Sequential Block Copolymer Self-Assemblies Controlled by Metal–Ligand Stoichiometry

Liyuan Yin,† Hongwei Wu,† Mingjie Zhu,† Qi Zou,*§ Qiang Yan,*† and Liangliang Zhu‡*,†

†State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai 200433, China
‡Department of Chemistry, Columbia University, New York, New York 10027, United States
§Shanghai Key Laboratory of Materials Protection and Advanced Materials in Electric Power, Shanghai University of Electric Power, Shanghai 200090, China

ABSTRACT: While numerous efforts have been devoted to developing easy-to-use probes based on block copolymers for detecting analytes due to their advantages in the fields of self-assembly and sensing, a progressive response on block copolymers in response to a continuing chemical event is not readily achievable. Herein, we report the self-assembly of a 4-piperazinyl-1,8-naphthalimide based functional block copolymer (PS-b-PN), whose self-assembly and photophysics can be controlled by the stoichiometry-dependent metal–ligand interaction upon the side chain. The work takes advantages of (1) stoichiometry-controlled coordination–structural transformation of the piperazinyl moiety on PS-b-PN toward Fe³⁺ ions, thereby resulting in a shrinkage–expansion conversion of the self-assembled nanostructures in solution as well as in thin film, and (2) stoichiometry-controlled competition between photoinduced electron transfer and spin–orbital coupling process upon naphthalimide fluorophore leading to a boost–decline emission change of the system. Except Fe³⁺ ions, such a stoichiometry-dependent returnable property cannot be observed in the presence of other transition ions. The strategy for realizing the dual-channel sequential response on the basis of the progressively alterable nanomorphologies and emissions might provide deeper insights for the further development of advanced polymeric sensors.

INTRODUCTION

Block copolymers (BCPs) are of great importance in the field of materials and their self-assembly has attracted considerable attention for many decades, due to their flexible self-assembly features to form a variety of ordered morphologies including spheres, rods, bicontinuous structures, lamellae, vesicles, and many other complex assemblies.1–7 These aggregates have shown great potential for practical applications in drug delivery, charge transfer, catalysis, and so forth.8–15 Since BCP self-assemblies are attributed to microphase segregations among different segments, their morphologies can be controlled by many parameters, such as molecular structure, molecular weight, polymerization degree of each segment, domain ratio of blocks, solvent and annealing conditions, and so on.16,17 As compared with these conventional strategies, BCP self-assembly driven by noncovalent interaction stands out for its diversity, reversibility, in situ operation, and so forth, and this methodology can normally serve as a corresponding sensing method during the stimuli-responsive self-assembly processes.18 Thus far, a lot of effort has been dedicated to develop these supramolecular BCP analogues.19–22 However, to the best of our knowledge, there remain big challenges to construct functional block copolymer systems that are able to respond to a dynamically variable noncovalent factor.

Metal–ligand interaction, a typically strong and smart noncovalent approach, has been largely employed to construct chemosensors,23–25 supramolecular architectures,26–30 and organic–inorganic hybrid materials.31,32 Several significant achievements in metal–ligand interaction for copolymer self-assembly have been demonstrated.21,22 Nevertheless, most of these cases are only related to one complexation equilibrium. It is very difficult to develop a stoichiometry-controlled and progressively alterable property upon one metal–ligand interaction. Interestingly, side-chain block copolymers are capable of presenting a synergic functionality due to the adjacency of the structural units and versatile self-assembly fashions,33,34 so as to offer rich choices to direct different complexation behaviors. With these considerations, we herein demonstrate a novel strategy that takes advantage of metal–ligand interaction between an optimized side-chain BCP and a well-selected metal-ion-center for realization of the above-
mentioned hypothesis. We expect that such a structural conversion relying on a stoichiometry-dependent coordination would integrate the self-assembly with optical property of the BCP so as to exhibit a sequential response effect.

Thus, a side-chain functional block copolymer poly(styrene)-block-poly(1,8-naphthalimide) (PS-b-PN) containing piperazinyl moiety was designed and shown in Figure 1A. The other domain, polystyrene, is a self-assembly initiator of block copolymer with good solution processability. As a recognition unit to transition metal ions with various coordination structures, the complexation ability of piperazinyl moiety can be further altered by changing stoichiometry or introducing different ions. Naphthalimide can serve as a fluorescent signal indicator with good performance. Overall, we utilize such a side-chain BCP design to control the complexation with certain metal ion species to achieve a progressive expression on self-assembly and emission for dual-channel response. Reference monomer PN and random copolymer PS-co-PN were also prepared for control experiments (see Methods section and SI for the synthesis and preparation details).

