

## Interaction of pyridine $\pi$ -bridge based poly-(methacrylate) dyes for fabrication of dye-sensitized solar cells with influence of the different strength of Phenothiazine, Fluorene and Anthracene sensitizers as donor units @ new anchoring mode†

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## Experimental Section

### Materials

The required materials, i.e., 4-hydroxy-3-nitrobenzaldehyde, 2-acetyl phenothiazine, 2-acetyl fluorene, 2-acetylanthracene and 2, 2'-Azobisisobutyronitrile (AIBN) were purchased from Sigma-Aldrich. Ammonium acetate, p-Toluenesulfonic acid (p-TSA), methacrylic acid, triethylamine (TEA) were purchased from Alfa Aesar. Dichloromethane (DCM), ethanol, methanol and tetrahydrofuran (THF) (SRL, India) solvents were purified by usual procedures. All column chromatographic separations were carried out using silica gel (60-120 mesh; analytical grade) (SRL, India). All the materials were used as received unless otherwise stated.

### Compound characterization and methods

FTIR spectra were recorded using Shimadzu FTIR 8400s. <sup>1</sup>H- and <sup>13</sup>C- NMR were measured using a Bruker Avance 300 or 500 MHz spectrometer with CDCl<sub>3</sub> or DMSO-d<sub>6</sub> as solvents. High-resolution mass spectrometry was performed on a JEOL GCMATE II GC-MS to record mass spectra (HRMS). UV-Visible spectra were recorded measured in DMF solution on a Shimadzu UV-1650PC UV-vis spectrometer. Thermogravimetric analysis (TGA) were recorded using a Mettler 851e TGA under nitrogen atmosphere at a heating rate of 10 °C/min. The glass transition temperature (T<sub>g</sub>) of the polymers were determined with a Mettler TA-3000 differential scanning calorimeter (DSC) at a heating rate of 10°C/min using air as the purge gas. The molecular weights (M<sub>w</sub>), average molecular weights (M<sub>n</sub>) and poly dispersity index (PDI) were determined by gel permeation chromatography (GPC) with tetrahydrofuran as an eluent and mono disperse polystyrene standards. All reactions were monitored by using thin layer chromatography (TLC) plates.

### Synthetic procedures and characterization data

#### 4-(2,6-di(10H-phenothiazin-3-yl)pyridin-4-yl)-2-nitrophenol (PPNP)

2-Acetylphenothiazine (2.649 g, 2 mmol) and 4-Hydroxy-3-nitrobenzaldehyde (2 g, 1 mmol) were charged under reflux condition for 6 h in the presence of ammonium acetate (2.115 g, 5 mmol) and p-Toluenesulfonic acid monohydrate (p-TSA) (0.25 mol% as catalyst) in ethanol medium. After the completion of the reaction, it was allowed to stand standing at room temperature for 4 h, and precipitate was collected by vacuum filtration, washed with methanol and dried.<sup>1</sup> The product obtained was further purified by column chromatography on silica gel using hexane:ethyl acetate as an eluent to get 4-(2,6-di(10H-phenothiazin-3-yl)pyridin-4-yl)-2-nitrophenol (PPNP). (94% yield). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz, δ ppm): 8.89 (s, 1H); 8.62 (s, 1H); 8.20 (d, 1H); 7.90 (t, 1H); 7.60 (d, 1H); 7.35 (d, 1H); 7.30 (d, 1H); 7.25 (m, 1H); 7.20 (d, 1H); 7.15 (d, 1H); 5.45(s, 4s). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz, δ ppm): 154.2; 153.8; 152.0; 142.8; 141.5; 138.0; 133.5; 128.0; 127.5; 127.3; 127.0; 126.5; 122.0; 120.5; 119.2; 117.3; 115.8. Anal. Calcd. for C<sub>35</sub>H<sub>22</sub>N<sub>4</sub>O<sub>3</sub>S<sub>2</sub>: C, 68.83; H, 3.63; N, 9.17; O, 7.86; S, 10.50. Found: C, 69.68; H, 4.78; N, 9.60; O, 8.49; S, 11.82. HRMS (m/z [M+H]<sup>+</sup>) calcd. For, 610.11; found 611.23.

