S_2 Emission from Chemically Modified BODIPYs

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Experimental

Synthetic General

The synthesis of BODIPYs is depicted on Scheme 2. Intermediate compound (**1**) was prepared by treatment of pyrrole with 1,3-dibromo-5,5-dimethylhydantoin in the presence of AIBN followed by amine protection with *p*-toluenesulfonyl chloride. Reaction of (**1**) with 4-methoxyphenylboronic acid under the conditions of Suzuki cross-coupling reaction yielded (**2**). After protection of the tosyl group with 15% ethanolic NaOH in ethanol, the resulting intermediate (**3**) was reacted with methyl 4-formylbenzoate to obtain (**4**), the oxidation of which was achieved by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, a stronger reactant than 1,4-benzoquinone. The reaction proceeded smoothly but separating the highly colored compound by column chromatography was difficult, which explains the somewhat low yield of this step. The oxidized compound (**5**) was then treated with boron trifluoride etherate in the presence of triethylamine in dried CH_2Cl_2 at room temperature to produce the precursor BODIPY (**6**). The ester group was hydrolyzed in presence of sodium hydroxide to yield BODIPY **1**. Further bromination at the 2 and 6 positions led to BODIPY **2**. Synthesized BODIPYs were characterized by elemental analysis, FT-IR, ^{1}H- ^{13}C-, and ^{19}F-NMR spectra (Figures S1-S6, Suppl. Information) MALIDO-TOF mass spectrometry (Figures S7-S8, Suppl. Information).

Reagents were purchased from Sigma-Aldrich, Fluka Inc., TCI Co, or Junsei Inc. and were used as received. Tetrahydrofuran (THF) was freshly distilled from sodium-benzophenone under N_2 atmosphere. Diethyl ether (Et_2O) and CH_2Cl_2 were freshly distilled from CaH_2 under N_2 atmosphere.

^{1}H-, ^{13}C- and ^{19}F-NMR spectra were recorded with the use of Varian Oxford 300 MHz spectrometer; chemical shifts are reported in ppm with respect to tetramethylsilane or hexafluorobenzene as internal standard. Elemental analysis was performed by the Center for microanalysis of KAIST (Daejeon, Korea) with a EA1110-FISONS elemental analyzer manufactured by ThermoQuest Italia S.P.A (accuracy: 0.3%). Infrared spectra were measured on KBr pellets using a Jasco FT/IR-4200 Spectrometer. MALDI-TOF mass spectrometry was performed on a Voyager-DETM STR BiospectrometryTM workstation from PerSeptive Biosystems.

Synthesis of BODIPY Derivatives

2-Bromo-1-tosyl-1H-pyrrole (1): 1,3-Dibromo-5,5-dimethyl-hydantoin (6.53 g, 22.4 mmol) was added to a solution of 3.1 mL of pyrrole (44.7 mmol) in 120 mL of freshly distilled THF in a dried flask under N_2 atmosphere at -78°C. The mixture was stirred for 30 min and allowed to stand for an additional 3.5 h at -78℃. To this solution were added 4 mL of Bu_3N and 180 mL of distilled Et_2O and the mixture was stirred for 10 min at -78℃. The resulting gray precipitate was removed by filtration and the solution was concentrated to remove Et_2O. p-Toluenesulfonyl chloride (17.04 g, 89.4 mmol) was then added and the inert atmosphere was re-established. The solution was cooled to 0℃ and 5.36 g (134.0 mmol) of NaH (60 % in mineral oil) was added. The mixture was stirred for 18 h and 60 mL of H_2O was added. The mixture was extracted with Et_2O and the ether extracts were washed with successive portions of 1M HCl and $NaHCO_3$. This mixture was combined with an equal volume of 2 M NaOH and was stirred for 2 h a room temperature The layers were separated and the organic extract was washed with H_2O and 2M NaOH. The organic layer was dried over $MgSO_4$ and concentrated to give a light brown solid. Recrystallization from isopropyl alcohol gave (**1**) in 23% yield. ^{1}H NMR (300 MHz, $CDCl_3$) = 2.43 (s, 3H), 6.23-6.29 (m, 2H), 7.32 (d, J=8.3Hz, 2H), 7.46 (dd, J=2.0, 3.5 Hz, 1H) and 7.81(d, J=8.4Hz 2H).

