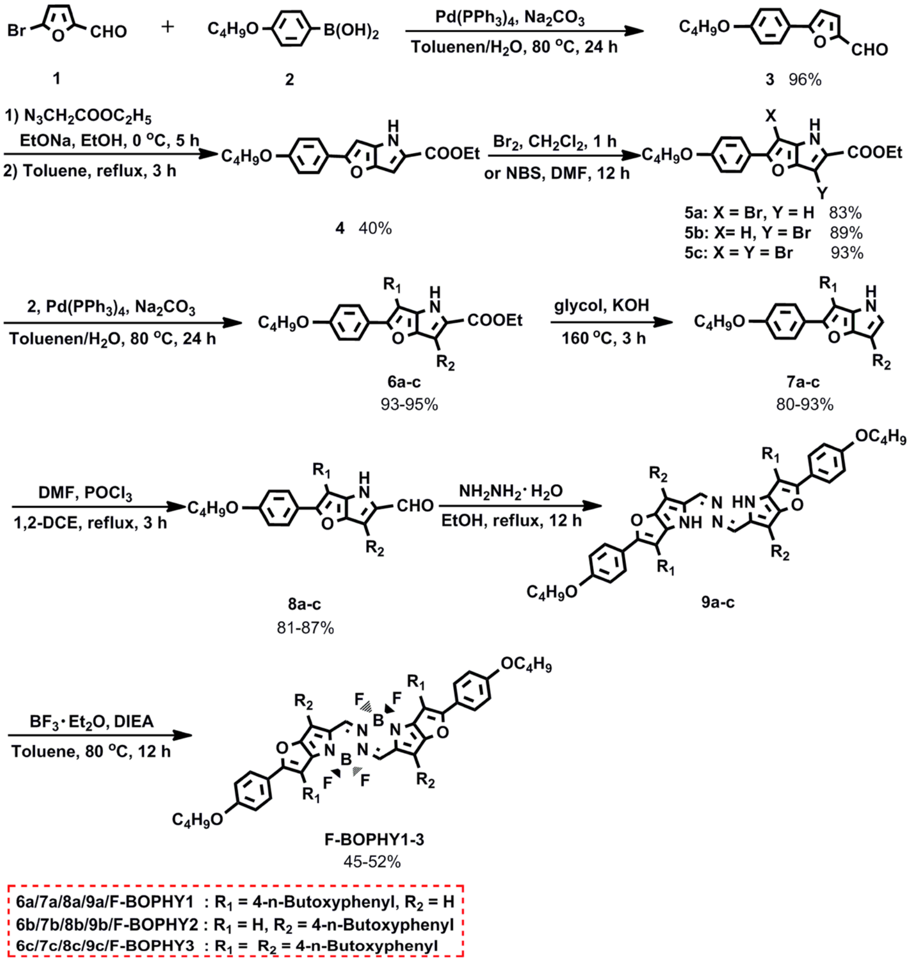
Scheme 3. Synthetic Routes for Dyes F-BOPHY1−3



observed slight dependence of the Stokes shifts of **F-BOPHY1** on the solvent. The above results thus indicate that the permanent dipole moments of **F-BOPHY1** in the ground and excited states are similar.[87]

To obtain further insight into the observed spectroscopic properties of **F-BOPHY1−3**, we performed DFT calculations on the three complexes at the B3LYP/6-31G(d) level using the Gaussian 09W program. As shown in Figure 2, it is clear that the LUMO state density of **F-BOPHY1** is mainly located on the β-furan-fused BOPHY core. In contrast, the electron density of the HOMO is mainly located on all atomic orbitals in the aromatic rings, except for two phenyls B. Thus, intramolecular charge transfer from the orbitals of the phenyls A, which connect to the α position of the furan ring, to the BOPHY core is possible in **F-BOPHY1**, thus partly reducing its fluorescence quantum yields. Rotations about the intramolecular C−Ar bonds (A and B rings) are also possible. As well, the HOMOs and LUMOs of **F-BOPHY2** and **F-BOPHY3** all show the similar electron distribution. The lifetime experiments of **F-BOPHY1−3** in CH_2Cl_2 by time-correlated single photon counting method and the slow component (nanosecond) of their lifetimes were observed.[82] The fluorescence decay of **F-BOPHY1−3** can be fitted with a single exponential function (Figures S7−S9). The measured fluorescence lifetimes (τ) of **F-BOPHY1−3** are 1.97, 2.59, and 2.56 ns, respectively (Table 1). Radiative ($k_f = \Phi_f/\tau$) and nonradiative ($k_{nr} = (1 - \Phi_f)/\tau$) rate constants were also calculated (Table 1). It is clear that there was little difference between the k_f values of **F-BOPHY1−3** (**F-BOPHY1**, 0.22×10^9 s^{-1}; **F-BOPHY2**, 0.15×10^9 s^{-1}; **F-BOPHY3**, 0.13×10^9 s^{-1}). Nonradiative deactivation processes in dichloromethane are slightly favored in **F-BOPHY1−3**, as the k_{nr} values range from 0.23×10^9 s^{-1} to 0.29×10^9 s^{-1}.

Photostabilities of F-BOPHY1−3. As novel dyes with potential practical applications, it is important for dyes **F-BOPHY1−3** to have good stability. We observed that solutions of **F-BOPHY1−3** in $CHCl_3$ remained unchanged over months in capacity bottles at room temperature (1×10^{-5} mol L^{-1}). We measured the photostabilities of the dyes in toluene in air under continuous irradiation with a 500 W Xe lamp in an attempt to compare them against that of the well-known commercial dye, 1,3,5,7-tetramethyl BODIPY. The tests showed that **F-BOPHY1−3** retained more than 96% of the fluorescence intensity after strong excitation for 40 min (Figure 3), which is less than unmodified BOPHY,[67] whereas 1,3,5,7-tetramethylBODIPY retained 84% under the same conditions. These results demonstrate that **F-BOPHY1−3** have high stability.

