

Solution-processed blue/deep blue and white phosphorescent organic light emitting diodes (PhOLEDs) hosted by a polysiloxane derivative with pendant mCP (1,3-bis(9-carbazolyl)benzene)

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ABSTRACT: The synthesis and characterization is reported of an efficient polysiloxane derivative containing the 1,3-bis(9-carbazolyl)benzene (mCP) moiety as a pendant unit on the polysiloxane backbone. In comparison with mCP, the

mCP-polysiloxane hybrid (PmCPSi) has significantly improved thermal and morphological stabilities with a high decomposition temperature ($T_d = 523$ °C) and glass transition temperature ($T_g = 194$ °C). The silicon-oxygen linkage of PmCPSi prevents intermolecular π -stacking and ensures a high triplet energy level ($E_T = 3.0$ eV). Using PmCPSi as a host, blue phosphorescent organic light emitting devices (PhOLEDs) effectively confine triplet excitons, with efficient energy transfer to the guest emitter and a relatively low turn-on voltage of 5.8 V. A maximum external quantum efficiency of 9.24% and maximum current efficiency of 18.93 cd/A are obtained. These values are higher than for directly analogous poly(vinylcarbazole) (PVK) based devices (7.7 V, 6.76%, 12.29 cd/A). Good color stability over a range of operating voltages is observed. A two-component “warm-white” device with a maximum current efficiency of 10.4 cd/A is obtained using a blend of blue and orange phosphorescent emitters as dopants in PmCPSi host. These results demonstrate that well-designed polysiloxane derivatives are highly efficient hosts suitable for low-cost solution-processed PhOLEDs.

Keywords: polysiloxane, high triplet energy, polymeric host, FIrpic, orange phosphor, phosphorescent organic light-emitting diode

INTRODUCTION

Phosphorescent organic light emitting diodes (PhOLEDs) based on heavy metal complexes continue to attract tremendous interest because by harvesting both singlet

and triplet excitons simultaneously for emission, internal quantum efficiency approaching 100% has been achieved.¹⁻⁹ However, for high performance it is necessary to blend the triplet emitters into host matrixes to prevent self-quenching and triplet-triplet annihilation.^{10,11} Recently, high external quantum efficiency over 25% has been achieved for blue and white phosphorescent OLEDs using small-molecule hosts.¹²⁻¹⁵ However, complicated co-evaporation techniques and precise processing controls are required for small-molecule based devices to ensure high reproducibility for commercialization of the product. Techniques that use Solution-processing, such as spin-coating or inkjet-printing, are more promising with respect to the reduction of fabrication costs and the realization of large-area displays for simple device configurations.¹⁶⁻¹⁸ Polymeric hosts are particularly suitable for solution processing technologies. This is driving academia and industry to develop new more efficient polymer hosts, and is a motivation for the current work. However, the performances of the polymeric hosts are still inferior to those of the small molecules. Efficient polymer hosts are especially needed for blue and white phosphorescent OLEDs. For the production of white OLEDs (WOLEDs) a two-component emitter layer is favored due to the simple device fabrication process.¹⁹⁻²⁴ In general, an orange emitter can be used instead of a green emitter as a way to eliminate the gap in emission wavelength between standard red and green emitters.²⁵⁻²⁷ Although orange emitters have been developed in numerous studies for vacuum-deposited two-emitting-component WOLEDs, there is still a huge potential to explore solution-processed WOLEDs,

owing to their lower production costs and suitability for commercially-competitive energy-saving large-area panels.

It is imperative to achieve high triplet energy (E_T) levels for both small-molecule and polymer host materials²⁸ for blue and white OLEDs to ensure that triplet excitons are confined within the emitting layer and thereby reverse energy transfer from guest to host is prevented.¹¹ In addition, to avoid phase separation upon heating, the host material should be thermally, electrochemically, and morphologically stable and form good quality films.^{29,30} Furthermore, a larger HOMO–LUMO energy gap (E_g) than the phosphorescent guest is required to ensure direct charge trapping on the emitter.³¹ Carbazole derivatives are established as hosts for PhOLEDs due to carbazole's high triplet energy and favorable hole-transporting properties.³²⁻³⁵ The small-molecule mCP [1,3-bis(9-carbazolyl)benzene] which has a triplet energy of 2.9 eV is widely used in this context.³⁶⁻⁴¹ However, mCP tends to crystallize as a consequence of its rather low T_g (glass transition temperature, 60 °C). It is a challenge to develop a polymeric host that has a higher T_g than mCP while maintaining mCP's desirable optoelectronic properties. One approach to novel host materials is to exploit organic-inorganic hybrid materials for which function and structure can be systematically varied on both the organic and the inorganic units., . As an example, polysiloxane is soluble in many common organic solvents, forms good quality films which are resistant to degradation under thermal, chemical and irradiation conditions, and the films adhere well to various substrates. To improve thermal, electrochemical, and morphological stability and to enhance the film-forming ability of organic

semiconductors, siloxanes have been combined with organic molecular structures; this has a minimal effect on the electronic properties of the materials.⁴²⁻⁴⁷