#### 4-(2,6-di(9H-fluoren-2-yl)pyridin-4-yl)-2-nitrophenol (FPNP)

2-Acetylaminofluorene is used instead of 2-Acetylphenothiazine in the above procedure to synthesis **FPNP** (92% yield). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz, δ ppm): 8.40 (s, 1H); 8.55 (s, 1H); 8.30 (s, 1H); 8.15 (d, 1H); 8.00 (d, 1H); 7.95 (d, 1H); 7.90 (d, 1H); 7.60 (d, 1H); 7.40 (t, 1H); 7.28 (t, 1H); 7.25 (t, 1H); 5.45 (s, 1H); 4.20 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz, δ ppm): 154.2; 152.8; 144.0; 143.5; 141.5; 140.0; 137.8; 136.0; 133.5; 130.8; 130.2; 128.5; 127.0; 125.8; 125.5; 122.8; 120.2; 116.0; 37.0. Anal. Calcd. for

C<sub>37</sub>H<sub>24</sub>N<sub>2</sub>O<sub>3</sub>: C, 81.60; H, 4.44; N, 5.14; O, 8.81. Found: C, 82.11; H, 5.48; N, 5.90; O, 9.73. HRMS (m/z [M+H]<sup>+</sup>) calcd. For, 544.18; found 545.32.

#### 4-(2-(anthracen-2-yl)-6-(anthracen-3-yl)pyridin-4-yl)-2-nitrophenol (APNP)

2-Acetylanthracene is used instead of 2-Acetylphenothiazine in the above procedure to synthesis **APNP** (93% yield). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz, δ ppm): 8.75 (s, 1H); 8.55 (s, 1H); 8.30 (s, 1H); 8.22 (s, 1H); 8.15 (d, 1H); 8.05 (d, 1H); 7.90 (d, 1H); 7.45 (t, 1H); 7.28 (d, 1H); 5.30 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz, δ ppm): 153.5; 152.2; 138.0; 133.2; 132.6; 132.0; 130.8; 130.0; 228.8; 127.5; 126.8; 125.8. Anal. Calcd. for C<sub>39</sub>H<sub>24</sub>N<sub>2</sub>O<sub>3</sub>: C, 82.38; H, 4.25; N, 4.93; O, 8.44. Found: C, 83.09; H, 5.31; N, 5.82; O, 9.28. HRMS (m/z [M+H]<sup>+</sup>) calcd. For, 568.18; found 569.26.

#### Synthesis of monomers PPNPM, FPNPM and APNPM

Compound **PPNP** (1 g, 1.50 mmol) dissolved in dry dichloromethane (DCM) was charged in a double-necked round flask and treated with freshly distilled methacryloyl chloride (0.3 mL, 3.0 mmol) in the presence of triethylamine (TEA), at 0-5 °C. The reaction mixture was stirred at room temperature in the presence of nitrogen atmosphere for 8 h.<sup>2</sup> The quaternary ammonium salt was filtered and the reaction mixture separated using excess of DCM and dried. The crude monomer was purified by column chromatography over silica gel eluting with a mixture of Chloroform and methanol (4:1) as eluent. The obtained monomer **PPNPM** was pale yellow coloured solid (yield 70%). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz, δ ppm): 8.71 (d, 1H); 8.22 (s, 1H); 8.18 (d, 1H); 7.69 (d, 1H); 7.52 (d, 1H); 7.50 (s, 1H); 7.31 (d, 1H); 7.28 (t, 1H); 7.20 (d, 1H); 7.11 (d, 1H); 7.05 (t, 1H); 6.55 (s, 1H); 6.20 (s, 1H); 2.06 (s, 3H) (Fig. S5). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 126 MHz, δ ppm): 166.8; 154.2; 152.5; 143.8; 143.2; 143.0; 137.8; 136.7; 136.0; 135.5; 135.0; 133.0; 131.0; 128.5; 128.1; 127.5; 123.1; 122.0; 118.1; 117.2; 115.6; 115.2; 114.8; 18.1 (Fig. S5). FT-IR (KBr pellet, cm<sup>-1</sup>): 3747; 3438; 3065; 2936; 2742; 2672; 2485; 2356; 1738; 1610; 1532; 1346; 1262; 1107; 947; 792; 740 (Fig. S4). Anal. Calcd. for C<sub>40</sub>H<sub>28</sub>N<sub>4</sub>O<sub>4</sub>S: C, 72.71; H, 4.27; N, 8.48; O, 9.69; S, 4.85. Found: C, 73.65; H, 5.08; N, 9.17; O, 10.51; S, 5.32. HRMS (m/z [M+H]<sup>+</sup>) calcd. For C<sub>40</sub>H<sub>28</sub>N<sub>4</sub>O<sub>4</sub>S, 660.18; found 661.42. Similarly, monomers **FPNPM** and **APNPM** were prepared using the same procedure described above.

