Silica sulfuric acid magnetic nanoparticles: Preparation and application in synthesis of mono-, di- and tri-[bis (6-aminopyrimidonyl) methanes]

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2. Experimental

2.1. General

All reagents were the best available purity and used without further purification. Fe₃O₄ nanoparticles (MNP), citric acid modified nanoparticles (CMNPs) and silica coated magnetic nanoparticles (Fe₃O₄/SiO₂ MNPs) were prepared according to the literature procedure [17]. Trialdehydes 2g-i were prepared according to the literature procedure [18]. The products 3a and 3c are known compounds and their structures were deduced by comparison of their physical and spectroscopic data (IR and ¹H NMR) with those of previously reported. The new products were characterized on the basis of their elemental analysis and IR, ¹H NMR and ¹³C NMR spectra. ¹³C NMR spectra of the products 3g, 3i and 3g-h have not been reported, because they were found to be insoluble in common organic solvents.

2.2. General procedure for the preparation of SSA-MNPs

One gram of silica coated magnetic nanoparticles (Fe₃O₄/SiO₂ MNPs) was poured within two neck balloon with a constant-pressure dropping funnel and a gas inlet tube for conducting of HCl gas over an adsorbing solution was used. Then, chlorosulfonic acid (1.5 mL) was added drop wise over a period of 30 minutes at room temperature and followed by mechanical stirring slowly to be a catalyst paste. HCl gas immediately evolved from the reaction vessel. After that the mixture was shaken well for 30 minutes. The SSA-MNPs were washed with acetone and distilled water for removing excess of chlorosulfonic acid and finally dried in oven at 60 °C for 6 h.

2.3. General procedure for the preparation of di-[bis(6-aminopyrimidonyl) methanes] 3e-f

A mixture of dialdehyde 2e-f or trialdehyde 2g-i (1 mmol), 6-amino-1,3-dimethyluracil (5 mmol for 2e-f or 7 mmol for 2g-i) and SSA-MNPs (0.1 gr) in ethanol (8 mL) was exposed to US irradiation at 50 °C for the appropriate time according to Table (2). Upon completion of the reaction as monitored by TLC, the SSA-MNPs were removed under applied external magnetic field. After that the solution was reduced in volume and left for slow evaporation. Then water and ethanol were added in a 5:1 ratio. The solid products that obtained were collected by filtration, washed with C₂H₅OH:water (5:1) for removing excess of 6-amino-1,3-dimethyluracil.
2.4. FT-IR spectra, SEM images, TGA curve and X-ray diffraction patterns of Catalyst

Figure S1 FT-IR spectra of (a) MNP, (b) CMNP, (c) Fe$_3$O$_4$/SiO$_2$ MNPs and (d) SSA-MNPs.

Figure S2 SEM images of SSA-MNPs.
2.5. Spectral data of the selected products

(3b): White; solid; isolated yield 90%. IR (KBr) (νmax, cm⁻¹): 3352, 3119, 2955, 2831, 1689, 1662, 1606, 1591, 1502, 1344. ¹H NMR (DMSO-d6, 300 MHz) δH (ppm): 3.34 (s, 6H, N-CH3), 3.36 (s, 6H, N-CH3), 5.66 (s, 1H, CHmethine), 7.30 (bs, 2H, NH2), 7.51 (t, 2H, J=7.8 Hz, H arom), 7.59 (d, 2H, J=7.6 Hz, H arom), 7.86 (s, 2H, NH2), 7.99 (d, 1H, J=7.8 Hz, H arom).

(3d): White; solid; isolated yield 87%. IR (KBr) (νmax, cm⁻¹): 3358, 3159, 3049, 2955, 1689, 1678, 1595, 1500. ¹H NMR (DMSO-d6, 300 MHz) δH (ppm): 3.33 (s, 6H, N-CH3), 3.36
(s, 6H, N-CH₃), 5.49 (s, 1H, CH₉methine), 6.97 (bs, 2H, NH₂), 7.28 (d, 1H, J=8.4 Hz, H₉arom), 7.34 (d, 1H, J=8.4 Hz, H₉arom), 7.43 (s, 1H, H₉arom), 7.48 (bs, 2H, NH₂).

