Living supramolecular polymerization achieved by collaborative assembly of platinum(II) complexes and block copolymers

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An important feature of biological systems to achieve complexity and precision is the involvement of multiple components where each component plays its own role and collaborates with other components. Mimicking this, we report living supramolecular polymerization achieved by collaborative assembly of two structurally dissimilar components, that is, platinum(II) complexes and π–π metal−metal interactions. Diverse supramolecular assemblies of platinum(II) complexes with noncovalent and π–π stacking interactions have been reported (10–35). Examples include metallogels (14–16), liquid crystals (17, 18), and molecular architectures (19–24) such as molecular hairpins, foldamers, tweezers, and rectangles, as well as nanostructures (25–31) such as nanofibers, nanosheets, vesicles, nanorings, helices, and nanotubes. Despite all these interesting developments, most of the supramolecular assemblies of platinum(II) complexes reported by our group and others are formed in single-component systems (13–35). Furthermore, despite recent interest in living supramolecular polymerization (36–55), living supramolecular assemblies based on the platinum(II) system has also been rarely studied (34).

Unlike the well-established living polymerization that involves the formation of polymers linked by covalent bonds, living supramolecular polymerization is a relatively new area of research that has only attracted much attention recently and has emerged as an efficient pathway for the fabrication of supramolecular assemblies with precisely controlled dimensions and diverse architectures (46–55). For example, living crystallization-driven self-assembly based on diblock copolymers containing crystallizable polyferrocenyl(dimethyl)silane blocks has been reported to achieve cylindrical micelles and block comicles with precise lengths, as well as various complex architectures (46–48). Besides, supramolecular polymerization of a special porphyrin-based monomer has been found to exhibit living characters to form nanofibers with controlled length and narrow polydispersity (51). Recently, a chain-growth supramolecular polymerization has been realized by rationally designed corannulene-based supramolecular monomer and initiator, which allows for the efficient control of chain length, sequence, and stereochemical structure of the linear supramolecular polymer chains formed (52). Moreover, nanotubular heterojunctions prepared from two types of hexabenzocoronene derivatives have been reported to exhibit long-range excitation energy transfer behaviors and enhanced charge transport properties compared with the homotropic nanotubular assemblies of both types of the hexabenzocoronene derivatives (49). One-dimensional heterojunctions may also show unique properties for their applications in optical, electrical, and optoelectronic devices (56). However, fabrication of segmented architectures with heterojunctions by living supramolecular polymerization remains challenging and less explored (47, 49), due to the relatively strict requirement of lattice matching of different supramolecular monomers for heterojunction formation; a lattice mismatch smaller than 15% has been regarded as a prerequisite for successful heterojunction formation (57, 58).

In the reported literature, another important feature of biological systems to achieve complexity and precision is the involvement of multiple components where each component plays its own role and collaborates with other components. This work achieves living supramolecular polymerization by the collaborative assembly of two structurally dissimilar components, namely, the platinum(II) complexes and the block copolymers. This work largely broadens the scope of supramolecular monomers for living supramolecular polymerization and in the construction of supramolecular-based heterojunctions with large lattice mismatch, which represents a distinct advantage over the existing methods based on single-component systems in devising living supramolecular polymerization. This work may open up new, simple one-pot strategies for the fabrication of segmented supramolecular-based heterojunctions with different optical, charge transport, and catalytic properties for directional excitation energy, electron and hole transport.

Significance

Living supramolecular polymerization has emerged as an efficient pathway for the fabrication of supramolecular assemblies with precisely controlled dimensions and diverse architectures. This work achieves living supramolecular polymerization by the collaborative assembly of two structurally dissimilar components, namely, the platinum(II) complexes and the block copolymers. This work largely broadens the scope of supramolecular monomers for living supramolecular polymerization and in the construction of supramolecular-based heterojunctions with large lattice mismatch, which represents a distinct advantage over the existing methods based on single-component systems in devising living supramolecular polymerization. This work may open up new, simple one-pot strategies for the fabrication of segmented supramolecular-based heterojunctions with different optical, charge transport, and catalytic properties for directional excitation energy, electron and hole transport.


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studies (46–55), the heterojunctions can only be prepared either from structurally similar supramolecular monomers (49) or from building blocks with a slight lattice mismatch of 6% (47). This has presented a major drawback as dissimilar components are sometimes preferred for the fabrication of high-performance heterojunctions for energy transport, charge transport, and catalytic functions.

