Supporting Information

Promising ZnO-based DSSCs Performance Using HMP Molecular Dyes of High Extinction Coefficients

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A. Supplementary Methods

(1) Experimental scheme, synthesis procedure and structural characterizations for HMP 9 sensitizer

(2) Experimental scheme, synthesis procedure and structural characterizations for HMP 11 sensitizer

(3) Preparation of ZnO NPs electrodes

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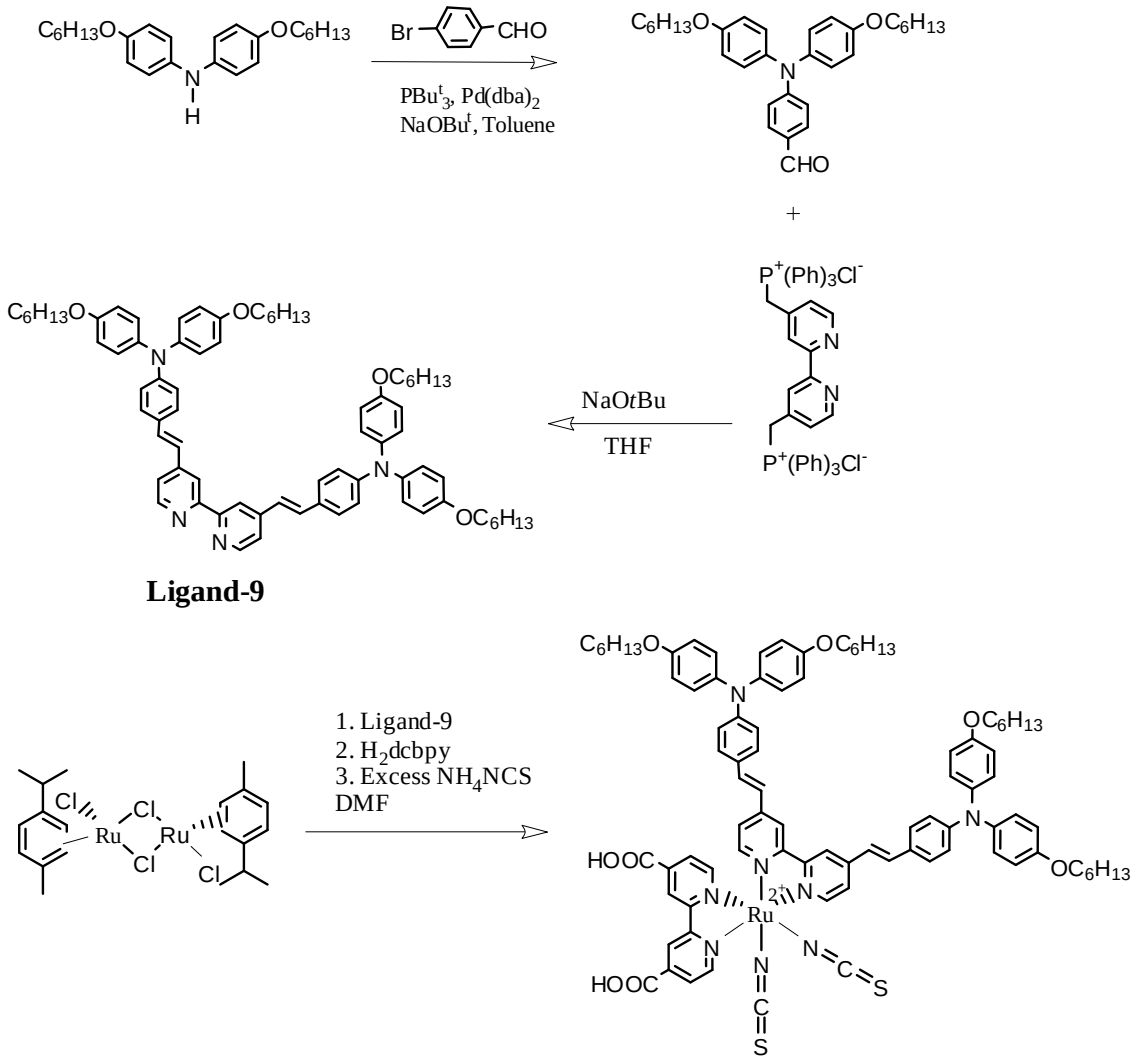
Figure S1. Cyclic voltammograms of dye molecules in DMF solvent.

