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Communication

Supermolecular Self Assembly of AIE-active Nanoprobes: Fabrication and Bioimaging Applications

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Luminescent polymeric nanoparticles (LPNs) have attracted great attention in the field of biosensor, bioimaging and therapy. In this work, we reported that novel aggregation induced emission dye based LPNs can be facilely and efficiently fabricated through supermolecular self assembly. TPE-Ad/β-CD LPNs possess strong luminescent intensity, uniform size, high water dispersibility and desirable biocompatibility, making them promising candidates for bioimaging applications.

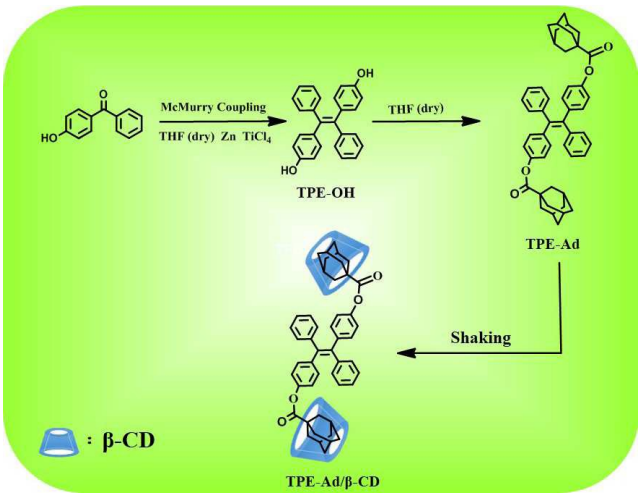
There has been a growing research interest to fabricate fluorescent multifunctional nanoparticles for various biomedical applications over the past few decades.[1-3] As compared with small organic dyes, these luminescent nanoparticles showed some advantages for biomedical applications, including better chemical stability, enhanced photostability and multifunctional potential.[4] A large number of luminescent nanoparticles with different compositions, surface coating and luminescent properties have been developed.[4-9] Among them, luminescent polymeric nanoparticles (LPNs) from self assembly of organic dyes contained amphiphilic polymers have attracted increasing attention because of their facile structure modification, admirable processibility, high sensitivity, faster response time and better anti-photobleaching capability.[4] Whereas, most of LPNs show intense photoluminescence in their diluted solution but often quench their emission in high concentration or in solid state. This phenomenon may be attributed to the strong intramolecular interaction which is referred to aggregation caused quenching (ACQ) effect. This will limit these LPNs for practical applications because it is difficult for us to fabricate LPNs with high luminescent intensity using conventional organic dyes . To tackle this problem, Tang et al. have found an abnormal phenomenon that was named as aggregation-induced emission (AIE).[10] Different from conventional organic dyes, dyes with AIE properties will emit enhanced luminescence in their high concentration solution or solid state. This will open up an effective route for overcoming the ACQ effect of conventional organic dyes, and provide elegant solution for fabrication of ultrabright LPNs. Up to now, a large variety of dyes with AIE-active properties were discovered.[11-14]

As a representative member of AIE-active dyes, tetraphenylethene (TPE) had attracted abundant attention in the fields of organic light emitting devices, chemosensors and biological imaging by taking advantage of high emission efficiency, facile synthesis and easy to functionalization.[15-19] Especially, the biological imaging application of these AIE active LPNs have been intensively investigated recently.[20] Despite of these impressive advances, design and synthesis of novel AIE-active LPNs with remarkable optical properties, superb water dispersibility and excellent biocompatibility is still highly desirable.

As a burgeoning interdisciplinary subject, supermolecular chemistry has gained considerable attention in recent years in the field of molecular recognition and the formation of ordered nanostructure, supermolecular hydrogels and many other functional materials by self assembly.[21-24] Supermolecular polymers with typical dynamic polymeric structure, can be formed by orthogonal assembly of monomers through supermolecular interactions at chain ends such as H-bonding, metal–ligand bonding, π-stacking and host–guest interaction.[21] For example, β cyclodextrin (β-CD) can form an exact 1:1 inclusion complex with adamantane via host-guest interactions. And then, stimuli-responsive polymeric materials obtained via supermolecular chemistry had attracted significant attention over the past years.[25-31] To the best of our knowledge, however, fabrication of AIE dyes based LPNs via supermolecular self assembly has seldom been reported.[32-35] And only very few reports have demonstrated the biomedical applications of these supermolecular self assemblies thus far.

