

## **Supporting Information**

### **Trigger-responsive, fast-degradable poly( $\beta$ -amino ester)s for enhanced DNA unpackaging and reduced toxicity**

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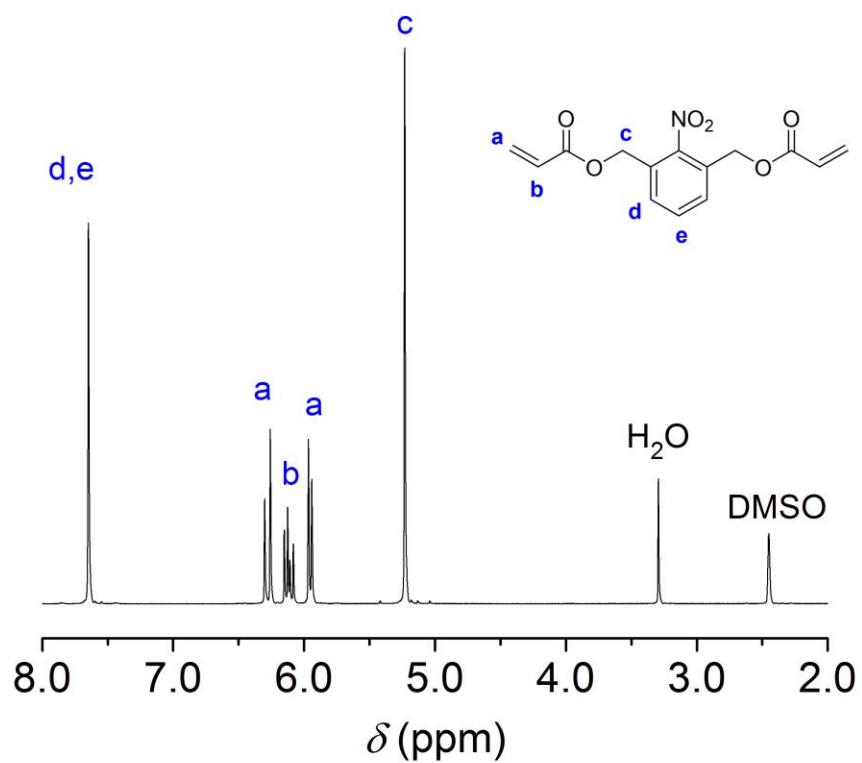
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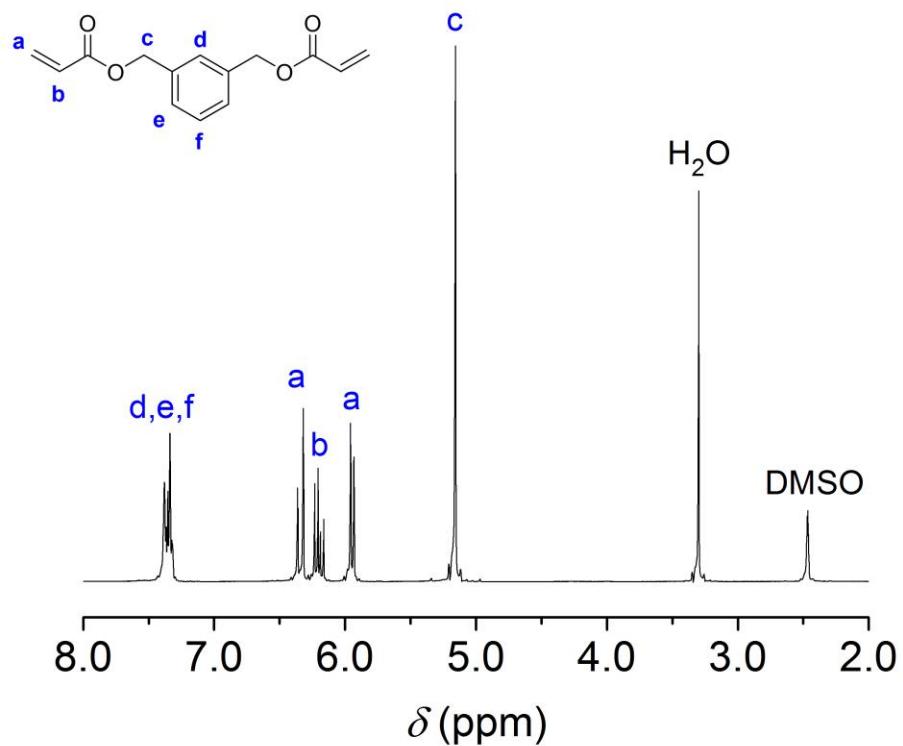
**Table S1. Preparation of PBAEs.**