Figure S2. Electronic absorption spectra of dye immobilized ZnO NPs electrodes of about 5 μm thick electrodes.

A. Supplementary Methods

(1) Experimental scheme, synthesis procedure and structural characterizations for HMP 9 sensitizer:



Scheme S1: Experimental scheme for the synthesis of **Ligand-9** and **HMP 9** sensitizer.

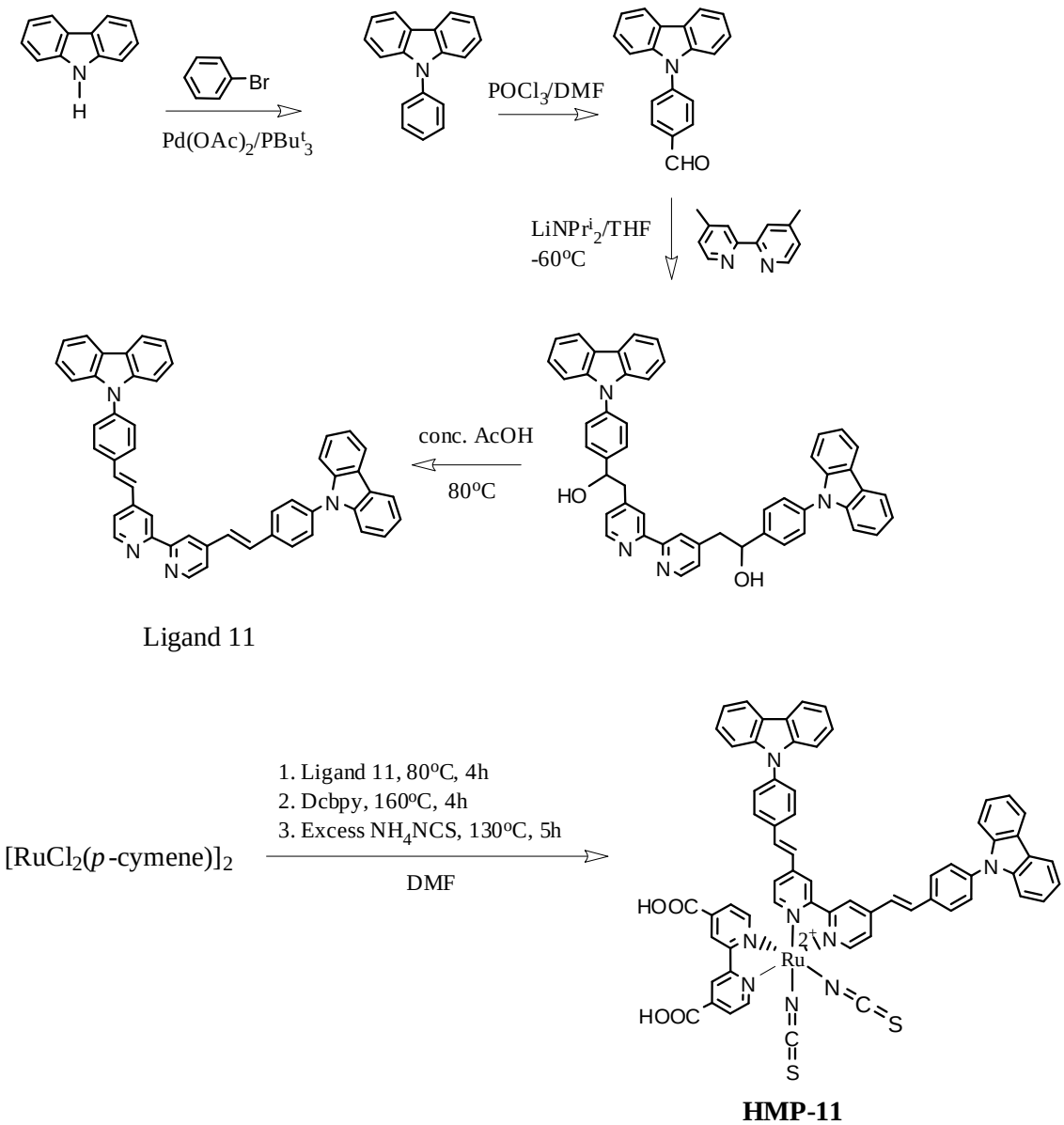
(1.1a) Synthesis procedure for *4,4'-Bis-(4-di-p-hexyloxyphenylamino)-styryl-2,2'-bipyridine* (**ligand-9**):

