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# Introduction

Photoluminescence materials based on small molecules or polymers have attracted a lot of attention due to their great potential in modern technologies such as color displays,<sup>1-10</sup> fluorescence dyes and paints.<sup>11-14</sup> There are several different kinds of light-emitting mechanisms, including fluorescence or phosphorescence from excitons, excimers, electromers, exciplexes, or electroplexes, that govern the color and quantum efficiency of the photoluminescence.<sup>15-33</sup> An exciplex is one kind of excited state complex that is formed by an electronically excited state donor molecule, D\* (or acceptor A\*), with a complementary acceptor molecule, A (or donor D), in their ground state. There are many competition processes existing in the medium, such as the normal fluorescent process, thermal

# The thermofluoric behavior of poly(fluorenetolyldiphenylamine)–oxadiazole pair in a polymer matrix<sup>†</sup>

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Under UV irradiation, 1,4-bis(5-(4-octan-2-ylphenyl)-1,3,4-oxadiazol-2-yl)naphthalene (NOXD) and poly(fluorenetolyldiphenylamine) (PFT) are blue light emissive in solid film. When NOXD and PFT were blended to form a neat thin-film, yellowish exciplex emission was observed. The emissive properties vary when the materials were blended into different kinds of polymeric hosts; while polystyrene–NOXD–PFT (5:1:1) and PMMA–NOXD–PFT (5:1:1) showed blue light emission, poly(acrylonitrile-co-methyl acrylate) (P(AN-co-MA))–NOXD–PFT (5:1:1) showed blue and yellow dual emissions. When the film was heated at 140 °C for 2 min, the yellow light exciplex emission was enhanced. However, upon cooling to ambient temperature, the exciplex emission intensity gradually dropped back. Similar thermofluoric behaviors were observed when the thermally crosslinked polyepoxy-polymercaptan–NOXD–PFT film (20:1:1) was heated at 160–170 °C; the blue light emission to the segregation of NOXD from the polymeric host at high temperature that allows NOXD to aggregate with PFT, leading to exciplex emission.

non-radiation decay and system crossing that could suppress the exciplex formation. To form the exciplex, the D\* (or acceptor A\*) and A (or donor D) have to collide with each other prior to any relaxation process. This would be strongly affected by the diffusion rate of the molecules, which is governed by the viscosity of the matrix and the effective concentration of D/A in the media.

In principle, an exciplex is composed of the D–A pair with an average separated distance of 0.3–0.4 nm,<sup>34–43</sup> in which partially charged components (0 <  $\delta$  < 1) with limited extents of charge separation between the donor–acceptor pair would be formed. Instead of having lower quantum yields, the exciplex emission spectrum is usually red-shifted so that a totally new emission profile, that is different from that of D or of A could be observed. During the past, many studies on enhanced exciplex emission of polymer systems suggested the possibility of using LED devices as a broadband emission source.<sup>15,30,31</sup>

Poly(fluorenetriphenylamine)s<sup>44</sup> form a class of hole-transporting fluorescent polymers that have been widely studied in the area of polymeric light emitting diodes. Due to their high fluorescence quantum yields as well as the excellent hole-injection and transport properties, this class of materials is highly useful for organic optoelectronic applications.

On the complementary side, oxadiazole (OXD) molecules are among the most widely studied electron-transport materials for organic electronics.<sup>45–47</sup> Many different types of OXDs, including

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dimeric,<sup>48–50</sup> trimeric,<sup>51–53</sup> starburst,<sup>54–56</sup> tetraphenylmethane<sup>57</sup> and arylsilane<sup>58</sup>-based OXDs have recently been reported. When OXDs have been blended in an electron-rich or donating matrix, with high-lying HOMO, photoluminescence from the exciplex emission could be observed. For example, exciplex formation was observed when 2-*tert*-butylphenyl-5-biphenyl-1,3,4-oxadiazole (PBD) was blended into polyvinylcarbazole (PVK). Since the exciplex formation phenomenon is not only an interesting issue in photophysical studies, but also in many organic electronic applications such as OLED and organic solar cell researches,<sup>59</sup> we have carried out systematic studies of the exciplex formation of the oxadiazole (OXD) derivatives in PVK blends as emitter.<sup>60-62</sup>

There are many factors affecting the exciplex formation. Besides the HOMO-LUMO matching factors, geometry factors and diffusion rate would also be essential. Therefore, one might expect that exciplex formation in a solid matrix would be complicated. At least, unlike molecules in solution in which conformational equilibrium is fast, conformational preferences and restrictions of molecules in a solid or highly viscous glassy matrix would be important factors to deal with. In the present article, we are going to present our study of the exciplex formation of 1,4-bis(5-(4-octan-2-ylphenyl)-1,3,4-oxadiazol-2-yl)-naphthalene (**NOXD**) with conjugated poly(fluorene-tolyldiphenylamine) **PFT**<sup>5</sup> in an poly(epoxy)-polymercaptan (PEPM) matrix and the unexpected thermofluoric phenomenon.<sup>63</sup>

# **Experimental section**

## Materials

All reagents were commercially available and were used without further purification. Polystyrene (PS,  $M_w$ : 250 000, Acros), poly(methyl methacrylate) (PMMA,  $M_w$ : 97 000, Acros), and poly(acrylonitrile-*co*-methyl acrylate) (P(AN-*co*-MA), Aldrich) were used as the host matrix.

