



Synthesis of platinum complexes of fluorenyl-substituted porphyrins used as phosphorescent dyes for solution-processed organic light-emitting devices



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ABSTRACT

Platinum(II) complexes of symmetrical *meso*-substituted A₄-porphyrins bearing four fluorene donor moieties 5,10,15,20-tetra(4-(2-methoxyfluorenyl)phenyl)porphyrin, referred to as TOFP, or eight fluorene arms, 5,10,15,20-octa(3,5-(2-methoxyfluorenyl)phenyl)porphyrin, OOFFP, were synthesised and characterised. The photophysical properties of the new compounds are reported and compared to those of PtTPP and PtTFP {TPP=tetraphenylporphyrin and TFP=tetra(2-fluorenyl)porphyrin}. The luminescence quantum yields of PtTOFP and PtOOFP are 11% and 4.2%, respectively, compared to 4.6% for the reference PtTPP and only 2.0% for the previously studied compound PtTFP. The electronic and optoelectronic behaviour of solution-processed organic light-emitting devices (OLEDs) are reported that incorporate these platinum porphyrins as phosphorescent dyes doped into different layers of a polyvinylcarbazole (PVK) host.

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1. Introduction

Organic light-emitting diodes (OLEDs) are of intense interest in the development of flat-panel display devices and for energy-efficient lighting.^{1,2} In both cases, three primary colours, blue, green, and red, are necessary. For commercial applications, the most success has been obtained for green emitters.³ For the blue light-emitting materials, such as polyfluorenes, high efficiency has been achieved, but there are frequent problems with stabilities and lifetimes.⁴ The development of red emitting systems is also challenging, partly due to the drop-off in emission quantum yield, that is, typically observed for lower energy excited states. This trend stems from the fact that non-radiative deactivation of excited states through intramolecular energy transfer into vibrations is favoured as the energy decreases (often referred to as the 'energy gap law') and also from the dependence of the radiative rate constant on ν^3 ,

according to the Einstein coefficient for spontaneous emission (ν =frequency of light emitted).

Many porphyrins emit quite strongly in the red region of the spectrum, owing to their rigid, highly conjugated structures. Moreover, they have quite narrow bandwidths, potentially favouring high colour purity if used in an OLED. Some studies have indeed used porphyrins as red OLED emitters; for example, a device comprising what is probably the most accessible of the porphyrin family, namely tetraphenylporphyrin (TPP), doped into a conjugated polymer, poly(9,9-dioctylfluorene), was described several years ago.⁵ The importance of fluorene units in organic electronics and photonics makes the combination of porphyrins and fluorenes particularly intriguing. For example, a series of star-shaped porphyrins bearing pendent oligofluorene arms were reported by Bo and co-workers.^{6,7} In previous work from our laboratory, we reported the synthesis of 5,10,15,20-tetrafluorenylporphyrin (TFP), incorporating fluorenyl substituents at the four *meso* positions of the porphyrin macrocycle, together with the catalytic properties of its ruthenium(II) complex.^{8–13} In terms of the photophysical properties, the fluorenyl substituents were found to lead to an increase in the fluorescence quantum yield of the free-base porphyrin

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($\Phi_F=0.24$) relative to that of TPP ($\Phi_F=0.13$ under the same conditions), apparently owing largely to an increase in the radiative rate constant associated with distortion of the porphyrin macrocycle.¹⁴ A density functional theory study on such compounds has been carried out by others.¹⁵ We have also prepared dendrimeric supramolecular assemblies bearing 12 and 24 fluorenyl peripheral donor groups surrounding the porphyrin core.^{16–18}

Over the past decade, many studies have focused on the use of luminescent organometallic complexes as emitting species in OLEDs. The high spin-orbit coupling constants associated with third-row transition metal ions, such as Ir(III) and Pt(II) promotes the emission of light from triplet states that are formed upon charge recombination in an OLED in ratios as high as 3:1 over the singlets. In a device comprising a purely organic emitting material, the emission from the triplet states is forbidden through the spin selection rule $\Delta S=0$, limiting the maximum attainable internal efficiency to 25%. Transition metal-based systems allow this limit to be raised to 100%. Platinum(II) complexes of porphyrins are therefore of interest as OLED emitters. Indeed, the first tests on the use of phosphorescent transition metal complexes as OLED phosphors were carried out with platinum octaethylporphyrin (PtOEP).¹⁹

Recently, we prepared the Pt(II) complex of the tetra-fluorenylporphyrin discussed above, PtTFP, and successfully incorporated it into a simple two-layer OLED device.²⁰ In the present paper, we describe two new platinum complexes of porphyrins based around a TPP core carrying either four or eight fluorene arms, PtTOFP and PtOFP, respectively (Fig. 1). In contrast to the PtTFP system, the fluorenyl units in these new compounds are not directly linked to, or conjugated with, the porphyrin ring. They are separated from the *meso*-phenyl rings via insulating $-\text{OCH}_2-$ linkers. The photophysical properties of the new compounds are investigated in solution, and we also report on the use of these complexes as emitters in simple OLED devices prepared by spin-coating procedures.

