Electronic Supplementary Information

Formation of Built-in Field at Porphyrin/ITO Interface Directly Proven by Time-Resolved Photovoltage Technique

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The structure and synthetic procedure of two porphyrin compounds are displayed in Figure S1. The porphyrin monomer, hydroxylphenyl porphyrin (H_2MHTPP, structure a), was synthesized by following the procedures described elsewhere.[1, 2] Typically, p-hydroxybenzaldehyde (2.3g, 18.9 mmol) and benzaldehyde (5.7 mL, 55.8 mmol) dissolved in 300 mL propionic acid were vigorously stirred and heated at reflux. Then the freshly distilled pyrrole (5.3 mL, 102.3 mmol) was added intomixture. After an additional 2 h, the reaction mixture was cooled, diluted with 100 mL ethanol and allowed to stand overnight. The black and purple powder was obtained after filtration and ethanol washing for five times to give a mixture, and then it was dried in a vacuum oven at 70 °C for 8 h. The crude product was separated further by using silica gel column chromatography with chloroform as eluent initially and with chloroform/ethanol solution of different ratio gradually. The porphyrin dimer (structure b) was synthesized by direct condensation between two hydroxylphenyl porphyrin.[3] H_2MHTPP (201.6 mg, 0.32 mmol) dissolved in 30 mL of dried CHCl3, and fumaryl chloride (50 μL, 0.46 mmol) was slowly added to the solution. The mixture was stirred for 48 h at room temperature. Then the crude product was chromatograhed on silica gel (100-200 mesh), with $CHCl_3$ as an eluent. The first fraction was the desired product of dimer.

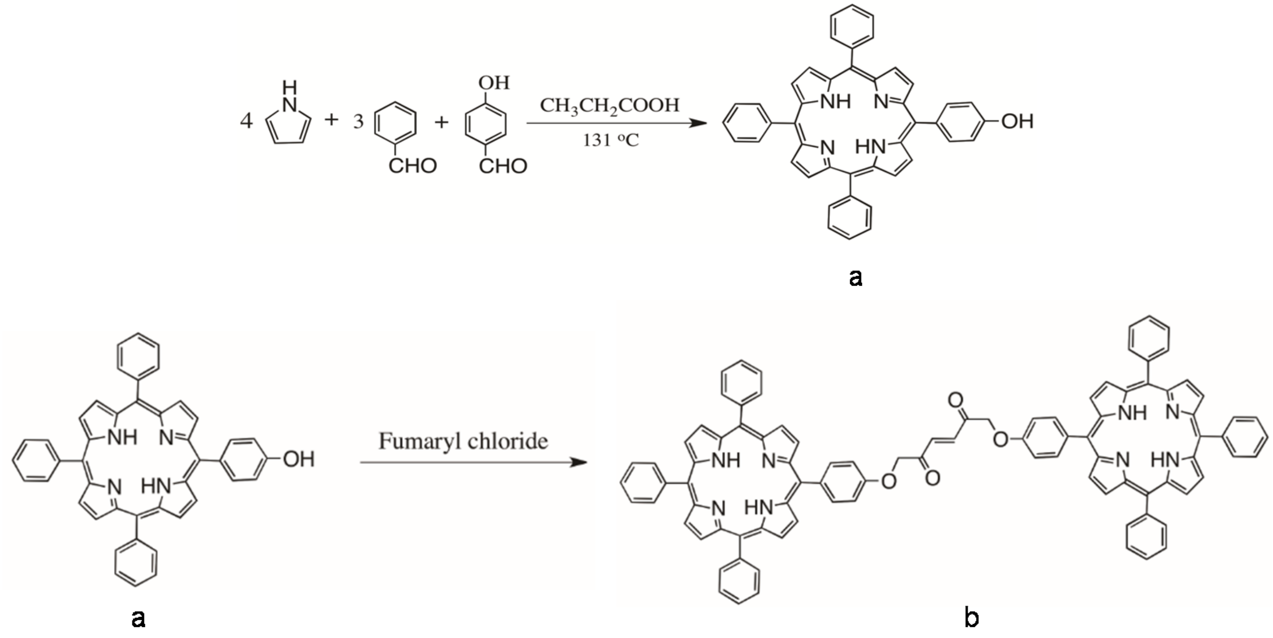

Figure S1. Structures and synthetic procedure of the porphyrin monomer (a) and dimer (b).

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1. R. G. Little, *Journal of Heterocyclic Chemistry*, 1981, **18**, 129-133.
2. Y. Y. Shi, W. Q. Zheng, X. Q. Li, L. X. Yu and X. Q. Wang, *Chem. J. Chin. Univ.-Chin.*, 2005, **26**, 9-12.
3. W. Q. Zheng, N. Shan and X. Q. Wang, *Chemical Research in Chinese Universities*, 2008, **24**, 20-23.

