

Solution processable phosphorescent dendrimers based on cyclic phosphazenes for use in organic light emitting diodes (OLEDs)[†]

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A novel solution processable phosphorescent dendrimer based on cyclic phosphazene (CP) cores has been prepared and used as emissive layers in simple OLED architectures, providing efficiencies of 24.0 cd A⁻¹ and 16.7 lm W⁻¹.

Organic and polymeric light emitting diode (OLED) technology has progressed immensely since the initial reports by Tang¹ and Friend² in 1987 and 1990 respectively. From these earliest discoveries through the late 1990's, almost all OLED reports were based on fluorescent emissive materials. As a result, champion OLED efficiencies were limited to around 10 lm W⁻¹ which made their application in display technology promising but no chance for solid-state lighting that requires efficiencies of >30 lm W⁻¹. With the discovery of platinum and iridium based *phosphorescent* complexes,^{3,4} OLED efficiencies >30 lm W⁻¹ have been achieved and thus application in both display and lighting applications have become even more promising.⁵

For these active materials, both small molecules and polymers are currently the preferred candidates. Small-molecules are advantageous as they can be highly purified and vacuum deposited in multi-layer stacks, both important for device lifetime and efficiency. However, vacuum deposition techniques generally require expensive equipment, a limitation to display size, and complicated full color display production processes at high volume using masking technologies.⁶ Polymers are generally of lower purity than small molecules but can access larger display sizes at much lower costs using solution-based deposition techniques such as spray coating, ink jet and screen printing.^{7,8}

Having a set of materials with properties intermediate between small molecules and polymers would be very advantageous. One such family of materials are dendrimers that have molecular weights in the favorable range between 1000–10 000 g mol⁻¹. Favorable because dendrimers can be purified to a high degree using chromatographic techniques, are soluble in common solvents, and allow synthetic versatility for tuning charge transport^{9–12} and emissive^{13–16} properties. Finally dendrimers of different emission colors can be physically blended together without phase separation for possible application in white lighting.

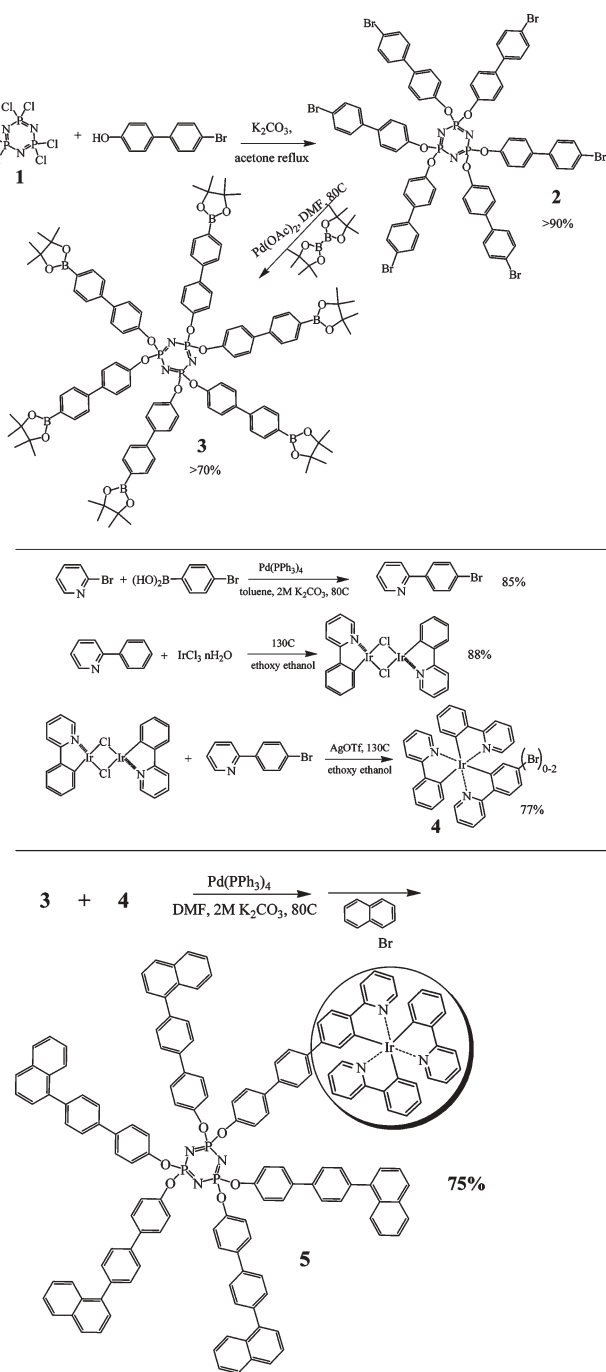
Cyclic phosphazenes (CP), with a planar non-delocalized cyclic ring consisting of alternating N and P atoms, are an interesting class of materials that offers access to dendrimeric materials. The inorganic phosphazenes have been well studied in both the cyclic and linear forms by several groups due to their diverse properties including excellent hydrolytic stability, thermal stability, flame retardant properties, and liquid crystalline behaviour to name a few.^{17–20} The CP core provides many advantageous properties towards useful materials for solution processable OLEDs. First, the chemistry to prepare functionalized CP cores is very straightforward. Second, the functionalized CP cores are very stable and do not breakdown even under very aggressive chemical conditions. Third, as the central CP core is inert, the optical and electronic properties are dependant on the dendrons. Individual free dendrons that may have interesting electronic and optical properties often cannot be used for devices as their thermal properties are poor. However, when attached to CP cores, thermal properties such as glass transition temperatures may be increased by as much as 100 °C in some cases while retaining the desired optical and electronic properties.²¹ Fourth, the functional groups are projecting in 3 dimensions thus producing a rigid spherical core from which to attach the dendrons of interest. These rigid spheres have been shown to promote amorphous properties that are known to be important for OLED devices.

