

Electronic Supplementary Information (ESI) for New Journal of Chemistry

Electronic Supporting Information

Enhanced Intracellular Uptake in Vitro by Glucose Functionalized Nanopesticides

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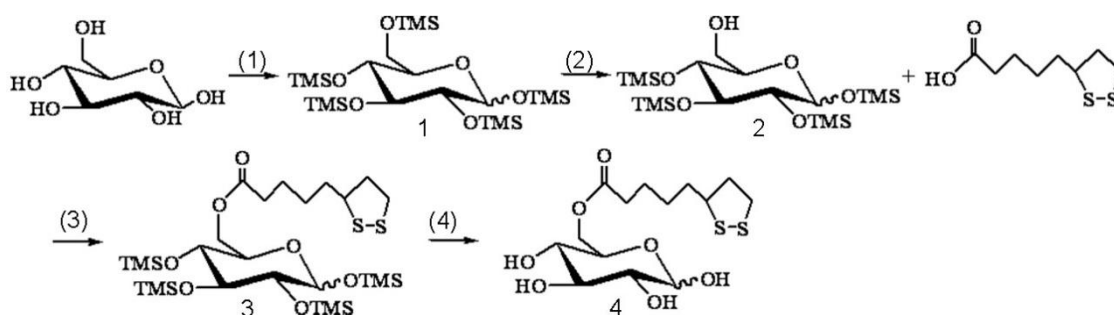
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Synthesis of the ligands



Scheme S1. Synthetic pathway of compound 4; Reagents and conditions: (1) TMSCl, HMDS, pyridine, r.t., overnight; (2) acetone, methanol, acetic acid, 40 °C, 4 h; (3) DCC, DMAP, CH₂Cl₂, 60 °C, 0.5 h; (4) TFA, CH₂Cl₂, 0 °C, 1.5 h.

Synthesis of compounds 1 and 2

Compounds 1 and 2 were prepared according to the procedure described in the

early reported literature.¹

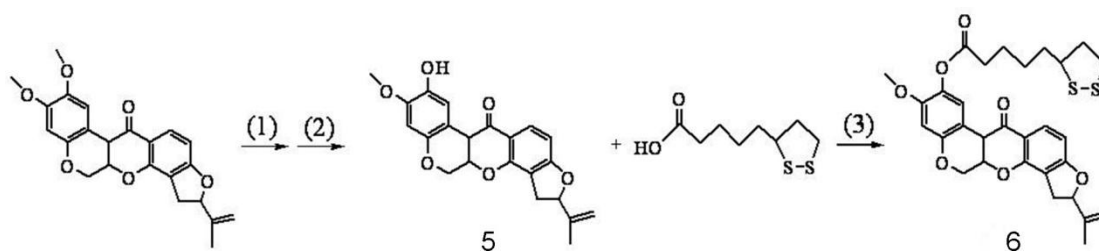
Synthesis of compound 3

A mixture of the prepared 2 (1.3754 g), DL-Thioctic acid (0.6390 g), DCC (0.7913 g) and DMAP (10.0 mg) in dry CH₂Cl₂ (35 mL) was stirred at 60 °C for 0.5 h. Then, the mixture was cooled down to room temperature, and the solution was stirred overnight. The solvent was evaporated under reduced pressure. Finally, the compound 3 was purified by the column chromatography.