■ CONCLUSIONS

In conclusion, we have successfully synthesized a series of novel β-furan-fused BOPHY fluorescent dyes **F-BOPHY1−3**. Their photophysical properties were investigated and examined by molecular structure analysis and quantum chemical calculations.

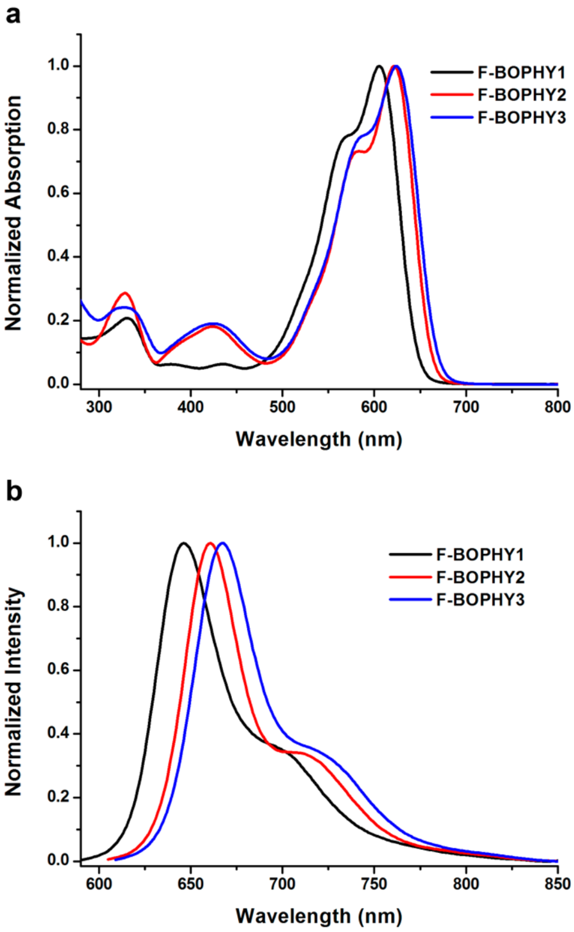


Figure 1. Normalized UV−vis absorption (a) and PL spectra (b) of dyes **F-BOPHY1−3** in dichloromethane measured at a concentration of 1.0 × 10^{-5} mol L^{-1}.

Dyes **F-BOPHY1−3** all exhibited high extinction coefficients that vary between 109 700 and 123 000 M^{-1} cm^{-1} in dichloromethane. Deep-red fluorescence emission of the dyes in solution, which could be tuned by aryl modification of the periphery of the BOPHY core, was observed. The reasonable fluorescence quantum yields of the dyes in various solvents were in the range of 0.30−0.45. Time-resolved fluorescence spectroscopy revealed that the slightly lower values of Φ_f for the complexes are attributed to the promotion of nonradiative processes. DFT calculations provided insight into the effects of substitution at the α position of the furan on their HOMO and LUMO levels. All of the dyes displayed high chemical stability and photostability. Considering their future prospects for broader ranges of absorption and emission in the visible red and NIR spectral regions, **F-BOPHY1−3** are potential candidates for photoelectric materials as well as molecular probes.

EXPERIMENTAL SECTION

General. NMR spectra were measured on a 400 MHz spectrometer (^{1}H: 400 MHz, ^{13}C: 100 MHz) by using $CDCl_3$ and DMSO-d_6 as the solvents. In ^{1}H and ^{13}C NMR measurements, chemical shifts (δ) are reported downfield from the internal standard Me_4Si. The absorption and fluorescence spectra were measured using UV−vis−NIR spectroscopy and a spectrofluorometer, respectively. High-resolution mass spectra (HRMS) spectra were recorded on ESI-TOF-MS and MALDI-TOF-MS. Elemental analyses were performed by investigation of C, H, and N. Fluorescence lifetime was measured in CH_2Cl_2 by time-correlated single photon counting method. The theoretical calculation in the present studies was performed at B3LYP/6-31G(d) level by using the Gaussian 09 program.

Materials. Toluene was distilled over sodium and benzophenone. Ethanol was dried with sodium. DMF was distilled from phosphorus pentoxide, and other chemicals were used as received without further purification.

Synthesis. *5-(4-Butoxyphenyl)furan-2-carbaldehyde (**3**).* A solution of **1** (16.00 g, 91.44 mmol), **2** (26.60 g, 137.09 mmol), $Pd(PPh_3)_4$ (140 mg, 0.121 mmol), and Na_2CO_3 (32.0 g, 301.92 mmol) in toluene/H_2O (300 mL, v/v = 1/1) was heated to reflux under nitrogen atmosphere for 24 h. Then the mixture was cooled to room temperature and the organic layer was separated, the aqueous layer extracted with CH_2Cl_2 (2 × 100 mL), the combined organic layer dried over anhydrous Na_2SO_4, and evaporated to dryness. The crude product was purified by column chromatography (silica gel; petroleum ether/ethyl acetate, v/v = 5/1) to give a light yellow solid (21.44 g), yield 96%; mp 59−62 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 9.60 (s, 1 H), 7.76 (d, J = 8.8 Hz, 2 H), 7.31 (d, J = 3.6 Hz, 1 H), 6.95 (d, J = 9.2 Hz, 2 H), 6.71 (d, J = 4.0 Hz, 1 H), 4.01 (t, J = 6.4 Hz, J = 6.8 Hz, 2 H), 1.83−1.76 (m, 2 H), 1.56−1.47 (m, 2 H), 1.00 (t, J = 7.6 Hz, J = 7.2 Hz, 3 H) (Figure S10); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 176.8, 160.5, 159.9, 151.6, 132.5, 127.0, 121.5, 114.9, 106.2, 67.9, 31.2, 19.2, 13.8 (Figure S11); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{17}O_3$ 245.1178; Found 245.1172 (Figure S12). Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.55; H, 6.41.

