Supporting Information

Visible-to-Near-Infrared Light-Driven Photocatalytic Hydrogen Production Using Dibenzo-BODIPY and Phenothiazine Conjugate as Organic Photosensitizer

Okta Suryani,[†] Yuta Higashino,[†] Haruka Sato,[†] and Yuji Kubo[*†,‡]

[†]Department of Applied Chemistry for Environment, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan
[‡]Research Center for Hydrogen Energy Society, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo, 192-0397 Japan

*Corresponding author: yujik@tmu.ac.jp

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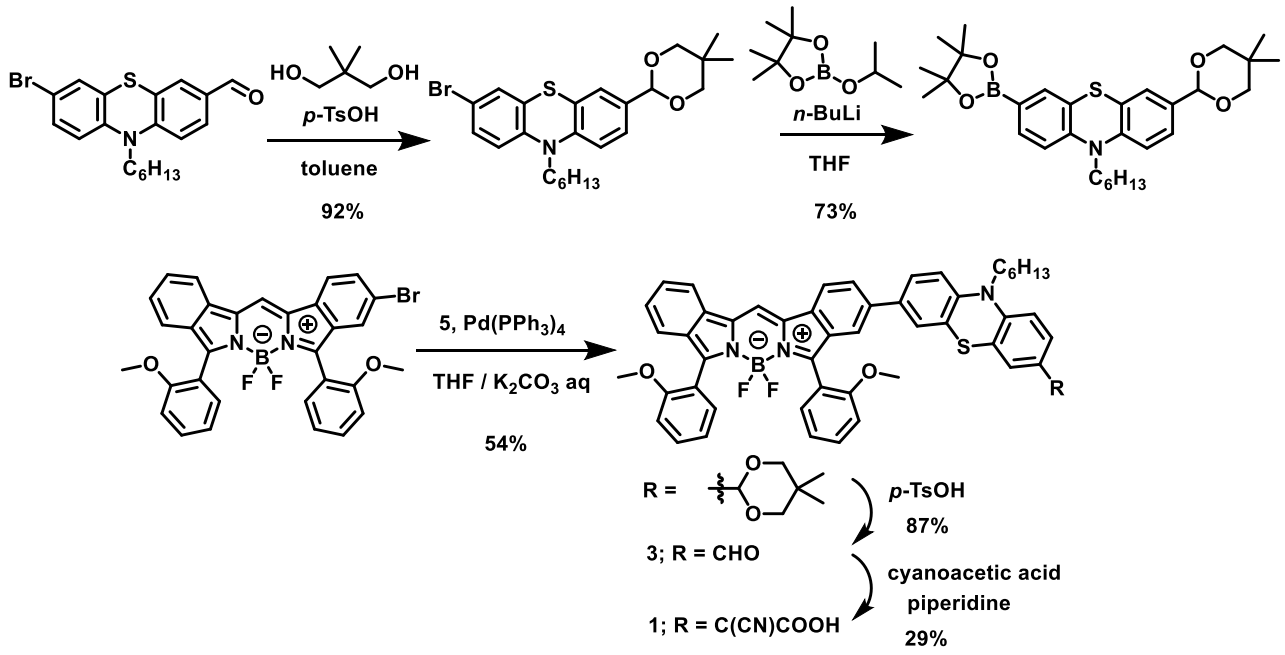
Synthesis of 1 and the structure assignment

The synthetic path is shown in Scheme S1. Its structure was confirmed by NMR measurements that were recorded on a Bruker Avance 500 spectrometer (^{1}H: 500 MHz,^{13}C: 125 MHz). Mass spectrometry data were obtained using a Bruker micrOTOF II-SDT1 spectrometer with the electrospray ionization (ESI) method.



Scheme S1. Synthetic route to **1**.

Difluoro[5-(7-(2-carboxy-2-cyanovinyl)-10-hexyl-10H-phenothiazin-3-yl)-1-[[3-(2-methoxyphenyl)-2H-isoindole-1-yl]methylene]-3-(2-methoxyphenyl)-1H-isoondolate-N^1,N^2]boron (**1**). To a dry THF solution (7.0 mL) of **3** (0.200 g, 0.246 mmol), a dry THF solution (3 mL) of 2-cyanoaceteic acid (0.0428 g, 0.503 mmol) and piperidine (0.090 mL, 0.91 mM) was added. The mixture was refluxed for 42 h, during which 0.090 mL each of piperidine was added to the solution four times. The resultant solution was poured into 1 N HCl aqueous solution (100 mL) and then extracted by CH_2Cl_2 and water. The organic phase was dried on Na_2SO_4 and evaporated. The residue was chromatographed on silica gel (Wacogel C-300) using a gradient of CH_3COOH (0-1%) in CH_2Cl_2 as an eluent to give **1** (0.0630 g) in 29% yield.

^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm) = 13.7 (2H, s), 8.67 (1H, s), 8.67 (1H, s), 8.21 (1H, dd, J = 8.58 and 3.38 Hz), 8.16 (2H, s), 8.15–8.17 (2H, m), 7.92 (2H, dd, J = 8.73 and 1.92 Hz), 7.84 (2H, d, J = 8.75), 7.82 (2H, d, J = 1.60 Hz), 7.56 (2H, ddd, J = 7.60, 6.69 and 0.91 Hz), 7.46–7.52 (8H, m), 7.45 (2H, d, J = 1.80 Hz), 7.42 (2H, s), 7.38–7.41(2H, m), 7.30 (2H, dd, J = 8.10 and 0.95 Hz), 7.28 (2H, d, J = 6.80 Hz), 7.17–7.25 (6H, m), 7.10–7.13 (2H, m), 7.06–7.09 (2H, m), 7.00–7.04 (2H, m), 3.96 (4H, t, J = 6.87 Hz), 3.74 (3H, s), 3.72 (3H, s), 3.69 (3H, s), 3.67 (3H, s), 1.70 (4H, quin, J = 7.29 Hz), 1.40 (4H, quin, J = 7.46 Hz), 1.24–1.28 (8H, m), 0.83 (6H, t, J = 6.90 Hz). ^{13}C NMR (125 MHz, DMSO-d_6) δ (ppm) = 163.7, 158.5, 157.4, 157.3, 157.3, 152.4, 149.1, 148.4, 141.7, 135.6, 135.2, 135.2, 132.2, 131.8, 131.6, 131.2, 129.3, 129.0, 128.8, 128.0, 127.0, 126.5, 126.2, 125.5, 125.2, 125.1, 123.1, 122.6, 122.6, 120.1, 119.9, 119.9, 119.8, 119.7, 119.5, 119.3, 119.2. 116.0. 119.0. 116.9. 116.7. 116.7. 115.5. 111.5. 111.4. 55.5. 55.4. 46.9. 30.7. 25.9. 25.6. 22.0. 13.7. ESI MS: 879.3 $[M-H]^-$.

