Synthesis of Core-Shell Magnetic Supramolecular Nanocatalysts based on Amino-Functionalized Calix[4] arenes for the Synthesis of 4H-Chromenes by Ultrasonic Waves

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# Supplementary information

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Fig. S1. $^1$H NMR spectrum of synthetic 5, 11, 17, 23-Tetra-4-tert-butyl-25, 27-di(ami-noethoxy)-26, 28-dihydroxy-calix[4]arene
Fig. S2. FT-IR spectrum of 5, 11, 17, 23-Tetra-4-tert-butyl-25, 27-di(amoioethoxy)-26, 28-dihydroxycalix[4]arene
1. Synthetic preparation of \( p \)-\( \text{tert-buty} \)lcalix[4]arene

The synthesis was performed according to method reported by Gutsche in 1990.[1] 100.00 g of \( p \)-\( \text{tert-buty} \)lphenol, 62 mL of formaldehyde solution (37%) and a distinctive solution of sodium hydroxide (1.2 g of sodium hydroxide in 3 mL of distilled water) were mixed under the mechanical stirring condition for 15 min at room temperature. After that, the mixture solution was heated for 2 h at 120 °C and the reaction mixture became light yellow and eventually after 2 h, the color of reaction mixture was turned to deep yellow or brown-yellow viscous product. Afterwards, 800 mL of warm diphenyl ether was appended to the cooled reaction mixture and the content of flask was kept under the stirring condition at least 1 h in order to dissolve the remained residues. In the next step, the reaction mixture was stirred and heated (100-120 °C) under the flow of nitrogen gas to remove water from the reaction mixture. In this step, the color of yellow mixture solution was turned to gray or a light brown. After water removal, the formed solid product was heated (150-160 °C) under the mechanical stirring condition for few minutes and then it was kept under the reflux condition and gentle flow of nitrogen for 4 h. During this process, the reaction solid was dissolved and a clear dark-brown to grayish-black solution was formed. After cooling the reaction mixture, 800 mL of ethyl acetate was appended in order to precipitate the final product. Then, the obtained product filtered and it was washed twice with 100 mL of acetic acid, distilled water and acetone respectively. In order to have pure crystalline product, the white to beige product from previous step was dissolved in boiling toluene (1000 mL) and on cooling, it recrystallized. Yield: 56%, mp: 344 °C. \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \( \delta \)H (ppm) = 10.3 (s, 4H, OH), 7.05 (s, 8H, Ar-H), 4.25 (d, 4H, \( J = 12 \), Ar-\( \text{CH}_2\)-Ar), 3.49 (d, 4H, \( J = 12 \), Ar-\( \text{CH}_2\)-Ar), 1.21 (s, 36H, t-Bu).
2. Synthetic Preparation of 5,11,17,23-Tert-tert-butyl-25,27-dicyanomethoxy-26,28-dihydroxycalix[4]arene

Based on previous studies in synthesis of chemically modified calix[4]arene supramolecules, 10.00 g of \( p \)-tert-butylcalix[4]arene, 8.53 g of potassium carbonate, 4 mL of chloroacetonitrile and 9.25 g of sodium iodide were mixed in 250 mL of dry acetone. Then, the mixture solution was stirred and kept under the reflux condition for 7 h. After the mentioned time, the mixture solution was cooled and it was filtered by using a bed of celite. In the next step, the filtrate concentrated to dryness and the final product obtained using recrystallization from ethanol.\cite{2} Yield: 57\%, mp > 290 °C. \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \( \delta \)H (ppm) = 7.11 (s, 4H, Ar-H), 6.72 (s, 4H, Ar-H), 5.56 (s, 2H, OH), 4.80 (s, 4H, OCH\(_2\)CN), 4.22 (d, 4H, J = 13.2 Hz, Ar-CH\(_2\)-Ar), 3.44 (d, 4H, J = 13.2 Hz, Ar-CH\(_2\)-Ar), 1.32 (s, 18H, t-Bu), 0.87 (s, 18H, t-Bu).
3. Synthetic preparation of 5,11,17,23-Tetra-4-tert-butyl-25,27-di(aminoethoxy)-26,28-dihydroxycalix[4]arene