In addition, the reported methods for living supramolecular polymerizations are mainly based on single-component systems, with exceptionally few examples of two-component systems that can be achievable only via the involvement of structurally similar building blocks (46–55). Since the realization of living supramolecular polymerization is largely dependent on the design of the specialized molecules or macromolecules, the types of supramolecular monomers that can be polymerized by living supramolecular polymerization are very limited (46–55). In contrast, biological systems use multicomponent systems where each component plays its own role and collaborates with other components to achieve complexity and precision. Recently, a platinum(II) complex/PEG-b-PAA two-component supramolecular coassembly process developed in our laboratory showed the formation of 1D core–shell crystalline nanostructures (59). Since they are connected by noncovalent metal–metal interactions, π–π interactions, and electrostatic attractions, the 1D crystalline nanostructures can be considered as one type of supramolecular polymers (36–55). In the present study, it is found that the ends of the 1D crystalline nanostructures formed by platinum(II) complexes and PEG-b-PAA diblock copolymers are active during the coassembly and remain active after the coassembly. Addition of more platinum(II) complexes to the 1D nanostructures leads to the growth of the nanostructures while the diameter of the nanostructures remains unchanged. Addition of a different platinum(II) complex to the nanostructures forms segmented nanostructures where segments of different platinum(II) complexes connect to form heterojunctions. At the heterojunctions, PAA blocks act as adapters for lattice matching between chemically and crystallographically different platinum(II) complexes. Heterojunctions with a lattice mismatch as large as 21% can be achieved. The present study represents an example of living supramolecular polymerization achieved by collaborative assembly of two structurally dissimilar components (46–55). The present study also broadens the scope of supramolecular monomers for living supramolecular polymerization and in the construction of supramolecular-based heterojunctions (46–55).

### Results and Discussion

Supramolecular coassembly of complex 1 (Fig. 1) and PEG_{45}-b-PAA_{69} in a mixed solvent of acetonitrile–methanol–water (1:1:8, vol/vol/vol) shows the formation of nanofibers with a diameter of 12.1 ± 1.2 nm and a length of several micrometers after incubation of the coassembly mixture for 1 d (Fig. S1). The nanofibers are found to possess a core–shell crystalline nanostructure with hexagonally packed platinum(II) complexes along the fiber axis (59). The formation mechanism of the nanofibers has been studied by

![Fig. 1. Chemical structures of platinum(II) complexes.](image)

![Fig. 2. Time course of the supramolecular coassembly process. (A) Changes of hydrodynamic radius $\langle R_h \rangle$ during supramolecular coassembly of complex 1 (0.15 mM) and PEG_{45}-b-PAA_{69} ([carboxylic acid] = 1 mM) in a mixed solvent of acetonitrile–methanol–water (1:1:8, vol/vol/vol). (B–F) TEM images of the nanoobjects formed by the supramolecular coassembly at different incubation time. (G) Schematic illustration of the nucleation-growth mechanism of the supramolecular coassembly.](image)
in the incubation time to 2 h leads to nanofibers with a diameter of 1.8 nm (Fig. 2A). TEM images of (A) nanofibers formed by supramolecular coassembly of complex 1 (0.06 mM) and PEG113-b-PAA69 ([carboxylic acid] = 1.2 mM) in a mixed solvent of acetonitrile–methanol–water (1:1:8, vol/vol/vol); (B) longer nanofibers formed after adding more complex 1 to the as-formed nanofibers of A at a final complex 1/carboxylic acid molar ratio of 0.1/1; (C) nanorods formed by supramolecular coassembly of complex 2 (0.11 mM) and PEG12-b-PAA51 ([carboxylic acid] = 1 mM) in a mixed solvent of acetonitrile–methanol–water (1:1:8, vol/vol/vol); (D) segmented nanostructures formed after adding complex 1 to the as-formed nanorods of C at a final complex 1/carboxylic acid molar ratio of 0.18/0.11/1.

