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Thiophene bridged naphthalimide-porphyrin complex with enhanced activity and stability in photocatalytic H_2 evolution

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Materials and Methods

All the chemicals used in this work were purchased from commercial sources and used as received. Solvents were dried by distilling over suitable dehydrating agents according to standard procedures. Purification of the compounds was performed by column chromatography with 100-200 mesh silica. ^{1}H and ^{13}C NMR spectra 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 Autoflex MALDI-TOF mass spectrometer. The optical absorption and emission spectra of the porphyrins were measured for the freshly prepared air equilibrated solutions at room temperature by using UV-Vis spectrophotometer and spectrofluorimeter, respectively. Cyclic voltammetry (CV) was recorded on an electrochemical workstation in THF 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 auxiliary electrode, a non-aqueous Ag/$AgNO_3$ reference electrode, ferrocene as internal standard and a glassy carbon working electrode.

Preparation of photocatalytic systems. A multichannel photochemical reaction system fixed with OLED white light (PCX50B, 148.5 mW/cm^2) was used as the light source. The photocatalytic hydrogen (H_2) evolution experiments were performed in a quartz vial reactor (20 mL) sealed with a rubber septum, gas-closed system, at ambient temperature and pressure Initially, the prepared sample powder (0.1 mM) was suspended in aqueous triethanolamine (TEOA) solution (Water: TEOA= 9 : 1 v/v) under constant stirring. Then, 3 wt.% of Pt as co-catalyst was loaded by in situ photoreduction deposition method, H_2PtCl_6 aqueous as Pt source. The suspension was purged with nitrogen gas for 30 min to ensure anaerobic conditions and then it was placed at the position of 15 cm away from lamp. After 1h irradiation, the released gas (400 μL) was collected by syringe from the headspace of the reactor and was analyzed by gas chromatography (Shimadzu, GC-2014, Japan, with ultrapure Ar as a carrier gas) equipped with a TDX-01(5 Å molecular sieve column) and a thermal conductivity detector (TCD). Eventually, the total content of photocatalytic H_2 evolution was calculated according to the standard curve. Continuous stirring was applied to the whole process to keep the photocatalyst particles in suspension state and get the uniform irradiation. The stability of the photocatalytic systems were investigated by measuring the ηH_2 over 50 hours. The turnover number (TON) was calculated at palateau by using the following formula:

$$\text{TON} = \frac{Number\ of\ moles\ of\ hydrogen\ produced\ in\ phtocatalytic\ system}{Number\ of\ moles\ of\ photcatalyst}$$

Photoelectrochemical Measurement.

The photoelectrochemical tests were performed according to our previous report.[1]

Fluorescence quantum yields (Φ_F). The Φ_F of the porphyrins in degassed THF solution were calculated by comparing with that of 5,10,15,20-tetraphenylporphyrin (**TPP**). **TPP** was used as fluorescence standard (λ_{exc} = 552 nm) with Φ_F = 0.12 in degassed toluene. The absorbance of the sample and reference solutions was measured by keeping at 0.1 and the emission of the sample and reference solutions was recorded at 552 nm excitation wavelength. The Φ_F was calculated according to the following equation.

$$\Phi_F^{sample} = \Phi_F^{ref}\left(\frac{S_{sample}}{S_{ref}}\right)\left(\frac{A_{ref}}{A_{sample}}\right)\left(\frac{n_{sample_2}}{n_{ref}^{2}}\right)$$

Where A_{ref}, S_{ref}, n_{ref}, *and* A_{sample}, S_{sample}, n_{sample} represent the absorbance at the excited wavelength, integrated area under the fluorescence curves and the solvent refractive index of the standard and the sample solutions.

Theoretical calculations

In order to further understand the effect of linkage on electronic structure of naphthalimide conjugated-porphyrins, we have performed density functional theoretical (DFT) calculations using Gaussian 09W program. The ground state geometry of the porphyrins (ethylhexyl groups were replaced with methyl unit) was optimized at the B3LYP/Genecp/ /LANL2DZ level. The computed frontier molecular orbitals, vertical excitation energies and their oscillator strengths, and orbital contribution are shown in Fig. S1.

