

Synthesis of Schiff-base porphyrin derivatives and their self-assemblies to enhance photocatalytic performance

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EXPERIMENT

Synthesis of TAPP 500 mg TNPP, 2.6 g Na₂S and 160 mg NH₄Cl were dissolved in 50 mL DMF and reacted at 70 °C for 8 h. After cooling, they were filtered, washed with deionized water, and dried in vacuum. Purified by column chromatography, the purple powder solid TAPP was obtained. (Fig S1)

¹H NMR (CDCl₃, 25 °C, 500 MHz), δ ppm: 8.90 (s, 8H, C-H, pyrrole), 7.99 (d, 8H, Ar-H), 7.08 (d, 8H, Ar-H), 5.29 (s, 8H, ph-NH₂), -2.72 (s, 2H, -NH-, pyrrole). (Fig S2)

Synthesis of porphyrin derivative TCyPPP, TbePPP and TPyPPP 0.5 g (0.7 mmol) TAPP, 60 mL ethanol and 3.5 mmol aldehyde were stirred and dissolved. Add a little glacial acetic acid as a catalyst. Reflux at 90 °C for 8 h. Leave to rest until the reaction is over. It is then filtered and washed with anhydrous ethanol until the filtrate is colorless and vacuum dried.

5,10,15,20-tetra [p-(4-cyanophenylmethylene imino)] phenyl porphyrin (TCyPPP)

According to the above method, 0.5 g (0.7 mmol) TAPP and 0.46 g (3.5 mmol) p-cyanobenzaldehyde were taken to prepare compound TCyPPP. (Fig S1)

¹H NMR (CDCl₃, 25 °C, 500 MHz), δ ppm: 10.06 (s, 8H, C-H, pyrrole), 8.94 (s, 4H, -N=CH-), 8.27-8.25 (d, *J*=8.0 Hz, 8H, Ar-H), 7.94-7.96 (d, *J*=8.0 Hz, 8H, Ar-H), 7.62-7.64 (d, *J*=8.0 Hz, 8H, Ar-H), 7.08-7.10 (d, *J*=8.0 Hz, 8H, Ar-H), -2.74 (s, 2H, -NH- pyrrole). (Fig S3)

5,10,15,20-tetra [p-(P-benzylidene imino)] phenyl porphyrin (TbePPP)

According to the above methods, 0.5g (0.7 mmol) TAPP and 360 μl (3.5 mmol)

benzaldehyde were used to prepare compound TbePPP. (Fig S1)

^1H NMR (CDCl_3 , 25 °C, 500 MHz), δ ppm: 10.03 (s, 8H, C-H, pyrrole), 8.95 (s, 4H, -N=CH-), 8.81-8.79 (d, $J=8.0$ Hz, 8H, Ar-H), 8.24-8.22 (d, $J=8.0$ Hz, 8H, Ar-H), 8.07-8.05 (d, $J=8.0$ Hz, 8H, Ar-H), 7.56-7.54 (d, $J=8.0$ Hz, 8H, Ar-H), 7.03 (s, 8H, Ar-H), -2.70 (s, 2H, -NH- pyrrole).(Fig S4)

5,10,15,20-tetra [p-(4-pyridylmethylene imino)] phenyl porphyrin (TPyPPP)

According to the above method, 0.5 g (0.7 mmol) TAPP and 336 μL 4-pyridyl formaldehyde (3.5 mmol) were used to prepare compound TPyPPP. (Fig S1)

^1H NMR (CDCl_3 , 25 °C, 500 MHz), δ ppm: 10.05 (s, 8H, C-H, pyrrole), 8.81 (s, 4H, -N=CH-), 8.27-8.25 (d, $J=8.0$ Hz, 8H, Ar-H), 8.76-7.74 (d, $J=8.0$ Hz, 8H, Ar-H), 7.61-7.59 (d, $J=8.0$ Hz, 8H, Ar-H), 7.05-7.03 (d, $J=8.0$ Hz, 8H, Ar-H), -2.71 (s, 2H, -NH- pyrrole).(Fig S5)

