# **Electronic Supporting Information**

# Disilanylene-bridged BODIPY-based D-σ-A architectures: a novel

## promising series of NLO chromophores

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### 1. Experimental Details

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 120 °C and cooled under a stream of inert gas before use. Tetrahydrofuran were distilled over sodium. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker DRX400 spectrometer and DRX500 spectrometer, and referenced to the residual proton signals of deuterated solvents. 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).

#### X-ray structure determination

The X-ray diffraction data were collected on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) using the  $\omega$ -2 $\theta$  scan mode. The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares methods using SHELX-2000.<sup>S1-S2</sup> All calculations and molecular graphics were carried out on a computer using the SHELX-2000 program package and Diamond 3.2. CCDC 1839779 (**1a**) and 1839780 (**1c**) contain the supplementary crystallographic data for this paper.

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data request/cif.

**1a:**  $C_{28}H_{33}BF_2N_2Si_2$ , A red block-like crystal of the approximate dimensions  $0.26 \times 0.09 \times 0.39$  mm<sup>3</sup> was measured. Triclinic, C2/c, a = 21.64(2) Å, b = 8.223(6) Å, c = 32.26(3) Å,  $\alpha = 90^{\circ}$ ,  $\beta = 97.40(2)^{\circ}$ ,  $\gamma = 90^{\circ}$ , V = 5693(9) Å<sup>3</sup>, Z = 8, F(000) = 2128,  $\rho = 1.173$  Mgm<sup>-3</sup>, R<sub>1</sub> = 0.0886, *w*R<sub>2</sub> = 0.2346, GOF = 1.015, residual electron density between 0.382 and -0.345 eÅ<sup>-3</sup>

**1c:**  $C_{30}H_{38}BF_2N_3Si_2$ , A red block-like crystal of the approximate dimensions  $0.13 \times 0.14 \times 0.16$ mm<sup>3</sup> was measured. Triclinic, P-1, a = 11.115(5) Å, b = 11.547(5) Å, c = 13.669(7) Å,  $\alpha = 69.556(8)^{\circ}$ ,  $\beta = 82.496(8)^{\circ}$ ,  $\gamma = 79.484(9)$ ,  $\vee = 1612.0(13)$  Å<sup>3</sup>, Z = 2, F(000) = 580,  $\rho = 1.124$  Mgm<sup>-3</sup>, R<sub>1</sub> = 0.0651, wR<sub>2</sub> = 0.2115, GOF = 1.072, residual electron density between 0.877 and -0.513 eÅ<sup>-3</sup>

#### Spectroscopic measurements

UV-visible absorption spectra were recorded on a Shimadzu 1800 spectrophotometer. Fluorescence spectra and the fluorescence lifetimes of the samples were determined with a Horiba Jobin Yvon Fluorolog-3 spectrofluorimeter. The goodness of the fit of the single exponential decays were judged using the chi-squared ( $\chi_R^2$ ) and the autocorrelation function C(*j*) values. Low residuals ( $\chi_R^2 < 1.2$ ) were consistently observed. 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. Fluorescein was used as the standard ( $\Phi_F = 0.86$  in 0.1mol/L NaOH).<sup>S3</sup> The quantum yield,  $\Phi$ , was calculated using equation

$$\Phi_{sample} = \Phi_{std} \left[ \frac{I_{sample}}{I_{std}} \right] \left[ \frac{A_{std}}{A_{sample}} \right] \left[ \frac{n_{sample}}{n_{std}} \right]^2$$
(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 ( $k_r$ ) and nonradiative ( $k_{nr}$ ) deactivation were calculated from the measured fluorescence quantum yield ( $\Phi_F$ ) and fluorescence lifetime ( $\tau$ ) according to equations (2) and (3):

$$k_{\rm r} = \Phi_{\rm F}/{\rm T} \tag{2}$$

$$k_{\rm nr} = (1 - \Phi_{\rm F})/\tau \tag{3}$$

## **DFT** calculations

The G09W software package was used to carry out a DFT geometry optimization using the CAM-B3LYP functional with 6-31G(d) basis sets.<sup>S4</sup> UV-visible were calculated by using the timedependent density functional theory (TD-DFT) approach with the CAM-B3LYP functional and 6-31G(d) basis sets. The calculations were made both in the gas phase and in toluene using the polarizable continuum model (PCM).

