View Article Online

Journal of Materials Chemistry C

Materials for optical, magnetic and electronic devices

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: J. H. Kim, K. H. Lee and J. Y. Lee, *J. Mater. Chem. C*, 2020, DOI: 10.1039/D0TC00178C.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/materials-c

Design of thermally activated delayed fluorescent sensitizers for high efficiency over 20% and long lifetime in the yellow fluorescent organic light-emitting diodes

Ji Han Kim, Kyung Hyung Lee, Jun Yeob Lee *

School of Chemical Engineering, Sungkyunkwan University

2066, Seobu-ro, Jangan-gu, Suwon-si, Gyeonggi-do, 440-746, Korea

Fax: (+) 82-31-299-4716

E-mail: leej17@skku.edu

* To whom correspondence should be addressed

Abstract

The yellow thermally activated delayed fluorescence (TADF) materials were synthesized using 2,4,6-triphenylpyrimidine-5-carbonitrile and 4-(3-cyanophenyl)-2,6diphenylpyrimidine-5-carbonitrile acceptors combined with a very strong donor moiety of 5,10-diphenyl-10,15-dihydro-5*H*-diindolo [3,2-*a*:3', 2'-c] carbazole. The strong electron acceptors and the strong donor twisted from the acceptor plane with a large dihedral angle decreased the singlet and triplet energy gap and managed the Dexter energy transfer. The 4-(4-(10,15-diphenyl-10,15-dihydro-5*H*-diindolo[3,2-*a*:3',2'-c]carbazol-5-yl)phenyl)-2,6diphenylpyrimidine-5-carbonitrile yellow TADF emitter showed short delayed fluorescence lifetime, high rate constant of reverse intersystem crossing and high external quantum efficiency (EQE) of 21.6%. The TADF emitter was used as the senstizer of the yellowing emitting 2,8-di-tert-butyl-5,11-bis(4-tert-butylphenyl)-6,12-diphenyltetracene and the TADF assisted fluorescent organic light-emitting diodes achieved high EQE of 20.2% and the device lifetime of 1,400 h up to 90% of initial luminance at 1,000 cd/m². This study provides a strategy for developing yellow TADF emitters to assist the fluorescent emission to achieve high EQE and long lifetime simultaneously.

Keywords: thermally activated delayed fluorescence, sensitizer, fluorescence, high efficiency, long lifetime

Introduction

The device performances of pure organic emitter based organic light emitting diodes (OLEDs) have been advanced rapidly by harvesting triplet excitons through the third generation of thermally activated delayed fluorescence (TADF) emitters in the red, green, and blue OLEDs. The TADF has the potential to have an internal quantum efficiency of 100% via a reverse intersystem crossing (RISC) process that converts excitons from a triplet excited state (T_1) to a singlet excited state (S₁) due to a small singlet and triplet energy gap (ΔE_{ST}).^[1-3] The external quantum efficiency (EQE) of the TADF OLEDs is close to or over 30% in all three colors, but the lifetime of the TADF OLEDs is much shorter than that of fluorescent and phosphorescent OLEDs.^[4-6] To tackle the short lifetime of the TADF OLEDs, a device approach introducing the TADF material as a sensitizer or assistant dopant for the red, yellow, green, and blue fluorescent emitters was proposed by Adachi group.^[7] The sensitizer strategy is advantageous for the device lifetime because of material stability of the fluorescence dopant and reduced contribution of triplet excitons in the light emission process. Management of the energy transfer processes by Förster energy transfer (FRET) and Dexter energy transfer (DET) have been known to be critical to the device performances of the TADF sensitized fluorescent OLEDs.^[7-10] The FRET should be activated, while the DET should be suppressed to obtain high EQE.^[11] In order to maximize the FRET from the TADF sensitizer to the fluorescent dopant, the TADF material should have a high RISC rate and the emission spectrum overlapped with the absorption spectrum of the fluorescent material. In previous work, (2s,4r,6s)-2,4,5,6tetrakis(3,6-dimethyl-9/+carbazol-9-yl)isophthalonitrile (4CzIPN Me) which has a high

RISC rate and a long wavelength spectrum was introduced as a sensitizer of a yellow-emitting 2,8-di[t-butyl]-5,11-di[4-(t-butyl)phenyl]-6,12-diphenylnaphthacene (TBRb) fluorescent

material, which provided high EQE of 19.1%.^[7] In addition, ketone type 1,2-bis(4-(3,6-ditertbutyl-9*H*-carbazol-9-yl)phenyl)ethane-1,2-dione (DC-TC) and 1,2-bis(4-(9,9-dimethylacridin-10(9*H*)-yl)phenyl)ethane-1,2-dione (DC-ACR) TADF emitters worked as the TADF sensitizers of the red-emitting dopant due to large spectral overlap and high RISC rate.^[12] From the previous studies, the requirements for the TADF sensitizer can be summarized as large spectral overlap with the fluorescent material (1), high RISC rate (2), the efficient upconversion process (3), control of DET to the fluorescent dopant (4), and good material stability. However, the TADF sensitizers satisfying these requirements are scarce and further development of the TADF sensitizer fulfilling the specification is necessary.

