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A multifunctional luminescent network film electrochemically deposited from a new AIEE emitter for OLEDs and explosive detection

Hongmin Hao^{a, †}, Haiyuan Luo^{a, †}, Aihua Yi^{b,*}, Cong Liu^{a,*}, Bingjia Xu^a, Guang Shi^a, Zhenguo Chi^c

^a Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, School of Chemistry and Environment, South China Normal University, Guangzhou 510006, China

^b School of Mechanical Engineering, Dongguan University of Technology, Dongguan 523808,

China

^c Materials Science Institute, School of Chemistry and Chemical Engineering, SunYat-sen University, Guangzhou 510275, China

Abstract :

Electrochemical polymerization (EP) has attracted considerable attention because of its high material utilization, simple process and low cost. In this work, a new AIEE-active blue-emitting molecule, TCzDPAn, was synthesized. The multifunctional luminescent network film, with TCzDPAn as the building block, was conveniently prepared by EP. The EP film exhibits smooth surface morphology and high thermal stability, which shows great potential as light-emitting materials. In addition, the EP film shows very sensitive detection for 2,4,6-trinitrophenol (TNP) in solution and vapor states, through the synergetic effect of photo-induced electron transfer(PET) and fluorescence resonance energy transfer (FRET). Overall, the study indicates the potential of

Corresponding author Tel: +86-769-22861122 fax: +86-20-22861122; E-mail address: <u>viaihua92751@163.com</u> (A.Yi),

Corresponding author Tel: +86-20-39310251 fax: +86-20-39310183; E-mail address: liucong_011@163.com (C.Liu),

[†] Hongmin Hao and Haiyuan Luo contributed equally to this work.

the multifunctional EP film as OLEDs materials and fluorescent sensors, which is attributed to the specific molecular features of TCzDPAn and the intrinsic properties of the EP film. **Keywords :** aggregation-induced enhanced emission; electrochemical polymerization film; organic light-emitting device; 2,4,6-trinitrophenol; fluorescent sensor

1. Introduction

Conventional organic luminophores generally exhibit partially or completely emission quenching in the aggregate state. However, luminophores are often used in the forms of films in a lot of practical applications. For example, films made of luminophores are used as active layer of organic light-emitting diodes (OLEDs) in optoelectronics applications ^[1-2]. In fluorescent sensing application, probes made of luminescent films are more practical than solution-based probes in view of recyclability, stability and portability, extensive suitability in gas/vapor sensing, and convenience in construction of the sensing devices. The phenomenon of aggregation-caused quenching (ACQ) is common in organic systems, which acts as one of major obstacle for the development of high-performance photoluminescent, electroluminescent materials and fluorescence-film probes.

In contrast, aggregation-induced emission (AIE) and aggregation-induced enhanced emission (AIEE) chromophores emit efficiently in the aggregated state, which may render organic luminophores to emit intensely in the solid state. Since the first report by Tang and co-workers in 2001, AIE and AIEE materials have been widely tested in broad applications of light-emitting diodes, fluorescence labeling materials, photonic devices, and chemo- and biosensing^[1-2].

Fluorescent thin films are often prepared by spin-coating, electrospinning, and electrostatic assembly. However, these traditional methods have some shortcoming yet to be solved, such as high material waste, poor control of the morphology, and complicated processing^[3-4]. In recent years, electrochemical polymerization (EP) has been successfully used in the synthesis of conducting polymers for the applications in organic electroluminescence^[5-8], fluorescent sensing^[9-10], electrochromic devices^[11], supercapacitors^[12-13], etc. Compared with the traditional methods, EP technology has the advantages of high material utilization, simple process, low cost and good application prospects, especially in the preparation of the large-size patterned

electroluminescent devices^[11]. Recently, due to the cross-linked network structure and chemically stable properties of EP films, they are used to construct the fluorescence-film probes. Jiang et.al. and Zhang et.al. reported the construction of microporous polymer networks films through EP, which exhibits good sensitive detection for TNP and 2, 4, 6-trinitrotoluene (TNT), respectively^[9-10]. However, there are still few reports on the application of EP films in good performance OLEDs and fluorescent sensors.

In this study, a multifunctional EP film, with TCzDPAn as the building block, was prepared. Its applications as active layer of OLEDs and explosive detection sensors were then investigated. The blue-emitting material TCzDPAn, in which the anthracene core was decorated with two triphenylethene groups and functionalized with four carbazole groups, has been designed and synthesized as outlined in Scheme 1. Anthracene derivatives possess outstanding photoluminescence and electroluminescence properties, which have been used widely as emitting materials in OLEDs^[14]. Triphenylethene is characterized by its AIE attribute^[15]. The four peripheral carbazole groups in TCzDPAn enable the formation of an insoluble interlocked network film via simple and effective EP method, because carbazole group is a highly electroactive group. The photophysical, electrochemical and thermal properties, as well as the morphology of the EP films were characterized, and their applications as OLEDs materials and explosive detection sensors were demonstrated. The results indicate that the EP film shows high potential as a multifunctional material for OLEDs and fluorescent sensing, attributed to both the specific molecular features of TCzDPAn and the intrinsic properties of the EP film.

