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PHOTOPHYSICAL PROPERTIES OF PORPHYRIN DENDRIMERS AS RED LIGHT-EMITTERS FOR ORGANIC LIGHT-EMITTING DIODE (OLED)

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ABSTRACT

We report on the investigation of photophysical properties of the free-base and metal chelated porphyrins bearing bulky stilbene dendron substituents at the *meso*-positions. The free-base and zinc chelated porphyrins emitted a red fluorescence in solution and solid state, while the copper derivatives were non-luminescent. The zinc porphyrin derivative with a G-1 stilbene dendron substituted on the *meso*-positions emitted the best red colour with a colour chromaticity close to a red colour using in a full-colour display screen. Upon excitation of the dendron units in dichloromethane an intramolecular energy transfer took place from the dendron units to the porphyrin core.

KEYWORDS: porphyrin, dendrimer, red-light emitter, organic light-emitting diodes (OLED)

1. INTRODUCTION

Since it was reported that conjugated poly(p-phenylene vinylene) (PPV) has been used as a light-emitting layer in OLED, producing a bright yellow-green emission when excited by flow of an electric current [1], OLED materials have attracted a large number of attentions. This is due to their potential applications in full-colour, flat-panel displays as well as being a perspective of academic research [2-4]. To develop a full-colour display, it is important to have a set of red, green and blue electroluminescent emitters with sufficiently high luminance and colour purity. Over the last few years organic materials for green and blue OLED with high luminance, high efficiency and high performance in the devices have been developed [5-6]. However, at the present time the development of organic materials for red-light emitter lags significantly behind that for the other two primary colours. So far, a number of both polymers and small molecular materials have been investigated as red-light emitters in electroluminescent devices (EL) such as dialkoxy-substituted PPV derivatives [7] and iridium chelated complexes [8-10]. However, to date the performance of such materials in the OLED is still significantly less effective compared to that of green and blue light emitters. Porphyrins have long been known to fluoresce or phosphoresce when chelated with platinum with a strong and pure red colour, but they are non-luminescent in solid state. This is in part due to their strong tendency towards π-π stacking and concentration quenching, resulting in poor fluorescence in solid state as well as their poor solubility and hence poor processing properties. Therefore only a few attempts have been made at using porphyrins as a red light-emitter in OLED. In an attempt to use porphyrins in OLED, they have been incorporated into a polymeric structure as copolymers [11] or side chains [12-13]. Saturated red emissions have been obtained from the metal chelated porphyrin complexe used as dopant red dye mixed with a suitable host. The phosphorescence quantum yield of platinum octaethylporphyrin (PtOEP)

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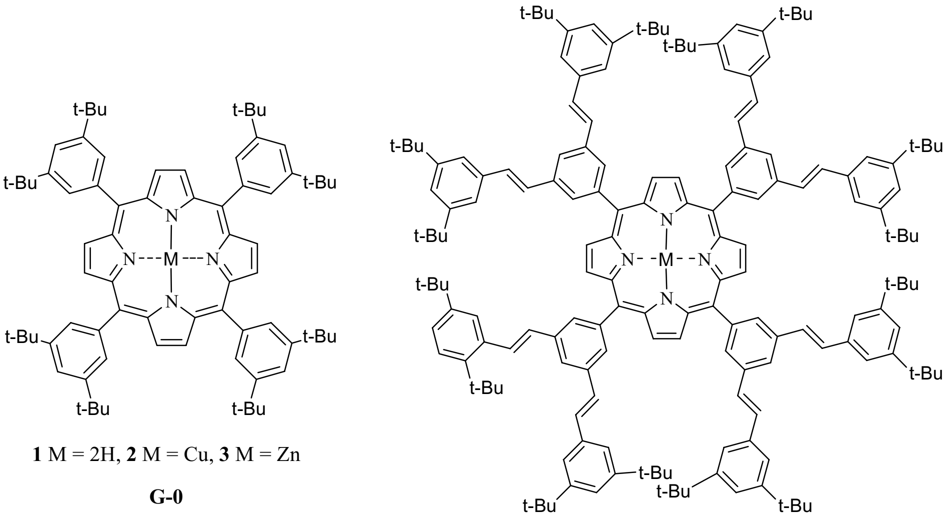
is about 0.45 in the deoxygenated toluene/DMF solutions at room temperature [14]. The devices with PtOEP doped into tris(8-quinolinolate) aluminium (Alq3) showed higher efficiency at a low injection current [14]. Currently, a number of porphyrin dendrimers have been synthesized, however their OLED properties have not been investigated [15-17]. It is of interest to design new porphyrin dendrimers as novel red light-emitting materials for OLED, therefore recently we have reported an alterative approach to reduce the possibility of porphyrins to π-π stacking as well as increasing porphyrin solubility by incorporating the porphyrin into a dendritic structure as a core. The porphyrin dendrimers bearing a rigid stilbene dendron attached on the porphyrin *meso*-positions were synthesized and fully characterized [18]. In this paper, we report on the study of photophysical properties of these free-base and metal chelated porphyrins.

