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Exciplex Formation and Electromer Blocking for Highly Efficient Blue Thermally Activated Delayed Fluorescence OLEDs with All-Solution-Processed Organic Layers

Xinxin Ban,^{*[a, b]} Feng Chen,^[a] Jie Pan,^[a] Yan Liu,^[a] Aiyun Zhu,^[a] Wei Jiang^{*[b]} and Yueming Sun^[b]

Abstract: Highly efficient solution-processable emitters are greatly desired to develop low-cost organic light-emitting diodes (OLEDs). The recently developed thermally activated delayed fluorescence (TADF) materials are promising candidates, but blue TADF materials compatible with the all-solution-process still not be achieved. Here, a serial of TADF materials, named X-4CzCN, are developed by introducing the bulky units through unconjugated linker, which realizes high molecular weight to enhance the solvent resistance ability without disturbing the blue TADF feature. Meanwhile, the peripheral wrapping groups efficiently inhibit the triplet-triplet and triplet-polaron quenching by isolating the energy transfer and charge transporting channels. The photophysical measurements indicate that a small variation in peripheral unit will have a noticeable effect on the luminescence efficiency. The enlarged volume of peripheral units will make the electroluminescent spectra blue-shift, while enhancing the energy transfer of exciplex and blocking the energy leakage of electromer can facilitate the exciton utilization. As a result, the fully solution-processed blue OLED achieves a CIE of (0.16, 0.27), a low turn on voltage of 2.9 eV and a high external quantum efficiency of 20.6%. As far as we known, this is the first report of all-solutionprocessed TADF OLEDs with blue emission, which exhibits a high efficiency even comparable to the vacuum-deposited devices.

Introduction

Thermally activated delayed fluorescent (TADF) materials have been extensively investigated due to their potential ability to harvest 100% internal quantum efficiency through a reverse intersystem crossing (RISC) process from the triplet state to the singlet state.^[1] Despite being a new technology, the maximum EQE values of vacuum-deposited TADF organic light emitting diodes (OLEDs) are over 30%, which is comparable to the stateof-the-art phosphorescent OLEDs.^[2] Recently, the intensive researches have been devoted to the development of solutionprocessed TADF OLEDs, which is cost effective both in preparation technics and material systems.^[3] However, the device performance of solution-processed TADF OLEDs are still far

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behind its vacuum-deposited counterparts due to the lack of functional TADF emitters, especially the blue one.

The molecular design plays a critical role in achieving highly efficient solution-processable TADF materials. One of the useful methods is the exploitation of small molecular or polymer TADF emitters with high solubility in aromatic solvents and good film forming ability through wet-process.^[4] By using these soluble TADF materials as emitters, solution-processed OLEDs with the EQE around 20.0% have been successfully achieved.^[5] However, due to the severe aggregation induced exciton quenching (ACQ) effect, these small molecular or polymer TADF emitters must be doped in appropriate host materials to achieve high electroluminescence efficiency.^[6] Unfortunately, the doping structure with small molecular hosts make the device not able to be fabricated by fully solution-process, because the solvent used to deposit upper layer will dissolve the bottom layers beneath it.^[7] Thus, most of the reported solution-processed TADF OLEDs usually contain a solution-processed emission layer (EML) and a vacuum-deposited electron transporting layer (ETL).^[8] In fact, the advantage of solution-processed devices for low-cost and largesize OLEDs require all the organic materials to be solutionprocessed.^[9] Normally, to design TADF emitters compatible with fully solution-process, the multifunctional properties must be centralized into one molecule, such as (1) good film forming ability through solution-process, (2) excellent resistivity toward orthogonal solvent, and (3) restricted exciton quenching effect in the congested non-doped film state.^[10] However, it is difficult to fulfill the tradeoff between blue TADF and solvent resistance, which require material not only enlarge π -conjugation and molecular weight to resist the solvent erosion, but also keep the small ΔE_{ST} and blue emission unchanged. Unfortunately, the fully solution-processed TADF blue OLEDs have been still unable to be achieved due to the lack of such multifunctional TADF blue emitters until now. Therefore, the developing of novel blue TADF emitters compatible with fully solution-process and deeply investigating the relationship between molecular structure and device performance is an urgent problem to be solved.

In this work, we present three solution-processable blue TADF emitters, MCz-4CzCN, PhCz-4CzCN and PhDCz-4CzCN, by utilizing 4CzCN as emissive core, which is chosen for its clear TADF feature with small ΔE_{ST} and efficient triplet harvesting. Photophysical investigation indicates that the introduced bulky units can effectively reduce the intermolecular interactions between the TADF cores, which ensure them to be used in non-doped devices. Meanwhile, the increased molecular weight makes the materials possess good resistivity toward orthogonal solvent, which enable the fabrication of fully solution-processed OLEDs. Furthermore, the detail relationship between molecular structures and EL performances indicates that the increased steric volume of wrapping units will make the electroluminescent

[[]a] Dr. X. X. Ban, Dr. F. Chen, Dr. J. Pan, Dr. Y. Liu, Dr. A. Y. Zhu Jiangsu Key Laboratory of Function Control Technology for Advanced Materials, School of Chemical Engineering, Jiangsu Ocean University, Jiangsu, 222005, China E-mail: banxx@hhit.edu.cn

[[]b] Title(s), Initial(s), Surname(s) of Author(s) School of Chemistry and Chemical Engineering, Southeast University, Nanjing, 211189, P. R. China E-mail: jiangw@seu.edu.cn

spectra blue-shift, while the blocking of energy leakage from TADF core to the peripheral electromer state is quite important for enhancing the exciton utilization. By using these new designed materials as emitters, fully solution-processed blue TADF OLEDs are successfully fabricated for the first time with high efficiency and stable emission. Particularly, PhCz-4CzCN based device achieves the considerable high performance with the current, power and external quantum efficiency of 40.8 cd A⁻¹, 27.5 lm W⁻ ¹ and 20.6%, respectively, which are comparable to the reported devices with vacuum-deposited ETL. Importantly, the turn on voltage was only 2.9 V and the EQE remains as high as 20.0% and 18.2% at the luminescence of 100 and 1000 cd m⁻², respectively. The extremely low turn-on voltage and small efficiency roll-off proves the superiority of exciplex formation in enhancing the charge injection and exciton utilization. This research provides reference for the further design of more efficient TADF materials for fully solution-processed OLEDs.

Results and Discussion

Synthesis and characterization: Scheme 1 exhibits the chemical structures of the designed TADF emitters and the detailed synthetic routes of the materials are shown in Scheme S1. The emissive core 4CzCN was synthesized in one-step reaction from a commercially available starting material 2,3,5,6tetrafluorobenzonitrile with 4-methoxy-9H-carbazole. According to the same strategy, the other three encapsulated compounds were synthesized from the corresponding branch frameworks. The peripheral units, MeCz, PhCz and PhDCz were achieved by connecting 4-methoxy-9H-carbazole to the halogenated compounds with different molecular-sized through Ullmann reaction. After demethylating by boron tribromide, the bulky units were combined with 4-(6-bromohexyloxy)-9H-carbazole by nucleophilic substitution. Finally, MeCz-4CzCN, PhCz-4CzCN and PhDCz-4CzCN were easily synthesized through aromatic nucleophilic substitution reaction with high yields above 80%. The molecular structures of the newly designed emitters were characterized by ¹H-NMR, ¹³C-NMR, mass spectrometry and elemental analysis.