In this contribution, the adamantane terminated TPE (TPE-Ad) was facilely obtained via esterification reaction between the hydroxyl group contained TPE (TPE-OH) and adamantane chloride. And then β-CD was mixed with TPE-Ad to form the final product (TPE-Ad/β-CD LPNs) (**Scheme 1**). Due to their amphiphilic properties, TPE-Ad/β-CD LPNs can self assemble into high luminescent LPNs with excellent water dispersibility and strong luminescent intensity. In which the hydrophobic TPE-Ad was aggregated in the interior as the core while the hydrophilic β-CD was as the shell. To evaluate the biomedical application potential, biocompatibility as well as cell uptake behavior of TPE-Ad/β-CD LPNs were also determined. As compared with previous strategies, the fabrication method developed in this work is rather simple, effective and universal. On the other hand, a number of AIE active LPNs with different function could also be fabricated when using different β-CD

derivatives through supermolecular self assembly. And these AIE active LPNs should be of significant impacts on the development of AIE dyes based materials



Scheme 1. The schematic diagram for preparation of AIE-active LPNs (TPE-Ad/β-CD LPNs) through host-guest interaction. The reaction can occur under room temperature within 1 h, and not involve in inert gas protection and toxic metal catalysts.

The detailed information for preparation of TPE-Ad/β-CD LPNs was described below. First, TPE-OH and 1-adamantoyl chloride were mixed at room temperature for 20 min using anhydrous tetrahydrofuran (THF) as reaction solution. Then, β-CD and TPE-Ad was mixed in water for 30 s. Finally, TPE-Ad/β-CD LPNs were obtained by centrifugation. The successful formation of fluorescence nanoparticles with AIE-active properties was confirmed by ^{1}H NMR measurement. As shown in **Fig. S1**, the results can be analyzed as follows. The proton peaks at 5.19 ppm can be ascribed to the -OH existed in TPE-OH. And the signal between 1-5 ppm in the ^{1}H NMR spectrum of TPE-OH should be attributed to the signal of H_2O in the sample. As compared with the spectrum of TPE-OH, no peaks could be found that were belonged to the free hydroxyl groups. And the new emergence of proton peaks in the presence of δ = 1.72, 1.93 and 2.03 ppm, that belonged to the adamantanine structure of TPE-Ad was observed. These results indicated that 1-Adamantoyl chloride was conjugated with TPE-OH through esterification reaction successfully. After an equal molar quantity of β-CD was mixed with TPE-Ad. The characteristic proton peaks at 4.98, 3.79, 3.56 and 3.49 ppm were emerged, indicating that β-CD was encapsulated with Ad to assemble into supermolecular complexes. Therefore, the ^{1}H NMR study provided an important insight into the formation of TPE-Ad/β-CD via esterification and host-guest interaction.

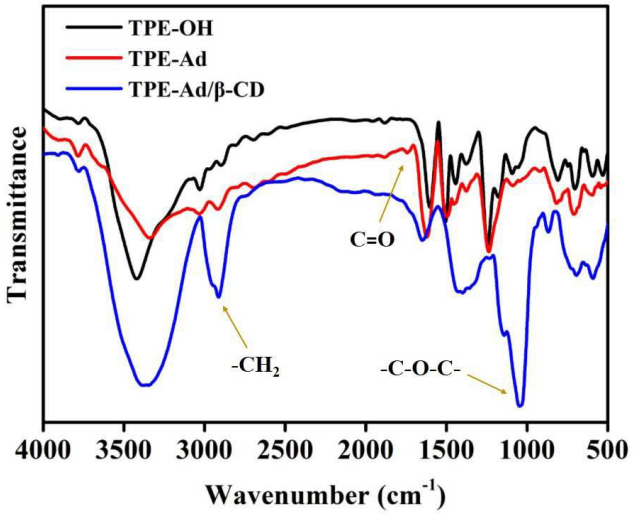


Fig. 1 FT-IR spectra of TPE-OH, TPE-Ad and TPE-Ad/β-CD, which provided significant evidence on successful self assembly into fluorescence nanoparticles with AIE active properties.