2. MATERIALS AND METHODS

The free-base porphyrins bearing rigid stilbene dendrons (G-0 and G-1) on the *meso*-positions and their zinc and copper chelated derivatives used in this study were synthesised according to the literature methods [18]. Molecular modelling of all porphyrin structures were performed using Chem 3D program published with optimization using the MM2 force field. UV-visible measurements were carried out by using a Perkin-Elmer UV Lambda 25 spectrometer and all measurements were performed in dilute solution of spectroscopic grade dichloromethane. Fluorescence spectra of porphyrins in dichloromethane solution were recorded using a Perkin-Elmer LS 50B Luminescence spectrometer with xenon lamp excitation.

3. RESULTS AND DISCUSSION

The molecular structures of the free-base and metal chelated porphyrin dendrimers (G-0 and G-1) used in this study are shown in Figure 1.



1 M = 2H, **2** M = Cu, **3** M = Zn

G-0

G-1 **4** M = 2H, **5** M = Cu, **6** M = Zn

Figure 1 Molecular structures of porphyrin dendrimers

The G-0 and G-1 *meso*-substituted free-base porphyrins 1 and 4 were synthesized using an acid catalysed condensation of the corresponding G-0 and G-1 aldehydes with pyrrole followed by oxidation. Chelation of divalent central zinc and copper into the porphyrin macrocycles was achieved with the reaction of the free-base derivatives with zinc and copper salts, refluxed using a dichloromethane-methanol solvent. The main features of the conjugated dendrimers consist of two parts: porphyrin core and four stilbene dendrons bearing tert-butyl groups as surface groups surrounding a core structure. The computer molecular modelling structures of the G-1 zinc porphyrin dendrimer 6 is shown in Figure 2. The structure is simple and adopts the three-dimensional conformation. The dendrons and porphyrin ring were all planar with the plane of G-1 stilbene dendron being aligned nearly orthogonal to the porphyrin plane due to steric interactions between the β-pyrrolic and the aryl ring protons. This creates a quasi-spherical structure, with the porphyrin core at the centre and the stilbene dendron cage surrounding it. As a result, there would be no possibility for the porphyrin molecules to π stacking, and so it was hope that good luminescence in solid state could be observed.