Synthesis of compound 4

Compound 4 was obtained through deprotection of 3 by trifluoroacetic acid (178 μL) in CH₂Cl₂ (20 mL) at 0 °C. The mixture was kept for 1.5 h. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography to yield 4 as a yellow oil. ¹H NMR(CD₃OD, 600 MHz): α: β = 4:1, δ 5.08 (d, 1H, *J* = 3.6 Hz, H-1-α), 4.47 (d, 1H, *J* = 7.8 Hz, H-1-β), 4.38 - 4.41 (m, 1H, H-6-1-β), 4.35 (d, 1H, *J* = 11.8 Hz, H-6-1-α), 4.19 (dd, 1H, *J* = 5.2 Hz, H-6-2-α), 4.16 - 4.17 (m, 1H, H-6-2-β), 3.93 - 3.96 (m, 1H, H-5), 3.67 (t, 1H, *J* = 9.3 Hz), 3.54 - 3.61 (m, 3H, S-CH₂, S-CH), 3.14 - 3.19 (m, 1H, CH), 3.06 - 3.14 (m, 1H, CH), 2.43 - 2.49 (m, 1H, S-CH-CH₂), 2.35 (t, 2H, *J* = 7.3 Hz, COCH₂-α), 2.28 (t, 2H, *J* = 7.3 Hz, COCH₂-β), 1.85-1.91 (m, 1H, S-CH-CH₂), 1.16-1.74 (m, 6H, CH₂). ¹³C (CD₃OD, 600 MHz): δ 173.89, 173.81, 96.77, 92.61, 76.46, 74.81, 73.94, 73.36, 72.38, 70.55, 70.31, 69.28, 63.91, 63.41, 56.10, 41.84, 39.88, 37.93, 34.24, 33.40, 29.87, 28.87, 28.39, 24.39, 23.03, 22.70, 13.01, 10.00.

Synthesis of Rotenone-Thioctic (R-TA)



Scheme S2. Synthetic pathway of compound 6; Reagents and conditions: (1) BBr₃, CH₂Cl₂, -5 °C, 4 min; (2) NaHCO₃, acetone, methanol, r.m, 2 h; (3) DCC, DMAP, CH₂Cl₂, r.m, overnight.

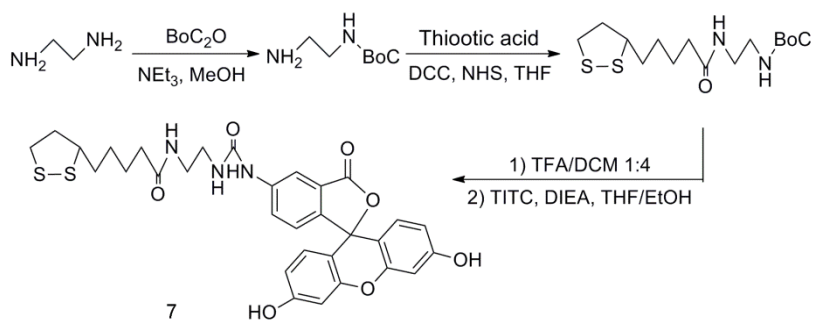
Synthesis of R-OH (5)

R-OH was synthesized as previously described.^{2,3} ¹H NMR (CDCl₃, 600 MHz), δ 7.83 (d, 1H, J = 8.52 Hz, 11-H), 6.82 (s, 1H, 1-H), 6.49 (d, 1H, J = 8.4 Hz, 10-H), 6.43 (s, 1H, 4-H), 5.23 (t, 1H, J = 8.9 Hz, 5'-H), 5.13 (s, 1H, 2-OH), 5.07 and 4.93 (brs, both 1H, 7'-H₂), 4.91 (m, 1H, 6a-H), 4.60 (dd, 1H, J = 12, 3 Hz, H-6a), 4.17 (d, 1H, J = 12 Hz, H-6b), 3.82 (s, 4H, OMe and 12a-H), 3.31 (dd, 1H, J = 15.7, 9.8 Hz, 4'-Hb), 2.95 (dd, 1H, J = 15.7, 8.1 Hz, 4'Ha), 1.76 (s, 3H, 8'-CH₃). ¹³C NMR (CDCl₃, 600 MHz) δ: 188.70, 167.26, 157.78, 146.88, 146.67, 143.08, 140.18, 130.03, 113.29, 113.11, 112.86, 112.54, 105.97, 104.83, 100.16, 87.79, 72.16, 66.23, 55.90, 44.58, 31.29, 17.12.