Fourier transform infrared spectroscopy (FT-IR) measurement provided significant further evidence that the successful formation of TPE-Ad/β-CD through host-guest interaction. And the characteristic peaks were clearly observed from **Fig. 1**. For example, the characteristic peaks appeared between 1602 and 1379 cm^{-1}, that can be defined as the stretching vibration of aromatic rings and flexural vibration of –OH, respectively. However, a distinct peak at 1722 cm^{-1} attributed to the stretching vibration of C=O can be observed in TPE-Ad. These results suggested that 1-Adamantoyl chloride was connected to TPE-OH successfully through esterification reaction. After Ad was employed, the hydrophobic TPE-Ad could interact with β-CD through host-guest interaction. The successful formation of TPE-Ad/β-CD can also be evidenced by FT-IR spectra. For example, intense stretching vibration of -OH located at 3410 cm^{-1} was obtained. Furthermore, another two strong characteristic peaks at 2922 and 1034 cm^{-1} were belonged to -CH- and -C-O-C. These results demonstrated that supermolecular complexes were generated triumphantly.

Due to amphipathic properties, the inclusion complexes with Ad can self assemble into core-shell microspheres in aqueous solution. Among them, the hydrophilic β-CD was diffused into water and hydrophobic AIE dyes were encapsulated in the core. Hence, the obtained fluorescence nanoparticles exhibited superb water dispersibility. Initially, the successfully assembled into nanoparticles were verified by the photoimages. As displayed in inset of **Fig. 2**, the particles were completely dispersed in aqueous. Furthermore, no obvious precipitation was observed after shelved for several days. Because of the aggregation of the supermolecular copolymers, the nanoparticles showed intensity blue-green fluorescence in aqueous solutions after irradiated by UV-lamp at 365 nm. After that, the photophysical properties of fluorescent nanoparticles were further investigated. According to the PL spectra, the maximum emission wavelength located at about 450 nm, while the excitation spectrum exhibited a broad excitation scope from 260 to 330 nm. Fluorescence quantum yield was another indispensable fluorescent property. The fluorescence quantum yield of polymeric supermolecular

nanoparticles were reached up to 26.5% using quinine sulfate as the standard. High quantum yield of TPE-Ad/β-CD LPNs make them possess high expectation for biolabeling or cell imaging. Furthermore, the photostability of TPE-Ad/β-CD LPNs was also evaluated using UV lamp continuous irradiation (**Fig. S2**). We demonstrated that almost no fluorescent intensity decrease was found after 30 min irradiation. These remarkable photophysical properties of TPE-Ad/β-CD LPNs are very important for their biomedical applications.

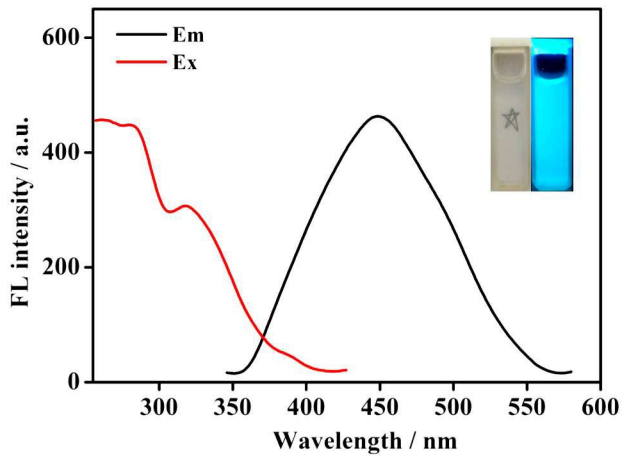


Fig. 2 Fluorescence excitation and emission spectra of TPE-Ad/β-CD LPNs. Inset is water dispersion of TPE-Ad/β-CD LPNs (left Cuvette) the fluorescent image of polymeric AIE nanoparticles taken at 365 nm UV light.