Theoretical calculation: To understand the electronic property of the compounds, theoretical calculations based on density functional theory (DFT) at the b3lyp/6-31g(d) level were performed for the emission core and encapsulated molecules. The calculated electron cloud distribution and geometrical structure are displayed in Figure 1. As can be seen, the whole molecule can be divided into three functional fragments: (1) the parent core ensures the emissive properties of the molecule; (2) the peripheral bulky units offer the steric shielding effect to reduce the intermolecular interaction of the emissive cores; (3) the flexible alkyl chains act as non-conjugated linker to connect the emission and wrapping units. The lowest unoccupied molecular orbital (LUMOs) are mainly centered on the benzonitrile moieties of the emission core, while the highest occupied molecular orbital (HOMOs) are mainly delocalized over the peripheral carbazolyl moieties, which indicates that the peripheral encapsulated units not only act as

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Scheme 1. The chemical structure of the encapsulated TADF emitter and its emissive core.

steric shields to reduce the interaction between emission cores, but also play the role of hole transporting groups in the molecule. The calculated HOMO and LUMO energy levels are -5.12/-1.87, -5.14/-1.88 and -5.21/-1.92 eV for MeCz-4CzCN, PhCz-4CzCN and PhDCz-4CzCN, respectively (Table 1). Additionally, the HOMO levels of wrapping units are calculated to be -5.13, -5.14 and -5.22 eV for MeCz, PhCz and PhDCz, respectively. Comparing with HOMO energy level of the emissive core (-5.24 eV for 4CzCN), the HOMO levels of the encapsulated emitters are similar to those of wrapping units, which further demonstrate that the hole-injection and transporting capabilities would be dominated by the peripheral units. The oscillator strength for absorption (f) are calculated to be 6.34, 7.36, 7.51 and 7.56×10^{-10} ² for 4CzCN, MeCz-4CzCN, PhCz-4CzCN and PhDCz-4CzCN, respectively. The enhanced f also demonstrates that encapsulated molecules possess the larger steric hindrance by the introduction of bulky wrapping units, which can suppress the geometries changes of the excited states and reduce nonradiative deactivation.[11]

The calculation of singlet and triplet energies were also performed by using time-dependent DFT (TD-DFT). The calculated singlet and triplet energies of MeCz-4CzCN, PhCz-4CzCN and PhDCz-4CzCN are all to be 2.64 and 2.74 eV, which are identical to that of 4CzCN. As expected, an extremely small ΔE_{ST} of 0.10 eV is achieved for the molecules, which would lead to an effective RISC process and benefit the utilizations of triplet excitons. Meanwhile, the singlet and triplet energies of the peripheral units are also calculated. As can be seen from Table S1, the S₁/T₁ of MeCz, PhCz and PhDCz are 4.09/3.14, 3.99/3.15, and 3.84/3.14 eV, which are much higher than that of emissive core. Thus, the designed wrapping units can efficiently suppress the back energy transfer from the emissive core to the peripheral groups. To demonstrate exciton confinement effect, the spindensity distribution (SDD) at T₁ state was further calculated. The SDDs of the encapsulated molecules are only distributed in the emission core, no triplet spin-densities are dispersed to peripheral units. Thus, the

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Figure 1. Optimized HOMO, LUMO and SDD density maps for X-4CzCN.

introduced bulky units around the emissive core will act as envelopes to effectively inhibit the intermolecular interaction in excited T_1 states. In contrast, the exposed triplet distribution of 4CzCN will lead to the severe triplet-triplet interaction induced exciton quenching in the tight stacking state, which is detrimental to obtain high efficiency in non-doped device. Moreover, the calculated molecular weight of MeCz-4CzCN, PhCz-4CzCN and PhDCz-4CzCN are 1943.9, 2191.9, 2852.2, respectively, which are much higher than that of 4CzCN (833.3). All the above theoretical results prove that the introduction of bulky unit by unconjugated alkyl chain can efficiently increase the molecular weight without disturbing the excited energy and energy-splitting property of the emitter.

Photophysical properties: The UV-vis absorption and photoluminescence (PL) spectra of MeCz-4CzCN, PhCz-4CzCN PhDCz-4CzCN and their parent core 4CzCN in toluene solution (10⁻⁵ M) are measured at room temperature. As shown in Figure 2a, the absorption spectra of the encapsulated emitters are similar to the parent core 4CzCN. The low-energy broad bands between 370 and 430 nm were attributed to the charge transfer (CT) excitations of the emissive core, while the strong absorption peaks at 280 and 330 nm can be assigned to the n- π^* and π - π^* transitions of the carbazolyl units. Thus, when the CT absorption intensity is fixed, the characteristic absorption peaks of carbazole are enhanced with the increased carbazolyl units. The optical energy gaps of MeCz-4CzCN, PhCz-4CzCN and PhDCz-4CzCN are all estimated to be 3.10 eV according to the absorption edges, which are equal to that of 4CzCN. Moreover, the emission peaks of the three encapsulated emitters are 452 nm, which is also identical to 4CzCN. Therefore, it can be concluded that the introduction of MeCz, PhCz and PhDCz groups through nonconjugated alkyl chains did not affect the ground or emissive excited state energies of the emissive core, which is consistent with the theoretical calculation. However, the photophysical properties of the molecules in condensed state are changed. The PL spectra in films are blue shift from 478 nm for 4CzCN to 470 nm for MeCz-4CzCN, PhCz-4CzCN and PhDCz-4CzCN. Furthermore, the half peak widths of the spectra are gradually diminished with the increased skeleton-volume of the wrapping units. The blue shift emission peak and reduced half peak width indicate that the intermolecular aggregations of emission units are inhibited by efficient molecular encapsulation.

Figure S1 depicts the phosphorescence (77 K) spectra of the emitters and encapsulated units in toluene solution. The triplet energy (T₁) of MeCz-4CzCN, PhCz-4CzCN and PhDCz-4CzCN are calculated to be 2.67 eV from the onset of the phosphorescence spectra, which is equal to the emissive core 4CzCN. As estimated from the first peak of phosphorescence spectra, the peripheral units, MeCz, PhCz and PhDCz, have the same triplet energy of 3.02 eV, which is high enough to suppress the reverse energy transfer and locate the triplet excitons in the emission core. The singlet energy (S_1) of the emitters are calculated to be 2.74 eV based on the fluorescence spectra at 300 K. Therefore, according to the energy-splitting of S_1 and T_1 , the ΔE_{ST} of MeCz-4CzCN, PhCz-4CzCN and PhDCz-4CzCN are calculated to be 0.22 eV. The PLQY of 4CzCN, MeCz-4CzCN, PhCz-4CzCN and PhDCz-4CzCN are measured to be 0.36, 0.53. 0.62 and 0.65, respectively, in neat films at room temperature. The enhanced PLQY of the encapsulated emitters can be attributed to the efficient wrapping effect by the introduced units. which eliminates the collision-induced peripheral intramolecular non-radiation transitions and bimolecular processes. Furthermore, the orderly increased PLQY of MeCz-4CzCN, PhCz-4CzCN and PhDCz-4CzCN indicates that the larger the skeleton-volume of the wrapping units, the better the encapsulation effect.



Figure 2. (a) Ultraviolet-visible (UV-vis) absorption and photoluminescence (PL) spectra in toluene solution; (b) PL spectra in film state. (c) Cyclic voltammogram of 4CzCN and X-4CzCNmin CH₂Cl₂ solution; (d) Transient PL decay characteristics of the 4CzCN and X-4CzCN films.

Electrochemical properties: The electrochemical properties of the materials were examined by cyclic voltammetry with ferrocene as the reference. As shown in Figure 2c, all the materials exhibit multiple irreversible oxidation curves. According to the onset of the oxidation peak, the HOMO energy levels of 4CzCN, MeCz-4CzCN, PhCz-4CzCN and PhDCz-4CzCN are estimated to be - 5.51, -5.33, -5.36 and -5.41 eV, respectively. The HOMO levels of the encapsulated molecules are smaller than their emissive core, which means the introduced wrapping units really influence the frontier orbitals. The electrochemical properties of the

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Table 1. Physical properties of 4C2CN and X-4C2CN.									
	λ _{ems} [nm]	E _g [eV]	S ₁ /T ₁ [eV]	∆E _{ST} [eV]	HOMO [eV]	LUMO [eV]	f [10 ⁻²]	PLQY [%]	
4CzCN	452 ^a	3.37°	2.74/2.64 ^c	0.10 ^c	-5.24 ^c	-1.87°	6.34	0.36	
	478 ^b	2.84 ^d	2.90/2.68 ^e	0.22 ^e	-5.51 ^f	-2.67 ^g			
MeCz-4CzCN	452 ^a	3.25°	2.74/2.64°	0.10 ^c	-5.12°	-1.87°	7.36	0.53	
	473 ^b	2.81 ^d	2.90/2.68 ^e	0.22 ^e	-5.33 ^f	-2.52 ^g			
PhCz-4CzCN	452 ^a	3.26°	2.74/2.64°	0.10 ^c	-5.14 ^c	-1.88°	7.51	0.62	
	471 ^b	2.81 ^d	2.90/2.68 ^e	0.22 ^e	-5.36 ^f	-2.55 ^g	1.51		
PhDCz-4CzCN	452 ^a	3.29°	2.74/2.64 ^c	0.10 ^c	-5.21°	-1.92°	7 56	0.65	
	469 ^b	2.83 ^d	2.90/2.68 ^e	0.22 ^e	-5.41 ^f	-2.58 ^g	7.50		

