Near-Infrared Thienyl-Bodipy Co-Sensitizer For High-Efficiency Dye-Sensitized Solar Cells

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Supporting Information

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1) General Methods

All reactions were performed under an atmosphere of dried argon using standard Schlenk tube techniques. All chemicals were used as received from commercial sources unless stated otherwise. THF was distilled from sodium and benzophenone under an Ar atmosphere. DMF was distilled from KOH under an argon atmosphere. 1H NMR (400.1 MHz) and 13C NMR (100.5 MHz) spectra were recorded at room temperature (rt) on a Bruker Advance 400 MHz spectrometer, 1H NMR (300.1 MHz) and 13C NMR (75.5 MHz) spectra were recorded at room temperature (rt) on a Bruker Advance 300 MHz spectrometer, 1H NMR (200.1 MHz) and 13C NMR (50.5 MHz) spectra were recorded at rt on a Bruker Advance 200 MHz spectrometer using perdeuteriated solvents as internal standards. Chromatographic purifications were performed using silica gel (40-63 μm). TLC was performed on silica gel plates coated with fluorescent indicator. Absorption spectra were recorded on a Schimadzu UV-3000 absorption spectrometer. The steady-state fluorescence emission and excitation spectra were obtained by using a HORIBA JOBIN YVON FLUOROMAX 4. All fluorescence spectra were corrected. The fluorescence quantum yield (fexp) was calculated from eq 1.

$$\Phi_{cmp} = \Phi_{ref} \frac{I \ OD_{ref} \ \eta^2}{I_{ref} \ OD \ \eta_{ref}{}^2} \quad (1)$$

Here, I denotes the integral of the corrected emission spectrum, OD is the optical density at the excitation wavelength and η is the refractive index of the medium. The reference systems used were rhodamine 6G (Φref = 0.78) in air equilibrated water and Tetramethoxydiisoindomethene-difluoroborate (Φref = 0.51). Luminescence lifetimes were measured on an Edimburgh Instruments spectrofluorimeter equipped with a R928 photomultiplier and a PicoQuant PDL 800-D pulsed diode connected to a GwInstect GFG- 8015G delay generator. No filter was used for the excitation. Emission wavelengths were selected by a monochromator. Lifetimes were deconvoluted with FS-900 software using a light-scattering solution (LUDOX) for instrument response.

2) Synthetic Experimental Part

General procedure A for Boron functionalization:

To a stirred solution of BODIPY (1eq.) an aldehyde (A and B) (2.2 eq), piperidine (2 mL) and a crystal of *p*-TsOH were added in a round bottom flask contains 20 ml toluene and equipped with a Dean stark apparatus. The reaction mixture was refluxed for 12 hours. After cooling to room temperature, the mixture was washed three times with water. The organic layer was dried over $MgSO_4$ or absorbent cotton and the solvent was evaporated under reduced pressure. The obtained crude residue was purified by silica-gel column chromatography as static phase to afford the target compound.

General procedure B for Boron functionalization:

In a Schlenk tube was added ethylmagnesiumbromide (3.3 eq, solution in THF 1.0 M) to a stirred solution of 3-(2-methoxyethoxy)prop-1-yne (4 eq.) in anhydrous THF. The reaction mixture was stirred at 60 °C for 2 h. Then the resulting anion was transferred via cannula to a solution of BOPIDY (1 eq.) in anhydrous THF. The solution was stirred at 60 °C overnight. Water was added, and the solution was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ or absorbent cotton and the solvent was evaporated under reduced pressure. The resulting crude residue was purified by silica-gel column chromatography as static phase to afford the desired compound.