In continuation of our research on solution processable hybrid materials,^{22–24} we report here the preparation of phosphorescent based CP materials for use as emissive layers in OLEDs. Our goal is to develop a platform from which many different solution processable phosphorescent materials can be prepared with optimal thermal, electronic and optical properties well suited for OLEDs. Scheme 1 shows the synthetic procedure for forming the phosphorescent CP material (**5**). We begin by using the commercially available starting precursor, hexachlorocyclotriphosphazene (**1**) that can easily undergo nucleophilic substitution reactions with 4-bromo-4'-biphenol using simple reagents such as acetone and K₂CO₃ at 60 °C to form the hexa(bromobiphenoxy) substituted CP (**2**) in high yield >(90%). Compound **2** is next reacted with a slight excess of bis(pinacolato)diboron, KOAc and 3 mol% Pd(OAc)₂ in DMF at 80 °C to provide the hexa(pinacolato-boranyl-biphenoxy) substituted CP (**3**) in good yield (>70%). Compound **4** (Br–Ir(ppy)₃) is prepared with a total yield of near 60% from the reaction of cyclometalated iridium chloro-bridged dimer [(ppy)₂Ir(μ-Cl₂)Ir(ppy)₂] with 2-(3-bromophenyl)pyridine. In this reaction, Ir(ppy)₃ and Br₂–Ir(ppy)₃ are also observed (≈30%) from MALDI analysis due to ligand scrambling. Compounds **3** and **4** were reacted together in a 1.0 : 1.0–1.2 molar ratio under Suzuki conditions using 2 M aqueous K₂CO₃, and Pd[PPh₃]₄ in DMF at 80 °C until complete consumption of **4** was observed *via*

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Scheme 1 Synthesis of the phosphorescent cyclic phosphazene based solution processable material.

TLC. At this stage additional base and catalyst were added along with excess 1-bromonaphthalene to cap the remaining pinacolatoboranyl sites. Upon completion the reaction mixture was precipitated into a methanol : water solution to give a yellow-orange solid. The material was finally purified by column chromatography using dichloromethane, and precipitated in methanol to recover a deep yellow solid in 75% yield. Residual Ir(ppy)₃ and higher molecular weight by-products formed from the reaction of Br₂-Ir(ppy)₃ and **3** were easily separated during purification. 1-Bromonaphthalene was chosen as it forms the corresponding naphthylbiphenoxy dendrons which are of sufficiently

high triplet energy level and thus compatible with the active Ir dendron. Furthermore the rigid dendrons give excellent material thermal properties, *i.e.* $T_g = 155\text{ }^\circ\text{C}$ and T_d (5% wt. loss) $> 400\text{ }^\circ\text{C}$. As the synthesis is performed by reacting one equiv. of **4** with the hexa-functionalized **3**, a mixture of products results, of which the target dendrimer (**5**) is the majority ($>70\%$) as determined by MALDI-TOF and GPC. The majority of the side products is the hexa-(naphthylbiphenoxy) CP material (without Ir substitution, $<25\%$) and a small portion of the di-Ir substituted product ($<5\%$) which do not seem to interfere with subsequent device results.

UV-Vis of **5** in dichloromethane shows a maximum at 292 nm corresponding to the $\pi-\pi^*$ transition absorption of the naphthylbiphenoxy dendrons. A broad lower intensity absorption from 350–480 nm with a peak of 390 nm corresponds to the metal to ligand singlet charge transfer state (MLCT). Similar UV-vis results have been reported for iridium (tris-2,2-phenylpyridine) Ir(ppy)₃ and other Ir dendrimers.²⁵

OLED devices were prepared by spin coating a 100 nm polyethylene dioxythiophene : polystyrene sulfonic acid (PEDOT : PSS) layer (obtained from HC-Starck) onto pre-cleaned ITO coated glass followed by drying at 120 $^\circ\text{C}$ for 10 min under N₂. Next a solution of the emissive layer (1 wt% total solids, 50 : 40 : 10, poly(*N*-vinylcarbazole) (PVK) : 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) : **5** in toluene) was spin coated to provide a 70 nm thick layer. The devices were completed by thermally evaporating 1,3,5-tris(1-phenyl-1*H*-benzimidazol-2-yl) benzene (TPBI) (20 nm), barium (5 nm) and silver (80 nm) at a base pressure of 1×10^{-6} mbar.

