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Flexible and highly fluorescent aromatic polyimide: design, synthesis, properties, and mechanism<sup>†</sup>

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To develop high-performance flexible fluorescent aromatic polyimides and to have a deeper insight into the fluorescence mechanism, two diamine monomers **PyDA** and **TzDA** with similar chemical structures but totally different electronic effects, were designed and synthesized. **PyDA** bears an electron-donor pyrrole group while **TzDA** bears an electron-acceptor 1,2,4-triazole group. The resulting aromatic polyimide **TzODPI** containing the triazole group showed bright green photoluminescence with a high quantum yield of up to 61% in solution and 13% in the film state. However, fluorescence was totally quenched in the pyrrole-containing polyimide **PyODPI**. The completely different phenomena were systematically elucidated with the aid of molecular simulations. Theoretical calculations for the molecular orbital distribution, oscillator strength, and the electron transition process between the ground state and excited state of model molecules were applied to clarify the fluorescence mechanism. Highly fluorescent aromatic polyimides can be obtained by appropriate control of the intra-molecular charge-transfer effects between the diamine and dianhydride moieties, and this demonstrates a simple strategy to develop wholly aromatic polyimides with high fluorescence for potential applications in the field of flexible displays.

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### Introduction

Flexible displays bring revolutionary changes to display modes, greatly expand display space forms, and are also the key technical requirements in the fields of wearable devices, smart phones, and other emerging displays.<sup>1</sup> Therefore, critical technologies and new materials in flexible displays have attracted increasing attention and have been rapidly developed recently. Among them, interest in polymeric light-emitting materials is growing in this most crucial field due to their flexible nature and facile film formation by spin coating<sup>2</sup> or inkjet printing.<sup>3</sup> Conjugated polymers, such as poly(*p*-phenylene vinylene),<sup>4</sup> poly(*p*-phenylene),<sup>5</sup> poly(thiophene)<sup>6</sup> and polyfluorene,<sup>7</sup> have become important light-emitting materials in large-area display devices, typically known as Polymer Light-Emitting Diodes (PLEDs), showing great potential in advanced flexible displays. However, the solubility, thermal stability, dimensional stability at high temperature, and photochemical stability of these conjugated polymers are critical problems,

which seriously restrict their applications and the development of PLEDs. These problems urgently need to be solved to meet the advancing fabrication processes in modern electronic and photonic industries, and to maintain a proper lifetime of the devices. Meanwhile, the development of a new generation of high-performance light-emitting polymeric materials is another efficient way to go.

Wholly aromatic polyimides (Ar-PIs), the well-established high-performance engineering polymers, possess excellent thermal stability, chemical and radiation resistance, mechanical strength and flexibility.<sup>8</sup> These properties are of significance in modern device fabrication processes for the requirement of a high glass transition temperature. Though Ar-PIs have great advantages in light-emitting device applications over conventional conjugated polymers, few attempts have been made to use them as light-emitting materials because the traditional polyimide is usually of non-luminance or luminance with a pretty low photoluminescence efficiency.

In order to make an improvement to the luminescence efficiency of Ar-PIs, fluorescent chromophores have been introduced into the polyimide backbone or used as the pendant groups.<sup>9</sup> However, strong  $\pi$ - $\pi$  interactions occurred between chromophores, and the strong intermolecular and intramolecular charge transfer between the occupied and unoccupied molecular orbitals on the diamine and dianhydride moieties respectively, caused unavoidable fluorescence quenching. To overcome this problem, aliphatic monomers were utilized.<sup>10</sup> These non-conjugated and low electron-donating moieties could boost the fluorescence intensity by effectively preventing

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PCFM Lab, GD HPPC Lab, Guangdong Engineering Technology Research Centre for High-performance Organic and Polymer Photoelectric Functional Films, State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, China. E-mail: ceszy@mail.sysu.edu.cn; Fax: +86 20 84112222; Tel: +86 20 84112222 † Electronic supplementary information (ESI) available: Experimental section, NMR spectra of the monomers and the polyimides; FTIR spectra, WAXD patterns, thermal properties, transmittance and absorption behavior of the polyimide films; cyclic voltammograms of polyimide solutions; chemical structures of model basic units. See DOI: 10.1039/c6tc03889a

#### Paper

charge-transfer-complex (CTC) formations, though, the thermal stability as well as the HOMO level decreased simultaneously, leading to instability of the devices, a mismatch in the work function of the cathode ITO and dielectric breakdowns.<sup>11</sup> Recent success has been gained by the introduction of triphenylamine building blocks to the polyimide backbone. It has been found to be an impactful way to develop wholly aromatic polyimides with a high fluorescence quantum yield,<sup>12</sup> which showed attractive potential applications in up-to-date flexible displays. However, the fluorescence mechanism of aromatic polyimide remains unknown and studies on this would be very important to guide the development of these materials, which may be the next generation of high-performance flexible light-emitting materials.