2-(4-Methoxyphenyl)-1-tosyl-1H-pyrrole (2): A mixture of (**1**) (10 g, 33.31 mmol), 4-methoxylphenylboronic acid (6 g, 39.48 mmol), $Pd(PPh_3)_4$ (1.8 g, 1.56 mmol), 30 mL of toluene, 30 mL of EtOH, and 30 mL of 2 M Na_2CO_3 was refluxed at 100℃ for 24 h under N_2 atmosphere and was extracted with ethyl acetate. The organic layer was washed with brine and water and dried over $MgSO_4$, filtered and concentrated in *vacuo*. The crude product was purified by recrystallization from isopropyl alcohol to give (2) as a white crystalline solid in 70% yield. ^{1}H NMR (300 MHz, $CDCl_3$) = 2.34 (s, 3H), 3.84 (s, 3H), 6.10 (dd, J=1.8, 3.0 Hz 1H), 6.28(t, J=3.4 Hz 1H), 6.81-6.86 (m, 2H), 7.09-7.17 (m, 4H), 7.25-7.26 (m, 2H) and 7.41 (dd, J=1.8, 3.1 Hz 1H).

2-(4-Methoxypheyl)-1H-pyrrole (3): A mixture of 0.050 g (0.15 mmol) of (**2**) in 0.6 mL of EtOH and 0.2 mL of 15 % ethanolic NaOH was stirred at reflux temperature for 3 h. The solution was concentrated in *vacuo* and the residue was dissolved in CH_2Cl_2 and washed with H_2O. The organic layer was dried over $MgSO_4$ and concentrated in *vacuo* to give 0.025 g of (**3**) as a white solid, in 95% yield. ^{1}H NMR (300 MHz, $CDCl_3$) = 3.81 (s, 3H), 6.27(dd, J=2.8, 5.7 Hz 1H), 6.40 (t, J=3.5 Hz, 1H), 6.79 (dd, J=2.4, 3.9 Hz 1H), 6.88-6.91 (m, 2H), 7.36-7.39 (m, 2H) and 8.32 (br s, 1H).

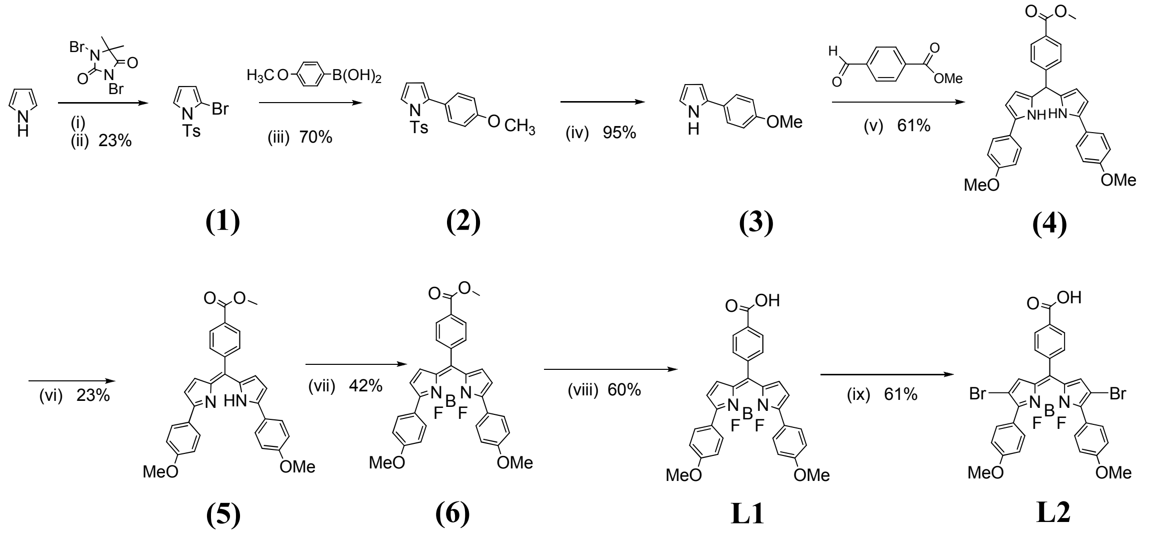
Methyl 4-(bis(5-(4-methoxyphenyl)-1H-pyrrole-2-yl)methyl)-benzoate (4): A mixture of 1.82 g (10.51 mmol) of (**3**), 0.69 g (4.2 mmol) of methyl 4-formylbenzoate, and 20 mL of ethyl acetate was added to a 250 mL 3-neck round flask and degassed with N_2 atmosphere for 5 min. Trifluoroacetic acid (0.03 mL, 0.42 mmol) was then added all at once. The solution was stirred under N_2 atmosphere at room temperature for 1 h. Then, 50 mL of 0.1N NaOH was added to the solution. The solution was extracted with ethyl acetate. The organic layer was washed with brine and water, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by recrystallization from hexane/CH_2Cl_2 mixture to give a violet solid in 61 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) = 3.80 (s, 6H), 3.91 (s, 3H), 5.58 (s, 1H), 5.93 (s, 2H), 6.33 (s, 2H), 6.88 (d, J=8.4 Hz, 4H), 7.32 (d, J=8.4 Hz, 4H), 7.38 (d, J=8.1 Hz, 2H), 8.01 (d, J=8.4 Hz, 2H) and 8.15 (s, 2H).

