Supplementary information

Enhanced dispersion stability of gold nanoparticles by the physisorption of cyclic poly(ethylene glycol)

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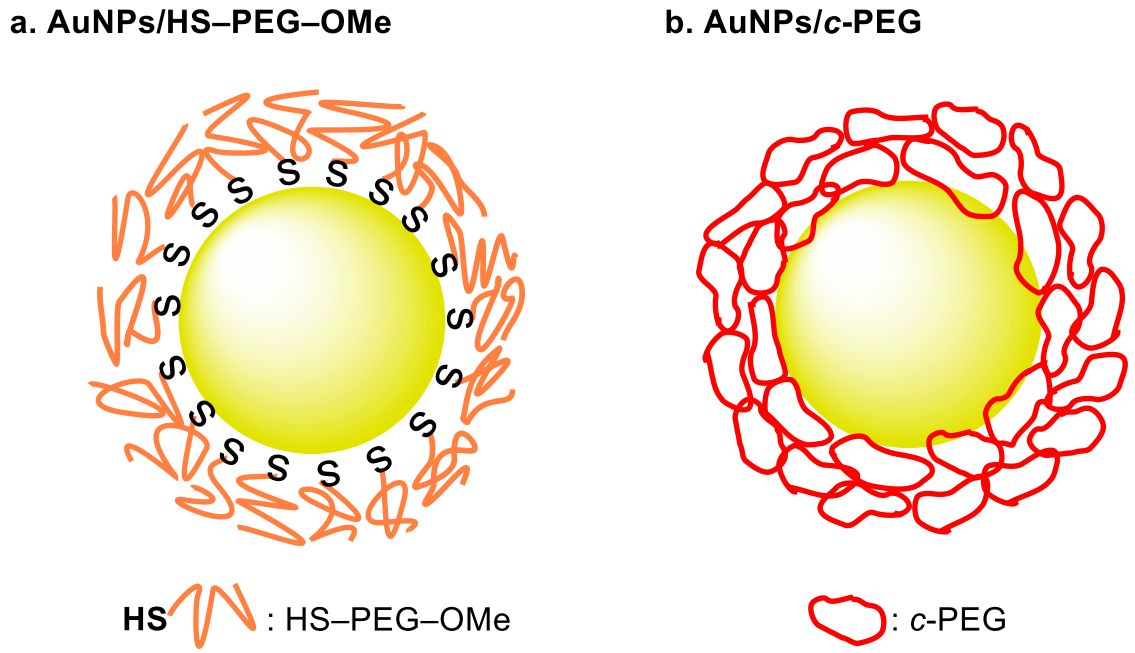
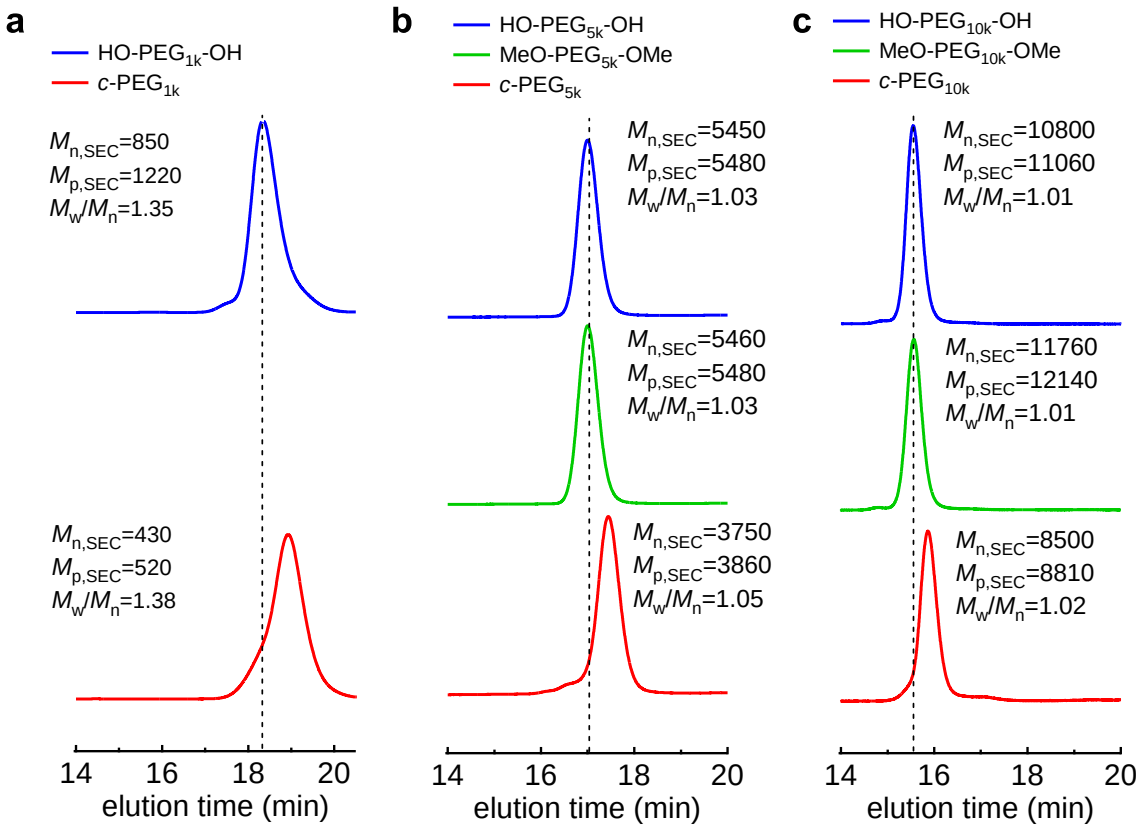
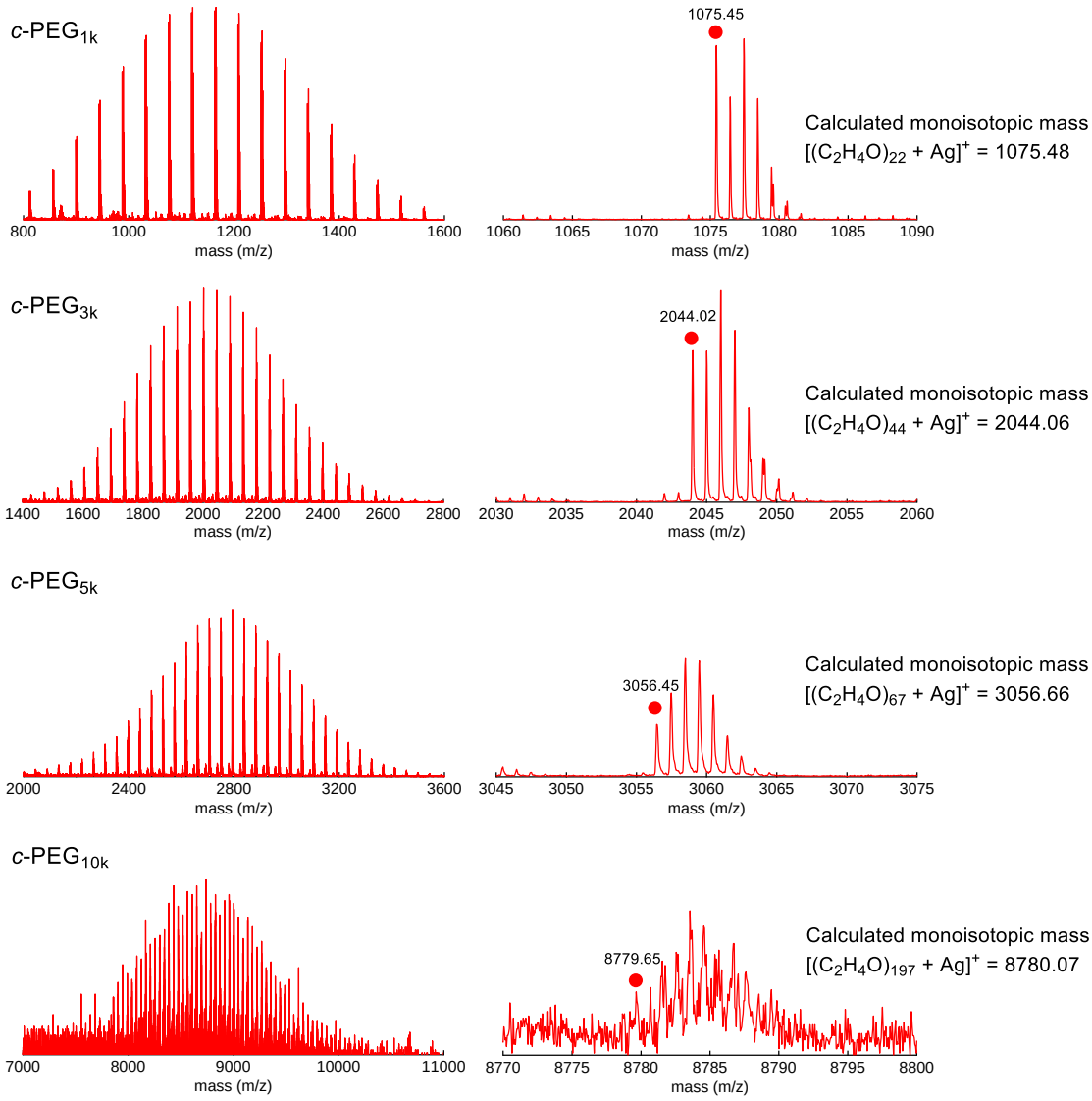