It is well-known that the charge-transfer (CT) character has a great impact on the photophysics, photochemistry and optical properties of polyimides, especially in fully aromatic polyimide systems.<sup>13</sup> Previous reports revealed that this character will quench the fluorescence, hence research rarely focuses on adjusting the CT effect to improve the quantum efficiency of Ar-PIs. However, it should be interesting to know if one could develop high efficiency fluorescent Ar-PIs by appropriate control the electron push-pull effect between the diamine moieties and the dianhydride moieties.

In this work, two diamine monomers **PyDA** and **TzDA** with similar chemical structures but totally different electronic effects were designed and synthesized (Scheme 1). **PyDA** bears an electron-donor pyrrole group while **TzDA** bears an electronacceptor 1,2,4-triazole group. Both of them contain a large nonplanar and non-polar tetraphenylmethane side group to avoid



Scheme 1 Synthesis routes of diamine monomers and their 3D structures.

the intermolecular interactions as far as possible. In this case, when these diamines were introduced into the polyimide backbone by reacting with the same dianhydride ODPA, the intramolecular charge-transfer (CT) interaction between the diamine and dianhydride became the main interaction in these two aromatic polyimide systems, and the electronic effect of the diamines played the primary role in the fluorescence properties, which was expected to regulate the charge-transfer strength and the donor-acceptor interaction intensity along the polymer backbone. Totally different fluorescence behavior was found for the resultant polymers. The aromatic polyimide containing the triazole group, TzODPI, showed bright green photoluminescence with a high quantum yield ( $\Phi_{\rm PL}$ ) of up to 61% in solution and 13% in the film state. However, the fluorescence was totally quenched in the pyrrole-containing polyimide PyODPI. The completely different phenomena were systematically elucidated with the aid of molecular simulations. Theoretical calculations for the molecular orbital distribution, oscillator strength, and the electron transition process between the ground state and excited state of model molecules were applied to clarify the fluorescence mechanism. The results indicate that the electron deficiency in diamine moieties could boost the photoluminescence efficiency by effectively suppressing the charge-transfer effects that weaken the fluorescence.

### **Results and discussion**

# Synthesis and characterization of the diamine monomers and polyimides

The diamine monomer **PyDA** was prepared according to our previous work.<sup>14</sup> **TzDA** was synthesized using the multi-step synthetic route shown in Scheme 1. Mass spectra, elemental analysis, IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopic techniques were applied to confirm that the intermediates and the diaminocompounds fully matched the proposed structures, as shown in the experimental section and Fig. S1 and S2 (ESI<sup>†</sup>). The proton resonance signals at around 5.05 ppm for diamine **PyDA** and 5.48 ppm for diamine **TzDA**, and the infrared absorptions at about 3450 cm<sup>-1</sup> and 3340 cm<sup>-1</sup>, which are characteristic of amino groups, indicate the successful preparation of the diamines. It is worthy to be mentioned that the amino protons of diamine **TzDA** undergo resonance at a much higher frequency (5.48 ppm)



**Fig. 1** <sup>1</sup>H NMR spectra of the diamines (a) **TzDA** and (b) **PyDA**.

than that of the diamine PyDA (5.05 ppm), as detailed in Fig. 1. Since the spatial structures of the two monomers are almost the same, the different proton resonance signals could be attributed to the distinct electron push-pull effect of the molecule core structures. The 1,2,4-triazole group, which is characterized as an electron acceptor due to the strong electro-negativity of the two sp<sup>2</sup>-hybridized nitrogen atoms, effectively reduces the electron density on the amino groups of diamine TzDA, causing a resonance shift to a higher frequency field. The absence of two nitrogen atoms, in contrast, brings the amino proton signals of diamine PyDA to a lower frequency field. We consider it an important indication because if such diamine monomers were polymerized with the same dianhydride respectively, the difference in the electron push-pull ability for the diamine moieties would certainly make an impact on the intramolecular charge-transfer characteristics of the polymers.

The optical properties of the diamines were also characterized using the absorption and photoluminescence spectra in both the solution and solid state. The results are displayed in Fig. 2 and summarized in Table 1. In tetrahydrofuran (THF) solution, **PyDA** and **TzDA** had absorption peaks at 307 nm and 303 nm, respectively. When excited at the wavelength of the maximum excitation peak ( $\lambda_{max}^{ex}$ ), 312 nm, **TzDA** showed an intense emission peak at 404 nm, with a photoluminescence efficiency of up to 29%. While, **PyDA** had a weaker and broader emission peak at 457 nm when excited at 317 nm, with a  $\Phi_{PL}$ value of 4.6%, which was much lower than that of **TzDA**. As for the solid state, the emission peak was blue-shifted to 398 nm and the  $\Phi_{PL}$  dropped to 14%, indicating that the aggregation-



Fig. 2 The optical spectra of the diamine monomers in (a) THF solution and (b) solid state.

Table 1 Optical properties of the diamine monomers

Diamine	In solu	ition <sup>a</sup>		Solid state			
	$\lambda_{\max}^{abs}$ (nm)	$\lambda_{\max}^{ex}$ (nm)	$\lambda_{\max}^{em}$ (nm)	$\Phi_{ m PL}\ (\%)$	$\lambda_{\max}^{ex}$ (nm)	$\lambda_{\max}^{em}$ (nm)	$\Phi_{ m PL}$ (%)
PyDA	307	317	457	4.6	381	413	5.5
TzDA	303	312	404	29	355	398	14

<sup>*a*</sup> Measured in THF solution ( $10^{-5}$  M).



