APPLIED PHYSICS LETTERS **89**, 061125 (2006)

Multifunctional platinum porphyrin dendrimers as emitters in undoped phosphorescent based light emitting devices

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(Received 3 May 2006; accepted 21 June 2006; published online 11 August 2006)

The authors report on a class of platinum porphyrin based phosphorescent multifunctional first generation dendrimers (Pt-8C*n*-TPP) incorporating a platinum porphyrin core as the emissive center and carbazole side groups as the hole, as well as energy transport fragments. Furthermore, the alkyl groups prevent aggregation and allow for the formation of transparent homogeneous films directly from solution. The intra- and intermolecular energy transfers by Förster and Dexter mechanisms from the carbazole side groups to the platinum porphyrin core have been investigated. Light emitting devices were fabricated and bright red electrophosphorescence was achieved from a single undoped emitting layer of Pt-8C4-TPP. The results indicate that platinum porphyrin dendrimers are very promising to make bright, red saturated and spin-coated phosphorescent devices with a simplified undoped emissive layer. © *2006 American Institute of Physics*.
[DOI: 10.1063/1.2335511]

The use of transition metal complexes as emitters in organic light emitting diodes (OLEDs) has become a relevant topic in the last few years,[1–3] due to the excellent photoluminescence (PL) properties and potential advantages of achieving maximum internal quantum efficiency up to 100%.[1] Among transition metal complexes particular attention has been given to Pt(II) octaethylporphine(PtOEP) as red emitter and to Ir(ppy)$_3$ as green emitter, which are commonly incorporated in organic molecules or polymer matrices as dopants.[4,5] However, in host/guest blends phase separation processes may occur, thus affecting the electroluminescence (EL) performances. Furthermore, fabrication of doped active layer devices is technologically more complicated and expensive than single-emitting-component emissive layer devices. In view of this, many efforts have recently been devoted to the synthesis of multifunctional emitters and many examples of OLEDs based on a single evaporated active layer have been reported.[6–9] However, in this scenario the development of organic materials for red phosphorescence lags significantly behind that for green and blue colors. A few results about red OLEDs fabricated by thermal evaporation with undoped, phosphorescent single-emitting-component emitters have been reported.[10–12] Even more critical is the progress in the synthesis of soluble compounds, since high performance phosphorescent OLEDs based on spin-coated undoped active layers are quite rare and limited to green emission.[13] The most promising red emitting dopants in transition metal complexes for OLEDs are platinum porphyrin compounds.[1,14] This class of materials can be functionalized with a variety of substituent groups allowing a fine tuning of the optical properties.[15–17] These characteristics are usually exploited by blending the active material with conductive polymers, such as polyvinyl carbazole (PVK), with a large Förster radius and a high energy, long lifetime triplet state T_1 to enhance the energy transfer processes to guest molecules.[18,19] In this work, soluble platinum porphyrin based phosphorescent first generation multifunctional dendrimers (Pt-8C*n*-TPP), incorporating platinum porphyrin core and carbazole side groups, are reported. The introduction of carbazole moiety strengthens the hole transport properties of the complex and allows for an efficient transport of the absorbed energy to the core. Moreover, the alkyl groups increase solubility in common organic solvents and allow for the formation of transparent homogeneous films directly by spin coating. The control of the intramolecular energy transfer mechanisms was accomplished by changing the distance between active groups (Pt-8C*n*-TPP, $n=4,6,8$), thus finely tuning the photoluminescence. Bright saturated red emitting undoped single emissive layer phosphorescent OLEDs are demonstrated.