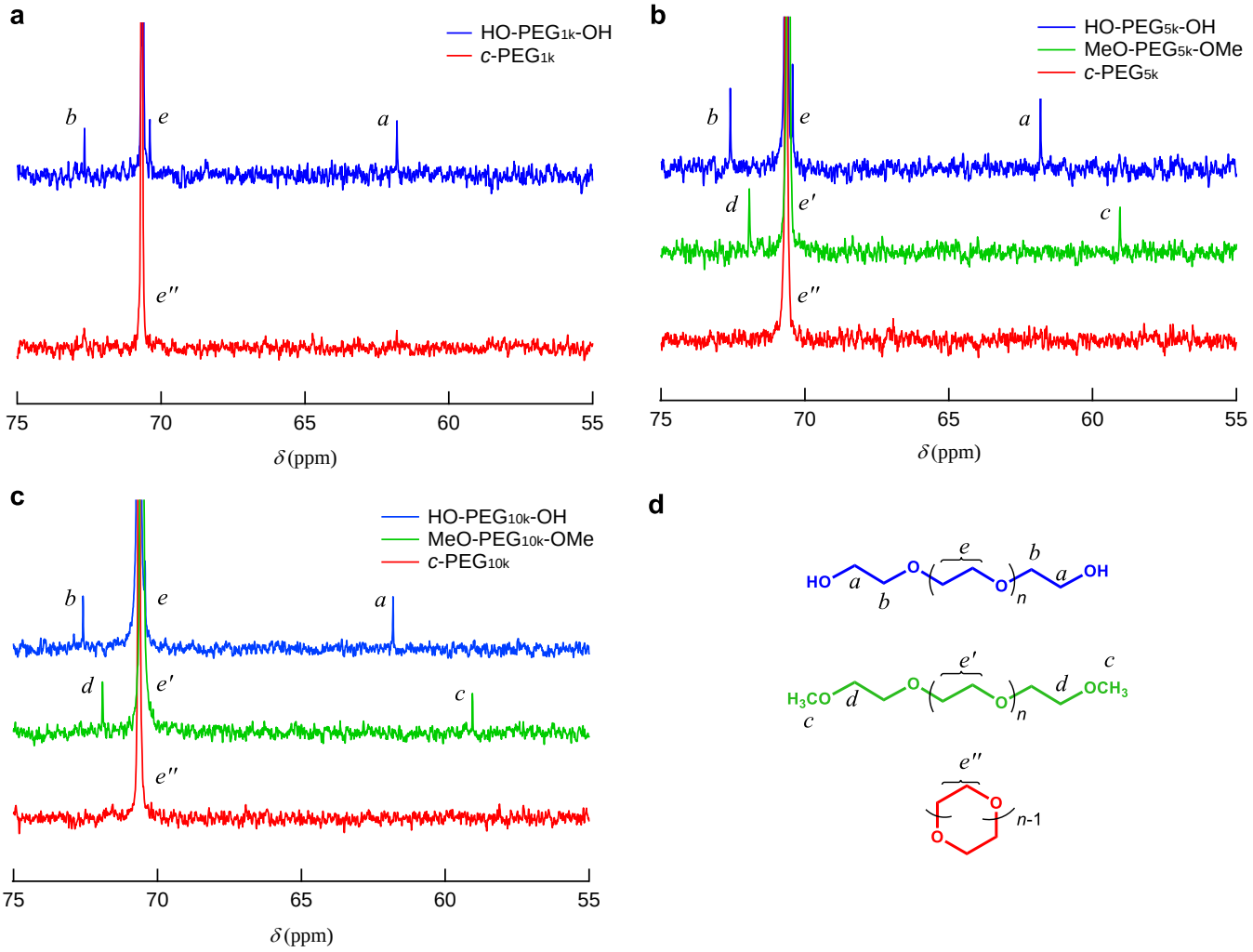
Supplementary Fig. 1 Schematic illustrations of PEGylated AuNPs. a AuNPs/HS–PEG–OMe and **b** AuNPs/*c*-PEG.