### RESULTS AND DISCUSSION

**Sequential Photophysics Controlled by Metal–Ligand Stoichiometry.** The block copolymer PS-b-PN was synthesized by reversible addition–fragmentation chain-transfer (RAFT) methodology. The polymerization degree of PS and PN is ~231 and ~12, respectively. Such a design indicates that the block copolymer prefers to aggregate into spherical microdomains via phase separation which induces chain stretching to lower the total interfacial energy of the polymer system. Having obtained the block copolymer, we turn to investigate the photoluminescence (PL) of PS-b-PN in the presence of a series of metal ions first. Figure 2A,B and S1 show the PL spectra with different stoichiometries of a series of transition metal ions. The variation traces of PL spectra were summarized in Figure 2D in which the arrows indicate the direction of the change of the maximum emission intensity. The results show that PL intensity of PS-b-PN either increases or decreases monotonously with the increasing equivalent of metal ions, except for the case with Fe³⁺ ions. To our surprise, PS-b-PN undergoes a gradual enhancement of PL intensity with the increasing concentration of Fe³⁺ ions when the concentration of Fe³⁺ ions is relatively low (less than 1.0 equiv, relative to the total numbers of the piperazinyl moiety, the same below), whereas its PL intensity begins to diminish upon further introduction of Fe³⁺ ions (up to 20 equiv). The variation traces of PL signal versus different concentrations of Fe³⁺ ions are summarized in Figure 2C and D.

We ascribed the above-mentioned returnable optical phenomena to be a coordination–structural transformation between the piperazinyl moiety of PS-b-PN and Fe³⁺ ions. At the relatively low equivalent range of Fe³⁺ ions, the complexation ratio is 2:1 between the piperazinyl unit and Fe³⁺ ion (two piperazinyl moieties coordinate one Fe³⁺ ion; see Figure 1B). When Fe³⁺ ion concentration further increased, the complexation ratio converted into 1:1 (one piperazinyl moiety coordinates one Fe³⁺ ion; see Figure 1B). The enhancement of PL intensity resulted from the suppression of the photoinduced electron transfer (PET) quenching after the coordination between Fe³⁺ ions and nitrogen atoms on the piperazinyl moiety. Subsequently, with the further increase of Fe³⁺ ions, spin–orbit coupling (SOC) dominates due to the heavy atom effect derived from the ferric center. Such a stoichiometry-controlled competition between PET and the SOC process from the piperazinyl moiety to naphthalimide fluorophore can also be evidenced by the change in absorption spectra of PS-b-PN (see Figure S2). Initially, the absorption band of PS-b-PN exhibited a blue shift upon the addition of...
Fe$^{3+}$ ions, indicating that the PET process narrowed the $\pi$-conjugation of the fluorophore. The unshifted band with the further increase of Fe$^{3+}$ ions suggests that the SOC process has no influence on $D-\pi-A$ system except for the quenching of the emission. For the cases of PS-b-PN interacting with other ions, the diameters of other ions are considered to mismatch such complexation mode transformation. Thus, only one photophysical mechanism was related in other cases so that the returnable phenomena were not shown for this BCP system.23,32,41

To further confirm this hypothesis, we performed electrospray ionization mass spectrometry (ESI-MS) by using a monomer of N in the presence of different amounts of Fe$^{3+}$ ions (see Figure S3). When 1 equiv of Fe$^{3+}$ ions was added, a peak at $m/z$ 364.6 attributed to the 2:1 coordination mode $[\text{Fe}/2\text{N}]^{3+}$ between piperazinyl unit and Fe$^{3+}$ ion was observed (Figure S3(A)). Upon further introduction of Fe$^{3+}$ ions, a peak at $m/z$ 239.2 appeared in the mass spectra (Figure S3(B)), which corresponds to $[\text{Fe}/\text{N} + 2\text{THF}]^{3+}$, indicating a coordination-structural transformation from 2:1 to 1:1 complexation ratio between piperazinyl unit and Fe$^{3+}$ ions. In addition, the emission changes of N interacted with different ions revealed the same trend as PS-b-PN shown in Figure 2D, signifying that the monomer is comparable to be employed for study from the perspective of the 4-piperazinyl-1,8-naphthalimide moiety.

