Supporting Information

The influence of polydopamine coating on gold nanorods for laser desorption/ionization time-of-flight mass spectrometric analysis

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Supporting figure

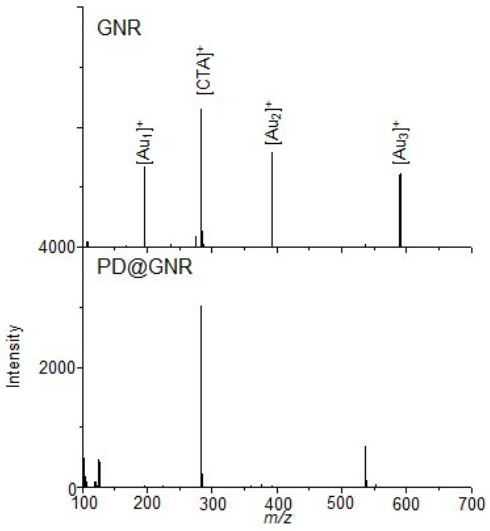

Figure S1. Mass spectra of gold nanorod (GNR) and polydoppamine coated GNR (PD@GNR) by laser desorption/ionization time-of-flight mass spectrometry (LDI-ToF-MS) analysis. The applied laser energy was 38 μJ.

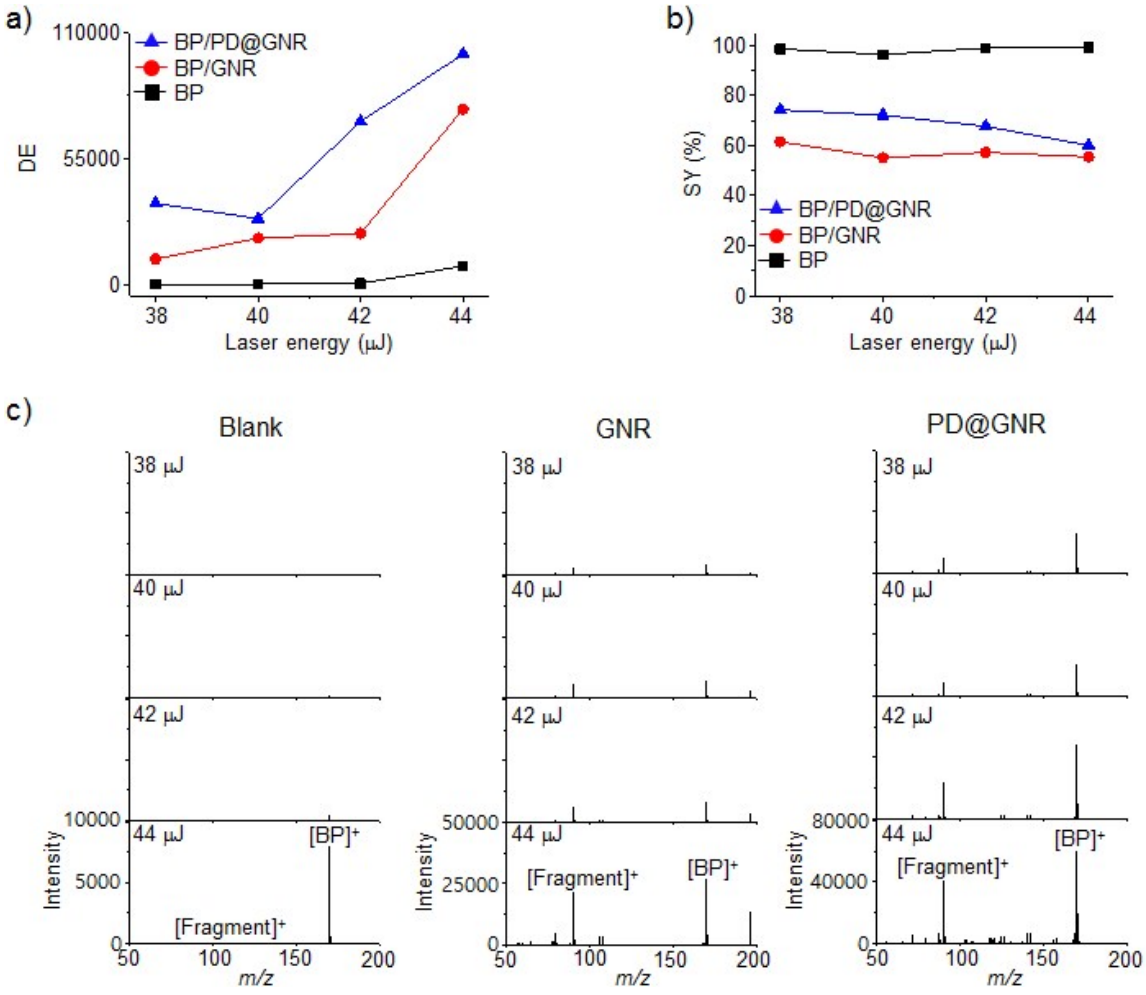

Figure S2. a) The DE and (b) SY values of BP itself and those obtained with GNR and PD@GNR as a function of the applied laser power. c) Mass spectra of BP itself and those obtained with GRN and PD@GNR with varying laser power (38 – 44 μJ). The DE value of BP with PD@GNR was higher than that of GNR but the SY value of BP with GNR was lower than that with PD@GNR. This result further confirms BP was softly desorbed and ionized with PD@GNR compared to GNR.