Under argon atmosphere 1.705 g (3.6 mmol) of compound **1** and 1.4 g (1.8 mmol) 4,4'-bis-(triphenylphosphoniummethyl)-2,2'-bipyridine chloride were dissolved in 50 mL dried THF and heated up to 50 ^{o}C. A suspension of 0.692 g (7.2 mmol) NaOtBu in THF was slowly added to the reaction mixture *via* dropping funnel followed by stirring at 50 ^{o}C for 4 h. After cooling to room temperature the reaction mixture was neutralized with acetic acid (10%) and extracted with CH_2Cl_2. The combined organic fractions were washed with water and aqueous solution of NaOAc. After drying over Na_2SO_4 and evaporation of the solvent, the residue was purified by column chromatography (n-hexane/ethylacetate = 7/3) yielding a yellow solid (0.985 g, 50 %). ^{1}H-NMR (400MHz, $CDCl_3$) δ_H[ppm]: 8.61 (d, 2H, Py-H), 8.48 (s, 2H, Py-H), 7.35 (d, 4H, Ph-H), 7.07 (d, 8H, Ph-H), 7.02 (d, 2H, vinyl), 6.94 (d, 2H, vinyl), 6.90 (d, 4H, Ph-H), 6.84 (d, 8H, Ph-H), 6.77 (d, 2H, Py-H), 3.94 (t, 8H, OCH_2), 1.74-1.81 (m, 8H, CH_2), 1.46 (m, 8H, CH_2), 1.33-1.37 (m, 16H, C_2H_4), 0.88-0.93 (m, 12H, CH_3). ESI-MS: m/z = 1094.6 $[M]^+$.

(1.1b) Synthesis procedure for *cis-[Ru(H_2dcbpy)(ligand-9)(NCS)$_2$]* (HMP-9)

$[RuCl_2(p\text{-cymene})]_2$ (0.08 g, 0.13 mmol) was dissolved in dry DMF (30 mL) and ligand-9 (0.284 g, 0.26 mmol) was added. The reaction mixture was heated at 80 °C for 4 h and then H_2dcbpy (0.063 g, 0.26 mmol) was added. The mixture was refluxed at 160 ^{o}C for 4 h in the dark to avoid the photo-induced *cis*-to-*trans* isomerization. Then, an excess of NH_4NCS (0.6 g, 7.8 mmol) was added to the reaction mixture and stirred at 130 ^{o}C for 5 h. After the reaction, the solvent was removed in vacuum and then water was added to the resulting semisolid to removed excess NH_4NCS. The water-insoluble product was collected on a sintered glass crucible by suction filtration and washed with distilled water, followed by diethyl ether and dried. The crude product was dissolved in a solution of *tetra*-butylammoniumhydroxide (0.3 g) in methanol (7 mL). The concentrated solution was charged on to a Sephadex-LH 20 column and eluted with methanol. The main red band was collected and concentrated to 4 mL. A few drops of 0.01 M $HNO_{3(aq)}$ was added to precipitate the product (0.117 g, 30%). FAB-MS: m/z = 1556.5 $[M]^+$, 1498.6 $[M\text{-}NCS]^+$. ^{1}H-NMR (400MHz, d_6-DMSO) δ_H[ppm]: 9.40 (d, 1H, Py-H), 9.04 (d, 1H, Py-H), 8.94 (d, 1H, Py-H), 8.90 (s, 1H, Py-H), 8.82 (d, 1H, Py-H), 8.74 (s, 1H. Py-H), 8.30 (s, 1H, Py-H), 7.95 (s, 1H, Py-H), 7.86 (d, 1H, Py-H), 7.70 (d, 1H, Py-H), 7.66 (d, 1H, Py-H), 7.56 (m, 4H, Ph-H), 7.44 (d, 4H, Ph-H), 7.20 (d, 2H, vinyl), 7.12 (d, 1H, Py-H), 7.07 (d, 4H, Ph-H), 6.95 (m, 8H, Ph-H), 6.87 (d, 2H, vinyl), 6.79 (d, 2H, Ph-H), 6.73 (m, 2H, Ph-H), 3.92 (m, 8H, OCH_2), 1.67-1.69 (m, 8H, CH_2), 1.38-1.41 (m, 8H, CH_2), 1.21-1.28 (m, 16H, C_2H_4), 0.85-0.88 (m, 12H, CH_3).