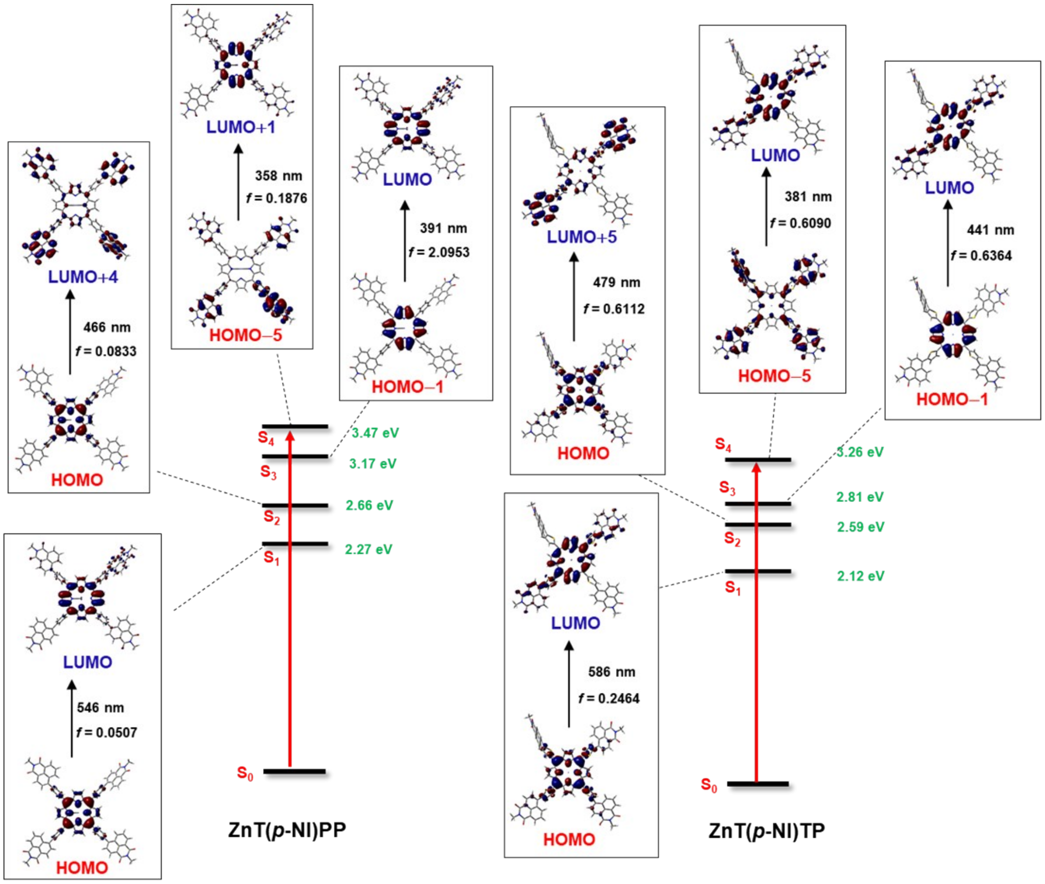
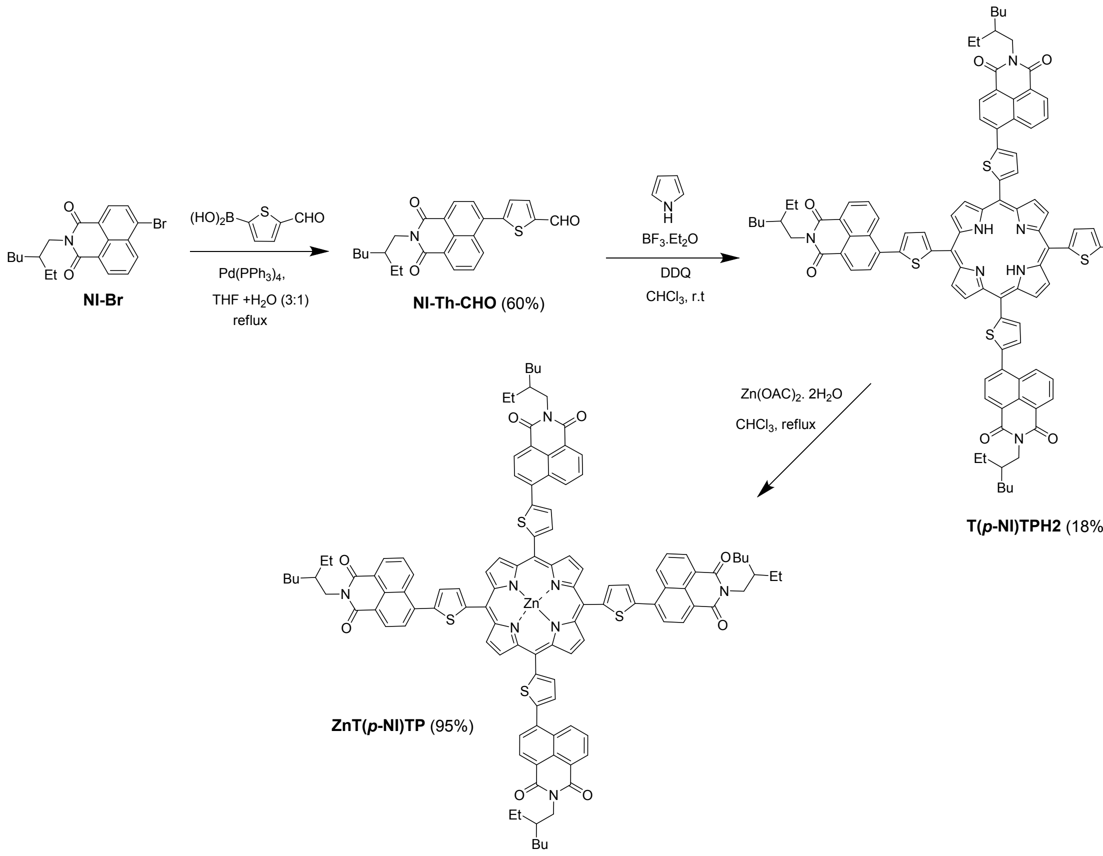


Figure S1. Jablonski energy diagram of the porphyrins based on the computation at B3LYP/GENECP/LANL2DZ level. Alkyl chains are simplified as methyl groups.

