Supplementary Information

Diketopyrrolopyrrole Linked Porphyrin Dimers for Visible-Near-Infrared Photoresponsive Non-fullerene Organic Solar Cells

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1. Materials and Characterizations

The material IT-M was purchased from Nano-C chemical company and PEDOT: PSS was obtained from Tokyo Chemical Industry Co; All solvents for the reactions were dried by using suitable dehydrating agents according to the standard procedures. Purification of the compounds was performed by column chromatography with 100-200 mesh silica. ^{1}H and ^{13}C NMR spectra were recorded in an NMR spectrometer operating at 400.00 and 100.00 MHz, respectively. The chemical shifts were calibrated from the residual peaks observed for the deuterated solvents chloroform ($CDCl_3$) at δ 7.26 ppm for ^{1}H and δ 77.0 ppm for ^{13}C, respectively. High-resolution matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained with a Bruker Auto flex MALDI-TOF mass spectrometer. The optical absorption of the porphyrin dimers was measured for the freshly prepared air equilibrated solutions at room temperature by using a UV-Vis spectrophotometer. Cyclic voltammetry (CV) experiments were performed on an electrochemical workstation in $CHCl_3$ solution by using 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as supporting electrolyte. The experiments were performed at room temperature with a conventional three-electrode cell assembly consisting of a platinum wire as the auxiliary electrode, a non-aqueous $Ag/AgNO_3$ reference electrode, ferrocene as internal standard and a glassy carbon working electrode.

2. Solar cell Device fabrication

We followed up a general solution-processing procedure for the fabrication of solar cells. Firstly, Indium tin oxide (ITO) coated on glass substrates which were washed by acetone, distilled water, and methanol. Secondly, the substrates were cleaned under UV-ozone treatment for 30 min and spin-coated the commercial PEDOT: PSS solution on the substrates at 3500 rpm for 80 s, and then dried over on a hot plate at 150 °C for 10 min. Subsequently, the substrates were cooled down to room temperature and transferred to the glove box in an argon atmosphere. The active layers of ETDPP-2P:IT-M and TDPP-2P:IT-M at the weight ratio of (1:1, w/w) were prepared by spin-coating from their solutions with a concentration of 20 mg/mL in a mixed solvent of chloroform (CF)/ diiodo-octane (DIO) (99.5:0.5 v/v) at 2500 rpm for 30 s. Then, the substrates were left to slow dry for 20 min in a petri dish, and followed by baking on a hot plate for 3 min at 100 ^{o}C. After cooled down to room temperature, an electron transport layer was spin-coated on the top of the active blend films from ZrAcac solution (0.5 mg/mL) in MeOH at 3000 rpm for 60 s. Finally, dried on a hot plate, Ag cathode (100 nm) was deposited in a high vacuum chamber (~10^{-6} mbar).

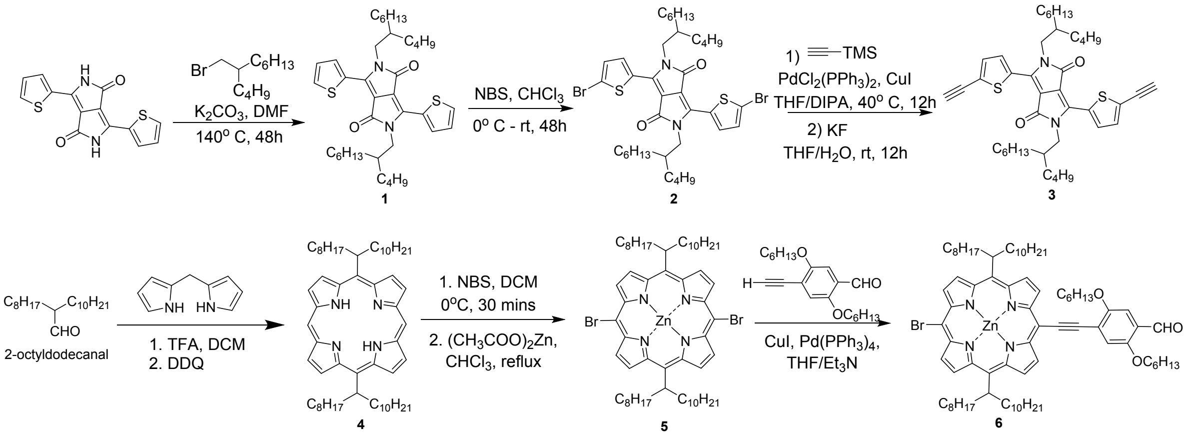
3. Morphology studies

Atomic force microscope operated in the tapping mode under ambient conditions. The thickness of the active layer of the device was measured using a Veeco Dektak 150 surface profiler. The spectral response was measured with a DSR100UV-B spectrometer with an SR830 lock-in amplifier. A calibrated Si photodiode was used as a reference before each measurement.

4. Abbreviations

3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2’,3’-d’]-s-indaceno[1,2-b:5,6-b’]dithiophene (ITIC), Indaceno[1,2-b:5,6-b′]dithiophene and 2-(3-oxo-2,3-dihydroinden-1-ylidene)malononitrile (IEIC), 9-Bis(2-methylene-((3-(1,1-dicyanomethylene)-6,7-difluoro)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2’,3’-d’]-s-indaceno[1,2-b:5,6-b’]dithiophene (IT-4F), 3,9-bis(2-methylene-((3-(1,1-dicyanomethylene)-6/7-methyl)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2’,3’-d’]-s-indaceno[1,2-b:5,6-b’]dithiophene (IT-M), and 2,2′-((2Z, 2′Z)- ((4,4,9,9-tetrahexyl-4,9-dihydro-s-indaceno[1,2b:5,6-b′] dithiophene-2,7-diyl)bis(methanylylidene))bis(3-oxo2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (IDIC).

