Preparation and Binding Evaluation of Histamine-Imprinted Microspheres via Conventional Thermal and RAFT-mediated Free Radical Polymerization

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Electronic Supplementary Information

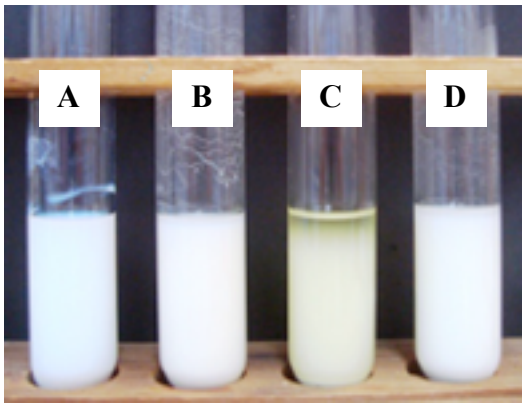


Figure S1. Microspheres obtained using ≤ 4% (w/w) monomer feed concentration with 1:4 mole ratios HTM:MAA (20 wt%) and EDGMA (80 wt%) in acetonitrile (MeCN) at 60 ^{o}C for 24 hours **(A)** CTP-N80, **(B)** CTP-M80, **(C)** CRP-N80, **(D)** CRP-M80.

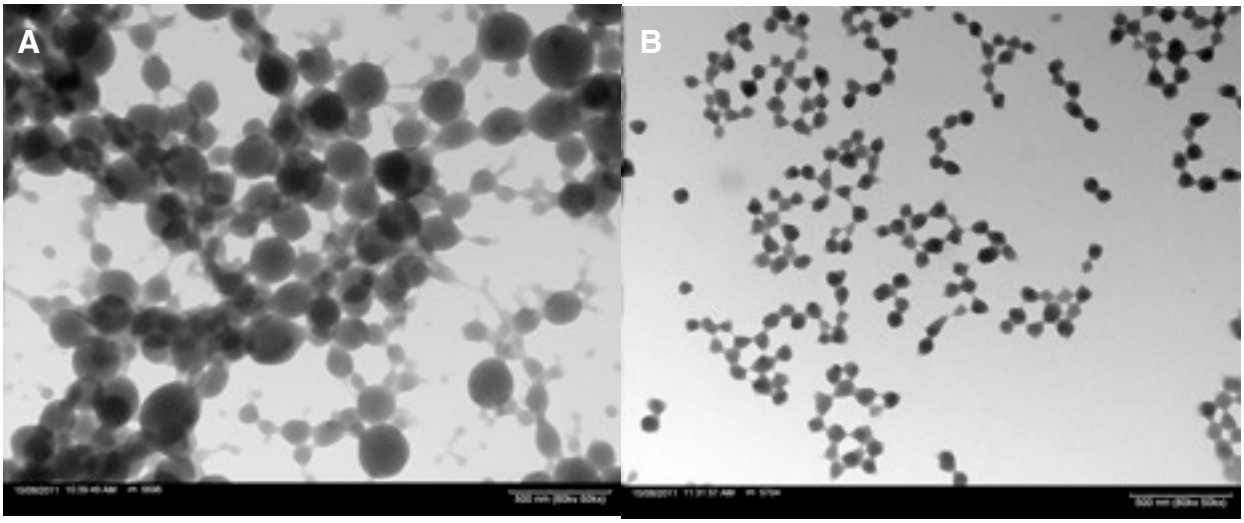


Figure S2. Sample micrograph of **(A)** CTP-M90 and **(B)** CTP-N90 prepared using ≤ 4% (w/w) monomer feed concentration with 1:4 mole ratios HTM:MAA (10 wt%) and EDGMA (90 wt%) in MeCN at 60 ^{o}C for 24 hours, viewed using a transmission electron microscope at 50,000x magnification.

