Supporting information

Self-Assembly of Discotic liquid crystal Decorated ZnO Nanoparticles for Efficient Hybrid Solar Cells

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Techniques.

The nuclear magnetic resonance (NMR) spectra were collected on a Bruker ARX 400 NMR spectrometer with deuterated chloroform as the solvent and with tetramethylsilane (δ=0) as the internal standard. The ultraviolet–visible (UV) spectra of the samples were recorded on a PerkinElmer Lambda 750 spectrophotometer. Fluorescence measurement for photoluminescence (PL) of the polymers was carried out on a Hitachi F-7000 PC spectrofluorophotometer with a xenon lamp as the light source. Texture observations by polarizing optical microscopy (POM) were made with a Nikon E600POL polarizing optical microscope equipped with an Instec HS 400 heating and cooling stage. Differential scanning calorimetry (DSC) was used to determine phase-transition temperatures on a Perkin-Elmer DSC 7 differential scanning calorimeter with a constant heating/cooling rate of 1 ^{o}C/min. The X-ray diffraction (XRD) study of the samples was carried out on a Bruker D8 Focus X-ray diffractometer operating at 30 kV and 20 mA with a copper target (λ =1.54 Å) and at a scanning rate of 1^{o}/min. Atomic force microscopy (AFM) measurement was carried out using a Digital Instrumental Nanoscope 31 operated in the tapping mode. Scanning electron microscopy (SEM) with gold vapor deposition was processed on FEI, QuanTA-200F environmental scanning electron microscope. Transmission electron microscopy (TEM) images were recorded using a JEOL-2100F transmission

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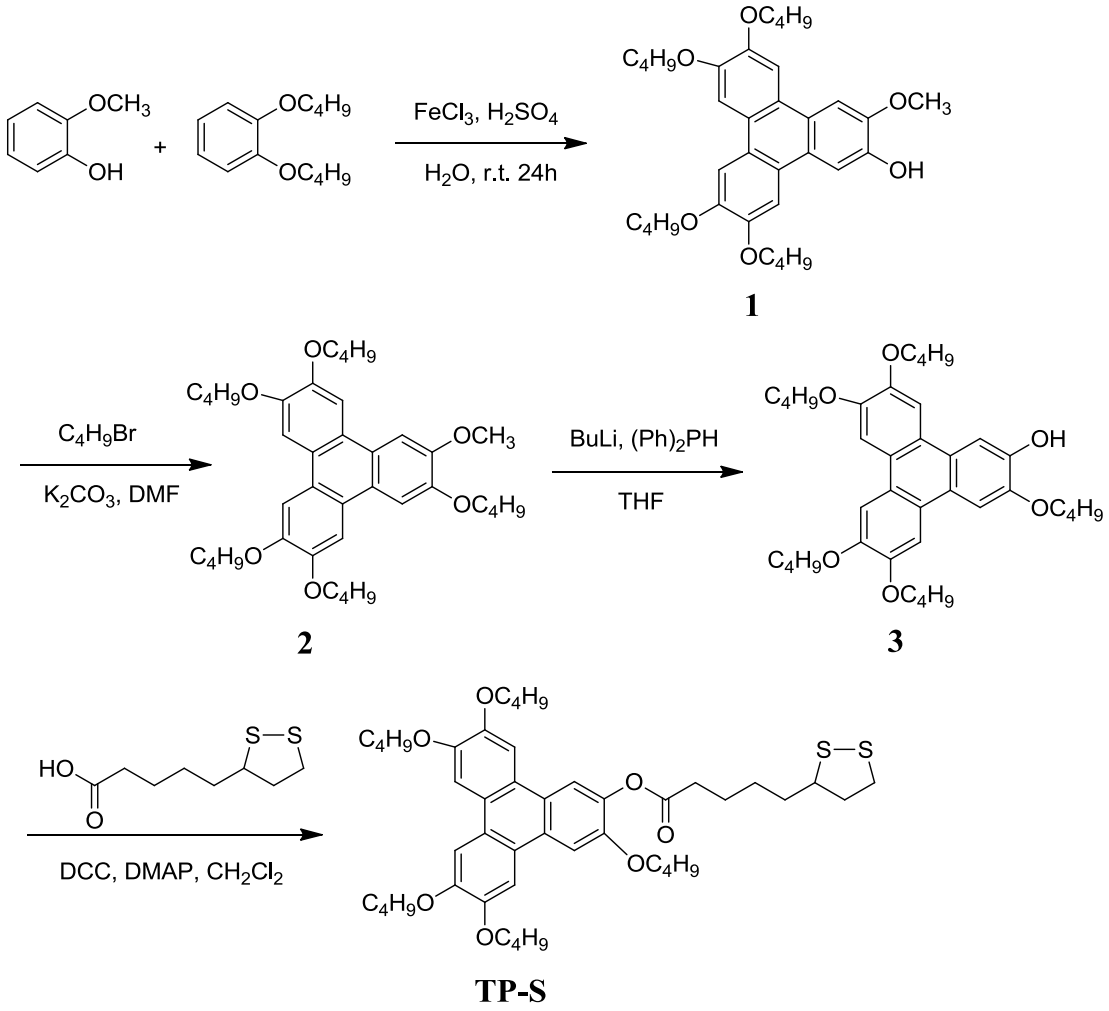
electron microscope and an internal charge-coupled device (CCD) camera.

