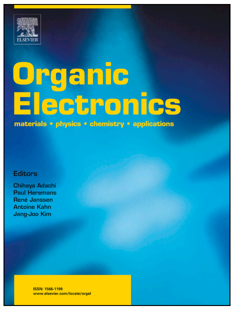

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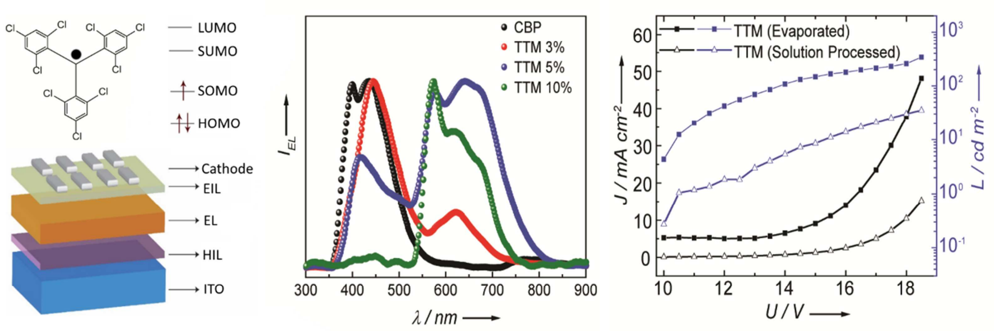
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λ / nm
TTM (Evaporated)
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J / mA cm^{-2}
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Solution-Processed Organic Light-Emitting Diodes with Emission from a Doublet Exciton; Using (2,4,6-trichlorophenyl)methyl as Emitter

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Abstract

Neutral-π radical based open shell molecules foster new potential in light emitting diodes because of their theoretical near-equity quantum efficiencies. In this study, we report organic light emitting diodes (OLEDs) based on a novel open shell molecule (2,4,6-trichlorophenyl)methyl (TTM) as the electroluminescent layer. The singly occupied molecular orbital (SOMO) level and optical bandgap of TTM was calculated using cyclic voltammetry and UV-visible absorption respectively. Thermogravimetric analysis showed a stable molecule capable of sublimation. Two decidedly different approaches, thermal evaporation and solution processing, were employed to deposit TTM:host blend thin films for OLED device fabrication. OLED devices fabricated via thermal evaporation and solution processing yielded external quantum efficiencies of 2.78% and 0.28% and luminances of 330 cdm^{-2} and 78 cdm^{-2} respectively. Further, the effect of doping ratios of the host materials on OLED device performance were investigated and optimal ratios were established. We report for the first time solution processed open shell organic molecules for light emitting diode applications. Our results elucidate the potential for low-cost and high efficiency optoelectronic devices.

1.1 Introduction

After three decades of development, organic light-emitting diodes (OLEDs) have undergone significant advances to become the preeminent technology for flat panel displays and solid-state lighting applications.[1],[2] OLEDs offer many advantages due to their ease of fabrication, low-cost, and mechanical robustness. Since their inception, several novel materials and device structures have been reported to enhance optoelectronic performance of OLEDs. Yet, until recently, mostly closed shell organic molecules were considered for OLED emitters. In the ground state of a closed shell organic molecule two electrons with opposite spin occupy the highest occupied molecular orbital (HOMO) and once excited, one of the electrons transitions to the lowest unoccupied molecular orbital (LUMO). Statistically, there is a 25% probability of forming a singlet state and 75% probability of forming a triplet state in such systems[3]. Thus, Pauli exclusion principle places a theoretical limit of 25% on the internal quantum efficiency of the fluorescent emitters[4]. Much of the OLED research effort was focused on harvesting these otherwise lost triplets by means of phosphorescent emitters[5], triplet fusion[6], and time delayed fluoresce[7]. Another approach is to use neutral conjugated radical molecules with an open outer shell where a transition from the singly unoccupied molecular orbital (SUMO) back down to the ground singly occupied molecular orbital (SOMO) state is spin allowed[8,9]. Because of this inherent property, open shell molecules have a theoretical upper limit of their internal quantum efficiency of 100% which makes them attractive for low-cost and high performance luminescent devices.

Several different device fabrication methods have been previously used to fabricate OLEDs from closed shell molecules. These methods involve vacuum based methods i.e. vapor jet[10] and thermal evaporation[11] and solution based techniques such as spin coating and inkjet printing[12]. Vacuum based methods have shown higher performance in OLEDs, although, solution processed techniques offer an alternative to further reduce fabrication costs and complexities. While the current research on solution based processing is limited to closed shell molecules, there has been no report for open shell molecules. Hence there is a need for low cost alternative fabrication techniques in addition to exploring novel open shell molecules to facilitate low cost and high efficiency OLEDs.