Scheme 2 Synthesis of the polyimides PyODPI and TzODPI.

caused fluorescence weakening effect occurred in **TzDA**. However, **PyDA** maintained its  $\Phi_{\rm PL}$  of 5.5% in the solid state, and underwent a blue-shift to 413 nm.

As shown in Scheme 2, the polyimide films were prepared by the reaction between the as-synthesized diamine and the commercial 4,4-oxydiphthalic anhydride (ODPA), using conventional two-step polymerization. The mix of the monomers in DMF produced a viscous precursor poly(amic acid) solution, which was subsequently cast on a clean dry glass plate followed by programmed thermal imidization. The resulting flexible and tough PI films were approximately 35 µm thick. The degree of polymerization was estimated by inherent viscosity  $(\eta_{inh})$  instead of gel permeation chromatography (GPC), because of the disparity in the structures of polar polyimide and nonpolar polystyrene, standardly utilized in GPC. It is more common to evaluate polyimide molecular weights using viscometry, as a higher viscosity generally indicates a higher degree of polymerization. The  $\eta_{inh}$  values measured using an Ostwald viscometer were 0.91 dL  $g^{-1}$  and 0.64 dL  $g^{-1}$  for PyODPI and TZODPI, respectively. As shown in Fig. S3 (ESI<sup>+</sup>), the infrared absorption bands at 1778  $\text{cm}^{-1}$  (asymmetric C=O stretching) and 1719 cm<sup>-1</sup> (symmetric C=O stretching) correspond to the imide ring, while no amide bands nor carboxyl absorption peaks are found. Furthermore, the amide and carboxyl proton signals disappear in the <sup>1</sup>H NMR spectra (Fig. S4, ESI<sup>+</sup>), indicating that the precursor poly(amic acid) was fully imidized. Fig. S5 (ESI<sup>+</sup>) presents the wide-angle X-ray diffraction patterns of both the polyimide films, which suggest the amorphous nature of these two films.

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	$T_{-a}^{a}$	$T_{-}^{b}$	$T_{-}^{c}$	$CTE^d$	$T_{\rm d}^{e} (^{\circ} {\rm C})$	)	Char vield-
PI	(°C)	(°C)	(°C)	$(\mu m \ m^{-1} \ ^{\circ}C^{-1})$	5 wt%	10 wt%	(wt%)
PyODPI	258	282	242	45	559	584	70
TzODPI	285	310	270	42	491	507	47

<sup>*a*</sup> The transition onset temperature, measured using DSC at a heating rate of 10 °C min<sup>-1</sup> under nitrogen. <sup>*b*</sup> Glass transition temperature, measured using DMA at a heating rate of 5 °C min<sup>-1</sup>. <sup>*c*</sup> Softening temperature, measured using TMA at a heating rate of 10 °C min<sup>-1</sup>. <sup>*d*</sup> Coefficient of thermal expansion, calculated using TMA curves (50 to 200 °C). <sup>*e*</sup> Decomposition temperature, measured using TGA at a heating rate of 20 °C min<sup>-1</sup> under nitrogen. <sup>*f*</sup> Residual weight percentage at 900 °C under nitrogen.

#### Thermal properties and solubility of the polyimides

Herein, TGA, DSC, DMA and TMA were applied to investigate the thermal properties of the polyimides. The results are shown in Table 2 and Fig. S6 (ESI<sup>†</sup>). The triazole-containing polyimide TzODPI possessed a much higher glass transition temperature  $(T_{\rm g})$  at 285 °C using the DSC measurement, or 310 °C using DMA, while the  $T_g$  for the pyrrole-containing polyimide **PyODPI** was lower and was observed at 258 °C using DSC, or 282 °C using DMA, suggesting a higher rigidity of the TzODPI polymer backbone or a stronger intermolecular interaction because of the existence of the triazole groups. Due to this property, the polyimide TzODPI film also showed relatively higher dimensional stability, with a coefficient of thermal expansion (CTE) of 42  $\mu$ m m<sup>-1</sup> °C<sup>-1</sup> in the recorded range of 50–200 °C, than that of the **PyODPI** film, which had a CTE of 45  $\mu$ m m<sup>-1</sup> °C<sup>-1</sup>. The softening temperatures  $(T_s)$  gauged by TMA, that were 270 °C for TzODPI and 242 °C for PyODPI, proved the stability order as well. Considering the similarity of the chemical structure for both polyimide units, the introduction of 1,2,4-triazole groups results in a more rigid polymer chain and a stronger intermolecular interaction thus leading to a higher dimensional and thermal stability. Between the char yields of the polyimides obtained from the TGA curves at 900 °C, the PyODPI ranked higher, which is coincident with its higher carbon content.

