Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Polysaccharide-Porphyrin-Fullerene Supramolecular Conjugates as a Photo-driven DNA Cleavage Reagent

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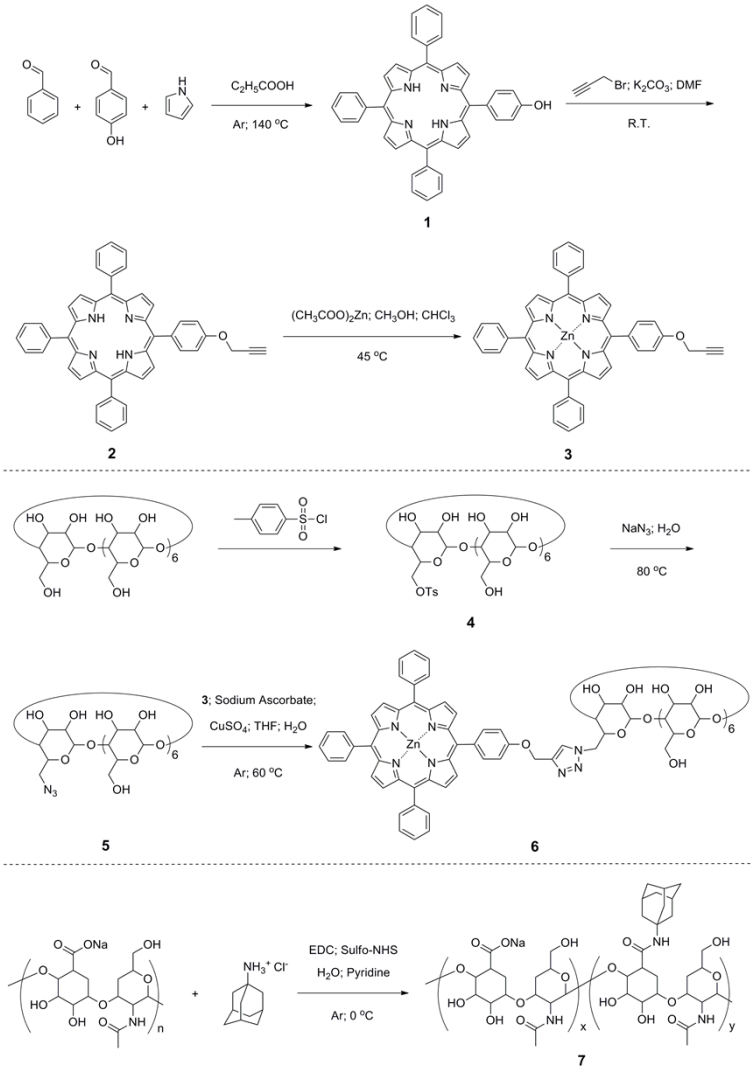


Scheme S1. Syntheses of triphenyl Zn-porphyrin-modified β-CD (**6**), adamantyl-modified hyaluronate (**7**).

Experimental Section

Material. All solvents and reagents were commercially available without further purification unless otherwise noted. All aqueous solutions were prepared from triple-distilled water. 6-Deoxy-6-azido-β-CD,[1] 5-(4'-hydroxyphenyl)-10,15,20-triphenylporphyrin (**1**),[2] and adamantyl-modified HA (**7**)[3] were synthesized according to the reported procedure.