Since the first persistent triarylmethyl radical was reported by Gomberg[13], several stable derivatives of this class of organic radicals have been reported.[14–19] Polychlorinated radicals such as tris(2,4,6-trichlorophenyl)methyl (TTM) radical[14] are particularly stable owing to the unique steric protection afforded to the triarylmethyl carbon by the chlorinated arene rings. Despite minor delocalization of the unpaired electron onto the *ortho*- and *para*-positions of each aryl ring,[20] the presence of the chlorine atoms at these positions imparts electronic shielding which kinetically stabilizes the TTM radical toward sigma dimerization and also enhances the stability of the radical toward oxygen.[15] However polyhalogenated triarylmethyl radicals are sensitive to electron transfer reactions, and easily undergo redox chemistry in the presence of electron donor and acceptor species.[18,21–23] This rich redox chemistry is also valuable in the areas of organic magnetic materials,[24–26] and recently for organic light-emitting diodes.[8] For these reasons we chose the TTM framework as a scaffold to support additional derivatization in an effort to tailor the photo-physical properties of this class of stable organic radicals.

We report a stable TTM radical as the emitter of OLEDs using thermal evaporation processes obtaining results comparable to the previous report.[8] Further we also show the versatility of this TTM molecule for solution processed devices. Albeit solution processed devices exhibit a lower performance, they provide processing advantages in their cost-effectiveness and printability.

1.2 Materials and Methods

Unless otherwise noted, all procedures were carried out using typical Schlenk techniques under an atmosphere of nitrogen or in a nitrogen-filled glove box. Solvents were dried and degassed by an Innovative Technology solvent purification system and stored over a 3 Å molecular sieves in a nitrogen-filled glove box. n-Butylammonium hydroxide 40% water, tetrabutylammonium perchlorate(anhydrous, TBAP), and magnesium sulfate (anhydrous powder) were purchased from T.C.I and J.T. Baker. Chloroform, hexanes and tetrahydrofuran were dried under nitrogen over CaH and Na/K, respectively and distilled prior to use. Aluminium trichloride (anhydrous) and 1,3,5-trichlorobenzene 98% were purchased from Sigma Aldrich and Beantown Chemical and used as received. Hydrochloric acid (0.1N) was prepared from concentrated hydrochloric acid. Melting points were recorded on a Mel-Temp apparatus in sealed capillary tubes and are uncorrected. All other reagents were used as received. NMR spectra were recorded on Bruker Avance 400 MHz/52mm spectrometer. Chemical shifts (δ) are given in ppm and are referenced to the residual solvent peak in $CDCl_3$: ^{1}H: 7.26 ppm; ^{13}C: 77.0 ppm. All column chromatography was performed using 20 cm column with silica gel (Aldrich), 700-230 mesh, 60 Å, and pore volume of 0.75 cm^3/g as the stationary phase. The synthesis of HTTM and TTM have been modified slightly from those reported in the literature.[14,16]

1.2.1 Synthesis of TTM

Synthesis of tris(2,4,6-trichlorophenyl)methane (HTTM)

In a nitrogen-filled glove box, a 50 mL pressure flask was charged with 1,3,5-trichlorobenzene (13.68 g, 75.40 mmol), 0.67 mL of chloroform (1.00 g, 8.37 mmol), aluminum trichloride (1.22 g, 9.14 mmol), and a magnetic stir bar. This mixture was heated to 90°C for 2 hr under an atmosphere of nitrogen. After this time the mixture was allowed to cool to room temperature and 20 ml of HCl (0.1N) was added drop-wise over this mixture which was cooled in an ice bath. The purple suspension immediately turned into a yellow solution that was then extracted from the aqueous byproducts using 50 mL of chloroform in a separatory funnel. The organic layer was dried over magnesium sulfate for 1 hr and filtered over a scintillated glass frit. The yellow solution was immediately concentrated under vacuum and the obtained oily material was added to 40 mL of hexanes which resulted in the immediate precipitation of a white solid.

The solid was collected on a frit, and washed with hexanes until the washings were colorless. The white solid was dried under vacuum to get an 80% yield which was used in the next step without further purification. m.p. 246-248oC. ^{1}H NMR (400 MHz) ($CDCl_3$): d 6.68 (s, 1H, CHPh), 7.23-7.24(d, 3H, J = 2.3 Hz), 7.35-7.36(d, 3H, J = 2.3 Hz). ^{13}C NMR (100.61 MHz): δ 49.80(CH), 128.43, 130.00, 133.78,133.82, 137.07, 137.90. The synthesis has been modified slightly and the purification process as well. Characterization data of this compound is in agreement with those reported in the literature.[16]

Synthesis of tris(2,4,6-trichlorophenyl)methyl radical (TTM)