Previously a polytetraphenylsilane derivative with a pendant carbazole unit⁴⁸ and a bipolar poly(phenylcarbazole-*alt*-triphenylphosphine oxide) siloxane⁴⁹ have served as hosts for blue and deep blue phosphors. We now report the synthesis of the new mCP-modified polysiloxane (PmCPSi) which incorporates mCP moieties as pendant groups linked via a phenoxy spacer unit, which is designed to remove the detrimental steric crowding between the siloxane backbone and the mCP units observed in a previous oligomer.⁴⁹ Rational tuning of material structure and morphology are essential for developing structure/property/efficiency relationships in OLEDs. In contrast to the previous polysiloxane⁴⁹ (which is a co-polymer) PmCPSi is a homo-polymer. Moreover, the two carbazole substituents per repeat unit of PmCPSi impart enhanced hole-injection properties compared to the previous polymers.^{48,49} This work establishes that PmCPSi possesses both a high E_T of 3.0 eV, because the polysiloxane prevents any π -stacking, and a higher HOMO (highest occupied molecular orbital) level than that of poly(vinylcarbazole) (PVK). Self-quenching of triplet excitons is greatly reduced because phosphorescent dyes doped into PmCPSi are prevented from aggregating. PmCPSi displays a dramatically increased T_g of 194 °C, a high degradation temperature, forms excellent quality films and is compatible with FIrpic ([bis(4,6-difluorophenyl)-pyridinato-N,C²]iridium(III) picolate) which is a standard blue emitter. Importantly, efficient blue PhOLEDs using PmCPSi and FIrpic as host and emitter, respectively, have been fabricated by

solution processing. This device shows a lower turn-on voltage, higher maximum current efficiency of 18.93 cd/A (6.32 lm/W, 9.24%) than a directly comparable PVK-based device. We also changed the ancillary ligand on Ir(MDQ)₂(acac) [bis(2-methyldibenzo[*f,h*]quinoxaline) (acetylacetonate) iridium(III)] which is a red phosphor to achieve an orange Ir complex, Ir(MDQ)₂(pic). A PmCPSi: FIrpic: Ir(MDQ)₂(pic) emitting layer gives a two-component “warm-white” PhOLED with a maximum current efficiency of 10.4 cd/A. We are not aware of any previous reports of polysilanes or polysiloxanes acting as hosts for white OLEDs. Therefore, the new polysiloxane PmCPSi is an excellent and versatile host material for blue and white PhOLEDs fabricated by solution processing.

EXPERIMENTAL SECTION

Materials. All reactants and solvents were supplied and used as described previously.⁴⁸ The details of monomer syntheses and characterization, which are based on modified literature procedures,^{48,50} are presented in the Supporting Information.

Device Fabrication. Details of device fabrication and characterization, using standard procedures,⁴⁸ are presented in the Supporting Information. The EQE values were calculated from the luminance, current density and electroluminescence spectrum according to reported methods.⁵¹ All measurements were performed at room temperature under ambient conditions.

PmCPSi (4): To a mixture of **3** (0.63 g, 1 mmol) and THF (30 mL), water (1 mL) and a drop of 1 M HCl were added. The mixture was stirred at 0 °C for 24 h. After the reaction was completed, the solvent was extracted with Et₂O and the organic layer was separated, washed with distilled water three times and dried over anhydrous magnesium sulfate. The filtrate was condensed by reduced pressure to give the dihydroxy monomer to which was added a solution of **3** (0.63 g, 1 mmol) in THF (30 mL) and two drops of tetra-*n*-butyl titanate as catalyst. The mixture was stirred at 70 °C for 7 days while monitoring the progress of the reaction with a Fourier Transform Infrared (FTIR) Spectrometer. After the reaction was completed, chlorotrimethylsilane (0.1 mL) was added and the mixture was stirred for another 12 h at 70 °C. The solvent was then evaporated in vacuum to give a sticky liquid, which was dissolved in toluene and precipitated with methanol to obtain the product (**4**) as a white powder. ¹H NMR (400 MHz, CDCl₃, δ): 8.1 (m, 4H; ArH), 7.7 (m, 2H; ArH), 7.3 (m, 17H; ArH), 0.42 (s, 3H; -CH₃). GPC (RI, polystyrene calibration) M_w = 3.48 kDa, M_w/M_n = 1.12.

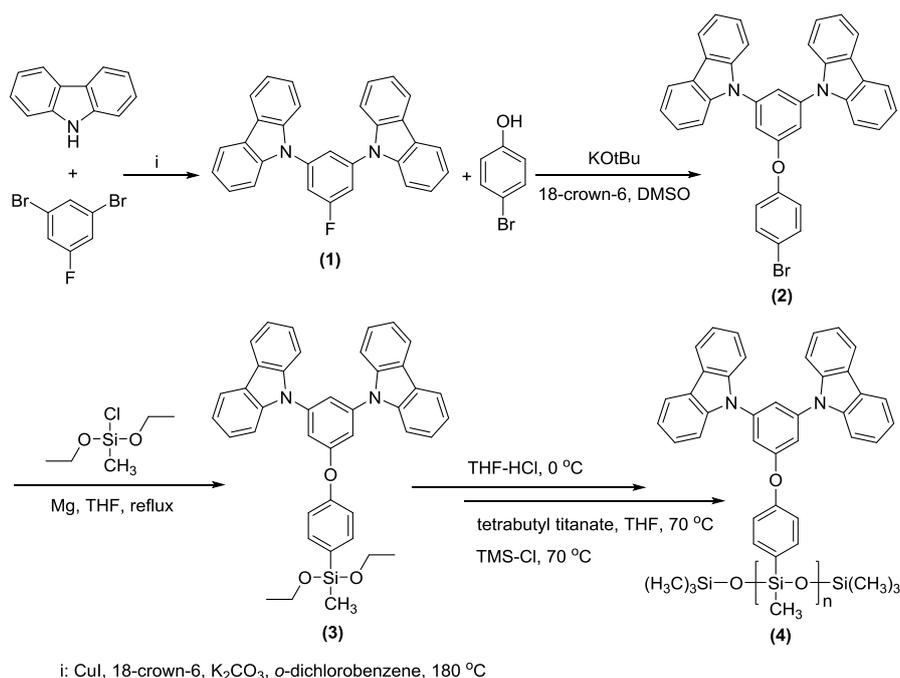
Ir(MDQ)₂(pic): 2-Methyl-dibenzo[*f,h*]quinoxaline (MDQ) was prepared according to the procedure reported in ref.⁵² To a solution of MDQ (2.46 g, 10 mmol) in 2-ethoxyethanol (60 mL) iridium trichloride hydrate (1.19 g, 4.0 mm) and water (20 mL) were added. The mixture was stirred under argon for 36 h at 120 °C and then allowed to cool to room temperature and the precipitate was collected and washed with acetone, ethanol, and dried in vacuum to yield the intermediate cyclometalated Ir^{III}-μ-chloro-bridged dimer. Then, a mixture of the chloro-bridged dimer (1.16 g, 0.8