(Z)-Methyl-4-((5-(4-methoxyphenyl)-1H-pyrrole-2-yl) (5-(4-methoxyphenyl)-2H-pyrrole-2-ylidene)methyl)benzoate (5): 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (0.4 g, 1.76 mmol) was added to a solution of 0.6 g (1.12 mmol) of (**4**) in 50 mL CH_2Cl_2. The mixture was stirred at room temperature for 1 h. The solution was concentrated in *vacuo*. The crude product was purified by flash column chromatography (silica, hexane/ethyl acetate). Yield: 23%. ^{1}H NMR (300 MHz, $CDCl_3$) = 3.90 (s, 6H), 3.98 (s, 3H), 6.61 (d, J=4.2 Hz, 2H), 6.77 (d, J=4.2 Hz, 2H), 7.03 (d, J=9.0 Hz, 4H), 7.62 (d, J=8.1 Hz, 2H), 7.86 (d, J=8.4 Hz, 4H) and 8.131 (d, J=7.8 Hz, 2H).

Boron dipyrromethene (6): A solution of 0.24 g (0.49 mmol) of (5) and 0.12 g (1.10 mmol) of triethylamine in 30 mL dried CH_2Cl_2 was stirred under N2 atmosphere at room temperature for 10 min. Then, boron trifluoride diethyl etherate (0.3 mL, 2.47 mmol) was added dropwise over 10 min. The resulting solution was stirred for 24 h at room temperature and the crude product was purified by flash column chromatography (silica, hexane/CH_2Cl_2). Yield: 42%. ^{1}H NMR (300 MHz, $CDCl_3$) = 3.85 (s, 6H), 3.99 (s, 3H), 6.62 (d, J=4.2 Hz, 2H), 6.78 (d, J=4.5 Hz, 2H), 6.96 (d, J=9.0 Hz, 4H), 7.65 (d, J=8.1 Hz, 2H), 7.88 (d, J=9.0 Hz, 4H) and 8.18 (d, J=8.4 Hz, 2H).

BODIPY-CO_2H (BODIPY 1): A solution of ethanolic NaOH (0.85 g, 21 mmol) was added to a stirred solution of 0.2 g (0.37 mmol) of (6) in THF/EtOH. The solution was stirred at room temperature for overnight. The solution was concentrated in *vacuo*. The crude product was purified by flash column chromatography (silica, CH_2Cl_2/MeOH), and then the product was acidified to pH 4 with a solution of 1M HCl. The water layer was extracted three times with ethyl acetate. The organic phase was dried over $MgSO_4$, filtered and concentrated in *vacuo*. The crude product was purified by recrystallization from hexane/CH_2Cl_2 mixture to give a green solid in 60% yield. Anal. calcd. for $C_{30}H_{23}BF_2N_2O_4$: C (68.72%), H (4.42%), N (5.34%); found : C (68.41%), H (4.46%), N (5.10%); ^{1}H NMR (300 MHz, $CDCl_3$) = 3.86 (s, 6H), 6.64 (d, J=3.6 Hz, 2H), 6.77 (d, J=3.5 Hz, 2H), 6.95 (d, J=9.0 Hz, 4H), 7.70 (d, J=8.1 Hz, 2H), 7.89 (d, J=9.0 Hz, 4H) and 8.26 (d, J=7.8 Hz, 2H); ^{13}C-NMR (226.4 MHz, DMSO) = 166.82, 160.5, 155.8, 142.5, 136.4, 133.4, 131.8, 131.7, 130.9, 129.5, 121.7, 114.1, 113.4, 109.6, 55.2; ^{19}F-NMR (282.3 MHz, DMSO) = -137.5 (s, 2F), MS(MALDI-TOF): m/z 524.06 524.96 (M^+), calc. 524.17.