Polymer	Solvent	Amine/diacrylate molar ratio	$M_n$ (kDa)	PDI ( $M_w/M_n$ )
P1-2800	DCM	1.3	2.8	1.87
P1-5100	DCM	1.2	5.1	2.32
P1-8900	DCM	1.1	8.9	2.31
P1-13700	DCM	1.05	13.7	1.91
P2-3000	DCM	1.3	3	2.23
P2-5200	DCM	1.2	5.2	2.41
P2-9200	DCM	1.1	9.2	2.11
P2-13400	DCM	1.05	13.4	2.61
P3-3600	DCM	1.3	3.6	1.67
P3-5500	DCM	1.2	5.5	1.85
P3-9300	DCM	1.05	9.3	1.86
P4-2700	DMSO	1.3	2.7	2.53
P4-6300	DMSO	1.2	6.3	2.66
P4-8800	DMSO	1.1	8.8	2.17
P5-3200	DMSO	1.3	3.2	2.09
P5-6100	DMSO	1.2	6.1	1.89
P5-9600	DMSO	1.1	9.6	2.63
P6-3000	DCM	1.3	3	1.77
P6-5800	DCM	1.2	5.8	1.99
P6-8300	DCM	1.1	8.3	2.21
P7-3000	DCM	1.3	3	2.88
P7-5300	DCM	1.2	5.3	2.42
P7-8200	DCM	1.05	8.2	2.49
P8-3200	DCM	1.3	3.2	2.47
P8-5500	DCM	1.2	5.5	2.44
P8-8000	DCM	1.1	8	2.14
P9-3100	DCM	1.3	3.1	2.66
P9-6900	DCM	1.2	6.9	2.47
P9-9200	DCM	1.1	9.2	2.19
P10-3100	DCM	1.3	3.1	2.11
P10-5900	DCM	1.2	5.9	1.76
P10-8500	DCM	1.1	8.5	1.98
P11-2800	DCM	1.3	2.8	2.64
P11-5800	DCM	1.2	5.8	2.39
P11-8900	DCM	1.1	8.9	2.63
P12-3400	DCM	1.3	3.4	1.92
P12-6200	DCM	1.2	6.2	2.78

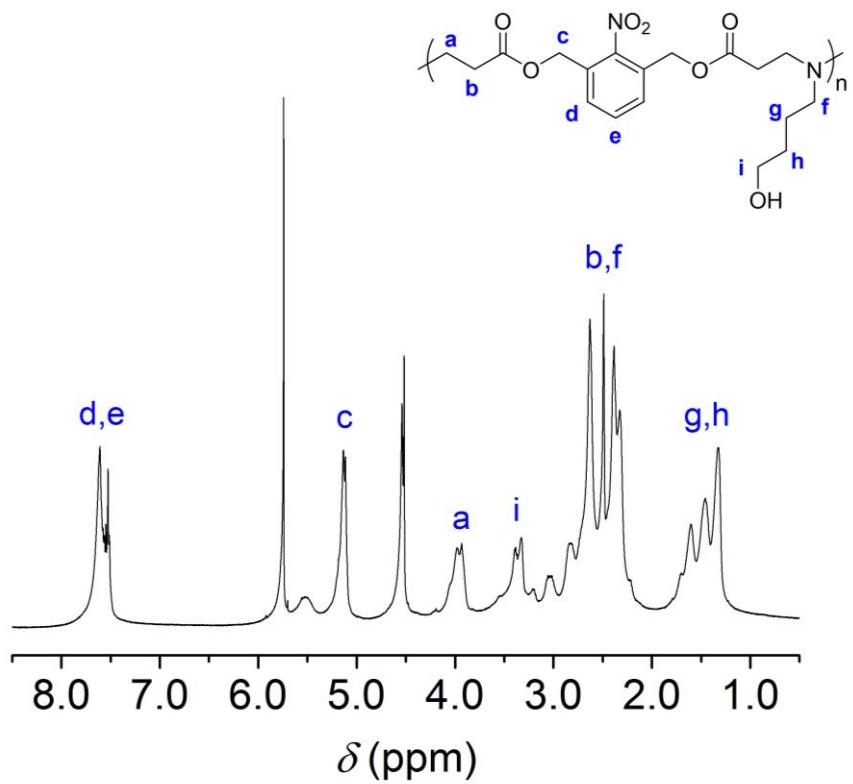
P12-8600	DCM	1.1	8.6	2.77
P13-3500	DCM	1.25	3.5	2.11
P13-6700	DCM	1.2	6.7	2.19
P13-9900	DCM	1.05	9.9	2.48
P14-3000	DCM	1.3	3	2.12
P14-5300	DCM	1.2	5.3	2.32
P14-9000	DCM	1.1	9	2.5
P15-3300	DCM	1.3	3.3	2.71
P15-5300	DCM	1.2	5.3	2.46
P15-9300	DCM	1.1	9.3	2.1
P16-3400	DCM	1.3	3.4	1.99
P16-5500	DCM	1.2	5.5	2.04
P16-9800	DCM	1.1	9.8	1.8
P17-11500	DCM	1.08	11.5	2.68



