Electronic Supplementary Information

For

Facile fabrication of glycopolymer-based iron oxide nanoparticles and their applications in carbohydrate-lectin interaction and targeted cell imaging

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Syntheses of compound 1, PFPA-COOH, compound 3 and 5

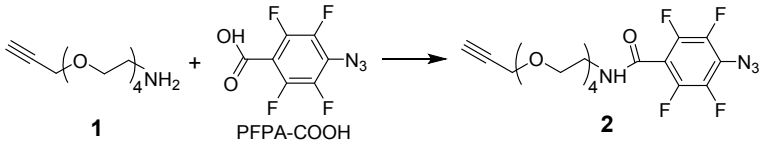
The amino-alkyne **1**,[1] PFPA-COOH,[2] 2-azidoacetohydrazide **3**,[3] azide-functionalized Rhodamine B **5**[4] were synthesized according to the published procedures, respectively. Their NMR spectra data are in agreement with those published.

Amino-alkyne (1) Pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.19 (d, J = 2.4 Hz, 2 H, HCCCH_2O-), 3.66-3.62 (m, 14 H, -OCH_2CH_2OCH_2CH_2NH_2), 3.50 (t, 2 H, -OCH_2CH_2NH_2), 2.86 (s, 2 H, -OCH_2CH_2NH_2), 2.42 (m, 1 H, -HCCCH_2O-) ppm.

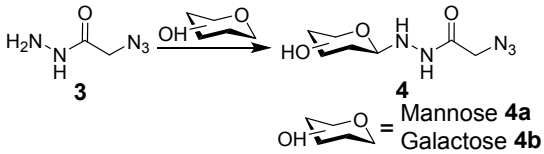
PFPA-COOH Colourless solid. ^{19}F NMR (500 MHz, $CDCl_3$): δ = -149.8 (m), -136.2 (m).

2-azidoacetohydrazide (3) Colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59 (s, 1 H, -NHNH_2), 4.06 (brs, 2 H, -CH_2-N_3), 3.92 (s, 2 H, -NHNH_2) ppm.

Azide-functionalized Rhodamine B (5) Thick red oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.34-8.28 (m, 1 H, Ar-H), 7.80 (t, J = 7.5 Hz, 1 H, Ar-H), 7.72 (t, J = 7.8 Hz, 1 H, Ar-H), 7.28 (d, J = 7.5 Hz, 1 H, Ar-H), 7.08 - 7.02 (m, 2 H, Ar-H), 6.89 (dd, J = 9.5, 2.4 Hz, 2 H, Ar-H), 6.79 (t, J = 5.7 Hz, 2 H, Ar-H), 4.16 (t, J = 4.6 Hz, 2 H, -COOCH_2-), 3.68 - 3.51 (m, 21 H, -OCH_2CH_2O-, Ar-CH), 3.36 - 3.32 (m, 2 H, N_3-CH_2-), 1.28 (t, J = 7.1 Hz, 12 H, -CH_3) ppm.



Scheme S1 Synthesis of alkyne-PFPA **2**. Reagent and condition: EDC, DCM, r.t., overnight.



Scheme S2 Synthesis of azide-modified mannose/galactose (**4a**/**4b**). Reagent and condition: EtOH : H_2O = 3 : 1, v/v, 80 °C, 8 h**.**

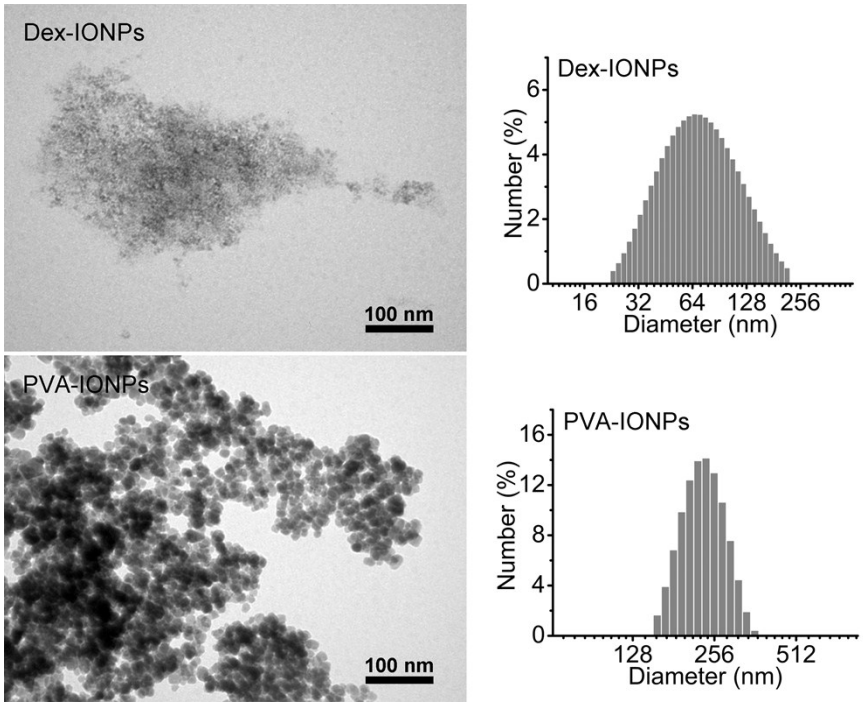


Fig. S1 TEM images and DLS analysis of Dex-IONPs and PVA-IONPs.