In a nitrogen-filled glove box, a 100 mL Schlenk flask was covered with aluminum foil and charged with HTTM (3 g, 5.41 mmol), and 4.60 mL of n-butylammonium hydroxide (4.56 g, 7.03 mmol) in 50 mL of THF was added to afford a deep-red solution. The reaction was stirred for 4 hr then p-chloranil (1.86 g, 7.57 mmol) dissolved in 25 mL of THF was added. The reaction mixture was allowed to stir for 12 hr, and then the resulting purple solution was concentrated *in vacuo* to give a purple dark solid. This solid was dissolved in 10 mL of dichloromethane and silica gel (1.0 g) was added. The resulting suspension was then dried *in vacuo* to give a purple solid that was loaded into the top of a silica gel-filled column, and the product was purified by chromatography using hexanes as the eluent. After removal of the hexanes *in vacuo*, the TTM radical was isolated as a red solid in 83% yield. Characterization data of this compound is in agreement with those reported in the literature.[14,16]

Cyclic voltammetry was performed using a CH Instruments (Model 600D) analyzer using a glassy platinum working electrode, and platinum wire counter electrode. The reference electrode was built from a silver wire inserted into a small glass tube fitted with a porous frit and filled with a $AgNO_3$ solution in THF (0.01 M). Ferrocene was used for calibration, and all reduction potentials are reported with respect to the $E_{1/2}$ of the Fc^+/Fc redox couple. All cyclic voltammograms were recorded in dichloromethane using tetrabutylammonium perchlorate(TBAP) as the electrolyte (0.1M) at a scan rate of 100 mVs^{-1}.

All electron paramagnetic resonance (EPR) spectra were recorded on an X-band Active Spectrum Benchtop Micro-ESR spectrometer (9.5 GHz, 300 Gauss sweep range). Field calibration was accomplished by using a standard of solid 2,2-diphenyl-1-picrylhydrazyl (DPPH), g = 2.0036. Spectra were recorded at room temperature in dichloromethane. Thermogravimetric analysis (TGA) were performed using TA Instruments TGA Q50. Temperature was ramped up at a rate of 5.00 °C/min from room temperature to 800°C with argon as carrier gas. UV-visible absorption spectra were obtained using a Shimadzu UV-2501PC UV-visible spectrometer. Absorption spectra were obtained from 1000 nm to 300 nm. Photoluminescence (PL) spectra were obtained using a quartz substrate and quartz cuvette from a 0.74 m double spectrometer (Spex) using a He-Cd Laser (Kimmon) with an excitation wavelength of 325 nm.

1.2.2 Materials

Bathophenanthroline (Bphen, 99.5%), N,N’-di-1-naphthyl-N,N’-diphenylbenzidine (NPB,99.5%) and 4,4-bis(carbozol-9-yl)biphenyl (CBP, 99.5%) were purchased from Jilin OLED Materials. Molybdenum trioxide (MoO_3, Puratronic 99.9995%) was purchased from Alfa Aesar. Lithium fluoride (LiF, 99.995%) and anhydrous chlorobenzene were purchased from Sigma-Aldrich. Aluminum pellets (Al, 99.999%) were purchased from Kurt J. Lesker.

1.2.3 OLED Device Fabrication and Characterization (Evaporation)

The organic light-emitting diodes (OLEDs) were created by evaporating the materials on glass substrates commercially pre-coated with an indium tin oxide (ITO)(110nm). The ITO coated glass substrates were cleaned in successive baths of detergent (Deconex OP 121), and deionized water for 20mins in an ultrasonic cleaner then baked at 100°C for 10 min. The substrates were then treated with air plasma for 10 min. The plasma cleaned substrates were loaded into a high vacuum evaporator (Travato 300C) and pumped down to ~ 10^{-8} Torr. The hole injection layer (HIL) was deposited by evaporating molybdenum trioxide(MoO3)(.75nm)/N,N'-di-1-naphthyl-N,N'-diphenylbenzidine(NPB)(40nm) onto the glass ITO substrate. Tris(2,4,6,-trichlorophenyl)methyl(TTM) material was doped through evaporation processes into a 4,4-bis(carbozol-9-yl)biphenyl(CBP) matrix: TTM: (CBP) (1wt%, 2wt%, 3wt%, 5 wt%, 10wt%, 15wt% ,20wt%, 40wt%, 40nm) forming the emissive layer of the OLED device. The electron injection layer (EIL) was formed by gradually evaporating (4,7-diphenyl-1,10-phenanthroline)(Bphen)(40nm)/lithium fluoride (LiF)(1nm) and aluminum(100nm) as a cathode. The fabricated OLEDs were then encapsulated in a flowing high-purity nitrogen gas environment. Luminance, current density, and external quantum efficiency characterization was performed using a Thor Labs PDA100A calibrated Si photo detector coupled to Labsphere model 2500 integrating sphere, and Agilent Technologies U3606B source meter unit.