The gradual increase of the lengths of the nanofibers as evidenced by both DLS and TEM can rule out the possibility that the supramolecular polymerization in the present study follows a mechanism like conventional radical polymerization; one distinct feature of conventional radical polymerization is the formation of long polymer chains at the early stage of polymerization. For the formation of long nanofibers from short nanofibers, there are three possible mechanisms, namely (i) the end–end coupling of the short nanofibers, (ii) Ostwald ripening process, and (iii) the growth process of a nucleation-growth mechanism. For the end–end coupling mechanism, the long nanofibers are formed by the fusion of the ends of two short nanofibers. Based on this, one would expect a progressively steep increase of hydrodynamic radius in the DLS time course since DLS is extremely sensitive to objects with large sizes. The end–end coupling mechanism cannot explain the results of gradual increase and the leveling off as observed in the DLS time course (Fig. 2D). For the Ostwald ripening process, platinum(II) complexes dissociate from a short nanofiber and add onto the ends of another short nanofiber. As mentioned above, the short nanofibers obtained by quenching the supramolecular polymerization at the early stage show insignificant change in lengths after incubation at room temperature for 2 d (Fig. S4). This finding suggests that since the short nanofibers have a crystalline nanostructure, the dissociation of platinum(II) complexes from the crystalline nanostructures should be relatively difficult and slow. Therefore, Ostwald ripening process plays an insignificant role for the formation of long nanofibers from short nanofibers.

Based on the above experiments and analysis, and in view of the crystalline nanostructures of the nanofibers, it is proposed that the two-component platinum(II) complex/block copolymer supramolecular polymerization follows a nucleation-growth mechanism (Fig. 2G). Upon the mixing of platinum(II) complexes and block copolymers, nanoaggregates would form as shown in Fig. 2B, and then a part of the nanoaggregates would undergo rearrangement to form nanorods of complex 2 and PEG45-b-PAA59, the nanorod-block-nanobelt nanostructures formed by addition of complex 1 to nanorods of complex 2, and the nanofibers formed by complex 1 and PEG45-b-PAA59.
the nucleus (60) (Fig. 2B and G). Addition of free platinum(II) complexes onto the nucleus would then lead to the formation and growth of the short nanofibers. It is noteworthy that the short nanofibers formed in the present study are different from the short patchy nanofibers in our previous study (59): the short patchy nanofibers possess less PEG protection and can couple with each other by attractive end patches, whereas the short nanofibers in the present study only allow the addition of free platinum(II) complexes onto their ends. In the present study, the free platinum(II) complexes are likely to be originated from the dissociation of the nanospecies of platinum(II) complexes and block copolymers (Fig. 2G). The dissociation of platinum(II) complexes is relatively easy and fast because the nanospecies possess large specific surface areas and the packing of platinum(II) complexes within the nanospecies is not quite regular. The binding constant of complex 1 and PEG_{133}-b-PAAn90 has been determined by UV-vis titration to be 6.5 × 10^4 M^{-1} (Supporting Information). The dissociation of free complex 1 is estimated to be 2.7 μM, i.e., 1.8% of the total amount of complex 1 in the assembly mixture. When the nanospecies have been exhausted, the growth of nanofibers and the two-component supramolecular polymerization end. In the present system, the ends of the nanofibers are found to be active during supramolecular polymerization, which is one of defining characters for living supramolecular polymerization.

Another defining character of living supramolecular polymerization is that the ends of the supramolecular polymers remain active after supramolecular polymerization. Nanofibers with a diameter of 10.6 ± 1.0 nm and an L of 251 nm (Lw/Ln = 1.21), prepared by the mixing of complex 1 and PEG_{133}-b-PAAn14 in a mixed solvent of acetonitrile–methylene–water (1:1:8, vol/vol/v) at complex 1/carboxylic acid molar ratio of 0.05/1, followed by incubation at room temperature for 1 d (Fig. 3A), are found to show insignificant change in both the diameter and the length upon further incubation. Interestingly, more of complex 1 in acetonitrile to the nanofibers at a final complex 1/carboxylic acid molar ratio of 0.1/1 followed by incubation has been found to produce longer nanofibers with an L of 562 nm (Lw/Ln = 1.26) and a diameter of 10.2 ± 1.3 nm (Fig. 3B). DLS analysis shows an increase of an Rg of 94 to 139 nm upon the addition and incubation. The length increase and the unchanged diameter of the nanofibers suggest that the nanofibers possess active ends that serve as sites to seed the growth of the added complex 1 onto their ends.

