

Supporting Information

Supramolecular Self-Assembly of a Polyelectrolyte Chain Based on Step-growth Polymerization of Hydrophobic and Hydrophilic Monomers

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Table 1S. Results of GPC analysis of poly(citramide imide) samples

Sample	Catalyst	T/°C	time/h	M _n	M _w	PDI
a	DMAP (1%)	170	6	4109	6549	1.59
b	Ti(OBu) ₄ (1%)	70	6	4037	5294	1.31
c	DMAP (1%)	70	6	5243	8039	1.53
d	DMAP (1%), LiCl (1%)	70	6	5057	6971	1.38
e	DMAP (1%)	70	12	5067	7544	1.49
f	DMAP (1%)	70	24	5070	6923	1.37
g	DMAP (1%)	70	3	4780	7903	1.65
h	DMAP (3%)	70	6	4445	7437	1.67

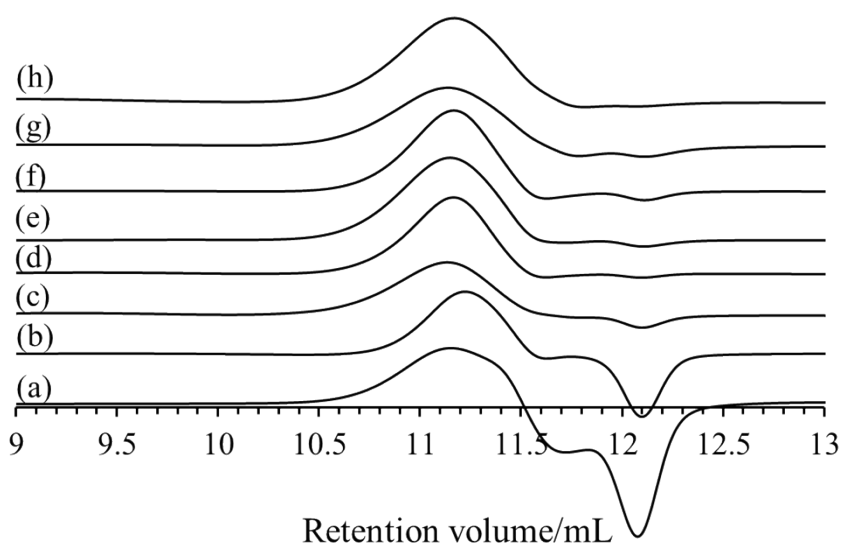


Figure 1S. GPC traces of poly(hexamethylene citramide imide) prepared under various conditions listed in Table 1S.

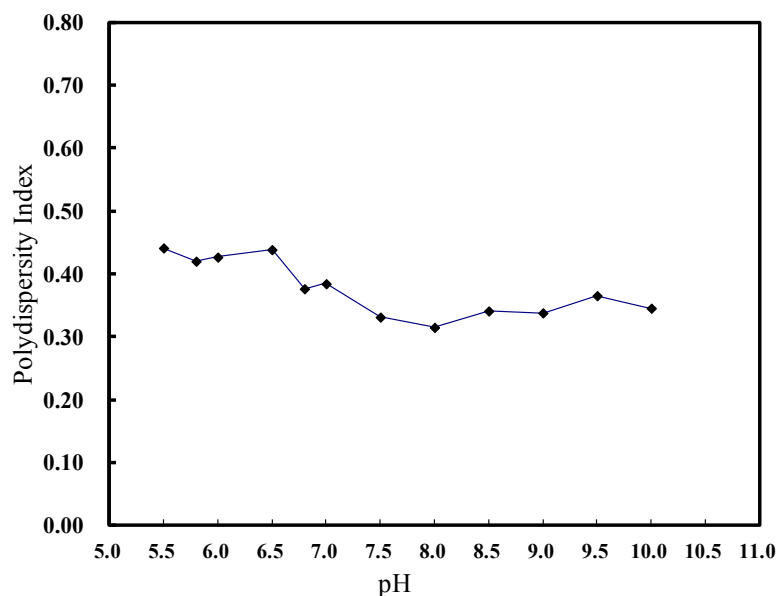


Figure 2S. Polydispersity index values of the hydrodynamic diameters (D_h) of the nanoparticles measured by dynamic light scattering.

