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# Stabilized Vesicles Consisting of Small Amphiphiles for Stepwise Photorelease via UV Light

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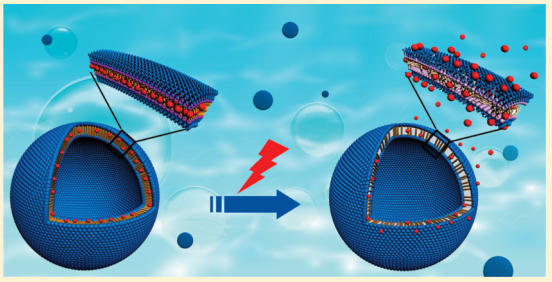
Supporting Information

**ABSTRACT:** A small amphiphile consisting of hydrophilic tetraethylene glycol monoacrylate and hydrophobic alkyl chain which were connected by an *o*-nitrobenzyl unit, a photolabile group, was designed and synthesized. The critical aggregate concentration of the synthesized amphiphile was determined to be about $3 \times 10^{-5}$ M by the fluorescence probe technique. Nanosized vesicles were prepared and stabilized by in-situ radical polymerization without altering the morphology. The polymeric vesicle was highly stable which retained vesicular shape under dilution or UV irradiation. Hydrophobic guests can be encapsulated within the vesicle membrane and released out of the vesicle by UV stimulus through splitting the amphiphilic structure of the amphiphile. Distinguished dose-controlled photorelease of the polymeric vesicle is achieved due to the maintenance of the vesicular shape integrity which makes the guest release depend on the cleavage amount of amphiphilic structure during UV irradiation. This study provides a promising strategy to develop stable drug delivery systems for sustained and phototriggered release.



## INTRODUCTION

Over the past several decades, numerous nanosized self-assembled systems have been developed in drug delivery,[1,2] such as micelles, vesicles, capsules, nanotubes, and nanoparticles which can carry drugs, prolong circulation time of drugs, and reduce systemic toxicity. Compared to the conventional drug carriers, the drug delivery systems capable of targeting and triggered release have received more attention due to their improved therapeutic activity. Thus far, various kinds of stimuli, such as pH,[3−5] temperature,[6−8] redox,[9−11] light,[12−15] gamma ray,[16] and enzyme,[17,18] have been explored for triggered release in drug delivery systems. Stimuli-responsive assemblies commonly undergo rapid dissociation or morphology change as long as the stimuli are applied, resulting in almost complete release of their payload suddenly which is called burst or rapid release.[19,20] Therefore, there is a growing challenge to the spatially and temporally controlled release in a sustained or dosage manner.[14,21]

Organic approaches toward stimuli-responsive drug carriers usually involve the assemblies of amphiphilic molecules, such as polymers, dendrimers, peptides, and surfactants. In particular, small amphiphiles (surfactant-type) have attracted widespread attention due to their easy synthesis, biocompatibility, and functional versatility.[20−22] However, a disadvantage encountered in the application of surfactant assemblies is the relatively low thermodynamic stability which leads to premature drug leakage. One of the practical routes to overcome this drawback is the utilization of polymerizable surfactants, and great efforts have been being made to the development of stable surfactant drug carriers.[22−24]

Herein, we describe a rational design of stable nanoassembly formed by photoresponsive small-molecule amphiphiles capable of highly controlled release. The prototype molecule **1** is composed of a hydrophobic alkyl chain and a hydrophilic tetraethylene glycol monoacrylate segment, which are connected by a photocleavable *o*-nitrobenzyl group (Scheme 1). The assembly behavior of the amphiphilic molecule was studied by the fluorescence probe technique, dynamic light scattering (DLS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The molecule **1** formed vesicular assemblies in water, and the vesicle was stabilized by polymerizing the terminal acrylate group. The encapsulation and phototriggered release properties of the stabilized vesicle were investigated by using a hydrophobic dye, Nile Red (NR), as a model drug. Experimental data demonstrated that the highly dose-controlled release was achieved by using the stabilized vesicle with UV irradiation.

## EXPERIMENTAL SECTION

**Materials.** All chemicals were purchased from Alfa Aesar or Aldrich or TCI and used without further purification, unless otherwise stated. Milli-Q water (18.2 MΩ·cm) was used in aqueous experiments. $CH_2Cl_2$ was distilled from $CaH_2$, and THF was purified by distillation from sodium with benzophenone.