(3e): White; solid; isolated yield 83%. IR (KBr) (νmax, cm⁻¹): 3396, 3167, 2953, 1666, 1608, 1589, 1494. ¹H NMR (DMSO-d₆, 300 MHz) δH (ppm): 3.31 (s, 12H, N-CH₃), 5.53 (s, 2H, CH methine), 6.90 (s, 4H, H₉arom), 7.33 (bs, 4H, NH₂), 7.56 (bs, 4H, NH₂).

(3f): White; solid; isolated yield 80%. IR (KBr) (νmax, cm⁻¹): 3454, 3360, 3111, 2962, 1683, 1601, 1496.¹H NMR (DMSO-d₆, 300 MHz) δH (ppm): 3.33 (s, 12H, N-CH₃), 5.52 (s, 2H, CH₉methine), 6.74 (s, 1H, H₉arom), 6.81 (d, 2H, J=7.7 Hz, H₉arom), 7.02 (t, 1H, J=7.5 Hz, H₉arom), 7.31 (bs, 4H, NH₂), 7.56 (bs, 4H, NH₂). ¹³C NMR (75 MHz, DMSO-d₆) δC (ppm): 28.0, 28.6, 29.9, 30.4, 35.7, 85.4, 87.1, 123.9, 127.7, 139.0, 150.7, 153.9, 155.1,162.4, 164.0.

(3g): White; solid; isolated yield 87%. IR (KBr) (νmax, cm⁻¹): 3379, 3130, 2955, 2810, 1687, 1610, 1564, 1500, 1456.¹H NMR (DMSO-d₆, 300 MHz) δH (ppm): 3.29 (s, 18H, N-CH₃), 5.59 (s, 3H, CH₉methine), 7.06 (d, 6H, J=8.4 Hz, H₉arom), 7.16 (d, 6H, J=8.4 Hz, H₉arom), 7.45 (bs, 12H, NH₂).

(3h): White; solid; isolated yield 88%. IR (KBr) (νmax, cm⁻¹): 3377, 3119, 2953, 2829, 1689, 1606, 1562, 1496, 1456.¹H NMR (DMSO-d₆, 300 MHz) δH (ppm): 3.30 (s, 18H, N-CH₃), 5.61 (s, 3H, CH₉methine), 6.92-7.02 (m, 9H, H₉arom), 7.25 (t, 3H, J=7.8 Hz, H₉arom), 7.34 (bs, 12H, NH₂). ¹³C NMR (75 MHz, DMSO-d₆) δC (ppm): 28.7, 30.4, 35.7, 85.2, 118.7, 119.8, 124.7, 129.1, 142.5, 150.9, 151.7, 153.9, 164.1, 173.4.

(3i): Pale yellow; solid; isolated yield 85%. IR (KBr) (νmax, cm⁻¹): 3398, 3119, 2953, 1691, 1614,1537, 1498, 1452, 1344.¹H NMR (DMSO-d₆, 300 MHz) δH (ppm): 3.34 (s, 36H, N-CH₃), 2.75 (s, 9H, O-CH₃), 5.66 (s, 3H, CH₉methine), 7.25 (s, 3H, H₉arom), 7.39 (s, 3H, H₉arom), 7.2-7.9 (bs, 12H, NH₂).
FT-IR: 3a

\(^1\)H-NMR-(DMSO-\(d_6\)): 3a
FT-IR: 3b

$^1$H-NMR-(DMSO-$d_6$): 3b
$^1$H-NMR-(DMSO-\textit{d}_6):3b

FT-IR: 3c
$^1$H-NMR-(DMSO-$d_6$): 3c

FT-IR: 3d
$^1$H-NMR-(DMSO-$_d_6$): 3d

FT-IR: 3e
$^1\text{H-NMR-(DMSO-}d_6\text{):} 3\text{e}$

FT-IR: 3f
$^1$H-NMR-(DMSO-$d_6$):3f

$^{13}$C-NMR-(DMSO-$d_6$):3f
FT-IR: 3g

$^1$H-NMR-(DMSO-$d_6$): 3g
FT-IR: 3h

$^1$H-NMR-(DMSO-$d_6$): 3h
$^{13}$C-NMR-(DMSO-$d_6$): 3h

FT-IR: 3i
$^1$H-NMR-(DMSO-$d_6$): 3i