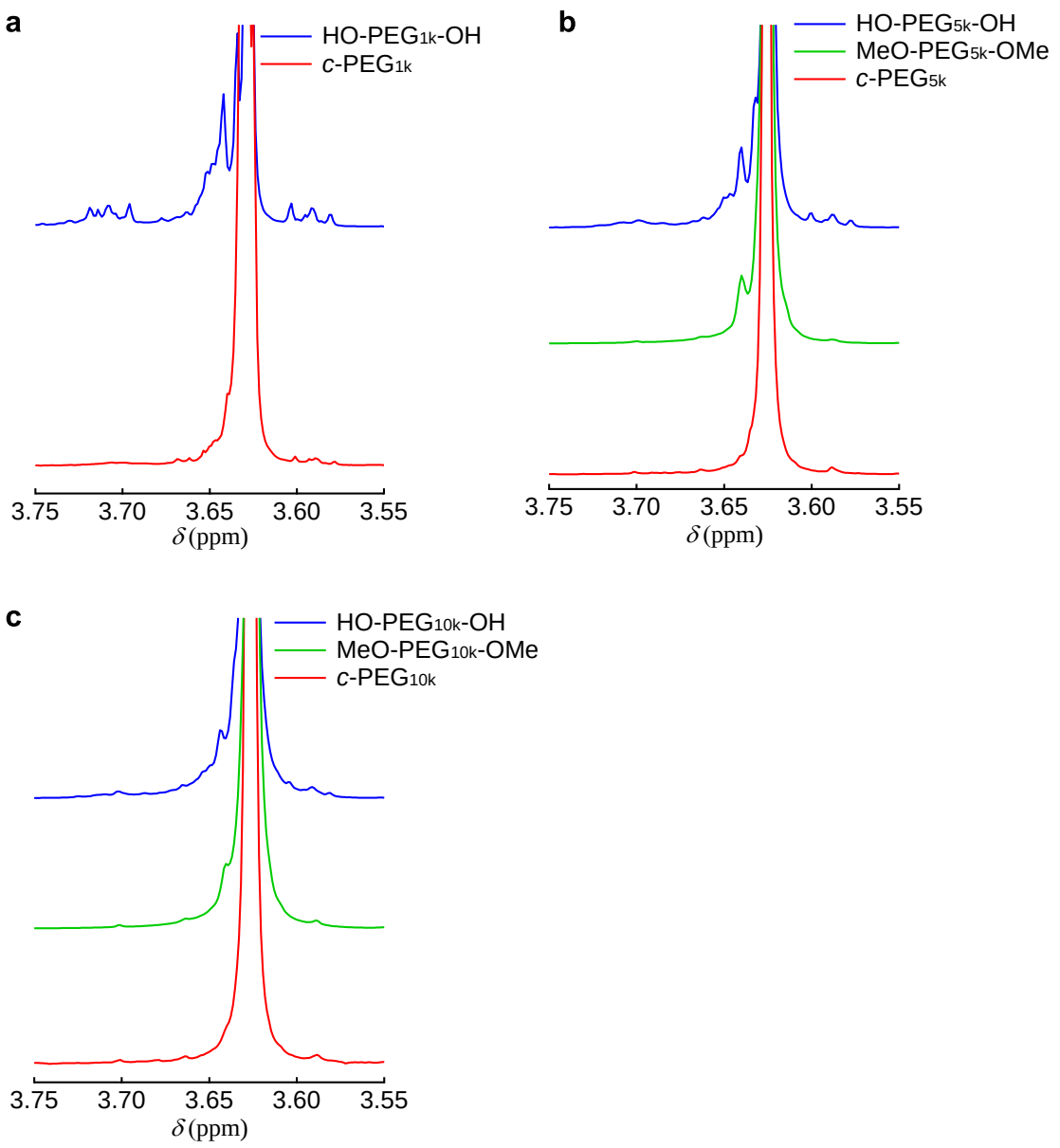
Supplementary Fig. 2 SEC traces of HO–PEG–OH (blue), MeO–PEG–OMe (green), and *c*-PEG (red). The molecular weight was **a** 1, **b** 5, and **c** 10 kDa.



