Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Environmentally Responsive Amino Acid-Bioconjugated Dynamic Covalent Copolymer as a Versatile Scaffold for Conjugation

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Reaction of an aromatic bisialdehyde compound and L-tyrosine methyl ester.

The aromatic bisaldehyde compound **1** (3.0 mg, 10 μmol) and L-tyrosine methyl ester (4.6 mg, 20 μmol) were dissolved in d_6-DMSO (0.5 mL) to give the solution. To the solution, DCl (1.5μL, 20 wt%) was added. The reaction was carried out at 60 ˚C. ^{1}H NMR spectroscopy was measured at specified intervals.

Reaction of an aromatic bisaldehyde compound and hydrazides

The aromatic bisaldehyde compound **1** (3.0 mg, 10 μmol) and L-tyrosine hydrazide (3.9 mg, 20 μmol) or acethydrazide (1.5 mg, 20 μmol) were dissolved in d_6-DMSO (0.5 ml) to give the solution. To the solution, DCl (1.5μL, 20 wt%) was added. The reaction was carried out at 60 ˚C. ^{1}H NMR spectroscopy was measured at specified intervals.

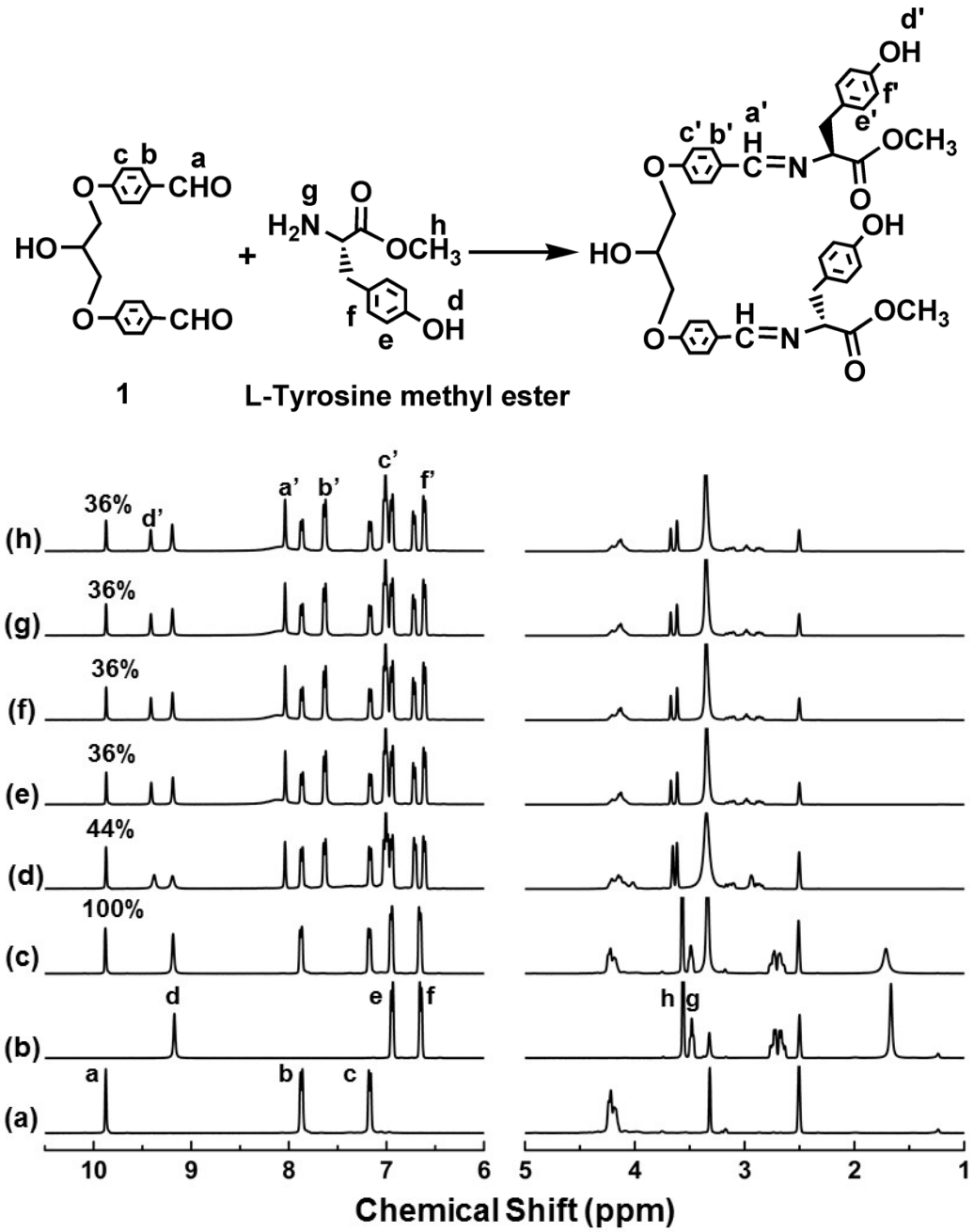

Figure S1. Imine bond formation. Partial ^{1}H spectrum in d_6-DMSO of a solution of (a) dialdehyde compound **1**, (b) L-tyrosine methyl ester, (c)-(h) solutions of **1** and L-tyrosine methyl ester (aldehyde/amine = 1:1 (molar ratio), d_6-DMSO+DCl) at specified intervals: (c) 0 h, (d) 1 h, (e) 2 h, (f) 6.5 h, (g) 12 h, (h) 24 h.

