

Tuning the electronic nature of aggregation-induced emission chromophores with enhanced electron-transporting properties†

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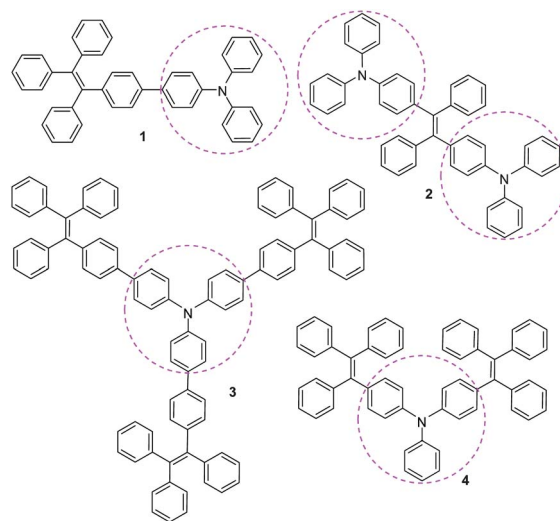
In organic light-emitting devices, materials with efficient electron-transporting properties, are essential. In this report, oxadiazole-containing tetraphenylethene TPE-Oxa is synthesized and its optical physics and electronic properties are investigated. The dye is almost nonluminescent when molecularly dissolved in solutions, but becomes highly emissive when aggregated in poor solvents or fabricated as thin films in the solid state. A quantum yield of unity has been achieved in its solid thin film. Inherited from the oxadiazole component, the dye molecule enjoys low-lying electronic band energies. Benefiting from the good electron-transporting and hole-blocking properties of the dye, the two-layer OLED devices using TPE-Oxa as both light-emitting and electron-transporting materials show superior performance, *i.e.*, lower turn-on voltage, higher brightness and efficiencies, to the devices of typical configuration with a dedicated electron-transporting layer.

Introduction

Organic materials with enhanced solid-state emissions have been well established in organic light-emitting diodes (OLEDs) in recent years.¹ Most of the organic conjugate chromophores emit strongly in their dilute solutions but become weak fluorophores when fabricated into solid films or aggregated in their poor solvents due to strong intermolecular interactions.² This problem must be solved because luminogenic molecules are commonly used as thin films in real-world applications.³ We have recently discovered an “abnormal” process of aggregation-induced emission (AIE). A series of propeller-shaped nonemissive dyes such as siloles and tetraphenylethenes (TPEs) can be induced to emit efficiently by aggregate formation.⁴ Because they are free of the common fluorescence “aggregation-caused quenching” effect, OLEDs utilizing AIE molecules exhibit outstanding performances.⁵

To enhance the device performance, OLEDs with multilayers are generally adopted to balance the charge injection and transportation. In reality, it would be nice to have emitters with

both efficient solid-state emissions and good charge-transporting properties because it will simplify the device fabrication procedure and lower the construction cost.⁶ In our previous work, AIE luminogens with good hole-transporting ability were demonstrated. By introducing triphenylamine (TPA) functionalities with hole-transporting properties into TPE derivatives, efficient solid emitters with good hole-transporting properties were achieved (Scheme 1).⁷ OLEDs using them as both emitting and hole-transporting layer showed superior performances to those with a dedicated hole-transporting layer.⁷ In comparison, electron



Scheme 1 Chemical structures of TPA (triphenylamine)-functionalized AIE-active tetraphenylethene derivatives with enhanced hole-transporting properties.