The activity of the ends of the supramolecular polymers has been further explored. Nanorods with a diameter of 45.7 ± 9.3 nm and an average length of ~1 μm are formed by the supramolecular coassembly of the alkynylplatinum(II) terpyridine complex 2 containing hydrogen-bonding moieties (Fig. 1) and PEG_{133}-b-PAAn90 (Fig. 3C), which are used as seeds. TEM-EDX (energy-dispersive X-ray) analysis indicates the presence of platinum in the nanorods (Fig. S5). Selected area electron diffraction (SAED) pattern confirms the existence of metal–metal and π–π stacking interactions within the nanorods (Fig. S6). Addition of complex 1 in acetonitrile to the nanorods followed by incubation has been observed to lead to the formation of 1D segmented nanostructures where the nanorod segments with a high electron contrast are found to connect to nanobelt segments with a low electron contrast in an end-to-end manner (Fig. 3D). At the heterojunction, the width of the nanobelt segment is equal to the diameter of the nanorod segment. In the control experiments, the seed nanorods show insignificant morphological and dimensional changes upon the addition of the same amount of acetonitrile followed by incubation (Fig. S7). Also, it is confirmed that without the presence of nanorod seeds, the supramolecular coassembly of complex 1 and PEG_{133}-b-PAAn90 under the same condition can form nanofibers only. Moreover, the diameter of the nanorod segments in the segmented nanostructures (42.3 ± 5.2 nm) shows insignificant change compared with that of the nanorod seeds. These findings indicate that the formation of the 1D segmented nanostructures can be exclusively attributed to the living growth of the nanobelt of complex 1 onto the nanorod seeds. The powder X-ray diffraction (PXRD) pattern of the nanorod-block-nanobelt nanostructures is quite similar to that of the seed nanorods, but both of them are very different from the PXRD pattern of the nanofibers formed by supramolecular coassembly of complex 1 and PEG_{133}-b-PAAn90 without the presence of the nanorod seeds (Fig. 4). These observations indicate that, for the formation of the nanorod-block-nanobelt nanostructures, supramolecular coassembly of complex 1 and PEG_{133}-b-PAAn90 gives up the types of molecular packing in the nanofibers to match the lattice of the seed nanorods to form the nanobelt segments. At the heterojunctions, PAAn blocks act as adaptors for lattice matching between the nanorods of complex 2 and the nanobelts of complex 1 in the transverse direction, and the noncovalent metal–metal and π–π interactions between complex 1 and complex 2 direct the formation of nanobelt segments in the longitudinal direction (Fig. 5). The nanorod-block-nanobelt nanostructures possess heterojunctions with a lattice mismatch of 21% as calculated from the principal peaks of PXRD patterns (Fig. 4), which is much larger than that in the literature (6%) (47) and breaks the 15% limit for heterojunction formation (57, 58).
To further demonstrate the capability of the supramolecular coassembly, alkynylplatinum(II) 2,6-bis(N-methylbenzimidazol-2-yl)pyridine complex 3 (Fig. 1), that possesses larger structural differences from complex 1, has been selected to build heterojunctions between complex 3 and complex 1 (Fig. 6). Complex 3, with a larger π-surface and hydrophobicity, has been found to undergo ready self-assembly in water to form nanorods on its own, which may serve as seeds for subsequent supramolecular growth. Nanorods of complex 3 with a diameter of 13.6 ± 1.4 nm and an average length of ∼900 nm are prepared by addition of complex 3 into water, followed by incubation at room temperature for 1 d (Fig. 6C). Nanorods of complex 3 show the emergence of a low-energy MMLCT absorption band at 570 nm in the UV-vis absorption spectrum and exhibit a drastic intensity enhancement of triplet MMLCT emission at 718 nm with respect to the monomeric form of complex 3 (Fig. 6 A and B). The nanorods show morphological and dimensional stability upon further incubation. By using the as-prepared nanorods as seeds, addition of complex 1 and PEG45-b-PAA69 to the nanorods followed by incubation has been found to form 1D segmented nanostructures where nanofiber segments of complex 1 connect nanorod segments of complex 3 to form heterojunctions (Fig. 6D). At the heterojunction, the diameter of the nanorod segment is equal to that of the nanofiber segment, which indicates that the living growth of the nanofiber segments of complex 1 occurs at the ends of the nanorod seeds. PXRD patterns show that the nanorods, the nanofibers, and the nanorod-block-nanofiber nanostructures possess hexagonally packed molecular columns of platinum(II) complexes within the nanostructures, and the lattice constants of these nanostructures are similar (Fig. S8).