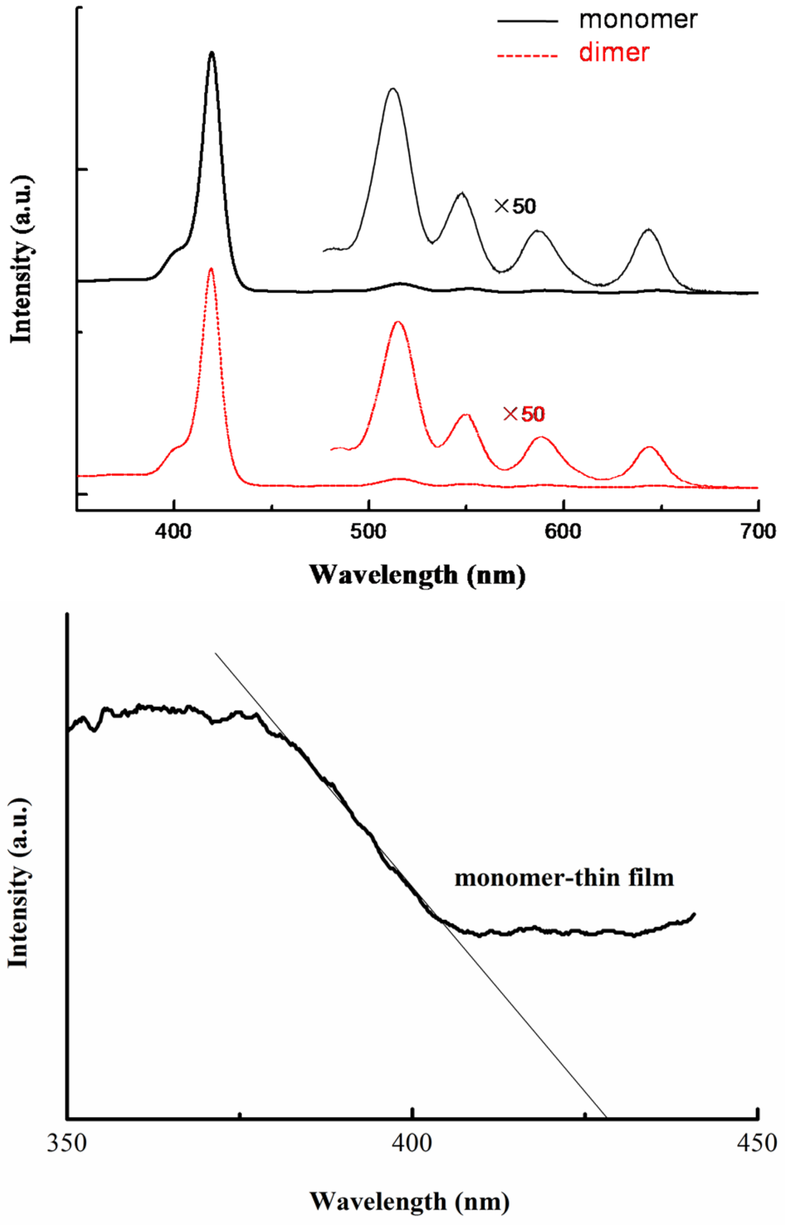

Figure S2. UV-Vis spectra of porphyrin powder (top) and porphyrin film (bottom). Both the monomer and dimer samples have nearly the same band gap and ground state. Also, the band gap is basically the same for both powder and film samples of porphyrin monomer. Effects of chemical modification or morphology engineering on the electronic structure of samples are thus negligible.

