Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

A Solvent-Free One-pot Multicomponent Tandem Polymerization of 3,4-Dihydropyrimidin-2(1*H*)-ones (DHPMs) Catalyzed by Ionic-Liquid@Fe_3O_4 NPs: Development of Polyamide Gels

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Table S4: Physical Properties and Efficiency of Recovered IL2@Fe_3O_4 NPs catalyst.

Procedure S1. Synthesis of IL1: IL1 was synthesized by using reported procedure.[1] Dissolved 1 eq of 1-methyl imidazole in acetonitrile solvent and then added 1eq of bromoacetic acid and refluxed the reaction mixture at 80°C for 6 hours. Pale yellow colored crystalline solid was separated after evaporation of the solvent on reduced pressure. Yield 74% and purity was characterized by IR (KBr thin film), ν(cm^{-1}): 3378.66 (broad), 3092.63, 3040.17, 1719.50, 1666.89, 1565.97, 1366.71, 1174.45, 1044.71, 771.36, 648.85, 455.78. ESI-MS m/z = 141.07 $[M + H]^+$.

Procedure S2. Preparation of Iron Oxide Nanoparticles: The iron oxide nanoparticles were prepared by using reported procedure.[2] Dissolved $FeSO_4.7H_2O$ in 100 ml of double distilled water to form a 0.1 M solution and dropwise added 0.45 M solution of NaOH as precipitating agent with continuous stirring. The black precipitates separated out after 45 min stirring. Filtered the precipitates and washed with water/ethanol mixture for 3 to 4 times.

Table S1: MCTPs of poly(DHPMs) (**P1-P8)**.

Entry	Poly(DHPMs)	Yield (%)	Mw[a] (g/mol)	PDI[a]	Solubility[b]
1.	P1	75	41,712	1.67	✓
2.	P2	70	37,315	1.20	✓
3.	P3	74	18,525	1.36	✓
4.	P4	80	83,384	1.78	✓

5.	P5	74	17,332	1.52	✓
6.	P6	70	11,427	1.75	✓
7.	P7	68	13,375	1.27	✓
8.	P8	75	35,860	1.65	✓

[a]Evaluated by GPC at room temperature in THF solvent and calibrated by linear polystyrene. [b]Solubility tested in organic solvents, such as Metanol, THF, DMSO, DMF and Acetonitrile:
✓ = Completely soluble.

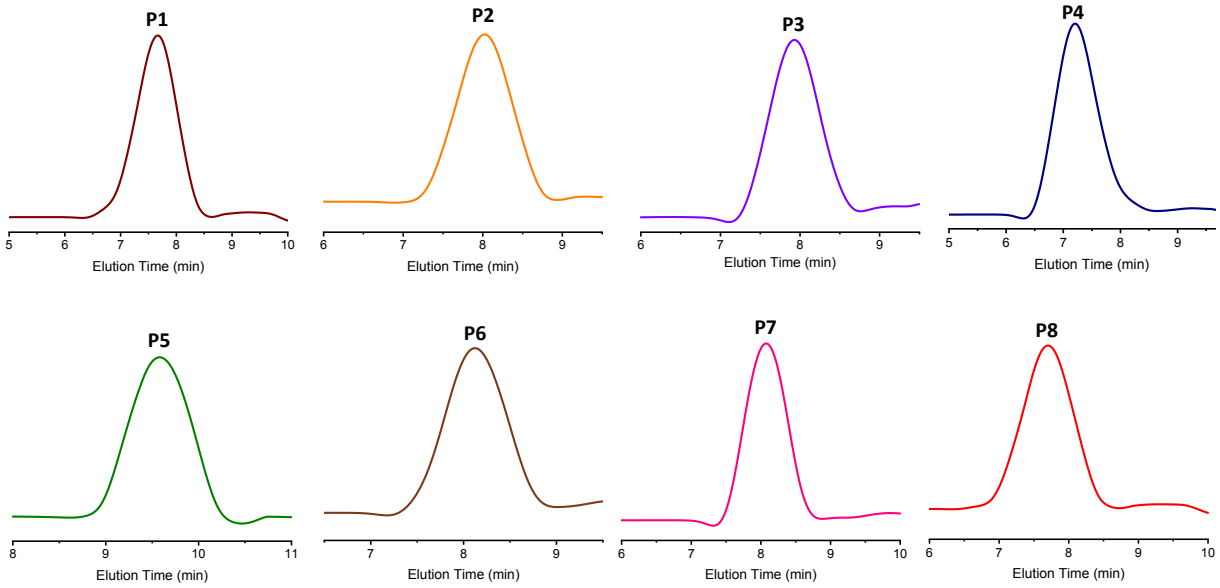
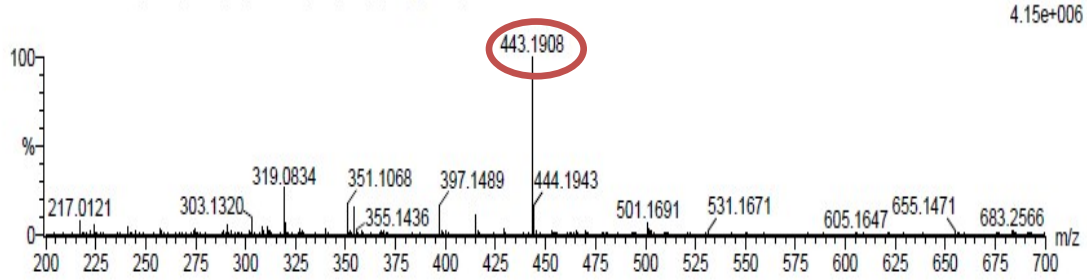


Figure S1. GPC traces of synthesized polyamides P1-P8.

Monoisotopic Mass, Odd and Even Electron Ions
25 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 10-25 H: 10-30 N: 0-4 O: 0-6

Sample Name : MR-19 INDIAN INSTITUTE OF TECHNOLOGY XEVO G2-XS QTOF
Test Name : HRMS ROPAR
170717-MR-19 19 (0.214) AM2 (Ar,18000.0,0.00,0.00); Cm (19:28) 1: TOF MS ES+
4.15e+006



Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
443.1908	443.1931	-2.3	-5.2	11.5	448.2	n/a	n/a	C22 H27 N4 O6

Figure S2. Mass spectra of Biginelli Product (B1).

