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# **Graphical Abstract**



# A Thermally Cross-Linkable Hole-Transporting Small-Molecule for Efficient Solution-Processed Organic Light Emitting Diodes

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#### Abstract

Fabrication of multilayered organic light-emitting diodes (OLEDs) through solution process involves several challenges, especially in preventing dissolution of prior layers during subsequent coating. To overcome, extensive efforts had been made in developing crosslinkable materials. In this work, a thermally cross-linkable hole-transporting material, (9,9'bis(4-vinylbenzyl)-9H,9'H-3,3'-bicarbazole) (VyPyMCz), is synthesized, characterized and successfully applied to multilayered OLEDs via solution-process. After cross-linking, the hole-transporting material forms robust, smooth and solvent-resistant network, enabling a subsequent spin-coating without deteriorating its film integrity. The measured energy level suggests that **VyPyMCz** facilitates the injection of hole and effectively blocks electron to realize high efficiency, especially at high luminance. At 1,000 cd  $m^{-2}$  for example, the power efficiency of a studied red device is increased from 7.5 to 11.9 lm W<sup>-1</sup>, an increment of 58%, and the maximum brightness improved from 7,724 to 13,560 cd m<sup>-2</sup>, an increment of 75%, as this electron confining, hole transporting material is incorporated. Remarkably, VyPyMCz also works for a high band gap (2.90 eV) with a high triplet energy (2.80 eV) blue emitter containing OLED device, the power efficiency is increased from 6.6 to 11.8 lm W<sup>-1</sup>, an increment of 78%, and the maximum luminance enhanced from 5,260 to 6,857 cd m<sup>-2</sup>, an increment of 30%, because of its higher triplet energy (2.87 eV).

Keywords: Thermal crosslinking, hole transporting materials, solution-processed OLEDs.

## 1. Introduction

Organic light-emitting diodes (OLEDs) have drawn enormous attention in academia and industries because of their amazing applications in both next generation full-color flat-panel display and solid-state lighting, owing to their potential for fabrication over a large area, light weight, rapid response, low power consumption, and wide viewing angle [1-10]. There are two general approaches to fabricate OLEDs, one is thermal evaporation process under high vacuum whereas another one is based on solution process feasible deposition [5,10]. Typically, the former methodology straightforwardly enables the successive deposition of multiple layers such as charge transport, multiple emissive layer or carrier blocking layers, which are highly crucial to improve the device performance and lifetime. Nevertheless, this process suffering with several serious downsides, amongst, low material utilization rates, poor scalability, high capital cost, and difficulty in patterning are the main [5,10]. The latter one seems to be more superior and attracted by the academia and industry because of its descriptive features such flexible, roll-to-roll manufacturability on larger area and cost effective with high efficiency if one can prevent the blending or dissolution of formerly deposited layers throughout the consecutive deposition of multilayer stacks [5,10-14].

Previously, in order to avoid the aforementioned issues, three major competitive approaches have been adopted by the scientists, i.e. (1) the usage of orthogonal solvents for successive layer deposition [15] (2) change of polarity of a precursor in a certain layer, and (3) usage of cross-linkable polymers [16-17]. In 2012, by using the first approach and a caesium carbonate (CsCO<sub>3</sub>) doped 1,3,5-tris(m-pyrid-3-yl-phenyl)benzene (TmPyPB) electron transporting layer (ETL), Jenekhe and co-workers developed a fully solution-processed blue phosphorescent OLED with a maximum current efficiency (CE) of 37.7 cd A<sup>-1</sup> at 1,300 cd m<sup>-1</sup> <sup>2</sup> [18]. In same year, they further reported a CE of 53.8 cd  $A^{-1}$  at 5, 900 cd  $m^{-2}$  for a green device with a 4,7-diphenyl-1,10-phenanthroline (BPhen) ETL [19]. In 2014, Bradley, Anthopoulos, Perumal and co-workers successfully develped a solution processed copper thiocyanate as hole injection layer (HIL) or hole transport layer (HTL) function layer for OLED and obtained a maximum efficacy (PE) of 22 lmW<sup>-1</sup> (CE 47 cd A<sup>-1</sup>) at 1,000 cd m<sup>-2</sup> for a green device [20]. Nevertheless, only a limited range of materials can readily be made compatible with this solubility criterion, critically diminishing the applicability of this method. The second approach has also proven to be of rather low importance, due to the difficulty of finding classes of materials, the polarity of which can be altered after deposition.

