Self-Assembly of Ultralong Polyion Nanoladders Facilitated by Ionic Recognition and Molecular Stiffness

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S *Supporting Information*

ABSTRACT: It is hard to obtain spatially ordered nanostructures via the polyion complexation process due to the inherent flexibility of polymers and isotropicity of ionic interactions. Here we report the formation of polyion assemblies with well-defined, periodically regular internal structure by imparting the proper stiffness to the molecular tile. A stiff bisligand TPE-C4-L2 was designed which is able to form a negatively charged supramolecular polyelectrolyte with transition metal ions. This supramolecular polyelectrolyte slowly self-assembled into polydispersed flat sheets with cocoon-like patterns. Upon the addition of an oppositely charged ordinary polyelectrolyte, the

polydispersed cocoons immediately transformed into ultralong, uniform nanoladders as a result of matched ionic density recognition. The supramolecular polyelectrolytes assembled side-by-side, and the negative charges aligned in an array. This structure forced the positively charged polymers to lie along the negative charges so that the perpendicular arrangement of the oppositely charged chains was achieved. Such precise charge recognition will provide insight into the design of advanced materials with hierarchical self-assembled structures.
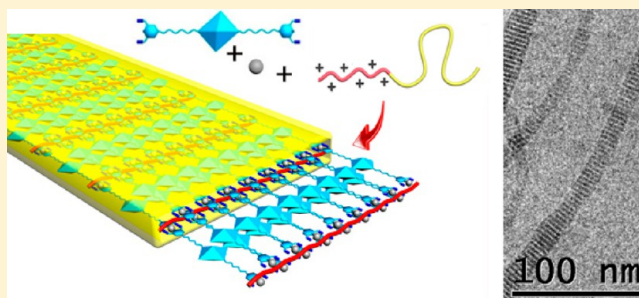
INTRODUCTION

Ionic interaction[1−5] has emerged as an important driving force for the fabrication of ionic self-assembly.[6−10] Well-known examples are the polyion assemblies formed in water by pairs of oppositely charged polyelectrolytes,[11−13] which can be forced into films[14−16] and capsules[17−21] with appropriate protocols, or made into micelles[2,22−27] and vesicles[28−30] by end-attaching uncharged water-soluble blocks to (at least one of) the polyelectrolytes. This is also the case when one of the polyelectrolytes was replaced by reversible or "soft" coordination polymers, namely, supramolecular chains in which organic bisligands and transition metal ions alternate in a regular fashion.[31−34] By proper choice of the bisligands, one can even obtain supramolecular polyelectrolytes,[35−39] which in turn can form polyion assemblies just like ordinary polyelectrolytes.[40−43] Usually, polyion assemblies formed with covalent polyelectrolytes[26,44] or coordination polymers[45−51] have internally random structures, since the polymers are flexible and the ionic interactions are isotropic between the flexible chains.

On the other hand, endeavors in creating hierarchical self-assembled structures from basic molecular tiles are increasingly directed toward advanced materials. Since the pioneering work by Lehn[52] and de Gennes,[53] supramolecular self-assembly has been verified as a marvelous approach to exotic self-assemblies. For instance, complex shapes were made by controlled assembly of single-strand DNA,[54] inorganic vesicles were found upon dispersing polyoxametalate (POM) solids in acetone,[55,56] and multicompartment micelles were created using properly designed block copolymers.[57−60] However, so far manipulation of structural hierarchy has not been achieved in polyion assemblies, because the ionic interactions usually are not sufficient to produce ordered structures.

In this work we show that precise alignment of polyelectrolyte chains inside polyion assemblies can be achieved by imparting proper stiffness to the molecular tiles. The stiff