In this work, we developed yellow TADF materials working as the sensitizer of fluorescent emitters to improve the EQE and lifetime of the yellow fluorescent OLEDs. Two new yellow emitters, 4-(4-(10,15-diphenyl-10,15-dihydro-5*H*-diindolo[3,2-a:3',2'-c]carbazol-5-yl)phenyl)-2,6-diphenylpyrimidine-5-carbonitrile (PyCNTruX) and 5-(4,6-diphenyl-1,3,5-triazin-2-yl)-2-(10,15-diphenyl-10,15-dihydro-5*H*-diindolo[3,2-a:3',2'-c]carbazol-5-yl)benzonitrile (TCNTruX), were introduced as the TADF sensitizers in the yellow fluorescent OLEDs doped with TBRb. It was demonstrated that the yellow fluorescent device based on the PyCNTruX sensitizer had an EQE of 20.6% and the device lifetime of 1,400 h up to 90% of

initial luminance at 1,000 cd/m^2 by managing the non-radiative loss processes in the emitting

layer.

Results and discussion

The TADF sensitizers have two strong electron withdrawing groups in the backbone structure. 2,4,6-Triphenylpyrimidine-5-carbonitrile (PyCN) has strong electron withdrawing properties by introducing a CN group in the pyrimidine core structure. Although a number of TADF materials using the pyrimidine unit have been reported,^[13-15] electron acceptor strength of the pyrimidine derivatives was not strong enough for long wavelength TADF emission. Therefore, we introduced the PyCN moiety with strong electron acceptor characteristics by the additional CN unit in the pyrimidine core. The 3-(4,6-diphenyl-1,3,5-triazin-2-yl) benzonitrile (TCN) with the diphenyltriazine based acceptor and the same CN secondary acceptor in the aromatic linker was also used as the strong acceptor. The donor was 5,10-diphenyl-10,15-dihydro-5*H*-diindolo [3,2-*a*:3', 2'-c] carbazole (TruX) which is a strong donor with a distorted geometry from the aromatic linker plane. The strong donor-acceptor based two TADF materials were strategically designed to have high RISC rate for efficient FRET to the fluorescent emitter as the TADF sensitizer while suppressing the undesirable DET by the distorted donor structure. The light emission process and the energy transfer process mentioned above are shown in **Figure 1**.



Journal of Materials Chemistry C Accepted Manuscript





Scheme 1. Synthetic scheme of PyCNTruX and TCNTruX.

The synthesis of the two TADF sensitizer materials is described in **Scheme 1**. The donor group, TruX, was synthesized via Buchwald-Hartwig amination reaction using iodobenzene. The first intermediate of the PyCN core was synthesized by condensation reaction using

piperidine as a base reagent and the PyCN core was synthesized by ring closing reaction. In addition, the first intermediate of the TCN core was synthesized by Suzuki-coupling reaction with palladium catalyst. All intermediates were purified by reprecipitation, recrystallization and column chromatography. PyCNTruX was synthesized through Buchwald-Hartwig amination raction, and TCNTruX was synthesized using C₂CO₃ base and anhydrous *N*,*N*-dimethylformamide. All final compounds have a purity higher than 99% through column chromatography and vacuum sublimation. Details of the synthesis processes are described in the experimental part of supporting information. All synthesized materials were identified by mass spectrometer, and ¹H and ¹³C nuclear magnetic resonance spectrometer.