General procedure C for Carboalkoxylation:

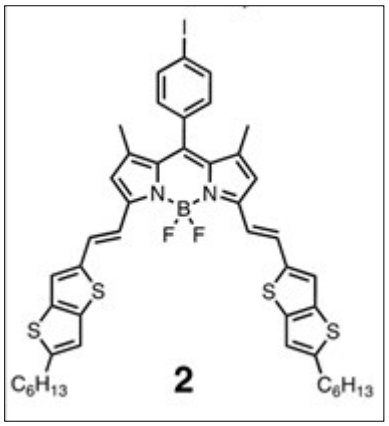
BODIPY (1 eq.), EtOH (5 mL), benzene (10 mL), triethylamine (5 mL) and $[Pd(PPh_3)_2Cl_2]$ (0.1 eq.) were added in a twin neck round bottom flask equipped with reflux condenser. Then a continuous flow of CO at atmospheric pressure and stirred along with heating (4 h at 70 °C) used to degassed the reaction mixture. After cooling to room temperature, dichloromethane was used to extract the mixture then washing using water for three times. The organic phase was dried over $MgSO_4$ or absorbent cotton and the solvent was evaporated under reduced pressure. The resulting crude residue was purified by silica-gel column chromatography as static phase to afford the desired compound.

General procedure D for Saponification:

In a round bottom flask equipped with a reflux condenser, were added BODIPY (1 eq.), EtOH (5 mL), THF (1 mL), water (1 mL) and NaOH (10 eq.). The mixture was stirred at 40 °C for 4 hours.

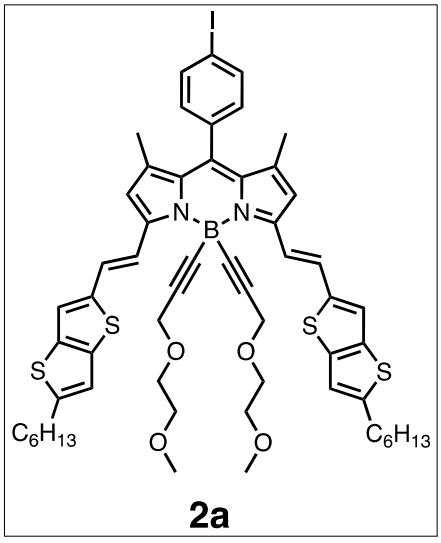
After cooling to room temperature, the reaction mixture was washed three times with water. The organic layer was dried over $MgSO_4$ or absorbent cotton and the solvent was evaporated under reduced pressure. The resulting crude residue was purified by silica-gel column chromatography as static phase to afford the desired compound.

Compound 2



2

Compound 2 was prepared according to the general procedure A from 114 mg (0.253 mmol) of compound 1 and 134 mg (0.532 mmol) of A. The purification was carried out by chromatography on silica gel as static phase with a mixture of petroleum ether/toluene/dichloromethane 55/35/10 as mobile phase and afforded 2 (110 mg, 0.120 mmol, 47%). ^{1}H NMR (200 MHz $CDCl_3$): 0.91 (m, 6H); 1.35-1.46 (m, 18H); 1.70-1.73 (m, 4H); 2.90 (t, ^3J = 6.9 Hz, 4H); 6.60 (s, 2H); 6.94 (s, 2H); 7.07 (d, ^3J = 8.0 Hz, 2H); 7.31-7.52 (m, 6H); 7.84 (d, ^3J = 8.0 Hz, 2H). ^{13}C NMR (50 MHz $CDCl_3$): 14.2, 15.1, 22.7, 28.9, 31.5, 31.6, 31.7, 94.8, 116.9, 117.8, 118.2, 120.9, 130.0, 130.8, 133.5, 135.0, 135.8, 138.1, 138.4, 140.4, 141.7, 142.9, 151.0, 150.2. Anal. Calcd for $C_{45}H_{46}BF_2IN_2S_4$ (Mr = 918.16): C, 58.82; H, 5.05; N, 3.05; Found: C, 58.61; H, 4.74; N, 2.83.



