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Supporting Information:

Asymmetric A-B-A' Metallo-Supramolecular Triblock Copolymer Linked by Ni^{2+} Bis-terpyridine Complexes at One Junction

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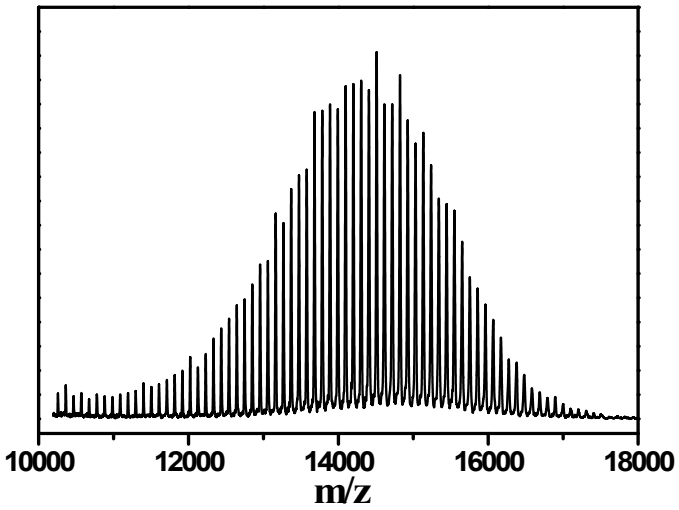

Figure S1. MALDI-TOF mass spectrum of S'-Tpy.

MALDI-TOF mass spectrum of Tpy end-functionalized polystyrene was obtained as shown in Fig. S1. Only one distribution can be revealed, where the spacing of peaks in the spectrum is 104 g/mol which corresponds to the molecular weight of the repeat unit of polystyrene. No evidence of un-functionalized PS which has a large mass unit difference from the neighboring peaks of functionalized polystyrene was observed, suggesting the successful functionalization process during the anionic polymerization.

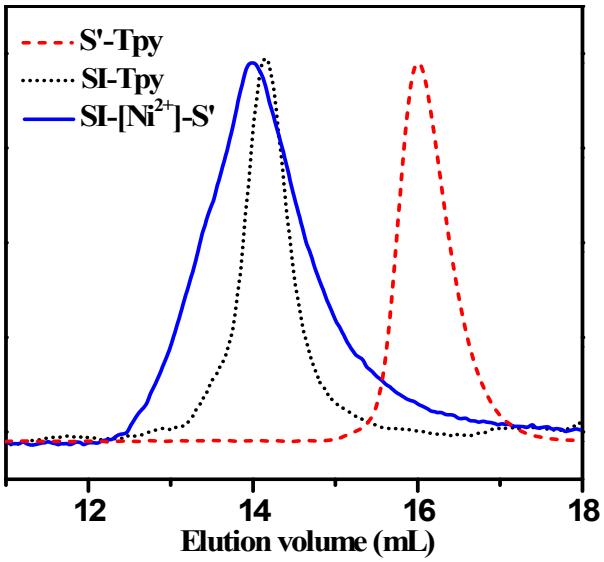

Figure S2. GPC profiles of SI-Tpy, S'-Tpy and SI-[Ni^{2+}]-S'.

The GPC traces of SI-Tpy, S'-Tpy and SI-[Ni^{2+}]-S' are shown in Fig. S2. The SI-Tpy and PS'-Tpy are highly monodisperse with M_w/M_n ~ 1.01. The evolution volume GPC of SI-[Ni^{2+}]-S' shifts towards a lower value compared to SI-Tpy, suggesting a higher molecular weight. The broadness of the evolution peak is caused by the aggregation of the metallo-supramolecular polymers in eluent of THF.

In order to further determine the molecular weight of the Tpy functionalized polymers, UV-vis titration experiments with Fe^{2+} ions were conducted. Fe^{2+} is chosen for titration experiment since it can form stable Fe^{2+} bis-Tpy of the association constant $K_2 = 1\times10^{13.8}$, which is also much larger than that of Ni^{2+} bis-Tpy ($K_2=1\times10^{11}$). The procedure is as following: SI-Tpy chloroform solution and $FeCl_2\cdot4H_2O$ methanol solution were freshly prepared. $FeCl_2$ methanol solution in a concentration of 0.04 mg/mL prepared from a stock solution was added into 2 mL SI-Tpy chloroform solution in a concentration of 1.06 mg/mL in equivalent steps of 25 μL $FeCl_2\cdot4H_2O$ methanol solution. Once the Fe^{2+} bis-Tpy complexes form, characteristic band at 325 nm belonging to ligand-centered (LC) band and the band at 562 nm originating from the metal-to-ligand-charge-transfer (MLCT) are observed as shown in Fig. S3 and Fig. S4. The intensities of the absorption at 325 nm against the amount of $FeCl_2$ were shown in the insets of the figures. The absorption intensity at 563 nm is initially proportional to the amount of $FeCl_2$, followed by a turning point, thereafter, the absorption intensity remains unchanged with the addition of the $FeCl_2$ further. The critical point which is identified at a ligand-to-metal ratio of 2:1 is used to calculate the molecular weight of the polymers. The molecular weight of the PS'-Tpy and SI-Tpy are 15 kg/mol and 108

kg/mol, respectively.