1.2.4 OLED Device Fabrication and Characterization (Solution Processed)

Solution processed OLEDs were created through spin deposition on glass substrates commercially pre-coated with an indium tin oxide anode (110nm). The substrates were cleaned as discussed previously. The hole injection layer (HIL) was formed by spin coating (poly(3,4-ethylenedioxythiophene)poly(styrenesul-phonate), (Clevios AI 4083 PEDOT:PSS) on the substrates at 4000 rpm for 30 seconds followed by baking at 145°C for 30 min in air. The emissive layer was formed by spin coating a blend solution of TTM and Poly(9-vinyl-carbozole)(PVK) dissolved in an anhydrous chlorobenzene solution with a concentration of

10mg/ml as TTM:PVK (5wt%, 10wt%, 15wt%, 20wt%, 50wt%, 50nm) inside a flowing-high purity nitrogen gas environment. The resulting TTM:PVK solution was spin coated onto PEDOT at 1000 rpm for 30 s and annealed at 80°C for 30 min. The substrates were then loaded into the evaporator for thermal evaporation of EIL as discussed before.

1.3 Results and Discussion

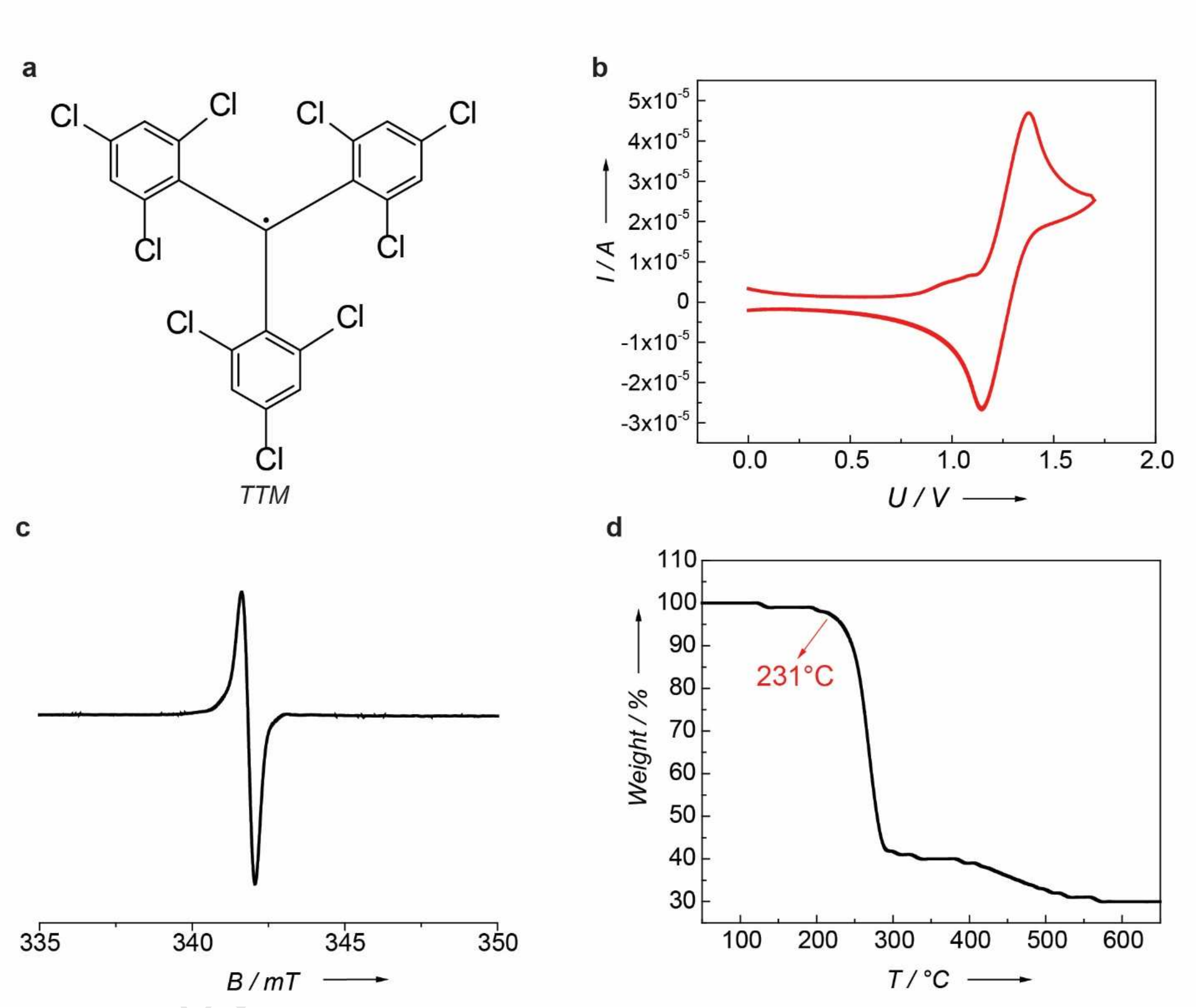

Figure 1. (a) Chemical structure of TTM (b) Cyclic-voltammetry in dichloromethane (c) The EPR spectrum in dichloromethane at room temperature (d) Thermogravimetric analysis spectrum of TTM