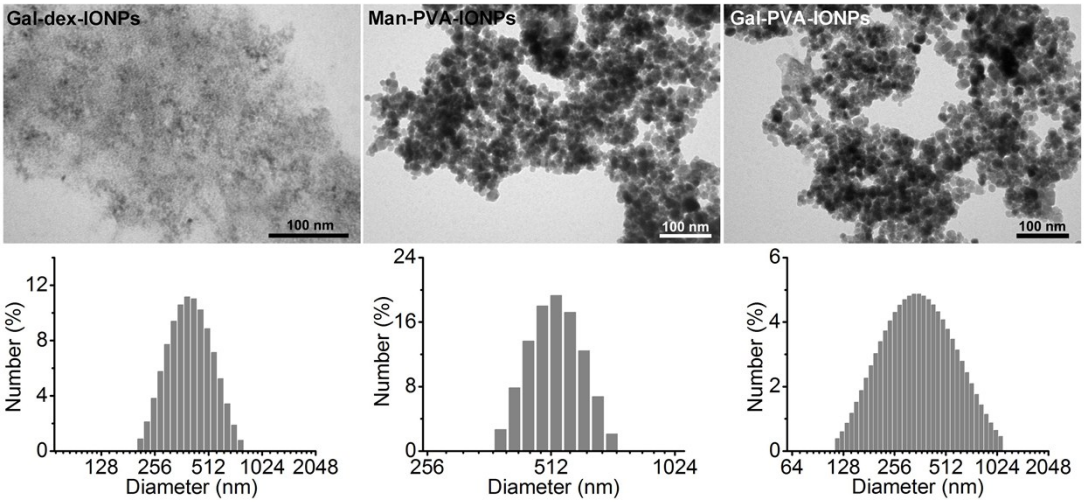


Fig. S2 TEM images and DLS analysis of three new made GIONs.

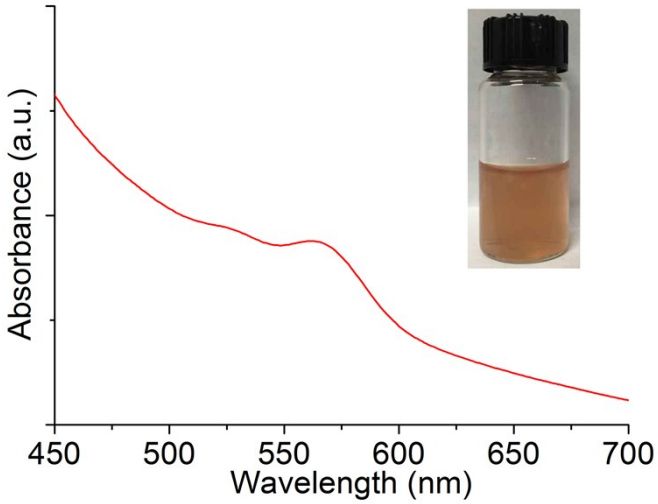


Fig. S3 The UV-Vis absorption spectra and the pictures (inset) of Gal-RhB-IONPs.

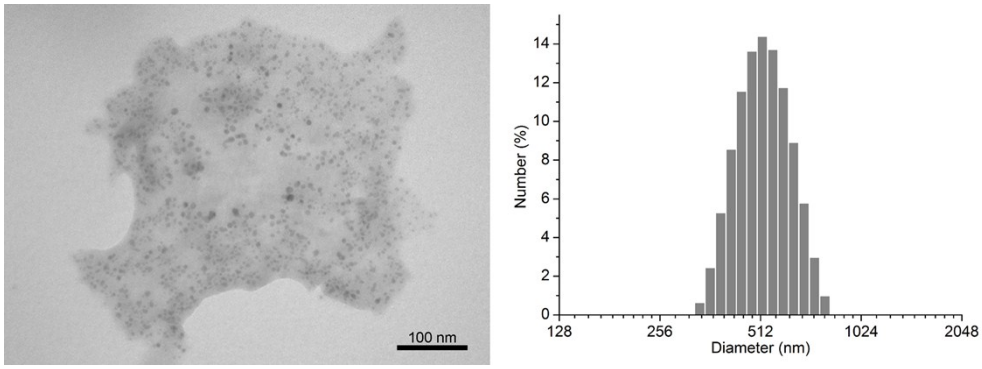


Fig. S4 TEM images and DLS analysis of Gal-RhB-IONPs.