5. Organic Synthesis



Scheme S1. Synthetic routes of precursors **3** and **6**

The intermediates **1**, **2** and **3** were synthesized according to the method reported and compared their ^{1}H NMR data with that provided in the literature (**Scheme S1**).[1]

Synthesis of 4-Ethynyl-2,5-bis(hexyloxy)benzaldehyde:

A mixture of 4-Bromo-2,5-bis(hexyloxy)benzaldehyde (7.706 g, 20.00 mmol), CuI (0.052 g, 0.28 mmol), and $Pd(PPh_3)_2Cl_2$ (0.475 g, 0.68 mmol) were combined in a reaction flask, then toluene (200 mL) and diisopropylamine (60 mL) were added under a nitrogen atmosphere. A solution of trimethysilyl acetylene (4.32 g, 6.22 mL, 44.0 mmol) in diisopropylamine (30 mL) was slowly added to the reaction mixture at room temperature. The reaction mixture was then stirred at 70 °C for 6 h to give a brown suspension. The solvent was then removed under reduced pressure, and purified by column chromatography on silica gel, using hexane and DCM mixture (1:1) as eluent to give 2,5-bis(hexyloxy)-4-(2-(trimethylsilyl)ethynyl)benzaldehyde (7.36 g, 92%) as a light yellow solid. Further, the aqueous KOH solution (15.0 mL, 20.0%) was diluted with methanol (50 mL) and added to a stirred solution of trimethylsilyl protected aldehyde (7.01 g, 12.0 mmol) in THF (100 mL) under a nitrogen atmosphere. The mixture was stirred at room temperature for 1 h and extracted with dichloromethane several times. The organic fraction was washed with water and dried over anhydrous $MgSO_4$. The crude product (5.28 g, 80%) was isolated as a pale-yellow solid.

^{1}H NMR (400.00 MHz, $CDCl_3$) δ 0.76-0.77 (t, J = 7.6Hz, 6H, CH_3), 1.20-1.30 (m, 8H), 1.3-1.5 (m, 4H), 1.65-1.80 (m, 4H), 3.08 (s, 1H, C≡CH), 4.01 (t, J = 6.3Hz, 2H), 4.02 (t, J = 6.3Hz, 2H), 7.22 (s, 1H), 7.30 (s, 1H), 10.41 (s, 1H) ppm.

Synthesis of compound 4

A solution of dipyrromethane (3 g, 21 mmol) and 2-octyldodecanal (21 mmol) in CH_2Cl_2 (1.5 L) was kept under nitrogen bubbling for 30 min. Then trifluoroacetic acid (TFA, 145 μL, 2.0 mmol) was added after the solution was stirred overnight at room temperature under nitrogen, then 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (7.28 g, 32 mmol) was added in one portion, and the reaction mixture was stirred for another 2h. Finally, the reaction was quenched by triethylamine (5 mL). The solvent was evaporated and the crude product was purified by silica chromatography using CH_2Cl_2/hexane (1:4) as the eluent, to give a purple product of the compound **4**, yield 5.5g, 30%.

^{1}H NMR (400.00 MHz, $CDCl_3$) δ 2.46 (s, 2H), 0.71-0.76 (m, 28H), 0.87-1.02 (m, 49H), 1.53 (m, 16H), 2.72-2.74 (m, 4H), 2.93-2.96 (m, 4H), 5.13 (m, 2H), 9.39-9.40 (m, J = 8.5 Hz, 4H), 9.64-9.73 (m, J = 8.5 Hz, 4H), 10.21 (m, 2H) ppm.

Synthesis of compound 5:

A solution of compound **4** (1.00 mmol) and NBS (373 mg, 2.10 mmol) in CH_2Cl_2 (200 mL) were stirred at 0°C for 30 min and continued the reaction under room temperature for overnight. The solvent was removed under reduced pressure. The residue was purified via chromatography on silica gel using CH_2Cl_2/hexane (1:4) as the eluent. Then, corresponding free-base porphyrin (1.00 mmol) and zinc acetate (1.095 g, 5 mmol) was refluxed in $CHCl_3$

(200 mL) for 4 h. The solvent was removed and the residue was purified via chromatography on silica gel using CH_2Cl_2/hexane (1:4) as the eluent to give a dark purple product of the compound **5**, yield 0.9 g, 76%.

^{1}H NMR (400.00 MHz, $CDCl_3$) δ 0.72 (m, *J* = 7.2 Hz,12H), 0.76–1.03 (m, 55H), 1.48–1.50 (m, *J* = 7.8 Hz, 4H), 2.69 (m, 4H), 2.89 (m, 4H), 5.14-5.18 (m, 2H), 9.66-9.76 (m, 8H) ppm; ^{13}C NMR ($CDCl_3$, 100.00 MHz) δ 14.01, 14.06, 22.53, 29.20, 29.47, 29.78, 29.93, 31.74, 31.81, 42.61, 47.18, 104.54, 122.06, 126.22, 130.77, 131.61, 131.82, 132.91, 133.25, 147.51, 147.76, 149.49, 149.75, 150.22, 150.27, 152.49, 152.56 ppm.

Synthesis of compound 6:

A mixture of compound **5** (1.0 mmol) and 4-ethynyl-2,5-bis(hexyloxy)benzaldehyde (350.7 mg, 0.950 mmol, ~0.9eq) in THF (40 mL) and Et_3N (20 ml) were taken in 100 ml RBF and degassed with nitrogen for 10 min, and then $Pd(PPh_3)_4$ (70 mg, 0.053 mmol) and CuI (10 mg, 0.053 mmol) were added to the mixture and stirred at 50^{o}C for 12 h under nitrogen. The solvent was removed under vacuum, and the solid residue was purified by preparative thin-layer chromatography using a $CHCl_3$/hexane (3:1) mixture as eluent to give a compound **6**, yield 0.35 g, 43%.

^{1}H NMR (400.00 MHz, $CDCl_3$) δ 0.70-1.57 (m, 84H), 1.59-1.96 (m, 38H), 1.96-2.03 (m, 5H), 2.73-2.76 (m, 2H), 2.77-2.91 (m, 8H), 4.25-4.34 (m, 4H), 5.22-5.35 (m, 2H), 7.44-7.5 (m, *J* = 3.2 Hz, 2H), 9.63-9.71 (m, *J* = 8.8 Hz, 6H), 9.72-9.90 (m, *J* = 8.8 Hz, 2H), 10.51 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100.00 MHz) δ 14.15, 22.72, 22.75, 25.85, 26.14, 29.21, 29.21, 29.71, 30.01, 30.06, 31.67, 31.78, 42.48, 42.54, 42.77, 47.19, 47.27, 106.32, 108.91, 116.02, 116.32, 120.71, 124.25, 125.09, 126.71, 126.90, 130.06, 130.24, 130.34, 130.74, 130.89, 131.21, 131.42, 132.87, 133.21, 135.27, 146.86, 147.11, 148.82, 149.51, 150.51, 151.76, 152.28, 152.62, 152.84,153.57, 153.69, 153.78, 155.30, 155.40 ppm.

