Electronic Supplementary Material (ESI) for ChemComm.

# Naphtho[*b*]-fused BODIPYs: one pot Suzuki-Miyaura-Knoevenagel synthesis and photophysical properties

Zhikuan Zhou,*[a,b] Jianping Zhou,[a] Lizhi Gai,[b] Aihua Yuan*[a] and Zhen Shen*[b]

a School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, P. R. China. E-mail: zkzhou@just.edu.cn, aihua.yuan@just.edu.cn; Fax: +86-511-85635850; Tel: +86-511-85639001.

b State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, P. R. China. E-mail: zshen@nju.edu.cn.

**I. Experimental section**

**II. Supplementary Figure**

# I Experimental Section

## I.1 Materials and instrumentations

All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. All air and moisture-sensitive reactions were carried out under nitrogen atmosphere in oven-dried glassware. Glassware was dried in an oven at 100 °C and cooled under a stream of inert gas before use. Both dichloromethane and triethylamine were distilled over calcium hydride. $^1$H NMR spectra were recorded on a Bruker DRX400 spectrometer and referenced to the residual proton signals of the solvent. HR-MS were recorded on a Bruker Daltonics microTOF-Q II spectrometer. All the solvents employed for the spectroscopic measurements were of UV spectroscopic grade (Aldrich).

## I.2 Synthesis and characterization

1. Synthesis of 2-iodo-1,3,5,7-tetramethyl-8-phenyl-4,4-difluoroboradiazaindacene (**4**)

**4** was obtained according to the literature reported procedure.[S1]

2. Synthesis of 2-(2-formylphenyl)-1,3,5,7-tetramethyl-8-phenyl-4,4-difluoroboradiazaindacene (**1**)

Compound **4** (100 mg, 0.22 mmol), 2-formylphenylboronic acid (50 mg, 0.33 mmol), and tetrakis(triphenylphosphine)palladium(0) (25 mg, 0.022 mmol) under nitrogen atmosphere were added to THF (20 mL). After addition of 2 mL of aqueous 2M sodium carbonate solution, the reaction mixture was heated at 80°C for 4h until no more compound **4** existing (monitored by TLC). The cooled crude mixture was poured into water (40 mL), extracted with $CH_2Cl_2$ (3 × 20 mL), and dried over anhydrous sodium sulfate. Silica-gel column chromatography (petroleum ether/ethyl acetate 85/15) gave **1** as a red solid (66 mg, 70% yield).

$^1$H NMR (400 MHz, $CDCl_3$): δ=9.86 (s, 1H), 8.01–7.98 (d, 1H), 7.64–7.60 (t, 1H), 7.53–7.45 (m, 4H), 7.34–7.30 (m, 2H), 7.22–7.20 (m, 1H), 6.06 (s, 1H), 2.60 (s, 3H), 2.43 (s, 3H), 1.41 (s, 3H), 1.18 ppm (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 192.30, 157.74, 152.57, 144.87, 142.51, 139.65, 137.79, 134.92, 134.07, 132.52, 132.24, 130.79, 129.51, 129.36, 129.32, 128.58, 128.29, 128.04, 127.90, 127.57, 122.28, 14.91, 14.67, 13.31, 12.77 ppm; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 511 nm; MALDI-TOF MS: m/z calcd for $[C_{26}H_{23}BF_2N_2O]^+$: 428.19; found: 428.61 $[M]^+$.

3. Synthesis of BODIPY **2a** without addition of TBAB

Compound **4** (100 mg, 0.22 mmol), 2-formylphenylboronic acid (50 mg, 0.33 mmol), and tetrakis(triphenylphosphine)palladium(0) (25 mg, 0.022 mmol) under nitrogen atmosphere were added to THF (20 mL). After addition of 2 mL of aqueous 2M sodium carbonate solution, the reaction mixture was heated at 80°C for 24h. The reaction was monitored by TLC. The cooled crude mixture was poured into water (40 mL), extracted with $CH_2Cl_2$ (3 × 20 mL), and dried over anhydrous sodium sulfate. Silica-gel column chromatography (dichloromethane/petroleum ether 35/65) gave **2a** as a purple solid (15 mg, 17% yield).

$^1$H NMR (400 MHz, $CDCl_3$): δ=8.22 (d, 1H), 7.88 (d, 1H), 7.80 (d, 1H), 7.69 (d, 1H), 7.57–7.56 (m, 3H), 7.48 (t, 1H), 7.41–7.37 (m, 3H), 6.16 (s, 1H), 2.69 (s, 3H), 2.01 (s, 3H), 1.45 ppm (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 161.57, 147.23, 146.21, 143.61, 135.57, 135.11, 135.03, 132.96, 132.48, 130.59, 130.15, 129.85, 129.52, 129.49, 128.50, 127.21, 125.60, 124.52, 124.30, 123.91, 116.29, 15.38, 15.26, 15.09 ppm; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 552 nm; MALDI-TOF MS: m/z calcd for $[C_{26}H_{21}BF_2N_2]^+$: 410.18; found: 410.57 $[M]^+$, 391.52 $[M-F]^+$.

4. Synthesis of BODIPY **2a** (Use TBAB as Phase Transfer Catalyst)

Compound **4** (50 mg, 0.11 mmol), 2-formylphenylboronic acid (25 mg, 0.17 mmol), tetrabutylammonium bromide (35 mg, 0.11 mmol) and tetrakis(triphenylphosphine)palladium(0) (13 mg, 0.011 mmol) were added to THF (20 mL) under nitrogen atmosphere. After addition of 3 mL of aqueous 2M sodium carbonate solution, the reaction mixture was heated at 80°C for 6h. The reaction was monitored by TLC. The cooled crude mixture was poured into water (20 mL), extracted with $CH_2Cl_2$ (3 × 20 mL), and dried over anhydrous sodium sulfate. Silica-gel column chromatography (dichloromethane/petroleum ether 35/65) gave **2a** as a purple solid (18 mg, 39% yield).

5. Synthesis of BODIPY **2b** (Use TBAB as Phase Transfer Catalyst)

Compound **2b** was obtained as a greenish solid in 45% yield by following a procedure similar to that of **2a**.

$^1$H NMR (400 MHz, $CDCl_3$): δ=7.88-7.77 (m, 3H), 7.67 (d, 1H), 7.59–7.56 (m, 3H), 7.41-7.38 (m, 2H), 7.16-7.11 (m, 1H), 6.18 (s, 1H), 2.70 (s, 3H), 1.97 (s, 3H), 1.46 ppm (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 163.06, 162.33, 160.62, 147.68, 145.98, 143.66, 135.84, 134.87, 132.88, 131.75, 131.65, 131.62, 131.29, 131.20, 129.64, 129.57, 128.46, 127.22, 124.61, 115.44, 113.24, 113.00, 109.32, 109.09, 15.45, 15.32, 14.80 ppm; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 545 nm.

