

Electronic Supplemental Information

Preparation and properties of magnetic Fe₃O₄/poly(pyrimidine-amide) nanocomposites: selective polyamidation of bis(2-amino-pyrimidine-4,6-diol) compound in an ionic liquid

Mehdi Taghavi, Raouf Alizadeh, Mousa Ghaemy*

Polymer Chemistry Research Laboratory, Faculty of Chemistry, University of Mazandaran, Babolsar, 47416-95447, Iran.

S1. Synthesis of 5,5'-((9-ethyl-9H-carbazol-3-yl)methylene)bis(2-aminopyrimidine-4,6-diol) (DATPhP) (1)

Compound (1), *DATPhP*, was synthesized according to the procedure given in the literature by some changes.¹ A mixture of 1.27 g (0.01 mol) 2-amino-4,6-dihydroxypyrimidine, 1.11 g (0.005 mol) 9-ethyl-3-carbazolecarboxaldehyde, and 10 mL DMSO was stirred for 6 h at 110 °C. After completion of the reaction which was tested by TLC, the solution was cooled to room temperature and then poured into 400 mL deionized water. The resulting violet powder was filtered, washed with water several times, dried in a vacuum oven at 100 °C. The yield of the reaction was 96% (2.20 g), the compound did not show sharp melting point and decomposed on heating above 350 °C. The purity and structure of the compound were proved by TLC, elemental analysis, and ¹H and ¹³C NMR, and FT-IR spectroscopy. The NMR spectrum was the most

* Corresponding author. Tel.: +98-112-5342353; FAX: +98-112-5342350.

E-mail address: ghaemy@umz.ac.ir (Mousa Ghaemy).

informative. FT-IR (KBr disk) at cm^{-1} : 3189-3447 (OH and NH_2), 3062 (C-H aromatic), 2931 (C-H aliphatic), 1612 (C=N), 1589 (C=C), 1237 (C-N), and 1162 (C-O). UV-vis spectrum (EtOH), λ_{max} nm (log ϵ): 261, 419. ^1H NMR ($\text{DMSO-}d_6$, δ in ppm): 1.28-1.31 (t, 3H, CH_3 , $J=7.0$ Hz), 4.36-4.41 (q, 2H, CH_2 , $J=7.0$ Hz), 5.53 (s, 1H, C-H), 6.78 (s, broad, 1H, NH_2), 7.09-7.13 (t, 1H, Ar-H, $J=7.4$ Hz), 7.19-7.21 (d, 2H, Ar-H, $J=8.4$ Hz), 7.37-7.43 (dd, 2H, Ar-H, $J=8.4$ Hz), 7.52-7.55 (d, 2H, Ar-H, $J=8.4$ Hz), 7.81 (s, 1H, Ar-H), 8.08-8.10 (d, 2H, Ar-H, $J=7.6$), 10.40-10.53 (m, 4H, broad, -OH). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$, δ in ppm): 14.25, 32.79, 37.34, 39.29, 92.49, 108.68, 109.24, 118.18, 118.66, 120.72, 122.26, 122.67, 125.57, 125.63, 130.28, 138.21, 140.07, 150.41, 154.86, 166.19. Elemental analysis calculated for $\text{C}_{23}\text{H}_{21}\text{N}_7\text{O}_4$: C, 60.12%; H, 4.57%; N, 21.35% and found: C, 60.04%; H, 4.97%; N, 21.29%.