#### Measurement

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Unity Plus 400 MHz spectrometer. Molecular weights and polydispersities of polymers were determined by gel permeation chromatography (GPC) analysis relative to polystyrene calibration (Waters Styragel columns of HR3 and HR4E) using THF as eluent at a flow rate of 1.0 mL min<sup>-1</sup>. Differential scanning calorimetry (DSC) analysis was performed under nitrogen at a heating rate of 10 °C min<sup>-1</sup>. Thermogravimetric analysis (TGA) was determined under nitrogen by measuring weight loss while heating at a rate of 10 °C min<sup>-1</sup>. Photoluminescence spectra were obtained on a Hitachi F-4500 luminescence spectrometer.

#### Synthetic procedures

The synthesis of **PFT** and **NOXD** are denoted in Scheme 1. The synthetic procedures are reported as follows.

**4-Bromo-***N***-**(**4-bromophenyl**)-*N*-*p***-tolylaniline** (1). To an icecooled solution of 4-methyl-*N*,*N*-diphenylaniline (2.5 g, 9.7 mmol, in 32 mL of DMF) was added dropwise NBS (*N*-bromosuccinimide) solution (3.58 g, 20.3 mmol, in 10 mL of DMF). After the addition, the mixture was stirred for a further 15 min. Then, when the reaction was completed, water was added to quench the reaction. The product was extracted with CH<sub>2</sub>Cl<sub>2</sub>, dried over anhydrous MgSO<sub>4</sub>, and concentrated under vacuum. The crude product was purified by column chromatography, eluting with hexane to give 1 (3.6 g, 90%) as white crystals. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.32–7.29 (m, 4H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.98–6.95 (m, 2H), 6.93–6.89 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  146.47, 144.07, 133.66, 132.05, 130.07, 125.03, 124.74, 114.82, 20.98. HRMS (FAB): calcd for C<sub>19</sub>H<sub>15</sub>Br<sub>2</sub>N, 414.9571 (M<sup>+</sup>); obsd, 414.9551.

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dibu-tylfluorene (2). To a solution of 2,7-dibromo-9,9-dioctylfluorene (10.0 g, 23.0 mmol) in THF (400 mL) at -78 °C was slowly



Scheme 1

added, by syringe, n-butyllithium (1.6 M in hexane, 31.7 mL, 50.7 mmol). The mixture was stirred at -78 °C for 1 h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11.4 mL, 55.8 mmol) was rapidly added to the solution, and the resulting mixture was warmed to room temperature and stirred for 24 h. After reaction, the mixture was poured into water and extracted with ether. The organic extracts were washed with brine and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed by rotary evaporation, and the residue was purified by column chromatography, using hexane- $CH_2Cl_2$  (10 : 1) as the eluent, to afford 2 (6.5 g, 53%) as white crystals. <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.78 (d, J = 8.0 Hz, 2H), 7.72–7.69 (t, J = 7.6 Hz, 4H), 2.02-1.98 (m, 4H), 1.38 (s, 24H), 1.07-1.01 (m, 4H), 0.63 (t, J = 7.2 Hz, 6H), 0.56–0.50 (m, 4H);  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ 150.24, 143.73, 139.49, 128.74, 119.26, 83.69, 55.15, 40.10, 25.93, 25.05, 23.06, 13.91; HRFAB m/z 530.3726, calcd for C33H48B2O4 530.3739.

**Octan-2-ylbenzene** (3). *n*-Hexylmagnesium bromide was prepared as follows: to Mg (4.40 g, 184 mmol) was added a small portion of *n*-hexyl bromide (8.70 g, 53.0 mmol) in ether (150 mL) to initiate the reaction. After initiation, an additional amount of *n*-hexyl bromide (20.0 g, 122 mmol) in ether (300 mL) was added dropwise. The solution was heated at reflux for 2 h.

To a solution of acetophenone (20.0 g, 166 mmol) in ether (200 mL) at -78 °C was added the freshly prepared n-hexylmagnesium bromide and stirred for 12 h at room temperature. The reaction was quenched by addition of diluted HCl, and the product was extracted with CH2Cl2 several times. The collected organic layer was dried over anhydrous MgSO4 and concentrated under vacuum to provide a mixture (crude alcohol and acetophenone, 31.2 g). The mixture was heated with stirring at 130 °C for 2 day to give dehydration product. Chromatography on silica gel, using hexanes as the eluent, gave a 2-substituted and 3-substituted alkene mixture (21.6 g, 115 mmol). Catalytic hydrogenation of the alkene mixture (21.6 g, 115 mmol) in methanol (380 mL), using 10% Pd/C catalyst (0.3 g) under atmospheric hydrogen for 48 h gave alkane crude product that was further purified by chromatography on silica gel, using hexane as the eluent to get 3 as colorless liquid (18.6 g, 59% in 3 steps). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.26-7.30 (m, 2H), 7.15-7.18 (m, 3H), 2.65-2.70 (m, 1H), 1.54-1.59 (m, 2H), 1.23-1.29 (m, 11H), 0.87 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ 147.45, 127.84, 126.60, 125.34, 40.21, 38.74, 32.13, 29.75, 28.05, 23.06, 22.72, 14.55; MS (EI) 190 (M<sup>+</sup>); HRMS (ESI) calcd for C<sub>14</sub>H<sub>22</sub> 190.1722 (M<sup>+</sup>), obsd 190.1723.