6. Synthesis of 2,6-diiodo-1,3,5,7-tetramethyl-8-phenyl-4,4-difluoroboradiazaindacene (**6**)

**6** was obtained according to the literature reported procedure. [S1]

7. Synthesis of BODIPY **3**

Compound **6** (50 mg, 0.087 mmol), 2-formylphenylboronic acid (39 mg, 0.26 mmol), tetrabutylammonium bromide (28 mg, 0.087 mmol) and tetrakis(triphenylphosphine)palladium(0) (7 mg, 0.0087 mmol) were added to THF (20 mL) under nitrogen atmosphere. After addition of 3 mL of aqueous 2M sodium carbonate solution, the reaction mixture was heated at 80℃ for 1.5 h. The reaction was monitored by TLC. The cooled crude mixture was poured into water (20 mL), extracted with $CH_2Cl_2$ (3 × 20 mL), and dried over anhydrous sodium sulfate. Silica-gel column chromatography (toluene/petroleum ether 80/20) gave **3** as a purple solid (15 mg, 35% yield).

$^1$H NMR (400 MHz, $CDCl_3$): δ=8.21 (d, 2H), 7.94 (d, 2H), 7.80 (d, 2H), 7.75 (d, 2H), 7.66-7.62 (m, 3H), 7.54-7.49 (m, 4H), 7.45-7.41 (m, 2H), 2.06 ppm (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 135.78, 135.56, 130.95, 130.38, 130.07, 129.96, 129.69, 129.15, 128.11, 125.58, 124.54, 116.73, 15.97 ppm; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 630 nm.

## I.3 X-ray structure determination

The X-ray diffraction data were collected on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) using the ω−2θ scan mode. The structure was solved by direct methods and refined on $F^2$ by full-matrix least-squares methods using SHELX-2000.[S2-S3] All calculations and molecular graphics were carried out on a computer using the SHELX-2000 program package and Mercury 3.8.

**2a**: $C_{26}H_{21}BF_2N_2$; A red block-like crystal of the approximate dimensions 0.30 × 0.20 × 0.20 mm$^3$ was measured. Monoclinic, space group C2/c, a = 21.110(8) Å, b = 10.940(4) Å, c = 20.341(12) Å, α = 90, β = 118.052(3), γ = 90, V = 4146(3) Å$^3$, Z = 8, F(000) = 1712, ρ = 1.315 g cm$^{-3}$, $R_1$ = 0.0772, $wR_2$ = 0.2344, GOF = 1.020.

**3**: $C_{33}H_{23}BF_2N_2$; A purple block-like crystal of the approximate dimensions 0.20 × 0.16 × 0.10 mm$^3$ was measured. Monoclinic, space group C2/c, a = 16.140(5) Å, b = 14.391(4) Å, c = 21.159(6) Å, α = 90, β = 103.057(3), γ = 90, V = 4784(2) Å$^3$, Z = 8, F(000) = 2064, ρ = 1.377 g cm$^{-3}$, $R_1$ = 0.0878, $wR_2$ = 0.2539, GOF = 1.155.

CCDC No. 1535183 for **2a** and No. 1535184 for **3** containing the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223–336–033; E-mail: deposit@ccdc.cam.ac.uk).

### 1.4 Spectroscopic measurements

UV-visible absorption spectra were recorded on a Shimadzu 3000 spectrophotometer. Fluorescence spectra were measured on a Hitachi F-2700 luminescence spectrometer with a 150 W xenon lamp. The fluorescence lifetimes of the samples were determined with a Horiba Jobin Yvon Fluorolog-3 spectrofluorimeter. Absorption and emission measurements were carried out in 1×1 cm quartz cuvettes. For all measurements, the temperature was kept constant at (298±2) K. Dilute solutions with absorbance of less than 0.05 at the excitation wavelength were used for the measurement of fluorescence quantum yields. For BODIPY **1**, **2a** and **2b**, rhodamine 6G was used as the standard ($\Phi_F$ = 0.95 in ethanol)[S4]. For BODIPY **3**, zinc phthalocyanine was used as the standard ($\Phi_F$ = 0.45 in PrOH)[S4].

The quantum yield, Φ, was calculated using equation (1):

$$\Phi_{sample} = \Phi_{std}\left[\frac{I\ sample}{I\ std}\right]\left[\frac{A\ std}{A\ sample}\right]\left[\frac{n2\ sample}{n2\ std}\right] \qquad (1)$$

where the *sample* and *std* subscripts denote the sample and standard, respectively, I is the integrated emission intensity, A stands for the absorbance, and n is refractive index.

When the fluorescence decays were monoexponential, the rate constants of radiative ($k_f$) and nonradiative ($k_{nr}$) deactivation were calculated from the measured fluorescence quantum yield ($\Phi_F$) and fluorescence lifetime (τ) according to equations (2) and (3):

$$k_f = \Phi_F/\tau \qquad (2)$$

$$k_{nr} = (1-\Phi_F)/\tau \qquad (3)$$

### I.5 DFT calculations

The G09W software package was used to carry out a DFT geometry optimization using the B3LYP functional with 6-31G(d) basis sets.[S5] The same approach was used to calculate the absorption properties based on time-dependent (TD-DFT) method.