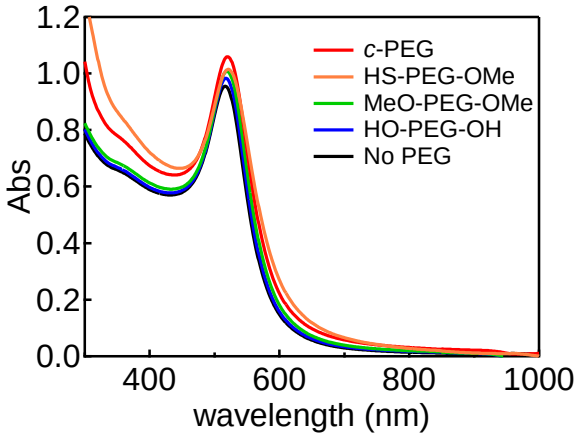
Supplementary Fig. 3 MALDI-TOF mass spectra of *c*-PEG$_{1k}$, *c*-PEG$_{3k}$, *c*-PEG$_{5k}$, and *c*-PEG$_{10k}$. Calculated monoisotopic mass and experimental *m*/*z* values of typical peaks are shown.



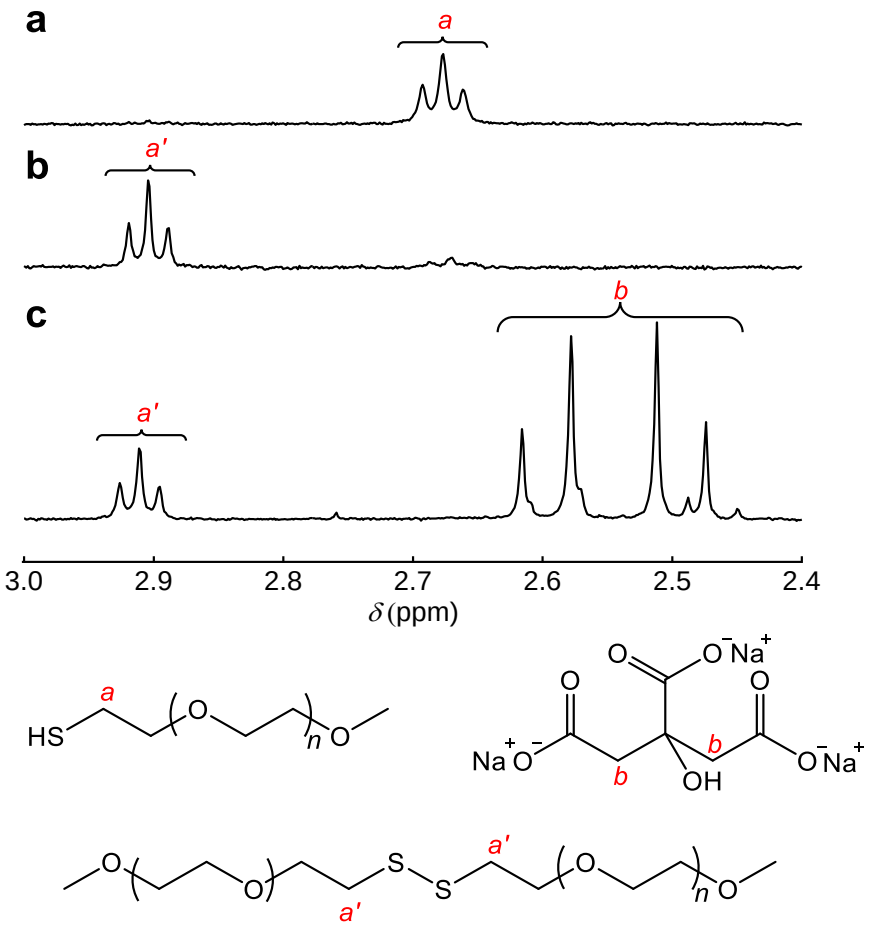
Supplementary Fig. 4 ^{13}C NMR spectra and chemical structures of HO–PEG–OH (blue), MeO–PEG–OMe (green), and *c*-PEG (red). The molecular weight was **a** 1, **b** 5, and **c** 10 kDa. The assigned peaks correspond to the chemical structures in **d**.



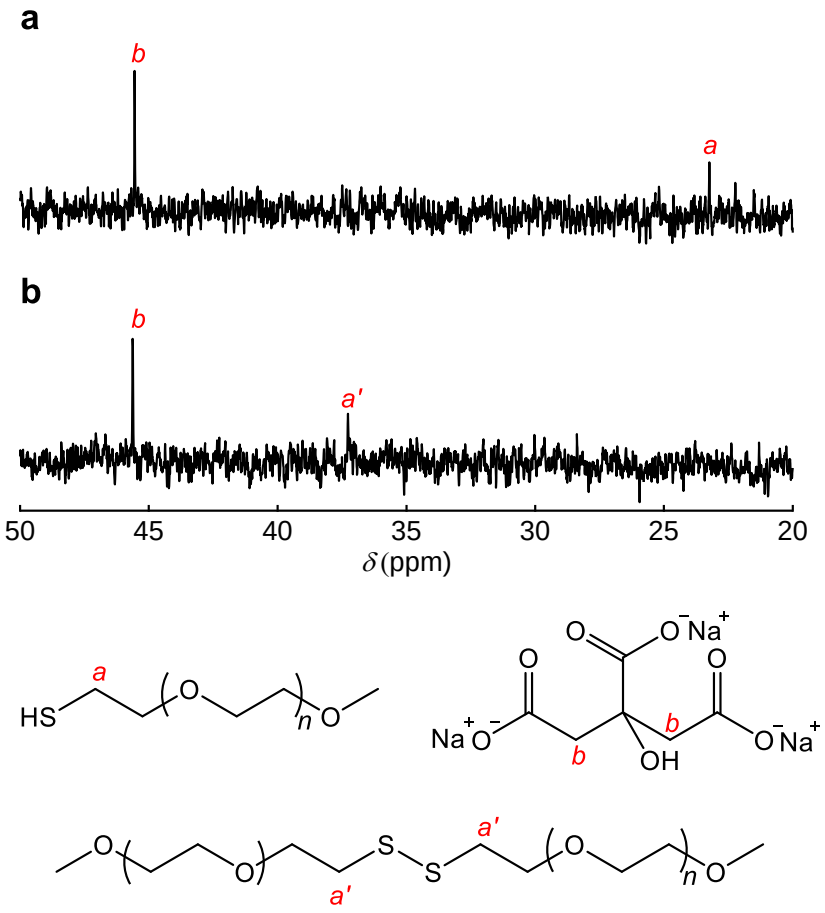
Supplementary Fig. 5 ^{1}H NMR spectra of HO–PEG–OH (blue), MeO–PEG–OMe (green), and *c*-PEG (red). The molecular weight was **a** 1, **b** 5, and **c** 10 kDa.