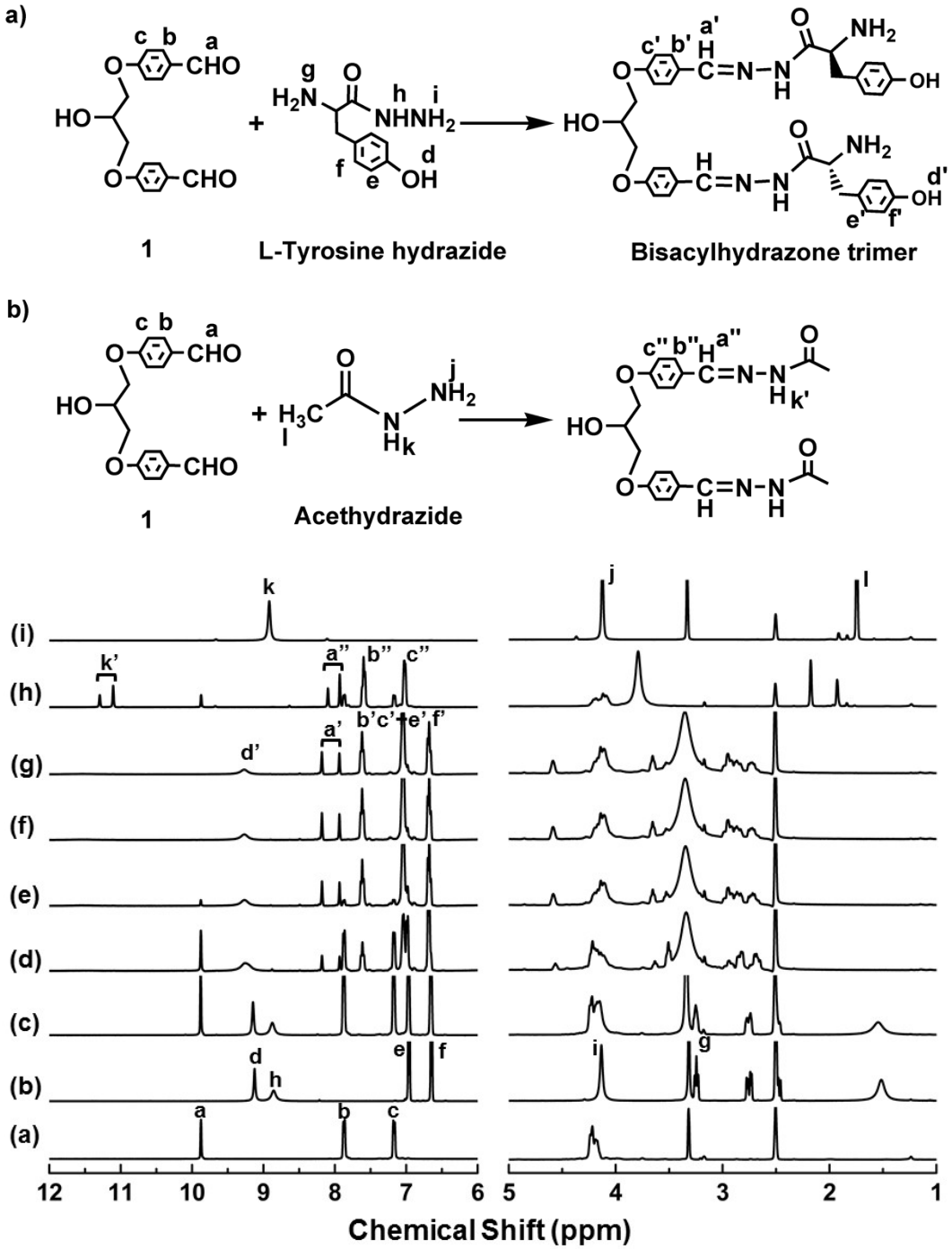

Figure S2. Acylhydrazone bond formation. Partial ^{1}H spectrum in d_6-DMSO of a solution of (a) dialdehyde compound **1**, (b) L-tyrosine hydrazide, (c)-(g) solutions of **1** and L-tyrosine hydrazide (aldehyde/hydrazide = 1:1 (molar ratio), DCl as the catalyst) at specified intervals: (c) 0 h, (d) 1 h, (e) 6.5 h, (f) 12 