2. Experimental section

2.1 Materials and analytical methods

The supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAPF₆, 98 %), was purchased from Alfa Aesar, and it was recrystallized twice and dried for 24 h under vacuum before use. Tetrahydrofuran (THF) was distilled in the presence of sodium benzophenone. All other chemicals and solvents were of analytical grade and used as received.

¹H and ¹³C NMR spectra were measured on a Mercury-Plus 300 spectrometer (CDCl₃ as the solvent and tetramethylsilane as the internal standard). Mass spectra (MS) were carried out on a Thermo DSQ MS spectrometer. Elemental analysis(EA) was measured on a Vario elemental

analysis cube (Vario EL cube). Fourier Transform Infrared (FT-IR) spectra were obtained on a Bruker Vector 33 spectrometer (KBr pellet). UV-visible absorption spectra (UV) were determined on a Shimadzu UV-1700 spectrophotometer. Fluorescence spectra (FL) were measured on a Hitachi FL-2500 spectrometer. Glass transition temperatures (T_g) were determined by differential scanning calorimetry (DSC) at a heating and cooling rate of 10 °C /min under N₂ atmosphere using a NETZSCH thermal analyzer (DSC-Q20) and recorded during the second heating run. Thermogravimetric analyses (TGA) were carried out using a thermal analyzer (NETZSCH, TG 209F3) under N₂ gas flow with a heating rate of 20 °C /min. The fluorescence quantum yields (Φ_{FL}) of the compound in THF or water/THF mixtures were evaluated using a Quantaurus-QY (Hamamatsu). Atomic Force Microscope (AFM) images were recorded using a Seiko SPA 400 with an SPI 3800 probe station. The high-resolution transmission electron microscopy (HR-TEM) experiment was performed using a JEOL model JEM-3010 at an acceleration voltage of 300 kV.

The cyclic voltammetric (CV) method was used to prepare EP films by using a standard one-compartment, three-electrode electrochemical cell attached to an Electrochemical Workstation (Model CHI760D, Shanghai Chenhua). The indium-tin oxide (ITO)-coated glass, titanium plate and Ag/Ag⁺ non-aqueous electrode was used as the working electrodes, the counter electrode, and the reference electrode respectively. All CV measurements were performed under an inert argon atmosphere with TCzDPAn (1 mg/mL) and supporting electrolyte of TBAPF₆ (0.1 M) in electrolyte solution of a mixed solvent of acetonitrile/dichloromethane (V/V=1:1). After the EP process, the resulting EP film was washed with a mixture of acetonitrile and CH₂Cl₂ (V/V = 1/1) to remove any unreactive precursors and supporting electrolytes, and then dried in a vacuum oven.

2.2 Device fabrication and testing

The ITO-coated glass substrates was cleaned, and then dried in an oven at 90°C. Poly(3,4 ethylenedioxythiophene) (PEDOT) was used as the hole-transporting layer and was coated from water solutions on the ITO substrate, yielding a 40 nm thick layer after drying (ca. 150 °C; 20 min). For spin-coated devices, the active layer was coated from toluene solutions containing 10 mg/mL TCzDPAn to give a film with a thickness of 70 nm. For EP devices, the emitting layers of

EP films were electropolymerized by the CV mode. Finally, CsF (1 nm) and Al cathodes (100 nm) were thermally deposited onto the emitting-layers in a vacuum with a back pressure of 5×10^{-4} Pa. The electroluminescent (EL) spectra were recorded using a PR-705 Spectroscan spectrometer. The brightness-current-voltage characteristics were recorded simultaneously with the measurement of the EL spectra by combining the spectrometer with a Keithley 2400 programmable electrometer. All measurements were carried out at room temperature under ambient conditions.