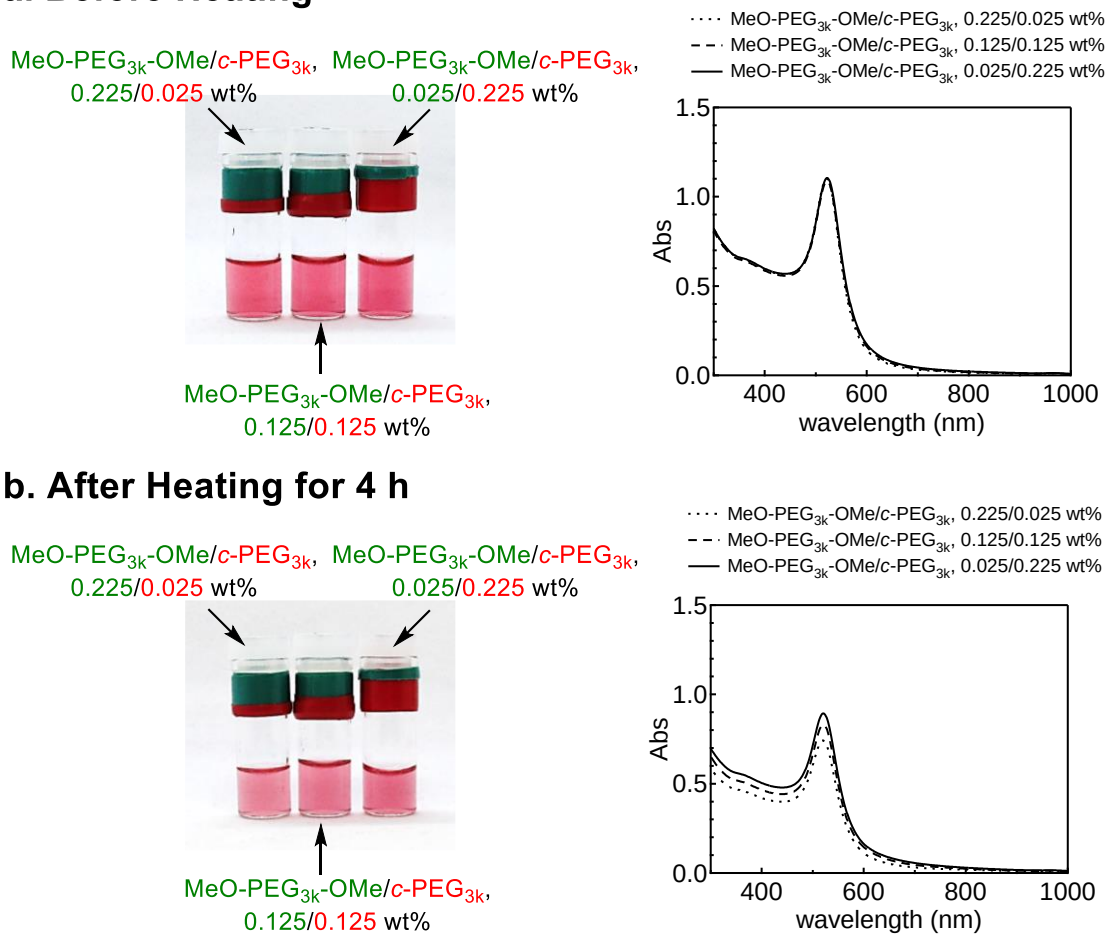
Supplementary Fig. 6 UV–Vis spectra before freezing and lyophilization. $AuNPs_{15}$/No PEG (black), $AuNPs_{15}$/HO–PEG_{3k}–OH (blue), $AuNPs_{15}$/MeO–PEG_{3k}–OMe (green), $AuNPs_{15}$/HS–PEG_{3k}–OMe (orange), and $AuNPs_{15}$/*c*-PEG_{3k} (red).



