Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information for

Turn on the singlet oxygen photosensitizers with intense visible light harvesting ability in aqueous solution

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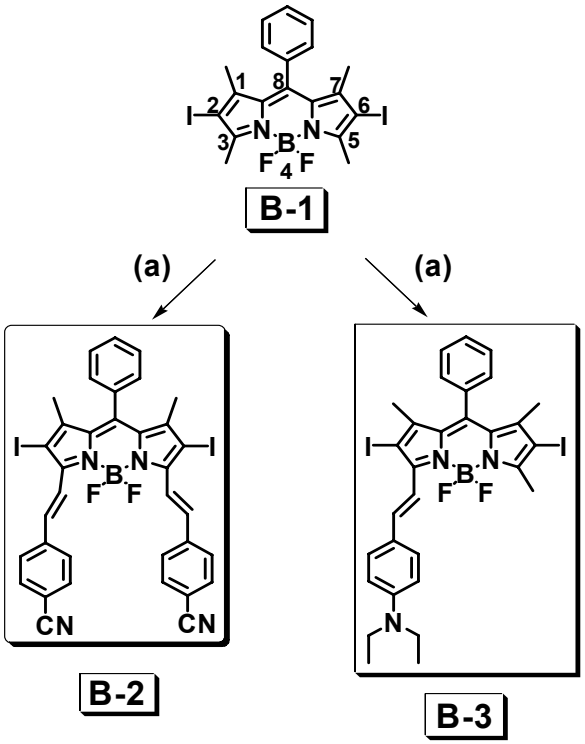


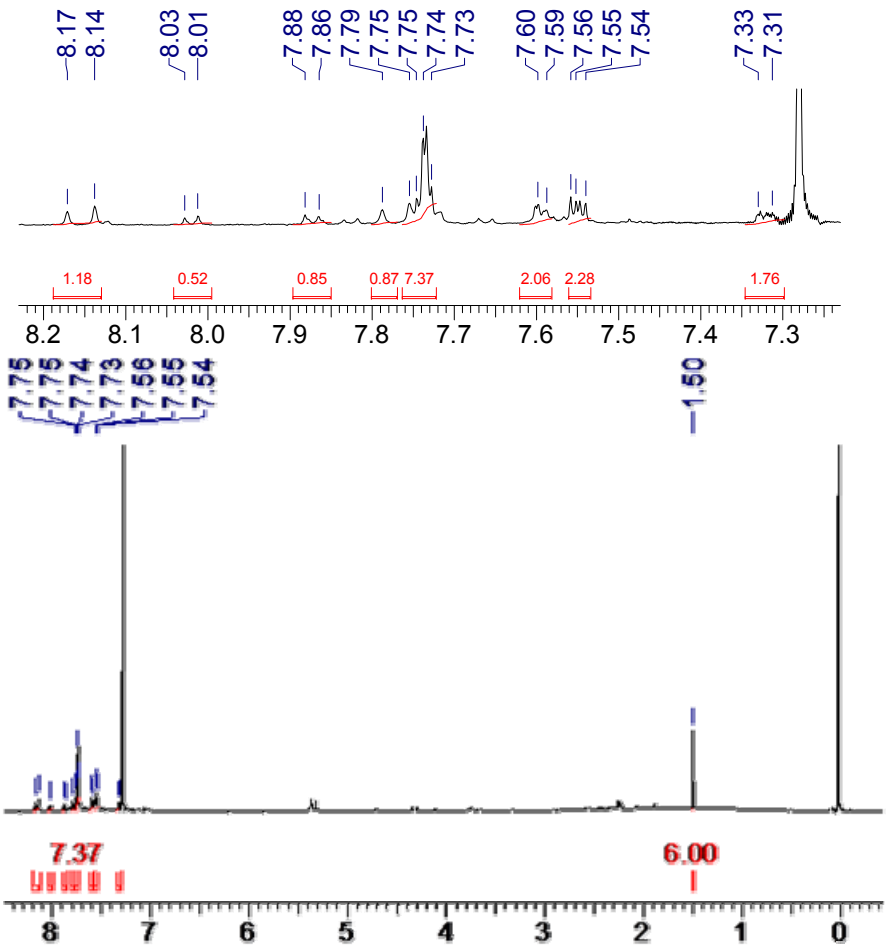
Scheme S1 Synthesis strategy of 2,6-diiodo-styryl-BODIPY derivatives. (a) Piperidine, AcOH, DMF, Microwave, 150 °C.

