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Light-Emitting Diodes Hot Paper

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Organic Light-Emitting Diodes Using a Neutral π Radical as Emitter: The Emission from a Doublet[**]

*Qiming Peng, Ablikim Obolda, Ming Zhang, and Feng Li**

***Abstract:** Triplet harvesting is a main challenge in organic light-emitting devices (OLEDs), because the radiative decay of the triplet is spin-forbidden. Here, we propose a new kind of OLED, in which an organic open-shell molecule, (4-N-carbazolyl-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)-methyl (TTM-1Cz) radical, is used as an emitter, to circumvent the transition problem of triplet. For TTM-1Cz, there is only one unpaired electron in the highest singly occupied molecular orbital (SOMO). When this electron is excited to the lowest singly unoccupied molecular orbital (SUMO), the SOMO is empty. Thus, transition back of the excited electron to the SOMO is totally spin-allowed. Spectral analysis showed that electroluminescence of the OLED originated from the electron transition between SUMO and SOMO. The magneto-electroluminescence measurements revealed that the spin configuration of the excited state of TTM-1Cz is a doublet. Our results pave a new way to obtain 100 % internal quantum efficiency of OLEDs.*

Organic light-emitting diodes (OLEDs) have been expected to be the next flat panel displays and lighting sources because of their special features, such as easy processing, lightweight, and flexibility.[1] During the evolution of OLEDs over the past two decades, many fluorescent and phosphorescent materials have been developed.[1,2] Although fluorescent materials are cost-effective, the theoretical upper limit of internal quantum efficiency (IQE) of fluorescent OLEDs is only 25 % according to the spin statistics.[3] In contrast, the IQE of phosphorescent OLEDs has achieved almost 100 %.[2a–c] However, practically useful phosphorescent materials are mainly concentrated to the expensive Ir and Pt complexes. Recently, thermally activated delayed fluorescence (TADF)-based OLEDs have been proposed to harvest both singlet and triplet excitons,[2d] and a very high efficiency has been reported.[2f]

In this work, different from the fluorescent, phosphorescent, and TADF-based materials, all of which are closed-shell molecules, an open-shell organic molecule was used as an emitter of OLEDs. For a ground-state closed-shell molecule, there are two electrons in the highest occupied molecular orbital (HOMO). When the molecule is excited, one electron stays in the HOMO and the other electron transits to the lowest unoccupied molecular orbital (LUMO). The spin configuration of the two electrons is either singlet or triplet, as shown in Figure 1 a.[4] According to the Pauli exclusion principle, the transition of a triplet exciton to the ground state is forbidden.[3a] However, if the emitting materials are open-shell molecules, the problem of triplets can be circumvented. Because for an ground-state open-shell molecule, there is only one electron in the highest molecular orbital, that is, the singly occupied molecular orbital (SOMO).[5] When this electron is excited to the lowest singly unoccupied molecular orbital (SUMO), the SOMO is empty, as shown in Figure 1 b. Thus, transition back of the excited electron to the SOMO is spin-allowed. So that the upper limit of internal quantum efficiency (IQE) of the OLEDs using open-shell molecules as emitter is theoretically 100 %. Because one electron has two spin states, the excited state of the open-shell molecules is called doublet.

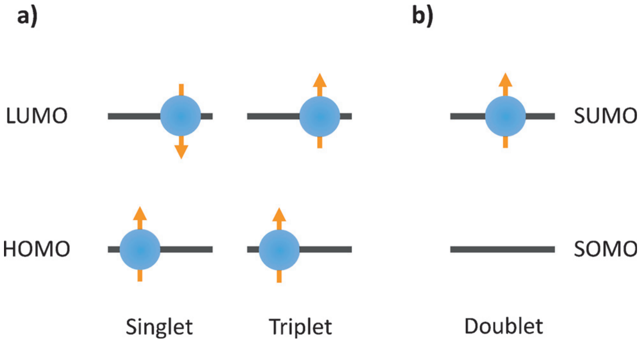

Figure 1. Schematic diagram of the spin configuration of the excited states. a) For closed-shell molecules, the spin configuration of the excitons can be either singlet or triplet. b) For open-shell molecules, the spin configuration is doublet.