Frontier molecular orbital of the two TADF emitters in ground state was calculated using B3LYP 6-31*G basis set. The distribution of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) was confirmed and the photophysical parameters were calculated. The calculation results are shown in **Figure S1**. The HOMO levels of the two TADF emitters were similar due to the same donor moiety, and the LUMO levels of the PyCN and TCN derivatives were also similar because of additional CN unit in the pyrimidine core. The HOMO of the two TADF emitters was distributed in the TruX donor moiety and the LUMO was distributed in the PyCN and TCN moieties. The LUMO of PyCNTruX was localized on the acceptor groups, while that of TCNTruX was widely distributed throughout the acceptor and the linker. This is due to the large dihedral angle of the PyCN acceptors from the phenyl plane by weak hydrogen bond between PyCN and the phenyl linker. In the case of TCNTruX, hydrogen bonding induced a planar molecular conformation between the diphenyltriazine acceptor and the linker, which extended the LUMO distribution to the phenyl linker. The dihedral angles of the donor from the aromatic linker of the TADF materials were 73 ° and 70 ° in the TCNTruX and PyCNTruX emitters, respectively, due to the

Journal of Materials Chemistry C Accepted Manuscript

large steric hindrance by bulky TruX donor moiety. The ΔE_{ST} values calculated from the frontier molecular orbital distribution were 0.04 eV for TCNTruX and 0.03 eV for PyCNTruX. The ΔE_{ST} values of the two emitters were small enough for RISC process and TADF characteristics.



Published on 02 March 2020. Downloaded on 3/2/2020 11:14:20 PM.

Figure 2. Excited state natural transition orbital distribution of PyCNTruX and TCNTruX.

Natural transition orbital (NTO) of the TADF emitters was also calculated to study the nature of electronic transition.^[16] To understand the origin of the fluorescence and phosphorescence

View Article Online DOI: 10.1039/D0TC00178C

of the two TADF emitters, structure optimization was performed in the excited state and NTO was calculated by ionization potential (IP)-tuned ωB97XD functional and 6-31+G* basis set. The NTO distribution of TADF emitters is shown in **Figure 2**. In the NTO calculation of PyCNTruX and TCNTruX, the transition probability from the highest occupied natural transition orbital (HONTO) to the lowest unoccupied natural transition orbital (LUNTO) was calculated as 85 and 83%, respectively, in the singlet transition. The HONTO and LUNTO in the two TADF materials were almost completely separated, indicating that the fluorescence is dominated by charge transfer (CT) rather than local emission. In the triplet transition, the HONTO to LUNTO transition probability of PyCNTruX and TCNTruX was calculated to be 73 and 67%, respectively. The NTOs were partially overlapped in the PyCNTruX and TCNTruX emitters with extensive separation of the HONTO and LUNTO, indicating that the origin of triplet emission is a CT dominated emission with a local emission character.^[17]

The photophysical analysis of two TADF emitters was carried out using ultraviolet-visible (UV-vis) absorption and photoluminescence (PL) measurements in dilute tetrahydrofuran solution. As shown in **Figure S2a**, two TADF materials showed broad and weak absorption spectra in the long wavelength region which can be assigned to the intramolecular charge transfer (ICT) transition from the TruX donor to acceptor moieties. The ICT absorption spectra of the PyCNTruX and TCNTruX emitters were similar due to strong acceptor character of the PyCN and TCN moieties. In addition, the TADF materials showed absorption below 350 nm due to n- π * and π - π * transitions from the TruX donor and acceptor groups. As shown in **Figure S2b**, the single energy and triplet energy of the materials were measured by the fluorescent and phosphorescent PL at 77K with and without delay time (10.0 ms). The PyCNTruX and TCNTruX showed onset wavelengths of 449 and 460 nm in the fluorescence measurement,

respectively, and the TCNTruX showed red-shifted emission due to the strong TCN acceptor moiety. As a result, the singlet energies of the PyCNTruX and TCNTruX were calculated as 2.76 and 2.70 eV, respectively. The triplet energies of the PyCNTruX and TCNTruX measured from phosphorescence after delay time of 10.0 ms were 2.75 and 2.75 eV, respectively, from the onset wavelengths of 451 and 450 nm. All materials showed a very small ΔE_{ST} of less than 0.01 eV for fast RISC process.

Electrochemical oxidation and reduction were measured using cyclic voltammetry (CV). The calibration was carried out using bis(cyclopentadienyl)iron (ferrocene) standard material. As shown in **Figure S3**, the CV results afforded HOMO levels of -5.72 and -5.76 eV in the PyCNTruX and TCNTruX emitters and LUMO levels of -3.49 and -3.51 eV, respectively. The slightly deepened HOMO and LUMO levels of the TCNTruX are due to the strongly electron accepting TCN acceptor and the wide LUMO extension to the phenyl linker.

Published on 02 March 2020. Downloaded on 3/2/2020 11:14:20 PM

Thermal analysis of PyCNTruX and TCNTruX was carried out by differential scanning calorimetry (DSC) and thermogravimetric analyzer (TGA) to calculate the glass transition temperature (T_g) and thermal decomposition temperature (T_d). The DSC and TGA thermograms of two emitters are displayed in **Figure S4**. The measured T_g values of PyCNTruX and TCNTruX were 198 °C and 134 °C, respectively. In addition, the T_d values of PyCNTruX and TCNTruX at 5% weight loss were measured to be 542 °C and 536 °C. Both emitters showed high T_g over 130 °C and high T_d above 500 °C, indicating high thermal stability in OLEDs.



