

Supporting information

Syntheses and Characterization of A₂BC Type Phthalocyanine and Its Visible-Light-Responsive Photocatalytic H₂ Production Performance on Graphitic Carbon Nitride

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Table of content

Fig. S1. UV-vis absorption spectra of Zn-*di*-PcNcTh in THF at different concentration.

Fig. S2. UV-vis absorption and Fluorescence emission spectra of Zn-*di*-PcNcTh in DCM solution with excitation fixed at 666 nm.

Fig. S3. Absorption wavelengths and oscillator strengths obtained by TDDFT calculations on the low-symmetry, metal-free H₂-*di(adj)*-PcNcTh and H₂-*di(opp)*-PcNcTh.

Fig. S4. UV-vis absorption spectra of H₂-*di(opp)*-PcNcTh and H₂-*di(adj)*-PcNcTh in DCM.

Fig. S5. Energy levels (in eV) of the frontier orbitals for the low-symmetry, metal-free H₂-*di(adj)*-PcNcTh and H₂-*di(opp)*-PcNcTh obtained by DFT calculations at B3LYP/6-31G(D) level.

Fig. S6. MALDI-TOF mass spectrum of Zn-*di*-PcNcTh.

Fig. S7. IR spectra of Zn-*di*-PcNcTh.

Fig. S8. Fourier transform infrared (FTIR) spectra of g-C₃N₄, Zn-*di*-PcNcTh and Zn-*di*-PcNcTh /g-C₃N₄.

Fig. S9. Typical cyclic voltammogram of Zn-*di*-PcNcTh in DCM containing 0.1 M [NBu₄][ClO₄] at a scan rate of 20 mV·S⁻¹.

Fig. S10. Photoluminescence (PL) spectra of Zn-*di*-PcNcTh solution and Zn-*di*-PcNcTh /g-C₃N₄ film.

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Fig. S11. Transient photocurrent curves of g-C₃N₄ and Zn-*di*-PcNcTh/g-C₃N₄ in suspension system under visible-light ($\lambda \geq 420$ nm) irradiation.

Fig. S12. UV-vis spectra of the desorbed Zn-*di*-PcNcTh solution before and after 10 h irradiation and the filtrate of Zn-*di*-PcNcTh/g-C₃N₄ suspension after 10 h irradiation (a); DRS spectra of the Zn-*di*-PcNcTh/g-C₃N₄ before 10 h irradiation and after 10 h irradiation with a desorption procedure (b).

Fig. S13. Molecular structures of the five fractions.

Table S1. UV-vis absorption spectra data for all the fractions in DCM.

Fig. S14. UV-vis absorption spectra of the first four fractions in DCM.

Fig. S15. IR spectra of the five fractions.

Fig. S16. MALDI-TOF mass spectrum of H₂Pc(OPh₃)₈.

Fig. S17. MALDI-TOF mass spectrum of H₂-*tri*-PcTh.

Fig. S18. MALDI-TOF mass spectrum of H₂-*di*-PcTh.

Fig. S19. MALDI-TOF mass spectrum of H₂-*tri*-PcNc.

Fig. S20. MALDI-TOF mass spectrum of H₂-*di(adj)*-PcNcTh.

Fig. S21. MALDI-TOF mass spectrum of H₂-*di(opp)*-PcNcTh.

Fig. S22. ¹H MNR (in CDCl₃) spectrum of the molecular ion of Zn-*di*-PcNcTh.

Fig. S23. ¹H MNR (in CDCl₃) spectrum of the molecular ion of H₂Pc(OPh₃)₈.

Fig. S24. ¹H MNR (in CDCl₃) spectrum of the molecular ion of H₂-*tri*-PcTh

Fig. S25. ¹H MNR (in CDCl₃) spectrum of the molecular ion of H₂-*di*-PcTh.

Fig. S26. ¹H MNR (in CDCl₃) spectrum of the molecular ion of H₂-*tri*-PcNc.

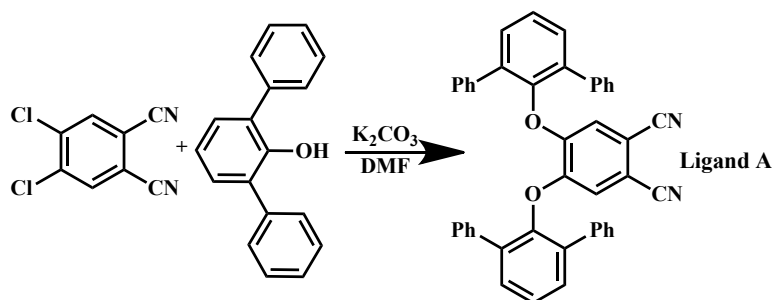
Fig. S27. ¹H MNR (in CDCl₃) spectrum of the molecular ion of H₂-*di(adj)*-PcNcTh.

Fig. S28. ¹H MNR (in CDCl₃) spectrum of the molecular ion of H₂-*di(opp)*-PcNcTh.

Experimental

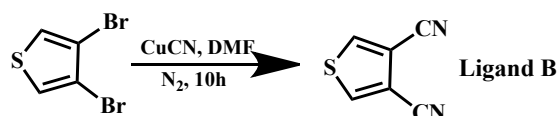
Overview on the preparation of ligands

Ligand A (4,5-bis(2',6'-diphenylphenoxy)-phthalonitrile): 4,5-Dichlorophthalonitrile (3.05 g, 15 mmol), 2,6-diphenylphenol (11.18 g, 48 mmol), K₂CO₃ (40.00 g, 285.7 mmol) were stirred in dry DMF (50 mL) at 100 °C under a nitrogen atmosphere for 48 h (Scheme S1). The reaction mixture was poured into water (150 mL), and the aqueous layer was extracted with 3 × 150 mL of CH₂Cl₂. After the mixture was dried over anhydrous MgSO₄, the organic layer was evaporated and the residue was purified by column chromatography on silica gel by eluting with petroleum ether-DCM. Recrystallization from methanol gave a white solid. Yield: 5.00 g, 54%. ¹H NMR (CDCl₃, 300MHz): δ=7.45 (d, 6H), 7.43-7.41 (d, 8H), 7.15-7.7.13 (d, 4H), 7.07-7.01 (m, 8H), 6.20 ppm(s, 2H).



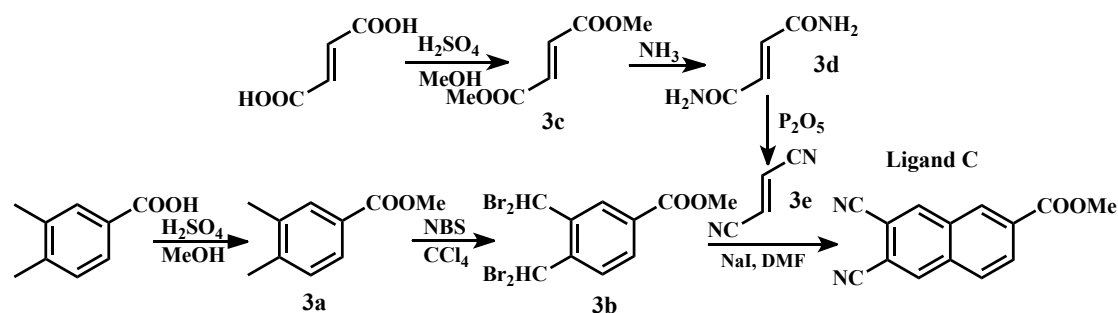
Scheme S1. Synthetic route of 4,5-bis(2',6'-diphenylphenoxy)-phthalonitrile.

Ligand B (3,4-dicyanothiophene): A solution of 3,4-dibromothiophene (10.06 g, 41.7 mmol), cuprous cyanide (8.96 g, 100 mmol) and DMF (50 mL) was refluxed 12 h (Scheme S2). The cooled reaction mixture was then poured into a solution of hydrated ferric chloride (5.40 g, 20.0 mmol) in 300 mL of 2 M hydrochloric acid and stirred vigorously for 1 h at 60-70 °C. After filtration the mixture was extracted four times with 1000 mL DCM. Each organic extract was washed successively with 6 M HCl, water, saturated sodium bicarbonate solution and water for two times. The organic phases were combined and dried over anhydrous MgSO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel by eluting with petroleum ether-DCM. Yield: 1.50 g, 27%. ¹H NMR (CDCl₃, 300MHz): δ=8.07 ppm(s, 2H).



Scheme S2. Synthetic route of 3,4-dicyanothiophene.

Ligand C (6-carboxymethyl-2,3-dicyanonaphthalene) were prepared through multi-step synthetic processes as shown in Scheme S3.



Scheme S3. Synthetic route of 6-carboxymethyl-2,3-dicyanonaphthalene.

Methyl 3,4-dimethylbenzoate (3a): Concentrated sulfuric acid (5.0 mL) was added to 3,4-dimethylbenzoic acid (5.00 g, 33.3 mmol) in MeOH solution (100 mL), and the mixture was refluxed with stirring for 12 h. At the end of this period, the solvent was removed under reduced pressure, and then mixed with water (20 mL), the product was extracted with ethyl acetate (3 × 50 mL). The combined extracts were washed with Na₂CO₃ solution (5%), water and saturated NaCl solution, dried over anhydrous MgSO₄ and then filtered and evaporated to dryness. Yield: 5.67 g, 95%. ¹H NMR (CDCl₃, 300MHz): δ=7.78-7.72 (m, 2H), 7.16-7.13 (d, 1H), 3.86 (s, 3H), 2.26 ppm(s, 6H).