Instrument. NMR spectra were recorded on a Bruker AV 400 spectrometer. Mass spectra were performed on a Varian 7.0 T FTICR-MS (MALDI). Thermogravimetric analysis (TGA) was recorded with a RIGAKU Standard type TG analyzer. Carefully weighed quantities of every sample were subjected at a heating rate of 10.0 K/min under nitrogen atmosphere from 25 °C to 800 ˚C. FT-IR spectra were recorded on a Bio-Rad FTS6000 spectrometer. UV-Vis spectra were recorded in a quartz cell (light path 5 mm) on a Shimadzu UV-3600 spectrophotometer equipped with a PTC-384WI temperature controller. Atomic force microscopy (AFM) images were examined by a Nanoscope IIIa Multimode 8 AFM (Bruker). Transmission electron microscopy (TEM) images were examined by a high-resolution TEM (Tecnai G2 F20 microscope, FEI) equipped with a CCD camera (Orius 832, Gatan) operation at an acceleration voltage of 200 kV. Each sample for TEM measurements was prepared by dropping a 50 μL of sample solution on a copper grid. The grids were then air-dried, and the samples were examined by a Philips EM400st transmission electron microscope. Agarose gels of 1% were prepared by heating 250 mg of agarose in 25 mL of 1 × TAE buffer (4.0×10^{-2} mol/L Tris, 2.0×10^{-2} mol/L acetic acid, 2×10^{-3} mol/L EDTA). Sample solutions containing pBR322 DNA and supramolecular conjugate were prepared by adding an appropriate volume of supramolecular conjugate and DNA solutions into Eppendorf tubes and then were diluted to the total volume of 10 μL. After incubation at 4 °C for 30 min, the sample solutions were subjected to electrophoresis at 60 V for 1 h (current 120 mA), and visualized by ethidium bromide staining. DNA bands were visualized and photographed by a UV transilluminator and

WD-9413B gel documentation system (Beijing Liuyi Instrument Factory, China).

Synthesis of 5-(4'-propargyloxyphenyl)-10,15,20-triphenyl Zn-porphyrin (3). **1** (630.7 mg, 1.0 mmol), propargyl bromide (594.8 mg, 5.0 mmol) and K_2CO_3 (691.1 mg, 5.0 mmol) in anhydro-DMF (40 mL) was stirred at 80 °C for 8 h, and then the solvent was removed under reduced pressure. The residue was washed by water and dried under vacuum for 12 h at 60 °C. The crude product was dissolved in methanol/chloroform (10 mL, v:v = 1:1), and zinc acetate (458.7 mg, 2.5 mmol) in methanol (10 mL) was added. The reaction mixture was refluxed for 8 h and then cooled to room temperature. The solvent was removed under reduced pressure, and the residue was purified by silica gel column by using chloroform/*n*-hexane (v:v = 5:3) to obtain the product as a purplish-red solid (653.1 mg, yield 89.2%). ^{1}H NMR ($CDCl_3$, 400MHz): δ (ppm) = 2.66-2.72 (t, J = 2.7 Hz, 1H), 4.95-5.01 (d, J = 5.0 Hz, 2H), 7.33-7.40 (d, J= 7.4 Hz, 2H), 7.68-7.82 (m, 9H), 8.10-8.18 (d, J= 8.2 Hz, 2H), 8.18-8.26 (m, 6H), 8.92-9.01 ppm (m, 8H); MALDI-HR-MS: m/z 730.185 [M^+].

Synthesis of porphyrin-modified β-CD (6). To a solution of **3** (365.1 mg, 0.5 mmol) in THF (5 mL), 6-deoxy-6-azido-β-CD (696.0 mg, 0.6 mmol) and $CuSO_4$ (159.6 mg, 1.0 mmol) in triple-distilled water (25 mL) was added with stirring, and then sodium ascorbate (594.3 mg, 3.0 mmol) was added. The reaction mixture was heated at 50 °C and stirred under an argon atmosphere for 8 h. The solvent was removed under reduced pressure, and the residue was purified by silica gel column by using propanol/water/ammonia (v:v:v = 6:3:1) to obtain the product as a dark purple solid (805.1 mg, yield 85.1%). ^{1}H NMR (DMSO-D_6, 400MHz): δ = 2.95-3.10 (m, 2H),

3.31-3.50 (m, 14H), 3.55-3.86 (m, 23H), 4.04-4.11 (t, J = 4.1 Hz, 1H), 4.34-4.61 (m, 5H), 4.65-4.74 (t, J = 4.7 Hz, 1H), 4.77-4.92 (m, 6H), 4.97-5.06 (d, J =5.0 Hz, 1H), 5.08-5.15 (s, 1H), 5.36-5.46 (s, 2H), 5.61-5.97 (m, 14H), 7.44-7.52 (d, J = 7.5 Hz, 2H), 7.73-7.92 (m, 9H), 8.06-8.14 (d, J = 8.1 Hz, 2H), 8.15-8.26 (m, 6H), 8.33-8.37 (s, 1H), 8.74-8.89 ppm (m, 8H); MALDI-HR-MS: m/z 1890.4594 $[M+H]^+$; elemental analysis calculated for **6**·10H_2O (%): C 51.58, H 5.79, N 4.73; found (%): C 51.37, H 5.69, N 4.85.