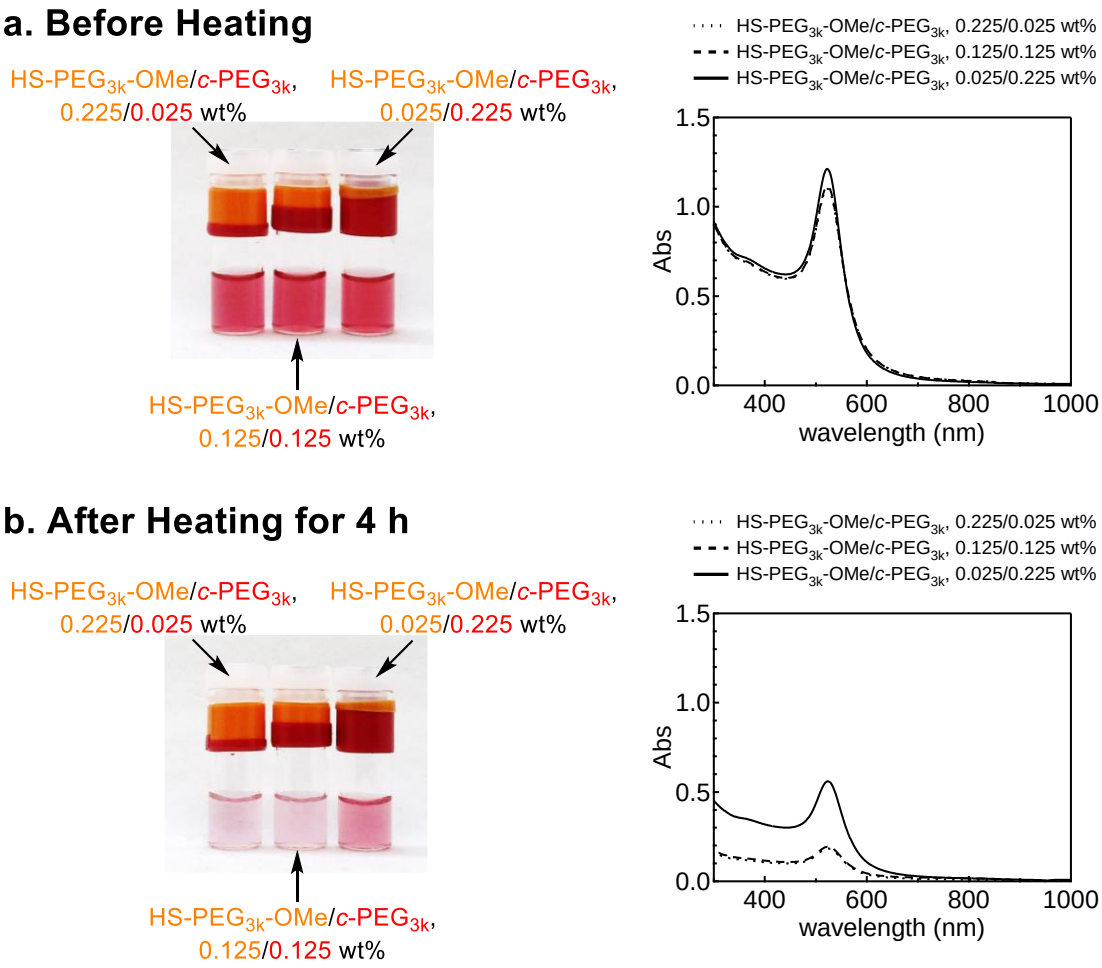
Supplementary Fig. 7 Formation of disulfide by heating. ^{1}H NMR spectra of **a** HS–PEG$_{3k}$–OMe, **b** MeO–PEG$_{3k}$–S–S–PEG$_{3k}$–OMe, and **c** AuNPs$_{15}$/HS–PEG$_{3k}$–OMe after heating at 85 °C for 4 h followed by exchange of the solvent to D_2O.



Supplementary Fig. 8 Formation of disulfide by heating. ^{13}C NMR spectra of $AuNPs_{15}$/HS–PEG_{3k}–OMe **a** before and **b** after heating at 85 °C for 4 h.



Supplementary Fig. 9 Heating test. Photographs and UV–Vis spectra of $AuNPs_{30}$/MeO–PEG_{3k}–OMe/*c*-PEG_{3k}. **a** Before heating and **b** after heating for 4 h at 85 °C. From left to right in each photograph, the concentrations of MeO–PEG_{3k}–OMe/*c*-PEG_{3k} were 0.225/0.025, 0.125/0.125, and 0.025/0.225 wt%. Rel. Abs was 67, 76, or 81%, respectively.



Supplementary Fig. 10 Heating test. Photographs and UV–Vis spectra of $AuNPs_{30}$/HS–PEG_{3k}–OMe/*c*-PEG_{3k}. **a** Before heating and **b** after heating for 4 h at 85 °C. From left to right in each photograph, the concentrations of HS–PEG_{3k}–OMe/*c*-PEG_{3k} were 0.225/0.025, 0.125/0.125, and 0.025/0.225 wt%. Rel. Abs was 17, 17, or 46%, respectively.

a. Immediately After Adding PBS

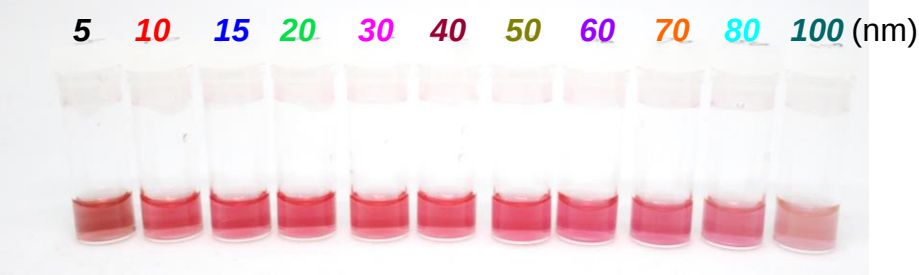
b. 7 d After Adding PBS

c. 14 d After Adding PBS

Supplementary Fig. 11 Photographs of AuNPs$_{15}$/*c*-PEG$_{3k}$ in a long-term stability test. a Immediately after, **b** 7 d after, and **c** 14 d after the addition of a tenfold-concentrated PBS solution kept at 37 °C.

