Supporting Information

A multi-stimuli-responsive fluorescence switch based on *E-Z* isomerization of hydrazone

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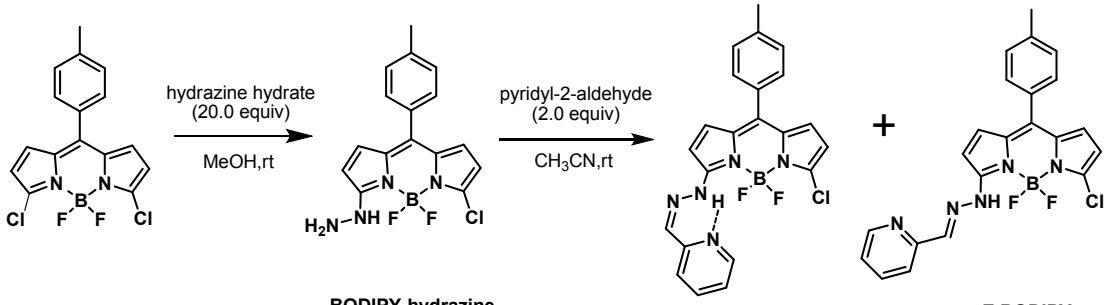
Materials and methods

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. NMR spectra were recorded with a Bruker Avance 400 spectrometer. High-resolution mass spectrometry experiments were performed with a Bruker Daltonics Apex IV spectrometer. Absorption spectra were determined on a Shimadzu UV-1601PC UV-Visible spectrophotometer. The photo reactions were carried out by using a high-pressure Hg lamp (500 W).

Synthesis of *Z*-BODIPY, *E*-BODIPY



BODIPY-hydrazine was synthesized according to the literature procedures[1]. 150 mg (0.44 mmol) 3, 5-dichloro BODIPY[2] was dissolved in 30 mL methanol under nitrogen. 0.5 mL (10 mmol) of hydrazine·hydrate was added and the reaction mixture was stirred in the dark at room temperature overnight. The solvent was evaporated under reduced pressure and the residue was purified by silica gel flash column chromatography (10:1 CH_2Cl_2:$C_2H_5OC_2H_5$) to afford the **hydrazine-BODIPY** as a dark solid (116 mg, 80% yield).

Synthesis of ***Z*-BODIPY**, ***E*-BODIPY**: Two equiv of pyridyl-2-aldehyde was added to hydrazine-BODIPY (320 mg, 0.092 mmol) in CH_3CN in the dark. The mixture was stirred overnight. The reaction was followed by TLC. The solvent was removed under reduced pressure. The crude residue was purified by silica gel flash column chromatography to afford the ***Z*-BODIPY (**32 mg, 8%**)** and ***E*-BODIPY(**326 mg, 81%**)**.

***Z*-BODIPY**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 16.18 (s, 1H), 8.92 (d, 1H, *J* = 4.0 Hz), 7.88 (td, 1H, *J* = 8.0, 2.0 Hz), 7.50-7.34 (m, 5H), 7.27 (d, 2H, *J* = 5.6 Hz), 6.95 (d, 1H, *J* = 4.8 Hz), 6.85 (d, 1H, *J* = 4.8 Hz), 6.43 (d, 1H, *J* = 4.0 Hz), 6.21 (d, 1H, *J* = 4.0 Hz), 2.44 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 160.2, 152.1, 148.7, 139.6, 137.8, 137.7, 135.0, 134.5, 134.0, 132.4, 131.4, 131.3, 130.5, 129.1, 124.9, 124.3, 121.5, 113.2, 112.2, 21.5. MS (ESI): $(M+H)^+$ 436.1310, found: 436.1312.

***E*-BODIPY:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.46 (s, 1H), 8.63 (d, 1H, *J* = 4.8 Hz), 8.05 (s, 1H), 7.96 (d, 1H, *J* = 8.0 Hz), 7.74 (t, 1H, *J* = 8.0 Hz), 7.35 (d, 2H, *J* = 5.6 Hz), 7.30-7.26 (m, 3H), 6.97 (d, 1H, *J* = 4.8 Hz), 6.81 (d, 1H, *J* = 4.8 Hz), 6.48 (d, 1H, *J* = 4.0 Hz), 6.23 (d, 1H, *J* = 4.0 Hz), 2.44 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 158.9, 152.6, 150.0, 147.3, 140.1, 136.6, 136.0, 135.2, 133.3, 132.4, 132.3, 130.9, 130.5, 129.2, 124.5, 122.9, 121.0, 113.8, 112.0, 21.5. MS (ESI): $(M+Na)^+$ 458.1130, found: 458.1129.