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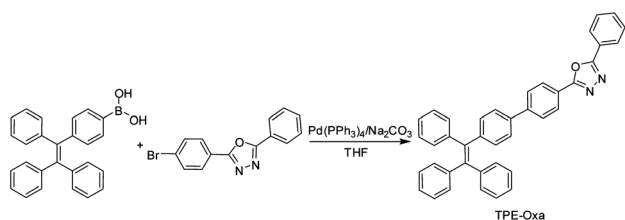
† Electronic supplementary information (ESI) available: Experimental procedures and characterization data for the synthesis of TPE-Oxa, UV absorption spectrum and CV spectrum. See DOI: 10.1039/c2jm16308j

mobilities in organic materials can be several orders of magnitude less than hole mobilities.⁸ There are a number of commercially available hole transport substances but just few electron transport materials with suitable parameters.^{8,9} Electron transport materials help transport electrons from the cathode and into the emitting layer. Charge injection is the limiting factors for device efficiency. In order to lower the barrier height, a suitable energy level relative to the adjacent layer is essential.⁸ Integrating the electron transport and emitting layers into one can also simplify the transport process and eliminate one of the barriers.¹⁰ Among the mostly used electron transport materials, besides some metal chelates such as the well-known Alq₃ (tris(8-hydroxyquinoline)aluminum)¹¹ and some N=C (imine)¹² containing heterocycle compounds, the 2,5-diaryl-1,3,4-oxadiazole (Oxa) building block is an attractive unit. Because it features electron deficient aromatic groups necessary for electron transport¹³ along with good stability and little negative effect on luminescence,¹⁴ the introduction of an oxadiazole ring into molecular structures is one of the promising approaches to the attainment of high charge-carrier mobility.¹⁵ Our purpose in this report is to combine the highly efficient solid-state emission of AIE-active luminogens and the good electron-transport property of the Oxa unit, leading to a new molecule with both enhanced electron transport and excellent optical properties. Next we present the synthesis of Oxa-containing tetraphenylethene TPE-Oxa and its photophysical properties. An efficient OLED using it as both emitter and electron-transporting layers was constructed. It showed superior performance to one with a dedicated electron-transporting layer.

Results and discussion

Synthesis

The Oxa chromophore is easy to build as part of a π -conjugated system. The synthetic route to the Oxa-containing TPE is depicted in Scheme 2.^{15d,16} The detailed procedures for the syntheses of the intermediates and final products are described in the ESI.† Briefly, the key reactant 1-(phenyl-4-boronic acid)-1,2,2-triphenylethene was prepared in high yield by lithiation of 1-(4-bromophenyl)-1,2,2-triphenylethene,¹⁷ followed by treatment with trimethyl borate and hydrolysis catalyzed by acid. 2-(4-Bromophenyl)-5-phenyl-1,3,4-oxadiazole was synthesized according to the reported literature method. Suzuki coupling reaction between the two reactants was catalyzed by Pd(PPh₃)₄, giving 1-[4'-(5-phenyl-2,1,3,4-oxadiazolyl)biphenyl-4-yl]-1,2,2-triphenylethene (TPE-Oxa) in good yield. The dye molecule was characterized by spectroscopic methods (¹H and ¹³C NMR,



Scheme 2 Synthetic route to 1-[4'-(5-phenyl-2,1,3,4-oxadiazolyl)biphenyl-4-yl]-1,2,2-triphenylethene (TPE-Oxa).

elemental analysis, and high-resolution mass spectra (HRMS). see ESI†).

Optical properties

TPE-Oxa is soluble in common organic solvents such as chloroform and tetrahydrofuran (THF) but insoluble in water, while it is almost nonluminescent when molecularly dissolved in its solvents. As shown in Fig. 1, the photoluminescence (PL) spectra of TPE-Oxa in THF are basically flat lines parallel to the abscissa. The fluorescence quantum yield (Φ_F) in THF is merely 0.23%. When a large amount of water is added into its THF solution, intense emission at ~ 480 nm is observed under identical measurement conditions. As seen from Fig. 1B, at a water fraction of 90%, its fluorescence intensity (I) is boosted by more than 550 times. Since water is a non-solvent for the dye molecules, the molecules must be aggregated in the solvent mixtures with high water fractions. Apparently, the emission of TPE-Oxa is induced by aggregation formation; in other words, it is AIE-active. The molecule in THF/water mixtures with high water fractions are, however, macroscopically homogenous with no precipitates, suggesting that the aggregates are of nano-dimensions, as proved by the TEM image shown in Fig. 2 and the level-off tails in the long wavelength region of their absorption spectra in the aqueous mixtures with high water contents due to the Mie effect of the dye nanoparticles.¹⁸ The photograph shown in the inset of Fig. 1 clearly manifests the nonluminescent and emissive natures of the molecular isolated species and aggregate particles. Like its aggregates suspended in aqueous media, TPE-Oxa is highly emissive in the solid state. Upon photoexcitation, its film emits at 466 nm (Fig. 6A). The Φ_F values measured by the integrating sphere method are much higher than those in the aqueous mixtures and reached 100%.

