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A Novel Complementary Absorbing Donor-Aceptor Pair in Block Copolymers Based on Single Materials Organic Photovoltaics

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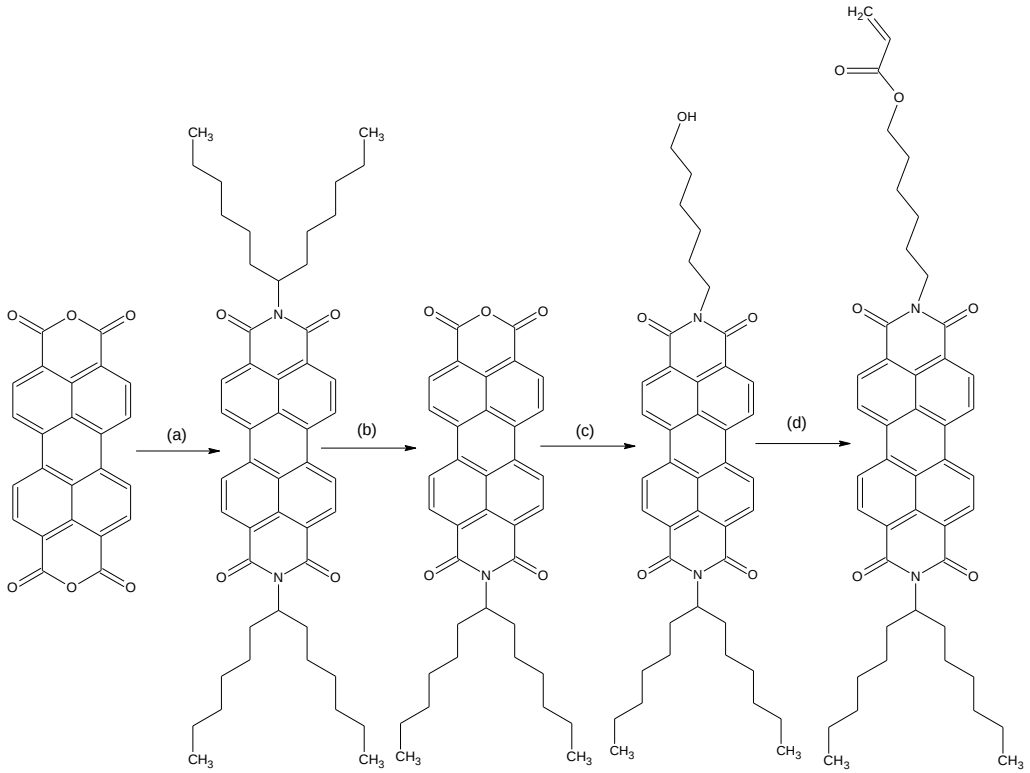
General Information: All used reagents were of commercial grade and used without any further purification. Perylene bisimide (PDI) based acrylic monomer was synthesized using standard procedures (Scheme-S1). [1,2]



a) pyridine, $Zn(COOH)_2$, 2-ethyl-hexylamine, 3h, reflux; b) t-BuOH, KOH, 2h, reflux; c) DMAc, 6-amino-1-hexanol, $Zn(COOH)_2$, 5h, reflux; d) Acryloyl chloride, triethyamine, dichloromethane, 24h, r.t.

Scheme-S1. Synthetic route to Perylene bisimide based acrylic monomer

On the other hand, diketopyrolopyroll (DPP) based low band gap macroinitator was synthesized by using following synthetic route (Scheme S2). 1,2,3[3], and 6,7[4] were prepared according to previously published procedures.

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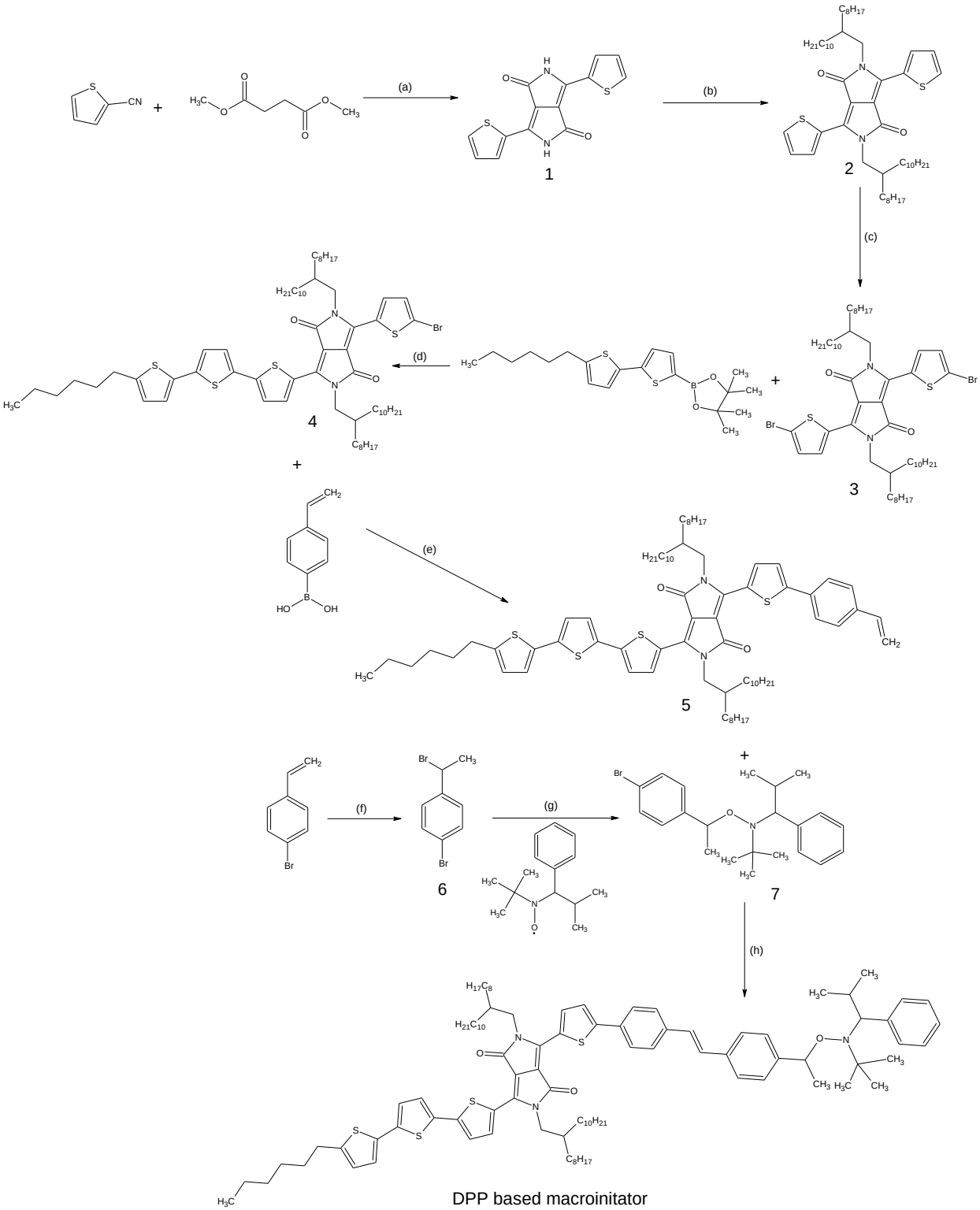