**1-Nitro-4-(octan-2-yl)benzene (4).** A mixture of concentrated nitric acid (46 mL, 65%, density: 1.40 g mL<sup>-1</sup>, 0.67 mmol) and sulfuric acid (30 mL, 98%, density: 1.84 g mL<sup>-1</sup>, 0.14 mmol) was added slowly to **3** (80 g, 0.42 mmol) with stirring at 0 °C (ice cooling) for 30 min, The mixture was stirred at 30 °C for 4 h, quenched by pouring on crushed ice (0.2 kg), and extracted with toluene ( $200 \times 3$  mL). The combined organic extracts were washed with aqueous NaHCO<sub>3</sub> (5%,  $200 \times 3$  mL) and distilled water (500 mL). The collected organic extracts were dried over anhydrous MgSO<sub>4</sub> and concentrated under vacuum. The undesired *o*-NO<sub>2</sub> isomer was removed by

chromatography on silica gel, using hexanes–CH<sub>2</sub>Cl<sub>2</sub> (20/1) as the eluent, followed by using hexane–CH<sub>2</sub>Cl<sub>2</sub> (10/1) to give 4 (58.4 g, 59%) as a yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 8.12 (d, J = 6.8 Hz, 2H), 7.30 (d, J = 6.8 Hz, 2H), 2.76–2.82 (m, 1H), 1.54–1.60 (m, 2H), 1.22–1.28 (m, 11H), 0.85 (t, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  155.62, 146.06, 127.63, 123.50, 40.13, 38.14, 31.78, 29.34, 27.61, 22.69, 22.05, 14.17; MS (EI) 235 (M<sup>+</sup>); HRMS (EI) calcd for C<sub>14</sub>H<sub>21</sub>NO<sub>2</sub> 235.1572 (M<sup>+</sup>), obsd 235.1574.

4-(Octan-2-yl)aniline (5). To a stirred suspension of 4 (10.0 g, 43.0 mmol) and 10% Pd-C (2.6 g) in DMF (86 mL) was added anhydrous (NH<sub>4</sub>)<sup>+</sup>(HCO<sub>2</sub>)<sup>-</sup> (33.0 g, 0.5 mol) in a single portion. The resulting solution was stirred at 80 °C for 3 h, extracted with ethyl acetate (200  $\times$  2 mL) and washed with distilled water  $(200 \times 2 \text{ mL})$  to remove any excess  $(NH_4)^+(HCO_2)^-$ . The catalyst was collected by filtration through a celite pad and rinsed with EtOAc (200 mL). The collected organic layer was extracted with saturated NH<sub>4</sub>Cl<sub>(aq)</sub>  $(200 \times 2 \text{ mL})$  to remove DMF. The collected organic filtrate was dried over anhydrous MgSO4 and concentrated under vacuum to give 5 (7.2 g, 83%). <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ):  $\delta$ 6.98 (d, J = 8.4 Hz, 2H), 6.64 (d, J = 8.4 Hz, 2H), 3.53 (bs, 2H), 2.55-2.60 (m, 1H), 1.51-1.56 (m, 2H), 1.19-1.28 (m, 11H), 0.90 (t, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  143.83, 138.01, 127.49, 115.05, 39.07, 38.70, 31.90, 29.49, 27.78, 22.75, 22.61, 14.20; MS (EI) 205 (M<sup>+</sup>); HRMS (EI) calcd for C<sub>14</sub>H<sub>23</sub>N 205.1830 (M<sup>+</sup>), obsd 205.1840.

1-Iodo-4-(octan-2-yl)benzene (6). Sulfuric acid (6.0 mL) was added dropwise to a suspension of 5 (4.0 g, 2.6 mmol) in H<sub>2</sub>O (80 mL) at 0 °C. The reaction mixture was stirred for 30 min. Acetone (30 mL) was then added to the slurry, and stirred for another 15 min. A solution of NaNO<sub>2</sub> (4.0 g, 58 mmol) in water (40 mL) was added dropwise. The resulting solution was stirred for 60 min. A solution of KI (16.0 g, 96.0 mmol) in water (40 mL) was added slowly to the reaction mixture. The resulting dark brown solution was allowed to warm to room temperature overnight. The reaction mixture was extracted with ethyl acetate (3  $\times$  200 mL). The combined organic layers were washed with  $HCl_{(aq)}$  (1 N, 1  $\times$  80 mL) to remove any residual amine. The organic phase was then washed with aqueous solution of  $Na_2S_2O_3$  (20% w/w, 3  $\times$  200 mL), dried, and concentrated under reduced pressure. The resulting residue was purified by chromatography on silica gel, using hexane as the eluent to get 6 as brown liquid (5.8 g, 94%). <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.38 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 8.4 Hz, 2H), 2.58-2.63 (m, 1H), 1.49-1.55 (m, 2H), 1.19-1.28 (m, 11H), 0.85 (t, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  146.72, 131.14, 128.64, 119.16, 39.56, 38.38, 31.87, 29.44, 27.69, 22.76, 22.38, 14.22; MS (EI) 316 (M<sup>+</sup>); HRMS (EI) calcd for C<sub>14</sub>H<sub>21</sub>I 316.0688 (M<sup>+</sup>), obsd 316.0685.

