Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supramolecular host-guest interaction of trityl-nitroxide biradicals with cyclodextrins: modulation of spin-spin interaction and redox sensitivity

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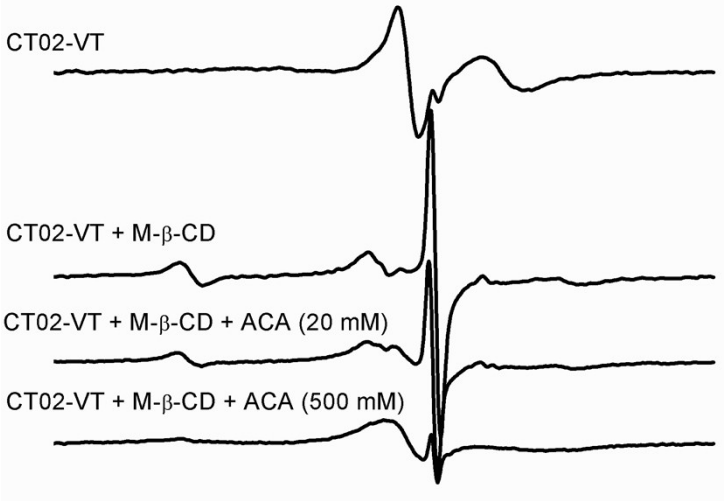

Figure S1. Competitive inclusion of CT02-VT (50 μM) and 1-adamantane carboxylic acid (ACA) with M-β-CD (100 mM) in phosphate buffer (pH 7.4, 20 mM).

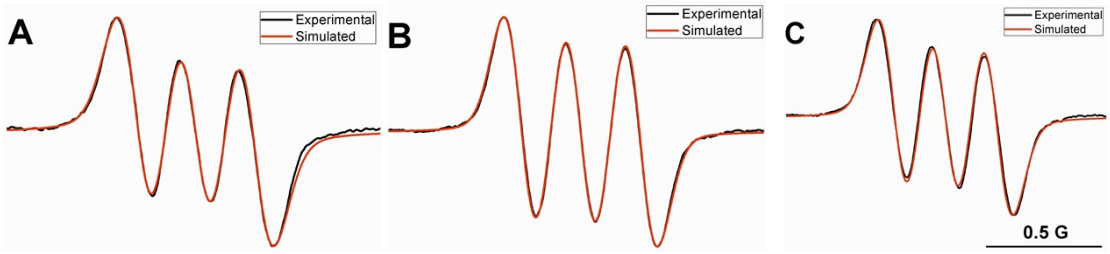

Figure S2. Experimental and simulated EPR spectra of trityl-hydroxylamine monoradicals obtained from the reduction of TN biradicals CT02-GT (A), CT02-AT (B) and CT02-VT (C) by ascorbate. Each TN biradical (50 μM) reacted with ascorbate (200 μM) in PBS (20 mM, pH 7.4). After two and half hours, the solution containing the trityl-hydroxylamine monoradicals was transferred into a gas-permeable Teflon tube (i.d. = 0.8 mm) and sealed at both ends. The sealed sample was placed inside a quartz EPR tube with open ends. Nitrogen gas was allowed to bleed into the EPR tube and after about 4 min EPR spectra were recorded. The following acquisition parameters were used: microwave power, 0.1 mW; modulation frequency, 10 kHz; time constant, 0.01 ms; conversion time, 5.12 ms; modulation amplitude, 0.02 G.

