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Supplementary Material

Morphology Induced Enhanced Photoconductivity of Phthalocyanine-Based Benzimidazole Linked Two-Dimensional Conjugated Covalent Organic Polymer

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Materials and Methods

All reagents and solvents were purchased from commercial suppliers and used without further purification. Ni(II) octa-amino phthalocyanine was synthesized according to the reported procedure.¹ Fourier transform infrared (FTIR) spectra were recorded between 4000 and 650 cm⁻¹ using a Perkin Elmer Spectrum 100 FT-IR spectrometer with an attenuated total reflection (ATR) accessory featuring a zinc selenide (ZnSe) crystal. The samples were analyzed with XPS using an Al K α x-ray (hv = 1486.6 eV) source and a hemispherical electron analyzer (Phoibos 100, SPECS GmbH). The base pressure of the analysis chamber was 1.33×10^{-8} Pa during the measurements. Diffuse reflectance spectra (DRS) were recorded in the wavelength range of 200-800 nm using an ISR-2600-Plus Shimadzu spectrophotometer with integrating spheres. Thermogravimetric analysis (TGA) was carried out on a Mettler Toledo Stare Thermal Analysis System at a heating rate of 10 °C min⁻¹ over a temperature range of 25–900 °C under a nitrogen flow (50 mL min⁻¹). Powder X-ray diffraction (PXRD) measurements were carried out on a Bruker Advanced D8 Xray diffractometer with Cu K α ($\lambda = 1.5405$ Å) radiation source operating at 30 kV and 30 mA. The patterns were recorded over the 2 Θ range of 1–50° with step size = 0.02°. The surface morphology and energy dispersive X-ray analysis (EDX) were recorded with an FEI (PHILIPS) XL30 SFEG scanning electron microscope (SEM). The elemental analysis measurement was performed by Thermo Scientific- Flash 2000. Dynamic light scattering (DLS) and zeta potential measurements were performed on a Malvern Zetasizer NanoSeries. The nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020M system. The samples were outgassed at 120 °C for 8 h before the measurements. Surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) methods. The pore-size-distribution curves were obtained from the adsorption branches using the non-local density functional theory (NLDFT) method.

Synthetic Procedures

Ni(II) octa-amino phthalocyanine was synthesized according to the previous reported procedures.^{1,2}



2,3,9,10,16,17,23,24-octa-tosylamidophthalocyanine Ni(II)

A mixture of 1.87 g (4.00 mmol) of compound 2, 0.52 g (4.00 mmol) of anhydrous NiCl₂, 0.9 ml (6.00 mmol) of DBU and 6 ml of dried n-hexanol was heated to reflux for 18 h under argon atmosphere. The solvent was completely removed under reduced pressure and the crude product was washed with ethanol several times, dissolved in 70 ml of a mixture of acetic acid– CH₂Cl₂ (1 : 5). Then, it was extracted with distilled water (4 100 ml) and the organic solution was dried over anhydrous Na2SO4 and concentrated. The dark green-blue product was purified over silica gel with CH₂Cl₂ as the eluent. Yield 0.75 g (%26); anal. Calc. for C₈₈H₇₂N₁₆NiO₁₆S₈: C, 54.91; H, 3.77; N, 11.64; found C, 54.63; H, 4.07; N 11.36%; IR v_{max}, cm⁻¹: 3547 (free NH), 3233 (H-bonded NH), 3068 (CHAr), 2925 (CH3), 1621 (C=N), 1598, 1534, 1468, 1438, 1402, 1338 (SO₂), 1294, 1161 (SO₂), 1090, 1055, 1020, 919, 812, 753, 706, 668, 546. MS (ES-MS), m/z (%): 1925 (100) [M+ 1]⁺, 1924 (88) [M]⁺.

Synthesis of 2,3,9,10,16,17,23,24-octaaminophthalocyanine Ni(II)

To a mixture of concentrated (98%) sulfuric acid (3 mL), and distilled water (0.4 mL) was added compound **1** (150 mg, 0.078 mmol), heated to 100 °C and stirred for 2 h at this temperature. Then

the reaction mixture was cooled to ambient temperature and poured into icewater (20 mL). Green precipitate was separated by centrifuge and washed with distilled water until filtrate become neutral. The obtained sulfate salt of the product was mixed with 10% NaOH (aq) solution (10 mL) to neutralize. The solid was washed with distilled water and then with ethanol. Yield: 30mg (56%). Anal. calcd. for $C_{32}H_{24}N_{16}Ni$: C, 55.49; H, 3.50; N, 32.42. Found C, 55.30; H, 3.68; N 32.65%. IR v_{max} , cm⁻¹ 3344 (NH), 1623 (C=N), 1530, 1480, 1430, 1356, 1294, 1216, 1113, 1052, 872, 801, 747, 515, 441. MS (ES-MS): *m/z* (%) 691 (100) [M + H]⁺. ¹H-NMR (DMSO-d⁶): δ , ppm 8.36 (s, 8 ArH), 5.59 (s, 8 NH).