Both the as-prepared polyimides showed not only good thermal stability, but also desirable solubility in common organic solvents. The solubility test was carried out by adding 10 mg of polyimide film into 1 mL of solvent. The results are summarized in Table 3. They could be well dissolved even in the weakly polar solvent  $CH_2Cl_2$  and in some common polar solvents like NMP at room temperature, and DMSO, DMF, DMAc and *m*-cresol at about 90 °C. The improved solubility mainly results from the bulky triphenyl methyl side groups as well as the contorted polymer backbone

Table 3	Solubility of the polyimides							
PI	<i>m</i> -Cresol	DMSO	DMF	DMAc	NMP	THF	$CH_2Cl_2$	
PyODPI TzODPI	+ +	+ +	+- +-	+- +-	++ ++	+ 	++ +	

"++", soluble at room temperature; "+", partially soluble at room temperature or soluble when heated at 90 °C; "+-", partially soluble when heated at 90 °C; "--", insoluble when heated at 90 °C. "--", insoluble at room temperature.

Table 4 Optical properties of the polyimides

	In solution <sup><i>a</i></sup>				Film state					
PI	$\lambda_{onset}^{abs}$ (nm)	$\lambda_{max}^{abs}\ (nm)$	$\lambda_{\max}^{em}$ (nm)	$\left( \substack{\Phi_{\mathrm{PL}}^{b} \\ (\%) } \right)^{b}$	$\lambda_0^c$ (nm)	$\lambda_{onset}^{abs}$ (nm)	$\lambda_{\max}^{ex}$ (nm)	$\lambda_{\max}^{em}$ (nm)	$\tau^d$ (ns)	$\left( \substack{\Phi_{\mathrm{PL}}^{b} \\ (\%) \end{array} \right)$
PyODPI TzODPI	377 339	329 288	N.D. 486	N.D. 61	419 372	394 350	N.D. <sup>e</sup> 439	N.D. 536	 13	N.D. 13

<sup>*a*</sup> Measured in dilute solution of  $CH_2Cl_2$  (*ca.*  $2 \times 10^{-2}$  mg mL<sup>-1</sup>). <sup>*b*</sup> Photoluminescence quantum yield determined using a calibrated integrating sphere. <sup>*c*</sup> Cut off wavelength and 80% transmittance wavelength. <sup>*d*</sup> Photoluminescence lifetime, not available for **PyODPI**. <sup>*e*</sup> Not detected.

when the flexible diphenyl ether structure in the dianhydride moieties is applied.

#### Optical properties of the polyimides

The optical properties of the polyimides were studied in both the solid state and the solution state by UV-vis and photoluminescence spectroscopy, and the results are listed in Table 4.

As shown in Fig. 3a and b, and Fig. S7 and S8 (ESI<sup>+</sup>), both of the polyimide films are tough and flexible, and exhibit good transparency in the visible region. The cutoff wavelength ( $\lambda_0$ ), the maximum absorption wavelength ( $\lambda_{max}^{abs}$ ), and the absorption onset wavelength ( $\lambda_{onset}^{abs}$ ) of the triazole-containing **TzODPI** thin film were 372 nm, 275 nm and 350 nm, respectively, which were much shorter than that of the pyrrole-containing PyODPI film, which showed 419 nm for  $\lambda_0$ , 332 nm for  $\lambda_{max}^{abs}$ , and 394 nm for  $\lambda_{onset}^{abs}$ . The  $\lambda_{max}^{abs}$  and  $\lambda_{onset}^{abs}$  values of the **TzODPI** film are obviously blue-shifted by about 57 nm and 44 nm when compared with the PyODPI film. Also, one can notice a subtle shoulder peak at around 307 nm in the TzODPI film, which indicates that certain intermolecular interactions exist because of the strongly polar 1,2,4-triazole moieties. It is well-known that the coloration of polyimide originates from the charge-transfer-complex (CTC) formation, which is greatly influenced by the intra- and intermolecular charge-transfer (CT) interactions. The stronger the CT interactions are, the deeper the color the polyimide has, and vice versa. Since both of the chemical structures of PyODPI and TzODPI have bulky triphenyl methyl side groups, the intermolecular CT interaction could be alleviated, resulting in a



Fig. 3 Photographs of the flexible polyimide films **PyODPI** and **TzODPI** under sunlight (a and b) and 365 nm UV light (c and d).



Fig. 4 The mechanistic charge-transfer intramolecular structure of **TzODPI** and **PyODPI**.

lighter color than conventional polyimides. On the other hand, when taking into account the intramolecular CT interaction (Fig. 4), for TzODPI, the electron acceptor triazole groups may help to weaken the intramolecular CT interaction, giving shorter  $\lambda_0$ ,  $\lambda_{max}^{abs}$  and  $\lambda_{onset}^{abs}$ , as well as a lighter color of the film. The alleviated CT interaction in TzODPI could be identified more clearly by the absorption behavior of the polyimides in dilute solution (Fig. 5), because the intermolecular interaction among the macromolecular chains could be ignored in this case. The  $\lambda_{max}^{abs}$  values of the **PyODPI** and **TzODPI** solutions were observed at 329 nm and 288 nm, respectively; and the  $\lambda_{onset}^{abs}$ values of them were observed at 377 nm and 339 nm, respectively. The absorption peak of TzODPI is obviously blue-shifted by about 41 nm when compared with that of PyODPI, which indicates that the dominant intramolecular CT effect was greatly weakened due to the strong electron-withdrawing effect of the 1,2,4-triazole moieties.