mmol), picolinic acid (0.31 g, 2.5 mmol), sodium carbonate (0.80 g) and 2-ethoxyethanol (100 mL) was refluxed at 120 °C for 12 h. After cooling to room temperature, the solvent was removed in vacuum, and the crude yellow product was washed with methanol to remove any unreacted picolinic acid. Column chromatography of the residue on silica gel with petroleum ether /ethyl acetate (1 / 1 v/v) as eluent gave **Ir(MDQ)₂(pic)** (0.44 g, 69%) as a reddish orange product. ¹H NMR (400 MHz, CDCl₃, δ): 9.19 (dd, J₁ = 8.0 Hz, J₂ = 1.7 Hz, 2H), 8.85 (s, 1H), 8.77 (t, J = 7.0 Hz, 2H), 8.18 (m, 4H), 7.99 (s, 1H), 7.91 (m, 2H), 7.85 (t, J = 7.5 Hz, 2H), 7.70 (d, J = 5.0 Hz, 1H), 7.57 (t, J = 6.5 Hz, 1H), 7.14 (m, 2H), 6.50 (d, J = 7.5 Hz, 1H), 6.28 (d, J = 7.5 Hz, 1H), 2.96 (s, 6H). Elemental analysis calcd for C₄₀H₂₆IrN₅O₂: C 59.99, H 3.27, N 8.74; found: C 60.03, H 3.27, N 8.70.

RESULTS AND DISCUSSION

Synthesis and Characterization

Scheme 1. Synthetic route to PmCPSi



Scheme 1 shows the synthetic route to PmCPSi (**4**). The starting material (**1**) was obtained by a modified Ullmann condensation of carbazole with 1,3-dibromo-5-fluorobenzene in the presence of catalytic copper(I) iodide. In the next step etherification of **1** with 4-bromophenol gave **2**. Transformation of **2** into the key reagent **3** by Barbier-Grignard reaction with chlorodiethoxy(methyl)silane, followed by hydrolysis in dilute THF-HCl solution gave the dihydroxy monomer (OH-Si). The desired polysiloxane was then obtained from the diethoxy monomer (OEt-Si) (**3**) and dihydroxy monomer (OH-Si) in a polycondensation reaction catalyzed by tetrabutyl titanate (TBOT). End-capping by reaction with trimethylchlorosilane gave the final polysiloxane (**4**). The ¹H NMR spectrum of (**4**) is shown in the Supporting Information. The weight average molecular weight was 3.48 kDa with a narrow polydispersity index of 1.12 as determined by gel permeation chromatography (GPC). Polymer (**4**) shows highly solubility in common organic solvents such as chloroform,

tetrahydrofuran, toluene and chlorobenzene. It is, therefore, suitable for thin film formation using spin-coating, dipping and casting procedures..

Thermal analysis

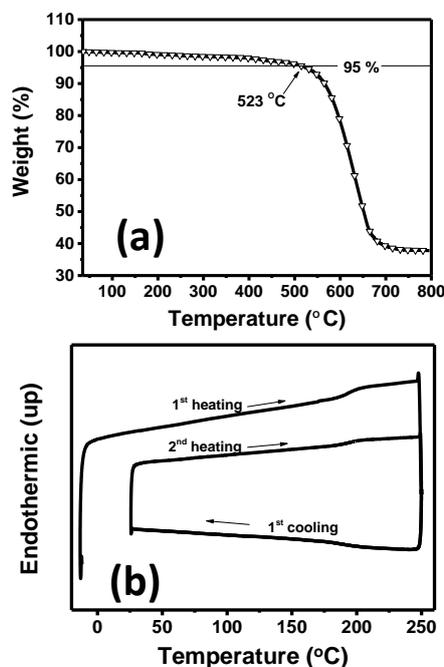


Figure 1. a) TGA trace of PmCPSi at a heating rate of 10 °C/min. b) DSC traces at a heating rate of 10 °C/min.