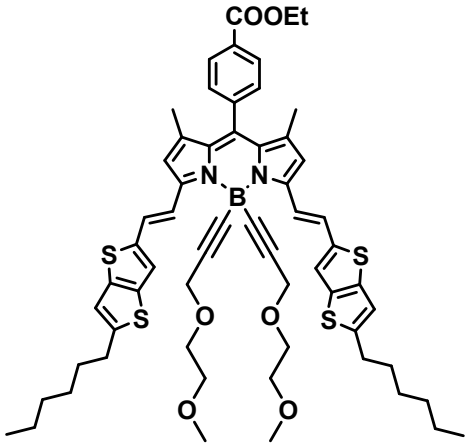
2a

Compound 2a

Compound 2a was prepared according to general procedure B from 0.96 mL (0.850 mmol) of ethylmagnesiumbromide, 124 µL (1.032 mmol) of 3-(2-methoxyethoxy)prop-1-yne and 132 mg (0.144 mmol) of compound 2. The purification was carried out by chromatography on silica gel as static phase with a mixture of dichloromethane/petroleum ether 80/20 as mobile phase and afforded 2a (124.7 mg, 0.113 mmol, 78%). ^{1}H NMR (200 MHz $CDCl_3$): δ = 0.90 (t, ^3J = 5.8 Hz, 6H), 1.25-1.42 (m, 12H), 1.44 (s, 6H), 1.66-1.76 (m, 4H), 2.90 (t, ^3J = 7.4 Hz, 4H), 3.15 (s, 6H), 3.20-3.26 (m, 4H), 3.56-3.68 (m, 4H), 4.23 (s, 4H), 6.60 (s, 2H), 6.93 (s, 2H), 7.09 (d, ^3J = 7.1 Hz, 2H), 7.21-7.37 (m, 4H), 7.84

(d, ^3J = 7.6 Hz, 2H), 8.00 (d, ^3J = 15.6 Hz, 2H). ^{13}C NMR (50 MHz $CDCl_3$): δ =14.2, 15.3, 22.7, 28.9, 31.5, 31.6, 31.7, 58.9, 59.6, 68.4, 71.7, 94.7, 116.9, 118.5, 119.9, 120.4, 128.1, 130.8, 135.3, 138.2, 138.3, 139.9, 140.0, 140.1, 143.6, 150.8, 151.4. Anal. Calcd for $C_{57}H_{64}BN_2O_4S_4$ (Mr = 1107.10): C, 61.84; H, 5.83; N, 2.53; Found: C, 61.77; H, 5.62; N, 2.27.

Compound 2b

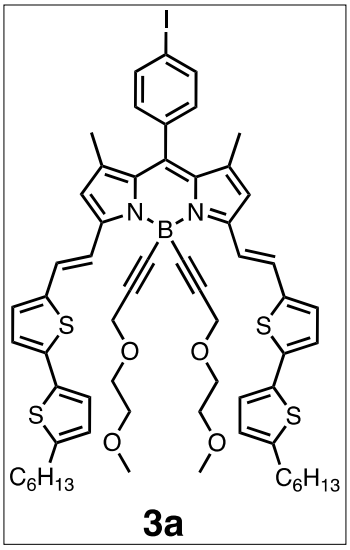


2b

Compound 2b was prepared according to general procedure C from 111 mg of compound 2a (0.100 mmol) and 12 mg of $[Pd(PPh_3)_2Cl_2]$ (0.017 mmol). The purification was carried out by chromatography on silica gel as static phase with a mixture of dichloromethane/ethyl acetate 95/5 as mobile phase and afforded 2b (85 mg, 0.081 mmol, 81%). ^{1}H NMR (200 MHz $CDCl_3$): δ = 0.90 (t, ^3J = 6.6 Hz, 6H), 1.27-1.48 (m, 21H), 1.64-1.76 (m, 4H), 2.90 (t, ^3J = 7.4 Hz, 4H), 3.16 (s, 6H), 3.21-3.26 (m, 4H), 3.61-3.66 (m, 4H), 4.24 (s, 4H), 4.43 (q, ^3J = 7.2 Hz, 3H), 6.61 (s, 2H), 6.94 (s, 2H), 7.27 (s, 2H), 7.21-7.33 (m, 2H), 7.45 (d, ^3J = 8.1 Hz, 2H), 7.84 (d, ^3J = 7.6 Hz, 2H), 8.02 (d, ^3J = 16.0 Hz, 2H), 8.18 (d, ^3J = 8.1 Hz, 2H). ^{13}C NMR (50 MHz $CDCl_3$): δ = 14.2, 14.4, 15.1, 22.7, 28.8, 31.5, 31.6, 31.7, 58.8, 59.5, 61.4, 68.4, 71.7, 91.9, 116.8, 118.5, 119.8, 120.4, 128.1, 129.2, 130.2, 131.0, 131.6, 136.6, 138.2, 139.9, 140.0, 140.5, 143.5, 150.8, 151.4, 166.2. Anal. Calcd for $C_{60}H_{69}BN_2O_6S_4$ (Mr = 1053.27): C, 68.42; H, 6.60; N, 2.66; Found: C, 68.17; H, 6.42; N, 2.75.

