

Supplementary Information

Bilayer Structured Supramolecular Light Harvesting Arrays Based on Zinc Porphyrin Coordination
Polymers for Enhanced Photocurrent Generation in Dye Sensitized Solar Cells

Jun-Xiang Zhang ^a, Yu Wu ^a, Jia-Cheng Liu* ^a and Ren-Zhi Li ^b

^a Key Laboratory of Bioelectrochemistry & Environmental Analysis of Gansu Province, Key Laboratory of Eco-Environment-Related Polymer Materials of Ministry of Education, Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, People's Republic of China.

^b Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (NanjingTech), People's Republic of China.

*Corresponding author.

Tel: +869317975636, fax: +869317971989.

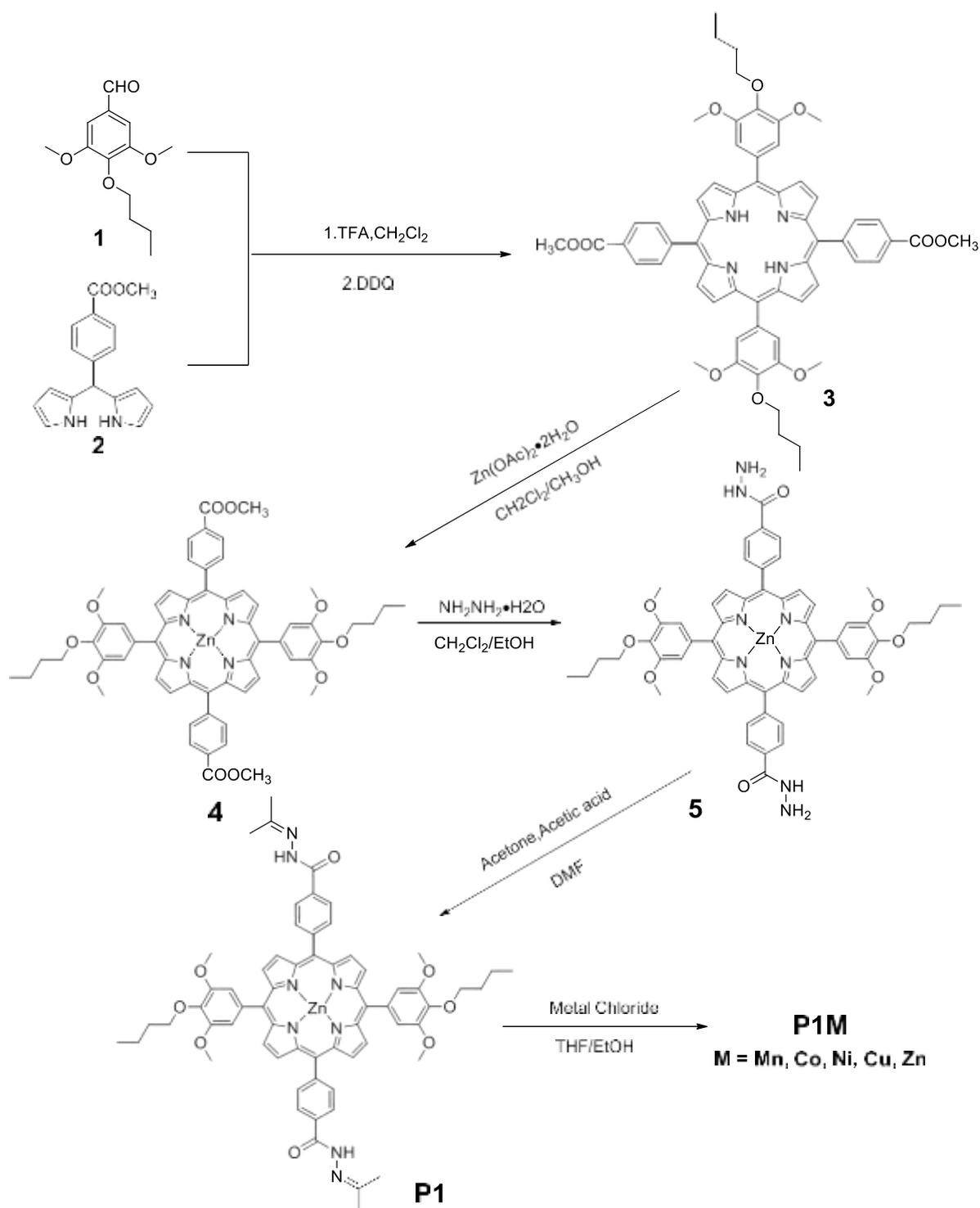
E-mail addresses: jcliu8@nwnu.edu.cn (J. C. Liu).

