

# Electronic Supplementary Information

## Enhanced nonlinear optical properties of a $\pi$ -conjugated porphyrin dimer-graphene nanocomposite

Lulu Fu,<sup>a,b,1</sup> Yan Fang,<sup>b,1</sup> Rui Yang,<sup>a,1</sup> Zihao Guan,<sup>b</sup> Zhiyuan Wei,<sup>b</sup> Naying Shan,<sup>b</sup> Fang Liu,<sup>b</sup> Yang Zhao,<sup>b</sup> Mark G. Humphrey,<sup>c</sup> Chi Zhang<sup>\*a,b</sup> (✉)

<sup>a</sup> School of Chemical and Material Engineering, Jiangnan University, Wuxi, 214122, China

<sup>b</sup> China-Australia Joint Research Center for Functional Molecular Materials, School of Chemical Science and Engineering, Tongji University, Shanghai, 200092, China

<sup>c</sup> Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia

### 1. Experimental Procedures

#### 1.1 Materials

All materials were of chemical or analytical grade from Titan, Energy, and T&K Co. Ltd. Some solvents were dried and pre-purified for a specific use, for example, tetrahydrofuran (THF) and diethyl ether were dried and distilled over sodium, dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) was refluxed with calcium hydride and solvents with a high boiling point such as N, N-dimethylformamide (DMF) were purchased from J&K Co. Ltd. Petroleum ether (boiling point range of 60-90 °C), o-dichlorobenzene (ODCB), ethanol (EtOH), methanol, acetonitrile, N-methyl pyrrolidone (NMP), chloroform ( $\text{CHCl}_3$ ), ethyl acetate and triethylamine ( $\text{Et}_3\text{N}$ ) were used without further purification. All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques and eluent mixtures are reported in volume: volume.

#### 1.2 Characterization methods

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 400 MHz spectrometer using tetramethylsilane as an internal standard. Mass spectra were determined using a Bruker Daltonics ultrafleXtreme matrix-assisted laser-desorption ionization time-of-flight (MALDI-TOF) mass spectrometer. The nanocomposite solutions were sonicated using an ultrasonicator (Kunshan Hechuang Sonicator Instrument Co., Inc.) operating at 200 W and 40 kHz for a duration of 15 min.

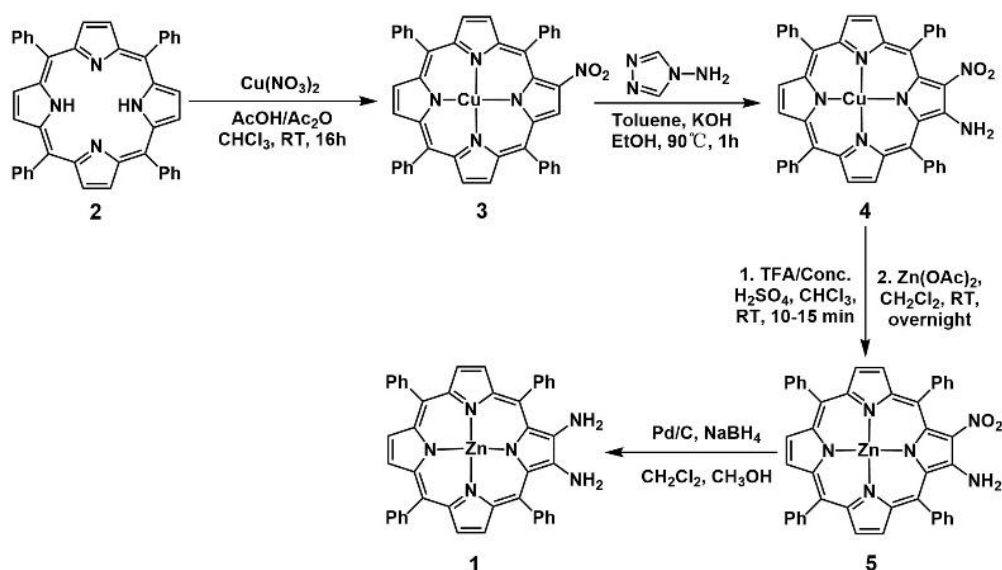


Fig. S1 Schematic depiction of the synthesis process of porphyrin 3, 4, 5, and 1.

#### 1.3 Preparation of porphyrin 3

Unlike traditional ways, the metallization of free radical porphyrins with copper ions and the nitration of porphyrin at  $\beta$  position were combined in one simple step with  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ . To a solution of 5,10,15,20-tetraphenylporphyrin (TPP, 1.23 g, 2.00 mmol) in 2,000 mL dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), was added a solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (1.33 g, 5.52 mmol) in mixed glacial acetic acid and acetic anhydride (1:6, 140 mL). The mixture was stirred for 16 h at ambient temperature and monitored by thin-layer chromatography (TLC). The resulting mixture was firstly washed with deionized water to remove a large amount of acid, after which the collected organic layer was further and successively washed with saturated  $\text{NaHCO}_3$  solution ( $2 \times 500$  mL) and deionized water. The finally combined organic layer was dried over  $\text{Na}_2\text{SO}_4$  and the solvents were evaporated under reduced pressure. Further purification was achieved by chromatography using silica gel and eluents of

CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (1:2), giving 2-nitro-5,10,15,20-(tetraphenylporphyrinato)copper(II) (3) (936 mg, yield 65%). (Since the copper ions metallized porphyrins are paramagnetic, porphyrin 3 and the following mentioned porphyrin 4 were not able to be confirmed with <sup>1</sup>H NMR and only characterized by MALDI-TOF-MS.) MS (MALDI-TOF): m/z calcd for C<sub>44</sub>H<sub>27</sub>CuN<sub>5</sub>O<sub>2</sub> 721.26, found 721.75 [M]<sup>+</sup>