Inspired by the weakened CT effect in **TzODPI**, we further looked into the photoluminescence properties of both polyimides to find out whether the mentioned effect would result in



Fig. 5 Normalized absorption spectra and emission spectra of the polyimides in  $CH_2Cl_2$  solutions (~2 × 10<sup>-2</sup> mg mL<sup>-1</sup>), and their images irradiated under 365 nm UV light.



Fig. 6 Excitation/emission spectra of the polyimide films (ca. 35 μm).

differences in the emission properties, and the results are shown in Fig. 3c, d, 5 and 6. For PyODPI, no matter whether it was in the solution or in the film state, it did not show fluorescent light. The fluorescence of the diamine PvDA was totally guenched when it was introduced into the polyimide backbone by polymerization with dianhydride ODPA (Fig. 3c and black line in Fig. 6). While for TzODPI, it showed a strong emission peak at 486 nm in dilute CH<sub>2</sub>Cl<sub>2</sub> solution (Fig. 5) when exited at 328 nm, with a high absolute fluorescence quantum yield of 61%, and as far as we know, this is the highest value ever reported for the luminescent aromatic polyimides. In the film state, it exhibited bright green fluorescence under 365 nm irradiation (Fig. 3d). A strong emission peak at 536 nm emerged when the film was excited at 439 nm with a short lifetime ( $\tau$ ) of 13 ns and a  $\Phi_{PL}$  of 13% (red line in Fig. 6), indicating that the polyimide film could give out fluorescence when placed under sunlight. The fluorescence quantum yield of this aromatic polyimide TzODPI is comparatively high, which has been rarely reported in literature.<sup>12</sup> The lower  $\Phi_{\rm PL}$ in the solid film state than in solution suggests that the mentioned intermolecular interaction by dense packing exists in TzODPI and will lower the electron-withdrawing effect of the 1,2,4-triazole moieties, thus from another point of view, it will enhance the intramolecular CT effect and subsequently weaken the fluorescence of the polyimide. Besides, the emission peak of TzODPI was obviously red-shifted by about 50 nm, from 486 nm to 536 nm, which was a result of the stacking of macromolecular chains in the solid film state.

The significant differences in the fluorescence behavior of **PyODPI** and **TzODPI** both in solution and the solid state may be mainly caused by the intensity of the intramolecular CT effect between the electron donor diamine moieties and the electron acceptor dianhydride moieties. In **PyODPI**, the strong intramolecular CT interaction between the electron-donor pyrrolecontaining diamine and the dianhydride ODPA, confirmed by its optical absorption behaviour (Fig. 5), totally quenched the fluorescence. However, when replacing the pyrrole unit with an electron-withdrawing unit of 1,2,4-triazole, the electron density of the diamine moiety is greatly lowered (Fig. 1), thus the intramolecular CT interactions would be greatly depressed, and finally this would result in the strong fluorescence emission of the **TzODPI** system. However, how these CT effects affect the

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fluorescence behavior of these aromatic polyimide systems still needs further study.

To gain a better insight into the photoluminescence phenomenon, theoretical calculations of the frontier molecular orbitals, oscillator strengths and the assignment of  $S_0$  to  $S_i$ transitions for the model basic units (MBUs) (TzM for TzODPI and PyM for PyODPI, Fig. S9, ESI<sup>+</sup>), were carried out using a Gaussian 09 program package.<sup>15</sup> Time-dependent density functional theory (TD-DFT) with long-range correction method at the cam-B3LYP/6-31+(d) level was used for dealing with the charge-transfer properties in the MBUs. The triphenylmethyl group was excluded since it is not conjugated to the polymer main chain and does not significantly affect the electronic properties of the basic units. The dianhydride moiety was simplified to make a clearer investigation for the influence of the electron properties in the diamine moiety. Similar to most fully aromatic polyimides, the highest occupied molecular orbitals (HOMOs) of both the MBUs are predominantly distributed on the diamine moieties, while the lowest unoccupied molecular orbitals (LUMOs) are located on the phthalimide moieties, as displayed in Fig. 7. However, the introduction of a triazole group brings the calculated HOMO level of TzDA down to -7.50 eV, which is much lower than that of **PyDA** (-6.71 eV), indicating the characteristics of donor and acceptor for the pyrrole and triazole structures, respectively. The total separation of these two frontier molecular orbitals would lead to the first exited state (S1) with CT effect via a one-electron HOMO to LUMO transition, which is characterized by a small value of oscillator strength (0.0021 for TzM and 0.0023 for PyM, Table 5). However, the higher frontier orbitals, LUMO+1 and LUMO+2, are distributed over the diamine moiety and the phthalimide moiety. Therefore, electrons in the HOMO are more initially inclined to hop up to LUMO+1 and LUMO+2 under sufficient energy to result in an excited state  $S_i$  (S<sub>4</sub> for TzM and the  $S_3$  for PyM, Table 5), owing to the much larger oscillator strength values for these transitions (1.1386 for TzM