1. Experimental

1.1 Materials and characterization

All solvents and reagents were used as commercially received without further purification unless stated elsewhere. The starting materials **1** and **2** were synthesized following a similar procedure presented in our previous work [1]. UV-Vis spectra were obtained on a UV-2550 spectrometer. The Luminescence spectrum was measured by LS-55 (PE USA Inc) fluorescence spectrophotometer at room temperature. ¹HNMR (600 MHz) was recorded on a Varian Mercury Plus spectrometer. Electrospray ionization (ESI) mass spectra was investigated on a ESI-TOF mass spectrometer. Elemental analyses of C, H, and N were recorded on a VxRio EL Instrument. The detailed synthesis processes of acylhydrazone zinc porphyrin coordination polymers **P1M** are shown in **Scheme S1**.

1.2 The synthesis of porphyrin coordination polymers **P1M**



Scheme S1 The synthetic routes of the coordination polymers **P1M**

Preparation of porphyrin **3**

Following a general procedure [2] with slight modification. To a solution of dipyrromethane **2** (0.56 g, 2 mmol), and **1** (0.48 g, 2 mmol) in dichloromethane (100 mL) was added trifluoroacetic acid (TFA) (0.24 mL, 3 mmol) dropwise under argon. After reacted for 30 min, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (1.2 g, 5 mmol) was added and the mixture was stirred for an additional 1 h. Evaporated the solvent at reduced pressure and the residue was redissolved in toluene. The solution was treated with a second portion of DDQ (1.2 g, 5 mmol) and refluxed for another 1 h. The toluene was removed at reduced pressure and the crude product was purified by column chromatography on silica gel using dichloromethane/petroleum ether as the eluent to afford the desired porphyrin as a purple solid, yield 17%. ¹H NMR (600 MHz, CDCl₃): δ 8.99 (d, J = 6.8 Hz, 4H, β-pyrrole H), 8.82 (d, J = 6.0 Hz, 4H, β-pyrrole H), 8.46 (d, J = 12.0 Hz, 4H, ph-H), 8.32 (d, J = 12.8 Hz, 4H, ph-H), 7.46 (s, 4H, ph-H), 4.33 (t, J₁ = 6.2 Hz, J₂ = 12.0 Hz, 4H, -OCH₂-H), 4.11 (d, J = 2.4 Hz, 6H, -COOCH₃-H), 3.95 (s, 12H, -OCH₃-H), 1.99 (m, 4H, -CH₂-H), 1.68 (m, 4H, -CH₂-H), 1.10 (t, J₁ = 6.0 Hz, J₂ = 11.8 Hz, 6H, -CH₃-H), -2.78 (s, 2H, -NH-H). ¹³C NMR (400 MHz, CDCl₃): δ 14.06, 19.02, 19.28, 29.71, 32.47, 52.46, 56.27, 56.43, 73.59, 76.84, 77.05, 77.27, 113.08, 118.90, 119.03, 119.24, 120.59, 120.72, 120.93, 127.99, 129.72, 129.77, 134.53, 137.10, 137.39, 146.77, 146.89, 151.73, 167.25, 167.28. HRMS (ESI, m/z): [M+H]⁺ calcd for C₆₀H₅₈N₄O₁₀, 994.42; found 995.2962.