(2) Experimental scheme, synthesis procedure and structural characterizations for HMP 11 sensitizer:



Scheme S2: Experimental scheme for the synthesis of **Ligand-11** and **HMP 11** sensitizer.

(2.1a) Synthesis procedure for *N-Phenylcarbazole* **(1).**

In a 100 mL two-necked round-bottomed flask, carbazole (Cz) (3 g, 18 mmol) and bromobenzene (3.3 g, 21 mmol) were stirred in 50 mL of xylene and potassium carbonate (3.73 g, 27 mmol) was added. Pd(OAc) (0.112 g, 0.5 mmol) and PBu^t_3 (0.1 g, 0.5 mmol) were suspended in 3 mL of xylene. The catalyst suspension was then added to the reactants and was stirred at 120 ^oC for 6 h. After the reaction, the mixture was poured into pentane (30 mL), filtered and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, *n*-hexane/ethylacetate = 8/2) to yield **1** as a pale yellow solid (3.06 g, 60%). ^{1}H-NMR (400MHz, $CDCl_3$) δ_H[ppm]: 8.15 (d, 2H, Cz-H), 7.58 (m, 4H, Cz-H), 7.46 (t, 2H, Ph-H), 7.40 (d, 2H, Ph-H), 7,28 (m, 2H, Cz-H), 7.11 (m, 1H, Ph-H).

(2.1b) Synthesis procedure for *4-(N-Carbazolyl)-benzaldehyde* **(2).**

To a solution of **1** (1.21 g, 5 mmol) in anhydrous 1, 2-dichloroethane (50 mL) at room temperature and anhydrous DMF (0.39 mL, 5 mmol) was added. $POCl_3$ (0.55 mL, 6 mmol) was added drop-wise and the mixture was refluxed for a night. After hydrolysis for 2 h under vigorous stirring at room temperature using an aqueous solution of sodium acetate 2 M (50 mL), the product was extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$ and evaporated in vacuo before a purification by chromatography on silica gel (eluent: CH_2Cl_2) to give **2** as a pale yellow solid (0.95 g, 70% yield). ^{1}H-NMR (400MHz, $CDCl_3$) δ_H[ppm]: 10.1 (s, 1H, CHO), 8.16 (d, 1H, Cz-H), 8.14 (d, 1H, Cz-H), 8.08 (d, 2H, Cz-H), 7.80 (d, 2H, Ph-H), 7.51 (d, 2H, Ph-H), 7.43 (t, 3H, Cz-H), 7.33 (t, 1H, Cz-H).