Compound 3a

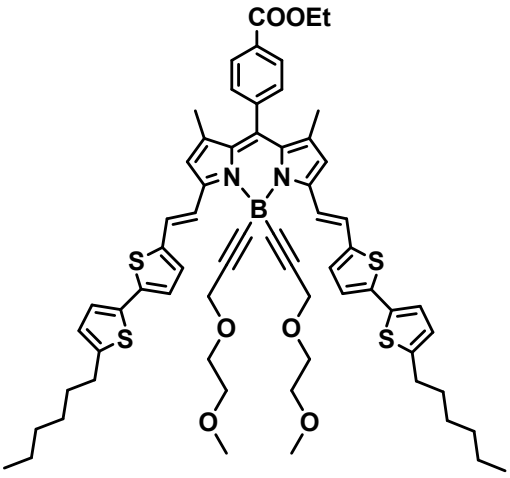
Compound 3a was prepared according to general procedure B from 0.8 mL (0.772 mmol) of ethylmagnesiumbromide, 111 µL (0.927 mmol) of 3-(2-methoxyethoxy)prop-1-yne and 150 mg (0.154 mmol) of compound 3. The purification was carried out by chromatography on silica gel as static phase with a mixture of dichloromethane/petroleum ether 80/20 as mobile phase and afforded 3a (111.0 mg, 0.096 mmol, 62%). ^{1}H NMR (300 MHz $CDCl_3$): δ = 0.91 (t, ^3J = 6.9 Hz,



3a

6H), 1.27-1.45 (m, 18H), 1.66-1.76 (m, 4H), 2.82 (t, ^3J = 7.5 Hz, 4H), 3.22 (s, 6H), 3.34-3.37 (m, 4H), 3.68- 3.71 (m, 4H), 4.25 (s, 4H), 6.60 (s, 2H), 6.73 (d, ^3J = 3.5 Hz, 2H), 7.05-7.26 (m, 10H), 7.84 (d, ^3J = 8.2 Hz, 2H), 7.99 (d, ^3J = 15.9 Hz, 2H). ^{13}C NMR (50 MHz $CDCl_3$): δ = 14.2, 15.2, 22.7, 28.9, 30.4, 31.7, 58.9, 59.5, 68.3, 71.8, 94.7, 118.6, 120.0, 124.1, 124.4, 125.2, 127.1, 129.2, 130.8, 131.9, 134.7, 135.3, 138.2, 139.5, 140.0, 141.3, 146.5, 151.5. Anal. Calcd for $C_{61}H_{68}BIN_2O_4S_4$ (Mr = 1159.18): C, 63.20; H, 5.91; N, 2.42; Found: C, 63.04; H, 5.77; N, 2.09.

