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Journal Name

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Pyridal[2,1,3]thiadiazole as Strong Electron-Withdrawing and Less Steric Hindrance Acceptor For Highly Efficient Donor-Acceptor type NIR Materials

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Pyridal[2,1,3]thiadiazole (PT) is an analog of common acceptor benzo[1,2,5]thiadiazole (BT) in charge transfer (CT) chromophore, exhibiting stronger electron-deficient ability and less steric hindrance. Here, we demonstrated the prominent effect of PT as proto-acceptor to construct D-A type NIR emitting materials. The compound *p*-TPA-PT-CN that combined donor triphenylamine (TPA) and cyano-substituent PT shows NIR emission of ~700 nm, and highly PL efficiency of 0.3 both in solution and solid. The strong D-A interaction in *p*-TPA-PT-CN results in low energy charge-transfer state. The pyridine nitrogen of PT lowers the steric hindrance between PT and the adjacent TPA donor segment, thereby induces planarity and strong mixing (hybridization) of CT and π - π states (HLCT). Such strong mixing contributes towards higher luminous efficiency. The OLEDs fabricated by utilizing *p*-TPA-PT-CN as the emitting layer showed an EQE of 1.47 % and Lmax= 640 cd m⁻² which is among the good NIR-OLED devices.

Introduction

High-performance near-infrared (NIR) organic light-emitting diodes (OLEDs) are rare. In the past decades, many types of NIR materials have been reported, because of their applications in organic light-emitting diodes (OLEDs), chemo-sensing, night-vision devices, and information-secured displays.¹⁻⁵ In the previous work, the applications of near-infrared phosphorescent OLEDs remained limited due to the expensive heavy metals and serious roll-offs.⁶⁻¹² While NIR fluorescent OLEDs prove their advantage in these aspects. However compared with the visible OLED, the efficiency of NIR OLED is still too low for practical application. This is because of the low energy NIR materials usually show lower photoluminescence (PL) efficiency at room temperature due to the energy gap law.^{13,14} Generally, there are two strategies to construct red/NIR materials:1) elongating conjugation;¹⁵⁻¹⁸ 2) introducing strong intermolecular charge transfer (ICT) emission by donoracceptor (D-A) architecture.¹⁹⁻²¹ The former strategy mainly include polycyclic arene derivatives, such as rubrene and pentacene, however, these polycyclic arenes usually tend to aggregate (strong π - π interactions) and exhibit weak or no

emission in the solid state as a result of aggregationcausedquenching.²² Comparatively, the later strategy has higher advantage for designing NIR materials because the emission properties of D-A materials can be judiciously tuned over a wide range, by varying the strength of donor or acceptor moieties.23,24 Additionally, the D-A architecture provides bipolar properties facilitating the hole/electron injection and transport.15,25,26 Recently, some D-A type NIR materials have been developed based on several electron deficient groups, such diphenylfumaronitrile (DBFN),²⁷ naphthothiadiazole as (NZ)^{28,29} 2,3-dicyanopyrazino phenanthrene $(DCPP)^{21}$ and [1,2,5] thiadiazolo[3,4-g]quinoxaline (QTD).^{18,30} Although the strong D and A architecture can realize NIR emission due to the strong CT state, this usually also lead to the frontier molecular orbitals distribute on corresponding D and A moieties.

The decoupling of frontier molecular orbitals is detrimental to obtain high photoluminescence efficiency due to competition from radiationless transitions.³¹ According to the twist intermolecular charge transfer (TICT) model, the overlap of the frontier molecular orbitals of the D-A compounds are dependent on the twist angle between the D and A.^{32,33} The overlap of the frontier molecular orbitals gradually decreased as the twist angle of the D-A compounds increased from 0° to 90° and completely decoupled at 90° with an orthogonal conformation.³⁴⁻³⁶ Therefore, control over D-A strength to obtain red/NIR emission, as well as relative small twist angle between the D and A to ensure enough overlap of frontier molecular orbitals is critical for allowed electronic transition to achieve high PL efficiency.