Closer inspection of the PL spectra of TPE-Oxa in the aqueous mixtures reveals that the emission maximum is blue-shifted slightly accompanying an increase in intensity when the water fraction is increased from 80 to 95% (from 487 to 480 nm). The electron diffraction microscopy analysis of the aggregates formed in the solvent mixtures with 90% water fraction displays many clear diffraction spots (Fig. 2 right), proving the crystalline nature of the aggregates. This blue-shift can be further developed when the sample is crystallized. As shown in Fig. 3, the crystalline clusters of TPE-Oxa showed intense deep blue fluorescence, with a maximum at 455 nm. One may notice that its film emits at 466 nm, a value between those of the nano-aggregates and the crystallites, which is probably due to its semi-crystallinity. In our previous study, we have observed similar phenomena on several AIE-active luminogens. The change in the packing order of the aggregates from an amorphous state to a crystalline one is expected to be the origin.¹⁹ That is, for these AIE-active luminogens, crystallization will enhance and blue-shift the emission.

Thermal properties

The thermal properties of TPE-Oxa are investigated by thermogravimetric (TGA) and differential scanning calorimetric (DSC) analyses. As shown in Fig. 4, TPE-Oxa enjoys good thermal stability with a T_d value of 377 °C. The sample melted at 240 °C to give an isotropic liquid in the first run of the DSC measurement.