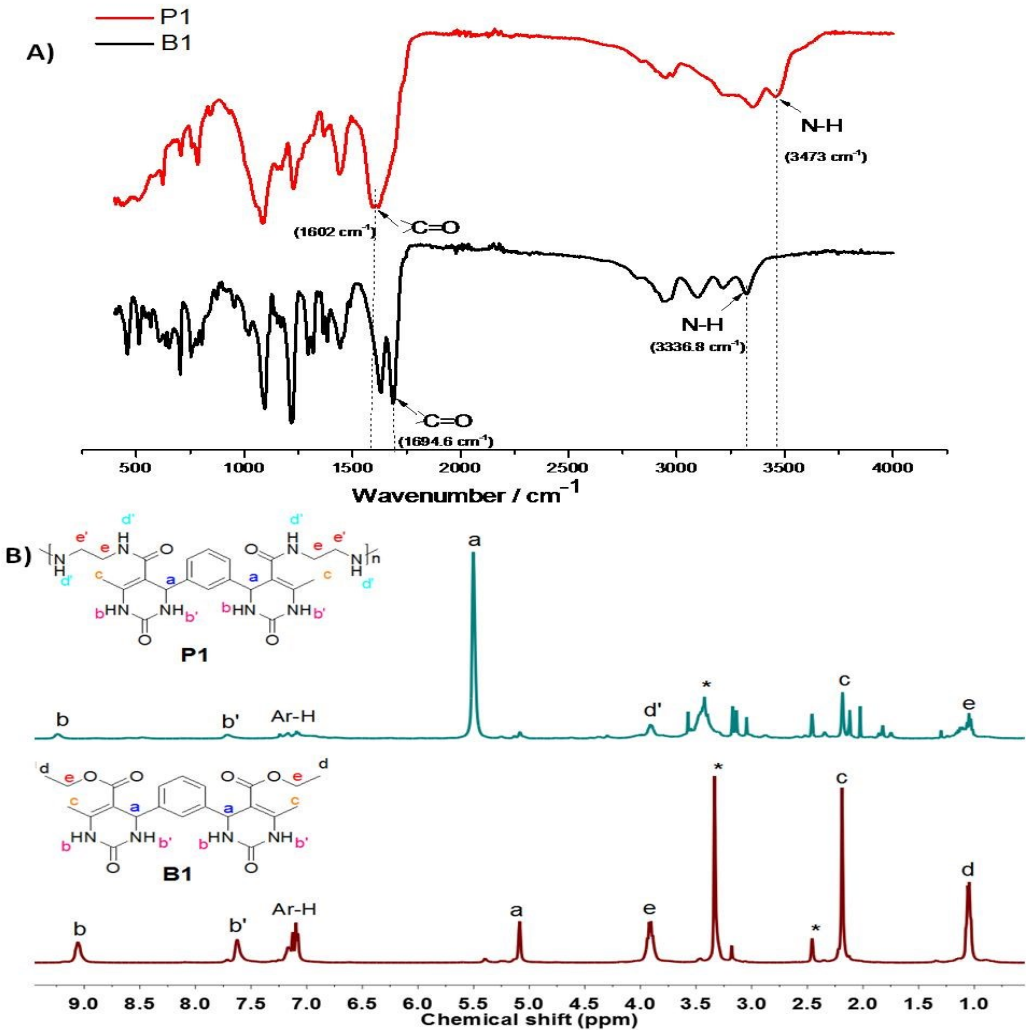


Figure S3: A) FT-IR spectra of B1 with N-H and C=O stretching vibrations at 3336.8 cm^{-1} and 1694.6 cm^{-1} whereas in P1, shifted at 3473 cm^{-1} and1602.6 cm^{-1} respectively. **B)** Comparison of ^{1}H NMR spectra of B1 and P1 in $CDCl_3$/DMSO-d_6.