Figure 1a shows the chemical structure of the TTM molecule with the centralized neutral radical surrounded by six chlorine atoms. The basis of the TTM molecule is the same as the one reported by Peng et al. where the authors reported its carbazole derivative.[8] However, we found that TTM without derivization is luminescent when coated as film and in solution (*vide infra*). We also found that the TTM molecule is stable credited to the protection offered by chlorinated arene rings, which help to shield the triarylmethyl carbon both electronically and kinetically similar to the stability reported for the carbazole derivative of TTM.[8] Cyclic voltammetry was utilized to measure the singly occupied molecular orbital (SOMO) level of TTM as shown in Figure 1b. From the oxidation reaction onset at 1.14V, the SOMO level was calculated as -5.54 eV measured with a ferrocene reference (4.5 eV). Furthermore, as seen in Figure 1c, we experimentally obtained electron paramagnetic resonance (EPR) spectrum and the spin resonance of the unpaired electron within the TTM organic radical, providing evidence of proper material synthesis. To ensure thermal stability and to measure the sublimation temperature of TTM, TGA was performed as shown in Figure 1d. A subsequent weight reduction of 5% occurs at an induced temperature of 231°C. The TGA spectrum provides evidence that the TTM material is capable of being evaporated at low temperatures and does not chemically decompose as it sublimes.

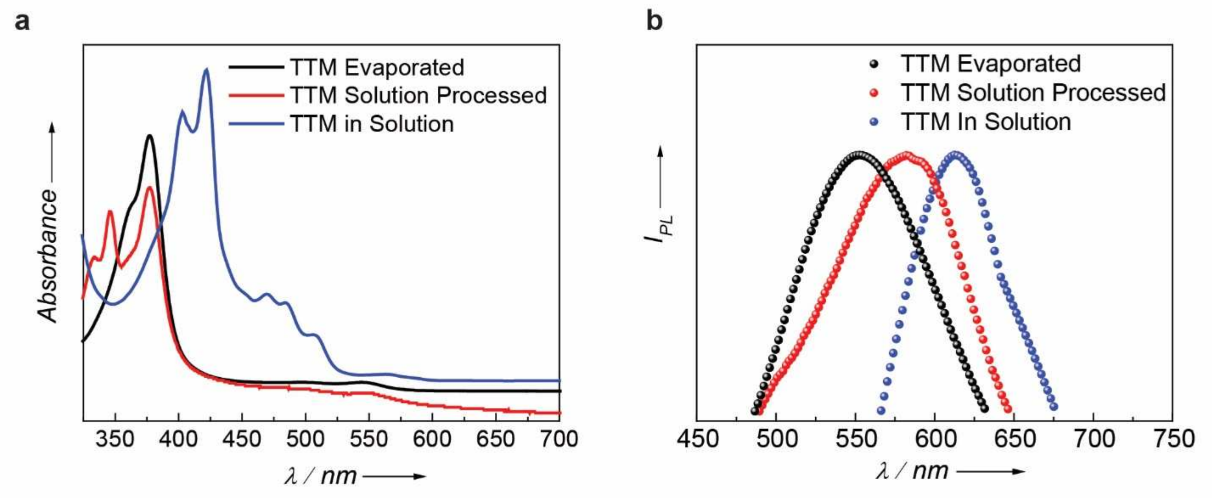

Figure 2. (a)UV-Visible absorption spectrum of evaporated TTM film, solution-processed TTM film and TTM in dichloromethane solution (b) The photoluminescence spectrum of TTM in dichloromethane solution and TTM evaporated as film.

The absorption spectra of evaporated and solution processed TTM thin films is shown in Figure 2a. The initial absorption onset of TTM in solution occurs at wavelength of 590 nm, with a secondary band centered at 525 nm representing energy gaps of 2.1 eV and 2.36 eV respectively. In the absorption spectrum of the evaporated TTM film there is a band centered at 575 nm representing an energy gap of 2.16 eV. The absorption spectrum of the solution processed sample shows a band centered at 563 nm representing an optical bandgap of 2.20 eV. The small difference between the optical bandgap of the evaporation and solution-processed devices could be due to the amorphous nature of the evaporated thin film compared to solvent induced ordering/aggregation in spin-coated films. This energy band gap represents a spin allowed transition from the SOMO to the SUMO of the doublet exciton. Unlike TTM in solution, the evaporated and solution-processed samples do not exhibit a secondary absorption band until near-UV possibly due to a forbidden energy transition. As seen in Figure 2b the PL spectrum for the evaporated TTM thin film is centered at 550 nm. A red shift occurs in the photoluminescence spectrum for both the solution processed sample (580nm) and as the pristine TTM material is dissolved in anhydrous chlorobenzene as solution (612nm).