#### Non-linear optical properties

The Z-scan method with a femtosecond laser pulse and a Ti:95 sapphire system was used to measure nonlinear absorption property. The nonlinear absorption data are fitted using the following equations:

$$T(z,s=1) = \sum_{m=0}^{\infty} \frac{[-q_0(z)]^m}{(m+1)^{3/2}} \text{ for } |q_0| < 1$$
(4)

$$q_{0}(z) = \frac{\beta I_{0} L_{eff}}{1 + \chi^{2}}$$
(5)

$$\sigma = \frac{h\gamma\beta}{N_A d \times 10^{-3}} \tag{6}$$

In equations (4) and (5),  $\beta$  is second-order nonlinear coefficient of the solution,  $I_0$  is the intensity of laser beam at focus (z = 0), Leff =  $[1-\exp(-\alpha_0 L)]/\alpha_0$  is the effective length with  $\alpha_0$  the linear absorption coefficient, L is the sample length, I is the wavelength of the beam, z is the sample position, and  $z_0 = \pi \omega_0^2 / \lambda$  is the diffraction length of the beam with  $\omega_0$  the spot size at focus. Where in equation (6),  $\sigma$  is molecular 2PA cross-section, h is the Planck's constant,  $\gamma$  is the frequency of incident laser, N<sub>A</sub> is the Avogadro constant, and d is the concentration of the sample. According to equations (4) and (5), the 2PA coefficient  $\beta$  (in units of cm/GW) can be deduced, then bring  $\beta$  into equation (6), 2PA cross section  $\sigma$  could be calculated.

The effective third-order NLO susceptibility  $\chi^{(3)}$  can be deduced using the following equations:

$$R_e \chi^{(3)} = 10^{-4} n_0^2 \varepsilon_0 c^2 \gamma / \pi$$
(7)

$$I_m \chi^{(3)} = 10^{-2} n_0^2 \varepsilon_0 c^2 \beta \lambda / 4\pi^2$$
(8)

$$\chi^{(3)} = \sqrt{(R_e \chi^{(3)})^2 + (I_m \chi^{(3)})^2}$$
(9)

In equations (7-9),  $\varepsilon_0$  is the vacuum permittivity, *c* is the speed of light in vacuum and  $n_0$  is the linear refractive index of the solvent. The third-order nonlinear refractive index  $\Box$  can be deduced from the equation:  $\Delta T_{pv} = 0.406(1 - S)^{0.25} I\Delta \phi I$ ,  $\Delta \phi = KL_{eff}\gamma I_0$ .  $\Delta T_{pv}$  is the difference between the peak and the valley of the normalized transmission, and S is the linear ratio of transmitted beam through the aperture.

## 2 Synthesis and characterization

#### 2.1 General synthesis of 1-(4-R-phenyl)-1,1,2,2-tetramethyldisilane



Under an argon atmosphere, phenylmagnesium bromide(100 mmol) in THF (100 mL) was added slowly to a solution of 1,1,2,2-tetramethyl-1,2-dichlorodisilane(10.2 mL, 110 mmol) in THF (50 mL) at -78 °C over 2 h, then the reaction mixture was warmed to room temperature. The mixture was cooled to 0 °C, and LiAlH<sub>4</sub> (3.795 g, 100 mmol) was added. The reaction mixture was warmed to room temperature and stirred overnight. The mixture was quenched with water very slowly and the aqueous layer was extracted three times with diethyl ether. The combined organic layer was washed with brine and dried over sodium sulfate. The solvent was purified by chromatography over silica gel (EA/hexane 1:100) to provide disilane in range of yields of 34-68% as a colorless oil.

