Supporting information

**Syntheses and Characterization of A$_2$BC Type Phthalocyanine and Its Visible-Light-Responsive Photocatalytic H$_2$ Production Performance on Graphitic Carbon Nitride**

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**Fig. S28.** $^1$H MNR (in CDCl$_3$) spectrum of the molecular ion of H$_2$-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), K$_2$CO$_3$ (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 CH$_2$Cl$_2$. After the mixture was dried over anhydrous MgSO$_4$, 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%. $^1$H NMR (CDCl$_3$, 300MHz): δ=7.45 (d, 6H), 7.43-7.41 (d, 8H), 7.15-7.13 (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.](image)

**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 MgSO$_4$. 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%. $^1$H NMR (CDCl$_3$, 300MHz): δ=8.07 ppm(s, 2H).

![Scheme S2. Synthetic route of 3,4-dicyanothiophene.](image)
**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.](image)

**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 ppm(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
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), 8.07-8.05 (d, 1H), 8.31 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 (logs): 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]porphyrin (H₂-tri-PcTh).

Yield: 10 mg, 4%. UV-vis $\lambda_{\text{max}}$ (DCM)/nm (log $\varepsilon$): 736 (4.95); 695 (4.57); 657 (4.63); 425 (4.40); 342 (4.64). $^1$H NMR (CDCl₃, 300MHz): $\delta$=8.53 (s, 2H, ThH), 7.80-7.60 (br, 48H, ArH), 6.90-6.80 ppm (br, 36H, ArH) (Fig. S24†). FT-IR (KBr): $\nu$ (cm$^{-1}$) = 3056, 3029, 1718, 1614, 1602, 1572, 1498, 1474, 1454, 1413, 1268, 1196, 1145, 1094, 1028, 999, 880, 791, 750, 700 (Fig. S15†). TOF-MS (m/z) calcd for C₁₃₈H₈₈N₈O₆S [M+1]$^+$ 1985.66, found 1984.33 (Fig. S17†); Elemental analysis calcd for C₁₃₈H₈₈N₈O₆S·CH₃OH·CH₂Cl₂: C 79.95, H 4.50, N 5.33. Found: C 80.23, H 4.68, N 5.69.

The third fraction, eluent CH₂Cl₂, 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]porphyrin (H₂-di-PcTh) and its isomer. Yield: 8 mg, 3%. UV-vis $\lambda_{\text{max}}$ (DCM)/nm (log $\varepsilon$): 736 (5.05); 700 (4.88); 426 (4.22); 337 (4.70). $^1$H NMR (CDCl₃, 300MHz): $\delta$=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†). FT-IR (KBr): $\nu$ (cm$^{-1}$) = 3290, 3055, 3028, 1719, 1612, 1602, 1498, 1474, 1456, 1413, 1328, 1267, 1196, 1145, 1028, 880, 787, 750, 698 (Fig. S15†). TOF-MS (m/z) calcd for C₁₀₀H₆₂N₈O₄S₂ [M+1]$^+$ 1503.44, found 1503.08 (Fig. S18†); Elemental analysis calcd for C₁₀₀H₆₂N₈O₄S₂·2CH₃OH·CH₂Cl₂: 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-tribenzonaphthoporphyrazine (H₂-tri-PcNc). Yield: 8 mg, 3%. UV-vis $\lambda_{\text{max}}$ (DCM)/nm (log $\varepsilon$): 732 (4.81); 694 (4.80); 433 (4.26); 342 (4.54). $^1$H NMR (CDCl₃, 300MHz): $\delta$=7.95 (s, 2H), 7.91(s, 2H), 7.81-7.60 (br, 50H), 6.89-6.80 ppm (br, 35H) (Fig. S26†). FT-IR (KBr): $\nu$ (cm$^{-1}$) = 3309, 3056, 3028, 1732, 1615, 1498, 1474, 1453, 1413, 1328, 1267, 1196, 1145, 1093, 1014, 880, 802, 750, 698 (Fig. S15†). TOF-MS (m/z) calcd for C₁₄₅H₉₂N₈O₈S [M+1]$^+$ 2074.33, found 2073.27 (Fig. S19†); Elemental analysis calcd for C₁₄₅H₉₂N₈O₈S·2CH₃OH·CH₂Cl₂: 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-dibenzonaphthothiophenoporphyrazine (H₂-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 $\lambda_{\text{max}}$ (DCM)/nm (log $\varepsilon$): 756 (4.73); 702 (4.48); 672 (4.52); 429 (4.31); 334 (4.54). $^1$H NMR (CDCl₃, 300MHz): $\delta$=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): $\nu$ (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,
TOF-MS (m/z): calcd for $\text{C}_{107}\text{H}_{66}\text{N}_8\text{O}_6\text{S} [\text{M+1}]^+$ 1591.78; found 1591.24 (Fig. S20†); Elemental analysis calcd for $\text{C}_{107}\text{H}_{66}\text{N}_8\text{O}_6\text{S} \cdot \text{CH}_3\text{OH} \cdot 2\text{CH}_2\text{Cl}_2$: 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-\textit{di}-PcNcTh in THF at different concentration.

**Fig. S2.** UV-vis absorption and fluorescence emission spectra of Zn-\textit{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.
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Fig. S7. IR spectra of Zn-dil-PcNcTh.
**Fig. S8.** Fourier transform infrared (FTIR) spectra of g-C$_3$N$_4$, Zn-*di*-PcNcTh and Zn-*di*-PcNcTh/g-C$_3$N$_4$.

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

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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-C$_3$N$_4$ suspension after 10 h irradiation (a); DRS spectra of the Zn-$di$-PcNcTh/g-C$_3$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

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<th>Compound</th>
<th>$\lambda_{\text{max}}$/nm (logs)</th>
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<td>$\text{H}_2\text{Pc(OPh$_3$)$_8$}$</td>
<td>352 (4.76) 426 (4.51) 677 (5.03) 711 (5.08)</td>
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<tr>
<td>$\text{H}_2\text{-tri-PcTh}$</td>
<td>342 (4.64) 425 (4.40) 657 (4.63) 695 (4.57) 736 (4.95)</td>
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<td>$\text{H}_2\text{-di-PcTh}$</td>
<td>337 (4.70) 426 (4.22) 700 (4.88) 719 (5.05)</td>
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<td>$\text{H}_2\text{-tri-PcNc}$</td>
<td>342 (4.54) 433 (4.26) 694 (4.80) 732 (4.81)</td>
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<tr>
<td>$\text{H}_2\text{-di(adj)-PcNcTh}$</td>
<td>334 (4.54) 429 (4.31) 672 (4.52) 702 (4.48) 756 (4.73)</td>
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<tr>
<td>$\text{H}_2\text{-di(opp)-PcNcTh}$</td>
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<tr>
<td>$\text{Zn-di-PcNcTh}$</td>
<td>357 (4.81) 697 (4.96) 732 (5.13)</td>
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</table>
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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.
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