2.3 Explosives detections

To explore the sensing properties of the EP films for the detection of nitroaromatic explosives, the fluorescence spectra of the EP films were recorded by immersing EP films in ethanol solutions of 2,4,6-trinitrophenol (TNP). To demonstrate its utility in vapor phase detection of TNP, the fluorescence spectra of the EP films were recorded in the presence of TNP vapor as a function of time. To explore the cycle performance, the EP film was immersed into the TNP ethanol solution (0.1 mM), and then measured with fluorescence spectrophotometer. The resulting film was then washed with ethanol, and heated under the vacuumed at 50 °C for 4 h to recover the fluorescence signal. The rinsed film was reused in the next-round sensing, and the whole process was repeated for multiple times. The Stern-Volmer constant (K_{sv}) was used to quantify the quenching efficiency. For static quenching process, the fluorescence intensity as a function of increasing quencher concentration([A]) was described by the Stern-Volmer equation $I_0/I-1 = K_{sv}[A]$, where I_0 and I were respectively the PL intensities in the absence and presence of the quencher, and K_{sv} was the Stern -Volmer constant(M^{-1}). Limit of detection (LOD) was calculated by the formula of LOD = $3\sigma/m$, where σ was the relative standard deviation, m was the slope of the calibration curve.

2.4 Synthesis

2.4.1 Synthesis of compound 1

A solution of 1-bromo-4-(bromomethyl)benzene (5.15 g, 16.3 mmol) was stirred under argon atmosphere at 140 °C for 15 min. Thereafter, triethyl phosphite (24.38 g, 146.7mmol) was added and the mixture was stirred for 7 h. After the excess triethyl phosphite was removed by vacuum distillation, the residue was cooled to room temperature. A colorless clear liquid was obtained (5 g, 98 % yield). ¹H NMR (500 MHz, CDCl₃) δ 7.43 (d, *J*=7.9 Hz, 2 H), 7.17 (dd, *J*=8.5,

2.5 Hz, 2 H), 4.06-3.96 (m, 4 H), 3.09 (d, J=21.7 Hz, 4 H), 1.25 (t, J=7.1 Hz, 6 H); MS (EIS), m/z : 307.0093 ([M+H]⁺, calcd for C₁₁H₁₆BrO₃P, 306.002).

2.4.2 Synthesis of compound 2

A solution of 9-(6-bromohexyl)-9H-carbazole (1.03 g, 3.1 mmol) and 4,4'-dihydroxy benzophenone (0.31 g, 1.4 mmol) in DMF (20 mL) was stirred under an argon atmosphere at 60°C. K_2CO_3 (0.26 g, 1.7 mmol) and NaI (0.18 g, 1.1 mmol) was added and the mixture was stirred for 48 h. After filtration, the filtrate was distilled under reduced pressure, and the crude residue was recrystallized from ethanol. A white powder was obtained (0.48 g, 45% yield). 1H NMR (500 MHz, CDCl3) δ 8.09 (d, J = 7.6 Hz ,4H),7.73 (d, J = 8.8 Hz ,4H), 7.43 (d, J = 16.2,8H),7.22 (d, J = 3.6 ,4H), 6.87(d, J = 8.8 Hz, 4H), 4.32 (t, J = 6.8 Hz, 4H), 3.97 (s, 4H), 1.92 (d, J = 14.0 Hz, 4H), 1.75 (d, J = 13.4 Hz, 4H), 1.55-1.38 (m, 8H); MS (MALDI-TOF), m/z: 713.401 ([M+H]⁺ calcd for C₄₉H₄₈N₂O₃, 712.366).

2.4.3 Synthesis of compound 3

A solution of compound 1 (1.38 g, 4.5 mmol) dissolved in THF (45 mL) was stirred under an argon atmosphere at 0 °C. Potassium tert-butoxide (0.05g, 0.4 mmol) was added quickly. After fully dissolved, compound 2 (0.36 g, 0.5 mmol) was added and the mixture was stirred continuously for 12 h at room temperature. The solvent was distilled by rotary evaporation after the reaction was completed. The crude product was poured into water and extracted with dichloromethane. The organic layer was dried over sodium sulfate (MgSO₄). Following filtration and evaporation of solvent under vacuum, the resulting crude product was purified on a silica gel column chromatography by dichloromethane/petroleum ether (V/V=1:2) to yield compound 3 as a light-yellow powder (0.41 g, 95 % yield). ¹H NMR (500 MHz, CDCl₃) δ 8.12 (dd, *J*=7.8, 0.5 Hz, 4 H), 7.51-7.40 (m, 8 H), 7.25-7.21 (m, 7 H), 7.08-7.04 (m, 2 H), 6.92-6.88 (m, 2 H), 6.83-6.78 (m, 4 H), 6.73 (s, 1 H), 4.34 (dd, *J*=15.7, 7.2 Hz, 4 H), 3.92 (td, *J*=6.4, 3.6 Hz, 4 H), 2.02-1.87 (m, 4 H), 1.84-1.68 (m, 4 H), 1.60-1.40 (m, 9 H); MS (MALDI-TOF), m/z: 864.318 ([M]⁺, calcd for C₅₆H₅₃BrN₂O₂, 864.329).

