Anisotropic assembly and fluorescence enhancement of conjugated polymer nanostructures

Xiaoju Men | Xiaofeng Fang | Zhihe Liu | Zhe Zhang | Changfeng Wu | Haobin Chen

Abstract
The electronic properties of conjugated polymers depend sensitively on their conformation and morphology. However, control over the morphology of conjugated polymers is highly challenging. Here, we demonstrate a facile approach for assembling conjugated polymers into anisotropic nanostructures. In a water–tetrahydrofuran (H₂O–THF) binary solvent, we prepared ellipsoidal nanoparticles, which can subsequently self-assemble into triangle-ring and rod-like nanostructures in a stepwise manner. The transitions among these morphologies can be rationally regulated by tuning the volume ratio of H₂O to THF and the polymer concentration. The nanostructures show shape-dependent absorption from 383 to 403 nm and significant fluorescence enhancement with a quantum yield up to 70%. The oxetane groups in the polymer side chains and the presence of surfactant in the solvent are decisive for the anisotropic assembly. We further demonstrate multicolor fluorescent nanowires with good structural integrity over doping of dye molecules or other fluorescent polymers. Single nanowires were characterized by high-order super-resolution optical fluctuation imaging, which revealed spatial distribution of the photooxidation sites along single nanowire for easily generating hole polarons.

KEYWORDS
nanostructure, nanowires, fluorescence, self-assembly, semiconducting polymers

1 | INTRODUCTION
Self-assembly of nanoparticles has led to a rapid growth in design and fabrication of next generation functional materials. The colloidal assemblies can have unique ensemble properties for various applications, which are otherwise difficult to achieve with individual nanoparticles. Precise control over the particle
shape and anisotropy is particularly meaningful as it contributes to the development of novel properties, functional versatility, and structural complexities of the colloidal assemblies. Over the past decades, self-assembly behaviors of semiconductor nanocrystals, magnetic nanoparticles, and metal nanorods have yielded a wide range of nanoparticle assemblies and hierarchical structures. On the other hand, self-assembly is also well known for soft materials such as block copolymers, Janus dendrimers, and polypeptide. The soft and flexible polymers can be assembled into micro- and nanostructures including vesicles, ellipsoids, wires, and tubes, which would find potential utility in drug delivery, nanoreactors, tissue engineering, and theranostics.

Creating π-conjugated nanostructures and controlling their self-organization are key issues in the fields of molecular, supermolecular and organic electronics. However, self-assembly is highly challenging for conjugated polymers owing to their rigid hydrophobic polymer backbones. In this regard, previous studies have been mostly focused on polythiophene-based block polymers, which have generated complex structures such as nanostars, nanoparticle bundles, isolated and branched nanofibers. In view of the existence of a large library of conjugated polymers, there is a crucial need to develop nanostructures of different conjugated polymers and further explore their optoelectronic properties.

Conjugated polymer nanoparticles (CPNs) have been shown as promising active materials for biomedicine and optoelectronics. Typical methods for preparing CPNs include reprecipitation of preformed polymer in aqueous solutions and direct synthesis from monomers by heterophane polymerization. As CPNs are amorphous with no preferred shape, most methods generate spherical nanoparticles with very few exceptions. Very recently, Mecking group reported ellipsoidal CPNs that were synthesized by heterophane polymerizations. The ellipsoidal CPNs have sizes in the range of 50–180 nm and uniform shape distributions, which are attractive for building blocks for photonic devices with potentially directional properties. Despite the impressive advances, small CPNs adopt an exclusively spherical morphology because of the high surface to volume ratio and the result of minimizing surface tension. Although physical methods such as lithography and stretching of thin films can generate anisotropic structures, a wet-chemistry approach is more preferable for solution-processed devices and biomedical applications.

Conjugated polymers are one of the most interesting materials with morphology-dependent optoelectronic properties. However, due to the rigid hydrophobic backbone of conjugated polymers, controlling their self-organization is very challenging. Herein, we address this challenge by development of a facile one-step preparation for assembling conjugated polymers into complex nanostructures, including nanospheres, nanoellipsoids, triangle-nanorings, and nanowires. A rapid mixing of a THF solution of conjugated polymer with water results in spherical nanoparticles alone. By adding Triton X-100 in water, we obtained ellipsoidal CPNs, which can subsequently self-assemble into triangle-nanorings and nanowires in a stepwise manner. The nanostructures exhibit shape-dependent absorption spectra and fluorescence quantum yields to 70%. The structures are stable and robust as doping with a portion of small molecules and other polymers do not change the morphology. We find that the oxetane groups in the polymer side chains are decisive for the nanoparticle assembly, which is inspiring to further explore conjugated polymer nanostructures by rational design of their side-chain functional groups.