Figure 3. Delayed (a) and prompt (b) transient PL decay curves of the 20 wt % doped thin films in PBICT measured at room temperature under nitrogen.

In order to measure the prompt fluorescence decay time and delayed fluorescence decay time of the synthesized TADF emitters, the transient PL was measured by doping them in the 12,12'-(6-phenyl-1,3,5-triazine-2,4-diyl)bis(11-phenyl-11,12-dihydroindolo[2,3-*a*]carbazole) (PBICT) host material at 20 wt% doping concentration. As shown in **Figure 3b**, the prompt decay time of the TADF emitter was in the order of PyCNTruX (68.1 ns) > TCNTruX (52.0 ns). The triazine based TCNTruX emitters showed short decay time because of relatively large overlap of the HOMO and LUMO by the wide distribution of the LUMO to the linker between donor and acceptor due to hydrogen bonding. In the case of the delayed fluorescence decay in **Figure 3a**, PyCNTruX and TCNTruX emitters exhibited very short decay times of 1.66 and 0.95 μ s due to small ΔE_{ST} less than 0.01 eV. The small ΔE_{ST} , distorted geometry, and hybrid triplet excited state accelerated the RISC process, resulting in the small delayed fluorescence lifetime. This is one of the shortest delayed fluorescence decay time reported in the TADF emitters.

The absolute PL quantum yields (PLQYs) of the emitters were measured to study the radiative and non-radiative processes from singlet and triplet excited states. The PLQYs of the PyCNTruX and TCNTruX emitters in the PBICT hosts were 0.76 and 0.44 under a nitrogen atmosphere, respectively. The PLQY values and the decay times were used to calculate the radiative rate constant (k_r ^S), the RISC rate constant (k_{RISC}) and the non-radiative rate constant (k_{nr} ^T) according to the following equation.^[18]

Published on 02 March 2020. Downloaded on 3/2/2020 11:14:20 PM

$$\tau_{p} = \frac{1}{k_{p}(1)}$$

$$\tau_{d} = \frac{1}{k_{d}} (2)$$

$$k_{ISC} = (1 - \Phi_{F})k_{p} (3)$$

$$k_{RISC} = \frac{k_{p}k_{d}\Phi_{TADF}}{k_{ISC} \Phi_{F}} (4)$$

$$\Phi_{F} = \Phi_{O_{2}}$$

$$\Phi_{TADF} = \Phi_{N_{2}} - \Phi_{O_{2}}$$

$$k_{r}^{S} = \Phi_{F}/\tau_{p} (5)$$

$$k_{nr}^{T} = k_{d} - \Phi_{F}k_{RISC} (6)$$

The τ_p and τ_d represent the prompt and delayed fluorescence decay times, the k_p and k_d are the prompt and delayed fluorescence rate constants, the k_{RISC} and k_{ISC} are the RISC and ISC rate constants, Φ_F is absolute PLQY measured under an oxygen atmosphere, Φ_{N_2} is absolute PLQY measured under a nitrogen atmosphere, Φ_{TADF} is absolute PLQY of TADF component. k_r^S is rate constant of radiative transition from singlet excited state to ground state, and k_{nr}^T is rate constant of non-radiative transition from triplet excited state.

 Table 1. Summerazied transient PL data and calculated constants of PyCNTruX and TCNTruX

 emitters.

Emitter	Prompt component		Delayed component		PLQY		Results			
	τ _p (ns) ^{a)}	k _p (×10 ⁷ s ⁻¹) ^{b)}	τ _d (us) ^{c)}	k _d (×10 ⁶ s ⁻¹) ^d)	$\Phi_{F}^{\ e)}$	$\Phi_{TADF}^{}^{f)}$	k_{ISC} (×10 ⁷ s ⁻¹) ^{g)}	k _{RISC} (×10 ⁵ s ⁻¹) ^h	k _r s (×10 ⁶ s⁻¹) ⁱ⁾	k _{nr} ^T (× 10 ⁵ s ⁻¹) ^{jj}
PyCNTruX	68.1	1.47	1.66	0.60	0.38	0.38	0.91	9.72	5.58	2.33
TCNTruX	52.0	1.92	0.95	1.05	0.30	0.14	1.35	7.02	5.77	8.42

^{a)} Excited state lifetime of prompt component. ^{b)} Rate constant of prompt component. ^{c)} Excited state lifetime of delayed component. ^{d)} Rate constant of delayed component. ^{e)} Absolute PL quantum yield measured under oxygen atmosphere. ^{f)} Absolute PL quantum yield of TADF component. ^{g)} Rate constant of intersystem crossing from S₁ to T₁. ^{h)} Rate constant of reverse intersystem crossing. ⁱ⁾ Radiative rate constant from S₁ to ground state of singlet (S₀). ^{j)} Nonradiative rate constant from T₁ to S₀.