Synthesis of R-TA (6)

Compound 5 (102.2 mg), DL-Thioctic acid (55.3 mg), DCC (110.6 mg) and DMAP (16.4 mg) were added into dry CH₂Cl₂ (20 mL). After 12 h of stirring at room temperature, the mixture was concentrated and purified by silica gel chromatography to give the corresponding compound 6 as a yellow solid. ¹H NMR(CDCl₃, 600 MHz), δ 7.83 (d, 1H, J = 8.52 Hz, 11-H), 6.95 (s, 1H, 1-H), 6.52 (s, 1H, 10-H), 6.51 (s, 1H, 4-H), 5.27 (t, 1H, J = 8.9 Hz, 5'-H), 5.09 and 4.96 (br s, both 1H, 7'-H₂), 4.94 (m, 1H, 6a-H), 4.65 (dd, 1H, J = 12.1 Hz, H-6a), 4.21(d, 1H, J = 12.1 Hz, H-6b), 3.84 (d, 1H, 12a-H), 3.77 (s, 3H, OMe), 3.31 (dd, 1H, J = 15.7, 9.8 Hz, 4'-Hb), 2.95 (dd, 1H, J = 15.7, 8.1 Hz, 4'Ha), 1.78 (s, 3H, 8'-CH₃); 3.58-3.63 (m, 1H, S-CH), 3.19-3.23 (m, 1H, S-CH₂), 3.12-3.16 (m, 1H, S-CH₂), 2.54 (t, 2H, J = 7.38, COCH₂), 2.47-2.51 (m, 1H, S-CH-CH₂), 1.91-1.97 (m, 1H, S-CH-CH₂), 1.71-1.77(m, 4H, CH₂), 1.27 (s, 1H, CH₂), 0.85-0.91(m, 1H, CH₂).

Synthesis of FITC-TA (7)



