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Morphology tailored Triazine-based Crystalline Organic Polymer for Efficient Mercury Sensing

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Section ES1: Thermo-gravimetric analysis

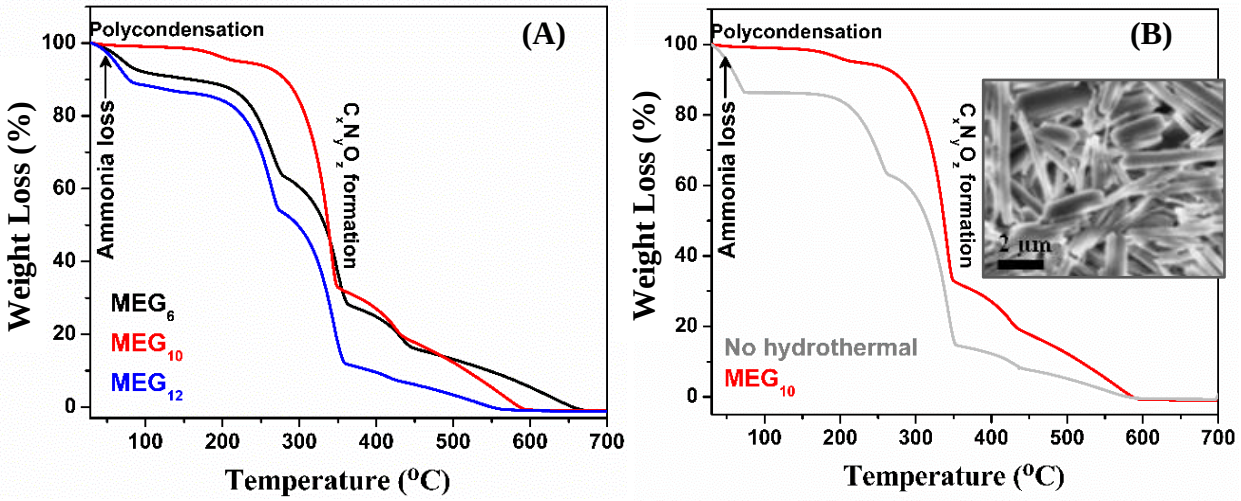

Fig. S1. (A) TGA curves of MEG_x polymers prepared at pH 6, 10 and 12. (B) TGA analysis and FESEM image (inset) of melamine-EG polymer prepared at pH 10 without hydrothermal treatment.

TGA analysis: The TGA curves of MEG_x, shown in Fig. S1A, reveal that the polymer prepared at pH 10 under hydrothermal treatment (MEG_{10}) is stable upto 300 °C whereas MEG_6 and MEG_{12} both loose considerable amount of weight (~10-12%) before 100 °C due to removal of adsorbed water or ammonia (from NH_4OH medium), and finally start decomposing beyond 200 °C.

Section ES2: XRD analysis

Table S1: Different structural parameters obtained by refining the XRD pattern of melamine.

Lattice parameters (Å)			Cell angle (deg)	Atom types	Fractional coordinates		
a	**b**	**C**	**β**		**x**	**y**	**Z**
				C1	0.1508	0.6056	-0.0054
				C2	0.0595	0.6847	0.3503
				C3	0.1268	0.7692	0.1470
				N1	0.2772	0.9509	-0.1753
				N2	0.1257	0.4270	0.4440
				N3	0.0574	0.9515	0.2355
				N4	0.0050	0.8184	0.2011
10.6036	**7.5045**	**7.2872**	**112.22**	N5	0.1971	0.7794	-0.0348
				N6	0.1367	0.5153	0.2622
				H1	0.3703	0.4166	-0.0822
				H2	0.2446	0.4667	0.0038
				H3	0.0545	0.2026	0.6081
				H4	0.0970	0.5337	0.5542
				H5	-0.0020	0.5011	0.2144
				H6	0.0039	0.0300	0.0726

The unit cell volume of polycrystalline melamine enhances from 517.25 $Å^3$ to 536.81 $Å^3$ with respect to its bulk counterpart primarily due the expansion of all the lattice parameters. However, the cell angle (β) reduces marginally from 113.30° to 112.22°. Coherently diffracting domain (crystallite) size and r.m.s. lattice strain of polycrystalline melamine are found to be 253.45 nm and 1.954×10^{-4} respectively.

Table S2: Different structural parameters obtained by refining the XRD pattern of MEG_{10}.