^a Measured in toluene solution at 300 K. ^b Measured in deposited films at 300 K. ^c Obtained from Gauss simulation. ^d Estimated from the absorption edges in Toluene. ^e Estimated from fluorescent and phosphorescent spectra. ^f Determined by the CV measurement. ^g Calculated from the energy gap and HOMO level.

wrapping units are also investigated and the HOMO levels of MeCz, PhCz and PhDCz are measured to be -5.30, -5.39 and -5.44 eV, respectively (Figure S2). It clearly can be seen that the HOMO levels of the encapsulated compounds are basically equal to their corresponding wrapping units and change as the molecular structure changes. Thus, the peripheral donor units will dominate the hole transporting of the molecules. Based on the optical energy band gaps, the LUMO energy levels of 4CzCN, MeCz-4CzCN, PhCz-4CzCN and PhDCz-4CzCN are calculated to be -2.67, -2.52, -2.55 and -2.58 eV, respectively. These experimentally calculated results are in agreement with the previous estimated ones from Gaussian simulation.

Transient PL properties: The transient PL decay of these compounds are measured in film state. As shown in Figure 2d, the prompt lifetimes (T_p) of 10, 13, 13 and 15 ns for 4CzCN, MeCz-4CzCN, PhCz-4CzCN and PhDCz-4CzCN are assigned to conventional fluorescence decay, whereas the delayed lifetimes (T_d) of 1.4, 2.6, 3.3, and 3.5 µs are caused by the reverse intersystem crossing process of triplet excited state. The clearly observed nanosecond-scale prompt and microsecond-scale delayed components at room temperature confirm their TADF characteristics. Moreover, time-resolved PL spectra of X-4CzCNs illustrated in Figure S4 shows the identical prompt and delayed PL spectra, which also proves the TADF emission of these compounds. Compared with the unprotected emissive core, the encapsulated emitters show delayed components with longer lifetimes due to the reduced ICT effect and dipole-dipole interactions between the emissive fragments. Based on the PLQY and the lifetime data, the photoluminescence quantum efficiency of the delayed part (Φ_d) are calculated to be 0.23, 0.47, 0.56 and 0.58 for 4CzCN, MeCz-4CzCN, PhCz-4CzCN and PhDCz-4CzCN, respectively (Table S2). The increased Φ_d with the volume of the peripheral units indicates that the larger steric wrapping units will facilitate to the reducing of triplet-triplet annihilation. Intriguingly, despite the same ΔE_{ST} , the rate of ISC process (k_{RISC}) of MeCz-4CzCN, PhCz-4CzCN and PhDCz-4CzCN are calculated to be 0.90-1.23 \times 10⁵ s⁻¹, which are higher than that of 4CzCN ($0.42 \times 10^5 \text{ s}^{-1}$). Besides, the efficiency of the RISC (Φ_{RISC}) of the encapsulated molecules are also enhanced comparing the emissive core, and the bigger steric shields will result in larger RISC efficiency. Therefore, the introduction of wrapping units to the emissive core can significantly increase the PL efficiency of the molecule, and a small variation in the size of wrapping units will have a noticeable effect on the encapsulation effect.

Thermal and morphological properties: Figure S5 shows the thermal analysis data of MeCz-4CzCN, PhCz-4CzCN and PhDCz-4CzCN. The glass transition temperatures (T_a), measured through differential scanning calorimetry (DSC), are 101, 115 and 148 °C for MeCz-4CzCN, PhCz-4CzCN and PhDCz-4CzCN, respectively. The high T_g is important for the formation of uniform amorphous films after annealing in solution-process, which will facilitate the improvement of device efficiency and long-term stability. The decomposition temperatures (T_d) were also determined through thermogravimetric analysis (TGA). According to 5% weight loss, the T_d of MeCz-4CzCN, PhCz-4CzCN and PhDCz-4CzCN were 399, 406, and 416 °C, respectively. It is noteworthy that the T_d and T_q are sequential increased with the enlarged peripheral bulky units, which imply that the thermal properties of the encapsulated molecules can strongly enhanced by adjusting the functional groups introduced at the peripheral position. As a result, the high T_d and T_a values resulting from the bulky substituent of carbazoles and the nonplanar structures demonstrate the good thermal stability of these newly designed encapsulated compounds.



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Figure 4. (a) Current density-voltage-luminance (J-V-L) characteristics; (b) External quantum efficiency versus current density plots; (c) EL spectra of the devices and the EL color coordinates on the CIE 1931 chromaticity diagram; (d) Photographs of the blue EL emission from X-4CzCN based devices.

In order to investigate the film forming ability, the morphologies of the spin-coating films were characterized by atomic force microscopy (AFM). As shown in Figure S6, the surface of MeCz-4CzCN, PhCz-4CzCN and PhDCz-4CzCN are quite smooth with the root-mean-square (RMS) values in the range of 0.39-0.52 nm. Although 4CzCN based film also do not exhibit any pinholes after annealing, the RMS value of 4CzCN film is 1.02 nm, which is a little high than that of encapsulated materials. The above results fully prove that the introduced wrapping units by flexible linkers can enhance the film forming ability of the materials, which facilitates the formation of amorphous defect-free films through solution process. Since the molecules are designed for multilayer solution-processed OLEDs, the solvent resistant abilities of the materials are tested. Figure S7 shows the UV-Vis absorption spectra of the corresponding films before and after rinsing process by isopropanol. The spectral intensity of the MeCz-4CzCN, PhCz-4CzCN and PhDCz-4CzCN remained almost similar to that of pristine films, which indicates that the encapsulated molecules with high molecular weight possess high resistance to alcohol. In contrast, the 4CzCN film was severely dissolved by alcohol, because only less than half of the absorption intensity was left. Therefore, it can be predicted that by using these encapsulated materials as non-doped emitter for fully solution-processed OLEDs, the orthogonal solvent will not damage the preceding emission layer during the sequential deposition alcohol-soluble electron transporting layer (ETL).

Electroluminescence properties: The OLEDs with fully solution-processed organic layers are fabricated and evaluated, Figure 3 shows the device structure and fabrication process. The optimal device architecture consisted of ITO/PEDOT:PSS (20 nm)/Blue TADF (60nm)/PHPO (40 nm)/Cs₂CO₃ (2 nm)/Al (100 nm), where the blue TADF materials were used as non-doped emitters to investigate their electroluminescence (EL) performance. The PEDOT:PSS was used as a hole injection layer (HIL) to decrease the energy barrier between the emission layer (EML) and the ITO anode (indium tin oxide). In order to optimize the carrier balance, PHPO was introduced as the electron transport layer (ETL). It should be noted that all the functional

organic layers (HIL, EML and ETL) in the devices are fabricated through solution-process. The OLEDs containing each of the three encapsulated emitters, MeCz-4CzCN, PhCz-4CzCN and PhDCz-4CzCN, are denominated as Device A, Device B and Device C, respectively. In addition, we also fabricated a reference device (Device D), which contains the parent core 4CzCN as emitter to estimate the other device results. Figure 4a and b show current density-voltage-luminance (J-V-L) curves and EQEluminance curves. Table 2 summarize the electroluminescent (EL) data of the devices. All devices showed the blue EL spectra, which indicates the emission from emissive core. The Device A based on MeCz-4CzCN exhibits a low turn-on voltage of 2.9 V at the luminescence of 1 cd m⁻². The maximum current efficiency (CE), power efficiency (PE) and external quantum efficiency (EQE) of Device A are 46.5 cd A⁻¹, 35.6 lm W⁻¹ and 21.8%, respectively. The maximum luminescence of Device A is above 14200 cd m⁻². Moreover, the efficiencies still remain as high as 41.2 cd A⁻¹, 25.8 lm W⁻¹ and 19.0% at the high luminescence of 1000 cd m⁻², which fully demonstrate the superiority of encapsulated TADF emitter in solution-processed OLEDs. Nevertheless, the EL spectrum of Device A is not blue enough with a peak of 486 nm and a Commission Internationale de L'Eclairage (CIE) coordinates of (0.17, 0.35).