The size and morphology of TPE-Ad/β-CD LPNs were characterized by TEM. As displayed in **Fig. S3**, the spherical microspheres with uniform particle size ranged from 100-200 nm were observed. The size distribution of supermolecular nanoparticles was calculated on the basis of TEM images. Results suggested that the size distribution of TPE-Ad/β-CD LPNs is 173 ± 15 nm. According to the TEM images, we could draw a conclusion that β-CD and TPE-Ad could self assemble into nanoparticles successfully in aqueous solution. Because β-CD can form inclusion complexes with TPE-Ad via host-guest interaction, thus obtained AIE active LPNs contained hydrophobic AIE dyes and hydrophilic β-CD can assemble into microspheres in aqueous solution. The self assembly of these amphiphilic supermolecular complexes can form water dispersible and ultrabright luminescent LPNs for the aggregation of AIE dyes. To explore their potential biomedical applications, the biocompatibility of TPE-Ad/β-CD LPNs should be first determined. After supermolecular modification, the compatibility of TPE-Ad/β-CD LPNs was expected to be significantly enhanced. In this case, the biocompatibility of TPE-Ad/β-CD LPNs to A431 cells was examined to prior to cellular imaging applications. In this study, CCK-8 assay was employed to evaluate the cell viability of the A431 cells after incubated with different concentrations of TPE-Ad/β-CD LPNs for both 8 h and 24 h.[36-39] As displayed in **Fig. S4**, the cell viability was almost unchanged both for 8 h or 24 h. Even the concentration was up to 120 μg mL^{-1}, the cell viability was remain greater than 95%, which give a powerful evidence of the supermolecular nanoparticles were biocompatible enough to accomplish cellular imaging and other biomedical applications.

It can be expected that TPE-Ad/β-CD LPNs were desirable candidates for fluorescence labeling and cell imaging by taking advantage of their excellent fluorescence properties, high water dispersibility and superb biocompatibility. The cell uptake behavior of TPE-Ad/β-CD LPNs was investigated by Confocal Laser Scanning Microscope (CLSM) observation to evaluate the potential biomedical applications.[40] As shown in **Fig. 3**, intense blue-green fluorescent signal could be observed from the A431 cells after incubated with 20 μg mL^{-1} of AIE dye based nanoparticles for 3 h. Moreover, many areas with weak fluorescent intensity were found in the cells, which possibly belonged to the location of cell nucleus (**Fig. 3A**). These results indicated that supermolecular nanoparticles could be uptaken by cells and mostly distributed in cytoplasm. More importantly, bright-field images demonstrated that cells still kept their natural morphology (**Fig. 3B**). Because no targeting agents were immobilized on the surface of TPE-Ad/β-CD LPNs, these LPNs should be internalized by cells through endocytosis. All the phenomenon manifested TPE-Ad/β-CD LPNs had superb dyeing effects and biocompatibility, which made them promising in biomedical applications. The fabrication and biomedical applications of AIE-active polymeric nanoprobes have attracted great research attention in recent years.[41-49] Various fabrication strategies such as surfactant-assissted self assembly, convalent conjugation, controlled living polymerization and ring-opening reaction etc have been developed.[8, 50-56] These AIE active nanoprobes could not only possess excellent water dispersibility, but also remarkable optical properties for bioimaging. However, the fabrication of AIE active polymeric nanoprobes through supermolecular chemistry has been rarely reported. In this work, we developed a rather simple and effective procedure for fabrication of AIE active nanoprobes through combination of esterification reaction and supermolecular chemistry. This procedure can be accomplished under air atmosphere, room temperature and absent of toxic agents within 1 h. More importantly, many other functional components can also be introduced into the AIE active LPNs when different β-CD derivatives were adopted. Therefore, the supermolecular strategy described in this work should be a novel route for fabrication of AIE active polymeric nanoprobes, which are expected usefulness for different biomedical applications.