**1-phenyl-1,1,2,2-tetramethyldisilane:** Yield 56%. Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.49 (dd, *J* = 6.3, 3.2 Hz, 2 H), 7.35 (dd, *J* = 4.9, 1.9 Hz, 3 H), 3.75 (s, 1 H), 0.39 (s, 6 H), 0.14 (d, *J* = 4.5 Hz, 6 H).

**1-(4-methoxyphenyl)-1,1,2,2-tetramethyldisilane:** Yield 57%. Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45 – 7.38 (m, 2 H), 6.96 – 6.89 (m, 2 H), 3.82 (s, 3 H), 3.74 (dd, *J* = 9.0 Hz, 4.5 Hz, 1 H), 0.36 (s, 6 H), 0.14 (d, *J* = 3.9 Hz, 6 H).

**1-(4-N,N-dimethylphenyl)-1,1,2,2-tetramethyldisilane:** Yield 68%. Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 8.2 Hz, 2H), 3.75 (dd, *J* = 9.0, 4.5 Hz, 1H), 2.98 (s, 6H), 0.37 (m, 6H), 0.12 (d, *J* = 4 Hz, 6H).

**1-(4-trifluoromethylphenyl)-1,1,2,2-tetramethyldisilane:** Yield 34%. Colorless oil. <sup>1</sup> H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.59 (s, 4 H), 3.75 (m, 1 H), 0.40 (s, 6 H), 0.14 (d, *J* = 4.5 Hz, 6 H).

#### 2.2 General synthesis of D(A)-Si-Si-BODIPY



Under an argon atmosphere, *N*, *N*-diisopropylethylamine (0.076 mL, 0.46 mmol) and 1-phenyl-1,1,2,2-tetramethyldisilane (45 mg, 0.23 mmol) were added to a solution of 2-iodo-*meso*-Mes-BODIPY (100 mg, 0.23 mmol) and bis(tri-*tert*-butylphosphine) palladium(0) (1.2 mg, 0.0023 mmol, 1% mol) in mesitylene (3 mL) at 0 °C. The mixture was stirred for 2 d at 0 °C. The reaction mixture was purified by column chromatography to afford **1a** (24 mg, 21%) and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Hexane. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.87 (s, 1 H), 7.76 (s, 1 H), 7.33 (dd, *J* = 6.7, 2.8 Hz, 2 H), 7.27 (d, *J* = 1.9 Hz, 2 H), 7.24 (s, 1 H), 6.96 (s, 2 H), 6.63 (d, *J* = 4.0 Hz, 1 H), 6.50 (s, 1 H), 6.45 (d, *J* = 2.5 Hz, 1 H), 2.39 (s, 3 H), 2.07 (s, 6 H), 0.31 (s, 6 H), 0.24 (s, 6 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  149.70, 146.64, 143.58,138.86, 138.47, 137.25, 136.88, 136.45, 135.41, 133.81, 129.94, 128.75, 128.32, 127.95, 118.50, 21.31, 20.14, -3.44, -4.03. HRMS-ESI: m/z: calcd [C<sub>28</sub>H<sub>33</sub>BF<sub>2</sub>N<sub>2</sub>Si<sub>2</sub>+Na]<sup>+</sup> m/z = 525.2141, found m/z = 525.2165.

Compounds **1b**,**1c** and **1d** were obtained as red solid by using a similar procedure to that for **1a** in yield of 18, 23 and 7%, respectively.