The hydrodynamic diameters of different concentrations of aqueous sample solutions were characterized by 3D cross-correlation analysis (photon cross correlation spectroscopy, PCCS) realized in a commercially available instrument (Nanophox, Sympatec GmbH, Germany). All the aqueous particle solutions were analyzed using disposable cuvettes. A laser light is split into two equal beams and focussed with the help of a lens into the sample vial. The crossing region forms the measurement volume. Two photon-detectors receive the scattered light at the right angle. The time resolved intensities measured by the photo-detectors are cross correlated. Data processing was carried out using non-negative least square (NNLS) analysis of the experimental correlation function and analyzed using *Stokes–Einstein equation* to calculate the hydrodynamic diameters of the samples. The advantage of the method has been discussed recently by J. Burdíková, F. Mravec, J. Wasserbauer, and M. Pekař, *Colloid Polym. Sci.* 2016 , 295 (1) :1-8.

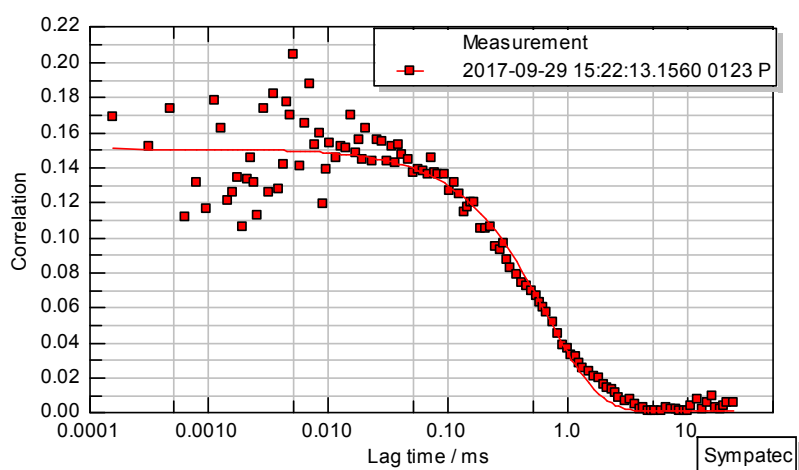
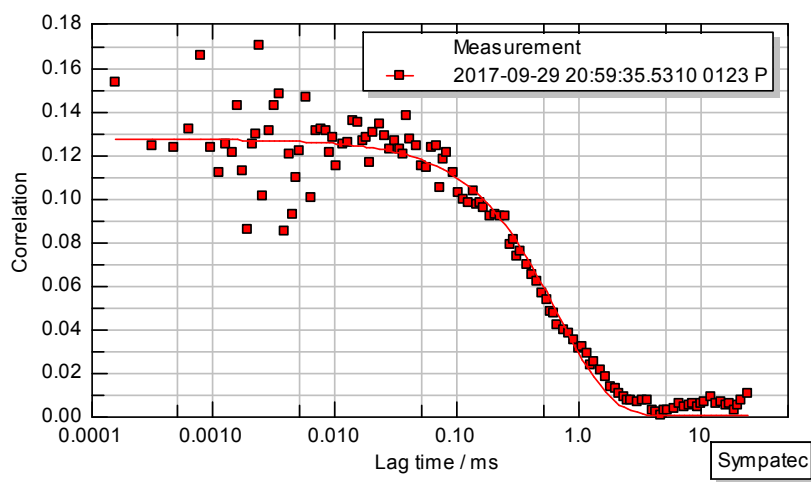
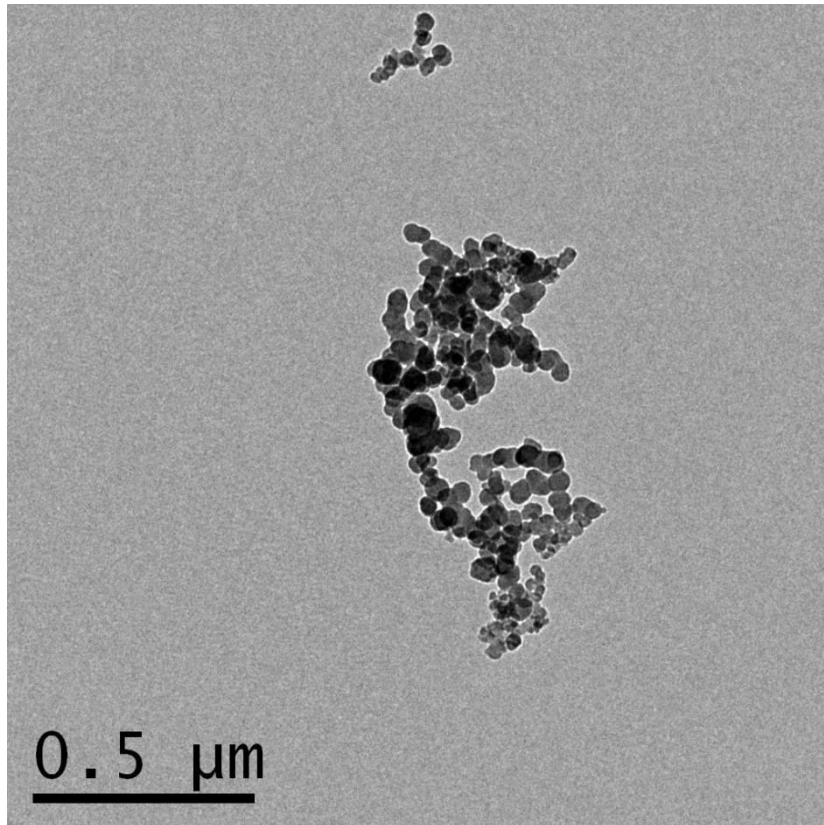