Synthesis of NiPc-COP1



2 neck 50 ml round bottom flash 40 mg (0.058 mmol) octa-amino Ni(II) phthalocyanine solved in 10 ml DMF under ice bath and argon atmosphere. 15 mg (0.012 mmol) terephthalaldehyde solved in 10 ml DMF and solution was dropped and mixture 1 hour. After dripping, air was bubbled through the reaction mixture for 20 minutes. The mixture was tightly sealed by placing it in a 50 ml reaction reactor and heated at 145 ° C for 7 days. After cooling to room temperature, the precipitate was collected by centrifugation, washed with ethanol, dichloromethane, DMF and acetone for several times and dried at 110 °C under vacuum 2 days.

Film preparation:

The Au / SiO2 / Si substrate half was covered with a teflon tape. The substrate was placed horizontally into the reactor from the solvothermal process. At the end of the reaction period, the substrate was carefully removed and dried at 110 $^{\circ}$ C for 2 days in the vacuum oven.



Figure S1. High resolution C1s XPS profile of NiPc-COP1

X-ray Photoelectron Spectroscopy

A survey spectrum was obtained from 0 eV–1400 eV to obtain elemental surface composition. High resolution spectra were then obtained at energy regions specific to elements observed in the survey spectrum (C 1s, N 1s, O 1s, Ni 2p 3/2).



Figure S2. High resolution N1s XPS profile of NiPc-COP1



Figure S3. High resolution Ni2p XPS profile of NiPc-COP1



Figure S4. EDS showing an even distribution of constituent elements C, N and Ni for NiPc-COP1

| 1 | Element % | | Ma: | | | |
|-----------------------------|-----------|--------------|--------------|--|--|--|
| Sample Name | Nitrogen | Carbon | Hydrogen | | | |
| Calculated | 25,74 | 65,25 | 2,74 | | | |
| | | 51 05 | | | | |
| 1 | 25,42 | 61,85 | 2,99 | | | |
| 2 | 24,99 | 61,99 | 3,01 | | | |
| 3 | 25,36 | 62,05 | 2,78 | | | |
| 3 Sample(s) in Group No : 1 | | | | | | |
| Component Name | Average | Std. Dev. | % Rel. S. D. | | | |
| Nitrogen | 25,26 | 0,23 | 0,92 | | | |
| Carbon | 61,96 | 0,10 | 0,17 | | | |
| Hydrogen | 2,93 | 0,13 | 4,35 | | | |

Figure S5. Elemental analysis of NiPc-COP1



Figure S6. SEM images of NiPc-COP1

Zeta Potential Distribution



Figure S7. Zeta potentials of NiPc-COP1 in water.

Size Distribution by Volume



Figure S8. Size distributions of NiPc-COP1 measured by DLS.



Figure S9. Tyndall effect of disperse NiPc-COP1 in H₂O.

Simulation methods.

A self-consistent ground-state calculation was performed with the ABINIT code to obtain the detailed electronic structure.³ The electronic structure calculations were performed in the generalized gradient approximation with the Perdew–Burke–Ernzerhof exchange–correlation energy functional.⁴ Orbitals were expanded in plane waves up to a cutoff of 30 Hartrees. The pseudopotential generated in our work was one of those of Troullier–Martins.⁵ The nonshift 4x26x4 (4x4x26) Monkhorst–Pack k-mesh was used to generate k-points in the irreducible Brillouin zone, which was enough to obtain a dense mesh of energy eigenvalues.⁶ To bring the atoms to their equilibrium positions, we performed structural relaxation as implemented in the ABINIT code, which was stopped after the forces on all atoms were less than 0.01 mRy/Å in the relaxed structure.

We report the theoretically predicted structures having the network topologies for NiPc-COP1. This compound has four isomers (Fig. S10) and we constructed the models for all isomers of given compounds followed by their simulation by ABINIT code. The calculated total energies for family compounds of NiPc-COP1 having the eclipsed structures are presented in Table S1. The found unit cell parameters for both eclipsed and staggered structures are presented in Table S2. The PXRD profile of studied compound contains the low angle diffraction peak in vicinity of $2\theta = 4.5 - 6.0^{\circ}$ which is characteristic for expected large unit-cell parameters. Meanwhile this broad peak indicates on presence of amorphous fraction in the sample. The comparison of observed experimental PXRD peaks and calculated ones for staggered and eclipsed constructed structures



Figure S10. Experimental background subtracted PXRD pattern of NiPc-COP1

revealed some corresponds between on eclipsed and staggered profiles in vicinity of low-angels peaks. However, experimental PXRD of **NiPc-COP1** is not exact match with neither structure which shows lack of specific alignment.