Synthesis

The NI-Br derivative and porphyrin, **ZnT(*p*-NI)PP** were synthesized and characterized according to our previous report.[1] Porphyrin **ZnTTP** was synthesized according to the procedure described in literature.[2]



Scheme S1 Synthesis of NI-conjugated porphyrin with thiophene linkage, **ZnT(*p*-NI)TP**.

NI-Th-CHO:

In a 100 mL two-neck round-bottom flask, **1** (1.0 g, 2.58 mmol), 5-formyl-2-thienylboronic acid (0.5 g, 3.1 mmol), potassium carbonate (1.1 g, 7.7 mmol) and 40 mL THF/H_2O (3:1, v/v) were taken and purged with nitrogen. After addition of $Pd(PPh_3)_4$ (150 mg, 2 mol %) the reaction mixture was refluxed for 12 h. After completion of reaction, it was diluted with dichloromethane and water. The organic layer was separated, dried over Na_2SO_4 and solvent removed under reduced pressure. The resulted crude reaction mixture containing product was purified by column chromatography with silica using dichloromethane/hexane (1:1, v/v) as eluent. Off-white solid; yield 0.65 g, 60.0%; ^{1}H NMR ($CDCl_3$, 400.00 MHz) δ ^{1}H NMR ($CDCl_3$, 400.00 MHz) δ 0.94-0.95 (m, 6 H), 1.25-1.42 (m, 8 H), 1.92-1.98 (m, 1 H), 4.09-4.19 (m, 2 H), 7.44 (d, J = 3.6

Hz, 1 H), 7.79-7.91 (m, 3 H), 8.52 (d, *J* = 8.4 Hz, 1 H), 8.63-8.68 (m, 2 H), 10.01 (s, 1 H). ^{13}C NMR (CDCl3, 100.00 MHz) δ 10.67, 14.13, 23.07, 24.05, 28.67, 30.73, 37.89, 44.20, 123.06, 123.18, 127.76, 127.81, 127.86, 128.61, 128.85, 129.52, 129.81, 130.06, 130.12, 130.29, 130.42, 130.53, 131.35, 131.57, 134.36, 134.42, 134.48, 136.54, 137.20, 145.01, 149.14, 163.86, 164.13, 182.78.

T(*p*-NI)TPH2:

In a 250 mL two-neck round-bottom flask, **NI-Th-CHO** (0.4 g, 0.96 mmol), pyrrole (80 μL, 1.05 mmol) and chloroform (100 mL) were taken and purged with nitrogen for 20 min. After BF_3-Et_2O (120 μL) was added and the reaction mixture was stirred for 6 h at room temperature under nitrogen and dark. After 2,3-dichloro-5,6- dicyanobenzoquinone (DDQ) (0.48 g, 1.92 mmol) was added, and the reaction mixture was stirred for 30 min. The reaction was quenched by the addition of triethylamine (5 mL). After completion of reaction, the solvent was removed and the resulted crude product was purified by column chromatography with silica using dichloromethane/hexane (1:1, v/v) as eluent. Green color solid: yield 0.32 g, 18.0%. ^{1}H NMR ($CDCl_3$, 400.00 MHz) δ – 2.64 (s, 2 H), 0.88-0.92 (t, *J* = 6.8 Hz, 12 H), 0.94-0.98 (t, *J* = 7.2 Hz, 12 H), 1.33-1.42 (m, 32 H), 1.94-2.00 (m, 4 H), 4.08-4.18 (m, 8 H), 7.80 (d, *J* = 3.6 Hz, 4 H), 7.86 (dd, *J* = 8.4 Hz, 7.2 Hz, 4 H), 8.13-8.16 (m, 8 H), 8.62-8.66 (m, 8 H), 9.03 (dd, *J* = 8.4 Hz, 1.2 Hz, 4 H), 9.34 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100.00 MHz) δ 10.71, 14.14, 23.12, 24.13, 28.77, 30.82, 37.99, 44.28, 112.15, 122.31, 123.16, 125.05, 127.46, 128.21, 128.82, 129.01, 129.88, 130.79, 131.53, 132.07, 134.82, 135.23, 138.41, 143.02, 144.92, 164.23, 164.45.