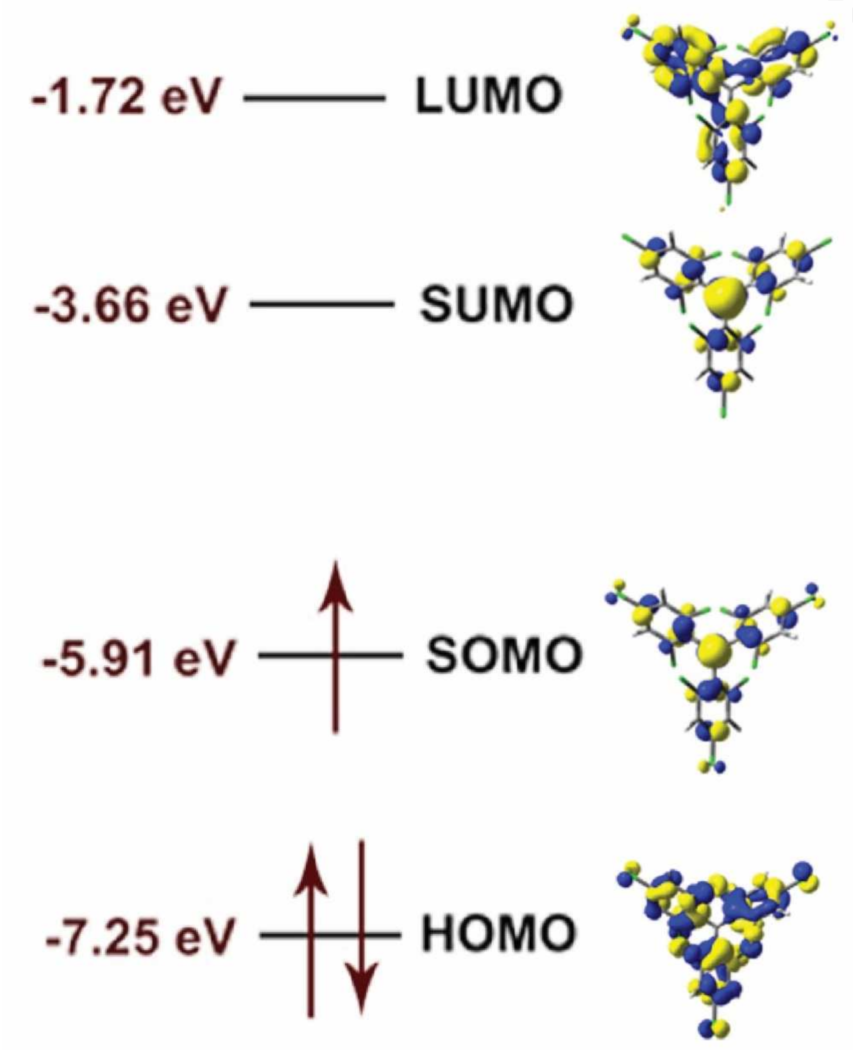

Figure 3. Density functional theory (DFT) calculations for each of the orbital states.

Using density functional theory calculations, we were able to calculate the energy levels of each of the orbital states: HOMO, SOMO, SUMO, and LUMO as -7.25eV, -5.91eV, -3.66eV, -1.72eV respectively as seen in Figure 3. The differences between the calculated energy level of the SOMO using CV and DFT data is due to the oxidation reaction of air. The optical bandgap, 2.25 eV, of TTM molecule calculated from absorption onset shows that the transition occurs from SOMO to SUMO.