HPLC analyses on stability of *E*-BODIPY to the *Z*-BODIPY

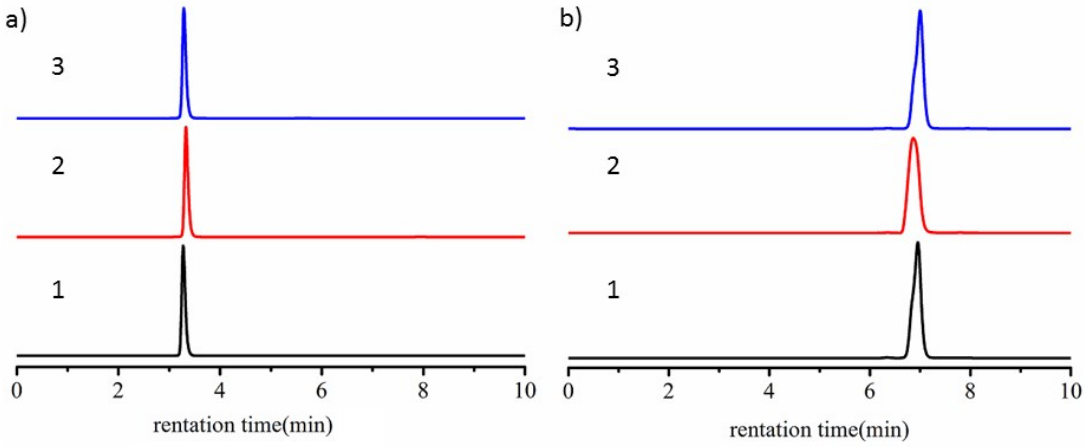


Fig. S1. HPLC charts of ***E*-BODIPY** (a) and ***Z*-BODIPY** (b). Charts 1, 2, 3 correspond to solutions under different conditions: 1 is kept in dark for 12 h, 2 is kept in daylight for 12 h, 3 is kept under 70℃ in dark for 12 h. HPLC was performed on a Hitachi ELITE LaChrom system. Silica gel column (YMC-Pack SIL) in normal phase (CH_2Cl_2/MeOH = 98/2) was used to analyze each isomer and 520 nm was used as the monitoring wavelength.

HPLC analyses on the conversion ratio from *E*-BODIPY to the *Z*-BODIPY

The photoconversion ratio from the ***E*-BODIPY** to the ***Z*-BODIPY** in CH_2Cl_2 upon irradiation using a high-pressure Hg lamp (500 W) with a filter ($300\ nm < \lambda < 400\ nm$) was measured with HPLC analyses. HPLC was performed on a Hitachi ELITE LaChrom system. Silica gel column (YMC-Pack SIL) in normal phase (CH_2Cl_2/MeOH = 98/2) was used to analyze the ratio of each isomer and 520 nm was used as the monitoring wavelength. Peak 1 (t = 4.2 min) corresponds to the ***Z*-BODIPY.** Peak 2 (t = 7.0 min) corresponds to the ***Z*-BODIPY**, the retention time of which shifts a little because of the change of concentration. The conversion ratio was estimated from the ratio of peak area between peak 1 and 2 to be about 60 % (A_2:A_3 = 12:9, Abs_E: Abs_Z = 1.1).

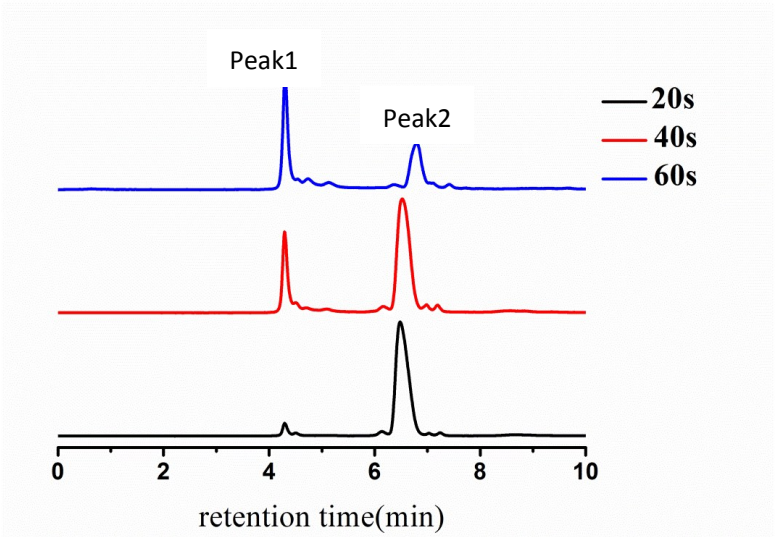


Fig. S2. HPLC charts of ***E*-BODIPY** upon irradiation using a high-pressure Hg lamp (500 W) with a filter (300 nm < λ < 400 nm).

