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Highly Efficient Thermally Activated Delayed Fluorescence via Unconjugated Donor-Acceptor System Realizing EQE of over 30%

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Here, two novel thermally activated delayed fluorescence (TADF) emitters, **2tDMG** and **3tDMG**, were synthesized for high-efficiency organic light-emitting diodes (OLEDs). The two emitters have a tilted face-to-face alignment of donor (D)/acceptor (A) units presenting intramolecular non-covalent interactions. The two TADF materials were deposited either by evaporation-process or by solution-process, both of them leading to high OLEDs performance. **2tDMG** used as the emitter in an evaporation-processed OLEDs achieves a high external

quantum efficiency (EQE) of 30.8% with a very flat efficiency roll-off of 7% at 1000 cd/m². The solution-processed OLEDs also displays an interesting EQE of 16.2%. **3tDMG** shows improved solubility and solution processability as compared to **2tDMG**, and thus a high EQE of 20.2% in solution-processed OLEDs is recorded. The corresponding evaporation-processed OLEDs also reach a reasonably high EQE of 26.3%. Encouragingly, this work provides a novel strategy to address the imperious demands for OLEDs with high EQE and low roll-off.

In the past decade, the development of organic light-emitting diodes (OLEDs) was reshaped by thermally activated delayed fluorescence (TADF) which can fully utilize both singlet/triplet manifold excitons through reverse intersystem crossing (RISC) and remove heavy metal by using environmentally benign pure organic molecules.^[1] Now, the cutting-edge TADF materials can exceed 30% external quantum efficiency (EQE) in electroluminescent devices, but these highly efficient TADF materials are basically limited to donor (D)- π -acceptor (A) molecular architecture.^[2] This type of molecular design, firstly proposed by Adachi et al. for TADF,^[1a] can tune their D or/and A groups, geometries and steric hindrance between them to generate twisted induced charge-transfer (TICT)-type emission.^[3] The twisted dihedral angle between D and A units can minimize the singlet-triplet splitting energy (ΔE_{ST}) for fast RISC,^[1c, 4] but the resulted TADF OLEDs still need to be significantly improved, notably in terms of efficiency roll-off at high brightness and concentration quenching because of the π - π intermolecular interactions in the solid-state.^[5] Another way to achieve TADF is to use D/A complex, in which the D/A blocks are spatially isolated, but their forming exciplexes are far less efficient than D- π -A analogues and the resulting OLEDs also display severe efficiency roll-off.^[6]

Recently, researchers conceptually consider that the intramolecular noncovalent interaction between D/A units in face-to-face alignment could be a new option to realize TADF.^[7]

Constructing TADF materials in this unconjugated way has the potential to combine the small ΔE_{ST} value with substantial transition dipole and achieve high luminescent efficiency.^[8] These two electron-rich and electron-poor π -systems need to be held close in space to form homoconjugation. In this regard, dozens of molecular frameworks have been employed but the performances remain around 10%~20% EQE,^[7,8] similar to those of D/A complexes. The problem may probably account for the D/A geometry not only the D/A distance. In other words, short D/A distance is essential for TADF but cannot ensure high efficiency which is more challenged and determinant for material and device performance. In addition, restriction of intramolecular motion (RIM) should also be taken into account in regard to enhancing photoluminescence quantum yield (PLQY).^[1b,5,7b,9] However, in previously reported structures, it is noted that both D and A units are extended in single bonds, indicating the molecular conrotatory motion cannot be thoroughly restricted.^[4,7c,7d] Even though these D/A units exist in a short distance and the excitation process is completed, the emission energy may be lost in free rotation.