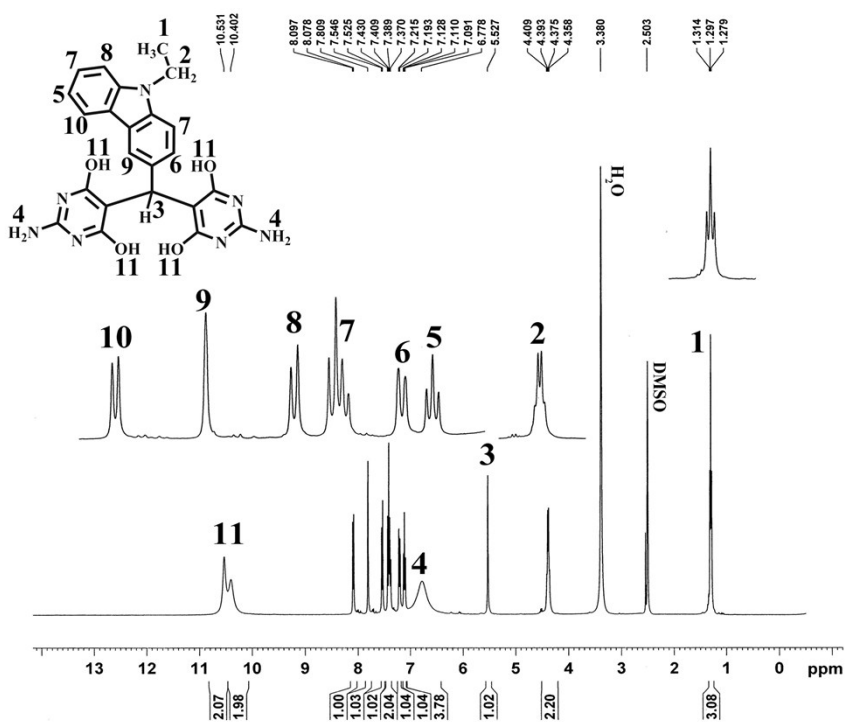


Fig. 2

Fig. 1S. ^1H NMR (A) and ^{13}C NMR (B) spectrum of DATPhP in $\text{DMSO-}d_6$.

S2. Polycondensation of DATPhP in TPP/IL

Into a 50 mL three-necked round-bottomed flask fitted with a water cooled condenser, a mechanical stirrer and a nitrogen gas inlet tube, a mixture of compound DATPhP (1 mmol), a dicarboxylic acid (1 mmol), 1,3-dipropyl imidazolium bromide {[1,3-(pr)₂im]Br} (0.70 g), and TPP (1.29 mmol) was placed. The mixture was heated at 110 °C for 2.5 h, the solution became viscous as the reaction proceeded. The reaction mixture was then cooled to room temperature and the resulting polymers were precipitated in 100 mL methanol. The precipitate was filtered and washed with hot water, and then was further purified by washing with refluxing methanol for 24 h in a Soxhlet apparatus to remove the low molecular weight oligomers. The inherent viscosity (η_{inh}) of the resulting PPAs, measured at a concentration of 0.5 g/dL in NMP at 25 °C, was in the range of 0.49-0.74 dL g⁻¹. The above procedure was used for the preparation of all PPAs, as shown in **Scheme 1**.

PPA1: Yield = 90 % and η_{inh} = 0.66 dL/g. FT-IR (KBr disk) at cm⁻¹: 3194-3413 (OH, NH amide), 3069 (C-H aromatic), 1689 (C=O amide), 1618 (C=N), 1568 (C=C), 1294 (C-N) and 1192 (C-O). UV-vis spectrum (NMP), λ_{max} , nm (log ϵ): 278, 425 in solvent and 282, 432 in film. ¹H NMR (DMSO-*d*₆, δ in ppm): 1.29-1.38 (t, 3H, CH₃, *J*= 7.0 Hz), 4.43-4.49 (q, 2H, CH₂, *J*= 7.0 Hz), 4.93 (s, 1H, C-H), 7.19-8.17 (m, 11H, Ar-H), 11.02 (s, 2H, broad, -NH amide), 11.73 (s, 4H, broad, -OH). Elemental analysis calculated for (C₃₁H₂₃N₇O₆)_n: C, 63.16%; H, 3.9%; N, 16.64%. Found: C, 62.98%; H, 4.37%; N, 16.59%.

PPA2: Yield = 80 % and η_{inh} = 0.58 dL/g. FT-IR (KBr disk) at cm⁻¹: 3203-3427 (OH, and NH amide), 3059 (C-H aromatic), 1672 (C=O amide), 1614 (C=N), 1529 (C=C), 1299 (C-N) and 1218 (C-O). UV-vis spectrum (NMP), λ_{max} , nm (log ϵ): 276, 422 in solvent and 279 and 423

in film. ^1H NMR (DMSO- d_6 , δ in ppm): 1.26-1.37 (t, 3H, CH_3 , $J= 7.0$ Hz), 4.42-4.47 (q, 2H, CH_2 , $J= 7.0$ Hz), 4.93 (s, 1H, C-H), 7.13-8.06 (m, 11H, Ar-H), 11.03 (s, 2H, broad, -NH amide), 11.86 (s, 4H, broad, -OH). Elemental analysis calculated for $(\text{C}_{31}\text{H}_{23}\text{N}_7\text{O}_6)_n$: C, 63.16%; H, 3.9%; N, 16.64%. Found: C, 63.01%; H, 4.41%; N, 16.62%.