(2.1c) Synthesis procedure for *4,4'-Bis-(4-(N-Carbazolyl)-phenyl-2-hydroxyethyl)-2,2'-bipyridine* **(3):**

Lithium diisopropylamide was formed by mixing BuLi (6 mmol) with diisopropylamine (0.97 mL, 7 mmol) in 30 mL THF for de-protonation at -60 °C. The $LiNPr^i_2$ solution was stirred at room temperature for 30 min and cooled to -40 °C. 4, 4'-Dimethyl-2, 2'-bipyridine (0.275 g, 1.5 mmol) dissolved in 10 mL THF was added drop-wise to the $LiNPr^i_2$. The black reaction mixture was stirred at room temperature for 1 h. After cooling to -60 °C, a solution of **2** (0.81 g, 3 mmol) in 10 mL of THF was added. Stirring was continued for 3 h, then the mixture was stirred into water and extracted with CH_2Cl_2 (100 mL). The organic phase was washed with brine and dried over $MgSO_4$. The solvent was removed on a rotary evaporator. The crude product was chromatographed using *n*-hexane-ethylacetate-Et_3N (50:48:2) to give compound **3** in 50 % yield (0.54 g). ^{1}H-NMR (400MHz, $CDCl_3$) δ_H[ppm]: 8.56 (d, 2H, Py-H), 8.37 (s, 1H, Py-H), 8.18 (s, 1H, Py-H), 8.14 (d, 2H, Cz-H), 7.61 (t, 4H, Cz-H), 7.55 (d, 4H, Ph-H), 7.47 (t, 2H, Cz-H), 7.42-7.36 (m, 10H, Cz-H, Ph-H), 7.30 (t, 2H, Cz-H), 7.17 (d, 2H, Py-H), 5.24 (s, 2H, Ph-CH), 3.29-3.18 (m, 4H, Py-CH_2), 2.17(s, 2H, OH).

(2.1d) Synthesis procedure for *4,4'-Bis-(4-(N-Carbazolyl)-phenyl-2-vinyl)-2,2'-bipyridine* (**ligand 11**)

Compound **3** (0.5 g, 0.68 mmol) was dissolved in conc. AcOH (20 mL, excess) and stirred at 80 ^{o}C for 18 h. The reaction mixture was poured into sat. aq. $NaHCO_3$ (100 mL) and extracted with CH_2Cl_2 (100 mL), dried over $MgSO_4$ and concentrated. The crude product was chromatographed (*n*-hexane/ethylacetate = 7/3) to give **ligand 11** in 45 % yield (0.21 g). ^{1}H-NMR (400MHz, $CDCl_3$) δ_H[ppm]: 8.7 (d, 2H, Py-H), 8.62 (s, 2H, Py-H), 8.19 (d, 2H), 7.67 (m, 4H), 7.62 (d, 4H), 7.58 (d, 5H), 7.51 (d, 2H), 7.46 (m, 2H), 7.42 (d, 6H), 7.31-7.35 (m, 3H), 7.20 (d, 2H). ESI-MS: m/z = 690.2 $[M]^+$.

(2.1e) Synthesis procedure for *cis*-[Ru(H_2dcbpy)(ligand 11)$(NCS)_2$] **(HMP 11)**

This compound was prepared according to the literature.[14] $[RuCl_2(p\text{-cymene})]_2$ (0.092 g, 0.15 mmol) was dissolved in dry DMF (30 mL) and ligand 11 (0.207 g, 0.3 mmol) was added. The reaction mixture was heated at 80 °C for 4 h and then 4, 4'-dicarboxylic acid-2, 2-bipyridine (H_2dcbpy, 0.071 g, 0.44 mmol) was added. The mixture was refluxed at 160 °C for 4 h in the dark to avoid the photo-induced *cis*-to-*trans* isomerization. Then, an excess of NH_4NCS (0.68 g, 9 mmol) was added to the reaction mixture and stirred at 130 °C for 5 h. After the reaction, the solvent was removed in vacuum. Water was added to the resulting semisolid to removed excess NH_4NCS. The water-insoluble product was collected on a sintered glass crucible by suction filtration and washed with distilled water, followed by diethyl ether and then dried. The crude product was dissolved in a solution of *tetra*-butylammoniumhydroxide (0.3 g) in methanol (10 mL). The concentrated solution was charged on to a Sephadex-LH 20 column and eluted with methanol. The main red band was collected and concentrated to 4 mL. A few drops of 0.01 M $HNO_{3(aq)}$ was added to precipitate the product (0.121 g, 35 %). FAB-MS: m/z = 1152.1 $[M]^+$, 1094.2 $[M\text{-}NCS]^+$. ^{1}H-NMR (400MHz, d_6-DMSO) δ_H[ppm]: 9.47 (s, 1H, Py-H), 9.15 (d, 1H, Py-H), 9.10 (s, 1H, Py-H), 8.94 (s, 1H, Py-H), 8.65 (d, 2H, Py-H), 8.37 (d, 2H, Cz-H), 8.31 (d, 2H, Cz-H), 8.15 (d, 1H, Py-H), 8.08 (s, 1H, Py-H), 7.95-7.91 (m, 4H), 7.80 (d, 2H), 7.74-7.65 (m, 8H), 7.58-7.54 (m, 4H), 7.50 (d, 2H), 7.46 (d, 2H), 7.44-7.38 (m, 4H), 7.34 (d, 2H).