2.4.4 Synthesis of compound 4

A solution of compound 3 (2.00 g, 2.31 mmol) in 1,4-dioxane(25 mL) was stirred under an argon atmosphere, followed by the sequent addition of bis(pinacolato)diboron (21.76 g, 6.93

mmol), potassium acetate (KOAc, 0.91 g, 9.24 mmol), and Pd(dppf)Cl₂ (0.14 g,0.18 mmol). The reaction mixture was gradually heated to 85 °C and stirred for 15 h. After that, the mixture was cooled to room temperature. The dioxane was removed by rotary evaporation. The residue was poured into a 5 % sodium hydroxide (NaOH) solution and extracted with CH₂Cl₂. The organic layer was dried over MgSO₄, and then filtered. Thereafter, the solvent was removed by rotary evaporation. The resulting crude product was purified by column chromatography on silica gel using dichloromethane/petroleum ether (V/V=1:1) as the eluent. Compound 4 was obtained as a light yellow solid (1.79 g, 85 % yield). ¹H NMR (500 MHz, CDCl₃) δ 8.11 (d, *J*=7.6 Hz, 1 H), 7.57 (d, *J*=7.4 Hz, 1 H), 7.50-7.38 (m, 2 H), 7.23 (t, *J*=7.4 Hz, 1 H), 7.05 (dd, *J*=19.9, 7.9 Hz, 1 H), 6.80 (dd, *J*=10.9, 8.4 Hz, 1 H), 4.34 (dt, *J*=10.1, 7.2 Hz, 1 H), 3.92 (t, *J*=6.3 Hz, 1 H), 1.93 (dt, *J*=20.9, 7.2 Hz, 1 H), 1.75 (dt, *J*=13.4, 6.5 Hz, 1 H), 1.50 (ddd, *J*=26.2, 18.2, 10.6 Hz, 3 H), 1.32 (s, 3 H); MS (MALDI-TOF), m/z: 913.617 ([M+H]⁺, calcd for C₆₂H₆₅BN₂O₄, 912.504).

2.4.5 Synthesis of TCzDPAn

The compound 4 (1.05 g, 1.15 mmol), toluene (60 mL), 2 M potassium carbonate aqueous (K₂CO₃) solution (2 mL) and appropriate phase transfer agents (AliquatR 336) were added to three-necked flask and stirred. Then, 9,10-dibromoanthracene (0.10 g , 0.29 mmol), tetrakis(triphenylphosphine)palladium (Pd(PPh₃)₄, (0.20 g, 0.17 mmol) were added into the reaction mixture in sequence under the anhydrous anaerobic condition. The mixture was refluxed at 90 °C for 24 h under an argon atmosphere. After cooling to room temperature, reaction mixture was poured into water and extracted with dichloromethane. The organic layer was dried over MgSO₄. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using dichloromethane/petroleum ether (V/V=1:1) as eluent, afforded TCzDPAn (0.19 g, 74 % yield) as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 8.12 (d, *J*=7.7 Hz, 4 H), 8.07 (d, *J*=7.7 Hz, 4 H), 7.70 (dd, *J*=6.8, 3.2 Hz, 4 H), 7.48 (t, *J*=7.5 Hz, 4 H), 7.45-7.40 (m, 8 H), 7.37 (d, *J*=8.1 Hz, 4 H), 7.32 (dd, *J*=9.4, 3.5 Hz, 8 H), 7.25-7.15 (m, 16 H), 6.99 (s, 2 H), 6.89 (d, *J*=8.6 Hz, 4 H), 6.85 (d, *J*=8.7 Hz, 4 H), 4.34 (t, *J*=7.1 Hz, 4 H), 4.29 (t, *J*=7.1 Hz, 4 H), 3.94 (q, *J*=6.3 Hz, 8 H), 1.98-1.86 (m, 8 H), 1.76 (dd, *J*=14.5, 9.4 Hz, 8 H), 1.59-1.41 (m, 20 H); ¹³C NMR (500 MHz, CDCl₃) δ 140.45, 131.60, 131.07, 129.85, 129.31,

128.90, 125.62, 125.58, 124.89, 122.87, 120.38, 120.33, 118.77, 118.73, 114.65, 114.18, 108.64, 67.99, 67.79, 67.69, 42.97, 42.91, 29.19, 28.95, 27.09, 25.96; MS (MALDI-TOF), m/z: 1747.961 ([M]⁺, calcd for C₁₂₆H₁₁₄N₄O₄, 1748.900); Anal. Calc. for C₁₂₆H₁₁₄N₄O₄: C 86.56, H 6.57, N 3.20, O 3.60; Found: C 86.82, H 6.71, N 3.12 %

3. Results and discussion

3.1 Synthesis

The strategy to synthesize TCzDPAn compound is outlined in Scheme 1. The TCzDPAn molecule was prepared through palladium-catalyzed Suzuki coupling reaction between 9,10-dibromoanthracene and corresponding boric acid ester. All the intermediate and final products were fully purified and characterized, and the result data satisfactorily corresponded to the expected molecular structures. The chemical structure and composition of the target compound TCzDPAn was characterized and confirmed by ¹H-NMR, ¹³C-NMR, MS and EA, which are included in the experimental section.