Neutral radicals are one typical kind of open-shell molecules.[6] Generally, neutral radicals are quite unstable. However, through the molecular design, stable neutral radicals can be obtained and they are able to withstand oxygen and light for an extremely long time at room

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[*] Q. Peng,[+] A. Obolda,[+] Prof. Dr. F. Li
State Key Laboratory of Supramolecular Structure and Materials
Institute of Theoretical Chemistry, Jilin University
Qianjin Avenue 2699, Changchun, 130012 (P. R. China)
E-mail: lifeng01@jlu.edu.cn

Prof. Dr. M. Zhang
State Key Laboratory of Supramolecular Structure and Materials
College of Chemistry, Jilin University
Qianjin Avenue 2699, Changchun, 130012 (P. R. China)

[+] These authors contributed equally to this work.

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temperature.[7] They are commonly studied in the fields of photophysics,[8] molecular magnetic materials,[9] spintronics,[10] and so forth, because the unpaired electron can easily take part in physical processes and chemical reactions.[6] Here, for the first time, we demonstrate a stable neutral π radical, (4-*N*-carbazolyl-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl (TTM-1Cz), as an emitter of OLEDs. For the details of the synthesis, characterization and purity of the material, please see the Supporting Information.

The chemical structure of TTM-1Cz is shown in Figure 2 a. Figure 2 b shows the steric configuration of the molecule optimized by DFT calculation. As can be seen, TTM-1Cz is stabilized by the six chlorine atoms surrounding the radical center carbon. The electron paramagnetic resonance (EPR) spectrum (Figure 2 c) shows that there is an unpaired electron in TTM-1Cz. One fundamental issue that needs to be addressed is the stability of the molecule. In our OLED, thin films of TTM-1Cz are fabricated using the method of organic molecular beam deposition. During fabrication the organic powder sample is heated in a high vacuum chamber until it sublimes. Most standard molecular semiconductors are thermally stable and do not chemically decompose during the deposition procedure. However, organic radicals are comparatively less stable, and one cannot take for granted that TTM-1Cz remains chemically unchanged upon heating under high vacuum. In other words, it must be experimentally proved that the chemical structure of TTM-1Cz in thin films after deposition should be the same as that drawn in Figure 2 a. In view of these, we carried out thermogravimetric analysis (TGA) of the pristine material (see Figure 2 d), which shows that TTM-1Cz can be vacuum-deposited (at approximately 90 °C) to fabricate OLEDs without any decomposition. In addition, we carried out EPR and nuclear magnetic resonance (NMR) measurements of the deposited sample. The EPR and NMR spectra of the deposited sample show that the chemical structure of TTM-1Cz was unchanged after vacuum deposition (Figures S2 and S3 in the Supporting Information).

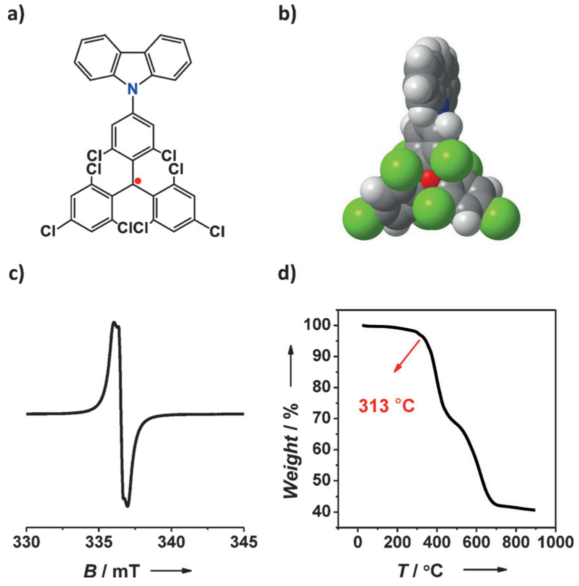

Figure 2. Material characteristics. a) The chemical structure of TTM-1Cz. b) The steric configuration of TTM-1Cz calculated by DFT. The unpaired electron is surrounded by six chlorine atoms. c) The EPR spectrum of TTM-1Cz powder measured at room temperature. d) The TGA spectrum of TTM-1Cz.