Fig. 7 The frontier molecular orbitals of TzM and PyM

Table 5Transition wavelength, oscillator strengths and the assignment of $S_0$  to  $S_i$  transitions for the model basic units (MBUs) **TzM** and **PyM**<sup>a</sup>

MBU	Excited state	Transition wavelength (nm)	Oscillator strength	Orbitals	Contribution
TzM	1	303	0.0021	HOMO $\rightarrow$ LUMO	0.53
				HOMO-1 $\rightarrow$ LUMO	0.21
	4	262	1.1386	HOMO $\rightarrow$ LUMO+1	0.51
				HOMO $\rightarrow$ LUMO+2	0.28
РуМ	1	323	0.0023	HOMO $\rightarrow$ LUMO	0.69
-				HOMO-2 $\rightarrow$ LUMO	0.19
	3	283	0.9756	HOMO $\rightarrow$ LUMO+1	0.36
				HOMO $\rightarrow$ LUMO+2	0.53
<sup>a</sup> Oth	er prohi	bited transi	tions are n	ot listed.	

and 0.9759 for **PyM**, Table 5). As LUMO+1 and LUMO+2 delocalize over the MBUs, the electrons in the excited states are capable of relaxing easily to the lowest excited state (S<sub>1</sub>) *via* rapid internal conversion. These plausible electronic excitation transition processes match the absorption spectra of the polyimides in solution. The  $\lambda_{onset}^{abs}$  at 339 nm for the **TzODPI** solution arises from the S<sub>1</sub> formation, consisting of dominant CT transitions HOMO  $\rightarrow$  LUMO and HOMO-1  $\rightarrow$  LUMO (calculated transition wavelength 303 nm). The maximum absorption peak at 288 nm corresponds to the formation of S<sub>4</sub>, which primarily comprises locally excited transitions HOMO  $\rightarrow$  LUMO+1 and HOMO  $\rightarrow$  LUMO+2 (calculated transition wavelength 262 nm). Analogous results could be found with regard to **PyODPI**.

After understanding the electron excitation process, we look into the subsequent transition. According to Kasha's rule, the conversion from the upper state  $S_i$  to the lowest excited state  $S_1$ occurs before the molecule reaches the ground state  $(S_0)$  to yield fluorescence emission. Hence, the nature of electron transition between S<sub>1</sub> and S<sub>0</sub> appears particularly crucial to clarifying the significantly different emission properties for these two similar structures. Herein, the analysis of the electron transitions was carried out with the aid of a Multiwfn program package<sup>16</sup> after the calculations using Gaussian 09 were finished. It can explain the electrostatic potential and electron localization functions of charge-transfer compounds visually by the use of wavefunction analysis and quantum chemical studies.<sup>17</sup> The primary results are summarized in Table 6. Hole and electron distributions respectively denoting the regions where an electron leaves and goes to were examined, as displayed in Fig. 8. Concerning the PyM, the hole region (blue) spreads through the pyrrole moiety and the adjacent phenyl ring, while the electron region (green) is located at the phthalimide moiety (Fig. 8b).

Table 6 The analysis of electron transition between  $\mathsf{S}_0$  and  $\mathsf{S}_1$  by Multiwfn program package

MBU	Integral of hole–electron distribution overlap (S)	Distance between the centroids of the hole and electron regions (D) (angstrom)	Norm of transition dipole moment (a.u.)
TzM	0.1947	3.74	0.076
PyM	0.0795	5.94	0.275

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Fig. 8 The hole (blue region) and electron (green region) distribution (a and b) and overlap (c and d) of **TzM** and **PyM**.

Almost no overlap region could be observed except for a tiny overlap lying on the carbonyl group, and the integral of the overlap of the hole-electron distribution (S) is tiny with a value of 0.0795. The calculated results show total separation of the hole and electron regions in PyM (Fig. 8d), presenting a typical CT transition mode. While for TzM, the hole region scatters over the 1,2,4-triazole moiety, the adjacent phenyl ring and the phthalimide moiety, and the electron region is also located at the phthalimide moiety. The overlap of the hole and electron regions can be easily noticed in Fig. 8c. The S value of TzM is much higher with a value of 0.1947, which is approximately 2.5 times that of PyM. Though the hole and electron regions are separated indicating that the CT effect still exists in TzM, this effect is suppressed resulting in the observed larger S value. Note that a large overlap integral allows effective transitions in theory. The higher photon emission efficiency of TzM or TzODPI makes sense. Another charge-transfer feature, the distance between the centroids of the hole and electron regions (D), is also provided. The larger the value, the longer distance the charge transfers. Again, TzM has a shorter D value of 3.74 angstroms, which exhibits a suppressed CT type characteristic, compared with PyM for which the D value is 5.94 angstroms. Similarly, the smaller value of transition dipole moment which TzM has, is in favor of the CT suppression as well.

Consequently, one could conclude that both polyimide structures perform though certain CT characteristics, with **TzODPI** having weaker donor-acceptor interactions and obvious fluorescence emission. However, the emission of **PyODPI** was quenched by the stronger CT effect between the pyrrole-containing diamine and dianhydride ODPA, due to the deficiency of the transition between  $S_1$  and  $S_0$ .