Methyl ω-tetrabromo-3,4-dimethylbenzoate (3b): A mixture of methyl 3,4-dimethylbenzoate (1.00 g, 6.1 mmol) and NBS (7.50 g, 42.5 mmol) in CCl₄ (30 mL) was refluxed and illuminated with a 125 W UV-lamp for 48 h. And then the resulting mixture was filtered, and the filtrate was evaporated. The crude product was recrystallized from hexane. Yield: 1.70 g, 60%. ¹H NMR (CDCl₃, 300 MHz): δ=8.29 (s, 1H), 8.04-8.02 (d, 1H), 7.83 (s, 1H), 7.27-7.26 (d, 2H), 3.97 ppm(s, 3H).

Dimethyl fumarate (3c): Concentrated sulfuric acid (5.0 mL) was added to a mixture of fumaric acid (30.0 g, 259 mmol) and MeOH (200 mL), and the mixture was refluxed with stirring for 12 h. After cooling to room temperature, the precipitation was collected and washed with water to get white solid compound. Yield: 31.20 g, 81%. ¹H NMR (CDCl₃, 300 MHz): δ= 7.44-7.42 (m, 2H), 4.38 ppm(s, 6H).

Fumaramide (3d): A mixture of dimethylfumarate (10.10 g, 87.7 mmol) and ammonia (50 mL) was stirred for 24 h at room temperature. The precipitation was collected and washed with water to get white solid compound. Yield: 8.02 g, 78.6%. ¹H NMR(DMSO-d₆, 300 MHz): δ=7.78

(s, 2H), 7.32 (s, 2H), 6.76 ppm(s, 2H).

Fumarodinitrile (3e): Fumaramide (20.00 g, 175.4 mmol) mixed with P₂O₅ (53.10 g, 377.1 mmol) was heated in vacuum. White needle-like product was collected from vessel wall. Yield: 7.50 g, 55%. ¹H NMR(CDCl₃, 300 MHz): δ=6.23 ppm(s, 2H).

Ligand C (6-carboxymethyl-2,3-dicyanonaphthalene): Anhydrous NaI (13.79 g, 91.9 mmol) was added to a solution of methyl ω-tetrabromo-3,4-dimethylbenzoate (6.72 g, 13.6 mmol) and fumarodinitrile (2.16 g, 27.7 mmol) in dry DMF (100 mL). The mixture was stirred for 24 h at 80 °C. The dark reaction mixture was added slowly to a solution of Na₂S₂O₃ (16.60 g, 65.0 mmol) in water (300 mL). The yellow precipitate was filtered off and purified by recrystallization from acetone. Yield: 2.25 g, 70%. ¹H NMR (CDCl₃, 300 MHz): δ=8.71 (s, 1H), 8.47 (s, 1H), 8.41 (s, 1H), 8.38-8.37 (d, 1H), 8.07-8.05 (d, 1H), 4.31 ppm(s, 3H).

Synthesis of 8,9,24,25-tetra(2',6'-diphenylphenoxy)-16(or17)-carboxyl zinc dibenzo naphtho-thiophenoporphyrazine (Zn-*di*-PhNcTh)

A solution of 3,4-dicyanothiophene (136.1 mg, 1.02 mmol), 4,5-bis(2',6'-diphenylphenoxy) phthalonitrile (209.5 mg, 0.34 mmol) and 6-carboxymethyl-2,3-dicyanonaphthalene (120.4 mg, 0.51 mmol) in dry n-butanol (10 mL) was heated to 100 °C with stirring for 3 h. To the reactant mixture was added slowly lithium metal (0.2 g) under stirring (Scheme 1). The solution immediately turned an intense green color and was heated to reflux for 6 h. When the mixture was allowed to cool to room temperature, glacial acetic acid (10 mL) was added and stirring was continued at 70 °C for 30 min. The mixture was cooled to room temperature and methanol (100 mL) was added. Then the mixture was filtered and the precipitation was washed with methanol. The residue was separated by silica gel column chromatography with DCM as a solvent and monitored by UV-vis spectra.

The first fraction identified as 2,3,9,10,16,17,23,24-octa(2',6'-diphenyl-phenoxy) phthalocyanine (H₂Pc(OPh₃)₈) was obtained by using petroleum ether-DCM(1:1) as eluant and recrystallized from DCM-MeOH to obtain a green solid. Yield: 5 mg, 2%. UV-vis λ_{max} (DCM)/nm (logε): 711 (5.08); 677 (5.03); 426 (4.51); 352 (4.76). ¹H NMR (CDCl₃, 300MHz): δ=7.77-7.66 (br, 63H, ArH), 6.88-6.80 ppm(br, 49H, ArH) (Fig. S23†). FT-IR (KBr): ν (cm⁻¹) = 3057 (w, ArCH), 3026 (w, ArCH), 1614, 1602, 1444, 1414, 1328, 1263, 1197, 1092, 1017, 879, 802, 750, 698 (Fig. S15†). TOF-MS (m/z) calcd for C₁₇₆H₁₁₄N₈O₈ [M+1]⁺ 2467.88, found 2465.91 (Fig. S16†); Elemental analysis calcd for C₁₇₆H₁₁₄N₈O₈·CH₃OH·2CH₂Cl₂: C 80.50, H

4.60, N 4.20. Found: C 80.49, H 5.12, N 3.98.

Change of eluent to petrol-DCM (1:3) provided a second fraction which was 8,9,15,16,22,23-hexa(2',6'-diphenylphenoxy)-28H,30H-tribenzothiopheno[3,4-q]porp-hyrazine(H_2 -*tri*-PcTh).

Yield: 10 mg, 4%. UV-vis $\lambda_{\max}$ (DCM)/nm (log ϵ): 736 (4.95); 695 (4.57); 657 (4.63); 425 (4.40); 342 (4.64). 1H NMR ($CDCl_3$, 300MHz): δ =8.53 (s, 2H, ThH), 7.80-7.60 (br, 48H, ArH), 6.89-6.80 ppm(br, 36H, ArH) (Fig. S24 $\dagger$). FT-IR (KBr): ν (cm^{-1}) = 3056, 3029, 1718, 1614, 1602, 1572, 1498, 1474, 1454, 1413, 1268, 1196, 1145, 1094, 1028, 999, 880, 791, 750, 700 (Fig. S15 $\dagger$). TOF-MS (m/z) calcd for $C_{138}H_{88}N_8O_6S$ $[M+1]^+$ 1985.66, found 1984.33 (Fig. S17 $\dagger$); Elemental analysis calcd for $C_{138}H_{88}N_8O_6S \cdot CH_3OH \cdot CH_2Cl_2$: C 79.95, H 4.50, N 5.33. Found: C 80.23, H 4.68, N 5.69.

The third fraction, eluent CH_2Cl_2 , was purified by column chromatography over silica and recrystallized from DCM-MeOH to obtain a mixture of 8,9,21,22-tetra(2',6'-diphenylphenoxy) - 28H,30H-dibenzodithiopheno[3,4-q]porphyr-a-zine(H_2 -*di*-PcTh) and its isomer. Yield: 8 mg, 3%. UV-vis $\lambda_{\max}$ (DCM)/nm (log ϵ): 719 (5.05); 700 (4.88); 426 (4.22); 337 (4.70). 1H NMR ($CDCl_3$, 300MHz): δ =8.60 (s, 2H, ThH), 8.35 (s, 2H, ThH), 7.86-7.62 (br, 32H, ArH), 6.98-6.85 ppm(br, 24H, ArH) (Fig. S25 $\dagger$). FT-IR (KBr): ν (cm^{-1}) = 3290, 3055, 3028, 1719, 1612, 1602, 1498, 1474, 1456, 1413, 1328, 1267, 1196, 1145, 1028, 880, 787, 750, 698 (Fig. S15 $\dagger$). TOF-MS (m/z) calcd for $C_{100}H_{62}N_8O_4S_2$ $[M+1]^+$ 1503.44, found 1503.08 (Fig. S18 $\dagger$); Elemental analysis calcd for $C_{100}H_{62}N_8O_4S_2 \cdot 2CH_3OH \cdot CH_2Cl_2$: C 74.85, H 4.39, N 6.78. Found: C 74.29, H 5.20, N 6.41.

The fourth fraction to be collected from a column, eluent DCM-MeOH (99:1), was 2,3,9,10,16,17-hexa(2',6'-diphenylphenoxy)-24(or 25)-carboxyl-31H,33H-triben-zonaphthoporphyr-a-zine (H_2 -*tri*-PcNc). Yield: 8 mg, 3%. UV-vis $\lambda_{\max}$ (DCM)/nm (log ϵ): 732 (4.81); 694 (4.80); 433(4.26); 342(4.54). 1H NMR ($CDCl_3$, 300MHz): δ =7.95 (s, 2H), 7.91(s, 2H), 7.81-7.60 (br, 50H), 6.89-6.80 ppm(br, 35H) (Fig. S26 $\dagger$). FT-IR (KBr): ν (cm^{-1}) = 3309, 3056, 3028, 1732, 1615, 1498, 1474, 1453, 1413, 1328, 1271, 1196, 1145, 1093, 1014, 880, 802, 750, 698 (Fig. S15 $\dagger$). TOF-MS (m/z) calcd for $C_{145}H_{92}N_8O_8$ $[M+1]^+$ 2074.33, found 2073.27 (Fig. S19 $\dagger$); Elemental analysis calcd for $C_{145}H_{92}N_8O_8 \cdot CH_3OH \cdot CH_2Cl_2$: C 80.57, H 4.51, N 5.11. Found: C 80.65, H 4.48, N 5.13.