## II Supplementary Figure

$^1$H NMR and $^{13}$C NMR spectra

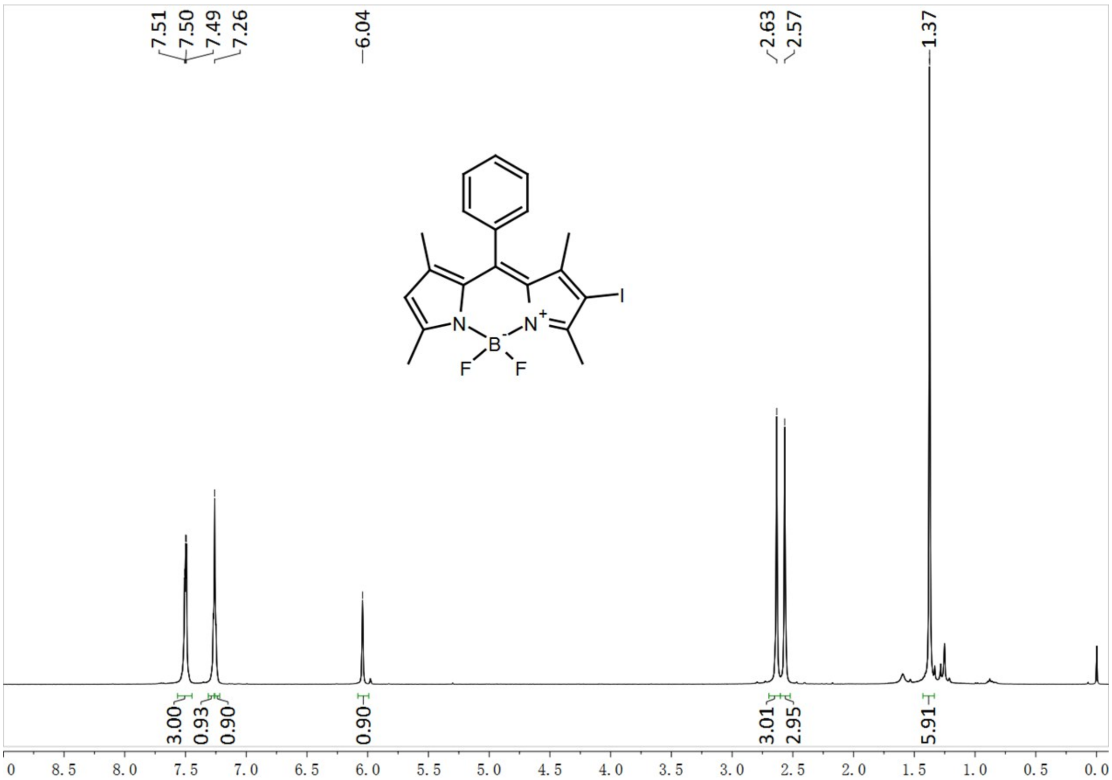

**Fig S1** $^1$H NMR spectra of the precursor **4** (400 MHz, CDCl$_3$).

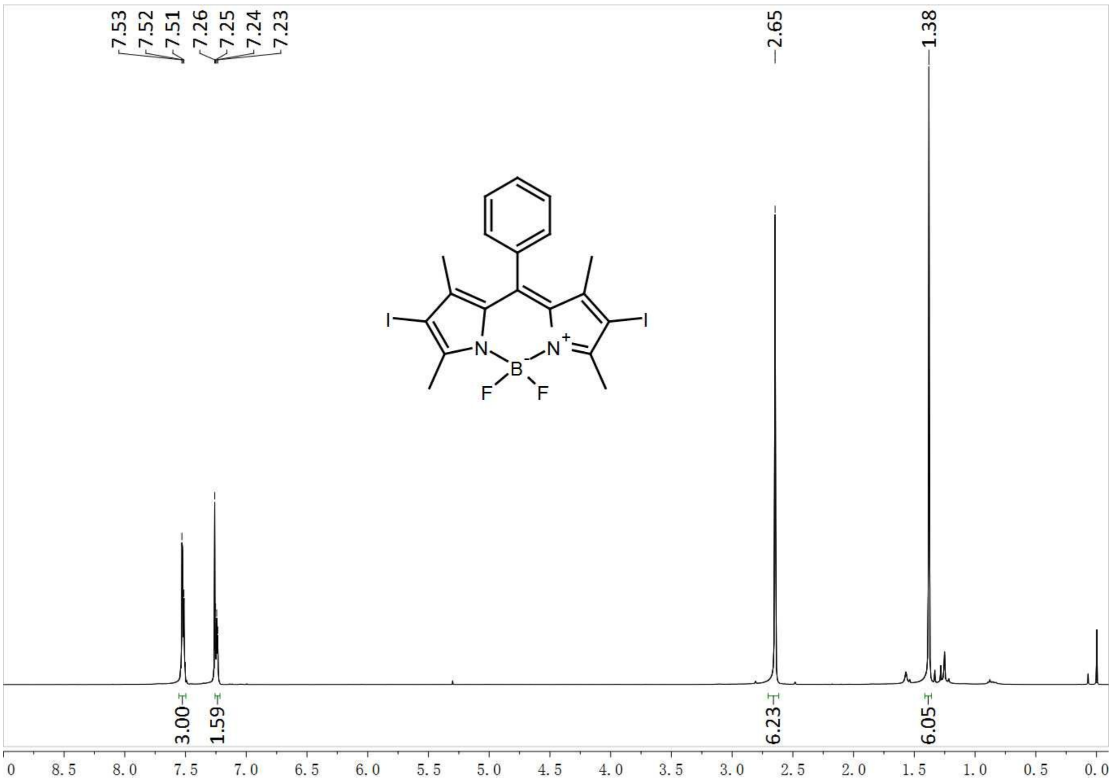

**Fig S2** $^1$H NMR spectra of the precursor **6** (400 MHz, CDCl$_3$).

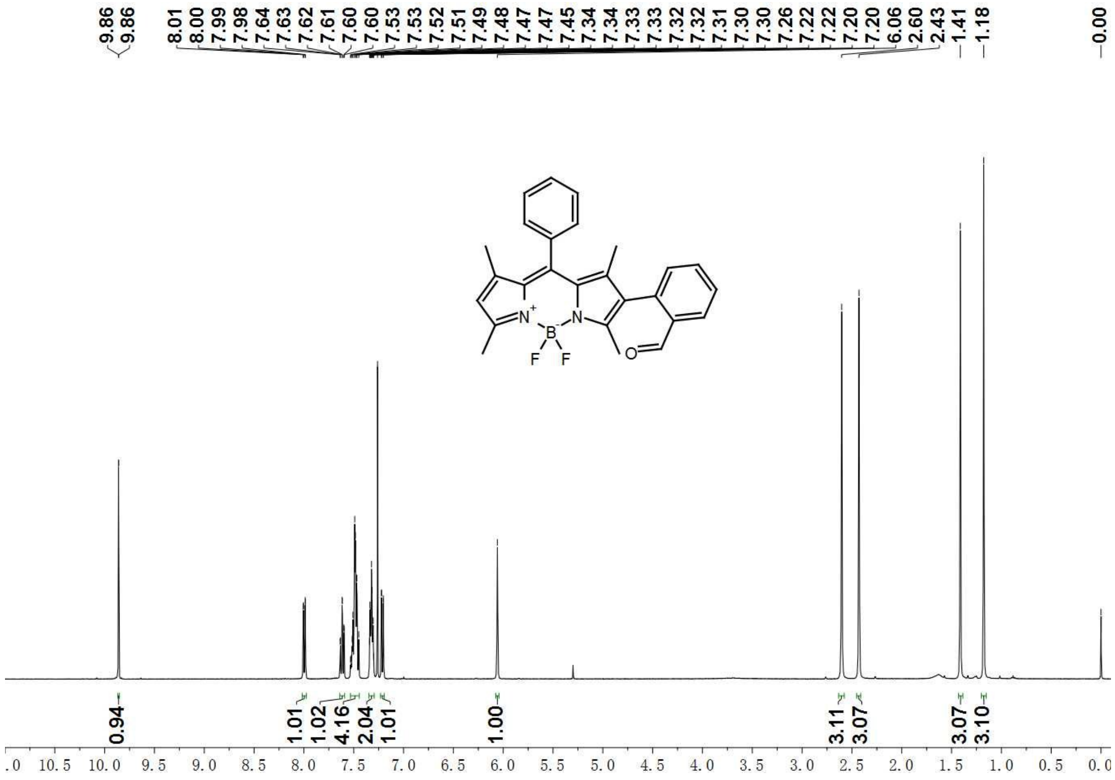

**Fig S3** $^{1}$H NMR spectra of the BODIPY **1** (400 MHz, $CDCl_3$).

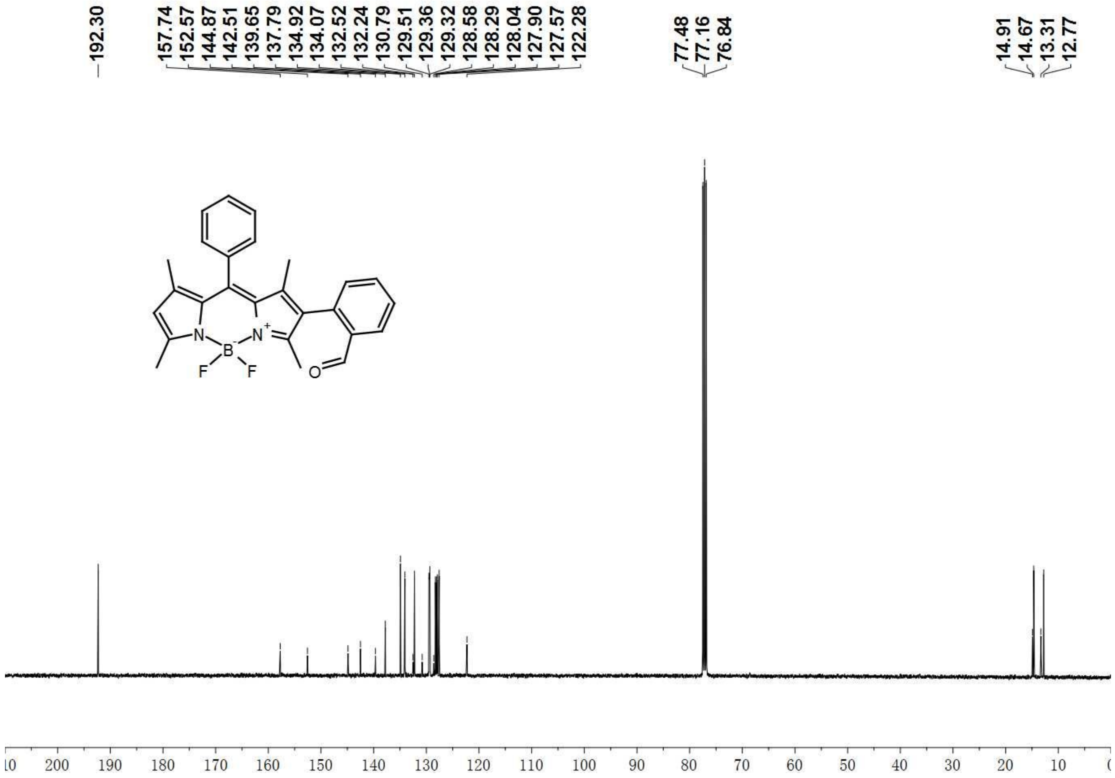

**Fig S4** $^{13}$C NMR spectra of the BODIPY **1** (100 MHz, $CDCl_3$).

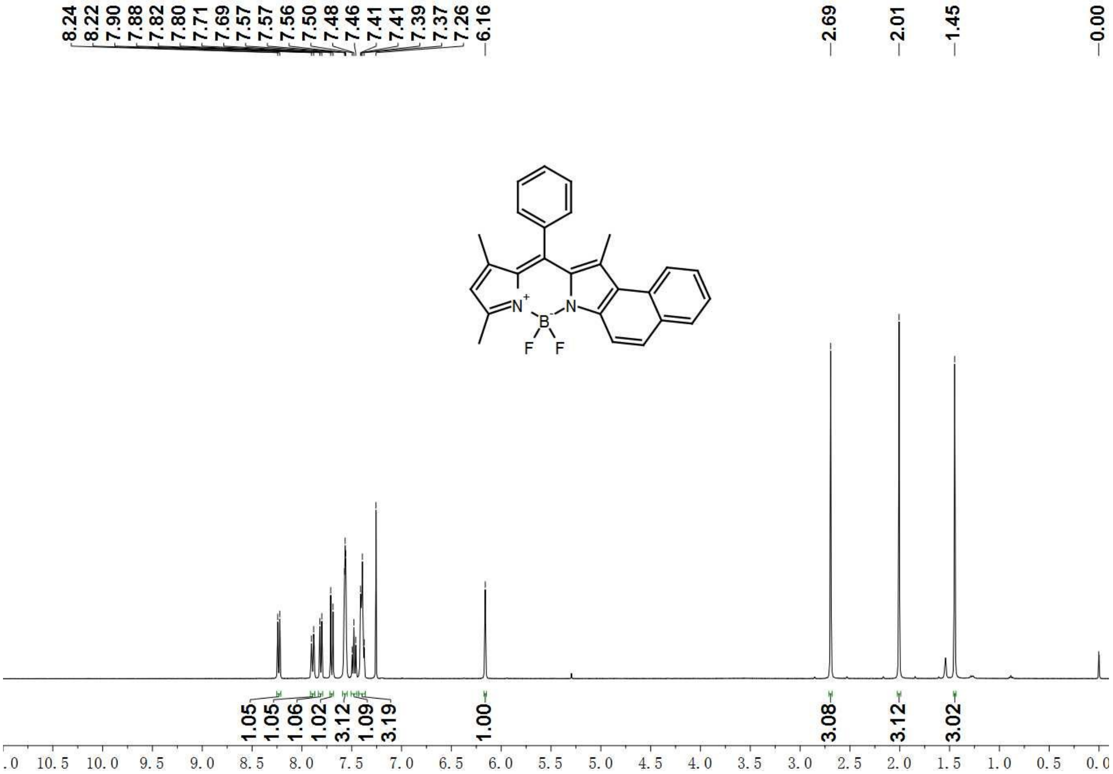