Following standard procedures for analogous polymers^{48,50} the thermal properties of PmCPSi (**4**) were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The data obtained from both techniques are listed in Table 1. PmCPSi exhibits high thermal stability with a decomposition temperature (T_d , corresponding to 5% weight loss) as high as 523 °C (Fig. 1). DSC data, as shown in Fig. 1, revealed an endothermic glass transition (T_g) at 194 °C for the heating scan. However, within the investigated temperature range, no exothermic peak due to crystallization or endothermic peak due to melting was observed during the first and

second heating cycles. As observed for a previous siloxane-based co-polymer,⁴⁸ PmCPSi is, therefore, shown to be a very stable amorphous material with a T_g value that is considerably raised compared to mCP ($T_g = 60$ °C). This is ascribed to the effective steric properties of the pendant units. These data imply that PmCPSi should form spin-coated thin films and devices that are durable and morphologically stable. These features are basic requirements for host materials in OLEDs.

Table 1. Physical properties of PmCPSi

E_T (eV) ^[a]	HOMO (eV) ^[b]	LUMO (eV) ^[c]	T_g (°C) ^[d]	T_d (°C) ^[e]
3.0	-5.65	-2.13	194	523

^[a]Triplet energy level; ^[b] Highest occupied molecular orbital; ^[c] Lowest unoccupied molecular orbital; ^[d] Glass-transition temperature determined by DSC; ^[e] Decomposition temperature determined by TGA at 5% weight loss.

Morphology Properties

Following literature precedents for analogous materials^{48,50} atomic force microscopy (AFM) was used to assess the film-forming ability and the morphological stability of PmCPSi together with its miscibility with the dopant FIrpic. Figure 2a reveals that a film of 10 wt% FIrpic doped into PmCPSi has smooth and homogeneous morphology: the root-mean-square (RMS) roughness value is low (0.56 nm). The images show no particle aggregation or phase separation. The thermal stability was further investigated by annealing the film at 190 °C, which is almost the same temperature as the corresponding T_g of PmCPSi, for 12 hours. Figure 2b shows that

the surface roughness changed slightly from 0.56 nm to 0.59 nm. Measurements at the same temperature after longer times showed that no obvious phase separation can be observed in the blended film (Figures 2c, 2d).

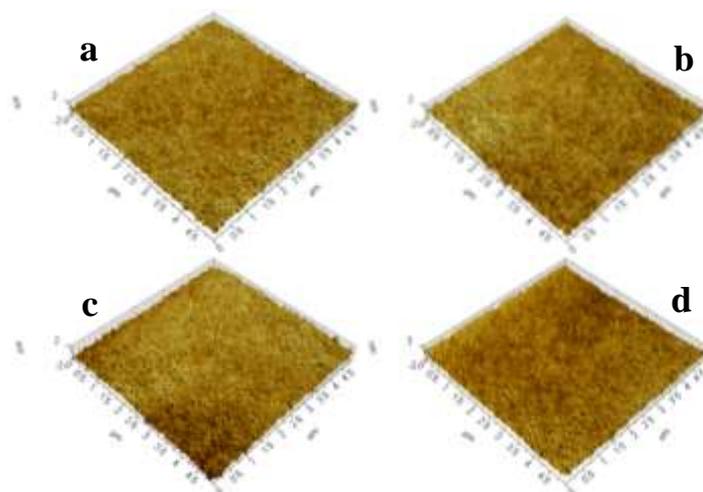


Figure 2. AFM topographical images of the solution processed films of PmCPSi doped with 10 wt% FIrpic: (a) unannealed (b) annealed at 190 °C for 12 h (c) annealed at 190 °C for 24 h and (d) annealed at 190 °C for 48 h.

The very stable film morphology is ascribed to good miscibility of PmCPSi and FIrpic, which means that the integrity of films should be retained during fabrication and operation of the PhOLEDs.

Photophysical properties

The absorption, photoluminescence (PL) (at room temperature) and phosphorescence spectra (at 77 K) spectra of PmCPSi were recorded in dilute dichloromethane solution (Figure 3a). The absorption peaks at around 294 nm are assigned to carbazole $\pi \rightarrow \pi^*$ transitions and weaker absorption peaks at 327 and 340

nm derive from the $n \rightarrow \pi^*$ transitions of extended carbazole conjugation. The absorption onset value gives an energy gap (E_g) of 3.52 eV.

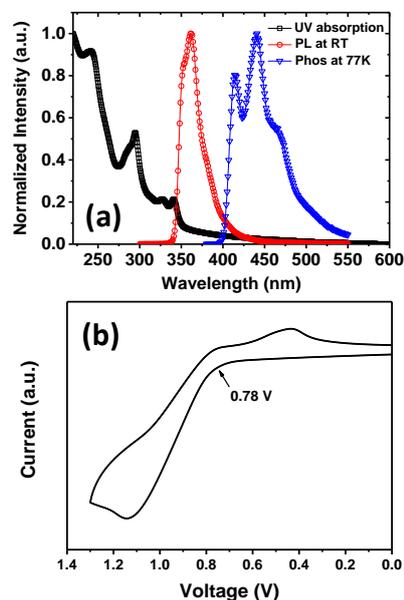


Figure 3. (a) The absorption, photoluminescence (at room temperature) and phosphorescence spectra (at 77 K) of PmCPSi in dichloromethane. (b) Cyclic voltammogram of PmCPSi in anhydrous dichloromethane with tetra(*n*-butyl)ammonium hexafluorophosphate (0.1 M) as a supporting electrolyte for the oxidation scan.