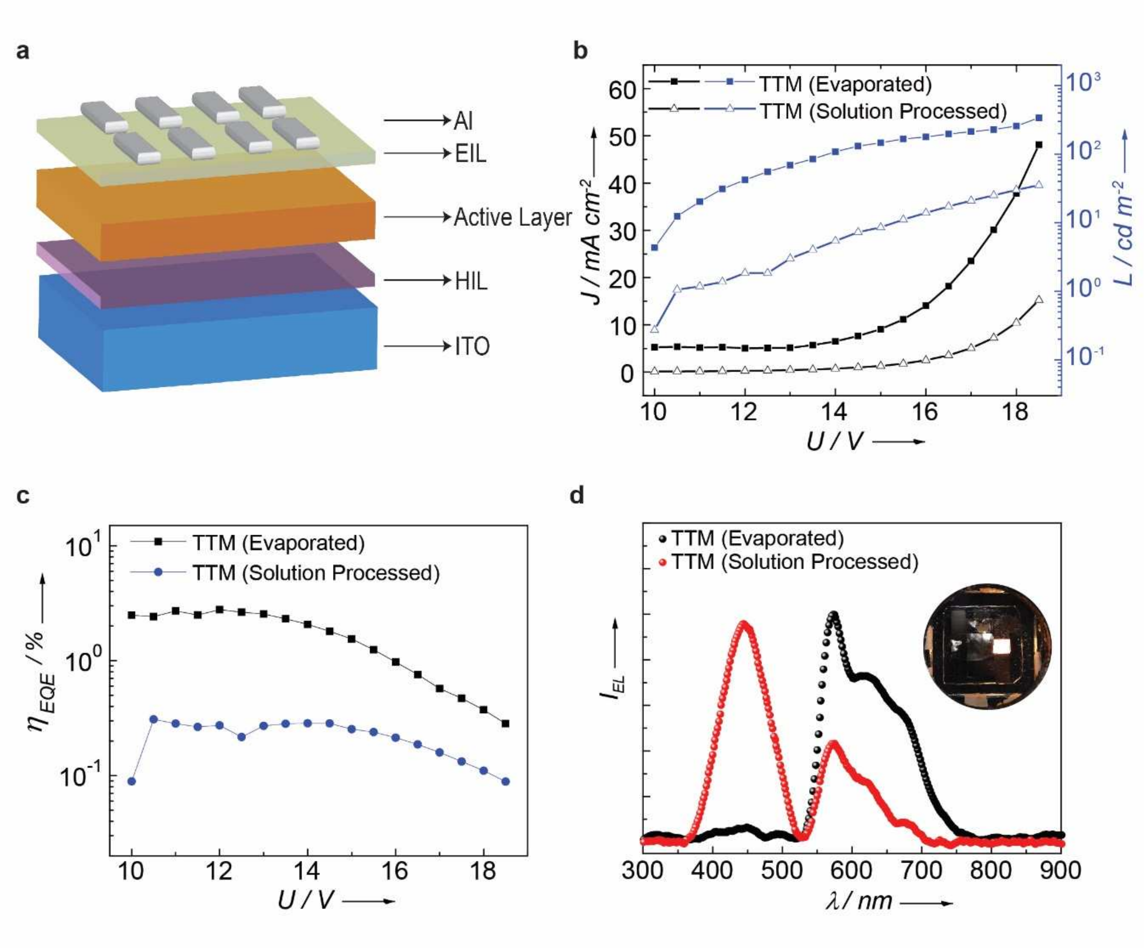

Figure 4 (a) Device structure of the TTM OLED. b) J-V-L characteristics of the TTM OLED devices (c) External quantum efficiency of the OLED devices vs. voltage. d) Electroluminescence of solution and evaporation based OLED devices. The inset shows an evaporated OLED device operating at 10 V.

Because organic radicals themselves are not emissive due to aggregate caused quenching, the TTM material must be doped into a matrix with a host material. Two distinct devices were designed in an effort to study the optoelectronic characteristics of OLEDs. The evaporated

OLED device structure was: ITO/MoO_3 (.75nm)/ NPB (40nm)/TTM:CBP (40nm)/Bphen (40nm)/LiF (1nm)/Al (100nm) which is schematically depicted in Figure 4a. Various doping ratios were investigated and the device with 5% TTM and 10% TTM doping ratios was found to be optimal for solution and evaporated processed devices respectively. The doping levels for evaporated devices were varied by adjusting the evaporation rate of TTM with respect to the evaporation rate of the CBP matrix. For solution processed devices, different doping ratios were obtained by mixing different volumes of PVK and TTM in chlorobenzene (10 mg/ml). The emissive/electroluminescent layer was achieved by spin coating a TTM:PVK thin films from chlorobenzene solution onto PEDOT:PSS coated substrates. The solution processed OLED device structure was: ITO/PEDOT PSS (50nm)/TTM:PVK (50nm)/Bphen (40nm)/LiF (1nm)/Al (100nm). Figure 4b shows the current density-voltage-luminance (J-V-L) plot of evaporated and solution processed TTM OLEDs. Each of the evaporated TTM devices showed a relative low turn on voltage of 7 V. The optimal current density-voltage-luminance (J-V-L) and external quantum efficiency (η_{EQE}) results were obtained from the evaporated TTM:CBP (10 wt.%) sample. Figure 4b shows the J-V-L characteristics of the evaporated and solution processed TTM devices. The evaporated TTM devices exhibited maximum luminance of 330 cd/m^2 and current density of 48 mA/cm^2 at 18 V bias voltage. On the other hand, solution processed devices showed a maximum luminance of 78 cd/m^2 and current density below 10 mA/cm^{-2} at 18 V bias voltage. Figure 4c shows the external quantum efficiency ($\eta_{EQE)}$ of each of the evaporate and solution processed devices. The maximum external quantum efficiency obtained from evaporated and solution processed devices were 2.78% at 12V and 0.28% at 10.5V respectively. The evaporated devices showed better optoelectronic performance than for the reported TTM-1cz OLED devices i.e. higher η_{EQE} and luminance.[8,9] While the luminance and efficiency of evaporation processed devices were superior to that of solution processed devices, the ease of solution-based processing points to advantages large scale OLED manufacturing. This type of fabrication technique allows for printability; providing a low-cost alternative for use in high-throughput OLED manufacturing. With further optimization of device fabrication protocols and novel open shell molecular design, the efficiencies can be further improved.

