

Supplementary information

Supramolecular nanoarchitectonics of propionylated polyrotaxanes with bulky nitrobenzyl stoppers for light-triggered drug release

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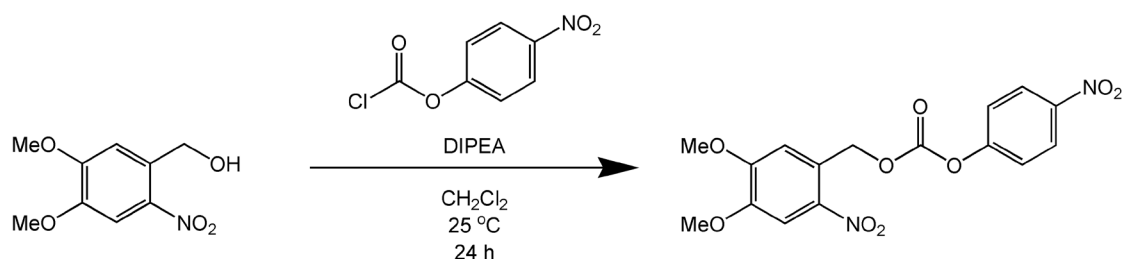
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S1. Instrumentations

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III 400 MHz spectrometer (Bruker BioSpin, Rheinstetten, Germany) at 25.0 °C. Electrospray ionization mass spectrometry (ESI-MS) was performed on a microTOF focus II (Bruker Daltonics, Bremen, Germany). Fourier-transform infrared (FT-IR) spectra were recorded using a Spectrum 100 FT-IR spectrometer (PerkinElmer, Waltham, MA, USA). The powder sample was mixed with KBr, ground in an agate grinding mill, and pressed to obtain transparent KBr pellets.

S2. Synthesis of 4,5-dimethoxy-2-nitrobenzyl 4-nitrophenyl carbonate



4,5-Dimethoxy-2-nitrobenzyl alcohol (1.95 g, 9.15 mmol; Tokyo Chemical Industry, Tokyo, Japan) was dissolved in CH_2Cl_2 (100 mL; Kanto Chemical, Tokyo, Japan), and *N,N*-diisopropylethylamine (DIPEA; 3.11 mL, 18.3 mmol; Tokyo Chemical Industry) and 4-nitrophenyl chloroformate (3.69 g, 18.3 mmol; Tokyo Chemical Industry) were successively added to the solution. The solution was stirred for 24 h at 25 °C. After the reaction, the solution was washed successively with 10 mM HCl (100 mL \times 5), distilled water (100 mL \times 3), and brine (100 mL \times 1). The organic layer was collected and dried over MgSO_4 . The product was purified via column chromatography using toluene/acetone (20:1). The collected product was recrystallized from toluene. The powder was collected by filtration and dried in vacuo to yield 4,5-dimethoxy-2-nitrobenzyl 4-nitrophenyl carbonate (1.82 g, 52.6% yield). ^1H NMR (400 MHz, CDCl_3): δ (ppm) = 3.96 (s, 3H, OMe), 4.00 (s, 3H, OMe), 5.69 (s, 2H, $-\text{CH}_2-$), 7.08 (s, 1H, 3-position in 4,5-dimethoxy-2-nitrobenzyl), 7.39 (d, 2H, 2- and 6-positions in 4-nitrophenyl), 7.75 (s, 1H, 6-position in 4,5-dimethoxy-2-nitrobenzyl), 8.28 (d, 2H, 3- and 5-positions in 4-nitrophenyl). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) = 56.5, 56.6, 67.7, 108.5, 110.7, 121.7, 125.1, 125.4, 140.1, 145.6, 148.9, 152.1, 153.7, 155.4. ESI-MS: m/z calcd. for $\text{C}_{16}\text{H}_{14}\text{N}_2\text{NaO}_9$ $[\text{M}+\text{Na}]^+$ 401.0592, found 401.1582.