#### Monomer FPNPM:

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz, δ ppm): 8.68 (s, 1H); 8.31 (s, 1H); 8.25 (s, 1H); 8.20 (d, 1H); 8.18 (d, 1H); 8.05 (d, 1H); 7.90 (d, 1H); 7.65 (d, 1H); 7.60 (d, 1H); 7.40 (t, 1H); 7.31 (t, 1H); 6.45 (s, 1H); 6.25 (s, 1H); 4.18 (s, 1H); 2.08 (s, 3H) (Fig. S7). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 126 MHz, δ ppm): 166.5; 153.8; 152.5; 144.0; 143.8; 143.5; 141.5; 140.4; 137.5; 136.8; 135.9; 135.5; 135.2; 1305; 130.2; 130.0; 128.6; 128.4; 126.9; 125.7; 125.5; 123.8; 120.1; 115.8; 36.8; 18.1 (Fig. S7). FT-IR (KBr pellet, cm<sup>-1</sup>): 3747; 3444; 3341; 3058; 2942; 2742; 2665; 2491; 2356; 1738; 1661; 1532; 1320; 1095; 811; 740 (Fig. S6). Anal. Calcd. for C<sub>41</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>: C, 80.38; H, 4.61; N, 4.57; O, 10.45. Found: C, 81.03; H, 5.72; N, 4.98; O, 11.29. HRMS (m/z [M+H]<sup>+</sup>) calcd. For C<sub>41</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>, 660.18; found 661.42. (yield 70%).

#### Monomer APNPM:

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz, δ ppm): 8.73 (s, 1H); 8.69 (s, 1H); 8.40 (s, 1H); 8.25 (s, 1H); 8.15 (d, 1H); 8.12 (d, 1H); 8.05 (d, 1H); 7.95 (d, 1H); 7.70 (d, 1H); 7.35 (t, 1H); 6.39 (s, 1H); 6.20 (s, 1H); 2.05 (s, 3H) (Fig. S9). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 126 MHz, δ ppm): 166.4; 154.0; 152.8; 143.8; 137.8; 137.0; 136.5; 135.8; 135.0; 133.6; 132.1; 130.8; 130.5; 130.0; 128.4; 128.1; 126.8; 126.6; 125.8; 124.2; 123.5; 115.8; 18.1 (Fig. S9). FT-IR (KBr pellet, cm<sup>-1</sup>): 3747; 3444; 3065; 2936; 2743; 2672; 2492; 2362; 1713; 1597; 1468; 1397; 1320; 1255; 1030; 805; 747; 708 (Fig. S8). Anal. Calcd. for C<sub>43</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>: C, 81.12; H, 4.43; N, 4.40; O, 10.05. Found: C, 82.01; H, 5.31; N, 5.75; O, 11.12. HRMS (m/z [M+H]<sup>+</sup>) calcd. For C<sub>43</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>, 636.20; found 637.38. (yield 74%).

### Synthesis of polymers PPNPP, FPNPP and APNPP

Monomer (**PPNPM**) and AIBN (0.5% wt. of monomer) in 10 mL THF solution were taken in a Schlenk tube under N<sub>2</sub> atmosphere, and the tube was tightly closed with rubber septum. The reaction mixture was then degassed by purging with N<sub>2</sub> gas for 25 min, and the Schlenk tube was sealed and kept at 75±5 °C oil bath with constant stirring.<sup>3</sup> After 52 hours, the polymer is cooled to room temperature, and then poured into methanol to precipitate the polymer. The precipitate of crude polymer (PPNPM) obtained was separated by filtration and purified by repeated precipitation from chloroform into methanol and then dried in vacuum at 40°C. The residue was collected and dried under vacuum to obtain **PPNPM** (70% yield). By the similar procedure, polymers **FPNPM** and **APNPM** were prepared (Scheme 1). The characterization data of **PPNPP**, **FPNPP** and **APNPP** are given below.