The third alternative- approach is the usage of cross-linkable materials [21-22]. Cross-linking has been used to improve the morphological stability and solubility of formerly spin-coated layer, hence allowing the successful deposition of the next layer [21-22]. As a result, much work is currently being dedicated to the development of cross linkable materials that display the physical properties requisite of a specific OLED layer. On the basis of reactive monomers present in the molecules and initiation method of cross-linking reaction, crosslinking mechanism can be classified into two categories, photo cross-linking and thermal crosslinking. Photo cross-linking assists the fine and thermal stress free patterning of layer at room temperature in a very short time period with the help of photoinitiators [23-26]. Among various kinds of photo cross-linking units, oxetanes [27-28], cinnamates [29], chalcones [29], thiol-ene-click-reactions [30], azides [31], and perfluoro azides [32] have been incorporated in the OLED devices as hole injecting (HIL) or transporting (HTL) materials. Regrettably, this process passes one very serious drawback, i.e. formation of undesired contaminations from the photoinitiators which may affect the operation of the devices [24-26]. Thermal cross-linking units are usually used for cross-linkable HTL materials because of the relatively simple deposition procedure. Remarkably, they can be proficiently applied for any type of material via annealing at high temperatures (>100 °C), with the necessities of cross-linkable moieties in the material [13,33-35]. Styrenes [36], acrylates [37], azides [38], trifluorovinylethers [39], phenylethynyl-groups [40], silanes [41], benzocyclobutenes [42], or alkyne-azide-cycloaddition [43] are the examples of such thermal cross-linking units applied to HTL materials.

In this study, we have designed and synthesized a thermally cross-linkable HTL material, **VyPyMCz** for solution-process based multilayer monochromatic and white OLEDs. The compound **VyPyMCz** exhibits high triplet energy and cross-linking function due to the presence of a carbazolyl moiety and two vinylphenyl groups, respectively. The synthesized material was examined by various characterization techniques, including thermogravimetry (TGA), UV-Vis spectroscopy, photoluminescence spectroscopy (PL), electron photoemission spectroscopy, and time of flight (ToF) method. The morphological behavior of the VyPyMCz thin films at different annealing temperatures was analyzed by atomic force microscopy (AFM). OLEDs with the cross-linking layer show low operating voltages and improved power efficiencies as compared with the corresponding reference devices (without HTL). For example, the studied red, blue, and green devices showed an increment of 58%, 78% and 40% in power efficacy at 1,000 cd m<sup>-2</sup> and an increment of 75%, 30% and 20% in maximum luminance, respectively. The reason why all the fabricated OLED devices show improved

efficiency at high brightness or voltage may be because of its relatively high lowest unoccupied molecular orbital (LUMO) energy-level (-2.0 eV). It's also notable that we did not observe any detrimental influence of the cross-linking process on the performance of OLED devices.

#### 2. Result and discussion

#### **2.1 Materials**

9H-carbazole (1), iron(III) chloride (FeCl<sub>3</sub>), chloroform, 4-vinylbenzyl chloride, potassium hydroxide (KOH), tetrabutylmmonium hydrogensulfate (TBAHS), tetrahydrofuran (THF) and chloroform were purchased from Aldrich and used as received.

9H,9'H-[3,3']Bicarbazole (2) was obtained by chemical oxidation of 9H-carbazole (1) in the presence of FeCl<sub>3</sub> as we described earlier [44].