(3) Preparation of ZnO NPs electrodes

To prepare ZnO nanoparticles (NPs) electrodes, ZnO (50% in H_2O) colloidal dispersion with dispersant was preferred as received. The film was formed using doctor blade technique; 1 ml of the ZnO dispersion was grounded along with binders for porous and uniform film formation with high thickness. The ZnO dispersion was grounded with 0.1 gm polyethylene glycol, 0.73 ml acetyl acetone and isopropyl alcohol. The doctor bladed film thickness was 10 μm. The additives and binders in the film were calcined at 300 °C for 1 h in air to remove the residual solvents and organic chemicals on ZnO NPs.

Further, this calcination increases the grain boundary between the ZnO nanoparticles. The film formation conditions were optimized to have high thickness and porosity, for easy penetration of dye molecule.

(4) Fabrication of ZnO NPs-based dye sensitized solar cells (DSSCs) electrodes

The ZnO NPs electrode was immobilized with dye by immersing it into a dye solution containing 0.3 mM of each sensitizer in the mixture of acetonitrile and *tert*-butanol (volume ratio: 1/1) for 30 min in N3 and 1 h for other sensitizers. After washing with acetonitrile and drying under inert conditions, the sensitized ZnO NPs electrodes were sandwiched with 100 nm thick Pt-sputtered conducting glass electrodes separated using a Surlyn-based polymer sheet (thickness: 80 μm), and sealed into which an electrolyte solution of 0.6 M 1-hexyl-2,3-dimethylimidazole iodide (C6DMI), 0.1 M lithium iodide (LiI), 0.05 M iodide (I_2), and 0.5 M 4-*tert*-butylpyridine (*t*-BPy) in 15 mL methoxyacetonitrile (98%) was injected using a fine 10 mL nontoxic Kovax syringe. The DSSCs measurements were performed with a photo-intensity of 100 mW/cm^2, with an electrode area of 0.25 cm^2. The cells were unmasked, keeping only 0.25 cm^2 area alone as the active region for DSSCs measurement.

(5) Electrochemical measurements

The electrochemistry of HMP dyes was analyzed in a single-compartment, three-electrode cell with a platinum disk working electrode and a Pt wire counter electrode. The reference electrode was Ag/AgCl and the supporting electrolyte was 0.1 M tetrabutylammonium tetrafluoroborate (TBA/TFB) in DMF/acetonitrile solvent (1:3). The cyclic-voltammetry measurements were done in Electrochemical Analyzer, BAS 100 B.

The electrochemical impedance analysis (EIS) was done to analyze the interfacial, charge and electron transfer phenomenon in DSSCs, using BAS-Zahner IM6 Impedance analyzer. The same DSSCs used in current density (*J*-*V*) characterizations were used for the EIS analysis under dark conditions. The open circuit potential (V_{oc}) obtained in the *J*-*V* analysis was used as an applied potential for the EIS analysis. The potential amplitude of *ac* was applied at 10 mV and its frequency region was maintained from 0.01 Hz to 1 MHz.