Synthesis.



Scheme S1. The synthetic route of **TP-S.**

Synthesis of 6,7,10,11-tetrakis(butoxy)-2-hydroxy-3-methoxytriphenylene (1)

To a vigorously stirred suspension of 1,2-dibutoxybenzene (22.3 g, 0.1 mol) and guaiacol (24.8 g, 0.2 mol) in H_2SO_4 (250 ml, 70% aqueous solution) was added carefully anhydrous $FeCl_3$ (64.9 g, 0.4 mol) in small portions over 1h at 0 °C. The cooling bath was removed and stirring was continued for 24 h. The suspension was poured into ice (500 g) and stirred for 1 h. The resulting dark precipitate was filtered through a fritted funnel, washed with water (500 ml) and EtOH (100 ml) and dissolved in CH_2Cl_2 (100 ml). After addition of EtOH (400 ml) a violet precipitate was obtained, which was filtered and dried over P_2O_5 at 50°C for 12 h in vacuo. The crude product was eluted over silica gel using petroleum ether : dichloromethane (1 : 1.5). The solvent was removed by rotary evaporation to yield the desired product (6.1 g, 20% yield) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.83 (6H, m, Ar-H), 5.91 (1H, s, OH), 4.26 (8H, m, OCH_2), 4.11 (3H, s, OCH_3), 1.96 (8H, m, OCH_2**CH_2**), 1.61-1.41 (8H, m, **CH_2**CH_3), 0.98 (12H, t, CH_3).

Synthesis of 3,6,7,10,11-pentakis(butoxy)-2-methoxytriphenylene (2)

6,7,10,11-Tetrakis(butoxy)-2-hydroxy-3-methoxytriphenylene **(1)** (8.4 g, 1.5 * 10^{-2} mol) and potassium carbonate (6.9 g, 5.0 * 10^{-2} mol) in DMF (340 mL) was heated at 80^{o}C for 1 h under an atmosphere of nitrogen. At which time, bromobutane (2.8 g, 2.0 * 10^{-2} mol) was added one portion to the mixture and the resulting solution was left under reflux for 12 h. The reaction mixture was then cooled down and filtered to remove the excess of base , the filtrate concentrated in vacuo and the crude product was purified by flash chromatography(petroleum ether : dichloromethane = 1 : 1.5) to give give a white solid (10.9 g, 96% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.83 (6H, m, Ar-H), 4.26 (10H, m, OCH_2), 4.11 (3H, s, OCH_3), 1.96 (10H, m, OCH_2**CH_2**), 1.61-1.41 (10H, m, **CH_2**CH_3), 0.98 (15H, t, CH_3).