(9,9'-bis(4-vinylbenzyl)-9H,9'H-3,3'-bicarbazole) (3/VyPyMCz) was prepared by the reaction of 9H,9'H-[3,3']bicarbazole (2) with an excess of 4-vinylbenzylchloride under basic conditions in the presence of TBAHS phase transfer catalyst. 2.0 g (6.02 mmol) of compound 2 and 2.02 g (13.24 mmol) of 4-vinylbenzylchloride were heated to reflux in 50 ml of THF at 65 °C. Then 1.01 g (18 mmol) of powdered KOH and a catalytic amount of TBAHS were added to the mixture, and it was refluxed for 24 hours. After thin layer chromatography (TLC) control the reaction mixture was filtered, the solvent was evaporated and the product was purified by column chromatography with silica gel using hexane/ethyl acetate (vol. ratio 5:1) as an eluent. Yield: 1.9 g (56 %) of yellow amorphous material. MS (APCI<sup>+</sup>, 20 V): 565.3 ([M +H], 100 %). <sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.47 (d, 2H, J = 1.8Hz, Ar), 8.30–8.22 (m, 2H, Ar), 7.81 (dd, 2H,  $J_1 = 1.8$  Hz,  $J_2 = 8.4$  Hz, Ar), 7.53–7.30 (m, 12H, Ar), 7.23–7.15 (m, 4H, Ar), 6.71 (dd, 2H,  $J_1 = 11.1$  Hz,  $J_2 = 17.7$  Hz, 2 × Ph-CH=CH<sub>2</sub>), 5.74 (dd, 2H, J<sub>1</sub> = 0.9 Hz, J<sub>2</sub> = 17.7 Hz, Ph-CH=CH<sub>2</sub>), 5.59 (s, 4H, 2 × Ph-CH<sub>2</sub>-Ar), 5.24 (dd, 2H,  $J_1 = 0.6$  Hz,  $J_2 = 10.8$  Hz, Ph-CH=CH<sub>2</sub>). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>,  $\delta$ , ppm): 141.12, 139.78, 139.94, 136.76, 136.32, 133.80, 126.69, 126,67, 125.99, 125.83, 123.66, 123.30, 120.54, 119.32, 119.06, 113.98, 109.15, 109.04, 46.51.

#### 2.2 Synthesis

The synthesis of the cross-linkable derivative 9,9'-bis(4-vinylphenylmethylen)[3,3']bicarbazole (**3**) was carried out by the synthetic route shown in Scheme 1. Firstly the key starting material 9H,9'H-[3,3']bicarbazole (**2**) was obtained by chemical oxidation of commercially

available 9H-carbazole (1) in the presence of FeCl<sub>3</sub> using procedure described in literature.<sup>1</sup> The bicarbazole (4) was then treated with an excess of 9-(6-bromohexyl)carbazole to afford the cross-linkable material (3), **VyPyMCz**. The synthesized derivatives were identified by mass spectrometry, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopies and resultant data were found to be in good agreement with the proposed structures. **VyPyMCz** inherited light yellow color and are rationally soluble in common organic solvents such as dichloromethane (DCM), toluene (TOL), chloroform (CHCl<sub>3</sub>), tetrahydrofuran (THF) and N,N-dimethylformamide (DMF) but insoluble in alcohols. Transparent thin films of the derivative could be prepared by spin coating from solutions.



Scheme 1. Schematic illustration of the synthesis of carbazole based cross-linkable hole transporting material VyPyMCz.

#### 2.3 Photophysical and electrochemical characteristics

The photophysical property of the dye was investigated by measuring absorption and emission spectra in THF at room temperature. The ultraviolet–visible (UV–Vis) and photoluminescence (PL) spectra of **VyPyMCz** are displayed in **Figure 1a** and the pertinent data are collected in Table 1. The molecule **VyPyMCz** show an energy band-gap of 3.38 eV, which is calculated from its intersection point of the absorption and emission spectra.