In this manuscript, we report [1,2,5]thiadiazolo[3,4-c]pyridine (PT) heterocycle as proto-type acceptor unit to construct D-A

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^{*}Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

materials with the donor triphenylamine (TPA) proximal to the N-atom (pyridyl), namely p-TPA-PT-CN. The choice of PT heterocycle is based on the following: 1) the pyridine heterocycle can increase electron-deficient properties when compared to the benzo[1,2,5]thiadiazole (BT), a red-shift of the absorption and fluorescence can be expected due to the strong CT character to realize low-energy emission; 2) the absence of steric hindrance around the nitrogen atom will result in smaller twist angle between PT and TPA units to provide more planar ground state conformation, which increases the overlap of the frontier molecular orbitals and consequently ensure large oscillator strengths to provide possible high PL efficiencies. In order to adjust the acceptor strength for a more red-shift emission, we additionally introduce the cyano-substituent to further increase the electron-deficient properties of the A moiety. Through systematic investigation and analysis, we revealed that the PT heterocycle is a promising acceptor to construct high efficient NIR-emission D-A materials with appropriate donors proximal to the N-atom of pyridyl.

Results and Discussion

Synthesis and Characterization

Published on 09 October 2017. Downloaded by Freie Universitaet Berlin on 09/10/2017 11:44:21

The Scheme 1 depicts the synthetic route to p-TPA-PT-CN. The synthesis started from the Stille coupling of 4,7-dibromopyridal-[2,1,3]thiadiazole with stannylated triphenylamine. The 4,7-dibromo-pyridal-[2,1,3]thiadiazole, has more reactive bromine at position 4, therefore Stille-coupling afforded an asymmetric precursor TPA-PT-Br with the triphenylamine proximal to the nitrogen. Next the precursor TPA-PT-Br undergoes suzuki coupling reaction with (4cyanophenyl)boronic acid to get the product p-TPA-PT-CN. The final product was purified using silica gel column chromatography, preparative HPLC and vacuum sublimation in sequence. The structure and purity of the final product is fully confirmed by the ¹H NMR, ¹³C NMR, mass spectrometry and elemental analysis.

Electrochemical Properties

Cyclic voltammetry (CV) provides the redox properties and the energy levels of a molecule. The oxidation and reduction process were performed in CH_2Cl_2 and DMF solution, respectively, using the 0.1 M n-Bu₄NPF₆ as the supporting electrolyte and ferrocene (Fc) as the internal standard (Fig. 1). The *p*-TPA-PT-CN showed reversible redox waves in the positive and negative scans. According to the half-wave potential ($E_{1/2}$) value of the oxidation and reduction process, its highest unoccupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels are -5.37 and -3.47 respectively (Table1), resulting in electrochemical



(ii) Pd(PPh₃)₄, 2M K₂CO₃, Methanol, Toluene(1:1:2), 90°C, 24h.
Scheme 1. Chemical structures and synthetic route of *p*-TPA-PT-CN.



bandgap of 1.9 eV. Crystal Structure

Single crystal of the compound was obtained by slow diffusion of ethanol into a methylene dichloride, and used for single crystal X-ray diffraction analysis (Table S3). The unit cell of p-TPA-PT-CN is monoclinic, space group C2/c, containing eight molecules. The torsional angle between the central PT ring and the triphenylamine is around 7.7° which is much smaller than that of the BT-based counterpart TPA-BT with a twist angle of 45°.²³ It is reasonable to infer that such a small torsion angle makes the molecule planar and rigid. In addition, the p-TPA-PT-CN cell contains dimer with inversely packed configuration, and the vertical distance between inversely neighboring PT rings is 3.45\AA (d₁). For the whole crystal, the *p*-TPA-PT-CN dimer is stacked along b-axis with the vertical distance of 3.41 Å (d₂). The distance between PT rings shows strong pi-pi interaction. The cyano group and TPA-H of neighboring p-TPA-PT-CN form C-H~N hydrogen bonds (Fig. 2b), and the length of these hydrogen bonds in the range of 2.916 Å \sim 3.793



Fig. 2 The Single-crystal structure of *p*-TPA-PT-CN. a) A single molecular structure of *p*-TPA-PT-CN crystal; b) The packing of the b axis (C-H~N hydrogen bonds length: 2.916 Å, 3.18 Å, 3.23 Å, 3.471 Å, 3.686 Å, 3.793 Å); c) The stack mode of the crystal (along with the b axis).

