

New Magnetic Phosphonate Organic-inorganic Hybrid Materials

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The synthesis and the characterization of new phosphonate organic-inorganic hybrid materials obtained by the incorporation of the monoazoic acid dyes (C1, C2, C3, C4) into a titanium dioxide phosphonate matrix is described in this study. The hybrid materials were obtained by simple sol-gel method and their morphology proved to be different depending on Ti/P ratio and of molecular structure of the incorporated dye. Furthermore, iron oxide magnetic nanoparticles (MNPs) were also incorporated in the above-mentioned matrix. The presence of phosphorus could be observed in all organic-inorganic hybrid materials. The obtained hybrid materials present good mechanical, chemical and optical properties and for these reasons they are very attractive candidates for different applications in fields like environmental chemistry or photocatalysis. Moreover, the materials containing MNPs are specially intriguing due to their advantage of easy separation from the reaction media by simple magnetic decantation increasing thus the reusability of this type of system.

Keywords: magnetic nanoparticles, monoazoic acid dyes, sol-gel, phosphonate organic-inorganic hybrid materials

Nanotechnology is a research area with growing interest, due to its applications ranging from information technologies to medicine [1]. In recent years, nanoscale materials including nanoparticles, nanofibers, and nanotubes have been the centre of research, in many fields. Moreover the use of magnetic nanomaterials has drawn a lot of attention due their unique characteristics. Their electronic, optical, and magnetic properties coupled with their specific dimensions make them very attractive candidates for different applications in environmental chemistry, catalysis and biomedicine [2].

The interest for the synthesis of new organic-inorganic hybrid materials has been increased in the last decade, because of their strong covalent bond between the organic and inorganic components, by using coupling molecules [3-5]. It is well known that metal-carbon bonds are not stable enough in regards to hydrolysis and for this reason coupling molecules are required in order to link the organic group to the inorganic network [6]. Moreover, many organic-inorganic hybrid materials reported in the literature show excellent characteristics in terms of mechanical, chemical and optical properties [7-10]. Recently, several metal oxide/phosphonate hybrid materials have been reported. The use of organophosphorus acids as the coupling molecules increases significantly the stability towards hydrolysis [11]. The non-hydrolytic sol-gel process offers a water-free route, in the first step, to organic-inorganic hybrids by reaction of metal precursor with an oxygen donor. The work published in [12] describes how this new method allows the obtaining of organic-inorganic hybrids. The non-hydrolytic sol-gel process could involve the reaction of phosphonic acid with an oxygen donor, leading to the formation of an inorganic oxide. The use of non-hydrolytic sol-gel chemistry for the synthesis of organic-inorganic hybrids is still in the beginning, in comparison with the progress of hybrid synthesis using hydrolytic sol-gel chemistry. Hay and Raval

reported the use of the non-hydrolytic sol-gel chemistry route to synthesize hybrids. The importance of these compounds for future studies was also proved in their work. These hybrids have a lot of potential applications [12].

One of the main applications of organic-inorganic hybrid materials phosphorus containing, is their use as flame retardants [13,14]. A new ethylene vinyl acetate-based hybrid material containing phosphorus has been developed by Bonnet et al. [13]. Flame retardancy in ethylene vinyl acetate copolymer based materials has been described in the literature [15,16]. Phosphorus based flame retardants [13,14] have shown high efficiency of fire retardance, depending on the type of the used phosphorus compound [13].

The preparation of new organic-inorganic hybrid compounds is of great interest nowadays, especially because they have properties of multifunctional materials [17]. This class of organic-inorganic hybrid compounds includes different types of functional hybrids, coordination complexes, donor-acceptor compounds, and so on [18]. Bauer et al. synthesized organic-inorganic hybrid materials by the reaction of a ligand with metal ions. They obtained a new hybrid organic-inorganic Ni(II) diphosphonate, prepared by the reaction of NiCl₂ with a diphosphonate ligand [18].

In our paper we report the development of new titanium dioxide/ organophosphorus materials. TiO₂ is a well known material for its multiple applications such as solar energy conversion, photo-catalysis, gas sensors, paint, UV protection and photovoltaic applications [19]. For this reason we believe that the hybrid materials containing TiO₂ and an organic phosphonic compound, N,N-bis (phosphonomethyl)glycine, and monoazoic acid dyes could present excellent properties for the areas mentioned above. Moreover, the functionalization of these materials with iron oxide magnetic nanoparticles was also studied.