PPA3: Yield = 88 % and $\eta_{\text{inh}} = 0.69$ dL/g. FT-IR (KBr disk) at cm^{-1} : 3212-3441 (OH, NH amide), 3033 (C-H aromatic), 1679 (C=O amide), 1616 (C=N), 1561 (C=C), 1291 (C-N) and 1211 (C-O). UV-vis spectrum (NMP), λ_{max} , nm (log ϵ): 285, 424 in solvent and 286, 428 in film. ^1H NMR (DMSO- d_6 , δ in ppm): 1.27-1.36 (t, 3H, CH_3 , $J= 7.0$ Hz), 4.42-4.46 (q, 2H, CH_2 , $J= 7.0$ Hz), 5.02 (s, 1H, C-H), 7.14-8.52 (m, 10H, Ar-H), 11.07 (s, 2H, broad, -NH amide), 11.76 (s, 4H, broad, -OH). Elemental analysis calculated for $(\text{C}_{30}\text{H}_{22}\text{N}_8\text{O}_6)_n$: C, 61.02%; H, 3.73%; N, 18.98%. Found: C, 60.99%; H, 3.89%; N, 18.90%.

PPA4: Yield = 91 % and $\eta_{\text{inh}} = 0.74$ dL/g. FT-IR (KBr disk) at cm^{-1} : 3232-3439 (OH, and NH amide), 3077 (C-H aromatic), 1682 (C=O amide), 1620 (C=N), 1519 (C=C), 1286 (C-N) and 1215 (C-O). UV-vis spectrum (NMP), λ_{max} , nm (log ϵ): 289, 442 in solvent and 295, 449 in film. ^1H NMR (DMSO- d_6 , δ in ppm): 1.37-1.41 (t, 3H, CH_3 , $J= 7.2$ Hz), 4.45-4.50 (q, 2H, CH_2 , $J= 7.0$ Hz), 4.91 (s, 1H, C-H), 7.11-8.07 (m, 15H, Ar-H), 11.06 (s, 2H, broad, NH amide), 11.86 (s, 4H, broad, -OH). Elemental analysis calculated for $(\text{C}_{37}\text{H}_{27}\text{N}_7\text{O}_8\text{S})_n$: C, 60.90%; H, 3.70%; N, 13.44%. Found: C, 60.76%; H, 4.13%; N, 13.39%.

PPA5: Yield = 92 % and $\eta_{\text{inh}} = 0.54$ dL/g. FT-IR (KBr disk) at cm^{-1} : 3196-3469 (OH, and NH amide), 3040 (C-H aromatic), 1688 (C=O amide), 1619 (C=N), 1529 (C=C), 1251 (C-N) and 1211 (C-O). UV-vis spectrum (NMP), λ_{max} , nm (log ϵ): 274, 421 in solvent and 277, 431 in film. ^1H NMR (DMSO- d_6 , δ in ppm): 1.32-1.64 (m, 7H), 2.15-2.20 (m, 4H), 4.44-4.50 (q, 2H, CH_2 , $J= 7.0$ Hz), 7.16-8.05 (m, 7H, Ar-H), 11.06 (s, 2H, broad, NH amide), 11.66-11.87 (m, 4H, broad, -

OH). Elemental analysis calculated for $(C_{29}H_{27}N_7O_6)_n$: C, 61.16%; H, 4.74%; N, 17.22%. Found: C, 61.05%; H, 5.19%; N, 17.14%.

PPA6: Yield = 95 % and $\eta_{inh} = 0.49$ dL/g. FT-IR (KBr disk) at cm^{-1} : 3202-3473 (OH, and NH amide), 3055 (C-H aromatic), 1688 (C=O amide), 1622 (C=N), 1528 (C=C), 1254 (C-N) and 1212 (C-O). UV-vis spectrum (NMP), λ_{max} , nm (log ϵ): 273, 421 in solvent and 277, 431 in film. 1H NMR (DMSO- d_6 , δ in ppm): 1.35-1.77 (m, 15H), 2.23-2.32 (m, 4H), 4.47-4.52 (q, 2H, CH_2 , $J = 7.0$ Hz), 7.10-8.09 (m, 7H, Ar-H), 11.03 (s, 2H, broad, NH amide), 11.79 (m, 4H, broad, -OH). Elemental analysis calculated for $(C_{33}H_{35}N_7O_6)_n$: C, 61.16%; H, 4.74%; N, 17.22%. Found: C, 61.05%; H, 5.19%; N, 17.14%.