Synthesis of B-2.

B-1 (50.0 mg, 0.09 mmol) and 4-cyanobenzaldenhyde (47.0 mg, 0.36 mmol) was dissolved in dry DMF (5 mL), followed by acetic acid (3 drops) and piperidine (3 drops). The mixture was put under Ar atmosphere before it was subjected to microwave irradiation (15 min, 150 °C, 1 min pre-stirring). After removal of the solvent under reduced pressure, the mixture was purified by column chromatography (silica gel, DCM), which gives a final deep purple solid. Yield: 11 % (10.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.17-8.14 (d, *J*=12.0 Hz, 1H), 8.03-8.01 (d, *J*=8.0 Hz, 1H), 7.88-7.86 (d, *J*=8.0 Hz, 1H), 7.79 (s, 1H), 7.75-7.73 (m, 7H), 7.60-7.59 (d, *J*=4.0 Hz, 2H), 7.56-7.54 (m, 2H), 7.33-7.31 (d, *J*=8.0 Hz, 2H), 1.50 (s, 6H). MALDI-HRMS calcd $[C_{35}H_{23}BF_2N_4I_2]^+$ m/z 802.0073, found m/z 802.0107.

Synthesis of B-3.

B-1 (50.0 mg, 0.09 mmol) and 4-diethylaminobenzaldehyde (16.0 mg, 0.09 mmol) was dissolved in dry DMF (5 mL), followed by acetic acid (3 drops) and piperidine (3 drops).The mixture was put under Ar atmosphere before it was subjected to microwave irradiation (15 min, 150 °C, 1 min pre-stirring). After removal of the solvent under reduced pressure, the mixture was purified by column chromatography (silica gel, petroleum ether: DCM= 2:1, v/v), which gives a final deep purple solid. Yield: 22 % (15.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.25-8.21 (d, *J*=16Hz, 1H), 7.56-7.28 (m, 6H), 6.70-6.68(d, *J*= 8 Hz, 2H), 3.46-3.42 (m, 4H), 1.58 (s, 2H), 1.45 (s, 3H), 1.39 (s, 3H), 1.27-1.21 (m, 9H). MALDI-HRMS calcd $[C_{30}H_{30}BF_2N_3I_2]^+$ m/z 735.0590, found m/z 735.0490.



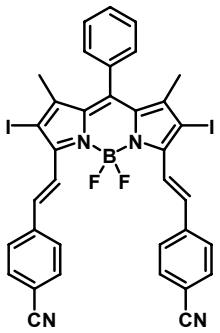
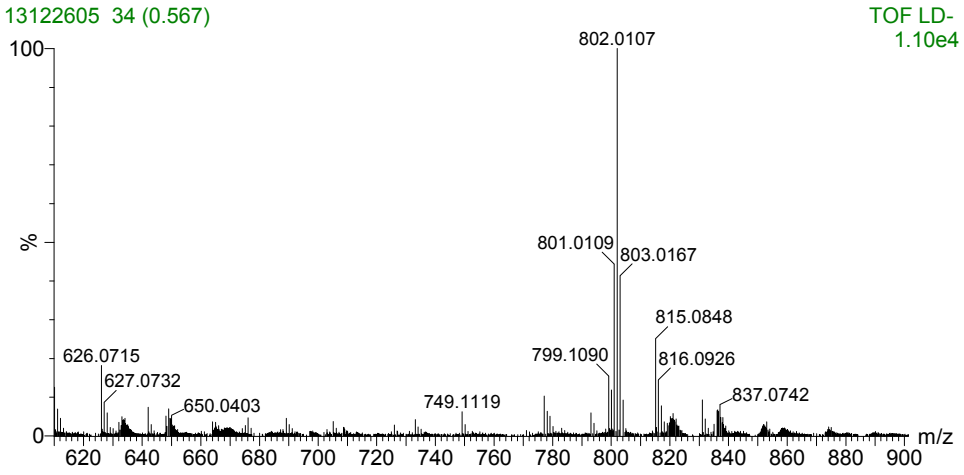