*Ethyl 2-(4-Butoxyphenyl)-4H-furo[3,2-b]pyrrole-5-carboxylate (**4**).* EtONa (14.00 g, 205.73 mmol) was dissolved in anhydrous ethanol (100 mL), keeping the temperature at 0 °C, a solution of **3** (13.00 g, 53.22 mmol) and ethyl azidoacetate (26.56 g, 205.70 mmol) in about 60 mL ethanol was added dropwise slowly into the mixture, and stirring was continued for 5 h at room temperature until the reaction was over. Excess saturated aqueous NH_4Cl solution was added to form a precipitate, which was collected by filtration. The precipitate was washed with water and dried in vacuo. The resulting residue was dissolved in toluene (100 mL) and heated to reflux for 3 h. After cooling, the solvent was evaporated. Solvent was removed under vacuum, and the residue was recrystallized from toluene/petroleum ether mixture to generate **4** as a yellow solid (7.00 g), yield 40%; mp 154−157 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.79 (s, 1 H), 7.66 (d, J = 8.8 Hz, 2 H), 6.94 (d, J = 8.8 Hz, 2 H), 6.82 (s, 1 H), 6.57 (s, 1 H), 4.40−4.34 (m, 2 H), 4.01 (t, J = 6.4 Hz, J = 6.8 Hz, 2 H), 1.83−1.76 (m, 2 H), 1.55−1.47 (m, 2 H), 1.40 (t, J = 6.8 Hz, J = 7.2 Hz, 3 H), 1.00 (t, J = 7.2 Hz, J = 7.6 Hz, 3 H) (Figure S13); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 162.0, 160.3, 159.3, 147.4, 130.6, 125.5, 123.8, 123.4, 114.8, 96.8, 91.9, 67.8, 60.4, 31.3, 19.2, 14.5, 13.8 (Figure S14); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{22}NO_4$ 328.1549; Found 328.1542 (Figure S15). Anal. Calcd for $C_{19}H_{21}NO_4$: C, 69.71; H, 6.47; N, 4.28. Found: C, 69.53; H, 6.38; N, 4.10.

Table 1. Photophyscial Properties of Dyes F-BOPHY1−3 in Dichloromethane

dye	λ_{abs}^{max} (nm)	ε (M^{-1} cm^{-1})	λ_{em}^{max} (nm)	Φ_f[a]	τ[b](ns)	$\Delta\nu_{st}$[c] (cm^{-1})	k_f[d]/k_{nr}[e] (10^9 s^{-1})
F-BOPHY1	606	123000	646	0.43	1.97	1022	0.22/0.29
F-BOPHY2	622	121300	661	0.40	2.59	949	0.15/0.23
F-BOPHY3	624	109700	667	0.34	2.56	1033	0.13/0.26

[a] Fluorescence quantum yields were determined using cresyl violet (Φ = 0.54 in methanol). [b] Fluorescence lifetime. [c] $\Delta\nu_{st} = \nu_{abs} - \nu_{em}$. [d] Radiative rate constant $k_f = \Phi_f/\tau$. [e] Nonradiative rate constant $k_{nr} = (1 - \Phi_f)/\tau$.

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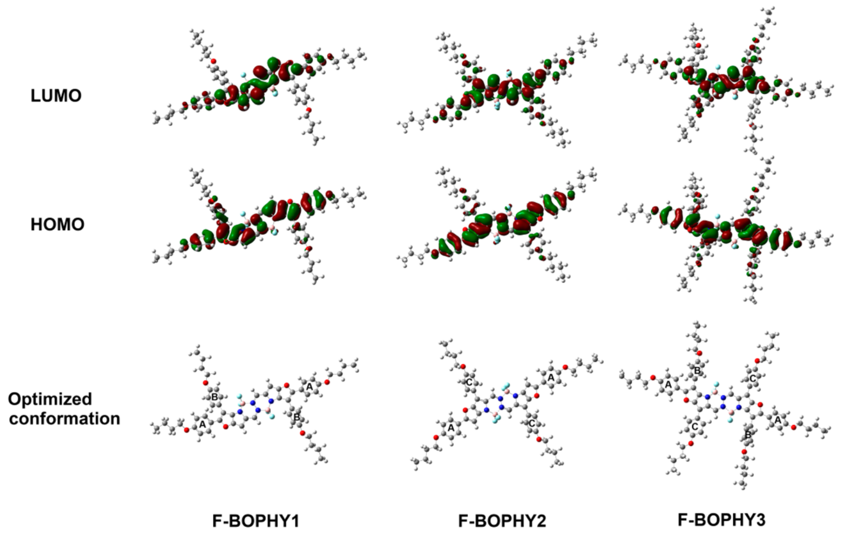

Figure 2. Electron density distributions in the HOMO and LUMO states calculated by DFT in Gaussian 09 at the B3LYP/6-31G(d) level, and the optimized conformation structures of dyes **F-BOPHY1−3**.

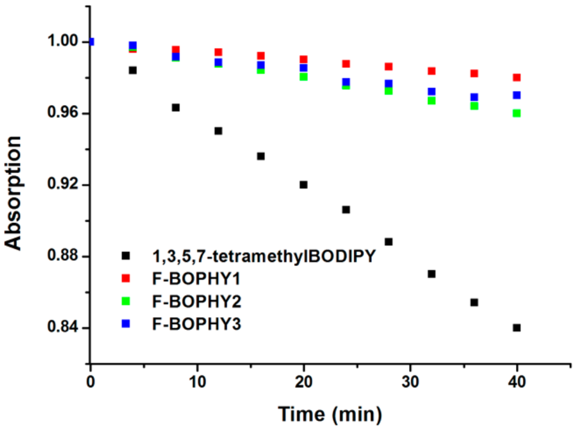

Figure 3. Comparison of the photostability of dyes **F-BOPHY1−3** (1×10^{-5} mol L^{-1}) and 1,3,5,7-tetramethylBODIPY (1×10^{-5} mol L^{-1}) in toluene under continuous irradiation with a 500 W Xe lamp over 40 min; 35 mW cm^{-2}; 25 °C.