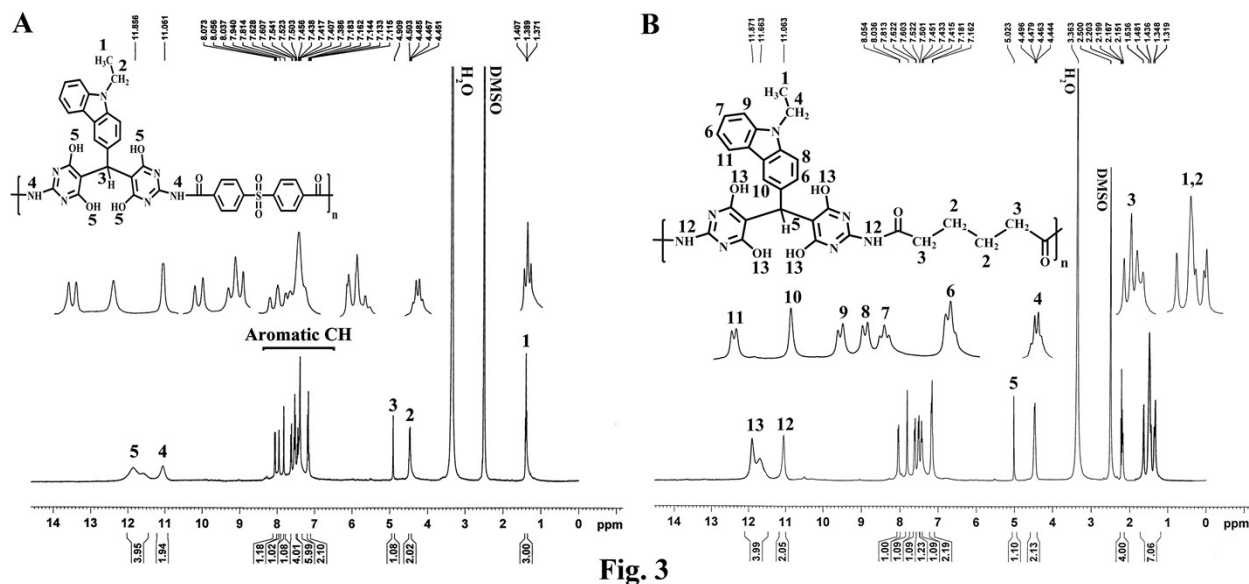


Fig. 2S. 1H NMR spectrum of PPA4 (A) and PPA5 (B) in DMSO- d_6 .

S3. Preparation of Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticle was prepared by the conventional coprecipitation method.² Firstly, 5.2 g $FeCl_3$ and 2.0 g $FeCl_2$ with 0.85 mL HCl solution (12 mol/L) were dissolved in 25 mL

diionized water. Then the resulting solution was added drop-wise into 250 mL NaOH solution (1.5 mol/L) under vigorous stirring. After completion of the reaction, the obtained precipitate was separated under the magnetic field and washed with diionized water for three times and ethanol for two times.

S4. Preparation of GPTES-Fe₃O₄ nanoparticles

A suspension of 1 g Fe₃O₄ nanoparticles in 30 mL ethanol and diionized water (50/50, v/v) was sonicated in 150 W ultrasonic water bath for 30 min. This suspension solution of Fe₃O₄ nanoparticles and 1 g GPTES were poured into a 50 mL round- bottomed flask equipped with a reflux condenser, a nitrogen gas inlet tube, and a magnetic stirrer bar. The flask was heated at 80 °C for 4 h with continuous stirring and then left to stay at room temperature for 24 h. Finally, the GPTES-coated Fe₃O₄ nanoparticles were separated from the mixture by the centrifugation and washed with ethanol for five times. Before the next step, the GPTES-Fe₃O₄ nanoparticles were dispersed in ethanol with the concentration of 1 g/L.²⁷