Compound 3b

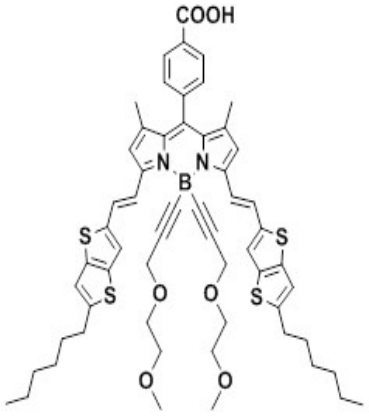


3b

Compound 3b was prepared according to general procedure C from 220 mg of compound 3a (0.190 mmol) and 13.3 mg of $[Pd(PPh_3)_2Cl_2]$ (0.019 mmol). The purification was carried out by chromatography on silica gel as static phase with a mixture of dichloromethane/ethyl acetate 95/5 as mobile phase and afforded 3b (178.2 mg, 0.169 mmol, 89%). ^{1}H NMR (300 MHz $CDCl_3$): δ = 0.91 (t, ^3J = 6.7 Hz, 6H), 1.30-1.39 (m, 12H), 1.40 (s, 6H), 1.45 (t, ^3J = 7.1 Hz, 3H), 1.70 (m, 4H), 2.82 (t, ^3J = 7.5 Hz, 4H), 3.22 (s, 6H), 3.34-3.37 (m, 4H), 3.67-3.70 (m, 4H), 4.25 (s, 4H), 4.44 (q, ^3J = 7.0 Hz, 2H), 6.60 (s, 2H), 6.72 (d, ^3J = 3.6 Hz, 2H), 7.05 (d, ^3J = 4.0 Hz, 2H), 7.11-7.13 (m, 4H), 7.22 (d, ^3J = 15.9 Hz, 2H), 7.47 (d, ^3J = 8.2 Hz, 2H), 7.99 (d, ^3J = 16.0 Hz, 2H), 8.19 (d, ^3J = 8.3 Hz, 2H). ^{13}C NMR (50 MHz $CDCl_3$): δ = 14.2, 14.5, 15.1,

22.7, 28.9, 30.4, 31.7, 58.9, 59.6, 61.5, 68.4, 71.8, 92.0, 118.6, 120.0, 124.1, 124.4, 125.2, 127.2, 129.2, 130.3, 131.1, 131.8, 134.7, 136.6, 139.6, 140.0, 140.5, 141.3, 146.5, 151.6, 166.2. Anal. Calcd for $C_{64}H_{73}BN_2O_6S_4$ (Mr = 1105.35): C, 69.54; H, 6.66; N, 2.53; Found: C, 69.38; H, 6.45; N, 2.17.

Compound T′$_2$P$_2$A



T′$_2$P$_2$A

Compound T′$_2$P$_2$A was prepared according to general procedure D from 72 mg of compound 2b (0.068 mmol) and 28 mg of NaOH (0.684 mmol). The purification was carried out by chromatography on silica gel as static phase with a mixture of dichloromethane/acetic acid 99/1 as mobile phase and afforded T′$_2$P$_2$A (47.6 mg, 0.046 mmol, 68%). ^{1}H NMR (300 MHz $CDCl_3$): δ = 0.90 (t, ^3J = 7.2 Hz, 6H), 1.24-1.38 (m, 12H), 1.41 (s, 6H), 1.68-1.78 (m, 4H), 2.90 (t, ^3J = 7.4 Hz, 4H), 3.17 (s, 6H), 3.23-3.27 (m, 4H), 3.63-3.66 (m, 4H), 4.24 (s, 4H), 6.62 (s, 2H), 6.94 (s, 2H), 7.25-7.33 (m, 4H), 7.52 (d, ^3J = 8.2 Hz, 2H), 8.02 (d, ^3J = 15.8 Hz, 2H), 8.25 (d, ^3J = 8.2 Hz, 2H). ^{13}C NMR (75 MHz $CDCl_3$): δ = 14.2, 15.2, 22.7, 28.9, 30.5, 31.7, 34.4, 58.9, 59.6, 68.4, 71.8, 92.0, 116.9, 118.6, 119.8, 120.5, 125.7, 128.4, 129.5, 129.8, 130.9, 131.6, 135.9, 138.2, 140.0, 140.0, 141.6, 143.6, 150.9, 151.7, 170.4. Anal. Calcd for $C_{58}H_{65}BN_2O_6S_4$ (Mr = 1025.22): C, 67.95; H, 6.39; N, 2.73; Found: C, 67.72; H, 6.17; N, 2.54.