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This leads to the development of new magnetic hybrid materials that combine the properties of the components, thus allowing their use in multiple research or industrial areas.

Experimental part

Methods

Unless otherwise stated, all commercial reagents were used as received without any purification and all reactions were carried out directly under open air. The monoazoic acid dyes (C1, C2, C3, C4), more exactly their sodium salts, were synthesized in our laboratory.

Elemental analyses were performed on a CHNS 932 micro-analyzer. SEM and EDX characterizations were made using a Jeol JSM 6400 Scanning Microscope coupled with an X ray microanalyzer EXL II System Link Analytical with a detector of 133eV. The samples were coated with a layer of gold prior to use. TEM images were recorded using a JEOL JEM 1011 microscope equipped with a lanthanum hexaboride filament, operated at an acceleration voltage of 100kV.

General procedure for the synthesis of the hybrid materials TiP01-TiP03 and TiPC1-TiPC4

To a solution containing 3g *N,N*-bis-(phosphonomethyl)-glycine in 10mL water, 14mL tetraethyl-orthotitanate was added and the mixture was stirred for 3 h at room temperature.

After this time different monoazoic acid dyes, 0.05g, were incorporated into the above-mentioned material resulting into four different hybrid materials.

The reaction time was different depending on the Ti/P ratio used. This ratio was varied between the range 0.5-3.0. The best results, in terms of gelification, were obtained using a ratio Ti/P= 3.0. Because of this, for obtaining monoazoic acid dyes incorporated in phosphonate gels, we used in the present work the ratio Ti/P= 3.0.

TiP01-TiP03 - phosphonate gels (molar ratios Ti/P01= 0.5 ; Ti/P02= 1.0 ; Ti/P03= 3.0)

TiC1-TiC4 - monoazoic acid dyes incorporated in phosphonate gels (quantitatively ratios Ti/C1= 2.258 x 10⁴ ; Ti/C2= 2.258 x 10⁴ ; Ti/C3= 2.136 x 10⁴ ; Ti/C4= 2.248 x 10⁴)

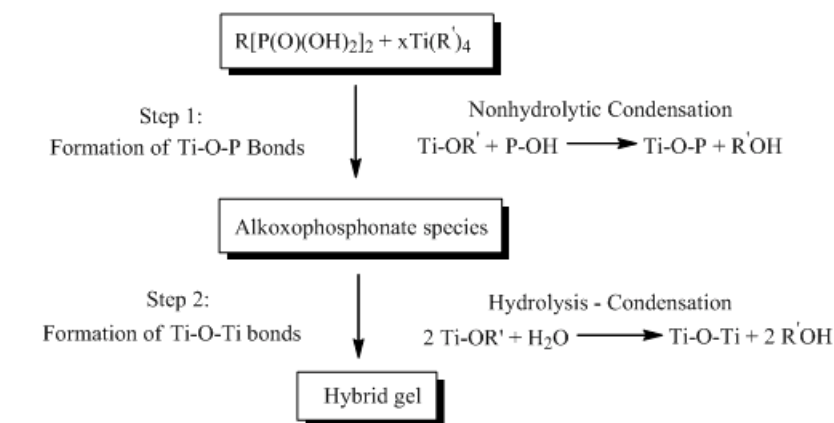
General procedure for the synthesis of the magnetic hybrid materials TiP03≡MNPs and TiPC4≡MNPs

To a solution containing 50mg TiP03 and TiPC4, respectively in 3mL toluene 50mg of iron oxide magnetic nanoparticles were added. The obtained mixtures were stirred at room temperature for 24h. After this time the magnetic hybrid materials were removed from the reaction media by magnetic decantation, washed several times with methanol and acetone and then dried in vacuo.