B. Supplementary figures

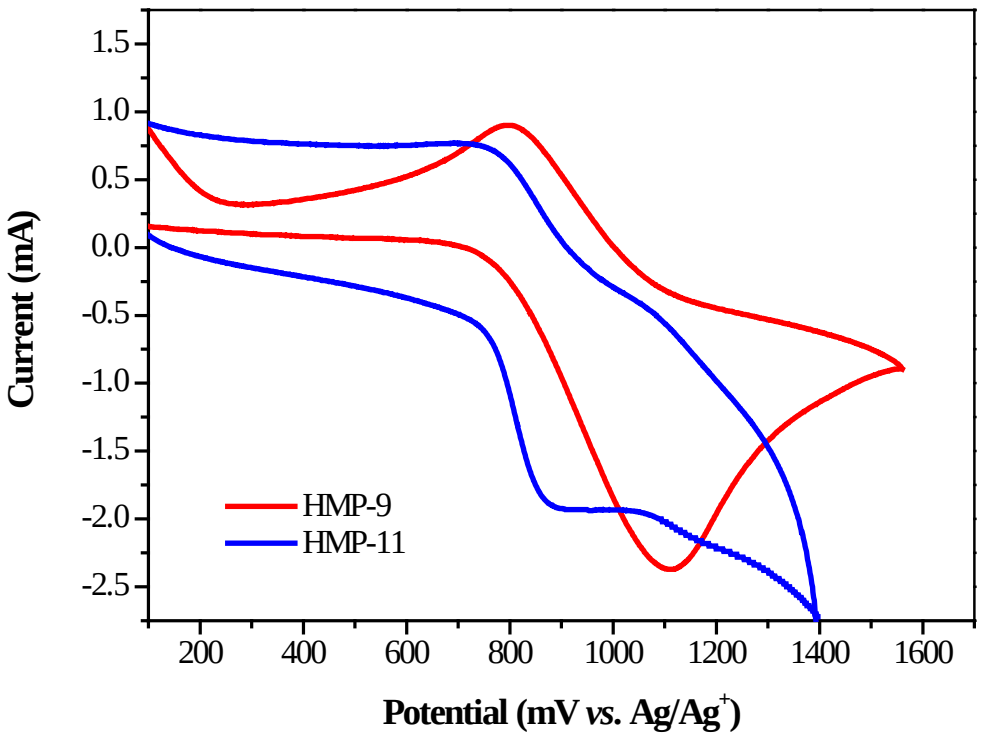


Figure S1: Cyclic-voltammograms of dye molecules in DMF/acetonitrile mixture (1:3) solvent.

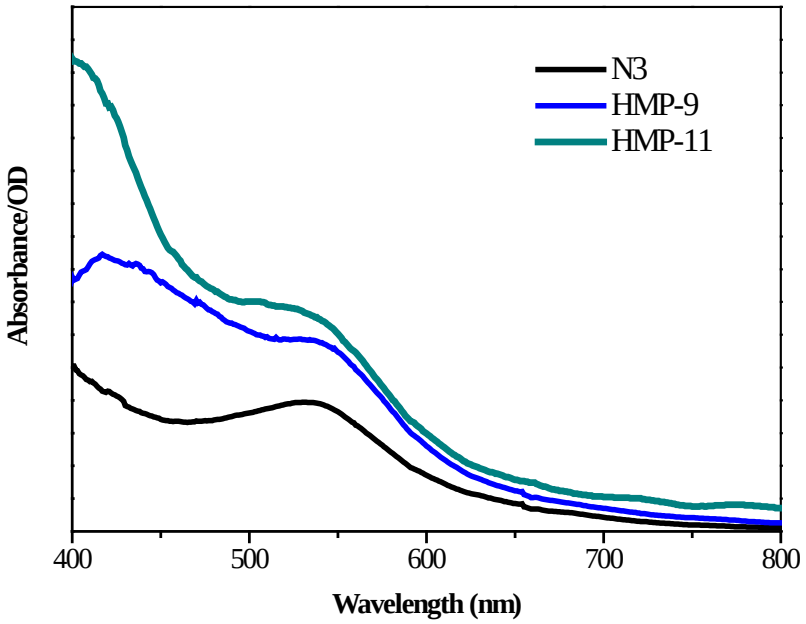


Figure S2: Electronic absorption spectra of dye molecules on ZnO NPs electrodes.