In this work, we designed highly efficient TADF materials based on D/A intramolecular noncovalent interaction; the key design rules include not only the short D/A distance but also the fixation of the D/A geometry. We connected the D/A units via a rigid linker, thereby confining them into a closely-packed coplanar configuration (**Figure 1a**).^[10] In light of the molecular construction, the target TADF materials could achieve very small ΔE_{ST} and high PLQY simultaneously. Besides, we also introduced *t*-butyl groups to improve the solubility of the TADF emitters. For the acceptor, the 2,4,6-triphenyl-1,3,5-triazine (TPZ) is a nearly planar structure because of strong hydrogen bonding, and the rigid structure contributes to space charge transfer and reduced molecular vibration leads to enhanced PLQY. Two greenish-blue TADF emitters, 2-(*tert*-butyl)-10-(4-(*tert*-butyl)phenyl)-1'-((4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-10*H*-spiro[acridine-9,9'-fluorene]) (**2tDMG**) and 2,7-di-*tert*-butyl-

10-(4-(tert-butyl)phenyl)-1'-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-10*H*-spiro[acridine-9,9'-fluorene] (**3tDMG**), were applied in both evaporation-processed and solution-processed TADF OLEDs. **2tDMG** achieved an extremely high EQE of 30.8% (evaporation-process) with efficiency roll-off while **3tDMG** also obtained a high EQE of 20.2% (solution-process) because of its better solubility. These excellent results open new avenues for the study of spatial electronic interactions in organic emissive materials.

The TADF materials of **2tDMG** and **3tDMG** can be facilely prepared through efficient three-step reactions (Supporting Information, **Scheme S1**). Although the overall yield of the optimized route is high, it should be noted that the reaction sequence is quite critical. We once tried to append the donor, the *t*-butyl substituted triphenylamine, at C9 site of fluorene to form spiro structure and then linked it with the acceptor, TPZ, to afford the target molecules. But due to the great steric hindrance at C1 site of fluorene,^[11] the last-step Pd-catalyzed coupling gave no product. The synthetic failure is an important hint: in previous reports,^[12] the researchers had not met similar difficulty when they introduced D/A units in short spatial distance via coupling reaction, indicating other molecular backbones to hold close D/A units were still somewhat flexible. But in our cases, the bulky and robust spiro-backbone prevented coupling reaction from happening at the adjacent C1 site.

The conjecture about D/A special conformation hinted by the above steric hindrance is confirmed by the single crystal structures of **2tDMG** and **3tDMG** (Supporting Information, **Figure S1-S3, Table S1**). Significantly, the presence of rigid spiro structure fixes the donor and refrains the acceptor from rotational and vibrational movement to a large extent. It indicates a short distance between donor and acceptor and a well D/A cofacial conformation, which are beneficial for spatial D/A charge transfer.^[7b,13] The minimum distances between A and the best fit plane of D are 3.09 Å of **2tDMG** and 3.11 Å of **3tDMG** which are similar to

the inter-ring distance (3.09 Å) of [2.2]paracyclophane,^[14] the closest stacked aromatic rings reported to date. Then, dihedral angles between the planes of the fluorene and the TPZ are 72.48° and 69.57° for **2tDMG** and **3tDMG**, respectively, indicating D/A planes in **2tDMG** are in more parallel conformation.

Following the fascinating cofacial D/A configuration seen in the crystal structure, the D/A interaction was further understood by the computational simulation. Ground-state and excited-state geometries at the B3LYP-D3BJ^[15,16]/def2-SVP^[17,18] and wb97xd^[19]/def2-SVP^[17,18] levels are respectively performed (Supporting Information, **Figure S4**, **Table S2**). In low-lying singlet (S_1) state, the hole/electron are separated to the donor and acceptor respectively, but in low-lying triplet (T_1) state, the hole/electron are localized on the fluorene linker, because the fluorene segment has the lowest triplet energy (Supporting Information, **Figure S5**). The calculation also shows a significant separation of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs). For both **2tDMG** and **3tDMG**, the HOMO is mainly located on the *t*-butyl substituted triphenylamine units and the LUMO is mostly situated at TPZ segments (**Figure 1b, c**). Because of the similar acceptor, **2tDMG** and **3tDMG** have similar LUMO energy levels of -2.091 and -2.093 eV, respectively. Meanwhile, **3tDMG** has a relatively higher HOMO (-4.896 eV) than **2tDMG** (-4.968 eV) owing to the stronger donor ability of the triphenylamine unit with one more *t*-butyl group. The detailed information is collected in **Table S2**. On the other side, the functions of reduced density gradient (RDG) and Sign (λ_2) ρ were calculated to show the intramolecular non-covalent interactions in **2tDMG** (**Figure 1d, f**) and **3tDMG** (**Figure 1e, g**). The green region and brown region of RDG analysis show the presence of obvious attractive interactions and large steric hindrance between D and A moieties respectively, which could be beneficial for suppressing the intramolecular vibrations and reducing energy loss of the excited molecules.^[20]