The target product, 8,9,15,16-tetra(2',6'-diphenylphenoxy)-23(or 24)-carboxyl-30H,32H-dibenzonaphthothiophenoporphyr-a-zine (H_2 -*di(adj)*-PcNcTh) was separated by using DCM- MeOH (97:3) as eluent and recrystallized from DCM-MeOH to obtain a green solid. Yield: 2 mg, 0.7%. UV-vis $\lambda_{\max}$ (DCM)/nm (log ϵ): 756 (4.73); 702 (4.48); 672 (4.52); 429 (4.31); 334 (4.54). 1H NMR ($CDCl_3$, 300MHz): δ =8.08 (s, 2H, ThH), 7.89-7.74 (br, 42H, ArH), 7.35-7.21 (br, 6H, ArH), 6.88-6.79 ppm(br, 36H, ArH). FT-IR (KBr): ν (cm^{-1}) = 3290 (w, COOH), 3057 (w, ArCH), 3029 (w, ArCH), 1718 (w, C=O), 1617 (w, C=N), 1600, 1498, 1474, 1454, 1413, 1270, 1196,

1091, 1030, 881, 790, 750, 699 (Fig. S15†). TOF-MS (m/z): calcd for $C_{107}H_{66}N_8O_6S$ $[M+1]^+$ 1591.78; found 1591.24 (Fig. S20†); Elemental analysis calcd for $C_{107}H_{66}N_8O_6S \cdot CH_3OH \cdot 2CH_2Cl_2$: C 76.62, H 4.25, N 6.56; Found: C 76.47, H 4.32, N 6.48.

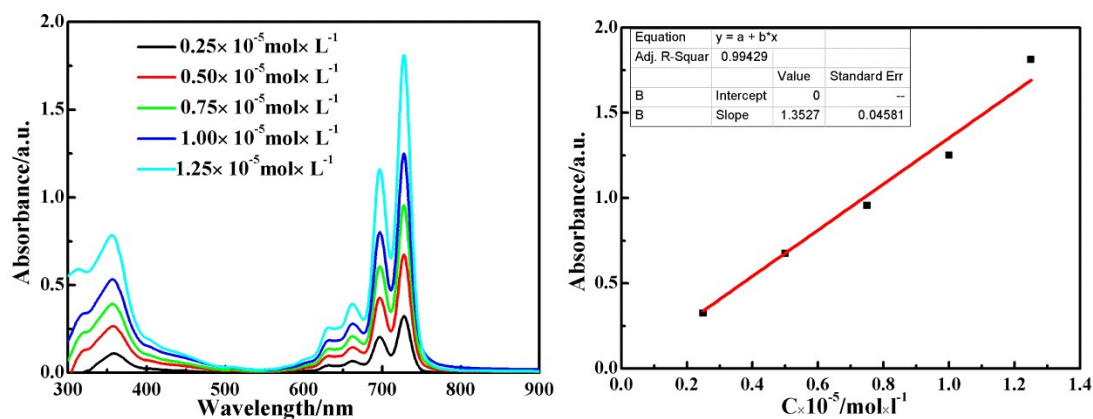


Fig. S1. UV-vis absorption spectra of Zn-*di*-PcNcTh in THF at different concentration.

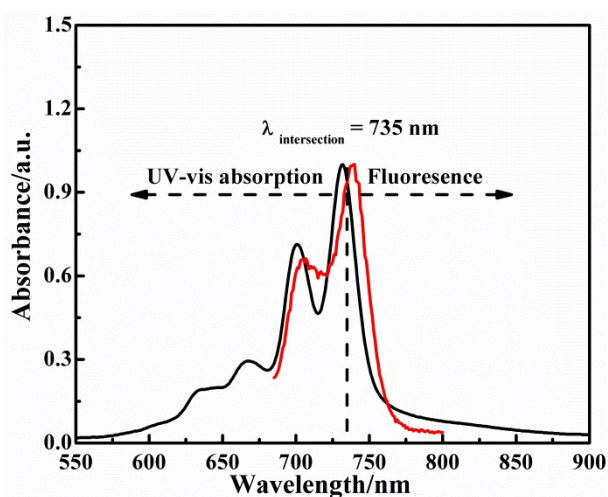


Fig. S2. UV-vis absorption and fluorescence emission spectra of Zn-*di*-PcNcTh in DCM solution with excitation fixed at 666 nm.

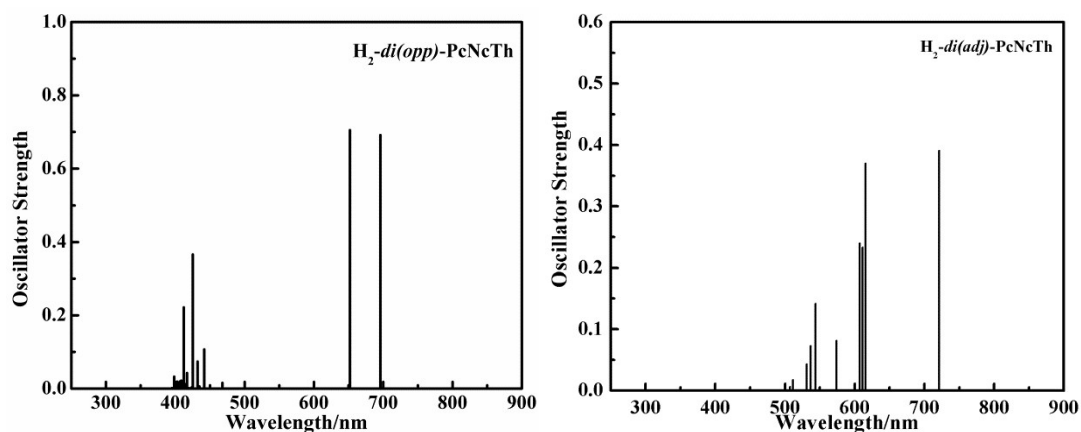


Fig. S3. Absorption wavelengths and oscillator strengths obtained by TDDFT calculations on the low-symmetry, metal-free H_2 -*di(adj)*-PcNcTh and H_2 -*di(opp)*-PcNcTh.

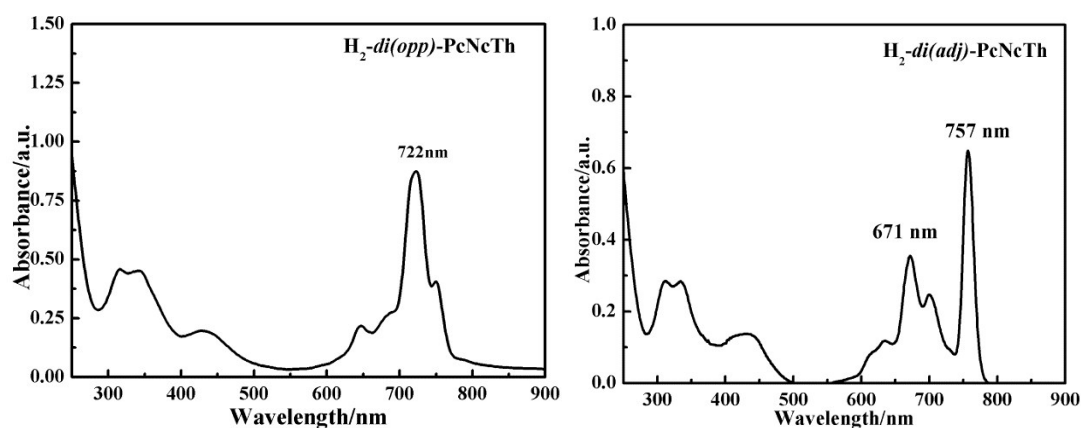


Fig. S4. UV-vis absorption spectra of H_2 -*di(opp)*-PcNcTh and H_2 -*di(adj)*-PcNcTh in DCM.

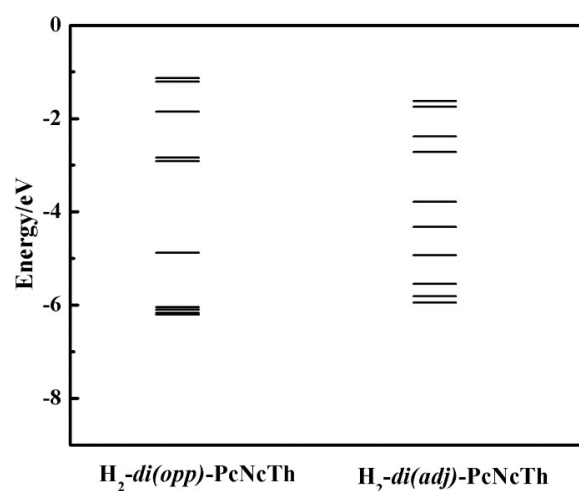


Fig. S5. Energy levels (in eV) of the frontier orbitals for the low-symmetry, metal-free H_2 -*di(adj)*-PcNcTh and H_2 -*di(opp)*-PcNcTh obtained by DFT calculations at B3LYP/6-31G(D) level.