ZnT(*p*-NI)TP:

A mixture of **T(*p*-NI)TPH2** (0.05 g, 0.03 mmol), $Zn(OAc)_2 \cdot 2H_2O$ (0.06 g, 0.3 mmol) and $CHCl_3$ (20 mL) was refluxed overnight. After completion of the reaction, solvent was removed and the resulted crude product was purified by column chromatography with silica using dichloromethane as eluent. Green color solid: yield 0.05 g, 95.0%. ^{1}H NMR (CDCl$_3$, 400.00 MHz) δ 0.71-0.75 (t, *J* = 7.2 Hz, 12 H), 0.81-0.85 (t, *J* = 7.8 Hz, 12 H), 1.10-1.25 (m, 32 H), 1.53-1.68 (m, 4 H), 3.40-3.45 (m, 8 H), 7.75 (d, *J* = 3.2 Hz, 4 H), 7.80-7.84 (m, 4 H), 8.08-8.21 (m, 16 H), 9.02 (d, *J* = 8.8 Hz, 4 H), 9.36 (s, 1H). ^{13}C NMR (CDCl$_3$, 100.00 MHz) δ 10.70, 14.12, 23.10, 24.12, 28.75, 30.80, 37.98, 44.26, 112.14, 122.27, 123.13, 125.04, 127.43, 128.20, 128.79, 128.97, 129.65, 129.84, 130.76, 131.49, 132.04, 134.81, 135.22, 138.38, 143.01, 144.91, 164.20, 164.42. (MALDI–TOF, m/z) calculated for $C_{116}H_{104}N_8O_8S_4Zn$: 1930.616 found 1930.612.

Table S1. Photophysical and electrochemical data of **ZnT(*p*-NI)TP** and **ZnTTP**, and life time data of **ZnT(*p*-NI)PP.**

Porphyrin	λ_{abs} (εx10^4)[a]	λ_{em}[b]	Φ_F[c] (%)	τ_F[d]	E_{Ox}, V[e] (vs NHE)	E_{red}, V[f] (vs NHE)	E_{0-0} /eV[g]
ZnT(*p*-NI)TP	367 (5.98), 443 (31.44), 569 (2.85), 614 (1.54)	652	19	2.6	1.18, 1.59	– 0.72, – 1.04	2.05
ZnTPP	430 (27.1), 563 (2.01), 610 (0.64)	652	10	1.2	1.26, 1.45, 1.69	– 0.83,	2.14
ZnT(*p*-NI)PP	-	-	-	1.6			

[a] Absorption in THF solution. [b] Emission in THF solution (λ_{ex}= 420 nm). [c] Fluorescence quantum yield. [d] Fluorescence life time. [e] E_{ox} (vs NHE) = 0.77 + E_{ox} (vs Ferrocene). [f] E_{red} (vs NHE) = 0.77 – E_{red} (vs Ferrocene). [g] Estimated from the intersection of the normalized absorption and emission spectra.

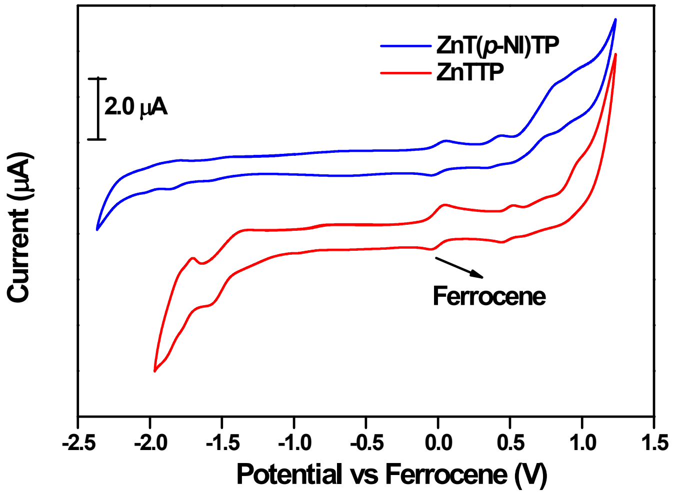


Fig. S2 Cyclic voltammograms of **ZnT(*p*-NI)TP** and **ZnTTP** recorded in THF (100 μM) solution.