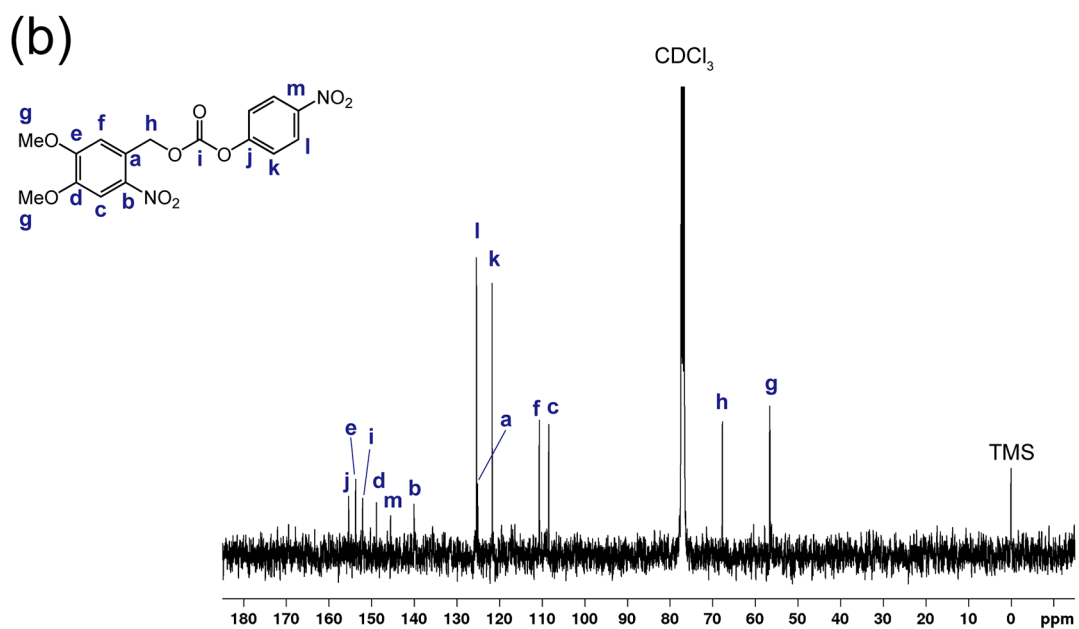
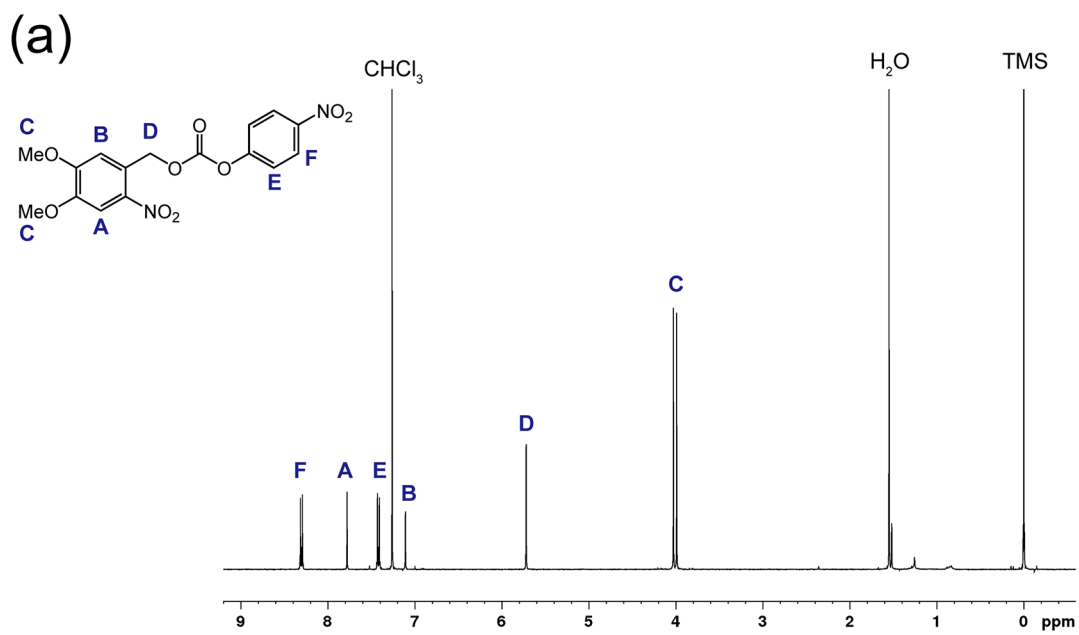