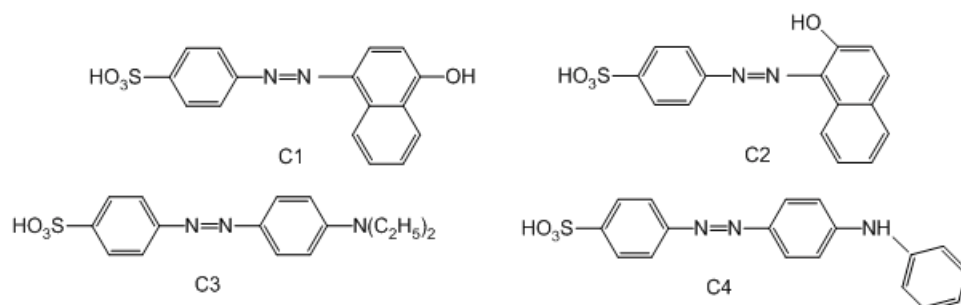
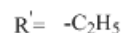
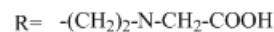
Results and discussions

The organic-inorganic hybrid materials containing titanium dioxide and the phosphonate were synthesized via a simple so-gel method (scheme 1). The monoazoic acid dyes were introduced in the above synthesized material as it is shown by scheme 2. The iron oxide MNPs were prepared according to a previously reported procedure [20], by the thermal decomposition of Fe(acac)₃ in the presence of oleylamine and oleic acid as surfactants. In this manner spherical, well dispersed MNPs were obtained, as it can be observed in the transmission electron microscopy (TEM) images. The average diameter of the nanoparticles is around 5nm.

In figure 1 is presented the IR spectrum of the hybrid material with the ratio Ti/P= 3.0. The bands in the regions of 1038cm⁻¹, 1380cm⁻¹ and 1625cm⁻¹, were attributed to stretching and vibrations of the Ti-O-Ti group, 3019cm⁻¹ and at 3732cm⁻¹ were attributed for Ti-O-P indicating the formation of the inorganic matrix. The band ascribed to superficial Ti-O vibrations appeared at 601cm⁻¹ and 455cm⁻¹. Also the IR spectrum of the phosphonate inorganic-organic hybrid material shows bands at: ν^(P-O) = 1038cm⁻¹, ν^(P=O) = 1122-1380cm⁻¹, ν^(OH) = 3732cm⁻¹, ν^(OH) = 3019cm⁻¹, ν^(C-O) = 1380cm⁻¹, ν^(C=O) = 1625cm⁻¹. These



Scheme 1. Working phases for phosphonate organic-inorganic hybrids synthesis



Scheme 2. The structures of the used monoazoic acid dyes

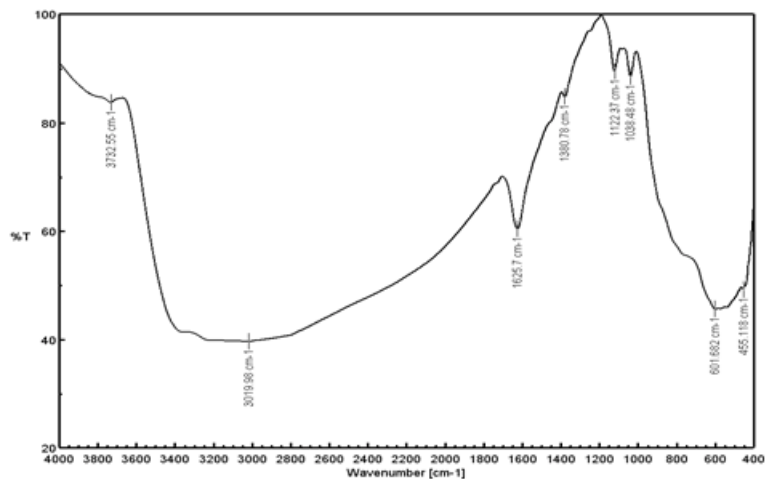


Fig. 1. IR spectra of the phosphonate organic-inorganic hybrid material at ratio Ti/P= 3.0