**1b:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.87 (s, 1 H), 7.77 (s, 1 H), 7.26 (s, 1 H), 7.24 (s, 1 H), 6.96 (s, 2 H), 6.83 (d, J = 8.5 Hz, 2 H), 6.63 (d, J = 3.7 Hz, 1 H), 6.55 (s, 1 H), 6. 45 (d, J = 2.4 Hz, 1 H), 3.80 (s, 3 H), 2.38 (s, 3 H), 2.07 (s, 6 H), 0.28 (s, 6 H), 0.23 ( s, 6 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  160.31, 149.80, 148.18, 143.51, 138.86, 136.89, 1 36.45, 135.18, 129.95, 129.71, 128.94, 128.31, 118.48, 117.17, 113.84, 55.12, 21.31, 20.1 4, -3.45, -3.79. HRMS-ESI: m/z: calcd [C<sub>29</sub>H<sub>35</sub>BF<sub>2</sub>N<sub>2</sub>OSi<sub>2</sub>+Na]<sup>+</sup> m/z = 555.2247, found m/z = 555.2266.

**1c** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.87 (d, *J* = 4.9 Hz, 1 H), 7.78 (s, 1 H), 7.21 (d, *J* = 7.8 Hz, 2 H), 6.96 (s, 2 H), 6.70 (s, 2 H), 6.61 (s, 2 H), 6.44 (s, 1 H), 2.96 (s, 6 H), 2.38 (s, 3 H), 2.09 (s, 6 H), 0.26(s, 6 H). 0.23(s, 6 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 150.12, 146.43, 143.23, 138.79, 137.36, 137.03, 136.49, 135.33, 134.92, 134.28, 130.03, 129.67, 128.31, 118.27, 112.41, 40.41, 21.30, 20.14, -3.39, -3.71. HRMS-ESI: m/z: calcd  $[C_{30}H_{38}BF_2N_3Si_2 +H]^+m/z = 546.2744$ , found m/z =546.2733.

**1d** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.90 (s, 1 H), 7.80 (s, 1 H), 7.49 (d, *J* = 7.9 Hz, 2 H), 7.42 (d, *J* = 7.9 Hz, 2 H), 6.96 (s, 2 H), 6.66 (d, *J* = 4.1 Hz, 1 H), 6.47 (s, 2 H), 2.38 ( s, 3 H), 2.05 (s, 6 H), 0.33 (s, 6 H), 0.25 (s, 6 H). HRMS-ESI: m/z: calcd [C<sub>29</sub>H<sub>32</sub>BF<sub>5</sub>N<sub>2</sub>Si <sub>2</sub>Na]<sup>+</sup> m/z=593.2015, found m/z=593.2029. calcd [C<sub>29</sub>H<sub>32</sub>BF<sub>4</sub>N<sub>2</sub>Si<sub>2</sub>-F]<sup>+</sup> m/z=551.2133, found m/z=551.2033.

#### 2.3 General synthesis of D-Si-Si-BODIPY-Si-Si-D



Under an argon atmosphere, *N*,*N*-diisopropylethylamine (0.12 mL, 0.72 mmol) and 1-phenyl-1,1,2,2-tetramethyldisilane (70.0 mg, 0.36 mmol) were added to a solution of 2,6-diiodo-*meso*-Mes-BODIPY (100 mg, 0.18 mmol) and bis(tri-*tert*-butylphosphine) palladium (0) (1.8 mg, 0.0036 mmol, 2 mol%) in mesitylene (3 mL) at 0 °C. The mixture was stirred for 2 d at 0 °C. The reaction mixture was purified by column chromatography to afford **2a** with yield of 13% and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Hexane. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.73 (s, 2 H), 7.33 (dd, *J* = 4.4, 3.0 Hz, 4 H), 7.27 (d, *J* = 1.7 Hz, 4 H), 7.24 (d, *J* = 1.3 Hz, 2 H), 6.97 (s, 2 H), 6.45 (s, 2 H), 2.41 (s, 3 H), 2.04 (s, 6 H), 0.30 (s, 12 H), 0.23 (s, 12 H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  148.96, 145.46, 138.72, 138.54, 137.41, 137.17, 136.51, 136.44, 133.83, 130.03, 128.73, 128.34, 127.94, 21.35, 20.17, - 3.42, -4.02. HRMS-ESI: calcd [C<sub>38</sub>H<sub>49</sub>BF<sub>2</sub>N<sub>2</sub>Si<sub>4</sub>+Na]<sup>+</sup> m/z=717.2932, found m/z=717.2944.