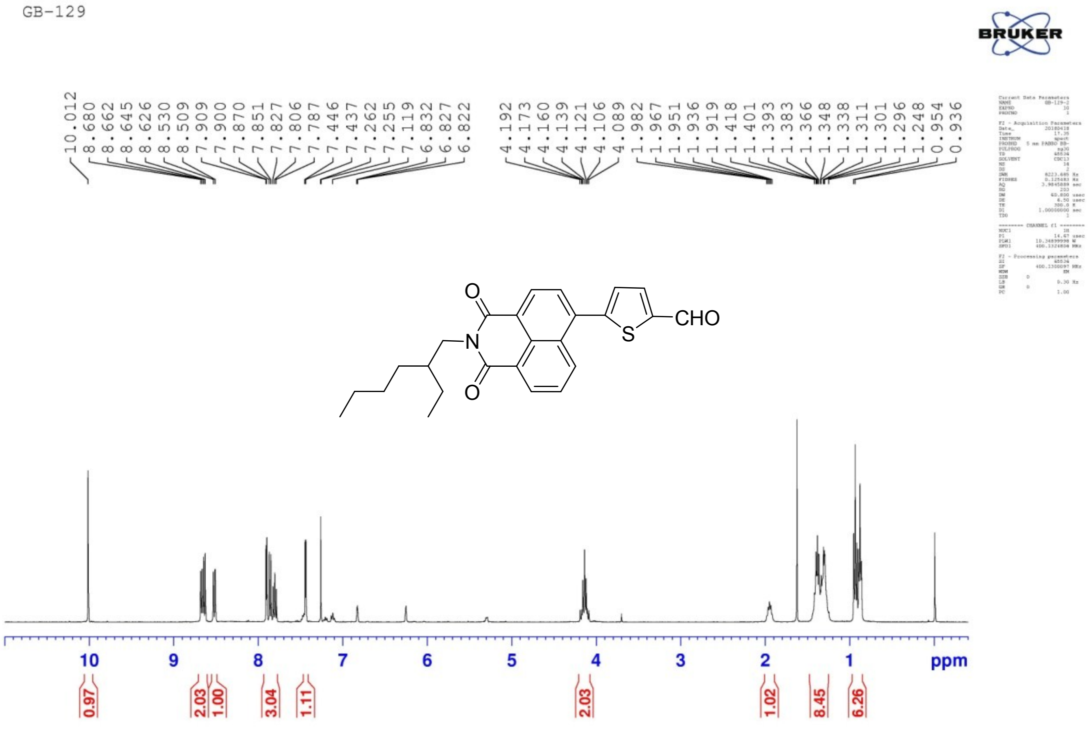


Fig. S3 ^{1}H NMR spectra of **NI-Th-CHO** recorded in $CDCl_3$.

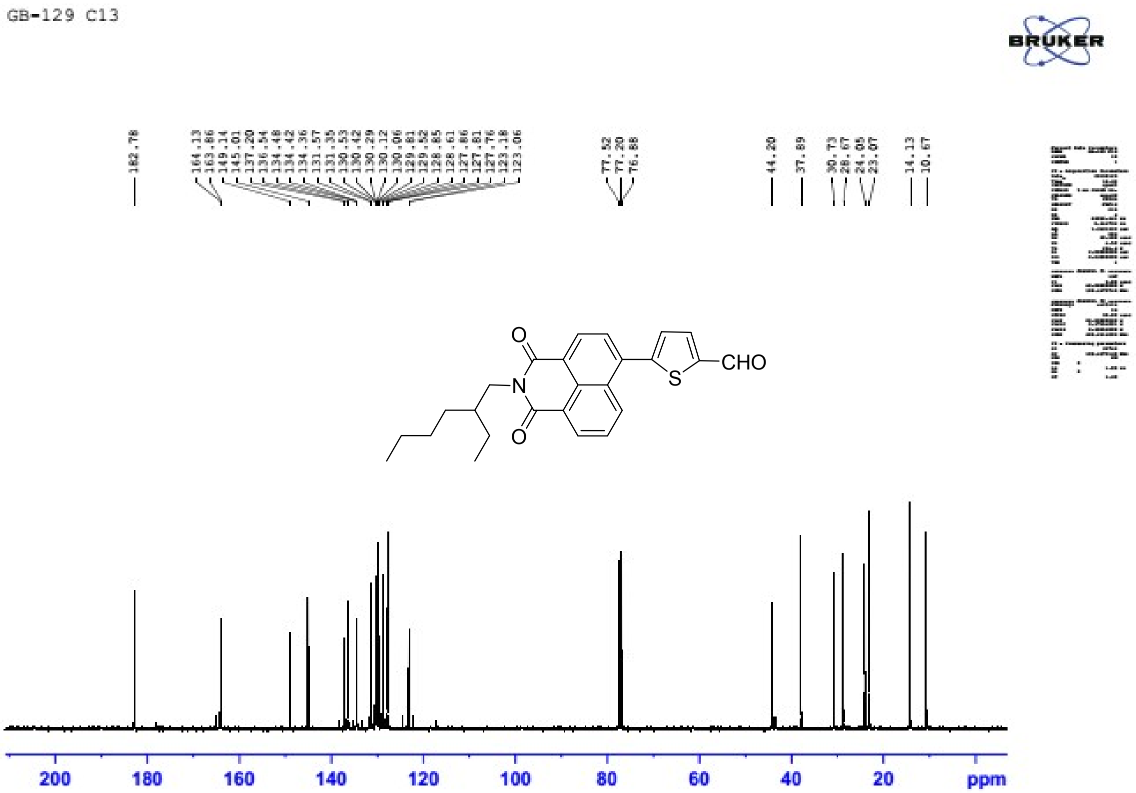


Fig. S4 ^{13}C NMR spectra of **NI-Th-CHO** recorded in CDCl$_3$.