**4-(Octan-2-yl)benzenenitrile (7).** To a mixture of CuCN (10.4 g, 117 mmol), and DMF (290 mL) under argon was added **6** (18.5 g, 58.5 mmol) at room temperature. The mixture was stirred at 150 °C for 48 h and then cooled to room temperature, diluted with  $CH_2Cl_2$  (500 mL), and washed with  $H_2O$  (3 × 200 mL). The organic phase was dried over anhydrous MgSO<sub>4</sub>, concentrated, and the residue was purified by flash chromatography on silica

with hexane–EtOAc (15/1) to give 7 (9.7 g, 77%). <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO):  $\delta$  7.73 (d, J = 8.8 Hz, 2H), 7.40 (d, J = 8.8 Hz, 2H), 2.74–2.80 (m, 1H), 1.51–1.56 (m, 2H), 1.03–1.25 (m, 11H), 0.82 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, d<sub>6</sub>-DMSO):  $\delta$  152.34, 131.41, 127.20, 118.23, 108.25, 38.89, 37.30, 31.20, 28.72, 27.04, 22.14, 21.65, 13.93; MS (EI) 215 (M<sup>+</sup>); HRMS (EI) calcd for C<sub>5</sub>H<sub>21</sub>N 215.1674 (M<sup>+</sup>), obsd 215.1670.

5-(4-Octan-2-ylphenyl)-1H-tetrazole (8). A mixture of 7 (12.9 g, 20.0 mmol), NaN<sub>3</sub> (7.7 g, 0.12 mol), and NH<sub>4</sub>Cl (6.5 g, 0.12 mol) in DMF (60 mL) was heated at 130 °C for 24 h. After cooling to room temperature, the solvent was removed under vacuum. The residue was poured into diluted HCl<sub>(aq)</sub> (1 N, 13 mL). After rinsing with distilled water, the resulting residue was purified by chromatography on silica gel, using ethyl acetate as the eluent to get 8 as white solid (10.6 g, 69%) m.p. 123-124 °C. <sup>1</sup>H NMR (400 MHz,  $d_6$ -DMSO):  $\delta$  7.94 (d, J = 8.4 Hz, 2H), 7.41 (d, J =8.4 Hz, 2H), 3.40 (b, 1H), 2.72-2.77 (m, 1H), 1.52-1.57 (m, 2H), 1.06–1.21 (m, 11H), 0.81 (t, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, d<sub>6</sub>-DMSO): δ 155.06, 150.45, 127.60, 126.83, 121.93, 38.90, 37.58, 31.26, 28.75, 27.12, 22.12, 22.03, 13.98; MS (EI) 258 (M<sup>+</sup>); HRMS (EI) calcd for C<sub>15</sub>H<sub>22</sub>N<sub>4</sub> 258.1844 (M<sup>+</sup>), obsd 258.1846. Anal. calcd for C<sub>15</sub>H<sub>22</sub>N<sub>4</sub>: C, 69.73; H, 8.58; N, 21.69. Found: C, 69.70; H, 8.62; N, 21.92%.

## Synthesis of NOXD

Tetrazole 8 (1.1 g, 4.3 mmol) in pyridine (4 mL) was stirred at room temperature under N2 till a homogenous mixture is formed. To this mixture, naphthalene-1,4-dicarbonyl dichloride<sup>64</sup> (0.5 g, 2.1 mmol) was added slowly. The reaction mixture was heated at 90 °C for 24 h and cooled to room temperature. Major portions of the solvent were removed under vacuum. The precipitated white solid was filtered and washed thoroughly with ethanol, and dried in oven to give NOXD (0.7 g, 53%). m.p. 180-182 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.42-9.45 (m, 2H), 8.38 (s, 2H), 8.13 (d, J = 8.4 Hz, 4H), 7.80–7.83 (m, 2H), 7.39 (d, J = 8 Hz, 4H), 2.78–2.83 (q, J = 7.2 Hz, 2H), 1.60–1.66 (m, 4H), 1.19–1.32 (m, 22H), 0.88 (t, J = 7.2 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 164.15, 163.08, 152.16, 130.19, 128.37, 127.51, 126.87, 126.67, 126.43, 123.75, 120.83, 40.41, 38.49, 32.10, 29.68, 27.98, 23.02, 22.48, 14.54; MS (ESI) 641 (M + 1)<sup>+</sup>; HRMS (ESI) calcd for  $C_{42}H_{48}N_4O_2$  641.3777 (M + 1)<sup>+</sup>, obsd 641.3856. Anal. calcd for C<sub>42</sub>H<sub>48</sub>N<sub>4</sub>O<sub>2</sub>: C, 78.71; H, 7.55; N, 8.74. Found: C, 78.40; H, 7.61; N, 8.85%.