Lattice parameters (Å)			Cell angle (deg)	Atom types	Fractional coordinates		
a	**b**	**c**	**β**		**x**	**Y**	**z**
				C1	0.2798	0.4466	0.0052
				C2	0.2045	0.5430	0.3230
				C3	0.0216	0.8022	0.3561
				N1	0.0964	0.3628	-0.3370
				N2	0.0917	-0.0213	0.4738
				N3	0.0017	0.2037	0.1936
				N4	-0.0017	0.6743	0.5033
10.1243	**8.2604**	**7.8860**	**116.85**	N5	0.3465	0.0740	0.1861
				N6	0.1108	0.2726	0.1151
				H1	0.5662	0.7102	0.3356
				H2	0.0400	0.8303	-0.0151
				H3	0.0072	0.0072	0.7706
				H4	0.0125	0.1735	0.6265
				H5	0.0353	0.8177	0.0061
				H6	0.0270	0.1663	0.6257

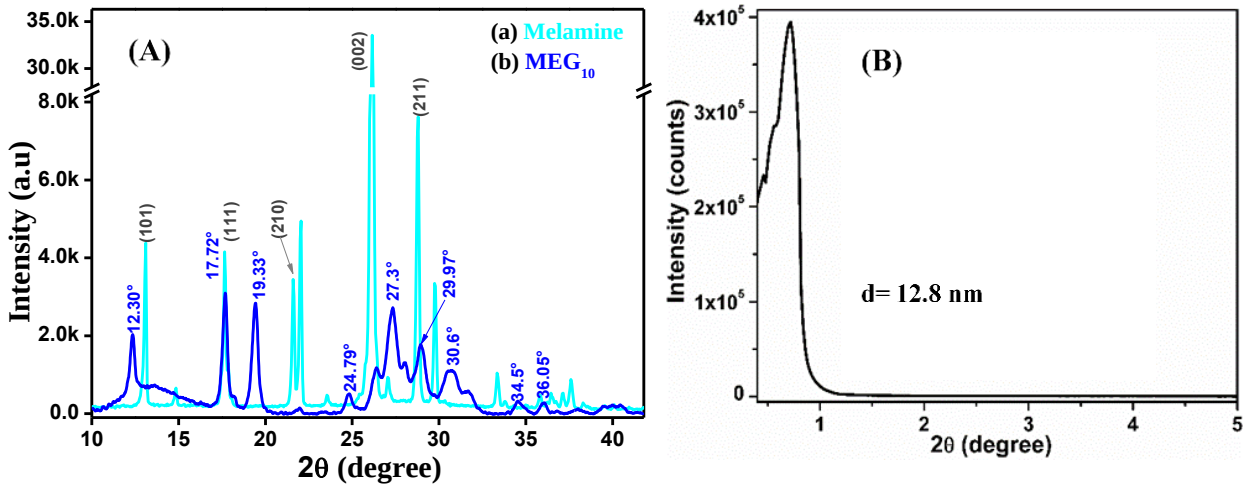

Fig.S2. (A) High angle XRD spectra of (a) pure melamine and (b) MEG_{10}. (B) low angle XRD shows mesoporous nature of MEG_{10} polymer.