Synthesis of compound 8:

A mixture of compound **6** (100 mg, 0.076 mmol) and compound **3** (25 mg, 0.036 mmol) in THF (15 mL) and Et_3N (5 ml) was degassed with nitrogen for 10 min, and then $Pd(PPh_3)_4$ (25 mg) and CuI (5 mg) were added to the mixture, and the solution was refluxed for 12 h under nitrogen. The solvent was removed under vacuum, and the solid residue was purified by preparative thin-layer chromatography using a $CHCl_3$/hexane (3:1) mixture as eluents.

Recrystallization from $CHCl_3$/methanol. Dark green solid: yield 0.15g, 64%.

Synthesis of compound 9:

A mixture of **6** (100 mg, 0.076 mmol) and **7** (25 mg, 0.036 mmol) in freshly distilled Toluene (30 ml) was degassed with nitrogen for 20 min and $Pd(PPh_3)_4$ (25 mg, 0.005 mmol) was added and the solution was refluxed for 24 h under nitrogen. The solvent was removed under vacuum, and the solid residue was purified by preparative thin-layer chromatography using a $CHCl_3$/hexane (3:1) mixture as eluents. Recrystallization from $CHCl_3$/methanol (1:3) gave **9** as dark green solid (0.18 g, 60%). The compound **9** does not show high-resolution ^1H NMR spectra due to the large π-extended structure but it was further confirmed by MALDI-TOF. The molecular formula of compound **9**: $C_{196}H_{284}N_{10}O_8S_2Zn_2$, the calculated m/z: 3102.0184, found: 3102.8480.

Synthesis of final products ETDPP-2P and **TDPP-2P**

The key precursor aldehyde **8** or **9** (110 mg, 0.034 mmol) was taken in a dried 100 mL RBF and kept under vacuum for 5 mins, filled with nitrogen atmosphere. Then 30 mL of dry $CHCl_3$ was added, 3-ethylrhodanine (70 mg, 0.34 mmol) and two drops of piperdine were added to the mixture. And allowed to stir about 24 h under ambient temperature. The reaction was completed and quenched with 50 mL of water. The organic layer was separated and extracted with $CHCl_3$, dried over $NaSO_4$. The solvent was removed by rotavapor and the residue was purified by column and preparative thin-layer chromatography as $CHCl_3$ and hexane (1:10) eluent. Finally, the two target products were recrystallized from a mixture of $CHCl_3$ and methanol to afford ETDPP-2P (90 mg, 80%) and TDPP-2P (70 mg, 72%) as a gray-green solid. MALDI-TOF, m/z, $[M]^+$, ETDPP-2P: $C_{210}H_{294}N_{12}O_8S_6Zn_2$, calculated 3435.9911, found: 3435.8898; TDPP-2P: $C_{206}H_{294}N_{12}O_8S_6Zn_2$, calculated 3387.9911, found: 3387.5439.

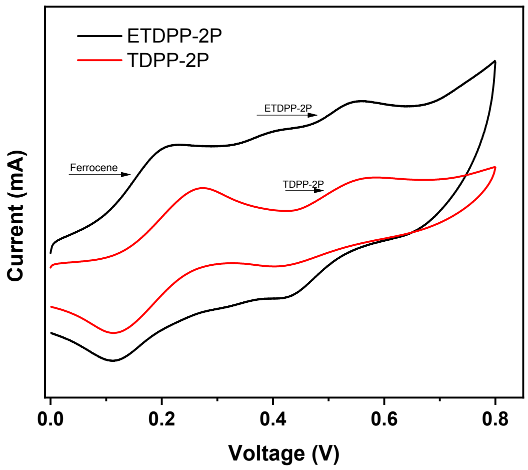


Figure S1. Cyclic voltammogram of ETDPP-2P and TDPP-2P measured in 0.1 mol L^{-1} $TBAPF_6$ in $CHCl_3$ solutions.

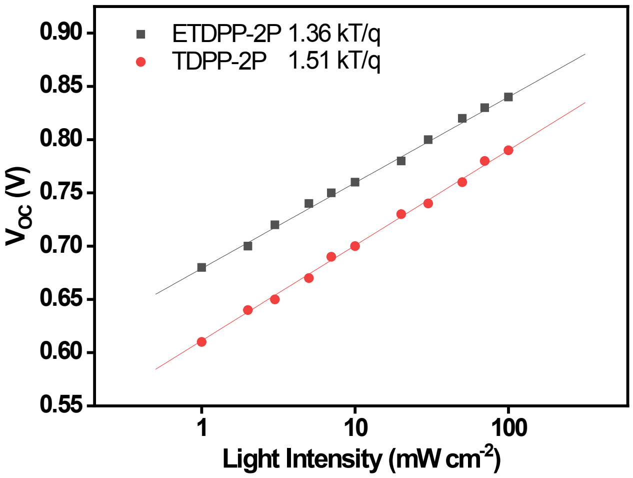


Figure S2. *V*oc versus light intensity plots of ETDPP-2P and TDPP-2P devices.

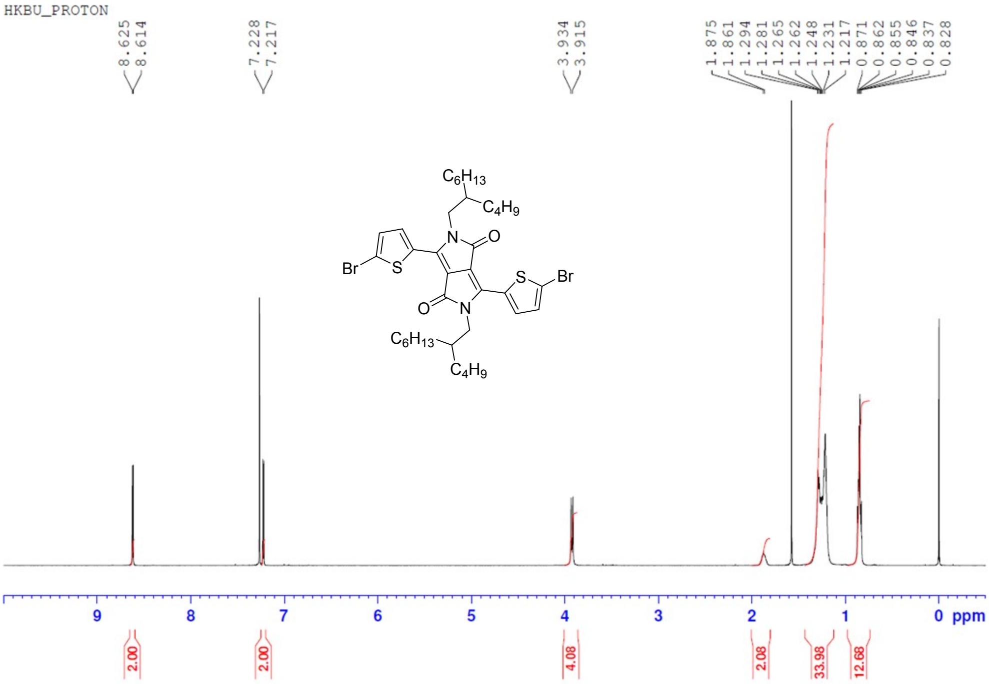


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1**.