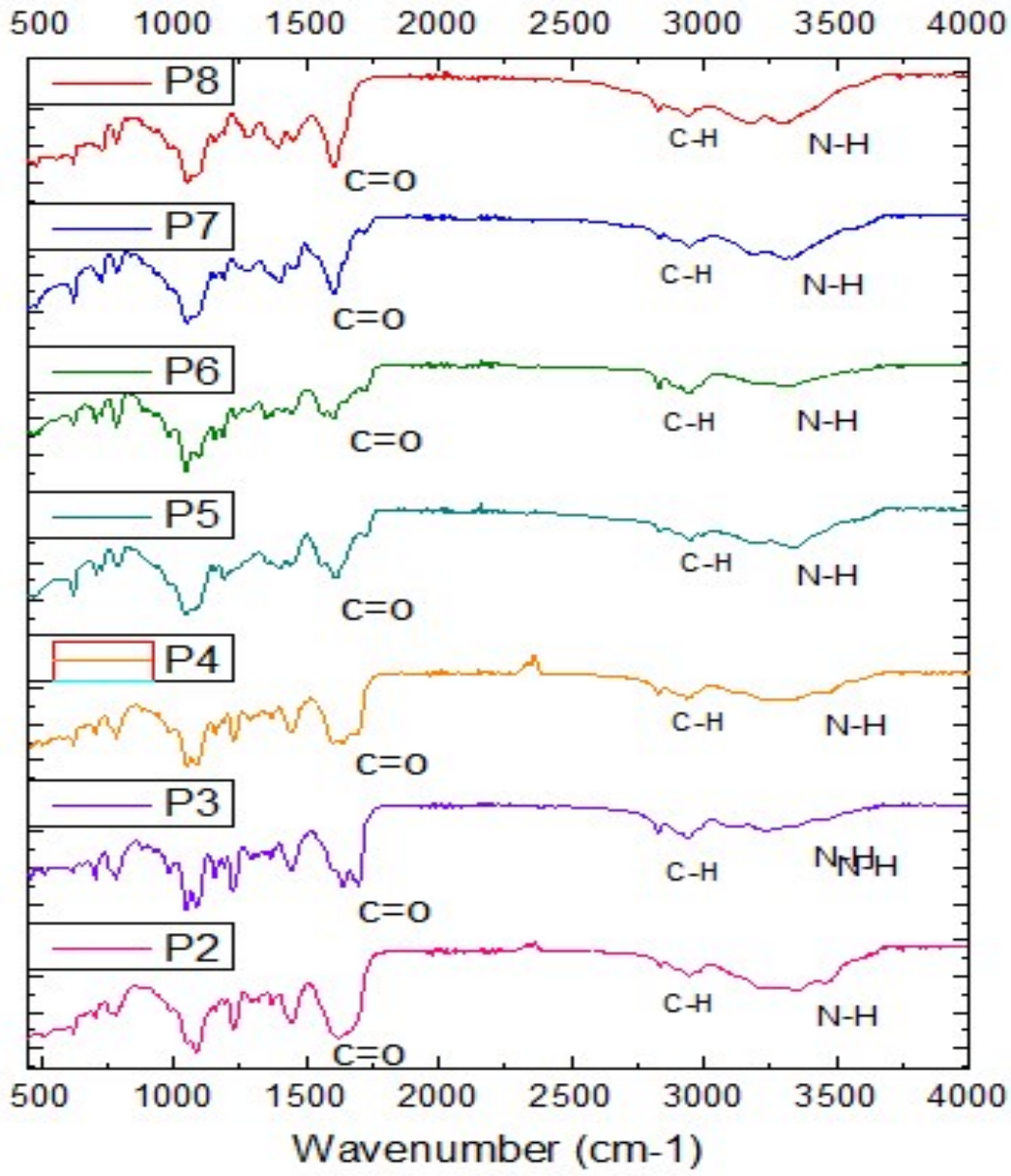


Figure S4. FT-IR spectra of polyamide adducts P2-P8.

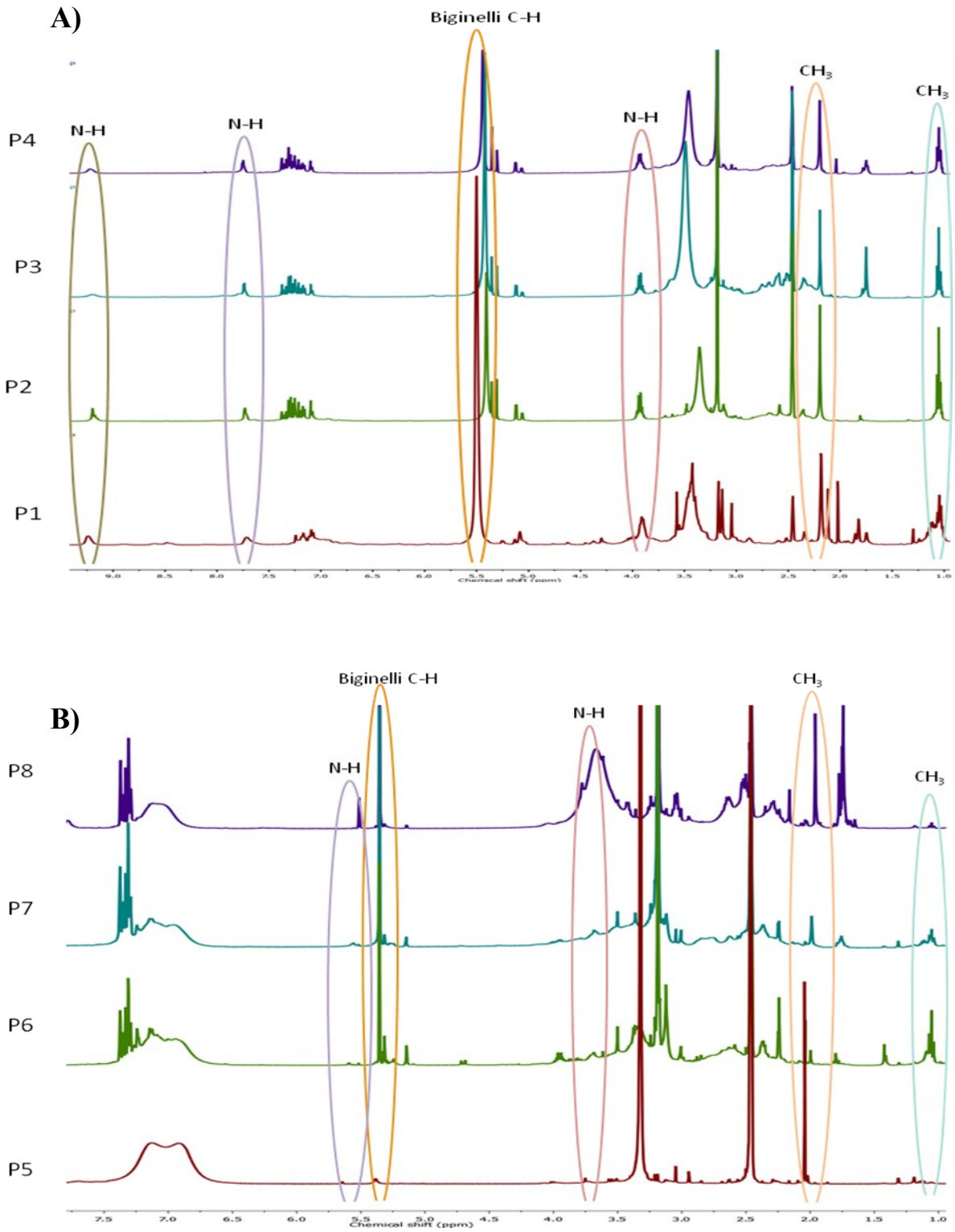


Figure S5.: A) ^{1}H NMR spectra in mixture of $CDCl_3$ and DMSO-d_6 of P1-P4 (Urea derivatives). **B)** ^{1}H NMR spectra in mixture of $CDCl_3$ and DMSO-d_6 of P5-P8 (thiourea derivatives).