Scheme 1 The synthetic routes of TCzDPAn

3.2 Optical properties of TCzDPAn and the AIEE effects

Fig.1a shows the absorption spectra of TCzDPAn in THF solutions(10 μ M). TCzDPAn exhibits three major absorption bands at 295 nm, 305-354 nm and 370-430 nm, respectively (Fig. 1a). The absorption peak at the position of 295 nm, 331nm and 378 nm were attributed to the π - π * transitions of carbazole, peripheral triphenylethene groups and anthracene, respectively^[14]. To determine the AIEE behavior of TCzDPAn, the changes of photoluminescence (PL) behaviors in

the solution and aggregate states were recorded. The FL spectra of TCzDPAn in the water/THF mixtures (10 μ M) with different contents of water are shown in Fig.1b. Since the molecules are completely insoluble in water, their existing forms will change from a solution or well-dispersed state in the pure THF to the aggregated nanoparticles, with an increase of the water fraction in the mixed solvent. The TCzDPAn in pure THF solution exhibits weak FL intensity and shows PL peak at 453 nm. However, the fluorescent intensity is significantly enhanced when the water fraction exceeded 50%. In the solvent mixture with 95% water, the PL intensity is 17-fold higher than that in the pure THF solution and shows strong blue fluorescence under UV irradiation (inset graph). Simultaneously, the fluorescence quantum yield ($\Phi_{\rm FL}$) values of TCzDPAn roses from 5.4 % in pure THF solutions to 46.3 % in the solvent mixture with 95% water. These results indicate that TCzDPAn exhibits significant AIEE effect. The emission images of TCzDPAn in water/THF mixtures with different water fractions are shown in Fig.S1. The compound exhibits stronger emission in water/THF mixtures with high water fractions than that in pure THF solution, which further demonstrating the AIEE-effects. The central anthracene core decorated with two triphenylethene groups which has twisted configuration, increases structural bulk and non-planarity, effectively diminishes its degree of intermolecular π - π stacking and enable the TCzDPAn exhibit AIEE-active^[1, 15]



Fig.1 (a) UV absorption spectra of TCzDPAn in pure THF solution(10 μ M). (b) FL spectra of TCzDPAn in water/THF mixtures(10 μ M). The inset depicts the changes of FL peak intensity and emission images in water/THF mixtures with water fractions of 0 % and 95 % under 365 nm UV illumination at room temperature, respectively

3.3 Preparation of the EP films

The EP films of TCzDPAn were produced on electrodes by the CV mode. The CV curves of TCzDPAn recorded for 10 scan cycles with a potential range from -0.6 to 0.86 V provided in Fig.2.

In the first cycle of the positive CV scan, the onset potential appeared at 0.76 and the oxidation peak is observed at 1.13 V, which is attributed to the oxidation of carbazole^[7] (Fig.S2). The fact that carbazoles transform into cationic radicals during oxidation and then couple effectively with each other to form dimeric carbazole cations has been verified by previous studies^[9, 16]. During the negative scan, an obvious reductive peak is detected at the potential of 0.45 V, which corresponds to the formation of the neutral dimeric carbazyl from the dimeric carbazyl cation^[21]. From the second scan, a new peak appears at 0.71 V, assigned to the oxidation of the formed dimeric carbazoles in the film. The current of each cycle rises gradually with increased scan cycle, indicating that the polymerization of the monomers and the growth of the film on the electrode upon successive CV scan. The thickness of network films can be controlled precisely by adjusting the numbers of scan cycles and the oxidative potentials, by around 0.7 nm per cycle under the potential range from -0.6 to 0.86 V (Fig.S3).



Fig.2 Cyclic voltammograms (-0.6~0.86 V) of TCzDPAn recorded for 10 scan cycles 3.4 Characterization of the EP film

The structure of the EP film and the formation of dimeric carbazole were evidenced by FT-IR spectra (Fig.S4). The peak at 723 cm⁻¹ and 749 cm⁻¹ in TCzDPAn is attributed to the vibrational bands of C-H bonds of the bisubstituted benzene groups of carbazole ring^[8]. The newly generated peak at 798 cm⁻¹ in the EP film is attributed to the vibrational bands of C-H bonds of the trisubstituted carbazole ring, which demonstrates the existence of dimeric cabazole^[4]. As there are four carbazole units in a TCzDPAn molecule, a cross-linked film is deposited by the electrochemical coupling reaction of carbazole groups, the schematic shown in Fig. S4. This EP

film is very stable and insoluble in many common solvents, which further demonstrating its cross-linking structures.