Besides, ethylenediamine tetraacetic acid (EDTA) was introduced to conduct an absorption experiment.43–45 Since the PL intensity of PS-b-PN diminished significantly with the addition of 30 equiv of Fe$^{3+}$ ions, it could recover after excess EDTA was introduced into the solution (Figure S4), signifying that an extremely strong complexation between EDTA and Fe$^{3+}$ ions causes the extraction of Fe$^{3+}$ ions from PS-b-PN to restore the emission. These experimental results suggest that addition of different amounts of Fe$^{3+}$ ions results in such a smart stoichiometry-controlled coordination-mode transformation between piperazinyl moiety and Fe$^{3+}$ ions. The coordination constant of the 1:1 complexation mode is less than that of the 2:1 complexation mode (see Figure S5), demonstrating that larger equivalents of Fe$^{3+}$ ions are necessary to raise the foldback of the PL trace as well as the returnable properties.

**Sequential Solution Self-Assembly Controlled by Metal–Ligand Stoichiometry.** To investigate the self-assembly of PS-b-PN upon progressive coordination–structural transformation, the nanomorphological change was first explored in solution upon the addition of different amounts of Fe$^{3+}$ ions. The aggregation condition of PS-b-PN self-assembly was examined by monitoring the variation of absorption spectra along with the concentration change in the THF/acetonitrile (v/v = 2:3) solution and was shown in Figure S6. The critical aggregation concentration (CAC) in the mixed solution was determined to be 43 $\mu$M. Accordingly, solutions of PS-b-PN (84 $\mu$M, above the CAC; see the Tyndall Effect in Figure S7) in THF/acetonitrile (v/v = 2:3) solution were mixed with a set of Fe$^{3+}$ ions in different stoichiometries for self-assembly studies.

The transmission electron microscopy (TEM) images are presented in Figure 3A and Figure S8 showing that the aggregates of PS-b-PN vary gradually from large size to small size when the stoichiometry of Fe$^{3+}$ ions increases up to 1.0 equiv; subsequently, the size of the BCP self-assemblies becomes large again when the stoichiometry of Fe$^{3+}$ ions continuously increases in the same solvent condition. This phenomenon suggests that the change of Fe$^{3+}$ ions content in PS-b-PN solution is responsible for such a sequential change of BCP self-assembly, which is indicative of the aforementioned Fe$^{3+}$-stoichiometry dependent coordination-mode conversion. The vesicle formation of PS-b-PN self-assembly was observed, as shown in Figure S9, suggesting that the segments of N serve as the internal and external coronas of the BCP self-assemblies as represented in Figure 3B. Upon adding low content of Fe$^{3+}$ ions, every two piperazinyl moieties from PS-b-PN coordinate with one Fe$^{3+}$ ion and the coronas of vesicle (∼500 nm) are electroactive in the same solvent condition. Therefore, it can be concluded that the repulsive force among coronas in one vesicle becomes dominant when the Fe$^{3+}$ ions concentrations are up to 1.0 equiv, which results in the relatively small size (∼200 nm) of side-chain BCP self-assembly. Besides, such a 2:1 coordination mode also causes one vesicle to be linked with another when some Fe$^{3+}$ ions coordinate with piperazinyl moieties between two different vesicles. When the concentration of Fe$^{3+}$ ions continuously increases, the repulsive force and the adjacent connection will weaken in a 1:1 coordination mode so that the vesicles become large (∼900 nm) and dispersed again.

Dynamic light scattering (DLS) technique can be used to accurately characterize the diameter of self-assemblies in solution.47,48 Figure 4 and Figure S10 show the DLS profile of PS-b-PN with different Fe$^{3+}$ ion equivalents in THF/acetonitrile (v/v = 2:3), which were collected according to the refractive index of as-prepared solution of PS-b-PN measured through an Abbe’s refractometer (see Table S1). As shown in Figure 4A, there is one peak centered at around 500 nm in the DLS spectrum, indicating that the average diameter of the vesicle without Fe$^{3+}$ ions is about 500 nm. When Fe$^{3+}$ ions (1.0 equiv) were introduced into the solution, a main peak around 200 nm appeared in the DLS spectrum (Figure 4B), indicating that the average diameter of the aggregates decreases greatly in accordance with the observations from TEM images in Figure 3. Subsequently, it can also be clearly observed that the average diameter of the BCP self-assemblies containing 2.5 equiv of Fe$^{3+}$ ions became large (∼900 nm) again (see Figure 4C). Such a shrinkage–expansion tendency can be more visualized by performing a set of experiments in detail (Figure S10) as well as the cryo TEM results (Figure S11). These results and the
consistency of self-assembly size among each other further confirm the round morphological formation of PS-b-PN in THF/acetonitrile (v/v = 2:3), rather than disk-like micelles or platelets.