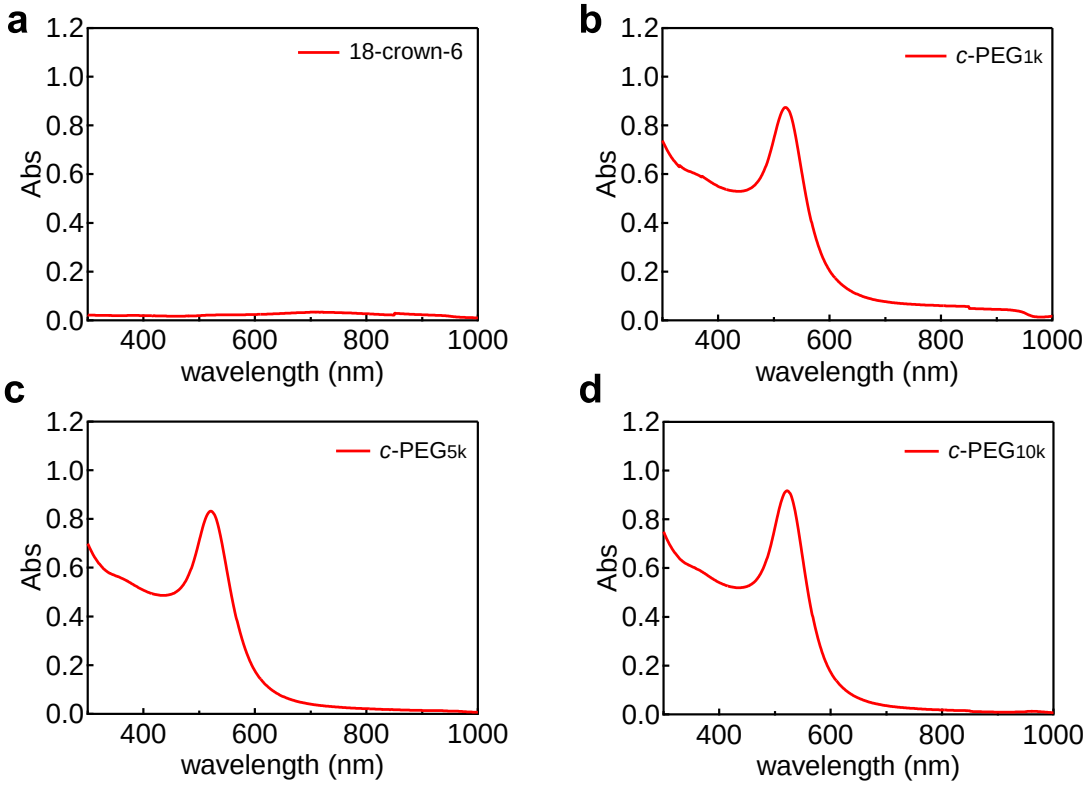
a. Before Adding PBS

b. Immediately After Adding PBS

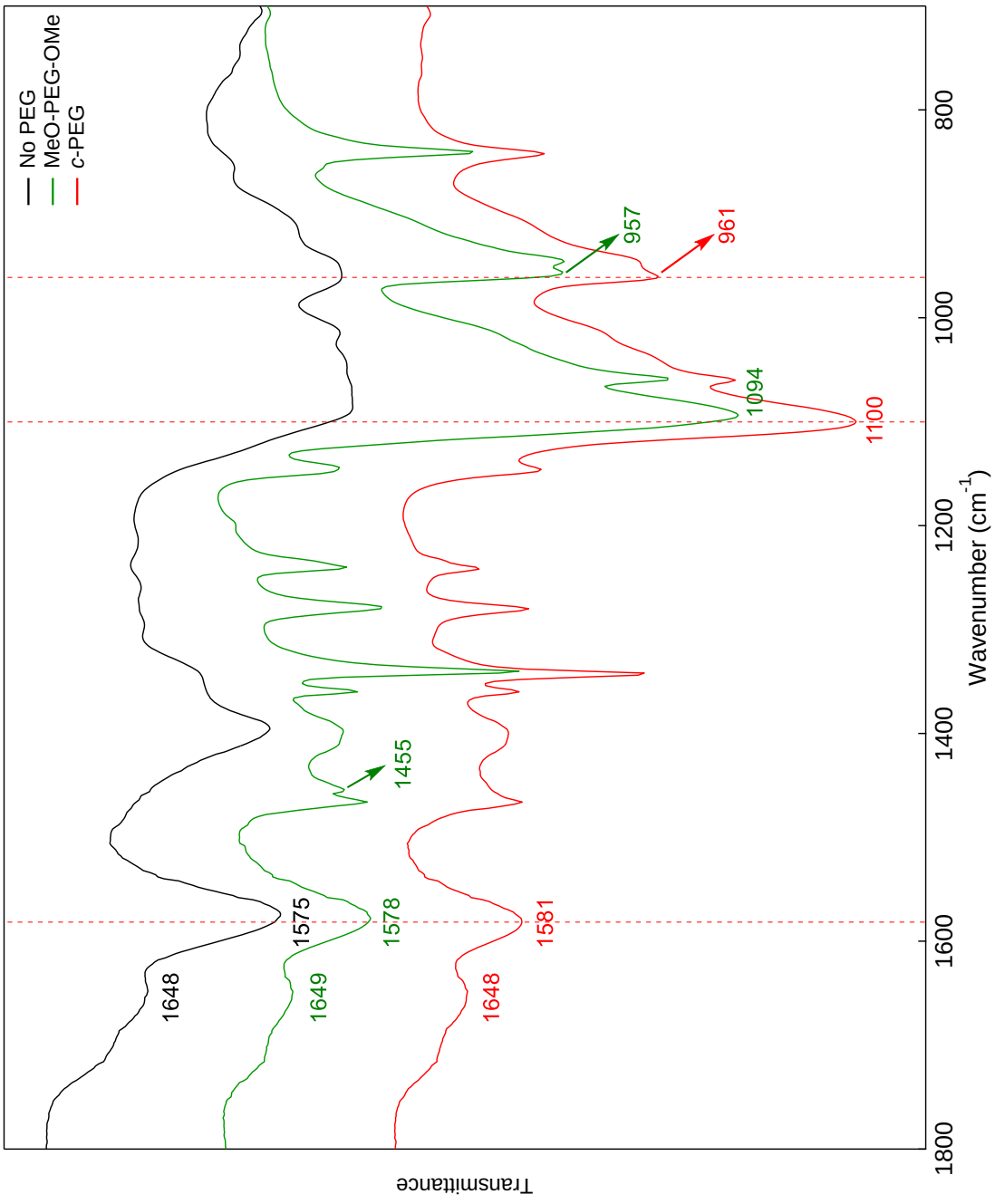


c. 850 min After Adding PBS

Supplementary Fig. 12 Physiological condition test with various diameters of AuNPs (5–100 nm). Photographs of AuNPs/*c*-PEG$_{3k}$ **a** before, **b** immediately after, and **c** 850 min after the addition of a tenfold-concentrated PBS solution. The resulting dispersions were pH 7.4 and 150 mM of NaCl. From left to right in each photograph, AuNPs$_5$/*c*-PEG$_{3k}$, AuNPs$_{10}$/*c*-PEG$_{3k}$, AuNPs$_{15}$/*c*-PEG$_{3k}$, AuNPs$_{20}$/*c*-PEG$_{3k}$, AuNPs$_{30}$/*c*-PEG$_{3k}$, AuNPs$_{40}$/*c*-PEG$_{3k}$, AuNPs$_{50}$/*c*-PEG$_{3k}$, AuNPs$_{60}$/*c*-PEG$_{3k}$, AuNPs$_{70}$/*c*-PEG$_{3k}$, AuNPs$_{80}$/*c*-PEG$_{3k}$, and AuNPs$_{100}$/*c*-PEG$_{3k}$.



Supplementary Fig. 13 Physiological condition test of AuNPs/18-crown-6 and AuNPs/*c*-PEG with various sizes. UV–Vis spectra of **a** $AuNPs_{15}$/18-crown-6, **b** $AuNPs_{15}$/*c*-PEG_{1k}, **c** $AuNPs_{15}$/*c*-PEG_{5k}, and **d** $AuNPs_{15}$/*c*-PEG_{10k} 1000 min after the addition of a tenfold-concentrated PBS solution. The resulting dispersions were pH 7.4 and 150 mM of NaCl.



Supplementary Fig. 14 FT-IR spectra of AuNPs$_{15}$/No PEG (black), AuNPs$_{15}$/MeO–PEG$_{3k}$–OMe (green), and AuNPs$_{15}$/*c*-PEG$_{3k}$ (red). Red dotted lines indicate the peak top wavenumbers of AuNPs$_{15}$/*c*-PEG$_{3k}$.

Supplementary Table 1 Experimental and calculated *m*/*z* values for the monoisotopic mass of *c*-PEG$_{3k}$.

DP_n	Experimental	Calculated
33	1559.73	1559.77
34	1603.76	1603.80
35	1647.80	1647.82
36	1691.81	1691.85
37	1735.83	1735.86
38	1779.86	1779.90
39	1823.89	1823.93
40	1867.90	1867.95
41	1911.94	1911.98
42	1955.96	1956.01
43	1999.98	2000.03
44	2044.02	2044.06
45	2088.03	2088.08
46	2132.06	2132.11
47	2176.07	2176.14
48	2220.10	2220.16
49	2264.13	2264.19
50	2308.16	2308.22
51	2352.17	2352.24
52	2396.20	2396.27
53	2440.22	2440.29
54	2484.25	2484.32
55	2528.27	2528.35