As shown in Fig. 1, resulting OLEDs had a turn-on voltage for light emission of 3 V, which is low considering the build-in potential for this device is approximately 2.4 eV. This low turn-on voltage confirms that the barrier for hole and electron injection is low. This is expected as the differences between the work functions of ITO and barium with the HOMO and LUMO of PEDOT : PSS respectively, is less than 0.1 eV.

A luminance of 3362 cd m⁻² is observed at 10 V with a corresponding current efficiency of 19.4 cd A⁻¹. The maximum current efficiency of 24.0 cd A⁻¹ is observed at a brightness level of 25 cd m⁻². Furthermore, the cd A⁻¹ *versus* luminance (see inset in Fig. 1) curve is rather flat, indicating that the device is quite independent of the applied bias and demonstrating the charge

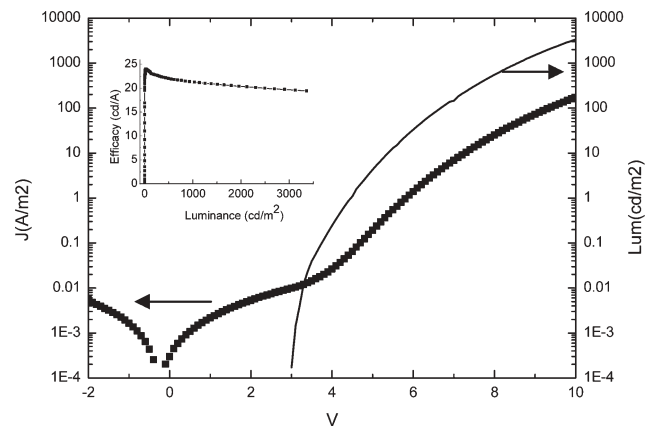


Fig. 1 Current density (symbols) and luminance (lines) for the ITO/PEDOT:PSS/PVK : PBD : (**5**)/TPBI/Ba/Ag OLED device. Inset shows the device efficacy *versus* the luminance.

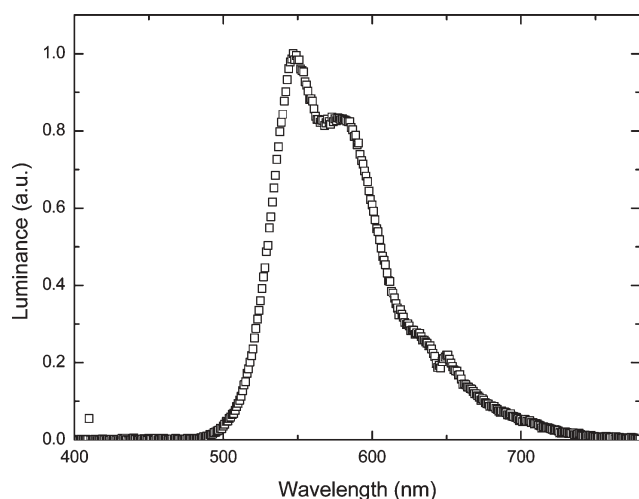


Fig. 2 Electro-luminescent spectrum obtained from an ITO/PEDOT-PSS/PVK : PBD : 5/TPBI/Ba/Ag device.

carrier balance is stable. This is an important factor that determines the usefulness of **5** for use in high brightness applications such as active matrix displays and illumination systems. Maximum external quantum efficiency (EQE) and lumens per watt (lm W^{-1}) were 7.0% and 16.7 lm W^{-1} respectively. As PVK is not the optimum host material for phosphorescent systems, we expect that our maximum efficiencies can be significantly improved with proper host selection.^{26,27} The electroluminescence spectrum of the device is yellow (CIE color coordinates $x = 0.45$, $y = 0.54$) and red shifted by 35 nm (Fig. 2) with respect to those using $\text{Ir(ppy)}_2\text{acac}$ (0.31, 0.57). This shift in emission spectrum is due to the increased conjugation from the phenylpyridine ligand with the biphenyl unit used to link the complex with the cyclic phosphazene core. This added conjugation stabilizes the LUMO slightly which in turn decreases the HOMO–LUMO gap. Control devices prepared using $\text{Ir(ppy)}_2\text{acac}$ as the light emitting species with similar device architectures consistently provided results 30–35% lower than devices using **5**.

In conclusion, reported here is a new class of solution processable amorphous phosphorescent materials based on cyclic phosphazene cores with many attractive properties for application in organic light emitting diode (OLED) technology including: ease of synthesis, high glass-transition temperatures (T_g), high solubility, good film-forming properties, and high-purity *via* column chromatography. Preliminary simple OLED devices achieve high current efficiencies of 24.0 cd A^{-1} at 25 cd m^{-2} and maintain current efficiencies of 19.4 cd A^{-1} at brightness levels over 3300 cd m^{-2} . Future work in this area will explore using more efficient host matrices to improve device efficiencies. We will also design and attach new emitting moieties to the CP core to achieve luminescence from blue to white to deep red.

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