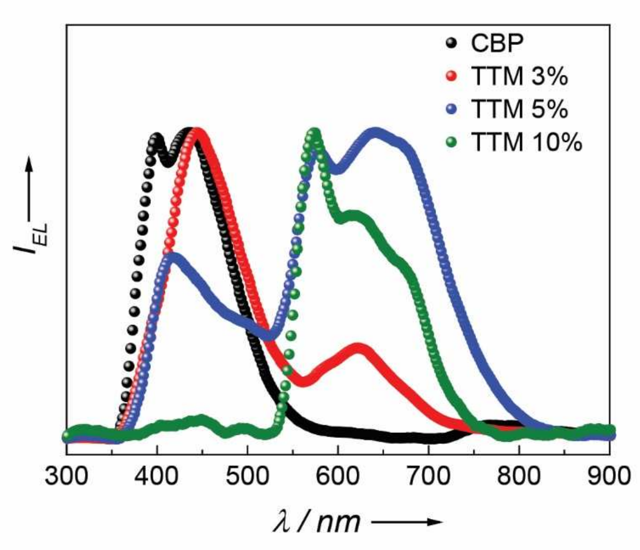

Figure 5. Electroluminescence of evaporated TTM OLED devices with different doping quantities.

It was found that the optimal doping ratio for each type of device architecture was directly related to the opto-electrical properties of the matrix used to create the emissive layer: CBP and PVK respectively. Figure 5 shows the electroluminescence (EL) of evaporated TTM OLEDs. For solution processed devices emission was only observed for 5% doping ratio and hence EL of the doping ratios were not compared. At low doping quantities, the majority of the light emission is produced from the CBP matrix alone. The devices with pure CBP host emitted a stable blue light with a peak at 436 nm which is the same blue band emission previously reported.[8] As the quantity of the dopant TTM increased to 3%, another band emerges in EL spectra with a peak at 642 nm indicative of emission from TTM. With 5% doping the emission from TTM was enhanced with a less dominant blue band emission from CBP. When the TTM doping ratio was increased to 10% all emission was contributed by TTM dopant itself revealing an orange light as observed in Figure 3d. Dopant ratios beyond 15% showed no luminance and hence were not compared.

1.4 Conclusions

In summary, we report a novel open shell neutral-π radical namely tris(2,4,6-trichlorophenyl)methyl (TTM) for application in OLEDs. Unlike closed shell molecules, neutral conjugated radicals have intrinsic advantages due to the radiative decay of the doublet exciton. Thermal gravimetric analysis showed thermal stability and the sublimation temperature of TTM was calculated at 231°C. Using DFT data, the HOMO, SOMO, SUMO and LUMO were found to be -7.25eV, -5.91eV, -3.66eV and -1.72eV respectively. The nature of the unpaired electron's ability to take part in many opto-electrical processes was shown with an absorption band centered at 563 nm, and a photoluminescence band centered at 580 nm representing optical bandgaps of 2.20 eV and 2.14 eV respectively. Two techniques were used namely evaporation and solution processing to fabricate TTM based OLED devices. The optimal TTM doping ratio for evaporated devices was 10% which exhibited a maximum η_{EQE} of 2.78% and luminance of 330 cd/m^2. Solution-processed devices with optimal doping ratio of 5% showed maximum η_{EQE} of 0.28% and luminance of 78 cd/m^2. Our results provide insight and lay the framework for novel open shell molecular design through derivitization. Further we show that solution processing of these open shell molecules can enable facile and low cost high efficiency OLEDs through systematic device optimization.

Acknowledgements

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- Solution-processed open shell organic molecules for OLED applications
- OLEDs based on (2,4,6-trichlorophenyl)methyl as the electroluminescent layer
- Open shell molecular design through derivitization