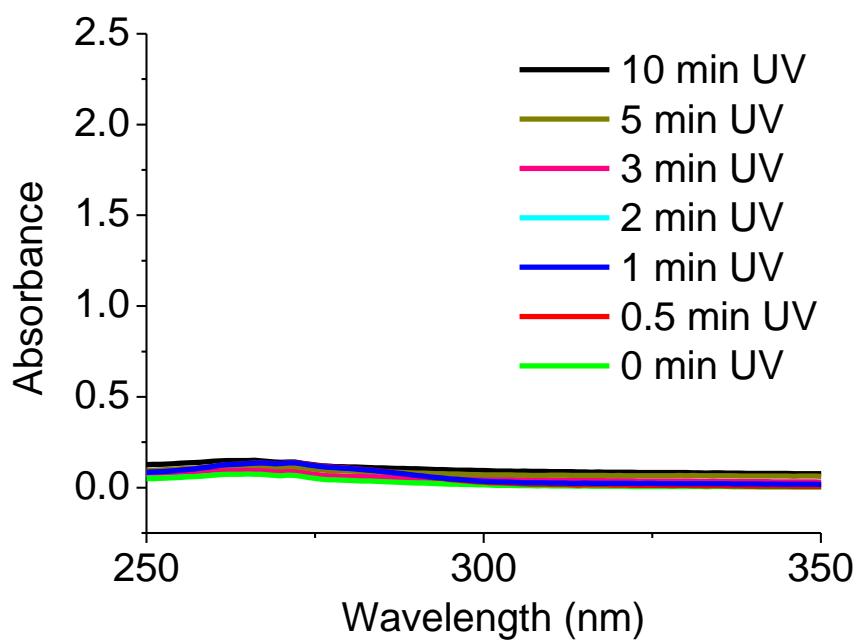
**Fig. S1.**  $^1\text{H}$  NMR spectrum of (2-nitro-1,3-phenylene)bis(methylene) diacrylate in  $\text{DMSO}-d_6$ .



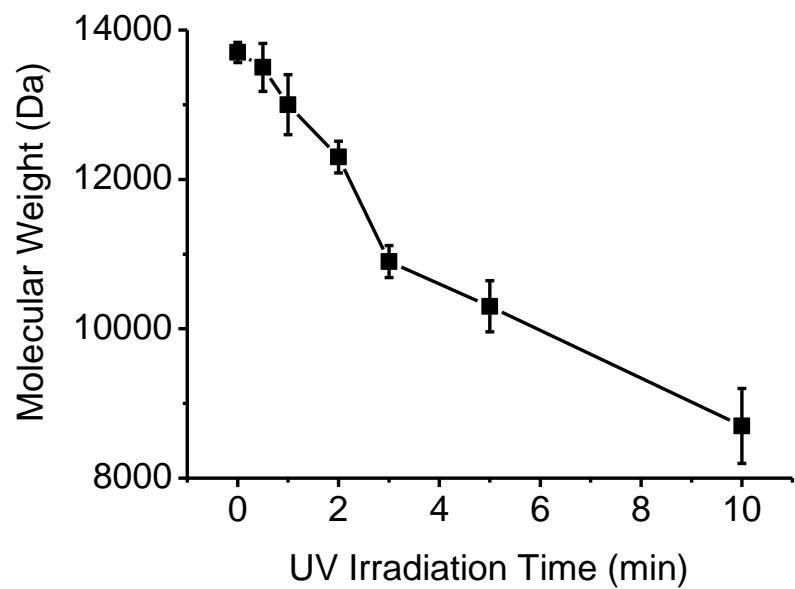
**Fig. S2.**  $^1\text{H}$  NMR spectrum of (1,3-phenylene)bis(methylene) diacrylate in  $\text{DMSO}-d_6$ .