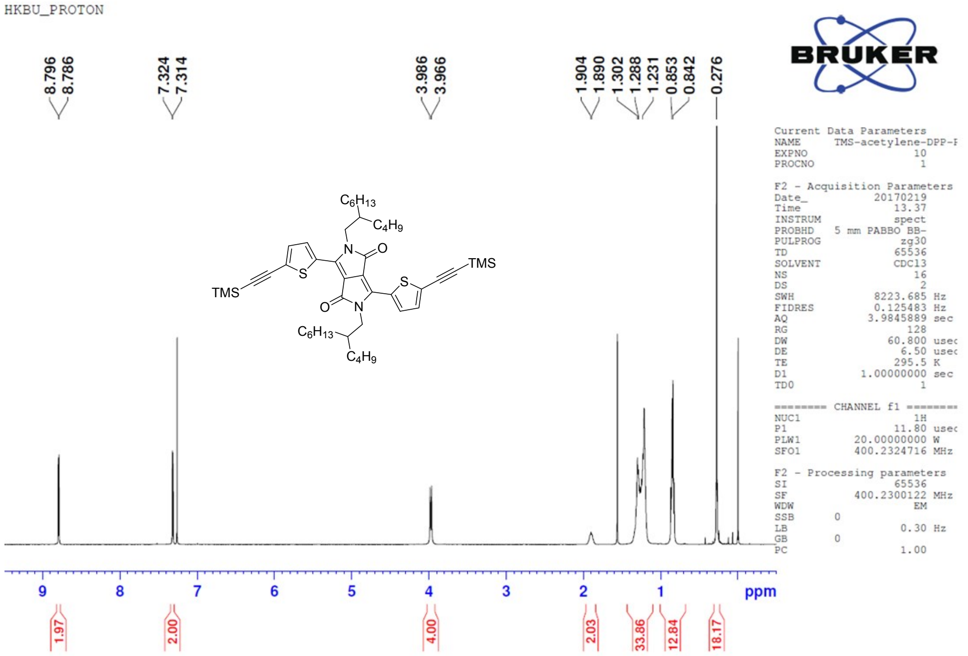


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Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2**.

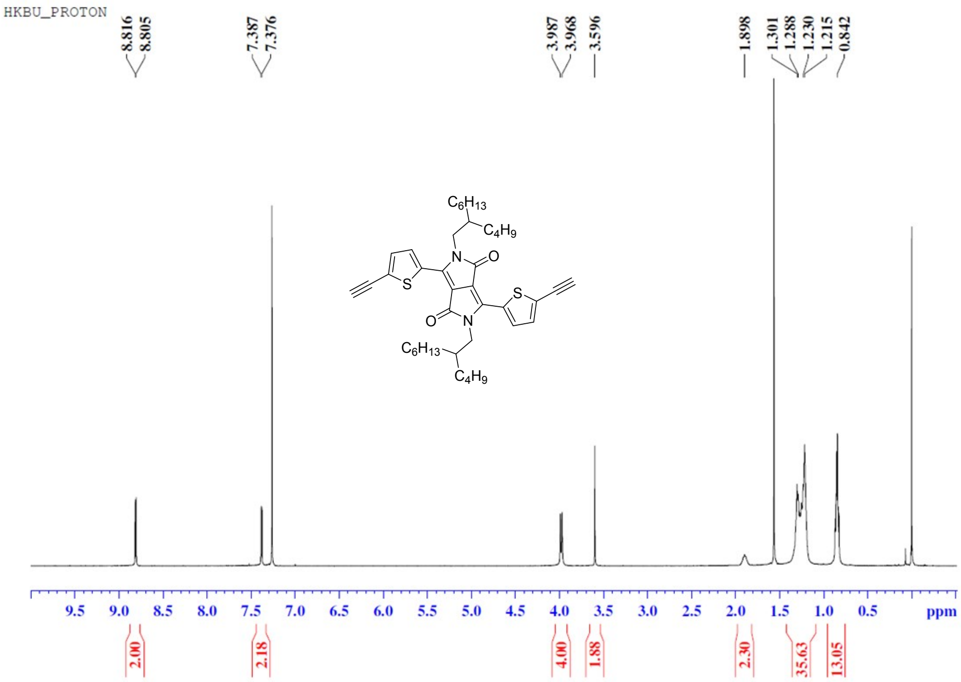

Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3**.

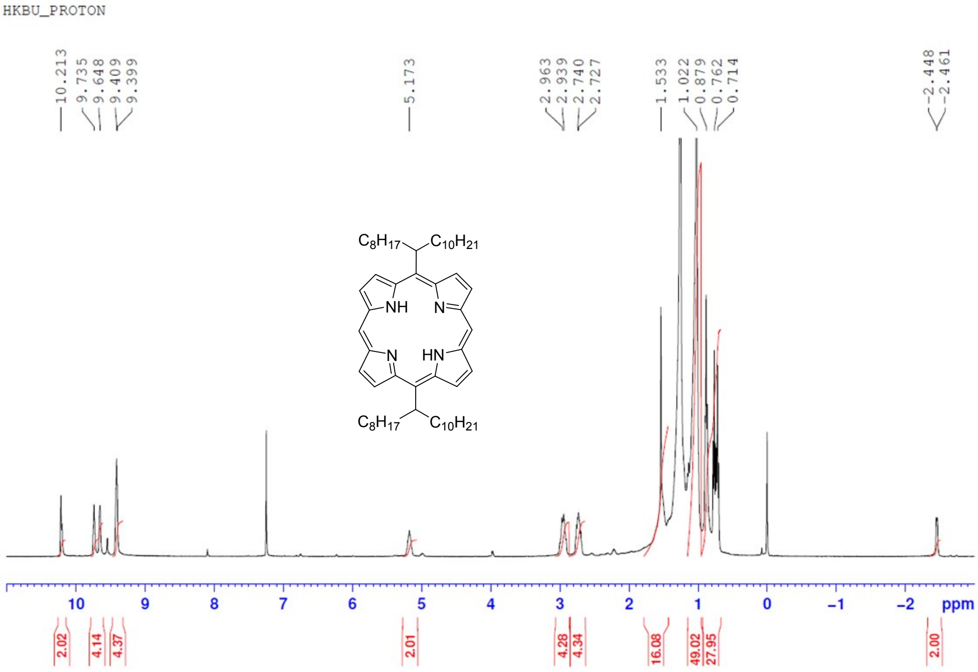

Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4**.