a)Tert-amyl alcohol, potassium tert-butoxide, 120 ℃, 2h; b) 2-octyldodecyl bromide, Cs_2CO_3, DMF, 120 ℃; c)NBS, $CHCl_3$, 0 ℃, 1h; d) K_2CO_3, Toluene/Water, TEAH, $Pd(PPh_3)_4$, 110 ℃, 5h; e) $NaCO_3$, THF/Water, 80 ℃, 5h; f) HBr 48%, 12h; g) CuBr/PMDTA, Toluene, 50 ℃, 1h, h) Pd2(dba)3, tri(t-butyl)phosphine, metyl dicyclohexane amine, THF, 55 ℃, 24h.

Scheme-S2. Synthetic route to DPP based low band gap macroinitator.

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Bromine terminated DPP-low band gap molecule 4. Under the protection of argon atmosphere, dibromo-DPP **3** (2.04 g, 2 mmol) and 5'-Hexyl-2,2'-bithiophene-5-boronic acid pinacol ester (0.752 g, 2 mmol) was put into a two-neck flask. Then 20 mL of degassed toluene and 5 mL of 2M K_2CO_3 solution in water were added to the mixture. The solution was flushed with nitrogene for 15 min, and then 25 mg of $Pd(PPh_3)_4$ was added. After another flushing with nitrogene for 15 min, the reactant was heated to 110 °C. After 5 min, 1 mL of tetraethlyammonium hydroxide solution (~40% in H_2O) was added and then the mixture was stirred for 5 h at 110 °C. The reactant was cooled to room temperature and poured into 200 mL of ethanol. The solvent was removed under vacuum and the residue was purified by column chromatography (by eluting with CH_2Cl_2-Hexane (1:1) to yield molecule **4**. (1.12 g, 47% yield). *^{1}H-NMR ($CHCl_3$ -d): δ ppm, 8.96 (d, 1H), 8.63 (d, 1H), 7.27 (d, 2H), 7.22 (d 2H), 7.05 (d, 2H), 6.73 (d, 1H), 4.04 (d 2H), 3.97 (d, 2H), 2.82 (t, 2H), 1.76-0.84 (m, 94H, CH aliphatic).*

Vinyl terminated DPP-low band gap molecule 5. . Under the protection of Argon atmosphere, a mixture of **4** (0.95 g, 0.8 mmol), 4-Vinylphenylboronic acid (0.148 g, 1 mmol) was put into a two-neck flask. Then 20 mL of degassed THF and 5 mL of 2M Na_2CO_3 solution in water were added to the mixture. The solution was flushed with nitrogene for 15 min, and then 25 mg of $Pd(PPh_3)_4$ was added. After another flushing with nitrogene for 15 min, the reactant was heated to 110 °C. Then the mixture was stirred for 5 h at 80 °C. The mixture was cooled to room temperature and then poured into a large amount of cold methanol (200 mL). The residue was obtained by filtration and purified by column chromatography (by eluting with CH_2Cl_2-Hexane (2:1) to yield molecule **5** (1.10 g, 92% yield). *^{1}H-NMR ($CHCl_3$ -d): δ ppm, 8.95 (d, 2H), 7.69-6.73 (m, 21H), 5.27 (d, 1H), 3.96 (dd, 4H), 2.71 (t, 2H), 1.91-0.84 (m, 94H, CH aliphatic).*

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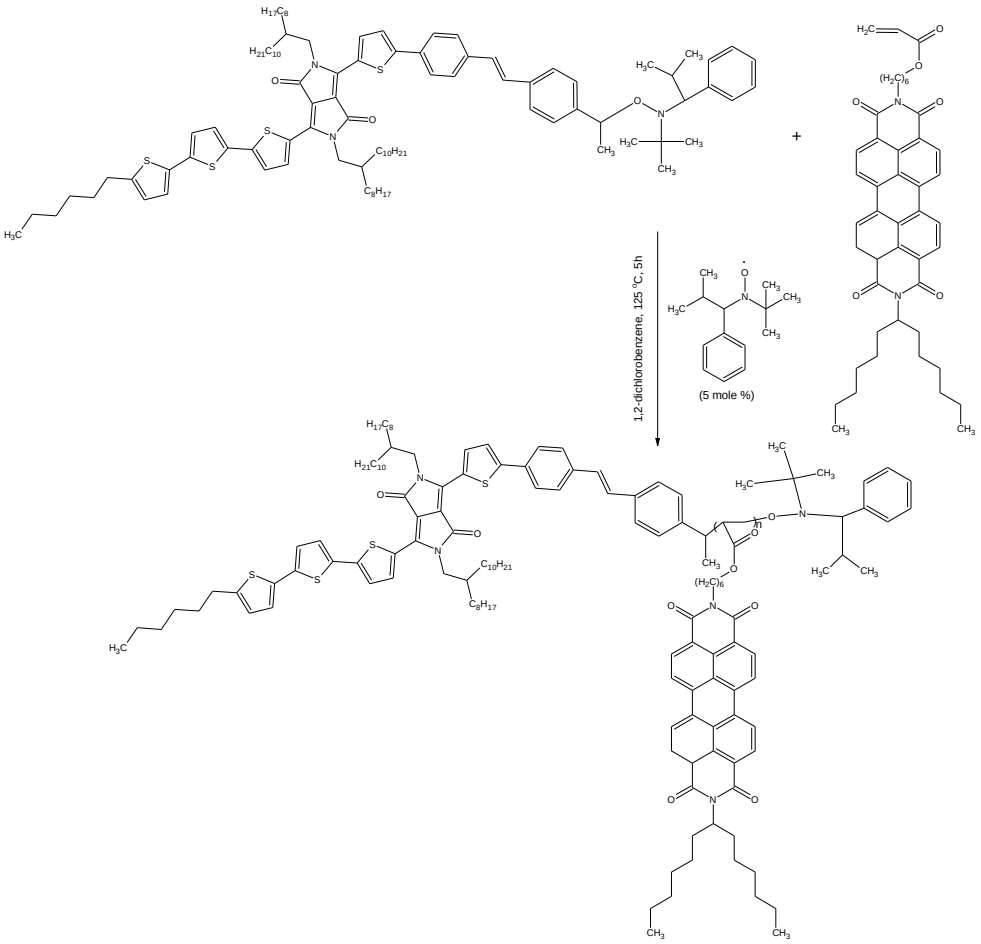
DPP alkoxyamine macroinitiator. A Schleck flask were dried by Head-gun under vacum and cooled down under argon. Vinyl-terminated DPP **5** (0.85 g, 0.7 mmol) was dissolved in anhydrous THF (75 mL) in this Schlenk flask under argon. To this was added $Pd_2(dba)_3$ (72 mg), tri(t-butyl)phosphine (60 mg), methyl dicyclohexane amine (3.60 g) and phenylbromide-alkoxylamine **7 (**0.3g, 0.75 mmol).The reaction mixture was stirred at 55 °C for 24 hrs. The residue precipitated repeatedly into methanol, then dried under vacuum to give DPP based macroinitiator (0.9 g, 83% yield). *^{1}H-NMR ($CHCl_3$ -d): δ ppm, 8.95 (d, 2H), 7.69-6.73 (m, 21H, CH aromatic), 4.96 (d, 1H), 4.09 (t, 4H), 3.43-3.32 (dd, 1H), 2.83 (t, 2H), 2.02-0.25 (m, 112H, CH aliphatic) MS [MALDI-TOF]: m/z* 1535.51 [M^+] .