Synthesis of zinc porphyrin **4**

To a solution of the porphyrin **3** (0.2 g, 0.2 mmol) in a co-solvents of dichloromethane/methanol (4/1, v:v, 50 mL) was added Zn(OAc₂) • 2H₂O (0.098 g, 0.45 mmol). The mixture was refluxed for 6 h, then diluted with dichloromethane (25 mL) and washed with water (75 mL) then 10% (wt%) solution of aqueous sodium bicarbonate. The organic phase was dried over Na₂SO₄, filtered, and evaporated the solvent to dryness to give the desired porphyrin **4** in quantitative yield. ¹H NMR (600 MHz, CDCl₃): δ 9.22 (d, J = 4.2 Hz, 4H, β-pyrrole H), 8.91 (d, J = 12.0 Hz, 4H, β-pyrrole H), 8.29 (m, 8H, ph-H), 7.43 (t, J₁ = J₂ = 6.4 Hz, 4H, ph-H), 4.23 (m, 4H, -OCH₂-H), 3.99 (t, J₁ = 13.2 Hz, J₂ = 18.6 Hz, 6H, -COOCH₃-H), 3.89 (q, J₁ = 12.6 Hz, J₂ = 6.0 Hz, J₃ = 12.2 Hz, 12H, -OCH₃-H), 1.92 (m, 4H, -CH₂-H),

1.65 (m, 4H, -CH₂-H), 1.10 (m, 6H, -CH₃-H). HRMS (ESI, m/z): [M+H]⁺ calcd for C₆₀H₅₆N₄O₁₀Zn, 1056.33; found 1057.1903.

Synthesis of acetohydrazide zinc porphyrin **5**

Excessive hydrazine hydrate (5 mL) in 10 mL ethanol was added to the solution of Porphyrin **4** (0.16 g, 0.15mmol) in 30 mL CH₂Cl₂, the mixture was refluxed at 70 °C for 30 h. Then the solution was cooled to room temperature and cold water (40mL) was added. The mixture was extracted with CH₂Cl₂. The organic layer was washed with water and dried over Na₂SO₄. Evaporation of the solvent to yield the desired porphyrin **5** in 92 % yield. ¹H NMR (600 MHz, DMSO-d₆): δ 10.17 (s, 2H, -CONH-H), 8.93 (s, 4H, β-pyrrole H), 8.76 (d, J = 3.6 Hz, 4H, β-pyrrole H), 8.25 (s, 8H, ph-H), 7.46 (s, 4H, ph-H), 4.19 (s, 4H, -OCH₂-H), 3.89 (s, 12H, -OCH₃-H), 1.83 (brs, 4H, -CH₂-H), 1.62 (brs, 4H, -CH₂-H), 1.05 (s, 6H, -CH₃-H). HRMS (ESI, m/z): [M+H]⁺ calcd for C₆₀H₅₆N₄O₁₀Zn, 1056.33; found 1057.2162.

Synthesis of acylhydrazone zinc porphyrin **P1**

Porphyrin **5** (0.16 g, 0.15mmol) was dissolved in a mixture of DMF and acetone (1/2, v/v, 30 mL) then 2 mL acetic acid was added, after refluxed at 60 °C for 24 h the solution was treated with cold water (40mL). Extracted with CH₂Cl₂ and the organic layer was washed with water and dried over Na₂SO₄. Remove the solvent at reduced pressure to yield **P1** in 86 % yield. ¹H NMR (600 MHz, DMSO-d₆): δ 10.82 (s, 2H, -CONH-H), 8.92 (d, J = 6.8Hz, 4H, β-pyrrole H), 8.79 (d, J = 6.0 Hz, 4H, β-pyrrole H), 8.31 (brs, 8H, ph-H), 7.47 (s, 4H, ph-H), 4.18 (m, 4H, -OCH₂-H), 3.88 (s, 12H, -OCH₃-H), 2.07 (s, 12H, -NCCH₃-H), 1.80 (m, 4H, -CH₂-H), 1.61 (m, 4H, -CH₂-H), 1.04 (t, J₁ = J₂ = 6.4 Hz, 6H, -CH₃-H). HRMS (ESI, m/z): [M+H]⁺ calcd for C₆₄H₆₄N₈O₈Zn, 1136.41; found 1137.2772. FT-IR (neat, cm⁻¹): 3415(br), 2928(m), 1718(w), 1651(s), 1604(m), 1578(s), 1488(s), 1460(s), 1407(m), 1346(s), 1288(w), 1234(m), 1124(s), 1071(m), 996(s), 942(w), 868(w), 796(w), 761(w), 720(w), 670(w).