**Fig S5** $^{1}$H NMR spectra of the BODIPY **2a** (400 MHz, CDCl$_3$).

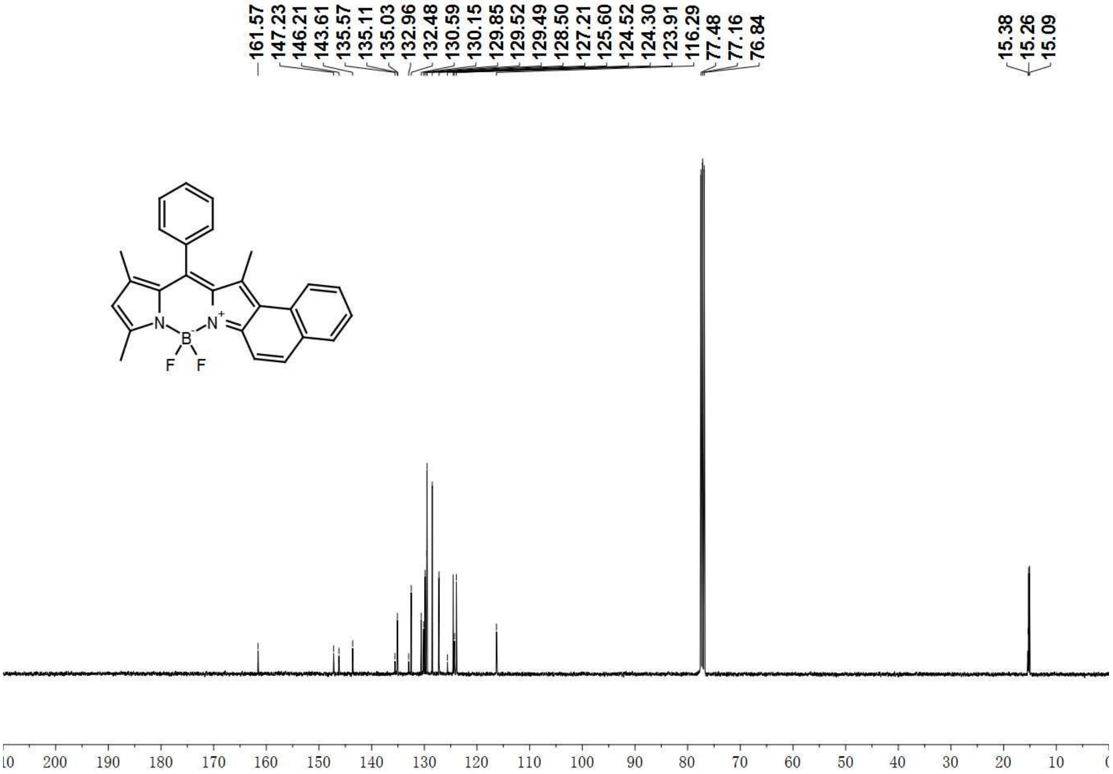

**Fig S6** $^{13}$C NMR spectra of the BODIPY **2a** (100 MHz, CDCl$_3$).

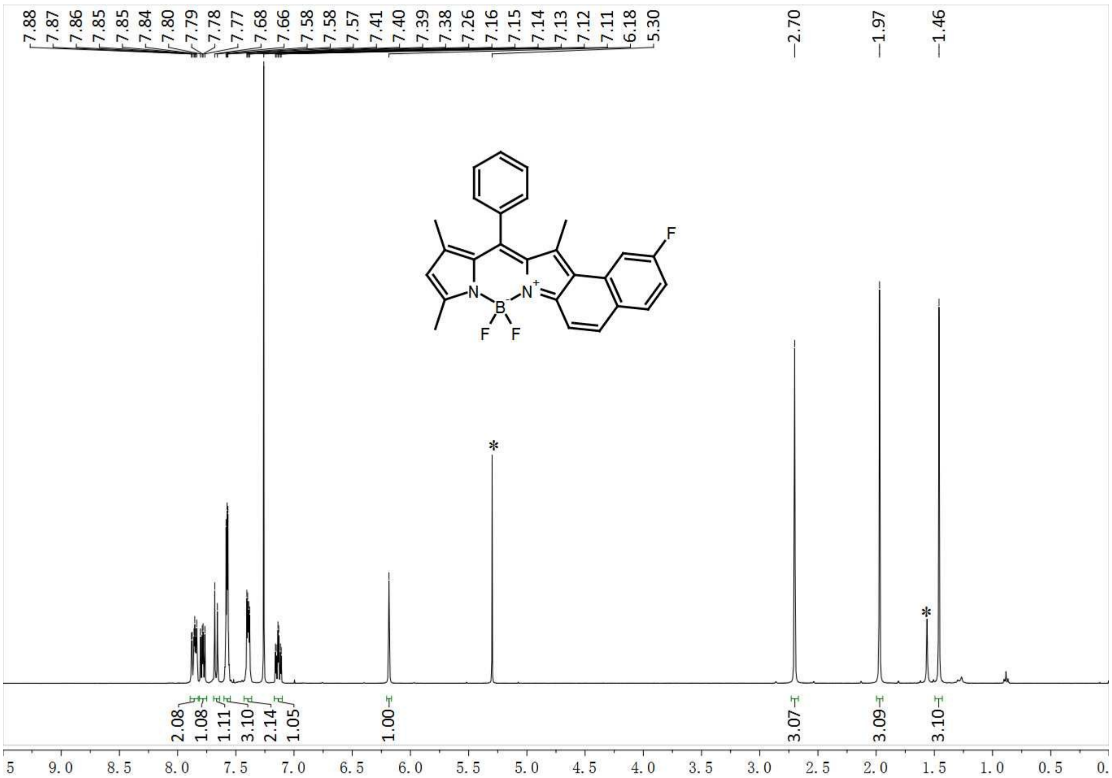

**Fig S7** $^1$H NMR spectra of the BODIPY **2b** (400 MHz, $CDCl_3$).

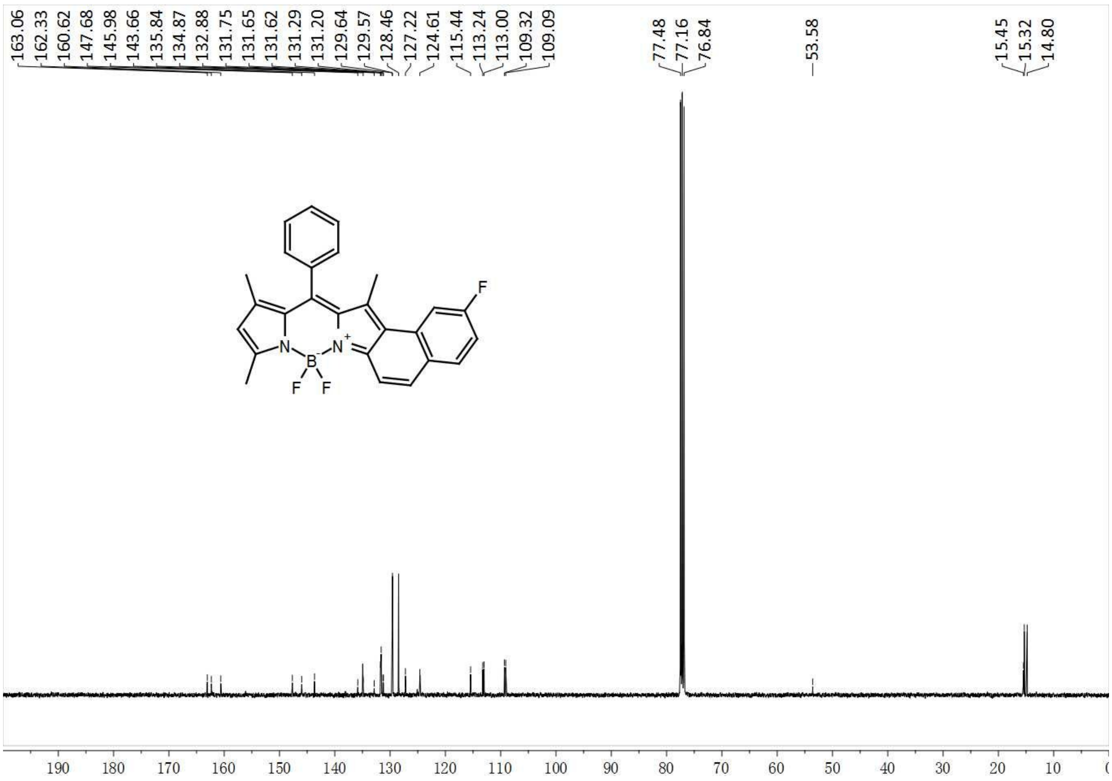

**Fig S8** $^{13}$C NMR spectra of the BODIPY **2b** (100 MHz, $CDCl_3$).

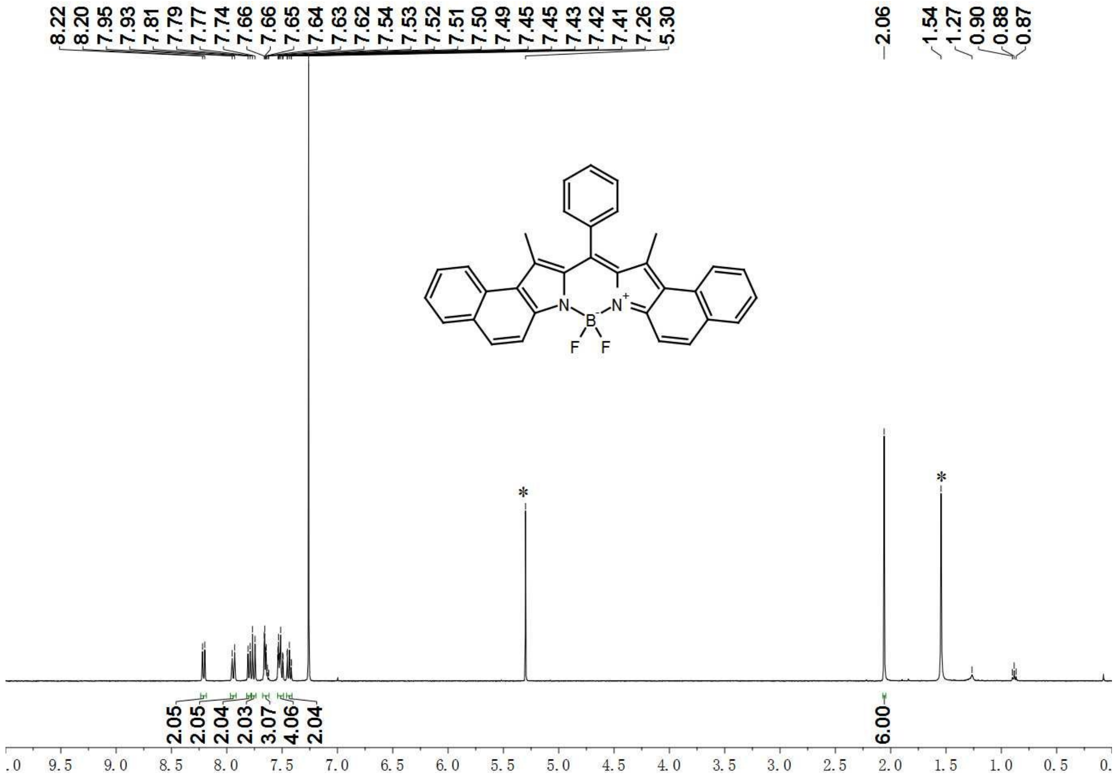

**Fig S9** $^{1}H$ NMR spectra of the BODIPY **3** (400 MHz, $CDCl_3$).

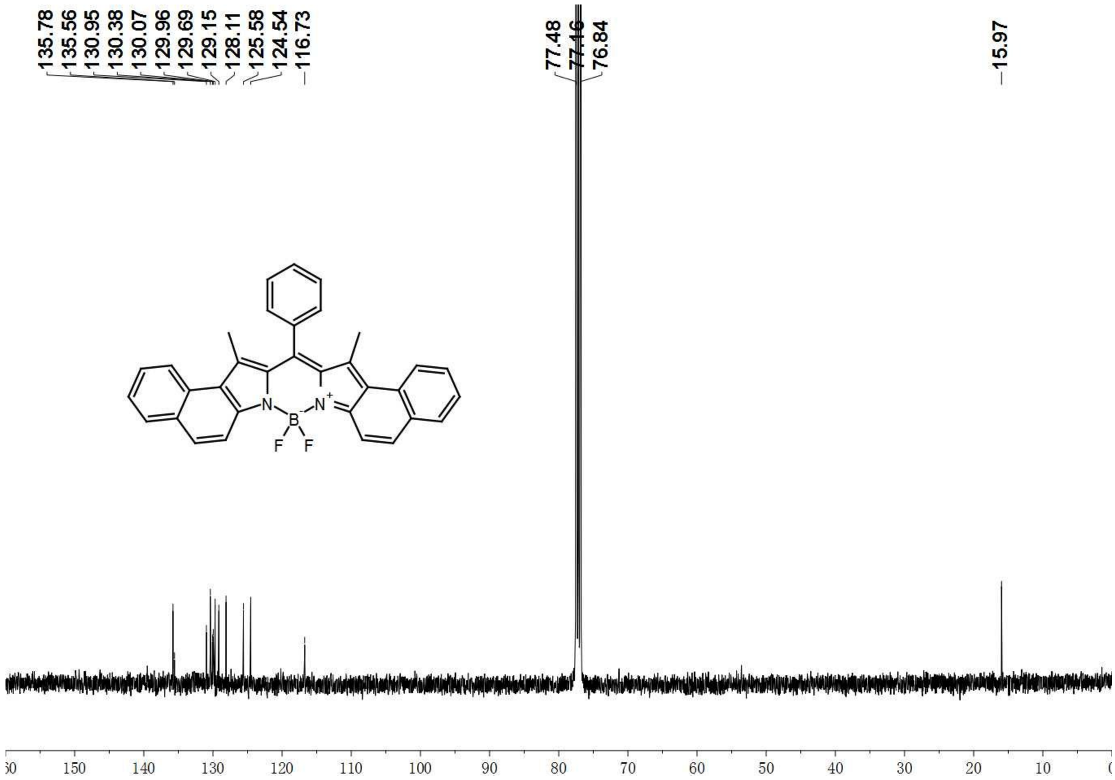