The electrochemical property of the dye was examined by using cyclic voltammetry (CV). The redox potential was calibrated by using the ferrocene/ferrocenium redox couple as an internal standard in the measurement as shown in **Figure 1b** and selected data are compiled in Table 1. The highest occupied molecular orbital (HOMO) energy level of this dye was estimated by using the ferrocene/ferrocenium redox couple as a reference (-4.8 eV) and its value was -5.25 eV. Its LUMO energy level was calculated from the energy difference

between HOMO energy level and bandgap of the molecule. The resulted HOMO and LUMO value of the molecules are -5.25 eV and -1.87 eV, respectively. The PL spectra of the HTM polymer thin films before and after cross-linking are identical as shown in **Figure S1**. It indicates that the cross-linking reactions of the vinyl moieties in the polymers produce networked structures without any decomposition of the polymer backbones. Furthermore, the robustness of the reported cross-linkable HTM also confirmed by solvent resistance experiment as discussed in our earlier report [45]

#### **2.4 Theoretical calculations**

The geometric and electronic properties of the synthesized polymer **VyPyMCz** at the molecular level are studied by density functional theory (DFT) and time-dependent DFT (TD-DFT) calculation by using B3LYP/6-31G (d, p) basis set [46] and obtained key parameters are summarized in **Table 1**. Figure 2 and 3 display the optimized geometries and spatial distributions of HOMO and LUMO energy levels of the synthesized polymer. Compound **VyPyMCz** exhibited an energy band gap of 4.0 eV, a HOMO level of -5.25 eV, and a LUMO level of -1.25 eV. It is notable that theoretical and experimental data are in good agreement with each other.

#### **2.5 Thermal Properties**

The thermal properties of the cross-linkable material, **VyPyMCz**, were investigated by using differential scanning calorimetry (DSC) (**Figure 1c**) and thermogravimetric analysis (TGA) (**Figure 1d**). The pertinent data are presented in **Table 1**. The compound **VyPyMCz** was obtained as an amorphous material after synthesis and purification. During the first DSC heating it became liquid at the glass transition temperature ( $T_g$ ) of 60 °C, and then the liquid sample polymerization started at about 230 °C and formed cross-linked and insoluble as well as not meltable polymeric network. This is well confirmed during the second DSC heating scan. It is evident that the formed polymer is well thermally cross-linked network. It does not have even glass transition state. The sample from the DSC pan was insoluble in any organic solvents when we tried to dissolve it after the DSC experiment.

The result of TGA of the cross-linkable material **VyPyMCz** is shown in **Figure 1d**. As mentioned earlier, the material is started thermally cross-linking from 230 °C. The cross-linking occurs also during the TGA test and finally thermal stability of the formed polymeric network is established during the experiment. It could be seen that the cross-linked sample

demonstrates very high thermal stability. Its mass loss of 5 % was determined at 423  $^{\circ}$ C as confirmed by the TGA test with a heating rate of 10 $^{\circ}$  C/min.

The material, **VyPyMCz**, during and after cross-linking has always the same chemical structure of chromophore, i.e. bicarbazole core, which is responsible for hole injecting/transporting properties. It seems that different efficiencies of the OLEDs that contain different layers of **VyPyMCz** cross-linked at various temperatures could be connected with the morphology of the films. At temperature below 230 °C the film is not cross-linked. At 230-260 °C, crosslinking reaction is rather fast; however, not all cross-linkable vinyl groups are reacted and crosslinkers in the polymeric network are still rare. At temperature higher than 260 °C, level of the crosslinking is higher. Some shrinkage is possible in the films, and maybe the changed morphology affects the performance of the OLEDs.

#### 2.6 Surface Morphology

Surface topographies of the cross-linkable **VyPyMCz** thin films annealed at different curing temperatures under nitrogen environment have been studied using atomic force microscopy (AFM) in the tapping mode. As shown in **Figure 4**, coating of **VyPyMCz** over the PEDOT:PSS layer decreases its roughness and hence increases its integrity and stability. We also observed that roughness and stability of **VyPyMCz** thin films highly depend on the annealing temperature. As we increased the temperature, roughness of the films decreased till 260°C. After that, its roughness started to increase. These observations show good agreement with the DSC and TGA analysis. Meanwhile, the HTL film annealed in between 240-260°C shows the lowest roughness along with no pinhole or crack, making it more suitable for solution processed OLED fabrication.