Determination of the amount of alkynyl group on A-IONP surface[4]

The amount of alkynyl group on the surface of A-IONP was determined by HPLC according to the following procedure:

15.0 mg A-IONPs were suspended in 5.0 mL mixture of DMSO and H_2O (DMSO:H_2O = 4 : 1, v/v), followed by the addition of benzyl azide (5.0 mg), $CuSO_4 \cdot 5H_2O$ (3.0 mg) and sodium ascorbate (5.0 mg). The mixture was incubated on a shaker at room temperature for 24 h. Thereafter, 1.0 mL reaction suspension was added to 1.0 mL acetone to precipitate NPs, then NPs were removed with a magnet, and the solvent was filtered with 0.22 μm filter. Then the concentration of benzyl azide in the filtrate was analyzed by HPLC (Shimadzu LC 20AT, 150 × 4.6 mm C18 analytical column with particle size of 5 μm). A control experiment was performed without the catalyst. The analysis was carried out at 25 °C using a mobile phase A (H_2O:MeCN 90:10, v/v, + 0.1 % TFA) and B (MeCN + 0.1 % TFA) at a flow rate of 1.0 mL/min. The following gradient was applied: A linear increase from solution 30 % to 100 % B in 8 min, then held for 2 min. The detection wavelength was 295 nm. The amount of alkyne group was calculated according to the following equation:

$$N = \frac{2 \times (C_0 - C) \times V}{m}$$

Where C stands for the concentration of benzyl azide in the supernatant after the reaction (μmol/mL); C_0 stands for the concentration of benzyl azide in control experiment (μmol/mL); m stands for the mass of A-IONPs (mg); V stands for the volume of the reaction solvent (mL); N stands for the amount of alkynyl group (μmol/mg NPs). For each sample, the amount of alkyne group was averaged from three independent measurements.

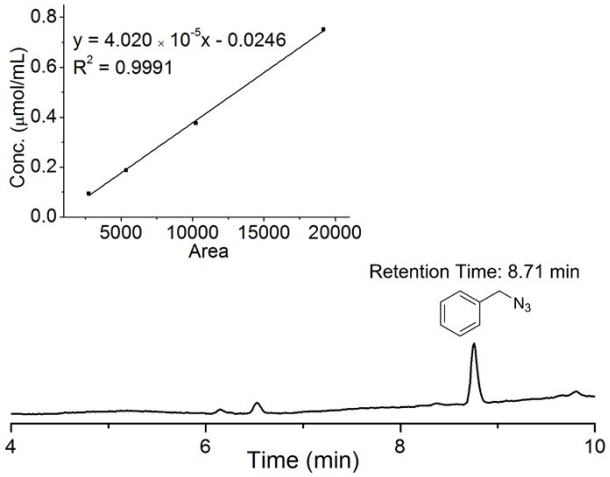


Fig. S5 HPLC chromatogram for the supernatant from the reaction mixture of A-IONPs and benzyl azide; Inset: the standard curve of benzyl azide.

Determination of galactose amount on Gal-RhB-IONP surface: Gal-RhB-IONPs (1.75 mg) were dispersed in deionized water (2.0 mL) in an ice bath. A freshly prepared 0.1% (w/w) solution of anthrone in sulfuric acid (8.0 mL) was added slowly to this solution. The resulting solution was gently mixed and heated to 100 °C for 10 min, then cooled in ice-water bath. The absorption of the solution was measured at 620 nm and compared with those that were obtained from a standard curve to determine the amount of galactose on the Gal-RhB-IONP surface. The reported amount of galactose was averaged from three independent measurements.

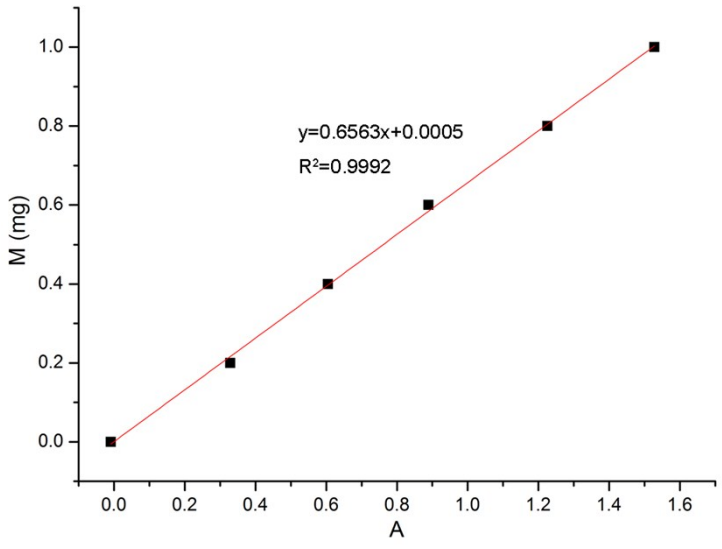


Fig. S6 The standard curve of galactose in determination of carbohydrate amount on Gal-RhB-IONP surface by anthrone–sulfuric acid colorimetric assay.

Determination of Rhodamine B amount on Gal-RhB-IONP surface: Gal-RhB-IONPs (0.5 mg) were dispersed in deionized water (20 mL). The absorption of the solution was measured at 571 nm (0.025 mg/mL PVA-IONPs in deionized water were used as control) and compared with those that were obtained from a standard curve to determine the amount of Rhodamine B on the Gal-RhB-IONP surface. The reported amount of Rhodamine B was averaged from three independent measurements.