Similar to Device A, the Device B based on PhCz-4CzCN also has a low turn on voltage of 2.9 V, a high luminescence of 18800 cd m⁻², and high device efficiency with the maximum CE, PE and EQE of 40.8 cd A⁻¹, 27.5 lm W⁻¹ and 20.6%, respectively. Importantly, the EL emission peak of Device B is blue shift to 475 nm with a CIE of (0.16, 0.27) due to the enlarged wrapping units, which can further isolate the emission core and reduce the aggregation states. Moreover, the efficiency roll-off of Device B was further diminished especially at high luminance with high current density, which can be attributed to the more efficient wrapping effect of PhCz units. Although Device C exhibits a further blue shift emission with EL peak at 465 nm due to the larger bulky unit of PhDCz, the device efficiencies of Device C are moderate with CE, PE and EQE of 18.9 cd A⁻¹, 11.2 lm W⁻¹ and 10.0%, respectively. To the best of our best knowledge, these devices are the first report of blue-emitting fully solutionprocessed TADF-OLEDs, which demonstrates that the molecular encapsulation is a practical way to enable the molecule to withstand the sequential orthogonal solvent possess without sacrificing their parent TADF nature. Besides, the different efficiency of Device A, B and C indicates that the molecular engineering of wrapping units is critical for achieving high performance encapsulated TADF emitters.

Figure S8 shows the EL spectra of the devices at different applied voltages and their corresponding device pictures. Since the parent material 4CzCN do not withstand the solvent erosion, the luminous point of Device D was destroyed. Thus, the detection of device efficiency of Device D is unavailable. Fortunately, the spectrum test can still be performed. As shown in Fig 4c, the EL spectrum of Device D was peaked at 497 nm and the CIE at 100 mA m⁻² was (0.22, 0.41). With the increase of applied voltage, a new emission was appeared at the longer wavelength region, which indicates 4CzCN tends to form severe aggregated state under electro-excitation.

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Table 2. Device Performances of the fully solution-processed TADF OLEDs.								
TADF emitter	V _{on} a [V]	CE _{max} ^b [cd A ⁻¹]	PE _{max} c [Im W ⁻¹]	EQE _{max} ^d [%]	EQE ₁₀₀ ^e [%]	EQE ₁₀₀₀ f [%]	L _{max} ^g [cd m ⁻²]	CIE [x, y] ^h
MeCz-4CzCN	2.9	46.5	35.6	21.8	21.3	19.0	14200	(0.17, 0.35)
PhCz-4CzCN	2.9	40.8	27.5	20.6	20.0	18.2	18800	(0.16, 0.27)
PhDCz-4CzCN	3.1	18.9	11.2	10.0	9.8	7.9	9600	(0.19, 0.28)

^{a)} V_{on} = turn-on voltage at 1 cd m⁻², ^{b)} CE_{max} = maximum current efficiency, ^{c)} PE_{max} = maximum power efficiency, ^{d)} EQE_{max} = maximum external quantum efficiency, ^{e)} EQE at 100 cd m⁻². ^{f)} EQE at 1000 cd m⁻². ^{g)} L_{max} = maximum luminance, ^{h)} CIE = the Commission Internationale de L'Eclairage coordinates at the luminance of 1000 cd m⁻².

In contrast, the EL spectra of Device A and B are nearly unchanged in the applied voltage of 5-15 V. The stable EL emission of Device A and B indicates that the molecular encapsulation by introducing bulky units can efficiently suppress the aggregation state of the emissive core. It is worthy to note that the EL spectra of the devices based on encapsulated emitters were all blue shift comparing to emissive-core based Device D, which exhibits an EL peak at 497 nm. Moreover, with increasing the steric volume of the wrapping units, the EL peak positions were gradually shifted to 486, 475 and 465 nm for Device A, B and C, respectively, which can be assigned to the further decreased intermolecular interaction between emission cores by more bulky peripheral wrapping units. As a result, the CIE coordinates of the MeCz-4CzCN, PhCz-4CzCN and PhDCz-4CzCN based devices were (0.17, 0.35), (0.16,0.27) and (0.19, 0.28), respectively, which are all in the blue emission range.

Exciplex and electromor properties: In addition to the high efficiency, the relationship between the molecular structure and device performance is also important. Since the device conformation and emissive core of the three emitters are the same, the relatively low EL performance of PhDCz-4CzCN comparing to MeCz-4CzCN, PhCz-4CzCN indicates that the introducing of PhDCz units may cause other potential energy leakage pathway. In the past reported investigations, much attention had been focused on the influence of the wrapping units on the emissive core. However, the strong interaction between the wrapping units themselves would also produce severe impact on the EL property, which is usually ignored in the previous studies. Moreover, the exciplex formation between the introduced peripheral units and electron transporting material may also participate the exciton formation and energy transfer process during the electroexcitation of the devices. Thus, deeply exploring the exciton formation and energy transfer process are benefit for fully understanding the relationship between molecular structure and device performance.

In order to investigate the fundamental exciton harvest process of the emitters and discover the real reason of different efficiency, the solution-processed devices only based on the wrapping groups are fabricated. As shown in Figure 5, since the wrapping units are electron-rich donors (D), the excited state (D*) could take part in three decay pathways: (1) straight back to the ground state to result in the intrinsic light of monomer emission; (2) combination with the ground state donor unit to exhibit the electromer emission; or (3) interaction with the ground state ETL molecule to form the exciplex state. As shown in Figure S9, the EL spectra of MeCz and PhCz based devices exhibit a deep blue emission with the peaks around 420 nm, while PhDCz based devices exhibit two emission peaks at 460 and 650 nm. To identify the attribution of the peaks, the PL spectra of MeCz, PhCz and PhDCz films are investigated.

As shown in Figure S10, MeCz, PhCz and PhDCz exhibit ultraviolet emission at the range around 350 nm. The fine structure of the emission peaks indicates that the excited excitons of MeCz, PhCz and PhDCz are local states, which are easily to form the exciplex emission with an electron acceptor unit. In order to investigate the exciplex formation ability, the 1:1 mixed films of MeCz:PhPO, PhCz:PhPO and PhDCz:PhPO are measured under photoexcitation. The emission spectra of MeCz:PhPO, PhCz:PhPO and PhDCz:PhPO are broad and red-shifted to 418, 400, and 404 nm compared with the 343, 340, 355, and 362 nm for MeCz, PhCz, PhDCz, and PhPO, respectively. The unstructured new emission of the mixed films can be attributed to exciplex states, which are formed through the intermolecular interaction between the excited state donor and acceptor units. Therefore, the blue range in the EL spectra of MeCz, PhCz and PhDCz based devices are exciplex emission between EML and ETL layers. The triplet energies of exciplexes are 2.96, 3.10 and 3.07 eV for MeCz:PhPO, PhCz:PhPO and PhDCz:PhPO, respectively, which are higher than that of 4CzCN (2.68 eV). Thus, the exciplex formation between the wrapping units and ETL molecules will not induce energy leakage of emissive core. Moreover, thanks to the exciplex formation, the turn-on voltage of these encapsulated TADF emitters are only around 2.9-3.1 V, which are lower than most of the reported solution-processed TADF blue OLEDs even with a vacuum deposited ETL.



Figure 5. Exciton formation and energy transfer diagram of the encapsulated molecules.

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Table 3. Comparison of solution-processed TADF OLEDs with blue emission.