The chemical structures of the synthesized platinum porphyrin dendrimers are shown in Fig. 1. All materials were characterized by ^{1}H NMR and mass and element analysis, and the synthesis details will be published elsewhere. The compounds consist of a platinum porphyrin core surrounded by a dendrimer structure of different length alkyl chains and

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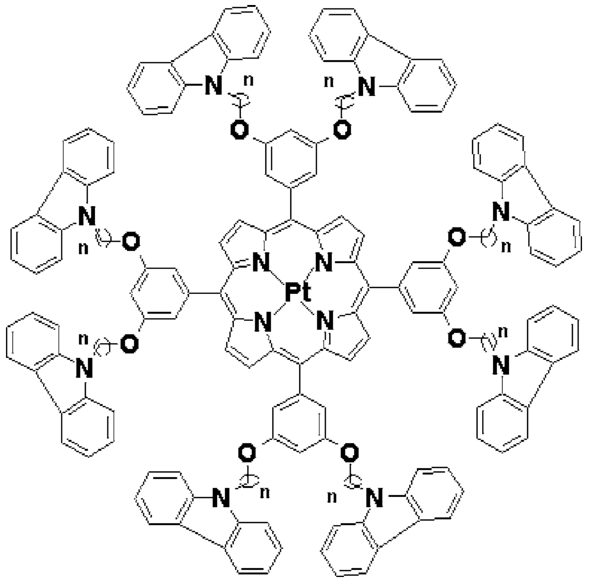


FIG. 1. *Meso*-substituted first generation platinum porphyrin dendrimers Pt-8C*n*-TPP (n=4,6,8).

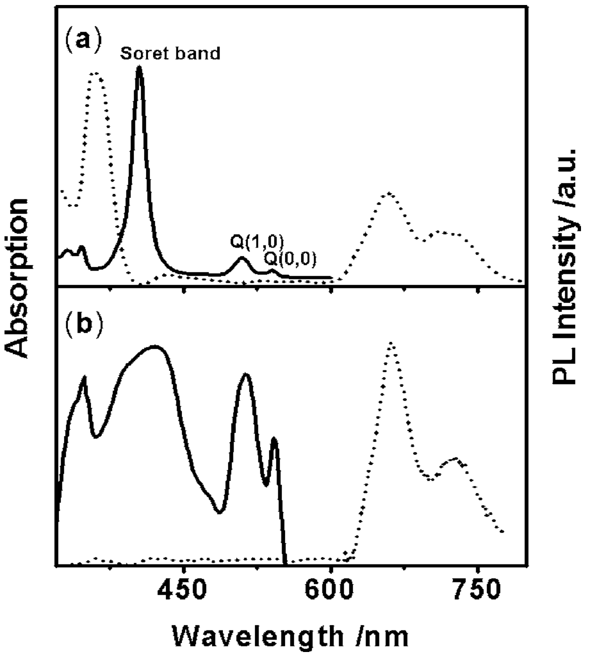


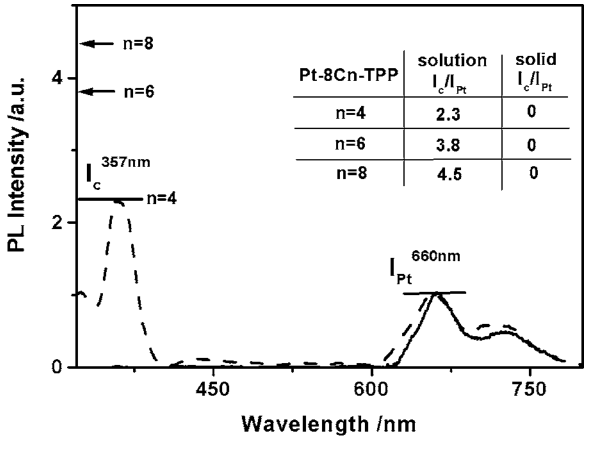
FIG. 2. Absorption and emission spectra of Pt-8C4-TPP. (a) Absorption (solid) and emission (dot) spectra of Pt-8C4-TPP in $CHCl_3$ solution; (b) absorption (solid) and emission (dot) spectra of Pt-8C4-TPP in the solid state.

carbazole side groups. The dendrimer structure allows one to separate the different functionalities of each active group, with the platinum porphyrin core acting as the emitting center and the external groups introducing enhanced conductive and mechanical properties. In particular, the alkyl chains provide good solubility for the dendrimers in organic solvents and excellent film forming properties by spin coating.