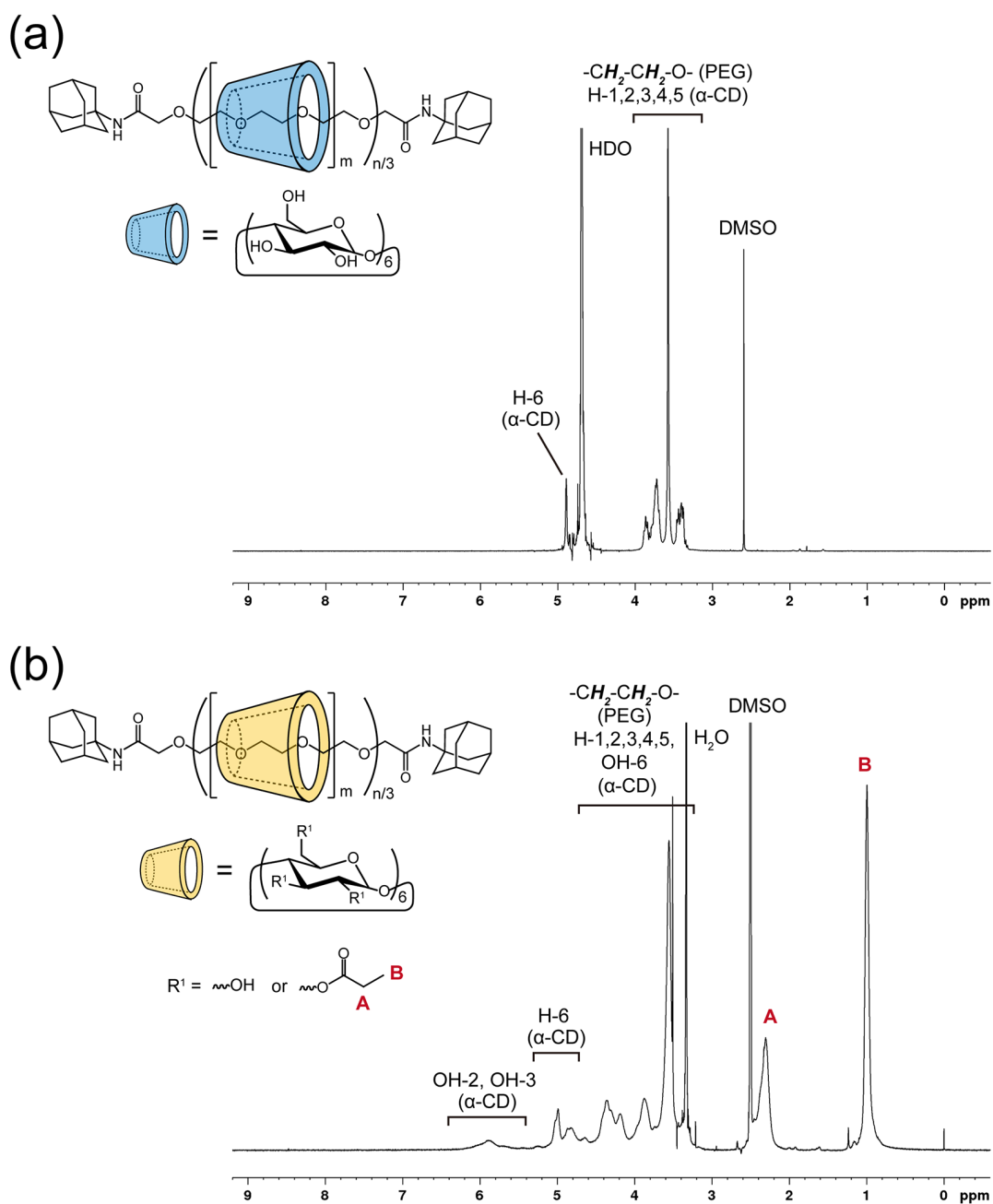