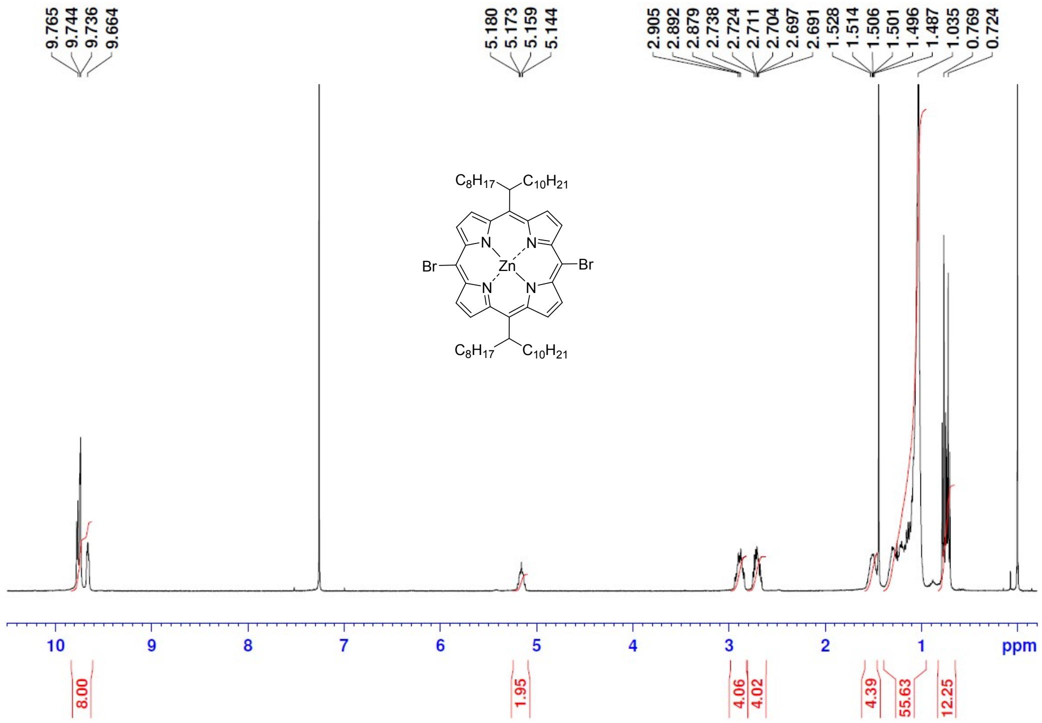

Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5**.