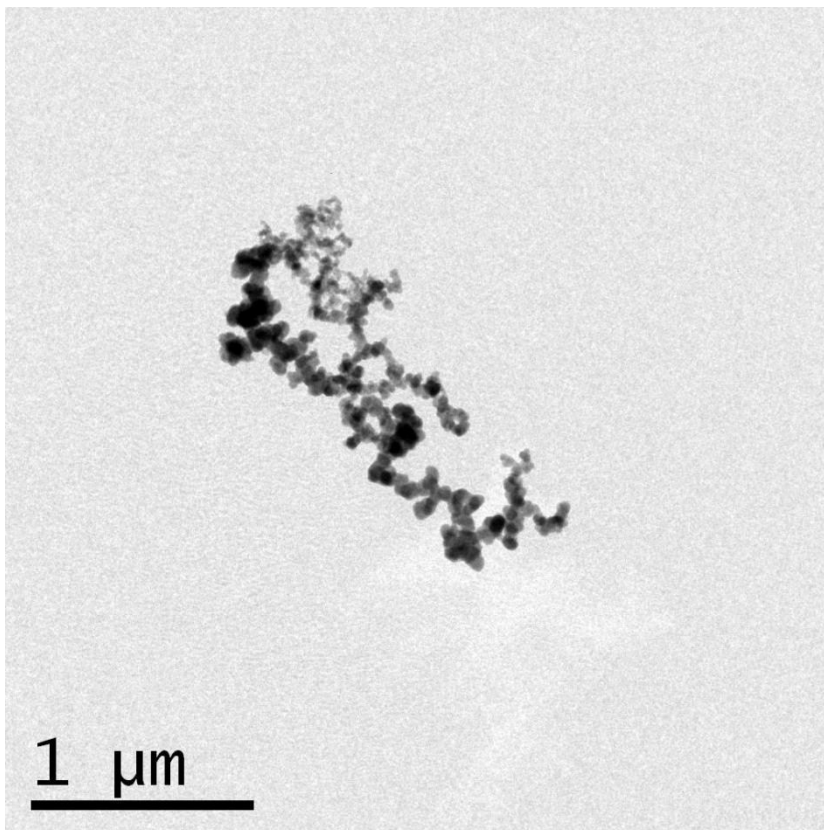
Figure 3S. Typical fitting analysis results in the DLS measurements of of the PHMC samples by photon cross correlation spectroscopy (PCCS).

Table 2S. NaCl salt concentration effect on the DLS and zeta potentials of the polymer at pH 8.0.

