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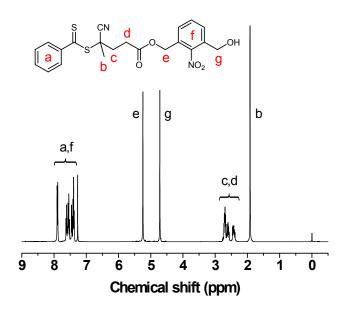
Supporting Information

Facile synthesis of photolabile dendritic-unit-bridged hyperbranched graft copolymers for stimuli-triggered topological transition and controlled release of Nile red

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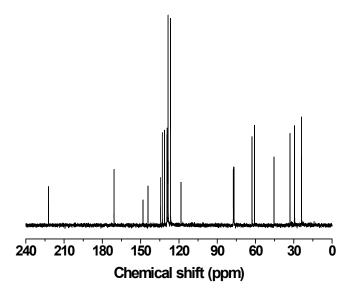
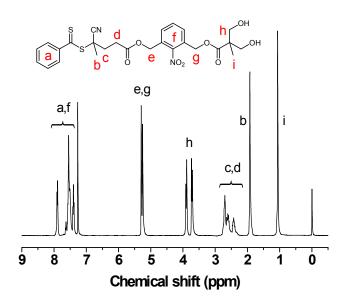


Fig. S1 ¹H (top) and ¹³C (bottom) NMR spectra of HNCP.



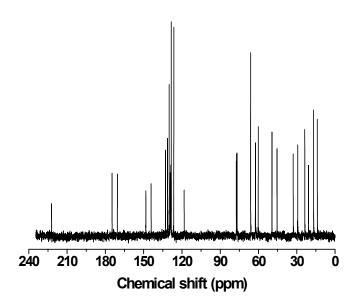


Fig. S2 ¹H (top) and ¹³C (bottom) NMR spectra of DNCP.

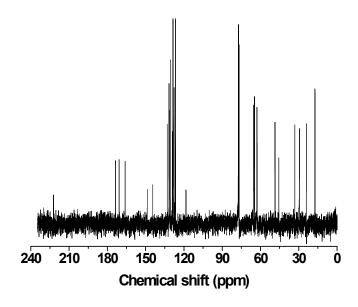


Fig. S3 ¹³C NMR spectrum of ANCP.

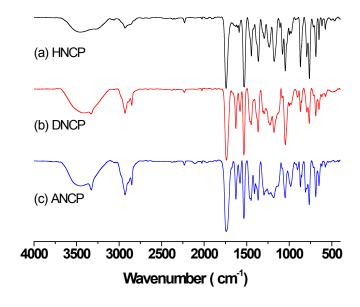


Fig. S4 IR spectra of ANCP and its precursors.

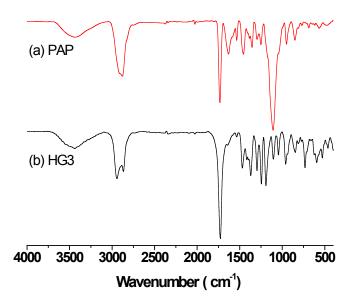


Fig. S5 IR spectra of hyperbranched PAP (a) and PAP-g-PCL (b).

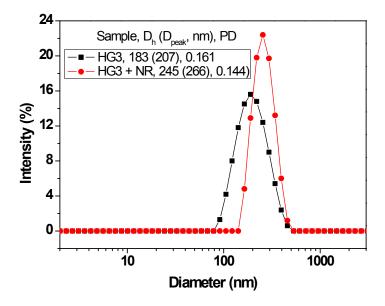


Fig. S6 DLS plots of blank ($c_{polymer} = 0.50 \text{ mg mL}^{-1}$) and NR-loaded ($c_{polymer} = 0.45 \text{ mg mL}^{-1}$) copolymer aggregates formed by HG3 in PBS solution (50 mM, pH 7.4) at 37 °C.

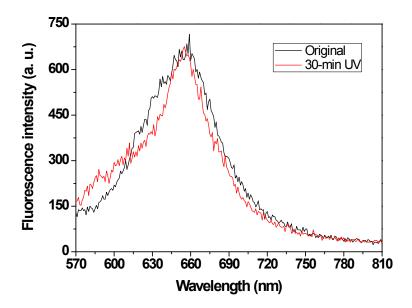


Fig. S7 Fluorescence spectra (λ_{ex} = 550 nm) of NR-bearing saturated aqueous solution before and after 30-min UV irradiation.