After the chemically modification of p-tert-butylcalix[4]arene, in order to prepare the 5,11,17,23-Tetra-4-tert-butyl-25,27-di(aminoethoxy)-26,28-dihydroxycalix[4]arene according to published method.[3] First of all, 3.00 g of LiAlH₄ was mixed with 50 mL of anhydrous THF under the N₂ atmosphere. Afterwards, a slurry was prepared and it was appended to the 15.00 g of 5,11,17,23-Tert-tert-butyl-25,27-dicyanomethoxy-26,28-dihydroxycalix[4]arene in 150 mL THF at 0 °C. The suspension solution was kept under the stirring condition for 4 h. After the mentioned time, 15 mL of NaOH solution (20%) and 5 mL of H₂O were added to the suspension solution and a white precipitate was prepared. The obtained white precipitate was filtered. Next, the evaporation of filtrate was accomplished under the reduced pressure and eventually, the residue recrystallized in dichloromethane/methanol solvents to attain white crystal. Yield: 77%, mp: 143-145 °C. ¹H-NMR (400 MHz, CDCl₃): δH (ppm) = 7.03 (s, 4H, Ar-H), 6.98 (s, 4H, Ar-H), 4.33 (d, 4H, J = 13 Hz, Ar-CH₂-Ar), 4.08 (t, 4H, J = 5.5 Hz, O-CH₂), 3.38 (d, 4H, J = 13 Hz, Ar-CH₂-Ar), 3.31 (t, 4H, J = 5.5 Hz, N-CH₂), 1.25 (s, 18H, t-Bu), 1.10 (s, 18H, t-Bu).
4. Synthetic preparation of Fe₃O₄ MNPs

Based on previous studies about synthesis of Fe₃O₄ MNPs by using coprecipitation method,[⁴] first 2.91 g of FeCl₃.6H₂O and 1.33 g of FeCl₂.4H₂O (with molar ratio of 2:1) were dissolved in 80 ml of distilled water. Second, the obtained mixture solution was stirred under the N₂ atmosphere condition and as well, it was followed by continuous heating up to 70 °C. In the next step, 10 mL of aqueous ammonia solution (25%) was added to the mixture solution dropwise during the 30 min. Then, the mixture solution was kept under the stirring condition and constant temperature (70 °C) for 2 h. After the mentioned time and cooling the mixture solution, the obtained black precipitate was separated by using an external magnet and finally, in order to remove the unreacted components and having neural pH (pH = 7), the black precipitate of Fe₃O₄ MNPs was eluted with distilled water for several times.
5. Functionalization process of Fe₃O₄ MNPs by silica layer

Conforming to the Stöber method with some modification and reformations\textsuperscript{[5]} and previous studies about the functionalization of Fe₃O₄ MNPs,\textsuperscript{[4]} the fabrication process of Fe₃O₄/SiO₂ nanostructure and placement of SiO₂ shell on the surface of Fe₃O₄ MNPs was accomplished by these following steps. First of all, a distinctive amount of obtained black Fe₃O₄ MNPs (0.22 g) was dispersed into the 50 mL of distilled water by using ultrasonic irradiation for 20 min. After the mentioned time, 7.5 mL of ammonia solution (25\%) was added to the mixture solution under the stirring condition. Then, 80 mL of ethanol was poured to the suspension. In the next step, 4 mL of TEOS solution was trickled to the mentioned suspension solution and it was stirred for 24 h at room temperature condition. Ultimately after 24 h, the Fe₃O₄ MNPs which are functionalized by SiO₂ layer, were separated from the reaction media by using external magnet. The obtained functionalized Fe₃O₄ MNPs washed with distilled water and ethanol and in order to dry the obtained product, it was kept in an oven (70 °C) for 12 h.
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