Isomerization yield measurements

The quantum yield experiments were started from solutions of *E* isomer and mixture of *E* and Z at the photostationary state. Quantum yields were calculated from the conversion of the recorded dc_E/dt profile using the following equation[3]:

$$\emptyset_{E\to Z}^{560nm} = \frac{d\left(c_z \cdot \varepsilon_Z^{560nm} + c_E \cdot \varepsilon_E^{560nm}\right) \cdot l}{dt} \cdot \frac{1}{1000 \cdot I_0 \cdot \varepsilon_Z^{560nm} \cdot \left(1 - 10^{-A^{560nm}}\right)}$$

I_0 [$E \cdot s^{-1} \cdot cm^{-3}$] is the light intensity as obtained from actinometry[3], ε is the molar absorptivity [$L \cdot mol^{-1} \cdot cm^{-1}$] and A is the total absorption at λ = 560 nm. c_Z and c_E were determined by HPLC, and quantum yield was obtained for ***E*-BODIPY** ($\emptyset_{E\to Z} = 0.41$).

Actinometry

Light intensity of 300-400 nm was determined by potassium ferrioxalate actinometry. 3 mL of potassium ferrioxalate solution (0.006 M in 0.05 M H_2SO_4) in a quartz cuvette was irradiated for 60 s, followed by addition of 0.5 mL of phenanthroline buffer (0.1 wt% in 0.5 M H_2SO_4/1.6 M NaOAc). A reference sample kept in the dark was treated the same way. The absorbance of both samples was measured and the difference at 510 nm was used for analysis. The light intensity I_0 is obtained from the following equation:

$$I_0 = \frac{\Delta A^{510\,nm}}{\Delta t \cdot 1000 \cdot \emptyset \cdot \varepsilon^{510\,nm}} \cdot \frac{3.5\,mL}{3\,mL}$$

$\Delta A^{510\,nm}$ is the difference in absorbance between the sample and the reference, $\varepsilon^{510\,nm} = 11100\,L \cdot mol^{-1} \cdot cm^{-1}$, and $\emptyset^{300-400\,nm} = 1.2$. The measured $\Delta A^{510\,nm} = 0.79$, and the light intensity is $I_0 = 1.19 \cdot 10^{-9} E \cdot s^{-1} \cdot cm^{-3}$.

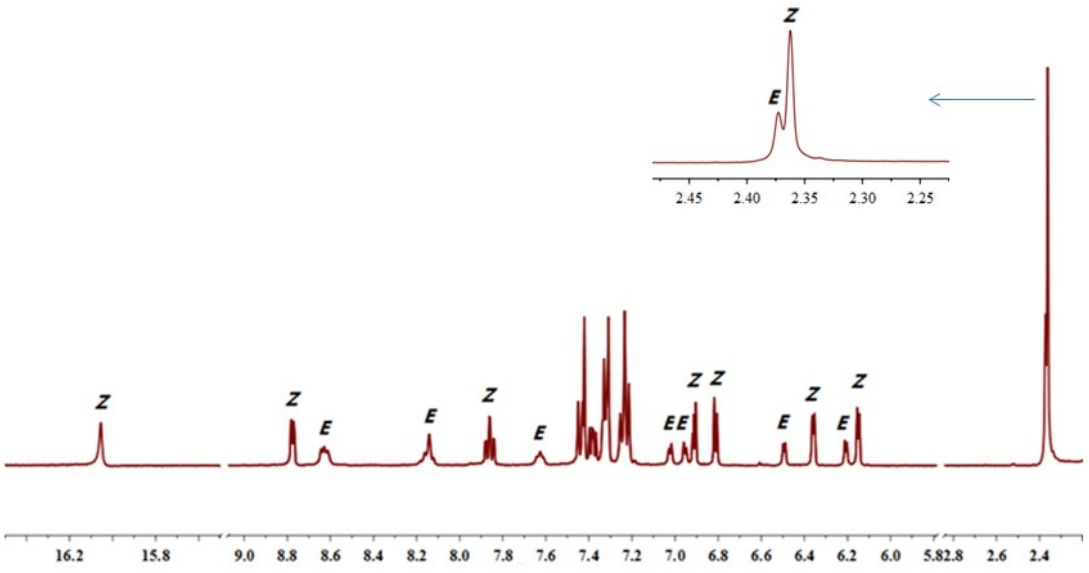


Fig. S3. ^{1}H NMR spectrum of ***E*-BODIPY** in CD_2Cl_2 after irradiation with a high-pressure Hg lamp (500 W) without filter for 6 h.