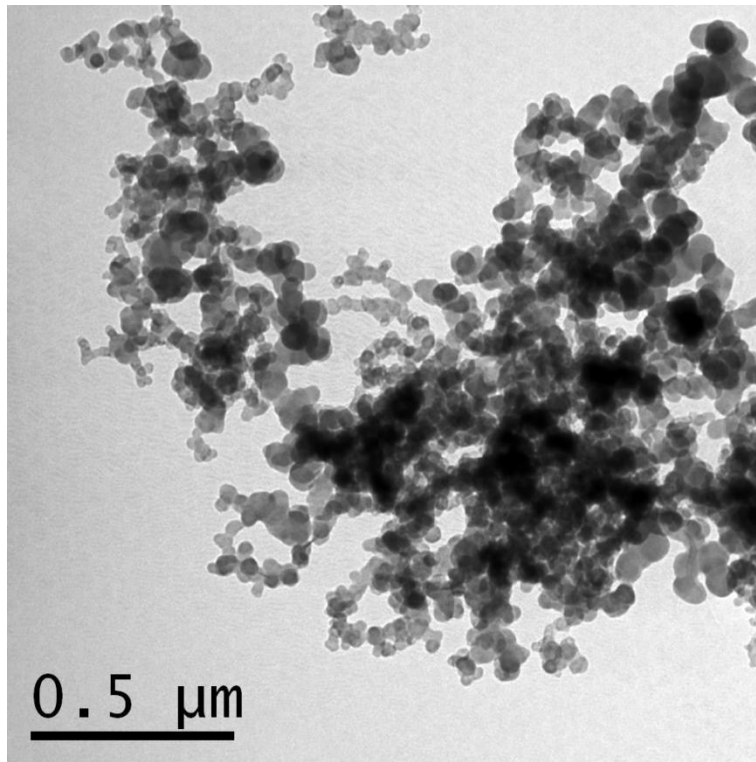
NaCl concentration /mM	D_h /nm	zeta potential/mV
20	218.87±8.29	-29.50±0.87
50	258.58±30.89	-29.23±1.50
80	218.78±23.47	-30.03±0.55
110	230.37±4.47	-28.70±0.31
140	230.76±5.06	-28.40±0.69
170	220.84±9.65	-28.50±0.89



