ELECTRONIC SUPPORTING INFORMATION

Method for Controlling Intracellular Protein Activity Using Photoresponsive Nanoparticles

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Fig. S1. (Color online) Free caspase activities with and without UV irradiation. The activity of free caspase exposed to UV light was measured under the same UV intensity as that used to release nanoparticles inside the cells (results in Fig. 5). The activity of caspase not exposed to UV light was confirmed under the same conditions as those shown in Fig. 4. These data suggest that the activity was sufficiently maintained, despite the reduction after UV light irradiation.

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Fig. S2. Physical properties (particle tracking analysis (PTA) images and concentration) of nanoparticles with encapsulated FITC-Dex. (a) 3-kDa FITC-Dex and (b) 10-kDa FITC-Dex. (i) Nanoparticle size and (ii) nanoparticle surface charge.



 $(a-i) \\ 151 \text{ nm} \\ 3.0 \times 10^9 \text{ nanoparticles/mL}$



(b-i) 143 nm 3.6 × 10⁹ nanoparticles/mL



(a-ii) 4.3 mV 5.6 × 10⁹ nanoparticles/mL



 $\begin{array}{c} (b\text{-}ii)\\ 1.4\ mV\\ 3.8\times10^9\ nanoparticles/mL \end{array}$



144 nm $1.9 \times 10^{10} \text{ nanoparticles/mL}$



 $\begin{array}{c} (\text{c-ii}) \\ 8.3 \text{ mV} \\ 2.8 \times 10^{10} \text{ nanoparticles/mL} \end{array}$

Fig. S3. Physical properties (particle tracking analysis (PTA) images and concentration) of nanoparticles with encapsulated caspase 3 at different concentrations: (a) 0.25μ unit, (b) 2.5μ unit, and (c) 25μ unit. (i) Nanoparticle size and (ii) nanoparticle surface charge.



Fig. S4. (Color online) (a) Illustration of photocleavable nanoparticle showing encapsulation and release of various proteins in cell. (b) Effect of FITC-Dex molecular weight on amounts of encapsulated and released molecules. FITC-Dex (1 mg) was encapsulated in each nanoparticle. After washing, the amount of FITC-Dex encapsulated in each nanoparticle was determined from its fluorescence intensity ($\lambda_{ex} = 494$ nm, $\lambda_{em} = 518$ nm). The nanoparticles were then UV-irradiated to release the FITC-Dex (n = 3).



Fig. S5. Transmission electron microscopy images of nanoparticles with encapsulated caspase 3 (2.5 μ unit). (a) Non-UV-irradiated and (b) UV-irradiated nanoparticles are 70–90 nm and 30–50 nm in size, respectively. These data suggest that the nanoparticles shrank under vacuum and retained their shapes without complete decay after UV irradiation. Scale bars: 100 nm.









 $Methyl \text{-}\beta\text{-}cyclodextrin$



Amiloride



Control



Fig. S7. (Color online) Separate fluorescence ($l_{ex} = 494$ nm and $l_{em} = 518$ nm) and bright-field images of cells with nanoparticles and three endocytosis inhibitors. The images are combined in Fig. 3.

Table S	1
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Physical properties of other nanoparticles with enzymes determined by ZetaView.

	Amount (µunit)	Nanoparticle size (nm)	ζ (mV)
Elastase	80	110	8.7
	800	116	0.9
	8000	123	2.7
Chymotrypsin —	800	101	2.7
	8000	132	0.03