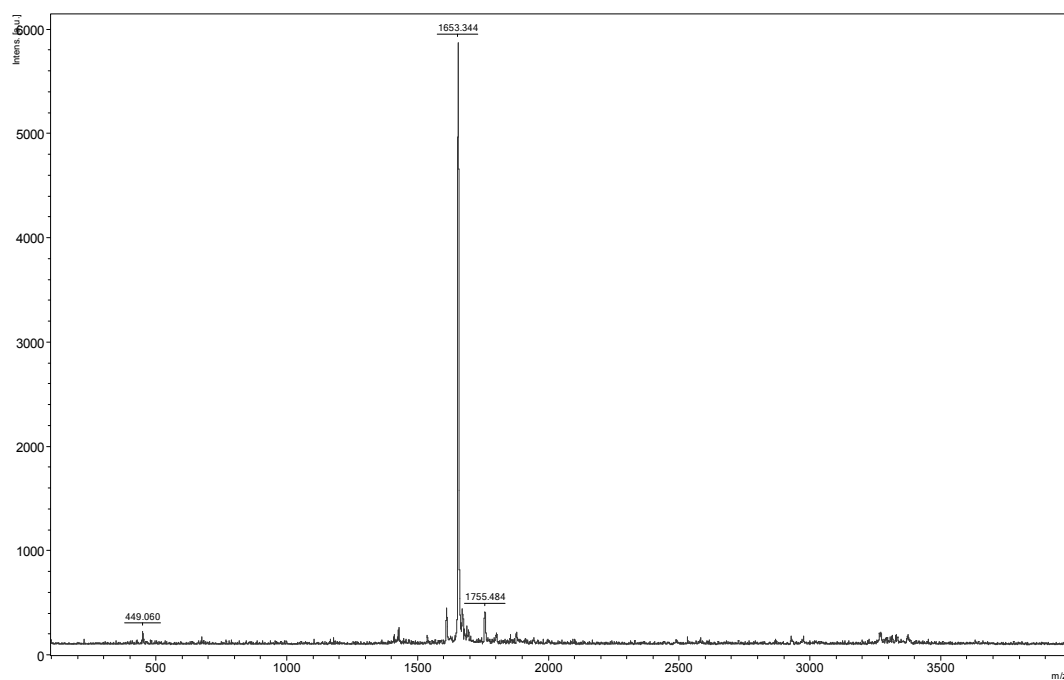


Fig. S6. MALDI-TOF mass spectrum of Zn-*di*-PcNcTh.

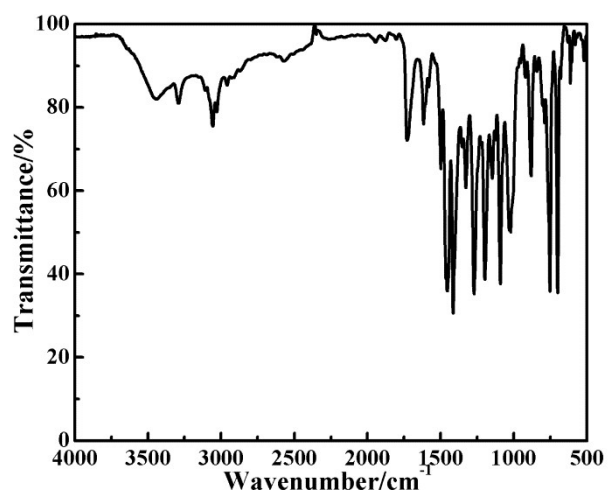


Fig. S7. IR spectra of Zn-*di*-PcNcTh.

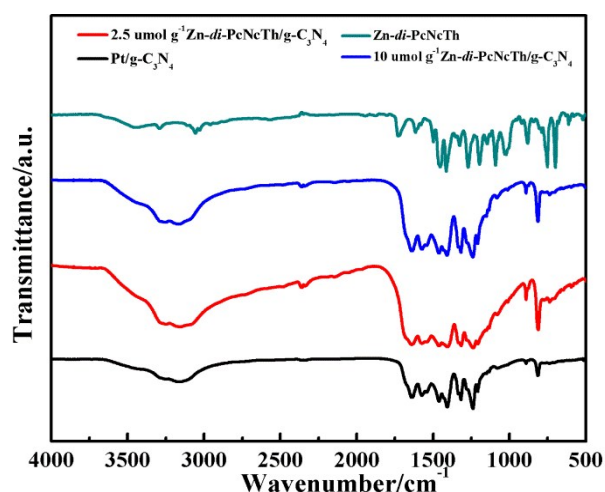


Fig. S8. Fourier transform infrared (FTIR) spectra of $\text{g-C}_3\text{N}_4$, Zn-di-PcNcTh and $\text{Zn-di-PcNcTh/g-C}_3\text{N}_4$.

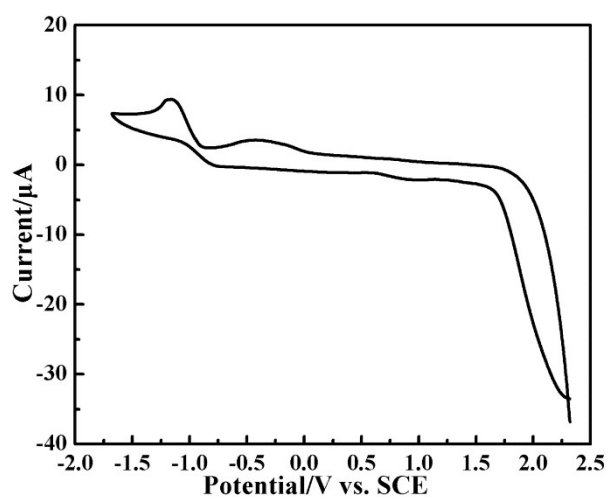


Fig. S9. Typical cyclic voltammogram of Zn-di-PcNcTh in DCM containing 0.1 M $[\text{NBu}_4][\text{ClO}_4]$ at a scan rate of $20 \text{ mV} \cdot \text{S}^{-1}$.

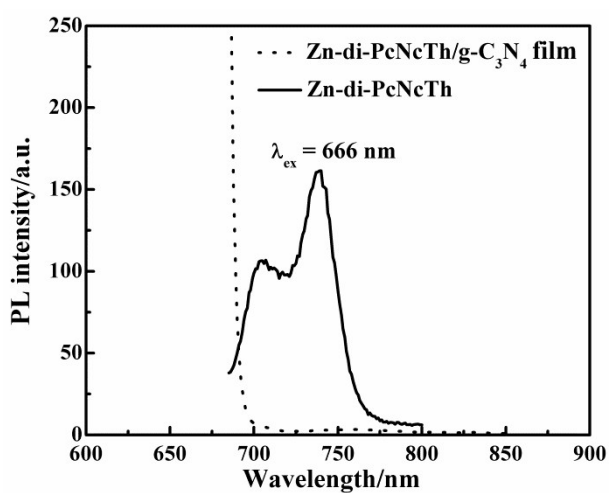


Fig. S10. Photoluminescence (PL) spectra of Zn-di-PcNcTh solution and $\text{Zn-di-PcNcTh/g-C}_3\text{N}_4$ film.

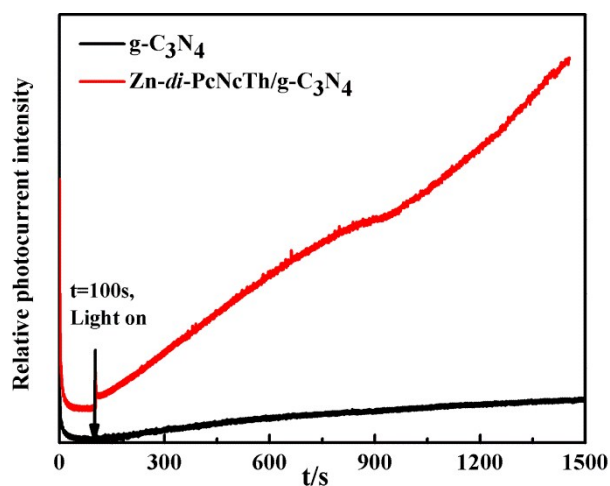


Fig. S11. Transient photocurrent curves of $g\text{-C}_3\text{N}_4$ and $\text{Zn-di-PcNcTh/g-C}_3\text{N}_4$ in suspension system under visible-light ($\lambda \geq 420$ nm) irradiation.

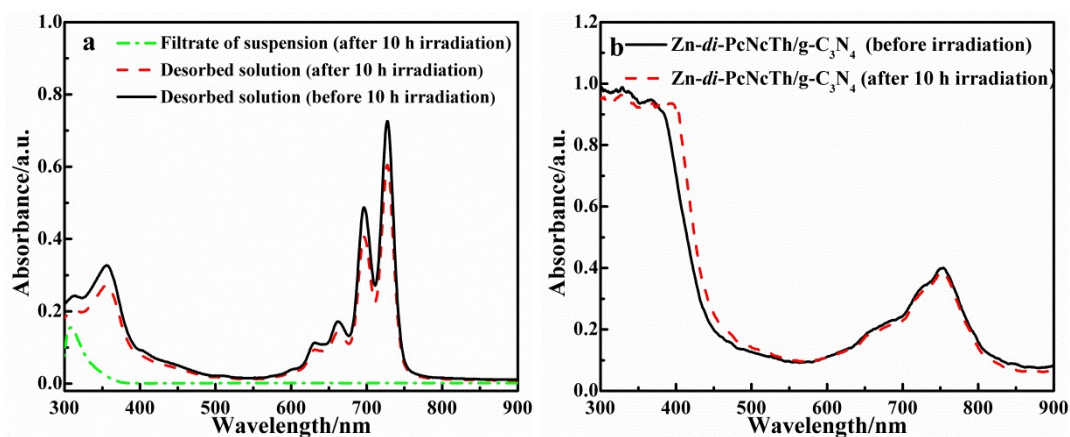


Fig. S12. UV-vis spectra of the desorbed Zn-di-PcNcTh solution before and after 10 h irradiation and the filtrate of $\text{Zn-di-PcNcTh/g-C}_3\text{N}_4$ suspension after 10 h irradiation (a); DRS spectra of the $\text{Zn-di-PcNcTh/g-C}_3\text{N}_4$ before irradiation and after 10 h irradiation (b).

