

Supporting Information

Self-Assembly of Metallopolymer with Graphene Nanoribbons

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PREPARATION OF GNRS

Preparation of Ribbon: MWCNTs of 110-170 nm diameter and 5-9 μm in length, hydrazine monohydrate (N₂H₄·H₂O) and ammonium hydroxide (NH₄OH) were used as received from Sigma-Aldrich Chemical Company, USA. Concentrated sulfuric acid (H₂SO₄), potassium permanganate (KMnO₄) and phosphoric acid (H₃PO₄) were procured from Fisher Scientific, USA. The chemicals were used as received. Silicon wafers (4") with 300 nm layer of thermal oxide and doped with P/Boron (100), SSP 500 micron, 0.001-0.005 ohm cm⁻¹ were procured from University Wafer.

MWCNTs (30 mg) were suspended in 7.2 mL of H₂SO₄ by stirring the mixture for a period of 1 h. Phosphoric acid (85%, 0.8 mL) was then added, and the mixture was allowed to stir for an additional 15 min before adding potassium permanganate (150 mg). The reaction mixture was then heated to 65 °C for 2 h, and allowed to cool to room temperature. The product from the oxidation reaction was poured into liquid nitrogen cooled 30% hydrogen peroxide (5 ml), which prevented the precipitation of potassium permanganate. The mixture was centrifuged at 11,150 rpm for 15 min in a Fisher Scientific Marathon

Micro H Centrifuge. The supernatant was pipette off and the precipitated solid was stirred in 5 ml of deionized water for 15 min, and then centrifuged. The supernatant was pipette off and the solid stirred in 5 ml of ethanol for 15 min, followed by 15min bath sonication. The isolated ribbons were sequentially washed in 5 ml each of hydrochloric acid (HCl, 20 vol% concentrated) and ether, then air dried. The resultant product was brown with a final yield of 35 mg, and was found to form a stable suspension in ethanol/H₂O (50:50) solution. AFM images were obtained while operating in noncontact mode; using 0.01-0.025 Ohm-cm Antimony (*n*) doped Si tips (Veeco, MPP-11123-10) at a scan rate of 2 Hz and 512 × 512 resolution.

ELECTRONIC STRUCTURE CALCULATIONS

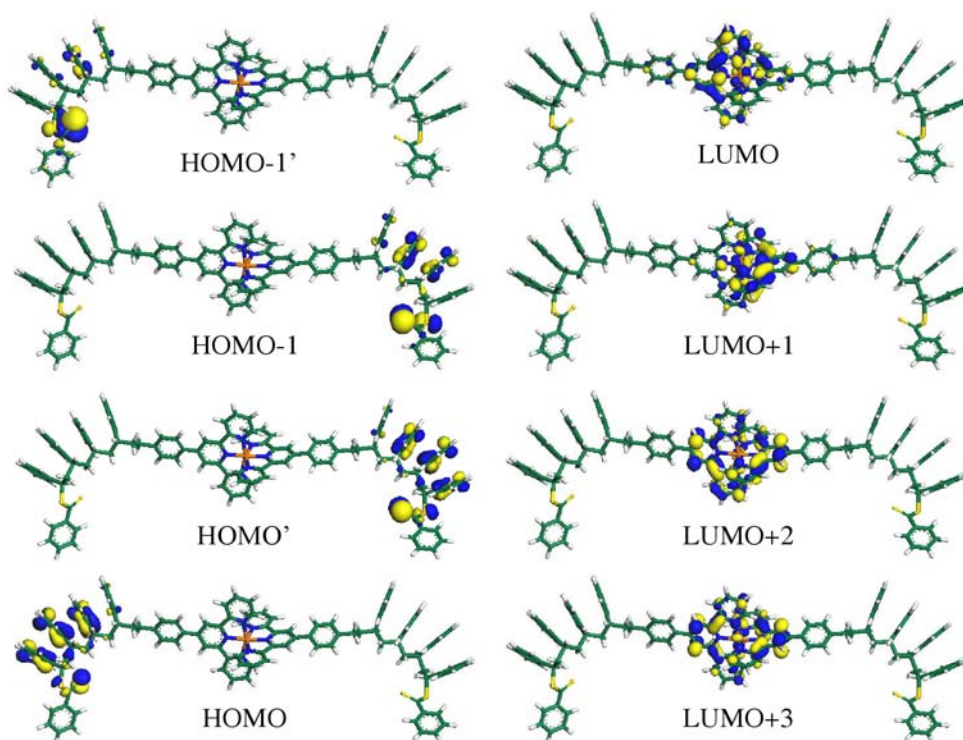


Figure S1. Wave function plot of the near gap states for PS-Ru(tpy)₂-PS. The wave function phases are distinguished by blue and yellow colors.

To facilitate an in-depth understanding of the self-assembly mechanism, we have performed calculations with 2 tpy piling on graphene. For GNRs of width about 300-500 nm, the electronic structure characteristic is similar to graphene. For additional tpy on graphene, the empty flat band close to the Fermi level shifts upwards (~ 0.05), indicating that the assembly of additional tpy is preferred for the stability of the hybrid structure.