h, (g) 24 h. (h) solution of **1** and acethydrazide (aldehyde/hydrazide = 1:1 (molar ratio), DCl as the catalyst), (i) acethydrazide.

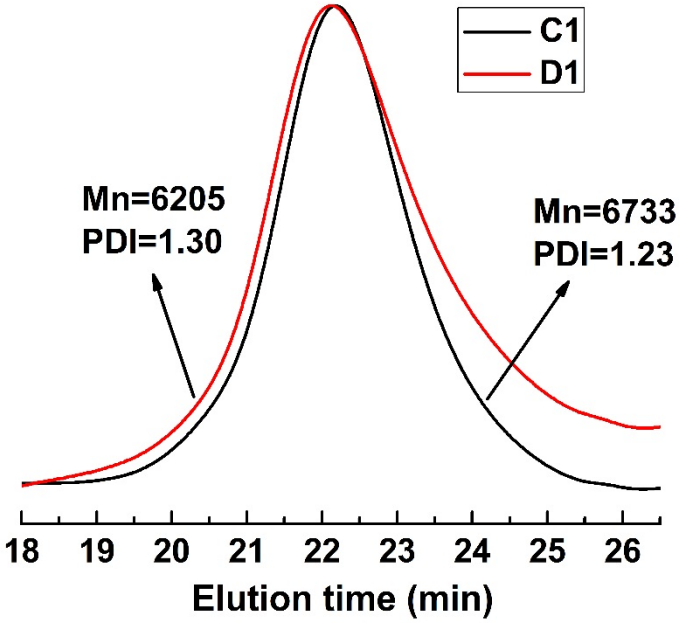

Figure S3. GPC curves of **C1** and **D1**.

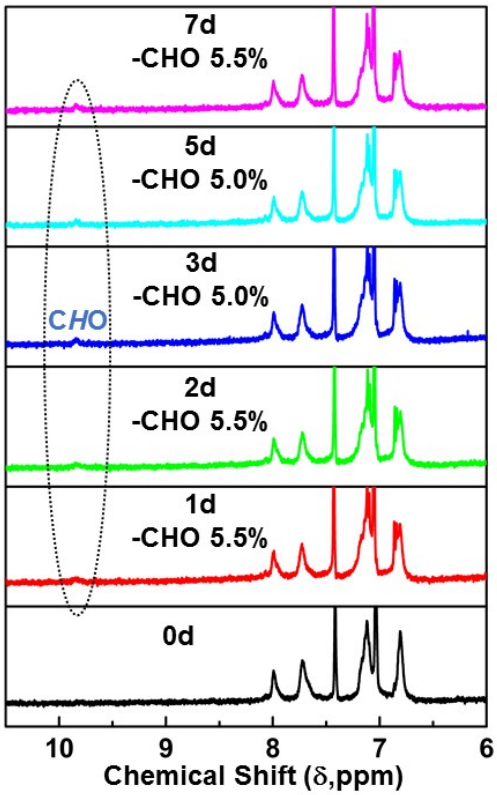

Figure S4. Partial ^{1}H NMR spectra of **D1** in D_2O/DCl recorded at specified intervals (pD = 5).