ESI-TOF-MS.

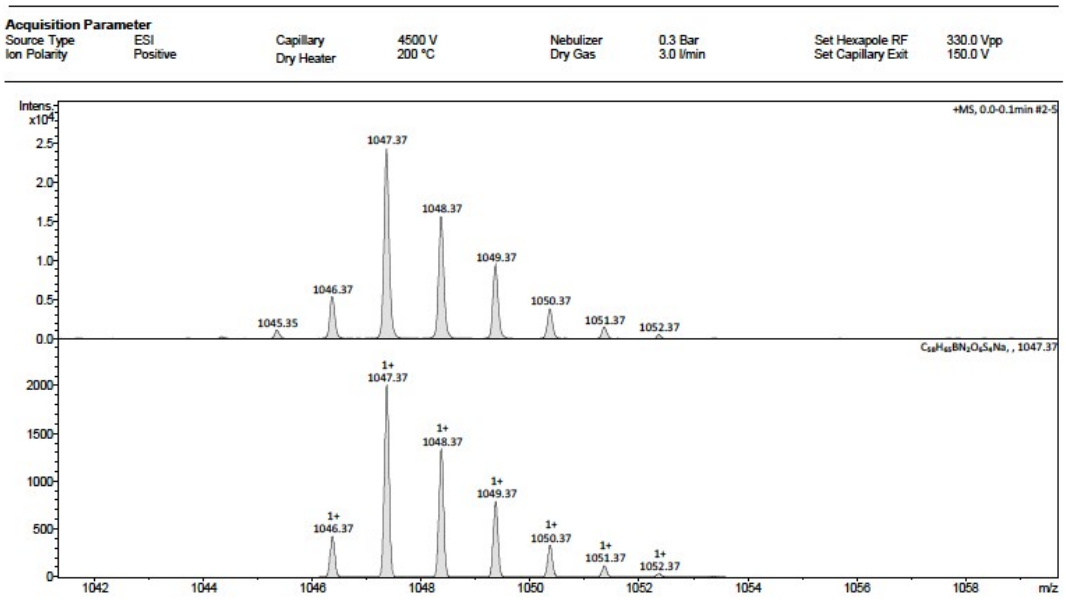
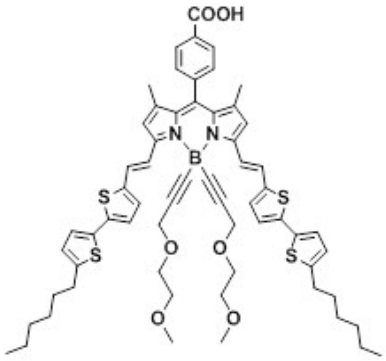


Figure S1. zoom (top) + simulation (bottom) analysis of T'_2P_2A

Compound T''_2P_2A



T''_2P_2A

Compound T''_2P_2A was prepared according to general procedure D from 148 mg of compound 3b (0.134 mmol) and 56 mg of NaOH (1.405 mmol). The purification was carried out by chromatography on silica gel as static phase with a mixture of dichloromethane/acetic acid 99/1 as mobile phase and afforded T''_2P_2A (95.3 mg, 0.089 mmol, 66%). ^{1}H NMR (300 MHz $CDCl_3$): δ = 0.91 (t, ^3J = 6.8 Hz, 6H), 1.30-1.38 (m, 12H), 1.40 (s, 6H), 1.66-1.75 (m, 4H), 2.82 (m, 4H), 3.22 (s, 6H), 3.35-3.38 (m, 4H), 3.68-3.71 (m, 4H), 4.26 (s, 4H), 6.61 (s, 2H), 6.73 (d, ^3J = 3.5 Hz, 2H), 7.06 (d, ^3J = 3.6 Hz, 2H), 7.11-7.26 (m, 6H), 7.51 (d, ^3J = 8.3 Hz, 2H), 7.99 (d, ^3J = 16.0 Hz, 2H), 8.26 (d, ^3J = 8.4 Hz, 2H). ^{13}C NMR (50 MHz $CDCl_3$): δ = 14.2, 15.2, 22.7, 28.9, 30.4, 31.7, 58.9, 59.6, 68.4, 71.8, 92.1, 95.5, 118.7, 112.0, 124.1, 124.4, 125.2, 127.3, 129.3, 129.5, 129.9, 130.9, 131.7, 134.7, 136.2, 139.7, 139.9, 141.3, 141.6, 146.6, 151.7, 170.7. Anal. Calcd for $C_{62}H_{69}BN_2O_6S_4$ (Mr = 1077.29): C, 69.12; H, 6.46; N, 2.60; Found: C, 68.94; H, 6.27; N, 2.37.