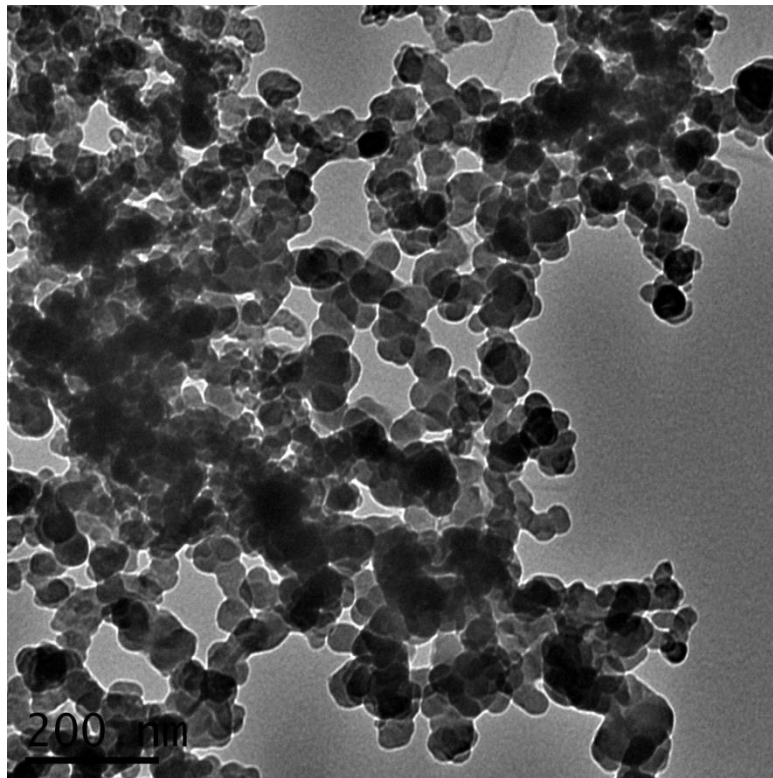
TEM of PHMC in pH=8.0 buffer



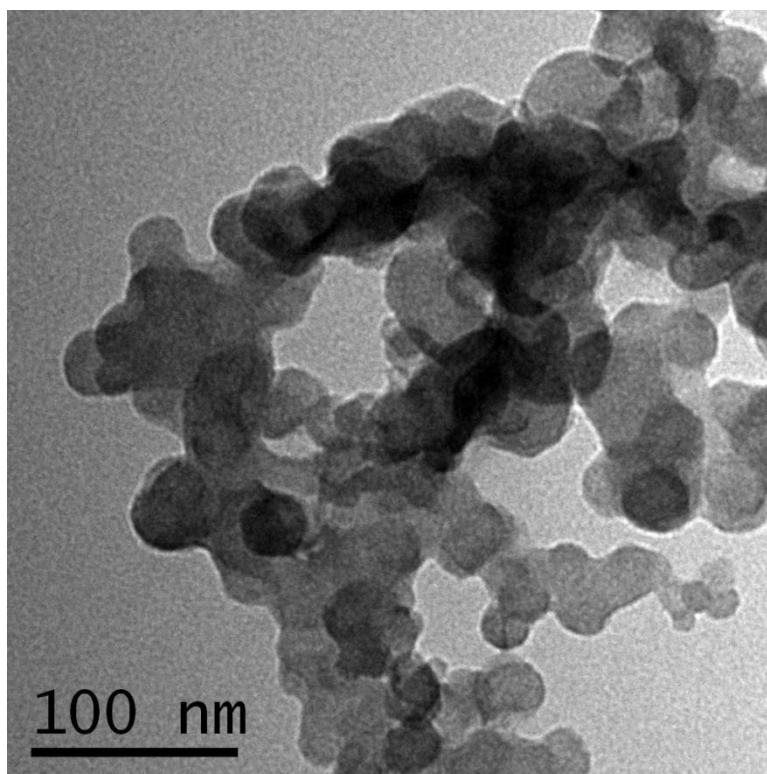
TEM of PHMC in pH=9.0 buffer



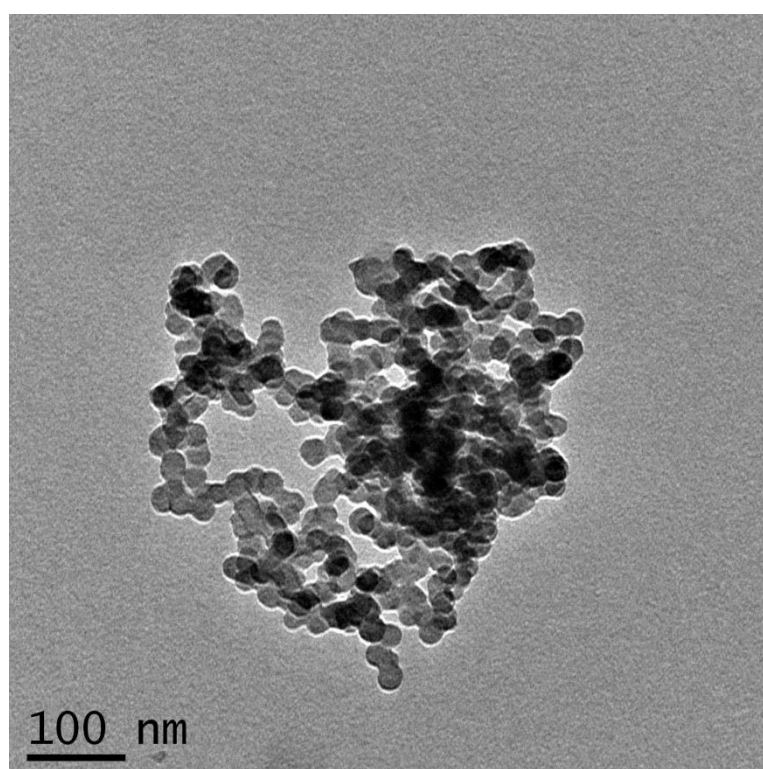
TEM of PHMC in pH=5.5 buffer



TEM of PHMC in pH=7.0 buffer

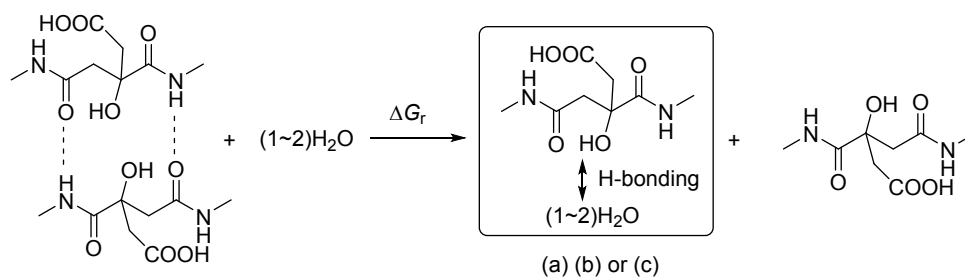


TEM of PHMC in pH=7.0 buffer



TEM of PHMC in pure water

Figure 4S. TEM images of PHMC particles.



$\Delta G_r = 1.8 \text{ kcal/mol}$ for (a), 1.7 kcal/mol for (b) and 7.3 kcal/mol for (c)

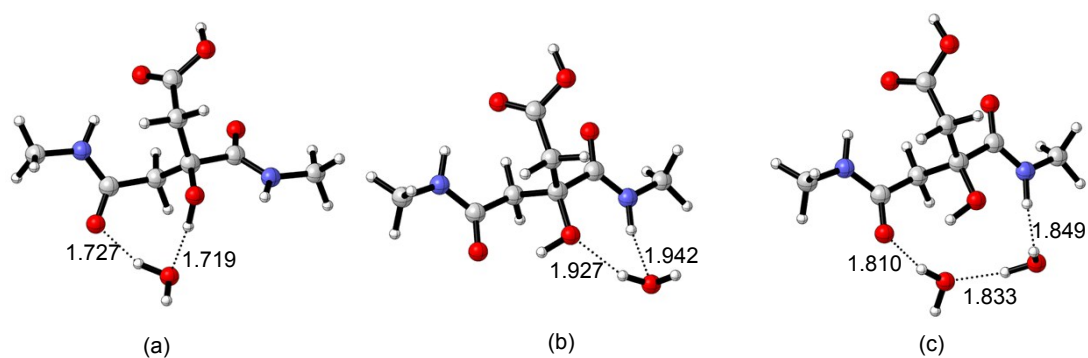