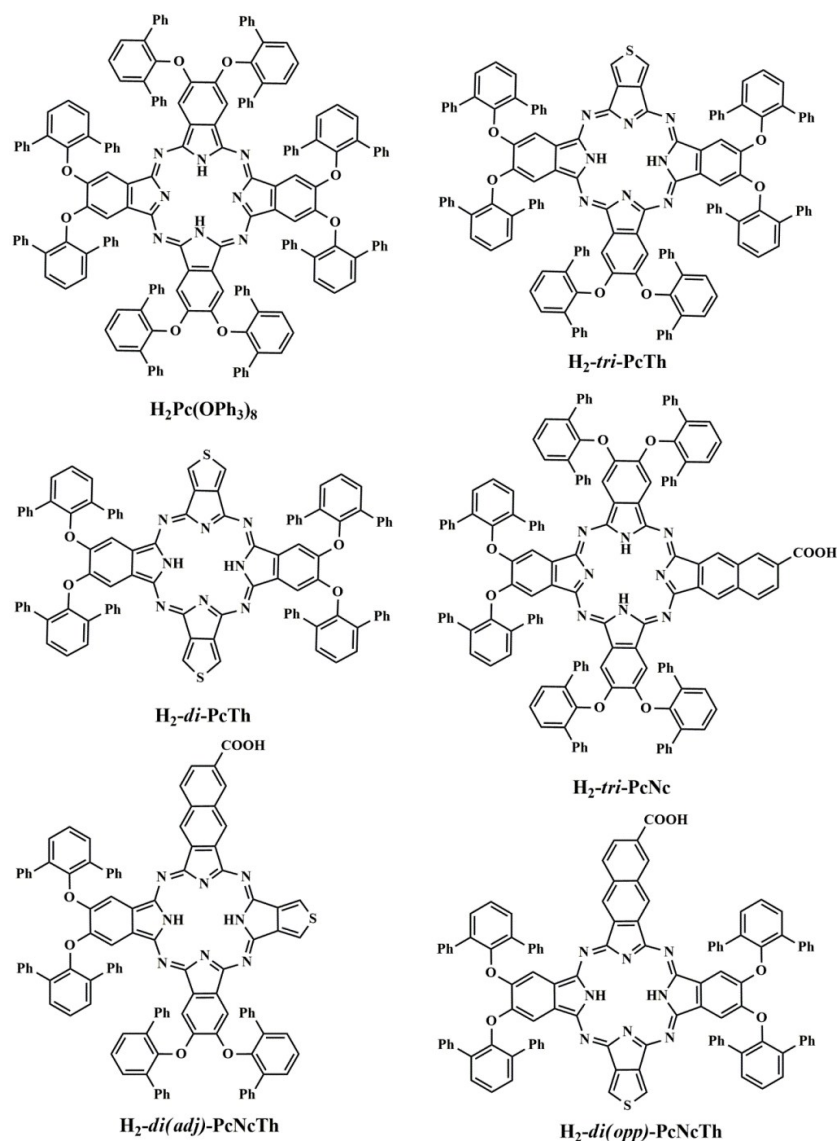


Fig. S13. Molecular structures of the five fractions.

Table S1. UV-vis absorption spectra data for all the fractions in DCM

Compound	$\lambda_{\max}$ /nm (log ϵ)				
H ₂ Pc(OPh ₃) ₈	352 (4.76)	426 (4.51)		677 (5.03)	711 (5.08)
H ₂ -tri-PcTh	342 (4.64)	425 (4.40)	657 (4.63)	695 (4.57)	736 (4.95)
H ₂ -di-PcTh	337 (4.70)	426 (4.22)		700 (4.88)	719 (5.05)
H ₂ -tri-PcNc	342 (4.54)	433 (4.26)		694 (4.80)	732 (4.81)
H ₂ -di(adj)-PcNcTh	334 (4.54)	429 (4.31)	672 (4.52)	702 (4.48)	756 (4.73)
H ₂ -di(opp)-PcNcTh	343 (4.71)	427 (4.32)		723 (4.90)	746 (4.74)
Zn-di-PcNcTh	357 (4.81)			697 (4.96)	732 (5.13)

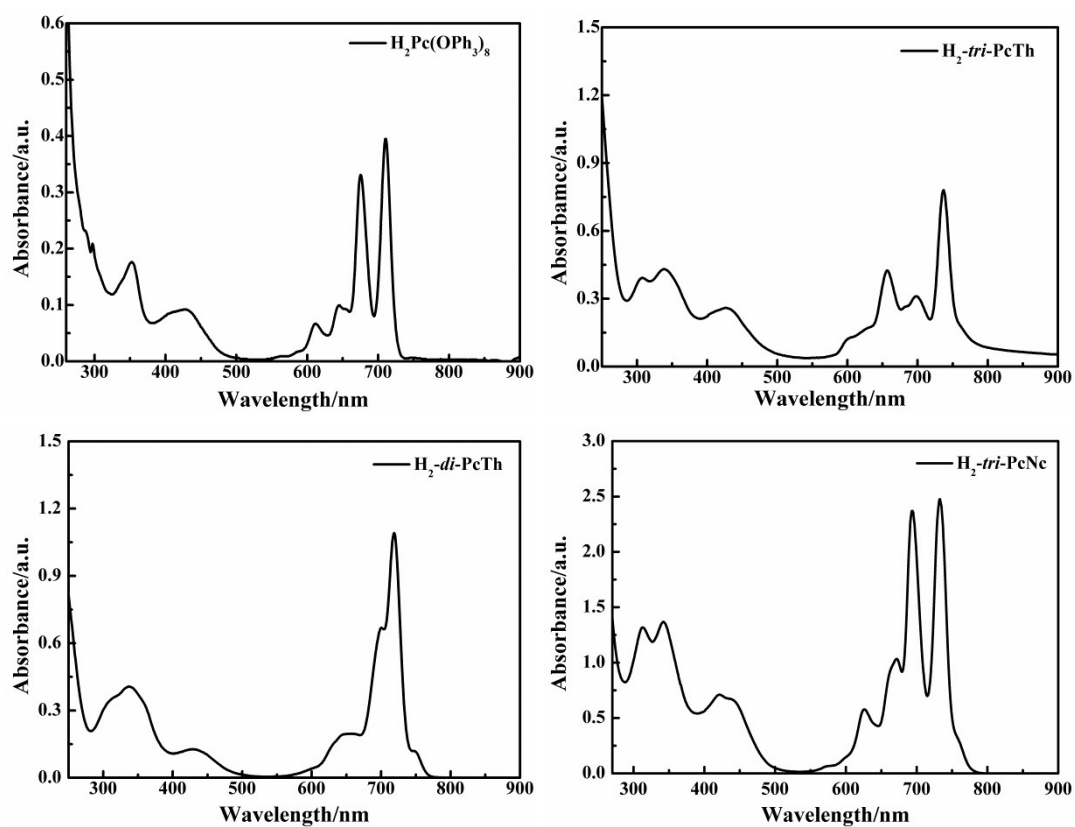


Fig. S14. UV-vis absorption spectra of the first four fractions in DCM.

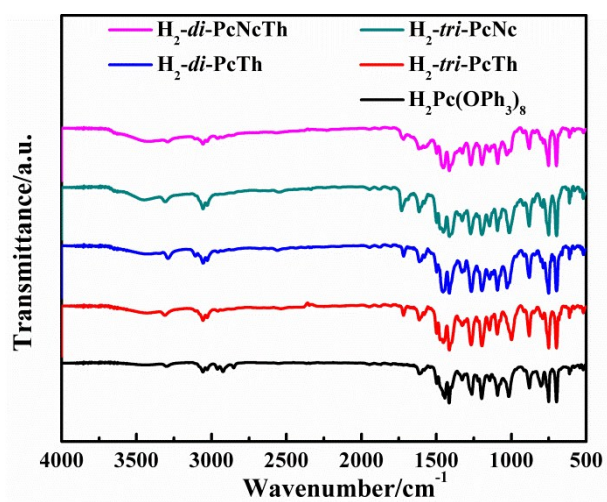


Fig. S15. IR spectra of the five fractions.

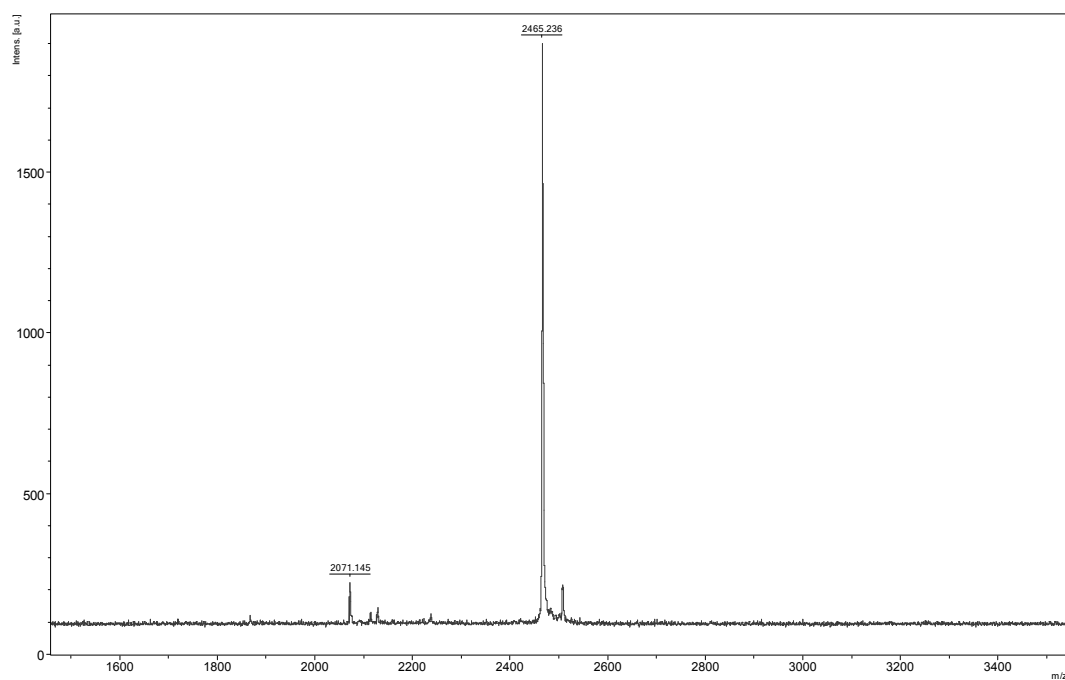


Fig. S16. MALDI-TOF mass spectrum of $\text{H}_2\text{Pc}(\text{OPh}_3)_8$.

