## **Electronic Supplementary Information**

# Zn-Phthalocyanine Functionalized Nanometal and Nanometal-TiO<sub>2</sub> hybrid materials: Aggregation behavior and Excited state dynamics

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## 1. Synthesis of Phthalonitrile derivatives

## a. Synthesis of 4- (p-amino) phenoxyphthalonitrile (4-APOPN)

To 0.692 g (0.004 M) of 4-nitrophthalonitrile (Scheme IV.2.1) and 0.528 g (0.0044 M) of p-amino benzoic acid, 1 equivalent of K<sub>2</sub>CO<sub>3</sub> was added and dissolved in 8 mL of DMF, stirred at room temperature under Argon atmosphere for 16 hr. The reaction mixture was poured into water and the precipitate obtained was filtered, washed and dried. Yield: 0.43 g (70%), m.p.108-110 °C, IR(KBr)  $\upsilon_{max}$ (cm<sup>-1</sup>): 3456.33 (NH<sub>2</sub>), 2235.31 (C=N), 1607.48 (N-H), 1562.26 (C=C), 1283.38 (C-N), 1254.02 (C-O-C), 1088.10 (C-H), <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, ppm): 8.02-8.05 (d, 1H; Ar-H), 7.62 (s, 1H, Ar-H), 7.23-7.27 (m, 1H; Ar-H), 6.84-6.87 (d, 2H, Ar-H), 6.62-6.65 (d, 2H, Ar-H), 5.21 (s, 2H, NH<sub>2</sub>). Presence of C=N, C-O-C, NH<sub>2</sub> vibrations in the IR spectrum and NH<sub>2</sub> signal in the <sup>1</sup>H NMR spectrum indicates the formation of 4-APOPN.

## b. Synthesis of 4- (p-thiocticamido) phenoxyphthalonitrile (4-TAPOPN)

About 0.47 g (0.002 M) of 4-(p-amino) phenoxyphthalonitrile (Scheme IV.2.1), 0.41 g (0.002 M) of thioctic acid and 0.52 g (0.003 M) of dicyclohexyl carbodiimide were taken in a 50 mL RB flask dissolved in 5 mL of dichloromethane, provided with water condenser and kept in an oil bath. The reaction mixture was stirred under argon atmosphere at 60 °C. To this 0.12 g (0.001 M) of dimethylaminopyridine in 2 mL of dichloromethane was added in drops and the reaction mixture was stirred for 24 hrs. After completion of the reaction, solvent was evaporated, purified by column chromatography using chloroform/methanol (v/v, 9:1) as eluent. Yield: 0.25 g (35%), m.p 106-108 °C, IR(KBr)  $\upsilon_{max}$ (cm<sup>-1</sup>): 2929.25, 1487.12 (CH<sub>2</sub>), 2850.60 (CH), 2230.66 (C=N), 1658.59, 1525.57 (CO-NH), 1591.33 C=C), 1244.26, 1157.76 (C-O-C), 1088.79 (C-H), <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, ppm): 10.03 (s, 1H; NH), 8.05-8.08 (d, 1H, Ar-H), 7.62-7.69 (m, 3H; Ar-H), 7.31-7.35 (m, 1H, Ar-H), 7.11-7.14 (d, 2H, Ar-H), 1.36-3.67 (m, 13H; Aliphatic-H). Presence of C=N, CO-NH and CH<sub>2</sub> group frequencies in the IR spectrum and <sup>1</sup>H NMR signals for NH proton and aliphatic protons indicates the formation of 4-TAPOPN.

### c. Synthesis of 4- aminophthalonitrile (4-APN)

About 0.692 g (0.004 M) of 4-nitrophthalonitrile (Scheme IV.2.2) was dissolved in 25 mL of ethanol, taken in a 100 mL RB flask kept. To this 0.3 g of iron powder<sup>1</sup> and 0.5 mL of saturated ammonium chloride solution and 2 drops of con.HCl were added and refluxed for 4

hrs. The reaction mixture was filtered and the filtrate was concentrated to 5 mL. The filtrate was poured into ice water. The precipitate obtained was collected and dried. Yield: 0.4 g (46%), m.p.179-181 °C, IR(KBr)  $\upsilon_{max}$  (cm<sup>-1</sup>): 3490.79 (NH<sub>2</sub>), 2232.45 (C=N), 1598.31 (N-H), 1507.20 (C=C), 1266.03 (C-N), 1100.83 (C=C), <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, ppm): 7.63-7.66 (d, 1H, Ar-H), 7.02 (s, 1H; Ar-H), 6.86-6.89 (d, 1H, Ar-H), 6.41 (s, 2H, NH<sub>2</sub>). Presence of NH<sub>2</sub> and C=N group vibrations in the IR spectrum and <sup>1</sup>H NMR signal for NH<sub>2</sub> protons indicates the formation of 4-APN.