#### 2.7 Electronics properties

#### 2.7.1 Ionization potential measurement

The ionization potential (Ip) of a thin layer of the **VyPyMCz** was measured by the electron photoemission method. The photoemission spectrum is presented in **Figure 1e**. The bicarbazole based VyPyMCz demonstrates Ip of 5.54 eV. It could be observed that Ip of the cross-linkable is notably lower than that of derivatives having electronically isolated carbazole rings (Ip>5.9 eV) [47-48]. Aforementioned feature reveals that thin layers of the newly synthesized derivatives could be as hole transporting layer materials for application in OLED devices.

#### 2.7.2 Carrier mobility measurement by time of flight method

The time-of-flight (ToF) measurement was used to elucidate the magnitudes of the hole mobility ( $\mu_h$ ) in a layer of the compound **VyPyMCz** [49-50]. It is noteworthy that the room temperature hole drift mobility shows linear dependencies on the square root of the electric field in the layers as shown in Figure . The  $\mu_h$  was calculated by the formula,

$$\mu_h = \mathrm{d}^2 / (\mathrm{V.}t_T) \tag{1}$$

where d is the layer thickness of the compounds, V applied bias, and  $t_T$  carrier transit time [51-52]. The  $t_T$  was calculated from the kink point in the double-logarithmic curve of transient photocurrent. Hole mobility of the compound **VyPyMCz** determined from the **Figure 1f** and calculated data is listed in Table 1, i.e. 3.6 x10<sup>-4</sup> cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> at an electric field of 3.3x 10<sup>5</sup> V cm<sup>-1</sup>. The synthesized compound **VyPyMCz** exhibits sound hole mobility, it may be because of high hole mobility of the carbazole core group [53-54].

#### 2.8 Electroluminescent properties

Inspired by noteworthy photophysical, thermal and crosslinakbe properties, high hole mobility, high triplet energy and suitable HOMO-LUMO, **VyPyMCz** incorporated as the hole transport layer into the solution processed multilayer blue, green and red multilayer OLEDs. The molecular structure of compound **VyPyMCz**, schematic representation of the fabricated OLED and electroluminescent spectra of the red, blue and green devices are demonstrated in the **Figures 5a**, **5b** and **5c**, respectively. Figure 5d shows the step-to-step patterning procedures of the fabricated OLED device, more detail information included in the supplementary information (S1.2). The designed device structure, their corresponding energy level alignment diagrams and proposed operational mechanism are displayed in **Figure 6**, which schematically prove that **VyPyMCz** not only enable the significant injection of hole but also successfully confine electron, which are one of the key factors in realizing high efficiency. **Figure 7 and Table 2** summarize the effect of absence and presence of cross-linkable hole transporting material VyPyMCz on the electroluminescence characteristics of all the studied blue, green and red OLED devices.

Remarkably, the incorporation of **VyPyMCz** HTL considerably improves the performance of all the studied devices. For example, we fabricated monochromatic red phosphorescent OLEDs with (R1) and without (R2) cross-linkable HTL, **VyPyMCz**, with following device structure: indium tin oxide (ITO) (125 nm)/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (35 nm)/with (R1) and without (R2) **VyPyMCz** /7.5 wt% Ir(2-phq)<sub>3</sub> doped in CBP (20 nm)/ 1,3,5-tris(N-phenyl-benzimidazol-2-yl)benzene (TPBi) (35

nm)/lithium fluoride (LiF) (1 nm)/ AluminAl (100 nm). At 100 cd m<sup>-2</sup>, Device R-2 shows a current efficiency of 13.5 cd A<sup>-1</sup>, which is increased to 20.6 cd A<sup>-1</sup>, an increment of 52%, as the **VyPyMCz** HTL is incorporated. At 1,000 cd m<sup>-2</sup>, the current efficiency is increased from 8.5 to 13.5 cd A<sup>-1</sup>, an increment of 59%, as shown in **Figure 7 and Table 2**.