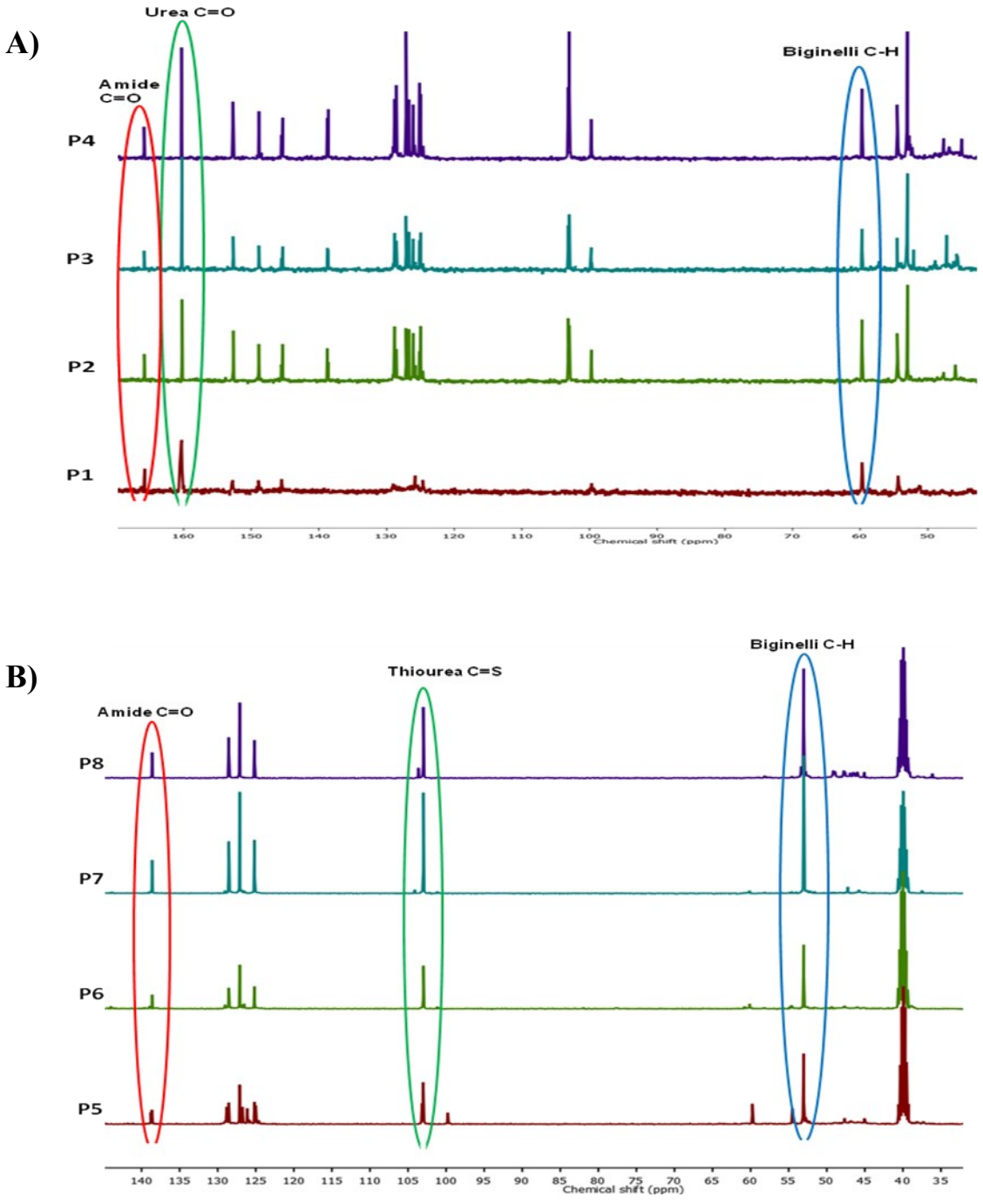


Figure S6. A). ^{13}C NMR spectra in mixture of $CDCl_3$ and DMSO-d_6 of P1-P4 (Urea derivatives). **B)** ^{13}C-NMR spectra in mixture of $CDCl_3$ and DMSO-d_6 of P5-P8 (thiourea derivatives).

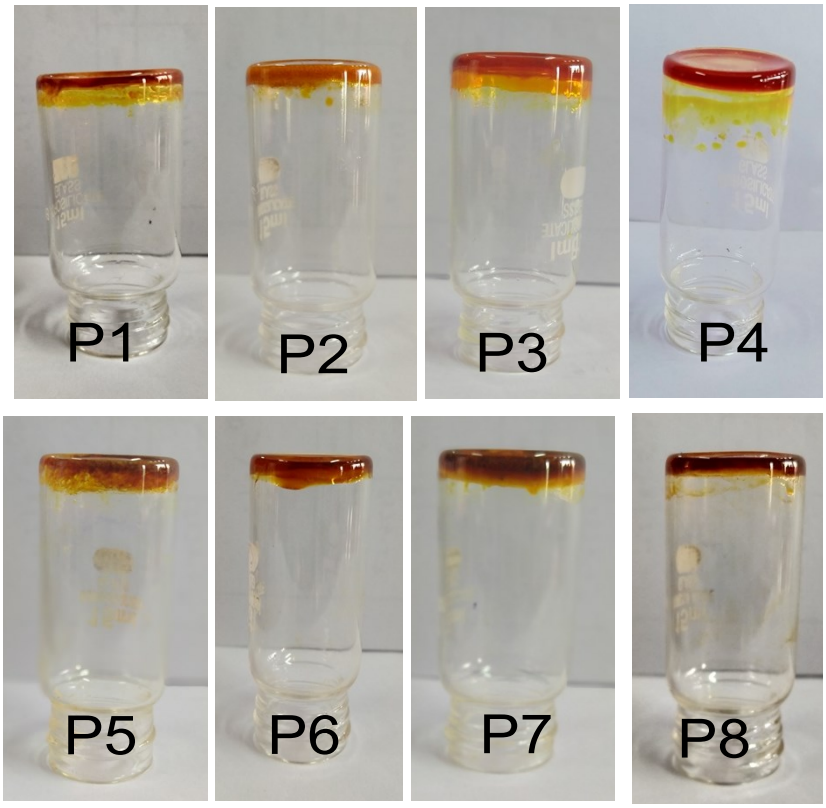


Figure S7: Photographs of Synthesized polyamide gels (P1-P8).

