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Functionalization of A_3B-type porphyrin with Fe_3O_4 MNPs. Supramolecular assemblies, gas sensor and catalytic applications

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ABSTRACT

The aim of this study was to synthesize different multifunctional materials containing 5-(4-carboxyphenyl)-5,10,15-tris(4-phenoxyphenyl)-porphyrin and iron oxide magnetic nanoparticles (MNPs). Besides, a new type of polymeric material comprising the same porphyrin and a polysaccharide, *k*-carrageenan, was also developed. All synthesized materials were characterized by FT-IR, TEM, XRD, ^{1}H NMR, HPLC, UV–vis and fluorescence spectroscopy and tested as catalysts for the Knoevenagel condensation of aldehydes at room temperature. The best performing porphyrin–based catalyst, which also contain MNPs and a silica linker, was additionally tested for its capacity to detect CO_2. All synthesized materials tested as catalysts for the above mentioned reaction proved comparable efficiency providing the desired adducts in short reaction times and with high yields. The novel designed catalytic systems met the sustainable chemistry requirements because they can be recovered and several times reused.

1. Introduction

One of the major demands of sustainable chemistry regarding catalysis is that the novel designed catalytic systems should be finally recovered in high purity and reused in the process. For this reason, magnetic nanoparticles, which present excellent properties as heterogeneous catalytic supports, have already been used for different porphyrinic compounds immobilization [1]. These types of organic-inorganic hybrid nanomaterials have been widely used in recent years, particularly in biomedicine, as carriers being able to easy penetrate the cell of living tissues [2–4].

Studies on synthetic porphyrins have increased significantly in recent years due to the many versatile optoelectronic and redox properties which makes them suitable candidates for a wide range of technical [5] and medical applications [6] and also for their supramolecular chemistry [7]. For this reason, they have been used as photosensitizers or imaging agents in medicinal chemistry [8–11], as sensitive materials in detection devices [12,13] and also as catalysts [14–16]. Hybrid materials comprising of porphyrins and a polymeric or an inorganic nanomaterial matrix have also drawn a lot of attention because the combined characteristics of the individual components can enhance a desired optical, electrical or redox property of the overall material [17–23].

Herein we designed three different multifunctional hybrid nanomaterials containing 5-(4-carboxyphenyl)-5,10,15-tris(4-phenoxyphenyl)-porphyrin (***COOH-POPP***), that are tested as catalysts for the Knoevenagel condensation of aldehydes at room temperature and for their ability to detect and monitor CO_2 in wet environment. Porphyrin based materials have previously been reported for selective oxidation reactions, as well as for the Knoevenagel condensation reaction [24], proving to be very efficient catalysts for these transformations. However, to the best of our knowledge, the use of porphyrin functionalized magnetic nanoparticles for such catalytic systems has not been studied so far. Even more, the materials reported herein possess several advantages compared to previous reports [14], such as good activity combined with short reaction times and mild conditions and easy recycling of the catalyst by simple magnetic decantation. Furthermore, one of the as-designed hybrid materials was also tested as optical sensor for CO2 detection, proving to be multifunctional.

The best results were obtained for the material containing the functionalized porphyrin, ***Fe_3O_4 MNPs*** and 1,2-bis(triethoxysilyl)ethane (***BTSE***) as silica linker (Fig. 1).

The increased interest in novel materials tailored to capture and convert CO_2 was the determining factor for studying these materials for gas detection as well. Porphyrins are used in metal–organic hybrids for capturing and CO_2 detection because of the presence of

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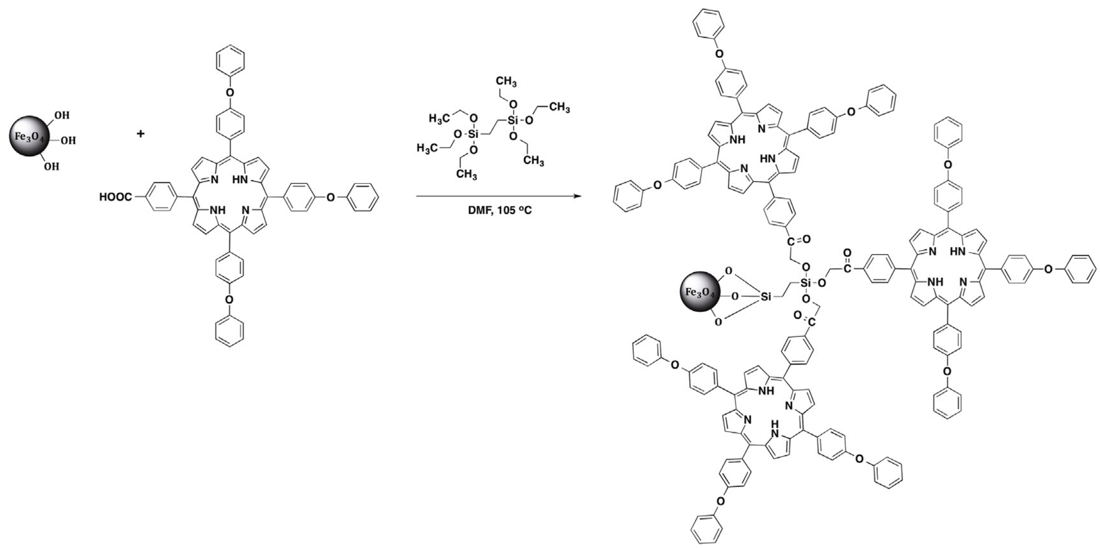

