

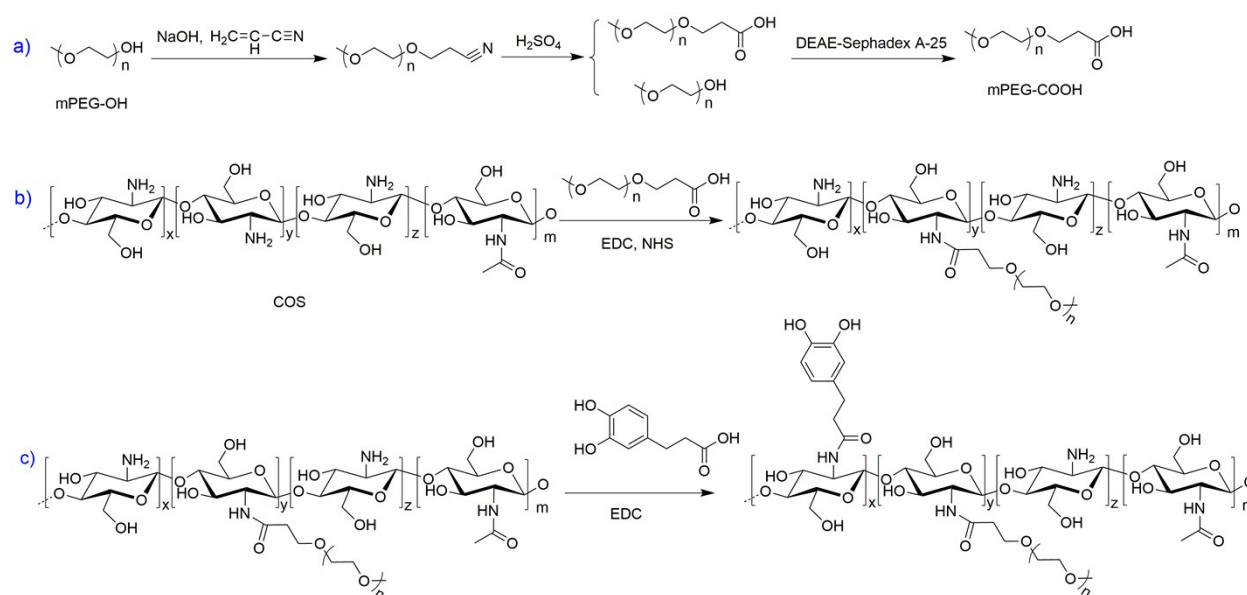
Supplementary Information

**Mussel-inspired chitooligosaccharide based multidentate ligand for
highly stabilized nanoparticles**

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Detailed Experimental

The catechol content was confirmed by the colorimetric assay at the maximum absorbance wavelength of the catechol (maximum wavelength, $\lambda_{\max} = 280 \text{ nm}$).¹⁻³ Standard solutions of hydrocaffeic acid (HCA) were used to generate a standard curve of catechol concentrations, and the quantification of the catechol content was performed. UV-Vis spectra were determined on a Cary 60 spectrophotometer (Agilent). Raman spectroscopy (PerkinElmer Flex-400, with 785 nm radiation and an output power of 80 mW).



Scheme S1. Synthetic procedures for chitooligosaccharide based multidentate ligand (ML). The number of monomers in a COS (3 kDa) chain molecule is approximately 18 ($x+y+z+m=18$), $x=5$, $y=5$, $m=2$.