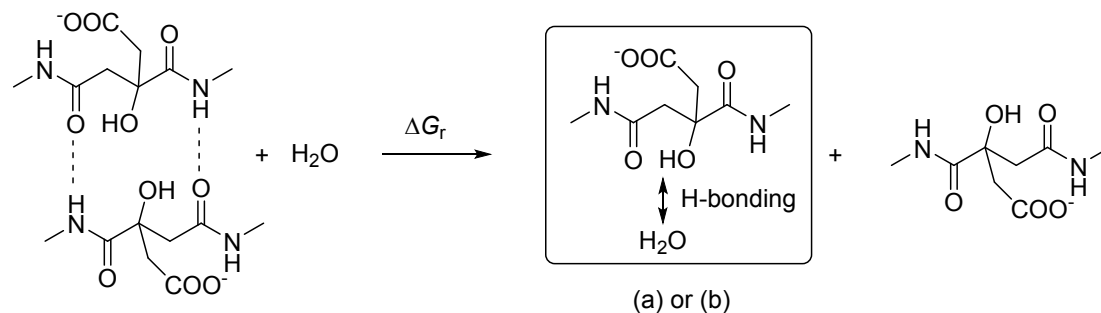


Figure 5S. H-bonding effect between the selected segment of the polycitramide (protonated state) and one water molecule (a) (b) or and two water molecules (c). The bond distances are in angstrom.



$\Delta G_r = 4.1 \text{ kcal/mol}$ for (a) and 1.6 kcal/mol for (b)

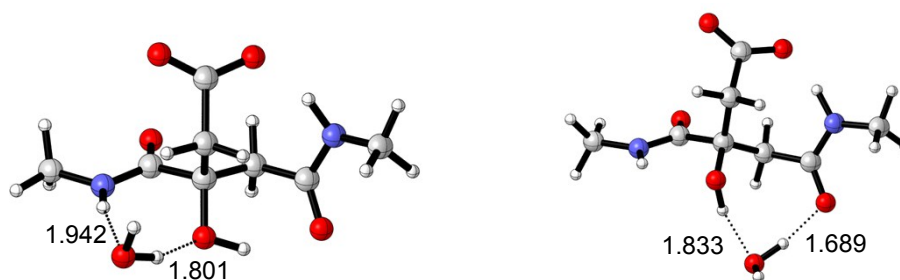


Figure 6S. H-bonding effect between the selected segment of the polycitramide (deprotonated state) and one water molecule. The bond distances are in angstrom.