*Ethyl 3-Bromo-2-(4-butoxyphenyl)-4H-furo[3,2-b]pyrrole-5-carboxylate (**5a**).* **4** (2.00 g, 6.11 mmol) was dissolved in dichloromethane (80 mL), and then bromine (0.98 g, 6.13 mmol) in 10 mL dichloromethane was added dropwise into the mixture at room temperature. The solution was stirred for 1 h until the reaction was over. The reaction mixture was evaporated to dryness. The solid residue was obtained and was recrystallized from methanol to give **5a** as a white solid (2.06 g), yield 83%; mp 179−181 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.93 (s, 1 H), 7.96 (d, J = 8.8 Hz, 2 H), 6.98 (d, J = 8.8 Hz, 2 H), 6.83 (s, 1 H), 4.45−4.37 (m, 2 H), 4.03 (t, J = 6.8 Hz, J = 6.4 Hz, 2 H), 1.84−1.77 (m, 2 H), 1.56−1.50 (m, 2 H), 1.41 (t, J = 7.2 Hz, J = 7.2 Hz, 3 H), 1.01 (t, J = 7.2 Hz, J = 7.6 Hz, 3 H) (Figure S16); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 159.5, 154.6, 145.5, 130.4, 127.8, 127.5, 125.5, 124.0, 122.8, 114.6, 97.3, 82.6, 67.8, 60.7, 31.3, 19.2, 14.5, 13.8 (Figure S17); HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{19}H_{21}BrNO_4$ 406.0654; Found 406.0647 (Figure S18). Anal. Calcd for $C_{19}H_{20}BrNO_4$: C, 56.17; H, 4.96; N, 3.45. Found: C, 55.98; H, 4.73; N, 3.32.

*Ethyl 6-Bromo-2-(4-butoxyphenyl)-4H-furo[3,2-b]pyrrole-5-carboxylate (**5b**).* **4** (2.50 g, 7.64 mmol) was dissolved in DMF (50 mL), and then NBS (1.40 g, 7.87 mmol) in 20 mL DMF was added dropwise into the mixture at 0 °C. The solution was stirred for 12 h at room temperature. The mixture was poured into water (500 mL), and the precipitate was collected by filtration. The solid residue was recrystallized from methanol to give **5b** as a white solid (2.76 g), yield 89%; mp 188−191 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.81 (s, 1 H), 7.69 (d, J = 8.4 Hz, 2 H), 6.95 (d, J = 8.4 Hz, 2 H), 6.58 (s, 1 H), 4.43−4.38 (m, 2 H), 4.02 (t, J = 6.4 Hz, J = 6.4 Hz, 2 H), 1.84−1.77 (m, 2 H), 1.57−1.48 (m, 2 H), 1.43 (t, J = 7.2 Hz, J = 6.8 Hz, 3 H), 1.00 (t, J = 7.6 Hz, J = 7.2 Hz, 3 H) (Figure S19); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 161.0, 159.6, 146.4, 129.3, 125.9, 123.2, 120.3, 114.8, 92.2, 84.4, 67.8, 60.7, 31.3, 19.2, 14.4, 13.8 (Figure S20); HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{19}H_{21}BrNO_4$ 406.0654; Found 406.0636 (Figure S21). Anal. Calcd for $C_{19}H_{20}BrNO_4$: C, 56.17; H, 4.96; N, 3.45. Found: C, 56.29; H, 4.82; N, 3.31.

*Ethyl 3,6-Dibromo-2-(4-butoxyphenyl)-4H-furo[3,2-b]pyrrole-5-carboxylate (**5c**).* By following the synthetic procedure for compound **5a**, **5c** was synthesized by using **4** (2.00 g, 6.11 mmol) and bromine (2.00 g, 12.52 mmol) as the reagents. The crude product was recrystallized from methanol to give **5c** as a white solid (2.76 g), yield 93%; mp 86−89 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.85 (s, 1 H), 7.98 (d, J = 9.2 Hz, 2 H), 6.99 (d, J = 8.8 Hz, 2 H), 4.45−4.40 (m, 2 H), 4.04 (t, J = 6.4 Hz, J = 6.4 Hz, 2 H), 1.85−1.78 (m, 2 H), 1.56−1.50 (m, 2 H), 1.44 (t, J = 6.8 Hz, J = 7.2 Hz, 3 H), 1.01 (t, J = 7.6 Hz, J = 7.2 Hz, 3 H) (Figure S22); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 160.8, 159.8, 155.4, 144.5, 129.1, 127.8, 127.5, 122.2, 120.9, 114.6, 97.3, 84.9, 82.6, 67.83, 61.0, 31.2, 19.2, 14.4, 13.8 (Figure S23); HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{19}H_{20}Br_2NO_4$ 485.9739; Found 485.9725 (Figure S24). Anal. Calcd for $C_{19}H_{19}Br_2NO_4$: C, 47.04; H, 3.95; N, 2.89. Found: C, 46.82; H, 3.73; N, 3.02.