Br-BODIPY-CO$_2$H (BODIPY 2): A mixture of BODIPY **1** (0.1 g, 0.19 mmol), NBS (0.075 g, 0.42 mmol) AIBN (0.004 g, 0.02 mmol) and 20 mL of CH_3Cl solution was refluxed at 100℃ for 24 h under N_2 atmosphere. The crude product was purified by flash column chromatography (silica, CH_2Cl_2/MeOH), and then the product was acidified to pH 4 with a solution of HCl (1M). The water layer was extracted with ethyl acetate three times. The organic phase was dried over $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by recrystallization from hexane/CH_2Cl_2 mixture to give a green solid. Br-BODIPY-CO$_2$H (BODIPY **2**): Yield: 61%. Anal. calcd. for $C_{30}H_{21}BBr_2F_2N_2O_4$: C (52.82%), H (3.10%), N (4.11%); found : C (52.62%), H (3.50%), N (4.00%). ^{1}H NMR (300 MHz, $CDCl_3$) = 3.85 (s, 6H), 6.92 (m, 6H), 7.62 (d, J=9.0 Hz, 4H), 7.68 (d, J=8.1 Hz, 2H) and 8.27 (d, J=7.8 Hz, 2H); ^{13}C-NMR (226.4 MHz, DMSO) 166.8, 160.6, 157.9, 140.8, 137.7, 135.4, 132.3, 131.0, 130.8, 130.7, 129.3, 124.3, 121.4, 113.9, 55.4; ^{19}F-NMR (282.3 MHz, DMSO) = -139.5. MS(MALDI-TOF): m/z = 681.87 (M^+), calc. 681.99.



Spectroscopic Measurements

Steady-state absorption and fluorescence spectra were measured using an UV/VIS spectrophotometer (Sinco, Neosys-2000) and a fluorophotometer (Sinco, FS-2), respectively. The fluorescence quantum yields are measured by an absolute PL quantum yield spectrometer (Hamamatsu, Quantaurus-QY C11347-01). The S2 fluorescence quantum yields are estimated and cross-checked using a toluene solution of anthracene as a standard, with a kwon value of 0.30.

The fluorescence lifetime in the sub-picosecond regime was estimated using the fluorescence up-conversion method. The second harmonic oscillation (390 or 430 nm) of the output of the femtosecond laser (780 or 860 nm) was used to excite the sample in a cell with a 1.0 mm optical path length. The residual fundamental and the fluorescence were focused in a BBO type I crystal to generate a sum-frequency oscillation, which was detected by a photomultiplier tube (Hamamatsu Photonics, H8259) and the photon counter (Stanford Research Systems, SR400) after passing through the monochromator (Nikon G250). The cross-correlation time of the apparatus was 100 fs fwhm.

Time-resolved fluorescence spectra were measured by the single photon counting method, using a streakscope (Hamamatsu

Photonics, C10627-03) equipped with a polychromator (Acton Research, SP2300). An ultrashort laser pulse was generated with a Ti:sapphire oscillator (Coherent, Vitesse, fwhm 100 fs) pumped with a diode-pumped solid-state laser (Coherent, Verdi) and the high power (1.5 mJ) pulses are generated with a Ti:sapphire regenerative amplifier (Coherent, Libra, 1 kHz). For excitation of the sample, the output of the Ti:sapphire regenerative amplifier was converted to 330 nm by using an optical parametric amplifier (Coherent, TOPAS). The instrument response function was also determined by measuring the scattered laser light to analyze a temporal profile. This method gives a time resolution of about 50 ps after the deconvolution procedure. The temporal emission profiles were well fitted into a single-exponential function. The residuals were less than 1.1 for each system.

