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The synthesis of 5,10,15,20-tetraarylporphyrins and their platinum(II) complexes as luminescent oxygen sensing materials

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ABSTRACT

5,10,15,20-tetraarylporphyrins TPP, TNP and TPyP (where TPP = 5,10,15,20-tetraphenylporphyrin, TNP = 5,10,15,20-tetranaphthalporphyrin and TPyP = 5,10,15,20-tetrapyrenyl-porphyrin) and the corresponding Pt(II) complexes were prepared. The photophysical properties of the porphyrin ligands and the Pt(II) complexes were studied using UV–vis absorption and photo-luminescence spectra; the geometry and electronic structure of the ligands and the complexes were studied via DFT/TDDFT calculations. UV–vis absorption and luminescence emission spectra showed that the added aryl groups did not contribute to the π-conjugation system of either the metal-free porphyrins or the Pt(II) complexes and, therefore, all ligands (and complexes) displayed similar photophysical properties. DFT/TDDFT calculations supported the proposed photophysical process and indicated very weak involvement of the aryl appendents in the low-lying electronic excited states. The luminescent oxygen sensing properties of the Pt(II) complexes were studied in solution as well as in polymer films (monitored via emission intensity and lifetime mode). The results demonstrated that in the case of both the pyrenyl and naphthyl groups, the oxygen sensing character of the complexes could be improved (quenching constant $K_{SV} = 0.068$ Torr^{-1} for Pt–TNP vs. $K_{SV} = 0.040$ Torr^{-1} for the parent complex Pt–TPP).

1. Introduction

Luminescent oxygen sensing has attracted much attention owing to its manifold applications in the chemical, biomedical, environmental and clinical sciences [1–9]. The pivotal issue of luminescent oxygen sensing is the selection of luminescent dyes with appropriate photophysical properties which can address various analytical demands, such as emission wavelength, dynamic oxygen partial pressure dynamic range, etc. Luminescent O_2 sensing can be quantitatively described by the Stern–Volmer equation (eq. (1)) [8].

$$\frac{F_0}{F} = \frac{\tau_0}{\tau} = 1 + K_D[Q] \tag{1}$$

where F_0 and τ_0 is the initial luminescent intensity and lifetime of the phosphorescent dyes in an inert atmosphere (such as N_2), F and τ are the luminescent intensity and lifetime, respectively, in the presence of O_2, K_D is the Stern–Volmer quenching constant and [Q] is the concentration of quenchers.

For heterogeneous luminescent O_2 sensing films, however, a modified Stern–Volmer or two-site model is required to study quenching because in "homogenous" polymers, the dyes reside in different microenvironments [7,8,10]. In the two-site model, the O_2-sensitive dyes are treated as two different portions and the fraction of these two portions are defined as f_1 and f_2, respectively ($f_1 + f_2 = 1$), the two portions showing different quenching constants (K_{SV1} and K_{SV2}, Eq. (2)).

$$\frac{I_0}{I} = \frac{1}{\dfrac{f_1}{1 + K_{SV1}p_{O_2}} + \dfrac{f_2}{1 + K_{SV2}p_{O_2}}} \tag{2}$$

The dyes used for luminescent O_2 sensing are usually triplet emitters with long luminescent lifetimes, such as ruthenium bipyridine complexes and the platinum porphyrin complexes [7–9]. These two families of triplet emitters display markedly different lifetimes insofar as Ru(II) complexes are usually <1 μs whereas Pt–porphyrin complexes are generally >50 μs. In order to meet the demand of various O_2 concentration ranges, dyes with a wide range of luminescent lifetimes are needed. However, it is often difficult to tune the luminescent lifetimes of fluorophores or phosphors [8,11].

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Recently, the present authors noticed that the luminescent lifetime of Ru(II) polypyridine complexes can be tuned by ligand modification (via a pyrene unit) to induce new excited states which energetically approximate to the ^{3}MLCT state (metal to ligand charge transfer). Usually an aromatic appendant with a triplet excited state that is energetically close to the ^{3}MLCT state (the emissive state of the Ru complex) is introduced, whereby equilibrium of ^{3}IL (intraligand)–^{3}MLCT can be established. As a result, the ^{3}IL can act as an energy reservoir to funnel energy to the emissive state of ^{3}MLCT and the luminescent lifetime of the Ru complexes can be extended. For example, pyrene has a T_1 state energy of 2.09 eV, the same as the ^{3}MLCT state of Ru(Phen)(bpy)$_2$ (2.09 eV) [12–14]; as a result, the lifetime of a typical Ru(II) complex can be extended to 58.4 μs for a pyrene-containing Ru complex, from 0.4 μs achieved for the parent complex Ru(bpy)$_3$ [12–14]. However, the mechanism of the lifetime extension varies for different compounds and, furthermore, the detailed mechanism of this triplet–triplet energy transfer is unclear. The present authors noticed that no attempts have been made to tune the luminescent lifetimes of Pt porphyrin complexes employing a similar supramolecular photochemical approach [15].

This paper concerns the preparation of 5,10,15,20-tetraarylsubstituted porphyrins (TPP, TNP and TPyP) and their platinum complexes in order to study both their photophysical properties and luminescent O_2 sensing properties. The design rational of the porphyrin ligands and the Pt(II) complexes was to examine the effect of these aromatic groups on the emission properties of the Pt–porphyrin complexes, especially the luminescent lifetimes and so attempt to elucidate the triplet–triplet energy transfer mechanism of the porphyrin dyads. UV–Vis absorption, emission spectra and DFT/TDDFT calculations reveal that electronic communication between the aryl appendants and the porphyrin core is weak, which is supported by experimental findings. The luminescent O_2 sensing properties of the complexes were studied by monitoring the emission intensity and luminescent lifetime variation of the complexes against O_2 partial pressure. These results may prove useful for future design of porphyrin-based triplet emitters.