To gain further insight into the unique BCP self-assembly behavior upon the coordination-structural conversion, we performed control experiments using PS-co-PN random copolymer instead of PS-b-PN block copolymer with respect to different stoichiometry of Fe$^{3+}$ ions. Followed by a similar preparation process for PS-co-PN self-assembly, the size of the random BCP self-assemblies originating from microphase separation is inhomogeneous in each content of Fe$^{3+}$ ions and there is no obvious average size change in the presence of different contents of Fe$^{3+}$ ions (see the TEM and DLS studies in Figure S12 and Figure S13, respectively), indicating that a random side-chain grafting cannot validly cause a shrinkage—expansion conversion of self-assembly behavior upon continuously increasing Fe$^{3+}$ ions. As compared with the PL studies of PS-b-PN, it is found that the operation for shrinkage—expansion conversion of the BCP self-assembled vesicles is synergetic with the boost—decline emission change of the system, implying that such a well-defined block copolymer with a Fe$^{3+}$-stoichiometry-controlled characteristic has great potential in the practical applications for Fe$^{3+}$ ion dual-channel dynamic sensing.

**Sequential Surface Self-Assembly Controlled by Metal–Ligand Stoichiometry.** In addition to those self-assemblies in solution, Fe$^{3+}$-stoichiometry-controlled surface self-assembly of PS-b-PN can also work well in thin film. The film samples were obtained by spin-coating the PS-b-PN solutions (84 μM in dioxane) with different Fe$^{3+}$ ion equivalents on silicon wafers at 9100 rpm for 45 s. Then these samples were placed in a 200 mL closed jar with the annealing of dioxane vapor for 36 h to facilitate the BCP self-assembly in solid states. It can be seen from Figure S4 that there are distinct changes in the self-assembly nanostructures with different Fe$^{3+}$ ion equivalents. Without Fe$^{3+}$ ions, the BCP nanostructures were composed of spherical micelles after solvent annealing of film. In terms of the fraction of the two domains, it is concluded that PN lay out around PS and the two segments coordinate and self-assemble into micelles. However, network nanostructures are found in the presence of 1.0 equiv of Fe$^{3+}$ ions since a 2:1 coordination-mode readily causes an intermolecular cross-linking. Additionally, the BCP self-assembly after solvent annealing became large-scale hollow structures while in the presence of 2.5 equiv of Fe$^{3+}$ ions. The schematic diagrams, as shown in Figure 5B, are used to visualize the variation of the surface self-assembly morphologies of PS-b-PN resulted from the change of Fe$^{3+}$-stoichiometry-controlled microphase segregation. The experiments with PS-co-PN were also conducted under identical conditions for comparison. As shown in Figure S14, there was no obvious change in morphologies of the surface self-assemblies of PS-co-PN with different Fe$^{3+}$ ion equivalents, agreeing with the findings of those self-assembly behaviors in solution.

Solid-state emission with respect to the surface self-assembly of the side-chain BCP was also explored (see Figure 6). The BCP backbone serves a matrix role which ensures that the resulting thin films can still emit with significant efficiency. Similar to that in solution, the PL behavior of the PS-b-PN film also undergoes a boost—decline conversion trend with continuously increasing Fe$^{3+}$ ion equivalents, indicating that the dual-channel dynamic response effect plays a dominant role in the solid state as well.