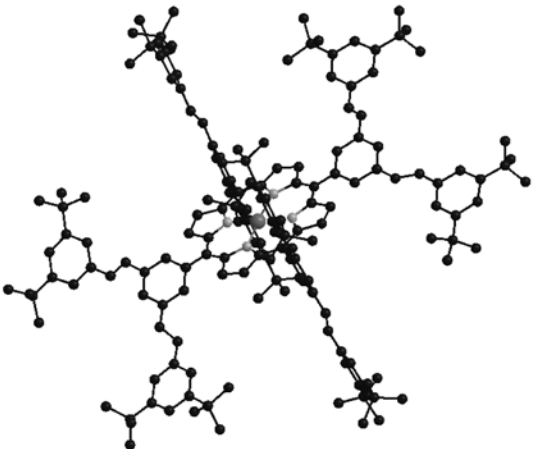


Figure 2 The optimised molecular structure of the G-1zinc porphyrin **6**

Figures 3 and 4 show the normalised electronic absorption spectra of the porphyrin dendrimers in dichloromethane solution. All dendrimers have two components to their UV-Visible absorption spectra. An absorption due to the central porphyrin chromophore as well as an absorption associated with the stilbene moiety containing *meso*-substituent dendron is observed as illustrated in Figure 3, which shows the UV-Visible absorption spectra of the free-base porphyrin dendrimers 1 and 4. The main features of the absorption of the porphyrin core of both molecules contain four low-intensity Q-bands (IV, III, II and I) in the visible region of 500-700 nm, which are a characteristic of the free-base porphyrin, and one very intense Soret band in the violet region of the spectrum at 420 and 431 nm for 1 and 4, respectively. The intensity ratio of these four Q-bands shows an ethio type spectrum confirming they are symmetrically *meso*-tetraarylporphyrins. The spectrum of 4 bearing stilbene subunit chromophore as the *meso*-substituent showed an additional absorption band of the dendrons at 311 nm.

Considering the effect of the *meso*-substituent on the electronic properties of the central porphyrin chromophore, there was a slight bathochromic shift of about 10 nm in the Soret absorption band on going from the G-0 porphyrin to the G-1 porphyrin despite the stilbene dendron being nearly perpendicular to the plane of the porphyrin core. The same effect was also observed for dendritic porphyrin systems possessing flexible aryl ether dendrons as the *meso*-substituent by Matos and co-workers [19] and Aida and co-workers [20], who suggested such bathochromic shift of the Soret band to be associated with either weak interactions between the core and the branches or with the encapsulation degree of the core into the dendrimer framework. In our opinion, this small bathochromic shift of the Soret band in the free-base porphyrins is an indication of the presence of the cross-conjugation between the rigid stilbene dendron and the core within the dendrimer.

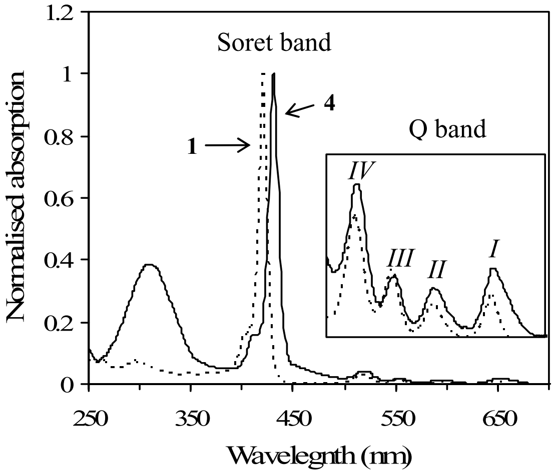


Figure 3 Normalised UV-Visible absorption spectra of the free-base porphyrin dendrimers in dichloromethane (10-5 M)