#### Copolymer synthesis of PFT

To a degassed solution of **1** (0.8 g, 1.9 mmol) and **2** (1.0 g, 1.9 mmol) in toluene (15 mL),  $K_2CO_{3(aq)}$  (2.0 M, 7.5 mL), Aliquat 336 (15 mg) and Pd(PPh<sub>3</sub>)<sub>4</sub> (32.7 mg, 1.47 mol%) was added under N<sub>2</sub>. The reaction mixture was heated at 90 °C for 3 days. The mixture was cooled and poured into aqueous MeOH (150 mL, 7 : 3 v/v). The crude polymer was collected and washed with excess MeOH. The crude **PFT** was re-dissolved in CH<sub>2</sub>Cl<sub>2</sub>, and then reprecipitated into MeOH. Finally, **PFT** was collected and washed with acetone for 48 h using a Soxhlet apparatus, and followed by washing with MeOH for 48 h to remove the oligomeric portions. The polymer was finally dried to give **PFT** (0.52

g, 50%).  $M_{\rm w} = 1.14 \times 10^4$  and  $M_{\rm w}/M_{\rm n} = 1.90$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.75–7.47 (m, 12H), 7.23–7.13 (m, 6H), 2.36 (br, 3H), 2.03 (br, 4H), 1.12–1.08 (br, 4H), 0.71–0.59 (br, 10H).

## **Results and discussion**

#### Preparation of NOXD and PFT

Conjugated fluorescent polymer **PFT** was prepared from Suzukicoupling of the corresponding bis(4,4'-bromophenylamine) **1** and bis(boronic ester) **2** (Scheme 1). While the electron-rich triphenylamine unit (with high lying HOMO) could function as an electron donor (D) in the exciplex formation, the presence of the fluorene units would enhance the photoluminescence quantum yield.

**NOXD** was prepared through a multi-step synthesis (Scheme 2). The synthesis was started from nitration of **3** to give **4**, followed by reduction with Pd catalyzed hydrogenation to give **5**. The arylamine **5** was then converted to **6** through diazonium salt intermediate. On treatment of **6** with CuCN, the corresponding nitrile **7** could be obtained in a reasonable yield. Reaction of **7** with NaN<sub>3</sub> gave the corresponding tetrazole **8**, a key intermediate for oxadiazole formation. Finally, two equivalents of **8** were coupled with naphthalene-1,4-diacyloyl dichloride<sup>64</sup> in pyridine at 90 °C to give **NOXD**.

#### Photophysical properties of NOXD and PFT

The UV-vis absorption and fluorescent spectra are shown in Fig. 1, with the data being summarized in Table 1. Bisoxadiazole **NOXD** shows two UV absorption bands peaked at 278 nm and



**Fig. 1** Photophysical properties of **NOXD** and **PFT**: (a) UV-vis absorption (UV), fluorescence (FL), and low-temperature fluorescence spectra (LTFL) of **NOXD**; (b) UV and FL in CHCl<sub>3</sub>, FL and LTFL in THF, and UV and FL in the film state of **PFT**.

Table 1 Photophysical properties of PFT and NOXD

$\lambda_{\max}^{UV}\left(nm\right)$	$\lambda_{\rm max}^{\rm fl},{\rm QY}$	$\lambda_{\max}^{\exp c}$ (nm)
386 378	443, 0.65 436, 0.43	395 399
360 350	423, 0.90 439, —	365 357
	λ <sup>UV</sup> <sub>max</sub> (nm) 386 378 360 350	$\begin{array}{c c} \lambda_{\max}^{UV} (nm) & \lambda_{\max}^{fl} QY \\ \hline 386 & 443, 0.65 \\ 378 & 436, 0.43 \\ 360 & 423, 0.90 \\ 350 & 439, - \end{array}$

<sup>*a*</sup> Comparing against coumarin 1 (ref. 5) ( $\Phi_{\rm PL} = 0.85$ ) in THF solution. <sup>*b*</sup> Comparing against poly(9,9-dioctylfluorene)<sup>5</sup> ( $\Phi_{\rm PL} = 0.55$ ) in thinfilm state. <sup>*c*</sup> Peaked wavelength in the excitation spectrum.

360 nm respectively in THF. Theoretical calculations reveal that the  $S_1 \leftarrow S_0$  band peaked at 360 nm involves  $\pi$ - $\pi^*$  electronic excitation from the HOMO to the LUMO (see ESI†). On the other hand, the band peaked at 278 nm involves more complicated state mixing. The fluorescent emission peaked at 423 nm shows moderate Stokes shift of 64 nm. The low temperature fluorescent spectrum at 77 K in THF glass is almost identical, with only small pattern change, in comparison to that in THF at room temperature. This result indicates that the structural relaxation of **NOXD** after photo-excitation in the S<sub>1</sub> is small.

Conjugated polymer **PFT** shows two absorption bands in CHCl<sub>3</sub>; one peaking at 386 nm and the other peaking at 300 nm. As discussed in previous publications, the absorption band at 386 nm is arising from the fluorene chromophore while the shoulder band peaking at about 300 nm originates from the absorption of the triphenylamine moieties.<sup>5</sup> The UV  $\lambda_{max}$  of the **PFT** film is slightly blue-shifted by about 8 nm to 378 nm. This may be due to the phenomenon of conformational restrictions that prohibit the polymer to align in coplanar conformations and therefore reduce the weight of  $\pi$ -conjugation.

**PFT** shows single strong emission band at 434 nm under UV irradiation in CHCl<sub>3</sub>. However, the photo-emission becomes relatively broad in THF with the emission maximum slightly red-shifted to 443 nm. When **PFT** is frozen in the organic glass at 77 K, photoluminescence shows emission bands peaked at 436 nm with a shoulder at 460 nm. In the film state, fine features with the major emission at 438 nm, a shoulder band at 460 nm, and other bands at 450–520 nm could be observed. This may be due to exciton migration and energy transfer in the solid film that favors the high energy excitons stepping down to the low energy one, leading to emission bands in bathochromic region.