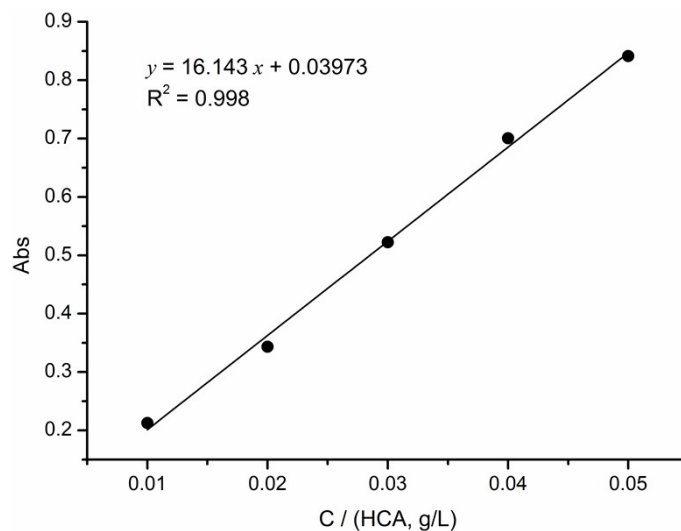
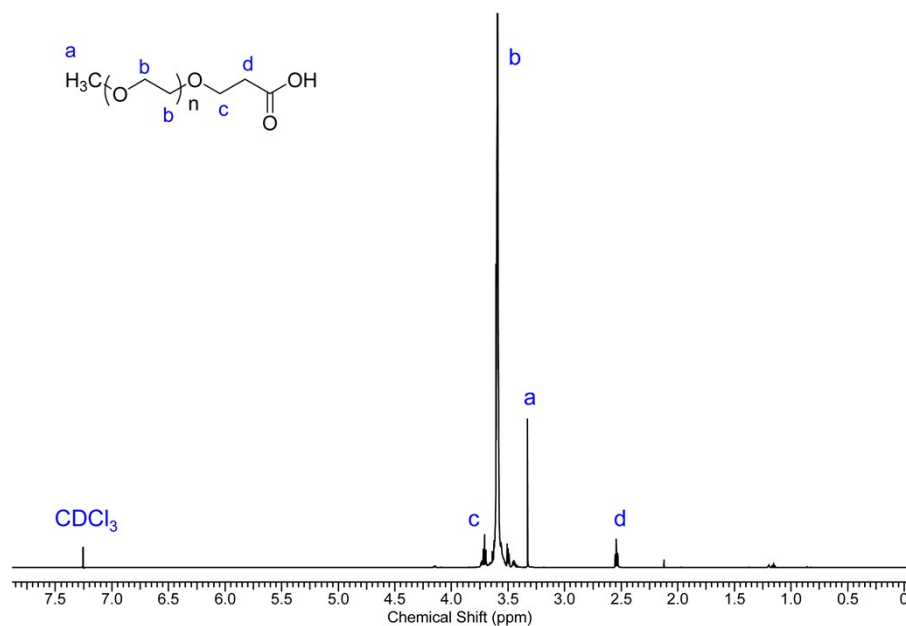
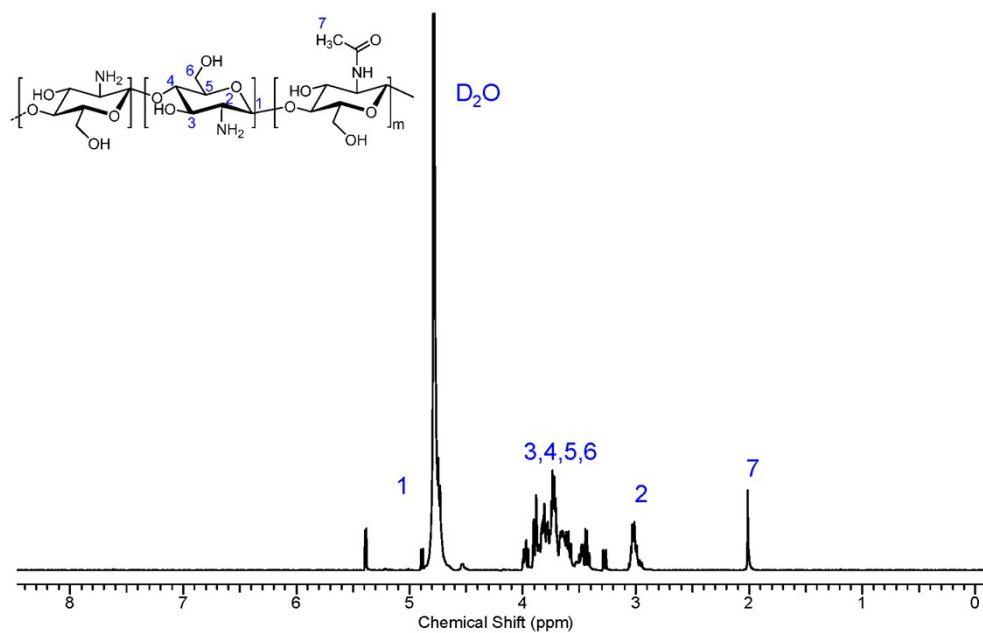