Fig. 1. Functionalization of magnetite nanoparticles (***MNPs***) with 1,2-bis(triethoxysilyl)ethane (***BTSE***) and 5-(4-carboxyphenyl)-5,10,15-tris(4-phenoxyphenyl)-porphyrin (***COOH-POPP***).

the two basic nitrogen atoms into the internal cavity, which facilitate strong interactions with CO_2, the same as those reported in human physiology. [25]

2. Experimental section

2.1. Reagents

2.1.1. 5-(4-carboxyphenyl)-5,10,15-tris(4-phenoxyphenyl)-porphyrin (COOH-POPP) synthesis

Although the most used method to obtain carboxylic acid porphyrins is through hydrolysis of ester type Zn-metalloporphyrins [26], the synthesis of A_3B unsymmetrical mixed substituted 5-(4-carboxyphenyl)-5,10,15-tris(4-phenoxyphenyl)-porphyrin was based on Adler -Longo multicomponent reaction [8] consisting in the condensation reaction of pyrrole and the two different substituted benzaldehydes 4-carboxylmethylbenzaldehyde and 4-phenoxybenzaldehyde in a particular ratio of 4:3:1, as previously reported [27]

2.1.2. Synthesis of Fe_3O_4 MNPs

Iron oxide magnetic nanoparticles were synthesized according to a previously reported method, by thermal decomposition of $Fe(acac)_3$ in the presence of oleic acid and oleylamine as surfactants. [28]

The syntheses of all conjugated materials: ***c1, c2, c3*** (structures in Fig. 2) were also done in accordance with the previous reported methods. [29,30] (see supporting information for detailed procedure).

All synthesized materials were fully characterized by FT-IR, TEM, AFM, XRD, 1H NMR, HPLC, UV–vis spectroscopy and elemental analysis (see supporting information for details).

2.1.3. General procedure for the Knoevenagel reaction

The corresponding aldehyde (0.2 mmol), malonitrile (0.3 mmol), and catalyst (2 mol% c1/c2/c3) were mixed and stirred at room tem-

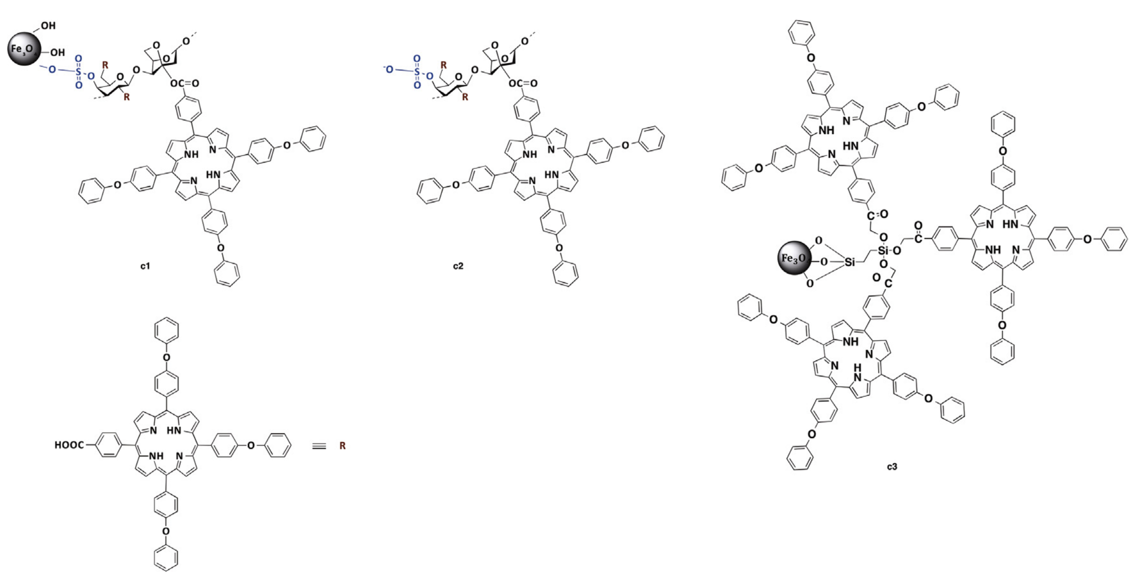

Fig. 2. Structures of the synthesized porphyrin-based materials.

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