Synthesis of 3,6,7,10,11-pentakis(butoxy)-2-hydroxytriphenylene (3)

Diphenylphosphine (10.2 g, 0.552 mol) was dissolved in 100ml of dried THF and the solution cooled in an ice bath under N_2. Butyllithium (50ml, 1.6 M in hexane) was

added slowly to this solution. 3,6,7,10,11-pentakis(butoxy)-2-methoxytriphenylene **(2)** (9.3 g, 1.5 * 10^{-2} mol) was added and the mixture heated at reflux for 12 h. Dilute aqueous HCl was added to the reaction mixture and the organic layer extracted with CH_2Cl_2 and dried over anhydrous $MgSO_4$. The solvent was distilled in vacuo and precipitation of a CH_2Cl_2 solution with CH_3OH gave a white solid. This was filtered off and further purified by column chromatography (petroleum ether : dichloromethane = 1:1.5) to give compound **(3)** (6.2 g, 58%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.83 (6H, m, Ar-H), 5.91 (1H, s, OH), 4.26 (10H, m, OCH_2), 1.96 (10H, m, $OCH_2\mathbf{CH_2}$), 1.61-1.41 (10H, m, $\mathbf{CH_2}CH_3$), 0.98 (15H, t, CH_3).

Synthesis of 2-[(5-(1,2-dithiolan-3-yl)pentanoate)]-3,6,7,10,11-pentakis(butoxy)-triphenylene (TP-S)

5-(1,2-dithiolan-3-yl)pentanoic acid (1.75 g, 8.5 mmol) was added to a solution consisting of 2 (6.92 g, 11.2 mmol), [4-(dimethylamino)pyridine] (DMAP) (1.37 g, 11.2 mmol), and (N,N′-dicyclohexylcarbodiimade) (DCC) (2.31 g, 11.2 mmol) in 100 mL of absolute dichloromethane. The solution was stirred for 24 h at room temperature under an argon atmosphere, was poured into 100 ml water, and then extracted with dichloromethane. The organic phase was dried with sodium sulfate and the solvent was removed. The residue was purified with column chromatography (silica gel; hexane/ethyl acetate = 2/1), followed by recrystallization with ethanol to give pale yellow solid 6.54 g. Yield 86.4 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.83 (6H, m, Ar-H), 4.26 (10H, m, OCH_2), 3.62 (1H, m), 3.23 (2H, m), 2.68 (2H, CH_2COO), 2.52 (1H, m), 1.96-1.3 (27H, m,), 0.98 (15H, t, CH_3).

Synthesis of ZnO nanoparticles

The synthesis of ZnO nanoparticles was accomplished using minor modification of the procedure previously described in the literature. The synthesis is carried out under N_2 atmosphere. At first, 1.23 g of $Zn(Ac)_2{\cdot}2H_2O$ was dissolved in 55 mL of methanol

at room temperature. Then, 25 mL of a methanol solution containing 0.48 g of KOH is added dropwise over a 20 min time interval at 60 ^{o}C with magnetic stirring. After the KOH solution is added, the solution is stirred at 60 ^{o}C for 2 h. The product appears as a white precipitate. After collecting by centrifugation, this white precipitate is washed three times with methanol until it transforms to a gel-like precipitate. Each washing process includes dispersion into methanol by sonication and subsequent centrifugation. Finally, the gel-like precipitate is redispersed in ortho-dichlorobenzene.

Modification of ZnO naoparticless with TP-S.

The modification of ZnO nanoparticles (60 mg/ml) with **TP-S** (30 mg/ml) was performed overnight in ortho-dichlorobenzene (o-DCB) solution at room temperature. Modified ZnO NPs (**HTph-S**@ZnO) were centrifuged twice in o-DCB solution to eliminate non-modified ligand molecules and then redispersed in o-DCB.