Figure S1. The regression curve in catechol content confirming of the multidentate ligand (280 nm). The catechol content of the ML was also confirmed by the UV absorbance of the catechol (280 nm, Abs = 0.42 in 0.5 g/L). Using this method, catechol content was determined to be 4.7 wt%, which is approximately 4 catechol per COS chain. The calculated degree of catechol substitution in the COS backbone was 21% (UV-vis spectrophotometer) and 28% (^1H NMR). The difference of the catechol conjugation results between the two measurements is possibly due to the potential error of a deacetylation rate provided by the manufacturer.

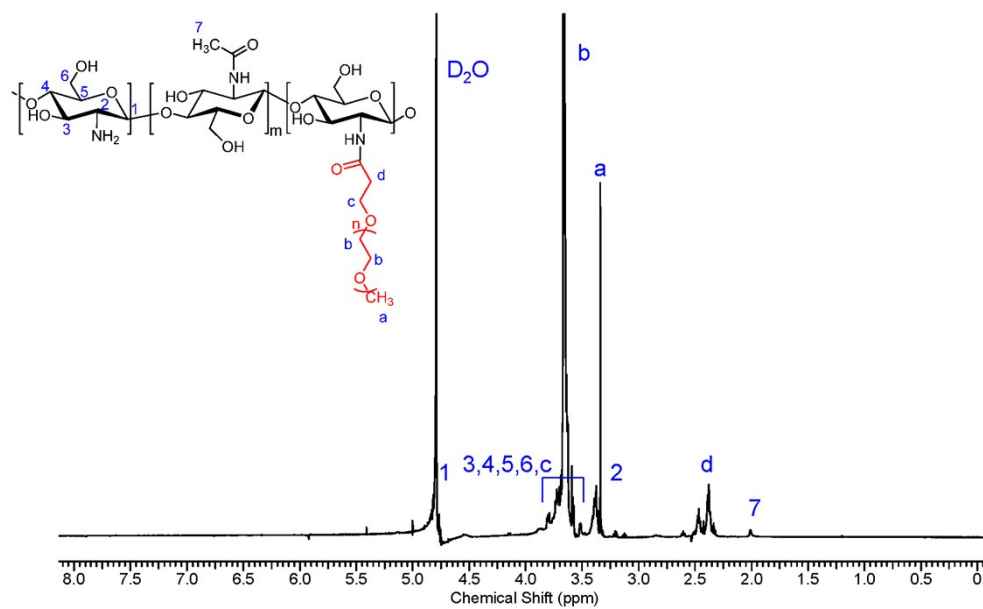
a) mPEG-COOH



b) Chitooligosaccharide (COS)