Section ES3: EDX analysis

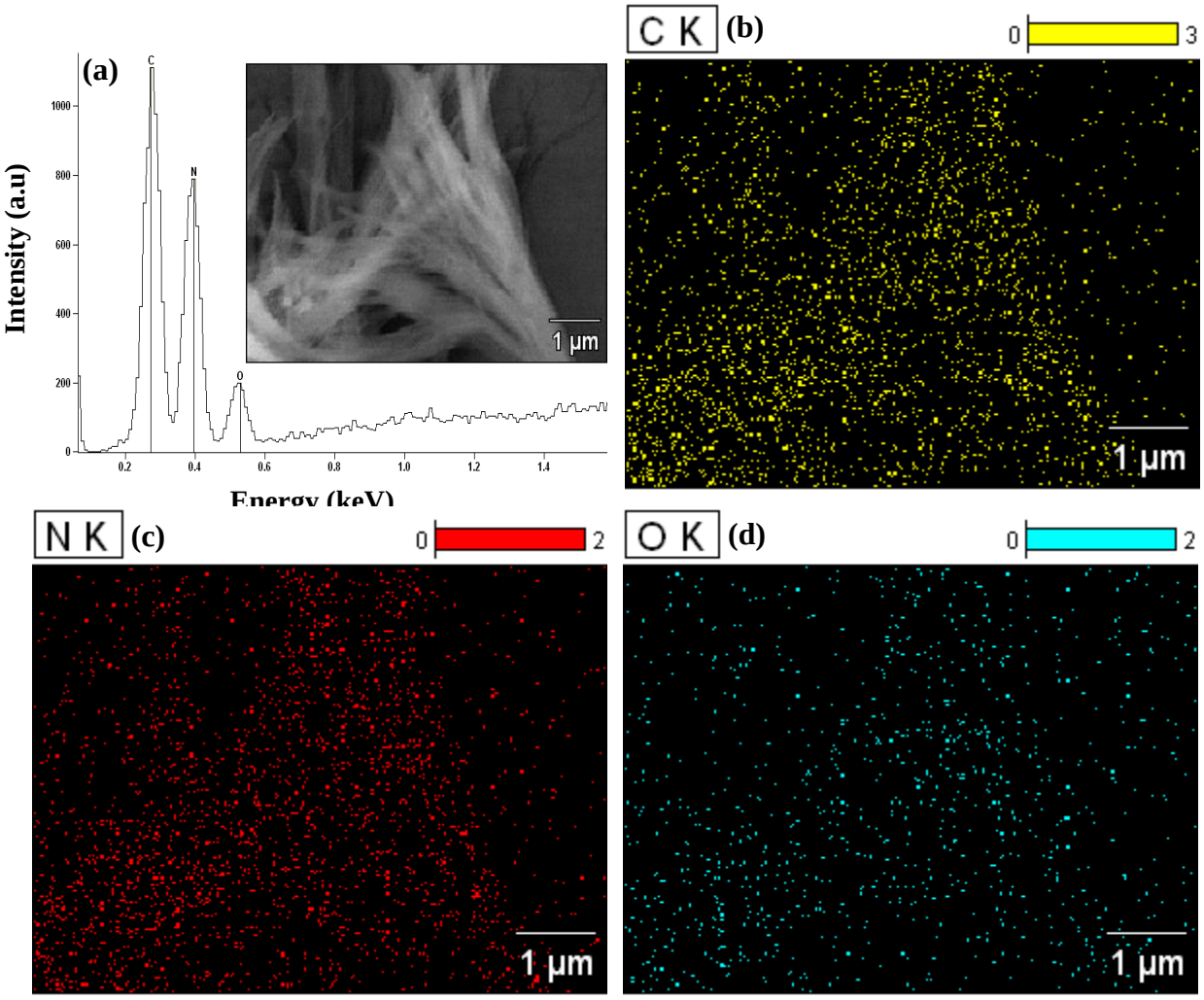

Fig.S3. (a) EDX spectra of MEG_{10} showing the presence of C, N and O; corresponding elemental mapping images are shown in (b),(c) and (d) for C, N and O respectively.

Section ES4: BET analysis

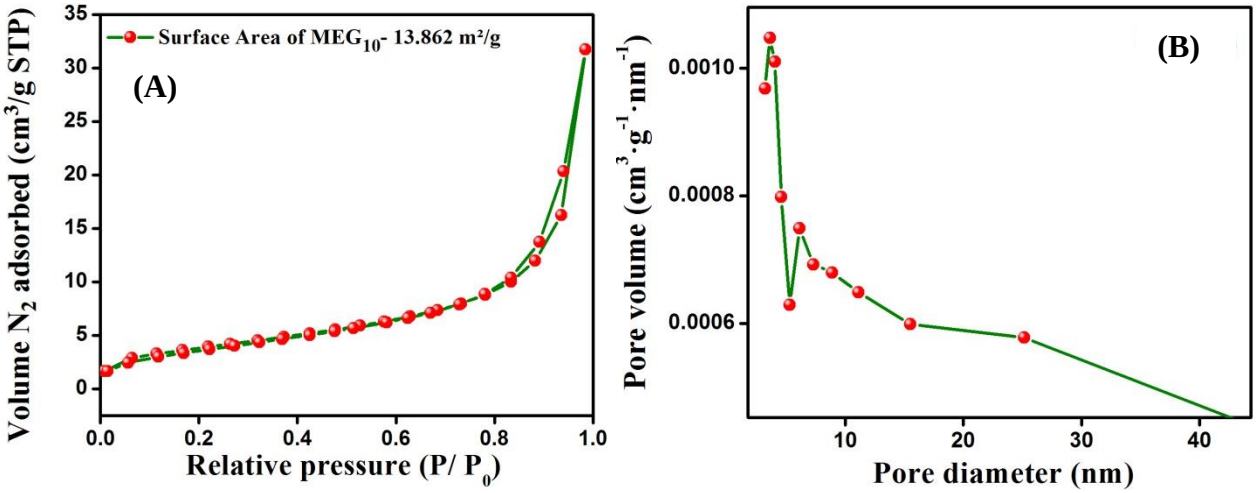

Fig.S4. (A) Nitrogen adsorption-desorption isotherm showing classical type III isotherm and (B) corresponding BJH pore-size distribution curve of MEG_{10} polymer with BJH pore diameter of 3.611 nm and average pore diameter of 13.9 nm (total pore volume = 0.03707 cc/g for pores smaller than 65 nm; P/P_0 = 0.98530).