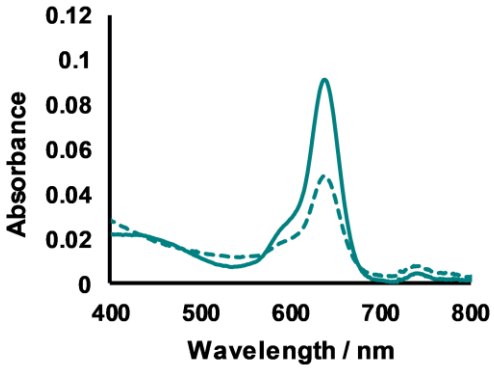


Figure S1. Absorption spectra of **1** in THF measured before (solid line) and after (dashed line) the dye deposition. The decrease in the absorbance indicates the adsorption of the substances onto Pt/HPT500.

Table S1. Assignment of the electronic transitions and oscillator strength (*f*) calculated for **1** and **2** using the B3LYP/6-31G(d,p) basis set.

Dye	State	λ (calcd.) / nm	*f* / a.u.	MO Transition Assignment
1	$S_0 \rightarrow S_1$	559	0.6125	HOMO →LUMO (22.8%)[a]
				HOMO →LUMO+1 (25.3%)
	$S_0 \rightarrow S_2$	540	0.3873	HOMO−1 →LUMO (2.3%)
				HOMO →LUMO (23.5%)
				HOMO →LUMO+1 (24.1%)
	$S_0 \rightarrow S_3$	486	0.1609	HOMO−1→LUMO (46.3%)
				HOMO →LUMO (2.8%)
	$S_0 \rightarrow S_4$	482	0.2078	HOMO−1 →LUMO+1 (46.9%)
2	$S_0 \rightarrow S_1$	415	0.7706	HOMO →LUMO (49.3%)

[a](CI coefficient)^2 × 100%

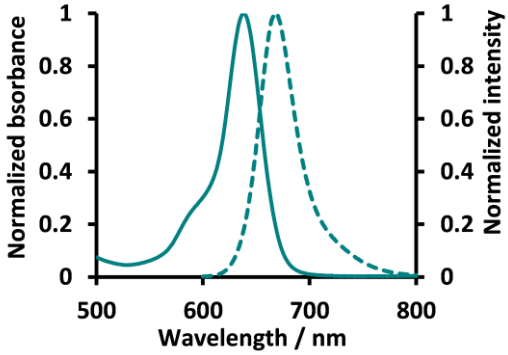


Figure S2. Absorption (solid line) and fluorescence (dashed line) spectra of **1** in THF (5 μM), showing the intersection at λ = 654 nm, which afforded the zeroth-zeroth transition energy $E_{0\text{-}0}$ 1.89 eV.

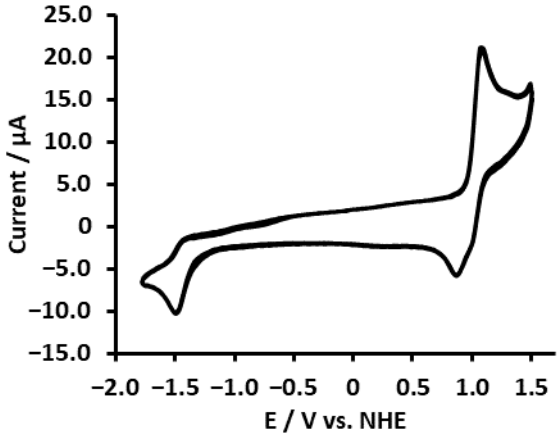


Figure S3. Cyclic voltammogram of **2** in THF (0.5 mM) in deaerated THF-CH_3CN (3:2 v/v) containing 0.1 M $TBAPF_6$ electrolyte.

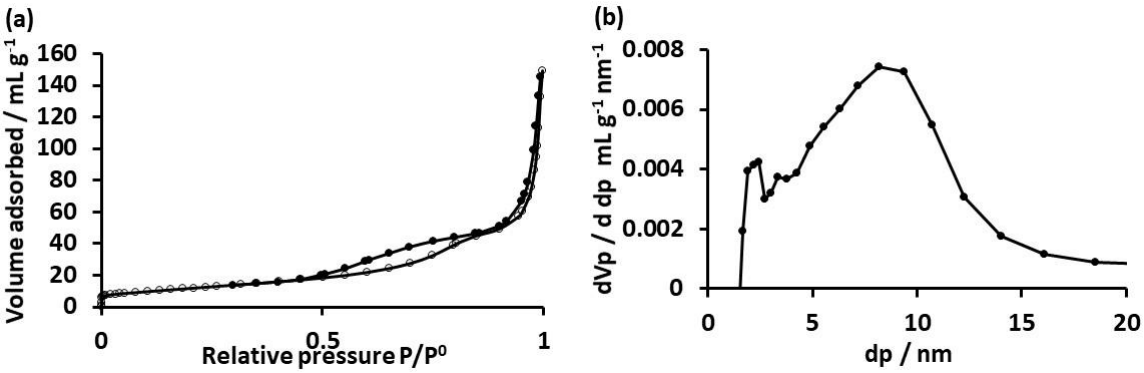


Figure S4. (a) Nitrogen adsorption/desorption isotherms and (b) BJH plot of the HPT500.

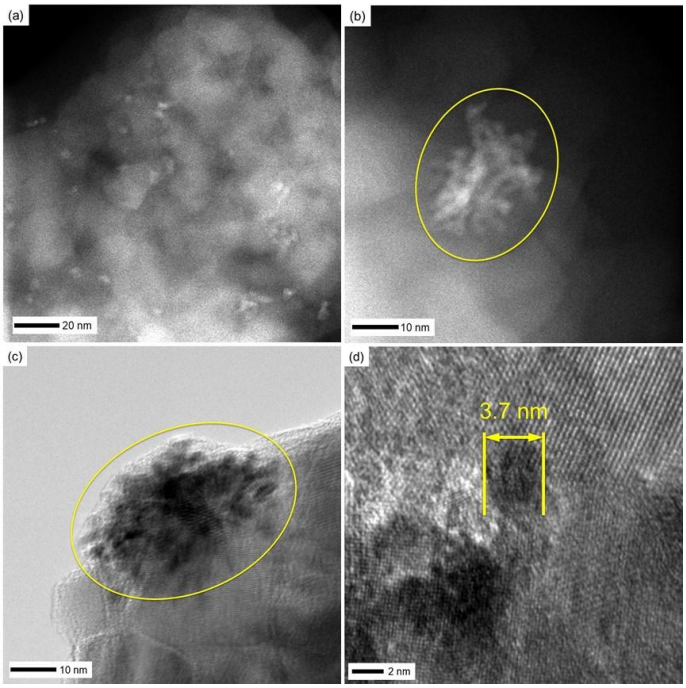


Figure S5. (a) and (b) High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images. (c) and (d) TEM images of Pt/HPT500.