Compounds **2b** and **2c** were obtained as red solid by using a similar procedure to that for **2a** in yield of 12 and 10 %, respectively.

**2b** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.73 (s, 2 H), 7.25 (m, 2 H), 7.23 (s, 2 H), 6.96 (s, 2 H), 6.83 (d, *J* = 8.5 Hz, 4 H), 6.50 (s, 2 H), 3.80 (s, 6 H), 2.40 (s, 3 H), 2.04 (s, 6 H), 0.27 (s, 12 H), 0.22 (s, 12 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.14, 148.85, 144.95, 138.7 2, 136.99, 136.29, 135.05, 129.89, 128.88, 128.71, 128.18, 113.68, 99.96, 55.26, 21.42, 20.0

4, -3.57, -3.90. HRMS-ESI: calcd  $[C_{40}H_{53}BF_2N_2O_2Si_4+Na]^+ m/z=777.3143$ , found m/z=777.31 55.

**2c** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.73 (s, 2 H), 7.21 (d, *J* = 8.2 Hz, 4 H), 6.96 (s, 2 H), 6.69 (s, 4 H), 6.56 (s, 2 H), 2.96 (s, 12 H), 2.39 (s, 3 H), 2.07 (s, 6 H), 0.26 (s, 12 H), 0.22 (s, 12 H).C<sup>13</sup> NMR(100 MHz, CDCl<sub>3</sub>)  $\delta$  152.06, 145.83, 139.14, 138.58, 137.73, 136.40, 134.90, 134.11, 131.57, 129.48, 128.43, 127.04, 29.84, 21.31, 20.18, -3.50, -3.79. HRMS-ESI: calcd  $[C_{42}H_{59}BF_2N_4Si_4+H]^+$  m/z=781.3956, found m/z=781.3969.

#### 2.4 Synthesis of A-Si-Si-BODIPY-Si-Si-A:



We have tried to optimize the reaction condition of 1-(4-trifluoromethylphenyl)-1,1,2,2tetramethyldisilane and 2,6-diiodo-*meso*-Mes-BODIPY by change of reaction temperature, catalyst, kind of solvent et al., the desired chromophore was not detected by Maldi-TOF mass, only 2-iodo-6-(4-trifluoromethylphenyl)dimethylsilyl-BODIPY was isolated with yield of 8%, due to the cleavage of Si-Si bond, which was markedly facilitated by electron-withdrawal in the substituent. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.95 (s, 1 H), 7.82 (s, 1 H), 7.59 (s, 4 H), 6.97 (s, 2 H), 6.83 (s, 1 H), 6.78 (s, 1 H), 2.37 (s, 3 H), 2.09 (s, 6 H), 0.49 (s, 6 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.81, 147.56, 146.79, 144.05, 142.35, 139.45, 138.27, 137.42, 136.65, 136.36, 135.30, 134.25, 130.34, 129.27, 128.54, 124.66, 21.30, 20.25, -2.00. HRMS-ESI: calcd [C<sub>27</sub>H<sub>25</sub>BF<sub>5</sub>IN<sub>2</sub>Si+Na]<sup>+</sup> m/z=661.0743. found m/z=661.0755.

# **3 Optical spectra**



Figure S1. Emission spectra of 1a-1d in kind of solvents with different polarity.