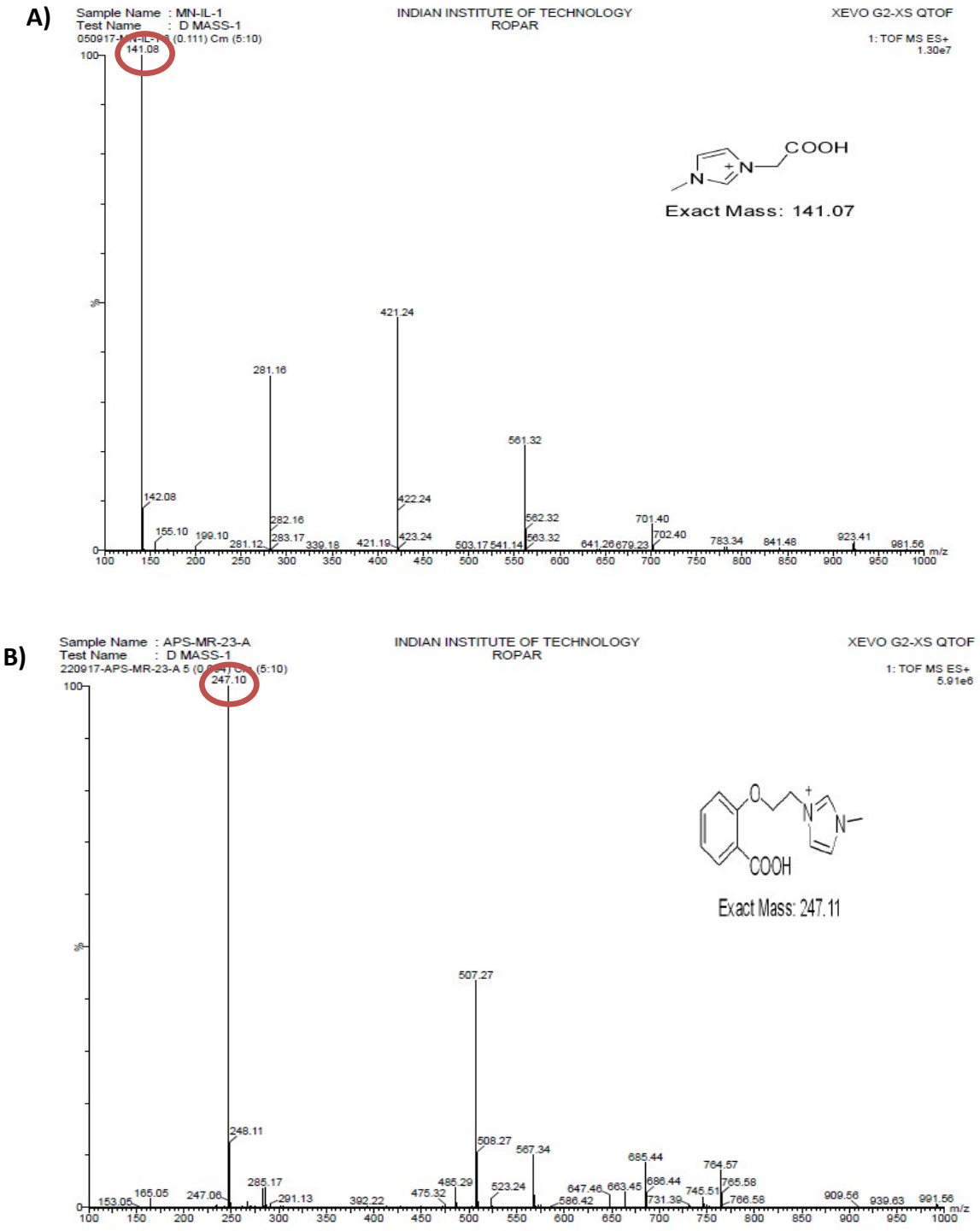
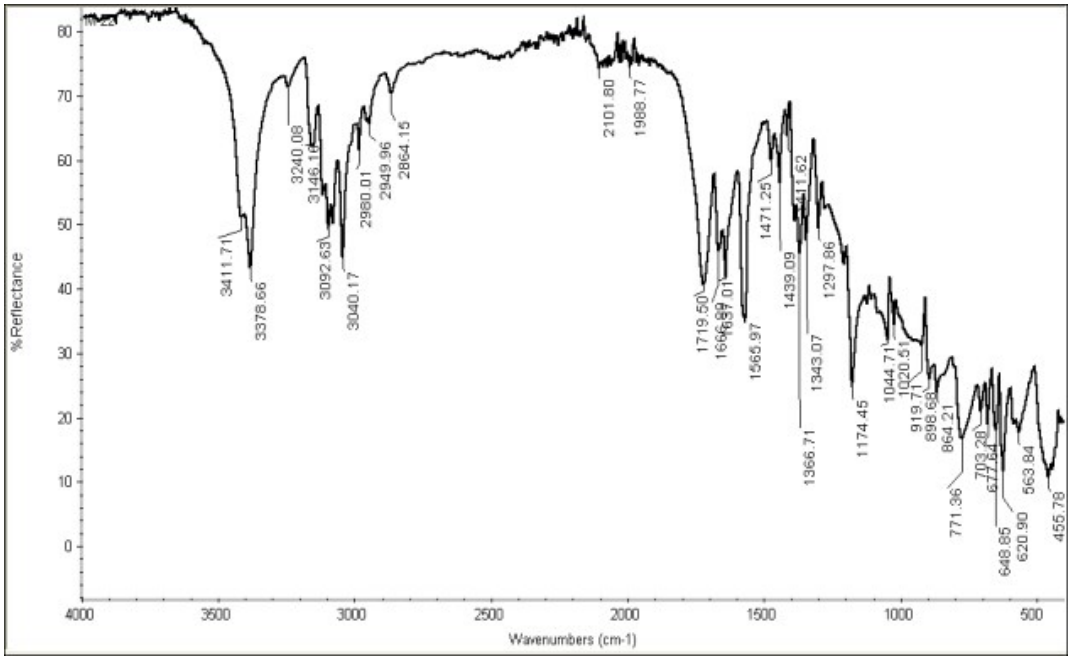


Figure S8. (A) Mass spectrum of IL1 and (B) Mass spectrum of IL-2.

A)



B)