In the PL spectrum of PmCPSi an intense UV emission peak is seen at 361 nm. These spectra of PmCPSi are very similar to those of phenylcarbazole and mCP derivatives.⁵³⁻⁵⁷ This confirms that the polysiloxane backbone has only minimal influence on the photophysical properties of the pendant mCP chromophore. The triplet energy (E_T) of PmCPSi was obtained from its phosphorescence spectrum at 77 K in dichloromethane: a well-structured band is observed in the 400-550 nm region. From the highest-energy vibronic sub-band of the spectrum an E_T of 3.0 eV was calculated. The slightly higher E_T of PmCPSi (compared to mCP) can be attributed to

the disruption of π conjugation as a result of the insertion of a Si-O bond between the pendant chromophores.⁵⁰

Electrochemical analysis

Cyclic voltammetry (CV) was used to probe the solution electrochemistry of PmCPSi was investigated by cyclic voltammetry (CV). Figure 3b shows an irreversible oxidation process which is typical of carbazole derivatives with free 3,6-positions.⁵⁸ The oxidation onset potential was recorded at 0.78 V for PmCPSi versus Ag/Ag⁺. The HOMO energy level of PmCPSi was calculated using the formula $E_{\text{HOMO}} = -(4.8 + E_{\text{ox}}^{\text{on}} - E_{\text{Fc}})$ eV. The LUMO energy level was obtained by adding the optical E_g to the HOMO level (Table 1). The HOMO level of PmCPSi is -5.65 eV, which is very similar to the values for mCP and CBP (4,4'-N,N'-dicarbazolylbiphenyl). These data indicates that the PmCPSi HOMO is mainly located at the carbazole sites and the polysiloxane backbone structure has a negligible influence on the HOMO energy level, as observed for other siloxane-carbazole composite materials^{48,50} Compared with PVK (HOMO = -5.8 eV) the lower HOMO energy level of PmCPSi will facilitate hole injection.

Solution-Processed Blue Phosphorescent Organic Light Emitting Diodes.

The foregoing data establish that PmCPSi possesses overall very desirable features of high morphological and thermal stability combined with a high E_T level. Therefore, PmCPSi was identified as an ideal host material for solution-processed blue PhOLEDs. Standard device architectures were used.^{48,50,63,65} A spin-coated device

(Device I) was fabricated using FIrpic as the phosphor with the following configuration: indium tin oxide (ITO)/ PEDOT:PSS (30 nm)/PmCPSi: 10 wt% FIrpic (40 nm)/ Tm3PyPB (5 nm) /TPBi (30 nm)/ LiF (1 nm)/Al (60 nm). For comparison, PVK-based devices were also fabricated. Device II replaced PmCPSi by PVK with the same device configuration as Device I; for Device III a PVK layer was inserted between the PEDOT:PSS layer and the emitting layer in Device I, acting as the hole injection layer. The doping concentration of FIrpic was 10 wt% in all the devices. The emitting layer was spin-coated from chlorobenzene solution onto the PEDOT:PSS-coated ITO glass substrate. Layers of Tm3PyPB and TPBi were added as hole/exciton-blocking and electron-transporting materials, respectively. It is known that an additional electron-transport layer enhances efficiency in FIrpic devices.⁵⁹ The E_T values of PmCPSi and Tm3PyPB (2.75 eV)^{15,60} are sufficiently high to confine triplet excitons in the emitting layer and to prevent luminescence quenching.