Synthesis of coordination polymers **P1M**

General procedure

P1 (0.16 g, 0.15mmol) was added to a co-solvent of THF/EtOH, the suspension was refluxed for 30 min to ensure the porphyrin be totally dissolved. Then metal chloride (**MCl₂**, **M** = Mn, Co, Ni, Cu, Zn. 2.0 equivalent) in 5 mL ethanol was added and keep refluxing for 8 h until precipitate was appeared. After remove the solvent by rotary evaporation, the residue was ultrasonic washed with water then methanol, centrifugalized to remove water and dried under vacuum to give the coordination polymers as dark red powder.

For **P1Mn**, yield 86%, Anal. Calcd. For [**P1MnCl₂**]_n: C, 60.79%; H, 5.10%; N, 8.86%. Found: C, 61.02%; H, 5.04%; N, 8.93%. ESI-MS (+MS, m/z): 1137.41, [**P1+H**]⁺; 1264.32, [**P1MnCl₂+H**]⁺; 1389.16, [**P1Mn₂Cl₂+H**]⁺. FT-IR (neat, cm⁻¹): 3429(br), 2953(s), 2872(m), 1716(s), 1604(s), 1577(s), 1489(m), 1460(m), 1408(s), 1348(s), 1269(m), 1238(m), 1126(s), 1068(m), 997(s), 866(w), 796(m), 765(w), 721(w).

For **P1Co**, yield 77%, Anal. Calcd. For [**P1CoCl₂**]_n: C, 60.60%; H, 5.09%; N, 8.83%. Found: C, 60.82%; H, 5.17%; N, 8.86%. ESI-MS (+MS, m/z): 1137.39, [**P1+H**]⁺; 1267.26, [**P1CoCl₂+H**]⁺; 1397.27, [**P1Co₂Cl₂+H**]⁺. FT-IR (neat, cm⁻¹): 3433(br), 3363(br), 2953(s), 2929(s), 2837(m), 1718(m), 1602(s), 1577(s), 1490(s), 1461(m), 1409(s), 1381(m), 1271(w), 1236(m), 1126(s), 1072(m), 999(s), 943(m), 864(w), 796(m), 765(w), 721(w).

For **P1Ni**, yield 91%, Anal. Calcd. For [**P1NiCl₂**]_n: C, 60.61%; H, 5.09%; N, 8.84%. Found: C, 60.95%; H, 5.03%; N, 8.92%. ESI-MS (+MS, m/z): 1137.42, [**P1+H**]⁺; 1267.02, [**P1NiCl₂+H**]⁺; 1397.83, [**P1Ni₂Cl₂+H**]⁺. FT-IR (neat, cm⁻¹): 3408(br), 2953(m), 2933(m), 2870(w), 1716(s), 1616(s), 1577(s), 1500(m), 1462(m), 1408(s), 1342(br), 1271(w), 1236(m), 1180(m), 1126(s), 1064(w), 1012(s), 972(w), 862(m), 802(w), 761(w), 729(w).