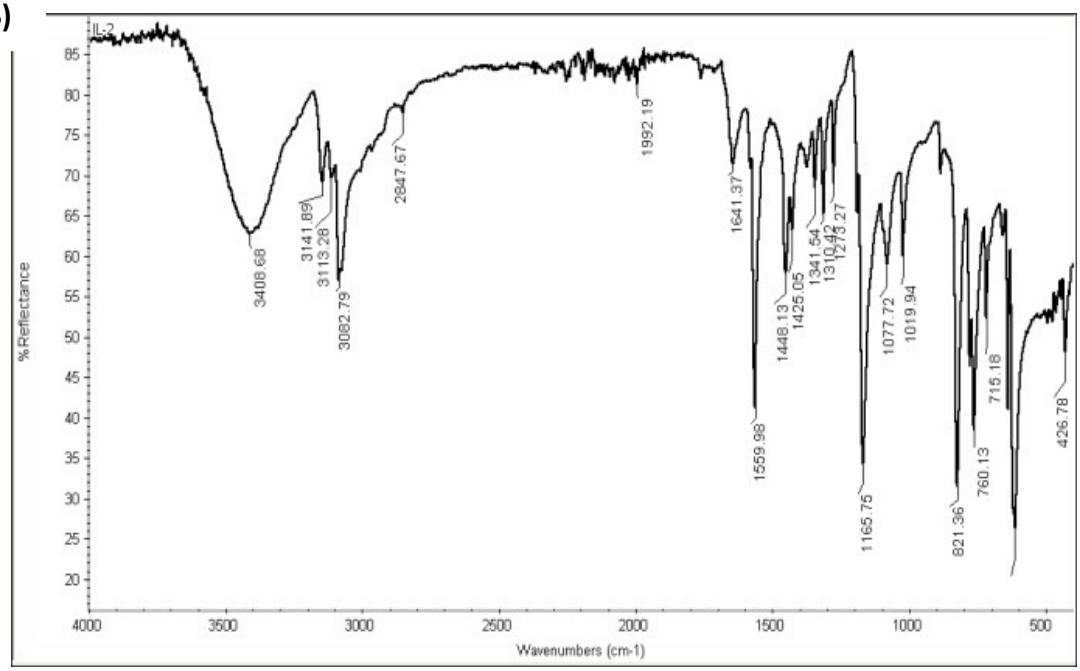


Figure S9. (A) FT-IR spectrum of IL1 and (B) FT-IR spectrum of IL-2.

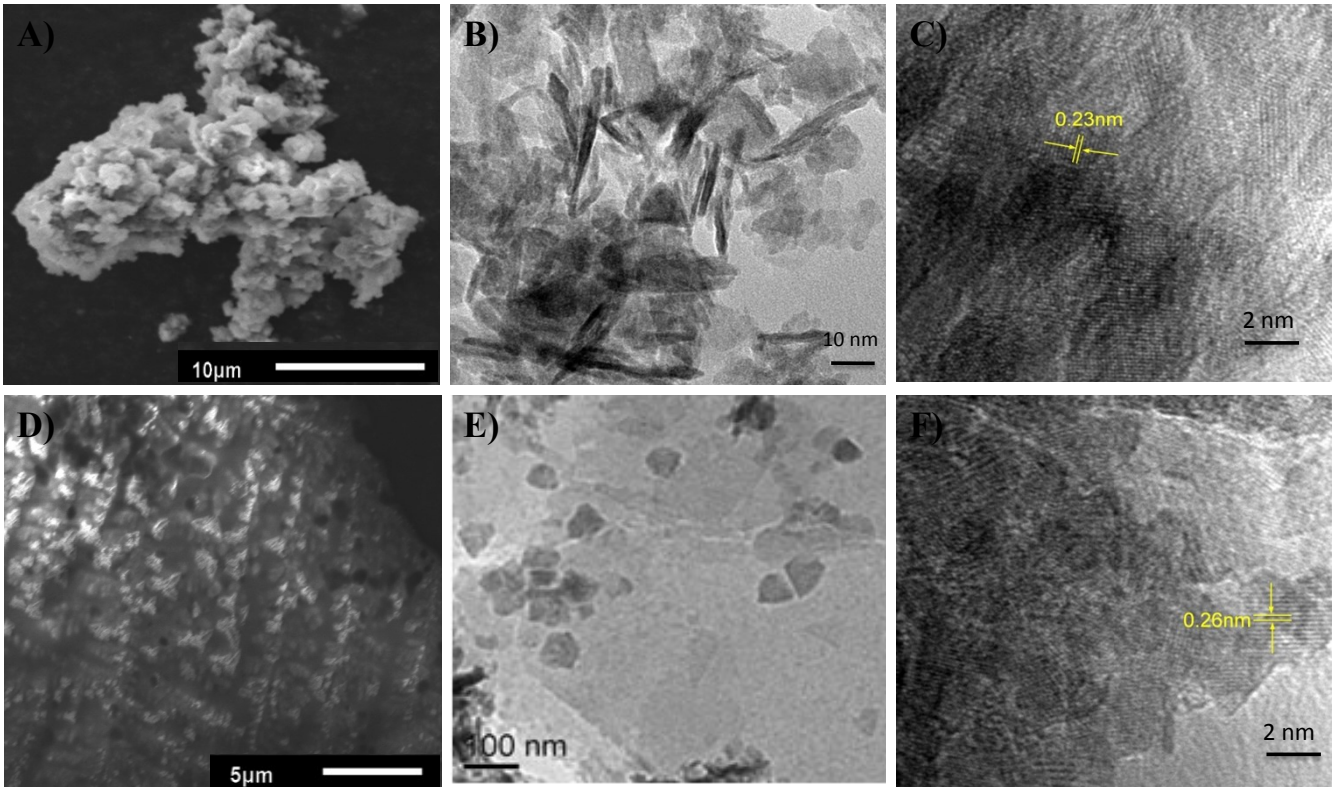


Figure S10: (**A-C**) SEM, TEM and HR-TEM images of IL2@Fe_3O_4 NPs respectively. (D-F) SEM, TEM and HR-TEM images of IL1@ Fe_3O_4 NPs respectively.