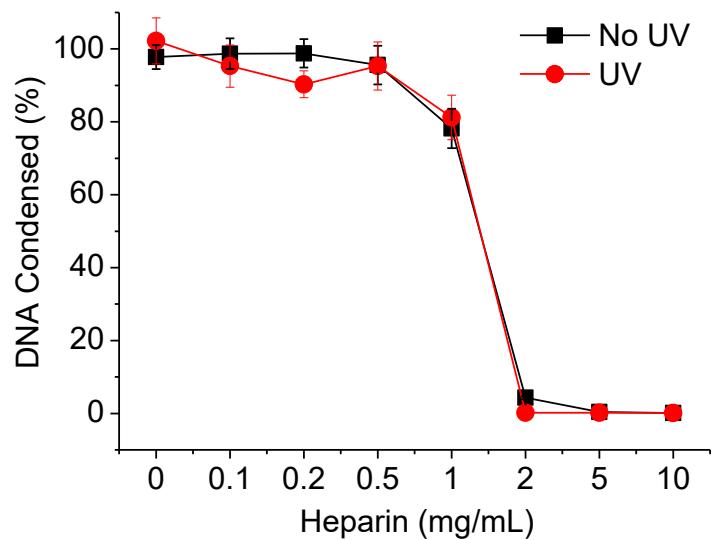
**Fig. S3.**  $^1\text{H}$  NMR spectrum of P1-13700 in  $\text{DMSO}-d_6$ .



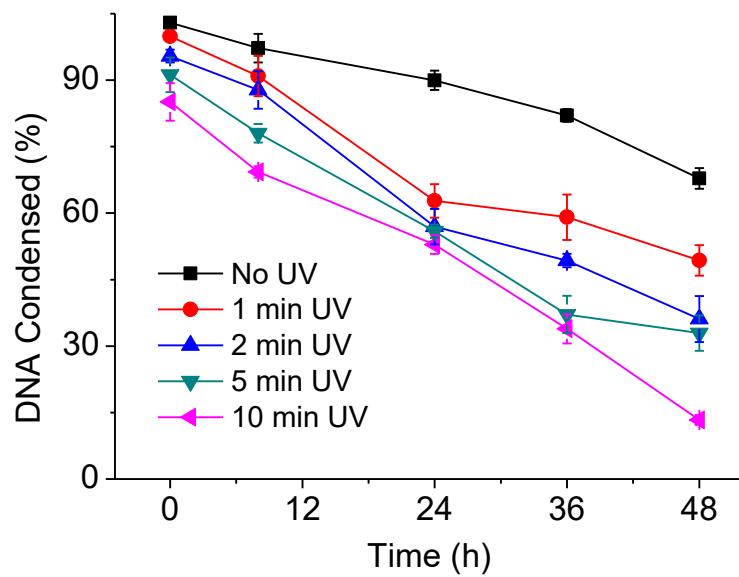
**Fig. S4.** UV-Vis spectrum of P17-11500 after UV irradiation ( $\lambda = 365$  nm,  $20$  mW/cm $^2$ ) for different time.



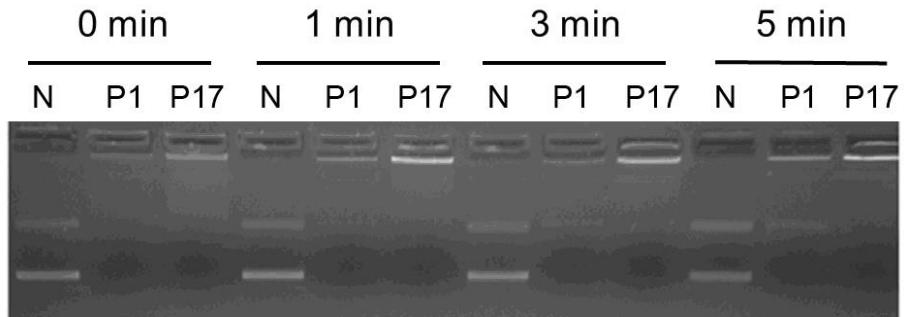
**Fig. S5.** Molecular weight change of P1-13700 upon UV irradiation for different time ( $n = 3$ ).