	Solvent	$\lambda_{abs}$ <sup>[a]</sup>	ε <sub>abs</sub>	$\lambda_{em}$ <sup>[b]</sup>	$\Delta v_{\text{em-abs}}$ <sup>[c]</sup>	$\Phi_{F}{}^{[d]}$	T <sub>f</sub> <sup>[e]</sup>	K <sub>r</sub> <sup>[f]</sup>	κ <sub>nr</sub> <sup>[g]</sup>
		[nm]		[nm]	[cm <sup>-1</sup> ]		[ns]	[10 <sup>8</sup> s <sup>-1</sup> ]	[10 <sup>8</sup> s <sup>-1</sup> ]
MesBDP	Toluene	503	65600	515	460	0.82	5.68	1.44	0.31
	Hexane	514	63500	534	729	0.61	6.31	0.97	0.62
	Toluene	516	64200	534	616	0.20	5.33	0.38	1.50
4-	$CH_2CI_2$	515	59700	517	75	0.09	6.89	0.13	1.32
Ta	THF	515	64600	516	38	0.08	7.04	0.11	1.31
	CH <sub>3</sub> CN	511	57400	513	76	0.09	7.30	0.12	1.25
	MeOH	511	59700	513	76	0.16	7.03	0.23	1.19
1b	Hexane	515	60600	536	761	0.34	4.65	0.73	1.42
	Toluene	517	58300	518	37	0.06	5.91	0.10	1.59
	$CH_2CI_2$	516	55300	517	37	0.10	6,78	0.15	1.33
	THF	515	56500	516	38	0.07	6.68	0.10	1.39
	CH₃CN	512	53000	513	38	0.04	5.62	0.07	0.99
	MeOH	510	52100	513	115	0.09	6.14	0.15	1.48
	Hexane	514	53400	528	515	0.015	4.52	0.033	2.18
	Toluene	516	51400	520	149	0.002	4.97	0.004	2.01
1c	$CH_2CI_2$	514	49200	516	75	< 0.001 <sup>[h]</sup>	n.d <sup>[i]</sup>	n.d	n.d
10	THF	514	52000	516	75	<0.001	n.d	n.d	n.d
	CH <sub>3</sub> CN	510	47500	513	115	<0.001	n.d	n.d	n.d
	MeOH	511	51500	513	76	<0.001	n.d	n.d	n.d
	Hexane	513	110300	529	589	0.87	7.40	1.17	0.18
	Toluene	516	111100	535	688	0.83	5.25	1.58	0.32
1d	$CH_2CI_2$	515	104500	516	37	0.10	7.17	0.14	1.25
i d	THF	514	110000	515	38	0.10	7.17	0.14	1.25
	CH₃CN	511	102700	513	76	0.09	7.87	0.11	1.15
	MeOH	512	101000	513	38	0.16	8.13	0.20	1.03

**Table S1.** Photophysical properties of the D(A)-Si-Si-BODIPY **1a-1d** in kind of solvents with different polarity and **MesBDP** in toluene.

[a] absorption maximum. [b] Fluorescence maximum. [c] Stokes-shift. [d] fluorescence quantum yield. [e] half-life period. [f] radiation rate constant. [g] non-radiation rate constant. [h] Could not be reliably determined. [i] Not determined



Figure S2. Emission spectra of 2a-2b in kind of solvents with different polarity.

 Table S2. Photophysical properties of the D-Si-Si-BODIPY-Si-Si-D 2a-2c in kind of solvents

 with different polarity.