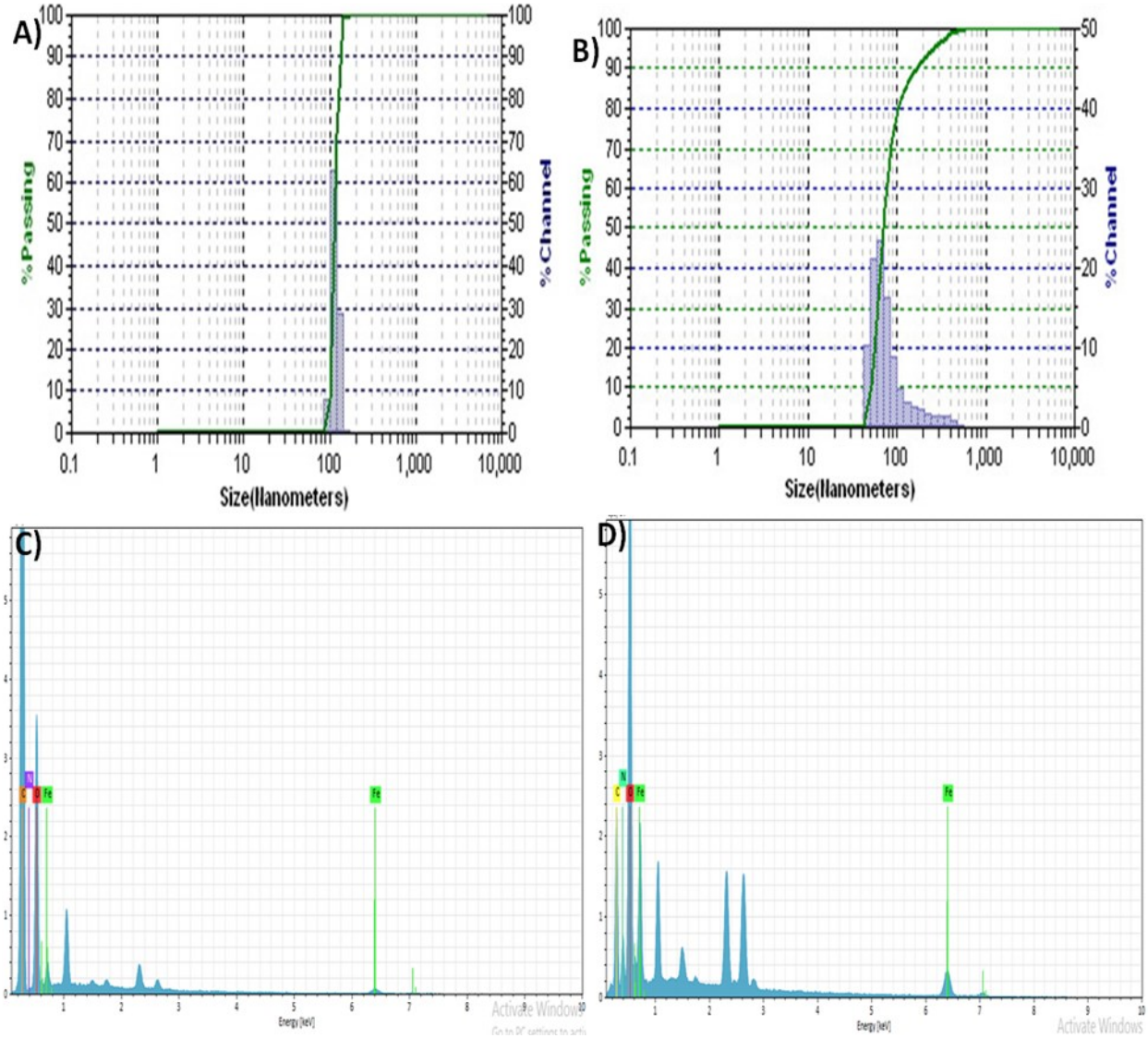


Figure S11. A-B) DLS of IL1-2@Fe_3O_4; **C-D**) EDX of IL1-2@Fe_3O_4.

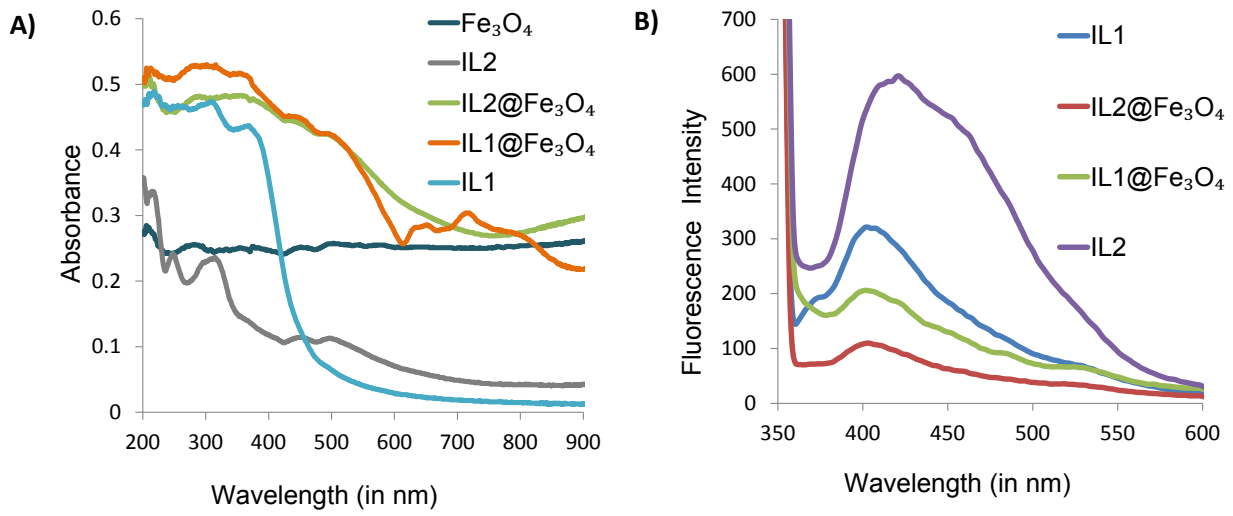


Figure S12: A) Solid state UV-Vis absorption spectra of Fe_3O_4 NPs, IL1-2 and IL1-2@Fe_3O_4; **C)** Solid state emission profile IL1 and IL1@Fe_3O_4NPs, IL2 and IL1@Fe_3O_4NPs.

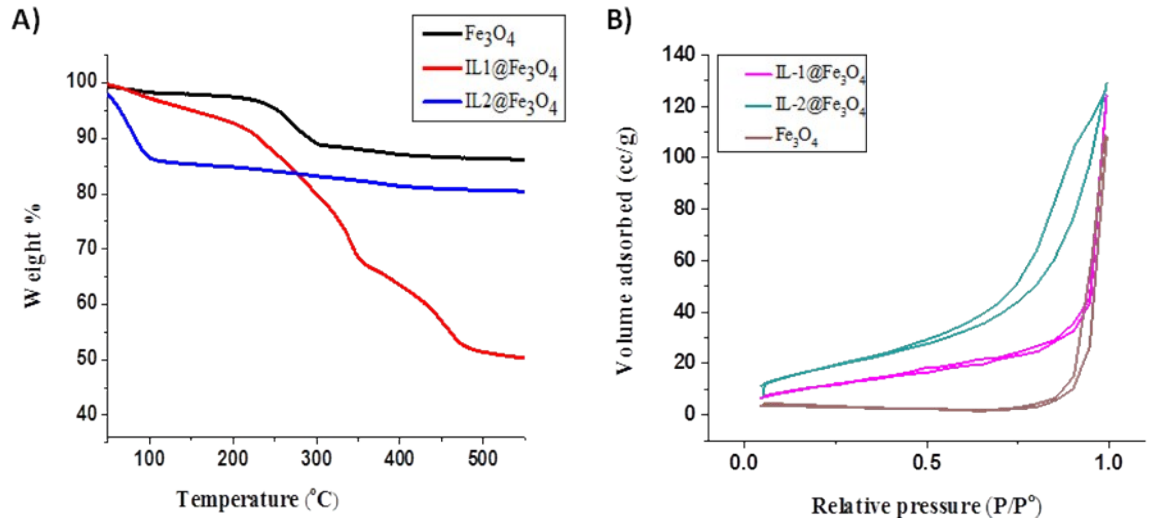


Figure S13. A) TGA-Plot of Fe_3O_4, IL1@Fe_3O_4 and IL2@Fe_3O_4. B) N_2 adsorption isotherm of Fe_3O_4, IL-1@Fe_3O_4 and IL-2@Fe_3O_4.