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Table 1 Thermal photophysical f	twist angles and energy	levels data of <i>n</i> -TPA-PT-CN

Molecule	T _g /T _d	In THF	:	In film	l	LUMO/HOMO ^{a)}	Twist angle (°)	
	(°C)	UV(nm)	PL(nm)	UV(nm)	PL(nm)	(eV)	DFT ^{b)}	Crytal ^{c)}
p-TPA-PT-CN	87/352	309,323,491	668	318,338,513	683	-3.47/-5.37	5.9	7.7

^{a)} HOMO/LUMO energy levels were calculated using cyclic voltammetry (CV) with ferrocene as an internal standard.

^{b)} Estimated from the optimized molecular geometry by DFT calculation, ^{c)} Estimated from the molecular geometry in crystal.

Å. We concluded that the π - π interactions and the intermolecular hydrogen bonds by the cyano group are the driving force to urge the long-range order in these molecules. As the Fig. 2c shows, the cyano group and the PT ring show the nitrogen-sulphur interactions (3.31 Å), responsible for the order along the c-axis.

Photophysical Properties

The photophysical properties of *p*-TPA-PT-CN were studied by the ultraviolet-visible (UV-vis) and PL spectra both in THF solution and evaporated film (Fig. 3a). The *p*-TPA-PT-CN exhibits similar absorption profiles in THF solution and evaporated film, only a moderate red-shift for film, which consist of two absorption bands. The short-wavelength absorption band around 310 nm is associated with the π - π * transitions of the D- A molecule, largely localized on the



Fig. 3 a) UV-vis spectra and PL spectra of p-TPA-PT-CN in THF and evaporated film; b) Solvatochromic PL spectra with increasing polarity of solvents (10⁻⁵ M).

triphenylamine moiety. The n- π^* transition originating from triphenylamine moiety is also expected to appear around 300 nm and likely overlapping with the π - π * transitions. The lowenergy absorption bands in 491 nm and 531 nm can be unambiguously assigned to the intramolecular charge transfer (ICT) transition ${}^{1}CT \leftarrow S_{0}$. As can be seen from the table S1, the molar extinction coefficients of the CT transition in various solutions remain at a relatively higher level (above $1.17*10^4$). These higher molar extinction coefficients likely originate from small twist angle between the D and A allowing easier electronic transition. The PL spectra of p-TPA-PT-CN (THF solution and film) are located in the NIR region. The broad and structureless features of PL spectra indicate a CT emission. The fluorescence spectra of p-TPA-PT-CN in different increasing solvent polarity (Fig. 3b) indicate that the emission peak (λ_{em}^{max}) shifted 118 nm (571-689 nm). In addition photoluminescent quantum yields decreased with increasing solvent polarity which is expected behavior due to CT phenomenon. However, even in the high polar solvent of tetrahydrofuran, the photoluminescent quantum yields still maintain at 0.2. In addition, the photoluminescent quantum yields of the evaporated film is also as high as 0.3, which is benefical to obtain high-performance non-doped OLEDs.

The UV-vis absorption spectra showed almost no change but obvious solvatochromic PL was observed on varying the solvent polarity (apolar n-hexane to highly polar acetonitrile). This is rationalized by the fact that the excited state is more



Fig. 4 Linear correlation of the orientation polarization (*f*) of solvent media with the Stokes shift (v_a - v_i , a: absorption; *f*: fluorescence) for the three materials. The lines in the low- and high-polarity regions were fitted to the solvent polarity with $f \le 0.15$ and $f \ge 0.15$, respectively.