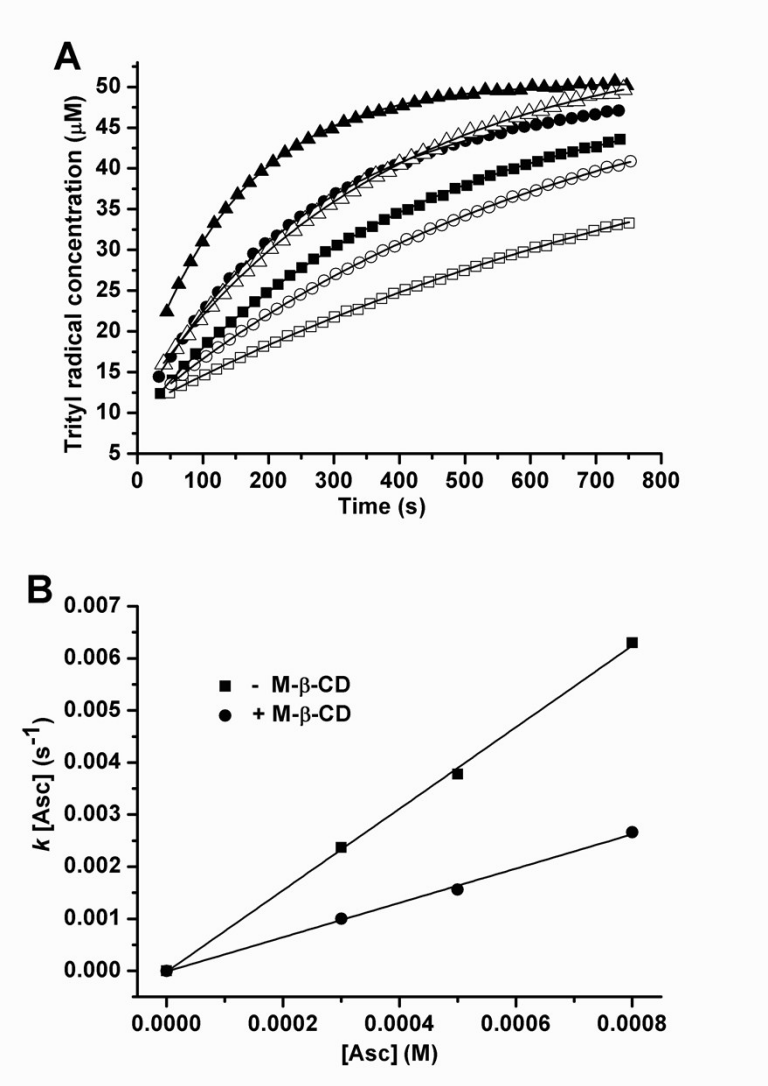

Figure S3. (A) Plot of the concentrations of trityl monoradicals as a function of time which were generated by the reaction of CT02-AT (50 μM) with 300 μM (square), 500 μM (circle) and 800 μM (triangle) of ascorbic acid in the presence (unfilled) or absence (filled) of M-β-CD (50 mM) in phosphate buffer (50 mM, pH 7.4). (B) Plot of *k*[Asc] as a function of the concentrations of ascorbic acid. Values of *k*[Asc] were obtained according to the data shown in Fig. S3 A. Linear regression of kinectic data to yield the second-order rate constants for reduction of CT02-AT by ascorbic acid in the presence (circle) or absence (square) of M-β-CD. Data were shown in Table 2.

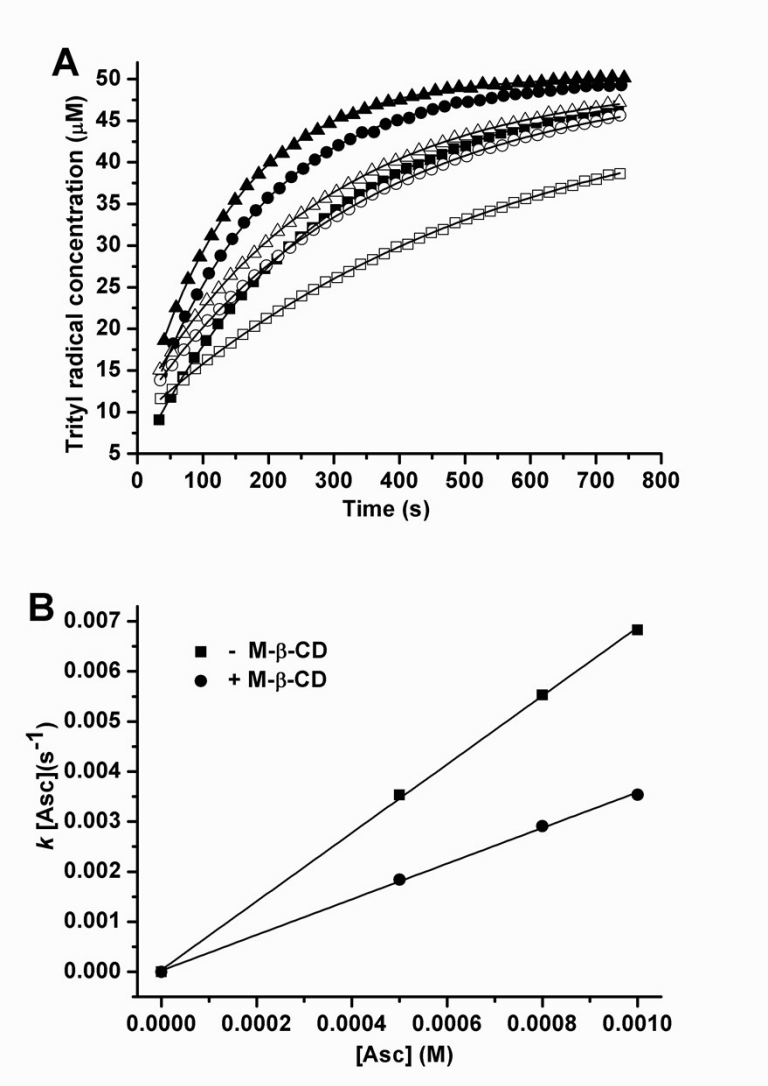

Figure S4. (A) Plot of the concentrations of trityl monoradicals as a function of time which were generated by the reaction of CT02-VT (50 μM) with 500 μM (square), 800 μM (circle) and 1000 μM (triangle) of ascorbic acid in the presence (unfilled) or absence (filled) of M-β-CD (50 mM) in phosphate buffer (50 mM, pH 7.4). (B) Plot of *k*[Asc] as a function of the concentrations of ascorbic acid. Values of *k*[Asc] were obtained according to the data shown in Fig. S4 A. Linear regression of kinectic data to yield the second-order rate constants for reduction of CT02-VT by ascorbic acid in the presence (circle) or absence (square) of M-β-CD. Data were shown in Table 2.