As routine analysis we carried out the sorption analysis using N_2 gas at 77K and 1 bar. A low surface area (~13.8 m^2/g) may be due to the common diffusional issues of N_2 molecules inside narrow pores.[1,2] The surface area can also be severly reduced due to the fusion of many pores probably during framework crystallization which results in structural variations like "pore expansion".[3] However the polymer material may also be non-porous with large number of π stackings and the surface area as obtained from the BET analysis arises mainly due to the external surfaces.

Section ES5: ^{1}H-NMR spectral analysis

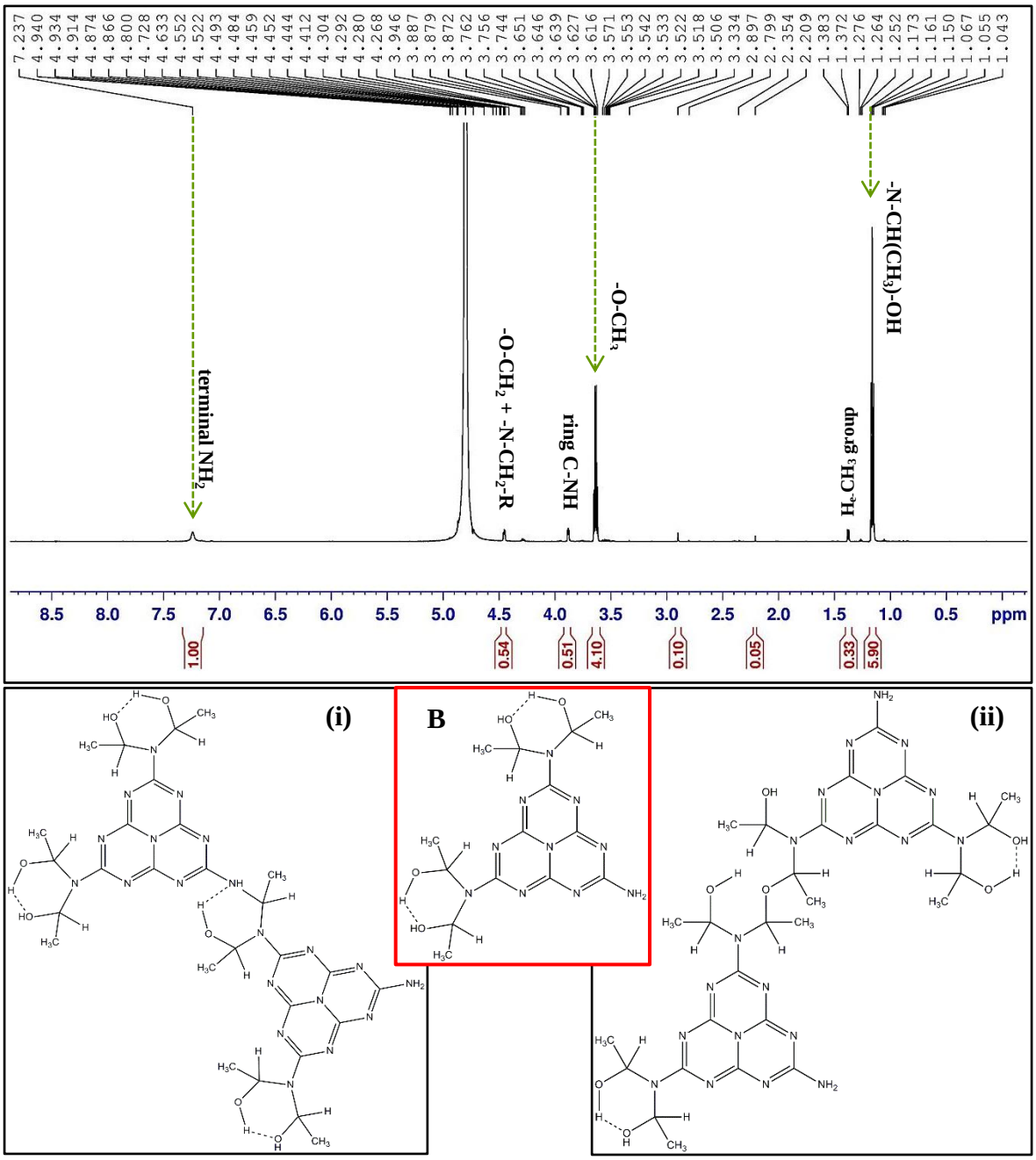

Fig.S5. (A) ^{1}H-NMR of MEG_{10}. Possible structures of the repeating unit created from the monomeric structure (B) are shown in (i) and (ii).