Preparation of 6/C_{60} Conjugate. A solution containing C_{60} (32.0 mg) and **6** (31.0 mg) in 12 mL of toluene/DMF (v:v = 5:1) was injected into 200 mL of triple-distilled water under vigorous stirring. The resulting solution was stirred for 2 days under an argon atmosphere. The organic solvents were then removed by dialysis (molecular weight cutoff 1000) in distilled water for 5 days, and the remaining aqueous solution was filtered by vacuum filtration. The filtrate was then freezen-dried to give **6**/C_{60} conjugate.

Preparation of 6/7/C_{60} Conjugate. A solution containing C_{60} (32.0 mg) and **6** (31.0 mg) solution in 12 mL of toluene/DMF (v:v = 5:1) was injected into a solution of **7** (24.0 mg) solution in 200 mL of triple-distilled water under vigorous stirring. The resulting solution was stirred for 2 days under an argon atmosphere. The organic solvents were then removed by dialysis (molecular weight cutoff 1000) in distilled water for 5 days, and the remaining aqueous solution was filtered by vacuum filtration. The filtrate was then frozen-dried to give **6**/**7**/C_{60} conjugate.

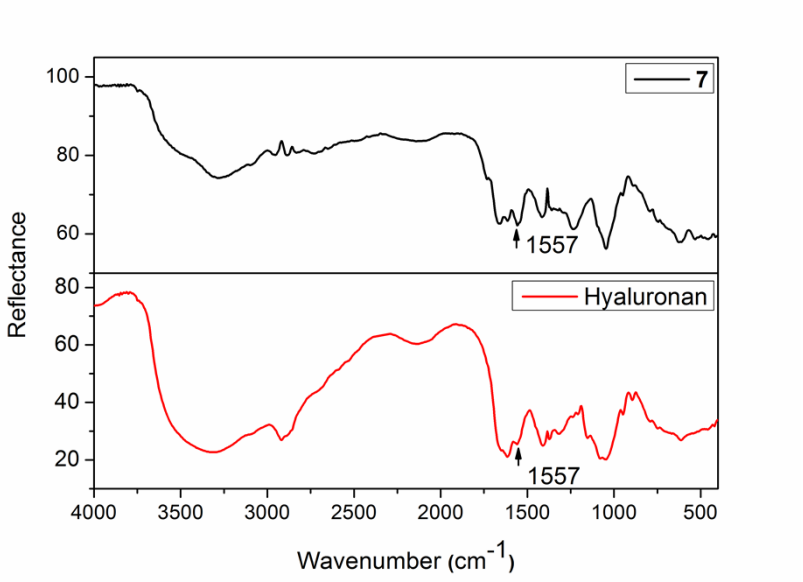


Figure S1. FT-IR spectra of **7** and sodium hyaluronate.

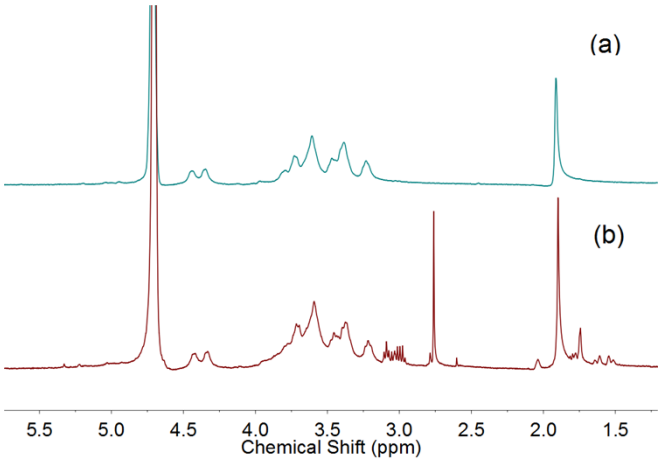
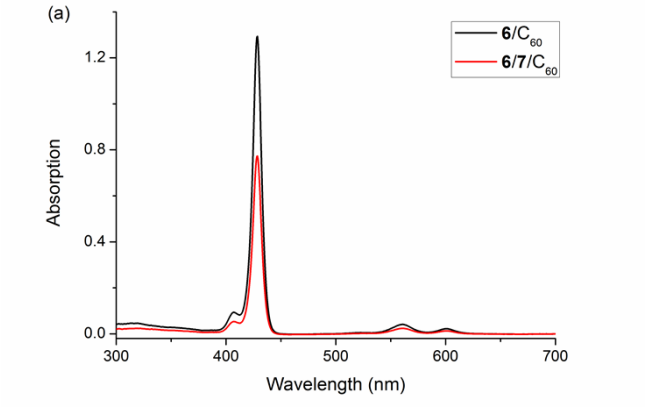