#### **PFT-NOXD** exciplex formation

To examine the exciplex from **PFT–NOXD**, homogeneous film of **PFT–NOXD** (1 : 1) was prepared by spin-coating (600 rpm) of the CHCl<sub>3</sub> solution (**PFT** (2 mg) and **NOXD** (2 mg) in CHCl<sub>3</sub> (1 mL)) onto a piece of ITO glass plate. We adopted an empirical weight ratio of **PFT–NOXD** (1 : 1) because this ratio provides an optimal performance about the thermofluoric phenomenon in latter studies. The emission spectra and excitation spectra of **PFT–NOXD** (1 : 1) were collected by Hitachi F4500 equipped with a film holder for analysis. In addition, the excitation spectra of

**PFT** and **NOXD** in film were also collected as reference for comparison. The emission spectrum of the **PFT-NOXD** (1 : 1) film was obtained by UV excitation at  $\lambda = 365$  nm. The excitation spectrum of the **PFT-NOXD** (1 : 1) film was obtained by monitoring the emission intensity at  $\lambda = 563$  nm. For the blue light emitting **NOXD** and **PFT**, the excitation spectrum of the neat films was monitored at 444 nm respectively.

Under UV irradiation at 365 nm, the photoluminescent spectrum of **PFT-NOXD** (1 : 1) in Fig. 2 shows broad emission, with the  $\lambda_{max}$  appearing at 564 nm (blue line). This is a typical exciplex emission, which is red-shifted from that of **PFT** ( $\lambda_{max}^{\rm fl}$  at 436 nm) or **NOXD** ( $\lambda_{max}^{\rm fl}$  at 439 nm). The exciplex formation was further confirmed with time-resolved measurements of the photoluminescence, in which the data are well-fitted by two single-exponential decay components, rendering lifetimes of  $\tau_1 \sim 18.3$  ns and  $\tau_2 \sim 80.0$  ns. Note that the remarkably long lifetime of  $\tau_2 \sim 80.0$  ns (64.5%) is comparable to that of the other oxadiazole-carbazole exciplex systems.<sup>60</sup>

The highest occupied molecular orbital (HOMO) of **PFT** and the lowest unoccupied molecular orbital (LUMO) of **NOXD** were evaluated respectively by cyclic voltammetry (CV). The oxidation half potential ( $E_{1/2}^{\text{ox}}$ ) of **PFT** was found to be 0.87 V, corresponding to the HOMO of -5.12 eV. On the other hand, the reduction half potential ( $E_{1/2}^{\text{red}}$ ) of **NOXD** was found to be -1.20 V, corresponding to the LUMO of -3.02 eV. The HOMO (**PFT**)– LUMO (**NOXD**) gap of 2.1 eV is consistent with the yellowish exciplex emission at  $\lambda_{\text{max}} = 564$  nm (2.2 eV). The small deviation may arise from the solvent and electrolyte effects in the CV analysis.

To further understand the exciplex formation mechanisms, excitation spectra of the above samples were examined (Fig. 2). For **NOXD**, the excitation spectrum shows two peaks at 300 and 350 nm. On the other hand, the excitation spectrum of **PFT** exhibits broad signals starting from 300 nm, with the band peaked at 350 and 400 nm, and extending to over 430 nm. However, the signal at around 300 nm is weak. These spectral differences allow us to differentiate which absorptions are important for the exciplex emission. For thin film of **PFT–NOXD**, the excitation spectrum covers the region from 300–400 nm with the spectral pattern similar to the overlay of the excitation spectra of **NOXD** and **PFT**, indicating that both



Fig. 2 Excitation spectra of NOXD (monitored at 444 nm), PFT (monitored at 444 nm), and emission and excitation spectra PFT–NOXD blend (monitored at 563 nm).

absorptions of **NOXD** and **PFT** have significant contribution to the exciplex emission at 563 nm.

The emission spectrum of the PFT/NOXD film evolves with time. After being allowed to stand at room temperature for 72 h, the emission intensity at 444 nm gradually arouse as shown in Fig. 3. This result indicates that the homogeneous blend, initially obtained by the spin-coating method, is morphologically unstable; phase separation might gradually occur to lead to domains of aggregates. Within these regions, NOXD and PFT are separated so that blue emission from NOXD or PFT might occur. Therefore, dual emissions at 444 and 561 nm were recorded. It is noteworthy to mention that differences in the excitation spectra for 444 nm and 520 nm could be found; the excitation spectrum of 300 and 366 nm for 444 nm is well matched with that of NOXD, indicating that NOXD were segregated from the homogeneous film and become the major source of the blue light emission at 444 nm. On the other hand, the emission spectrum of the exciplex contains two components from the absorption of NOXD and PFT.

## PFT-NOXD exciplex formation in polymer matrix

To evaluate the behavior of the exciplex in polymeric hosts, aprotic polymers spanning a wide range of polarity, including polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(acrylonitrile-*co*-methyl acrylate) (acrylonitrile 94%) (P(AN-*co*-MA)), were adopted as the host matrix for **PFT** and **NOXD**. In a typical procedure, the polymeric host and the fluorescent components in CHCl<sub>3</sub> were stirred for 4 h. The solution was spin-coated (600 rpm) onto a piece of ITO glass that has UV cutoff at 300 nm. The plate was then dried at 50 °C for 30 min and at 120 °C for 10 min, during the course of which the polymer film will be solidified.