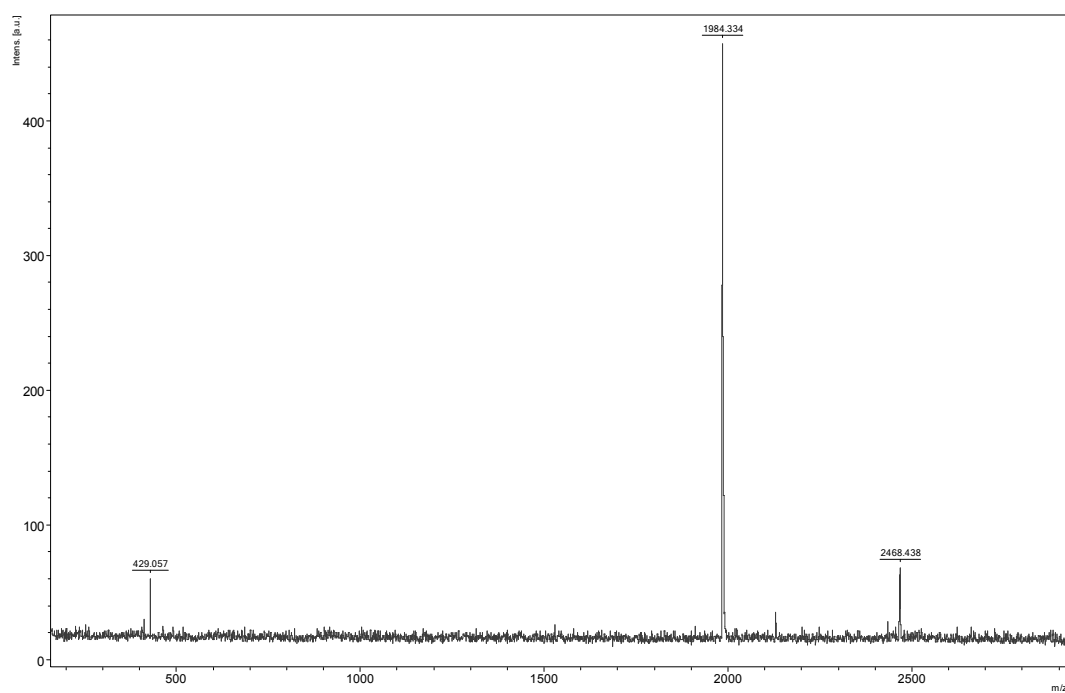


Fig. S17. MALDI-TOF mass spectrum of $\text{H}_2\text{-tri-PcTh}$.

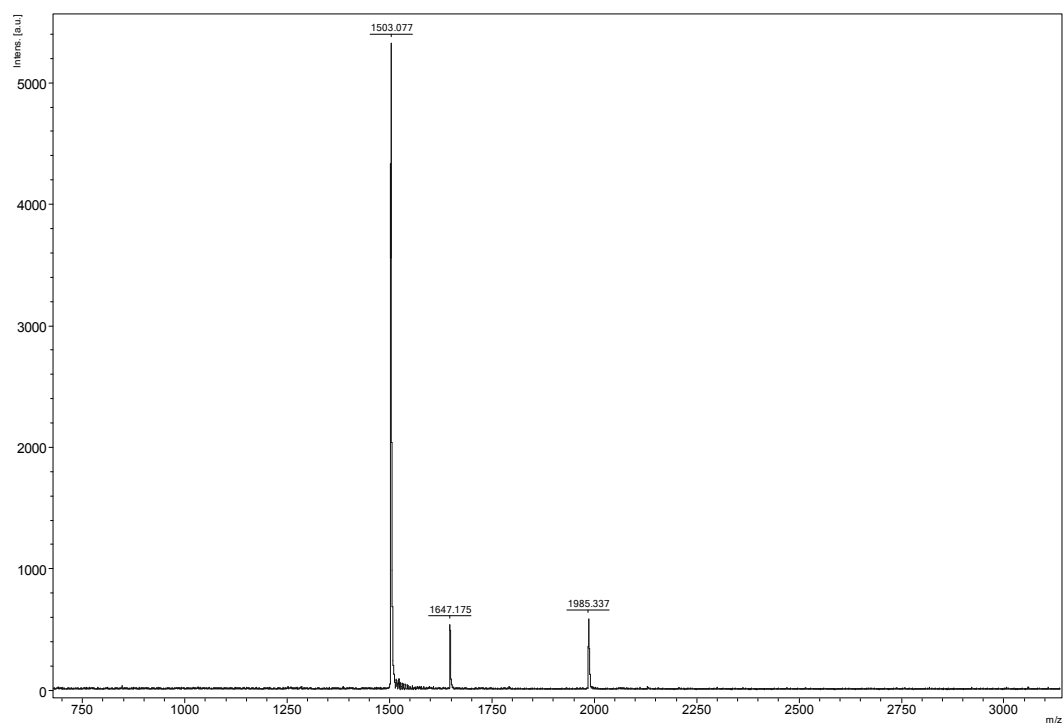


Fig. S18. MALDI-TOF mass spectrum of H_2 -*di*-PcTh.

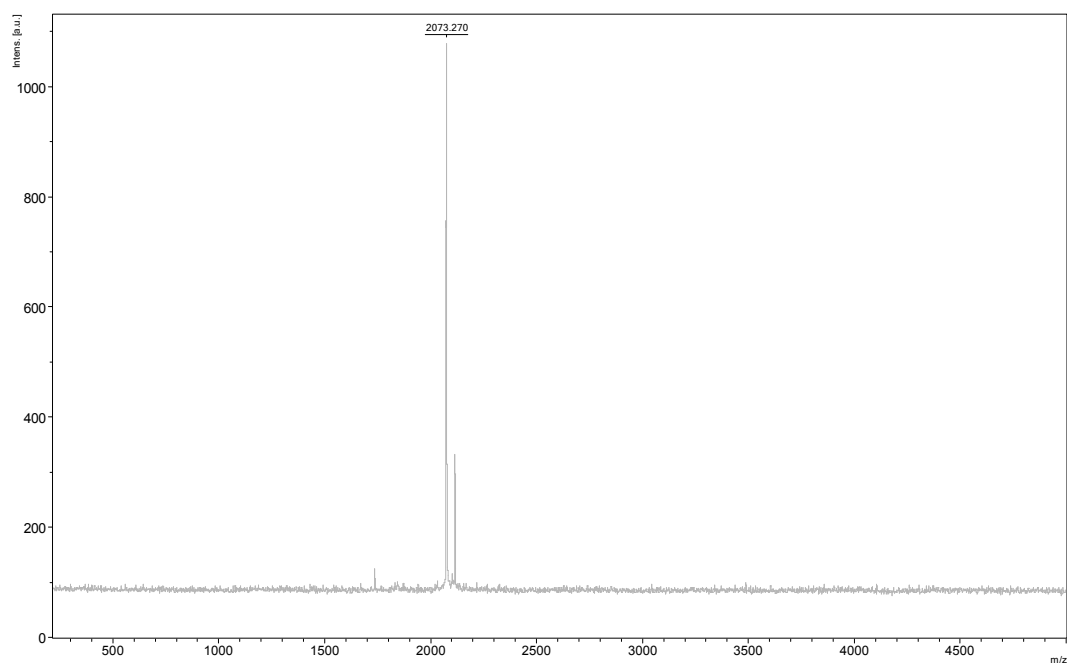


Fig. S19. MALDI-TOF mass spectrum of H_2 -*tri*-PcNc.

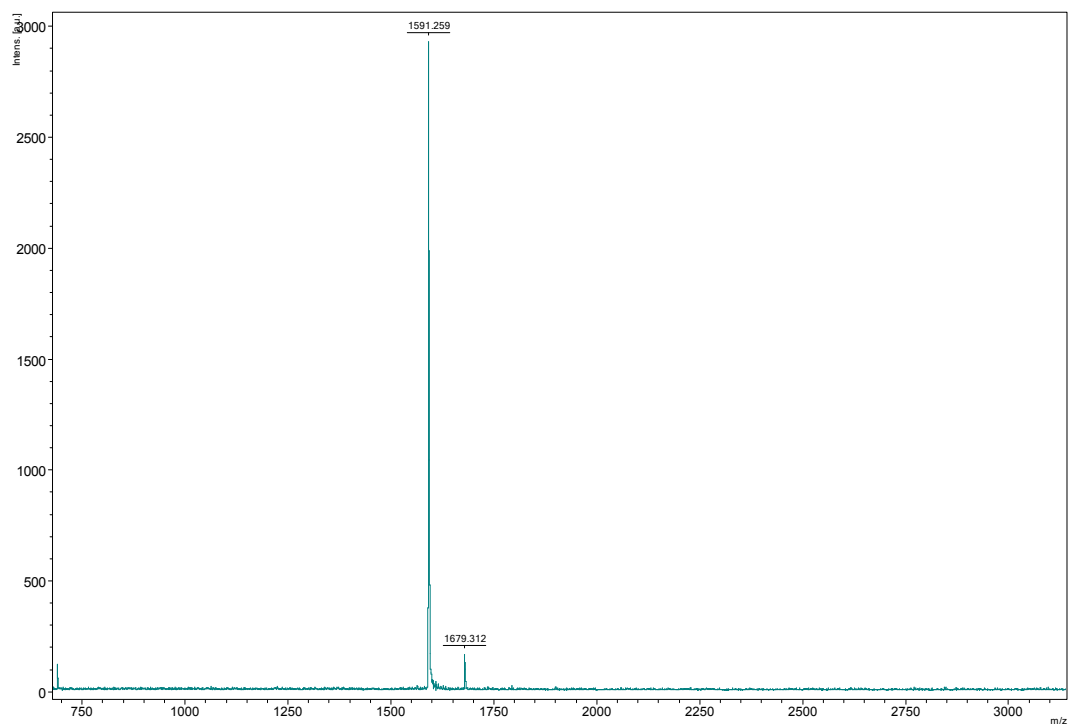


Fig. S20. MALDI-TOF mass spectrum of H_2 -*di(adj)*-PcNcTh.