Finally, DPP based macroinitator was used for polymerization of acryloyl based perylene bisimide monomer (Scheme S3).



Scheme-S3. Synthetic route to DPP-PDI block copolymer

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DPP-PDI diblock copolymer. A mixture of DPP alkoxyamine macroinitiator (0.32 g, 0.2 mmol), perylene bisimide acrylate monomer (PDI) (0.72 g, 1 mmol), nitroxide radical (0.46 mg, 0.002 mmol) and 1,2-dichlorobenzene (400 μL) were subjected to three freeze pump-thaw cycles, sealed under vacuum, and heated at 125 °C for 24 h. The reaction mixture was cooled, dissolved in THF, and precipitated in methanol. The black precipitate was filtered and dried to give the desired DPP-PDI block copolymer (480 mg). GPC: Mn 7200 $gmol^{-1}$, PDI 1.16. *^{1}H-NMR ($CHCl_3$ -d): δ ppm, 8.95 (d, 2H-DPP), 8.65 (d, 8H-PDI), 7.98-6.73 (m, 21H, CH aromatic), 5.20, 4.19, 4.06, 3.51, 2.83, 2.64, 2.25-0.83 (m, CH aliphatic).*

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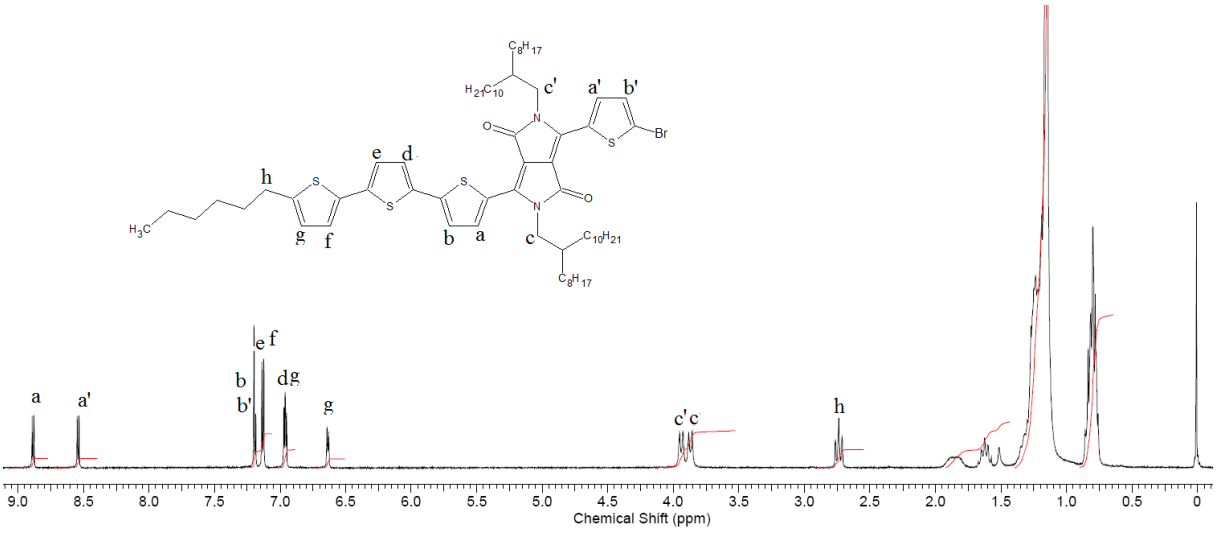

Figure S1. ^{1}H-NMR spectrum of bromine terminated DPP- low band gap molecule **5**

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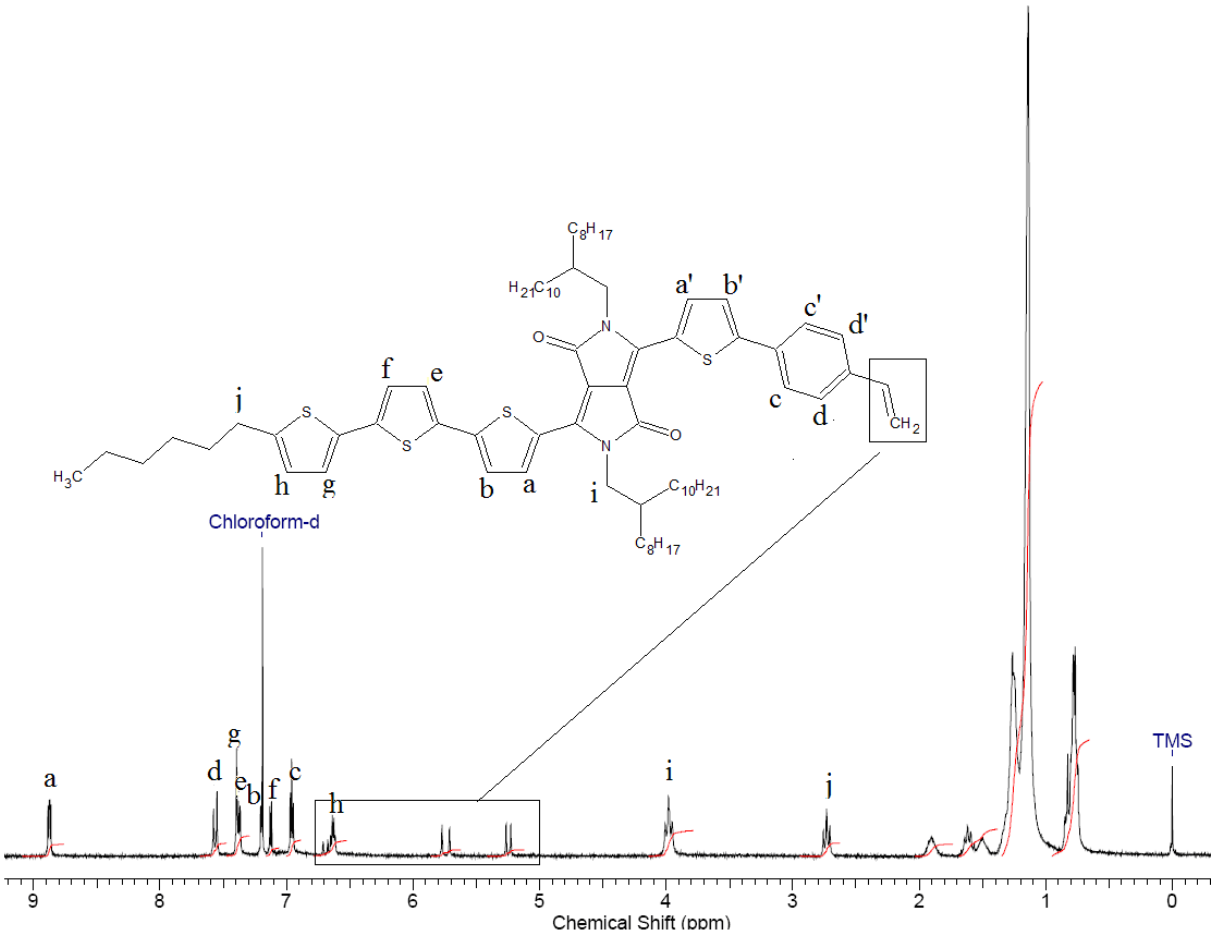