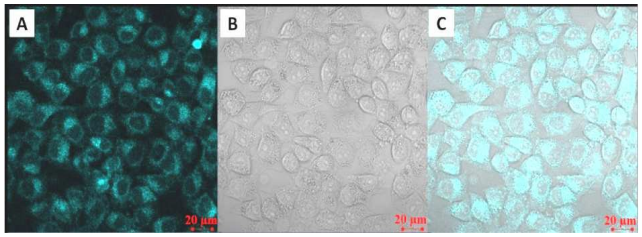


Fig. 3 CLSM images of A431 cells which were incubated with 20 μg mL^{-1} of TPE-Ad/β-CD LPNs for 3 h. (A) excited with 405 nm laser, (B) bright field and (C) merge image of A and B.

In summary, for the sake of creation of AIE-active supermolecular luminescent nanoparticles with favorable biocompatibility, superb water dispersity and fluorescence properties, a facile and effective synthetic protocol was proposed based on self assembly of TPE-Ad with β-CD. By virtue of series of characterization techniques, it can draw a conclusion that the

AIE-active LPNs were obtained through esterification and host guest interaction. Compared with other reported synthetic strategies, this method provides simple and facile treatment (just stirring or shaking at room temperature), rapid response time (< 30 s) and high yield. Notably, according to the biocompatibility evaluation and cell imaging results, the supermolecular nanoparticles exhibited capability for other bio-applications for its low cytotoxicity and intense luminescence. More importantly, this methods could provide a high-efficiency platform for preparation diverse AIE active luminescent nanoparticles via design various Ad-capped structure and using different β-CD derivatives. Hence, this study could open up a new avenue for development of high potential nanoparticles for various biomedical applications.

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Notes

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† Electronic Supplementary Information (ESI) available: [^{1}H NMR spectra TEM images and cell viability results of TPE-Ad/β-CD LPNs *et al* were provided in supplementary information]. See DOI: 10.1039/b000000x/

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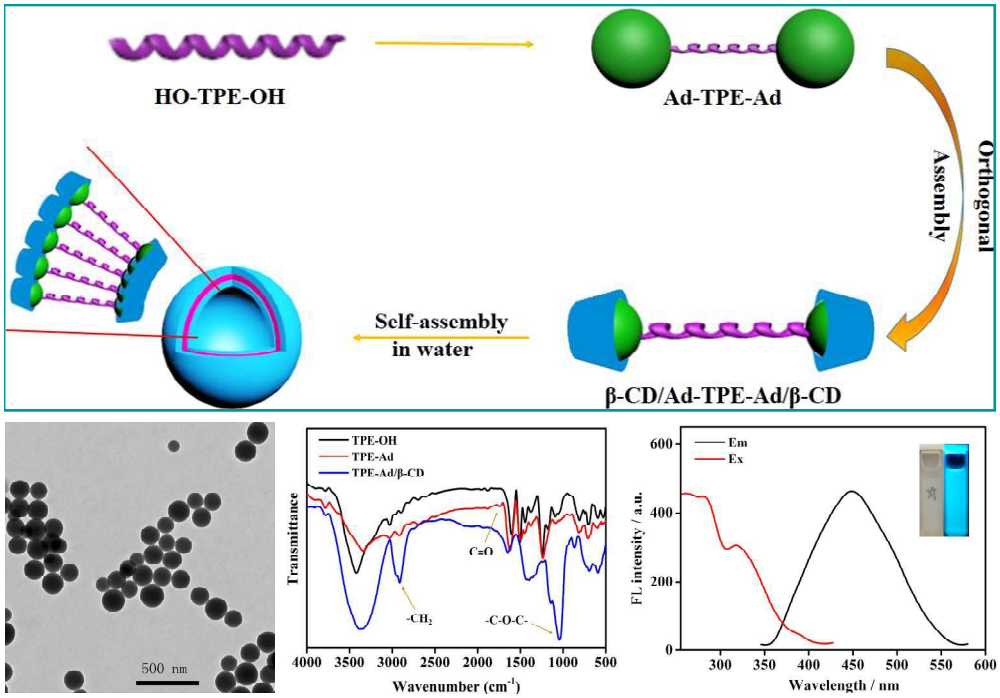

The AIE active luminescent polymeric nanoprobes were fabricated for the first time via formation of supermolecular complexes between the adamantane capped AIE dye and β cyclodextrin