

Novel high-efficiency PL polyimide nanofiber containing aggregation-induced emission (AIE)-active cyanotriphenylamine luminogen†

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Two aggregation-induced emission (AIE)-active high-performance polymers and their electrospun (ES) nanofibers were synthesized and prepared. Strong luminescence is induced when they are aggregated in poor solvents or fabricated into solid films and this is further enhanced when they are prepared as ES nanofibers, demonstrating their AIE feature and great potential for opto-electronic applications.

Recent studies have shown that heteroatom-containing luminogens, such as cyano substituents and triphenylamine (TPA) derivatives, possess excellent light emission attributes. While these luminogens are almost non-fluorescent in solution they fluoresce strongly in the aggregated 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 aggregation-caused quenching (ACQ)² effect observed in most conventional chromophores,³ and paves a new way in the design and synthesis of efficient solid-state emitters.⁴

Because of its structural simplicity and high molar polarization, the cyano (CN) group has been frequently utilized as a functional unit in the design of advanced optoelectronic materials.⁵ As a result, a great number of AIE luminogens containing cyano groups have been developed due to the internal steric hindrance arising from the cyano group.⁶ In dilute solution, the twisted geometry allows intramolecular rotation, which annihilates its excitons non-radiatively. In crystals, such molecular motions are restricted. The C–H...N hydrogen bonds formed between the cyano groups of one molecule and the hydrogen atoms of an adjacent molecule thus rigidify the molecules and intensify their light emission.⁷

In addition, TPA derivatives also are well known as their photo- and electroactive properties show potential for opto-electronic applications, such as photoconductors,^{8a} hole-transporters,^{8b} light-emitters,^{8c} electrochromic,^{8d–f} and memory devices.^{8g–i} Although TPA itself is not AIE active, its propeller-like structure and electron-donating characteristics make it a useful building block for the construction of AIE luminogens, and the emission colors can be tuned through judicious combinations of the TPA units with various electron-accepting moieties. This is demonstrated by AIE luminogens containing donor–acceptor pairs, which can emit green or red light due to the different extents of push–pull interactions.⁹

Recently, electrospinning (ES) has emerged as a new technique to produce various functional nanofibers because of the advantages of low cost, flexible operation conditions, and an efficient continuous production process. The ES procedure probably results in smaller phase separated domains than those of the spin-coated films.¹⁰ Furthermore, the resulting nanofibers may produce a more extended chain conformation along the fiber axis, thus enhancing the orientation and alignment in comparison with the spin-coated films. As reported in the literature, ES fibers showed different photoluminescence (PL) characteristics to the corresponding thin films with much higher PL efficiency.¹¹

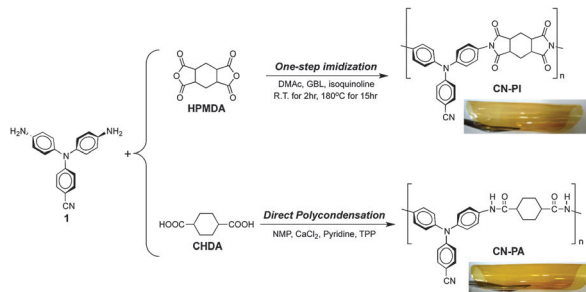
Based on this concept, our molecular design strategy is based on the embedding of a CN-TPA luminogen into high-performance polymers, which have been widely used in gas separation membranes, composites, fuel cells, optical, electrochromic, and polymer memory applications due to their excellent thermal stability, high mechanical strength, low flammability, good chemical and radiation resistance, and good electronic properties.¹² In this communication, we therefore synthesized two high-performance polymers from CN-TPA containing diamine monomer (Scheme 1).

The model compounds **M-PI** and **M-PA** were readily synthesized by condensation and the detailed synthetic routes and characterization are described in the ESI† (Chart 1, ESI†).