Figure S2. ^{1}H-NMR spectrum of vinyl terminated DPP- low band gap molecule **6**.

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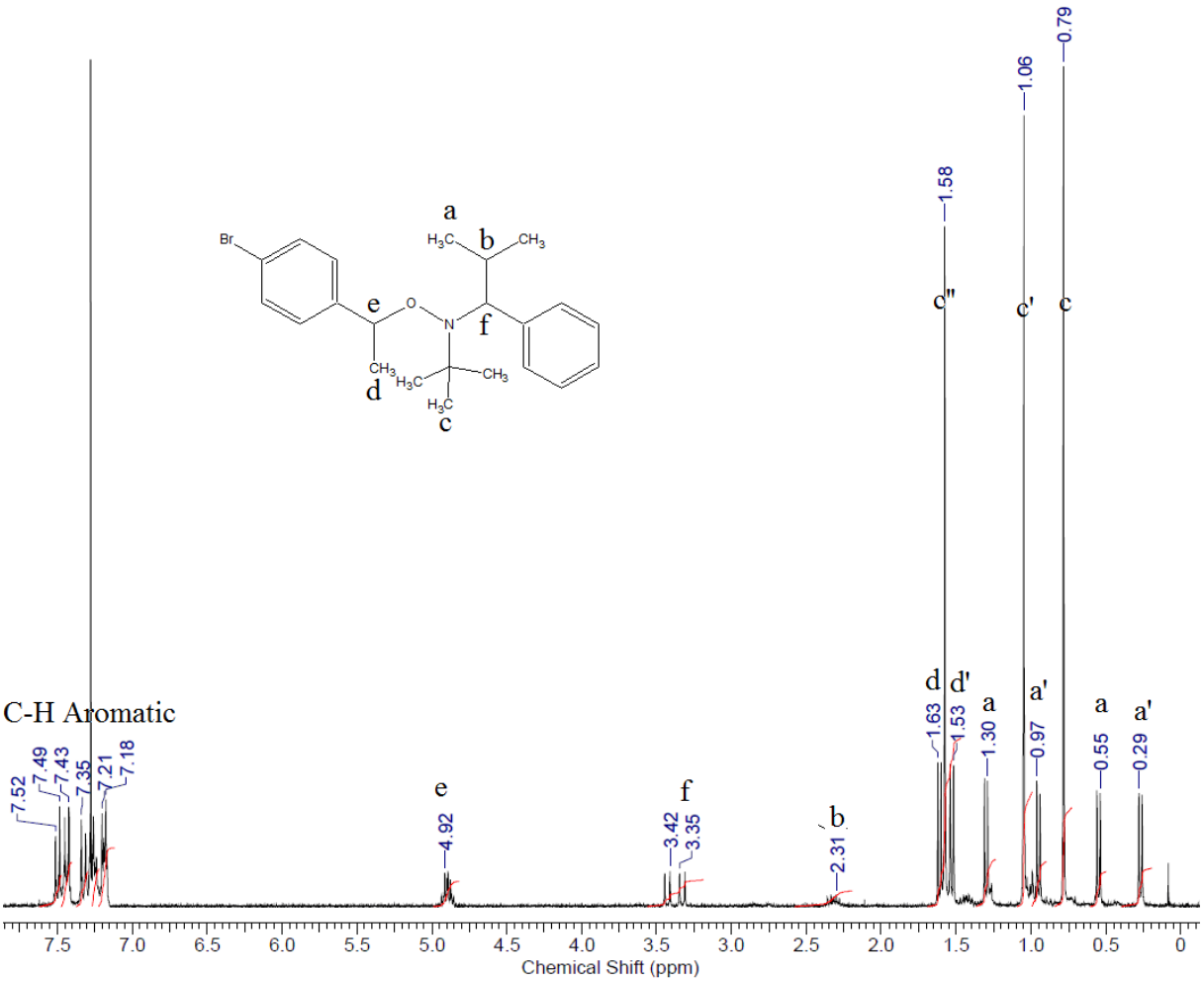

Figure S3. ^{1}H-NMR spectrum of 2,2,5-Trimethyl-(1'-p-bromophenylethoxy)-4-phenyl-3-azahexane (TIPNO) macroinitator.