Scheme 1. Structure of (a) TPE-C4-L2 and (b) PMVP$_{41}$-b-PEO$_{205}$ and (c) Schematic Representation of the Structures Formed by TPE-C4-L2 and Metal Ions without and with Polymer^a
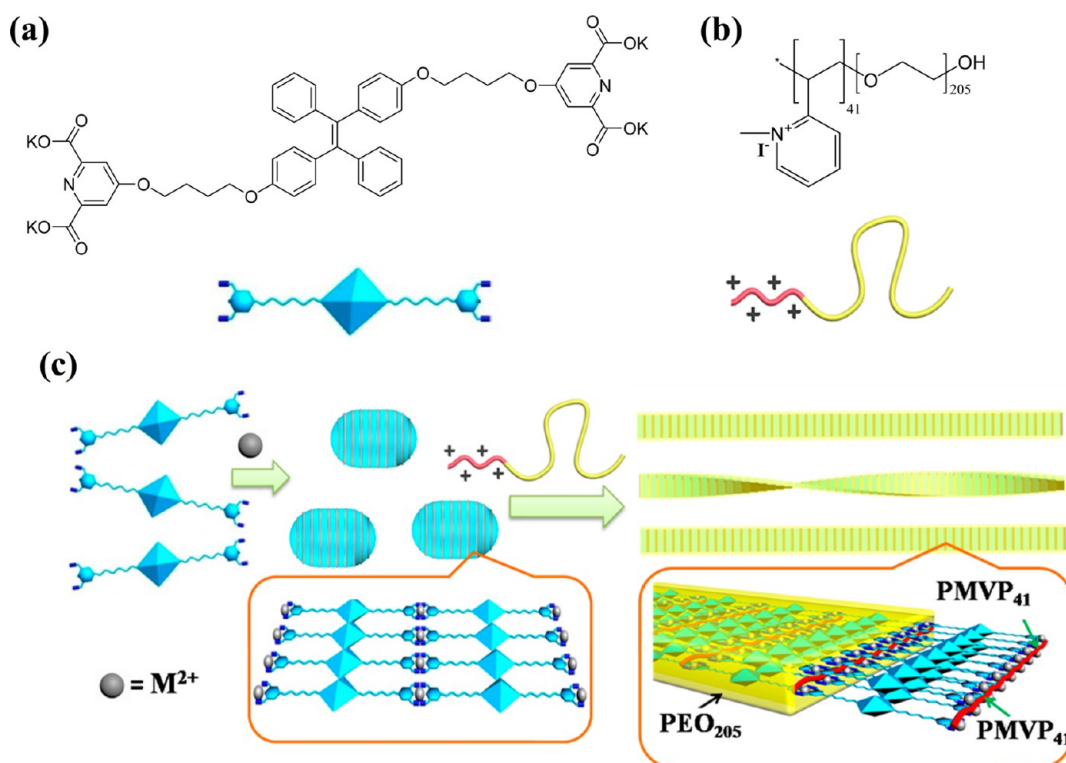
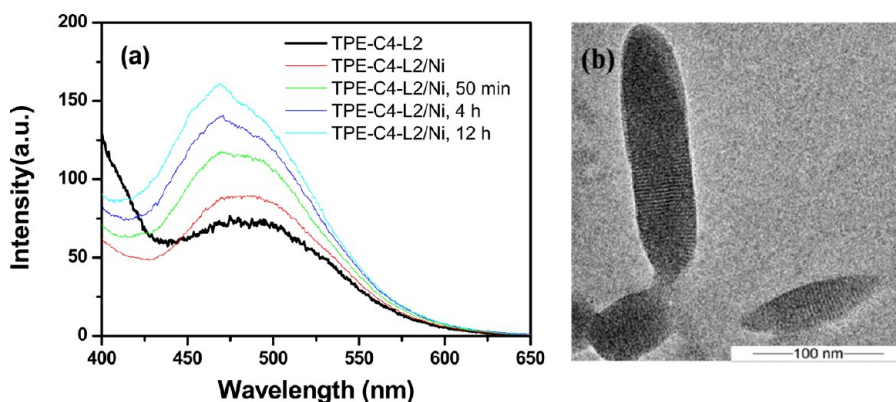^{a}The PE0$_{205}$ block is illustrated as the yellow shell that covers the ultralong nanoladders.