The polyimide **CN-PI** and polyamide **CN-PA** were prepared by a one-pot high-temperature solution polycondensation method¹³

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† Electronic supplementary information (ESI) available: Experimental section. Tables: inherent viscosity, molecular weights, solubility behavior, thermal, and photophysical properties. Figures: NMR, IR, and PL behavior of model compounds, NMR, IR, TGA, and TMA traces of polymers. See DOI: 10.1039/c2cc37857d



Scheme 1 Synthesis of CN-TPA based high-performance polymers. The photographs show the appearance of the flexible films (thickness: $\sim 60\ \mu\text{m}$).

and phosphorylation polycondensation,¹⁴ respectively (Scheme 1). The detailed synthetic procedures and basic properties are described in the ESI†

The optical properties of the polymers were investigated and summarized in Table 1. These soluble polymers exhibited maximum UV-vis absorption bands at around 310–313 and 313–316 nm in *N*-methyl-2-pyrrolidinone (NMP) solutions and solid film states, respectively, due to the π - π^* transitions of the aromatic TPA chromophores. Fig. 1 depicts the UV-vis absorption and PL behavior of these resulting CN-TPA-based polymers. In the case of NMP solutions (conc.: $10^{-5}\ \text{mol L}^{-1}$), polyimide **CN-PI** and polyamide **CN-PA** exhibited blue and green PL emission with a PL quantum yield of 34 and 14% at the maximum peaks of 443 and 497 nm, respectively. In the solid film state, the obviously high PL emission could be observed (as shown in Fig. S6, ESI†), and the polymers both showed a hypsochromic shift in PL emission relative to those of the solutions. Moreover, the PL quantum yields of the films are as high as 65% and 46% for **CN-PI** and **CN-PA**, respectively, which are greatly enhanced compared with those of the solution state. The phenomenon could be attributed to the solvatochromism and AIE effect resulting from the introduction of the CN-TPA luminogens.

In order to demonstrate the solvatochromic behavior, the optical absorption and PL of model compounds **M-PI** and **M-PA** were investigated in solvents (conc.: $10^{-5}\ \text{mol L}^{-1}$) with different polarity. Fig. S7 and S8 (ESI†) exhibit the normalized PL spectra of **M-PA** and **M-PI** in various solvents, together with fluorescence images of their dilute solutions, respectively, and the absorption and PL emission data are summarized in Tables S4 and S5 (ESI†). These results clearly indicate the PL emission spectra show strong solvent-polarity dependence, revealing a dominant broad emission band that undergoes remarkable

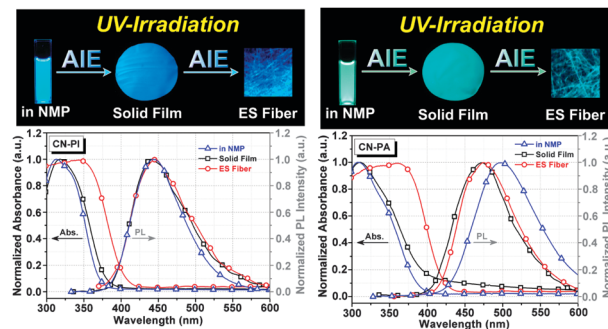


Fig. 1 Normalized absorbance and photoluminescence (PL) spectra of polyimide **CN-PI** (left) and polyamide **CN-PA** (right) in solution, solid film, and ES fiber states. Photographs were taken under illumination of a 365 nm UV light.

bathochromic shift with an increase of the solvent polarity. For the amide-type model compound **M-PA**, the emission color changes from violet-blue in cyclohexane (CH) ($\lambda_{\text{em}} = 415\ \text{nm}$) to yellowish-green in DMSO ($\lambda_{\text{em}} = 508\ \text{nm}$).

It is reasonable that the model compounds showed higher PL quantum yields as compared with the corresponding polymers (Table 1). The solvatochromism could be attributed to the fast interconversion process from the emissive local excited state to the low emissive state. In addition, they exhibit much stronger emission in nonpolar solvents or in the solid state due to the restricted molecular transitions.^{6,15}

To further confirm the AIE attribution, PL spectra of the **CN-PA** NMP–water diluted mixtures were studied with different water fractions, and the results are summarized in Table S6 (ESI†). Since the polyamide was insoluble in water and soluble in NMP, increasing the water fraction in the mixed solvent could change their existing forms from a solution in pure NMP to aggregated luminogen particles in the mixtures, which will result in changes in their UV and PL spectra. The PL spectra and images of $10\ \mu\text{M}$ of **CN-PA** in NMP–water mixtures with different water contents are shown in Fig. 2. Polyamide **CN-PA** in pure NMP exhibited green PL emission with a maximum peak at 497 nm, while the PL emission was blue-shifted and the intensity enhanced with increasing water fraction.