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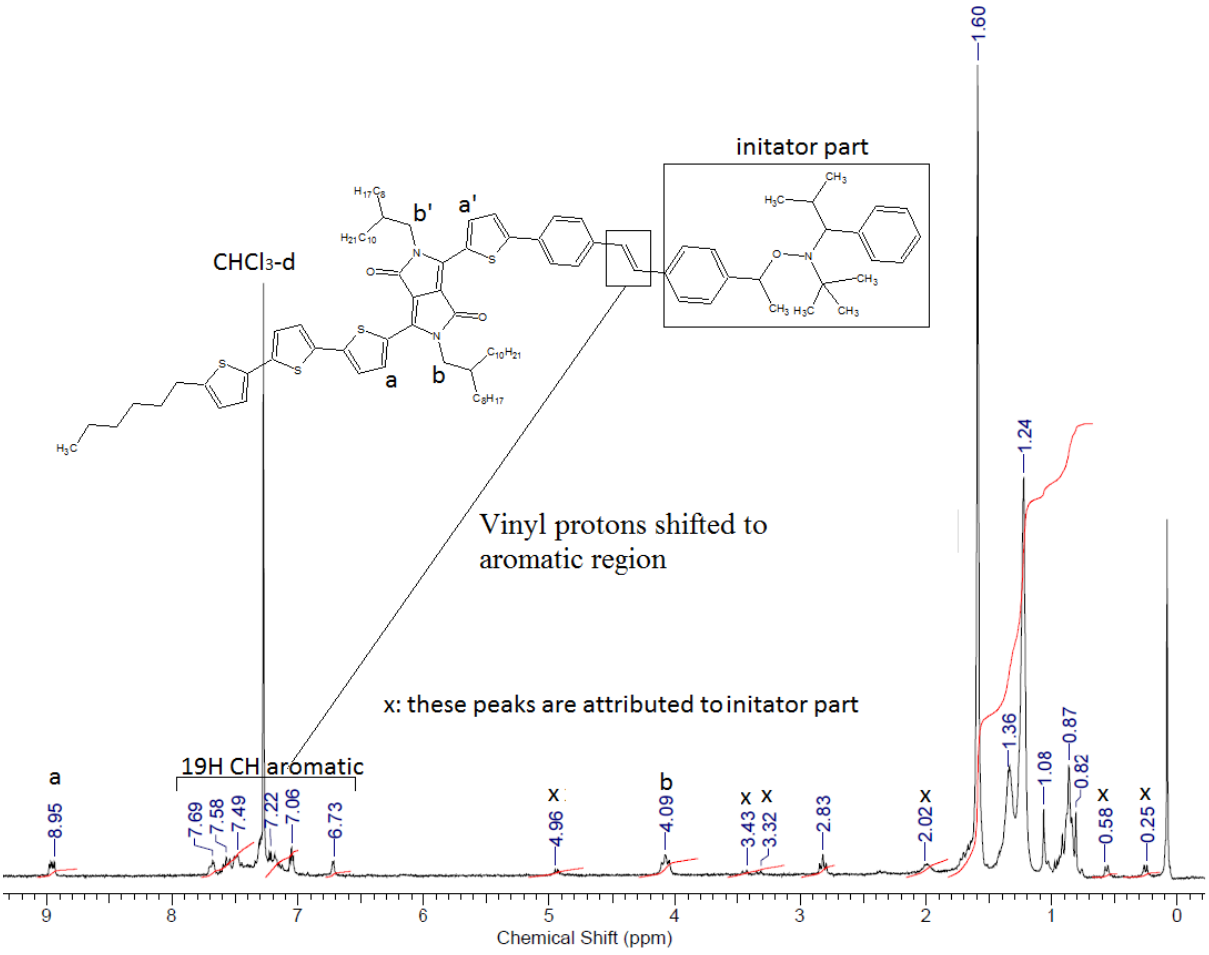

Figure S4. ^{1}H-NMR spectrum of DPP based macroinitator.

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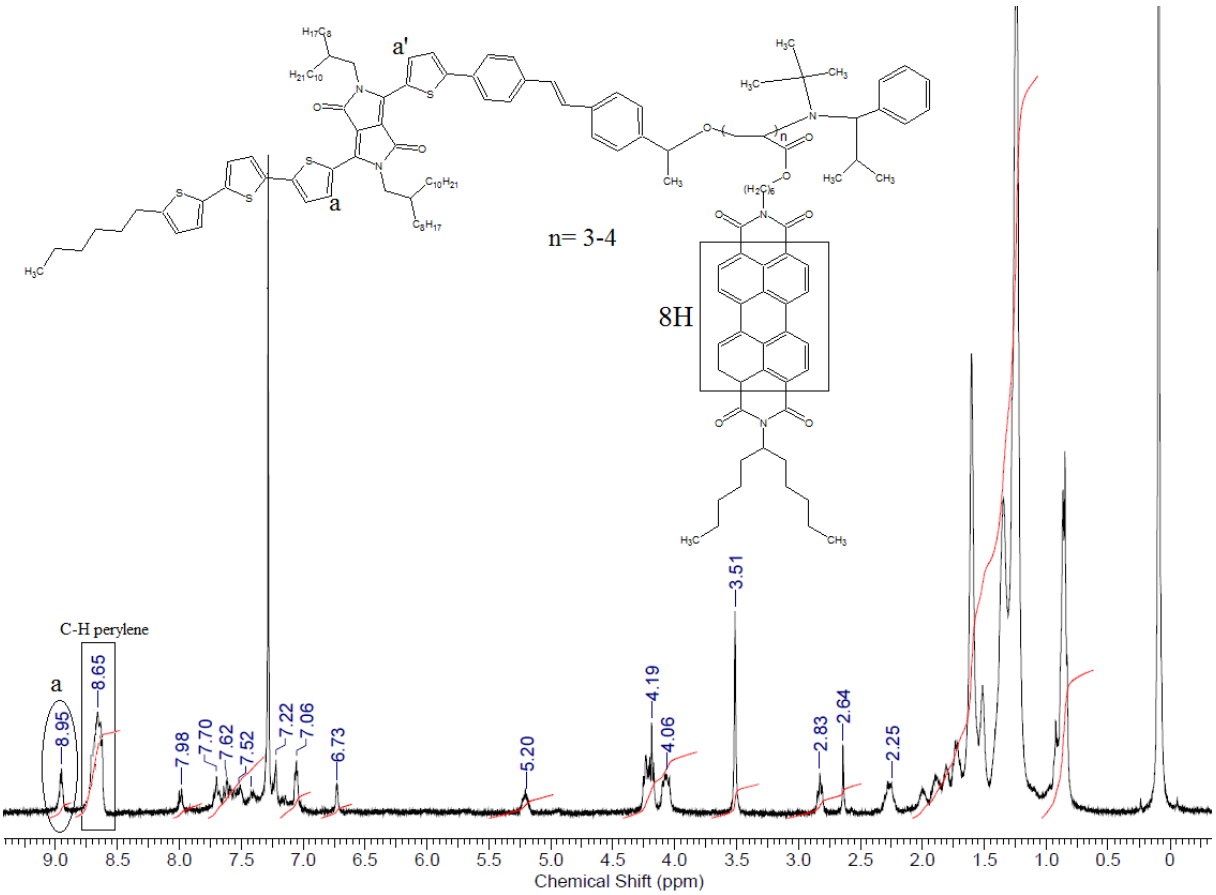

