



Synthesis of organic motif tailored hybrid nanoframes: Exploiting *in vitro* bioactivity and heavy metal ion extraction applications

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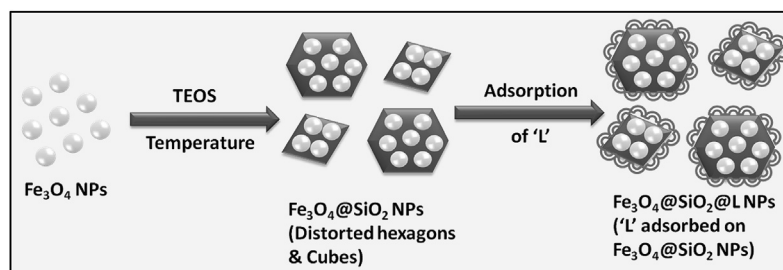
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HIGHLIGHTS

- New hybrid nanoparticles (NPs) shown good to high antibacterial activity.
- NPs showed barely compromised magnetism and thermal stability.
- Macroporous NPs depicted harmonious Zn(II) ion extraction efficiency.
- Extraction of Zn(II) ions by NPs exhibited no matrix interference.

GRAPHICAL ABSTRACT



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ABSTRACT

Hybrid nanoparticles (NPs) were designed by adsorbing a (13*E*,19*E*)-N₁'N₃'-bis[4-(diethylamino)-2-hydroxybenzylidene]malonohydrazide (L) motif, on Fe₃O₄@SiO₂ distorted hexagonal and cubic NPs. Electronic images of the synthesized hybrid NPs revealed distorted topographies with size of ~50–70 nm. We exploited key *in vitro* features, topographies, thermal behaviours, spectroscopic data, magnetic properties and heavy metal ion extraction efficiencies of the prepared hybrids. Additionally, the discrete discussion on the surface areas of the synthesized NPs tackled with BET, are introduced. Characterization with FT-IR, SEM, TEM, XRD, BET, VSM, TGA, particle size analysis and Raman spectroscopic techniques revealed that the organic scaffold L is attached to the prepared Fe₃O₄@SiO₂ NPs surface via adsorption or covalent interactions or some sort of charge/proton transfer. Antibacterial tests depicted that, L and Fe₃O₄@SiO₂ NPs exhibited moderate to good antifungal activity against *C. albicans*, while synthesized key hybrids has shown good to high antibacterial activity against Gram-positive bacterium, *S. aureus*, two Gram-negative bacteria's, *E. coli* and *P. aeruginosa*, and antifungal activity against *C. albicans*. Also, the Zn²⁺ ion extraction efficiency of the key hybrids was tackled and validated with commercial pharmaceutical tablet analysis.

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1. Introduction

Contests in developments of newer materials produced a plethora of substances; amongst which organic scaffolds tethered

nanomolecular structures leading to appealing artificial changes confronted researchers attention [1]. These hybrid motifs are endowed with noteworthy applications such as, bacterial isolation [2], chemosensing as well as biosensing [3], extraction of heavy metal ions [4], and other remarkable applications [5–8]. Pristine Fe₃O₄ also has myriad of applications such as information storage material [9], wave-absorbing material [10], medical diagnosis [11], as a catalyst [12], etc. Albeit, pristine Fe₃O₄ NPs have number of

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lacunae, such as lack of selectivity, low binding capacity, spontaneous aggregation and the loss of magnetism upon air exposure [13]. These lacunae can be removed with silica coatings, as the mesoporous silica coated materials put together them as potential sorbents in adsorption based methods. However, most part of as-prepared mesoporous silica shells indexed limited adsorption capacity, which in turn is indiscriminate and reversible. Conversely, to magnify the selectivity as well as specificity and to craft stronger and lasting interactions, these materials should be chemically doped with explicit organic motifs to get hold of hybrid mesoporous silica nanoframes. As a consequence, the organic motifs modified mesoporous silica shells, leads to alluring artificial changes has become an important research area of material chemistry with myriad of sustainable applications [14]. In topical epoch, terrifying belongings of microbes as well as heavy metal ions and their related precautions, have cached the forecasting apprehension [15–19]. Thus, because of these wide-ranging scattering of contagious diseases and critical perilous effects of heavy metal ions, antibacterial materials that can concurrently arrest the growth of such microbes and the material with selective and sensitive extraction efficiency is still noteworthy research concern [20,21].

Quite a few metal ions play a decisive role in physiological mechanisms provided that they don't go beyond the cellular requirements [22]. Zinc has become the focal point of the research in support of its well recognized functions in myriad of fundamental processes such as energy transduction, metalloenzyme functions, etc, amongst all the metals of biological relevance. Also, this second most plentiful transition element in human body stimulates more than 100 enzymes [23]. Neurobiology revealed that, neuronal passing can occur owing to the deserted Zn^{2+} ions released subsequent to the traumatic brain injury, stroke, or seizure [24]. Zn^{2+} ion stimulated creation of α -amyloid, which may leads to Alzheimer's disease and additional neurological threats [25]. Furthermore, excess of Zn^{2+} ions also leads to prostate cancer [26] and diabetes [27]. The surfeit Zn^{2+} ions present in the soil may perhaps dangles the actions of a number of essential microbes. Thus, the in harmony quantities of Zn^{2+} ions are imperative for the proper physiological carrying out of bionetwork [28], thus Zn^{2+} ions are over and over considered as an appealing threat to life and draw attention to the significance of preconcentration, recognition and detection of Zn^{2+} in environmental and biological samples.

