

Synthesis and characterization of tin(II) 5,10,15,20-tetrakis(4-phenylbenzoate)porphyrin and tin(II) 5,10,15,20-tetrakis(4-[1,1'-biphenyl]-4ylbenzoate)porphyrin

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Abstract

Herein we reported the synthesis and characterization of a new type of metalloporphyrins, tin(II)5,10,15,20-tetrakis(4-phenylbenzoate)porphyrin and tin(II)5,10,15,20-tetrakis(4-[1,1'-biphenyl]-4ylbenzoate)porphyrin. We identified the products by FT-IR and UV-Vis techniques. The photocatalytic degradation of methylene blue under visible light irradiation is investigated by the photocatalysts sensitized with 5, 10, 15, 20 tetrakis(4-carboxyphenyl)porphyrin We investigated the effect of functional groups phenol and 1, 1'-biphenyl – 4- ol in photocatalytic degradation of methylene blue under visible light irradiation in the same conditions.

Keywords: Photocatalyst, Porphyrin, Light irradiation, Methylene blue

1. Introduction

Porphyrins are very important structural components in the life on our planet, and also the essential components in the chemistry processes [1]. The studies of porphyrins and metalloporphyrins have had great concern during the past years in particular part of chemistry [2]. Due to their broad applications in light absorption and photoelectric activity, porphyrin derivatives are a favorable photoactive agent for various applications, such as solar energy conversion, medical imaging, photocatalytic activity and photocatalytic processes [3]. It should be noted that photocatalysis is a low-cost intermittent method for the purification of contaminated water compared with other technologies [4]. Recently, there have been several attempts to enhance visible photocatalytic activity of metalloporphyrins. Metalloporphyrins with different functional groups (–COOH, –

OH, etc.) in the porphyrin structure have been utilized as photocatalysts for pollutant photodegradation [5].

In the present work, synthesis of new kinds of metalloporphyrins have been reported and then photocatalytic degradation of methylene blue catalyzed by these new structural metalloporphyrins have been investigated.

2. Experimental processes

2.1. Synthesis of porphyrin 3,4

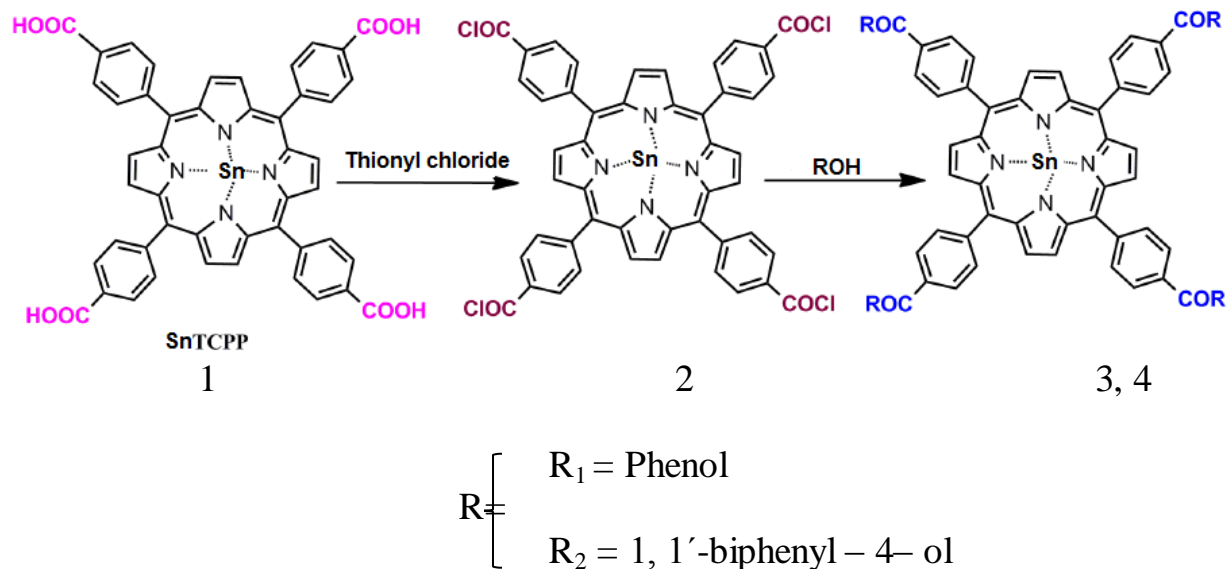
Porphyrin derivatives were prepared according to the literature [6]. First SnTCPP (0.102 g) was synthesized and dissolved in 10mL THF, and then thionylchloride (1 mL) was slowly added into solution to start reaction under stirring at 70 °C for 2h (scheme. 1). The excess thionylchloride must be removed. Then phenol or 1, 1'-biphenyl – 4- ol (0.0434 g) was added to the solution and the mixture was stirred and refluxed for 8h, then THF in the crude product was evaporated with a rotary evaporator at 50 °C and thus the corresponding products (5,10,15,20-tetrakis(4-phenylbenzoate)porphyrin and 5,10,15,20-tetrakis(4-[1,1'-biphenyl]-4yl benzoate)porphyrin) were obtained.