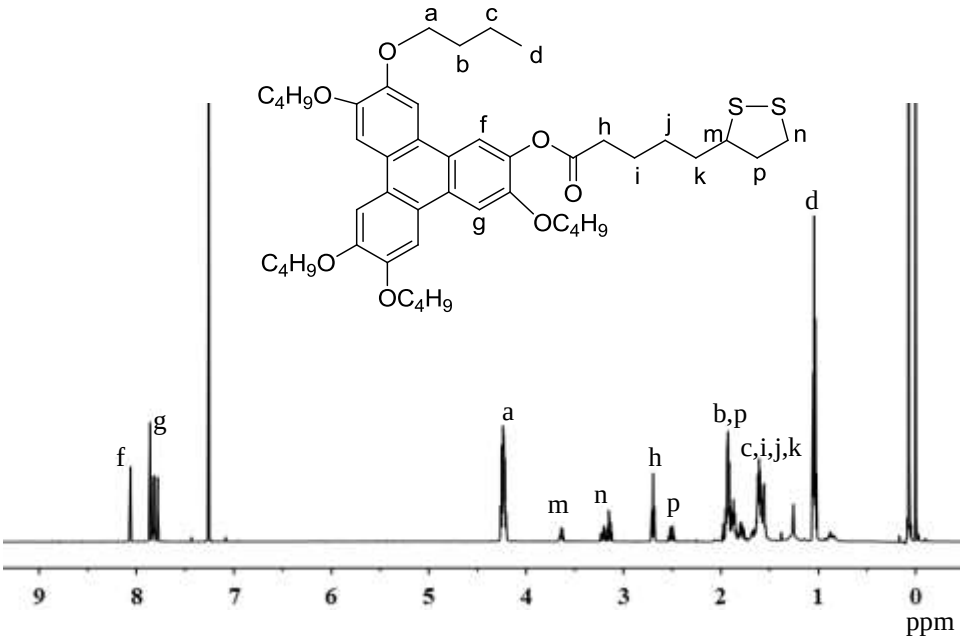


Figure S1. ^{1}H NMR spectrum of **TP-S**.

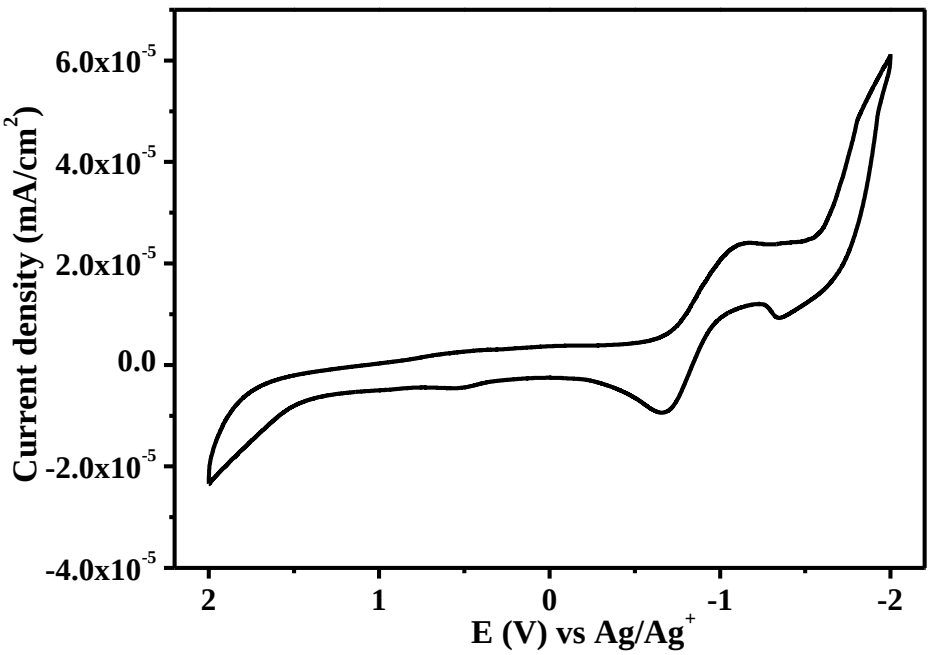


Figure S2. Cyclic voltammetry (CV) of the TP-S thin film, measured in a 0.1 M solution of Bu_4NPF_6 in CH_3CN with a Pt electrode and an Ag/AgNO3 reference electrode.