UV-VIS SPECTRA

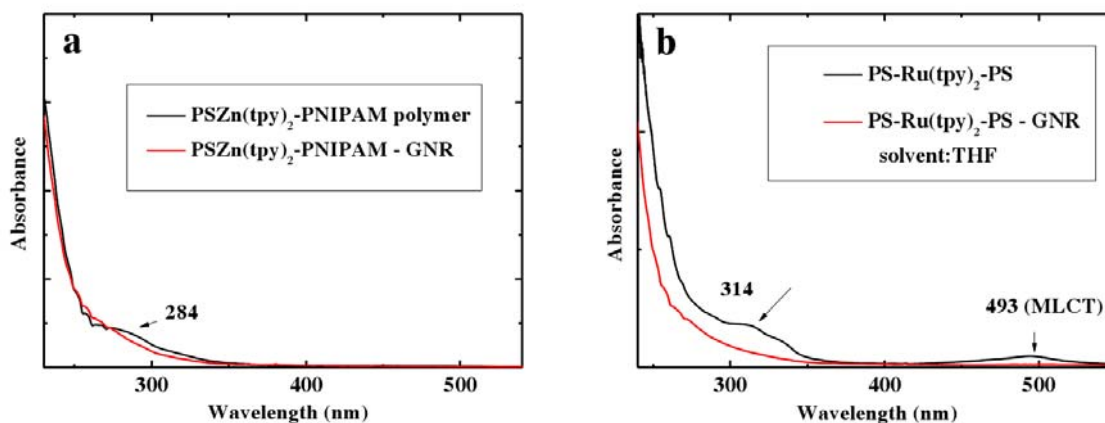


Figure S2. UV-vis spectra of PS-Ru(tpy)₂-PS, PS-Zn(tpy)₂-PNIPAM and metallopolymers cast onto graphene ribbons in THF solvent. Left panel: PS-Zn(tpy)₂-PNIPAM absorption at 284 nm disappears after interaction with graphene; right panel: PS-Ru(tpy)₂-PS absorption peaks at 314 and 493 nm (metal-ligand charge transfer MLCT) are not present after interaction with graphene in THF (all samples concentration were 4 mg/ml).

Displayed in Figure S2 are the UV-vis spectra of PS-Ru(tpy)₂-PS, PS-Zn(tpy)₂-PNIPAM, compared with those of PS-Ru(tpy)₂-PS, PS-Zn(tpy)₂-PNIPAM with GNRs (red lines). As seen in Figure S2, the UV-vis spectra undergo quenching of the characteristic peaks of PS-Ru(tpy)₂-PS, PS-Zn(tpy)₂-PNIPAM themselves, after interacting with GNRs. This demonstrates that GNRs interact strongly with metallopolymers in solution.

CONFOCAL MICROSCOPE IMAGES

Confocal microscope images of PNIPAM-Zn(tpy)₂-PS and GNRs in left and right panels, respectively, are shown in Figure S3. It is evident that there is no peculiar ordering.

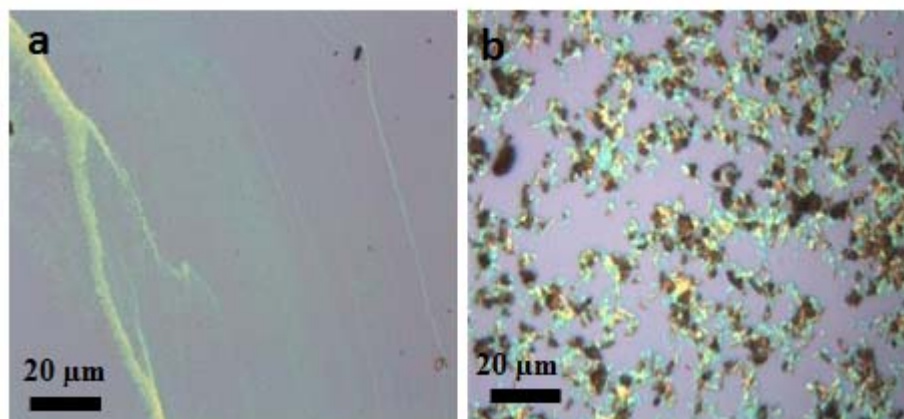


Figure S3. Confocal microscope images of PS-Zn(tpy)₂-PNIPAM and a few layers of GNRs. (a) PNIPAM-Zn(tpy)₂-PS polymer on SiO₂. (b) GNRs from unzipped MWCNTs after centrifugation and spin casting onto Si/SiO₂ surface from an ethanol/H₂O solution.