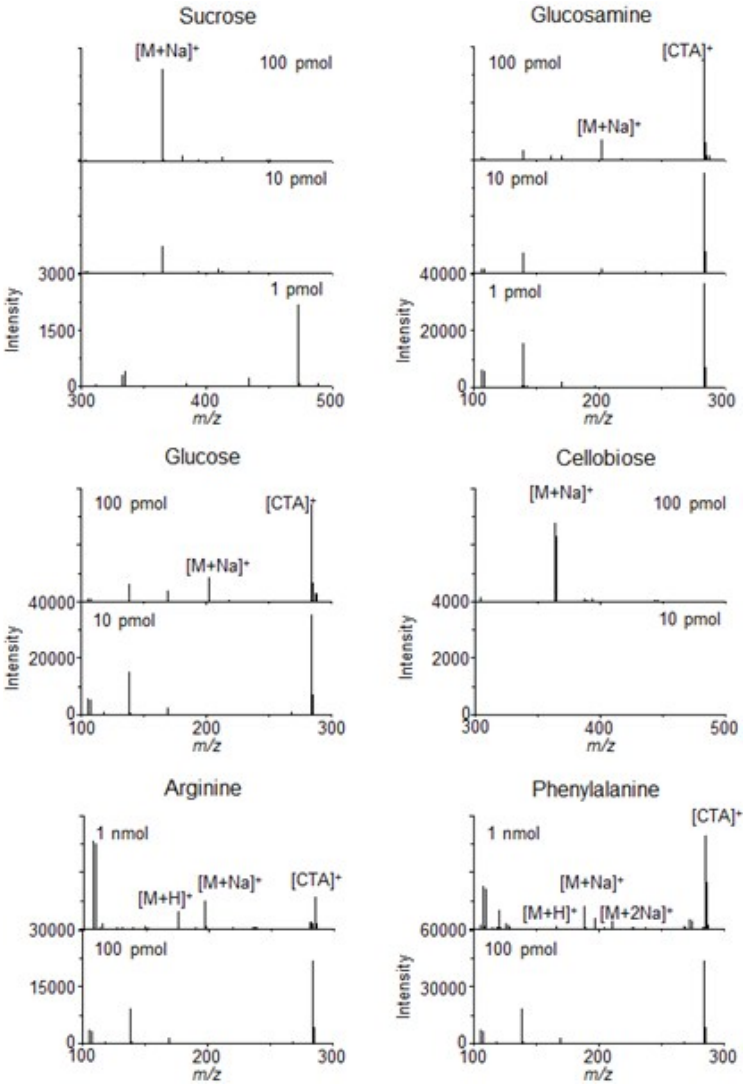

Figure S3. Detectable concentration ranges of small molecules such as glucose, glucosamine, sucrose, arginine, phenylalanine and cellobiose obtained by laser desorption/ionization time-of-flight mass spectrometry (LDI-ToF-MS) analysis with assistance of PD@GNR. The laser energy was 44 μJ.

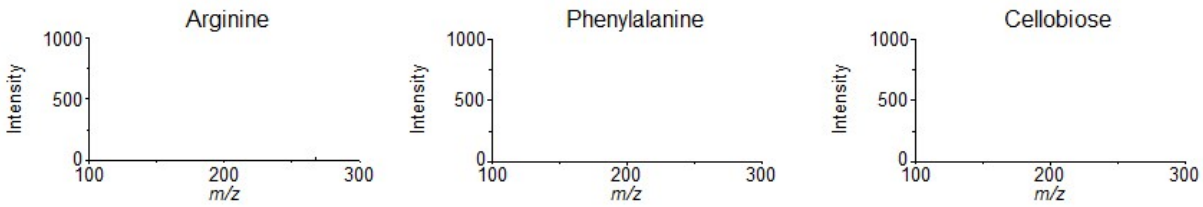

Figure S4. Mass spectra of arginine, phenylalanine and cellobiose obtained from blank targets by laser desorption/ionization time-of-flight mass spectrometry (LDI-ToF-MS) analysis without GNR and PD@GNR. The laser energy was 44 μJ.