For **P1Cu** yield 83%, Anal. Calcd. For [**P1CuCl₂**]_n: C, 60.38%; H, 5.07%; N, 8.80%. Found: C, 60.64%; H, 5.02%; N, 8.92%. ESI-MS (+MS, m/z): 1137.41, [**P1+H**]⁺; 1274.32, [**P1CuCl₂+H**]⁺; 1389.16, [**P1Mn₂Cl₂+H**]⁺. FT-IR (neat, cm⁻¹): 3423(br), 2953(m), 2931(m), 2872(w), 2357(w),

2339(w), 1716(m), 1606(s), 1577(m), 1496(br), 1462(m), 1408(m), 1346(m), 1273(m), 1234(m),
1205(w), 1176(w), 1126(s), 1068(w), 997(m), 943(w), 866(w), 796(m), 767(w), 721(w).

For **P1Zn**, yield 84%, Anal. Calcd. For $[\mathbf{P1ZnCl}_2]_n$: C, 60.29%; H, 5.06%; N, 8.79%. Found: C, 60.61%; H, 5.02%; N, 8.92%. (+MS, m/z): 1137.41, $[\mathbf{P1}+\mathbf{H}]^+$; 1273.28, $[\mathbf{P1ZnCl}_2+\mathbf{H}]^+$; 1411.06, $[\mathbf{P1Zn}_2\mathbf{Cl}_2+\mathbf{H}]^+$. FT-IR (neat, cm^{-1}): 3549(br), 3413(br), 2956(w), 2933(w), 2867(w), 2362(w), 2023(w), 1716(s), 1637(s), 1616(s), 1577(m), 1523(w), 1489(m), 1462(m), 1406(s), 1346(s), 1269(m), 1234(m), 1203(w), 1126(s), 1070(m), 997(s), 943(m), 866(w), 796(m), 763(w), 719(w)

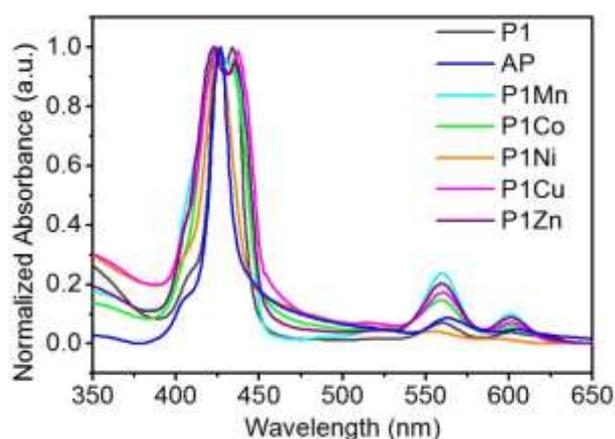


Fig. S1 Normalized UV-vis absorption spectra of the porphyrin **P1** and porphyrin coordination polymers **P1M** in CHCl_3 solution.