In consideration of the above design concept to develop high performance polyimides for advanced optical and electronic applications, it is quite reasonable to question whether the stronger the electron-withdrawing effect of the diamine moieties, the higher the emission efficiency of the resulting polyimide is. Further investigation has been in progress in this lab and the results are to be reported in the near future.

#### **Electrochemical properties**

Cyclic voltammetry was employed to determine the oxidation potential of the polymers in NMP solution, as shown in Fig. S10

Table 7 Electrochemical properties of the polyimides

PI	$E_{\mathrm{onset}}^{\mathrm{ox}}\left(\mathbf{V}\right)$	$E_{g}^{a}$ (eV)	$HOMO^{b}$ (eV)	$LUMO^{c}$ (eV)
TzODPI PyODPI	0.63 0.50	3.66 3.29	$\begin{array}{c} -5.05 \\ -4.92 \end{array}$	$-1.39 \\ -1.63$

<sup>*a*</sup> Energy gap =  $1240/\lambda_{onset}^{abs}$  of the polyimide solution in CH<sub>2</sub>Cl<sub>2</sub>. <sup>*b*</sup> The HOMO energy levels relative to ferrocene (-4.80 eV) were calculated from  $E_{onset}$ . <sup>*c*</sup> LUMO = HOMO +  $E_{g}$ .

(ESI<sup>†</sup>) and the results are summarized in Table 7. For TzODPI and PyODPI, the onset potentials were measured to be 0.63 V and 0.50 V versus Ag/AgCl, respectively. It is noted that the oxidation potential of external standard ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) was measured to be 0.38 V versus Ag/AgCl in NMP. Assuming that the HOMO level for the  $Fc/Fc^+$  standard is -4.80 eV with respect to the zero vacuum level, the HOMO level was determined to be -5.05 eV for TzODPI and -4.92 eV PyODPI. Also note that the band gaps estimated from the absorption edge of the polymer solutions were 3.66 eV and 3.29 eV or TzODPI and PyODPI, respectively. The lowest unoccupied molecular orbital (LUMO) energy levels were calculated to be -1.39 eV for TzODPI and -1.63 eV PyODPI. The lower HOMO level of TzODPI compared with that of PyODPI reveals the electron-deficiency of the diamine moieties in TzODPI. However, the still relatively high HOMO level value of TzODPI indicates its potential for facile device fabrications.

### Conclusions

Two novel wholly aromatic polyimides were prepared from diamines with totally different electron affinities. They had facile film forming abilities, high thermal stability and desirable solubility. The electron acceptor 1,2,4-triazole containing polyimide, TzODPI, exhibited bright green fluorescence with a quantum yield of up to 61% in solution and 13% in the film state, while PyODPI, bearing electron donor pyrrole moieties, suffered a fluorescence quenching effect. The entirely opposed optical properties were expected to originate from the varied CT interaction intensities, which were elucidated with the aid of optical spectra and molecular simulations. Highly fluorescent aromatic polyimides can be obtained by appropriate control of the intra-molecular charge-transfer effects between the diamine and dianhydride moieties. This demonstrates a convenient way for developing novel wholly aromatic polyimides with high fluorescence efficiency for potential optoelectronic applications.

### Experimental

The instrumentation and all commercially available starting compounds are listed in the ESI.† The diamine monomers and the corresponding polyimides were synthesized by the routes outlined in Schemes 1 and 2, respectively. The intermediate 4-tritylaniline and the pyrrole containing diamine monomer 4,4'- (1-(4-tritylphenyl)-pyrrole-2,5-diyl)dianiline (**PyDA**) were synthesized according to a previously reported procedure.<sup>14</sup>

#### Synthesis of 1,2-bis(4-nitrophenyl)hydrazine (1)

4-Nitrobenzoyl chloride (9.23 g, 50.0 mmol) was dissolved in 80 mL of anhydrous *N*-methyl-2-pyrrolidone (NMP). After triethylamine (4.18 mL, 30.0 mmol) was added, the formed suspension was cooled in an ice-water bath. Then hydrazine monohydrate (1.50 g, 30.0 mmol) was added dropwise under vigorous stirring. The mixture was allowed to react at room temperature for 5 h and then poured into water (200 mL). The pale yellow precipitation was filtered off and washed with water and ethyl acetate, and dried under vacuum to give a white powder (6.70 g, 81%). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 10.99 (s, 2H), 8.38–8.35 (d, 4H) and 8.15–8.12 (d, 4H). <sup>13</sup>C NMR (500 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 124.29, 129.50, 138.37, 149.96 and 164.72. MS (EI, *m*/*z*): [M]<sup>+</sup> calcd for C<sub>14</sub>H<sub>10</sub>N<sub>4</sub>O<sub>6</sub>: 330.06. Found: 330. IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3222 (N–H, stretching), 1614 (C=O, stretching), 1530 (NO<sub>2</sub>, v<sub>as</sub>) and 1350 (NO<sub>2</sub>, v<sub>s</sub>).