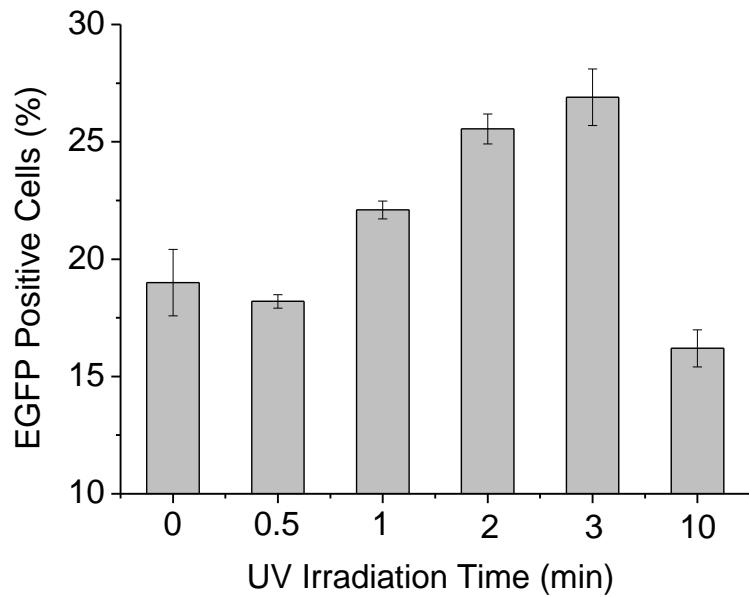
**Fig. S6.** DNA release from UV-irradiated and non-irradiated P17-11500/DNA polyplexes in the presence of heparin at various concentrations ( $n = 3$ ).



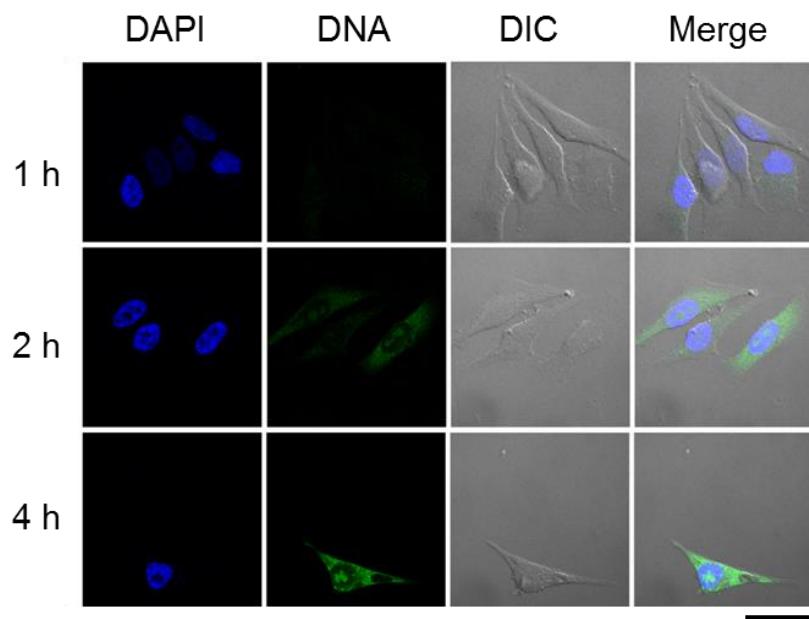
**Fig. S7.** DNA release from P1-13700/DNA polyplexes (weight ratio of 50) irradiated with UV light for different time ( $\lambda = 365$  nm,  $20\text{ mW/cm}^2$ ) following incubation up to 48 h ( $n = 3$ ).



**Fig. S8.** DNA release from polyplexes (polymer/DNA weight ratio of 50) irradiated with UV light ( $\lambda = 365$  nm,  $20$  mW/cm $^2$ ) for different time as demonstrated by the gel retardation assay. N represents naked DNA, P1 represents P1-13700, and P17 represents P17-11500.



**Fig. S9.** Effect of UV irradiation time ( $\lambda = 365$  nm,  $20$  mW/cm $^2$ ) on the transfection efficiencies of P5-6100/DNA polyplexes (weight ratio of 50, n = 3).



**Fig. S10.** CLSM images showing the cellular internalization and distribution of P1-13700/YOYO-1-DNA polyplexes (weight ratio of 50) in HeLa cells following incubation at 37 °C for different time. Cell nuclei were stained with DAPI. Bar = 50 μm.