Figure S2. Partial ^{1}H NMR spectra of sodium hyaluronate and **7** in D_2O.



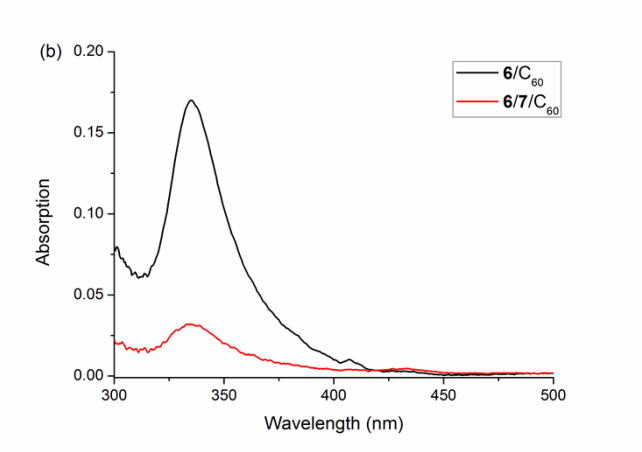


Figure S3. UV-vis spectra of **6**/C_{60} and **6**/**7**/C_{60} in DMSO (a) and toluene (b) at 25 °C.

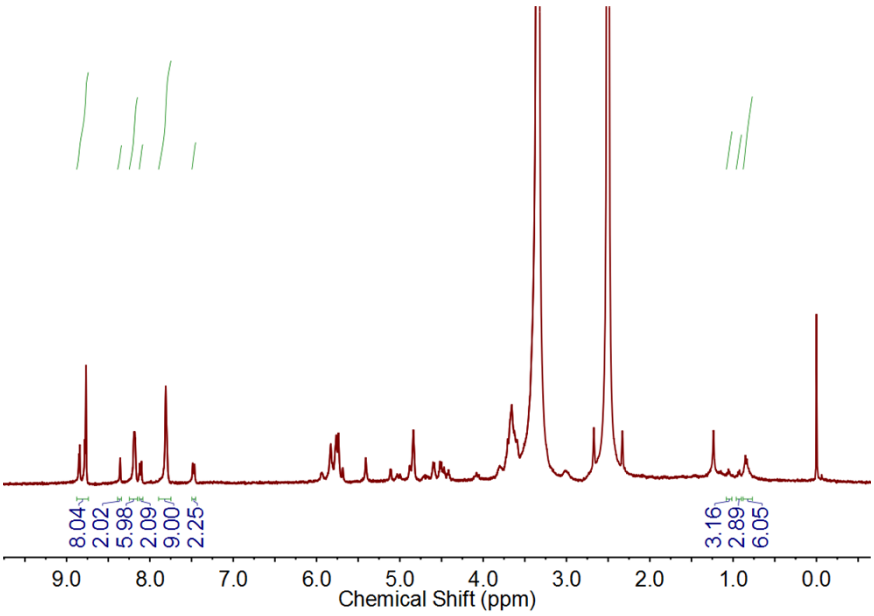


Figure S4. ^{1}H NMR spectra of **6**/**7**/C_{60} in DMSO-D_6.

Reference

1. Hbaieb, S.; Kalfat, R.; Chevalier, Y.; Amdouni, N.; Parrot-Lopez, H. *Mater. Sci. Eng. C* **2008**, *28*, 697–704.

2. Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.

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