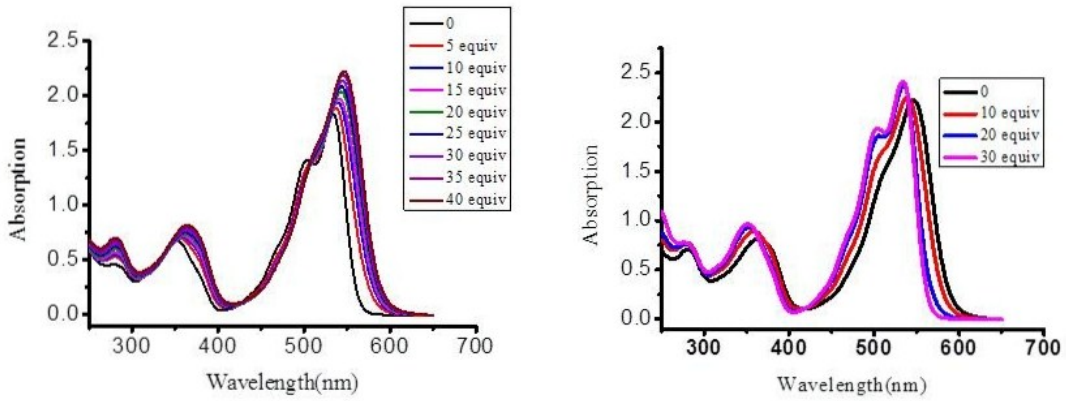


Fig. S4. UV-vis spectrum of ***E*-BODIPY** (40 μM) upon addition of TFA (left) and **protonated BODIPY** (40 μM) upon addition of DIPEA (right).

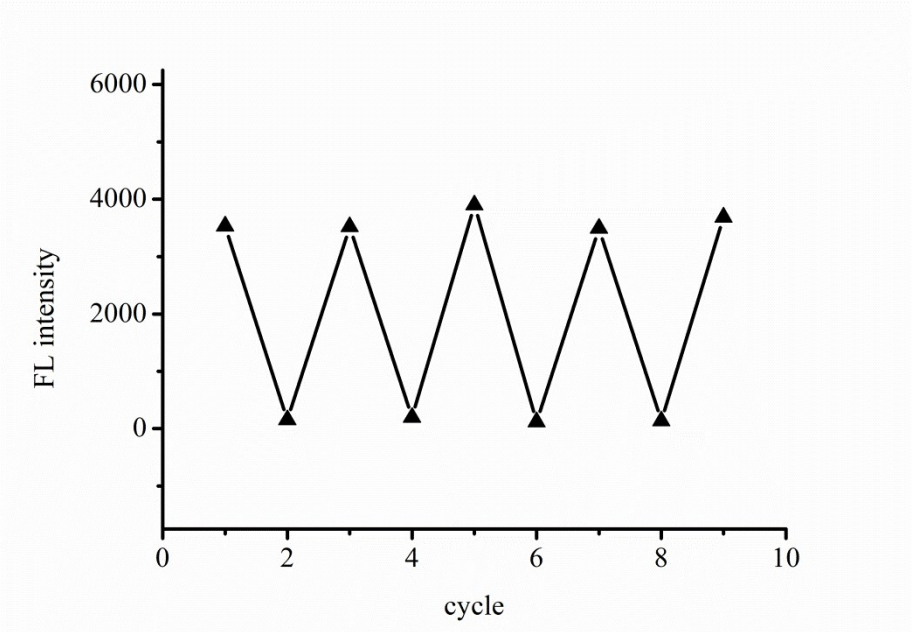


Fig. S5. pH cycling experiment of ***E*-BODIPY** (40 μM) upon alternate addition of acid (TFA) and base (DIPEA).