	Device structures of organic layers		L _{max} [cd m ⁻²]	CE _{max} [cd A ⁻¹]	EQE _{max} [%]	CIE [x, y]	
Ν	PEDOT:PSS PhCz-4CzCN PhPO	2.9	18800	40.8	20.6	0.16, 0.27	
	PEDOT:PSS POCz-DPS TPBi	5.4	2700	12.6	7.3	0.18, 0.30	[13]
	PEDOT:PSS PhCzDSO2 TPBi	5.0	4546	8.8	4.0	0.19, 0.37	[8c]
	PEDOT:PSS m-DTPACO TmPyPB	3.9		4.8	2.4	0.15, 0.28	[14]
	PEDOT:PSS DCzDMAC-DPS TPBi	5.2		3.8	2.2	0.18, 0.27	[15]
	PEDOT:PSS TPPOCz TmPyPB TPBi	6.2	6119	3.2	2.0	0.26, 0.31	[16]
	PEDOT:PSS PBD-10 DPEPO TmPyPB	3.8		13.5	7.3	0.20, 0.29	[4c]
	PEDOT:PSS P-Ac95-TRZ05 TSPO1 TmPyPB	3.2	6150	24.8	12.1	0.18, 0.27	[4d]
	PEDOT:PSS TFB B-oTC DPEPO TyPMPB	3.9	4351	37.3	19.1	0.15, 0.26	[17]
	PEDOT:PSS poly-TPD P3-P12 TmPyPB	3.2		9.0	4.0	0.22, 0.37	[18]
	PEDOT:PSS PVK TB14CZ-ACTRZ TPBi	4.0	2622	13.9	5.5	0.21, 0.42	[19]
D	PEDOT:PSS PVK SiCz:4CzFPN EMPA TPBi			36.1	20.0	0.16, 0.25	[5]
	PEDOT:PSS PVK CzSi:MA-TA TSPO1 TPBi				22.1	0.15, 0.19	[6c]
	PEDOT:PSS PVK SiCz:5CzCN TSPO1 TPBi				19.7	0.17, 0.30	[6d]
	PEDOT:PSS mCP:PCzDP-10 TmPyPB			38.6	16.1	0.24, 0.40	[6b]
	PEDOT:PSS CzSi:TB-2PXZ TmPyPB	5.8		21.0	8.9	0.18, 0.40	[8d]
	PEDOT:PSS polymers:mCP TmPyPB	3.9		26.0	8.7	0.23, 0.40	[8e]
	PEDOT:PSS PYD2:emitter TPBi	4.5	10 413	9.5	5.6	0.18, 0.23	[3b]
	PEDOT:PSS mCP:5CzCF3Ph TmPyPB	3.9		11.8	5.2	0.21, 0.33	[3c]

^{a)} N = Non-doped device; ^{b)} D = Doped device; ^{c)} Blue font means the organic materials are fabricated by solution-processed; ^{d)} Red font means the organic materials are fabricated by vacuum deposition.

The exciplex formation will not only reduce the turn-on voltage of the device, but also eliminate the triplet-polaron quenching (TPQ) of the TADF emitter. Since the hole carrier are transported in the peripheral wrapping units and the triplet state are mainly located in the core, the exciplex formation at the interface of the encapsulated emitter and ETL molecule will lead to the independent channels for charge transport and energy transfer. Therefore, the triplet state of the emissive core will not directly contact with the polarized charge transporting units. It has been reported that triplet-polaron interactions are the main reason for the unstable EL spectra and reduced device efficiency during the continuous operation.^[12] The steric bulky units introduced to our designed TADF emitters could efficiently increase the distance from exciton to polaron and reduce the TPQ effect. As a result, both Me-4CzCN and PhCz-4CzCN can exhibit the high device efficiency at high luminescence and stable EL emission with unchanged spectra in a wide range applied voltages. Nevertheless, the EL spectra of PhDCz-4CzCN exhibits a slight change at the long emission range, and the color purity is not satisfactory comparing to Me-4CzCN and PhCz-4CzCN, even though PhDCz-4CzCN possesses a bigger wrapping unit. Thus, the 650 nm emission in PhDCz based devices indeed has some influence on the EL performance of PhDCz-4CzCN.

In addition to the interaction with the ETL to form the exciplex state, the excited wrapping unit will also interact with the ground state itself to form the electromer emission. Moreover, the electromer and exciplex formation will compete with each other under electric field, and which pathways will dominate the decay process really depends on the molecular structure of the wrapping units. As shown in the EL spectra, the intense electromer emission band at 650 nm was observed in PhDCz based device. Such low energy electromer state of |PhDCz* PhDCz > will lead

to a sever energy leakage during device operation, which is the main reason of the low device efficiency of PhDCz-4CzCN. In contrast, the bimolecular interaction of |MeCz* MeCz) and |PhCz* PhCz) was extremely weak, which result in a negligible electromer comparing with the dominated exciplex emissions in MeCz and PhCz based device. Notably, the high device efficiencies were obtained in MeCz-4CzCN and PhCz-4CzCN based device, which means most of the excited excitons will achieve radiative transition in the emission core without energy leakage from the emissive core to the electromer state. However, the severe electromer formation in PhCz-4CzCN based device will not only decrease the electroluminescence efficiency, but also damage the EL purity. Therefore, it is can be concluded that blocking the serious exciton quenching channel of low energy electromer state is important for design efficient wrapping units for encapsulated TADF materials, which was usually ignored by the previous reports.

Based on the above investigations, designing efficient wrapping units for encapsulated TADF blue emitters, the high triplet energy to confine the reverse energy transfer is not the only consideration, the other three factors should also be taken into account. (1) The larger steric volume of the wrapping units will provide more effective shield effect to reduce the aggregation of the emissive cores, which would suppress the concentration quenching and lead to a blue shift EL spectrum. (2) The exciplex formation between the wrapping units and the ETL will facilitate the charge transportation and injection, which can inhibit the triplet-polaron quenching and lead to a low turn-on voltage. (3) The electromer state of the wrapping units under electro-excitation is a severe energy leakage pathway, which will destroy the color purity and reduce the device efficiency. The newly designed wrapping unit PhCz, which possess suitable bulky volume, efficient exciplex formation and almost no electromer state, make the PhCz-4CzCN based device achieve a blue emission with the emission peak of 475 nm, a low turn-on voltage of 2.9 eV, a high luminescence of 18800 cd m⁻² and a high device efficiency with EQE above 20 %. To the best of our knowledge, this is the first report of non-doped TADF blue OLEDs with fully solution-processed organic layers, and the device efficiencies are among the highest of the recently reported solution-processed TADF OLEDs (Table 3).

Conclusions

In summary, we have successfully achieved highly efficient fully solution-processed TADF blue OLEDs by designing and synthesizing three encapsulated TADF blue emitters. Photophysical investigation demonstrate that the introduced bulky wrapping units to the emissive core not only enable the high molecular weight for sequential orthogonal solvent process, but also build a large steric hindrance effect for enhancing the RISC and suppressing the TTA, which makes the encapsulated emitters can be competent with non-doped devices. The thoroughly study of the EL properties indicates that even the small modulation in the molecular structure of wrapping units will dramatically affect the encapsulation effect. The enlarged volume of wrapping units will make the electroluminescent spectra blueshift, while enhancing the energy transfer of exciplex and blocking the energy leakage of electromer can facilitate the exciton utilization of the devices. As a result, the achieved fully solutionprocessed TADF blue OLEDs exhibits a low turn-on voltage and an excellent EL efficiency, which outperform most of the reported doped device with vacuum deposited EML. This work would provide critical guidelines for the design of more efficient TADF blue materials used to future cost-effective solution-processed organic electroluminescence application.

Experimental Section

General methods

¹H and ¹³C NMR spectra were measured on a Bruker NMR spectrometer operating at 600 MHz with tetramethylsilane (TMS) as the internal standard. Molecular masses were measured by a BRUKER DALTONICS time-of-flight Matrix-assisted laser desorption-ionization mass spectrometry (MALDI-TOF-MS). TGA was performed on a Netzsch simultaneous thermal analyzer (STA) system (STA 409PC) under a N2 flow at a heating rate of 10 °C min-1. DSC measurements were operated on a DSC 2910 modulated calorimeter under a N₂ flow at a heating rate of 10 °C min⁻¹ and a cooling rate of 20 °C min⁻¹. UV-vis absorption spectra were recorded on a SHIMADZU UV-2450 spectrophotometer while photoluminescence (PL) spectra, photoluminescence quantum yields (PLQYs) and low tempertrature phosphorescence spectra were measured using a HORIBA FLUOROMAX-4 fluorescence spectrophotometer. Cyclic voltammogram (CV) was measured on a CHI750C voltammetric analyzer in a typical three-electrode cell with a nitrogen-saturated CH₂Cl₂ solution of 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate as conductive medium, a platinum plate working electrode, a platinum wire counter electrode, and a silver wire reference electrode. The transient PL spectra were measured with Edinburgh FL920 fluorescence spectrophotometer.

