Synthesis and photophysical evaluations of β-fused Uracil-Porphyrin derivatives

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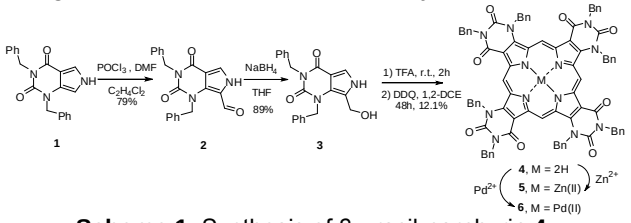
Keywords: Porphyrin, uracyl, photodynamic therapy

INTRODUCTION

Porphyrin systems bearing fused rings have been a subject of intense research, since they constitute a viable approach to obtain new compounds with improved photophysical and photobiological properties.[1,2,3] New β-fused uracil-porphyrin conjugates were synthesized by the tetramerization of uracil-pyrroles under acidic conditions, followed by oxidation. Complexation effects were also studied as well as aggregation in solution. Preliminary photophysical experiments were also performed in order to evaluate the potential of these new compounds for use in PDT, materials science or as fluorescent markers.

RESULTS AND DISCUSSION

Pyrrole **2** was prepared in 79% yield from the compound **1**[4] according to the Vilsmeier-Haack methodology (Scheme 1). Reduction of **2** with $NaBH_4$ in THF provided compound **3** (89 % yield). Several attempts to condense pyrrole **3** to porphyrin **4** were carried out with different acid catalysts and oxidation conditions. Success was finally obtained using TFA and then DDQ in 12.1% yield.



Scheme 1. Synthesis of β-uracil-porphyrin **4**.

The synthesis of a novel class of β-fused uracil-porphyrins prompted us to explore the facility of these macrocycles to complex different metals such as Zn(II) and Pd(II). Porphyrin **4** was reacted with $Zn(OAc)_2$ and $Pd(OAc)_2$ and the corresponding porphyrinic complexes **5** and **6** were obtained in 95 and 93 % yields, respectively. All compounds were purified, and the structures confirmed by ^1H and ^{13}C NMR, HRMS and UV/Vis. Neither photobleaching decays nor aggregation were observed in THF solutions (1-120 μM) for all three porphyrin derivatives. Studies on singlet oxygen generation (Figure 1) showed that Pd(II)-porphyrin **6** was more effective when compared with the corresponding Zn(II)-porphyrin **5** and the metal free porphyrin **4**. The fluorescence emission quantum yields (Table 1) were also calculated for all three porphyrins.

Figure 1. DPBF absorbance decay at 410 nm in the presence of different photosensitizers.

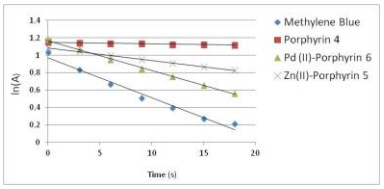


Table 1. The fluorescence quantum yields (Φf) of porphyrins **4**, **5** and **6**.

Compound	Fluorescence λ_{max}[nm] Q(0-0)	Q(0-1)	Φf
4	671	735	0.150
5	630	671	0.006
6	672	729	0.070

CONCLUSION

The synthesis of β-fused uracil-porphyrins starting from a functionalized pyrrole derivative was successfully accomplished. The new porphyrin derivatives demonstrated their potential in porphyrin chemistry, considering their photophysical parameters and related potential applications.

ACKNOWLEDGEMENTS

The authors thank FAPESP (2013/06532-4, 2012/04964-1, 2011/13993-2, 2011/17177-5), CNPq and CAPES for financial support and scholarships.

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