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Coordination-Assisted Assembly of 1-D Nanostructured Light-Harvesting Antenna

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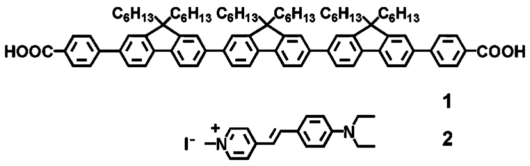
The coordination-directed assembly of metal ions and organic bridging ligands can produce coordination polymers (CPs) with intriguing properties and potential applications in catalysis,[1] gas storage,[2] nonlinear optics,[3] molecular recognition, and separations.[4] Scaling down these materials has recently afforded an exciting new class of highly tailorable nanomaterials known as nanoscale coordination polymers (NCPs).[5−10] Compared with purely inorganic or organic nanomaterials, new or enhanced phenomenon can arise in NCPs by the careful selection of organic building blocks and metal species. However, many properties of nanomaterials depend not only on the size, shape, and composition but also to a large extent on the spatial arrangement of the building blocks with respect to one another within a material. This is particularly true with linear π-conjugated systems, which play crucial roles in electronic devices, as the charge-transport properties of conjugated molecules are strongly influenced by the long-range ordering of the chromophores.[11] Owing to the general lability of the metal coordination geometries, it is very challenging to control such hierarchical assemblies through a preferred packing of the individual molecules to give functional and morphological NCPs. In this Communication, we report the first metal ion coordination-assisted self-assembly of two distinct chromophores into nanoscale supramolecular coordination polymers (NSCPs) with efficient light-harvesting.

Fascination with the architecture and mechanism by which natural photosynthesis operates has been the driving force for research on artificial light-harvesting systems.[12] Research in this direction is further driven by the recent developments in the area of advanced materials, particularly in the design of optoelectronic devices, where energy- and electron-transport processes over nanometer scale spatial dimensions are crucial.[13] Covalently bound, polymeric multichromophoric systems generally offer much greater stability than supramolecular complexes. However, complicated and multistep syntheses limit their availability and applicability. In this work, we demonstrate an efficient coordination-assisted approach to stable 1-D nanostructured light-harvesting antenna that transforms ultraviolet (UV) directly to red radiation.

We initially designed π-conjugated donor **1** and acceptor **2** to investigate the self-assembly and energy transfer between them (Scheme 1). Donor **1** was synthesized by successive Suzuki coupling and characterized by MALDI-TOF, ^{1}H NMR, and IR (Supporting Information). **1** exhibits very strong blue emission with quantum yield (Φ) of about 95% in DMF, while **2** exhibits very weak emission (Φ < 1% in DMF) due to the very efficient intramolecular charge transfer. The UV−vis and PL spectra of **1** and **2** are shown in Figure 1 (left, top). The good overlap between the emission band of **1** and absorption of **2** favors the energy transfer between them. However, when these two compounds mixed in DMF with a ratio of 1:2, it resulted in the quenching of the strong blue emission of **1** and a reduction in the weak emission of **2**, which is indicative of efficient interaction but an absence of fluorescence resonance energy transfer (FRET) between them. No enhancement of FRET was observed even after deprotonation of **1** using base or amine, which was performed in order to facilitate the formation of supramolecular complex with the cation of **2**.

Scheme 1. Molecular Structures of Donor **1** and Acceptor **2**



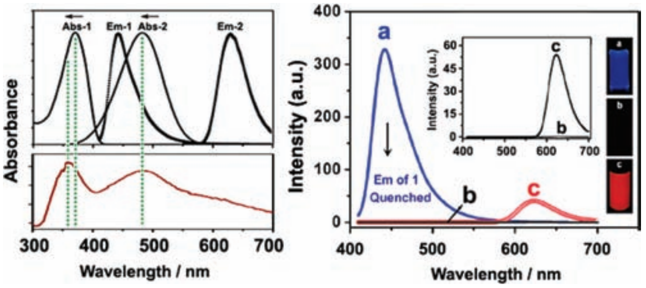


Figure 1. (Left, top) Normalized UV−vis absorption and PL spectra of **1** and **2** in DMF; (left, bottom) UV−vis spectrum of nanowire dispersion. (Right) The emission spectra of **1** (curve a), **1** + **2** (curve b), and **1** + **2** + $Zn(OAc)_2$ (curve c) in DMF. All of the spectra were obtained by excitation at 370 nm. The inset shows fluorescence images under 365-nm UV shine and expansion of the curves b and c.