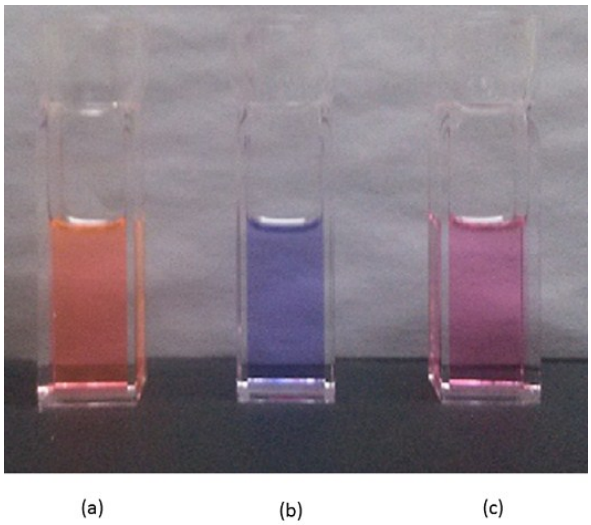


Fig. S6. Photograph of ***E*-BODIPY** (a), **protonated BODIPY** (b), ***Z*-BODIPY** (c) in CH_2Cl_2.

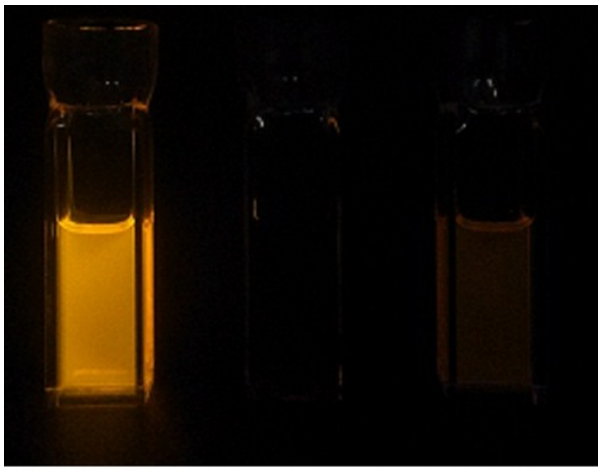


Fig. S7. Photograph of ***E*-BODIPY** (a), **protonated BODIPY** (b), ***Z*-BODIPY** (c) under irradiation with UV light (λ = 365 nm) in CH_2Cl_2.

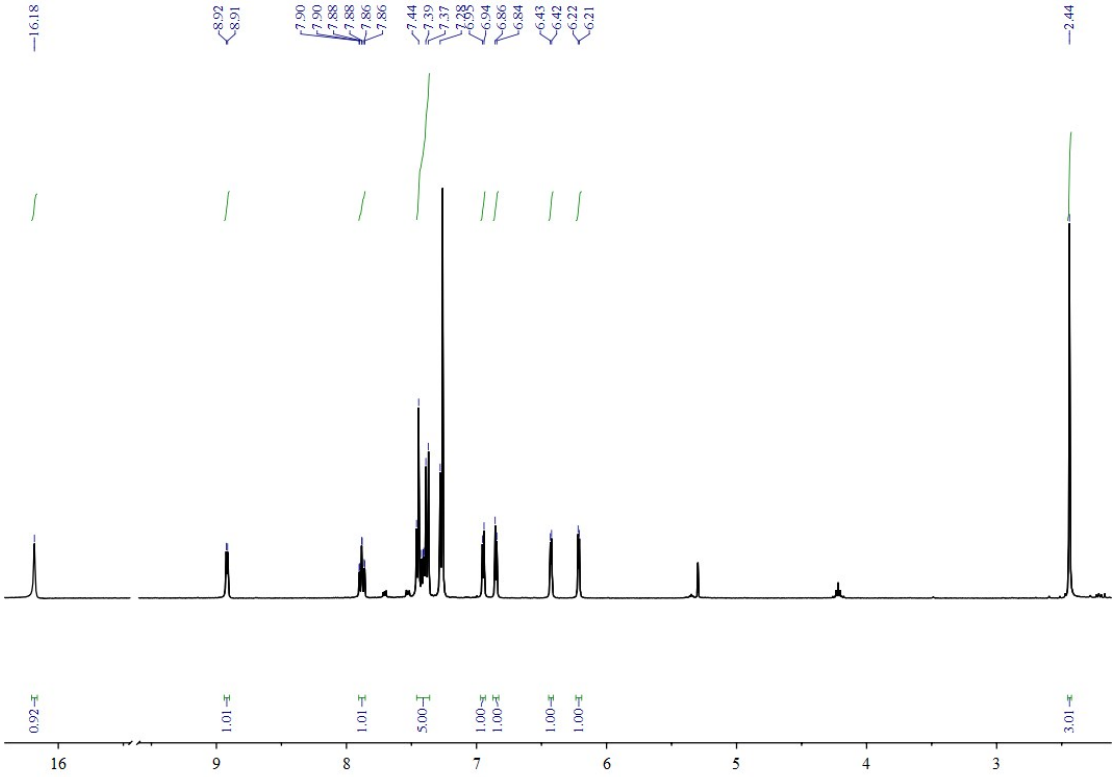
Reference:

[1] O. Dilek and S. Bane, *J. Fluoresc.* **2011**, *21*, 347-354.