Supplementary Table 2 DLS size, *c*-PEG layer thickness, and grafting density (σ) of $AuNPs_{15}$/*c*-PEG_{3k} at various concentrations of *c*-PEG_{3k}.

c-PEG conc. (wt%)	0.05	0.15	0.25	0.50	0.75
DLS size (nm)	20.3	25.0	27.4	27.1	28.7
c-PEG layer thickness (nm)	1.0	3.3	4.6	4.4	5.2
σ (chains/nm^2)	0.029	0.094	0.13	0.12	0.15

Supplementary Table 3 Estimated numbers of Au atoms and PEG molecules per one AuNP in the case of a PEG concertation of 0.25 wt%.

AuNPs size (nm)	Number of Au atoms per one AuNP (10^4)	Number of PEG (M_n = 3,000 Da) per one AuNPs (10^4)
5	0.39	1.41
10	3.10	11.3
15	10.5	38.2
20	24.8	90.4
30	83.3	303
40	198	723
50	386	1410
60	665	2430
70	1070	3880
80	1580	5780
100	3090	11300

Supplementary Table 4 Absorption wavenumbers in the FT-IR spectra of AuNPs$_{15}$/No PEG, AuNPs$_{15}$/MeO–PEG$_{3k}$–OMe, and AuNPs$_{15}$/*c*-PEG$_{3k}$.

	AuNPs/No PEG (cm^{-1})	AuNPs/MeO–PEG–OMe (cm^{-1})	AuNPs/*c*-PEG (cm^{-1})
C–O, C–C stretching, CH_2 rocking of PEG[1]	–	841	842
CH_2 rocking, CH_2 twisting of PEG[1]	–	946	946
CH_2 rocking, CH_2 twisting of PEG[1]	**–**	**957**	**961**
C–O, C–C stretching, CH_2 rocking of PEG[1]	–	1059	1060
C–O, C–C stretching of PEG[1]	**–**	**1094**	**1100**
C–O stretching, CH_2 rocking of PEG[1]	–	1145	1146
CH_2 twisting of PEG[1]	–	1240	1242
CH_2 twisting of PEG[1]	–	1279	1280
CH_2 wagging of PEG[1]	–	1340	1343
Symmetric stretching of COO^- of sodium citrate[2]	1396	1398	1399
CH_2 scissoring of PEG[1]	**–**	**1455**	**–**
CH_2 scissoring of PEG[1]	–	1466	1466
Asymmetric stretching of COO^- of sodium citrate[2]	**1575**	**1578**	**1581**
Asymmetric stretching of COO^- of Au–citrate[2]	1648	1649	1648

Noticeable differences are shown in bold.

Supplementary references

1. Vrandečić, N.S., Erceg, M., Jakić, M. & Klarić, I. Kinetic analysis of thermal degradation of poly(ethylene glycol) and poly(ethylene oxide)s of different molecular weight. *Thermochim. Acta* **498**, 71-80 (2010).

2. Wulandari, P. et al. Characterization of citrates on gold and silver nanoparticles. *J. Colloid Interface Sci.* **438**, 244-248 (2015).