Quantum chemical calculations

The optimized structures of the designed materials were calculated by Gaussian 09 at the B3LYP functional with 6-31G (d) basis sets. The excitation energies in the singlet and triplet states were obtained using the TD-DFT method based on an optimized molecular structure for the ground state.

Device Fabrication and Measurements

The ITO-coated glass with a sheet resistance of 10 Ω sq⁻¹ were used as the substrate, which were rinsed in deionized water and then ultrasonicated sequentially in acetone and ethanol. After cleaning, the ITO substrate was treated in a UV-ozone oven for 20 min. Then 40 nm PEDOT:PSS was spin-coated onto the ITO substrate and dried at 200 °C for 10 min. The substrates were then taken into a nitrogen glove box, where the 60 nm emission layer was spin coated onto the PEDOT:PSS layer from chlorobenzene and annealed at at 100 °C for 30 min. After that, 40 nm PhPO was spin coated onto the EML as the electron transporting layer. Finally, Cs₂CO₃ (2 nm) and AI (100 nm) were deposited as the cathode for the devices. The EL spectra, device luminance, and current density-voltage characteristics were recorded using a combination of a Photo-Research PR-655 SpectraScan and a Keithley 2400 Sourcemeter. The device was tested in the condition of the atmosphere with no protective encapsulation.

Synthesis and characterization

All the reagents used for the synthesis of the compounds were purchased from Aldrich and Acros companies and used without further purification. The anhydrous tetrahydrofuran (THF) solvent was dewatered according to standard procedures. The intermediates M1 and M2 are synthesized according to the references.^[20]

4-methoxy-9-phenyl-9H-carbazole (PhCz)

A mixture of M1 (1.97 g, 10.0 mmol), iodobenzene (2.04 g, 10.0 mmol), Cul (0.06 g, 0.30 mmol), 1,10-phenanthroline (0.06 g, 0.30 mmol), and K₂CO₃ (0.78 g, 6.0 mmol) was added to 30 mL DMF solution. The mixture was refluxed under nitrogen for 24 h. After cooling, the mixture was poured into 100 mL water and filtered. The product was then obtained by column chromatography on silica gel to yield a white solid (1.64 g, 61%). ¹H NMR (600 MHz, DMSO, δ): 8.27 (d, *J* = 7.4 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.61 (dt, *J* = 8.4, 1.7 Hz, 2H), 7.56 – 7.53 (m, 1H), 7.41 – 7.32 (m, 3H), 7.27 (dt, *J* = 14.1, 3.6 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 4.07 (s, 3H). ¹³C NMR (126 MHz, CDCl₃, δ): 156.35, 142.36, 140.22, 137.88, 129.83, 127.49, 127.29, 126.68, 125.02, 123.19, 122.76, 120.13, 112.58, 109.19, 102.78, 100.94, 55.58. HRMS (ESI) m/z: calcd for C₁₉H₁₅NO; C 83.49, H 5.53, N 5.12; found: C 83.52, H 5.51, N 5.12.

4-methoxy-9-methyl-9H-carbazole (MeCz)

This compound was prepared according to the procedure for the synthesis of PhCz, giving a yield of 70%. ¹H NMR (600 MHz, DMSO, δ): 8.17 (d, J = 7.7 Hz, 1H), 7.56 (d, J = 8.2 Hz, 1H), 7.45 – 7.31 (m, 2H), 7.27 – 7.12 (m, 2H), 6.77 (d, J = 7.9 Hz, 1H), 4.03 (s, 3H), 3.86 (s, 3H). ¹³C NMR (126 MHz, CDCl₃, δ): 156.34, 142.52, 140.25, 126.49, 124.75, 123.08, 122.20, 119.13, 111.88, 107.89, 101.52, 100.06, 55.49, 29.30. HRMS (ESI) m/z: calcd for C1₄H1₂NO, 211.0997; found, 211.1032. Anal. calcd for C1₄H1₂NO: C 79.59, H 6.20, N 6.63; found: C 79.58, H 6.22, N 6.68.

9-(4-(9H-carbazol-9-yl)phenyl)-4-methoxy-9H-carbazole (PhDCz)

This compound was prepared according to the procedure for the synthesis of PhCz, giving a yield of 55%. ¹H NMR (600 MHz, DMSO, δ): 8.31 (dd, *J* = 7.6, 3.5 Hz, 3H), 7.97 – 7.89 (m, 4H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.51 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 2H), 7.48 – 7.41 (m, 2H), 7.37 – 7.30 (m, 3H), 7.20 (d, *J* = 8.1 Hz, 1H), 6.92 (d, *J* = 7.9 Hz, 1H), 4.10 (s, 3H). ¹³C NMR (126 MHz, CDCl₃, δ):156.43, 142.19, 140.78, 140.05,

136.82, 136.68, 128.50, 128.31, 126.90, 126.15, 125.20, 123.58, 123.34, 122.96, 120.47, 120.28, 112.78, 109.79, 109.16, 102.70, 101.30, 55.62. HRMS (ESI) m/z: calcd for $C_{31}H_{22}N_2O$, 438.1732; found, 483.1738. Anal. calcd for $C_{31}H_{22}N_2O$: C 84.91, H 5.06, N 6.39; found: C 84.86, H 5.09, N 6.40.

9-phenyl-9H-carbazol-4-ol (PhCz-OH)

PhCz (2.73 g, 10 mmol) was dissolved in 100 mL dry CH₂Cl₂. The solution was stirred at 0 °C and BBr₃ (1.2 mL 1 M solution in CH₂Cl₂, 12 mmol) was added dropwise. After stirring for 12 h, the reaction was returned to room temperature and carefully quenched with methanol. After that, a saturated solution of NaHCO3 was added, and the mixture was washed with water for three times. The organic lavers were combined and dried with MgSO₄. The product was then obtained by column chromatography on silica gel to yield a brown solid (2.0 g, 79%). ¹H NMR (600 MHz, DMSO, δ): 10.28 (s, 1H), 8.26 (d, J = 7.7 Hz, 1H), 7.70 - 7.65 (m, 2H), 7.60 (dd, J = 8.4, 1.2 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.31 (d, J = 8.1 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.20 (t, J = 8.0 Hz, 1H), 6.80 (d, J = 7.7 Hz, 1H), 6.69 (d, J = 7.4 Hz, 1H). ¹³C NMR (126 MHz, DMSO, δ): 154.37, 142.55, 139.91, 137.63, 130.55, 128.02, 127.52, 127.20, 125.36, 123.00, 122.99, 120.40, 111.61, 109.35, 106.14, 100.95. HRMS (ESI) m/z: calcd for C₁₈H₁₃NO, 259.0997; found, 259.1012. Anal. calcd for C₁₈H₁₃NO: C 83.37, H 5.05, N 5.40; found: C 83.34, H 5.06, N 5.41.

9-methyl-9H-carbazol-4-ol (MeCz-OH)

This compound was prepared according to the procedure for the synthesis of PhCz-OH, giving a yield of 80%. ¹H NMR (600 MHz, DMSO, δ): 10.10 (s, 1H), 8.17 (d, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 8.1 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.24 (t, *J* = 7.9 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.61 (d, *J* = 7.7 Hz, 1H), 3.81 (s, 3H). ¹³C NMR (126 MHz, DMSO, δ): 154.08, 143.04, 140.30, 127.01, 124.81, 122.61, 122.20, 119.08, 110.82, 108.82, 104.99, 100.47, 29.56. HRMS (ESI) m/z: calcd for C₁₃H₁₁NO, 197.0841; found, 197.0884. Anal. calcd for C₁₃H₁₁NO: C 79.16, H 5.62, N 7.10; found: C 79.15, H 5.65, N 7.12.