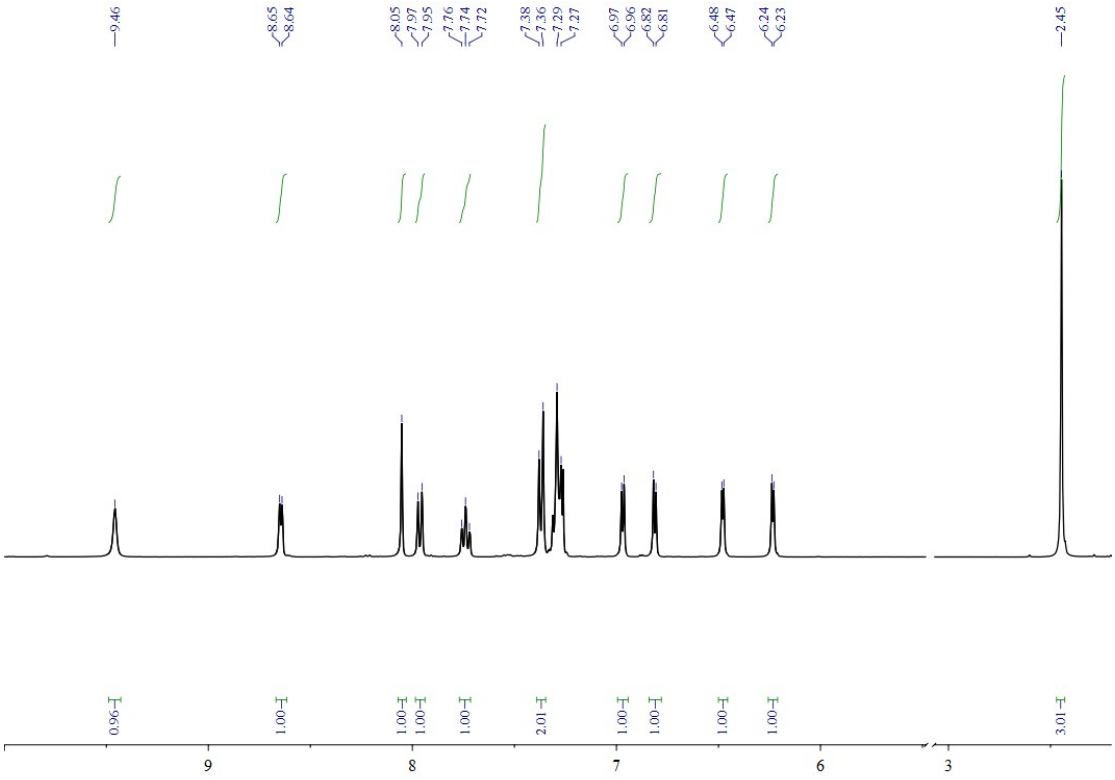
[2] (a) Baruah, M.; Qin, W.; Basarić, N.; De Borggraeve, W. M.; Boens, N. *J. Org. Chem.* **2005**, *70*, 4152; (b) Domaille, D. W.; Zeng, L.; Chang, C. J. *J. Am. Chem. Soc.* **2010**, *132*, 1194.

[3] D. J. van Dijken, P. Kovaříček, S. P. Ihrig and S. Hecht. *J. Am. Chem. Soc.* **2015**, 137, 14982-14991.