The k_r^S (× 10⁶ s⁻¹) values of PyCNTruX and TCNTruX were 5.58 and 5.77, respectively, and k_{RISC} (× 10⁵ s⁻¹) values were calculated as 9.72 and 7.02. The k_{RISC} value was relatively high in the PyCNTruX emitter due to high fluorescence quantum yield (Φ_{TADF}) in spite of relatively long delayed fluorescence lifetime compared to that of TCNTruX. The k_{nr}^T (× 10⁵ s⁻¹) values of PyCNTruX and TCNTruX were calculated to be 2.33 and 8.42, respectively. The PyCNTruX emitter showed high PLQY, large k_{RISC} and small k_{nr}^T for efficient TADF process.

To evaluate the potential of the TADF compounds as the TADF emitters and sensitizers, the TADF and TADF sensitized fluorescent OLEDs were fabricated to evaluate electroluminescence (EL) performances. The emitting layer of the TADF devices was the 20 wt% TADF doped PBICT layer and that of the TADF sensitized fluorescent OLEDs was the 0.5% TBRb dopant and 20% TADF emitter co-doped PBICT layer. The PBICT was chosen as the host material because the LUMO level of the synthesized TADF materials are very deep. In order to minimize the electron trapping by the TADF emitter, the PBICT host with a deep LUMO level was selected. The electron trapping will localize the emission zone near the electron trapport layer, which is not good for device lifetime.

The overall device structure and energy level diagram are shown in **Figure S5**. The current density-voltage-luminance (J-V-L), EQE-L data, and EL spectra of these devices are presented in **Figure 4**. The PyCNTruX, TCNTruX and 4CzIPN-Me emitters were tested as the greenish yellow TADF emitters and sensitizers of the yellow fluorescent dopant. As shown in **Figure 4a**, J of the TADF and TADF sensitized fluorescent devices was quite similar. Since the three TADF emitters showed similar HOMO and LUMO levels, the J was not largely different in the three devices. The L value of PyCNTruX based devices was larger than that of the TCNTruX based devices because the PyCNTruX TADF and TADF sensitized fluorescent devices was larger than that of the TCNTruX based high efficiency.

Published on 02 March 2020. Downloaded on 3/2/2020 11:14:20 PM

The maximum EQEs of the PyCNTruX, TCNTruX and 4CzIPN-Me TADF devices were 21.6, 12.8% and 15.6%, respectively, as shown in **Figure 4b**. The EQE of the TADF devices followed the trend of the PLQY. The PyCNTruX emitter with a high PLQY of 0.76 performed better than the TCNTruX emitter with a PLQY of 0.44. The efficiency roll-off of the two TADF OLEDs was negligible because of short delayed fluorescence lifetime. The fast RISC process

Journal of Materials Chemistry C Accepted Manuscript

of the TADF emitters suppressed efficiency loss mechanism by the triplet excitons, resulting in the constant EQE even at high J and L.

The peak wavelengths of the PyCNTruX, TCNTruX and 4CzIPN-Me TADF devices were 539, 540 and 546 nm (**Figure 4c**), and the Commission Internationale de L'Eclairage (CIE) coordinates were (0.40, 0.57), (0.40, 0.57) and (0.41, 0.57), respectively. The EL spectra of the three TADF emitters were suitable for sensitizing the fluorescence emission of the yellow fluorescent dopant.



Figure 4. Current density–voltage–luminance (J–V–L) (a), EQE–luminance characteristics (b) and EL spectra of TADF and sensitized TBRb devices (c).