Similarly, we also fabricated monochromatic blue and green phosphorescent OLED devices with and without cross-linkable HTL, VyPyMCz, with following device structures:

Device B1: ITO (125 nm)/PEDOT:PSS (35 nm)/ 15 wt% FIrpic doped in CBP (20 nm)/ TPBi (35 nm)/LiF (1 nm)/Al (100 nm).

Device B2: ITO (125 nm)/PEDOT:PSS (35 nm)/ **VyPyMCz**/ 15 wt% FIrpic doped in CBP (20 nm)/ TPBi (35 nm)/LiF (1 nm)/Al (100 nm).

Device G1: ITO (125 nm)/PEDOT:PSS (35 nm)/ 15 wt% Ir(ppy)<sub>3</sub> doped in CBP (20 nm)/ TPBi (35 nm)/LiF (1 nm)/Al (100 nm).

Device G2: ITO (125 nm)/PEDOT:PSS (35 nm)/ **VyPyMCz**/ 15 wt% Ir(ppy)<sub>3</sub> doped in CBP (20 nm)/ TPBi (35 nm)/LiF (1 nm)/Al (100 nm).

The current efficiency of the studied blue OLED device increases from 15.4 to 19.3 cd  $A^{-1}$ , an increment of 25.32%, at 100 cd m<sup>-2</sup> and from 12.8 to 15.7 cd  $A^{-1}$ , an increment of 22.65%, at 1,000 cd m<sup>-2</sup>, as the **VyPyMCz** HTL is incorporated. Furthermore, the incorporation of VyPyMCz HTL also increases the CE of green OLED device from 48.1 to 55.3 cd  $A^{-1}$ , an increment of 14.90%, at 100 cd m<sup>-2</sup> and from 45.0 to 51.9 cd  $A^{-1}$ , a increment of 15.3%, at 1,000 cd m<sup>-2</sup>.

We observed significant improvement in the efficiency of the all the studied OLED devices consisting of low and high bandgap emitters, as the **VyPyMCz** HTL was introduced. The reasons why the **VyPyMCz** HTL containing devices showed the improvement in efficiency can be attributed to two important structural factors. First, the **VyPyMCz** HTL can effectively facilitate the injection of hole because its incorporation breaks the original hole injection barrier of 1.1 eV into two smaller ones, i.e. 0.35 eV and 0.75 eV, as shown in Figure 5(a). Second, its incorporation also helps confine the electron to prevent the overflow of electrons from EML into the hole injection layer especially at high current density or high brightness. It is because **VyPyMCz** HTL possesses a relatively high LUMO value, -1.85 eV, which is 1.03

eV higher than that of the CBP host, or 0.93 eV, 1.03 eV and 1.13 eV higher than that of the red, blue and green emitters, respectively.

We observed an only 7.0 % efficiency-roll-off into the red OLED and 2.67 % into the blue OLED, as brightness increases from 100 cd m<sup>-2</sup> to 1,000 cd m<sup>-2</sup>. These results confirm that **VyPyMCz** HTL effectively facilitates the injection of the hole as well as effectively confine the electron and prevent the overflow of the electrons entering into the hole injection layer especially at high current density or high brightness. In the past, numerous attempts have been made to elucidate the mechanisms behind these roll-off characteristics. These studies revealed that triplet-triplet annihilation, triplet-polaron quenching or dissociation of excitons into free charge carriers are the main reasons behind efficiency decrement at high current density. Both these mechanisms are highly correlated with the balance dynamics of carrier injection. The reason why the **VyPyMCz** HTL possesses an effective electron confining function is because it has a relatively high LUMO value (-1.87 eV).