Section ES6: Molecular Weight determination from GPC:

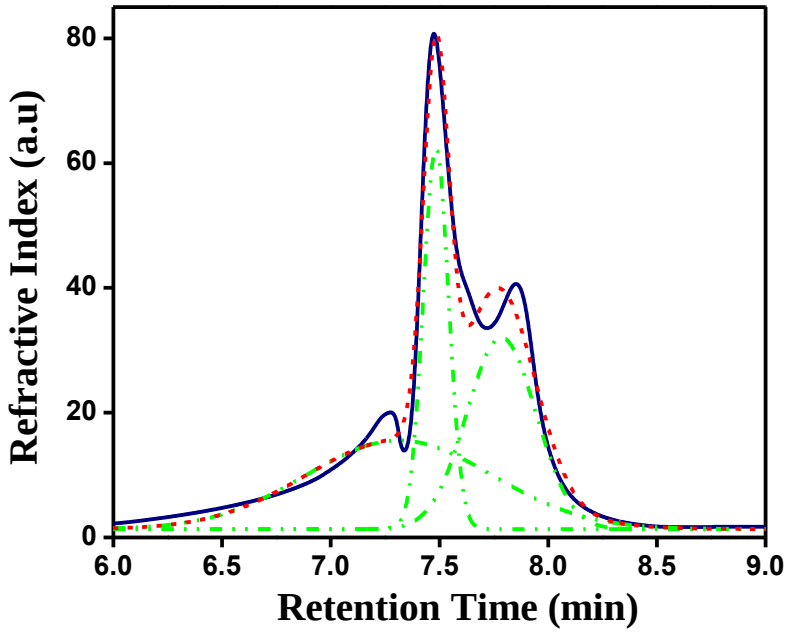

Fig.S6. Molecular weight distribution of MEG_{10} as obtained from GPC.

Section ES7: Zeta Potential Analysis

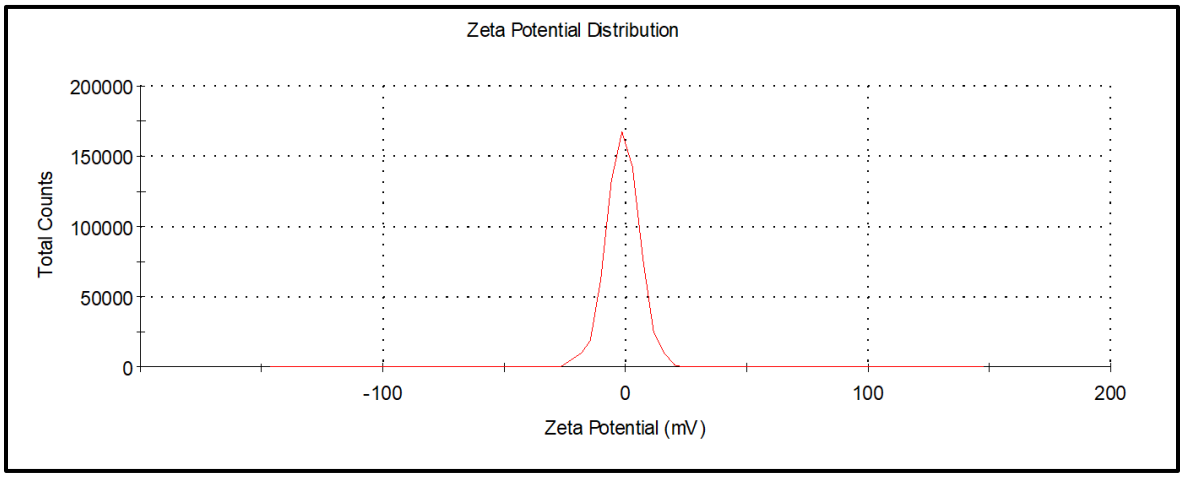

Fig.S7. Zeta Potential distribution curve of MEG_{10} dispersed in deionized water measured at pH 6.