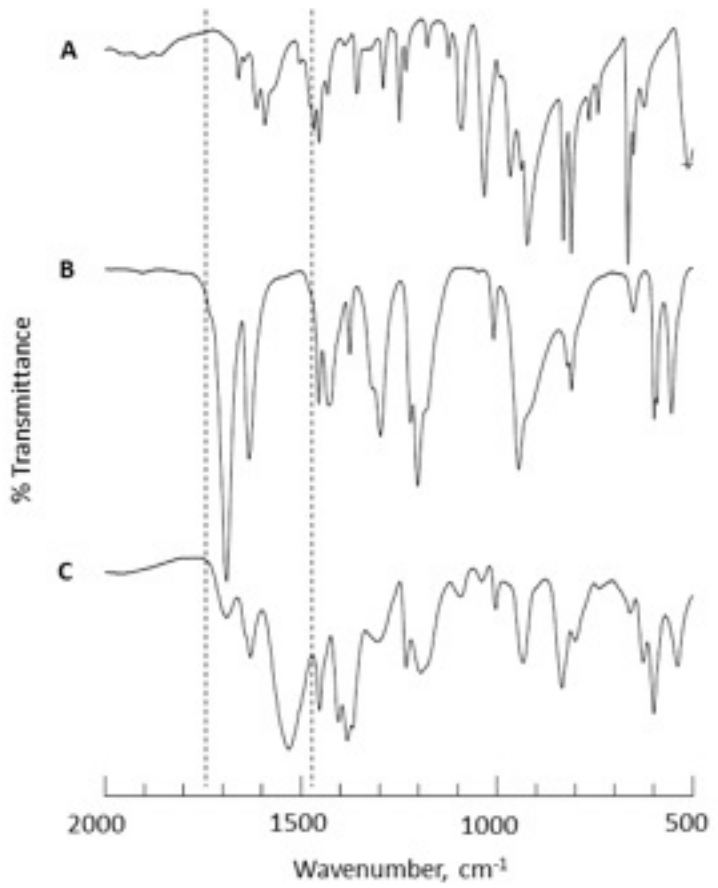


Figure S3. Representative FTIR spectra of: **(A)** histamine (HTM), **(B)** methacrylic acid (MAA), and **(C)** 1:1 HTM-MAA mixture highlighting changes between ~1500 and ~1700 cm^{-1} due to the interaction of HTM with MAA.

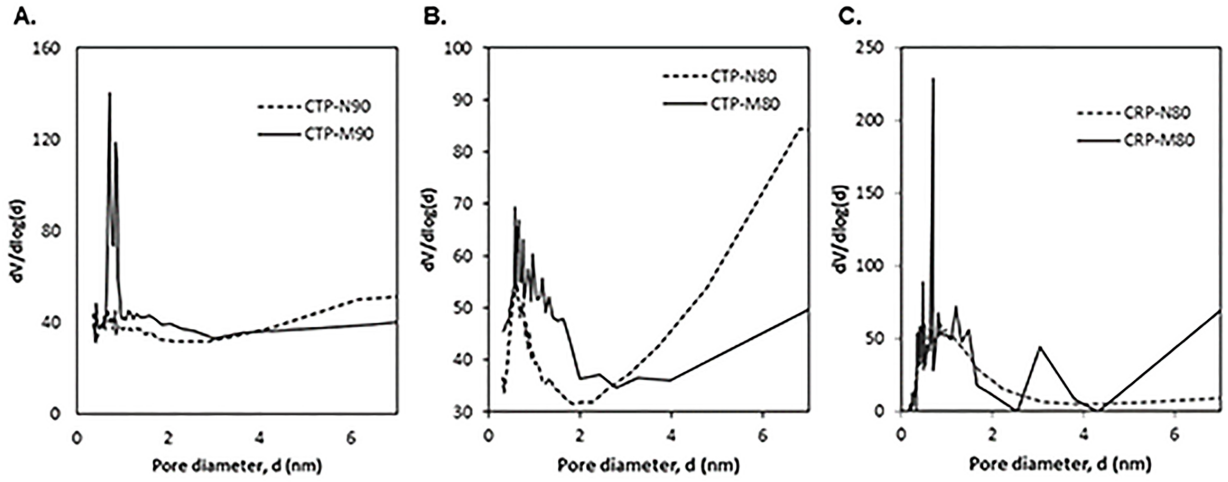


Figure S4. Micropore size distribution of **(A)** CTP-M90 and CTP-N90; **(B)** CTP-M80 and CTP-N80; and **(C)** CRP-M80 and CRP-N80, measured by N_2 gas adsorption.