*Ethyl 2,3-bis(4-Butoxyphenyl)-4H-furo[3,2-b]pyrrole-5-carboxylate (**6a**).* A solution of **5a** (1.80 g, 4.43 mmol), **2**(1.29 g, 6.65 mmol), $Pd(PPh_3)_4$ (40 mg, 0.035 mmol), and Na_2CO_3 (2.00 g, 18.87 mmol) in toluene/H_2O (80 mL, v/v = 1/1) was heated to reflux under nitrogen atmosphere for 24 h. Then the mixture was cooled to room temperature and the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL), the combined organic layer was dried over anhydrous Na_2SO_4, and was evaporated to dryness. The crude product was purified by column chromatography (silica gel; petroleum ether/CH_2Cl_2, v/v = 1/3) to give a light yellow solid (1.96 g), yield 93%; mp 124−127 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.81 (s, 1 H), 7.53 (d, J = 8.8 Hz, 2 H), 7.40 (d, J = 8.8 Hz, 2 H), 6.96 (d, J = 8.4 Hz, 2 H), 6.84 (d, J = 8.4 Hz, 3 H), 4.35−4.30 (m, 2 H), 4.05−3.96 (m, 4 H), 1.86−1.75 (m, 4 H), 1.57−1.48 (m, 4 H), 1.38 (t, J = 6.8 Hz, J = 7.2 Hz, 3 H), 1.04−0.97 (m, 6 H) (Figure S25); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 162.0, 159.0, 158.7, 154.5, 146.0, 131.4, 130.0, 129.9, 128.0, 124.0, 123.9, 123.5, 115.1, 114.4, 109.6, 97.0, 67.8, 67.7, 60.4, 31.4, 31.3, 19.3, 19.2, 14.5, 13.9, 13.8 (Figure S26); HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{29}H_{34}NO_5$ 476.2437; Found 476.2432 (Figure S27). Anal. Calcd for

$C_{29}H_{33}NO_5$: C, 73.24; H, 6.99; N, 2.95. Found: C, 72.98; H, 7.05; N, 2.82.

*Ethyl 2,6-bis(4-Butoxyphenyl)-4H-furo[3,2-b]pyrrole-5-carboxylate (**6b**).* By following the synthetic procedure for compound **6a**, **6b** was synthesized by using compound **5b** (2.65 g, 6.52 mmol) and **2** (1.90 g, 9.79 mmol) as the reagents. The crude product was purified by column chromatography (silica gel; petroleum ether/CH_2Cl_2, v/v = 1/5) to give a light yellow solid (2.95 g), yield 95%; mp 111−114 °C; ^1H NMR (400 MHz, $CDCl_3$): δ ppm 8.73 (s, 1 H), 7.84 (d, J = 8.8 Hz, 2 H), 7.68 (d, J = 8.8 Hz, 2 H), 7.01 (d, J = 8.8 Hz, 2 H), 6.94 (d, J = 8.8 Hz, 2 H), 6.58 (s, 1 H), 4.36−4.31 (m, 2 H), 4.05 (t, J = 6.4 Hz, J = 6.4 Hz, 2 H), 4.01 (t, J = 6.4 Hz, J = 6.4 Hz, 2 H),1.86−1.77 (m, 4 H), 1.59−1.48 (m, 4 H), 1.33 (t, J = 7.2 Hz, J = 6.8 Hz, 3 H),1.04−0.99 (m, 6 H) (Figure S28); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 161.9, 160.7, 159.3, 158.5, 147.0, 131.2, 129.3, 129.0, 128.2, 125.7, 123.8, 123.7, 118.4, 114.8, 114.0, 91.9, 67.8, 67.7, 60.3, 31.4, 31.3, 19.3, 19.2, 14.4, 13.9 (Figure S29); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{34}NO_5$ 476.2437; Found 476.2423 (Figure S30). Anal. Calcd for $C_{29}H_{33}NO_5$: C, 73.24; H, 6.99; N, 2.95. Found: C, 73.08; H, 6.80; N, 2.76.

*Ethyl 2,3,6-tris(4-Butoxyphenyl)-4H-furo[3,2-b]pyrrole-5-carboxylate (**6c**).* By following the synthetic procedure for compound **6a**, **6c** was synthesized by using **5c** (2.50 g, 5.15 mmol) and **2** (3.00 g, 15.46 mmol) as the reagents. The crude product was purified by column chromatography (silica gel; petroleum ether/CH_2Cl_2, v/v = 1/3) to give a light yellow solid (3.00 g), yield 93%; mp 130−133 °C; ^1H NMR (400 MHz, $CDCl_3$): δ ppm 8.76 (s, 1 H), 7.84 (d, J = 8.8 Hz, 2 H), 7.54 (d, J = 8.8 Hz, 2 H), 7.42 (d, J = 8.4 Hz, 2 H), 7.00 (d, J = 8.8 Hz, 2 H), 6.97 (d, J = 8.8 Hz, 2 H), 6.84 (d, J = 8.8 Hz, 2 H), 4.33−4.28 (m, 2 H), 4.07−3.96 (m, 6 H), 1.86−1.74 (m, 6 H), 1.60−1.46 (m, 6 H), 1.32 (t, J = 7.2 Hz, J = 7.2 Hz, 3 H), 1.05−0.97 (m, 9 H) (Figure S31); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 162.0, 159.1, 158.7, 158.5, 154.8, 145.6, 131.2, 130.1, 129.9, 129.4, 128.1, 124.0, 123.9, 123.7, 120.4, 118.4, 115.1, 114.4, 114.0, 109.6, 67.8, 67.7, 60.3, 31.4, 19.3, 19.2, 14.4, 13.9, 13.8 (Figure S32); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{39}H_{46}NO_6$ 624.3325; Found 624.3317 (Figure S33). Anal. Calcd for $C_{39}H_{45}NO_6$: C, 75.09; H, 7.27; N, 2.25. Found: C, 74.88; H, 6.95; N, 2.36.