Summary and Prospects

In conclusion, living supramolecular polymerization has been achieved by collaborative assembly of two structurally dissimilar components, that is, platinum(II) complexes and PEG-b-PAA diblock copolymers. In the collaborative assembly, the PAA blocks neutralize the charges of the platinum(II) complexes, while the noncovalent metal–metal and π–π interactions direct the longitudinal growth of the platinum(II) complexes into 1D crystalline nanostructures, and the PEG blocks inhibit the transverse growth of the platinum(II) complexes and provide the entire system with excellent solubility. For the formation of segmented crystalline nanostructures, the PAA blocks act as adapters for lattice matching between different platinum(II) complexes, and living growth of the platinum(II) complexes is achieved by the metal-metal and π–π stacking interactions in the longitudinal direction. Owing to the strategy of the two-component collaborative assembly, the heterojunctions of the segmented nanostructures in the present study possess supramolecular monomers with many more structural and crystallographical differences than those formed by single-component living supramolecular polymerization in the reported literature (47). The unique aggregation behaviors of the platinum(II) complexes, together with the advantages of block copolymers for supramolecular assembly and their collaborations, have been well demonstrated in the present study. It is believed that this strategy of two-component collaborative assembly will further broaden the scope of supramolecular monomers for living supramolecular polymerization that may lead to a new class of supramolecular polymers with diverse compositions, precisely controlled dimensions, and complicated architectures, as well as intriguing spectroscopic and luminescence properties and other functional properties. Since the two-component strategy allows for the fabrication of heterojunctions with large structural differences and large lattice mismatch, it may also open new and simple one-pot strategies for the construction of diverse arrays of segmented supramolecular-based heterojunctions for applications in optical, catalytic, electrical, and optoelectronic devices via directional excitation energy, and electron and hole transport.

Materials and Methods

Nanostructure Growth Experiment for the Preparation of Longer Nanofibers by Using Nanofibers of Complex 1 and PEG113-b-PAA49 as Seeds. PEG113-b-PAA49 in methanol was first mixed with water, and then platinum(II) complex 1 in acetonitrile was added. The complex 1/carbonic acid molar ratio in the mixture was 0.05:1. The mixture was homogenized by gentle shaking and incubated at room temperature for 1 d. Nanofibers were formed with a diameter of 10.6 ± 1.0 nm and an Lν of 251 nm (Lν/Lνc = 1.21). To perform the nanostructure growth experiment, additional amounts of complex 1 in acetonitrile were added to the as-formed nanofibers, followed by incubation at room temperature for 1 d. The final molar ratio of complex 1/carbonic acid was 0.1/1.

Nanostructure Growth Experiment for the Fabrication of Nanorod-Block-Nanobelt Nanostructures of Complex 2 and Complex 1 by Using Nanorods of Complex 2 and PEG45-b-PAA69 as Seeds. PEG45-b-PAA69 in methanol was first mixed with water, and then platinum(II) complex 2 in acetonitrile was added. The complex 2/carbonic acid molar ratio in the mixture was 0.11/1. The mixture was homogenized by gentle shaking and incubated at room temperature for 1 d. Nanorods were formed with a diameter of 45.7 ± 9.3 nm and a length of ∼1 μm. To perform the nanostructure growth experiment, complex 1 in acetonitrile was added to the as-formed nanorods, followed by incubation at room temperature for 1 d. The final molar ratio of complex 1/complex 2/carbonic acid was 0.180/1.1/1.

Nanostructure Growth Experiment for the Construction of Nanorod-Block-Nanofiber Nanostructures of Complex 3 and Complex 1 by Using Nanorods of Complex 3 as Seeds. Platinum(II) complex 3 in N,N-dimethylformamide (DMF) incubated in methanol at room temperature for 1 d. Nanorods were formed with a diameter of 13.6 ± 1.4 nm and an average length of ∼900 nm. To perform the nanostructure growth experiment, PEG45-b-PAA69 in methanol was first mixed with platinum(II) complex 1 in acetonitrile, and then the mixture of complex 1 and PEG45-b-PAA69 was added to the as-formed nanorods. The mixture was homogenized by gentle shaking and allowed to stand at room temperature for 1 d. The final molar ratio of complex 1/complex 2/carbonic acid was 0.150/1.3/1.