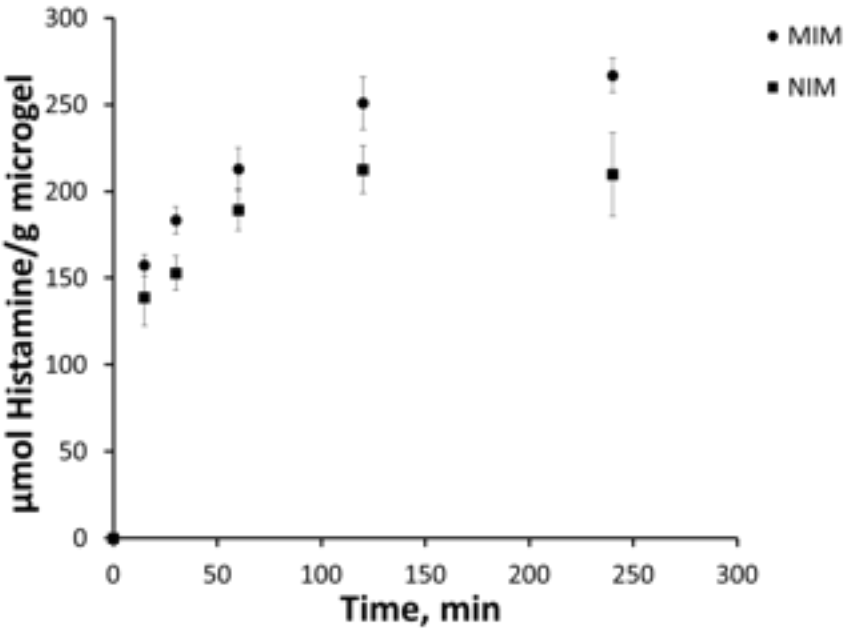
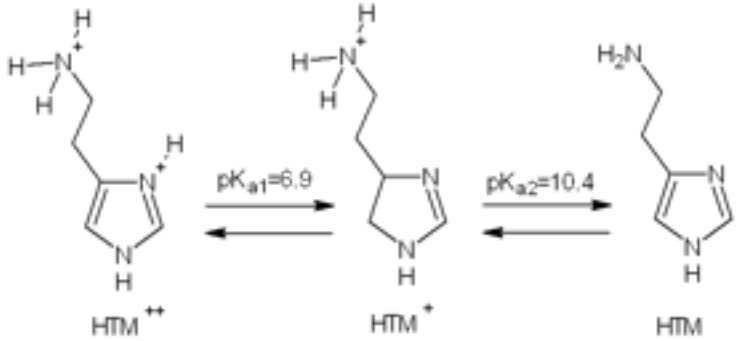


Figure S5. HTM sorption of CTP-M80/N80 microspheres at various times from 15 to 240 min. Binding conditions: 2 mg microspheres in 1 mM HTM aqueous solution at pH 7.

A.



B.

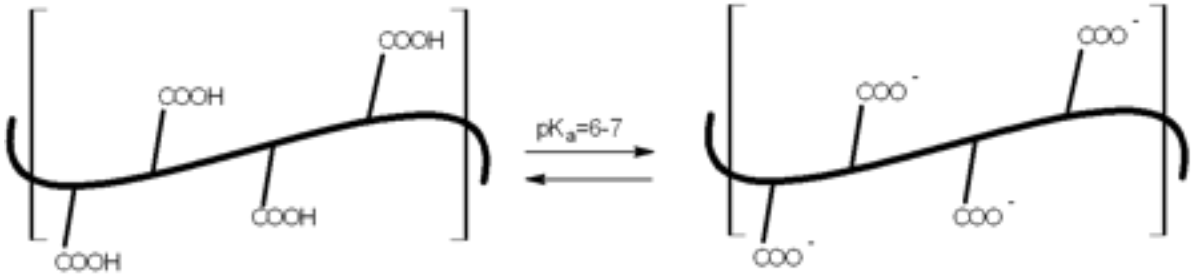


Figure S6. (**A)** Different forms of HTM at different pHs. HTM has pK_a values of 6.9 and 10.4. At pH 5, HTM^{++} is predominant, HTM^{++} and HTM^{+} exist at pH 7 while at pH 9, HTM^{+} is more predominant. **(B)** Deprotonation of MAA-based microspheres at different pH. pK_a of PMAA is between 6-7. At pH below the pK_a, microspheres are almost protonated whereas above the pKa value (i.e. pH= 9) MAA-based microspheres are deprotonated.