Energy levels of the frontier molecular orbitals (i.e. HOMO, SOMO, SUMO, and LUMO) were identified by density functional theory (DFT) calculations using the Gaussian 09 series of programs.[11] As presented in Figure 3 a, the energy levels of HOMO, SOMO, SUMO, and LUMO were calculated to be −5.94, −5.47, −3.37, and −1.43 eV, respectively. The absorption (Abs) and photoluminescence (PL) spectra of TTM-1Cz in chloroform solution are shown in Figure 3 b. In the Abs spectrum, there is a band centered at approximately 600 nm corresponding to the energy gap of 2.07 eV, which is assigned to the electronic transition from SOMO to SUMO. The shorter-wavelength bands of the Abs spectrum are attributed to the transitions from SOMO/HOMO to higher-energy orbitals. The PL spectrum (centered at 660 nm) demonstrated that the emission was originated from the transition of SUMO to SOMO, that is, the radiative decay from the doublet excitons.

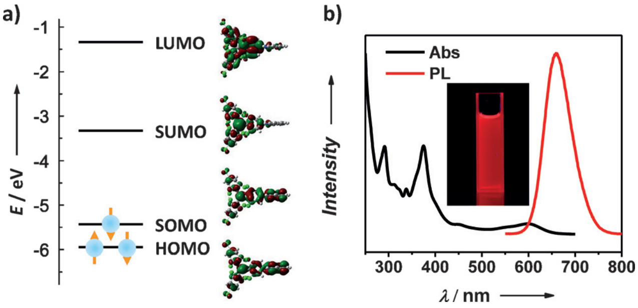

Figure 3. Molecular orbital energy levels and spectra analysis. a) The energy levels (left panels) and contour plots (right panels) of the molecular orbitals (LUMO, SUMO, SOMO, and HOMO) of TTM-1Cz. b) The UV/Vis Abs and PL spectra of TTM-1Cz in chloroform solution.

The thin film of pure TTM-1Cz is not emissive, because of the aggregation-caused quenching. Thus the only way to make TTM-1Cz emissive is doping it into some matrix. We then fabricated OLEDs using the structure of indium tin oxide (ITO)/*N*,*N*′-di-1-naphthyl-*N*,*N*′-diphenylbenzidine (NPB) (30 nm)/TTM-1Cz:4,4-bis(carbazol-9-yl)biphenyl (CBP) (5 wt %, 40 nm)/1,3,5-tri(phenyl-2-benzimidazolyl)-benzene (TPBi) (35 nm)/lithium fluoride (LiF) (0.8 nm)/aluminum (100 nm), as schematically depicted in Figure 4 a, where NPB, CBP, and TPBi serve as the hole-transporting, doping-host, and electron-transporting materials, respectively. Figure 4 b shows the electroluminescence (EL) spectrum of the OLED (at 7 V) accompanied by the PL spectra of the TTM-1Cz:CBP (5 wt %) thin film. It can be found from Figure 4 b that the PL and EL come from the radiative decay of the doublets of TTM-1Cz. The EL is broader compared to the PL, because of some effects from the electrical excitation. There is a tiny emission band in the blue region (< 500 nm) of the EL