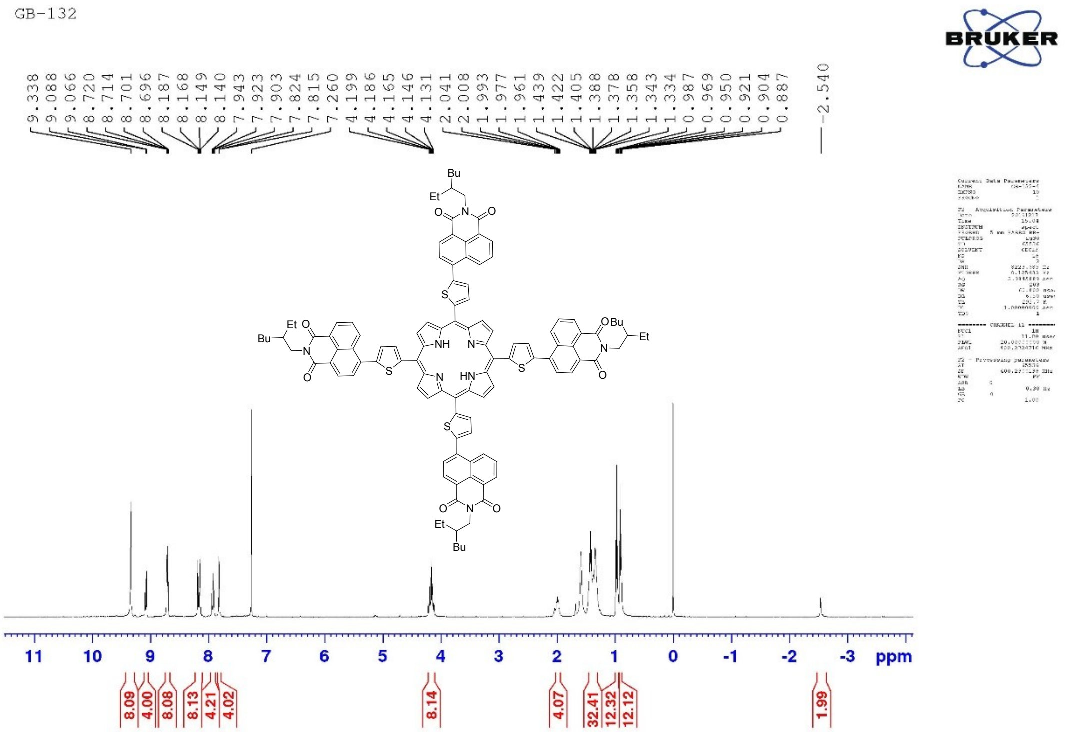


Fig. S5 ^{1}H NMR spectra of **T(*p*-NI)TTH2** recorded in $CDCl_3$

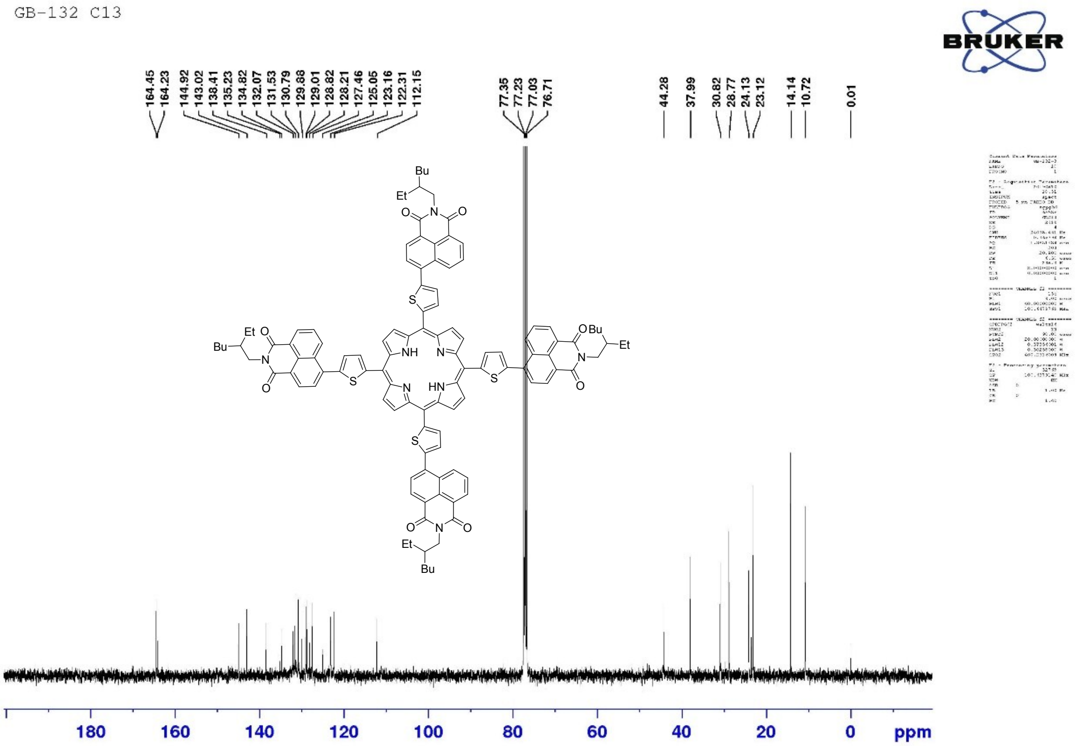


Fig. S6 ^{13}C NMR spectra of **T(*p*-NI)TTH2** recorded in $CDCl_3$.