	Solvent	$\lambda_{abs}$ <sup>[a]</sup>	ε <sub>abs</sub>	$\lambda_{\text{em}}$ <sup>[b]</sup>	$\Delta v_{\text{em-abs}}^{[\text{c}]}$	$\Phi_{F}{}^{[d]}$	T <sub>f</sub> <sup>[e]</sup>	κ <sub>r</sub> <sup>[f]</sup>	κ <sub>nr</sub> <sup>[g]</sup>
		[nm]		[nm]	[cm <sup>-1</sup> ]		[ns]	[10 <sup>8</sup> s <sup>-1</sup> ]	[10 <sup>8</sup> s <sup>-1</sup> ]
	Hexane	531	72600	552	716	0.58	6.76	0.86	0.62
	Toluene	534	68000	558	805	0.20	3.18	0.63	2.51
2a	$CH_2CI_2$	533	67200	558	841	<0.001 <sup>[i]</sup>	n.d <sup>[i]</sup>	n.d	n.d
	THF	532	71300	556	811	<0.001 <sup>[i]</sup>	n.d	n.d	n.d
	CH₃CN	529	74400	_[h]	-	-	-	-	-
	MeOH	529	64900	548	655	<0.001 <sup>[i]</sup>	n.d <sup>[i]</sup>	n.d	n.d
	Hexane	531	82500	552	716	0.51	5.53	0.93	0.88
2b	Toluene	534	75700	556	741	0.03	4.36	0.07	2.22
	$CH_2CI_2$	533	72200	520	-	<0.001 <sup>[i]</sup>	n.d <sup>[i]</sup>	n.d	n.d
	THF	533	72200	520	-	<0.001 <sup>[i]</sup>	n.d	n.d	n.d
	CH₃CN	529	66900	518	-	<0.001 <sup>[i]</sup>	n.d	n.d	n.d
	MeOH	524	62100	517	-	<0.001 <sup>[i]</sup>	n.d	n.d	n.d
	Hexane	534	65400	_[h]	-	-	-	-	-
	Toluene	537	58700	_[h]	-	-	-	-	-
2c	$CH_2CI_2$	535	57900	_[h]	-	-	-	-	-
	THF	535	65500	_[h]	-	-	-	-	-
	CH₃CN	531	54700	_[h]	-	-	-	-	-
	MeOH	531	59000	_[h]	-	-	-	-	-

[a] absorption maximum. [b] Fluorescence maximum. [c] Stokes-shift. [d] fluorescence quantum yield. [e] half-life period. [f] radiation rate constant. [g] non-radiation rate constant. [h] No fluorescence could be detected. [i] Could not be reliably determined.



Figure S3. Open-aperture Z-scan data for 1a-1d and 2a-2c in toluene at 100  $\mu M.$ 



Figure S4. Normalized close-aperture Z-scan spectra for 1a-1c and 2a-2c in toluene at 100 µM.

### 4 Crystallographic structures



**Figure S5**. X-ray crystal structures of **1a** (left) and **1c** (right). The thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms are omitted for clarity in both views.

## **5 DFT calculations**



**Figure S6.** Optimised structure of **1c** and **2c** in the twisted and parallel conformations. Calculations were performed at CAM-B3LYP/6-31G(d) level.

**Table S3.** SCF energies in Hartrees for the folded, extended conformations of **1c** and **2c** in the gas phase and toluene with the polarisable continuum model (PCM) by using the CAM-B3LYP functional with 6-31G(d) basis sets.

The Folded optimised structure of **1c** and **2c** is more stable than the extended structure, being in consistent with the X-ray structure.

Conformation	E/ Hartrees	
Folded 1c	-2133.2491	gas phase
Extended 1c	-2133.2482	gas phase
Folded 2c	-3236.6338	gas phase
Extended 2c	3236.6314	gas phase
Folded 1c	-2133.2558	toluene
Extended 1c	-2133.2549	toluene
Folded 2c	-3236.6419	toluene
Extended 2c	-3236.6398	toluene



**Figure S7.** Frontier MOs and their energy levels of MesBDP and all the chromophores. Calculations were performed at CAM-B3LYP/6-31G(d) level in toluene with the polarisable continuum model (PCM).

**Table S4.** Calculated electronic excitations energies, oscillator strengths and the related wave functions for **MesBDP**, **1a-1d** and **2a-2c** in toluene calculated with the polarisable continuum model (PCM) by using the CAM-B3LYP functional with 6-31G(d) basis sets

	State <sup>[a]</sup>	Energy	λ	<b>f</b> [b]	Oribitals (coefficient) <sup>[c]</sup>
		(eV)	(nm)		
MesBDP	S1	3.01	412	0.56	H→L (97%)
1a	S1	2.91	426	0.74	H→L (95%)
1b	S1	2.91	427	0.74	H→L (78%), H-1→L (19%)
1c	S1	2.89	428	0.75	H-1→L (83%), H→L (14%)
1d	S1	2.97	417	0.70	H→L (97%)
2a	S1	2.83	439	0.96	H→L (95%)
2b	S1	2.82	440	0.98	H→L (84%), H-2→L (13%)
2c	S1	2.80	443	1.00	H-2→L (74%), H→L (14%)

[a] Excited state. [b] Oscillator strength. [c] MOs involved in the transitions; H and L denote the HOMO and LUMO of the system, respectively.