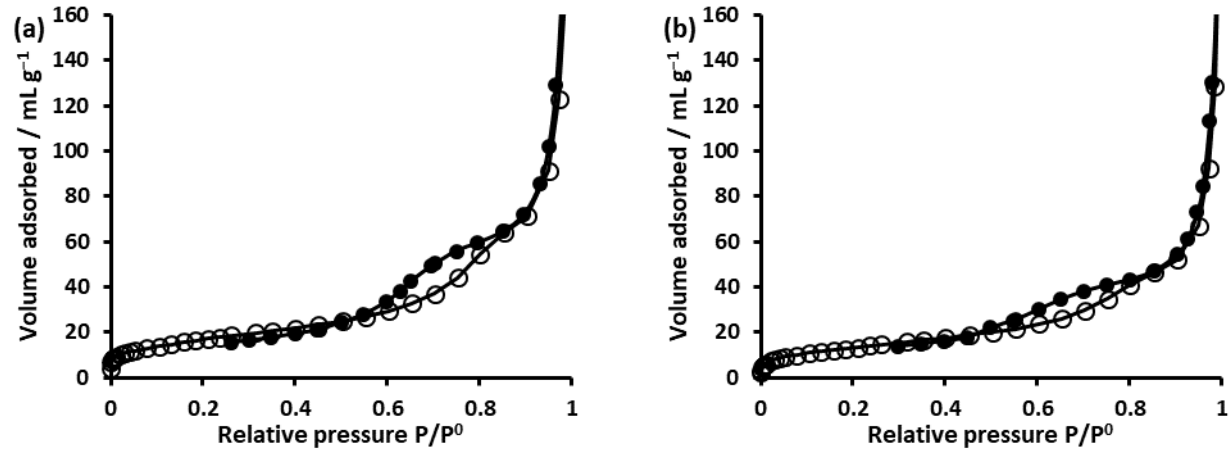


Figure S6. Nitrogen adsorption/desorption isotherms of Pt/HPT500 (a) and Pt/HPT500/**1** (b).

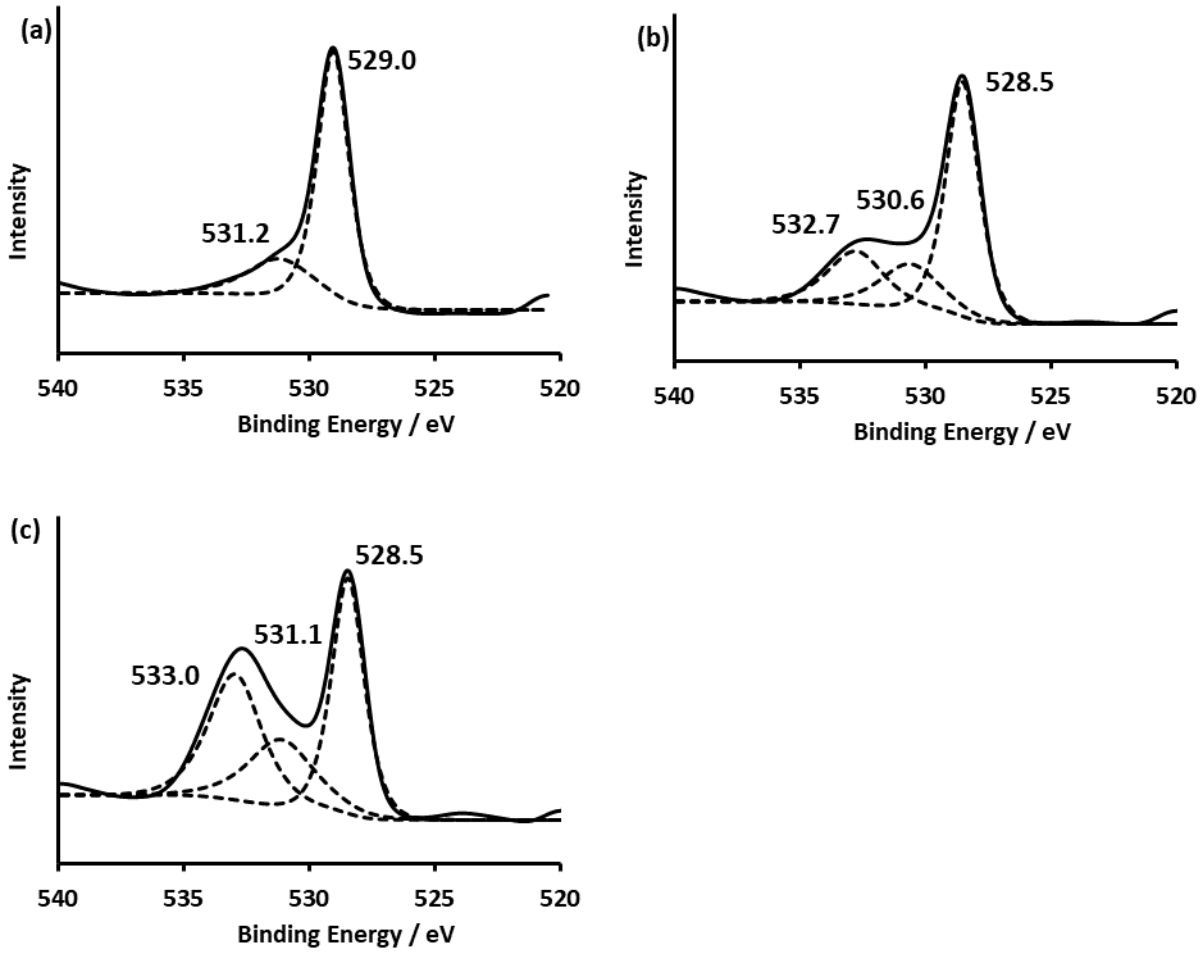


Figure S7. O 1s peak (solid line) of Pt/HPT500 (a), Pt/HPT500/**1** (b), and Pt/HPT500/**2** (c). Dashed line is one deconvoluted in symmetric gaussian curves.