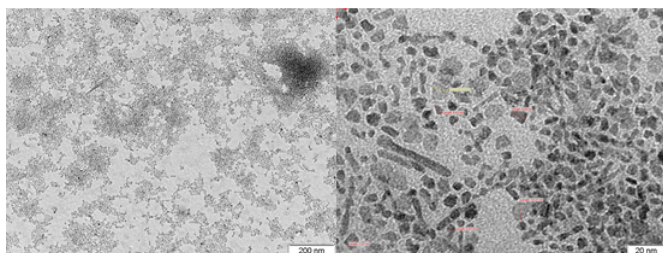


Fig. 2. TEM images of hybrid materials TiP03

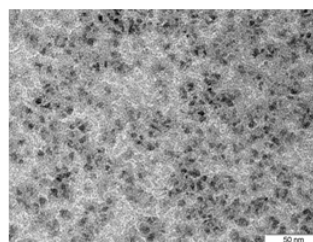


Fig. 3. TEM image of hybrid material TiPC4

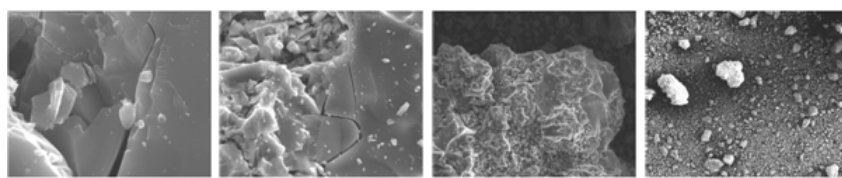


Fig. 4. SEM images obtained for the compound TiP01 at different resolutions

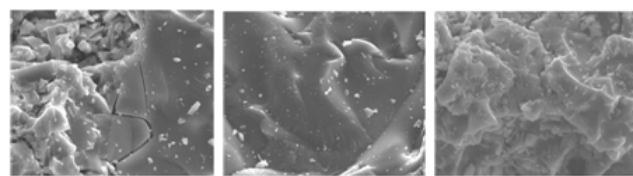


Fig. 5. SEM images obtained for TiP01 ÷ TiP03, at 20μm

results confirm the presence of the organic-inorganic hybrid materials.

In order to check the size, shape and dispersity of the above synthesized hybrid materials, transmission electron microscopy was used. Based on figure 2 and it can be observed that the inorganic part of the material appears under the form of nanoparticles varying in shape as well as in size, the latter ranging from 5 to 10nm.

There is an obvious difference in shape between the material that does not contain the dye (TiP3) and the one which has incorporated the dye (TiPC4) that can be observed in figure 3. The presence of an extra organic molecule in the material affects the shape and distribution of the nanoparticles in the matrix.

Unfortunately just by TEM the organic part of the material can not be observed, so for this reason scanning electron

microscopy was also used to characterize the synthesised hybrid organic-inorganic materials. This method reveals information about the sample including external morphology or texture, as well as chemical composition and crystalline structure. The images were made at different resolutions, from 5μm to 1mm.

SEM images obtained for the compound TiP01, at different resolutions (5, 20, 100μm and 1mm) are presented in figure 4. SEM images obtained for all compounds described in this paper (TiP01 ÷ TiP03, TiPC1 ÷ TiPC4), at 20μm, are presented in figures 3 and 4.

SEM analysis of TiP01, TiP02 and TiP03 showed similar structures, starting from few microns, up to the order of millimeters. For the compound TiP01 the aggregates could be up to 500μm in size, but for TiP02 and TiP03 the maximum size observed was around 200μm. In the case of TiP03, as showed in figure 5, the aggregates presented a surface more fragmented than TiP01 and TiP02. With other words, the microstructures formed at the aggregates surface are more visible for TiP03.

The compounds TiPC1, TiPC2 and TiPC3 present similar morphology with that of TiP01, TiP02 and TiP03, but the aggregates are smaller than those in the case of previous compounds (fig. 6). The aggregates are for TiPC1 and TiPC2 up to 40-50μm and for TiPC3 material up to 100μm.