**Polymer PPNPP:** (70% yield). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz, δ ppm): 8.69 (s, 1H); 8.31(s, aH); 8.19 (d, 1H); 7.50 (d, 1H); 7.45 (s, 1H); 7.30 (d, 1H); 7.25 (t, 1H); 7.23 (d, 1H); 7.20 (d, 1H); 7.00 (t, 1H); 1.55 (m, 2H); 1.31 (s, 3H) (Fig. S5). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 126 MHz, δ ppm): 174.8; 153.8; 152.6; 145.7; 143.7; 143.0; 142.8; 137.5; 135.5; 135.0; 132.2; 130.8; 128.7; 127.5; 123.5; 122.8; 118.5; 117.1; 115.7; 115.0; 114.08; 44.7; 34.5; 23.2 (Fig. S5). FT-IR (KBr pellet, cm<sup>-1</sup>): 3747; 3444; 3058; 2974; 2742; 2685; 2491; 2356; 1751; 1686; 1538; 1352; 1268; 1088; 1023; 805; 740 (Fig. S4). GPC: M<sub>w</sub> = 29600 g·mol<sup>-1</sup>, M<sub>w</sub>/M<sub>n</sub> = 1.61.

**Polymer FPNPP:** (72% yield). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz, δ ppm): 8.70 (s, 1H); 8.35 (s, 1H); 8.25 (s, 1H); 8.23 (d, 1H); 8.21 (d, 1H); 8.05 (d, 1H); 7.90 (d, 1H); 7.65 (d, 1H); 7.58 (d, 1H); 7.40 (t, 1H); 7.31 (t, 1H); 4.15 (s, 1H); 1.60 (m, 3H); 1.32 (s,3H) (Fig. S7). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 126 MHz, δ ppm): 174.6; 153.7; 152.6; 146.0 143.9; 143.7; 143.3; 141.5; 140.0; 138.1; 135.5; 135.3; 130.0; 129.2; 128.4; 127.0; 125.9; 125.3; 123.6; 120.0; 116.0; 44.8; 36.3; 34.60; 25.2 (Fig. S7). FT-IR (KBr pellet, cm<sup>-1</sup>): 3352; 3060; 2986; 1950; 1794; 1695; 1590; 1527; 1447; 1354; 1285; 1193; 1093; 1018; 882; 783; 739 (Fig. S6). GPC: M<sub>w</sub> = 30200 g·mol<sup>-1</sup>, M<sub>w</sub>/M<sub>n</sub> = 1.50.

**Polymer APNPP:** (72% yield). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz, δ ppm): 8.65 (s, 1H); 8.60 (s, 1H); 8.35 (s, 1H); 8.28 (s, 1H); 8.20 (d, 1H); 8.15 (d, 1H); 8.03 (d, 1H); 7.98 (d, 1H); 7.65 (d, 1H); 7.40 (t, 1H); 1.55 (m, 2H); 1.30 (s, 3H) (Fig. S9). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 126 MHz, δ ppm): 174.5; 154.0; 152.6; 146.0; 143.8; 137.8; 136.9; 135.6; 132.9; 132.5; 131.5; 131.9; 130.6; 130.4; 128.8; 127.3; 126.7; 126.0; 124.2 123.6; 44.5; 34.6; 25.5 (Fig. S9). FT-IR (KBr pellet, cm<sup>-1</sup>): 3747; 3348; 3058; 2968; 2936; 2749; 2678; 2491; 2356; 2227; 1758; 1661; 1532; 1474; 1390; 1171; 1043; 792; 734 (Fig. S8). GPC: M<sub>w</sub> = 28900 g·mol<sup>-1</sup>, M<sub>w</sub>/M<sub>n</sub> = 1.53.