It is also interesting to note that all the **VyPyMCz** HTL contains OLED devices display higher brightness when compared to reference device. It may be because of crosslinking properties of the reported HTL, which significantly reduce the roughness of HIL layer and improved thinfilm integrity. AFM analysis of spin coated thin film also confirmed the aforementioned hypothesis. These results show that designed and synthesized crosslinkable polymer is suitable and advantageous to be used as HTL materials in OLEDs as it enables the subsequent solutionprocessing of the emission layer without mixing in the previously deposited layer.

### **Conclusion:**

In this study, a class of solution process feasible and thermally cross-linkable holetransporting material, **VyPyMCz**, has been designed, synthesized and successfully incorporated in the multilayered OLEDs. This compound features a larger bandgap and a higher triplet energy level. **VyPyMCz** can be thermally cross-linked to form a solventresistant layer upon isothermal heating at 250 °C for 30 min. The crosslinked **VyPyMCz** layer possesses not only hole-collecting ability (HOMO = -5.25 eV) but also electron-confining capability (LUMO = -1.87 eV), which significantly improve the number of exciton into the desired recombination zone, hence noticeable efficiency enhancement for red, green, and blue OLEDs, especially at higher voltage. The OLED device consisting of low band gap red emitter displays 58 and 45% increments in the PE and CE at 1,000 cd cm<sup>-2</sup>, respectively, that is 78 and 47% for high band gap blue emitter. The approach presented herein could become a general method fabricate a highly efficient solution processed OLEDs by significantly injecting holes in the desired emissive layer and preventing the overflow of electrons into the non-radiative HIL.

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**Figure 1.** (a) UV-Vis and PL spectrum of the cross-linkable hole transporting material (VyPyMCz) recorded in chlorobenzene at room temperature. (b) Cyclic voltammograms of the VyPyMCz dye. (c) and (d) show the TGA and DSC curves of the material VyPyMCz, heating rate  $10^{\circ}$ C/min. (e) Electro-photoemission spectra of the VyPyMCz thin film. (f) The hole mobility of the HTM VyPyMCz as a function of the square root of electric field.



Figure 2. Optimized structures of the synthesized cross-linkable dye VyPyMCz.



Figure 3. Electron Density Contours of frontier molecular orbitals (FMO).



**Figure 4.** AFM images of cross-linkable hole transporting material (**VyPyMCz**) spin-coated and cured on ITO, recorded in trapping mode. After coating the **VyPyMCz** HTL, the substrate was baked at 120 °C for 20 min to remove residual solvent, then it was annealed at different curing temperature (T<sub>c</sub>) for 40 min: (a) PEDOT: PSS (b) PEDOT: PSS/ **VyPyMCz** (c) PEDOT: PSS/ **VyPyMCz** (T<sub>c</sub>=160 °C) (d) PEDOT: PSS/ **VyPyMCz** (T<sub>c</sub>=200 °C) (e) PEDOT: PSS/ **VyPyMCz** (T<sub>c</sub>=250 °C) (f) PEDOT: PSS/ **VyPyMCz** (T<sub>c</sub>=300 °C). The root mean square roughness are being 1.26 nm, 0.815 nm, 0.542 nm, 0.472 nm, 0.359 nm, and 1.1 nm, respectively.



**Figure 5.** (a) Chemical structure of synthesized cross-linkable hole transporting material (**VyPyMCz**), (b) schematic illustration of OLEDs using **VyPyMCz** as a hole transporting layer, (c) electroluminescent spectra of fabricated red, blue and green OLEDs, and (d) solution processed step-to-step fabrication of OLED using material, **VyPyMCz**.



**Figure 6**. Schematic diagram of the energy levels of the fabricated solution-processed red, green, and blue OLED devices consisting of CBP and VyPyMCz as the host and cross-linkable hole transporting HTL, respectively.



**Figure 7.** Effect of the presence and absence of the solution-processed cross-linkable hole transporting and electron confining layer, VyPyMCz, on the (1) luminance-voltage-current density, (2) power efficiency-luminance-current efficiency and (3) electroluminescent characteristics of the (a-c) red device, (c-f) blue device and (g-i) green device consisting of CBP as a host.