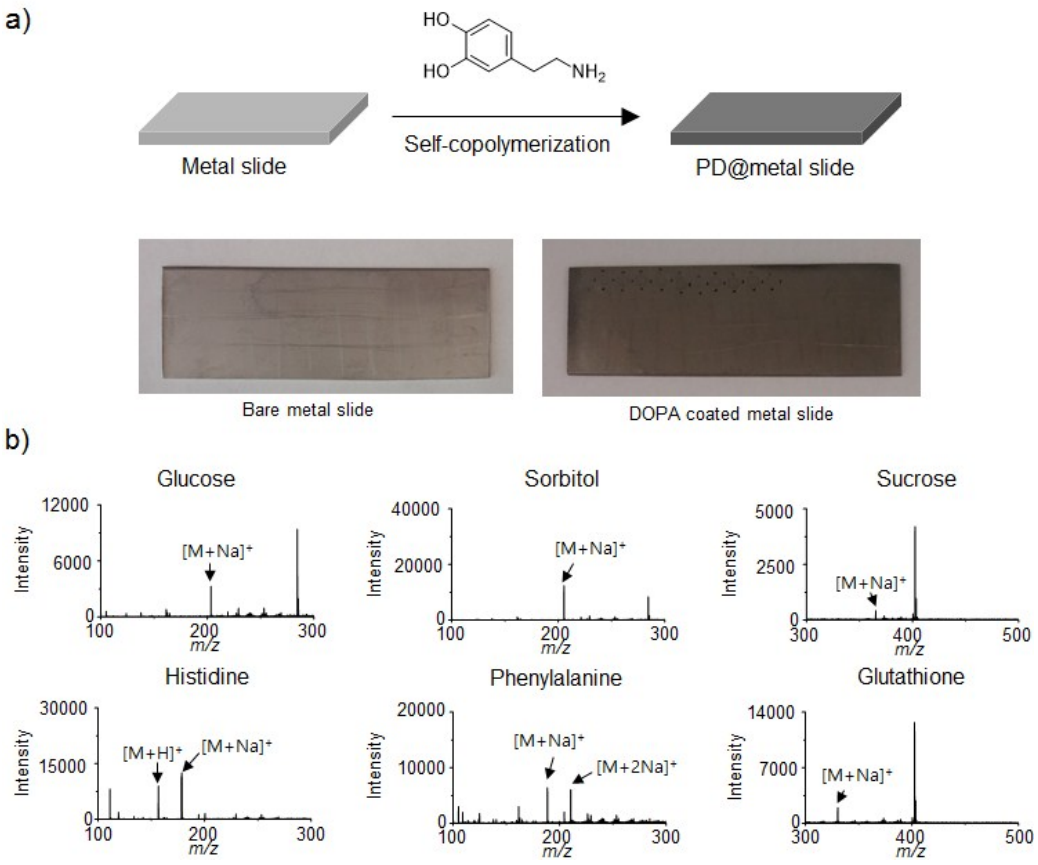

Figure S5. a) Schematic diagram of polydopamine (PD) coating on a metal slide. b) Photographs of bare and PD coated metal slides. c) Mass spectra of small molecules obtained on the PD coated metal slide. No mass signal was detected on the bare metal slide. The laser energy was 44 μJ. Small molecules were detected as cationic adducts with proton and sodium at *m/z* 202 $[glucose+Na]^+$, 205 $[sorbitol+Na]^+$, 364 $[sucrose+Na]^+$, 156 $[histidine+H]^+$ and 177 $[histidine+Na]^+$, 188 $[phenylalanine+Na]^+$ and 210 $[phenylalanine+2Na]^+$, and 329 $[glutathione+Na]^+$.

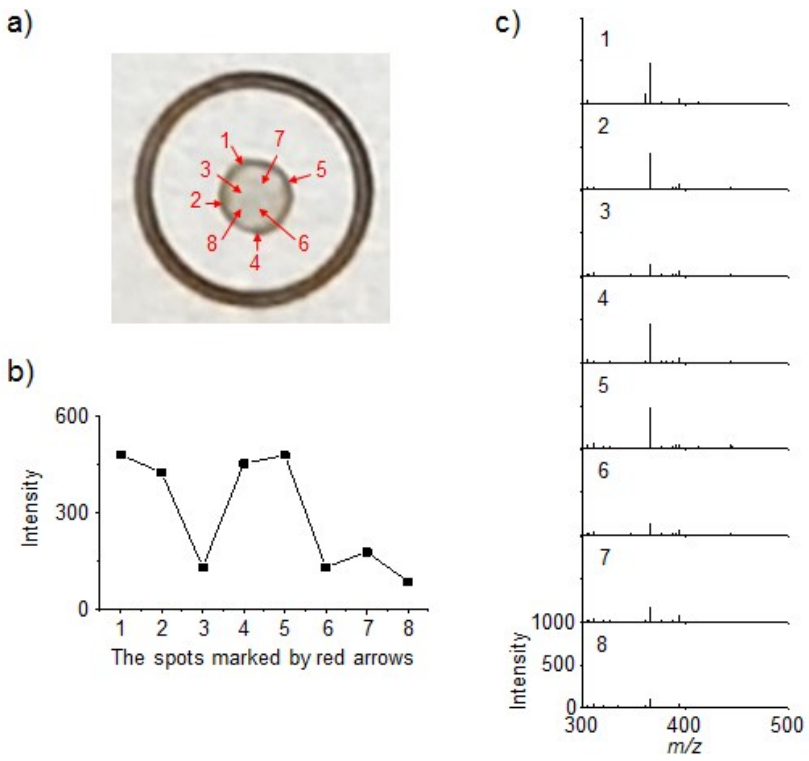

Figure S6. a) Photograph of the dried spot of cellobiose and PD@GNR mixture with designated by red arrows that indicated the laser irradiated positions. b) The LDI-ToF-MS mass signal intensities and mass spectra (c) of cellobiose obtained with PD@GNR at the designated region by red arrows. The applied laser energy power was 44 μJ.