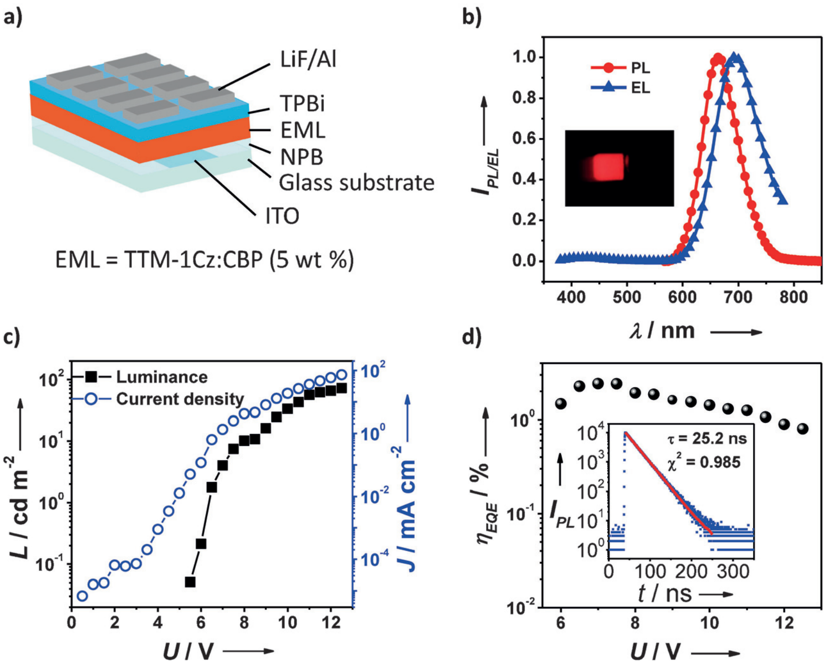

Figure 4. Device performance. a) The schematic diagram of the structure of TTM-1Cz-based OLEDs. b) The EL spectrum (7 V) of the OLEDs accompanied by the PL spectra of the doped thin film. The inset shows a photograph of the TTM-1Cz-based OLEDs operating at 7 V. c) The *J–V–L* characteristics of the OLEDs. d) The η_{EQE} of the OLEDs as a function of voltage. The inset shows the lifetime of the excited states of TTM-1Cz in toluene solution.

spectrum, which originates from the emission of CBP and NPB. The intensity of the blue band increased with the voltage (Figure S4). A photograph of the OLED at 7 V is given as an inset of Figure 4b. For photographs of the OLED at other voltages, please see the Supporting Information (Figure S5). The current density–voltage–luminance (*J–V–L*) characteristics of the OLED are shown in Figure 4c. Figure 4d shows the external quantum efficiency (η_{EQE}) of the OLED as a function of voltage. The maximum η_{EQE} is 2.4%, which lies in the same level of most deep-red/near-infrared OLEDs (Table S2). For the device performance of the TTM-1Cz-based OLED with other structure, please see the Supporting Information (Figures S6–S11 and Table S1).

In an effort to confirm that the emission of TTM-1Cz originated from the radiative decay of the doublets, we carried out the magneto-electroluminescence (MEL) measurement. The MEL describes the change of the EL of an OLED when an external magnetic field of tens of millitesla was applied. There are several mechanisms underlying the MEL in OLEDs, such as the electron–hole pair mechanism and the triplet–triplet annihilation mechanism.[13] However, each of the mechanism relates to the triplet excitons.[13] Thus, if the spin configuration of the excited states of TTM-1Cz is the same as that of the conventional closed-shell organic fluorescent molecules, that is, the singlet and triplet excitons, the MEL should be detected. We can verify whether the emission of the OLED comes from the radiative decay of a doublet or a singlet through the MEL measurement. Herein we fabricated a well-designed OLED in which the electroluminescence contains the emission from TTM-1Cz and a conventional fluorescent material, NPB. The device structure of the OLED is ITO/NPB (30 nm)/CBP (10 nm)/TTM-1Cz:CBP (5 wt %, 40 nm)/TPBi (35 nm)/LiF (0.8 nm)/Aluminum (100 nm). In this OLED, the CBP layer of 10 nm inserted between the two emission layers was used to avoid the influence of the triplets of NPB on TTM-1Cz. A short-wavelength-pass filter chopped at 540 nm and long-wavelength-pass filter chopped at 550 nm were used to separate the blue emission of NPB and red emission of TTM-1Cz. The EL spectra of the total emission, the blue emission, and the red emission are shown in Figure 5a. As the magnetic field increased from 0 to 200 mT with a step of 20 mT (Figure 5b), the EL intensity of NPB and TTM-1Cz was measured. Figure 5c shows the blue emission from NPB when the magnetic field was applied. An obvious MEL can be detected, indicating the existence of triplet excitons in the NPB layer. Whereas no MEL was observed for the red emission from TTM-1Cz, as shown in Figure 5d. The results demonstrate that there is no triplet exciton in the TTM-1Cz layer. The spin configuration of the excited states of TTM-1Cz in the OLED is neither singlet nor triplet, but doublet.