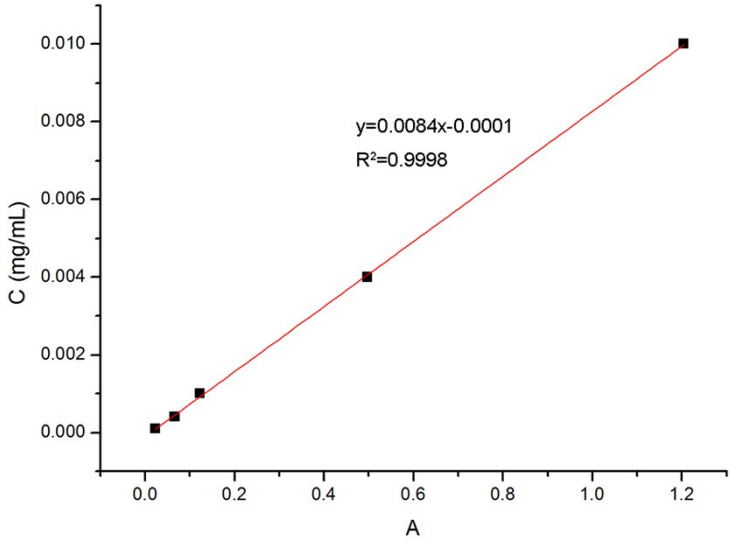


Fig. S7 The standard curve of compound **5** in determination of Rhodamine B amount on Gal-RhB-IONP surface by UV-visible absorbance.

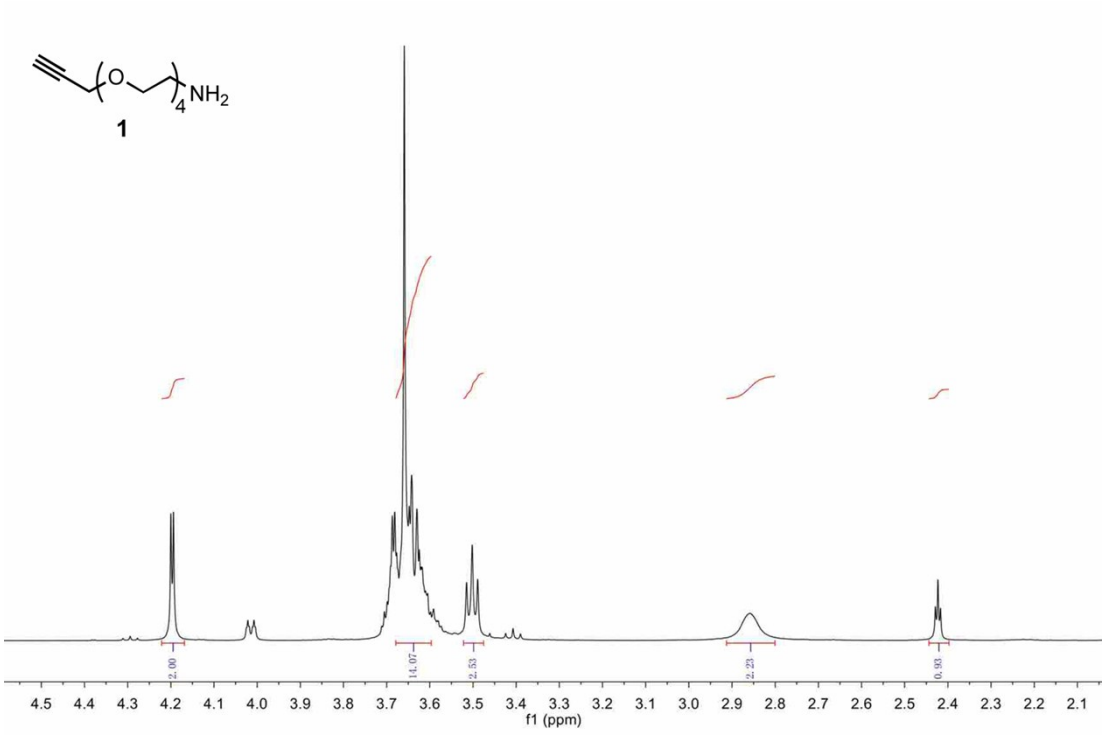


Fig. S8 ^{1}H NMR spectrum of amino-alkyne **1**.