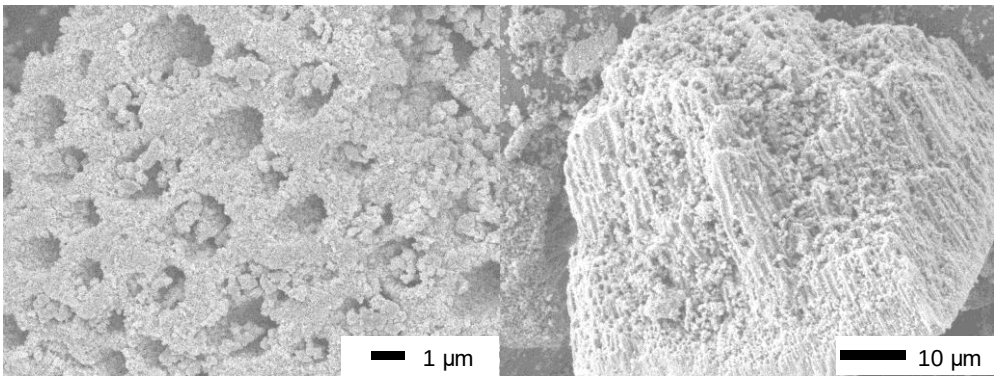


Figure S8. FE-SEM image of Pt/HPT500/**1**.

Figure S9. A photograph of the photoreactor of the dye sensitized photocatalyst Pt/TiO_2/**1** in phosphate buffer solution containing ascorbic acid (0.5 M) as the sacrificial electron donor. A 300 W Xenon lamp with a light guide was used to irradiate the photocatalyst from the top side of the photoreactor.

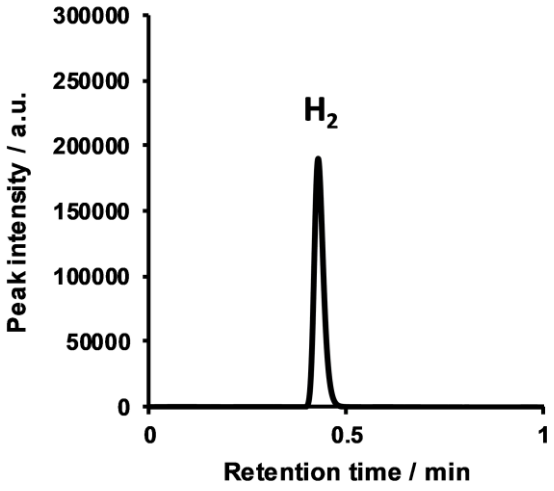


Figure S10. Gas chromatogram showing the hydrogen peak at 0.42 min retention time taken after 1 h photolysis of Pt/HPT500/**1** at pH 3.6.

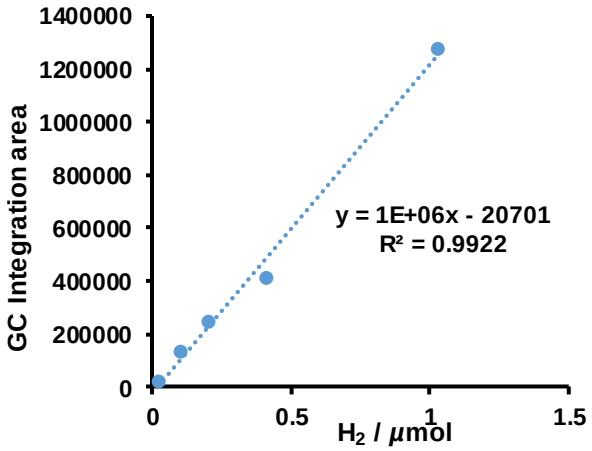


Figure S11. Calibration curve used for the calculation the amount of produced hydrogen

Table S2. Photocatalytic activity of Pt/HPT500/**1** and Pt/HPT500/**2.**

	Pt/HPT500/**1**						Pt/HPT500/**2**					
Time / h	1st cycle		2nd cycle		3rd cycle		1st cycle		2nd cycle		3rd cycle	
	TON	TOF	TON	TOF	TON	TOF	TON	TOF	TON	TOF	TON	TOF
1	2340	2340	1990	1990	1170	1170	650	650	240	240	190	190
2	3170	1590	3060	1530	2030	1020	852	426	317	159	210	105
3	4540	1510	4040	1350	2540	850	1080	360	429	143	195	65.0
4	5840	1460	5190	1300	3160	790	1290	323	480	120	397	99.3
5	6460	1290	6120	1220	3860	770	1330	266	558	112	392	78.4
6	7960	1330	7350	1230	3560	590	1460	243	560	93.3	460	76.7
7	8880	1270	6620	950	4310	620	1480	211	603	86.1	580	82.9
8	9710	1210	7970	1000	4970	620	1530	191	655	81.9	533	66.6
9	9260	1030	8630	959	5410	600	1690	188	676	75.1	604	67.1
10	11100	1110	8650	865	5650	570	1720	172	762	76.2	596	59.6

[a]Dye loading amount **1** = 18.0 nmol mg $^{-1}$. [b]Dye loading amount **2** = 15.2 nmol mg $^{-1}$.

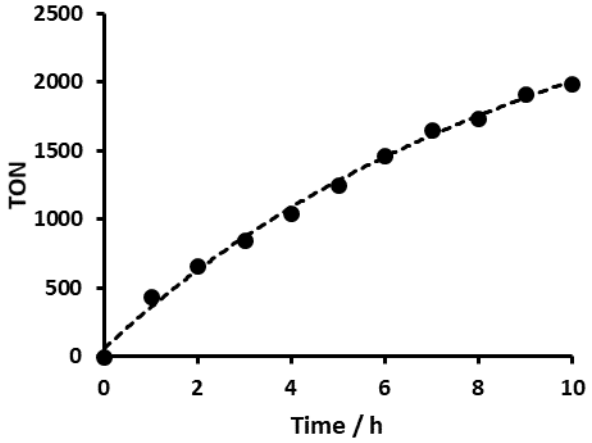


Figure S12. Photocatalytic activity of Pt/HPT500/**1** in aqueous solution involving ascorbic acid at pH 7.2. Dye loading amount of **1** = 18.0 nmol mg^{-1}.