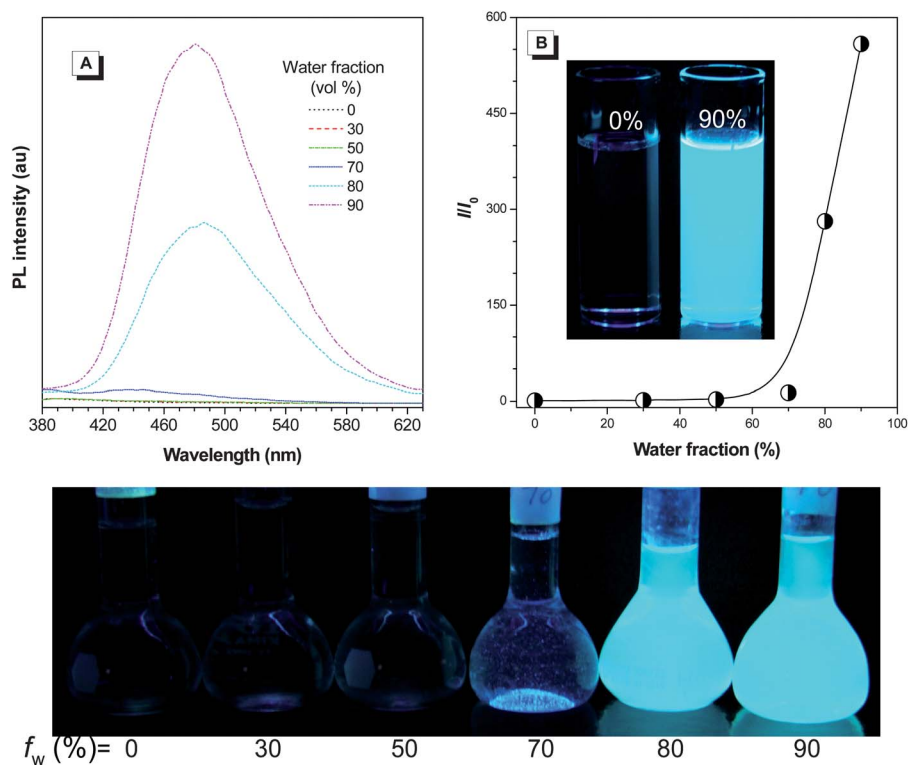


Fig. 1 (A) Photoluminescence spectra of TPE-Oxa in THF/water mixtures with different water fractions. Concentration: 10 μ M; excitation: 355 nm. (B) Plots of (I/I_0) values *versus* compositions of the THF/water mixtures. Inset: fluorescent images of TPE-Oxa in THF/water mixtures with different water fractions.

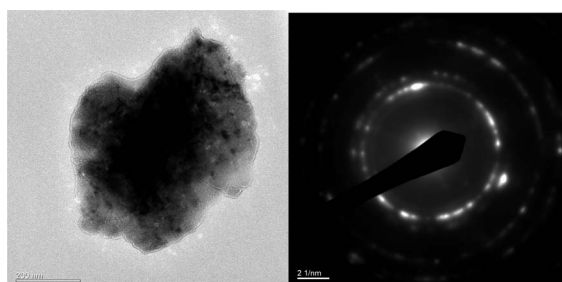


Fig. 2 TEM image of the nanoaggregates of TPE-Oxa formed in a THF/water mixture with 90% water fraction and the electron diffraction (ED) pattern.

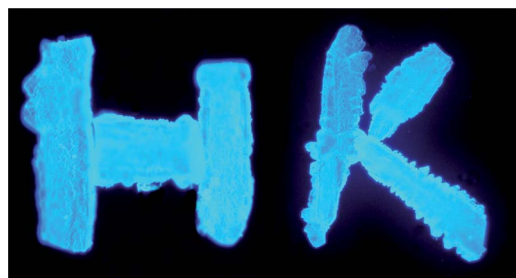


Fig. 3 Fluorescence microscopic image of crystalline clusters of TPE-Oxa.

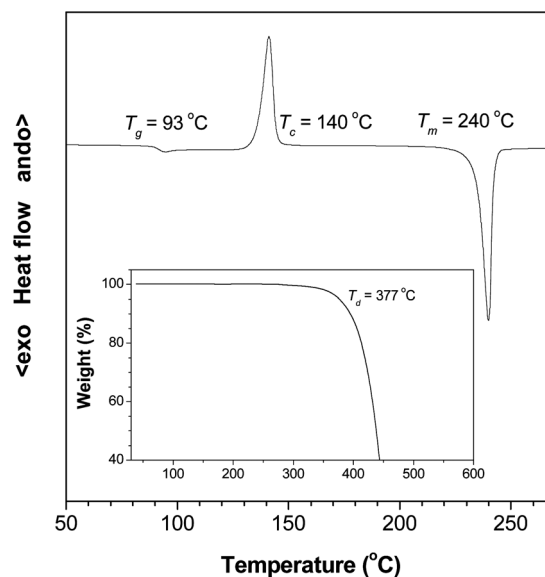


Fig. 4 TGA and DSC thermograms of TPE-Oxa (recorded under N_2 at a heating rate of 20 (TGA) and 10 (DSC) $^{\circ}C\ min^{-1}$.)

Upon cooling, the isotropic liquid changed into a glassy state. As the glassy sample was reheated for the second run, a glass transition was observed at 93 $^{\circ}C$, which is defined as the glass transition temperature (T_g) of TPE-Oxa. Upon further heating beyond T_g , an exothermal crystallization was observed at 140 $^{\circ}C$. Due to its low molecular weight, the T_g of TPE-Oxa is not high.