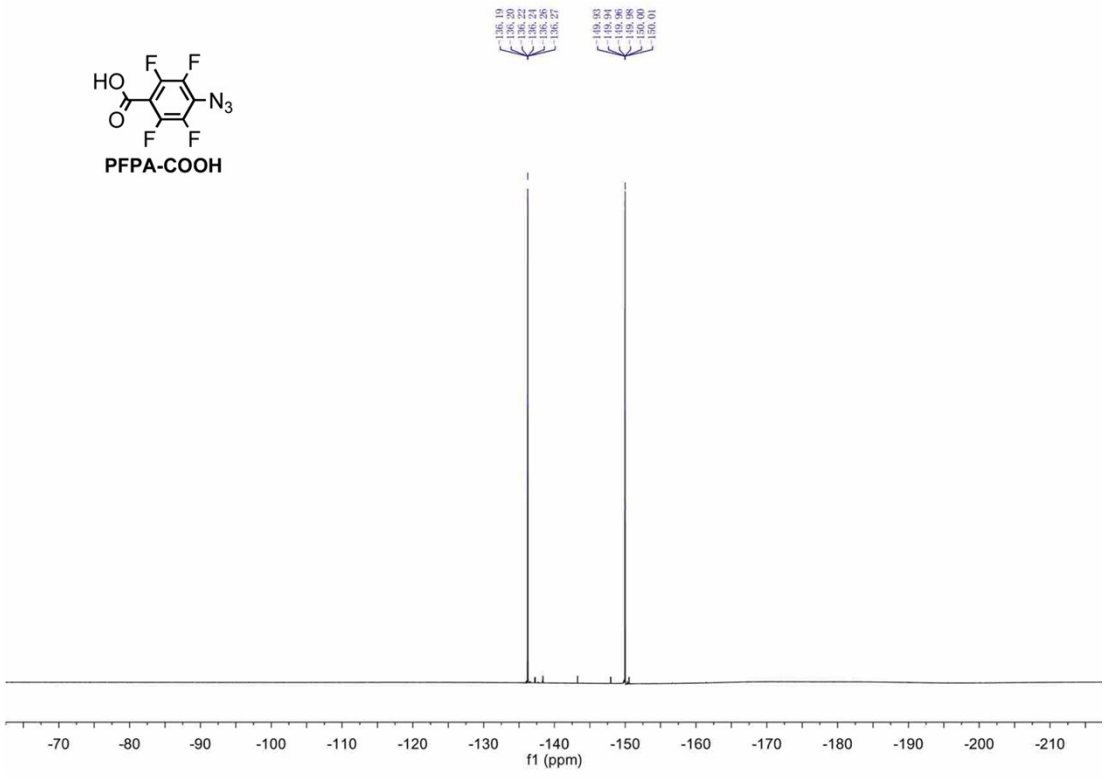


Fig. S9 ^{19}F NMR spectrum of PFPA-COOH.

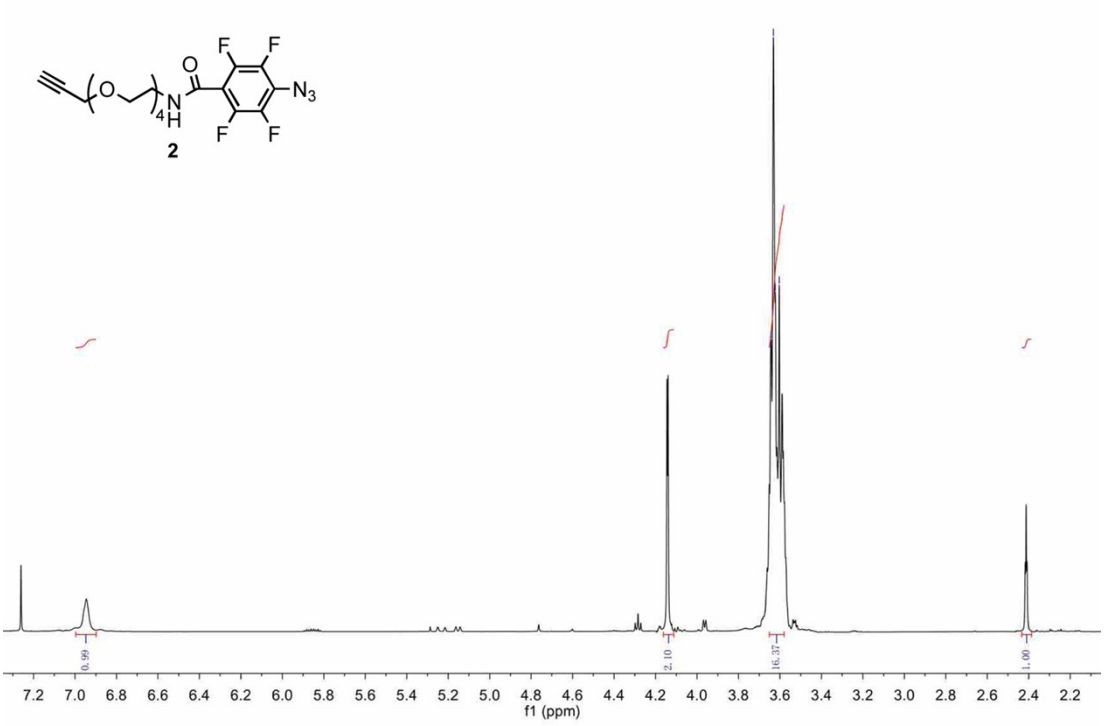


Fig. S10 ^{1}H NMR spectrum of alkyne-PFPA **2**.