The compound of FITC-TA (7) was synthesized according to the literature.⁴

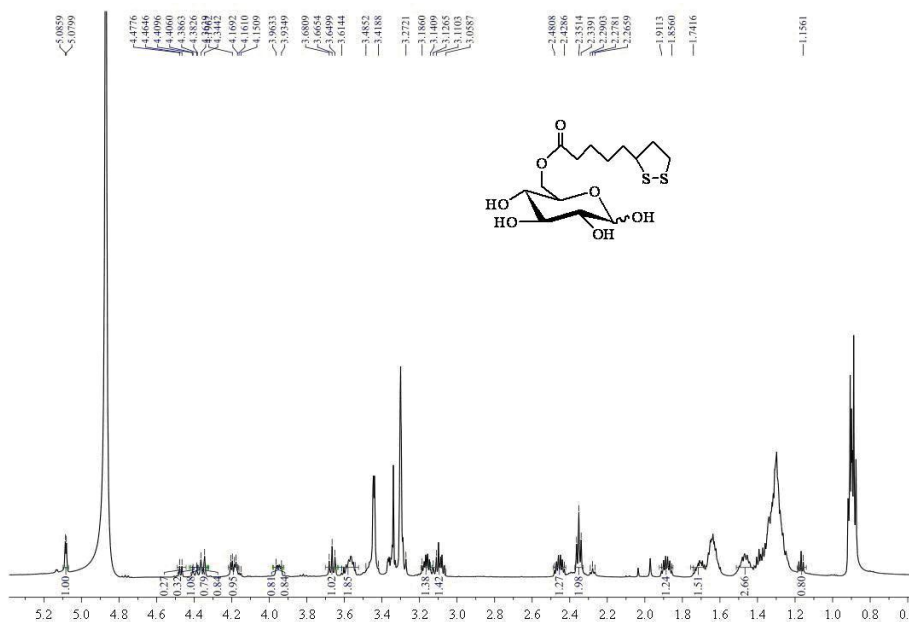


Fig. S1 ¹H NMR spectrum of compound 4

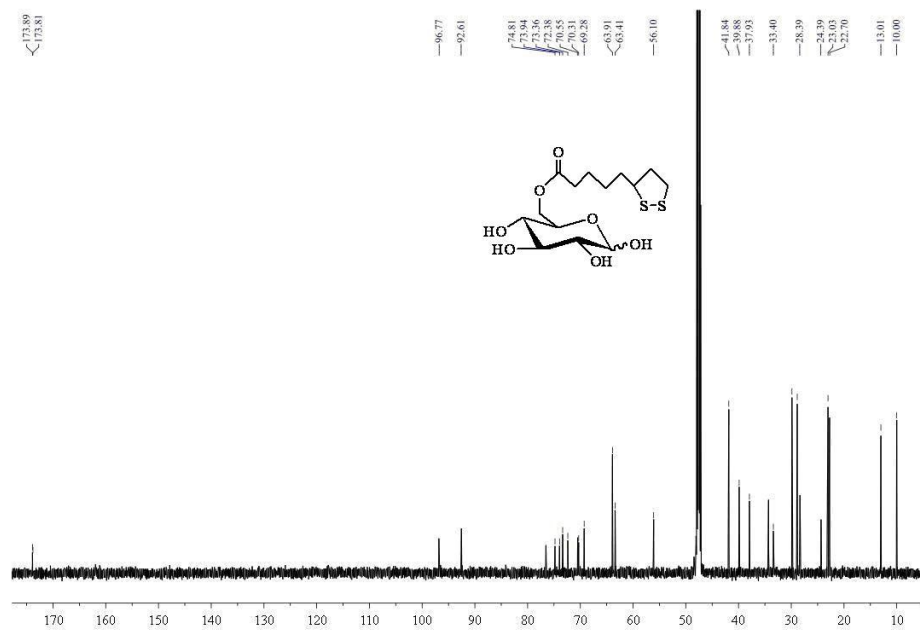


Fig. S2 ^{13}C NMR spectrum of compound 4

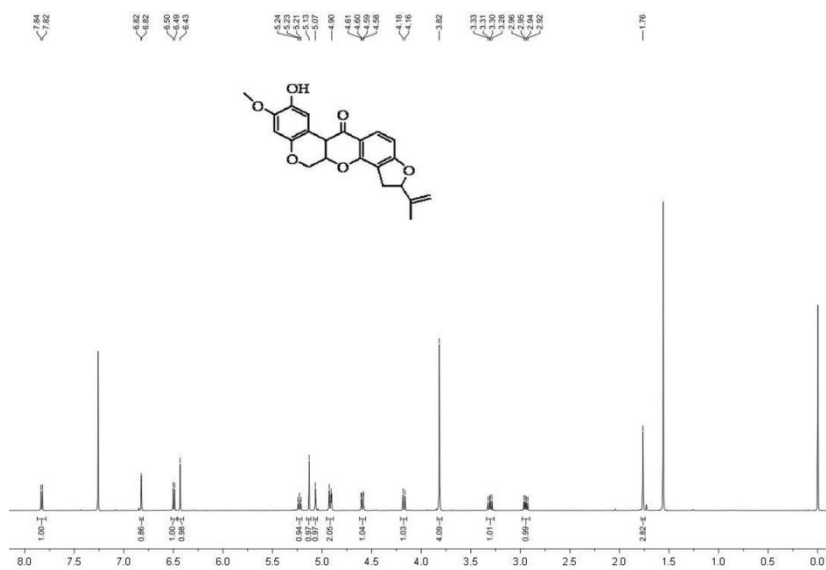


Fig. S3 ^1H NMR spectrum of compound 5

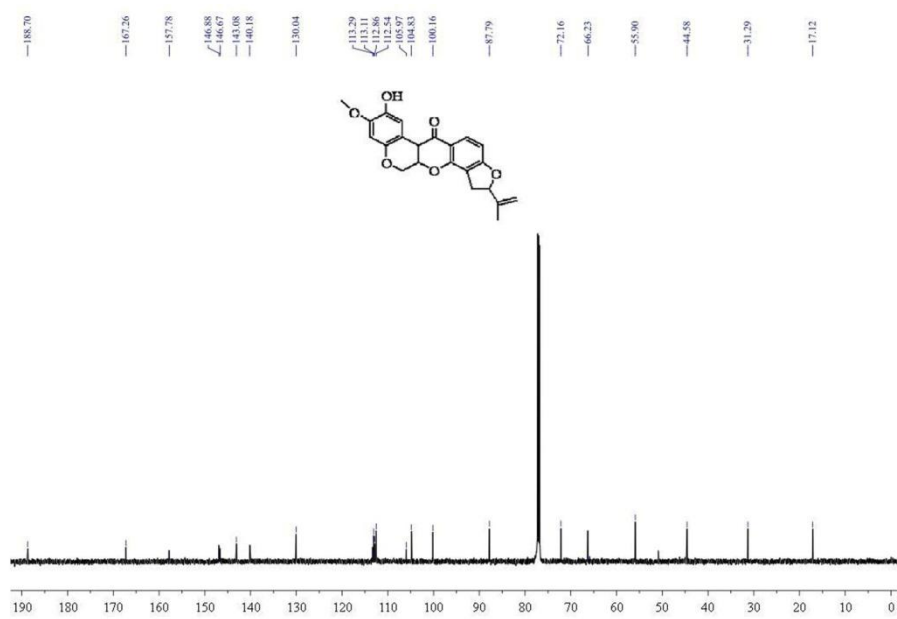