The three TADF emitters were used as the sensitizers of the yellow-emitting TBRb fluorescent dopant. The device performances of the TADF sensitized TBRb yellow fluorescent devices are in Figure 4. The EQEs of the TBRb OLEDs with the PyCNTruX, TCNTruX and 4CzIPN-Me sensitizers were 20.2, 12.8 and 14.9%, respectively. Surprisingly, the EQE of the TBRb doped devices was quite similar to that of the TBRb free TADF devices. Little EQE loss was detected in the TADF sensitized fluorescent OLEDs. In other works, the EQE of the TADF sensitized fluorescent OLEDs was generally deteriorated compared to that of the pristine TADF device by the energy loss process through DET.^[8,19-20] In previous work, the efficiency loss mechanism was managed only when a very large blocking groups to prevent the DET was introduced.^[11] However, the loss mechanism was effectively controlled in the PyCNTruX and TCNTruX sensitized devices even without large blocking groups in the TADF sensitizer and the TBRb emitter. In the PyCNTruX and TCNTruX devices, the bulky TruX donor twisted from the phenyl linker. The bulk TruX donor makes the very fast RISC process and short delayed fluorescence lifetime (1.66 and 0.95 us) suppressed the loss process. The bulky TruX donor manages the DET by steric effect and the high RISC rate of the PyCNTruX emitter lowers the probability of DET, but increases the probability of FRET, which resulted in the high EQE over 20% in the PyCNTruX sensitized TBRb devices. The increased PLQY by energy transfer from non-radiative singlet excitons in the TADF sensitizer to the TBRb dopant is also partially responsible for the high EQE. The PLQY values of the PyCNTruX and PyCNTruX films doped with TBRb fluorescent dopants were 0.87 and 0.67, respectively. In all films, PLQY values were significantly increased by doping with TBRb, and the nonradiative singlet exciton contributed to the TBRb emission by FRET.

EL emission wavelengths of the PyCNTruX, TCNTruX and 4CzIPN-Me sensitized TBRb devices were 555, 557 and 559 nm, respectively, and CIE coordinates were (0.45, 0.53), (0.46,

0.53) and (0.47, 0.53). The CIE color coordinates of the two devices were similar becuase the EL emission was mostly from the TBRb fluorescent dopant. The device data of the PyCNTruX, TCNTruX and 4CzIPN-Me based devices are summarized in **Table 2**.

Table 2. Characteristics of TADF and sensitized TBRb device performances.

Published on 02 March 2020. Downloaded on 3/2/2020 11:14:20 PM

Emitter	Turn on Voltage (V)	External quantum efficiency (%)		Power efficiency (lm/W)		Color coordinates	
		$[1000 \text{ cd/m}^2]$	[Max]	$[1000 \text{ cd/m}^2]$	[Max]	х	у
PyCNTruX (20 wt%)	4.5	21.6	21.6	49.0	53.9	0.41	0.56
PyCNTruX:TBRb (20 wt%:0.5 wt%)	4.5	20.2	20.2	46.5	50.7	0.45	0.53
TCNTruX (20 wt%)	5.0	12.8	12.8	25.4	29.5	0.43	0.55
TCNTruX:TBRb (20 wt%:0.5 wt%)	4.9	14.6	14.6	30.2	34.2	0.46	0.53
4CzIPN-Me (20 wt%)	4.8	15.3	15.6	34.4	41.0	0.41	0.57
4CzIPN-Me:TBRb (20 wt%:0.5 wt%)	5.5	14.7	14.9	27.4	36.0	0.47	0.53

To investigate the light emission process of the TADF sensitized TBRb fluorescent devices, the transient PL of the TADF sensitized TBRb films was analyzed. As shown in **Figure 5**, the delayed fluorescence decay was accelerated and the delayed component was weakened by the TBRb doping in the TADF emitter. The acceleration of the delayed fluorescence is due to reduced singlet exciton density through FRET from the TADF sensitizer to the fluorescent dopant. The fast FRET process reduces the singlet exciton populations and facilitated the transition from triplet excited state to singlet excited state. The weakened delayed fluorescence is attributed to the suppressed ISC process by the fast FRET process. The triplet exciton population is decreased by the FRET from singlet excited state of the TADF sensitizer to the fluorescent dopant because singlet exciton population in the singlet excited state of the TADF.

sensitizer is reduced. Therefore, the delayed fluorescence was weakened by the fluorescent dopant.



Figure 5. Transient PL decay curves of the PBICT:PyCNTruX and PyCNTruX (with TBRb) (a) and the PBICT:TCNTruX and TCNTruX (with TBRb) (b) thin films measured at 300 K under nitrogen.