c) mPEG-g-COS



d) ML

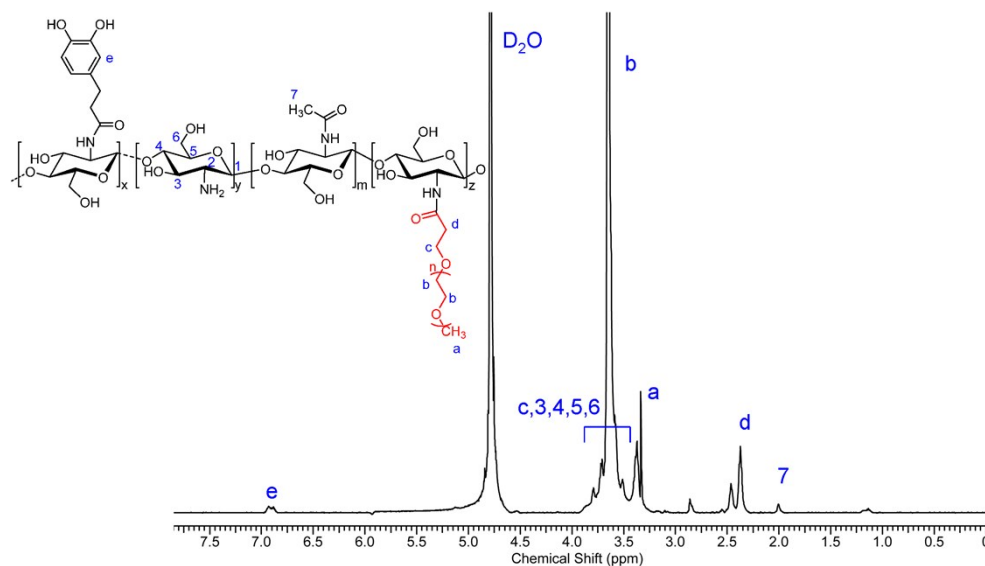


Figure S2. ¹H-NMR analysis of (a) mPEG-COOH, (b) COS, (c) mPEG-g-COS, (d) ML.

Table S1. Molecular characteristics of ligands in this study.

Copolymer	Molecular weight of blocks			DS of mPEG ^a	DS of catechol ^{a,b}	M_n ^a
	COS	mPEG	HCA			
mPEG-g-COS	3,000	2,000	182	0.25	0	12,910
ML	3,000	2,000	182	0.25	0.28 ^a ; 0.21 ^b	13,730

^a As determined by the ¹H NMR.

^b As determined by the colorimetric assay.

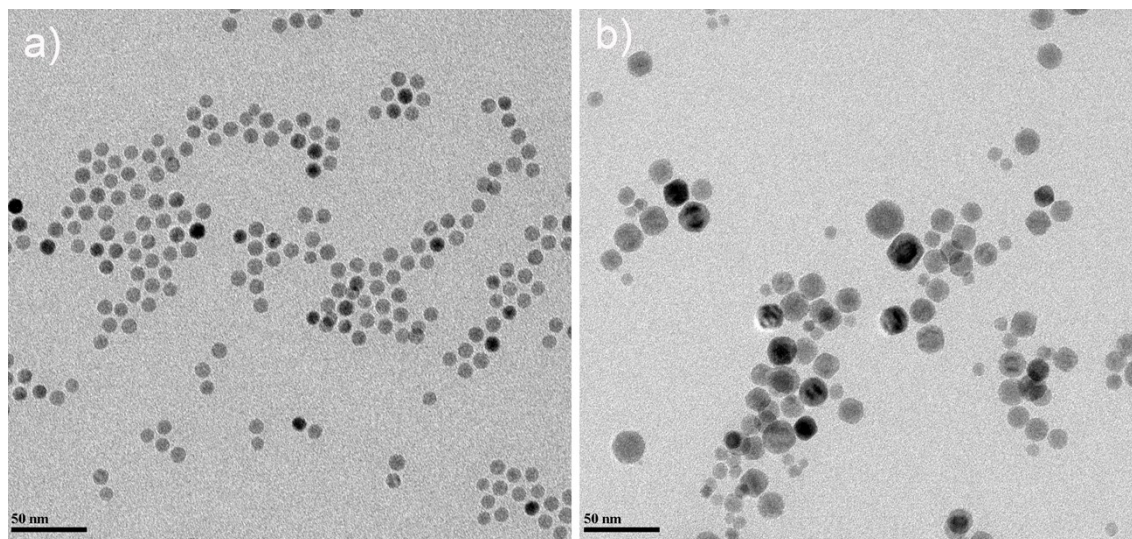


Figure S3. TEM images of (a) ML-stabilized IONPs and (b) mPEG-g-COS-stabilized IONPs. It was observed that mPEG-g-COS stabilized IONPs became obvious aggregates, but ML-stabilized IONPs well dispersed as single particles. It could be ascribed to the interaction of amino groups of COS with the IONPs surface resulted in crosslinking of the nanoparticles and induced aggregation of nanoparticle during the ligand exchange process.