### Synthesis of 1,2-bis(4-nitrophenyl)chloromethylene)hydrazine (2)

Compound **1** (9.91 g, 30.0 mmol) and anhydrous toluene (100 mL) were added to a 250 mL three-neck flask, followed by addition of PCl<sub>5</sub> (16.66 g, 80.0 mmol) in batches. The suspension was stirred at 120 °C for 5 h. Then toluene was removed by rotary evaporation under vacuum. Water (100 mL) was added and the mixture was refluxed for 30 min. After filtration and cooling to room temperature, a tan crude product was obtained, which was afterwards purified on a silica-gel column using ethyl dichloromethane/ *n*-hexane (v/v = 1/1) as an eluent to give compound **2** as yellow needle crystals (8.49 g, 77%). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 8.43–8.37 (d, 4H) and 8.33–8.28 (d, 4H). <sup>13</sup>C NMR (500 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 124.73, 130.16, 138.18, 142.97 and 150.17. MS (EI, *m*/z): [M]<sup>+</sup> calcd for C<sub>14</sub>H<sub>8</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>4</sub>: 365.99. Found: 366. IR (KBr,  $\nu$ , cm<sup>-1</sup>): 1586 (C==N, stretching), 1526 (NO<sub>2</sub>, v<sub>as</sub>) and 1342 (NO<sub>2</sub>, v<sub>s</sub>).

# Synthesis of 3,5-bis(4-nitrophenyl)-4-(4-tritylphenyl)-1,2,4-triazole (3)

4-Tritylaniline (8.05 g, 24.0 mmol) and 2 (7.34 g, 20.0 mmol) were mixed and dissolved in *N*,*N*-dimethylaniline (80 mL). The resulting solution was stirred at 100 °C under argon for 48 h. After cooling to room temperature, the mixture was poured into *n*-hexane (300 mL) to precipitate the crude product. After filtration, washing with methanol and purification by column chromatography, a light yellow crystalline solid was obtained (8.87 g, 70%). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 8.22–8.19 (d, 4H), 7.65–7.62 (d, 4H), 7.46–7.44 (d, 2H), 7.33–7.29 (m, 6H), 7.24–7.19 (m, 5H) and 7.14–7.11 (d, 6H). <sup>13</sup>C NMR (500 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 62.14, 124.35, 124.71, 125.12, 128.79, 130.14, 131.05, 135.74, 138.16, 142.97, 150.15, 150.67 and 164.73. MS (EI, *m/z*): [M]<sup>+</sup> calcd for C<sub>39</sub>H<sub>27</sub>N<sub>5</sub>O<sub>4</sub>: 629.21. Found: 629. IR (KBr,  $\nu$ , cm<sup>-1</sup>): 1603 (C—N, stretching), 1524 (NO<sub>2</sub>, v<sub>as</sub>) and 1346 (NO<sub>2</sub>, v<sub>s</sub>).

### Synthesis of 4,4'-(4-(4-tritylphenyl)-1,2,4-triazole-3,5diyl)dianiline (TzDA)

Compound 3 (6.30 g, 10.0 mmol),  $SnCl_2 \cdot 2H_2O$  (22.56 g, 100.0 mmol) and ethanol (250 mL) were charged into a 500 mL

three-neck flask. The mixture was refluxed with stirring under argon for 4 h. Then ethanol was removed by rotary evaporation under vacuum, and the resulting vicious solution was poured into 4 M NaOH (250 mL). The mixture was stirred vigorously for 2 h, extracted with CH2Cl2 and dried under vacuum. Purification of the residue by column chromatography and further recrystallization from ethanol afforded diamine TzDA as a white crystalline solid (4.69 g, 82%). <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 7.36–7.31 (m, 6H), 7.26-7.21 (m, 5H), 7.16-7.07 (m, 8H), 6.97-6.95 (d, 4H), 6.44-6.41 (d, 4H) and 5.48 (s, 4H, NH<sub>2</sub>). <sup>13</sup>C NMR (500 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 64.79, 113.52, 114.38, 126.84, 128.35, 129.59, 130.97, 132.36, 134.34, 146.26, 148.12, 150.33 and 154.43. Anal. calcd for C<sub>39</sub>H<sub>31</sub>N<sub>5</sub>: C, 82.22; H, 5.48; N, 12.29. Found: C, 82.01; H, 5.47; N, 12.21. MS (EI, m/z):  $[M]^+$  calcd for  $C_{39}H_{31}N_5$ : 569.26. Found: 569. IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3457, 3339 (N-H, v), 1610 (C=N, stretching) and 1298 (C-N, stretching).

### Preparation of polyimides

The synthesis of polyimide **TzODPI** is used as an example for the general synthetic route of both polyimides (Scheme 2). To a solution of diamine **TzDA** (0.4856 g, 0.8524 mmol) in 5 mL of anhydrous DMF, was added dianhydride ODPA (0.2644 g, 0.8524 mmol) in one portion. After stirring at room temperature under argon for 8 h, the viscous poly(amic acid) solution was subsequently coated on a clean glass plate, followed by thermal imidization in a vacuum oven at 80 °C/1 h, 150 °C/1 h, 230 °C/1 h and 300 °C/1 h. After cooling to room temperature, the plate was soaked in warm water and the polyimide film (approximate 35 µm) peeled off automatically.

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