The PL spectra of the TCzDPAn spin-coated film and the EP film deposited on ITO are presented in Fig.3. The TCzDPAn spin-coated film emits blue luminescence with the peak of 457 nm, while that of EP films at about 500 nm. There is about 43 nm red-shifted of the PL spectra of EP film comparing with that of spin-coated film. This phenomenon is also observed in other fluorescent EP films owing to their cross-linked-network structures and the relative close packing of chromophores in the EP films^[3,5-6].



Fig.3 The PL spectra of spin-coated film and EP film of TCzDPAn on ITO

The thermal property of TCzDPAn and the EP film were examined by TGA and DSC measurements. As display in Fig S5a, TCzDPAn and the EP film show good thermal stability and T_d (5% -weight-loss temperature measured by TGA) is 390°C and 408 °C, respectively. The good thermal stability of TCzDPAn can be ascribed to the large molecular weight and rigid carbazole peripheries. The higher level of thermal stability of the EP film comparing with TCzDPAn is attributed to its crosslink structure. The glass transition temperature (T_g) of TCzDPAn is detected at 75 °C, while such thermal transition is not detected in the EP film(Fig.S5b), suggesting that the EP film has a very high degree of cross-linking. The DSC curves of TCzDPAn reveals no peaks associated with crystallized or melting transitions, indicating that TCzDPAn and its EP film have excellent thermal stability which is beneficial for the application as photoelectric materials in OLED devices.

3.5 Morphologic studies of the EP film

The morphology of EP film was studied by AFM and TEM. As revealed by AFM, the EP film exhibits a uniform surface and the root mean square roughness (RMS) is only 1.7 nm, which is importance for its application in optoelectronic devices (Fig.4). The uniform microporous structure with diameter of less than 1 nm of the EP film is observed directly by TEM (Fig.4). The permanent structural micropores of EP film will make it a promising candidate of excellent fluorescence-film probe.



Fig.4 AFM and TEM images of the EP film.

3.6 Electrochemical characterization

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are related to the redox potentials. They are two important parameters for electroluminescent materials on account of their relationship with hole/electron-injecting capability ^[17-18]. The electrochemical properties of TCzDPAn and the EP film as shown in Fig.S6. As the onset reduction potential of TCzDPAn cannot be observed clearly, the LUMO energy level is calculated from the HOMO energy level and the energy band gap which was estimated from the absorption edge (LUMO =HOMO- ΔE_g). The calculated HOMO and LUMO energies of TCzDPAn are -5.40 eV and -2.93 eV respectively. The HOMO and LUMO energies of the EP film are calculated to be -5.17 eV and -2.34 eV, respectively, according to the equation $E_{\text{HOMO/LUMO}} = -(E_{\text{onset(ox/red),FOC}}+4.8) eV^{[19]}$.

^{3.7} Electroluminescence properties

In order to investigate the potential application of TCzDPAn and EP film as the emitting layers (EML) in OLEDs, undoped devices with simple configuration of ITO/PEDOT:PSS (40 nm)/Spin-coated film (~70 nm)/CsF (1 nm)/Al (100 nm) (Device I) and ITO/PEDOT:PSS (40nm)/EP film (~70 nm)/CsF (1 nm)/Al (100 nm) (Device II) were fabricated. A well-known hole injection material PEDOT:PSS was used to lower the leakage current, CsF was used as the modificatory layer of the cathode Al, which could enhance the electron injection, and ITO coated glass was used as the substrate and anode^[20]. All the characterization data for devices were summarized in Supporting Information Table S1. The turn-on voltage(V_{on}), maximum luminance(L_{max}) and maximum luminescent efficiency($\eta_{C,max}$) of Device I is 4.8 V, 1282 cd/m² and 0.38 cd/A, respectively (Table S1). The electroluminescent device using the EP film as EML displays a maximum luminance of 923 cd/m² and a maximum luminance efficiency of 0.28 cd/A with very low roll-off of the efficiency, which demonstrates the great potential in EL devices of this new AIEE compound and its EP film. Device I emits blue light with a maximum at 468 nm and CIE coordinates of (0.16, 0.24) (Fig.5c and Table S1). Device II exhibits blue-green emission with a maximum at 520 nm, which is about 52 nm red-shifted in contrast with that of Device I, attributed to the their cross-linked-network structures and the relative close packing of chromophores in the EP films. Although the EL performance of these Devices are not high, it demonstrates the great potential in EL devices of this new AIEE compound and its cross-linked polymer network films fabricated by simple EP technology. The device performances may be further improved by the configuration of the EL devices and the optimization of the EP conditions.