Figure 1. (a) Fluorescence intensity and (b) TEM image of TPE-C4-L2/Ni = 1/1 solution ([Ni^{2+}] = 0.5 mM).

bisligand TPE-C4-L2 (Scheme 1a) and transition metal ions (Ni^{2+}, Zn^{2+}, Ca^{2+}, etc.) can form a negatively charged supramolecular polyelectrolyte which alone can slowly self-assemble into polydispersed flat cocoon-like sheets. Upon the addition of a properly designed positively charged block polyelectrolyte PMVP$_{41}$-b-PEO$_{205}$ (Scheme 1b), the polydispersed cocoons immediately transformed into uniform ultralong nanoladders as a result of matched charge density. The negatively charged coordination supramolecular polymer chains aligned parallel to each other and were perpendicularly interconnected by the positively charged block of PMVP$_{41}$-b-PEO$_{205}$ to form an ordered grid-like structure (Scheme 1c). To the best of our knowledge, this is the first time the spatially ordered arrangement of the polyion chains upon the charge attraction has been obtained.

The synthesis of the bisligand TPE-C4-L2 is given in Supporting Information. The TPE group is well-known for its aggregation-induced emission,[61] which acts as a reporter group in this work. Without the presence of metal ions, the solution of TPE-C4-L2 exhibited negligible fluorescence, indicating no aggregation of TPE-C4-L2. Upon addition of transition metal ions at a stoichiometric ratio, the dilute solution did not exhibit noticeable fluorescence first, but the fluorescence increased slightly over time (Figure 1a) due to the slow aggregation of TPE-C4-L2. Both TEM (Figure 1b) and cryo-TEM (Supporting Information Figure S4) images revealed the formation of flat, cocoon-like sheets. The presence of regularly separated dark and light lines indicated that metal ions have aligned in an array. This indicates the formation of coordination polymer chains with alternatively arranged metal ions and TPE-C4-L2. In Figure 2a we show the molecular modeling of one repeating
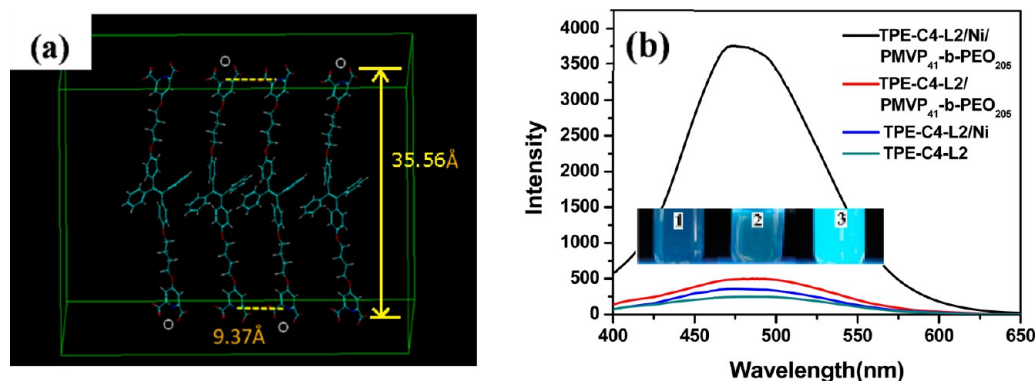
Figure 2. (a) Hyper Chem 8.0 simulation of the $\pi-\pi$ stacking between the TPE groups in the side-by-side alignment of TPE-C4-L2/metal system. The distance between two neighboring coordinating centers (or the butyl chains) is 9.37 Å. The extending length of the TPE-C4-L2 is 35.56 Å. (b) Fluorescence spectra of different solutions. The inset images are the photos of the solution of (1) TPE-C4-L2/Ni, (2) TPE-C4-L2/PMVP$_{41}$-b-PEO$_{205}$, and (3) TPE-C4-L2/Ni/PMVP$_{41}$-b-PEO$_{205}$ irradiated at 365 nm.

unit of this arrangement with Chem Hyper 8.0. The details of such molecular alignment will be discussed further in the following text.