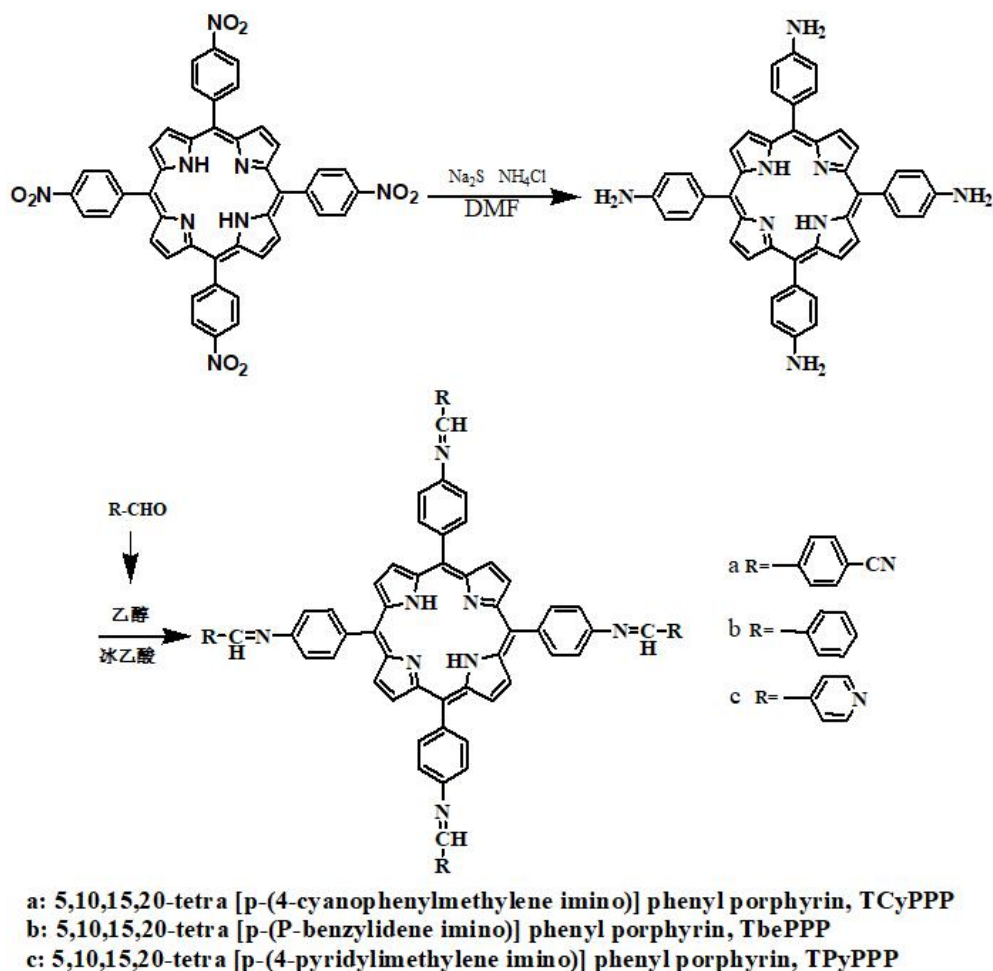


Fig S1 Synthetic routes of TAPP, TCyPPP, TbePPP and TPyPPP.