Furthermore, transient PL was analyzed by doping with 9-([1,1':2',1"-terphenyl]-2-yl)-10phenylanthracene (AnTP) fluorescent dopant^[21] in order to confirm whether the PyCNTruX and TCNTruX prevent DET to the fluorescent dopant. AnTP has higher S_1 and lower T_1 than the TADF material as a blue fluorescent material, and is suitable as the fluorescent material for DET. 2,4-Diphenyl-6-(4-(5-phenylindolo[3,2-a]carbazol-12(5H)analyzing yl)phenyl)pyrimidine-5-carbonitrile (4PyCNICz) emitter with 5-phenyl-5,12dihydroindolo[3,2-a]carbazole (InCZ) donor instead of the TruX donor in the same backbone structure of PyCNTruX was compared to confirm the DET managing role of the TruX donor.^[22] As shown in Figure S6, the transient PL decay of the PyCNTruX and TCNTruX emitters was not changed by doping of AnTP. Whereas, the delay component of the 4PyCNICz emitter was largely weakened by doping of AnTP, proving the DET preventing role of the TruX donor.

The operational lifetime of the TADF and TADF sensitized fluorescent OLEDs was measured at a constant current operation mode from an initial luminance of 1,000 cd/m². Figure 6 shows the operational lifetime of the TADF and TADF sensitized fluorescent OLEDs. Comparing the device lifetime of the TADF and TADF sensitized fluorescent OLEDs, the device lifetime of the TADF sensitized fluorescent OLEDs was longer than that of the TADF device. The reason for the extended device lifetime in the TADF sensitized fluorescent OLEDs is the reduction of the long decay time component as shown in transient PL data in Figure 5. The sinlget excitons of the TADF sensitizer transfer the singlet emission energy to the fluorescent dopant by FRET process, which reduces triplet exciton polulation by ISC process and singlet up-conversion of the triplet excitons. The reduced triplet exciton density suppresses triplet exciton triggered degradtion mechanisms such as triplet-triplet annihilation and triplet-polaron annihilation, which extends the device lifetime of the TADF sensitized fluorescent OLEDs. The 1,000 h lifetime of the TADF device and 1,400 h lifetime of the TADF sensitized device are the state of the lifetime of the TADF and TADF sensitized OLEDs. The device lifetime of the PyCNTruX and TCNTruX devices was much longer than that of the 4CzIPN-Me device because of high RISC rate of the TADF sensitizers. As the device lifetime greatly depends on the excited state lifetime of the excitons, the fast up-conversion is advantageous for the device lifetime. The PyCNTruX and TCNTrux showed a much higher RISC rate than 4CzIPN-Me^[8], which largely extended the device lifetime.



Figure 6. Lifetime curves of PBICT:PyCNTruX, PBICT:TCNTruX and :PBICT:4CzIPN-Me devices with or without TBRb at an initial luminance of 1,000 cd/m².

As shown in **Table 3**, the PyCNTruX sensitized yellow fluorescent OLED shows higher efficiency than other TADF sensitized yellow fluorescent OLEDs. In addition, the lifetime of the device was about 6 times longer than that of other TADF sensitized fluorescent OLED.

Host	TADF materials	Fluorescen t emitter	EQE _{max} (%)	Measurement Method	Device lifetime (h)	Color coordinate	Reference
mCBP	4CzIPN-Me	TBRb	19.1	Initial luminance 1,000 cd/m ² <i>LT90</i>	250	(0.43, 0.54)	8
mCBP	PXZ-TRZ	TBRb	18.0	Initial luminance 3,225 cd/m ² <i>LT90</i>	13	(0.45, 0.53)	7
-	4CzIPN	C ₄ -DFQA	13.5	-	-	(0.44, 0.55)	23
-	4CzIPN	C ₄ -TCF ₃ QA	14.6	-	-	(0.45, 0.54)	23

 Table 3. Summarized device performances of TADF sensitized yellow fluorescent OLEDs.

PBICT	4CzIPN-Me	TBRb	14.9	Initial luminance	251	(0.47, 0.53)	This work
PBICT	PyCNTruX	TBRb	20.2	1,000 cd/m ²	1400	(0.45, 0.53)	This work
PBICT	TCNTruX	TBRb	14.9	L190	750	(0.46, 0.53)	This work

Conclusions

Published on 02 March 2020. Downloaded on 3/2/2020 11:14:20 PM

In conclusion, two new TADF sensitizers, PyCNTruX and TCNTruX, were developed for high efficiency and long lifetime in the yellow fluorescent OLEDs. Among the two TADF materials, the PyCNTruX TADF sensitizer with a PyCN acceptor and TruX donor achieved high EQE of 20.2% and the device lifetime of 1,400 h up to 90% of initial luminance at 1,000 cd/m² in the TADF sensitized yellow fluorescent OLEDs doped with a TBRb emitter. Detailed analysis of the emission mechanism revealed that supression of the DET related non-radiative loss processes by high k_{RISC} of the TADF material due to small ΔE_{ST} and bulky TruX donor is the main mechanism for the high EQE and long lifetime. Therefore, the TADF molecular design introducing a stong electron acceptor and a strongly electron donating and bulky donor for DET control is promising as the material design of the TADF sensitizers for fluorescent OLEDs.