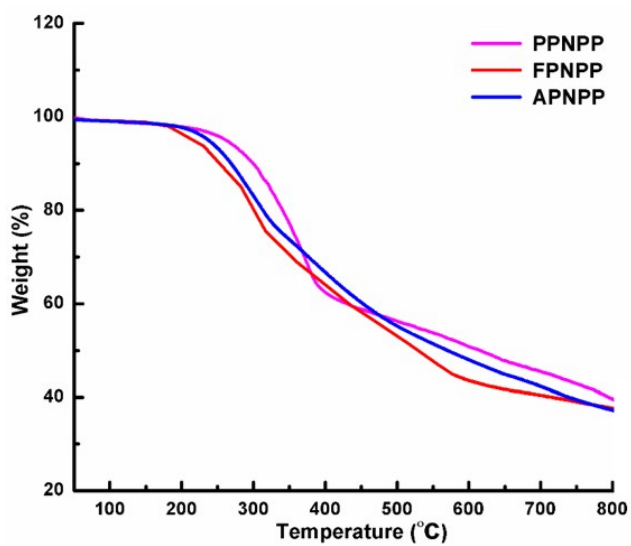


Fig. S1. TGA curves of PPNPP, FPNPP and APNPP

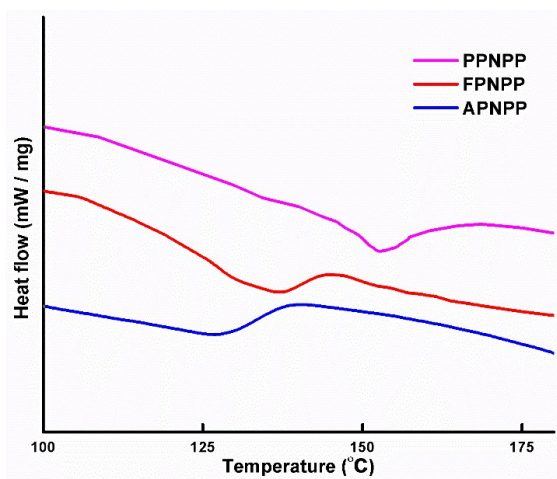
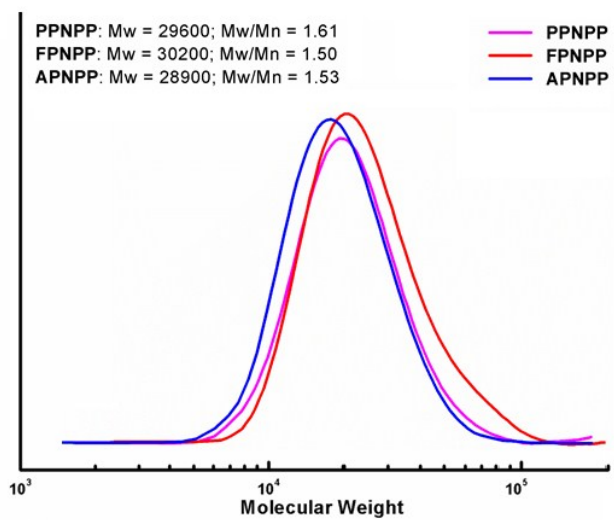


Fig. S2. DSC curves of PPNPP, FPNPP and APNPP



**Fig. S3.** GPC curves of polymers **PPNPP**, **FPNPP** and **APNPP**

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1. A. Hariharan, K. Subramanian, M. Alagar and K. Dinakaran, *High Perform. Polym.*, 2015, **27**, 724–733.
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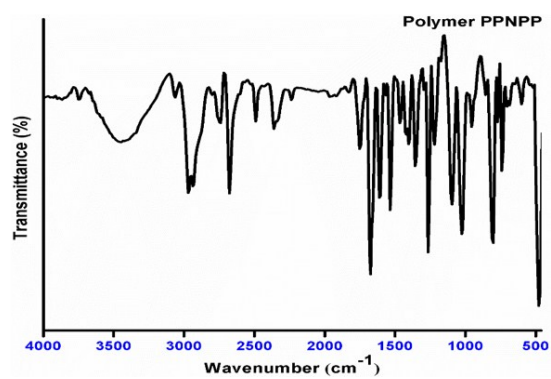
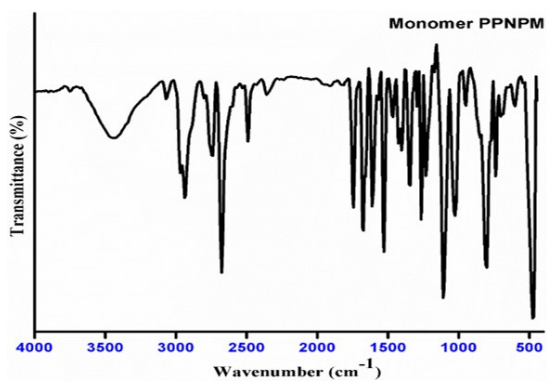