Surprisingly, as soon as a neutral-cationic diblock copolymer poly-N-methyl-2-vinyl pyridinium iodide-b-poly(ethylene oxide), PMVP$_{41}$-b-PEO$_{205}$ (Scheme 1b), was added at charge stoichiometry, the significant enhancement of the fluorescence was detected (Figure 2b), indicating the strong aggregation of the TPE moieties. The solution also appeared bluish, and the light scattering intensity increased 30-fold (Supporting Information Table S1). Both were likely due to the presence of large aggregates in the solution. In Figure 3 we showed the cryo-TEM micrographs of the polyion complexes formed by the coordination polymer and PMVP$_{41}$-b-PEO$_{205}$ mixed at charge stoichiometry. Flexible, ribbon-like structures with length over 1 μm were shown in Figure 3a. Moreover, strikingly fine "ladder"-like periodic structure of thin dark stripes normal to the ribbon long axis was clearly shown in the zoomed-in pictures (Figure 3b,c). It is amazing that the well-ordered periodic structures are uniform in the whole system, and the length of the ladders persists up to a few micrometers. The average width of the ladders is around 10.7 nm which features these structures "nanoladders". The nanoladders are thin and sometimes twisted, as shown in Figure 3c. At places where two nanoladders overlap (indicated by the arrow), the overlay of the dark lines can be easily identified (Figure 3c), suggesting the thickness of the nanoladders is within the focusing depth of the cryo-TEM.

The dark/light periodicity measured from the Fourier analysis was determined to be about 3.6 nm (inset in Figure 3b), which agrees well with the fully extended length of the TPE-C4-L2 obtained from molecular simulations by Chem Hyper 8 (Figure 2a). This indicates that the "nanoladders" (dark lines) are the side-by-side aligned coordination polymers as illustrated in Scheme 1c. Compared with the cocoon-like structures in the solutions without the presence of PMVP$_{41}$-b-PEO$_{205}$, it is clear that neutralization of the negative charges at the coordination center promoted the striking parallel alignment of the coordination polymer chains to such a large length scale.

Charge density of the coordination polymers and of PMVP$_{41}$-b-PEO$_{205}$ was analyzed to understand the molecular arrangement in the nanoladders. The negative charge density perpendicular to the long axis of the ribbons is two negative elementary charges per 9.37 Å (Figure 2a). The charge density
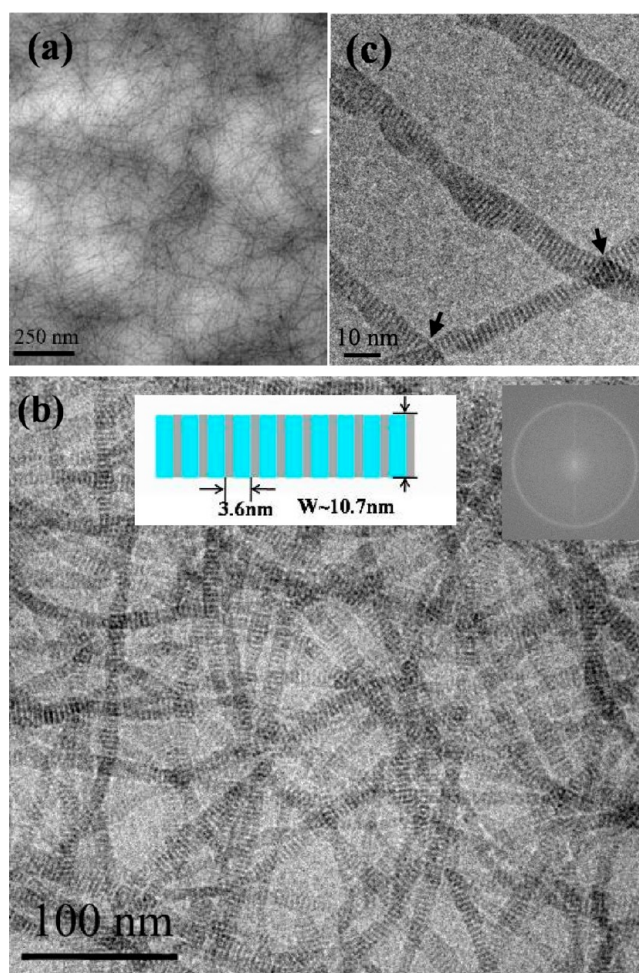

Figure 3. Cryo-TEM images of the aggregates formed in the TPE-C4-L2/Ni/PMVP$_{41}$-b-PEO$_{205}$ mixed system. Panels a–c are the images obtained at different magnifications. The insets in part b are the illustration of the nanoladders (left) and the FFT analysis (right) of them, respectively.