#### 1.4 Preparation of porphyrin 4

The procedure for porphyrin 3 was according to the reported protocol.<sup>1</sup> A solution of porphyrin 3 (900 mg, 1.25 mmol) dissolved in 300 mL toluene was added to a solution of 4-amino-4H-1,2,4-triazole (3.11 g, 37.2 mmol) in 15 mL ethanol. The reaction mixture was heated to 90 °C. After the temperature of the mixture was stable, KOH (6.92 g, 123 mmol) was added and the system was further heated to 110 °C. The consumption of porphyrin 2 monitored by TLC took about 10 minutes and the reaction mixture was poured into cold water. Through several-time washing with deionized water, the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvents were evaporated under reduced pressure. The residue was further purified through chromatography using silica gel with CH<sub>2</sub>Cl<sub>2</sub>/ petroleum ether (1:1) as eluents and the fraction with higher polarity was collected as porphyrin 4 (825 mg, 1.13 mmol), yield 90%. MS (MALDI-TOF): m/z calcd for C<sub>44</sub>H<sub>28</sub>CuN<sub>6</sub>O<sub>2</sub> 735.16, found 735.77 [M]<sup>+</sup>

#### 1.5 Preparation of porphyrin 5

The demetallization process of porphyrin was based on a general procedure using mixed Conc. H<sub>2</sub>SO<sub>4</sub> and trifluoroacetic acid (TFA).<sup>2</sup> The obtained porphyrin 4 (733 mg, 1 mmol) was dissolved 35 mL CH<sub>2</sub>Cl<sub>2</sub>, to which a mixture of 35 mL Conc. H<sub>2</sub>SO<sub>4</sub> and 50 mL TFA was added dropwise and quickly. The reaction was carefully poured into 2000 mL cold water after vigorous stirring for 10-15 min at room temperature. The collected organic layer was further washed successively with saturated aqueous NaHCO<sub>3</sub> solution and deionized water. After dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the brown-green organic layer was directly reacted with the solution of Zn(OAc)<sub>2</sub> (1.28g, 7.00 mmol) in 15 mL methanol. The resulting mixture was stirred overnight under ambient temperature. After removal of solvents under reduced pressure, the residue was purified by chromatography using silica gel with CH<sub>2</sub>Cl<sub>2</sub>/ petroleum ether (3:2) as eluents and the bright-green fraction was collected as porphyrin 5 (515 mg, 0.70 mmol), yield 90%. <sup>1</sup>H NMR (600 MHz, CHCl<sub>3</sub>-d, δ (ppm)): 8.96 (1H, d, J = 15.0 Hz, H-pyrrole), 8.88 (1H, d, J = 15.0 Hz, H-pyrrole), 8.72 (1H, d, J = 15.0 Hz, H-pyrrole), 8.69 (1H, d, J = 15.0, H-pyrrole), 8.59 (1H, d, J = 15.0 Hz, H-pyrrole), 8.43 (1H, d, J = 15.0 Hz, H-pyrrole), 8.18-8.01 (10H, m, H-phenyl), 7.90-7.77 (8H, m, H-phenyl), 6.89 (2H, br s, NH<sub>2</sub>). MS (MALDI-TOF): m/z calcd for C<sub>44</sub>H<sub>28</sub>ZnN<sub>6</sub>O<sub>2</sub> 736.21, found 736.34 [M]<sup>+</sup>

#### 1.6 Preparation of porphyrin 1

The reduced procedure was according to the reported protocol.<sup>3</sup> Porphyrin 5 (400 mg, 0.54 mmol) was dissolved in a mixture of CH<sub>2</sub>Cl<sub>2</sub> and methanol (10: 1, 220 mL). After bubbling with N<sub>2</sub> for 20 minutes, the mixture was added with 600 mg 10% palladium on activated carbon (Pd/C) and vigorously stirred under an N<sub>2</sub> atmosphere for further 10 minutes. To the resulting mixture, NaBH<sub>4</sub> (532 mg, 14.4 mmol) was added in portions and the mixture was stirred under monitoring until the complete consumption of porphyrin 5 (ca. 2h). The mixture was then filtered through a plug of Celite using CH<sub>2</sub>Cl<sub>2</sub> as the eluent (100 mL), giving a crude product of porphyrin 1 in CH<sub>2</sub>Cl<sub>2</sub>. Due to the instability of two amino groups at neighbouring β positions on porphyrin, the crude solution of porphyrin 1 was directly used in the next step without further purification.

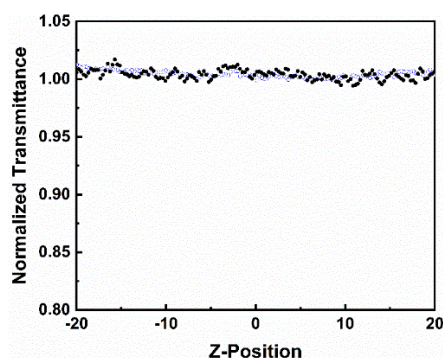


Fig. S2 Open-aperture Z-scan curves for blank solvent DMF at 532 nm wavelength with an input influence of 20 μJ.

## Notes and References

- 1 K. P. Birin, I. A. Abdulaeva, A. I. Poddubnaya, Y. G. Gorbunova and A. Y. Tsivadze, *Dyes Pigments*, 2020, **181**,108550.
- 2 S. Ostrowski and S. Grzyb, *Tetrahedron Lett.*, 2012, **53**, 6355.
- 3 K. P. Birin, A. I. Poddubnaya, A. Abdulaeva, Y. G. Gorbunova and A. Y. Tsivadze, *Dyes Pigments*, 2018, **156**, 243.