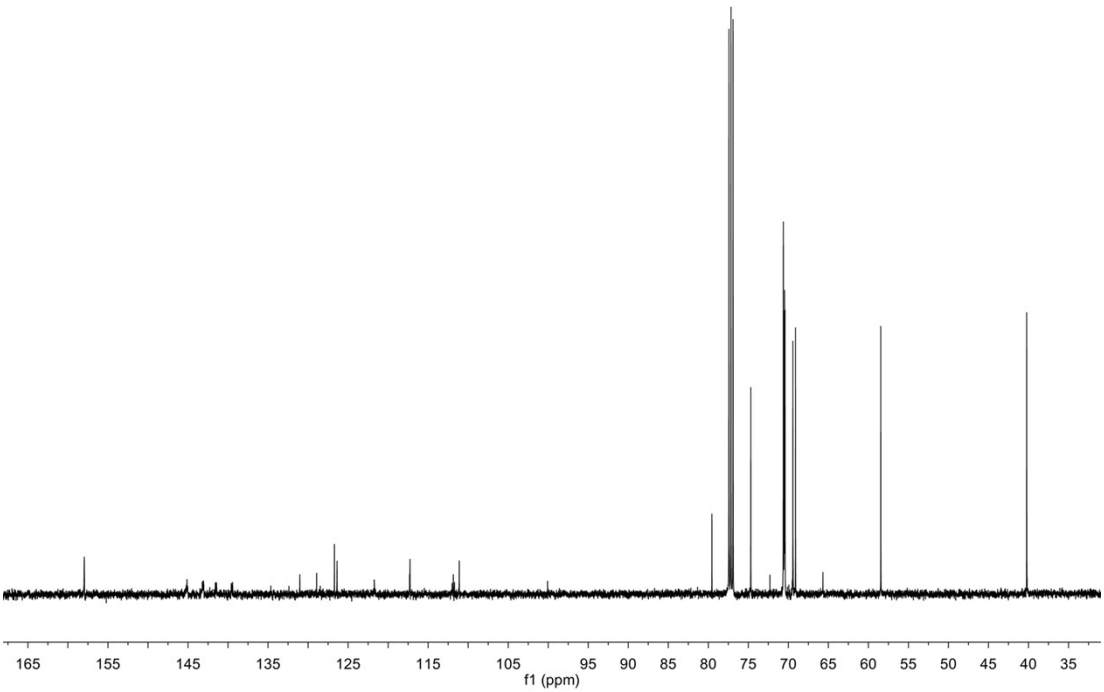


Fig. S11 ^{13}C NMR spectrum of alkyne-PFPA **2**.

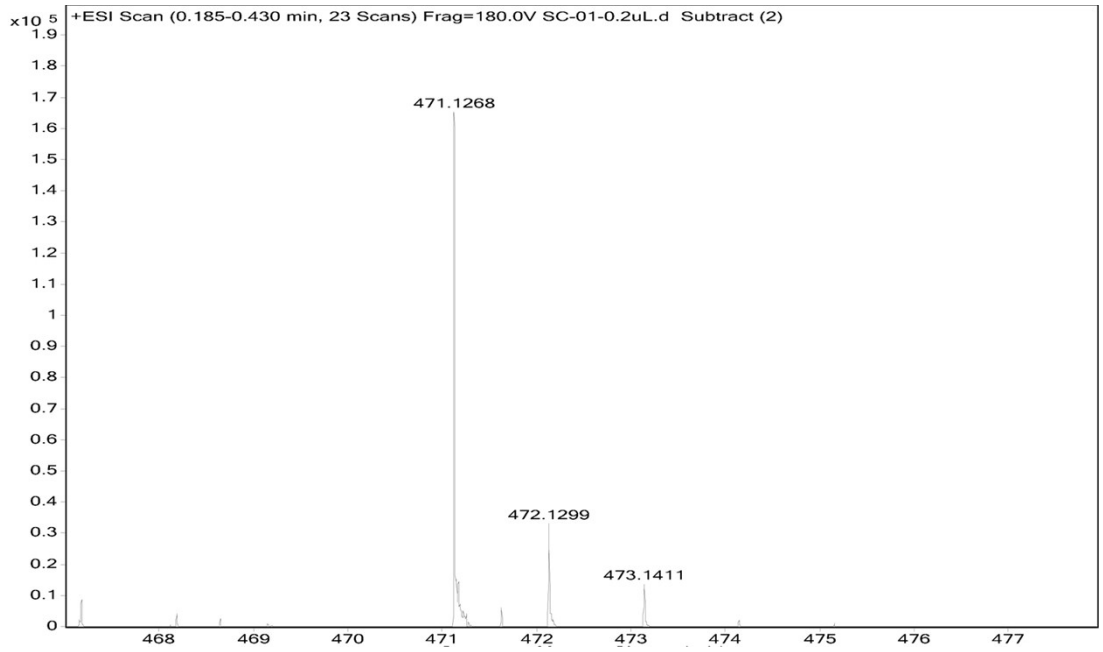


Fig. S12 ESI HRMS spectrum of alkyne-PFPA **2**.