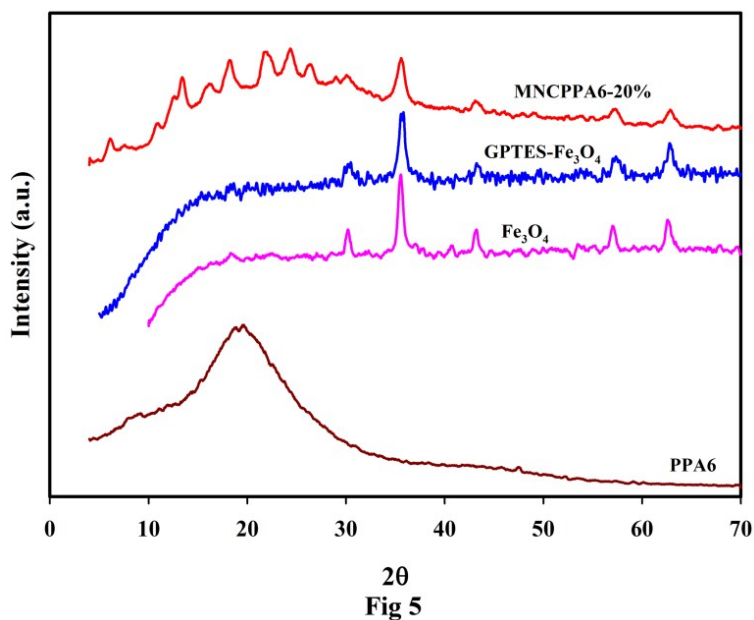


Fig. 3S X-ray diffraction patterns of Fe₃O₄, mNS, PPA6 and MNCPPA6-20%.

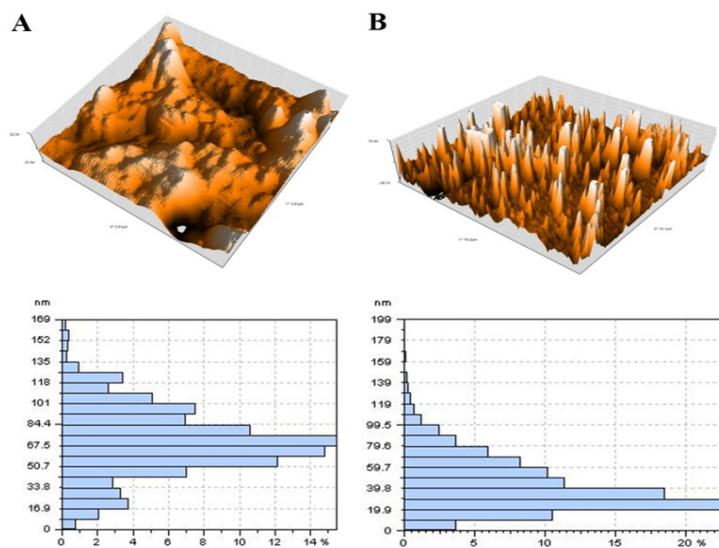
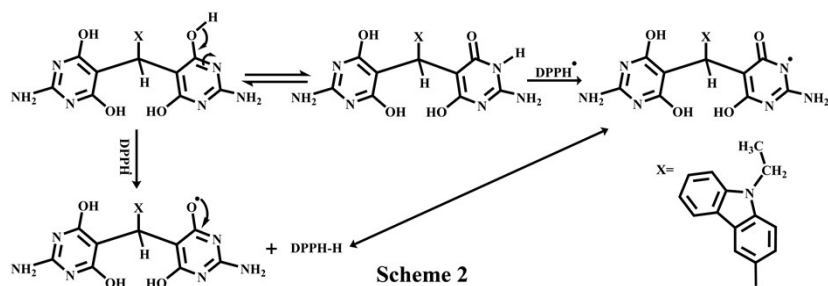


Fig. 7

Fig. 4S AFM images of GPTES-Fe₃O₄ (A) and MNCPPA4-20% (B).



Scheme 2

Scheme 1S Mechanism of antioxidant activity

References:

- 1 A. V. Moskvina, N. R. Reznikova, M. P. Meshcheryakov and B. A. Ivin, *Russ. J. Gen. Chem.*, 2001, **71**, 1096-1098.
- 2 N. R. Nagireddy, M. M. Yallapu, V. Kokkarachedu, R. Sakey, V. Kanikireddy, Alias, J. Pattayil and M. R. Konduru, *J. Polym. Res.*, 2011, **18**, 2285-2294.