When **PFT** and **NOXD** were blended into relatively non-polar PS and PMMA matrix, the major emission occurred at the range of 400–500 nm that is corresponding to the independent emission from **PFT** and **NOXD** (Fig. 4). Small shoulder at 560 nm is assigned to the **PFT-NOXD** exciplex emission. These results indicated that **PFT** and **NOXD** might be phase separated and isolated by the host matrix, as illustrated in Fig. 5 in the phase-



Fig. 3 The photophysical properties of the film of PFT-NOXD blend after standing at ambient temperature for 72 h.



Fig. 4 Photoluminescence of PFT–NOXD films: in neat PFT–NOXD; in PMMA– PFT–NOXD (5 : 1 : 1); in PS–PFT–NOXD (5 : 1 : 1); in P(AN-co-MA)–PFT–NOXD (5 : 1 : 1).



Fig. 5 Schematic diagram for PFT–NOXD. Phase-separation model and the PFT– NOXD entanglement models for PFT and NOXD in polymeric hosts. Exciplex emission from the PFT–NOXD pairs is expected.

separation model, and hence the exciplex formation was retarded. On the other hand, when **PFT** and **NOXD** were blended into P(AN-*co*-MA) matrix, dual emissions at 450 nm and 550 nm were observed. The stronger emission at 550 nm clearly arouse from the exciplex emission; this result implies that certain extents of **PFT** and **NOXD** were entangled in P(AN-*co*-MA), allowing the exciplex formation to be effective under radiation. As illustrated in the **PFT**-**NOXD** entanglement model in Fig. 5, the  $\pi$ - $\pi$  interactions between **PFT** and **NOXD** may indeed benefit their aggregation in a polar media. This will enhance the probability of exciplex formation under photo-excitation.

# Thermofluoric behavior of PFT-NOXD exciplex formation in P(AN-*co*-MA) matrix

It is noteworthy to mention that when the **PFT/NOXD**/P(AN-*co*-MA) (1 : 1 : 10) film was heated at 140 °C for 2 min, the exciplex emission intensity at 550 nm was significantly enhanced. This may be due to the fact that more **NOXD** molecules diffuse from the **NOXD** aggregates into the polymer matrix at high temperature. This would increase the chances of **PFT–NOXD** exciplex formation. Noteworthy to mention is that this exciplex emission could also be reversed back slowly when cooling at ambient temperature. The evolution of the photoluminescent spectra



Fig. 6 The evolution of the photoluminescent spectra of the 140  $^\circ$ C annealed PFT/NOXD/P(AN-*co*-MA) with time.

with time were recorded as shown in Fig. 6. The exciplex emission intensity dropped back to 1/3 of the initial intensity after 20 h of relaxation.

# The thermofluoric phenomenon of PFT-NOXD exciplex formation in a cross-linked poly(epoxy) matrix

The photoluminescent behavior of fluorescence compounds in a cross-linked matrix is also interesting target to study. In the following study, we adopted commercially available epoxy glue, including an epoxy resin and a polymercaptan hardener (Chern-Young 0367, PowerBon 2996, or Sellery 09-652) as the basic material for the cross-linked matrix. In a typical procedure, epoxy resin with polymercaptan hardener (PEPM, 1:1), fluorescent components and chloroform were mixed and stirred for 4 h. The solution was spin-coated (600 rpm) onto a piece of ITO glass plate that has UV cut-off at 300 nm. The plate was then dried at 50 °C for 30 min and at 120 °C for 10 min, during the course of which the epoxy-glue could be solidified and reached to the full strength. The absorption behavior and the fluorescent properties of the plate were recorded. After then, the plate was heated to 160-170  $^\circ \mathrm{C}$  and then cooled in the ambient temperature. The spectral changes were monitored by photoluminescence, and excitation spectrum measurements at specific time.

When **NOXD** and **PFT** were blended into the PEPM matrix, the fluorescence behavior is highly dependent on the mixing ratio. After the cross-linking treatment at 120 °C, all the PEPM films exhibited blue fluorescence under UV irradiation. The result indicated that at the beginning the **NOXD** and **PFT** are phaseseparated into the PEPM matrix. Upon thermal annealing at 160– 170 °C for 2 min under nitrogen atmosphere, the **NOXD–PFT–** PEPM (1 : 1 : 10) turned into yellow emission under UV irradiation. The yellow emission status maintained even after 24 h. On the other hand, when the film of **NOXD–PFT–**PEPM (1 : 1 : 20) was annealed under the same conditions, the intensity of the yellowish photoluminescence decayed with time (Fig. 7). However, the yellowish emission could be resumed if the plate was re-annealed again at 160–170 °C for 2 min. The emission color change could be repeated for several thermal annealing–





Fig. 7 The thermofluoric behavior of the NOXD–PFT–PEPM (1 : 1 : 20) film: (a) before thermal annealing; (b) after thermal annealing at 170 °C; (c) after standing at ambient temperature for about 60 min.

cooling cycles. However, if the mixing ratio of **NOXD-PFT**-PEPM was reduced to 1 : 1 : 40, blue emission maintained even after thermal annealing, indicating that the concentrations of **NOXD** and **PFT** are too low to generate the exciplex.