2tDMG and **3tDMG** were analyzed by ultraviolet–visible (UV-vis) absorption and photoluminescence (PL) measurements in the toluene solution (**Figure 2a**). In the absorption spectra, **2tDMG** and **3tDMG** both show strong absorption at nearly 300 nm attributed to the local π - π^* transitions. On the other hand, they also exhibited an intramolecular charge transfer (ICT) transition band around 400 nm displaying weak absorption between 370 and 440 nm, indicating a non-trivial level of interaction between the D/A moieties. Then, based on the absorption edges, the corresponding optical bandgaps can be calculated to be 2.75 eV for **2tDMG**, and 2.66 eV for **3tDMG**, respectively. When excited at 340 nm in the toluene solution at room temperature, a strong emission is observed for both **2tDMG** and **3tDMG**, at 502 and 505 nm respectively. We can obtain the S_1 energies and the T_1 energies of **2tDMG** and **3tDMG** from the fluorescence spectra and phosphorescent spectra in toluene at 77 K (Supporting Information, **Figure S6**). Therefore, the ΔE_{STS} of **2tDMG** and **3tDMG** were calculated to be 0.03 and 0.01 eV, respectively. The ΔE_{STS} are quite small and would be beneficial for the efficient RISC process. **Figure 2b** shows transient PL decay curves which were measured by vacuum-deposited process. Transient PL measurements of **2tDMG** and **3tDMG** dispersed in bis[2-(diphenylphosphino)phenyl]ether oxide (DPEPO) host material were investigated to analyze the excited-state lifetime for the delayed PL emission. The doped films exhibited a prompt decay component and a delayed emission decay profile. The prompt decays of **2tDMG** and **3tDMG** doped film with lifetimes of 106 and 91 ns are observed respectively, meanwhile, the delayed sections of these two TADF materials are respectively 3.43 and 2.28 μs measured at 300 K. With the temperature decreasing from 300 to 100 K, the delayed sections were reduced gradually. Because the delayed fluorescence emission process is triggered by RISC of TADF materials which is a thermally activated process, it reaffirms the TADF nature of **2tDMG** and **3tDMG**. To further compare exciton utilization, PLQY was

measured under nitrogen atmosphere and the PLQY of **2tDMG**: DPEPO film (87%) is slightly higher than **3tDMG**: DPEPO film (86%) (Supporting Information, **Table S3**).

The HOMO energy levels of **2tDMG** and **3tDMG** are determined by the onset of the first oxidation wave (Supporting Information, **Figure S7**), and the LUMO energy level can be calculated from the optical bandgap based on UV-vis absorption spectra and the HOMO energy level. The HOMO energy level of **2tDMG** is estimated to be -5.12 eV, and **3tDMG** has a higher HOMO of -5.03 eV corresponding to the more *t*-butyl groups. For comparison, the spirophenylacridine-fluorene compound, not bearing *t*-butyl groups displays a lower HOMO energy level (-5.33 eV obtained from $E^{1/2}$).^[21] This translates the significant impact of the number of *t*-butyl groups located at the donor for HOMO energy level. The LUMO energy levels of **2tDMG** and **3tDMG** are both estimated to be -2.37 eV as their acceptor is identical. Therefore, the electrochemical bandgaps (E_{gs}) of **2tDMG** and **3tDMG** are calculated to be 2.75 and 2.66 eV, respectively.