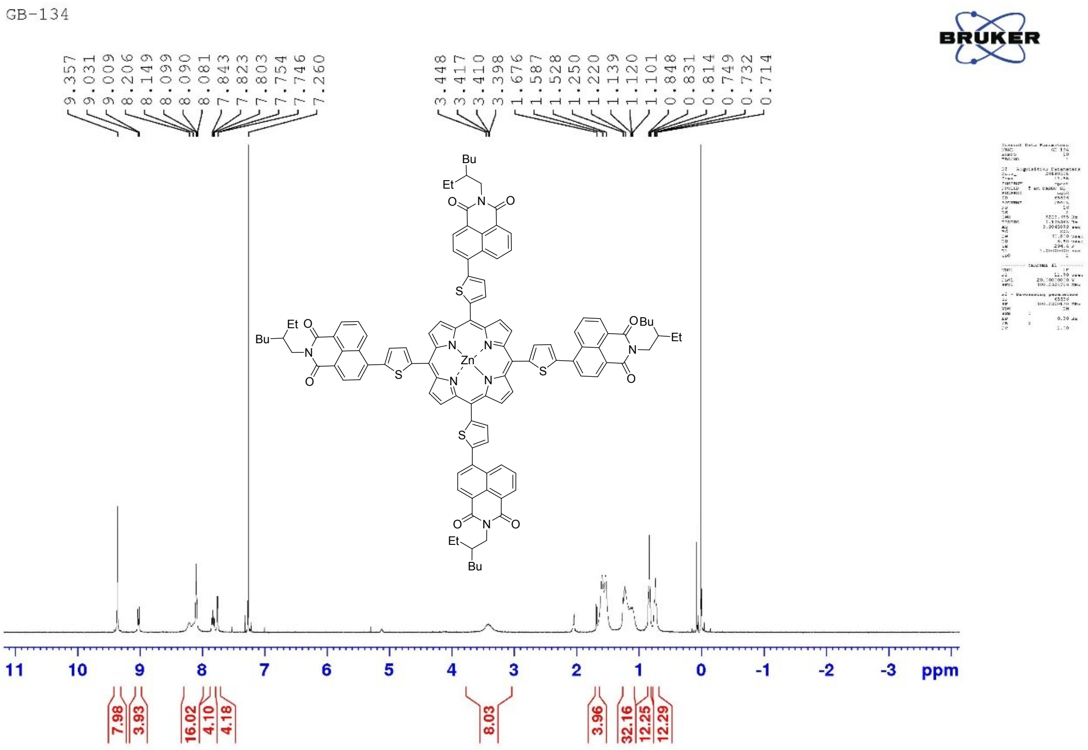


Fig. S7 ^{1}H NMR spectra of **ZnT(*p*-NI)TP** recorded in $CDCl_3$.