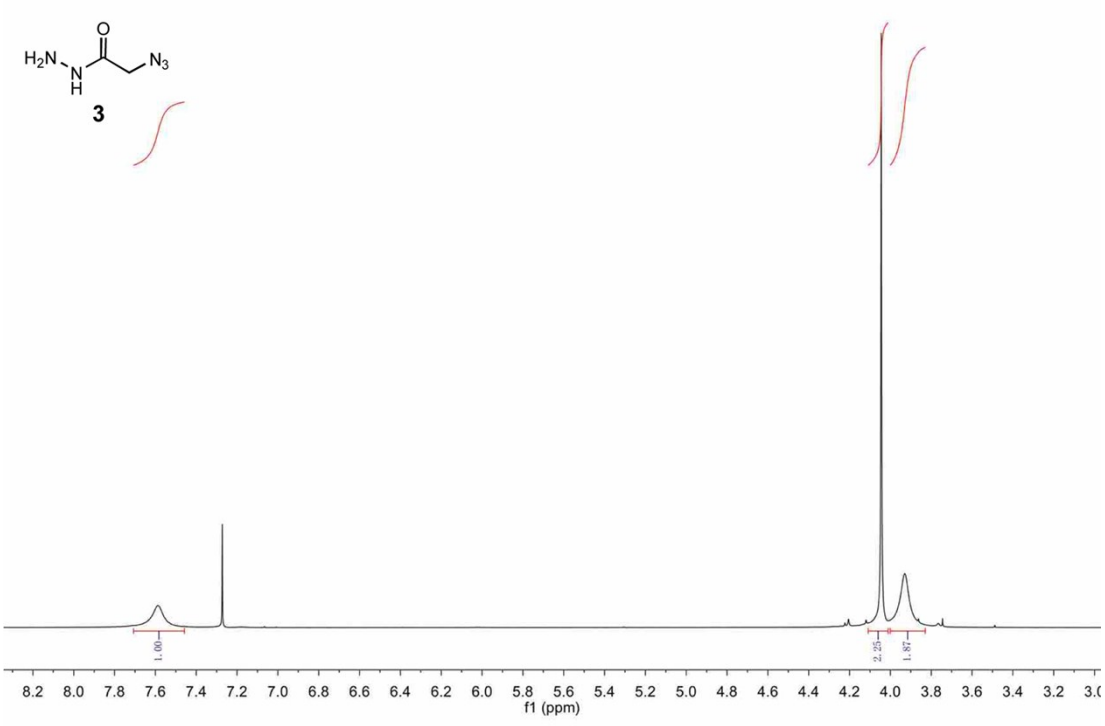


Fig. S13 ^{1}H NMR spectrum of 2-azidoacetohydrazide **3**.

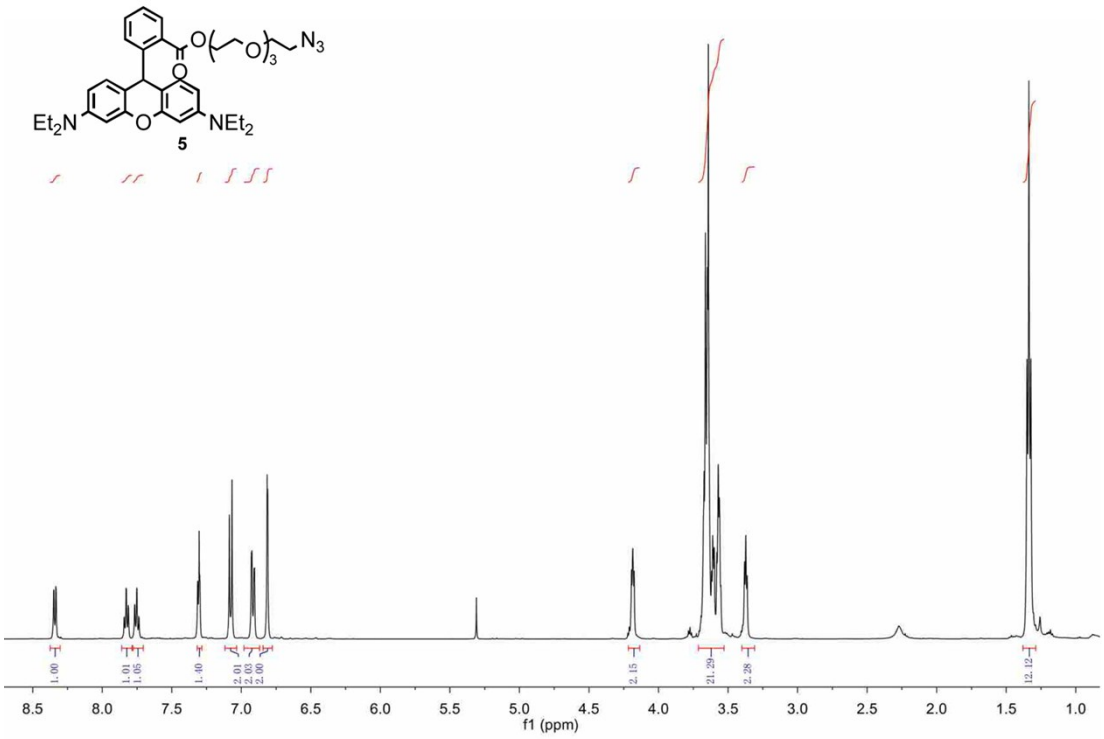


Fig. S14 [1]H NMR spectrum of azide functionalized Rhodamine B **5**.