Section ES8: Diffuse Reflectance Spectra and Photoluminescence Spectra

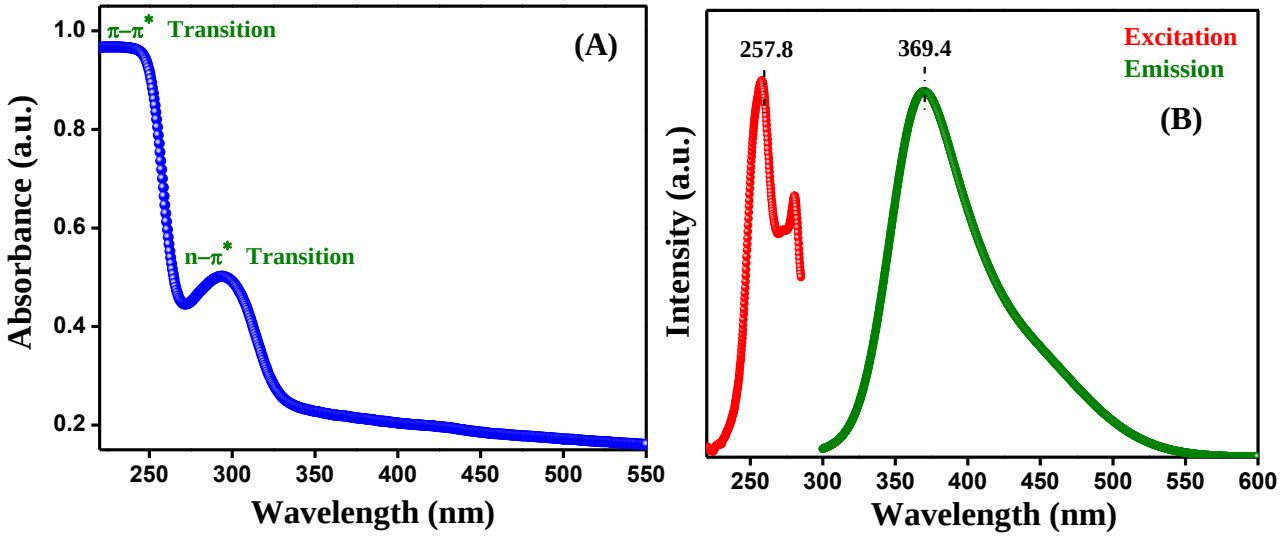

Fig.S8. (A) Absorbance spectrum of MEG_{10} at pH 6; and (B) Photoluminescence excitation and emission spectra of MEG_{10}.

Section ES9: MEG_{10} as metal ion sensor

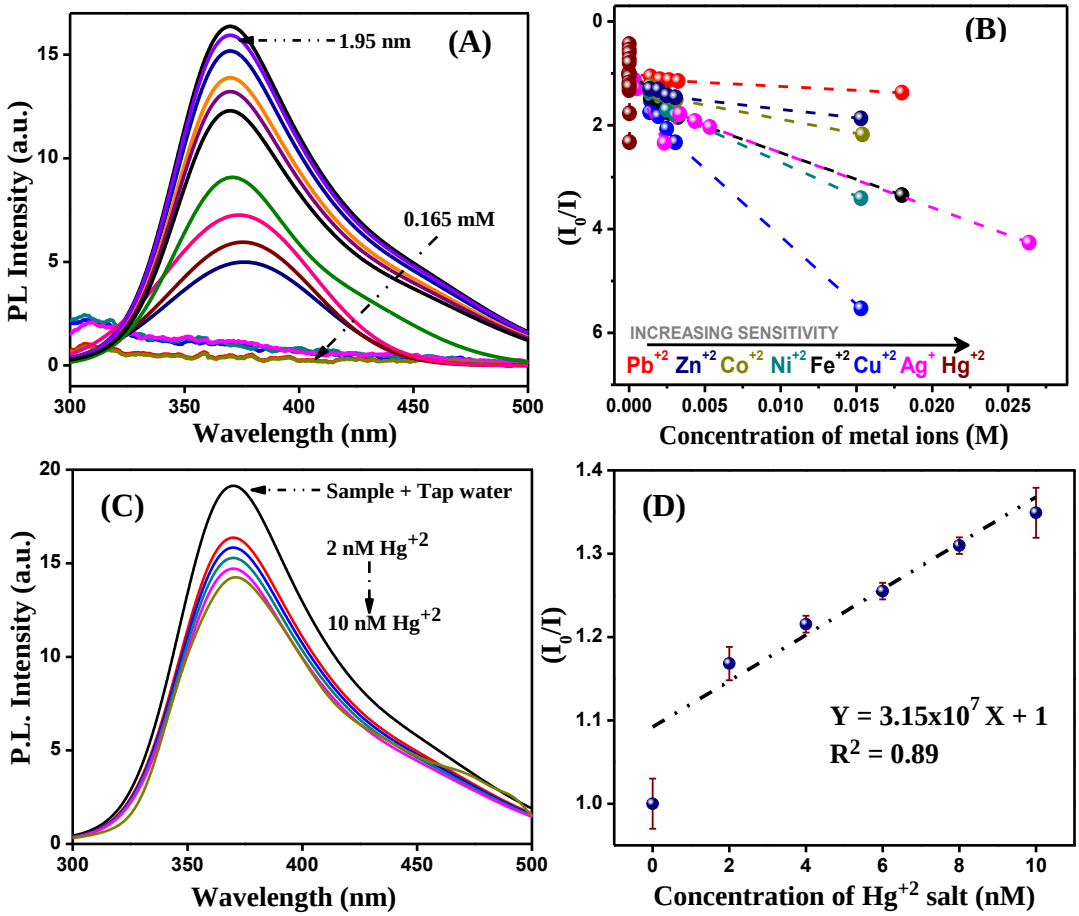

Fig.S9. (A) Room temperature PL quenching of aqueous MEG_{10} solution in presence of different concentration of Hg^{+2} salt at 25 °C. (B) Change in PL intensity $[(I_0\text{-}I)/I]$ versus concentration of different transition metal ions ($[MEG_{10}]$ = 0.5 mg/mL, 25 °C). (C) Room temperature PL quenching of aqueous MEG_{10} solution in tap water in presence of different concentration of salts. (D) Change in PL intensity $[I_0/I]$ versus different concentration of Hg^{+2} metal ions in tap water $[MEG_{10}]$ = 0.5 mg/mL.