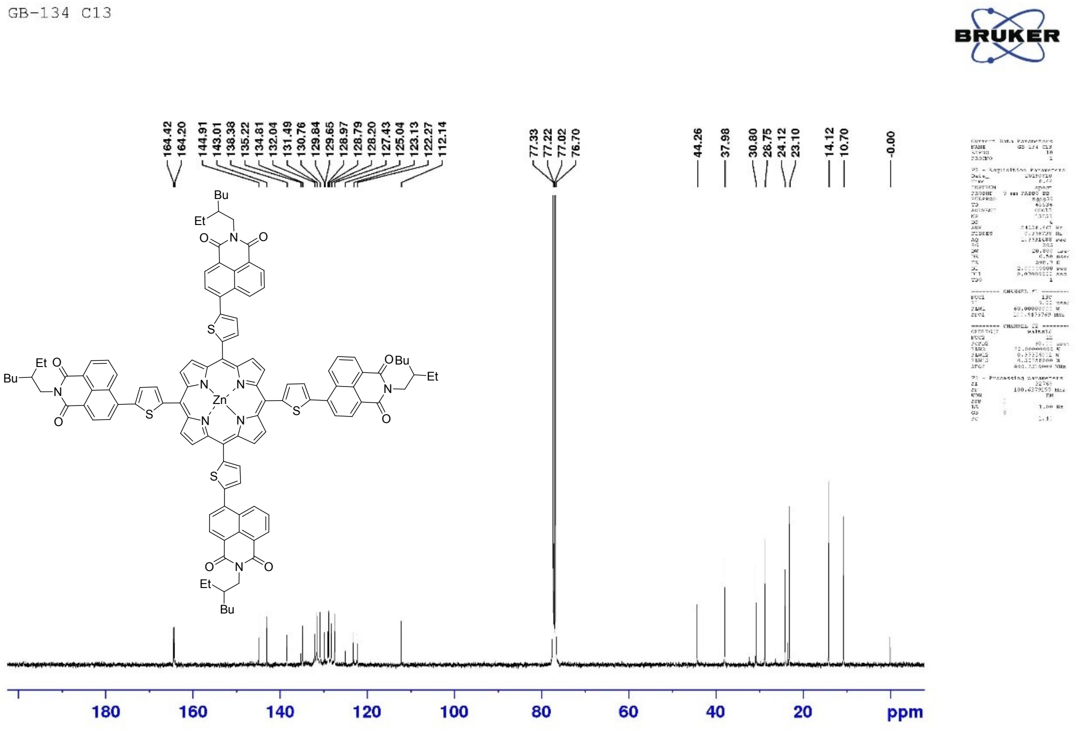
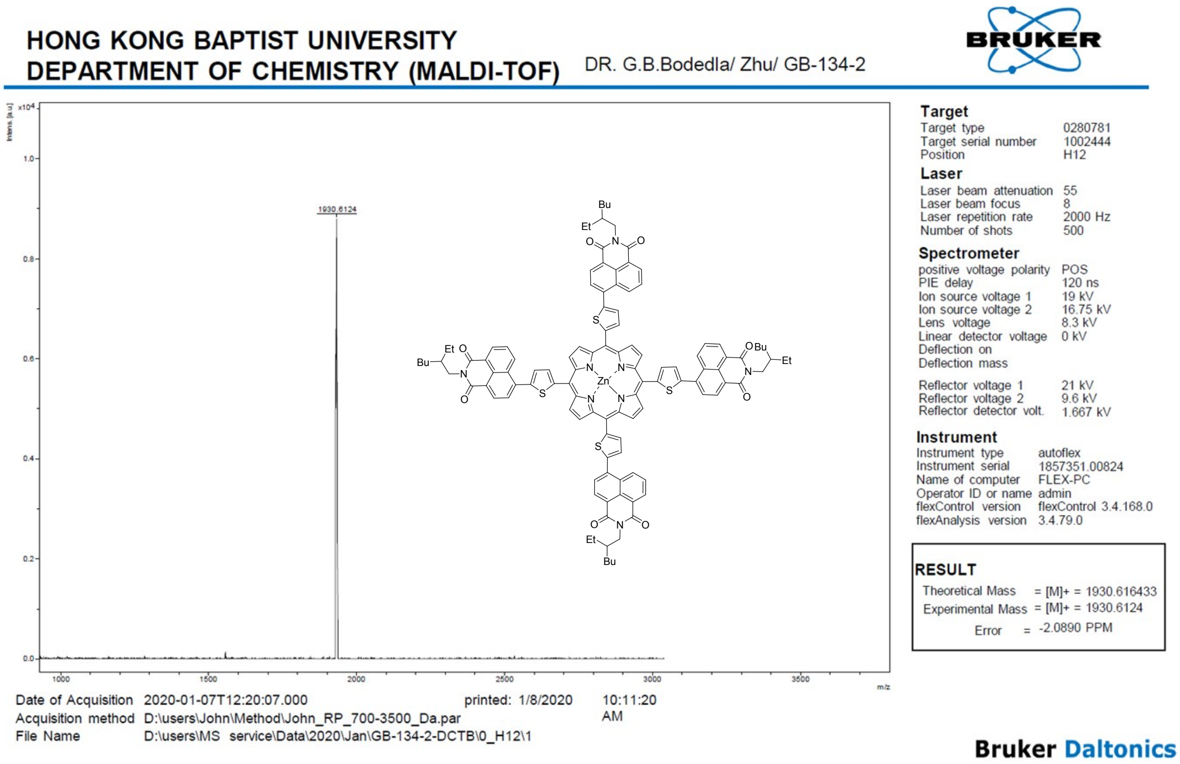


Fig. S8 ^{13}C NMR spectra of **ZnT(*p*-NI)TP** recorded in $CDCl_3$



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Target serial number	1002444
Position	H12

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Laser beam focus	8
Laser repetition rate	2000 Hz
Number of shots	500

Spectrometer

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PIE delay	120 ns
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Ion source voltage 2	16.75 kV
Lens voltage	8.3 kV
Linear detector voltage	0 kV
Deflection on	
Deflection mass	
Reflector voltage 1	21 kV
Reflector voltage 2	9.6 kV
Reflector detector volt.	1.667 kV

Instrument

Instrument type	autoflex
Instrument serial	1857351.00824
Name of computer	FLEX-PC
Operator ID or name	admin
flexControl version	flexControl 3.4.168.0
flexAnalysis version	3.4.79.0

RESULT

Theoretical Mass = [M]+ = 1930.616433
Experimental Mass = [M]+ = 1930.6124
Error = -2.0890 PPM

Fig. S9 MALDI–TOF spectra of **ZnT(*p*-NI)TP**.

References

1. G. B. Bodedla, L. Li, Y. Che, Y. Jiang, J. Huang, J. Zhao and X. Zhu, *Chem. Commun.*, 2018, **54**, 11614-11617.
2. Y. Zhou, F. Liu, H. Wu, B. Qu and L. Duan, *Asian J. Chem.,* 2015, **27**, 616-620.