Scheme S.1. Synthesis of 4-APOPN, 4-TAPOPN

## d. Synthesis of 4- thiocticamidophthalonitrile (4-TAPN)

Reaction of 0.29 g (0.002 M) of 4-aminophthalonitrile with (Scheme IV.2.2) 0.41 g (0.002 M) of thioctic acid and 0.52 g (0.003 M) of dicyclohexyl carbodiimide in 5 mL of dichloromethane were stirred at 60 °C in an oil bath under argon atmosphere. To this 0.12 g (0.001 M) of 4-dimethylaminopyridine in 2 mL of dichloromethane was added in drops and the reaction mixture was stirred for 24 hrs. After completion of the reaction, solvent was evaporated, purified by column chromatography using chloroform/methanol (v/v, 9:1) as eluent. Yield: 0.16 g (39%), m.p 80-82 °C, IR(KBr)  $\upsilon_{max}$ (cm<sup>-1</sup>): 2923.16 (CH<sub>2</sub>), 288.50 (C-H), 2229.80 (C=N), 1634.63, 1521.20 (CO-NH), 1598.48 (C=C), 1080.15 (C-H), <sup>1</sup>H NMR

(DMSO-d<sub>6</sub>, ppm): 10.73 (s, 1H; NH), 7.67-7.70 (d, 1H, Ar-H), 7.06-7.07 (d, 1H; Ar-H), 6.90-6.94 (m, 1H, Ar-H), 1.46-3.68 (m, 13H; Aliphatic-H). Presence of  $C\equiv N$ , CO-NH and CH<sub>2</sub> group frequencies in the IR spectrum and <sup>1</sup>H NMR signals for NH proton and aliphatic protons indicates the formation of 4-TAPN.



Scheme S.2. Synthesis of 4-APN, 4-TAPN

# 2. NMR Spectrum of TAZnPc1/2/3



Figure S.1. <sup>1</sup>H NMR spectrum of TAZnPc1



Figure S.2. <sup>1</sup>H NMR spectrum of TAZnPc2



Figure S.3. <sup>1</sup>H NMR spectrum of TAZnPc3

## 3. HR-MS Spectrum of TAZnPc1/2/3

#### **Elemental Composition Report**

#### Single Mass Analysis

Tolerance = 200.0 mDa / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions 93 formula(e) evaluated with 1 results within limits (all results (up to 2000) for each mass)



## Figure S.4. HR-MS spectrum of TAZnPc1



Figure S.5. HR-MS spectrum of TAZnPc2

#### **Elemental Composition Report**

Single Mass Analysis Tolerance = 200.0 mDa / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

93 formula(e) evaluated with 1 results within limits (all results (up to 2000) for each mass)



Figure S.6. HR-MS spectrum of TAZnPc3

#### 4. Synthesis of TAZnPc Functionalized Nanoparticles

#### a. Synthesis of TAZnPc Functionalized Gold Nanoparticles

The TAZnPc (TAZnPc1, TAZnPc2 & TAZnPc3) functionalized gold nanoparticles was synthesized by stirring a mixture of 2 ml of (0.2 mM) TAZnPc and 0.2 ml of (0.2 M) NaBH<sub>4</sub> in a 50 mL RB flask at room temperature. After 2 min. of stirring 0.2 mL of (20 mM) HAuCl<sub>4</sub> was added in drops and then stirred for 2 hrs. The color of the solution was changed from green to dark pink color. The solution was centrifuged thrice and the precipitate obtained was collected, dispersed in DMF and used for studies.

### b. Synthesis of TAZnPc Functionalized Silver Nanoparticles

The TAZnPc (TAZnPc1, TAZnPc2 & TAZnPc3) functionalized silver nanoparticles was synthesized by stirring a mixture of 2 ml of (0.2 mM) TAZnPc and 0.2 ml of (0.2 M) NaBH<sub>4</sub> in a 50 mL RB flask at room temperature. After 2 min. of stirring 0.2 mL of (20 mM) AgNO<sub>3</sub> was added in drops and stirred for 2 hrs. The color of the solution changes from green to dark brown color. The solution was centrifuged thrice and the precipitate obtained was collected, dispersed in DMF and used for studies.

- **5.** Characterization of Functionalized Nanoparticles
- a. HR-TEM Image



Figure S.7. HR-TEM Image of a) TAZnPc1/GNP, b) TAZnPc1/SNP



Figure S.8. HR-TEM Image of a) TAZnPc2/GNP, b) TAZnPc2/SNP



Figure S.9. HR-TEM Image of a) TAZnPc3/GNP, b) TAZnPc3/SNP

## 6. Synthesis of TAZnPc/TA Functionalized Gold and Silver Nanoparticles

Synthesis of TAZnPc/TA/GNP and TAZnPc/TA/SNP (Scheme IV.13) were done by taking 1.5 mL (0.2 mM) of TAZnPc, 0.25 mL (2 mM) of thioctic acid (TA) and 0.1 mL (0.2 M) of NaBH<sub>4</sub> in a 50 mL RB flask and stirred at room temperature. After 2 minutes of stirring 0.1 mL of (20 mM) HAuCl<sub>4</sub>/AgNO<sub>3</sub> was added in drops and then stirred for 2 hrs. The prepared solution was used for sensitization of TiO<sub>2</sub> film. The dithiol group was reduced to SH group and covalently linked to the nanoparticle surface. The COOH end of thioctic acid was used to adsorb on TiO<sub>2</sub> film.

## 7. Preparation of TAZnPc functionalized nanoparticle-TiO<sub>2</sub> hybrid film

4-µm TiO<sub>2</sub> nanocrystalline films were prepared from a commercially available TiO<sub>2</sub> paste (Solaronix SA, Ti-Nanoxide HT/SC series). This paste was deposited on a transparent glass substrate by using the doctor blade technique. The prepared films were annealed for 30 mins at 450 °C. The TiO<sub>2</sub> films were sensitized with TAZnPc/TA functionalized gold/silver nanoparticle solution at room temperature for 5h. After removal from the dye bath, the non-adsorbed molecules were washed off by rinsing the film with the same solvent and the film was dried at room temperature for ~20 s.

## 8. References

 Synak, A.; Gil, M.; Organero, J. A.; Sánchez, F.; Iglesias, M.; Douhal, A.; J. Phys. Chem. C, 2009, 113, 19199-19207.