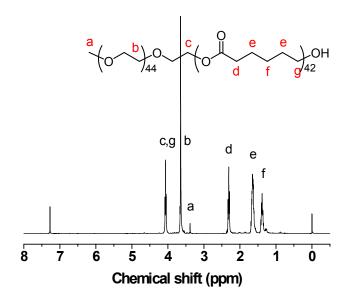
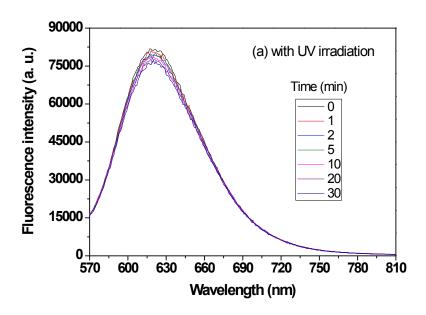


Fig. S8 ¹H NMR spectrum of PEG-*b*-PCL. The copolymer ($M_{n,NMR} = 6800$, PDI = 1.18) was synthesized by CL polymerization initiated with MPEG using Sn(Oct)₂ catalyst in toluene at 90 °C.



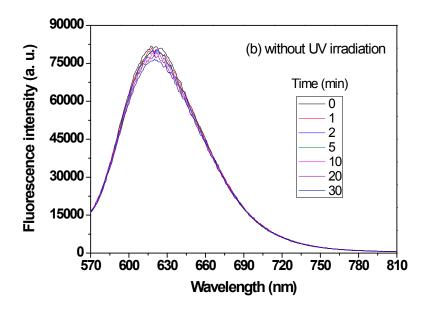


Fig. S9 Influence of time (with (a) or without (b) UV irradiation (365 nm, 10.0 mW cm⁻²)) on fluorescence spectra ($\lambda_{\rm ex} = 550$ nm) of NR-loaded PEG-*b*-PCL aggregates ($c_{\rm polymer} = 0.50$ mg mL⁻¹, DLC = 8.24%) in PBS solution (50 mM, pH 7.4) at 37 °C.

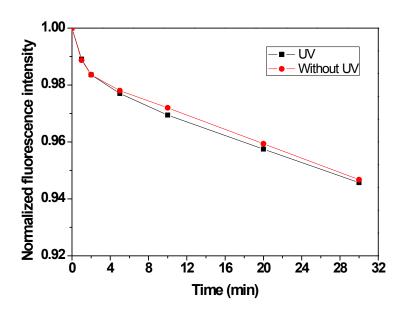
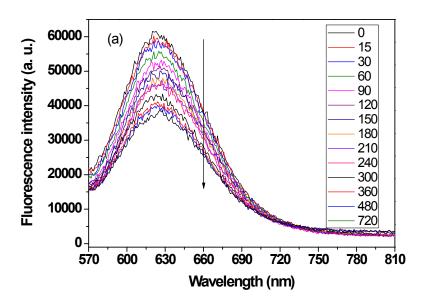
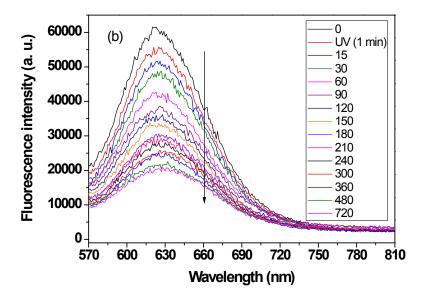


Fig. S10 Influence of UV irradiation time on normalized fluorescence intensity of NR-loaded PEG-b-PCL aggregates ($c_{\text{polymer}} = 0.50 \text{ mg mL}^{-1}$, DLC = 8.24%) in PBS solution (50 mM, pH 7.4) at 37 °C, in which the experimental errors were within ± 0.005 .





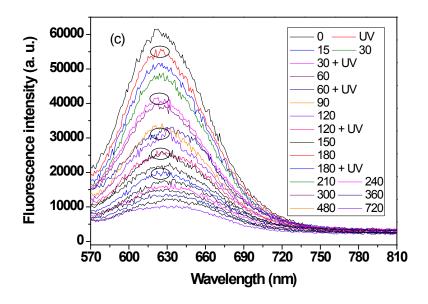


Fig. S11 Evolution of fluorescence spectra of NR-loaded HG3 aggregates (c = 0.45 mg mL⁻¹, $\lambda_{ex} = 550$ nm) in PBS solution (50 mM, pH 7.4) at 37 °C with time (unit: min): (a) without UV irradiation; (b) with 1-min light irradiation at the beginning of release process; (c) with 1-min light irradiation at each particular time of 0, 30, 60, 120 and 180 min (the circles were inserted to denote the fluorescence spectra after UV irradiation).