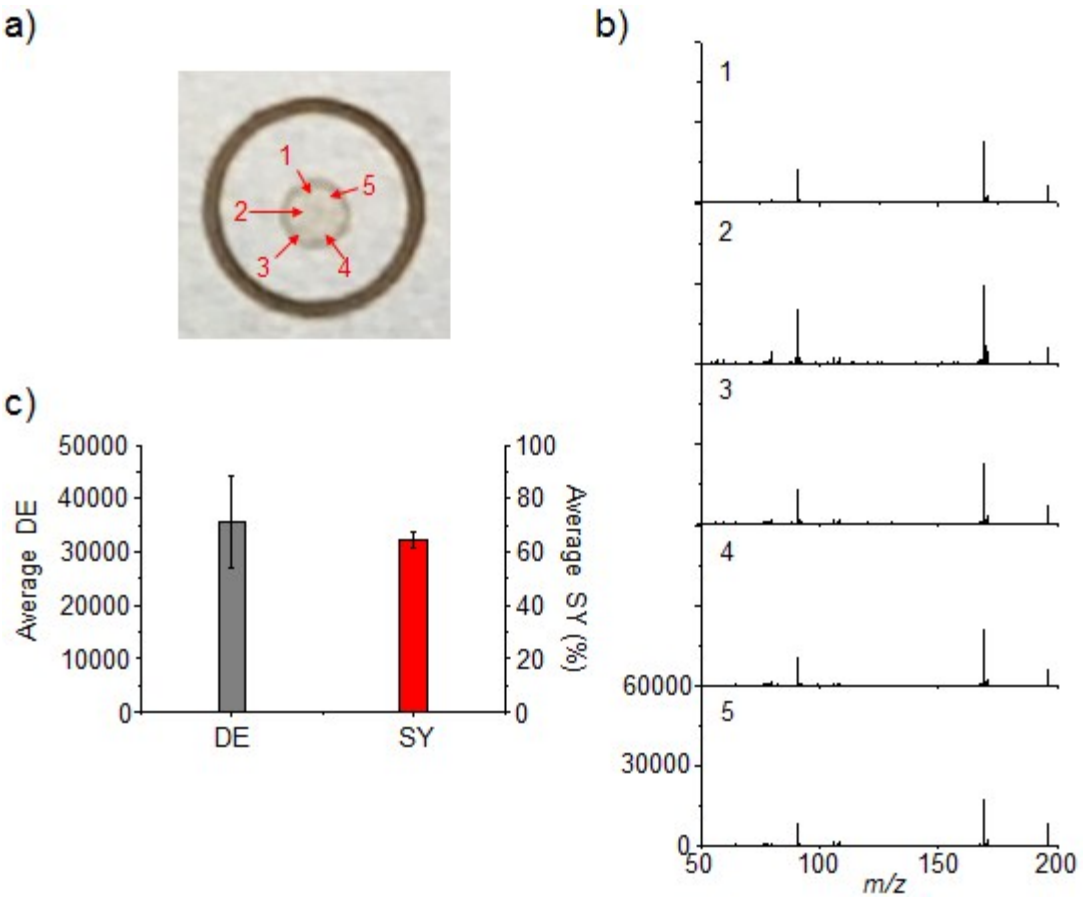

Figure S7. a) Photograph of the dried spot of BP and GNR mixture with designated by red arrows that indicated the laser irradiated positions. b) The LDI-ToF-MS mass signal intensities and mass spectra (c) of BP obtained with GNR at the designated region by red arrows. The applied laser energy power was 44 μJ.