Thermal and morphological stabilities are fundamental to the fabrication and operation of OLED. To investigate the thermal stability, thermogravimetric analysis (TGA) was carried out under a nitrogen atmosphere. As presented in **Figure S8**, the decomposition temperatures (T_d) of **2tDMG** and **3tDMG** with 5% weight loss are recorded at 369 and 375 °C, respectively. Differential scanning calorimetry (DSC) of **2tDMG** and **3tDMG** have also been measured showing high glass transition temperatures of 165 and 154 °C, respectively (Supporting Information, **Figure S9**). The results of TGA and DSC suggest that these two TADF materials can be fabricated in vacuum deposition and solution process for OLED manufacture because of great morphological stability. All these energy levels and physical properties are summarized in **Table 1**.

To investigate the electroluminescence (EL) properties of **2tDMG** and **3tDMG**, we fabricated the devices using these materials as emitters (Device 1-6). The OLED devices based on DPEPO as the host material exhibited a high efficiency at driving voltages lower than 3 V, (**Figure S10-S15**). There is a trend that the operating voltages decrease as the doping ratios increase, implying charge-carrier transport property of TADF emitters is better than that of the DPEPO host material. Then, we added the hole and exciton blocking layers and fabricated device 1 (**2tDMG**) and 2 (**3tDMG**). The optimal device performance achieved with this structure of: ITO/ 1,4,5,8,9,11-hexaazatriphenylenehexacarbonitrile (HAT-CN, 10 nm)/ 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC, 40 nm)/ 4,4',4''-tris-(carbazol-9-yl)-triphenylamine (TCTA, 8 nm)/ 1,3-di(9*H*-carbazol-9-yl)benzene (*m*CP, 8 nm)/ DPEPO: 40 wt% emitters (20 nm)/ DPEPO (8 nm)/ 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB, 40 nm)/ 8-hydroxyquinolinolato-lithium (Liq, 2 nm)/ Al (100 nm). The device configuration and molecular structures of functional materials are shown in **Figure S10**. HAT-CN and Liq were employed as the hole and electron-injection materials, respectively; TAPC and TmPyPB served as the hole-transporting layer and electron-transporting layer; emitter doped in DPEPO host utilized as the emitting layer (EML); TCTA was used as the exciton blocking layer, and the high T_1 of *m*CP and DPEPO can confine triplet excitons within the EMLs. **Figure 3** shows the performances of the vacuum-deposited OLEDs based on **2tDMG** and **3tDMG** and the EL maximum peaks are 504 and 518 nm respectively, agreeing well with their photoluminescence behaviors. The best EL efficiency is found with **2tDMG** (device 1: 30.8%, 88.5 cd/A, 71.8 lm/W) whereas **3tDMG** displays lower performance (device 2: 26.3%, 85.0 cd/A, 73.9 lm/W) and both devices show a small roll-off. **2tDMG** has much shorter D/A distance, meanwhile, the fit planes of donor and acceptor are near to parallel which is beneficial for space charge transfer. Then, we also designed devices 3 and 4, in which *m*CP was used as host instead of DPEPO, device structure: ITO/ HAT-CN (10 nm)/ TAPC (40 nm)/ TCTA (8 nm)/ *m*CP: emitters (20 nm, 30 wt% for **2tDMG**, 20 wt% for **3tDMG**)/

TmPyPB (40 nm)/ Liq (2 nm)/ Al (100 nm). However, the EL efficiencies of **2tDMG** and **3tDMG** were lower than those using DPEPO. Actually, it is believed that n-type hosts, such as DPEPO, are suitable to realize stable delayed fluorescence organic electroluminescent devices.^[22]