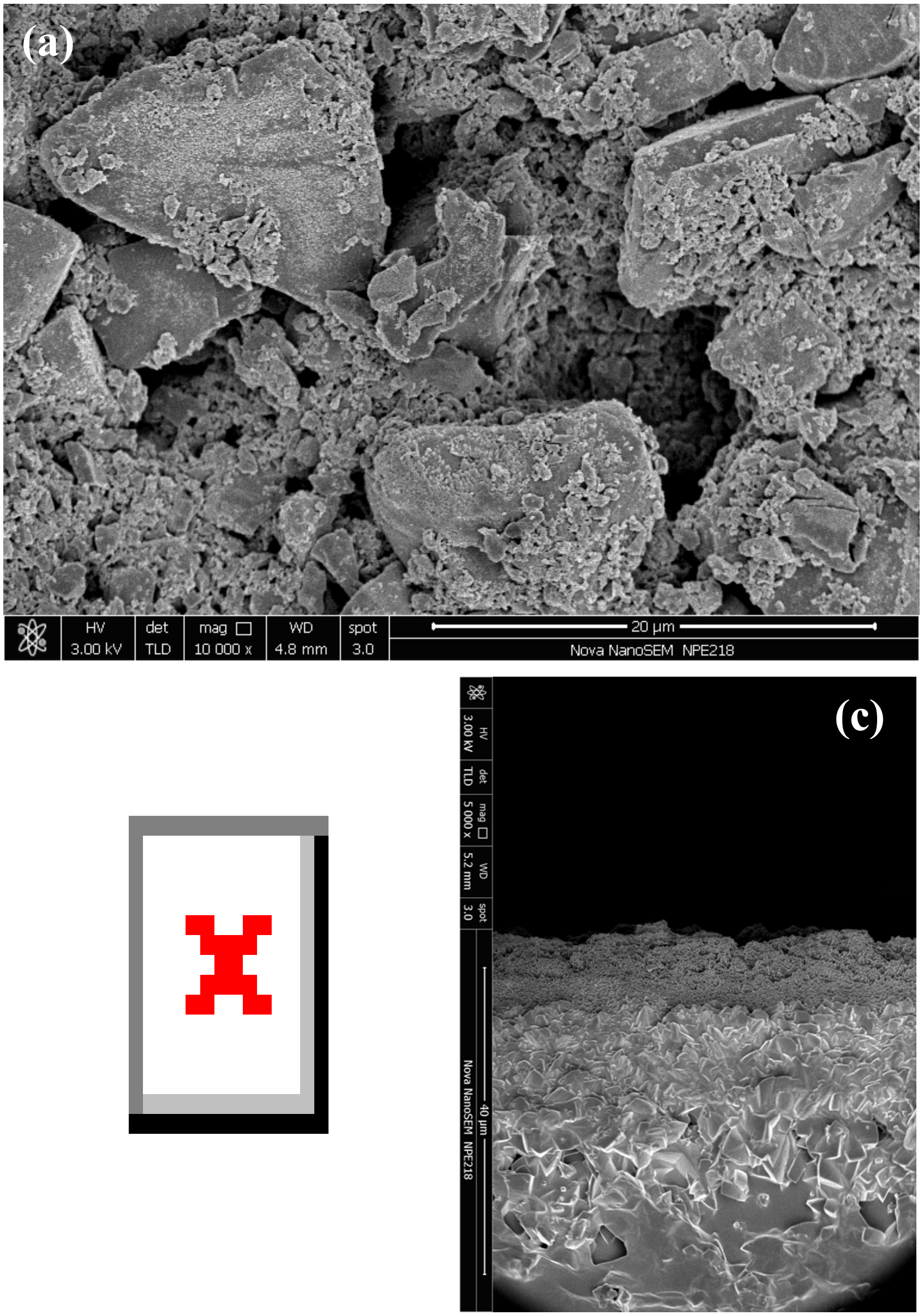

Figure S3. SEM images of porphyrin monomer in the form of powder (a) and supported thin film (b-c). SEM observations suggested that the formation of thin film didn't disturb the morphology of porphyrin too much, which are mainly irregular aggregations of particles. Obviously, the excellent contact between ITO surface and porphyrin aggregations was ensured in the thin film tested here, which could be further reflected by much higher PV response as compared with that of powder sample. Note that the film tested here was not crystalline thin film, the electronic structure of which largely depended on the arrangement of molecule assemblies (e.g. H-aggregate or J-aggregate).