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Fig. 5 B3LYP/6-31G calculated the optimized conformations, relevant molecular frontier molecular orbital and natural transition orbitals (NTO) distribution (f is the oscillator strengths of the S₁ state transition).

polar than the ground state. In the excited state, electrons are excited from HOMO to LUMO causing redistribution of the charge and conformational change to form a TICT state in a D-A material. The polarized excited state can be stabilized by the high polar solvents because the solvent molecules reorient around the molecule to lower the energy of the system thereby leading to a red shift in the emission spectra. The dipole moment (μ_e) of lowest excited state (S₁), can be determined from the slope of the Stokes shift (v_a-v_f) versus the solvent polarity function (f) plot by Lippert-Mataga equation.^{37,38} The p-TPA-PT-CN shows linear relationship (Fig. 4) in the whole range of solvent polarity. However, the μ_e of p-TPA-PT-CN (15.0 D) is smaller than the well-known CT molecule, 4-(N,Ndimethylamino)benzonitrile (DMABN) (23 D). Moreover, PL quantum yield of p-TPA-PT-CN is high in low- and moderatepolarity solvents, indicating that S1 state of p-TPA-PT-CN is an intercrossed excited state of LE and CT rather than a pure CT state. This shows that small twist angle between D and A in p-TPA-PT-CN makes the hybridization of LE and CT states more efficient.

The transient PL delayed lifetime curves of p-TPA-PT-CN (solvents and film, Fig. S7) indicate single-exponential fluorescence decay process with a lifetime of 6.33 ns, 6.82 ns, 2.72 and 4.96 ns for hexane, ether, tetrahydrofuran and evaporated film respectively. Therefore, in all conditions, p-TPA-PT-CN possesses only onefold lowest excited state. As revealed in the X-ray crystal structures, photophysical properties and DFT calculations (next section and SEI, Fig. S8), p-TPA-PT-CN has a planar D-A conformation, thereby increase the probability of electronic transition. Thus, p-TPA-PT-CN showed larger radiative rates (k_r) . Although p-TPA-PT-CN exhibit a large (k_{nr}) , likely because of low band gap supporting the non-radiative process, it still reached a high PL efficiency of 0.28. It should be noted that there other factors also affect their photophysical properties, such as aggregation model, here we suggest the twist angle is one of the factor responsible for high PL efficiencies.





Luminance (cd m⁻²)

Theoretical Calculations

Density functional theory (DFT) calculation s (B3LYP/6-31G*) were performed to characterize the ground-state geometries, HOMO/LUMOs and the natural transition orbitals (NTO) distribution. The optimized conformation of p-TPA-PT-CN (Fig. 5) shows a twist angle of 5.9° between the D and A, which is much smaller than that of the BT-based counterpart TPA-BT with an optimized twist angle of 35.4°.23 The orbital contour plots (Fig. 5), show that the HOMO is delocalized over the whole molecule, while LUMO is mainly distributed on the acceptor and adjacent CN-phenyl, suggesting large orbital overlap between HOMO and LUMO. The calculated energy levels (HOMO and LUMO) are -5.22 eV and -2.94 eV. To characterize the excited state, the energy levels of natural transition orbitals (NTOs) were calculated (Fig. 5). The "hole" are distributed over the whole molecular skeleton while the "particle" are localized over the central PT core and the adjacent CN-phenyl. The overlap of hole and particle demonstrates the hybridization of CT and LE components (HLCT). In addition, because of the small twist angle between the D and A, causes the higher oscillator strength (0.83) for p-TPA-PT-CN, much larger than the known ICT compounds.

Electroluminescence Properties

We fabricated non-doped OLED based on p-TPA-PT-CN as the emissive layer with the following device configuration: ITO (95nm) / dipyrazino (2,3- f:2 ' ,3 ' -h) - quinoxaline-2,3,6,7,10,11 - hexacarbonitrile (HATCN) (5nm)/Di-[4-(N,Nditolyl -amino)-phenyl] cyclohexan(TAPC) (40 nm)/EML(20 nm) /1,3,5-tri[(3-pyridyl) -phen-3-yl]benzene(TmPyPB) (40 nm)/LiF (1 nm)/Al (90 nm). The device has HATCN as the anode buffer layer; TAPC as the hole-transport layer and the electron/exciton-blocking layer; TmPyPB as the electrontransporting layer (ETL)/ hole-blocking layer. As listed in Table 2, the device showed low turn-on voltage of 3.3 V, implying small injection barriers between the emitter and transport layers, attributed to the electron-transport nature of PT and hole-transport nature of TPA units. The external quantum efficiency (EOE) versus luminance characteristics and the EL spectra at a brightness of 100 cd m⁻² (Fig. 6) indicate NIR emission with a λ_{max}^{em} at 700 nm and CIE (0.70, 0.30).