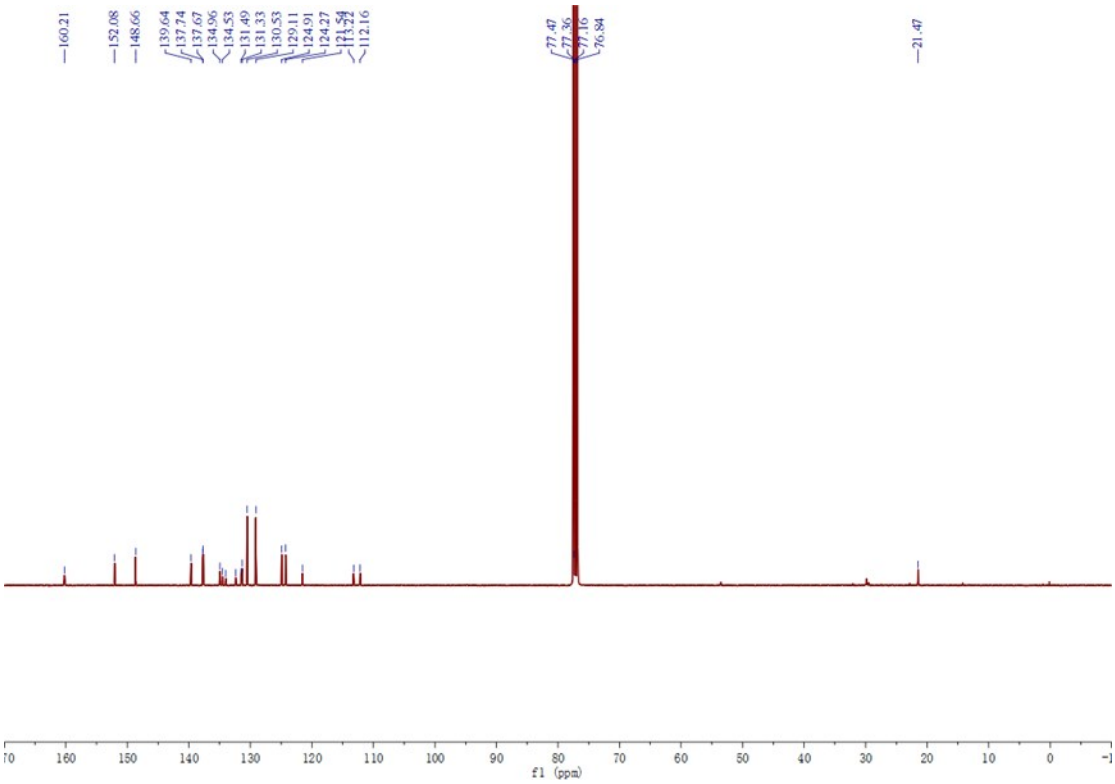
[1]H NMR and HRMS of *E*-BODIPY and *Z*-BODIPY



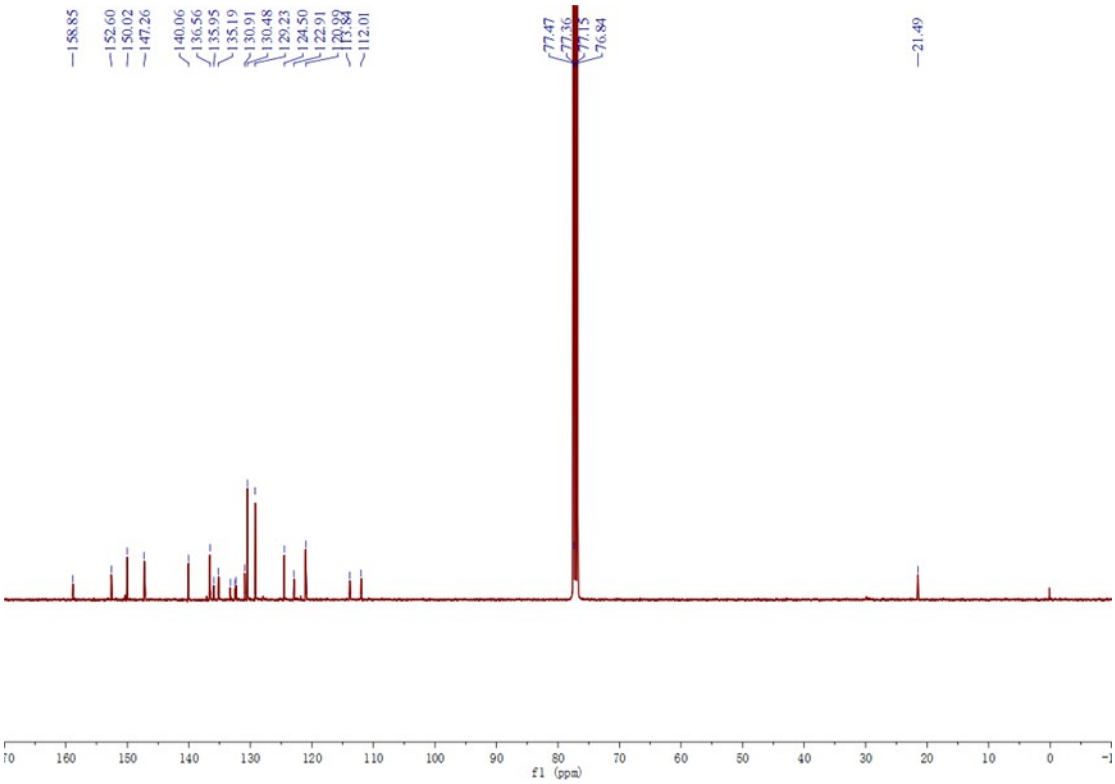
[1]H NMR spectrum of ***Z*-BODIPY**.