Fig. S4. FT-IR spectra of monomers PPNPM and polymers PPNPP

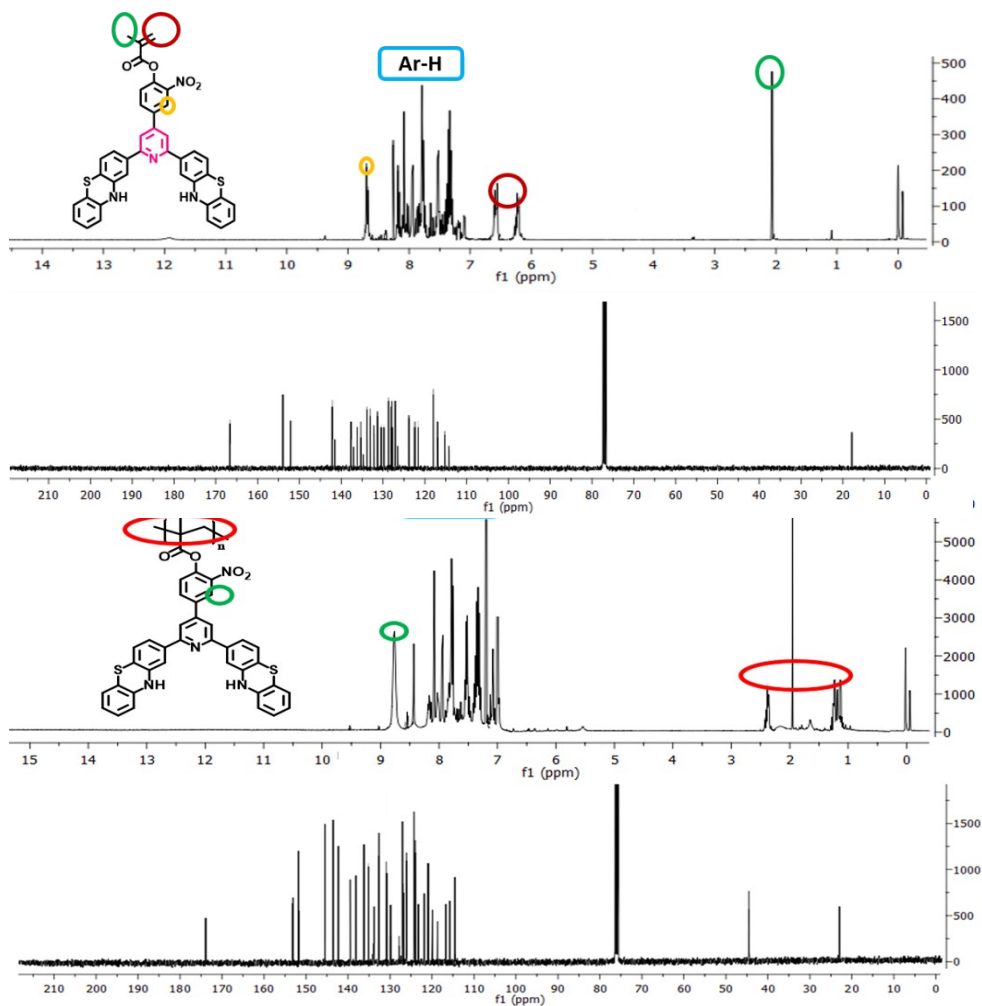


Fig. S5. <sup>1</sup>H-NMR, <sup>13</sup>C-NMR Monomer PPNPM and Polymer PPNPP

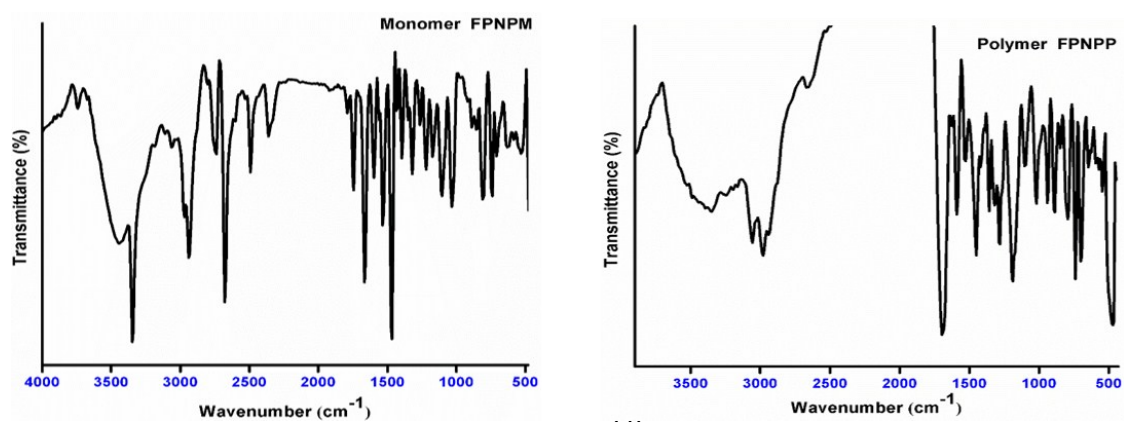