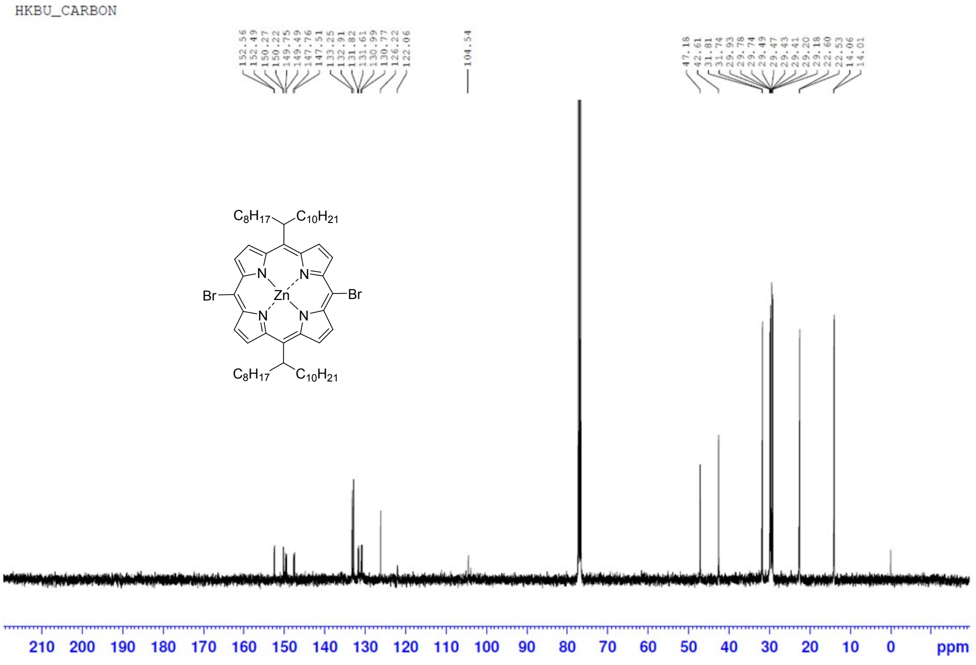

Figure S8. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5**

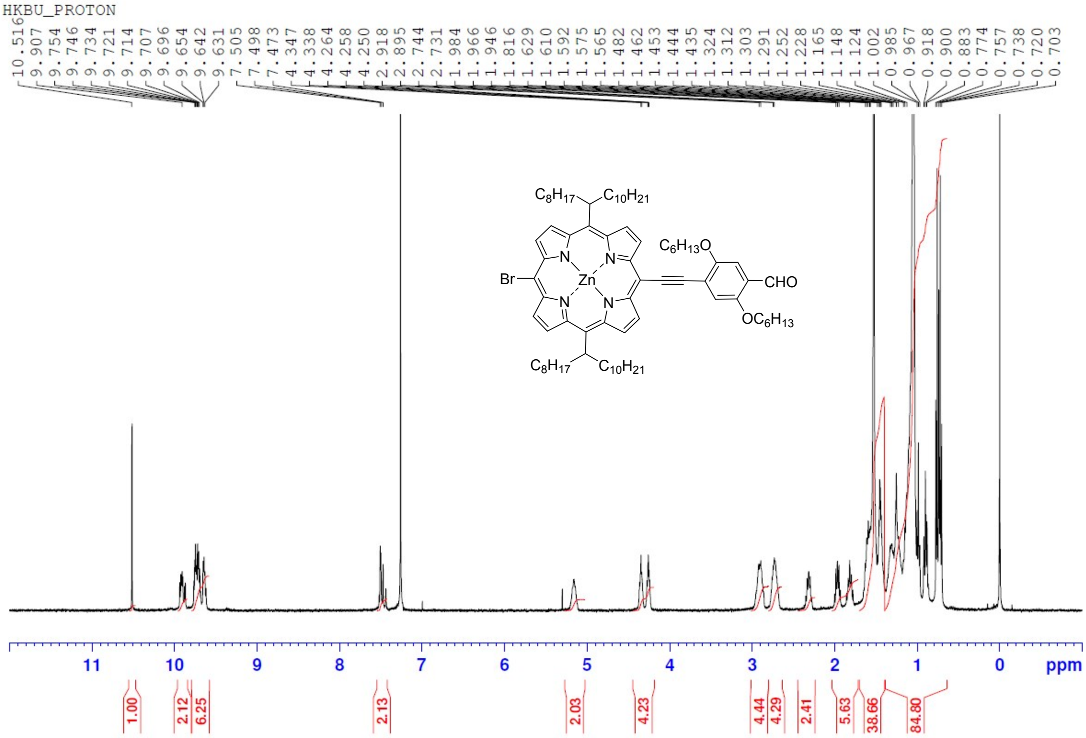

Figure S9. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **6**.

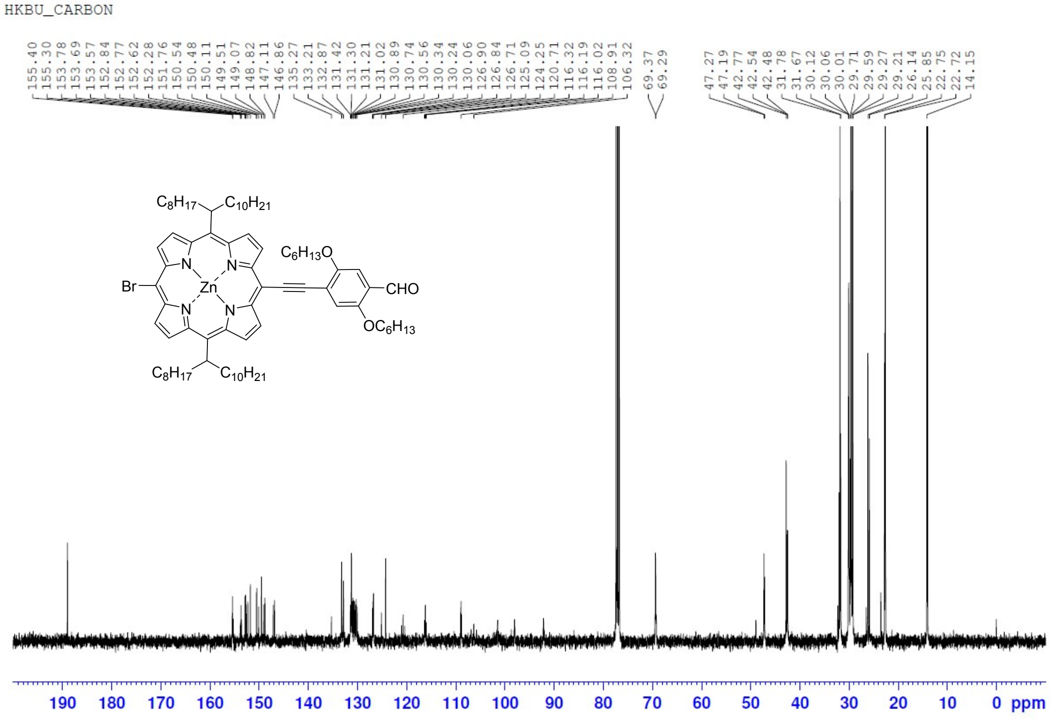

Figure S10. ^{13}C NMR (100 MHz, CDCl$_3$) spectrum of **6**

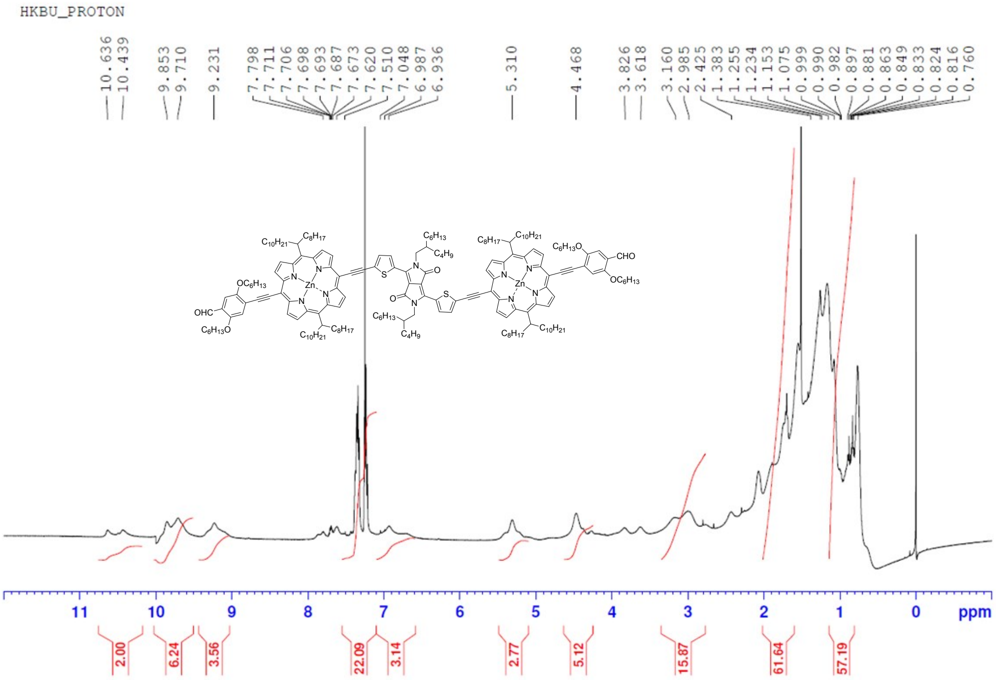

Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8**.