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# 7 <sup>1</sup>H NMR Spectra and HR-MS Spectra





19



560

m/z

555.2247

err

-1.9

[mDa

565

err

] -3.4

[ppm

mSig

ma

30.6

570

rdb e<sup>-</sup>

Conf

14.5 even

550

1 C 29 H 35 B F 2 N 2 Na O Si 2

555

Score

100.00

545

# Formula

Meas. m/z

555.2266

m/z

N-R

ule

ok







1c





22

#### **Compound 2a**









Compound 2c				
$\int_{-1}^{-1} \frac{7.73}{7.26}$ $\int_{-1.20}^{-1.20} \frac{7.23}{6.69}$ $\int_{-1.20}^{-1.20} \frac{6.69}{6.56}$		- 2.96 - 2.39	- 2.07	۲ 0.26 0.22
	N-C-Si-Si-V-Si B-N-Si-Si-V-Si F F	-\$i-{>-N<		
₽ 56. 2.39 ¥ 2.09 Å		2.45₌ .31 ₌	₽ 00.	2.04 1.96
3.5 8.0 7.5 7.0 6.5 6.0 	5.5 5.0 4.5 4.0 3 f1 (p)	.5 3.0 2.5 pm)	2.0 1.5 1.0	0.5 0.0 -0.5
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Analysis Name D:\Data\QTOF- Method tune_100-1000 Sample Name Comment	LUH-170426- <b>zxh-NN-SI-4_</b> 01. -170426.m	d	Operator Jia Instrument / Ser# m	ang icrOTOF-Q II 10324
Acquisition Parameter           Source Type         ESI           Focus         Active           Scan Begin         100 m/z           Scan End         1000 m/z	Ion Polarity Set Capillary Set End Plate Offset Set Collision Cell RF	Positive 4500 V -500 V 120.0 Vpp	Set Nebulizer Set Dry Heater Set Dry Gas Set Divert Valve	0.5 Bar 250 °C 2.6 l/min Source
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6000 -		[M+H] <sup>+</sup> 781.3969		
4000-				
2000-			803.3758	
0+				
700 720	740 760	780	800 820	840 m/z
Meas.m/z # Formula 781.3969 1 C 42 H 60 B F 3	Score m/z err 2 N 4 Si 4 100.00 781.3959	-1.1 err [ppm] -1.1 -1.3	mSigma rdb e Conf 20.2 18.5 even	ok

2-lodo-6-(4-trifluoromethylphenyl)dimethylsilyl-BODIPY

4 7 8 9 7 8 8	N 1	0	•
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N N N N O O O	n	2	0
1 1	1	1	1



		Mass	Spectr	rum Sn	nartFo	rm	ula F	Repo	rt			
Analysis Info							Acquisition Date 12/13/2017 10:27:				10:27:5	7 AM
Method Sample Name Comment	D:\Data\Q1OF-LuH-zxh-1/1213-SI-CF3-Siduan_01.d tune_100-1000-170517.m						Operator Jiang Instrument / Ser# micrOTOF-Q II 10324				324	
Acquisition Par	ameter											
Source Type	ESI		Ion Polarit	ty	Positive			Set Nebu	lizer	0.5	Bar	
Focus	Active		Set Capill	ary	4500 V			Set Dry H	leater	250	°C	
Scan Begin	100 n	VZ	Set End F	Plate Offset	-500 V			Set Dry C	5as	2.6	l/min	
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1500				1]	M-F]+		[M+N	la]+				
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661.07	55 1	C 27 H 25 B F 5	IN 2 Na Si	100.0	0 661.0	742	-1.3	-1.9	22.	4 14.5	even	ok