9-(4-(9H-carbazol-9-yl)phenyl)-9H-carbazol-4-ol (PhDCz-OH)

This compound was prepared according to the procedure for the synthesis of PhCz-OH, giving a yield of 80%. ¹H NMR (600 MHz, DMSO, δ): 10.36 (s, 1H), 8.31 (dd, J = 7.0, 6.3 Hz, 3H), 7.96 – 7.87 (m, 4H), 7.61 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 8.2 Hz, 1H), 7.51 (ddd, J = 8.2, 7.1, 1.1 Hz, 2H), 7.46 – 7.40 (m, 1H), 7.37 – 7.33 (m, 2H), 7.32 – 7.25 (m, 2H), 7.03 (d, J = 7.8 Hz, 1H), 6.75 (d, J = 7.5 Hz, 1H). ¹³C NMR (126 MHz, DMSO, δ): 154.42, 142.45, 140.54, 139.83, 136.55, 136.14, 128.76, 128.67, 127.66, 126.84, 125.50, 123.34, 123.14, 123.06, 121.08, 120.77, 120.69, 111.74, 110.31, 109.61, 106.41, 101.16. HRMS (ESI) m/z: calcd for C₃₀H₂₀N₂O, 424.1576; found, 424.1345. Anal. calcd for C₁₃H₁₁NO: C 79.16, H 5.62, N 7.10; found: C 79.15, H 5.65, N 7.12.

4-(6-(9-phenyl-9H-carbazol-5-yloxy)hexyloxy)-9H-carbazole (PhCz-Cz)

A mixture of PhCz-OH (1.26 g, 5.0 mmol), M2 (1.75 g, 5.0 mmol) and K₂CO₃ (1.7 g, 15.0 mmol) was added to 100 mL acetone solution. The reaction was heated at 60 °C under nitrogen for 24 h. After cooling, the mixture was poured into 200 mL water. The crude product was filtered and purified by silica gel column chromatography to give the white product (2.25 g, 82%). ¹H NMR (600 MHz, CDCl₃, δ): 8.42 (d, J = 7.7 Hz, 1H), 8.33 (t, J = 13.5 Hz, 1H), 8.01 (s, 1H), 7.62 – 7.51 (m, 4H), 7.44 (dd, J = 17.5, 10.4 Hz, 1H), 7.40 – 7.33 (m, 4H), 7.32 – 7.25 (m, 3H), 7.22 (d, J = 7.0 Hz, 1H), 4.32 – 4.22 (m, 4H), 2.09 (d, J = 6.2 Hz, 4H), 1.81 (s, 4H). ¹³C NMR (126 MHz, CDCl₃, δ): 155.89, 155.80, 142.49, 141.02, 140.34, 138.80, 137.96, 129.92, 127.55, 127.35, 126.89, 126.79, 125.13, 124.95, 123.28, 123.10, 123.01, 122.85, 120.32, 119.71, 112.73, 110.11, 109.34, 103.47, 102.67, 101.83, 101.17, 68.07, 67.92, 29.58, 26.23, 26.22. HRMS (ESI) m/z: calcd

for $C_{36}H_{32}N_2O_2,\,524.2464;$ found, 524.2341. Anal. calcd for $C_{36}H_{32}N_2O_2;$ C 82.41, H 6.15, N 5.34; found: C 82.39, H 6.17, N 5.33.

4-(6-(9-methyl-9H-carbazol-5-yloxy)hexyloxy)-9H-carbazole (MeCz-Cz)

This compound was prepared according to the procedure for the synthesis of PhCz-Cz, giving a yield of 80%. ¹H NMR (600 MHz, CDCl₃, δ): 8.34 (dd, J = 15.1, 7.7 Hz, 2H), 8.04 (s, 1H), 7.46 – 7.34 (m, 2H), 7.31 (t, J = 8.1 Hz, 1H), 7.22 (t, J = 7.3 Hz, 2H), 7.05 – 6.99 (m, 2H), 6.67 (t, J = 7.9 Hz, 2H), 4.27 (q, J = 6.4 Hz, 4H), 3.84 (s, 3H), 2.08 (s, 4H), 1.80 (s, 4H). ¹³C NMR (126 MHz, CDCl₃, δ): 155.75, 155.73, 142.54, 140.92, 140.24, 138.69, 126.69, 126.48, 124.85, 124.66, 123.04, 123.02, 122.82, 122.30, 119.64, 119.11, 112.72, 111.94, 109.89, 107.81, 103.26, 101.25, 101.10, 100.77, 67.85, 67.82, 29.49, 29.30, 26.13. HRMS (ESI) m/z: calcd for C₃₁H₃₀N₂O₂; C 80.49, H 6.54, N 6.06; found: C 80.46, H 6.58, N 6.02.

9-(4-(4-(6-(9H-carbazol-5-yloxy)hexyloxy)-9H-carbazol-9-yl)phenyl)-9H-carbazole (PhDCz-Cz)

This compound was prepared according to the procedure for the synthesis of PhCz-Cz, giving a yield of 75%. ¹H NMR (600 MHz, CDCl₃, δ): 8.46 (d, J = 7.7 Hz, 1H), 8.35 (d, J = 7.7 Hz, 1H), 8.19 (d, J = 7.6 Hz, 2H), 8.04 (s, 1H), 7.81 (s, 4H), 7.57 (d, J = 8.1 Hz, 2H), 7.53 (d, J = 7.7 Hz, 1H), 7.48 (t, J = 7.4 Hz, 2H), 7.43 (t, J = 7.6 Hz, 1H), 7.35 (ddd, J = 28.5, 20.6, 12.3 Hz, 8H), 7.23 (d, J = 7.0 Hz, 1H), 7.15 (d, J = 7.8 Hz, 1H), 7.04 (d, J = 8.1 Hz, 1H), 6.77 (d, J = 7.6 Hz, 1H), 7.15 (d, J = 7.8 Hz, 1H), 4.33 (t, J = 5.3 Hz, 1H), 6.77 (d, J = 5.6 Hz, 2H), 2.11 (d, J = 6.0 Hz, 4H), 1.83 (s, 4H). ¹³C NMR (126 MHz, CDCl₃, δ): 155.85, 155.73, 142.22, 140.94, 140.78, 140.05, 138.70, 136.87, 136.63, 128.49, 128.30, 126.91, 126.71, 126.13, 122.51, 124.87, 123.56, 123.28, 123.04, 122.83, 120.49, 120.45, 120.25, 119.65, 112.83, 109.90, 109.78, 109.11, 103.28, 102.45, 102.00, 101.11, 99.99, 68.02, 67.82, 29.50, 26.15. HRMS (ESI) m/z: calcd for C48H₃₉N₃O₂, 689.3042; found, 689.3218. Anal. calcd for C48H₃₉N₃O₂: C 83.57, H 5.70, N 6.09; found: C 83.52, H 5.75, N 6.12.

2,3,5,6-tetrakis(4-methoxy-9H-carbazol-9-yl)benzonitrile (4CzCN)

In the nitrogen atmosphere, the prepared M1 (0.88 g, 4.5 mmol) was added to the anhydrous THF solution (40 mL) contain of NaH (0.60 g, 5 mmol). The mixture was stirred at 0 °C for 0.5 h, then 2,3,5,6tetrafluorobenzonitrile (0.17 g, 1 mmol) in anhydrous THF (20 mL) was added dropwise. The solution was stirred for another 12h at room temperature. After the reaction is over, the reaction was quenched with the addition of 250 mL water. The mixture was extracted with CH₂Cl₂ for three times. The combine organic layer was dried with anhydrous MgSO4 and the solvent was removed under vacuum. The precipitate was purified by column chromatography on silica gel, resulted in the bright green product (0.75 g, 83%). ¹H NMR (600 MHz, DMSO, δ): 8.58 (s, 1H), 7.94 (dd, J = 14.9, 7.8 Hz, 6H), 7.87 (dd, J = 13.3, 6.4 Hz, 2H), 7.59 (dd, J = 8.2, 4.1 Hz, 2H), 7.50 (ddd, J = 8.4, 7.2, 2.5 Hz, 2H), 7.25 (ddd, J = 10.3, 5.3, 2.7 Hz, 4H), 7.18 (ddd, J = 7.9, 6.8, 4.2 Hz, 4H), 7.14 (t, J = 7.0 Hz, 2H), 7.09 (t, J = 7.5 Hz, 2H), 6.73 (dd, J = 8.1, 1.6 Hz, 2H), 6.68 (d, J = 8.1 Hz, 2H), 3.95 - 3.84 (s, 12H). ¹³C NMR (126 MHz, CDCl₃, δ): 156.04, 156.02, 155.97, 140.88, 140.41, 140.38, 138.73, 138.26, 138.11, 137.21, 137.14, 126.76, 126.73, 124.93, 124.86, 123.64, 123.62, 123.30, 123.25, 123.15, 123.09, 121.40, 121.35, 121.17, 121.11, 118.48, 113.50, 113.16, 112.76, 109.26, 108.79, 108.72, 102.86, 102.60, 102.56, 102.31, 102.27, 102.22, 55.41. MALDI-TOF MS: calcd for C₅₉H₄₁N₅O₄, 883.3; found, 883.2 [M+]. Anal. calcd for C₅₉H₄₁N₅O₄: C 80.16, H 4.67, N 7.92; found: C 80.11, H 4.72, N 7.85.