TAPP

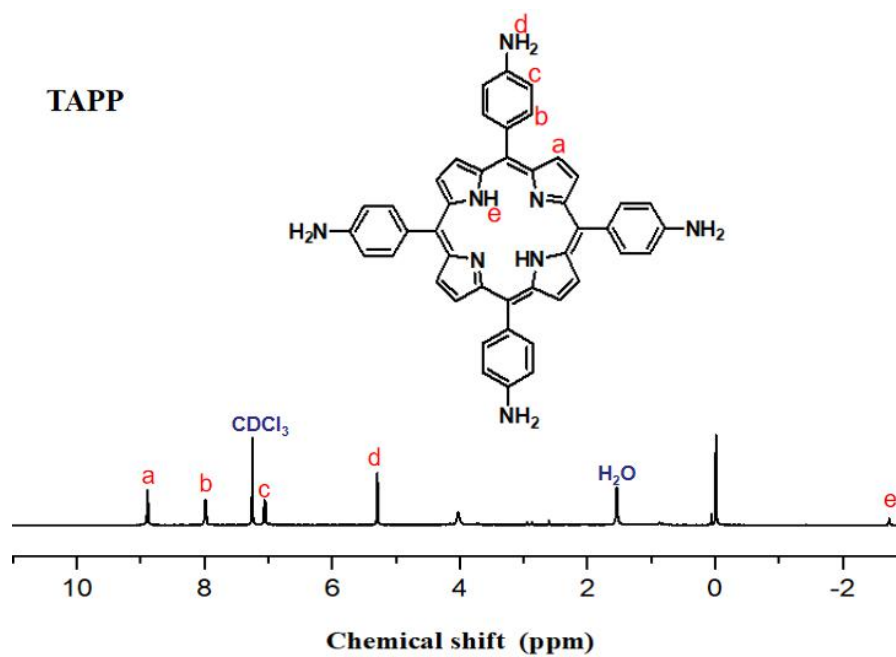


Fig S2 ¹H NMR spectrum of TAPP.

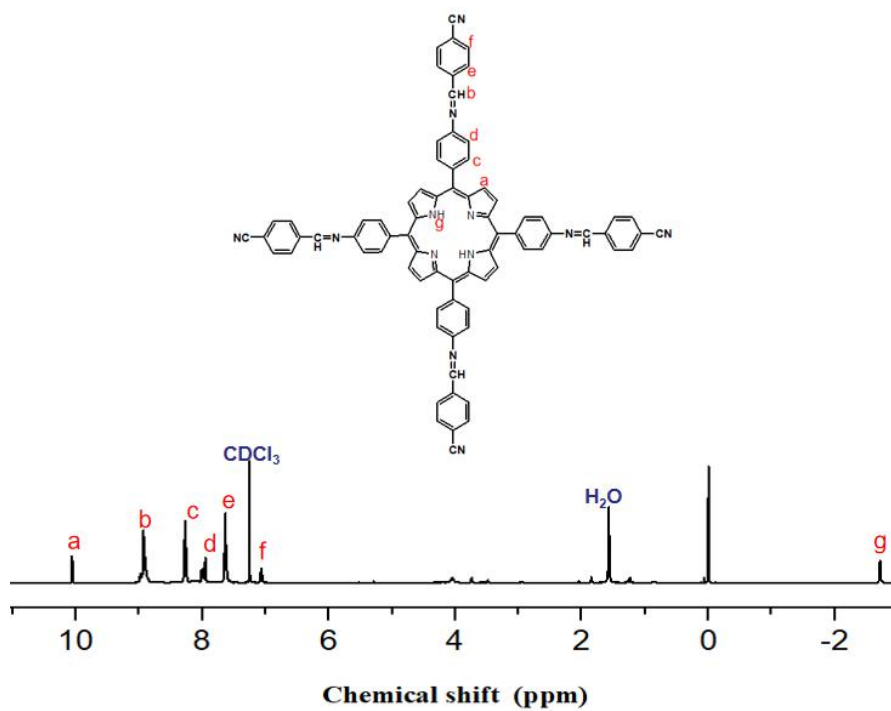


Fig S3 ¹H NMR spectrum of TCyPPP.