Fig. S1 ^{1}H NMR of **B-2** (400 MHZ, $CDCl_3$).



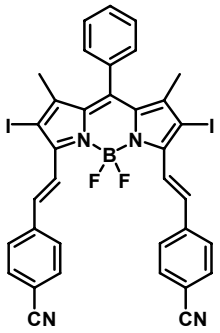


Fig. S2 TOF HRMS MALDI of **B-2**.

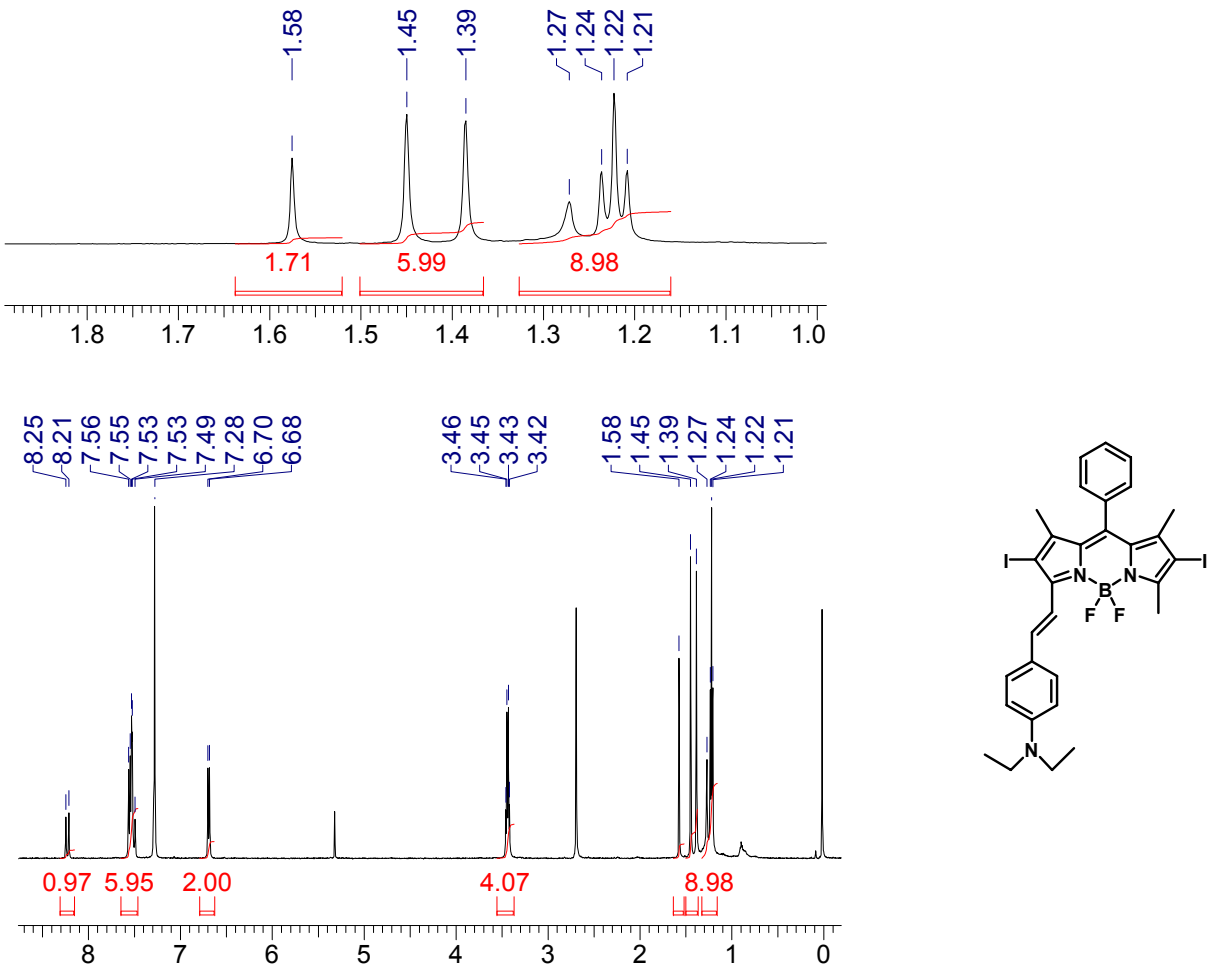


Fig. S3 ^{1}H NMR of **B-3** (400 MHZ, $CDCl_3$).