Because of the *t*-butyl groups, **2tDMG** and **3tDMG** have the potential for solution-processed OLEDs. Therefore, we fabricated solution-processed OLEDs (Device 5-6) as shown in **Figure 3**, and the best structure was: ITO/ poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS, 40 nm)/ 10-(4-(4-(9*H*-carbazol-9-yl)phenylsulfonyl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (CzAcSF): 10 wt% emitters (40 nm)/ DPEPO (10 nm)/ TmPyPB (50 nm)/ Liq (1 nm) / Al (100 nm). In these devices, PEDOT:PSS and Liq acted as the hole-injection layer and electron-injection layer respectively, TmPyPB served as the electron-transporting layer, and CzAcSF was selected as the host. DPEPO was used as the hole-blocking layer to optimize the devices (Supporting Information, **Figure S16, S17**). These solution-processed OLEDs show blue-shift EL emission peaks, 486 (**2tDMG**) and 504 nm (**3tDMG**), compared to the vacuum-processed devices. Moreover, these solution-processed OLEDs achieve competitive high efficiencies with maximum EQEs of 16.2% (**2tDMG**) and 20.2% (**3tDMG**). It is believed that the better solubility of **3tDMG** than **2tDMG** due the presence of two *t*-butyl groups is one of the reasons of its better device performance in solution process OLEDs (**Figure S18**). To our best knowledge, this is also the first time reaching 20% EQE threshold out of the traditional D- π -A TADF series.^[7a,7c,23] All the device performances of **2tDMG** and **3tDMG** are summarized in **Table 2**.

In summary, we designed and synthesized greenish-blue TADF emitters based unconjugated D/A blocks interacted in confined space. These materials rely on the rigid backbone and short D/A distance which in turn restrict the free rotations of constitutional blocks and impose D/A

to adopt a favorable cofacial conformation. t-butyl groups are introduced to make the TADF emitters **2tDMG** and **3tDMG** suitable for both evaporation and solution processed devices. As a result, both materials show small ΔE_{ST} and high PLQY as well as high T_g because of the rigid backbone. In evaporation-processed TADF devices, **2tDMG** and **3tDMG** achieve 30.8% and 26.3% EQEs respectively; notably, the efficiency can retain as high as 28.5% and 23.2% at the 1000 cd/m² respectively, indicating very flat efficiency roll-offs. In solution-processed OLEDs, the maximum EQEs are 16.2% and 20.2% for **2tDMG** and **3tDMG** respectively. These excellent performances clearly demonstrate a disruptive motif in constructing highly efficient TADF materials out of conventional D- π -A architecture. We thus believe our results could shed a new light on the development of optoelectronic functional materials in noncovalent interactions.

[CCDC-1992381 (**2tDMG**) and CCDC-1992382 (**3tDMG**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