2. Results and discussion

2.1. Synthesis

The two free-base porphyrins H₂TOFP and H₂OFP were synthesised as we reported previously.¹⁶ Their platinum(II) complexes were prepared by using a method adapted from that used for the formation of PtTPP.²¹ The platinum salt PtCl₂ was dissolved in benzonitrile and pre-heated at 100 °C for 1 h under an argon atmosphere, followed by addition of the free-base porphyrin and reflux for a further 2 h (Scheme 1). The crude products were purified by chromatography on silica to give the desired compounds PtTOFP and PtOFP as reddish-purple solids, which were characterised by NMR and UV–visible spectroscopy and mass spectrometry. It should be noted that the key difference between H₂OFP and H₂TOFP (and likewise between the two platinum complexes) is in the number of appended fluorenyl groups: eight versus four, respectively. Although the fluorenyl groups are linked to the pendent aryl groups at different positions (*meta* vs *para* in H₂OFP and H₂TOFP, respectively), this differing substitution pattern is expected to have minimal effect on the porphyrin-based electronic excited state, given the expected twist of the pendent aryls groups relative to the porphyrinic plane. Indeed, we have previously found that the corresponding model 4-methoxyphenyl and 3,5-dimethoxyphenyl-substituted porphyrins differ by less than 5 nm in their fluorescence emission maxima.

2.2. Absorption and emission spectra in solution

(i) *Free-base porphyrins.* The UV–visible spectra of the free-base porphyrins exhibit a combination of bands as anticipated from the constituent units. Spectra for H₂TOFP are shown in Fig. 2, and data for both it and for H₂OFP are compiled in Table 1. The intense Soret bands around 420 nm and Q bands around 590 and 650 nm, characteristic of *meso*-tetra-arylporphyrins, are accompanied by

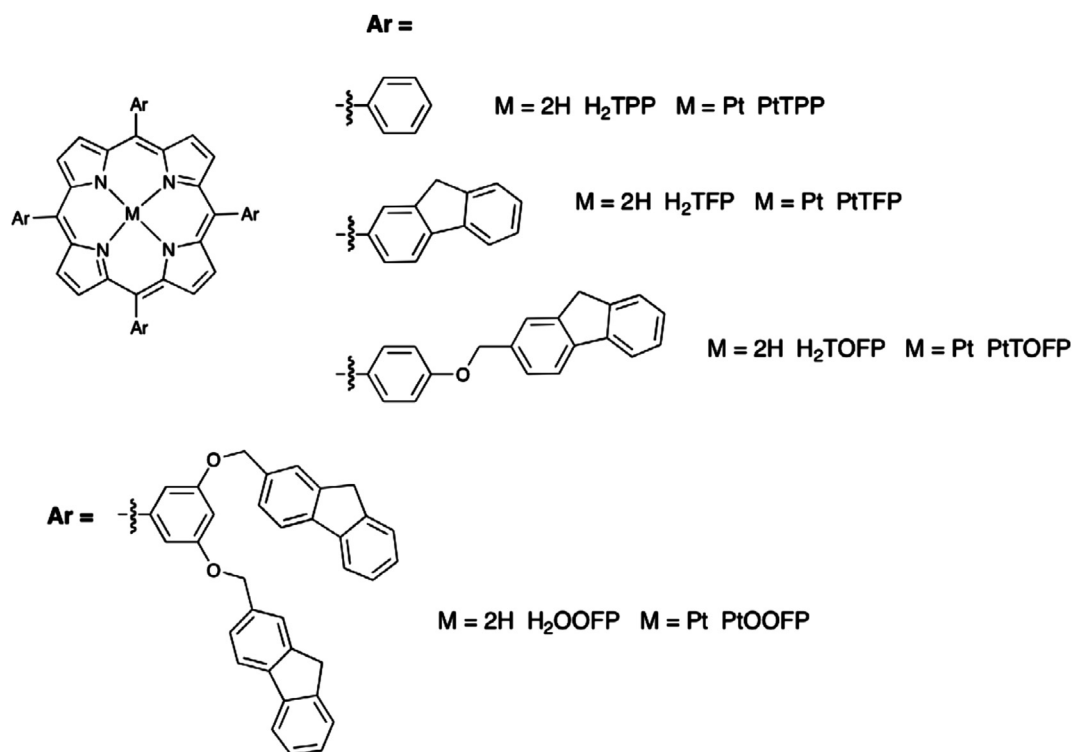


Fig. 1. Structures of the free-base porphyrins and their platinum(II) complexes.

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