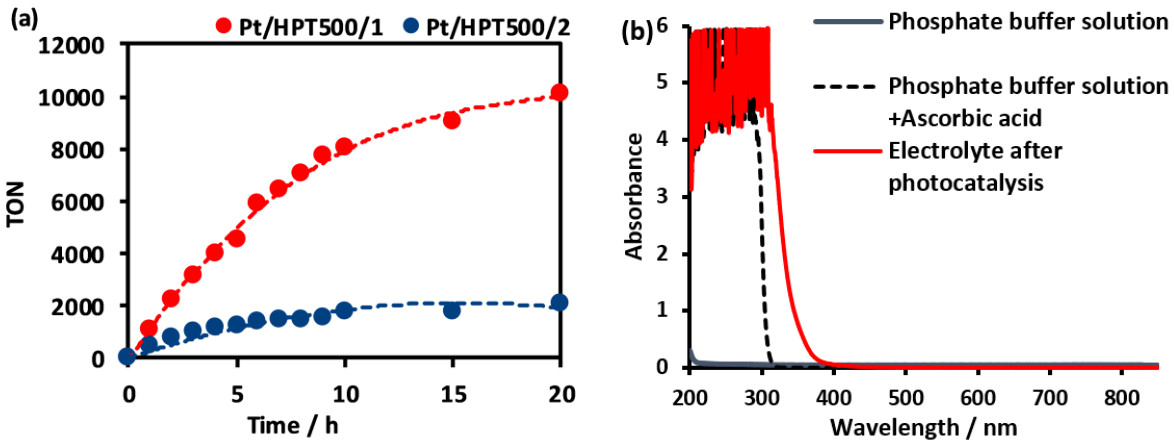


Figure S13. (a) Photocatalytic activity of Pt/HPT500/**1** under 20-h irradiation. Dye loading amounts of **1** and **2** were 18.0 nmol mg^{-1} and 15.2 nmol mg^{-1}, respectively. (b) UV-Vis absorption spectra of electrolyte after 20-h photocatalysis using Pt/HPT500/**1**.

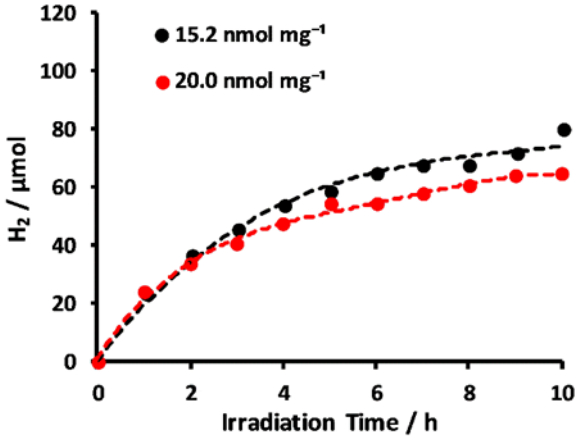


Figure S14. Plots of hydrogen evolved over Pt/HPT500/**2** upon 10-h irradiation using 300 W Xe lamp (λ > 400 nm, 100 mW cm^{-2} light intensity).

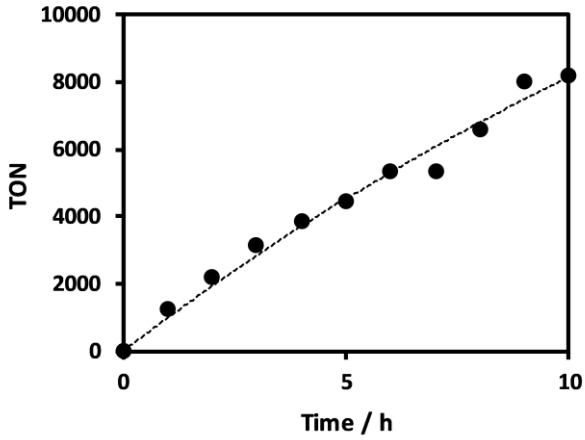


Figure S15. Photocatalytic activity of Pt/P25/**1** in the presence of ascorbic acid (0.5 M) under 100 mW cm^{-2} light irradiation (λ > 400 nm) at pH 3.6. Dye loading amount **1** on P25 = 30.0 nmol mg^{-1}.

Table S3. Hydrogen production of Pt/HPT500/**1**, Pt/P25/**1**, and Pt/ HPT500/**2**.

Irradiation time / h	Pt/HPT500/**1**			Pt/HPT500/**2**			Pt/P25/**1**		
	μmol	μmol g^{-1}[a]	TON[b,c]	μmol	μmol g^{-1}[a]	TON[b,d]	μmol	μmol g^{-1}[a]	TON[b,e]
1	126	21000	2340	29.7	4940	650	113	18900	1260
2	171	28500	3170	38.9	6480	852	195	32500	2170
3	245	40900	4540	49.2	8200	1080	284	47400	3160
4	316	52600	5840	58.8	9800	1290	348	57900	3860
5	349	58200	6460	60.8	10100	1330	400	66700	4450
6	430	71700	7960	66.5	11100	1460	477	79500	5300
7	479	79900	8880	67.8	11300	1480	479	79900	5330
8	524	87400	9710	69.9	11600	1530	593	98900	6590
9	500	83300	9260	76.9	12800	1690	722	120000	8020
10[f]	597	99500	11100	78.6	13100	1720	737	123000	8180

[a]Activity = Photocatalytic activity of the system is defined as number of micromole of H_2 evolved per gram of photocatalyst (μmol H_2 / g photocatalyst). [b]TON = 2 × mol H_2 / mol dye. [c]Dye loading amount **1** =18.0 nmol mg^{-1}. [d]Dye loading amount **2** on HPT500 = 15.2 nmol mg^{-1}. [e]Dye loading amount **1** on P25 = 30.0 nmol mg^{-1}. [f]The experiment was terminated since the amount of hydrogen production reached the plateau.