of PMVP$_{41}$ block is one elementary positive charge per 2.3 Å, or four positive charges per 9.2 Å (Supporting Information). The complete charge neutralization could be achieved if two arrays of coordination centers (metal ions) interact with one PMVP$_{41}$ block. Therefore, the PMVP$_{41}$ blocks would be
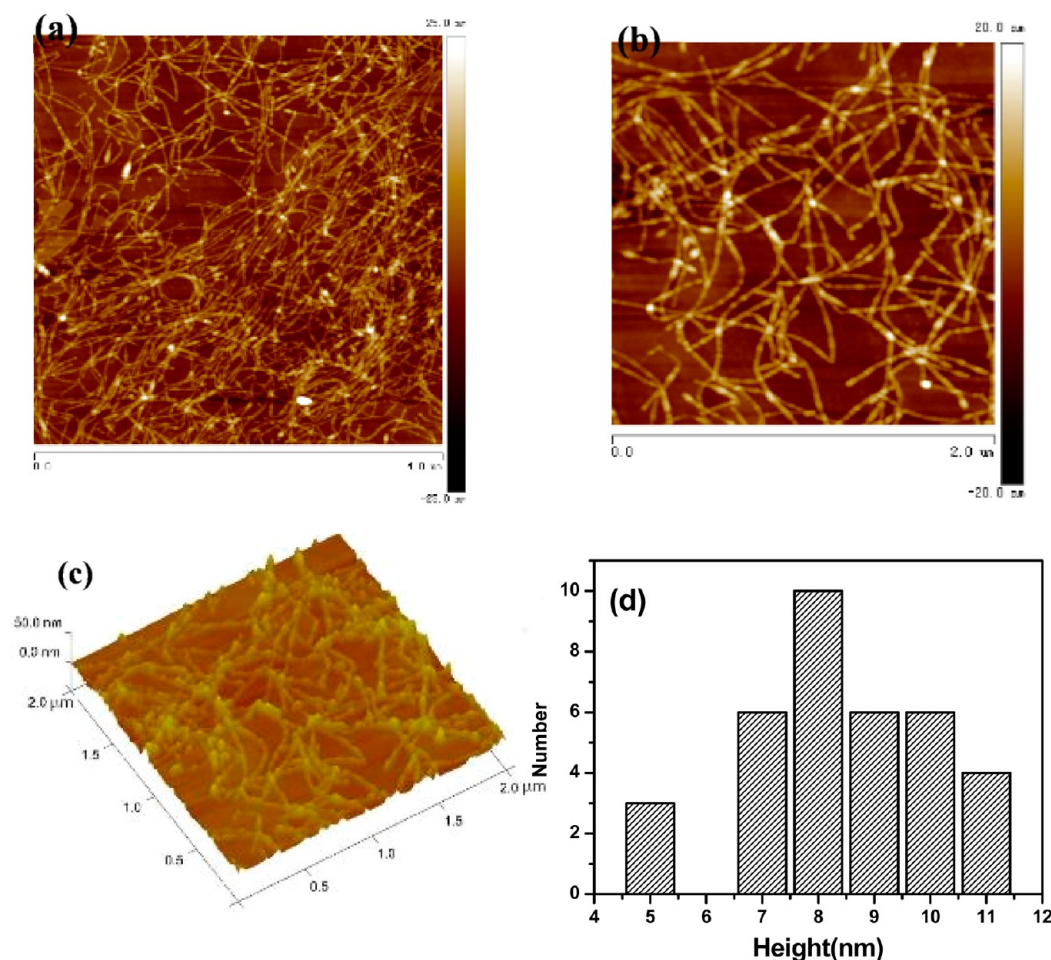
Figure 4. AFM image of the aggregates formed in the TPE-C4-L2/Ni/PMVP$_{41}$-b-PEO$_{205}$ mixture system. Panels a and b are the images obtained at different magnifications. Panel c is the 3D image of panel b. (d) Height distribution of TPE-C4-L2/Ni/PMVP$_{41}$-b-PEO$_{205}$.

sandwiched between two sheets of coordination polymers (Scheme 1c). The fully extended length of the PMVP$_{41}$ block is around 9.5 nm which coincides with the width of the long nanoladders (10.7 nm), possibly indicating the fully extended chain configuration of the PMVP$_{41}$ block inside the polyion complex and supporting the structural model proposed in Scheme 1c. The model in Scheme 1c clearly demonstrates that the molecular stiffness at atomic level in the ligand has been successfully amplified to macroscopic level.