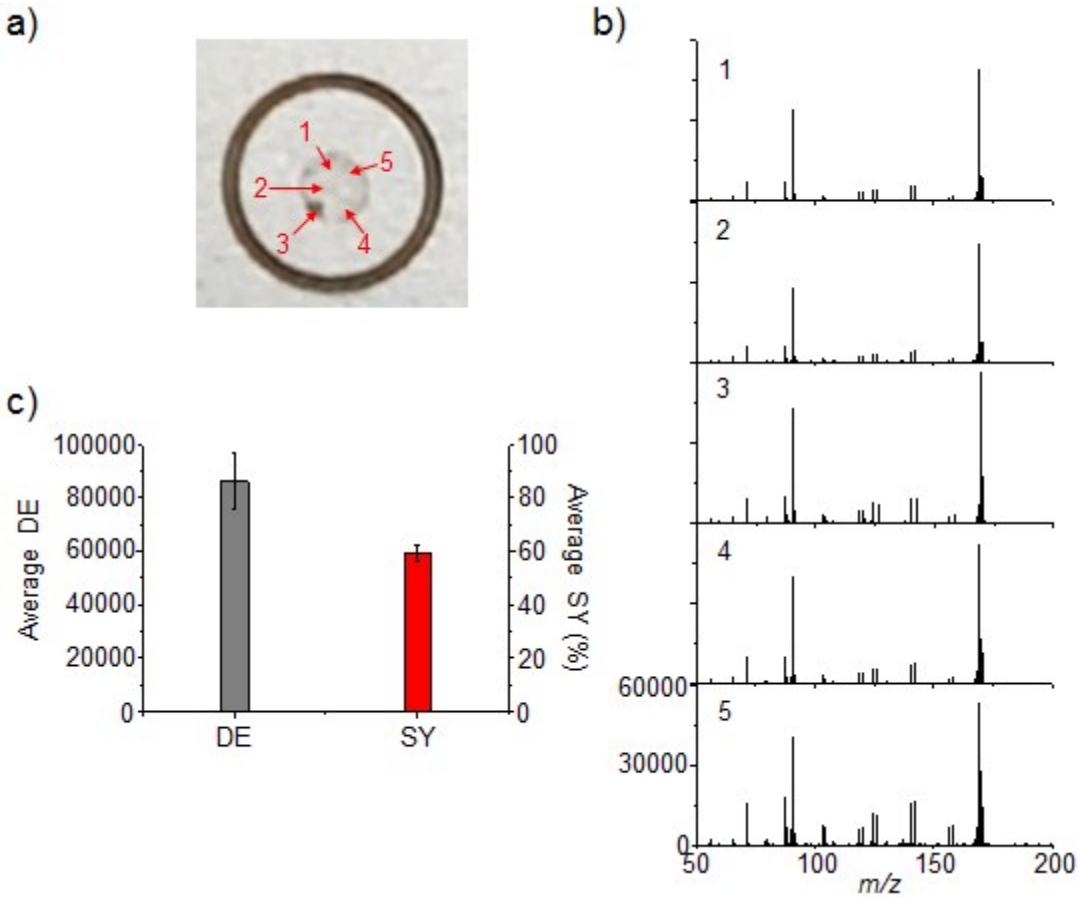

Figure S8. a) Photograph of the dried spot of BP and PD@GNR mixture with designated by red arrows that indicated the laser irradiated positions. b) The LDI-ToF-MS mass signal intensities and mass spectra (c) of BP obtained with PD@GNR at the designated region by red arrows. The applied laser energy power was 44 μJ.