Section ES10: XRD Analysis of Hg^{+2}@MEG_{10} complexes at different pH values:

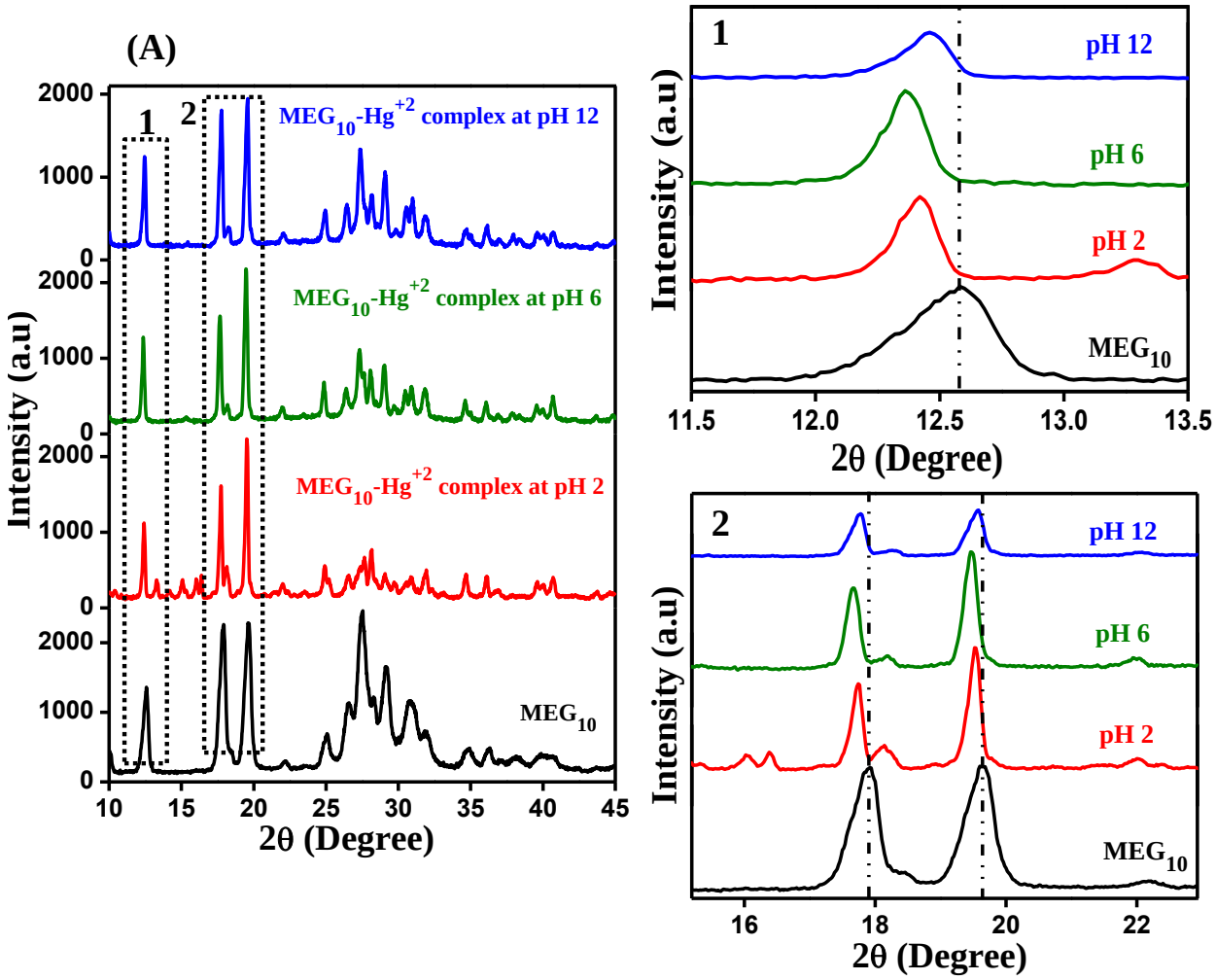

Fig. S10. (A) XRD analysis of MEG_{10} after Hg^{2+} adsorption at different pH values of 2, 6 and 12. Magnified XRD plot of the (1) (001) plane and (2) (-201) and (200) planes of MEG_{10} after Hg^{2+} adsorption.