2.2. Photocatalytic activity

The process of photocatalytic degradation of organic dyes methylene blue with concentration 10 ppm (10 ml) in the presence of photocatalysts (1 gL⁻¹) were evaluated for 3h and done with Shimadzu UV-1700 spectrophotometer.

3. Result and Discussion

In order to explain synthesis of new of metalloporphyrins, we chose a reaction (Scheme 1) to show that the effect of functional groups in metalloporphyrins structure can be efficient in photocatalytic degradation [6].



Scheme 1. Synthesis of new porphyrins derivatives

3.1. Fourier transforms infrared spectroscopy

FT-IR spectra of tin(II) 5,10,15,20-tetrakis(4-phenylbenzoate)porphyrin and tin(II) 5,10,15,20-tetrakis(4-[1,1'-biphenyl]-4ylbenzoate)porphyrin measured in the range of 400–4000 cm^{-1} show in Fig. 1. The absorption peak at 1735 cm^{-1} and the double peak appeared at 1263 cm^{-1} were related to the C=O for ester bond and carbon-oxygen (C-O) single bond vibration, respectively, which proved the formation of covalent bonding between functional groups and metalloporphyrin by FT-IR spectra. As show in Fig. 1 the peak for COOH in SnTCPP has been eliminated in these new Structures.

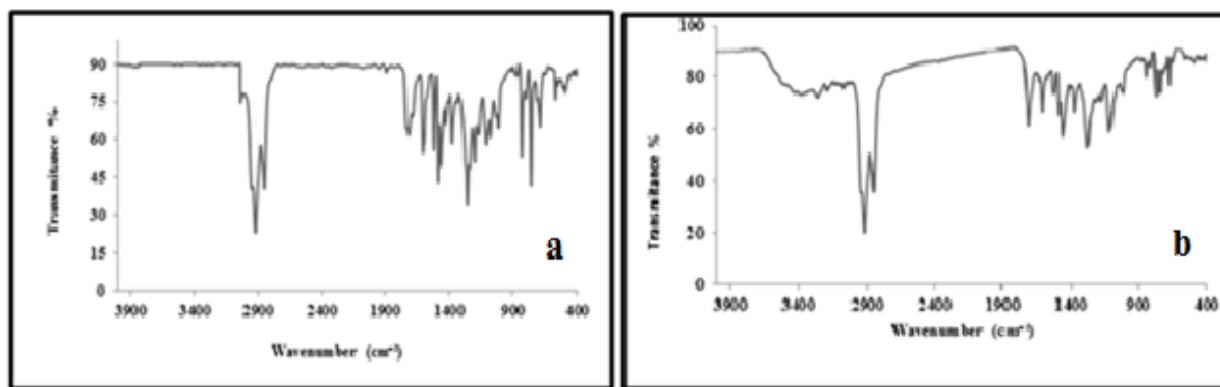


Fig. 1. The FT-IR spectrum of the synthesized a: tin(II) 5,10,15,20-tetrakis(4-phenylbenzoate)porphyrin b: tin(II) 5,10,15,20-tetrakis(4-[1,1'-biphenyl]-4ylbenzoate)porphyrin.

3. 2. UV-Vis spectroscopy

The absorption spectra of two porphyrin compounds were recorded in CHCl_3 (Fig. 2). The absorption spectrum of tin(II) 5,10,15,20-tetrakis(4-phenylbenzoate)porphyrin and exhibit a Soret and Q bands at 433, 565, 604 nm tin(II) 5,10,15,20-tetrakis(4-[1,1'-biphenyl]-4ylbenzoate)porphyrin exhibit a Soret and Q bands at 429, 561, 604 nm, respectively. The presence of soret band and two Q band has seen in Fig. 2.

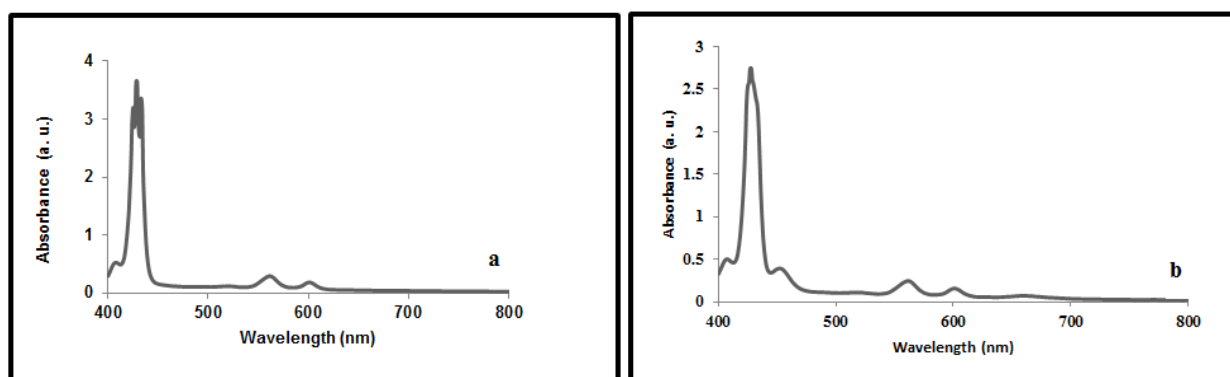


Fig. 2. UV-Vis of the synthesized a: tin(II) 5,10,15,20-tetrakis(4-phenylbenzoate)porphyrin b: tin(II) 5,10,15,20-tetrakis(4-[1,1'-biphenyl]-4ylbenzoate)porphyrin.