These nanoladders are stabilized against further aggregation by the PEO$_{205}$ blocks. Although the presence of PEO$_{205}$ blocks is not directly visible in cryo-TEM because they are well-solvated, their presence can be indicated by the lack of bundling of the ladders. The PEO$_{205}$ blocks would form a very thin layer surrounding the ladders in solutions. This can provide steric repulsions to prevent the ladders from further bundling. The presence of PEO blocks on the surface of the nanoladders was also verified by the AFM measurements. As shown in Figure 4, the stripes cannot be observed in the AFM images, and the height measurements suggest the presence of mountains up to 10 nm on each ribbon. These mountains should be the dried PEO coils which act as a thick corona shell surrounding the ladders. For the same reason, the stripes cannot be observed either with normal TEM (Supporting Information Figure S5), just because the ladders were deeply buried under the dried thick PEO coils.

Ionic recognition and charge balancing are very crucial to the formation of ultralong nanoladders. When the coordination polymer was in excess, the negative charges could not be completely balanced by the positive charges on PMVP$_{41}$-b-PEO$_{205}$. Subsequently, not all cocoons were transformed into ultralong nanoladders (Figure 5a). This implies that the complete transformation from cocoons into uniform nanoladders requires complete charge neutralization. On the other hand, as PMVP$_{41}$-b-PEO$_{205}$ is in excess, the nanoladders were significantly shortened (Figure 5b). In addition, if the linear PMVP$_{41}$-b-PEO$_{205}$ was replaced by a branched polyelectrolyte polyetheneimine (PEI), only spheres were obtained (Figure 5c and Supporting Information Figure S6) because the branched structure of PEI does not allow charge density matching between the positive and negative charges.