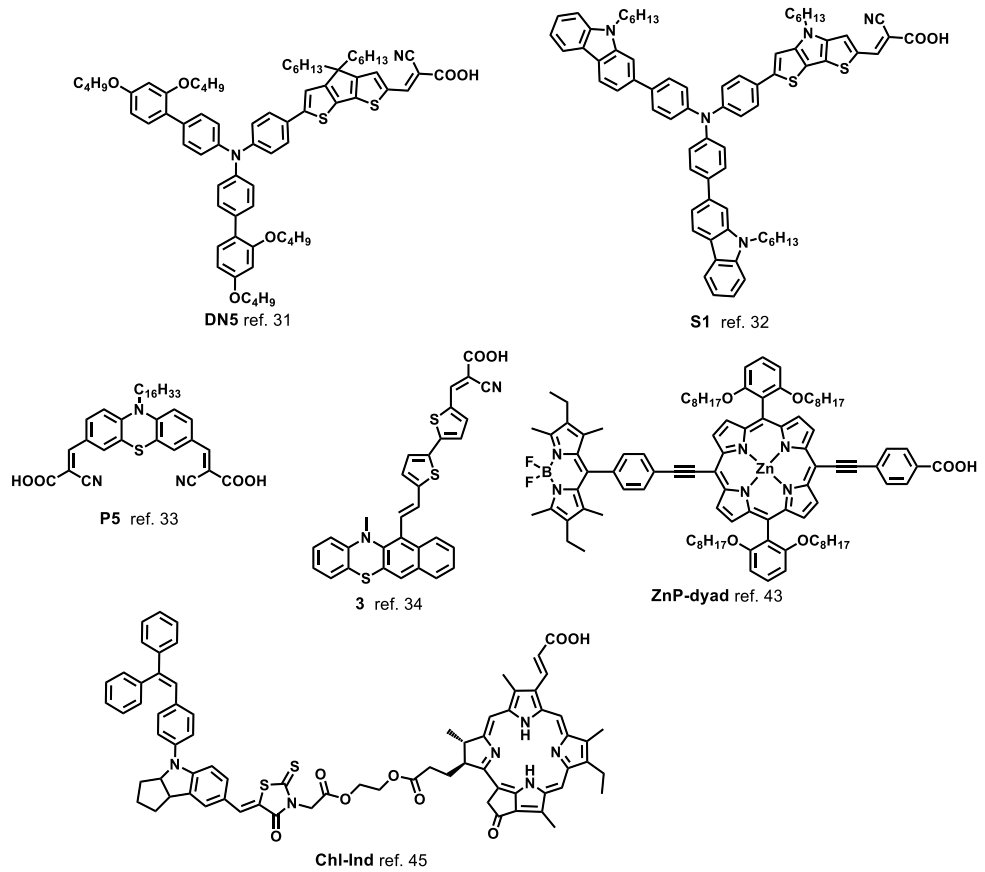


Figure S16. Reported metal-free organic photosensitizers for DSP system.

Table S4. The hydrogen production of Pt/HPT500/**1** using ascorbic acid (0.5 M) under light irradiation 100 mW cm^{-2} (λ > 400) nm in comparison with the other metal-free organic photosensitizers.

Photocatalyst	Cocatalyst	λ_{max} (ε) / nm (M^{-1} cm^{-1})	Irradiation time/ h	AQY / %	TON[a]	TOF[b]	Activity[c] / μmol g^{-1}	Activity[d] / μmol g^{-1}	Ref.
Pt/HPT500/**1**	Pt 0.42 wt%	638 (123 000)	10	3.56 (670 nm)	11 100	1110	99 500	23 700 000	
Pt/TiO_2/**DN5**	Pt 1 wt%	542 (66 778)	6	–[e]	1 864	–[e]	–[e]	–[e]	31
Pt/TiO_2/**S1**	Pt 0.5 wt%	531 (77 760)	48	12.3 (520 nm)	10 200	213	–[e]	478 000	32
Pt/TiO_2/**P5**	Pt 1 wt%	463 (13 500)	5	–[e]	1 026	205	–[e]	–[e]	33
Pt/TiO_2/**3**	Pt 1 wt%	443 (22 239)	16	1.65 (420 nm)	4460	278	–[e]	–[e]	34
Pt/TiO_2/**ZnP-dyad**	Pt 0.5 wt%	659 (48 100)	120	2.59 (556 nm)	12 800	107	–[e]	173 000	43
Pt/TiO_2(P25)/ **Chl-Ind**	Pt 1 wt%	380-750	6	1.27 (420 nm)	1 044	–[e]	4 176	–[e]	45

[a] TON = 2 × mol H_2 / mol dye. [b] TOF = TON / irradiation time (h). [c]Activity = Photocatalytic activity of the system is defined as number of micromole of H_2 evolved per gram of photocatalyst (μmol H_2 / g photocatalyst). [d]Activity = Initial photocatalytic activity of the system is defined as number of micromole of H_2 evolved per gram of platinum loaded (μmol H_2 / g Pt). [e]No data provided in the reference.