2,3,5,6-tetrakis(4-(6-(9-methyl-9H-carbazol-5-yloxy)hexyloxy)-9H-carbazol-9-yl)benzonitrile (MeCz-4CzCN)

This compound was prepared according to the procedure for the synthesis of 4CzCN, giving a yield of 85%. ¹H NMR (600 MHz, CDCl₃, δ): 8.32 (dd,

J = 20.1, 7.9 Hz, 5H, 8.11 - 8.02 (m, 4H), 7.43 - 7.36 (m, 6H), 7.35 - 7.27 (m, 10H), 7.21 (dt,*J*= 7.9, 4.4 Hz, 4H), 7.18 - 7.14 (m, 4H), 7.13 - 6.98 (m, 12H), 6.98 - 6.93 (m, 4H), 6.60 (ddd,*J*= 12.2, 7.9, 3.7 Hz, 4H), 6.57 - 6.48 (m, 4H), 4.22 - 4.14 (m, 8H), 4.07 (d,*J*= 4.8 Hz, 8H), 3.77 (d,*J*= 12.4 Hz, 12H), 2.04 - 1.95 (m, 8H), 1.95 - 1.86 (m, 8H), 1.67 (ddd,*J* $= 21.2, 15.0, 7.3 \text{ Hz}, 16\text{H}). ^{13}\text{C} NMR (151 \text{ MHz}, \text{CDCI}_3, \delta): 155.71, 155.68, 142.50, 142.48, 141.04, 140.20, 140.19, 138.22, 137.33, 126.71, 126.45, 126.43, 124.83, 124.78, 124.63, 124.60, 123.77, 122.99, 122.94, 122.28, 122.24, 119.09, 119.03, 118.51, 113.59, 111.92, 111.89, 107.76, 101.19, 101.17, 100.79, 100.77, 100.73, 77.23, 77.02, 76.81, 67.87, 67.84, 67.78, 67.73, 29.37, 29.30, 29.23, 29.21, 26.03, 25.99, 25.92. MALDI-TOF MS: calcd for C1₃₁H₁₁₇N₉O₈, 1943.9; found, 1943.8 [M+]. Anal. calcd for C1₃₁H₁₁₇N₉O₈: C 80.88, H 6.06, N 6.48; found: C 80.85, H 6.02, N 6.47.$

2,3,5,6-tetrakis(4-(6-(9-phenyl-9H-carbazol-5-yloxy)hexyloxy)-9Hcarbazol-9-yl)benzonitrile (PhCz-4CzCN)

This compound was prepared according to the procedure for the synthesis of 4CzCN, giving a yield of 82%. ¹H NMR (600 MHz, CDCl₃, δ): 8.38 (dd, J = 15.9, 7.7 Hz, 4H), 8.31 (s, 1H), 8.13 - 8.04 (m, 4H), 7.58 - 7.51 (m, 16H), 7.46 - 7.41 (m, 4H), 7.40 - 7.29 (m, 12H), 7.28 - 7.20 (m, 10H), 7.19 - 6.99 (m, 14H), 6.99 - 6.94 (m, 4H), 6.64 (dd, J = 13.4, 5.4 Hz, 4H), 6.61 - 6.48 (m, 4H), 4.21 (dt, J = 8.9, 6.4 Hz, 8H), 4.14 - 4.05 (m, 8H), 2.06 – 1.97 (m, 8H), 1.92 (t, J = 22.0 Hz, 8H), 1.77 – 1.60 (m, 16H). ¹³C NMR (151 MHz, CDCl₃, δ): 155.72, 155.69, 142.32, 140.52, 140.48, 140.16, 138.20, 137.89, 137.85, 137.31, 137.21, 129.76, 127.39, 127.37, 127.23, 127.21, 126.66, 126.65, 124.90, 124.89, 123.09, 123.04, 122.84, 122.81, 120.11, 120.06, 118.51, 112.59, 112.56, 109.10, 109.09, 102.47, 102.44, 101.66, 101.64, 101.60, 101.59, 77.23, 77.01, 76.80, 67.88, 67.84, 29.40, 29.38, 29.33, 29.27, 26.92, 26.05, 26.03, 26.00, 25.96, 25.95, 22.66. MALDI-TOF MS: calcd for C151H125N9O8, 2191.9; found, 2191.9 [M+]. Anal. calcd for C151H125N9O8: C 82.68, H 5.74, N 5.75; found: C 82.65, H 5.70, N 5.71.

2,3,5,6-tetrakis(4-(6-(9-(4-(9H-carbazol-9-yl)phenyl)-9H-carbazol-5yloxy)hexyloxy)-9H-carbazol-9-yl)benzonitrile (PhDCz-4CzCN)

This compound was prepared according to the procedure for the synthesis of 4CzCN, giving a yield of 80%. ¹H NMR (600 MHz, CDCl₃, δ): 8.42 (dd, J = 16.2, 7.8 Hz, 4H), 8.33 (s, 1H), 8.17 (d, J = 7.8 Hz, 8H), 8.14 - 8.05 (m, 4H), 7.78 – 7.73 (m, 16H), 7.54 (dd, J = 8.2, 0.9 Hz, 8H), 7.47 (tt, J = 12.6, 6.5 Hz, 12H), 7.42 - 7.36 (m, 6H), 7.36 - 7.26 (m, 18H), 7.22 - 6.95 (m, 20H), 6.69 (td, J = 8.6, 4.8 Hz, 4H), 6.64 - 6.52 (m, 4H), 4.27 - 4.19 (m, 8H), 4.16 - 4.06 (m, 8H), 2.09 - 1.99 (m, 8 H), 1.98 - 1.89 (m, 8H), 1.78 - 1.62 (m, 16H). ¹³C NMR (151 MHz, CDCl₃, δ): 155.82, 155.79, 142.16, 140.74, 140.00, 137.33, 136.83, 136.80, 136.60, 136.57, 128.42, 128.25, 126.90, 126.11, 125.10, 123.54, 123.25, 123.21, 123.07, 123.04, 120.50, 120.43, 120.25, 120.23, 112.77, 109.77, 109.75, 109.10, 109.09, 102.43, 102.40, 102.03, 102.02, 101.98, 101.97, 67.94, 67.90, 67.85, 29.39, 29.34, 29.28, 26.06, 26.03, 25.99, 25.97, 22.69, 22.67, 22.62. MALDI-TOF MS: calcd for C199H153N13O8, 2852.1; found, 2852.1 [M+]. Anal. calcd for C199H153N13O8: C 83.73, H 5.40, N 6.38; found: C 83.70, H 5.45, N 6.29.

Acknowledgements

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FULL PAPER

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FULL PAPER

The molecular engineering of TADF emitter has been successfully used to enable the fabrication of fully solutionprocessed blue OLEDs. The excellent device efficiency with a high EQE above 20% can be attributed to the efficient exciplex formation and electromer blocking.



Xinxin Ban,* Feng Chen, Jie Pan, Yan Liu, Aiyun Zhu, Wei Jiang* and Yueming Sun

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Exciplex Formation and Electromer Blocking for Highly Efficient Blue Thermally Activated Delayed Fluorescence OLEDs with All-Solution-Processed Organic Layers