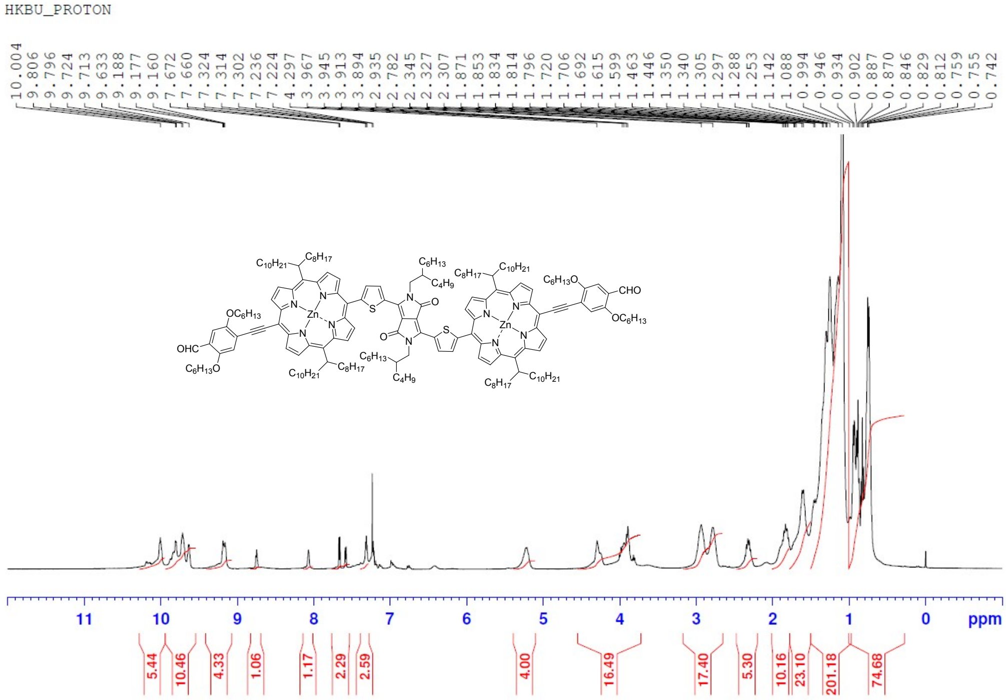

Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **9**

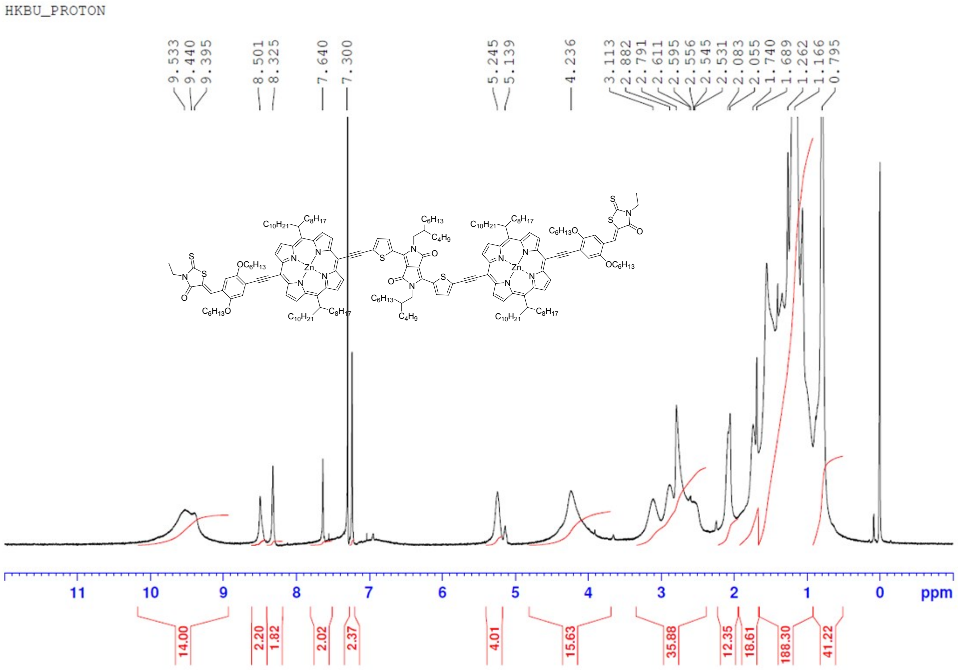

Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **ETDPP-2P**

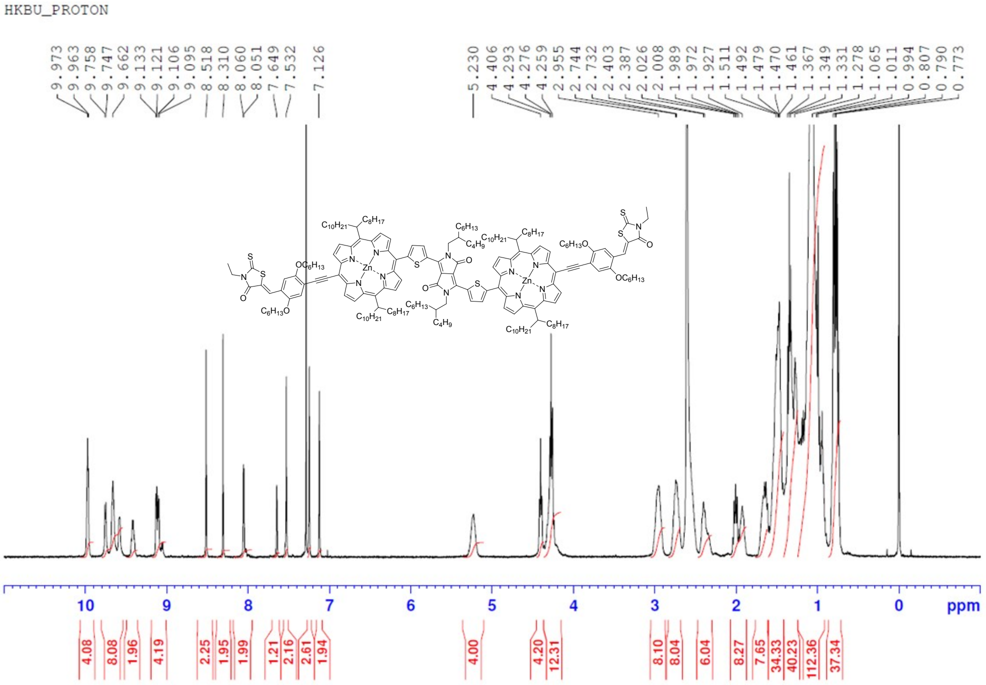

Figure S14. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **TDPP-2P**.