The surface topography of spin-coated Pt-8Cn-TPP films on poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT-PSS) was investigated by atomic force microscopy. The typical film morphology shows root-mean-square (RMS) roughness of 1.3±0.1 nm. The excellent film forming properties of Pt porphyrin dendrimer play an important role in device fabrication.

The optical properties of the dendrimers have been investigated by carrying out absorption and photoluminescence measurements on all the compounds in solution and in the solid state. In Fig. 2 we display the absorption and photoluminescence spectra of compound Pt-8C4-TPP. An intense Soret band at 404 nm and two Q bands at 540 and 510 nm are observed in the absorption spectrum. The Q band is attributed to the spin-triplet excited state, whereas the Soret band to the singlet state, consistent with previous observations from platinum porphyrin complexes.[15,16,20] An emission band of Pt-8C4-TPP is observed with a sharp $Q(0,0)$ peak at 660 nm and vibronic $Q(1,0)$ sidebands at 725 nm, as reported by several investigators.[15,16,20] In solution [see Fig. 2(a)], the Pt porphyrin dendrimer emits phosphorescence from the Pt porphyrin core at 660 nm and a strong fluorescence from the carbazole side groups around 357 nm, as expected for carbazole derivatives.[21] Conversely, in the solid state [see Fig. 2(b)], only phosphorescence from the Pt porphyrin core is detected. These results indicate that in the solid state the energy absorbed by the carbazole group is completely transferred to the core, due to efficient energy transfer induced by intermolecular and intramolecular interactions. In order to get dominant emission from the Pt porphyrin core, the absorbed energy from carbazole groups must efficiently be transferred to the core by both Förster (dipole-dipole) and Dexter (electron-exchange) energy transfer processes, which require good spectral overlap. This is verified in Pt-8C*n*-TPP complexes which show a partial spectral overlap between the emission spectrum of carbazole groups and the Soret band of Pt porphyrin dendrimer, suggesting that Förster energy transfer from side groups to Pt dendrimer is possible. Moreover, the triplet energy level of carbazole groups according to that of PVK (2.46 eV) reported by literature[19] fits well with the Pt dendrimer Q bands, leading to good Dexter energy transfer.

In order to deeply investigate the energy transfer mechanisms, different length alkyl chain compounds have been synthesized (Pt-8C*n*-TPP, n=4,6,8) to finely tune the distance between the Pt porphyrin core and the carbazole side groups. Figure 3 indicates the emission spectra of Pt-8C*n*-TPP in $CHCl_3$ solution and in the solid state. The intensity ratio of the photoluminescence from the carbazole



Pt-8Cn-TPP	solution I_c/I_{Pt}	solid I_c/I_{Pt}
n=4	2.3	0
n=6	3.8	0
n=8	4.5	0

FIG. 3. Emission spectra of Pt-8C*n*-TPP (n=4,6,8) in $CHCl_3$ solution (dash) and in solid state (solid). Inset: Intensity ratios of photoluminescence from carbazole side groups and Pt porphyrin core with different numbers of alkyl groups.