2 RESULTS AND DISCUSSION

2.1 Design and synthesis of oxetane-functionalized conjugated polymers

Polyfluorenes are well-known blue-emitting conjugated polymers and exhibit great flexibility in tuning their emission color from blue to near-infrared region by the introduction of low-band-gap monomers into the polymer backbone. In particular, poly(9,9-dialkylfluorene) can form disordered glassy phase, partially crystalline β-phase, or liquid crystalline phase depending on the side-chain structures. Oxetanes are commonly reactive functional groups for cationic photopolymerization. In this study, we discover that oxetane as a side chain terminus of polyfluorenes enabled self-assembly of conjugated polymer nanostructures. We use poly(9,9-dioctylfluorene) (PFO) polymer and the same polymer backbone with side-chain oxetane groups (oxe-PFO) for the self-assembly study. The polymer synthesis is described in supporting information (Figures 1(A) and S1). In a typical reprecipitation (Figure 1(B)), a solution of conjugated polymer in THF was rapidly mixed with water under sonication, yielding exclusively spherical nanoparticles for both PFO and oxel-PFO polymers (Figures 2(A) and S2). However, by adding a small amount of Triton X-100 in the water solution (0.25 wt%), the preparation produced different nanostructures such as ellipsoids, triangle-rings, and wires-like morphologies for oxel-PFO polymer (Figures 2(B)–2(D)), while spherical nanoparticles were exclusively obtained for PFO polymer under the same conditions. The 1H NMR spectra of PFO and oxel-PFO are shown in Figure 2(E), which confirmed the presence of oxetane groups (δ = 4.3
and $\delta = 4.4$, two $-\text{CH}_2-$ in the oxetane ring) in oxe-PFO polymer. For oxe-PFO nanoparticles prepared in absence of Triton X-100, only spherical nanoparticles were obtained, revealing the critical role of Triton X-100 in the formation of non-spherical nanostructures. The aspect ratios of the nanostructures were characterized by TEM images. For triangle rings, the aspect ratio was estimated by measuring the perimeters relative to the radius of the side wires. The average aspect ratio of the ellipsoids was estimated to be 1.8, while those for triangle-rings and nanowires were determined to be 8.6 and 19.3, respectively (Figure 2(F)). The peculiar triangle-ring structure and nanowires with such large aspect ratios were first discovered, indicating that highly ordered nanostructures of conjugated polymers are available by self-assembly.

2.2 Control of the morphological evolution

We explore the shape evolution of the nanostructures by varying the preparation conditions (Figure 3). Detailed protocols were provided in Table S1. Starting with a constant water solution (10 ml, 0.25 wt% Triton X-100), we varied the volume and concentration of the polymer in THF solution that was rapidly injected into water under sonication. With a small injection volume (1 ml) and different oxe-PFO concentrations (100–300 $\mu$g/ml), ellipsoidal CPNs were solely obtained (Figures 3(A), 3(D), and 3(G)). However, by using a constant polymer concentration (300 $\mu$g/ml) and increasing the injection volume (2 and 4 ml), morphological evolution from
ellipsoids to triangle rings was clearly observed in the samples (Figures 3(A)–3(C)). Triangle-rings were dominantly prepared when the injection volume was increased to 4 ml (Figure 3(C)). The unique triangle shape was likely generated by self-assembly of three individual ellipsoids via the end-to-end linking. This is somewhat surprising for ellipsoidal CPNs as they have to overcome the strong hydrophobic interactions and $\pi-\pi$ stacking. The end-to-end assembly of inorganic nanowires was also rarely reported because van der Waals or dipole–dipole attraction usually keeps them aligned side-by-side.\textsuperscript{56} Here, it appears that the oxetane group plays a key role in self-assembly into this structure. Because according to our previous work,\textsuperscript{57} oxetane groups can not only reduce the surface zeta potential of CPNs, but themselves can also be connected to each other by covalent coupling.