Figure S1. (a) ^1H and (b) ^{13}C NMR spectra of 4,5-dimethoxy-2-nitrobenzyl 4-nitrophenyl carbonate in CDCl₃ at 25 °C.



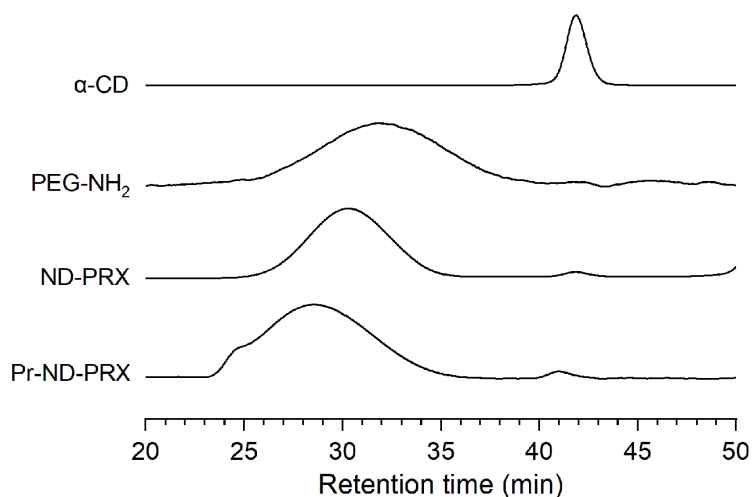


Figure S3. SEC charts of α -CD, PEG-NH₂, ND-PRX, and Pr-ND-PRX eluted with DMSO containing 10 mM LiBr at 60 °C. The peaks were detected with RI.

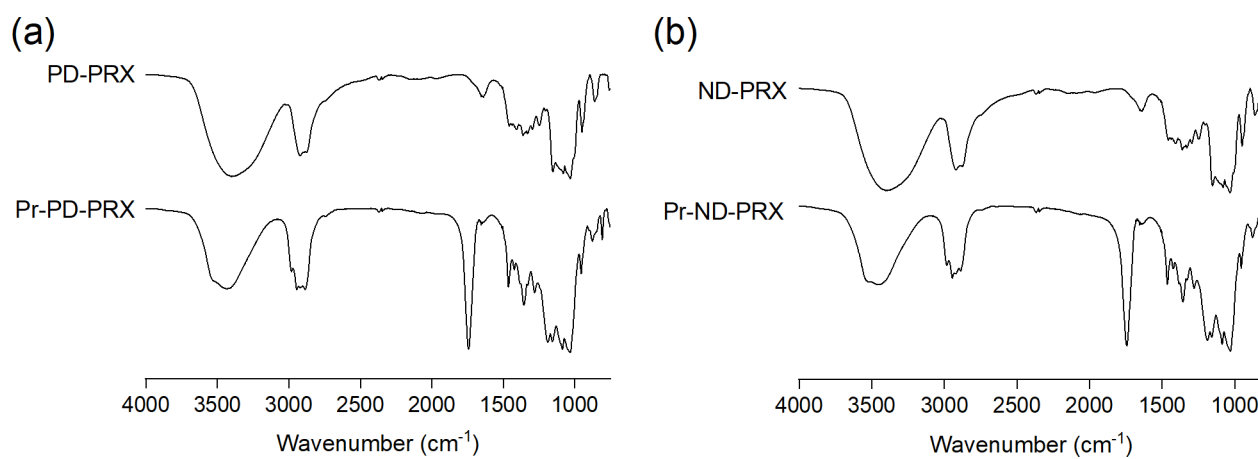


Figure S4. (a) FT-IR spectra of PD-PRX and Pr-PD-PRX. (b) FT-IR spectra of ND-PRX and Pr-ND-PRX.