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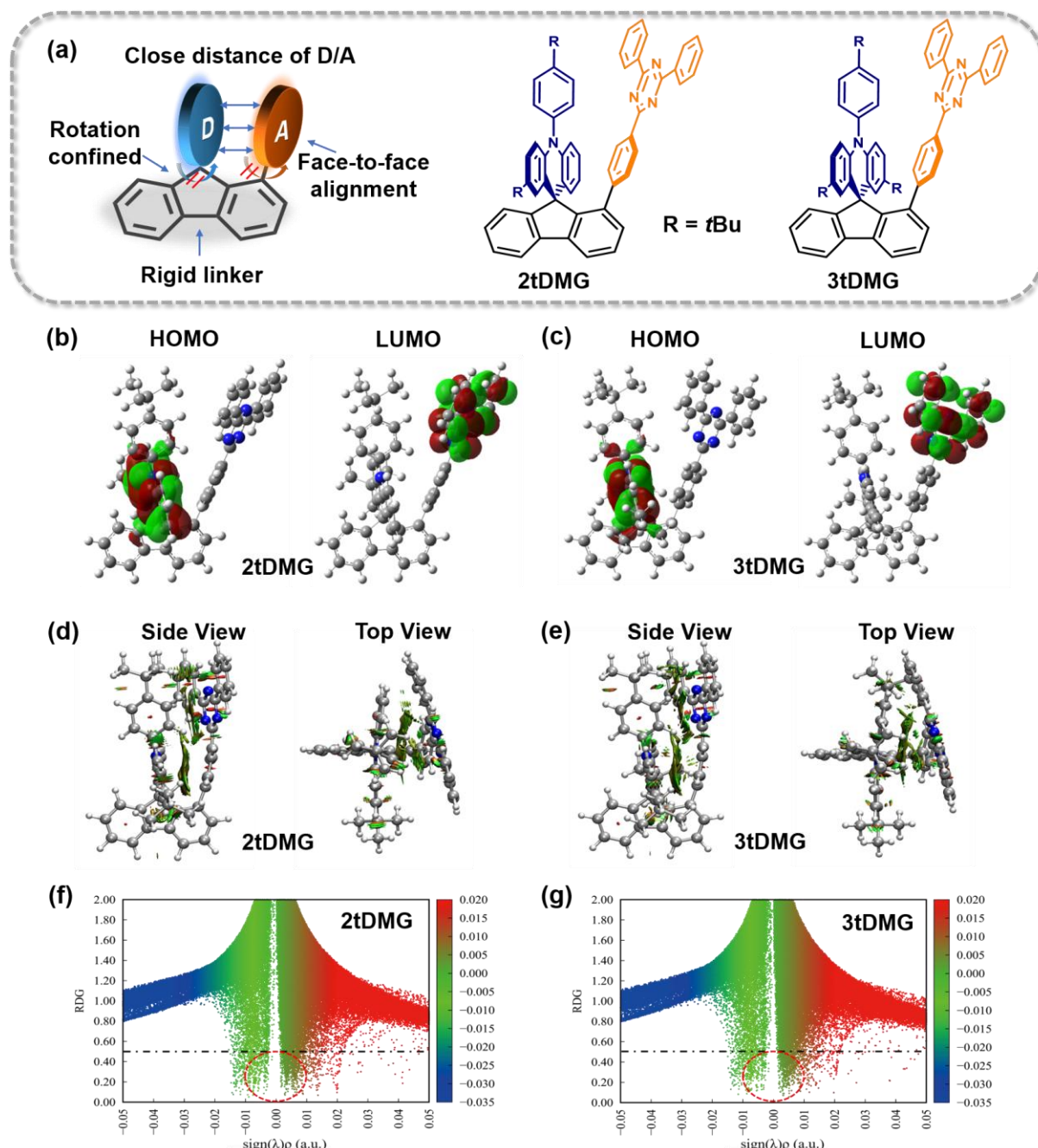


Figure 1. Configuration and molecular structures (a) of **2tDMG** and **3tDMG**; HOMO and LUMO orbital distributions of (b) **2tDMG** and (c) **3tDMG**. Reduced density gradient (RDG)

isosurface map with an isovalue of 0.5 for (d) **2tDMG** and (e) **3tDMG**. The functions of RDG and $\text{Sign}(\lambda_2)\rho$ for (f) **2tDMG** and (g) **3tDMG**.