Two types of nanostructures (i.e., triangle-rings and wires) were simultaneously observed by using 200 $\mu$g/ml oxe-PFO concentration and increasing the injection volume (Figures 3(E) and 3(F)). In Figure 3(F), we found that some short nanowires were composed of 2–4 ellipsoidal CPNs, indicating that the formation also occurred via the end-to-end assembly of the ellipsoidal CPNs. When using a relatively diluted solution (100 $\mu$g/ml), triangle-rings were not observed by varying the injection volume from 1 to 4 ml. Instead, morphology evolution from ellipsoids to short wires, and further to nanowires were clearly observed, confirming the end-to-end assembly of ellipsoidal CPNs in a stepwise manner (Figures 3(G)–3(I)). The triangle rings and nanowires can be reliably prepared in water consisting of Triton X-100 in the range of 0.05–0.5wt%, indicating that moderate variation of the surfactant does not affect the shape of nanostructures.
FIGURE 3  Morphology evolution of conjugated polymer nanostructures by self-assembly in water in presence of 0.25 wt% Triton X-100. (A) Ellipsoids, (B) ellipsoids and triangle-rings, (C) triangle-rings, (D) ellipsoids, (E) ellipsoids, triangle-rings and wires, (F) triangle-rings and wires, (G) ellipsoids, (H) ellipsoids and wires, (I) wires. (J) Hydrodynamic size of different shaped nanoparticles. (K) Morphology diagram of the oxe-PFO self-assemblies in water (10 ml) versus the polymer concentration and the THF volume.
TABLE 1  Summary of particle size and optical properties of different oxe-PFO nanostructures

| Morphology      | Diameter (nm) | Length (nm) | Aspect ratio | Size (nm) | ζ (Mv) | λ_{max}^{abs} (nm) | λ_{max}^{ems} (nm) | ϕ (%) |
|-----------------|--------------|------------|--------------|-----------|--------|-------------------|-------------------|--------|
| Sphere          | 47           | 47         | 1.0          | 50        | -46.5  | 383               | 436               | 26     |
| Ellipsoid       | 48           | 86         | 1.8          | 66        | -40.0  | 397               | 436               | 33     |
| Triangle-ring   | 18           | 155        | 8.6          | 76        | -41.4  | 399               | 436               | 54     |
| Wire            | 26           | 502        | 19.3         | 122       | -48.5  | 403               | 436               | 70     |

*a* Hydrodynamic size.

*b* Zeta potential.

*c* Absorption maximum.

*d* Fluorescence maximum.

*e* Quantum yield.

2.3 Characterization of conjugated polymer nanostructures

Dynamic light scattering (DLS) confirmed the distinctive self-assembly of oxe-PFO nanostructures. The DLS results of oxe-PFO samples in aqueous solutions varied from 50 to 122 nm (Figure S3), accompanied by the shape evolution from nanospheres to nanowires. In contrast, the CPNs of PFO polymer from the same preparations remained unchanged, indicating that the side-chain oxetane groups indeed play an indispensable role in the nanoparticle assembly. The apparent increase of hydrodynamic sizes clearly reveal the self-assembly does occur in aqueous solution (Figure 3(J)). The nanostructures show a good colloidal stability. No obvious changes in size and morphology were observed for 7 days (Figure S4), indicative of the long term colloidal stability of both triangle-nanorings and nanowires at room temperature. Figure 3(K) showed the morphology diagram with respect to the concentration and volume of the polymer in THF solution in the preparation. As clearly indicated, ellipsoidal CPNs were exclusively formed with low injection volume (1 ml) and different concentration (100–300 μg/ml). By increasing the injection volume, the ellipsoidal CPNs tends to self-assemble into triangle-rings at a high concentration (300 μg/ml), nanowires at a low concentration (100 μg/ml), and mixed structures at a mediate concentration (200 μg/ml).