Fig. S4 ^{13}C NMR spectrum of compound 5

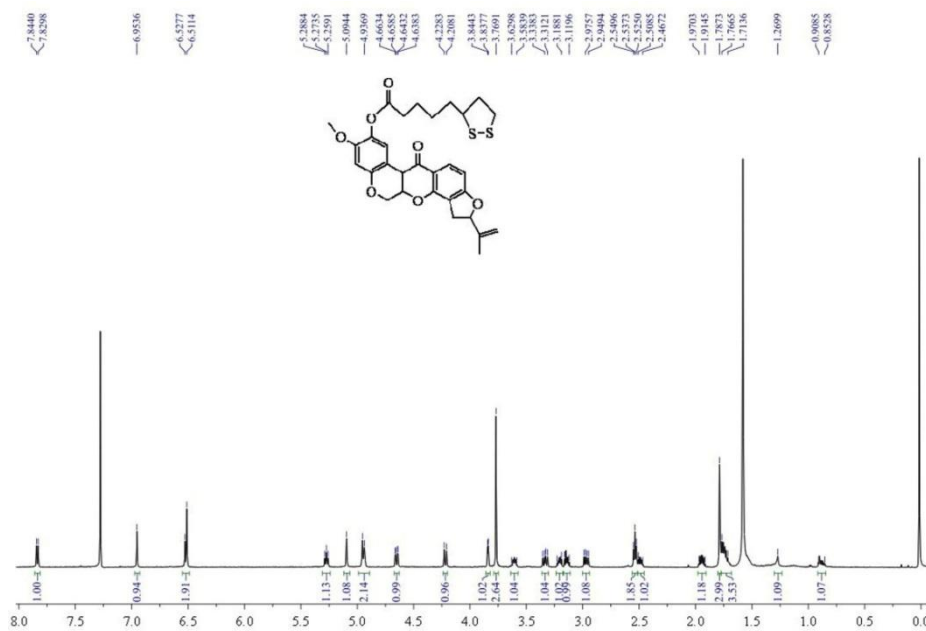


Fig. S5 ^1H NMR spectrum of compound 6

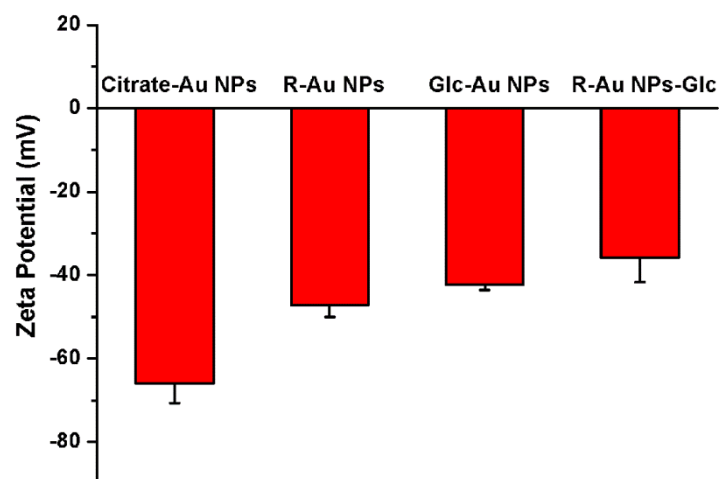


Fig. S6 Zeta potentials of as-prepared Citrate-Au NPs, R-Au NPs, Glc-Au NPs and R-Au NPs-Glc dispersed in aqueous solution.

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