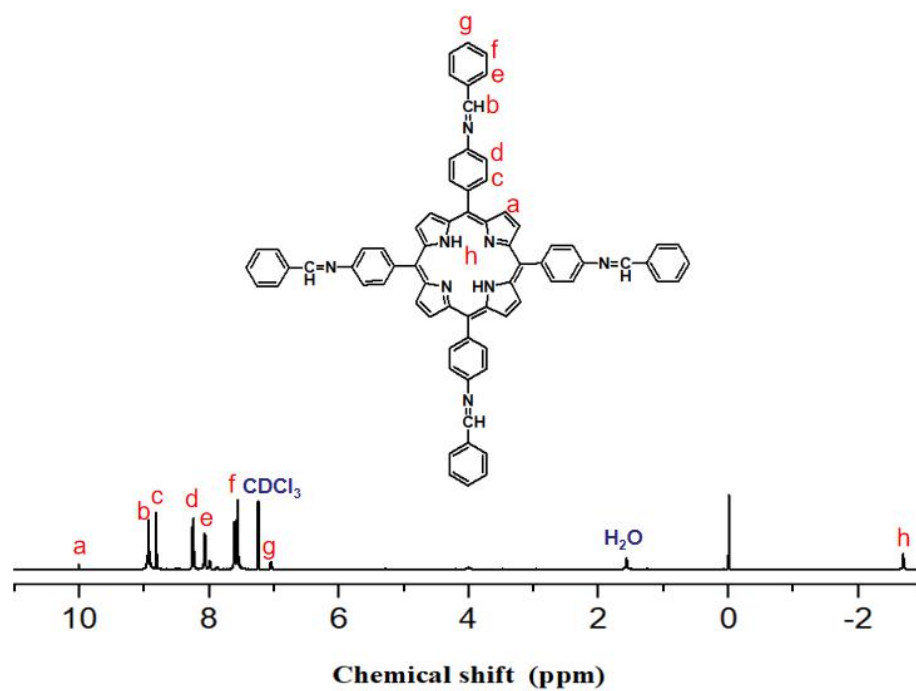


Fig S4 ¹H NMR spectrum of TbePPP.

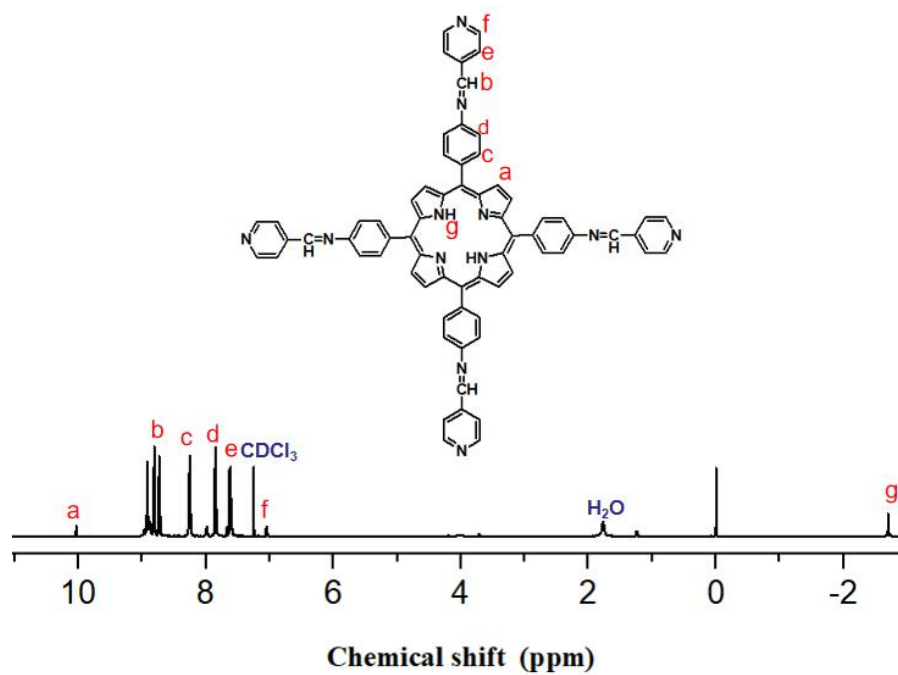


Fig S5 ¹H NMR spectrum of TPyPPP.