*2,3-bis(4-Butoxyphenyl)-4H-furo[3,2-b]pyrrole (**7a**).* The mixture of **6a** (1.80 g, 3.78 mmol) and KOH (7.50 g, 133.68 mmol) in ethylene glycol (50 mL) was heated at 160 °C for 3 h under nitrogen. Then the mixture was cooled to room temperature and poured into water, and the precipitate was collected by filtration. The crude product was purified by column chromatography (silica gel; petroleum ether/CH_2Cl_2, v/v = 1/3) to give a light yellow solid (1.35 g), yield 88%; mp 112−115 °C; ^1H NMR (400 MHz, $CDCl_3$): δ ppm 7.80 (s, 1 H), 7.49 (d, J = 8.8 Hz, 2 H), 7.41 (d, J = 8.8 Hz, 2 H), 6.94 (d, J = 8.8 Hz, 2 H), 6.83 (d, J = 8.8 Hz, 2 H), 6.79 (t, J = 2.8 Hz, J = 2.8 Hz, 1 H), 6.24−6.23 (m, 1 H), 4.01 (t, J = 6.8 Hz, J = 6.4 Hz, 2 H), 3.97 (t, J = 6.8 Hz, J = 6.4 Hz, 2 H), 1.83−1.73 (m, 4 H), 1.56−1.46 (m, 4 H), 1.03−0.97 (m, 6 H) (Figure S34); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 158.4, 158.3, 150.5, 146.7, 132.4, 129.8, 127.5, 127.0, 125.2, 125.1, 120.0, 114.9, 114.4, 110.3, 92.6, 67.7, 31.4, 31.3, 19.3, 19.2, 13.9, 13.8 (Figure S35); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{30}NO_3$ 404.2226; Found 404.2219 (Figure S36). Anal. Calcd for $C_{26}H_{29}NO_3$: C, 77.39; H, 7.24; N, 3.47. Found: C, 77.48; H, 6.95; N, 3.32.

*2,6-bis(4-Butoxyphenyl)-4H-furo[3,2-b]pyrrole (**7b**).* By following the synthetic procedure for compound **7a**, **7b** was synthesized by using compound **6b** (2.50 g, 5.26 mmol) and KOH (10.50 g, 187.15 mmol) as the reagents. The crude product was purified by column chromatography (silica gel; CH_2Cl_2) to give a white solid (1.70 g), yield 80%; mp 154−157 °C; ^1H NMR (400 MHz, $CDCl_3$): δ ppm 8.22 (s, 1 H), 7.68−7.62 (m, 4 H), 7.03 (d, J = 2.0 Hz, 1 H), 6.94−6.89 (m, 4 H), 6.61 (s, 1 H), 3.99 (t, J = 6.4 Hz, J = 6.4 Hz, 4 H),1.83−1.76 (m, 4 H), 1.57−1.48 (m, 4 H), 1.01 (t, J = 7.2 Hz, J = 7.2 Hz, 6 H) (Figure S37); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 158.3, 157.2, 156.4, 145.7, 127.0, 126.2, 126.0, 124.9, 124.8, 115.7, 114.8, 114.7, 109.1, 92.9, 67.8, 31.4, 31.3, 19.3, 13.9 (Figure S38); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{30}NO_3$ 404.2226; Found 404.2221 (Figure S39). Anal. Calcd for $C_{26}H_{29}NO_3$: C, 77.39; H, 7.24; N, 3.47. Found: C, 77.22; H, 6.98; N, 3.29.

*2,3,6-tris(4-Butoxyphenyl)-4H-furo[3,2-b]pyrrole (**7c**).* By following the synthetic procedure for compound **7a**, **7c** was synthesized by using compound **6c** (2.50 g, 4.01 mmol) and KOH (8.00 g, 142.59 mmol) as the reagents. The crude product was purified by column chromatography (silica gel; petroleum ether/CH_2Cl_2, v/v = 1/3) to give a light yellow solid (2.05 g), yield 93%; mp 100−102 °C; ^1H NMR (400 MHz, DMSO-d_6): δ ppm 10.97 (s, 1 H), 7.67 (d, J = 8.4 Hz, 2 H), 7.46−7.40 (m, 4 H), 7.27 (d, J = 2.4 Hz, 1 H), 7.01−6.92 (m, 6 H), 4.03−3.94 (m, 6 H), 1.76−1.67 (m, 6 H), 1.50−1.42 (m, 6 H), 0.98−0.91 (m, 9 H) (Figure S40); ^{13}C NMR (100 MHz, DMSO-d_6): δ ppm 158.4, 156.9, 149.7, 144.5, 130.2, 127.8, 127.3, 126.6, 126.0, 125.1, 124.7, 117.8, 115.3, 115.1, 111.2, 107.6, 67.6, 31.3, 31.2, 19.3, 19.2, 14.2 (Figure S41); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{36}H_{42}NO_4$ 552.3114; Found 552.3096 (Figure S42). Anal. Calcd for $C_{36}H_{41}NO_4$: C, 78.37; H, 7.49; N, 2.54. Found: C, 78.42; H, 7.25; N, 2.38.

*2,3-bis(4-Butoxyphenyl)-4H-furo[3,2-b]pyrrole-5-carbaldehyde (**8a**).* $POCl_3$ (0.32 mL,3.43 mmol) was added dropwise into dry DMF (0.30 mL, 3.89 mmol) at 0 °C, and the mixture was stirred for 0.5 h, then compound **7a** (1.30 g, 3.22 mmol) in 1,2-dichloroethane (60 mL) was added to the mixture while controlling the temperature of 0 °C. The mixture was heated to reflux for 3 h. The solution was poured into distilled water and extracted with dichloromethane after the pH value of mixture was adjusted to 10 by adding 2 M NaOH. The residue was purified by column chromatography with dichloromethane as the eluent to afford a light yellow powder (1.15 g), yield 83%; mp 151−153 °C; ^1H NMR (400 MHz, $CDCl_3$): δ ppm 9.44 (s, 1 H), 9.19 (s, 1 H), 7.56 (d, J = 8.8 Hz, 2 H), 7.39 (d, J = 8.8 Hz, 2 H), 6.95 (d, J = 8.8 Hz, 2 H), 6.85 (d, J = 8.8 Hz, 2 H), 6.78 (d, J = 1.6 Hz, 1 H), 4,03−3.97 (m, 4 H), 1.86−1.75 (m, 4 H), 1.59−1.46 (m, 4 H), 1.04−0.97 (m, 6 H) (Figure S43); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 178.7, 159.5, 158.9, 156.9, 146.5, 134.94, 133.9, 130.8, 129.9, 128.3, 123.5, 123.2, 115.1, 114.5, 109.5, 67.8, 67.78, 31.3, 19.3, 19.2, 13.9, 13.8 (Figure S44); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{27}H_{30}NO_4$ 432.2175; Found 432.2169 (Figure S45). Anal. Calcd for $C_{27}H_{29}NO_4$: C, 75.15; H, 6.77; N, 3.25. Found: C, 74.82; H, 6.55; N, 3.33.