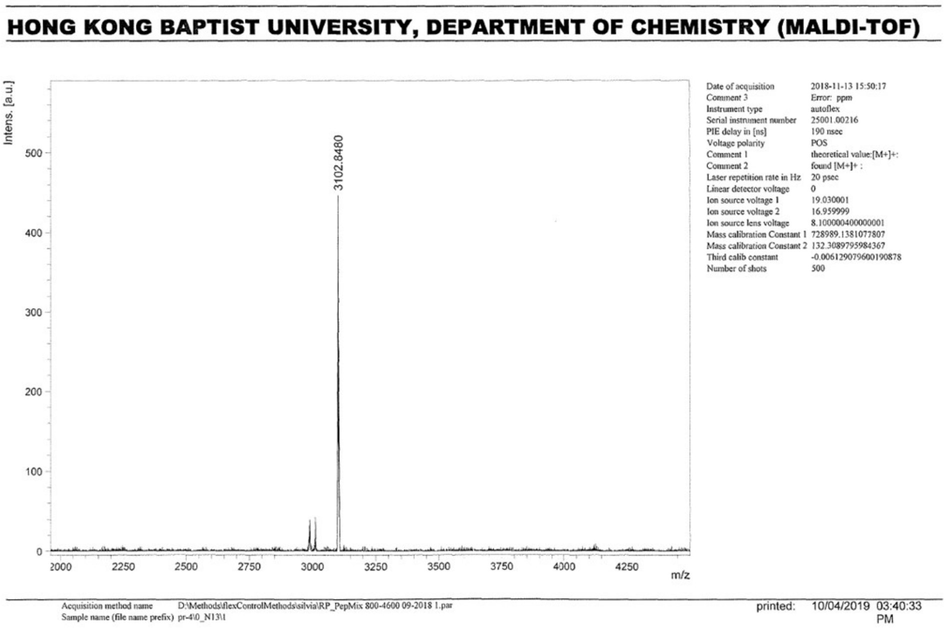

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Figure S15. MALDI-TOF of compound **9**.

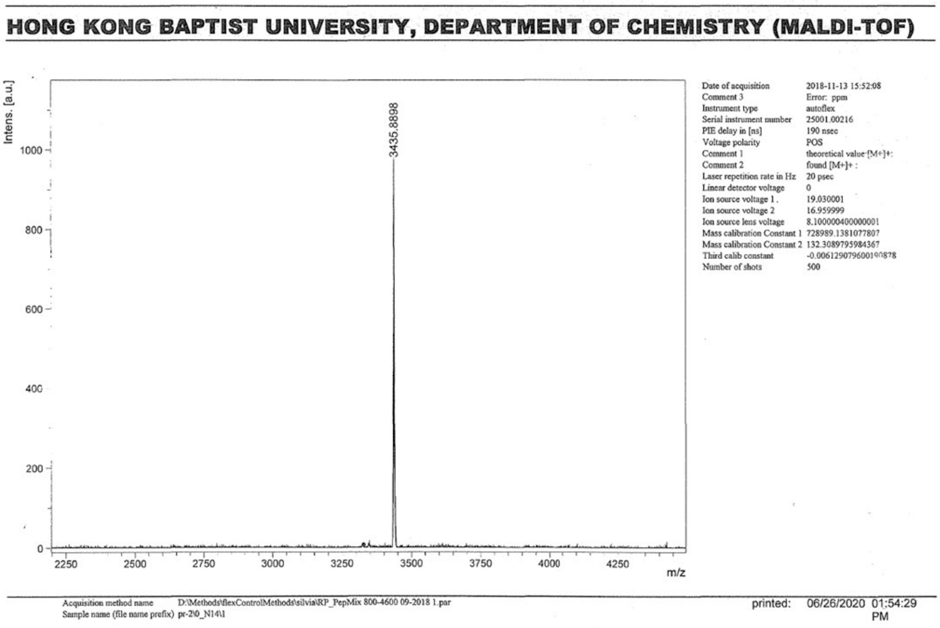

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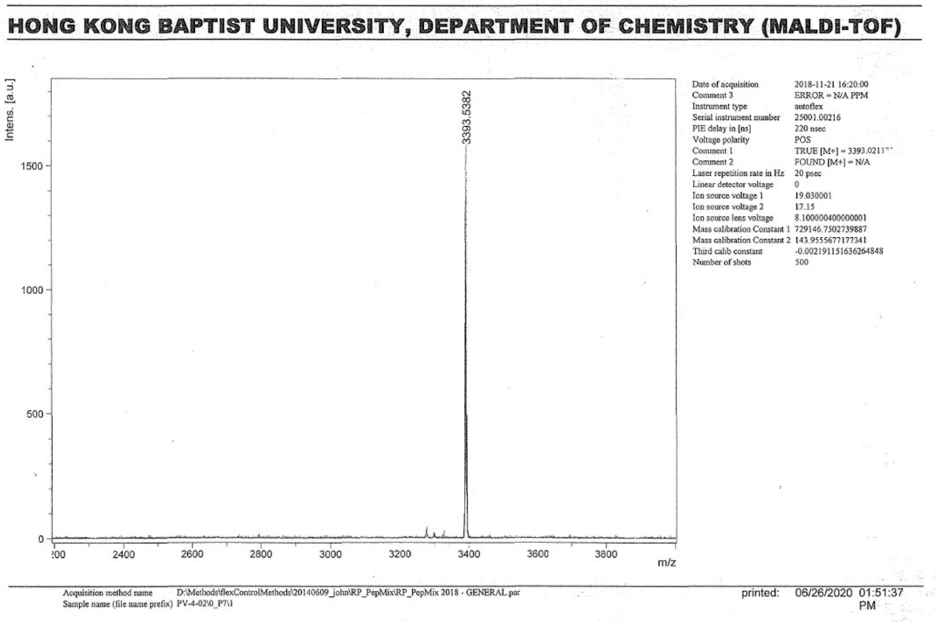
Figure S16. MALDI-TOF of compound **ETDPP-2P**.



HONG KONG BAPTIST UNIVERSITY, DEPARTMENT OF CHEMISTRY (MALDI-TOF)

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Figure S17. MALDI-TOF of compound **TDPP-2P**.

References

1. V. Piradi, X. Xu, Z. Wang, J. Ali, Q. Peng, F. Liu and X. Zhu, *ACS applied materials & interfaces*, 2019.