Novel High-Performance Polymeric PL Nanofibers Containing Aggregation-Induced Emission (AIE)-active Cyanotriphenylamine Luminogens

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Introduction

Recent studies have depicted that the heteroatom-containing luminogens, such as cyano (CN) substituents and tripheylamine (TPA) derivatives, possess an excellent attribute in light emission. While these luminogens are almost non-fluorescent in solutions but fluoresce strongly in the aggregate state, which is attributed to the restriction of intramolecular rotation in the condensed phase.[1] Such a novel phenomenon, named "aggregation-induced emission (AIE)", is exactly the opposite of the ACQ effect observed in most conventional chromophores, and paves a new avenue for the design and synthesis of efficient solid-state emitters.[2]

Our molecular design strategy is based on the embedment of CN-TPA luminogen into the high-performance polymers (*e.g.*, polyimides and polyamides; HPPs), which have been widely used in gas separation membranes, composites, fuel cells, optical, electrochromic, and polymer memory applications due to their excellent thermal stability, high mechanical strength, low flammability, good chemical and radiation resistance, and good electronic properties.[3] In this article, we therefore synthesized two HPPs from CN-TPA containing diamine monomer. The incorporation of CN-TPA luminogen was expected to enhance AIE effect for developing efficient solid-state emitters. Furthermore, these light-emitting electrospun (ES) nanofibers were also prepared, investigated, and demonstrated the potential as high-performance efficient luminescent materials for optoelectronic applications.

Results and Discussion

The preparation of the polyimide **CN-PI** was carried out by a one-pot, high-temperature solution polycondensation method. In this procedure, the dianhydride **HPMDA** and the diamine **1** were polymerized in *N,N*-dimethylacetamide (DMAc) and γ-butyrolactone (GBL) at 180 °C in the presence of isoquinoline as catalyst.[4] On the other hand, polyamide **CN-PA** was synthesized from the diamine **1** and dicarboxylic acid **CHDA** according to the phosphorylation technique using triphenyl phosphite and pyridine as condensing agents described by Yamazaki[5] (Scheme 1). As shown in Scheme 1 and Figure 1a, the polymers could be solution cast into flexible, transparent, and tough films with pale yellowish color.

The optical properties of the polymers were investigated by UV-vis and photoluminescence (PL) spectroscopy. In solid film state, the obviously high PL emission could be observed (as shown in Figure 1b). Moreover, the PL quantum yields of the films are as high as 65 % and 46 % for polyimide **CN-PI** and polyamide **CN-PA**, respectively, estimated by integrating sphere, which are greatly enhanced compared with that of the solution state.

The polymeric ES fibers of AIE-active **CN-PI** and **CN-PA** were further fabricated to investigate and confirm the phenomenon of high quantum yield in solid film state. The FE-SEM images of these two ES fibers having smooth fiber-like structure without beads formation were shown in Figure 2. Interestingly, the ES fibers of **CN-PI** and **CN-PA** exhibited notable PL emission with enhanced quantum yield up to 70 % when compared with their solid films. The further enhancement of PL quantum yields of the AIE luminogen in fiber state implying the judicious combination of the AIE feature and ES nanofiber fabrication is an essential approaching and could be potentially used for the application of optoelectronic materials.

Conclusions

Two AIE-active high-performance polymers and their ES nanofibers were readily synthesized and prepared. While they are fluorescent in solutions, the stronger luminescence is induced when aggregated in poor solvents or fabricated into solid films with high PL quantum yields up to 65 %, demonstrating their aggregation-induced emission (AIE) feature. Moreover, the ES nanofibers revealed higher PL quantum yield up to 70 %, implying the great potential for optoelectronic applications.

Reference

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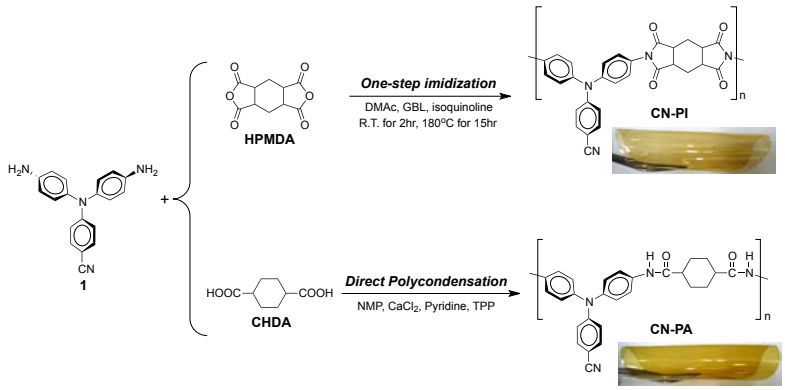

Scheme 1. Synthesis of CN-TPA based high-performance polymers. The photograph shows appearance of the flexible films (thickness: ~60μm).

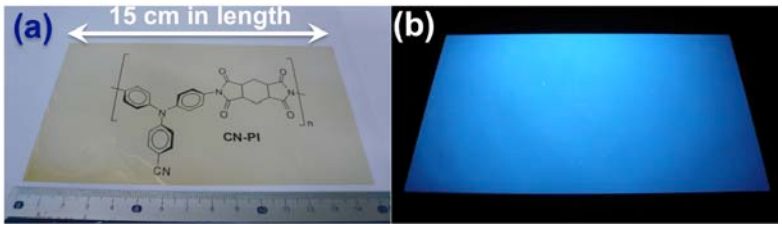

Figure 1. (a) The photograph of self-standing and flexible **CN-PI** film with *ca.* 35 μm thickness. (b) The PL photograph of **CN-PI** was taken under illumination of a 365 nm UV light.

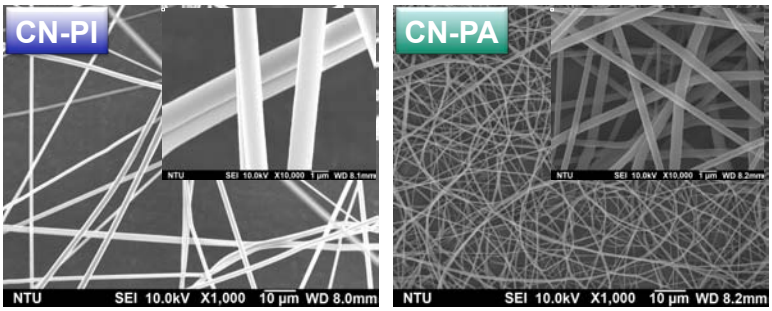

Figure 2. SEM images of ES nanofibers of **CN-PI** (left) and **CN-PA** (right).