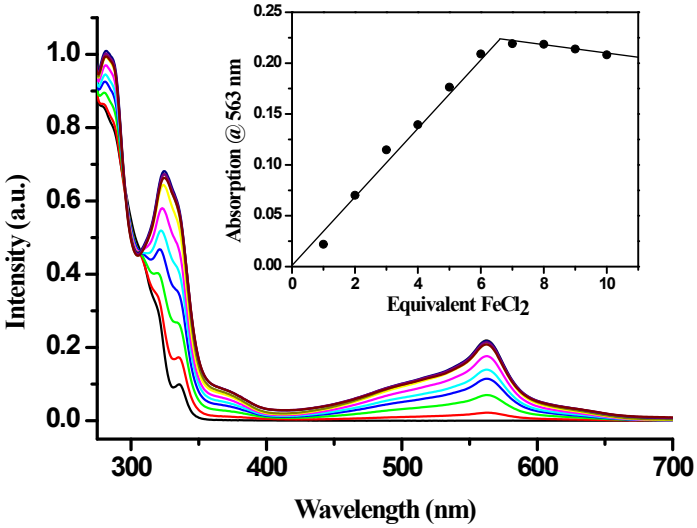

Figure S3. UV-vis spectra of S'-Tpy chloroform solution titrated with $FeCl_2$ methanol solution. Inset is the plot of the absorbance at 325 nm *versus* the equivalents of $FeCl_2$.

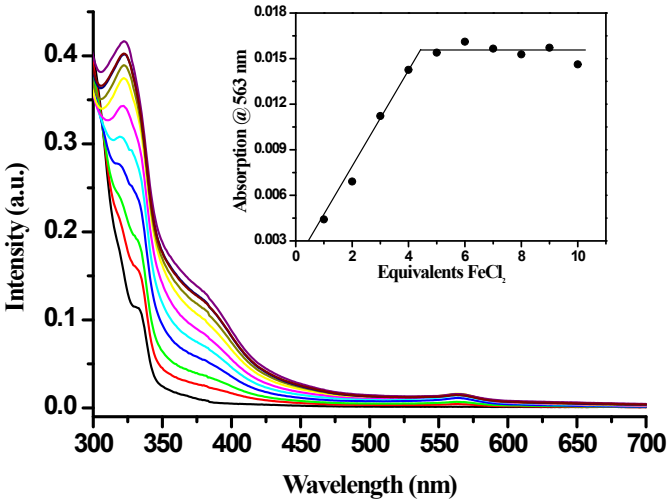

Figure S4. UV-vis spectra of SI-Tpy chloroform solution titrated with $FeCl_2$ methanol solution. Inset is the plot of the absorbance at 325 nm *versus* the equivalents of $FeCl_2$.

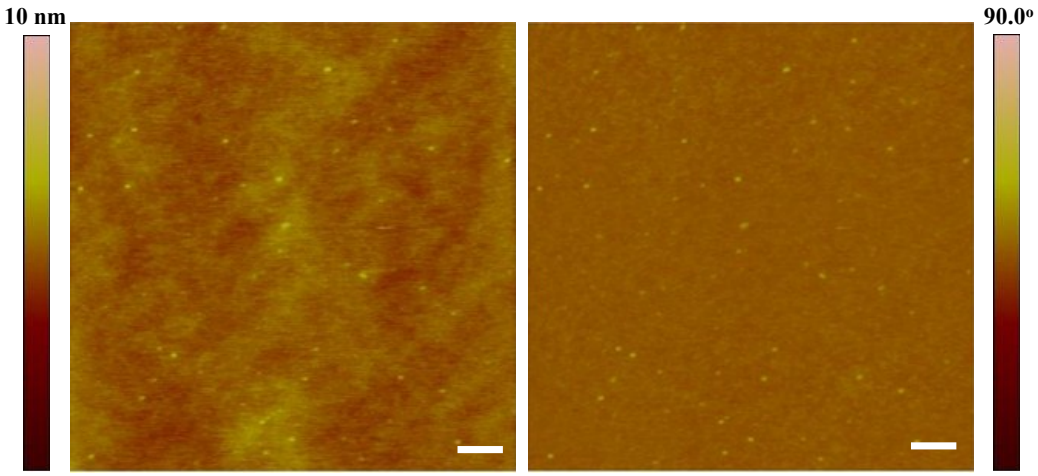

Figure S5. AFM height image (the left) and phase image (the right) of SI-Tpy diblock copolymer. The scalar bar represents 100 nm.