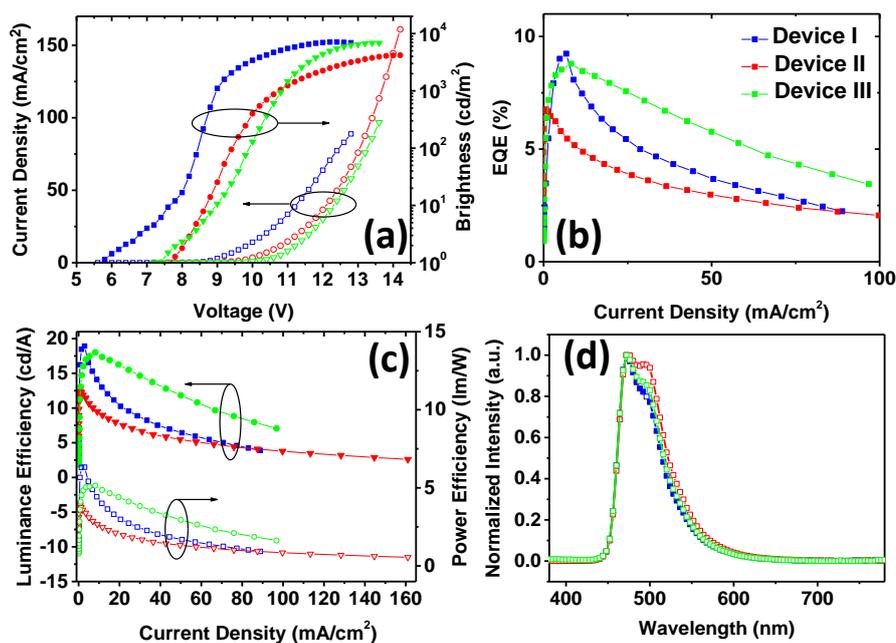


Figure 4. (a) J - V - L characteristics of 10 wt% FIrpic-doped PhOLEDs; (b) External quantum efficiency versus current density of FIrpic-doped PhOLEDs; (c) Current efficiency and power efficiency versus current density of FIrpic-doped PhOLEDs; (d). Electroluminescence spectra at 9 V for these FIrpic-doped PhOLEDs. Device structures: Device 1: ITO/PEDOT:PSS (35nm) /PmCPSi:FIrpic (40 nm)/Tm3PyPB (5 nm)/TPBi (35 nm)/LiF/Al; Device 2: ITO/PEDOT:PSS (35 nm) /PVK:FIrpic (40 nm)/Tm3PyPB (5 nm)/TPBi (35 nm)/LiF/Al; Device 3: ITO/PEDOT:PSS (35 nm) /PVK (10 nm)/PmCPSi:FIrpic (40 nm)/Tm3PyPB (5 nm)/TPBi (35 nm)/LiF/Al.

Current density-voltage-brightness (J - V - L) curves are shown in Figure 4a for the blue PhOLEDs. The PmCPSi device (Device I) exhibits lower operation voltage and higher luminance compared to comparable PVK devices (Devices II and III). As shown in Table 2, the turn-on voltage (at 1 cd/m²) was 5.8 V for Device I, 7.7 V for Device II and 7.4 V for Device III, which is attributed to the smaller carrier injection barrier for PmCPSi compared to PVK. Additionally, Figure 4b shows that the maximum external quantum efficiency of 9.24% for Device I is higher than that for Device II. Power and current efficiencies plotted with respect to current density are depicted in Figure 4c. Device I shows a current efficiency of 18.93 cd/A and a maximum power efficiency of 6.32 lm/W, over a wide high luminance range. The overall performance is significantly improved by comparing Device I with Device II. Moreover, in Device III, a PVK layer was inserted between the PEDOT:PSS and PmCPSi-based emitting layer: the turn-on voltage increased to a value close to that of Device II due to the large hole injection barrier from PEDOT:PSS to PVK layer,⁶¹ but the power and current efficiencies decreased more gently than Device I owing to the exciton block layer especially at the range of high luminance. The excellent

performance of PmCPSi can be further assigned to the simultaneous incorporation of mCP units into the polysiloxane backbone, since the former have been shown to be good hole-transporting hosts³²⁻³⁵ and the latter has good thermal and morphological stability.⁴²

Table 2. Performance of Firpic-based PhOLED devices

	V _{on} (V) [a]	L _{max} (cd/m ²) [b]	η _{c,max} (cd/A) [c]	η _{p,max} (lm/W) [d]	η _{ext,max} (%) ^[e]	CIE(x,y) ^[f]
Device I	5.8	6930	18.93	6.32	9.24	0.15, 0.33
Device II	7.7	4194	12.29	4.19	6.76	0.17, 0.35
Device III	7.4	6835	18.02	5.14	8.79	0.16, 0.33

[a] Turn-on voltage; [b] Maximum luminance; [c] Maximum luminous efficiency; [d] Maximum power efficiency; [e] External quantum efficiency; [f] Commission Internationale de l'Eclairage coordinates.
Device 1: ITO/PEDOT:PSS (3.5 nm) /PmCPSi:Firpic (40 nm)/Tm3PyPB (5 nm)/TPBi (35 nm)/LiF/Al;
Device 2: ITO/PEDOT:PSS (35 nm) /PVK:Firpic (40 nm)/Tm3PyPB (5 nm)/TPBi (35 nm)/LiF/Al;
Device 3: ITO/PEDOT:PSS (35 nm) /PVK (10 nm)/PmCPSi:Firpic (40 nm)/Tm3PyPB (5 nm)/TPBi (35 nm)/LiF/Al.

The electroluminescence spectra of the blue PhOLEDs are shown in Figure 4d. All of the devices exhibit emission exclusively from Firpic at λ_{max} 472 nm with the expected vibrational peaks at long wavelengths.⁶² It is clear, therefore, that triplet excitons are not transferred from phosphor to host. Importantly, stable emission spectra were observed throughout the operating voltage (up to 13 V).

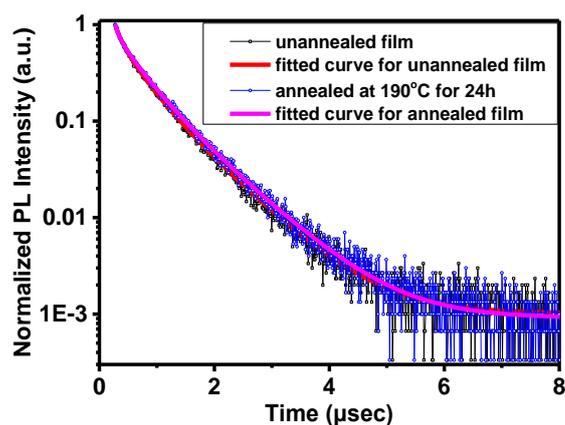


Figure 5. Transient photoluminescence decay (excited at 343 nm) curves and the corresponding fitting curves at room temperature at 475 nm for the unannealed 10 wt% FIrpic co-deposited with PmCPSi and the film annealed at 190 °C for 24 h.