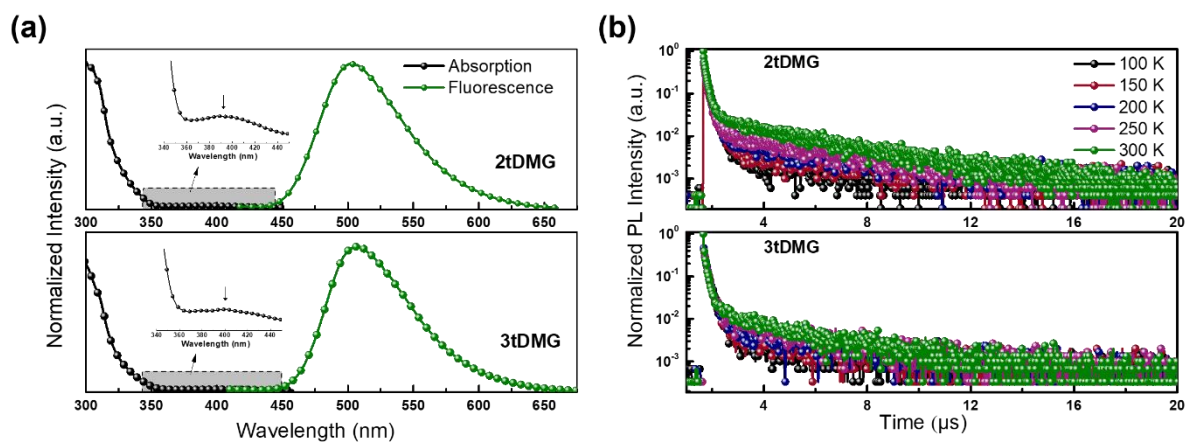


Figure 2. (a) UV-vis absorption, fluorescence (298 K) of **2tDMG** and **3tDMG** respectively. (b) Temperature-dependent PL decay curves from 300 to 100 K of **2tDMG** (40 wt%) and **3tDMG** (40 wt%) doped in DPEPO film respectively.