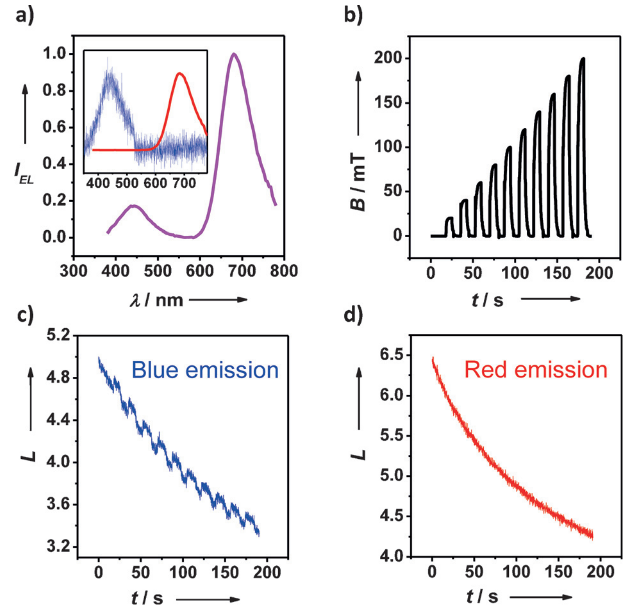

Figure 5. MEL measurements. a) The EL spectrum of the OLED used in the MEL experiments. The inset shows the separated blue emission of NPB and red emission of TTM-1Cz. b) The magnetic field applied in the MEL experiments. c) The EL intensity of the blue part of the OLED emission at 7 V when the magnetic field was applied. d) The EL intensity of the red part of the OLED emission at 7 V when the magnetic field was applied.

Besides TTM-1Cz, another neutral π radical, (TTM-2Cz), was also synthesized. The parallel electroluminescent experiments of TTM-2Cz were performed and similar results were obtained, please see the Supporting Information (Figures S12 and S13).

This study paves a new way to obtain 100% IQE of an OLED. However, the following aspects of open-shell molecules still need to be improved to achieve high efficient and stable OLEDs. I) The stability: It was reported that by carefully designing the molecular structure, some open-shell molecule can maintain its properties for almost 30 years.[14] II) The PL efficiency: For TTM-1Cz, the PL lifetime is 25.2 ns (see the inset in Figure 4d), which is relatively long thus the radiative transition may be not totally allowed. For a molecule, the probability of the radiative transition, R_{ij}^2, can be expressed as shown in Equation (1).[3a]

$$R_{ij}^2 \propto |\langle\psi_{ei}|M|\psi_{ej}\rangle|^2 |\langle\chi_{vi}|\chi_{vj}\rangle|^2 |\langle\psi_{si}|\psi_{sj}\rangle|^2 \quad (1)$$