Fig. S6. FT-IR spectra of monomers FPNPM and polymers FPNP

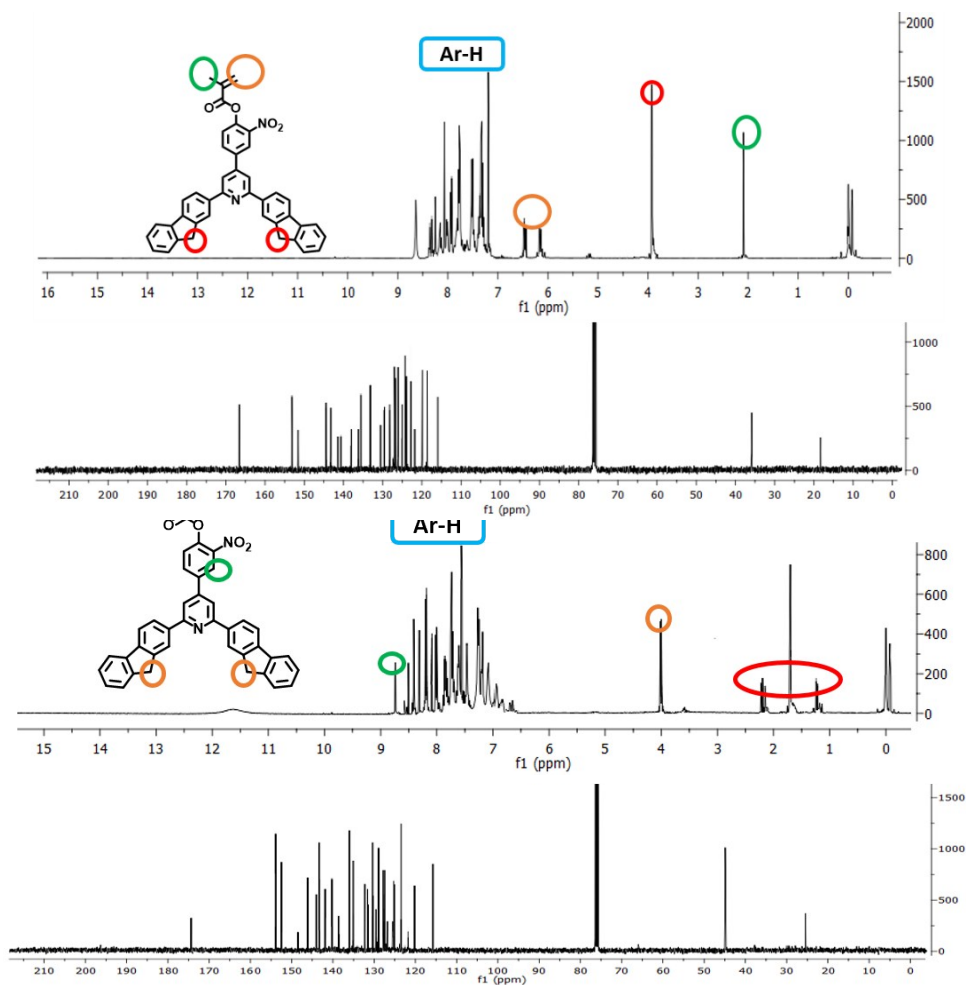


Fig. S7. <sup>1</sup>H-NMR, <sup>13</sup>C-NMR Monomer FPNPM and Polymer FPNP