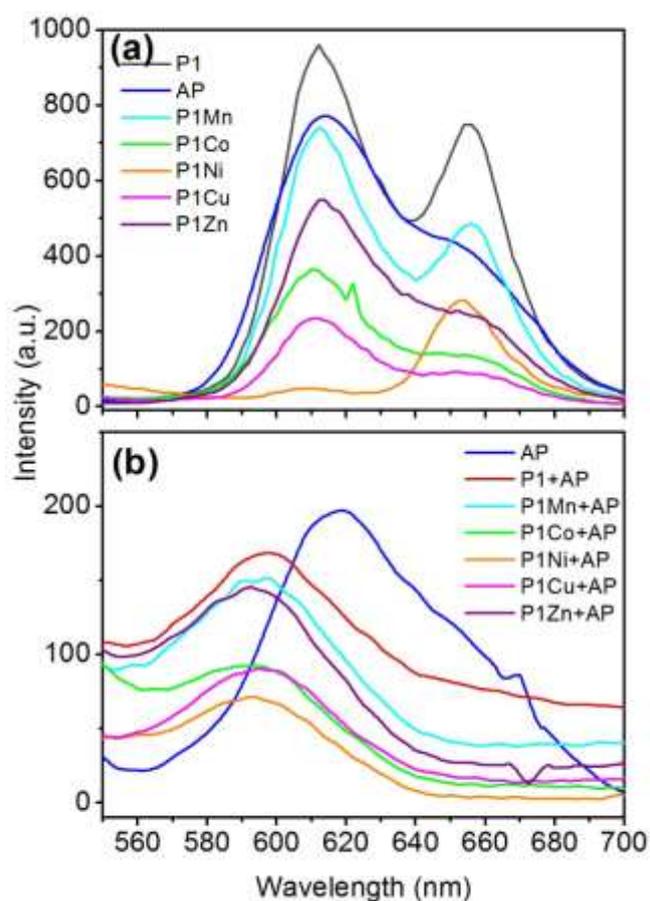


Fig. S2 Photoluminescence spectra of (a) the dyes in CHCl₃ solution and (b) adsorbed onto TiO₂ films. The emission spectra were recorded by exciting at 425 nm.

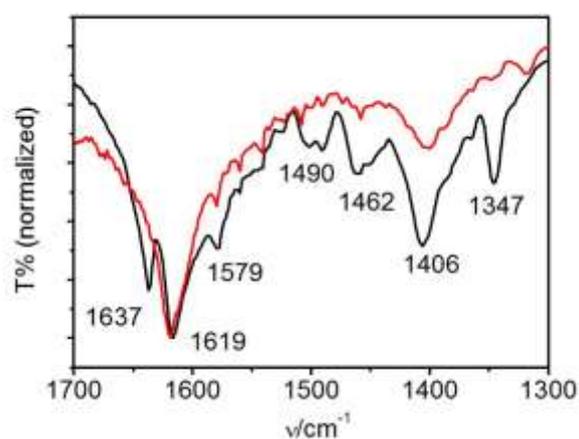


Fig. S3 FT-IR spectra of AP in solid state (black line) and after adsorbed on TiO₂ surface (red line).

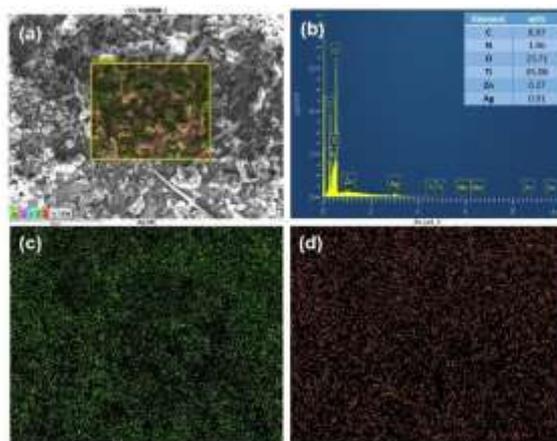


Fig. S4 SEM-EDS plane scan analysis of **P1+AgAP** sensitized TiO₂ interface:(a) SEM image (plane scan region of the interface), (b) EDS spectrum, the inset summarized the mass fractions (wt%) of the chemical elements at the TiO₂ interface, (c) element Ag, (d) element Zn.

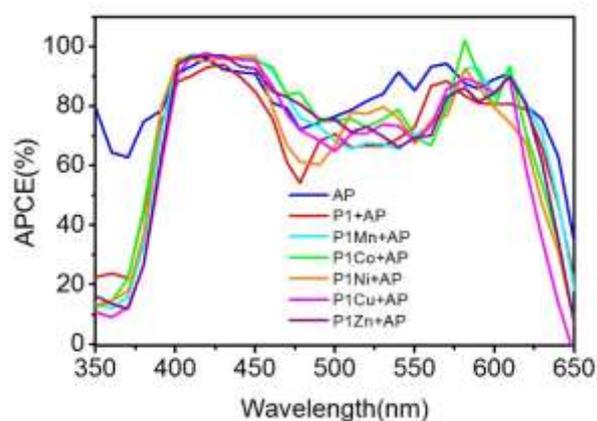


Fig. S5 APCE value of the porphyrin and porphyrin coordination polymers based solar cells.

References

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