A comparison of the absorption spectra of the free-base G-0 porphyrin 1 and G-1 porphyrin 4 with their metal chelated derivatives 2 and 3, and 5 and 6, respectively, was illustrated in Figure 4. On going from the free-base porphyrins to metalloporphyrins, the UV-Visible absorption spectra are simplied due to the symmetry of the planar porphyrin macrocyclic fragment (of π-the electron cloud of the macrocycle) increases. The Soret band of the zinc and copper derivatives (peaks at 418, 422, 424 and 430 nm for 2, 3, 5 and 6, respectively) changed only slightly about 1-7 nm from their corresponding free-base porphyrins depending on the complex formation. The Q-bands in the visible region have two absorption peaks (II and I) (a characteristic of the metalloporphyrins) in which the band II corresponding to the electronic-vibrational transition is stronger than the band I corresponding to the electron transition. In all cases, the UV-Visible absorption spectra of the copper chelated porphyrins are shifted to the low-frequency region compared to those of the corresponding zinc porphyrins. This can be explained in terms of a greater electronegativity of the copper metal (1.9) leading to a lowering of the electron density on the occupied π-orbitals of the porphyrin molecule, which is accompanied by hypsochromic shifts of the spectra. Moreover, such hypsochromic shifts also indicate that the strength of the Cu-N coordination bond in the metalloporphyrins containing the planar MN_4 coordination unit is greater than that of the Zn-N coordination bond. Indeed to remove the central copper chelate from the porphyrin macrocycle requires stronger acid (conc. H_2SO_4) compared to the zinc derivative (HCl) [21]. As with the case of free-base porphyrin 4, the effect of the *meso*-substituent on the electronic properties of the porphyrin core was also observed in the copper 5 and zinc 6 derivatives by a slight bathochromic shift of the Soret band (6-8 nm) with the absorption peak due to the dendron remained unaltered at 311 nm.

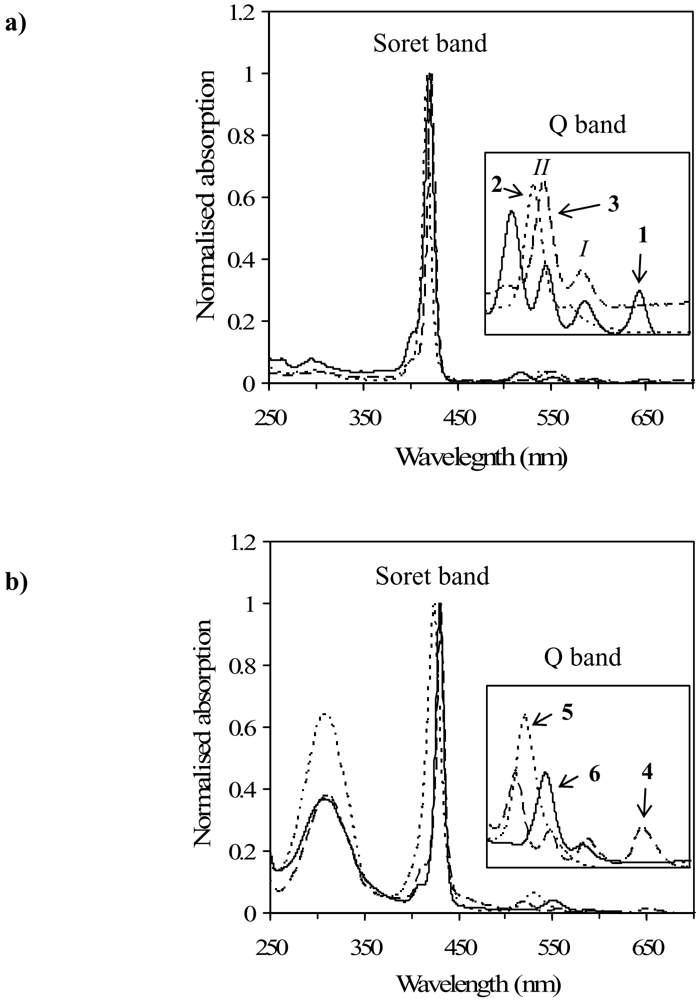


Figure 4 Normalised UV-Visible absorption spectra of
a) G-0 porphyrins; b) G-1 porphyrins in dichloromethane (10-5 M)

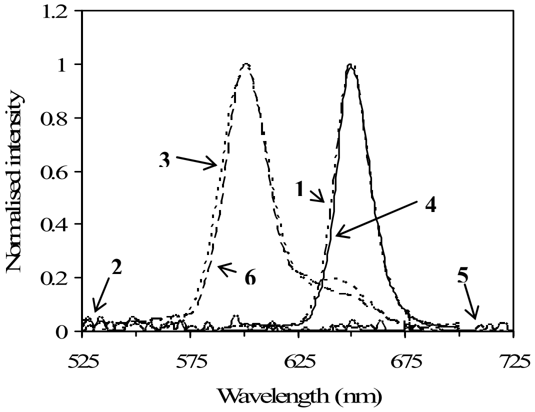


Figure 5 Normalised photoluminescence spectra of porphyrin dendrimers in dilute dichloromethane solution excited at the Soret band.