Figure S5. ^{1}H-NMR spectrum of DPP-PDI block copolymer

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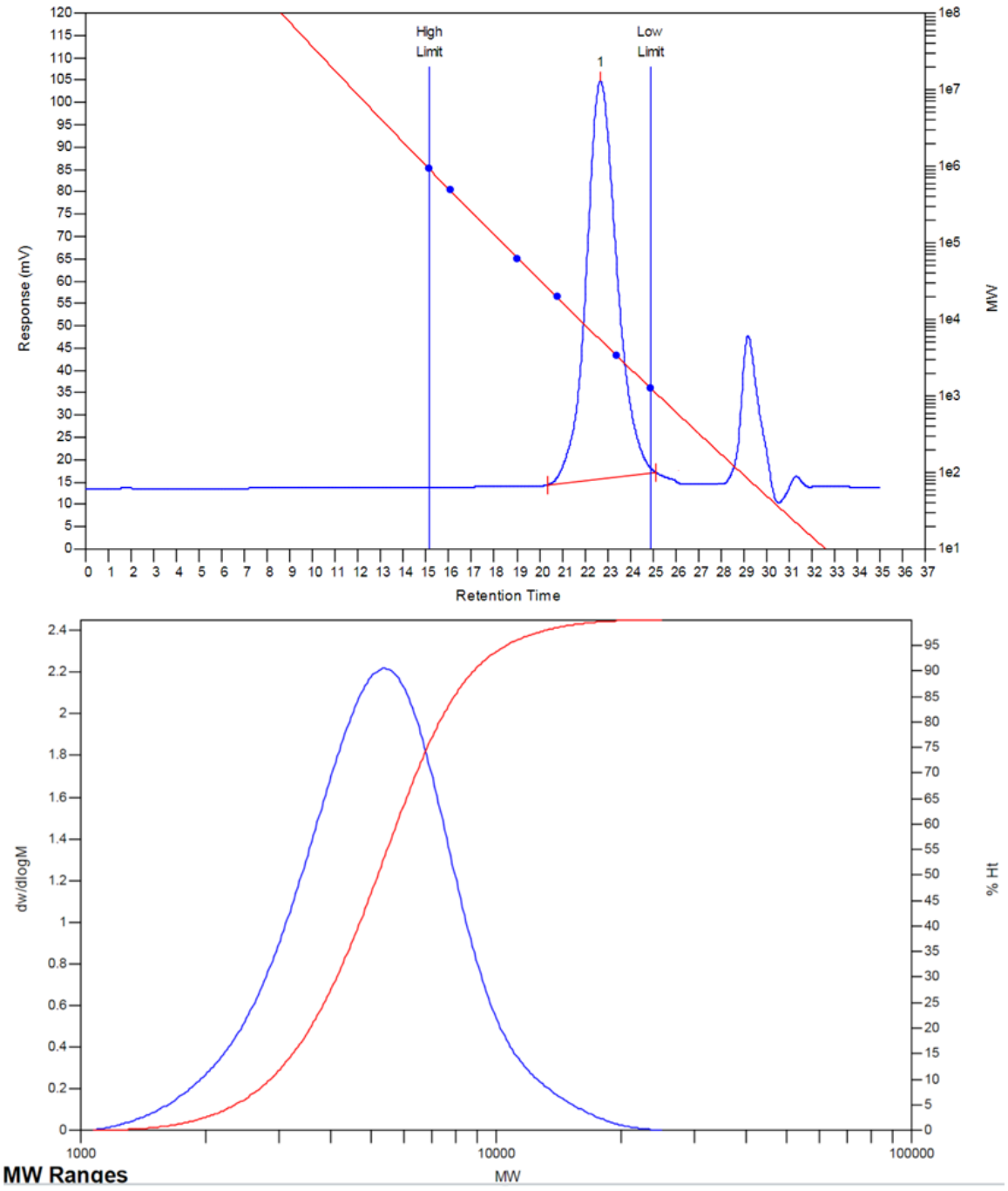

Figure S6. GPC curve of DPP-PDI block copolymer.

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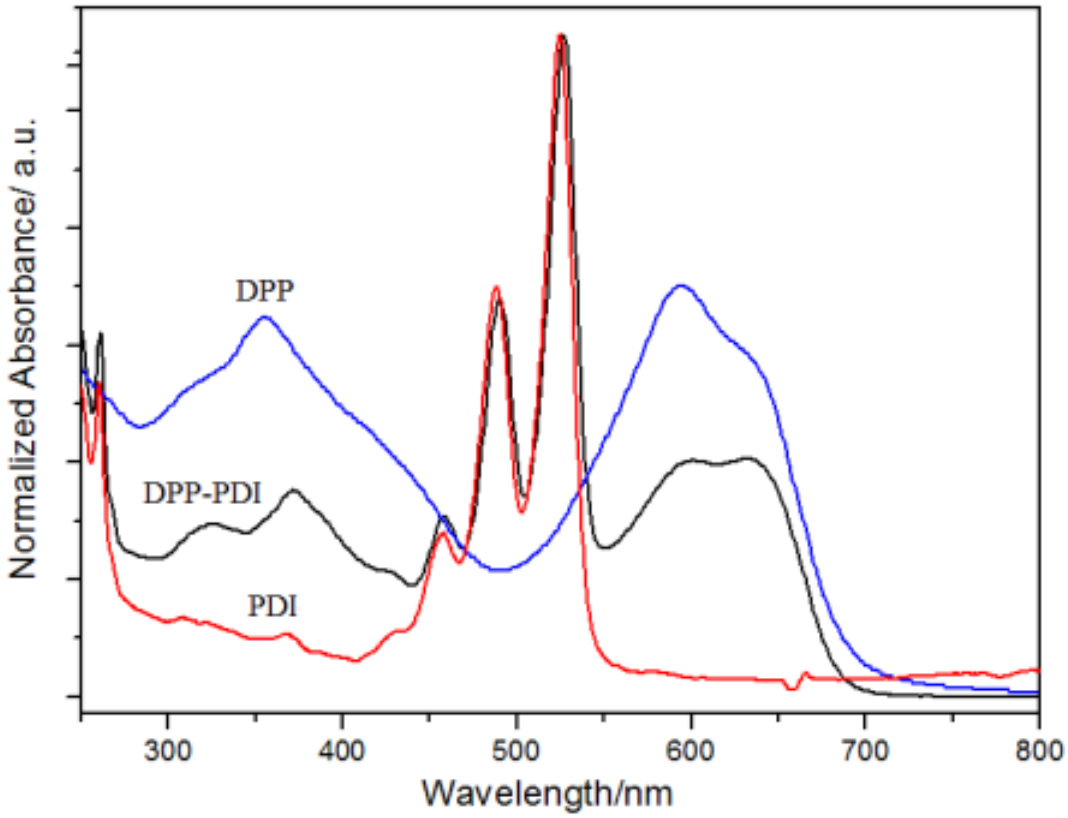

Figure S7. Absorption spectra of initial compounds and DPP-PDI block copolymer in DCM solution