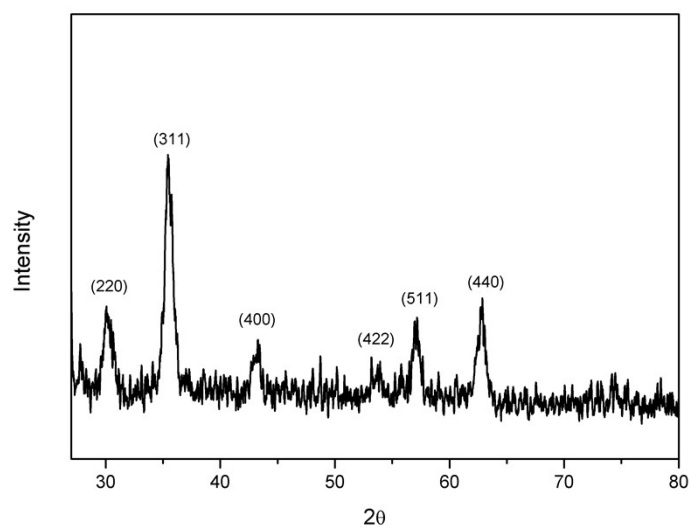


Figure S4. The power X-ray diffraction (XRD) pattern of the ML-stabilized IONPs. The position and relative intensity of all diffraction peaks match well with those from the JdPCS card (19-0629) for magnetite.

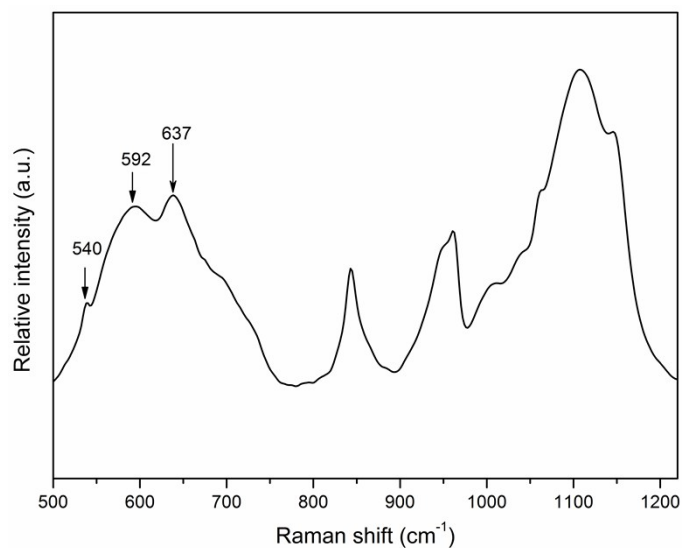


Figure S5. Raman spectra of the ML-stabilized IONPs.

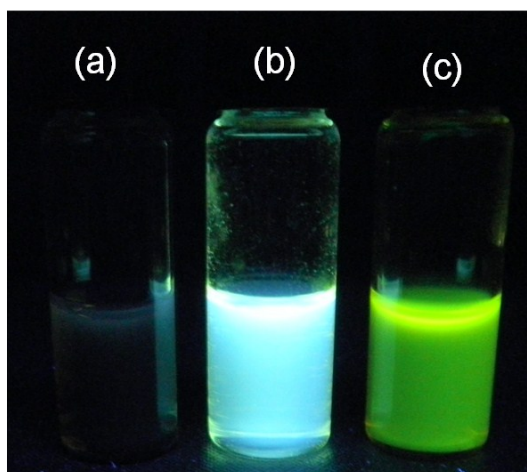


Figure S6. Photograph of aqueous suspensions of (a) un-conjugated ML-IONPs, (b) FITC, and (c) FITC-conjugated ML-IONPs under UV illumination.

References

- [1] L. E. Arnow, *J. Biol. Chem.* **1937**, 118, 531.
- [2] J. H. Waite and M. L. Tanzer, *Anal. Biochem.* **1981**, 111, 131.
- [3] D. W. Barnum, *Anal. Chim. Acta.* **1977**, 89, 157.