3. 3. Photocatalytic degradation of methylene blue

The photocatalytic activities of two kinds of catalysts were investigated by the degradation of methylene blue in aqueous solution under light irradiation. The characteristic absorption of MB at 664 nm was chosen to monitor the photocatalytic degradation process. As the Fig. 3 shows the photodegradation of these photocatalysts under visible light irradiation were higher than blank sample of MB. The Percent degradation observed for tin(II) 5,10,15,20-tetrakis(4-phenylbenzoate)porphyrin was about 40% and for tin(II) 5,10,15,20-tetrakis(4-[1,1'-biphenyl]-4ylbenzoate)porphyrin was 53%. Therefore as we seen for 5,10,15,20-tetrakis(4-[1,1'-biphenyl]-4ylbenzoate)porphyrin is better than tin(II) 5,10,15,20-tetrakis(4-phenylbenzoate)porphyrin because the π system extended.

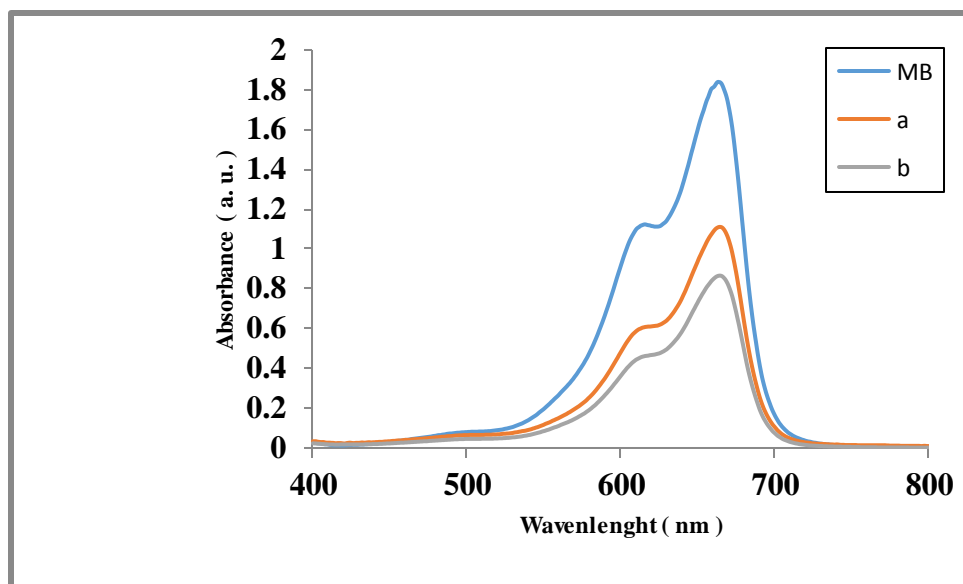


Fig. 3. The absorption spectra of the MB solution: in presence of a: (tin(II) 5,10,15,20-tetrakis(4-phenylbenzoate)porphyrin) and b: (tin(II) 5,10,15,20-tetrakis(4-[1,1'-biphenyl]-4-ylbenzoate)porphyrin) catalyst under visible light irradiation.

4. Conclusion

Porphyrins are stable molecules with a macrocyclic conjugated system that increase the photodegradation. We synthesis two kind of porphyrins with different functional groups and the conjugated system would be spread. The photocatalytic degradation of MB by these porphyrins was studied under visible light irradiation. The obtained results indicate that the photodegradation of methylene blue was affected by the initial MB concentration and type photocatalyst. The photocatalytic activity of 5,10,15,20-tetrakis(4-[1,1' biphenyl]-4-ylbenzoate)porphyrin was higher than photodegradation tin(II) 5,10,15,20-tetrakis(4-phenylbenzoate) porphyrin.

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References

- [1] B. J. Littler, Y. Ciringh, j. S. Lindsey, *J. Org. Chem*, **1999**, 64, 2864.

- [2] D. Li, W. Dong, S. Sun, Z. Shi, S. Feng, *J. Phys. Chem. C*, **2008**, 112, 14878.
- [3] H. Noriko, A. Yutaka, *Energ. Fuel*, **2003**, 17, 1641.
- [4] W. Sun, J. Li, X. Lu, F. Zhang, *Res. Chem. Intermed.*, **2013**, 39, 1447.
- [5] W. Y. Sun, J. Li, G. Y. Yao, F. X. Zhang, J. L. Wang, *Appl. Surf. Sci.*, **2011**, 258, 940.
- [6] C. Zhang, X. Li, S. Kang, L. Qin, G. Li, J. Mu, *Chem. Commun.*, **2014**, 50, 9064.