**CONCLUSION**

We have demonstrated a unique Fe$^{3+}$-stoichiometry-controlled self-assembly of functional block copolymer (PS-b-PN) via metal–ligand interaction in the 4-piperazinyl-1,8-naphthalimide...
based side chain. In this work, selective recognition of Fe^{3+} ions in a progressing fashion was achieved through the chelation–structural transformation between 4-piperazinyl-1,8-naphthalimide and the metal-ion center. When relatively small amounts of Fe^{3+} ions are complexed with PS-b-PN, the 2:1 coordination mode between piperazinyl moiety and Fe^{3+} ion causes a shrinkage of the self-assembled nanostructure accompanied by an enhanced emission signal. On the other hand, upon the introduction of much more Fe^{3+} ions to the PS-b-PN system, the resulting 1:1 coordination mode between piperazinyl moiety and Fe^{3+} ion leads to a re-expansion of the self-assembled nanofeature along with a gradual quenching of the emission. Such a returnable self-assembly and optical property have both been observed in solution and in thin film, which were confirmed by TEM, DLS, AFM, and PL studies, but cannot emerge in the presence of other transition ions, allowing a promising dual-channel sequential response function of PS-b-PN. The current results could be valuable for the design of the next generation polymeric probes that fit for detecting the dynamically variable process of chemical events as well as pertinent advanced intelligent materials.

## METHODS

**General.** ¹H NMR and ¹³C NMR spectra were measured on a Bruker 400L spectrometer. The electrospray ionization (ESI), fast atom bombardment (FAB) mass spectra, and high-resolution mass spectrometry (HR-MS) were recorded on a Shimadzu 1800 spectrometer (ionization mode: FAB+). The molecular weight of polymers was determined with a Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive index detector and calibrated with polystyrene standard samples. Absorption spectra were recorded on a Shimadzu 1800 spectrophotometer, while the fluorescent emission spectra were taken with a Jobin Yvon Fluorolog-3 spectrofluorometer (Model PL-TAU13). TEM images were collected on a Tecnai G2 20 TWIN microscope operated at 100–120 kV. The atomic force microscopy (AFM) images were collected on a PSI XE100 Atomic Force Microscope (Park System). The dynamic diameters of self-aggregates were measured by dynamic light scattering (DLS) using Zetasizer Nano ZS90 system (Malvern). The refractive index of these colloidal solutions was measured by an Abbe’s refractometer. The photo images were photographed by a Nikon COOLPIX S8000 digital camera.

**Synthesis of Compounds 1 and 2.** These two compounds were prepared according to a similar procedure described in the literature.⁵¹,⁵²

**Synthesis of Compound 3.** Compound 2 (1.32 g, 3.68 mmol) was added to a DMF solution (6 mL) containing 1,6-dibromohexane (8.13 g, 33.3 mmol). The mixture solution was then mixed with K₂CO₃ (1.0 g, 7.25 mmol). The solution was stirred for 8 h at 80 °C under Ar protection. Then it was poured into deionized water (30 mL) and kept overnight. The crude solid was collected through filtration and then purified through silica gel chromatography (petroleum ether:ethyl acetate = 3:1, v/v) to afford yellow compound 3 (1.65 g, 85%). H NMR (400 MHz, CDCl₃, 298 K): δ = 8.58 (d, J = 7.2 Hz, 1H), 8.52 (d, J = 8.0 Hz, 1H), 8.41 (d, J = 7.6 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.21 (d, J = 8.4 Hz, 1H), 4.16 (t, J = 7.6 Hz, 2H), 3.43 (t, J = 7.2 Hz, 2H), 3.32 (br, 4H), 2.78 (br, 4H), 2.49 (t, J = 7.6 Hz, 2H), 1.91 (m, 1H), 1.73 (m, 2H), 1.59 (m, 2H), 1.50 (m, 2H), 1.42 (m, 4H), 1.35 (m, 4H), 0.89 (t, J = 7.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 164.53, 163.06, 156.00, 132.55, 130.26, 129.90, 126.18, 125.57, 123.34, 114.88, 59.19, 54.54, 51.04, 40.67, 34.32, 33.33, 30.58, 29.54, 29.27, 28.57, 27.36, 26.82, 21.47, 14.07. HRMS (FAB) m/z: [M+H]⁺ calcd for C₂₈H₃₉N₃O₂Br₂, 528.2226; found m/z 528.2238.