**Fig S10** $^{13}C$ NMR spectra of the BODIPY **3** (100 MHz, $CDCl_3$).

**Table S1**. Spectroscopic and photophysical properties of **1-3** in various solvents at 298K.

| | *Solvent* | $\lambda_{abs}$ [nm] | $\varepsilon_{abs}$ | $\lambda_{em}$ [nm] | $\Delta\nu_{em\text{-}abs}$ [cm$^{-1}$] | $\Phi_F$ | $\tau_f$ ns |
|---|---|---|---|---|---|---|---|
| 1 | Hexane | 511 | 101800 | 524 | 486 | 0.78 | 3.72 |
| | Toluene | 514 | 95800 | 527 | 480 | 0.99 | 3.85 |
| | $CH_2Cl_2$ | 511 | 95200 | 525 | 522 | 0.82 | 4.02 |
| | THF | 511 | 92500 | 525 | 522 | 0.89 | 4.22 |
| | $CH_3CN$ | 508 | 86800 | 522 | 528 | 0.86 | 3.78 |
| | MeOH | 508 | 95700 | 522 | 528 | 0.73 | 3.92 |
| 2a | Hexane | 559 | 131200 | 568 | 283 | 0.37 | 3.67 |
| | Toluene | 560 | 118600 | 575 | 466 | 0.41 | 3.90 |
| | $CH_2Cl_2$ | 552 | 100000 | 573 | 664 | 0.30 | 3.70 |
| | THF | 552 | 96800 | 571 | 603 | 0.38 | 4.19 |
| | $CH_3CN$ | 544 | 81000 | 570 | 838 | 0.27 | 4.35 |
| | MeOH | 547 | 97100 | 571 | 768 | 0.26 | 4.11 |
| 2b | Hexane | 551 | 141900 | 558 | 228 | 1.11 | 2.95 |
| | Toluene | 553 | 110600 | 566 | 415 | 0.46 | 3.26 |
| | $CH_2Cl_2$ | 545 | 86400 | 562 | 555 | 0.37 | 2.80 |
| | THF | 545 | 91800 | 561 | 523 | 0.40 | 3.53 |
| | $CH_3CN$ | 537 | 73900 | 560 | 765 | 0.38 | 3.35 |
| | MeOH | 540 | 85200 | 559 | 629 | 0.32 | 3.52 |
| 3 | Hexane | 632 | 77300 | 637 | 124 | 0.05 | 3.72 |
| | Toluene | 636 | 212200 | 643 | 171 | 0.06 | 3.82 |
| | $CH_2Cl_2$ | 630 | 175660 | 640 | 248 | 0.06 | 3.29 |
| | THF | 629 | 103900 | 640 | 273 | 0.04 | 3.55 |
| | $CH_3CN$ | 622 | 146900 | 635 | 329 | 0.03 | 2.72 |
| | MeOH | 625 | 108900 | 636 | 277 | 0.03 | 2.59 |