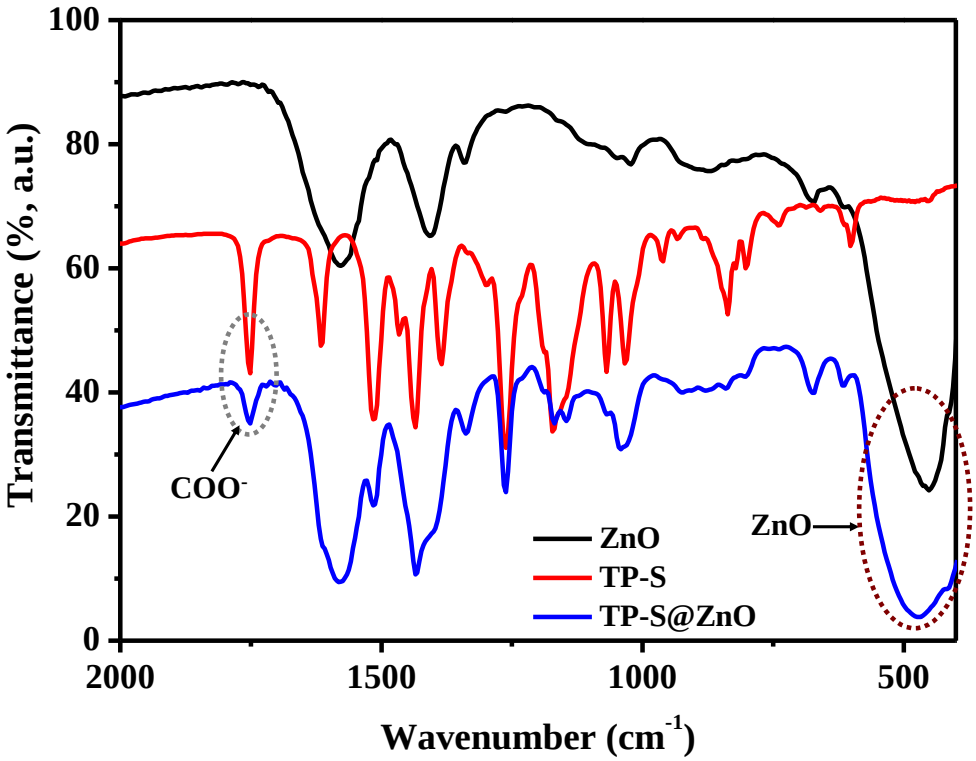


Figure S3. FT-IR spectra of pure ZnO NPs, TP-S and TP-S modified ZnO NPs (**TP-S@ZnO**).

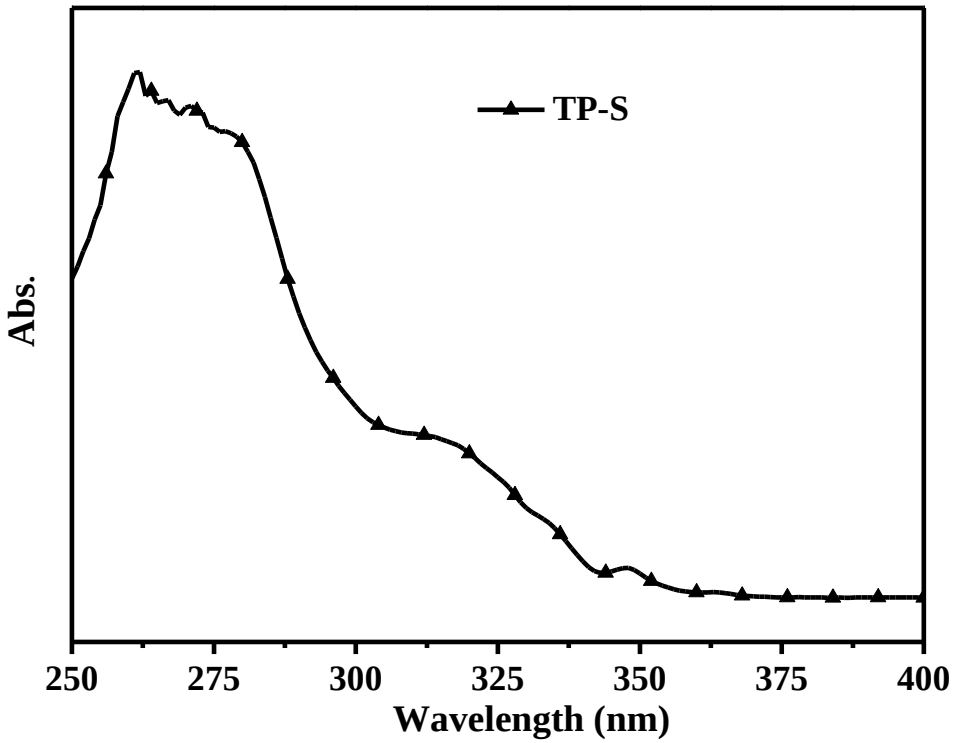


Figure S4. UV-vis absorption spectrum of TP-S.