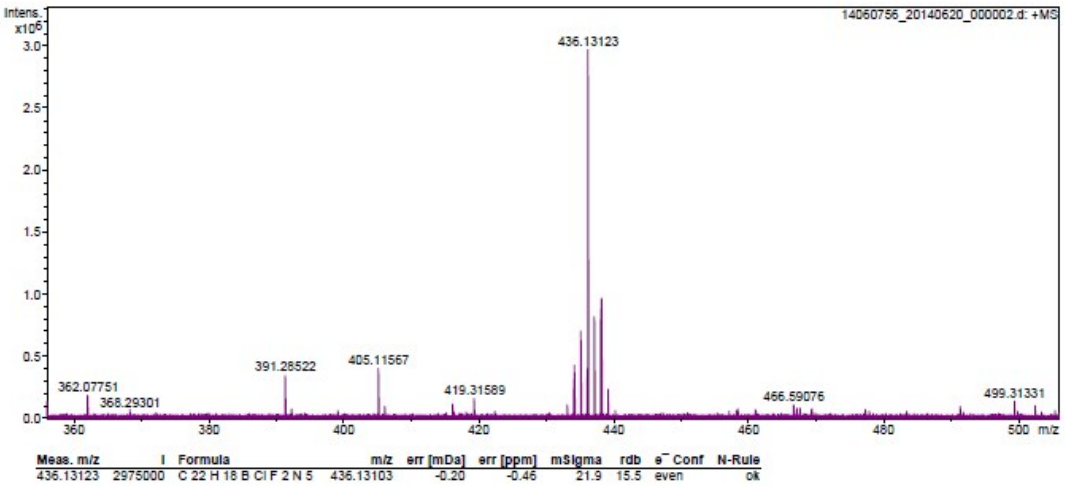
[1]H NMR spectrum of ***E*-BODIPY**.



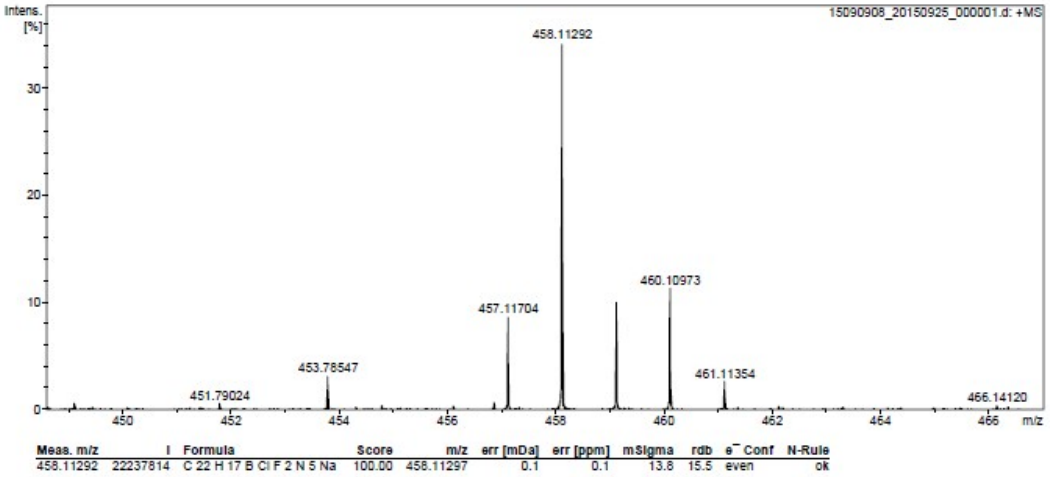
^{13}C NMR spectrum of ***Z*-BODIPY**.



^{13}C NMR spectrum of ***E*-BODIPY**.



HR-ESI-MS of ***E*-BODIPY**.



HR-ESI-MS of ***Z*-BODIPY**.