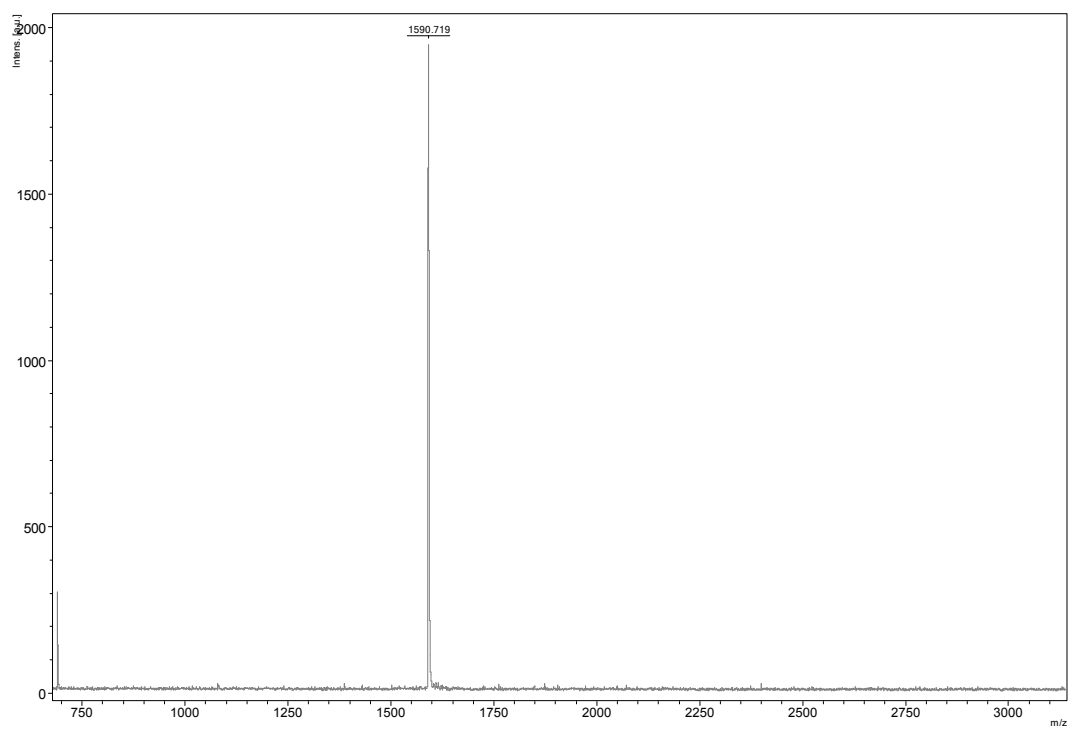


Fig. S21. MALDI-TOF mass spectrum of H_2 -*di(opp)*-PcNcTh.

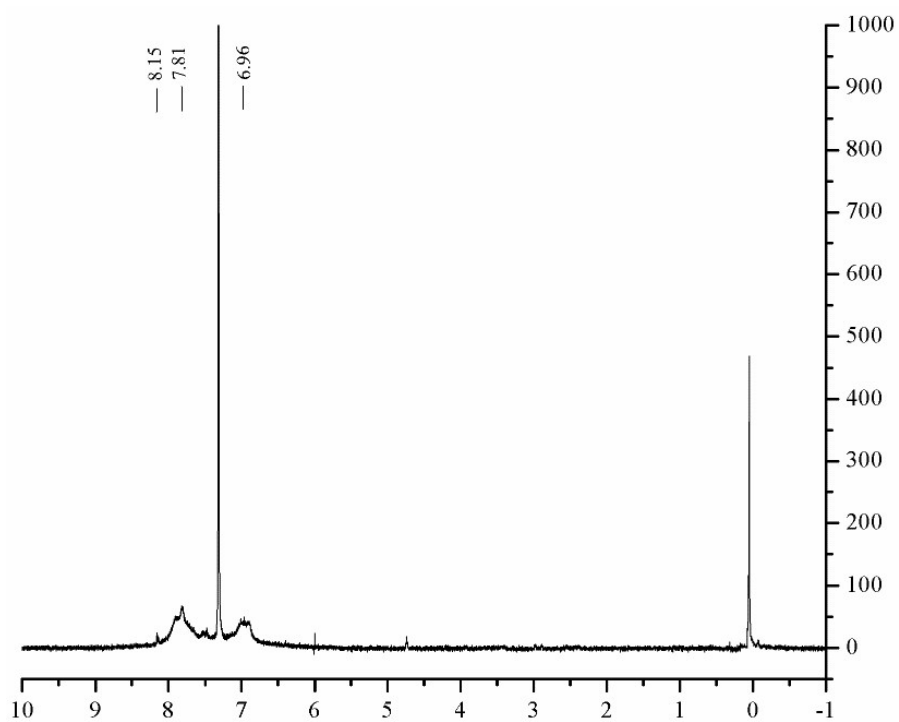


Fig. S22. ^1H MNR (in CDCl_3) spectrum of the molecular ion of Zn-di-PcNcTh .

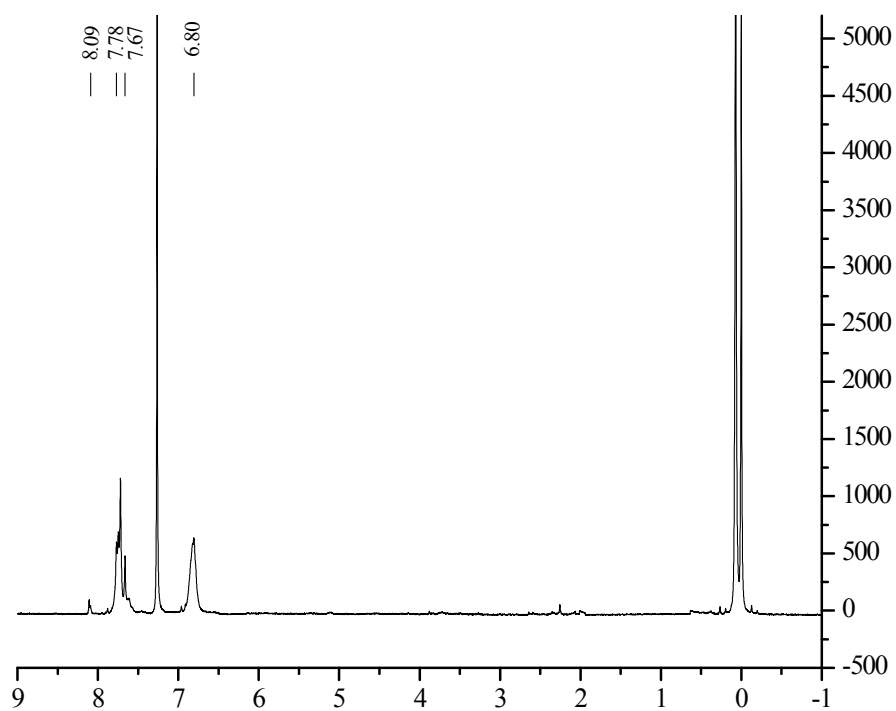


Fig. S23. ^1H MNR (in CDCl_3) spectrum of the molecular ion of $\text{H}_2\text{Pc}(\text{OPh}_3)_8$.

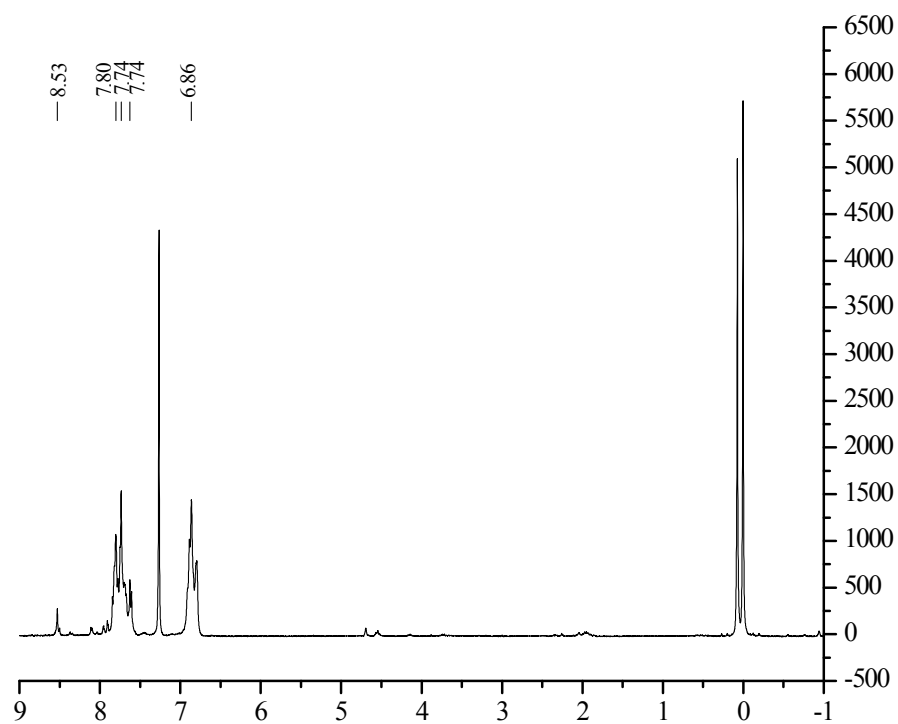


Fig. S24. ^1H MNR (in CDCl_3) spectrum of the molecular ion of $\text{H}_2\text{-tri-PcTh}$