Section ES11: XPS Analysis of Hg^{+2}@MEG_{10} post sensing:

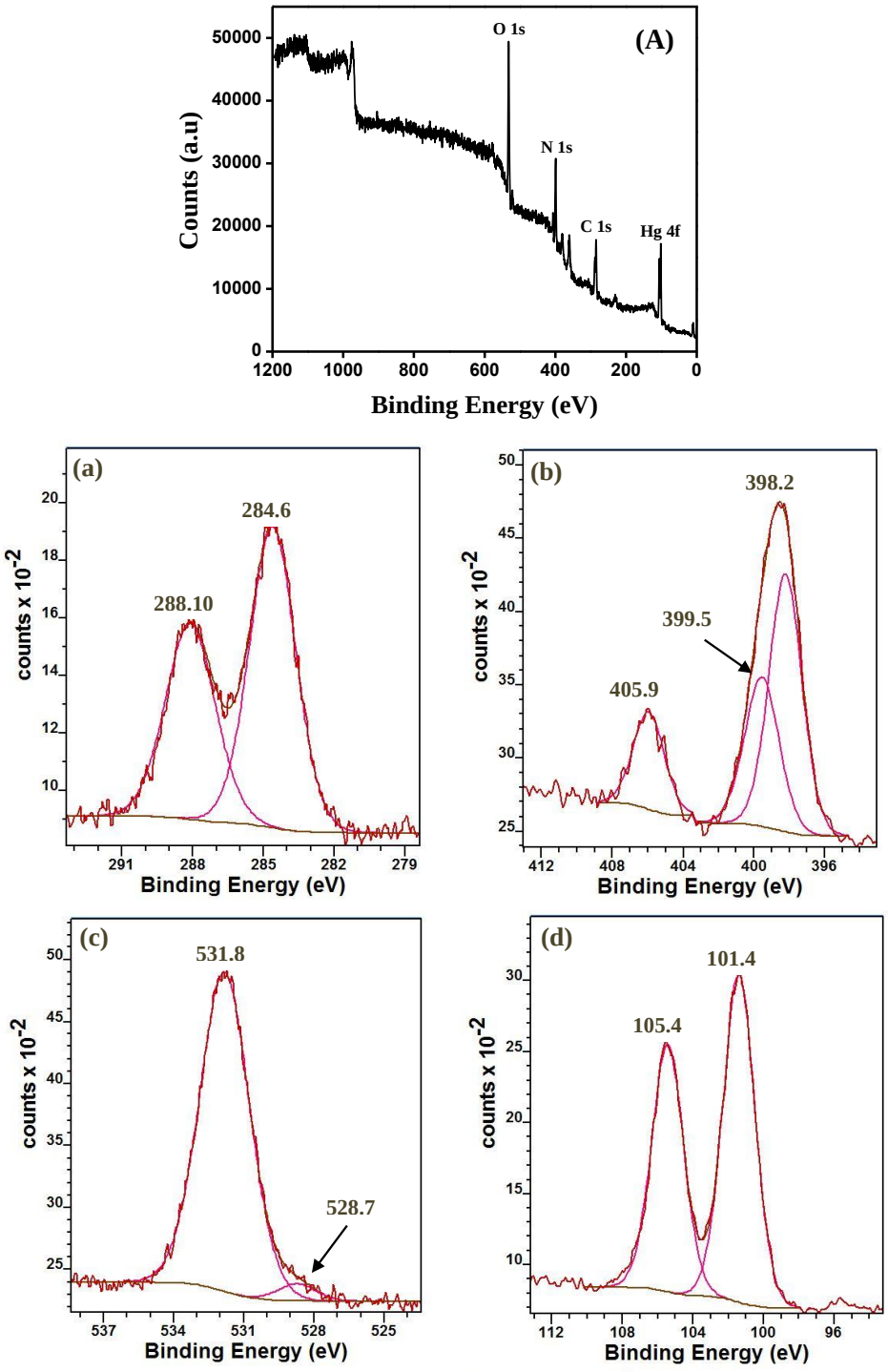

Fig. S11. XPS spectra of MEG_{10} after Hg^{2+} adsorption: (A) XPS survey scan; Elemental scan of (a) C1s, (b) N1s, (c) O1s spectra and (d) Hg4f spectra. The individual deconvoluted profiles are also given.

References

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2. P. Kaur, J. T. Hupp and S. T. Nguyen, *ACS Catal.*, 2011, **1**, 819-835.

3. L.K. Shrestha, Y. Yamauchi, J. P. Hill, K. Miyazawa and K. Ariga, *J. Am. Chem. Soc.*, 2012, **135**, 586-589.