The solution photoluminescence (PL) spectra of the porphyrin dendrimers were recorded in dichloromethane solution and the spectra of 1, 2, 3, 4, 5 and 6 are shown in Figure 5. The PL spectra of the free-base porphyrins 1 and 4 on excitation of the Soret band of the porphyrin core were identical, showing a singlet absorption peak at 600 nm. The emission spectra of the zinc chelated porphyrins 3 and 6 were also alike and substantially hypsochromic shifted with maxima emission band at 650 nm. In contrast, the copper derivatives 2 and 5 were non-luminescent. From these emission spectra the Commission International d'Eclairage 1931 (CIE) coordinate (x, y) for the porphyrin dendrimers 1, 3, 4 and 6 were determined to be (0.716, 0.283), (0.619, 0.381), (0.718, 0.282) and (0.629, 0.370), respectively, which correspond to red emission as illustrated in Figure 6. The zinc porphyrins 3 and 6 emitted a red fluorescence close to a red colour using in a full-colour display screen. The latter 6 bearing large *meso*-substituent emitted the best red colour. This could be explained in terms of the bulky G-1 stilbene dendrons on the *meso*-positions well prevent a π-stacking of the porphyrin core resulting highly fluorescent core as it was predicted by molecular modelling study. When the dendritic porphyrins 4 and 6 were excited at 311 and 430 nm, where the G-1 stilbene dendron units and the porphyrin core absorb, respectively, in both case the emission was mostly from the porphyrin core, and the residual fluorescence from the dendron units was very weak. This result indicates that there is an efficient intramolecular excitation energy transfer from the outer stilbene dendron units to the inner porphyrin core within the dendrimer. In fact that the high excited energy migration over the continuous dendritic array of stilbene building units within the life time of the excited state to the porphyrin core even through the dendrons are rigid and held orthogonally to the plane of the porphyrin can be ascribed to the efficiency flow through the cross-conjugation of stilbene dendron units. This energy transfer was also observed in the case of aryl ether dendronised porphyrin systems [20].

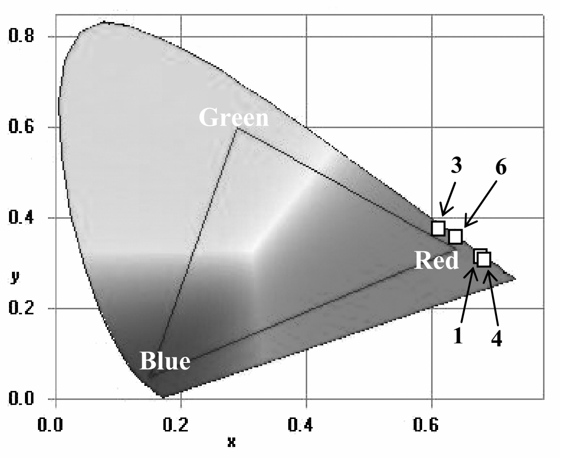


Figure 6 *CIE* coordinate of the porphyrin dendrimers

4. CONCLUSIONS

The bulky *meso*-substituents limited porphyrin molecules a π-stacking, resulting in a strong red fluorescent porphyrin core, as well as allowing electronic properties to be independently varied. The energy transfer from the dendron units to the porphyrin core occurred with high efficiency due their unique structures. Chelation of porphyrin macrocycles with different metals altered the electronic properties and allowed the tuning of emission colour with the zinc porphyrins emitted a perfect red colour. These porphyrin dendrimers have a potential application as a red light-emitter for OLED.

5. ACKNOWLEDGEMENTS

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