**Synthesis of Compound N.** Compound 3 (1.25 g, 2.37 mmol) was added to a DMSO solution (6 mL) containing potassium acrylate (1.04 g, 9.48 mmol). The mixture solution was stirred for 12 h at 90 °C under Ar protection. Then it was poured into deionized water (50 mL) and kept overnight. The crude solid was collected through filtration and then purified through silica gel chromatography (petroleum ether:ethyl acetate = 3:1, v/v) to afford yellow compound N (0.885 g, 72%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 8.58 (d, J = 7.2 Hz, 1H), 8.51 (d, J = 8.0 Hz, 1H), 8.41 (d, J = 7.6 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.20 (d, J = 8.4 Hz, 1H), 6.42 (dd, J₁₁ = 16 Hz, J₂ = 1.6 Hz, 1H), 6.13 (m, 1H), 5.81 (dd, J₁₂ = 10.4 Hz, J₂₂ = 1.6 Hz, 1H), 4.17 (t, J = 7.6 Hz, 2H), 3.29 (t, J = 7.2 Hz, 2H), 2.75 (br, 4H), 2.48 (t, J = 7.6 Hz, 2H), 1.73 (m, 4H), 1.59 (m, 4H), 1.42 (m, 4H), 1.33 (m, 4H), 0.88 (t, J = 7.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 171.51, 164.53, 163.08, 156.01, 132.56, 131.35, 131.03, 126.16, 125.57, 123.34, 114.88, 59.19, 54.54, 51.04, 40.67, 34.32, 33.33, 30.58, 29.54, 29.27, 28.57, 27.36, 26.82, 21.47, 14.07. HRMS (FAB) m/z: [M+H]⁺ calcd for C₃₂H₄₀N₅O₉Br₂, 643.57; found m/z 643.56.

DOI: 10.1021/acs.langmuir.6b01787

Langmuir 2016, 32, 6429-6436

Figure 7. Synthetic route for the preparation of the monomer and polymers.
Preparation of PN. To a 25 mL Schlenk flask, equipped with a Teflon-coated stir bar, was added N (0.519 g, 1 mmol), the transfer agent (2-(1-(butylthio)vinylthio)propanenitrile, 20.0 mg, 0.1 mmol), AIBN (3.2 mg, 0.002 mmol), and distilled dioxane (3 mL). The flask was capped with a rubber septum and the mixture was stirred until all the stuff dissolved, resulting in a clear yellow solution that was degassed by three cycles of freeze/pump/thaw. After the final thaw cycle, the flask was backfilled with Ar and the flask was sealed and immersed in a 75 °C oil bath for 8 h. Then the flask was immersed in liquid nitrogen to quench the polymerization. The frozen mixture was allowed to warm to room temperature and the crude polymer was then precipitated into a 1:1 mixture of icy water and methanol from minimal dioxane three times. The precipitates were filtered out and dried in vacuum overnight to yield 335 mg of yellow polymer compound. Mₙ = 5700 Da, Mₛ = 6100 Da, Mₚ/Mₑ = 1.06. The polymerization degree of N is ~12.¹¹H NMR (400 MHz, CDCl₃, 298 K): δ = 8.58–8.52 (br), 8.51–8.43 (br), 8.42–8.27 (br), 7.72–7.58 (br), 7.22–7.11 (br), 4.22–3.97 (br), 3.38–3.20 (br), 2.86–2.66 (br), 2.55–2.27 (br), 1.92–1.22 (br), 0.97–0.80 (br). A scheme showing the syntheses of PN, PS-co-PN and PS-b-PN is displayed in Figure 7.

Preparation of PS-co-PN. To a 25 mL Schlenk flask, equipped with a Teflon-coated stir bar, was added N (0.3 g, 0.58 mmol), styrene (0.2 g, 1.9 mmol), the transfer agent (11.6 mg, 0.058 mmol), AIBN (3.2 mg, 0.002 mmol), and distilled dioxane (1 mL). The flask was capped with a rubber septum and the mixture was stirred until all the stuff dissolved, resulting in a clear yellow solution that was degassed by three cycles of freeze/pump/thaw. After the final thaw cycle, the flask was backfilled with Ar and the flask was sealed and immersed in an 75 °C oil bath for 12 h. Then the flask was immersed in liquid nitrogen to quench the polymerization. The frozen mixture was allowed to warm to room temperature and the crude polymer was then precipitated into methanol from minimal dichloromethane three times. The precipitates were filtered out and dried in vacuum overnight to yield 308 mg of yellow polymer compound. Mₙ = 20 900 Da, Mₛ = 24 100 Da, Mₚ/Mₑ = 1.15. Mₛ (PS) = 18 K, Mₛ (PN) = 6 K, determined from¹¹H NMR. The polymerization degrees of S and N are ~173 and ~12, respectively.¹¹H NMR (400 MHz, CDCl₃, 298 K): δ = 8.61–8.28 (br), 7.71–7.55 (br), 7.21–6.87 (br), 6.83–6.29 (br), 4.22–3.98 (br), 3.34–3.18 (br), 2.82–2.64 (br), 2.54–2.37 (br), 2.27–1.02 (br), 0.98–0.80 (br).