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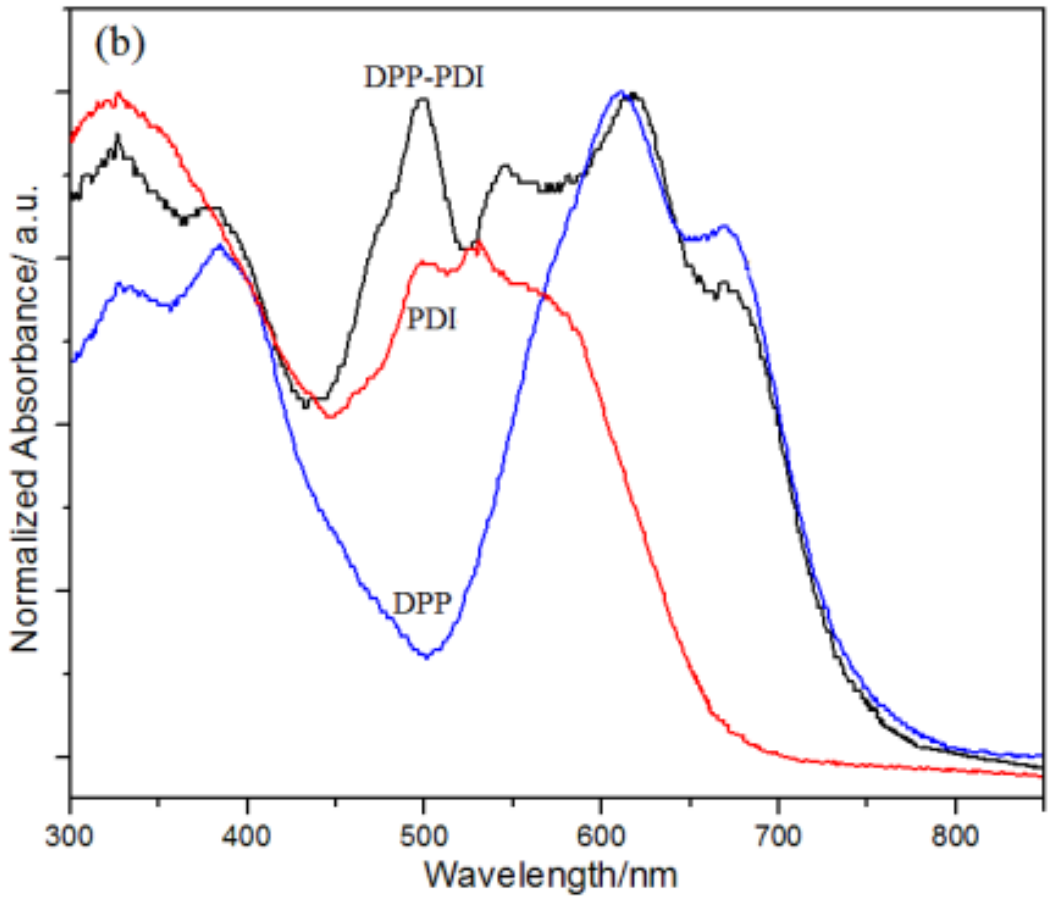

Figure S8. Absorption spectra of initial compounds and DPP-PDI block copolymer on thin film

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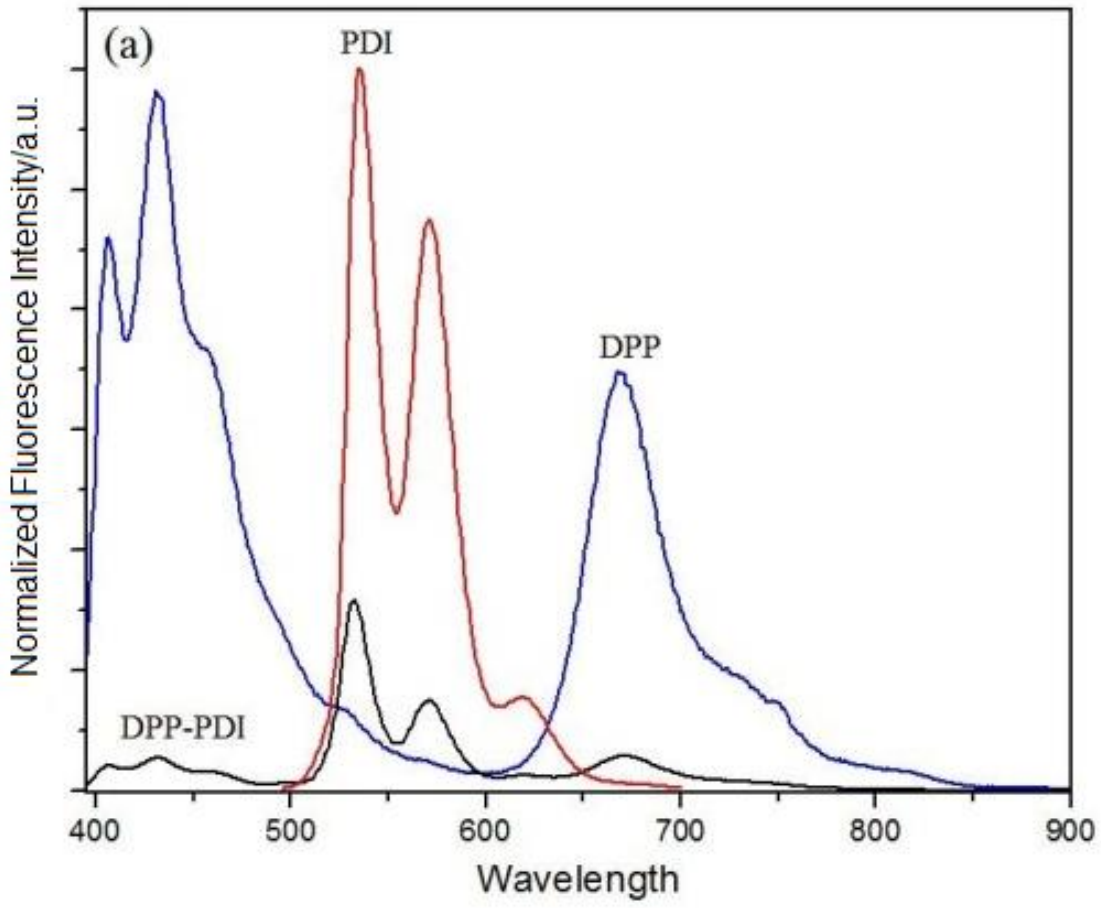

Figure S9. Photoluminescence spectra of initial compounds and DPP-PDI block copolymer in DCM solution