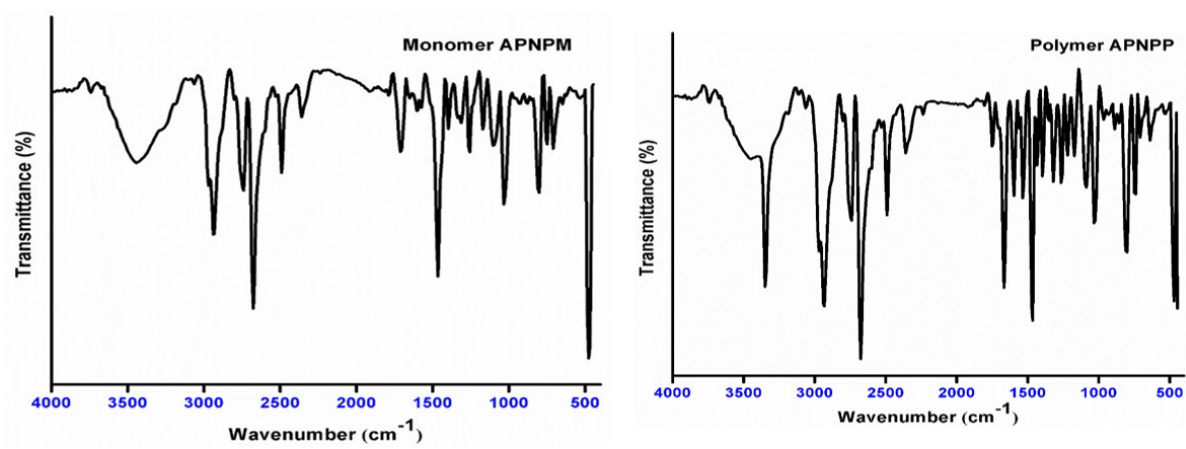


Fig. S8. FT-IR spectra of monomers APNPM and polymers APNPP

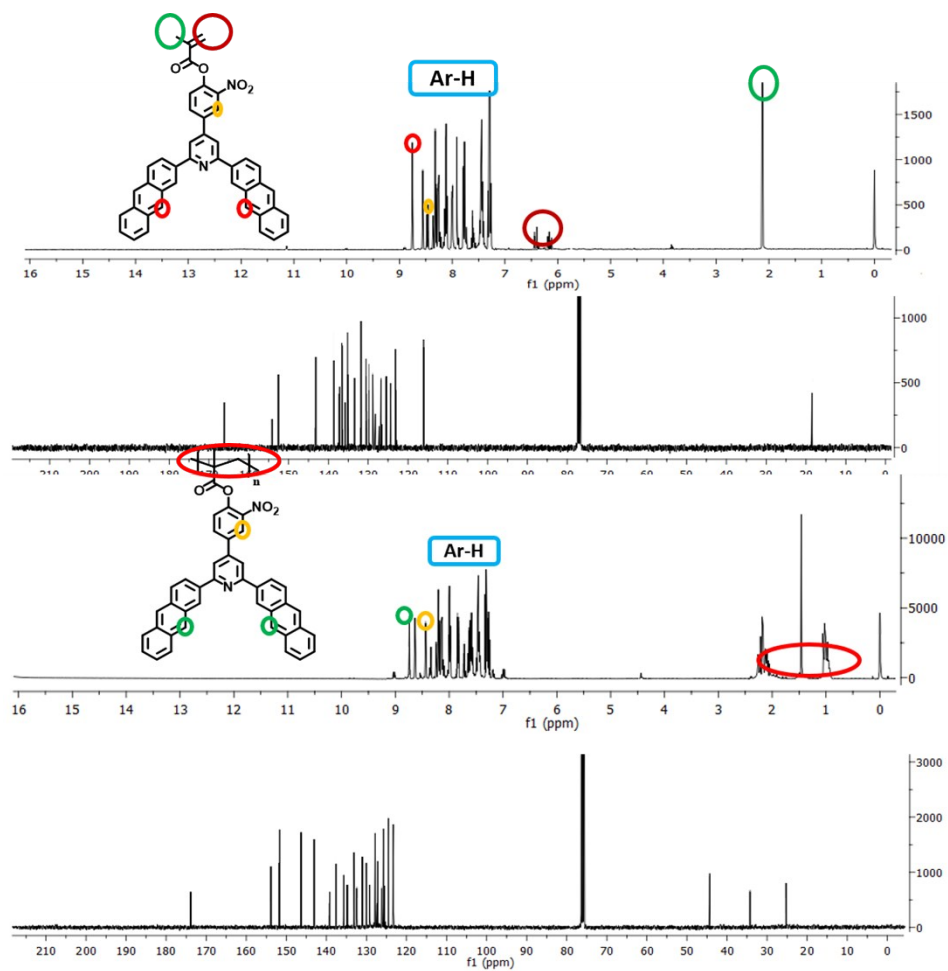


Fig. S9. <sup>1</sup>H-NMR, <sup>13</sup>C-NMR Monomer APNPM and Polymer APNPP