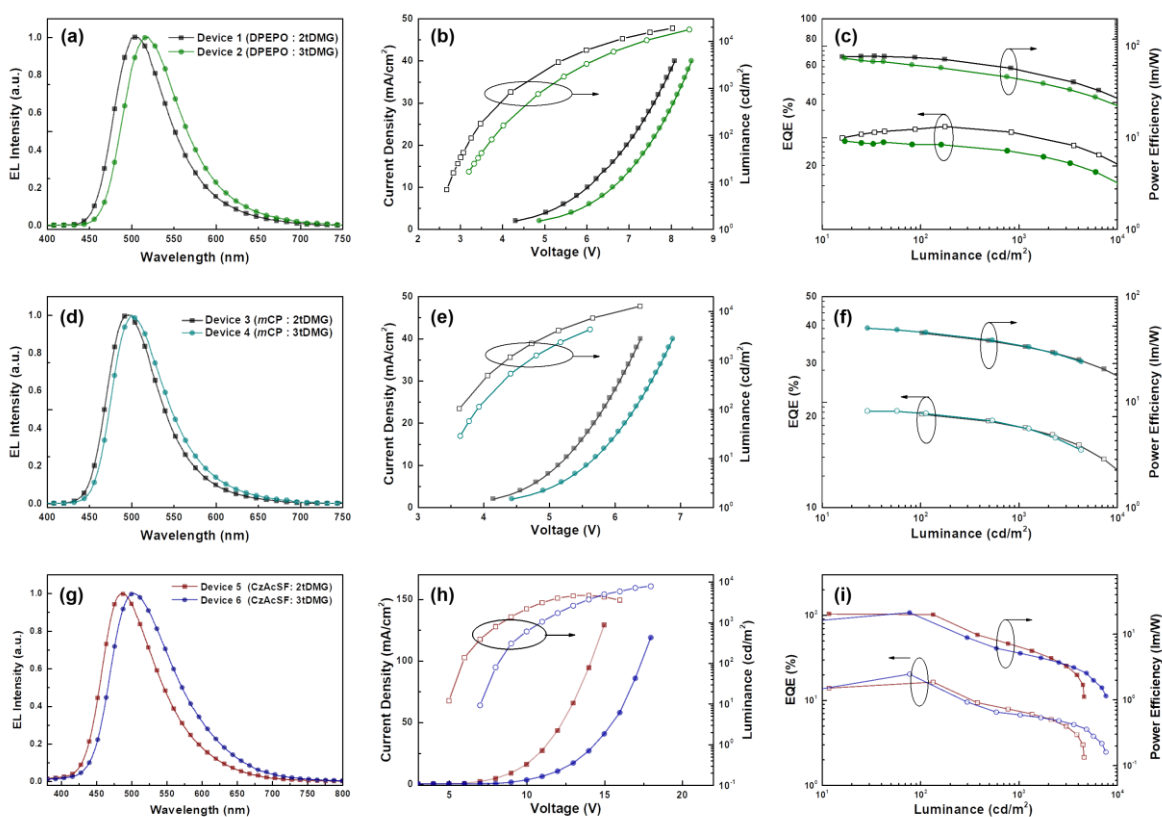


Figure 3. OLED device performances based on different device structures (Device 1-6). (a, d, g) EL spectra curves; (b, e, h) current density to voltage to luminance (J - V - L) curves; (c, f, i) EQE to luminance curves and power efficiency (PE) to luminance curves.

Table 1. Summary of photophysical, electrochemical and thermal properties of **2tDMG** and **3tDMG**.

Compounds	$\lambda_{\text{abs}}^{\text{a)}$ [nm]	$\lambda_{\text{em}}^{\text{a)}$ [nm]	$S_1^{\text{b)}$ [eV]	$T_1^{\text{b)}$ [eV]	ΔE_{ST} [eV]	HOMO ^{c)} [eV]	LUMO ^{c)} [eV]	$T_g^{\text{d)}$ [°C]	$T_d^{\text{e)}$ [°C]
2tDMG	297, 389	502	2.96	2.93	0.03	-5.12	-2.37	165	369
3tDMG	289, 403	505	2.91	2.90	0.01	-5.03	-2.37	154	375

^{a)} In toluene (10^{-5} M) solution at room temperature; ^{b)} determined from the fluorescence and phosphorescence spectrum measured in toluene solution at 77 K. ^{c)} estimated from the redox potential in cyclic voltammetry; ^{d)} T_g obtained from DSC measurements; ^{e)} T_d obtained from TGA measurements.

Table 2. Summary of device performances utilizing **2tDMG** and **3tDMG**.

Device	Process	Host: Dopant	EL [nm]	EQE ^{a)} [%]	PE ^{a)} [lm/W]	CE ^{a)} [cd/A]	CIE [x, y]
1	evaporation	DPEPO: 2tDMG	504	30.8, 28.5, 24.6	71.8, 55.5, 38.8	88.5, 81.9, 70.3	(0.24, 0.53)
2	evaporation	DPEPO: 3tDMG	518	26.3, 23.2, 20.1	73.9, 44.3, 31.5	85.0, 74.3, 64.2	(0.29, 0.57)
3	evaporation	<i>m</i> CP: 2tDMG	496	20.4, 18.5, 16.1	50.1, 34.0, 25.2	52.0, 47.3, 41.2	(0.20, 0.46)
4	evaporation	<i>m</i> CP: 3tDMG	501	20.8, 18.4, 15.6	45.0, 32.7, 24.4	58.0, 51.8, 43.8	(0.24, 0.52)
5	solution	CzAcSF: 2tDMG	486	16.2, 7.4, 3.6	20.1, 6.4, 2.4	37.5, 17.2, /	(0.22, 0.37)
6	solution	CzAcSF: 3tDMG	504	20.1, 6.7, 4.9	21.1, 5.1, 2.9	53.6, 17.9, 12.0	(0.28, 0.46)

^{a)} Values of external quantum efficiency (EQE), power efficiency (PE) and current efficiency (CE) at the maximum, 1000 cd/m², and 4000 cd/m², respectively.

The table of contents entry: The thermally activated delayed fluorescence emitter 2tDMG is designed and synthesized based on donor (D)/acceptor (A) spatially intramolecular noncovalent interaction. The D/A units are connected via a rigid linker, thereby confining them into a close-packed coplanar configuration for small singlet-triplet splitting energy (ΔE_{ST}). 2tDMG achieves a high external quantum efficiency of 30.8% with a low efficiency roll-off in evaporation-processed.

Keyword: thermally activated delayed fluorescence; organic light-emitting diodes; high efficiency; intramolecular spatial charge transfer; spiro structure

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