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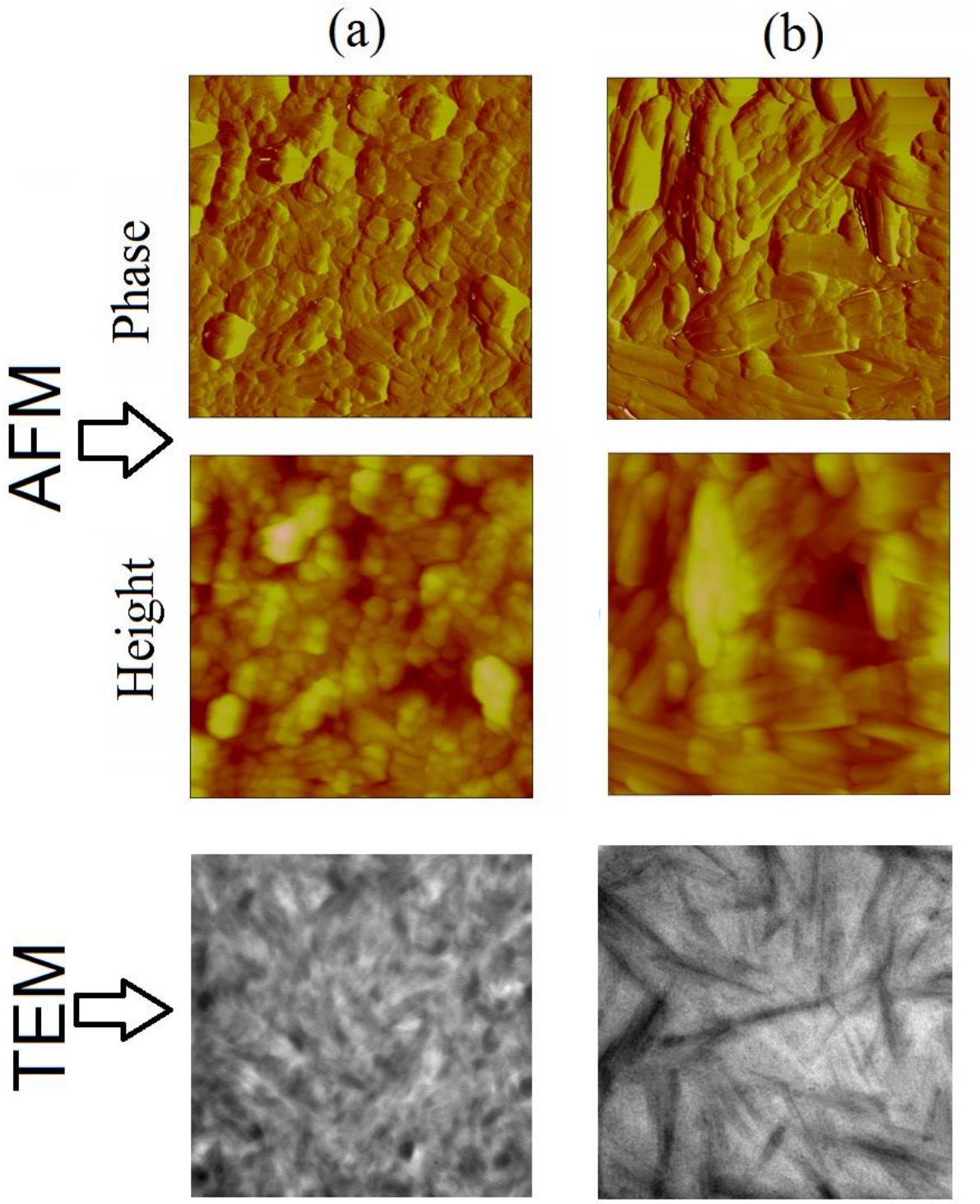

Figure S10. AFM and TEM images for the DPP-PDI block copolymer film (from a 2 wt % CF solution at 3000 rpm) a) pristine b) after thermal annealing at 100 °C for 10 min (each scale 3μm x 3μm).

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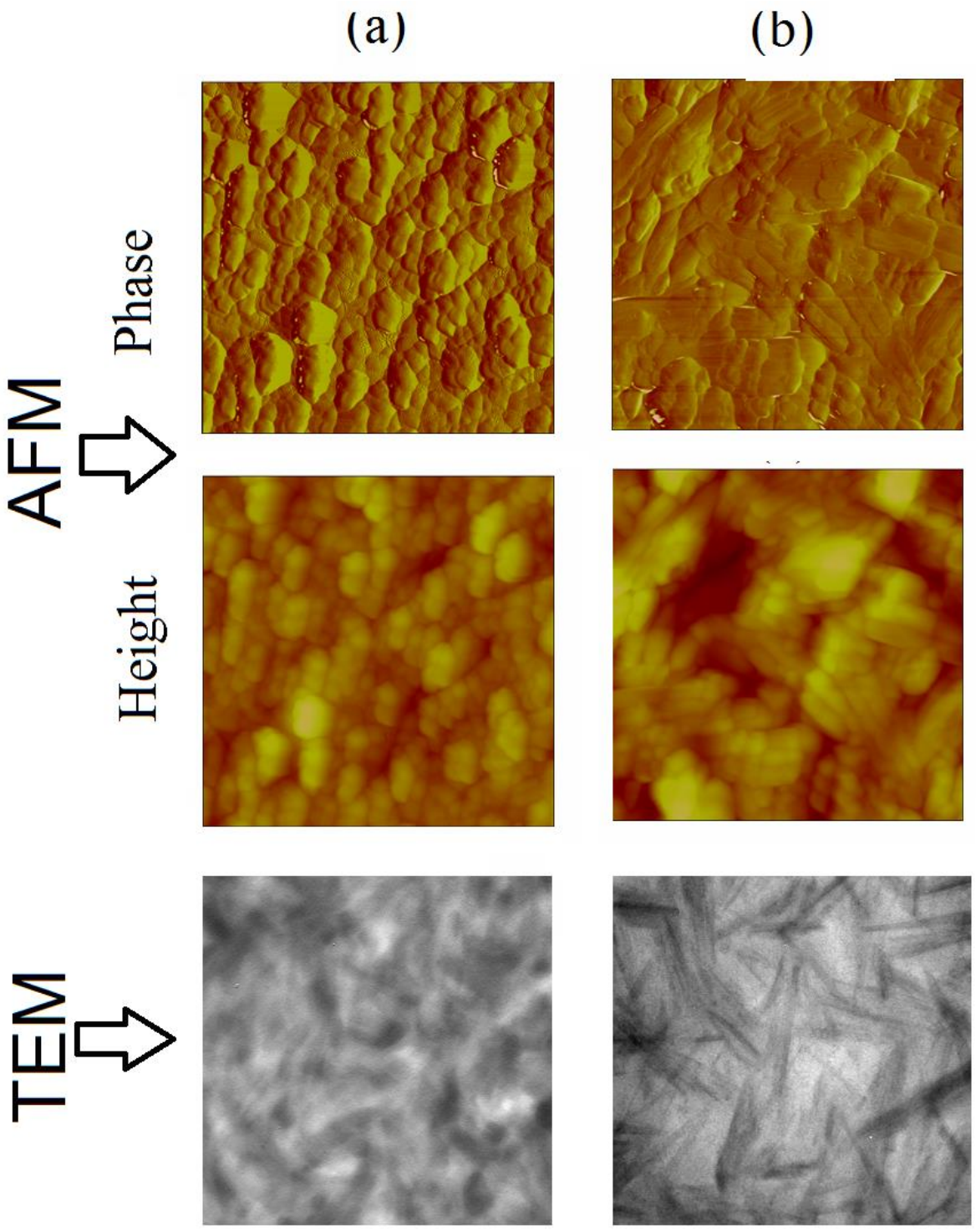

Figure S11. AFM and TEM images for the DPP-PDI block copolymer film (from a 2 wt % CB solution at 1000 rpm) a) pristine b) after thermal annealing at 100 °C for 10 min (each scale 3μm x 3μm)