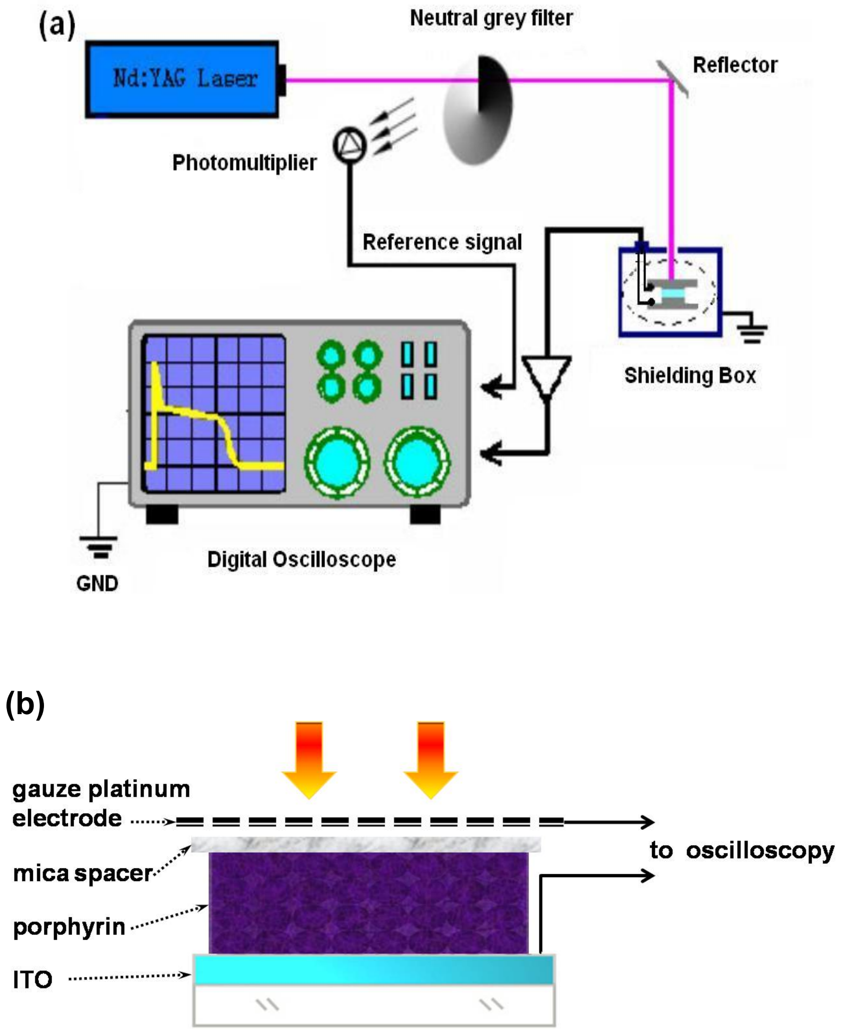

Figure S4. (a) Sketch of the TPV measurement equipment; (b) details of the sample chamber and the illumination geometries. During the measurement, the gauze platinum electrode was connected to the core of a BNC cable which inputs the signals to the oscilloscope. In our measurement, powder samples or thin films were loaded in the schielding box and excited with a laser radiation pulse (wavelength of 355 nm and pulse width of 5 ns) from a second-harmonic Nd:YAG laser. The intensity of the pulse was regulated with a neutral gray filter and determined with an EM500single-channel joulemeter (Molectron, Inc.). And the illuminated area is 0.1 cm^2. The time-resolution and input resistance are nano-second level and 100 MΩ.

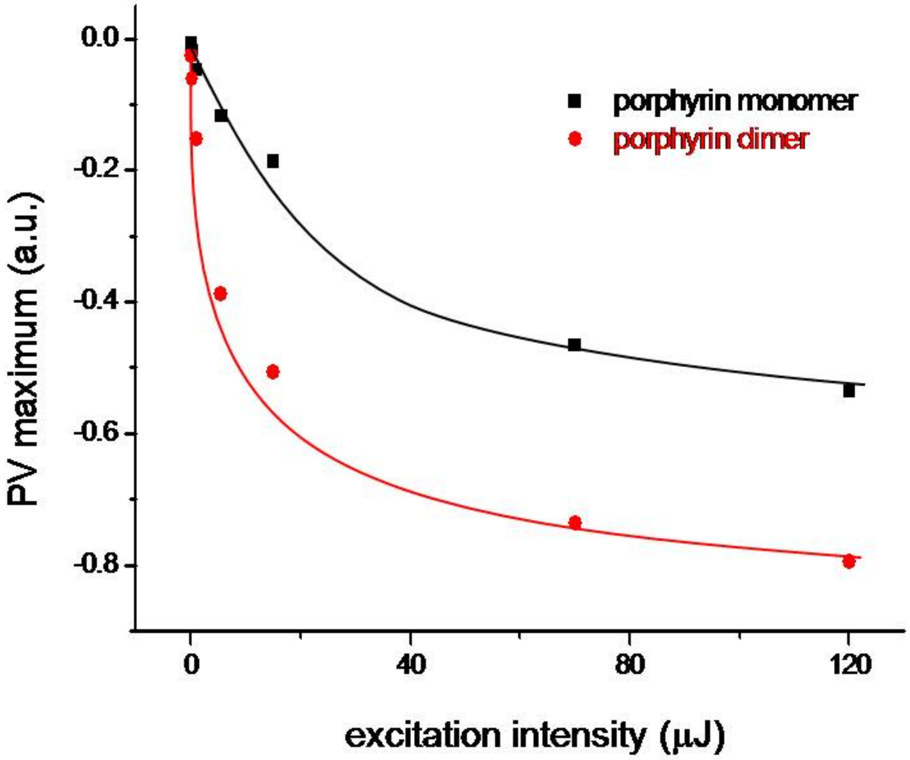

Figure S5. Dependence of the time-resolved photovoltage amplitude (maximum) on the excitation level for porphyrin monomer powder/ITO (black square) shown in Figure 1 and porphyrin dimer powder/ITO (red dot) shown in Figure 3a. The PV response tend to become saturated under the irradiation of high-intensity laser.