*2,6-bis(4-Butoxyphenyl)-4H-furo[3,2-b]pyrrole-5-carbaldehyde (**8b**).* By following the synthetic procedure for compound **8a**, **8b** was synthesized by using $POCl_3$ (0.38 mL, 4.08 mmol), dry DMF (0.36 mL, 4.67 mmol), and compound **7b** (1.45 g, 3.59 mmol) as the reagents. The crude product was purified by column chromatography (silica gel; CH_2Cl_2/ethyl acetate, v/v = 8/1) to give a yellow solid (1.35 g), yield 87%; mp 162−164 °C; ^1H NMR (400 MHz, $CDCl_3$): δ ppm 9.83 (s, 1 H), 9.36 (s, 1 H), 7.72 (d, J = 8.8 Hz, 2 H), 7.65 (d, J = 8.8 Hz, 2 H), 7.05 (d, J = 8.8 Hz, 2 H), 6.96 (d, J = 8.8 Hz, 2 H), 6.65 (s, 1 H), 4.07−4.00 (m, 4 H), 1.87−1.77 (m, 4 H), 1.58−1.48 (m, 4 H), 1.04−0.99 (s, 6 H) (Figure S46); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 177.1, 164.4, 160.1, 159.4, 146.5, 135.5, 131.4, 130.9, 129.8, 127.4, 126.3, 123.0, 122.4, 118.6, 115.1, 114.9, 92.0, 67.9, 31.3, 31.2, 19.3, 19.2, 13.9 (Figure S47); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{30}NO_4$ 432.2175; Found 432.2168 (Figure S48). Anal. Calcd for $C_{27}H_{29}NO_4$: C, 75.15; H, 6.77; N, 3.25. Found: C, 74.96; H, 6.53; N, 3.28.

*2,3,6-tris(4-Butoxyphenyl)-4H-furo[3,2-b]pyrrole-5-carbaldehyde (**8c**).* By following the synthetic procedure for compound **8a**, **8c** was synthesized by using $POCl_3$ (0.36 mL, 3.86 mmol), dry DMF (0.34 mL, 4.54 mmol), and compound **7c** (1.90 g, 3.44 mmol) as the reagents. The crude product was purified by column chromatography (silica gel; CH_2Cl_2) to give a yellow solid (1.62 g), yield 81%; mp 185−188 °C; ^1H NMR (400 MHz, DMSO-d_6): δ ppm 12.07 (s, 1 H), 9.61 (s, 1 H), 7.72 (d, J = 8.4 Hz, 2 H), 7.48−7.43 (m, 4 H), 7.09 (d, J = 8.4 Hz, 2 H), 7.00−6.95 (m, 4 H), 4.07−3.98 (m, 6 H), 1.76−1.67 (m, 6 H), 1.52−1.41 (m, 6 H), 0.98−0.92 (m, 9 H) (Figure S49); ^{13}C NMR (100 MHz, DMSO-d_6): δ ppm 179.3, 159.6, 158.9, 158.8, 156.2, 145.0, 133.6, 131.0, 130.8, 128.7, 123.7, 123.1, 123.0, 115.4, 115.2, 110.5, 79.8, 79.5, 79.1, 67.7, 31.3, 31.2, 31,1, 19.2, 14.2 (see Figure S50); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{37}H_{42}NO_5$ 580.3063; Found 580.3043 (Figure S51). Anal. Calcd for

$C_{37}H_{41}NO_5$: C, 76.66; H, 7.13; N, 2.42. Found: C, 76.43; H, 6.92; N, 2.31.

*bis(Difluoroboron)-1,2-bis((2,3-bis(4-butoxyphenyl)-4H-furo[3,2-b]pyrrol-5-yl)methylene)hydrazine (**F-BOPHY1**).* **8a** (0.80 g, 1.85 mmol) and hydrazine hydrate (46 mg, 0.92 mmol) were dissolved in 60 mL of ethanol, a few drops of acetic acid were added, then the mixture was heated to reflux for 12 h under nitrogen. Then the mixture was cooled to room temperature and the precipitate was collected by filtration. After being rinsed with cold ethanol and dried under vacuum to afford **9a** as an orange solid, the resultant solid was dissolved in dry toluene (60 mL), and DIEA (2.43 mL, 1.90 g, 14.70 mmol) was added to the solution, followed by dropwise addition of boron trifluoride diethyl ether complex (2.34 mL, 2.63 g, 18.55 mmol). Then the reaction mixture was heated at 80 °C under an atmosphere of nitrogen for 12 h. The solvent was evaporated, washed with water, and extracted with CH_2Cl_2. The solvent was removed and the crude product was purified by column chromatography (silica gel; petroleum ether/CH_2Cl_2, v/v = 1/2) to give a coppery solid (0.46 g), yield 52%; mp 292−295 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.91 (s, 2 H), 7.49 (d, *J* = 9.2 Hz, 4 H), 7.42 (d, *J* = 8.4 Hz, 4 H), 7.01 (d, *J* = 8.8 Hz, 4 H), 6.81 (d, *J* = 9.2 Hz, 4 H), 6.71 (s, 2 H), 4.05 (t, *J* = 6.4 Hz, *J* = 6.4 Hz, 4 H), 3.97 (t, *J* = 6.4 Hz, *J* = 6.4 Hz, 4 H), 1.88−1.80 (m, 4 H), 1.79−1.73 (m, 4 H), 1.61−1.44 (m, 8 H), 1.04 (t, *J* = 7.2 Hz, *J* = 7.6 Hz, 6 H), 0.98 (t, *J* = 7.6 Hz, *J* = 7.2 Hz, 6 H) (Figures S52 and S53); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 163.0, 160.3, 159.2, 150.2, 136.8, 131.5, 130.7, 128.7, 127.2, 122.7, 122.2, 115.6, 114.6, 111.2, 102.4, 67.8, 67.6, 31.5, 31.2, 19.4, 19.2, 13.9, 13.8 (Figure S54); ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm −139.47 (Figure S55); HRMS (MALDI-TOF) *m/z*: $[M]^+$ calcd for $C_{54}H_{56}B_2F_4N_4O_6$ 954.4322; Found 954.4304 (Figures S56 and 57). Anal. Calcd for $C_{54}H_{56}B_2F_4N_4O_6$: C, 67.94; H, 5.91; N, 5.87. Found: C, 67.76; H, 5.62; N, 5.66.