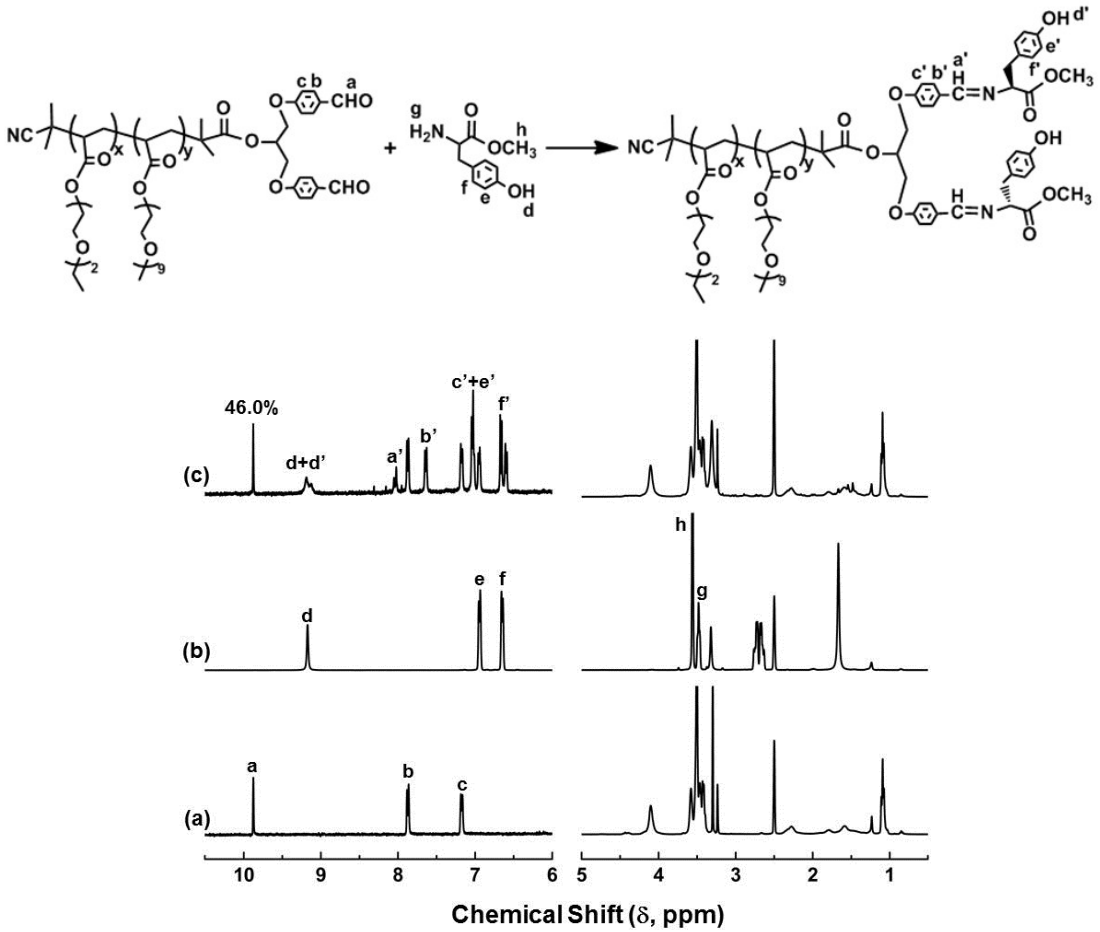

Figure S5. Partial ^{1}H NMR spectra of (a) copolymer **C1**, (b) L-tyrosine methyl ester, (c) polymer sample obtained via the condensation of **C1** and L-tyrosine methyl ester after 24 reaction in the aqueous solution of pH 5.

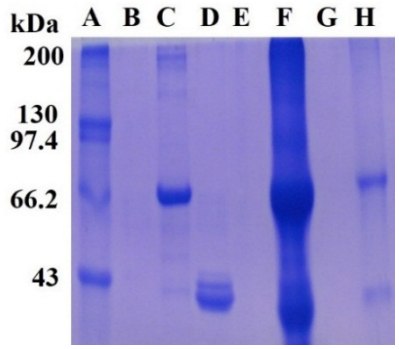

Figure S6. SDS-PAGE analysis of the chain exchange reaction of biodynamer-BSA bioconjugate with HP. Line A: protein maker; Line C: BSA; Line D: HRP; Line F: biodynamer-BSA; Line H: after chain exchange reaction.