Here ψ_{ei} and ψ_{ej} denote the initial and final electronic-state wavefunctions, respectively. M is the dipole moment operator. χ_{vi} and χ_{vj} denote the initial and final vibrational state wavefunctions, respectively. ψ_{si} and ψ_{sj} are the spin wavefunctions of the initial and final states, respectively. In the right side of Equation (1), the first term refers to the dipole selection rule. For a dipole allowed transition, ψ_{ei} and ψ_{ej} should be of opposite symmetry with respect to the inversion operator; the second term refers to the Franck–Condon factor, which depends on the vibrational overlap integrals; the third term refers to the spin selection rule. Spin-allowed transition can only occur between states with the same spin quantum number. If any of the three terms is small, the transition could be partially forbidden. For TTM-1Cz, the transition is clearly spin-allowed, thus the relatively slow transition rate is attributed to the first and second terms, which correlate with the molecular structure. Therefore, to enhance the PL efficiency of open shell molecules, researchers should make efforts to rationally design the molecular structure.

In summary, we have fabricated OLEDs using stable neutral π radicals, TTM-1Cz and TTM-2Cz, as emitters. There is only one electron in the SOMO of the two open-shell molecules. This feature renders the excited state of the open-shell molecules to doublet. The key issue of harvesting the triplet energy in an OLED is circumvented, as the radiative decay of the doublet is totally spin-allowed. In the TTM-1Cz- and TTM-2Cz-based OLED, the emission was confirmed to be from the electronic transition from SUMO to SOMO by the spectral analysis. The spin configuration of excited states of TTM-1Cz is doublet according to the magneto-electroluminescence measurements. The maximum η_{EQE} of the TTM-1Cz-based OLED was achieved to be of 2.4%, which is comparable to most deep-red/near-infrared OLEDs. We believe the device performance will be further improved when better emitting open-shell molecules and more effective device structures are found. Nevertheless, using neutral π radicals as emitter to fabricate OLED paves a new way to obtain 100% IQE of OLEDs. We anticipate that our work will be a starting point for further research, leading to high performance organic OLEDs based on open-shell compounds.

Experimental Section

TGA measurement: Thermal gravimetric analysis (TGA) was carried out on the Pyris1 TGA thermal analysis system at heating rate of 20°C min^{-1} in nitrogen.

EPR measurements: EPR spectrum of the powder of TTM-1Cz was measured using the JES-FA200 EPR spectrometer at ambient temperature.

DFT calculations: The DFT calculations were performed with the Gaussian 09 series of programs using the B3LYP hybrid functional and 6-31G(d) basis set.

Spectral measurements: For the Abs and PL measurements, TTM-1Cz was dissolved at a concentration of 1×10^{-5} mol L^{-1}. Then the spectra were measured using a UV/Vis spectrophotometer (Shimadzu UV-2550) and a spectrofluorophotometer (Shimadzu RF-5301PC).

Lifetime measurements: For the lifetime measurements, an Edinburgh fluorescence spectrometer (FLS980) was used. Then the lifetime of the excited states was measured by the time-correlated single-photon-counting method (detected at the peak of the PL) under the laser excitation at 375 nm and a pulse width of 50 ps.

OLED fabrication and characterization: The OLEDs were fabricated by the multiple source organic molecular beam deposition method at 2×10^{-4} Pa. The current density–voltage (J–V) characteristics were measured by a Keithley 2400 source meter. The luminance–voltage (L–V) characteristic and the EL spectrum were measured by a PR650 spectroradiometer. For measuring the spectrum of the blue emission of the OLED used in the MEL measurements, a high-sensitivity Maya2000 Pro Spectrometer was used.

MEL measurements: After fabrication, OLEDs were immediately placed on a Teflon stage between the poles of an electromagnet with the magnetic field perpendicular to the current. A Keithley 2612 sourcemeter was used to provide a constant voltage from channel A. The emission of the devices was collected by an optic fiber (2 m) connected to a Hamamatsu photomultiplier (H10721-20). The photomultiplier was connected to channel B of the Keithley 2612 to record the EL intensity. In order to eliminate the interference of the magnetic field on the photomultiplier, we placed the photomultiplier far away from the electromagnet.

Keywords: doublet · luminescence · open-shell molecules · organic light-emitting diodes · radicals

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