Table S2: N_2 adsorption BET measurements of Fe_3O_4, IL-1@Fe_3O_4 and IL-2@Fe_3O_4

S. No.	Catalyst	Surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Average pore diameter (nm)
1.	Fe_3O_4	18.00	0.181	32.55
2.	IL-1@ Fe_3O_4	57.57	0.198	3.77
3.	IL-2@ Fe_3O_4	90.63	0.209	9.54

Table S3: Acidic strength calculation for Fe_3O_4, IL-1@Fe_3O_4 and IL-2@Fe_3O_4

Sr.No	Catalyst	Volume of 0.5 N HCl[a] (ml)	Basic unit count[b] (BU) (mmol/g)	(RBA)[c] (mmol/g)	Relative basic units[d] (RBA/0.25)
1.	Fe_3O_4	0.5	0.25	0.25	1
2.	IL1@ Fe_3O_4	0.4	0.2	0.63	2.55
3.	IL2@ Fe_3O_4	0.7	0.35	1.76	7.04

[a]Volume of 0.5 N HCl required to neutralize 1 mg of catalyst (ml) calculated via back titration; [b]Number of unit's equivalent to ''OH'' present in 1 mg of sample; [c]Relative SA based exposure of BU to reactants, calculated using the formula: BU × SA of catalyst/SA of Fe_3O_4 (SAs from Table 3); [c]Calculated using the formula: RBU×RBU/RBU for Fe_3O_4.

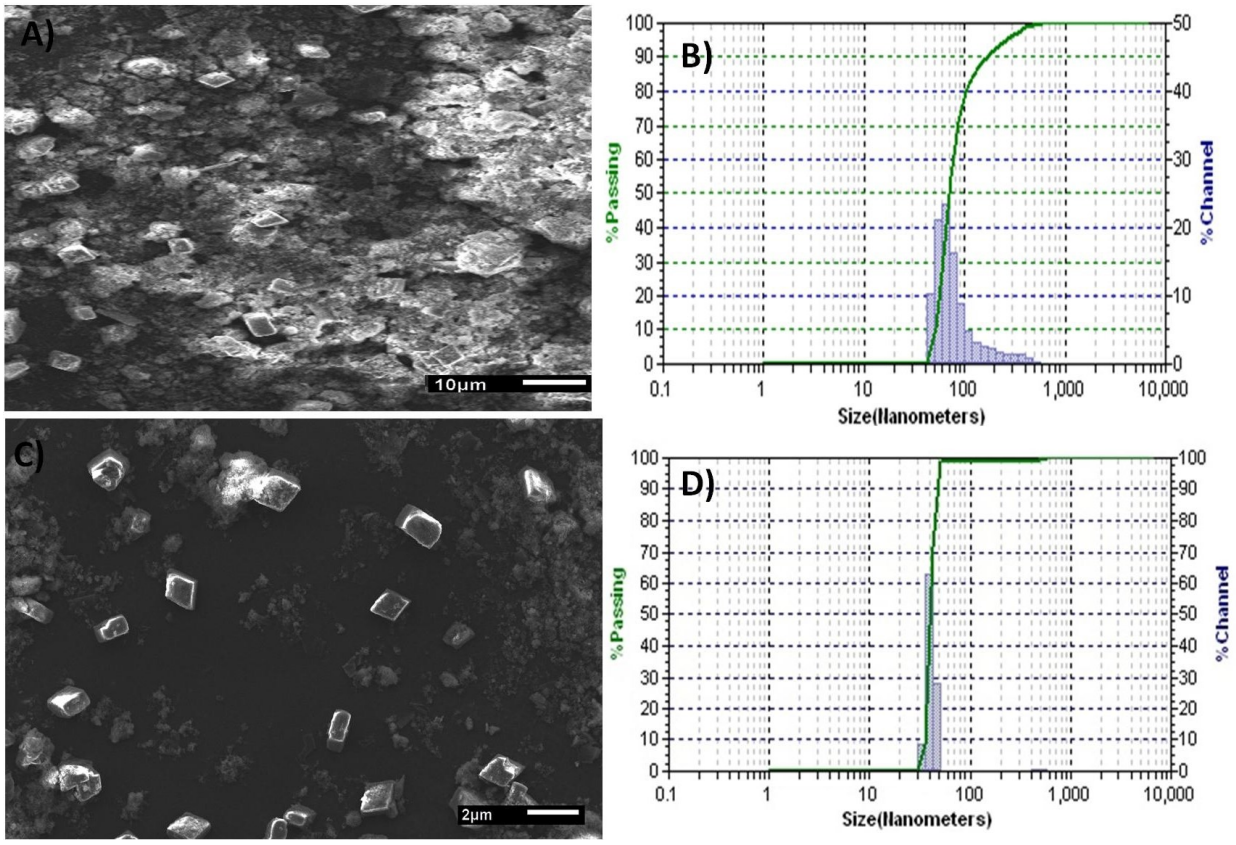


Figure S14: A-B) SEM and DLS images of IL2@ Fe_3O_4 after the fifth recycling cycle, respectively; **C-D**) SEM and DLS images of IL2@ Fe_3O_4 after the tenth recycling cycle, respectively.

Table S4: Physical Properties and Efficiency of Recovered IL2@Fe_3O_4 NPs catalyst.

Entry	Catalyst	Size (nm)[a]	(%) Yield of P1
1.	IL2@Fe_3O_4[b]	67	91
2.	IL2@Fe_3O_4[c]	49	84

[a]Measured by DLS. IL2@Fe_3O_4recoveredafter [b]fifth and [c]tenth catalytic reaction cycle.

REFERENCES

1. Mayank, A. Singh, P. Raj, R. Kaur, A. Singh, N. Kaur and N. Singh, *New J. Chem*., **2017**, 41, 3872-3881.

2. D. D. Suppiah and S. B. A. Hamid, *J. Magn. Magn. Mater*., **2016**, 414, 204-208.