Electrochemical properties

As the introduction of the oxadiazole unit into our AIE system is to tune its electronic nature, measuring its energy level to validate the effect is essential. The electrochemical behaviour of TPE-Oxa was studied by cyclic voltammetry. Its electrochemical potential was calibrated with the ferrocene/ferrocenium (Fc/Fc⁺) standard (4.8 eV below the vacuum level) to determine the HOMO energy level (Fig. S5†) From the onset of the oxidation, its HOMO energy level is 6.1 eV. The LUMO energy level deduced from the difference between the HOMO level and the optical band gap is 3.1 eV (Fig. 5). Just like other traditional oxadiazole-containing materials, TPE-Oxa shows low-lying electronic band energies.¹⁵ Comparing with the most famous electron-transporting material TPBi, they possess a similar low-lying HOMO level, which will benefit hole-blocking. On the other hand, its LUMO lies lower than that of TPBi (3.1 vs. 2.7 eV) and is almost equal to the work function of the electron injecting cathode (LiF/Al). This may lower the charge injection barrier and the device operating voltages. These electronic properties indicate that besides light-emitting, TPE-Oxa can also play a role as electron-transporting hole-blocking material. Thus according to the energy level diagrams, two different device architectures are adopted to validate its optoelectronic behaviour. One is the typical device structure with both hole-transporting and electron-transporting layers and the other one only has a hole-transporting layer, as shown in Fig. 5.

Electroluminescence properties

Under the typical multilayer device structure: ITO/NPB(60 nm)/TPE-Oxa(20 nm)/TPBi(10 nm)/Alq₃(30 nm)/LiF/Al(200 nm), the device emits deep blue light with the EL maximum (λ_{EL}) of 466 nm, which is quite close to that of the PL in film. Fig. 6A depicts the EL spectra and the PL spectrum of the thin film. Under the two layer device structure: ITO/NPB(60 nm)/TPE-Oxa(60 nm)/LiF/Al(200 nm), the device emits a little longer wavelength than the former one with the EL maximum (λ_{EL}) of 476 nm. Both the EL show spectral stability with hardly any changes along with the operating bias increasing from 8 V to 15 V. Fig. 6B shows the current density and luminance–voltage characteristics of the two kinds of devices based on TPE-Oxa. We can see with the simple device structure (no dedicated electron-transporting layer (ETL)), it shows better electronic character. The charge transfer in the simple device is more efficient than that in the device with ETL, *i.e.*, to reach the same current density/brightness, the applied bias needed for the former one is

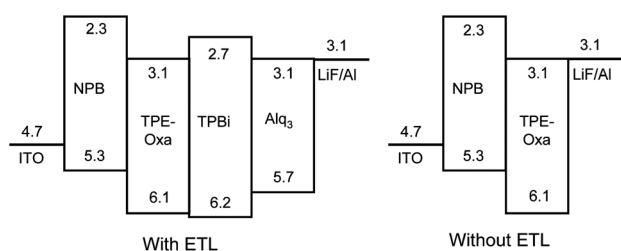


Fig. 5 Energy level diagrams of multilayer EL devices of TPE-Oxa with and without electron-transporting layers (ETL).

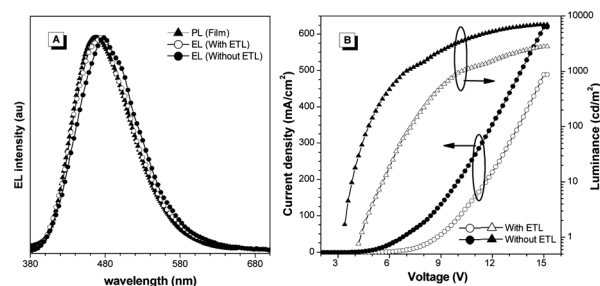


Fig. 6 (A) PL and EL spectra of solid thin film of TPE-Oxa. (B) Current density and luminance–voltage characteristics of devices based on TPE-Oxa.