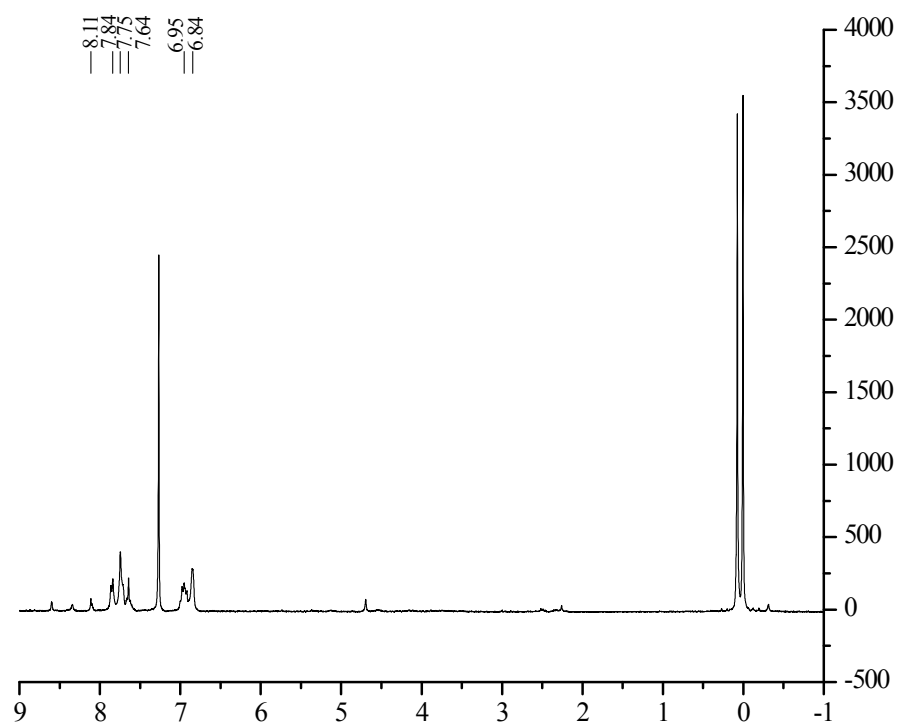


Fig. S25. ^1H MNR (in CDCl_3) spectrum of the molecular ion of $\text{H}_2\text{-di-PcTh}$.

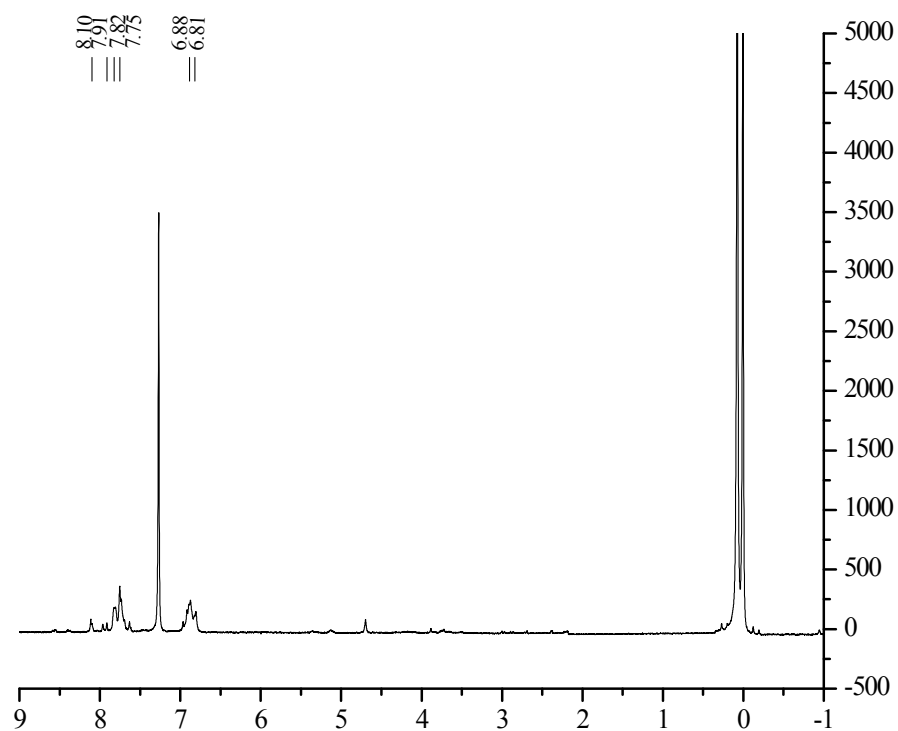


Fig. S26. ^1H MNR (in CDCl_3) spectrum of the molecular ion of $\text{H}_2\text{-tri-PcNc}$.

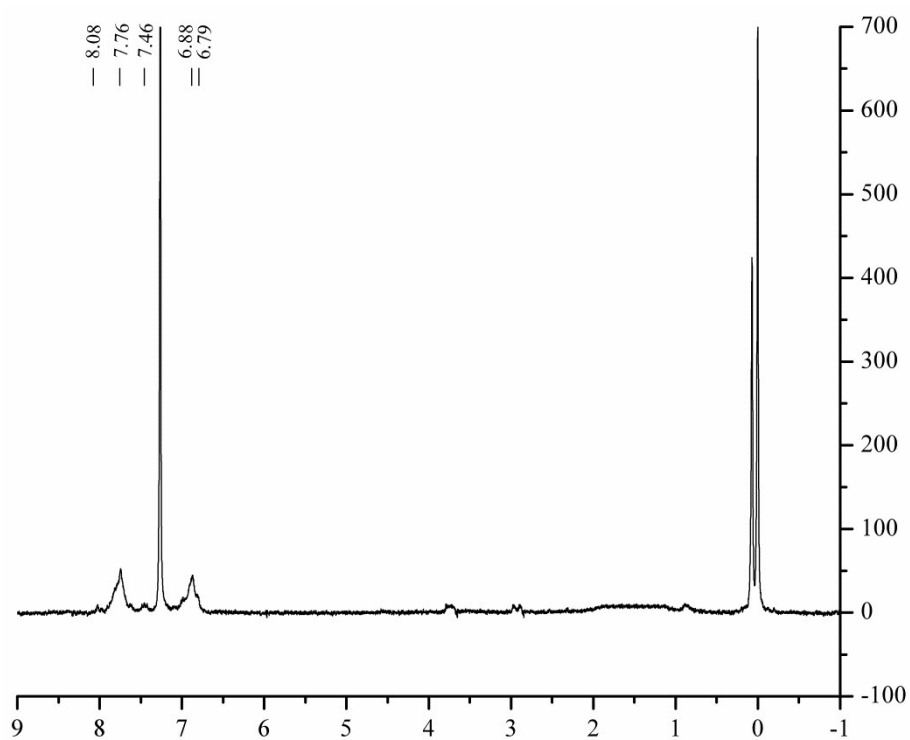


Fig. S27. ^1H MNR (in CDCl_3) spectrum of the molecular ion of $\text{H}_2\text{-di(adj)-PcNcTh}$.

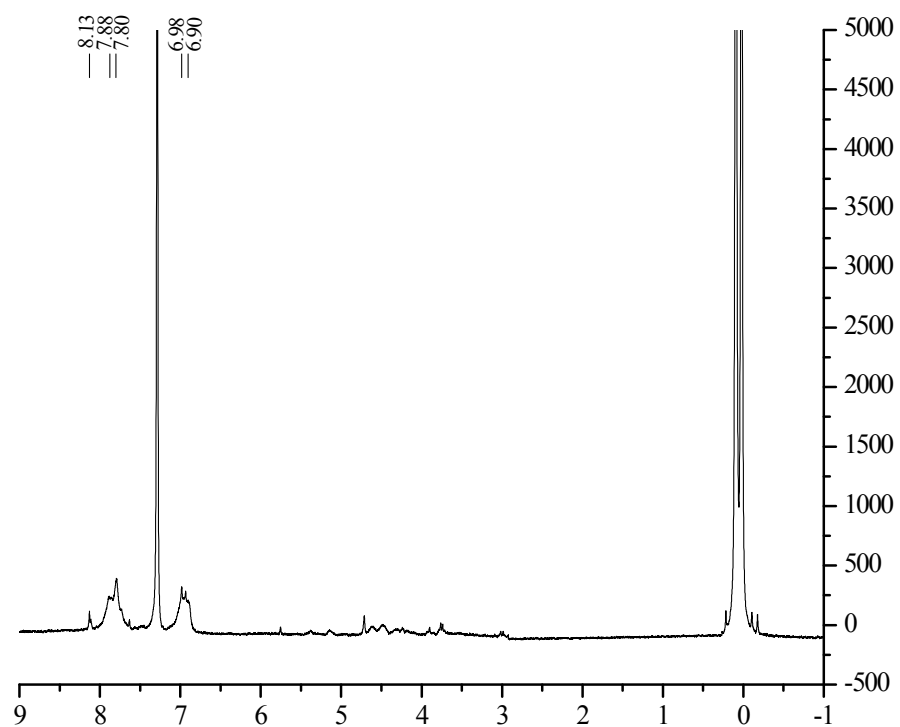


Fig. S28. ^1H MNR (in CDCl_3) spectrum of the molecular ion of $\text{H}_2\text{-di(opp)-PcNcTh}$.