The anisotropic nanostructures show distinct optical properties as compared with spherical CPNs. The absorption and fluorescence of conjugated polymers are largely dependent on their conformation. For a comparison, four samples of PFO polymer were prepared by using the same conditions to the four types of oxe-PFO nanostructures. As shown in Figures 4(A) and 4(B), the four PFO samples show very similar absorption and fluorescence spectra. However, the absorption of oxe-PFO nanostructures was apparently red-shifted from 383 to 403 nm (Figure 4(C)), as the morphology changes from nanospheres to nanowires. The red-shifted absorption in the triangle-rings and nanowires are consistent with the overall increase in the conjugation length, as compared with the spherical nanoparticles that consist of much bending and kinking of the polymer backbone. In fact, the optical properties of conjugated polymers changed slightly after being prepared into nanoparticles, such as hypochromic shift in absorption and reduced in fluorescent quantum yields as the conjugated polymer changes from the initial extended state to the condensed state within the nanoparticle. 58,59 Compared with spherical structures, conjugated polymers are apparently more likely to be in an extended state in anisotropic nanostructures, thus exhibiting higher fluorescence quantum efficiencies. Moreover, the nanowires show the highest fluorescence quantum yield (~70%) among these nanostructures (Figure 4(D)), most likely due to the well-organization of the polymer backbones in the nanowires which consist of much less defects as compared with other nanostructures. Moreover, the nanowires show the highest fluorescence quantum yield (~70%) among these nanostructures (Figure 4(D)), most likely due to the well-organization of the polymer backbones in the nanowires which consist of much less defects as compared with spherical CPNs. Table 1 summarized the shape, particle size, and optical properties of the self-assembled oxe-PFO nanostructures. Particularly, the distinctive absorption profiles provide a facile spectroscopic approach to identify the respective morphology as compared with the expensive and time-consuming TEM imaging.

2.4 Dye-doped and blended multicolor conjugated polymer nanostructures

We further explore encapsulation of hydrophobic fluorescent dyes and blending of other conjugated polymers in the nanostructures. A fluorescent dye (Coumarin 6, 0.5 wt%) or conjugated polymers (oxe-PF5DTBT, oxe-PF10BT, 10 wt%) were mixed with oxe-PFO in the precursor
solutions for sample preparation, respectively. Absorption spectroscopy showed that the doped samples exhibit morphology-dependent red-shifted absorption peaks as those observed for undoped nanostructures (Figure S5). TEM images confirmed the formation of different nanostructures in the doped samples (Figure S6), indicating that encapsulation of small amount of fluorescent dye and other conjugated polymers do not affect the anisotropic assembly. It is worth noting that the fluorescence properties were significantly modified because of the efficient Förster resonance energy transfer (FRET). As shown in Figure 4(E), although the absorption profiles of the dye or polymer-doped nanowires were similar to that of the pure nanowires, the fluorescence exhibited the characteristic emissions from the dopant molecules (Figure 4(F)), indicating the great flexibility for tuning their optical properties.

2.5 Single-particle fluorescence imaging and high-order SOFI analysis

Finally, we characterize the nanostructures by single-particle fluorescence imaging. As shown in Figures 5(A)–5(D), fluorescence brightness of individual nanoparticles was clearly enhanced, as the morphology evolved from spheres, ellipsoids, triangle-rings to wires. Particularly, one dimensional fluorescence patterns were exclusively observed for nanowires, while the other three samples show diffraction-limited spots. We have recently demonstrated super-resolution optical fluctuation imaging (SOFI) by using small photoblinking CPNs. In single-particle imaging, we observed concrete fluorescence fluctuations from these nanostructures. By high-order SOFI analysis, individual nanowires were clearly resolved with enhanced spatial resolution (Figure 5(E)–5(L)).
radial size of the nanowire by conventional TIRF imaging was \(~472\) nm, while the spatial resolution was improved to \(~74\) nm by 8th-order SOFI analysis (Figures 5(M) and 5(N)), indicating the potential to characterize the nanowire structure by optical microscope. Moreover, Figure 5(L) showed that the single nanowire was discontinued and appeared as isolated spots. As high-order SOFI requires continuous and robust fluorescence fluctuation from the object, the isolated spots indicated that these sites exhibited more pronounced photoblinking than the lost parts along the nanowire. There is evidence that photoblinking in conjugated polymers is induced by hole polarons. Therefore, high-order SOFI reveals spatial distribution of the photooxidation sites that easily generate hole polarons. This information is valuable for using conjugated polymers in molecular and organic electronics.
CONCLUSION

In summary, a facile approach was developed for self-assembly of conjugated polymers into complex nanostructures. The preparation in a binary solvent yielded ellipsoidal nanoparticles, which can subsequently self-assemble into triangle nanorings and nanowires in a stepwise manner. The oxetane groups in the polymer side chains and the presence of surfactant in the solvent are decisive for the anisotropic assembly. The resulting nanostructures show robust structural integrity over doping of dye molecules or other fluorescent polymers. This study represents a critical step toward fine control of the structure and organization of conjugated polymers. Further exploration of their properties and applications is underway. Self-assembly of conjugated polymers is a significant advance for their optoelectronic applications and we believe this approach can be extended to a broader scope of conjugated polymers.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

ORCID

Haobin Chen https://orcid.org/0000-0003-3111-9824

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