These results demonstrate that the CN-TPA unit is indeed AIE-active.

FE-SEM images of these two ES fibers having smooth fiber-like structure without bead formation are shown in Fig. 3. The absorption spectra of the ES fibers showed a bathochromic shift to their solution and film states, suggesting the higher orientation and alignment of the polymer chains in the fiber state.

Table 1 Optical properties of polymers

Index	NMP ($10\ \mu\text{M}$) solution (nm)			Solid film (nm)			ES fiber (nm)		
	λ_{abs}	λ_{em}^a	$\Phi_{\text{PL}} (\%)^b$	λ_{abs}	λ_{em}^a	$\Phi_{\text{PL}} (\%)^c$	λ_{abs}	λ_{em}^a	$\Phi_{\text{PL}} (\%)^c$
CN-PI	313	443	34	316	440	65	350	446	70
CN-PA	310	497	14	313	472	46	360	475	57

^a They were excited at λ_{abs} for solid and solution states. ^b The quantum yield was measured by using quinine sulfate (dissolved in 1 N H_2SO_4 with a concentration of $10\ \mu\text{M}$, assuming photoluminescence quantum efficiency of 0.546) as a standard at 24–25 °C. ^c PL quantum yields in the solid state were determined using a calibrated integrating sphere.

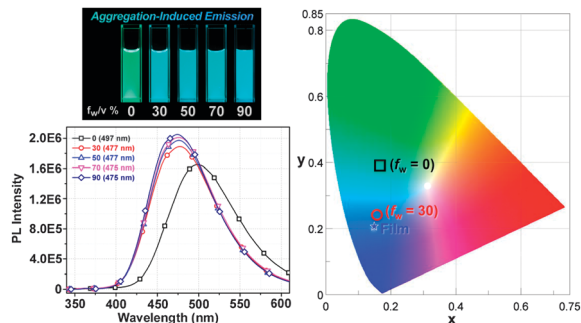


Fig. 2 PL spectra of polyamide **CN-PA** in NMP–water with different water fractions (f_w /vol%) (solution concentration is 10 μ M and excited with abs_{max} respectively). Photographs were taken under illumination of a 365 nm UV light.

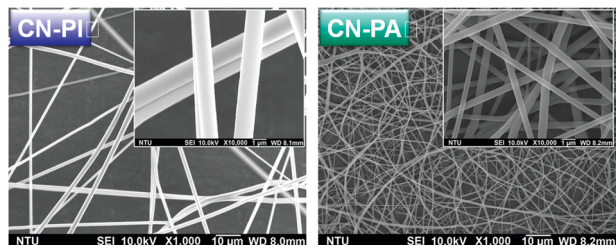


Fig. 3 SEM images of ES nanofibers of **CN-PI** (left) and **CN-PA** (right).

Comparing the optical properties summarized in Table 1, **CN-PA** in the fiber state showed a larger bathochromic absorption shift from NMP solution than the case of **CN-PI**, which could be attributed to the stronger inter-chain interactions of **CN-PA** (e.g., hydrogen-bonding of amide linkage) than **CN-PI**. Fig. 1 shows the optical properties and PL photographs of dilute solutions, thin films, and ES fibers of these two polymers. 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.

In summary, two newly AIE-active cyanoarylamine-containing high-performance polymers, polyimide **CN-PI** and polyamide **CN-PA**, were prepared *via* one-step imidation and direct phosphorylation polycondensation, respectively, and could be utilized to prepare nanofibers by an ES method. SEM results showed that the obtained nanostructures were quite uniform without any beads on the nanofiber surfaces. Notably, the CN-TPA-based polymers having an AIE feature are highly emissive in the solid state with PL quantum yield up to 65%, which could be further enhanced in the form of ES nanofibers (up to 70% of PL quantum yield). These results demonstrate that incorporation of the CN-TPA luminogen into high-performance polymers is a feasible approach to prepare efficient luminescent materials for optoelectronic applications.

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