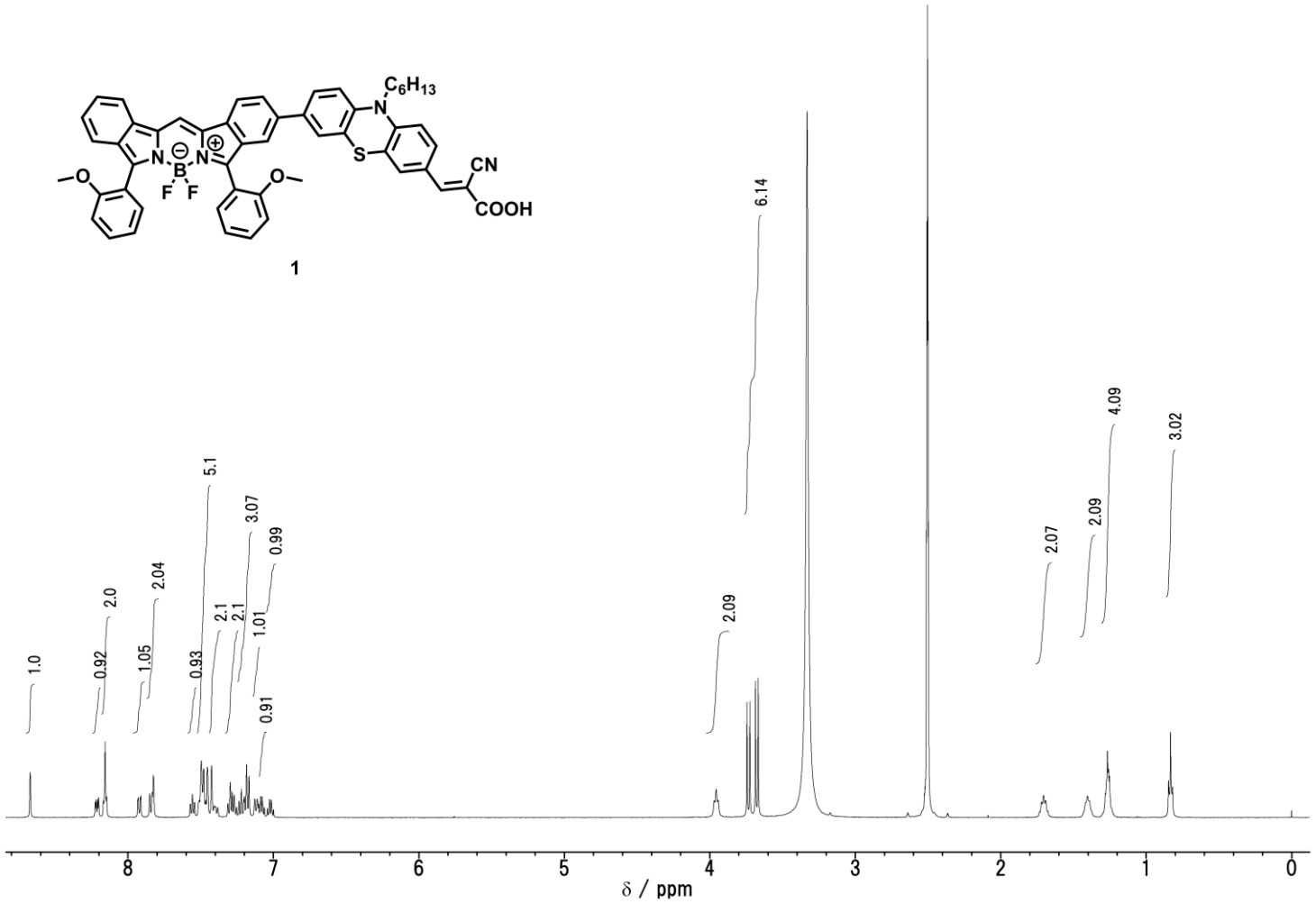


Figure S17. ^{1}H NMR spectrum of **1** in DMSO-d_6.

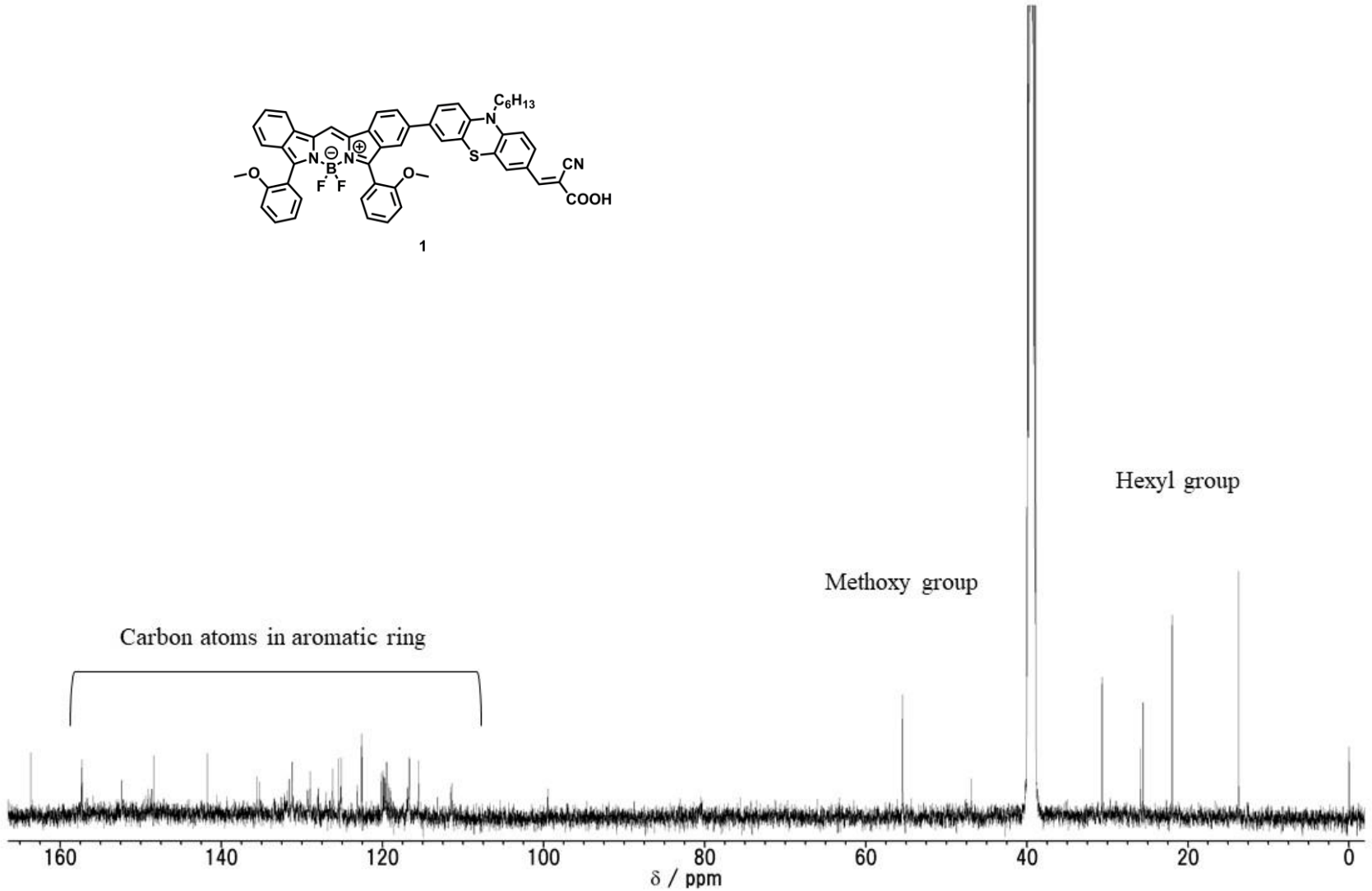


Figure 18. ^{13}C NMR spectrum of **1** in DMSO-d_6.