The exciton confinement property of the host was further verified by transient photoluminescence decays at 475 nm for thin films on quartz substrates with a dispersion of 10 wt% FIrpic in PmCPSi. The decay lifetimes are fitted based on the previous theory.⁶³ Figure 5 shows a nearly mono-exponential decay curve for the unannealed film with a relatively long lifetime of 1.43 μ s, indicating complete suppression of the triplet energy transfer from phosphor to host, with confinement of the energy in the emission layer. It is notable that the lifetime after annealing the film at 190 °C for 24 hours was essentially unchanged due to the very stable doped film. Thus a stable emission layer can be expected when it is processed at high temperature to remove residual solvent.

We have also investigated the ability of PmCPSi to host the deep blue phosphor FCNIrpic ([bis((3,5-difluoro-4-cyanophenyl)pyridine)]iridium(III) picolinate) with a device configuration of ITO/ PEDOT:PSS (30 nm)/PVK (10 nm)/PmCPSi: 3 wt%

FCNIrpic (40 nm)/ Tm3PyPB (5 nm) /TPBi (30 nm)/ LiF (1 nm)/Al (60 nm). The doping concentration of FCNIrpic was chosen as 3 wt% due to the strong intermolecular interactions of polar F and CN functional groups in the ligands at a high doping concentration.^{48,64} Figure 6a shows the current density-voltage-luminance curves for the deep blue PhOLEDs. The devices turn-on at 8 V and reach a maximum brightness of 5167 cd m⁻². As depicted in Figures 6b and 6c, the maximum power efficiency, current efficiency and external quantum efficiency values are 1.48 lm W⁻¹, 6.11 cd A⁻¹ and 4.32%, respectively, which are maintained over a wide high luminance range. In Figure 6d, the electroluminescence (EL) spectra of the PmCPSi-FCNIrpic device exhibited a peak maximum at 460 nm and a shoulder at 484 nm with a color coordinate of (0.14, 0.20) within the range 9-13 V. The CIE value deviation in response to the voltage change is negligible which indicates excellent color stability. These findings demonstrate a stable device structure during operation due to PmCPSi's high thermal and morphological stability.

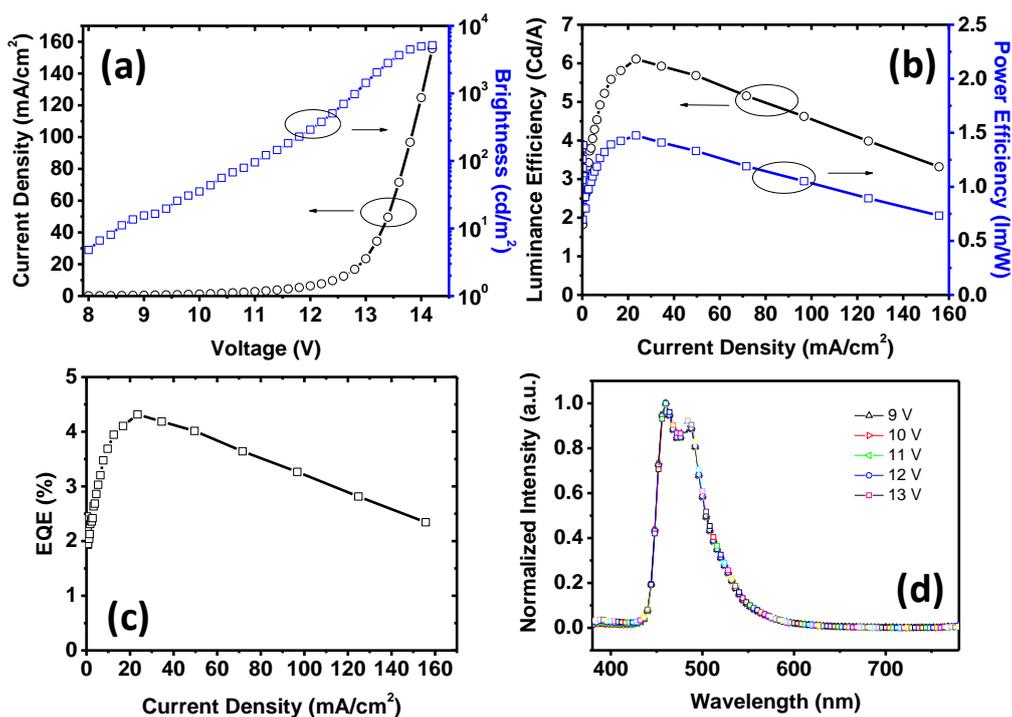


Figure 6. (a) J - V - L characteristic of 3 wt% FCNIrpic-doped PhOLED; (b) External quantum efficiency versus current density of FCNIrpic-doped PhOLED; (c) Current efficiency and power efficiency versus current density of FCNIrpic-doped PhOLED; (d). Electroluminescence spectra for FCNIrpic-doped PhOLED at 9-13 V.