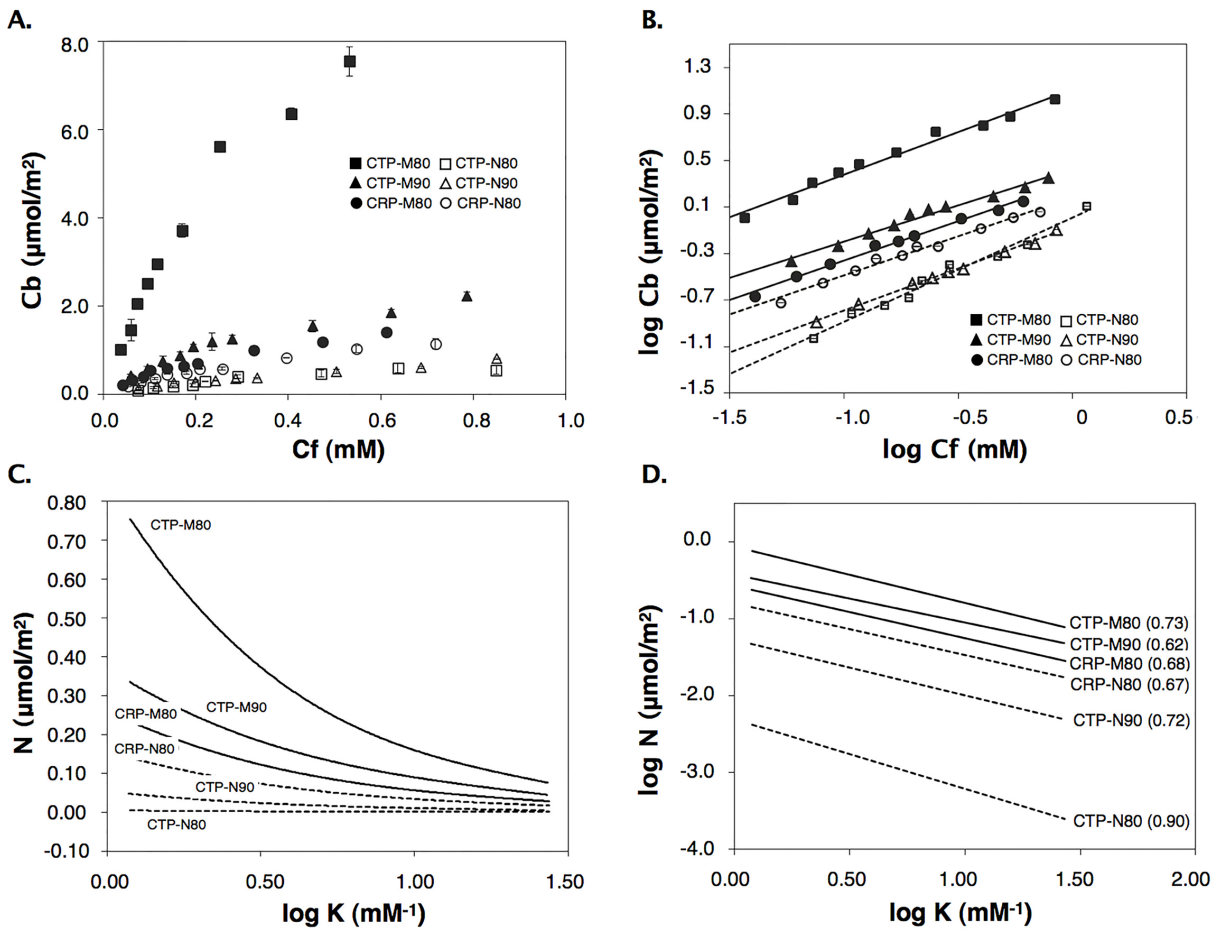


Figure S7. **(A)** Freundlich binding isotherms, **(B)** linearized log-log Freundlich binding isotherms, **(C)** Freundlich affinity distribution expressed in the *N* vs log *K* format, and **(D)** Freundlich linearized affinity distribution expressed in log *N* versus log *K* format, using calculations based on surface area. *N* and *K* were obtained from the slope (*m*) and y-intercept *a* of **B** (see Table 2). HTM binding results were obtained between 0.10 and 1.0 mM HTM concentration range (aqueous solution, 25 mM buffer, pH 7) using 2 mg of MIMs and NIMs. Affinity distributions have been generated using the equation $N(K) = 2.303am(1 - m^2)K^{-m}$ over concentration ranges $K_{min} = 1/F_{max}$ and $K_{max} = 1/F_{min}$.