The above calculations were performed using Gaussian 09 packages.¹M06-2X functional² with the 6-31G(d) basis set was used for the gas-phase geometry optimization. Frequency calculations were performed to confirm each stationary point as a real minima (zero imaginary frequency). Single-point energy calculations were then performed by using M06-2X functional with a larger basis set, i.e. 6-311++G(2df,2p) in aqueous solution with the SMD model³. The Gibbs free-energy correction from frequency calculation was added to the single-point energy to obtain the solution-phase Gibbs free energy. Note that all solution-phase free energies reported

correspond to the reference state of 1 mol/L, 298.15 K. The 3D structures were drawn using CYLview software.

(1) Frisch, M. J.; et al. Gaussian 09, R. D. 01, Gaussian, Inc., Wallingford CT, **2009**.

(2) (a) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2006**, *110*, 13126-13130. (b) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157-167. (c) Zhao, Y.; Truhlar, D. G. *Chem. Phys. Lett.* **2011**, *502*, 1-13.

(3) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378-6396.

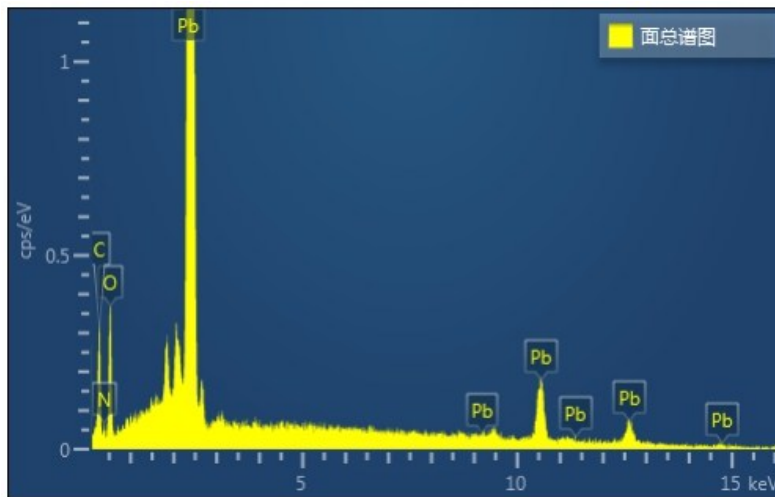
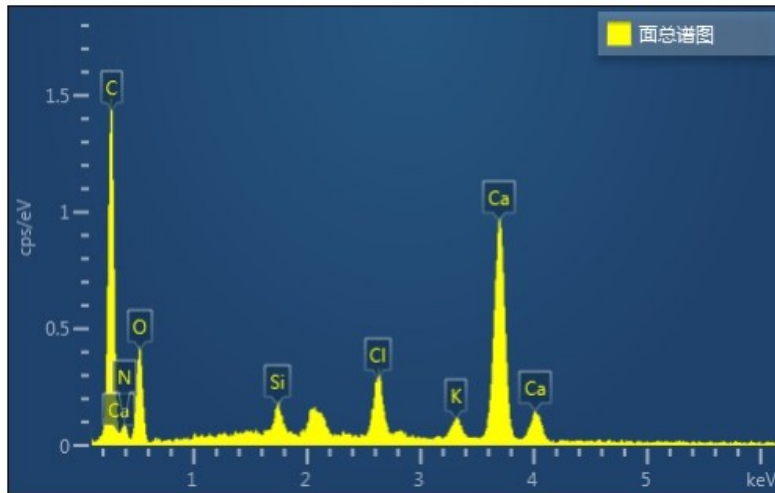


Figure 7S. Energy dispersive spectroscopic analysis (EDS) (performed by using Oxford Instruments) results of the PHMC polymers after Ca^{2+} ion chelation (top) and after Pb^{2+} ion chelation (bottom).