Solution processed WOLEDs based on two emitters

We have constructed two-component white OLEDs with a single emission layer by combining blue and orange emitters²⁷ [FIrpic and Ir(MDQ)₂(pic), respectively] with the PmCPSi host Ir(MDQ)₂(pic) (Scheme 2) is the picolate (pic) analog of the standard red emitter, Ir(MDQ)₂(acac) [bis(2-methyldibenzo[*f,h*]quinoxaline)(acetylacetonate) iridium(III)].²⁶ It is known that the ancillary ligand pic is blue-shifts emission of heteroleptic Ir complexes by lowering the HOMO level that can affect the metal-to-ligand charge-transfer (MLCT) transition energy, e.g. in the sky-blue emitter, FIrpic.⁶⁵

Scheme 2. Synthetic route for Ir(MDQ)₂(pic)

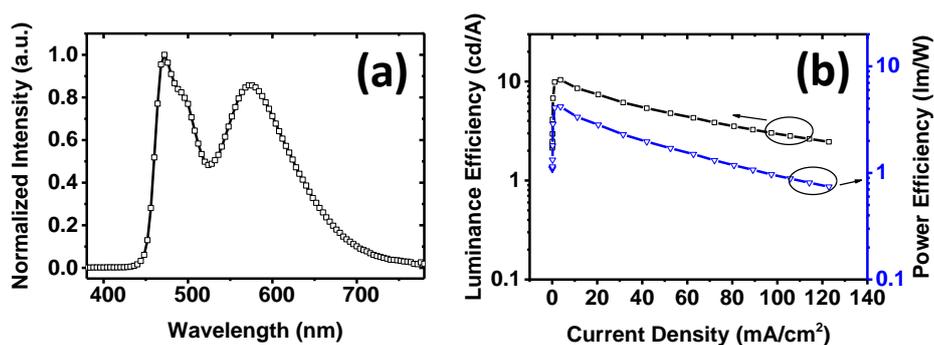
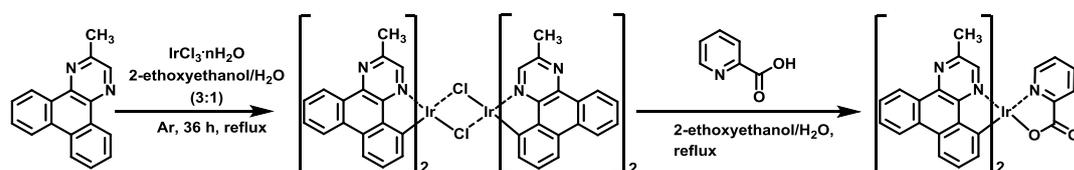


Figure 7. (a) EL spectrum and (b) efficiencies of the solution-processed white OLEDs based on FIrpic and Ir(MDQ)₂(pic) emitters

Figure 7 shows the EL spectrum (at 100 cd/m²) and the luminance and power efficiencies for the two-component white OLED with a standard architecture.⁶⁶ ITO/PEDOT:PSS (30 nm)/ PmCPSi: FIrpic: Ir(MDQ)₂(pic) (40 nm) Tm₃PyPB (5 nm) /TPBi (30 nm)/LiF (1 nm)/Al, where the concentration of FIrpic is 10 wt%, and of Ir(MDQ)₂(pic) is 0.7 wt%. Figure 7a shows the peaks at 472 and 572 nm corresponding to FIrpic and Ir(MDQ)₂(pic) emission, respectively. Their relative intensities vary strongly with the applied voltage: the orange emission decreases relative to the blue at higher voltage. This effect which results from the higher energy excitation of the blue emitter has been observed previously in multi-chromophore OLEDs.^{67,68} The “warm-white” device has CIE coordinates of (0.34, 0.41) and color rendering index (CRI) of 70 with color temperature (CT) of 4855 K at ca. 100 cd/m².

A maximum current efficiency of 10.4 cd/A and a maximum power efficiency of 4.2 lm/W are obtained. The efficient generation of “warm-white” light is a priority topic due to its beneficial effects on the human physiology and well-being.^{69,70} It should also be emphasized that the solution-processing approach is more convenient than vacuum-evaporation to fabricate two-component emissive layer (EML) devices⁶⁶ because the desired composition of the EML can be accurately achieved by weighting the dopants, instead of a more complicated co-evaporation process which is harder to control.

CONCLUSIONS

The purpose of this work was to extend the scope of polysiloxane derivatives and to develop an efficient host for solution-processed PhOLED applications. This has been achieved with the new polymer PmCPSi which incorporates pendant mCP moieties into the polysiloxane backbone. In comparison with mCP, PmCPSi exhibits greatly enhanced thermal and morphological stability. The silicon-oxygen bonds disrupt the π conjugation, therefore, PmCPSi retains a high E_T of 3.0 eV. PmCPSi has been shown to be a better host material than PVK for blue PhOLEDs. The PmCPSi-based devices exhibit lower operation voltage, higher luminance efficiency, improved CIE coordinates and enhanced EL efficiency compared to PVK devices under directly comparable conditions. Studies on FCNIrpic-based devices confirmed that PmCPSi can also serve as a stable host for deep blue PhOLEDs. A two-component phosphorescent WOLED with a single emitting layer has been achieved by blending

blue FIrpic and orange Ir(MDQ)₂(pic) into the PmCPSi host. In particular, to our knowledge, this is the first example of a polysiloxane host for WOLED fabrication. The versatility of PmCPSi as a host for efficient and stable monochromatic PhOLEDs and two-element WOLEDs has been established. There is clearly further scope to use polysiloxane-based host materials in OLEDs possessing a wide range of emission colors combined with enhanced efficiency and stability. This strategy should facilitate the fabrication of reduced-cost OLEDs for applications in display and lighting technologies.

ASSOCIATED CONTENT

Supporting Information. Details of synthesis and characterization; ¹H NMR and ¹³C NMR spectra of compounds; procedures for OLED fabrication; *J-V-L*, CIE and CRI characteristics of PmCPSi:Ir(MDQ)₂(pic) based devices. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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