The spectral changes of NOXD-PFT-PEPM (1:1:20) with time were recorded and shown in Fig. 8a. While the yellow emission gradually (560 nm) faded away, the blue emission intensity increased. The excitation spectra about the bands at 449 nm and at 560 nm are shown in Fig. 8b. Again, while the emission band at 560 nm is strongly related to the PFT absorption, the blue emission band at 449 nm corresponds to the NOXD emission. These results are governed by the equilibrium between the PFT-NOXD entanglement state and the PFT-NOXD phase-separation state. At room temperature, NOXD crystallized from PEPM matrix. The concentration of NOXD in the PEPM matrix was below the critical concentration so that exciplex emission could not be observed. When the film was annealed at 160-170 °C, the high temperature environment allowed the NOXD molecules to be segregated from the crystalline regions. Increasing of the concentration of NOXD in the matrix led to higher probability of exciplex formation with PFT. Under this situation, the yellow emission increased and the blue emission decreased. After then, when the plate was cooled at ambient temperature, the NOXD might gradually diffuse back to the crystalline regions; this reverse process led to decrease of the yellow emission and enhancement of the blue emission.



**Fig. 8** Thermofluoric studies of the **NOXD–PFT**–PEPM (1 : 1 : 20) film: (a) photoluminescence spectral change of **NOXD–PFT**–PEPM (1 : 1 : 20) with time. (b) Excitation spectrum of the **NOXD–PFT**–PEPM (1 : 1 : 20) film after thermal annealing at 170 °C.



Fig. 9 Comparison of the DSC analyses: (a) for NOXD:PFT:PEPM; (b) for the PEPM:NOXD films against PEPM.

To further understand the details about the temperaturedependent fluorescence changes, the **NOXD-PFT-PEPM** films were examined by differential scan calorimetry (DSC). The results are summarized in Fig. 9. In the absence of **NOXD-PFT**, the PEPM does not show any  $T_g$  in this temperature region (Fig. 9a). **NOXD** alone showed a sharp melting point at 176 °C, indicating that **NOXD** crystallized in solid film (Fig. 9b). When the film of **NOXD-PFT-PEPM** (1 : 1 : 20) was subjected to DSC analysis, a small transition was observed at 167 °C (Fig. 9a) that is consistent with the aforementioned thermofluoric temperature. Since neither **PFT** nor PEPM shows any transition in the temperature range, we suspect that the transition originates from the melting of **NOXD** crystalline regions.

To further understand this observation, samples of **NOXD** in PEPM were prepared for examination. A flat line was obtained from the sample of **NOXD**-PEPM (1:40), suggesting that **NOXD**-PEPM (1:40) formed a homogeneous film in this formulation (Fig. 9b); no sign about crystallization of **NOXD** from the matrix was evidenced. However, when the fraction of **NOXD** in PEPM increased to (1:30), a small signal peaked at 173 °C was observed. Increasing the amounts of the **NOXD**-PFT component in PEPM led to more intense signal, indicating crystallization of **NOXD** from the matrix becomes more significant. Perhaps due to the donor acceptor interactions, the presence of **PFT** in PEPM would lead to reduction of melting point of **NOXD** from 173 °C in **NOXD**-PEPM (1:20) to 167 °C in **NOXD**-PFT-PEPM (1:1:20).



**Fig. 10** Images of **NOXD–PFT**–PEPM (1 : 1 : 10): (a) cross-polarized microscope; (b) SEM image.

Photoluminescence Response of NOXD:PFT in polymer matrix 443 nm 433 nm 443 nm, 544 nm Non-Polar Polar  $* + (++)_n^* * (++)_v^*$ 

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Microcrystals formed in the matrix could be directly observed by cross-polarized microscope. Fig. 10a shows an image of **NOXD-PFT**-PEPM (1:1:10) under illumination by cross-polarized light. Observation of the dark background suggested that the film of **NOXD-PFT**-PEPM (1:1:10) is mainly homogeneous. However, small bright dots that correspond to the crystalline **NOXD** with varies sizes could be clearly observed.

The film was further explored by using scanning electron microscope, from which sub-micron features could also be observed. Fig. 10b revealed that formation of particles with the size about hundred nanometers are evidenced.

## Conclusions

The use of exciplex formation in polymer blend has played an important role in modern organic electronic applications.65 In the present study, we reported the exciplex formation behavior of NOXD and PFT in various polymer matrix. Our aforementioned observations are summarized in Scheme 3: when NOXD and PFT were mixed with non-polar polymers such as polystyrene and PMMA, perhaps due to poor miscibility, NOXD and PFT were separated so that the exciplex emission could not be observed. On the other hand, dual-emissions were observed when NOXD and PFT were blended into P(AN-co-MA). This observation indicated that heterostructures exist in P(AN-co-MA) matrix; when the blue emission arises from isolated NOXD or PFT, the yellow emission arises from the exciplex of NOXD-**PFT.** The equilibrium could be altered so that the yellow exciplex emission was enhanced by increasing temperature. This process was found to be reversible, even though the process was slow in the highly viscous polymer matrix. Similar thermofluoric phenomenon were observed in cross-linked poly(epoxy) matrix, and the process can be recyclable for few times. In summary, we have successfully demonstrated the thermofluoric behavior of NOXD-PFT in polymeric matrix. By controlling the exciplex formation through phase-separation, we can create thermofluoric film with blue-yellowish switching mechanism at specific temperature.

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