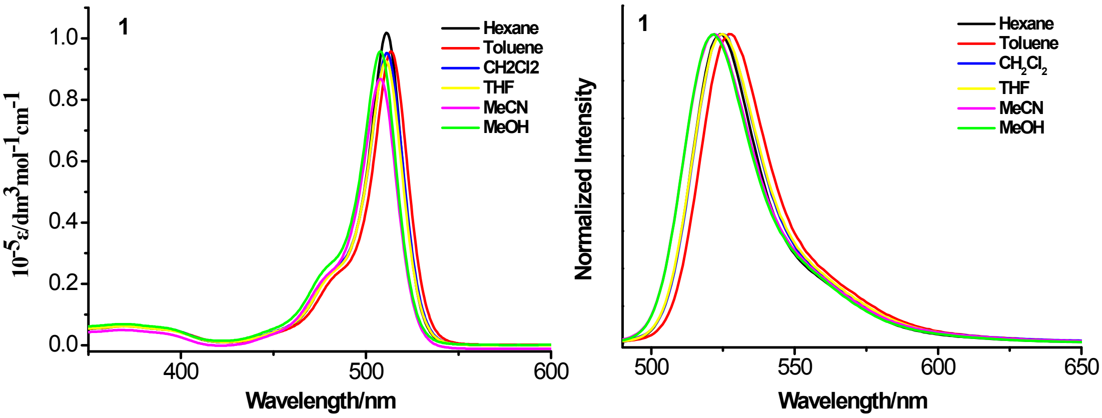

**Fig S11**. Absorption and emission spectra of **1** in a range of different solvents.

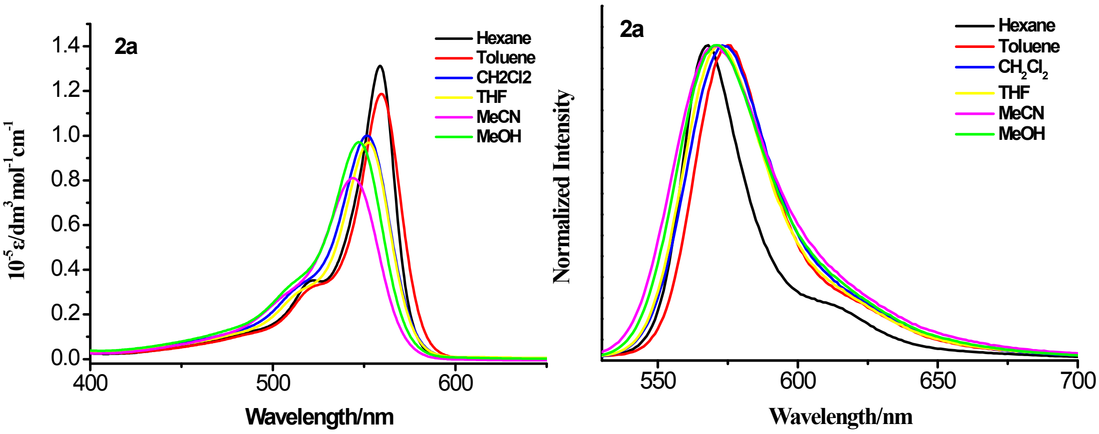

**Fig S12**. Absorption and emission spectra of **2a** in a range of different solvents.

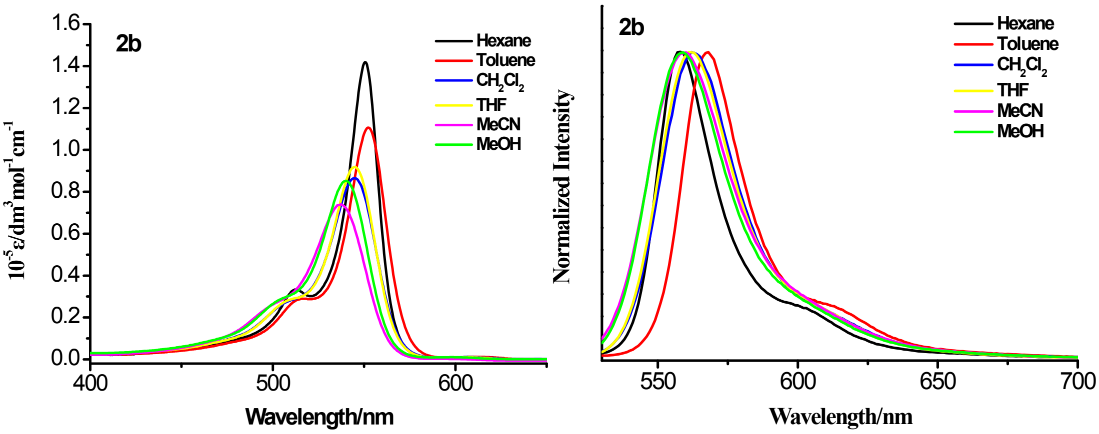

**Fig S13**. Absorption and emission spectra of **2b** in a range of different solvents.

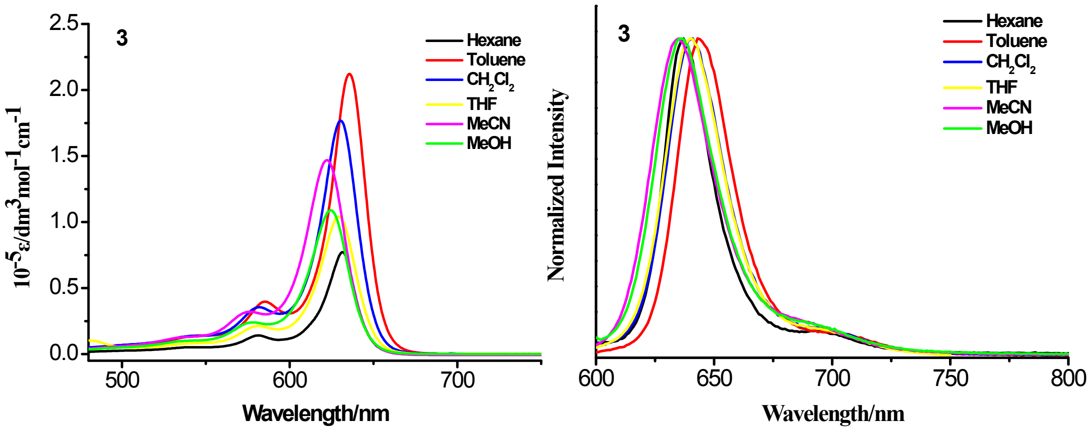

**Fig S14**. Absorption and emission spectra of **3** in a range of different solvents.

**Table S2.** Selected transition energies and wave functions of **1**, **2a**, **2b**, and **3** calculated by the TDDFT method (B3LYP/6-31G(d))

| compd. | energy [nm] | f[b] | wave function[c] |
|---|---|---|---|
| 1 | 425 | 0.54 | +0.662｜L←H>+… |
|  | 378 | 0.01 | -0.109｜L+1←H-3>-0.208｜L←H-1>-0.121｜L+1←H-1>-0.118｜L←H>+0.641｜L+1←H>+… |
|  | 374 | 0.19 | +0.617｜L←H-1>+0.227｜L←H>+0.216｜L+1←H>+… |
|  | 350 | 0.03 | +0.690｜L←H-2>+… |
| 2a | 493 | 0.01 | +0.695｜L←H-1>-0.112｜L←H>+… |
|  | 474 | 0.77 | +0.693｜L←H>+… |
|  | 365 | 0.06 | +0.607｜L←H-3>+0.346｜L←H-2>+… |
|  | 357 | 0.10 | -0.355｜L←H-3>+0.583｜L←H-2>+… |
| 2b | 494 | 0.17 | +0.555｜L←H-1>-0.434｜L←H>+… |
|  | 467 | 0.59 | +0.550｜L←H>+… |
|  | 366 | 0.09 | +0.525｜L←H-3>+0.503｜L←H-2>+… |
|  | 336 | 0.01 | +0.698｜L←H-4>+… |
| 3 | 547 | 0.21 | +0.605｜L←H-1>+0.364｜L←H>+… |
|  | 532 | 0.97 | +0.609｜L←H>+… |
|  | 508 | 0.01 | +0.705｜L←H-2>+… |

| | | |
|---|---|---|
| 415 | 0.07 | +0.690 \| L←H-3>+… |
| 361 | 0.09 | +0.692 \| L←H-4>+… |
| 352 | 0.03 | +0.697 \| L←H-5>+… |

[a] Oscillator strength. [b] MOs involved in the transitions with H and L denoting the HOMO and LUMO, respectively.

## III References

S1 H. Lu , Q. Wang, L. Gai, Z. Li, Y. Deng, X. Xiao, G. Lai and Z. Shen, Chem. - Eur. J., 2012, 18, 7852-7861.

S2 C. L. Picou, E. D. Stevens, M. Shah and J. H. Boyer, Acta Crystallogr. Sect. C 1990, 46, 1148.

S3 SMART, SAINT, SADABS and SHELXTL, Bruker AXS Inc., Madison, 2000.

S4 A. M. Brouwer, Pure. Appl. Chem., 2011, 83, 2213–2228.

S5 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford, CT, 2009.