CHARATERIZATION of PNIPAM-Zn(tpy)₂-PS

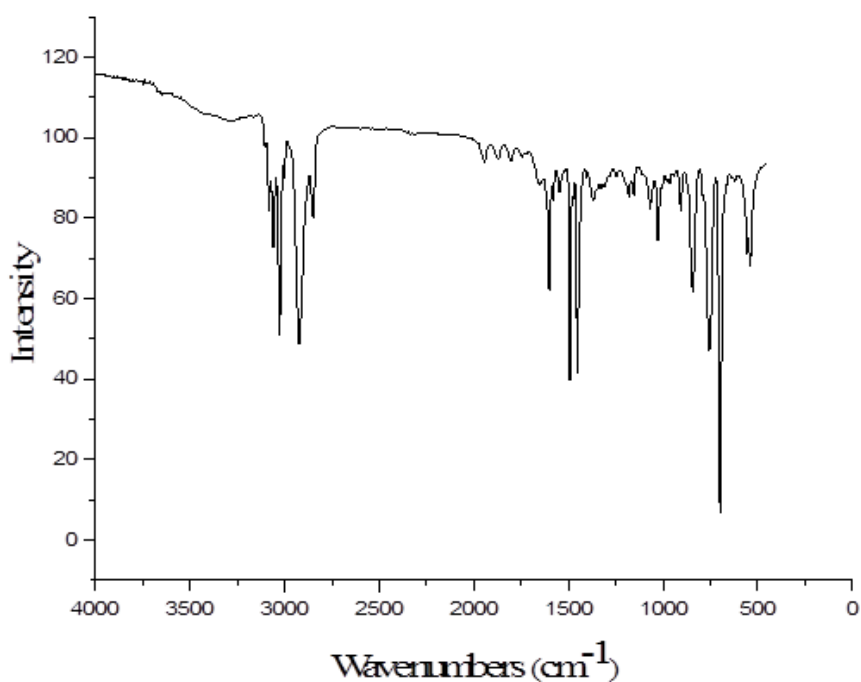


Figure S4. The FTIR spectrum of PS-Zn(tpy)₂-PNIPAM (KBr pellet).

The structure of PNIPAM-Zn(tpy)₂-PS was characterized with Proton NMR and FTIR spectrometers:

^1H NMR (500 MHz, CDCl_3): (ppm) 8.70-6.40 (broad, m, Ph), 4.00 (br, s, CH-N), 2.00-1.84 (br, s, PhCH_2), 1.57 (s, $\text{C}(\text{CH}_3)_2$) 1.41-1.14 (broad, m, CH_2CH)

FTIR (KBr cm^{-1}): 3400 w (NH); 3061m (ArH), 3030s(ArH); 2922s (CH_3); 2852m(CH_2); 1646w(NHC=O), 1602m(ArC=C), 1492s (NCH₃), 1453m(CH_2), 839m(ArH), 755s (ArH), 693s(ArH).

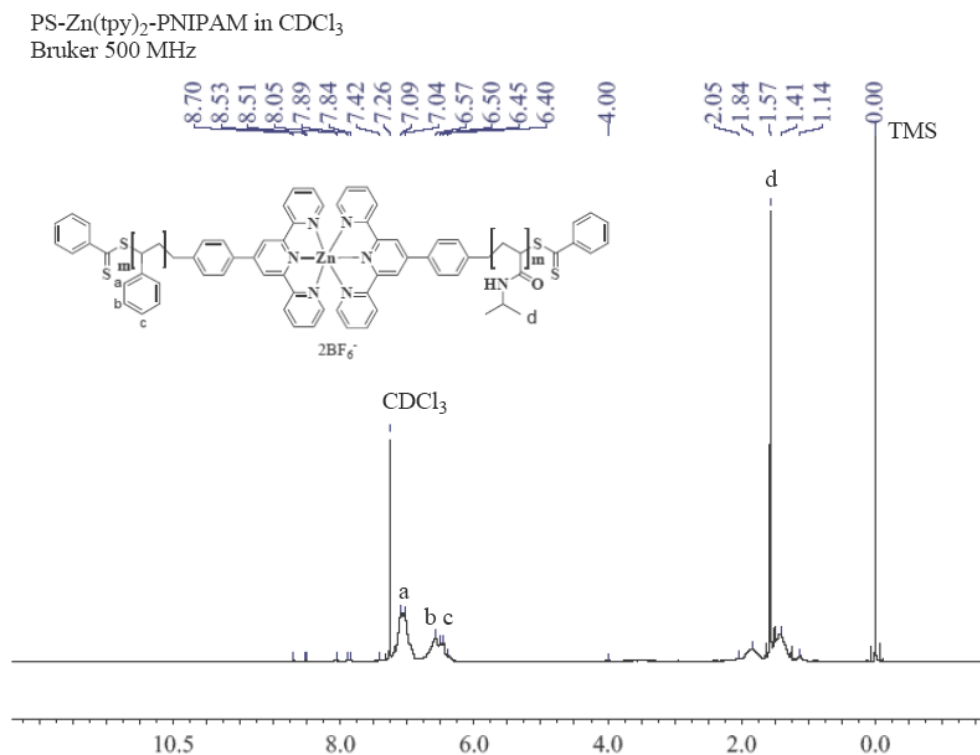


Figure S5. The proton NMR spectrum of PS-Zn(tpy)₂-PNIPAM (500 MHz, CDCl_3).