Finally, the molecular stiffness of the bisligand is also critical to the formation of ultralong nanoladders. When the butyl group in TPE-C4-L2 was replaced with the foldable four ethylene oxide (EO) group, TPE-(EO)$_4$-L2 (inset in Figure 5d), only spherical structures were formed (Figure 5d) even if the TPE group was preserved. Molecular simulations (Supporting Information) suggest that the $\pi-\pi$ stacking between the TPE groups occurred (Figure 2a) in the system. Although $\pi-\pi$ stacking by its own may drive self-assembly formation,[62] only the $\pi-\pi$ stacking between the TPE groups is not enough to lead to the formation of the nanoladders. It should also be clarified that the change of the spacer length and
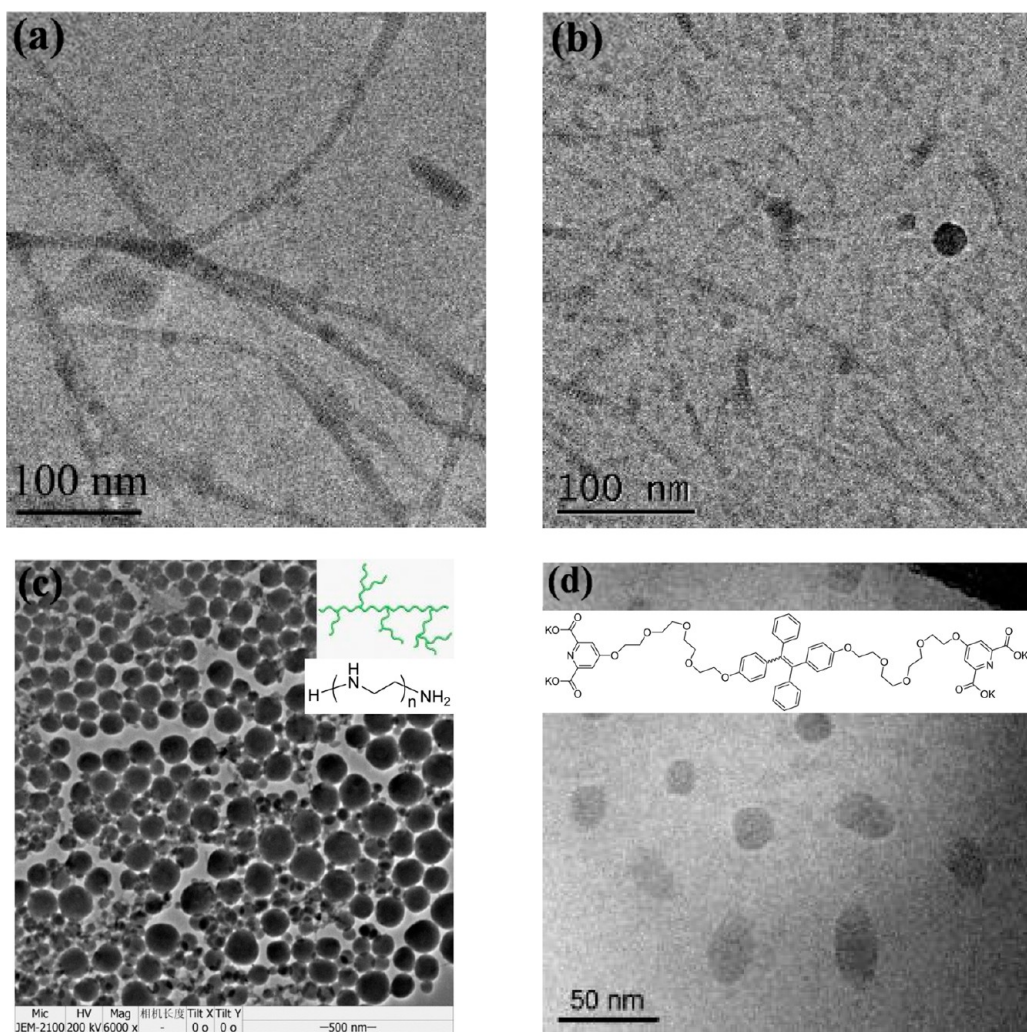
Figure 5. (a, b) Cryo-TEM image of the aggregates formed in the TPE-C4-L2/Ni/PMVP$_{41}$-b-PEO$_{205}$ mixture. (a) [−] = 2[+]. (b) [+] = 2[−] ([+] = concentration of positive charges carried by PMVP$_{41}$ block and [−] = concentration of negative charges carried by TPE-C4-L2/Ni). (c) TEM image of TPE-C4-L2/Zn/PEI mixture. (d) Cryo-TEM image of TPE-(EO)$_4$-L2/Ni/PMVP$_{41}$-b-PEO$_{205}$. The insets in parts c and d are the structure demonstration of PEI and TPE-(EO)$_4$-L2, respectively.

hydrophilicity aroused by replacing the butyl group with the (EO)$_4$ does not influence our conclusion, either. First of all, the main effect of the (EO)$_4$ group is to make the chain foldable. Alkyl chains of even longer length always take a stretched conformation in molecular self-assemblies.[63] Second, the hydrophobic interaction does not contribute to the side-by-side alignment of the coordination polymers since the interchain distance is as far as 9.37 Å, which is much larger than the length scale of hydrophobic interactions.[64] Therefore, it is the molecular stiffness that governs the topology of the self-assembled structures.

The results presented here are universal for most transition metal ions (nickel, zinc, copper, calcium, gold, cobalt, iron, barium, strontium, etc.; see Supporting Information Figures S7−S11). We infer that the bisligand demonstrated here can also be replaced by other properly designed stiff ones. This suggests that controlled organization of stiff polymers into ordered hierarchical polyion assemblies requires the concerted effects of molecular stiffness and charge recognition, each of which is necessary to obtain the precise alignment that we observed in these supramolecular structures. Since ionic interaction is prevalent in nature and artificial systems, the

fabrication of hierarchical structures in polyion assemblies signifies a new protocol to prepare novel controlled structures. In this strategy, the molecular stiffness at atomic level can be amplified into supramolecular stiffness of macroscopic level. In addition, the precise alignment of metal elements in this work may also provide an approach that leads to controlled printing in nanoscale.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials and methods, syntheses, and characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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