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Supporting Information

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Synthesis of Platinum(II) Complexes

Complexes 1–3 were synthesized according to the literature methods (10, 61, 62).

Synthesis of Polymers

Poly(ethylene glycol)-b-poly(tert-butyl acrylate) (PEG-b-PBA) diblock copolymers were synthesized via atom transfer radical polymerization (63), using PEG-Br and methyl α-bromoisobutyrate as initiator, respectively (64). PEG_{45-b}-PBA_{69} (M_w/M_n = 1.17) and PEG_{113-b}-PBA_{31} (M_w/M_n = 1.20) were obtained (the subscript represents the degree of polymerization of each block). The degrees of polymerization and M_w/M_n were determined by ^1^H NMR spectroscopy and gel permeation chromatography, respectively. To prepare poly(ethylene glycol)-b-poly(acrylic acid) (PEG-b-PAA), PEG-b-PBA was first dissolved in dichloromethane at ~50 mg/mL, and then trifluoroacetic acid was added at a trifluoroacetic acid/dichloromethane volume ratio of 1/10 to the solution to selectively hydrolyze the tert-butyl ester groups. After hydrolysis for 2 d, the reaction mixture was evaporated under reduced pressure to dryness. The obtained PEG-b-PAA was purified by four cycles of dissolution in methanol/precipitation in hexane. The deprotection of the tert-butyl ester groups was confirmed by FTIR and ^1^H NMR spectroscopy. PEG_{45-b}-PAA_{69} and PEG_{113-b}-PAA_{31} were obtained.

Time-Course Experiments of the Supramolecular Coassembly

PEG_{45-b}-PAA_{69} in methanol was first mixed with water, and then platinum(II) complex 1 in acetonitrile was added. The mixture was homogenized by gentle shaking, and time-course experiments including UV-vis, steady-state emission, and DLS measurements were allowed to be performed.

Determination of the Binding Constant by UV-Vis Titration

For UV-vis titration, the concentration of complex 1 was fixed at 50 μM and the concentration of carboxylic acids of PEG_{45-b}-PAA_{69} was varied from 5 to 100 μM. The pH of the mixture of complex 1 and PEG_{45-b}-PAA_{69} was 5. The corresponding UV-vis spectra were recorded. The binding constant was calculated according to the following equation (65): [carboxylic acid]/(ε_A−ε_F) = [carboxylic acid]/(ε_B−ε_F) + 1/K_θ(ε_B−ε_F), where ε_A, ε_B, and ε_F were A_{obs}/[complex]_{total} ([complex]_{total} = [complex]_{free} + [complex]_{bound}), the extinction coefficient for complex 1 in the fully bound form, and the extinction coefficient for free complex 1, respectively. The absorbance of MMLCT band at 605 nm was selected as A_{obs}. Since free complex 1 in their monomeric form shows no absorption at 605 nm, the value of ε_F is 0. A plot was made of [carboxylic acid]/(ε_A−ε_F) versus [carboxylic acid] (Fig. S9). The binding constant (K_θ) could then be obtained by the ratio of the slope to the intercept. The binding constant of complex 1 and PEG_{45-b}-PAA_{69} has been determined by UV-vis titration to be 6.5 × 10^4 M^{-1}. In the supramolecular coassembly of complex 1 (0.15 mM) and PEG_{45-b}-PAA_{69} ([carboxylic acid] = 1 mM), the concentration of free complex 1 was calculated to be 2.7 μM. The percentage of free complex 1 and the aggregated complex 1 is 1.8% and 98.2%, respectively.