Compound	$\lambda_{em}{}^a$	$T_g^{b}$	$T_d^{c}$	$\mu_h^{\rm d}$	HOMO <sup>e</sup>	LUMO <sup>e</sup>	HOMO <sup>f</sup>	HOMO <sup>f</sup>	Band Gap <sup>g</sup>	$E_T^{\rm f}$
	[nm]	[ <sup>°</sup> C]	[°C]	$[cm^2V^{-1}s^{-1}]$	[eV]	[eV]	[eV]	[eV]	[eV]	[eV]
VyPyMCz	402	60	423	3.6 x10 <sup>-4</sup>	-5.25	-1.87	-5.25	-1.25	3.38	2.87

**Table 1** Thermal, photophysical, and electrochemical characteristics of the cross-likable hole

 transporting material VyPyMCz.

<sup>a</sup>Emission peak; <sup>b</sup>Glass transition temperature; <sup>c</sup>Decomposition temperature; <sup>d</sup>Hole mobility at the electric field of 3.3 x 10<sup>5</sup> cm<sup>-1</sup>; <sup>e</sup>HOMO and LUMO were calculated from the redox potentials measured by cyclic voltammetry (CV) method. The semi-oxidation potential  $(E_{1/2}^{ox})$  was calculated from  $(E_{p1} + E_{p2})/2$ –0.48, where 0.48 is the correction value obtained in the oxidation system as the Ferrocenium/Ferrocene  $(Fc^+/Fc)$  was added as the internal standard. The energy of HOMO was then obtained from the  $E_{HOMO} = -(E_{1/2}^{ox} + 4.8)$ . The energy of LUMO was estimated by subtracting the bandgap from the HOMO energy level,  $[E_{LUMO} = -E_{HOMO} + Eg]$ .; <sup>f</sup>Calculated by using B3LYP/6-31G (Density functional theory (DFT) and time-dependent DFT (TD-DFT)); <sup>g</sup>Calculated from its intersection point of the absorption and emission spectra.

**Table 2:** Effects of the presence and absence of the cross-linkable hole transporting and electron confining layer on the operation voltage (OV), power efficiency (PE), current efficiency (CE), external quantum efficiency (EQE), maximum luminance, and CIE coordinates of the fabricated solution-processed red, blue and green devices.

Device	HTL	@ 100/1000/1	Maximum Luminance				
		OV[V]	PE[lm W <sup>-1</sup> ]	CE[cd A <sup>-1</sup> ]	EQE[%]	CIE <sub>xy</sub> coordinates	(cd m⁻²)
R1	-	5.1/6.8/-	14.0/7.5/-	22.6/16.1/-	10.0/7.1/-	(0.57, 0.43)	7,724
R2	VyPyMCz	4.8/6.3/9.6	18.3/11.9/4.2	28.1/23.7/12.8	12.7/10.7/-	(0.58, 0.42)	13,560
B1	-	4.8/6.1/-	10.2/6.6/-	15.4/12.8/-	6.2/5.5/-	(0.17, 0.40)	5,260
B2	VyPyMCz	4.6/5.5/-	15.4/11.8/-	19.3/17.7/-	9.5/6.0/-	(0.17, 0.39)	6,857
G1	-	4.8/6.0/8.4	41.7/28.8/12.6	48.1/45.0/32.2	14.5/16.3/10.6	(0.33, 0.62)	21,960
G2	VyPyMCz	4.1/5.4/8.1	48.9/40.3/17.0	55.3/51.9/41.2	13.4/14.6/9.7	(0.33, 0.62)	26,230

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## **Highlights:**

- Design, synthesis, and characterization of a thermally cross-linkable hole transporting material VyPyMCz has been demonstrated.
- Preventing the dissolution of formerly deposited layers throughout the consecutive deposition of multilayer stacks
- > Facilitating the injection of holes and effectively confine electrons to realize high efficiency
- Solution process feasible highly efficient red, green and blue OLED devices have been designed and fabricated.