Fig.5(a) Current-voltage-luminance characteristics of the OLEDs. (b) luminous efficiency-current

density characteristics of the OLEDs. (c) EL spectra of TCzDPAn and EP film

3.8 Explosive detection by EP film

The stable cross-linked structure and good fluorescence properties of the EP film inspired us to explore their applications as fluorescence-film sensor for nitroaromatic explosives. The 2,4,6-trinitrophenol (TNP) that commercial available is used as a model explosive. The fluorescence changes of EP films in response to different amount of TNP in ethanol were studied. Their PL intensity decrease significantly with the increasing loading amount of TNP but with no change in spectral profiles(Fig. 6a). The fluorescence quenching rate is 96.86% with addition of 0.1mM TNP. To further quantify the quenching efficiency, the Stern-Volmer plot of relative PL intensity ($I_0/I-1$) of EP film versus TNP concentration is investigated and shown in Fig. 6b. The Stern-Volmer plot is almost linear at low concentrations, and gives a quenching constant (K_{sv}) of $1.14 \times 10^5 \,\mathrm{M}^{-1}$ (Fig. 6b), which is found to be higher than many other fluorescent chemosensors for TNP^[18, 21-22]. The limit of detection calculated by the formula of LOD= $3\sigma/m$ can reach 500 nM, revealing the excellent sensitivity to TNP of the EP film. Afterward, the curve bent upward, suggesting the super amplification effect upon increasing the TNP concentration. The nonlinear nature of the Stern-Volmer plot of TNP may be due to the energy transfer process^[23]. In addition, the cross-linked-network microstructure and porous nature of the EP film ensures its stability and the easy and fast migration of exciton, which is benefit for the enhancement of sensing efficiency^[18, 24]. Furthermore, the reusability of the EP film was examined (Fig. 6c). Approximately the same state of fluorescence quenching is observed after each cycle, and the fluorescence intensities of the EP film recover to a similar level. The EP film is reusable for TNP detection, which may be due to the stable cross-linked network structure of EP film.



Fig. 6 (a) Fluorescence emission spectra of EP film with the addition of different amounts of TNP in ethanol solution(10 μ M-100 μ M). (b) Stern-Volmer plots of I₀/I-1 versus TNP concentration. I₀ and I are the fluorescence intensities of the EP film in the absence and presence of TNP, respectively. Inset: The fitting diagram at low concentration (0- 50 μ M). (c) The cyclic performance of the EP film in the detection of 0.1mM TNP solution

The efficient system for vapor phase sensing of TNP is extremely challenging because TNP has very low vapor pressure $(7.4 \times 10^{-7} \text{ mm Hg at } 25 \text{ °C})$ compared to several other nitroaromatic explosives (including TNT and DNT)^[25]. To demonstrate the utility of EP film in detection of TNP in vapor state, the fluorescence spectra of the EP films were recorded in the presence of saturated TNP vapor (Fig. 7a). As shown in Fig. 7b, fluorescence quenching is observed immediately by exposing EP film to saturated TNP vapor, and the fluorescence quenching is 48 % in 100 s exposure, and reaches 70 % in 240 s. Thus, the EP film displayed high sensitivity to TNP vapor.



Fig. 7 (a) Time-dependent PL spectra of EP film upon exposure to TNP saturated vapor at room temperature for 0-240 s. Film thickness: 60 nm; excitation wavelength: 365 nm. (b) Time-dependent fluorescence quenching studies of EP film upon exposure to saturated vapor phase of TNP.

3.9 Mechanism for TNP detection

Generally, the photo induced electron transfer or energy transfer between the sensor molecules and the nitroaromatics account for the fluorescence response of sensors^[21, 26]. The conduction band of fluorescent sensors usually lies at higher energies than the LUMOs of electron-deficient analytes, thus resulting in the electron transfer and leading fluorescence quenching. The calculated LUMO energy level of TNP is -3.92 eV, which is much lower than that of the EP film (-2.34 eV), thus facilitates the occurrence of the photoinduced electron transfer^[18, 27]. The non-linear Stern-Volmer plot for TNP also suggests an energy transfer mechanism. To further account for the intrinsic reason for the quenching behaviors, the UV spectra of TNP and the PL spectrum of EP films were investigated. It can be seen that the absorption of TNP overlaps with the emission of EP film in the range of 385 to 470nm, which suggests that energy transfer quenching process may be one of the quenching pathway (Fig. 8). The resonance energy transfer can occur from fluorophore to non-emissive analyte, especially at the high concentration when the fluorophore and the analyte are close to each other, which dramatically enhance fluorescence-quenching efficiency. Based on these results, the quenching mechanism of the EP film dominated by both charge and energy transfer.