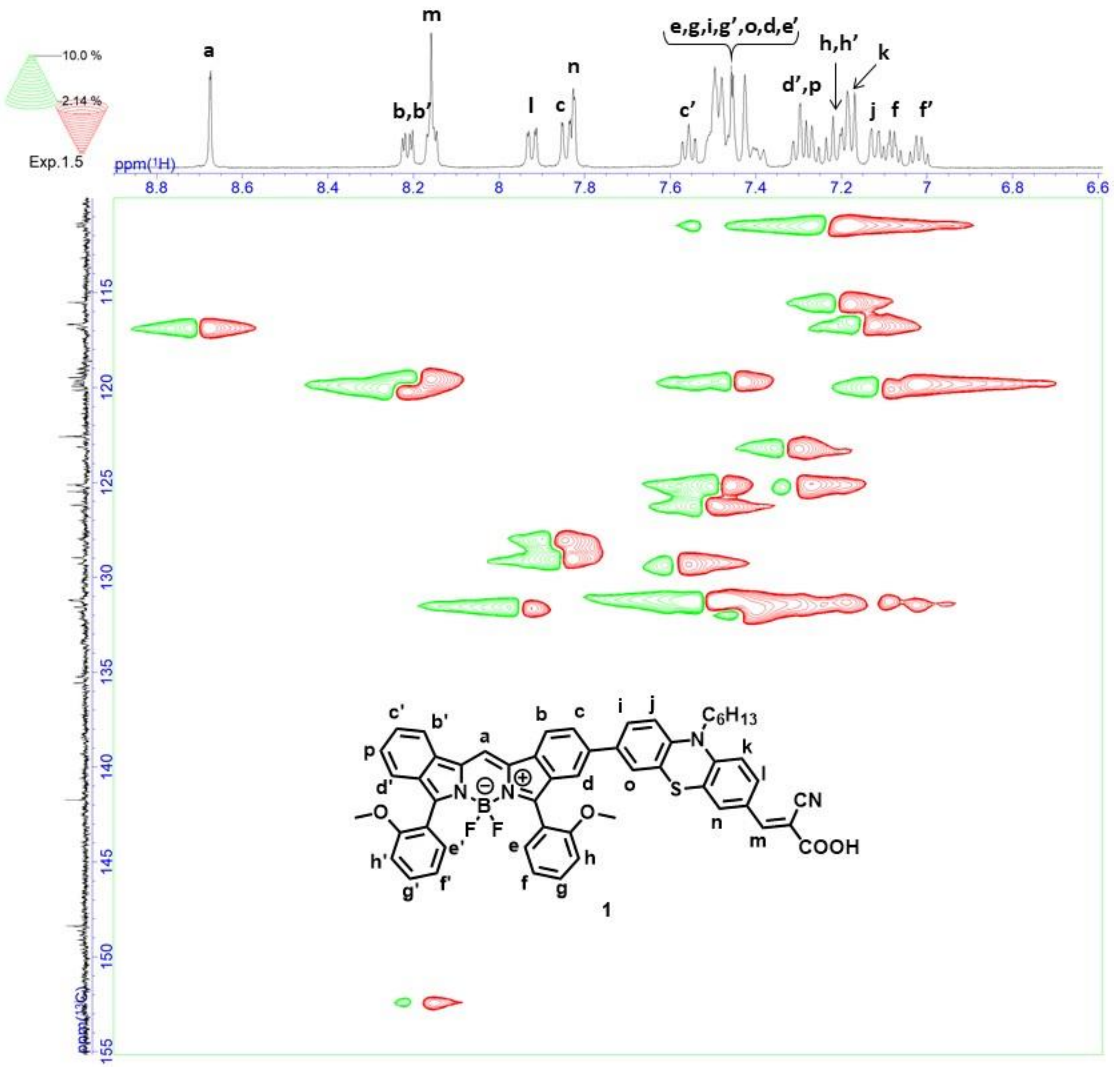


Figure 19. ^{1}H-^{13}C HSQC spectrum of **1** in DMSO-d_6 in low magnetic field.

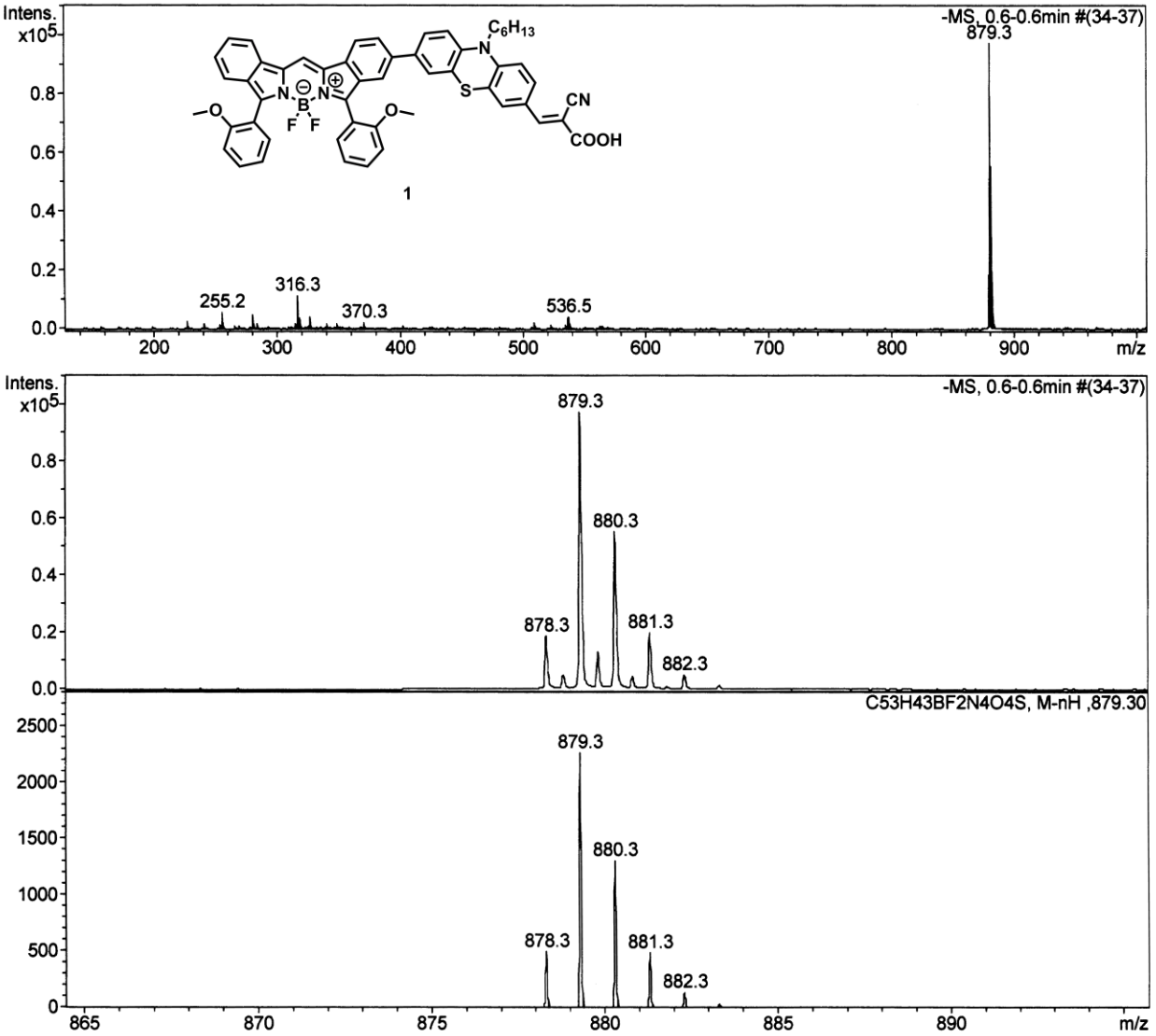


Figure S20. ESI MS (negative ion mode) of **1**.