References

- [1] Y. J. Cho, S. K. Jeon, B. D. Chin, E. Yu and J. Y. Lee, Angew. Chem., 2015, 54, 5201.
- [2] R. Komatsu, H. Sasabe, Y. Seino, K. Nakao and J. Kido, J. Mater. Chem. C, 2016, 4,

2274.

- [3] G. Xie, X. Li, D. Chen, Z. Wang, X. Cai, D. Chen, Y. Li, K. Liu, Y. Cao, S. J. Su, Adv. Mater., 2015, 28, 181.
- [4] W. Zeng, H. Y. Lai, W. K. Lee, M. Jiao, Y. J. Shiu, C. Zhong, S. Gong, T. Zhou, G. Xie,
- M. Sarma, K. T. Wong, C. C. Wu, C. Yang, Adv. Mater. 2018, 30, 1704961.
- [5] S. P. Xiang, X. L. Lv, S. Q. Sun, Q. Zhang, Z. Huang, R. D. Guo, H. G. Gu, S. Y. Liu, L.
- Wang, J. Mater. Chem. C, 2018, 6, 5812-5820.
- [6] S. Y. Byeon, J. Kim, D. R. Lee, S. H. Han, S. R. Forrest, J. Y. Lee, Adv. Opt. Mater.,2018, 6. 1701340
- [7] H. Nakanotani, T. Higuchi, T. Furukawa, K. Masui, K. Morimoto, M. Numata, H.
- Tanaka, Y. Sagara, T. Yasuda, C. Adachi, Nat. Commun. 2014, 5, 4016.
- [8] T. Furukawa, H. Nakanotani, M. Inoue, C. Adachi, Sci. Rep. 2015, 5, 8429.
- [9] X. K. Liu, Z. Chen, C. J. Zheng, M. Chen, W. Liu, X. H. Zhang, C. S. Lee, Adv. Mater. 2015, 27, 2025.
- [10] D. D. Zhang, X. Z. Song, M. H. Cai, L. Duan, Adv. Mater. 2018, 30, 1705250.
- [11] J. H. Kim, K. H. Lee, J. Y. Lee, Chem. Eur. 2019, 25, 9060 9070.
- [12] D. J. Chen, X. Y. Cai, X. L. Li, Z. Z. He, C. S. Cai, D. C. Chen, S. J. Su, J. Mater. Chem. C, 2017, 5, 5223.
- [13] K. Wu, T. Zhang, L. Zhan, C. Zhong, S. Gong, N. Jiang, Z. –H. Lu, C. Yang, Chem.Eur. J., 2016, 22, 10860.

- [14] P. Ganesan, R. Ranganathan, Y. Chi, X. -K. Liu, C. -S. Lee, S. -H. Liu, G. -H. Lee, T.
- -C. Lin, Y. -T. Chen, P. -T. Chou, Chem. Eur. J., 2017, 23, 2858.
- [15] I. S. Park, J. Y. Lee, T. Yasuda, J. Mater. Chem. C, 2016, 4, 7911.
- [16] H. Sun, C. Zhong, J.-L. Bredas, J. Chem. Theory Comput., 2015, 11, 3851.
- [17] K. Le, D. Kim, J. Phys. Chem. C. 2016, 120, 28330.
- [18] K. Masui, H. Nakanotani, C. Adachi, Org. Electron., 2013, 14, 2721-2726.
- [19] H. J. Jang, J. Y. Lee, J. Kwak, D. Lee, J. -H. Park, B. Lee, Y. Y. Noh, J. Inf. Disp. 2019, 20, 1.
- [20] I. H. Lee, W. Song and J. Y. Lee and S-H. Hwang, J. Mater. Chem. C, 2015, 3, 8834-8838.
- [21] J. H. Yun, C. H. Lee, K. S. Yook, J. Y. Lee, Synth, Met., 2016, 217, 216.
- [22] J. S. Jang, H. L. Lee, K. H. Lee, J. Y. Lee, J. Mater. Chem. C, 2019, 7, 12695-12703.
- [23] S. P. Wang, Y. W. Zhang, W. P. Chen, J. B. Wei, Y. Liu, Y. Wang, Chem. Commun.
- 2015, 51, 11972-11975.

[24] S. Y. Byeon, J. H. Kim, J. Y. Lee, ACS Appl. Mater. Interfaces, 2017, 9, 13339-13346.