Preparation of PS-b-PN. To a 25 mL Schlenk flask, equipped with a Teflon-coated stir bar, was added N (0.2 g, 0.58 mmol), styrene (0.2 g, 1.9 mmol), AIBN (3.2 mg, 0.002 mmol), and distilled dioxane (1 mL). The flask was capped with a rubber septum and the mixture was stirred until all the stuff dissolved, resulting in a clear yellow solution that was degassed by three cycles of freeze/pump/thaw. After the final thaw cycle, the flask was backfilled with Ar and the flask was sealed and immersed in a 75 °C oil bath for 12 h. Then, the flask was immersed in liquid nitrogen to quench the polymerization. The frozen mixture was allowed to warm to room temperature and the crude polymer was then precipitated into methanol from minimal dichloromethane three times. The precipitates were filtered out and dried in vacuum overnight to yield 212 mg of yellow polymer compound. Mₛ = 28 000 Da, Mₚ = 30 400 Da, Mₛ/Mₑ = 1.09. Mₛ (PS) = 24 K, Mₛ (PN) = 6 K, determined from¹¹H NMR. The polymerization degrees of S and N are ~231 and ~12, respectively.¹¹H NMR (400 MHz, CDCl₃, 298 K): δ = 8.61–8.28 (br), 7.71–7.55 (br), 7.21–6.87 (br), 6.83–6.29 (br), 4.22–3.98 (br), 3.34–3.18 (br), 2.82–2.64 (br), 2.54–2.37 (br), 2.27–1.02 (br), 0.98–0.80 (br).

Ion Titration for the Sequential Photophysics. The PS-b-PN solution of 10 μM in THF was prepared. First, we collected the PL spectrum at 298 K (Jₑ = 365 nm) without addition of any ions. After that, metal ions of different equivalents of metal ions (0.2, 0.4, 0.6, 0.8, 1.0, 1.4, 2.0, 4.0, 6.0, 10, 16, 20, and 45 equiv) were added and the PL spectra of every mixture were collected. A series of transition metal ions (Ag⁺, Mn²⁺, Al³⁺, Cd²⁺, Ni²⁺, Co²⁺, Fe⁺³, Fe²⁺, Cr³⁺, Zn²⁺, Cu²⁺, and Hg²⁺) were monitored. Figure S1 shows the emission spectra of PS-b-PN solution before and after the addition of different ions with increasing equivalents and Figure 2D summarizes the emission intensity variations of PS-b-PN after the addition of different ions.

Solution Self-Assemblies. Solutions of PS-b-PN or PS-co-PN (6.25 mg/mL in THF) were mixed with different equivalents of Fe³⁺ ions (0, 0.5; 0.75, 1.0; 1.5; 2.5, and 15 equiv) relative to the total numbers of piperazinyl moiety. Then, those mixtures were mechanically stirred for 1 h at room temperature in order to dissolve copolymer fully. Then, acetonitrile was added slowly (the volume ratio of THF and acetonitrile = 2:3). TEM, DLS, and UV/vis were used for the analysis of the solutions.

Surface Self-Assemblies. Solutions of PS-b-PN or PS-co-PN (6.25 mg/mL in dioxane) were spin-coated (9100 rpm, 45 s) on silicon chips. The optimal solvent vapor annealing conditions found for our system involve annealing in a 200 mL closed-jar with dioxane vapor for 36 h. Thin films were analyzed by AFM and applied for optical tests.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.6b01787.

Supporting experimental data (including PL, TEM, AFM, DLS, UV/vis) (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: qzou@shiep.edu.cn.
*E-mail: yanq@fudan.edu.cn.
*E-mail: zhuliangliang@fudan.edu.cn.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Research Grant for Talent Introduction of Fudan University (JH1717006) and partially from Columbia University (award number W911NF-12-1-0252 to L. M. Campos) and National Program for Thousand Young Talents of China. Q. Z. acknowledges financial support by the National Natural Science Foundation of China (21406137) and the Shanghai Sailing Program (14YF141090). L. Z. thanks Prof. Dr. L. M. Campos and Prof. Dr. W.-D. Jang for helpful discussions.

REFERENCES