*bis(Difluoroboron)-1,2-bis((2,6-bis(4-butoxyphenyl)-4H-furo[3,2-b]pyrrol-5-yl)methylene)hydrazine (**F-BOPHY2**).* By following the synthetic procedure for compound **F-BOPHY1**, **F-BOPHY2** was prepared from **8b** (0.80 g, 1.85 mmol) and hydrazine hydrate (46 mg, 0.92 mmol), followed by reaction with DIEA (2.43 mL, 1.90 g, 14.70 mmol) and boron trifluoride diethyl ether complex (2.34 mL, 2.63 g, 18.55 mmol). The crude product was purified by column chromatography (silica gel; petroleum ether/CH_2Cl_2, v/v = 1/2) to give a coppery solid (0.41 g), yield 46%; mp 294−296 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.10 (s, 2 H), 7.78 (d, *J* = 8.8 Hz, 4 H), 7.66 (d, *J* = 8.4 Hz, 4 H), 7.09 (d, *J* = 8.4 Hz, 4 H), 6.97 (d, *J* = 8.4 Hz, 4 H), 6.80 (s, 2 H), 4.08 (t, *J* = 6.4 Hz, *J* = 6.4 Hz, 4 H), 4.02 (t, *J* = 6.4 Hz, *J* = 6.8 Hz, 4 H), 1.88−1.77 (m, 8 H), 1.59−1.49 (m, 8 H), 1.05−0.98 (m, 12 H) (Figures S58 and S59); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 168.2, 160.9, 159.9, 148.9, 144.9, 135.5, 130.6, 127.1, 125.0, 122.4, 122.0, 119.4, 115.5, 115.0, 93.1, 67.9, 31.3, 31.2, 19.3, 19.2, 13.9 (Figure S60); ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm −145.11 (Figure S61); HRMS (MALDI-TOF) *m/z*: $[M]^+$ calcd for $C_{54}H_{56}B_2F_4N_4O_6$ 954.4322; Found 954.4304 (Figures S62 and S63). Anal. Calcd for $C_{54}H_{56}B_2F_4N_4O_6$: C, 67.94; H, 5.91; N, 5.87. Found: C, 68.16; H, 5.69; N, 5.61.

*bis(Difluoroboron)-1,2-bis((2,3,6-tris(4-butoxyphenyl)-4H-furo[3,2-b]pyrrol-5-yl)methylene)hydrazine (**F-BOPHY3**).* By following the synthetic procedure for compound **F-BOPHY1**, **F-BOPHY3** was prepared from **8c** (1.00 g, 1.72 mmol) and hydrazine hydrate (43 mg, 0.86 mmol), followed by reaction with DIEA (2.26 mL, 1.77 g, 13.67 mmol) and boron trifluoride diethyl ether complex (1.96 mL, 2.21 g, 15.53 mmol). The crude product was purified by column chromatography (silica gel; petroleum ether/CH_2Cl_2, v/v = 2/3) to give a coppery solid (0.49 g), yield 45%; mp 283−286 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.00 (s, 2 H), 7.59 (d, *J* = 8.4 Hz, 4 H), 7.49 (d, *J* = 8.8 Hz, 4 H), 7.45 (d, *J* = 8.8 Hz, 4 H), 7.06 (d, *J* = 8.8 Hz, 4 H), 7.01 (d, *J* = 8.4 Hz, 4 H), 6.81 (d, *J* = 8.8 Hz, 4 H), 4.09−4.04 (m, 8 H), 3.96 (t, *J* = 6.4 Hz, *J* = 6.8 Hz, 4 H), 1.88−1.75 (m, 12 H), 1.59−1.48 (m, 12 H), 1.03 (t, *J* = 7.6 Hz, *J* = 7.2 Hz, 12 H), 0.98 (t, *J* = 7.2 Hz, *J* = 7.6 Hz, 6 H) (Figures S64 and S65); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 162.9, 160.2, 159.9, 159.2, 147.8, 145.2, 136.0, 131.5, 130.7, 128.8, 125.0, 122.8, 122.4, 121.9, 119.4, 115.5, 114.6, 114.5, 111.4, 67.9, 67.8, 31.5, 31.3, 31.2, 19.3, 19.2, 13.9, 13.8 (Figure S66); ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm −140.25 (Figure S67); HRMS (MALDI-TOF) *m/z*: $[M]^+$ calcd for $C_{74}H_{80}B_2F_4N_4O_8$ 1250.6098; Found 1250.6078 (Figures S68 and S69). Anal. Calcd for $C_{74}H_{80}B_2F_4N_4O_8$: C, 71.04; H, 6.45; N, 4.48. Found: C, 70.82; H, 6.28; N, 4.32.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01018.

> Selected geometrical parameters of optimized **F-BOPHY1−3**; UV/vis spectra and photophysical data of **F-BOPHY1−3** recorded in different solvents; time-resolved emission-decay curves of **F-BOPHY1−3**; ^{1}H and ^{13}C NMR spectra and MS of **3**, **4**, **5a−c**, **6a−c**, **7a−c**, **8a−c**, and **F-BOPHY1−3** (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: liuxl1219@163.com.
*E-mail: hanaixia@tsinghua.org.cn.

Author Contributions

[§]L.Z. and D.X. equally contributed to the paper.

Notes

The authors declare no competing financial interest.

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