DOI: 10.1039/C7TC03978F

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Table 2. Electroluminescence characteristics of the devices											
- · a)	Von	L _{max} [cd m ⁻²] ^{c)}	EQE _{max} [%]	CE _{max} [cd A ⁻¹]	PE _{max} _ [Im W ⁻¹]	at 100 cd m ⁻²			at 500 cd m ⁻²		
Device"	[V] ^{b)}					V[V]	EQE[%]	CIE[x,y]	V[V]	EQE[%]	CIE[x,y]
<i>p</i> -TPA-PT-CN	3.3	640	1.47	0.20	0.17	5.2	1.35	(0.70, 0.30)	8.0	1.30	(0.69, 0.29)

a) Device structure: ITO (95 nm) /HATCN (5 nm)/TAPC (40 nm/D-A materials (20 nm)/TmPyPB (40 nm)/LiF (1 nm)/Al (90 nm); b) Calculated with a luminance of 1 cd m⁻²; c) L_{max} = maximum luminance; EQE_{max} = maximum external efficiency; CE_{max} =maximum current efficiency; PE_{max} =maximum power efficiency; CIE = Commission International del'Eeclairage coordinates (1931 CIE chromaticity diagram).

Although our instrument (PR-650 Spectroscan spectrometer) could not detect the EL luminance signal over 780 nm, the *p*-TPA-PT-CN based device still reach a maximum brightness of 640 cd m⁻². When compared with the PL emission in the pristine film, the EL spectra exhibit obviously red-shift, due to the space charge induced spectra shift originating from the space charge redistribution as the response to dipole moment change in electronic excitation. Although the device displayed NIR emission, it still maintained a high EQE value of 1.47%, which is among the good performance of NIR OLEDs. Notably, the devices also demonstrated very low roll-off. The devices based on *p*-TPA-PT-CN at high luminance of 1000 cd m⁻² and 500 cd m⁻² (Table 2), keep an EQE of 1.30% respectively. All these characteristics suggest that PT is a promising unit to construct D-A materials for the NIR OLED applications.

Conclusions

In summary, we have used PT heterocycle as proto-type acceptor to construct a D-A (p-TPA-PT-CN) NIR electroluminescent material. Experimental and DFT analysis revealed that donor TPA positioned proximally to the N-atom of PT can result in a small twist angle between D and A due to the absence of steric hindrance. This planar ground state geometry endows the materials with larger oscillator strengths to provide high PL efficiencies both in solvent and pristine films. The addition of cyano-phenyl onto the PT can significantly affect the solid state conformation, which enables the p-TPA-PT-CN to adopt more planar conformation. These factors contributed towards higher PL efficiency (0.28) with a NIR emission. As expected, the NIR emission device based on p-TPA-PT-CN achieved a maximum EQE of 1.47%. These experimental results demonstrate that the PT is an effective unit to design D-A materials for highly efficient NIR emitters.

Acknowledgements

The authors express their thanks to the Natural Science Foundation of China (21334002, 51521002, 51403063), the Ministry of Science and Technology of China (2013CB834705, 2015CB655003), the Fundamental Research Funds for the Central Universities (2015ZP001, 2015ZM042), Introduced Innovative R&D Team of Guangdong (201101C0105067115), Major Science and Technology Project of Guangdong Province

(2015B090913002), Foundation of Guangzhou Science and Technology Project (201504010012), China Postdoctoral Science Fund (Grant No. 2014M562174) for their support.

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Pyridal[2,1,3]thiadiazoleas as Strong Electron-Withdrawing and Less Steric Hindrance Acceptor For Highly Efficient Donor-Acceptor type NIR Materials

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High efficiency NIR emissive materials is rational deigned based on PT with strongly mixed S1 of

LE and CT states.