Fig. 8 Overlap of the absorption spectrum of TNP and the emission spectrum of EP film.

4 Conclusions

A luminescent network film, with a new AIEE-activity blue-emitting molecule, TCzDPAn as the building block, has been constructed conveniently by EP technology. The EP film exhibits smooth morphology and high thermal stability, which demonstrates the great potential as EML in EL devices. Additionally, the EP film is promising reusable sensitive sensors for solution and vapor phase sensing of TNP due to good luminescent properties, cross-linked network structure and microporous morphology. The K_{sv} is found as high as 1.14×10^5 M⁻¹, which is comparable to the best performances of the fluorescence-film probes for TNP. The quenching mechanism of the EP film dominated by both charge and energy transfer. Overall, the study indicates the potential of the EP film as OLEDs materials and fluorescent sensors.

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Figure captions

Scheme 1 The synthetic routes of TCzDPAn

Fig.1. (a) UV absorption spectra of TCzDPAn in pure THF solution(10 μ M). (b) FL spectra of TCzDPAn in water/THF mixtures(10 μ M). The inset depicts the changes of FL peak intensity and emission images in water/THF mixtures with water fractions of 0 % and 95 % under 365 nm UV illumination at room temperature, respectively.

Fig.2. Cyclic voltomogram (-0.6~0.86 V) of TCzDPAn recorded for 10 scan cycles.

Fig.3. The PL spectra of spin-coated film and EP film of TCzDPAn.

Fig.4. AFM and TEM images of the EP film.

Fig.5. (a) Current-voltage-luminance characteristics of the OLEDs. (b) luminous efficiency–current density characteristics of the OLEDs. (c) EL spectra of TCzDPAn and EP film.

Fig. 6. (a) Fluorescence emission spectra of EP film with the addition of different amounts of TNP in ethanol solution(10 μ M-100 μ M). (b) Stern-Volmer plots of I₀/I-1 versus TNP concentration. I₀ and I are the fluorescence intensities of the EP film in the absence and presence of TNP, respectively. Inset: The fitting diagram at low concentration (0- 50 μ M). (c) The cyclic performance of the EP film in the detection of 0.1mM TNP solution.

Fig. 7 (a) Time-dependent PL spectra of EP film upon exposure to TNP saturated vapor at room temperature for 0-240 s. (b) Time-dependent fluorescence quenching studies of EP film upon exposure to saturated vapor phase of TNP.

Fig. 8. Overlap of the absorption spectrum of TNP and the emission spectrum of EP film.

Supporting Information

A multifunctional luminescent network film electrochemically deposited from a new AIEE emitter for OLEDs and explosive detection

Hongmin Hao^a, Haiyuan Luo^a, Aihua Yi^{b*}, Cong Liu^{a*}, Bingjia Xu^a, Guang Shi^a, Zhenguo Chi

0%	10%	20%	30%	40%	50%	60%	70%	80%	85%	90%	95%	96%

Fig. S1 The emission images of the compound in water/THF mixtures with different water fractions under 365 nm UV illumination at room temperature



Fig.S2 Cyclic voltomogram (-0.6~1.5 V, 200 mV/s) of TCzDPAn(first and second cycle).



Fig. S3 Plot of the TCzDPAn EP film thickness versus the CV (-0.6~0.86 V and -0.6~0.83 V)



Fig. S4 FT-IR spectra of TCzDPAn and EP film







Fig. S6 Electrochemical voltammograms measured for (a) TCzDPAn and (b) the EP film

Table S1 EL performances of OLEDs^a

Device	$V_{\rm on}[V]$	$L_{\rm max} [{\rm cd/m}^2]$	$\eta_{\rm C,max}$ [cd/A]	$\lambda_{\rm EL}$ [nm]	CIE _{x,y}
Ι	4.8	1282	0.38	468	(0.16,0.24)
Π	4.2	923	0.28	520	(0.30, 0.51)

^aAbbreviations: V_{on} =turn-on voltage at 1 cd/m², L_{max} =maximum luminance, $\eta_{C,max}$ =maximum current efficiency, λ_{EL} =EL maximum,. $CIE_{x,y}$ =Commission international de l'Eclairage chromaticity coordinates collected at 2 mA.

Device configuration:

I : ITO/PEDOT:PSS (40 nm)/Spin-coated film (~70 nm)/CsF (1 nm)/Al (100 nm)

II : ITO/PEDOT:PSS (40 nm)/EP film (~70 nm)/CsF (1 nm)/Al (100 nm)

Highlights

- > A new AIEE-activity blue-emitting molecule, TCzDPAn, has been synthesized.
- > Luminescent network film has been prepared by electrochemical polymerization (EP).
- > The EP film demonstrated great potential as OLED materials and fluorescence sensor.

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