much lower than the latter one (~ 2 V). Subsequently, the turn-on voltage of the simple device (3.2 V) is lower than that of the multilayer one (4.4 V). Profiting from the better electronic properties, the simple OLED radiates more brightly with the maximum luminance (L_{max}) value reaching 7000 cd m^{-2} at 15 V, which is much higher than the with ETL counterpart of 2800 cd m^{-2} . And also, the simple device exhibits high performance in efficiency. Fig. 7 shows the current efficiency, power efficiency and external quantum efficiency *versus* voltage characteristics of the two kinds of devices based on TPE-Oxa. The simple device worked at almost twice the efficiency of the multilayer one in the whole bias range, *e.g.*, 2.4 vs. 1.5 cd A^{-1} of the maximum current efficiency (η_C), and 2.2 vs. 1.1 lm W^{-1} of the power efficiency (η_P), for details see Table 1. These results verified the enhanced electron-transporting and hole-blocking behaviour of TPE-Oxa, clearly demonstrating that the EL properties of AIE luminogens can be readily tuned by molecular engineering endeavors. Combination of electronic tuning groups into AIE-luminogens has led to their use as both light-emitting and electron-transporting hole-blocking materials in OLEDs.

Conclusions

In this paper, oxadiazole-containing tetraphenylethene TPE-Oxa is synthesized and its optical physics and electronic properties are investigated. The dye possesses typical AIE characteristics; it becomes highly emissive when aggregated in poor solvents or fabricated as thin films in the solid state. A quantum yield of unity has been achieved in its solid thin film. Inherited from the oxadiazole component, the dye molecule enjoys low-lying electronic band energies. The two-layer OLED devices using

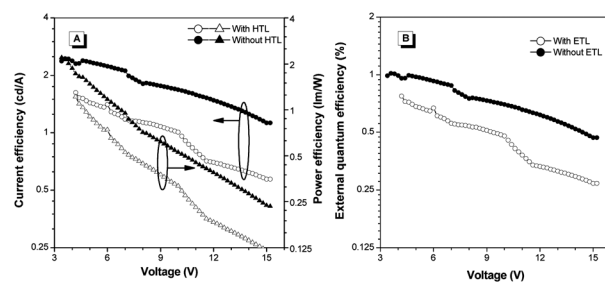


Fig. 7 (A) Current efficiency and power efficiency *versus* voltage characteristics of device based on TPE-Oxa. (E) External quantum efficiency *versus* voltage characteristics of device based on TPE-Oxa.

Table 1 Electroluminescence performances of TPE-Oxa^a

ETL	λ_{EL} (nm)	V_{on} (V)	L_{max} (cd m ⁻²)	CE_{max} (cd A ⁻¹)	PE_{max} (lm W ⁻¹)	EQE_{max} (%)
✓	466	4.4	2800	1.5	1.1	0.7
✗	476	3.2	7000	2.4	2.2	1.0

^a Device configurations, with ETL: ITO/NPB(60 nm)/TPE-Oxa(20 nm)/TPBi(10 nm)/Alq₃(30 nm)/LiF/Al(200 nm); without ETL: ITO/NPB(60 nm)/TPE-Oxa(60 nm)/LiF/Al(200 nm). Abbreviations: λ_{EL} = EL maximum, V_{on} = turn-on voltage at 1 cd m⁻², L_{max} = maximum luminance, CE_{max} = maximum current efficiency, PE_{max} = maximum power efficiency, EQE_{max} = maximum external quantum efficiency.

TPE-Oxa as both light-emitting and electron-transporting materials show superior performances to the devices of typical configuration with a dedicated electron-transporting layer. Benefiting from the good electron-transporting and hole-blocking properties of the dye, the device with simple structure shows much lower turn-on voltage, higher brightness and efficiency. The carrier mobility of the material in other kinds of devices, e.g., organic field-effect transistors (OFETs) or measured by the time of flight (TOF) method will be studied in future works, to see whether the material has potential in organic light-emitting transistors (OLETs). Using this combination strategy developed in this work, it is anticipated that more AIE luminogens with versatile functionalities will be generated.

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