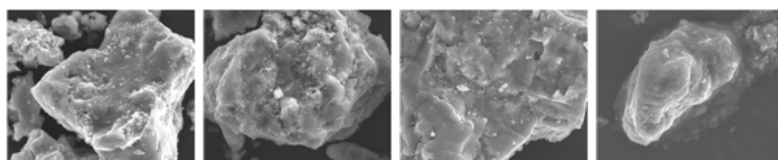


Fig. 6. SEM images obtained for TiPC1 ÷ TiPC4, at 20 μm

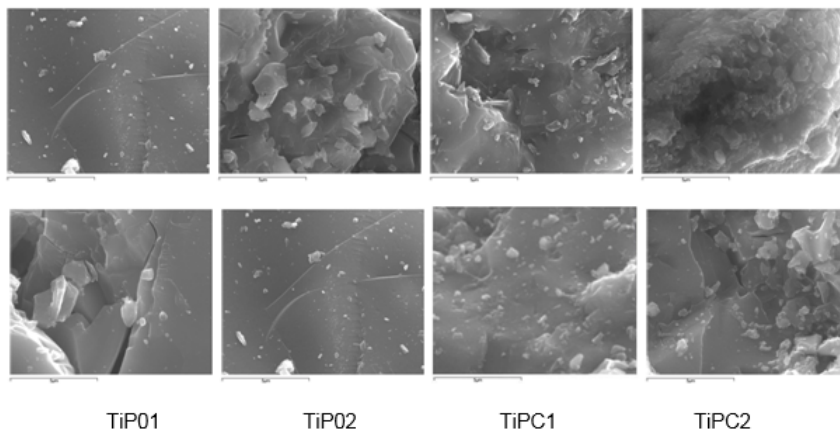


Fig. 7. Comparison of SEM images obtained for TiPC4, at resolution of 5 μm , with the images of other compounds

Fig. 8. Comparison of few of the materials surface, at resolution of 5 μm

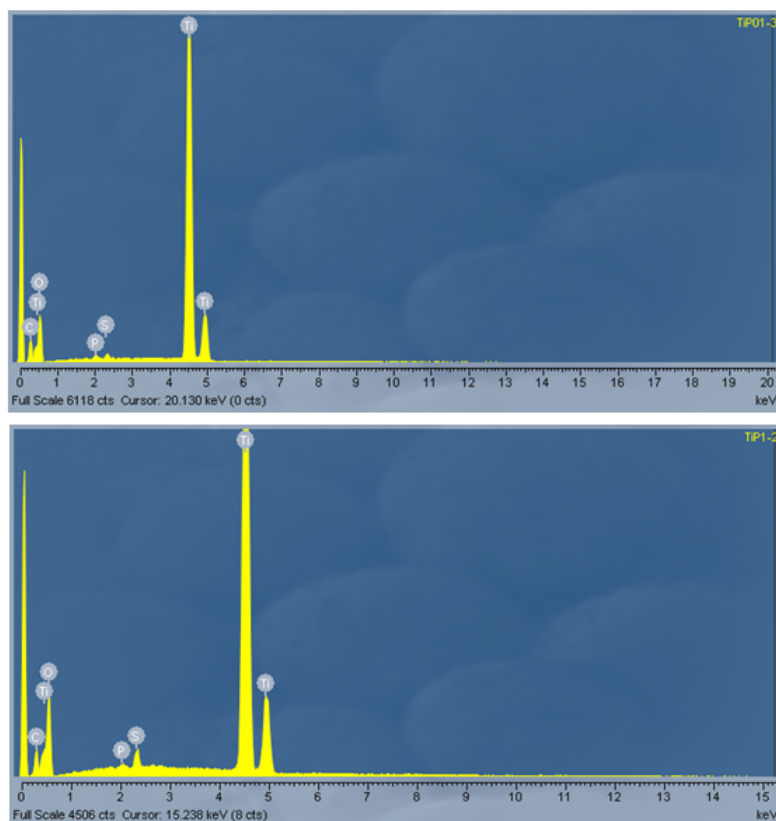


Fig. 9a. EDX spectra of TiP03

Fig. 9b. EDX spectra of TiPC4

The compound TiPC4 showed different morphology and different structures, when compared with the other materials studied here. In size, the aggregates of TiPC4 are from 10 to 60-70 μm .

However, the structures formed by TiPC4 are not so compact like the aggregates formed by the other materials. The shape of the aggregates in this case is also much different. If we look to the SEM images obtained with a resolution of 5 μm (fig. 7) we can observe that TiPC4 is very fragmented at the surface compare to previous materials studied here and also it shows many small circular structures at the surface.

TiP02 is the most compact at the surface, and in the same time TiP03 and TiPC3 are more fragmented. TiP01 has a surface almost the same compact as TiP02, but with small fragmentations (fig. 8). According to chemical structures is expected that those hybrid materials to have similar morphology. The fact that TiPC4 is so different than the other compounds can be explained by its molecular structure.

Energy dispersive X-ray spectroscopy was used to analyze the elemental composition of the organic-inorganic hybrid materials. In the case of the samples TiP01, TiP02 and TiP03, the ones which do not contain the

organic dye, the presence of phosphorus can be observed in all cases.