On the basis of our interest in metal-compound-induced self-assembly of nanostructures,[14] and also inspired by the recent elegant strategy for NCPs,[5−10] we attempted coordination-assisted approach to assemble the chromophores. The two-carboxylate in **1** can link to metal cations after deprotonation, which facilitates the formation of coordination polymers. We selected Zn(II) as metal center here because of its affinity with carboxylate[15] and its nondetrimental nature to fluorescence. With the addition of $Zn(OAc)_2$ into the mixture of **1** and **2**, the solution became turbid, and the red emission was dramatically enhanced (Figure 1, right) by 85 times (curve areas) compared with that before the addition of $Zn(OAc)_2$. It is noted that the excitation wavelength of 370 nm here is the optimal excitation for donor **1** rather than acceptor **2**. In addition, the red emission intensity excited at 370 nm is much stronger than that excited at 480 nm (the optimal excitation for **2**), which is indicative of an efficient light-harvesting antenna effect in the assembled system. TEM and SEM (Figure 2) analysis revealed the formation of nanowires after the addition of $Zn(OAc)_2$. The nanowires are relatively uniform with diameters of 20−30 nm and lengths up to several micrometers. Note that efficient FRET occurs only in nanowires but not in the clear solution before the addition of

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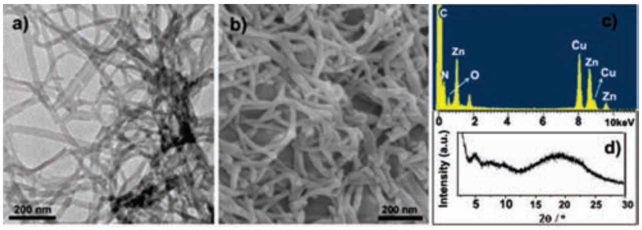
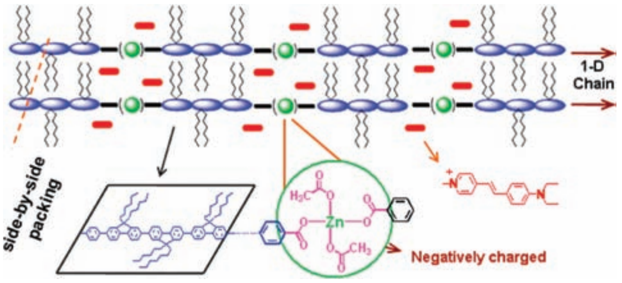


Figure 2. As synthesized NSCPs: (a) TEM image; (b) SEM image; (c) EDX data; (d) XRD data.

$Zn(OAc)_2$; thus, the ordered arrangement of the chromophores in the 1-D nanostructure is crucial for the continuous unidirectional energy transfer.[12]

The energy-dispersive X-ray (EDX) analysis (Figure 2c) of the nanowires confirmed the existence of Zn, O, and N, but the loss of I. This indicated that the counteranion I^- in compound **2** was exchanged by other anion in the self-assembly process. Elemental analysis results confirmed that the ratio between **1**, cation of **2**, and $Zn(OAc)_2$ is 1:2:1. IR spectrum of the nanowire sample revealed that the carboxylate groups adopted the monodentate coordination ($\nu_{as} - \nu_s = 203\ \mathrm{cm}^{-1}$, Figure S5) mode.[15b] UV−vis absorbance of the nanowire dispersion showed that the absorption peaks of **1** and **2** have intensity ratio of 1.03:1. Taking the extinction coefficient (153660 and 70160 ε/ $M^{-1}\ cm^{-1}$ for **1** and **2**, respectively) into account, the molecular ratio between **1** and cation of **2** is roughly 1:2 in the nanowires, which agrees well with elemental analysis results. In addition, the absorption peak of **1** blue-shifted about 12 nm in nanowire (Figure 1, left bottom) compared with that in DMF solution, which is indicative of H-aggregation (face-to-face packing) of molecule **1** via $\pi-\pi$ interactions in the nanowires.[16] This was further supported by the powder X-ray diffraction result (Figure 2d) of the nanowires. The dominant peak at about 4.4 Å ($2\theta = 20°$) originates from the side-by-side packing. The multiple orders of the peaks were also observed with 2θ at 10° and 5°, respectively. On the basis of these experimental results, the mechanism of the self-assembly was proposed and illustrated in Scheme 2. The dicarboxylate **1** was linked by Zn(II) to form 1-D chain. The two acetic carboxylic groups further linked to the Zn atom to saturate the coordination. As a result, the coordination polymeric chain was negatively charged, and the cations of **2** electrostatically attached to the chains. The $\pi-\pi$ interactions and hydrophobic forces perpendicular to the chain direction also play significant roles in the whole process. Therefore, the formation of 1-D coordination polymers mediated by strong metal−ligand bonding is dominant in the self-assembly process, which undergoes side-by-side packing to form arrays of supramolecular polymeric structures.

Scheme 2. Proposed Self-Assembly Mechanism for 1-D NSCPs



In conclusion, we have demonstrated the first example of Zn(II)-coordination-assisted self-assembly of 1-D nanostructured light-harvesting antenna. Efficient FRET is favored in the assembled 1-D nanostructure. Superior to the self-assembly of all-organic nanostructures, the NSCPs can form stable dispersion and are not disassembled by organic solvents, thus affording the possibility of spin-coating for further application. Preliminary experimental results showed that this scheme is also suitable for the self-assembly of other linear oligomers and positively charged species. By rational tuning of the optical properties of the chromophores and proper selection of the metal species, the coordination-assisted assembly strategy is expected to open up new possibilities in the development of new generation of photofunctional materials.

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Supporting Information Available: Synthesis procedures and characterization of **1**, self-assembly mechanism study. This material is available free of charge via the Internet at http://pubs.acs.org.

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