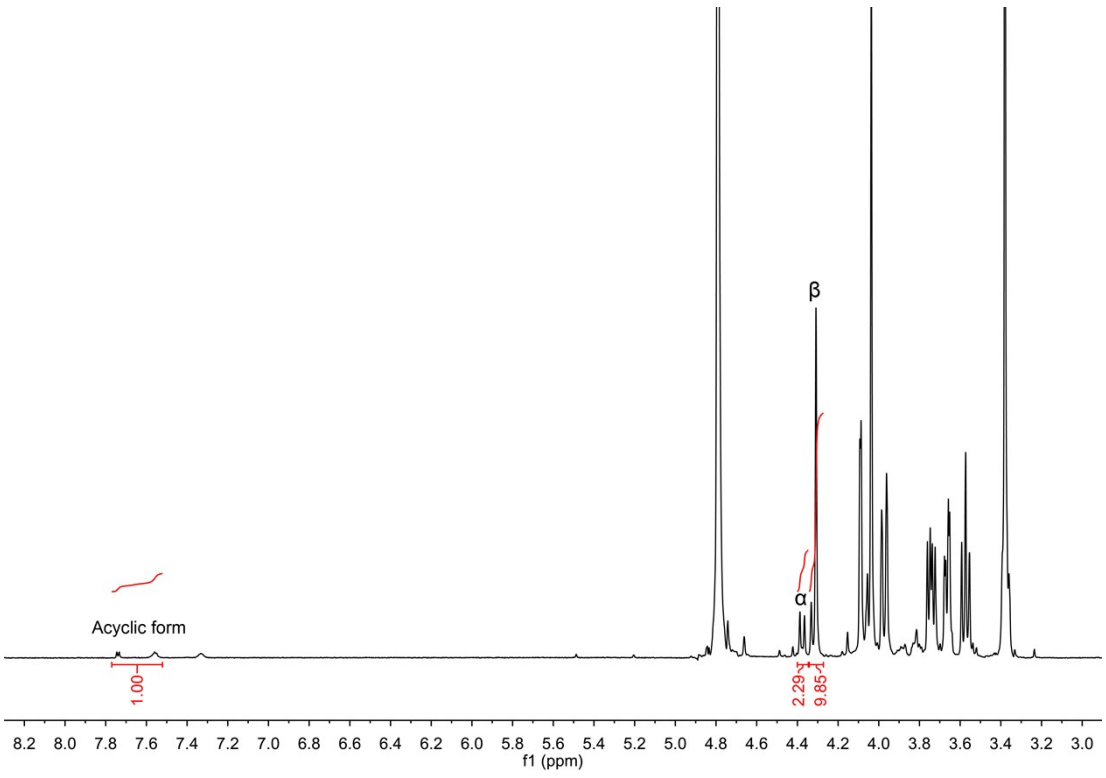


Fig. S15 [1]H NMR spectrum of azide modified mannose **4a**.

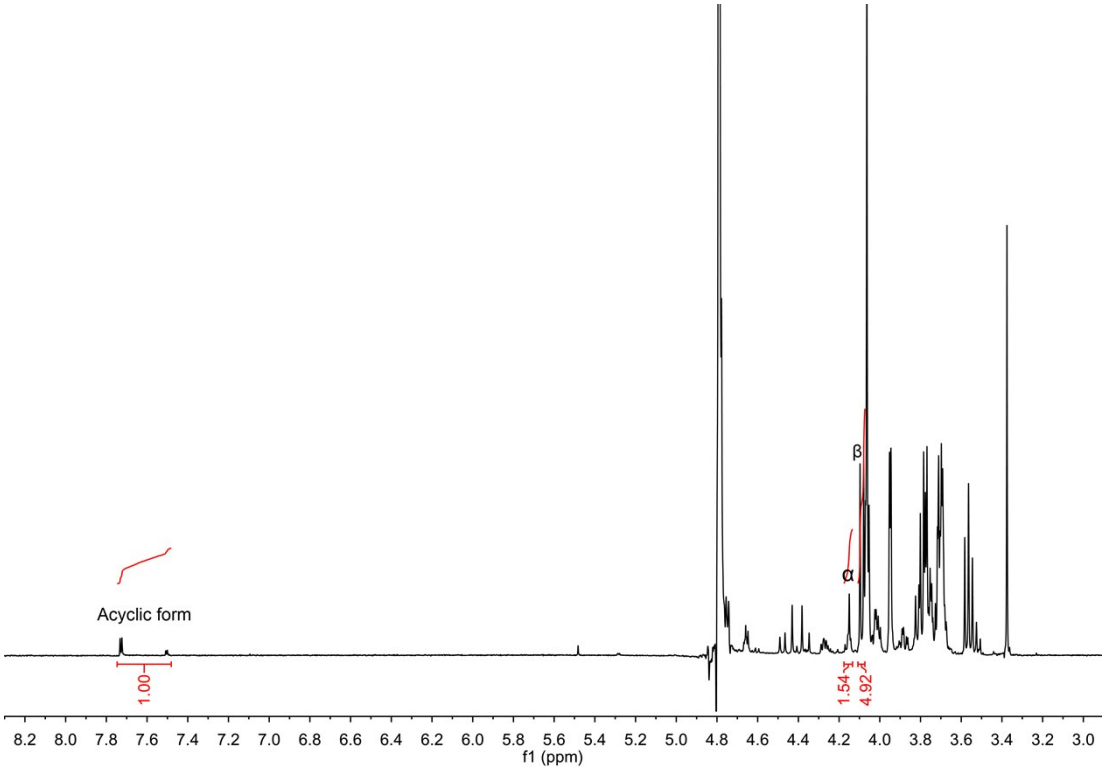


Fig. S16 ^{1}H NMR spectrum of azide modified galactose **4b**.

Reference

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