	Repeating unit	By LDI-ToF-MS					By gel-permeation chromatography (GPC)		
		Mn	Mw	PD	S/N	Resolution	Mn	Mw	PD
PEG_{500}	44	599	617	1.03	56.5	2654	550	580	1.06
PEG_{500}/GNR		612	630	1.02	244.2	4078			
PEG_{500}/PD@GNR		612	635	1.03	363.5	2749			
PEG_{1000}	44	959	993	1.03	55.0	3000	900	940	1.05
PEG_{1000}/GNR		934	976	1.04	53.7	2845			
PEG_{1000}/PD@GNR		967	1002	1.03	90.0	3027			
PEG_{2000}	44	1997	2003	1.00	4.0	6032	1900	1960	1.03
PEG_{2000}/GNR		1951	1956	1.00	4.8	4876			
PEG_{2000}/PD@GNR		1950	1974	1.01	46.4	4230			
PEG_{4000}	44	-	-	-	-	-	4120	4240	1.03
PEG_{4000}/GNR		-	-	-	-	-			
PEG_{4000}/PD@GNR		3965	3993	1.00	12.5	2010			

Figure S9. The figures of merit (FOM) such as M_n, M_w, polydispersity (PD), signal to noise ratio (S/N) and resolution from the LDI-ToF-MS analysis of PEG itself, and with GNR and PD@GNR. The values of M_n and M_w obtained by our strategy were slightly higher than those by using gel-permeation chromatography (GPC) from the supplier information. The PD values obtained by our strategy were slightly lower that those by GPC from supplier information. The slight deviation might be originated from the methodological difference. Importantly, the S/N values of PEG derivatives increased in order of PEG itself, PEG/GNR and PEG/PD@GNR. This result also suggested that the PD coating layer improves the LDI-ToF-MS analysis and our strategy is suitable for the analysis of synthetic polymers.

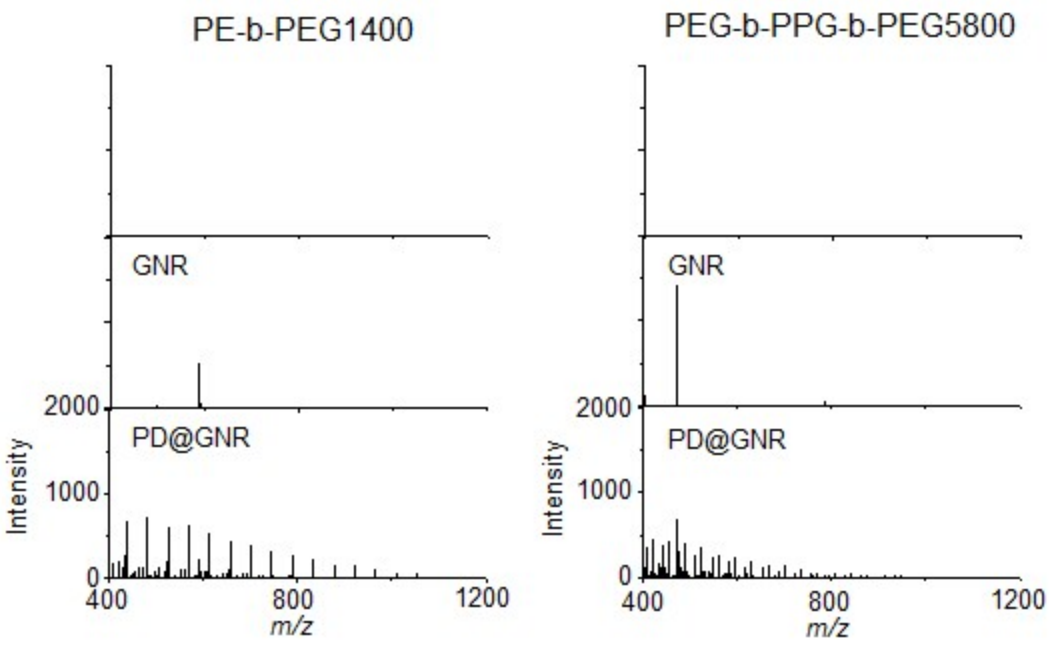

Figure S10. LDI-TOF-MS spectra of PE-*b*-PEG_{1500} and PEG-*b*-PPG-*b*-PEG_{5800} and their LDI-TOF-MS spectra obtained with GNR and PD@GNR. The applied laser energy was 54 μJ.