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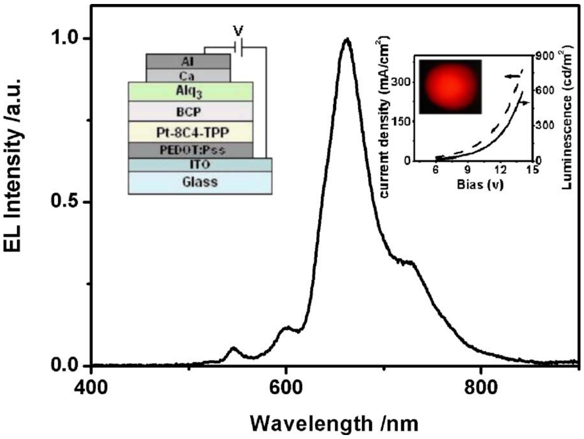

FIG. 4. (Color online) EL spectrum of device II. Insets: Device structure and characteristics.

side groups and the Pt porphyrin core with increasing alkyl chain length $(n=4,6,8)$ is shown in the inset of Fig. 3. In all samples the emission originating from the carbazole side groups quenches in the solid state, demonstrating a clear intermolecular energy transfer process. In addition, the PL intensity in solution of the carbazole groups decreases as the length of the alkyl chains (see inset of Fig. 3) is reduced, indicating that intramolecular energy transfer processes are favored by a reduced distance between the central core and the external groups. This result clearly demonstrates that Pt-8C4-TPP is a molecule with enhanced intramolecular energy transfer processes and pure saturated red emission, independent of the external environment, i.e., of the deposition conditions. These characteristics, together with the excellent film forming properties by spin coating, make these molecules suitable for electroluminescence applications.

Two kinds of OLED devices based on Pt-8C4-TPP were fabricated: (I) indium tin oxide ITO/PEDOT-PSS/Pt-8C4-TPP/Ca/Al and (II) ITO/PEDOT-PSS/Pt-8C4-TPP/BCP/Alq_3/Ca/Al. A hole transporting layer of PEDOT-PSS, used to lower the hole injection barrier at the ITO surface, was spin coated onto the cleaned ITO-coated glass substrate (120 nm, 15 Ω/sq). Then, a layer of platinum porphyrin dendrimer Pt-8C4-TPP was spin coated from a chloroform solution on the surface of the PEDOT-PSS (total 100 nm). Finally, 30 nm thick 2,9–dimethyl-4,7–diphenyl-1,10–phenanthroline (BCP), acting as electron transferring/hole blocking layer, 20 nm thick layer Alq_3, acting as electron injecting/transferring material, and a 50 nm thick Ca cathode covered with a 150 nm thick Al layer were deposited by thermal evaporation at pressure of 4×10^{-6} mbar.

The introduction of BCP as hole blocking layer and Alq_3 as electron transport layer in device II resulted in a well balanced charge injection in the platinum porphyrin dendrimer and in greatly enhanced EL performance. Figure 4 shows the EL spectrum and the characteristics of the device (II). Four emission peaks are observed at about 540, 590, 660, and 720 nm, which correspond to coordinates (0.60, 0.30) of the 1931 Commission Internationale De L'Eclairage chromaticity diagram. Comparing with the previously observed PL spectra, the strong 660 nm emission band is attributed to phosphorescence from the Pt compound whereas the 720 nm emission is attributed to the vibronic sideband. A weak fluorescence band around 590 nm is observed,[22] while another weak peak around 540 nm could be attributed to either the transition from thermally populated triplet state "hot band"[11,23] or to weak singlet emission from *T-T* annihilation.[24] Bright phosphorescence was observed in both devices, with a maximum value up to 600 cd/m^2 for device II. This value is by far higher than those previously measured in pure PtOEP[11] or PVK: PtOEP based devices.[18]

In summary, the properties of the porphyrin compounds can be finely tuned by chemical modification of the porphyrin framework. The key design components to be used in bright OLED devices include hole transport and energy transport side groups, together with alkyl chains that lead to a good solubility and film forming properties. In this work we report on multifunctional platinum porphyrin based first generation phosphorescent dendrimers in which energy transfer mechanisms are finely tuned to obtain a saturated red electroluminescence. This report of spin-coated OLED based on multifunctional red phosphorescent emitters indicates that platinum porphyrin dendrimers are a very promising way of making bright, red saturated and spin-coated phosphorescent devices with a simple undoped emissive layer.

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