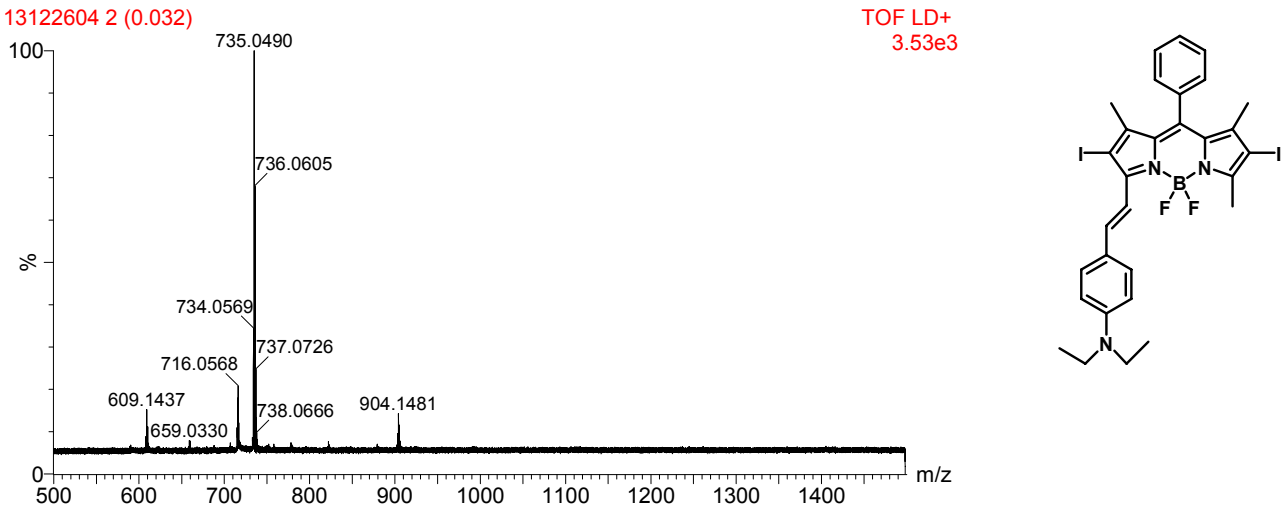


Fig. S4 TOF HRMS MALDI of **B-3**

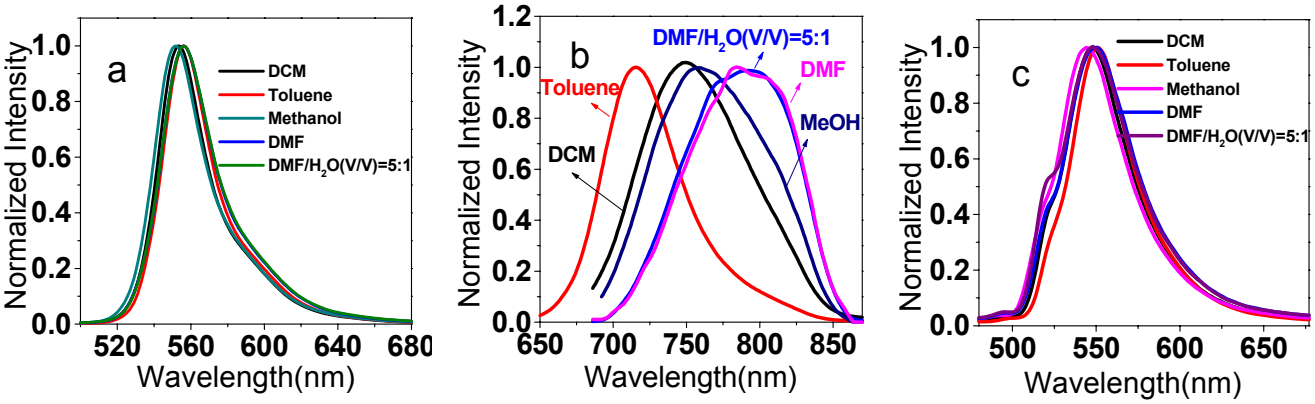


Fig. S5 Normalized fluorescence emission spectrum of **B-1** (a), **B-3** (b) and **B-4** (c) in different solvents. (1.0×10^{-5} M; 20 °C)

Table S1 Summary of photophysical properties in different solvents of **B-1**, **B-2**, **B-3** and **B-4**.

	λ_{abs} [a] (nm)	ε [b]	λ_{ems} (nm) /Φ_F (%) [c]				
			Toluene	CH_2Cl_2	Methanol	DMF	DMF/H_2O=5:1(V/V)
B-1	535	0.80	553/0.95	556/1.00	552/0.90	555/1.1	557/0.91
B-2	643	0.60	666/5.10	660/5.00	655/4.70	664/3.70	664/3.60
B-3	653	0.67	717/1.20	743/0.21	750/0.04	790/0.01	800/0.02
B-4	519	0.66	551/0.32	548/0.24	544/0.25	549/0.21	548/0.20

[a] In CH_2Cl_2 (1.0×10^{-5} M); [b] Molar extinction coefficient at the absorption maxima. ε: 10^5 $M^{-1}cm^{-1}$; [c] With 2,6-diiodo-styryl-BODIPY (Φ_F = 0.01 in CH_2Cl_2) as the standard.[1]

Table S2 Summary of redox potential properties of **B-1**, **B-2**, **B-3** and **B-4**.

	E_{OX} (eV) [a]	E_{red} (eV) [b]	$E_{0,0}$ (eV) [c]	$\triangle G^0$ (eV) [e]
B-1	1.41	−0.86	2.32	−0.05
B-2	1.25	−0.86	1.93	0.18
B-3	0.87	−0.86	1.90	−0.17
B-4	1.58	−0.86	2.33	0.11

[a] E_{OX}: oxidation potential of the electron donor; [b] E_{red}: reduction potential of the electron acceptor (O_2);[2] [c] $E_{0,0}$: excitation energy; [d] $\triangle G_0$: free energy changes of the potential PET effect with Rehm – Weller Equation.[3]

Reference

1. L. Huang, J. Z. Zhao, S. Guo, C. Zhang and J. Ma, *J. Org. Chem.* 2013, **78**, 5627.
2. T.i Kawashima, K. Ohkubo and S, Fukuzumi. Phys. Chem. Chem. Phys. 2011, **13**, 3344.
3. X. Zhang, L. Chi, S. Ji, Y. Wu, P. Song, K. Han, H. Guo, T. D. James, J. Zhao. 2009, **131**, 17452.