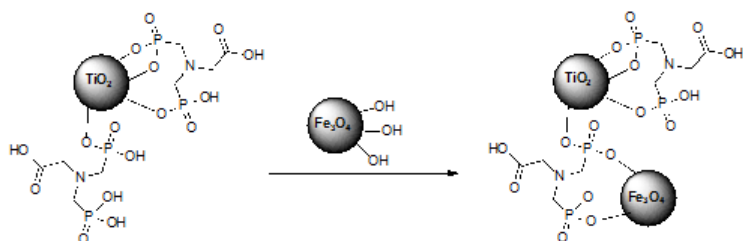
The presence of the very small amount of sulfur in the sample (fig. 9a) can be explained by the fact that many elements can have overlapping peaks. In this case the peaks of sulfur and phosphorus can be confused since they are detected at very similar energies.

In the case of the samples TiPC1, TiPC2, TiPC3 and TiPC4, the ones which have incorporated the organic dyes, the presence of phosphorus can also be observed.

The dyes incorporated into the organic-inorganic hybrid materials are, as mentioned above, the sodium salts of the specific sulfonic monoazoic acids, so for this reason in these samples we can observe the presence of sodium and sulfur in the measured samples (fig. 9b). In this case it should be mentioned that the presence of silicon also observed in the spectra is due to the detector. The EDX instrument operates using a silicon detector which sometimes creates *false peaks* that can be confused with other peaks in the sample.

The presence of phosphorus can be thus observed in all organic-inorganic hybrid materials.

The magnetic organic-inorganic hybrid materials were easily synthesized by the incorporation of the iron oxide MNPs into the hybrid material containing titanium dioxide



Scheme 3. Synthesis of the magnetic organic-inorganic hybrid material

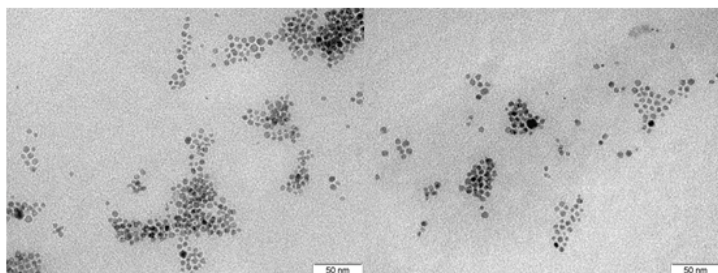


Fig. 10. TEM images of the magnetic hybrid materials
a) TiP03=MNPs and b) TiPC4=MNPs

and the phosphonate. We believe this is due to the free OH units present at the surface of the MNPs, which also make this material very easy to be functionalized.

Based on the TEM images (fig. 10) obtained we could observe that the nanoparticles do not aggregate or form clusters, but they are fairly well dispersed, forming a mixture of magnetic-nonmagnetic materials in which the two types of nanoparticles are bound together by means of the organic component present in the matrix, as shown in scheme 3.

The presence of the organic part in the material could be confirmed by elemental analysis. The percentage of nitrogen, 0.36% in the case of TiP03=MNPs and 0.62% in the case of TiPC4=MNPs clearly show that the organic component is present in the matrix.

Conclusions

We report the synthesis of new phosphonate organic-inorganic hybrid materials obtained by sol-gel method, using different Ti/P ratios and also by the incorporation of four different monoazoic acid dyes. Also we also report the functionalisation of the synthesized material with iron oxide magnetic nanoparticles obtaining thus a new magnetic hybrid material. All the materials were fully characterised in order to confirm the presence of the organic-inorganic components in the matrix. This has been done using FT-IR, SEM and EDX, TEM and EA. Based on the FT-IR analysis we could confirm the presence of the Ti-O-P band in all samples which indicates the formation of the phosphonate organic-inorganic hybrid materials. From the SEM analysis it was observed that the phosphonate organic-inorganic hybrid materials showed similar structures, with aggregates from a few μm up to 500 μm in size. In some cases the aggregates presented small or bigger fragmentations on the surface, fact that can be associated with molecular structure of the analysed material. The TEM images show the size and distribution of the nanoparticles in the cases of both magnetic and nonmagnetic hybrid materials. Elemental analysis confirms the presence of the organic components in the synthesized materials.

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