The sub-picosecond time-resolved absorption spectra were collected by a pump-probe transient absorption spectroscopy system (Ultrafast Systems, Helios). The pump light was generated by using a regeneratively amplified titanium sapphire laser system (Coherent, Libra-F, 1 kHz) pumped by a diode-pumped Q-switched laser (Coherent, Evolution). The seed pulse was generated by a titanium sapphire laser (Coherent, Vitesse). The fourth harmonic generation (410 nm) generated from an optical parametric amplifier (Coherent, TOPAS) was used as the excitation pulse. And a white light continuum pulse, which was generated by focusing the residual of the fundamental light to a thin sapphire crystal after the computer-controlled optical delay, was used as a probe beam and directed to the sample cell with 1.0mm of optical path and detected with the CCD detector installed in the absorption spectroscopy. The pump pulse was chopped by the mechanical chopper synchronized to one-half of the laser repetition rate, resulting in a pair of the spectra with and without the pump, from which absorption change induced by the pump pulse was estimated.

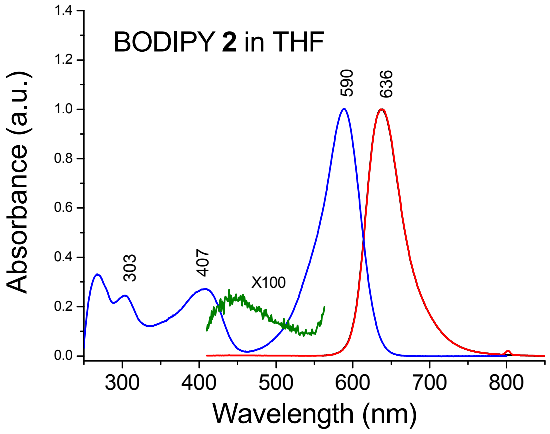


Fig. S1. Absorption (blue line) and fluorescence (red line, λ_{ex} = 400 nm and black line, λ_{ex} = 550 nm) spectra of BODIPY **2** in THF. Green lines indicate enlarged spectra for S2-emission.

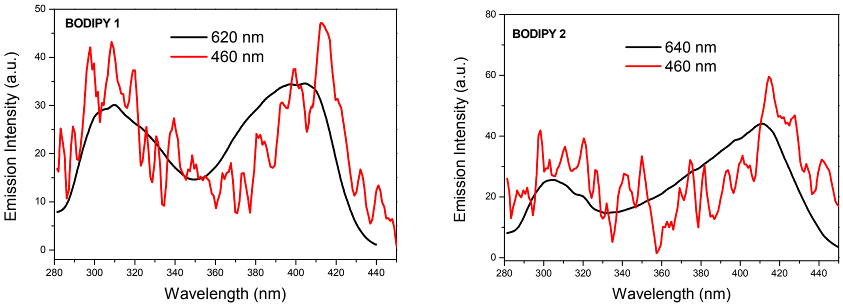


Fig. S2. Excitation spectra of BODIPY **1** and **2** in THF. Monitoring wavelengths are 620 (black line) and 460 nm (red line).

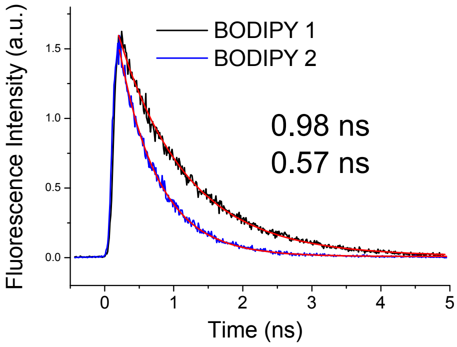


Fig. S3. S1-emssion decay profiles of BODIPY **1** (black line) and **2** (blue line) in THF. Excitation wavelength is 400 nm. Red lines are the best fit to the data using single exponential function.

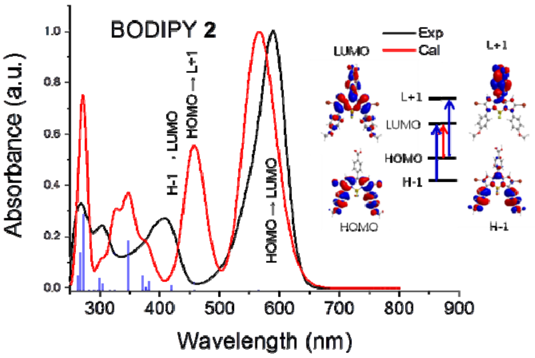


Fig. S4. Absorption and simulated spectra and orbital diagram BODIPY **2** calculated by B3LYP/6-31G(d) level.