Solid phase extraction is recognized as an efficient preconcentration technique, obligatorily helps to go up to the lower detection and quantitation limits of the analyte of interest that further determined by other sophisticated instruments [29]. In view of this fact and in continuation to our work on heavy metal ions [30], the current expansion and strategy gifted a newer organic/inorganic hybrid nanoframe, with its alluring *in vitro* application as well as Zn^{2+} ion extraction properties, along with thorough characterization which is the requisite of such type of study.

2. Experimental section

2.1. Materials

Anhydrous Ferric chloride (FeCl_3), Ferrous Chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and liquor ammonia were obtained from Sigma Aldrich, India and Tetra Ethyl Ortho Silicate (TEOS), glycerol, anhydrous ethanol, methanol as well as acetonitrile were procured from Arcos Organics, Germany. The other reagents were analytical grade and used without any purification unless and otherwise mentioned.

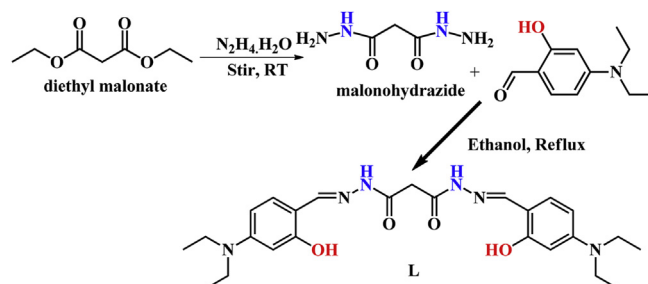
2.2. Synthesis of (13E,19E)- N_1' , N_3' -bis[4-(diethylamino)-2-hydroxybenzylidene] malonohydrazide (L)

(13E,19E)- N_1' , N_3' -bis[4-(diethylamino)-2-hydroxybenzylidene] malonohydrazide (L) was synthesized by the literature reported procedure [31]. Diethyl malonate (0.16 g, 1 mmol) and hydrazine hydrate (0.10 g, 2 mmol) were stirred at high speed under solvent free condition at 40 °C temperature for 15–20 min in a flat bottom flask. The obtained malonohydrazide was washed with hexane and dissolved in 20 mL of ethanol. Further, the solution of 4-diethylamino-salicylaldehyde in 30 mL ethanol (0.22 g, 2 mmol) was added to it. The resulted reaction mixture was refluxed for 2 h with continued stirring (Scheme 1). The progress of reaction was monitored by TLC. The solution colour was changed from dark purple to bright yellow. The reaction mixture was cooled and the obtained crystals were filtered, washed with hexane and dried under vacuum to obtain the key organic motif L in quantitative yield. Yield: 0.39 g (82% yield), mp > 154–156 °C. ^1H NMR (300 MHz, CDCl_3 , 25 °C ppm) δ : = 1.18–1.22 (t, J = 6.9 Hz, 12H, 4 CH_3), 1.57 (s, 2H, CH_2), 3.36–3.43 (q, J = 6.6 and 7.2 Hz, 8H, 4 CH_2), 6.23–6.27 (t, J = 4.2 and 8.7 Hz, 4H, 4Ar-H), 7.08–7.11 (d, J = 8.4 Hz, 2H, CHQN), 8.46 (s, 2H, Ar-H), 11.83 (s, 2H, 2NH) ppm; ^{13}C NMR (75 MHz, DMSO, 25 °C): δ = 12.9, 40.4, 44.2, 97.9, 104.1, 106.5, 150.6, 159.9, 166.2, 166.6 ppm; FTIR (nujol, cm^{-1}): ν 3301, 3197, 3140, 2924, 2854, 1681, 1666, 1635, 1598, 1518, 1463, 1417, 1363, 1297, 1248, 1174, 1134, 1053, 1006, 956, 907, 824, 787, 695, 593, 566, 502 cm^{-1} ; Mass spectrometry: $[\text{M}+\text{H}]^+$ Calculated: 483.27; Found: 483.35.

2.3. Synthesis of supermagnetic Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{SiO}_2$ NPs

Supermagnetic Fe_3O_4 NPs were synthesized by adding, anhydrous FeCl_3 (3.244 g, 20 mmol) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (1.988 g, 10 mmol) in 200 mL previously degassed deionised water, in a three necked vessel. Afterward, the reaction vessel was placed in an oil bath heated to attain a constant temperature of 358 K, with under nitrogen and with continued stirring. As the desired temperature was achieved, 30 mL of liquor ammonia was added to the reaction mixture, so that the resulting orange coloured reaction mixture turned black. Consequently, the Fe_3O_4 magnetic nanostructures were washed several times with water, twice with sodium chloride solution (20 mM L^{-1}) and again with water by centrifugation/dispersion cycles. Further these washed Fe_3O_4 NPs were stored in deionised water at a concentration of 40 g/L.

From above solution, 20 mL aliquot was withdrawn in a beaker and the NPs were allowed to settle, with the help of a strong permanent magnet at the bottom of the container. Subsequently, the supernatant water was discarded followed by addition of, 10% aqueous emulsion of TEOS (80 mL) and glycerol (60 mL). Using acetic acid and ammonia, the pH of the resultant mixture was adjusted at 4.6. This reaction mixture was added in a two necked flask, kept stirred and heated for 2 h at 363 K under nitrogen



Scheme 1. Synthetic route of abiotic motif L.

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