Physical Measurements and Instrumentation

^1^H NMR spectra were recorded on a Bruker AVANCE 300 or 400 (300 and 400 MHz) Fourier-transform NMR spectrometer with chemical shifts reported relative to tetramethylsilane. UV-vis absorption spectra were recorded on a Cary 50 (Varian) spectrophotometer equipped with a xenon flash lamp. Steady-state emission spectra were recorded using a Spex Fluorolog-3 model FL3-211 fluorescence spectrophotometer equipped with an R2658P PMT detector. Step-scanned PXRD data were collected by the Bruker AXS D8 ADVANCE (Philips PW1830) powder X-ray diffractometer in Bragg–Brentano (θ/2θ) reflection mode with a graphite monochromatized Cu–Kα radiation (λ = 1.5406 Å) and nickel filter. TEM experiments were performed on Philips CM100 with an accelerating voltage of 100 kV. EDX analysis and SAED experiments were carried out on FEI Tecnai G2 20 Scanning TEM with an accelerating voltage of 200 kV. DLS experiments were performed on a Malvern Zetasizer 3000HSA with an internal HeNe laser (λ = 632.8 nm). In the DLS study, the hydrodynamic radius of the measured objects, which is calculated from the diffusion coefficient by the Stokes–Einstein equation, is the radius of an equivalent sphere which has the same diffusion coefficient as the measured objects even though the true shape of the measured objects may differ from a sphere. The equivalent sphere hydrodynamic radius is used to represent the size of the measured objects.
Fig. S1. TEM image of the nanofibers formed by supramolecular coassembly of complex 1 (0.15 mM) and PEG₄₅-b-PAA₆₉ ([carboxylic acid] = 1 mM) in a mixed solvent of acetonitrile–methanol–water (1:1:8, vol/vol/v) after incubation for 1 d.

Fig. S2. (A) UV-vis absorption spectra and (B) absorbance at 605 nm of the mixture of supramolecular coassembly of complex 1 (0.15 mM) and PEG₄₅-b-PAA₆₉ ([carboxylic acid] = 1 mM) in a mixed solvent of acetonitrile–methanol–water (1:1:8, vol/vol/v) at different incubation time.

Fig. S3. (A) Steady-state emission spectra and (B) relative emission intensity at 785 nm of the mixture of supramolecular coassembly of complex 1 (0.15 mM) and PEG₄₅-b-PAA₆₉ ([carboxylic acid] = 1 mM) in a mixed solvent of acetonitrile–methanol–water (1:1:8, vol/vol/v) at different incubation time.
Fig. S4. (A) TEM image of the nanofibers obtained by quenching the assembly mixture of complex 1 (0.15 mM) and PEG₄₅-b-PAA₆₉ ([carboxylic acid] = 1 mM) in an ice bath at incubation time of 15 min. (B) TEM image of the quenched nanofibers after incubation of the nanofibers of A at room temperature for 2 d.

Fig. S5. EDX spectrum of the nanorods prepared from complex 2 (0.11 mM) + PEG₄₅-b-PAA₆₉ ([carboxylic acid] = 1 mM) in a mixed solvent of acetonitrile–methanol–water (1:1:8, vol/vol/v).

Fig. S6. TEM image and SAED pattern (Inset) of the nanorods formed by supramolecular cosassembly of complex 2 (0.11 mM) + PEG₄₅-b-PAA₆₉ ([carboxylic acid] = 1 mM) in a mixed solvent of acetonitrile–methanol–water (1:1:8, vol/vol/v).
Fig. S7. TEM image of the seed nanorods formed by supramolecular coassembly of complex 2 (0.11 mM) + PEG45-b-PAA69 ([carboxylic acid] = 1 mM) upon the addition of acetonitrile followed by incubation as a control for nanostructure growth experiment for the fabrication of nanorod-block-nanobelt nanostructures of complex 2 and complex 1.

Fig. S8. PXRD patterns of the nanorods formed by complex 3, the nanorod-block-nanofiber nanostructures formed by addition of complex 1 and PEG45-b-PAA69 to nanorods of complex 3, and the nanofibers formed by complex 1 and PEG45-b-PAA69. All of the PXRD patterns show a series of Bragg peaks in the region of $3^\circ < 2\theta < 18^\circ$. The distances obtained from the Bragg peaks follow the ratios of $1: \sqrt{3}: \sqrt{4}: \sqrt{7}$, characteristic of a hexagonal packing of molecular columns of platinum(II) complexes. The PXRD patterns also show that all of the nanostructures possess similar lattice constants.
Fig. S9. Plot of $[\text{carboxylic acid}] / (e_A - e_F)$ versus $[\text{carboxylic acid}]$ for the determination of the binding constant. The binding constant ($K_b$) could be obtained by the ratio of the slope to the intercept.

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