ESI-TOF-MS.

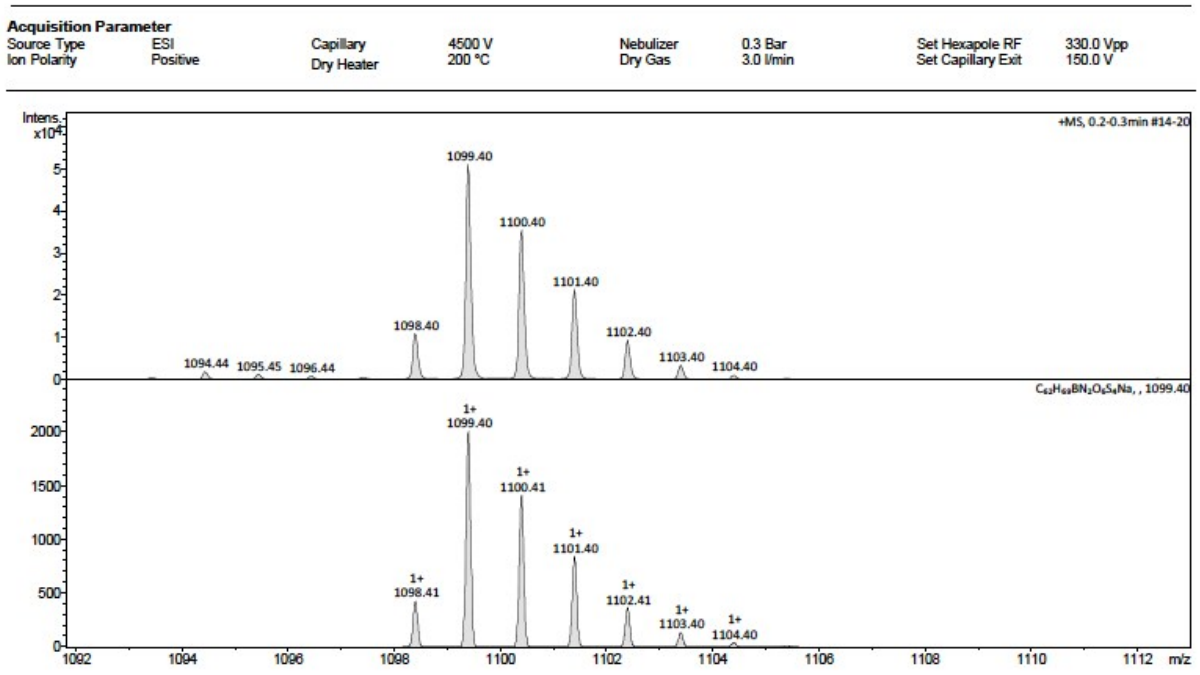


Figure S2. zoom (top) + simulation (bottom) analysis of T''_2P_2A

3) Electrochemical Measurements:

The cyclic voltammetry was recorded with a conventional 3-electrode system using a BAS CV-50W voltammetric analyser equipped with a Pt microdisk (2 mm^2) working electrode and a silver wire counter-electrode. Ferrocene was used as an internal standard and was calibrated against a

saturated calomel reference electrode (SCE) separated from the electrolysis cell by a glass frit presoaked with electrolyte solution. Solutions contained the electro-active substrate (about 1.5 mM) in deoxygenated and anhydrous dichloromethane containing tetra-n-butylammonium hexafluorophosphate (0.1 M) as supporting electrolyte [electrochemical window from +1.7 to -2.2 V], at a solute concentration of ca. 1.5 mM and at rt. The quoted half-wave potentials were reproducible within ≈ 15 mV. Potentials were standardized versus ferrocene (Fc) as internal reference and converted to the SCE scale assuming that E1/2 (Fc/Fc+) = +0.38 V (Δ Ep = 60 mV) vs SCE. Error in half-wave potentials is ±10 mV. For irreversible processes the peak potentials (Eap or Ecp) are quoted. All reversible redox steps result from one-electron processes. Onset potentials determined on the 10% current increase.

4) Absorption, emission and excitation spectra of T'_2P_2A and T''_2P_2A photosensitizers

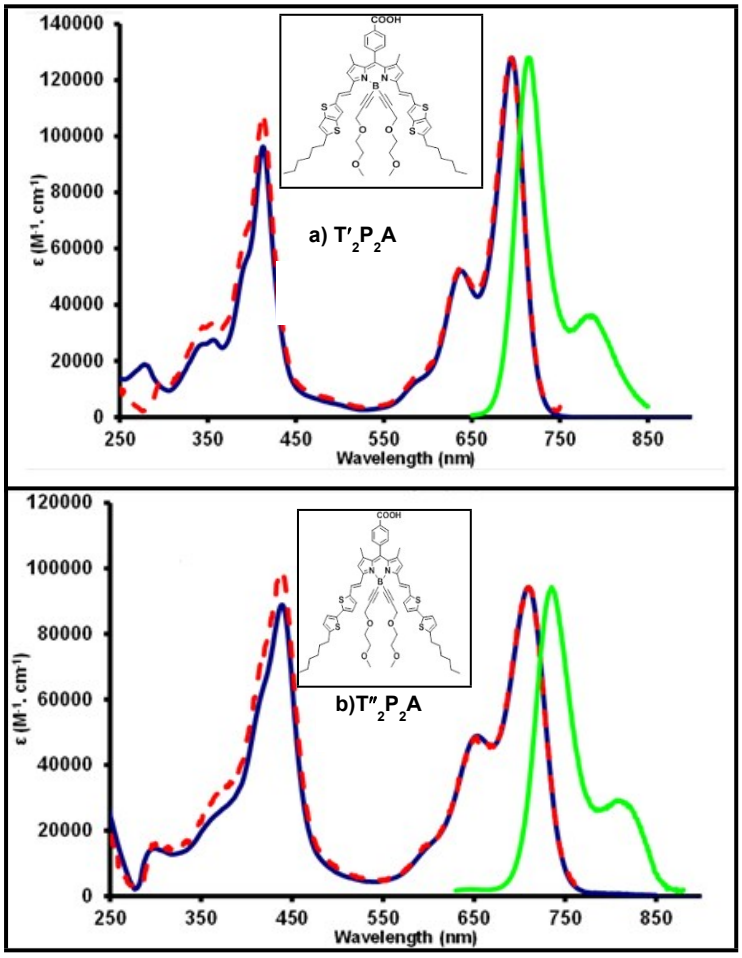


Figure S3. Absorption spectra (orange), emission spectra (green) and the excitation spectra (dashed l) in THF of a) T′$_2$P$_2$A and b) T″$_2$P$_2$A photosensitizers

Table T1. Reproducible photovoltaic parameters of the fabricated DSSCs

Dye	Device No.	J_{SC} [mA cm^{-2}]	V_{OC} [V]	*FF*	η [%]
TP$_2$A	1	11.3	0.524	0.698	4.13
	2	11.5	0.52	0.703	4.20
T$_2$′P$_2$A	1	16.23	0.524	0.705	6.00
	2	15.97	0.533	0.687	5.85
T$_2$″P$_2$A	1	11.8	0.46	0.625	3.39
	2	11.86	0.454	0.615	3.31
TP$_2$A + T$_2$′P$_2$A	1	17.66	0.553	0.674	6.58
	2	17.55	0.55	0.692	6.68