2. Experimental

2.1. Materials

The chemicals were used as received without further purification. $PtCl_2$ is a product of J&K Chemical LTD., Ltd. O_2 and N_2 of high purity were used in the studies.

The polymer for the fabrication of the O_2 sensing films was poly(aryl ether ketone) (IMPEK-C) (Scheme 1) [16] (Scheme 1). The number-average molecular mass ($\overline{M_n}$) of IMPEK-C is 250 460 g/mol, with a polydispersity index (PDI) of 1.94.

2.2. Characterization

NMR spectra were recorded using a 400 MHz Varian Unity Inova spectrophotometer. Mass spectra were recorded using a Q-TOF Micro MS spectrometer and MALDI micro MX. UV–Vis absorption spectra were obtained using a PerkinElmer Lambda 35 UV–Vis spectrophotometer. Emission spectra were recorded on either a JASCO FP-6500 or a Sanco 970 CRT spectrofluorometer. Fluorescence and phosphorescence quantum yields were measured using 5,10,15,20-tetraphenylporphyrin (TPP) ($\Phi = 0.11$, in benzene) and TPP-Pt ($\Phi = 0.046$, in CH_2Cl_2) as reference [17]. Fluorescence lifetime was measured using the frequency-domain instrument of Chronos 95 145 fluorescence lifetime spectrometer (ISS, Inc., Champaign, IL, USA). The regression of the experimental decay curves was carried out employing VINCI Analysis (BETA 1.6) software. The home-assembled time-domain luminescent lifetime device has been described elsewhere [7].

Typical film preparation was undertaken by dissolving 10.0 mg of IMPEK-C polymer in 0.5 mL acetone to which was added 0.2 mL of Pt porphyrin complex solution in chloroform (1.0×10^{-3} mol dm^{-3}). After thorough mixing, ~0.3 mL of the solution was applied to a silica glass disk (diameter: 1.6 cm) and the solvent was evaporated at room temperature to realize a transparent film [the thickness of the film of TPP–Pt was estimated as 22 μm, according to the mass of the film (5.1 mg) and the density of the polymer (1.14 g cm^{-3})]. Similarly the thickness of the film of TNP–Pt, and TPyP–Pt were estimated as 21 μm and 24 μm, respectively.

2.3. Theoretical calculations

The structure of the porphyrins and the Pt complexes were optimized using density functional theory (DFT) with B3LYP functional and the 6-31G (d)/LanL2DZ basis set. The excited state related calculations were carried out employing time dependent DFT (TD-DFT) with optimized ground state geometry. The 6-31G (d) basis set was employed for C, H, N and the LanL2DZ basis set was used for Pt (II). There were no imaginary frequencies for any of the optimized structures. All calculations were performed with Gaussian 09 [18].

2.4. Synthesis of 5,10,15,20-tetrakisphenylporphyrin (TPP)

The compound was prepared by a reported method [19]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 8H), 8.20 (d, 8H, $J = 8.0$ Hz), 7.79–7.71 (m, 12H), −2.76 (s, 2H). ESI-MS *m*/*z*: calcd for $C_{44}H_{30}N_4$ ([M + H]$^+$) 614.2471, found 615.0590.

2.5. Synthesis of platinum complex of 5,10,15,20-tetrakisphenylporphyrinTPP (Pt–TPP)

$PtCl_2$ (caution:deliquescent; protect from moisture; protect from light; 37.0 mg, 0.14 mmol) was added to 35 mL benzonitrile and the mixture was refluxed for 4 h, after which time, $PtCl_2$ was completely dissolved in benzonitrile and 5,10,15,20-tetraphenylporphyrin (28.0 mg, 0.046 mmol) was added to the solution. The system was refluxed for 2 h. Benzonitrile (35 mL) was removed under reduced pressure and the crude product was purified using column chromatography (silica gel, $CHCl_3$). A red solid was obtained (30.0 mg, 81.7%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 8H), 8.14 (d, 8H, $J = 8.0$ Hz), 7.75–7.72 (m, 12H). HR MALDI-MS *m*/*z*: calcd for $C_{44}H_{28}N_4Pt$ ([M]$^+$) 807.1962, found 807.1922.

2.6. Synthesis of pyrene-1-carbaldehyde [20]

Under an Ar atmosphere, pyrene (6.06 g, 29.8 mmol), dry chloroform (22.5 mL) and *N*,*N*-dimethylformamide (4.6 mL) were mixed and stirred for 10 min. After pyrene had dissolved, $POCl_3$ (caution: Reacts violently with water; incompatible with many metals, alcohols, amines, phenol, DMSO, strong bases; 9.2 g, 60.4 mmol) was added while the reaction mixture was cooled with ice/water. The ensuing solution was stirred at 60 °C for 20 h after which time, the reaction mixture was concentrated by evaporation and then saturated sodium acetate solution was added. The precipitated solid was filtered and washed with water and then dried under vacuum. The crude product was purified by column chromatography (silica gel, petroleum ether: $CH_2Cl_2 = 1:1$, V/V). A yellow powder was obtained (0.64 g, 2.78 mmol, 9.3%). ^{1}H NMR (400 M Hz, $CDCl_3$) δ 7.95–8.04 (m, 2H), 8.11–8.13 (m, 2H), 8.18–8.22 (m, 3H), 8.30 (d, 1H, $J = 8.0$ Hz), 9.27 (d, 1H, $J = 12.0$ Hz), 10.68 (s, 1H). EI-MS *m*/*z*: calcd for $C_{17}H_{11}O$ ([M + H]$^+$) 231.0810, found 231.0723.