Figure S11. Isomers of NiPc-COP1

Table S1. Total energy of isomers of NiPc-COP1

| | E _{total} , eV | | | | | |
|-----------|-------------------------|----------|----------|----------|--|--|
| | İsomer 1 | İsomer 2 | İsomer 3 | İsomer 4 | | |
| NiPc-COP1 | -479.363 | -479.360 | -479.322 | -479.357 | | |



Figure S12. Comparison of NiPc-COP1 observed PXRD and calculated profiles for eclipsed and staggered structures.

| Table S2 | . The | lattice | constants | of | for | ecli | psed | and | staggered | structures. | |
|----------|-------|---------|-----------|----|-----|------|------|-----|-----------|-------------|--|
| | | | | | | | 1 | | 00 | | |

| | eclipsed | staggered |
|----------------|----------|-----------|
| Q | | |
| <i>a=b</i> , Å | 22.710 | 22.745 |
| <i>c</i> , Å | 3.4898 | 7.0860 |
| Space group | Pm | C2/m |
| ? ±= ?? = ?? | | 90?° |



Figure S13. N₂ adsoption/desorption isotherms of **NiPc-COP1** measured at 77 K, filled and empty symbols represent adsorption and desorption, respectively.

Optical Band Gap Measurement

The optical band gap of **NiPc-COP1** has been investigated with evaluation of reflectance (DRS) with the following relational expression (1) proposed by Tauc, Davis^{7,8}, and Mott⁹ is used. Data for



Figure S14. Pore size distribution of NiPc-COP1 calculated from N₂ isotherms calculated using NLDFT.

these plots were obtained from the diffuse reflectance versus wavelength spectral data run using Schimadzu 2600 UV-Vis-NIR spectrometer.

$$(h\nu\alpha)^{1/n} = A(h\nu - Eg) \tag{1}$$

Where:

h: Planck's constant, **v**: frequency of vibration, **α**: absorption coefficient, **Eg**: band gap, **A**: proportional constant.

The value of the exponent **n** denotes the nature of the sample transition. For direct allowed transition **n** = **0.5** and for indirect allowed transition **n** = **2**. The band gap values were determined from the intersect of the tangent of the onset of reflection, expressed as $(hv\alpha)^{1/n}$ with the x-axis. We found that the indirect allowed transition Tauc factor (n=2) cannot provide a satisfactory fitting. However, a decent linear fit was obtained for n = 0.5 which indicates that band gap of **NiPc-COP1** possess allowed direct transitions. Therefore, the direct allowed transition Tauc factor **n** = 0.5 is used for all our calculations.

Electrical and photoconductivity measurements,

To investigate the photovoltaic and photoconductive properties of NiPc-COP1, monochromatic light was used within the wavelength range of 500–1000 nm. To produce this tunable monochromatic light, the radiation from a 300 W Xenon lamp (by Thermo Oriel) was passed through a Triax 550-type UV-visible spectrophotometer. Photoconductivity and I-V measurements were performed using a programmable electrometer (Keithley 6517b). A Janis closed-cycle optical type helium cryostat was used to cool the samples. A control sensor (diode DT 470) and a resistive heater were used to adjust the temperature within an accuracy of ~0.1 K by using Lake Shore 340 temperature controller.

For electrical and photoconductivity measurements, the films were grown on Au/SiO₂/Si substrates. Then, Au electrodes with a thickness of ca. 100 nm were coated on the grown films via thermal evaporation method. The base pressure of the thermal evaporation chamber was 5×10^{-4} Pa and a wolfram boat (Kurt Lesker, 3.5" length \times 0.5" width \times 0.125" deep) was used for evaporation of metallic Au. Two different electrode structures were performed, sandwich and parallel contact, to understand the effect of the film formation on the electrical behavior (See

Figure 1). We used top contacts for surface measurements and sandwich contacts for bulk measurements.

For I-V and photoconductivity measurements, samples were kept at ~ 0.6 Pa vacuum, and at 300 K. I-V measurements were performed in the range of from -10 to +10 V with 50 mV steps. In addition, current vs. temperature measurement was performed with a constant voltage of 10 V at a step rate of 1 K between 30 K and 300 K. The dc conductivity dependent temperature is defined using the relation:

$$\sigma_{dc} = \sigma_0 \exp^{-E_A / kT}$$

where E_A is the activation energy, *T* is the temperature, *k* is the Boltzmann's constant, and σ_0 is the constant proportionally.



Figure S15. Wavelength-dependent on-off switching of photocurrent of **NiPc-COP1** at a bias voltage of 10 V

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