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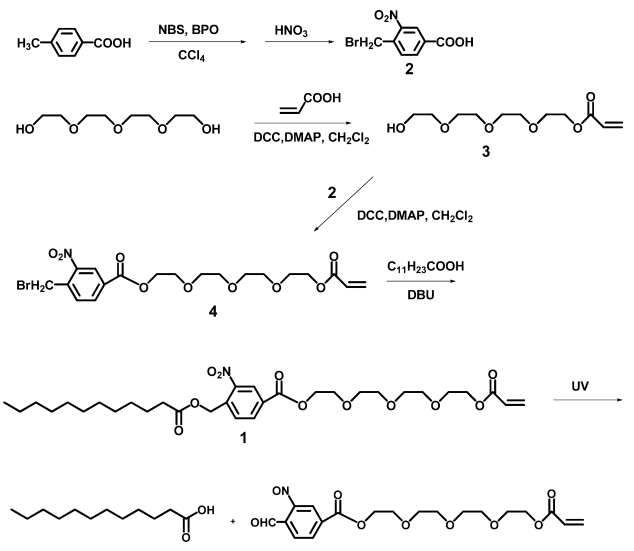
**Scheme 1. Synthetic Route and Photolysis of Photoresponsive Amphiphile 1**




**Instruments.** IR spectra were recorded on a Varian Excalibur 3100 spectrometer. $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were performed on a Bruker Avance Π-400 spectrometer. ESI mass spectra were obtained from a Waters LCT Premier XE apparatus. UV/vis absorption and fluorescence emission spectra were run on a Shimadzu UV-1601PC spectrometer and a Hitachi F-4500 spectrometer, respectively. Dynamic light scattering measurements were performed using a Malvern Zetasizer 3000HS. The turbidity measurement was carried out on a Shimadzu UV-1601PC spectrometer. The SEM images were obtained from a Hitachi S-4300 scanning electron microscope operated at 10 kV. The TEM images were recorded by a JEM200CX or a FEI TECNAI F20 transmission electron microscope performed at 200 kV. Photolysis and photorelease experiments were carried out by using a mercury lamp equipped with a long-pass filter with cutoff wavelength at 315 nm, and the light intensity before the sample vessel was ca. 12 mW/cm$^2$.

**Synthesis of Compound 2.** 3-Nitro-4-(bromomethyl)benzoic acid was prepared according to the literature[25] and obtained as light yellow needles: mp 129 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) 10.8 (s, 1H), 8.6 (d, 1H), 8.2 (d, 1H), 7.8 (d, 1H), 4.9 (s, 2H).

**Synthesis of Compound 3.** *N*,*N*′-Dicyclohexylcarbodiimide (DCC, 4.5 g, 22 mmol, dissolved in 20 mL of distilled $CH_2Cl_2$) was slowly added to 30 mL of $CH_2Cl_2$ solution of tetraethylene glycol (5.9 g, 30 mmol), acrylic acid (1.0 g, 13.9 mmol), and a catalytic amount of 4-(dimethylamino)pyridine (DMAP) under vigorous stirring at 0 °C. The reaction mixture was stirred for 1 h in an ice bath and then brought to room temperature over 24 h. After that, the reaction mixture was filtered, and the solvent was removed in a rotary evaporator. The crude product was purified by silica gel column chromatography eluting with a mixture of ethyl acetate:methanol (50:1 v/v) to yield 2.1 g (51%) of colorless oil. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 6.44 (d, 1H), 6.18 (dd, 1H), 5.84 (d, 1H), 4.41 (t, 2H), 4.13 (t, 2H), 3.74–3.58 (m, 12H), 2.4 (s, 1H). IR (KBr pellet, cm$^{-1}$): 3438.2, 2877.3, 2360.1, 1723.9, 1636.1, 1104.0. HRMS (ESI): calcd $[M + Na]^+$ $m/z$ 271.1158; found 271.1147.

**Synthesis of Compound 4.** DCC (0.82 g, 4 mmol, dissolved in 5 mL of distilled $CH_2Cl_2$) was slowly added dropwise to 20 mL of $CH_2Cl_2$ solution of 3-nitro-4-(bromomethyl)benzoic acid (1.04 g, 4 mmol), compound **3** (1.0 g, 4 mmol), and DMAP (0.043 g, 0.35 mmol) at 0 °C. The mixture was stirred for 1 h at 0 °C and then reacted at room temperature over 24 h. The product was collected after filtration. The solvent was removed in a rotary evaporator, and the crude product was purified by silica gel column chromatography eluting with a mixture of petroleum ether:ethyl acetate (3:2 v/v) to yield 1.76 g (90%) as colorless oil. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm), 8.66 (d, 1H), 8.26 (m, 1H), 7.68 (d, 1H), 6.43 (d, 1H), 6.17 (dd, 1H), 5.83 (d, 1H), 4.84 (s, 2H), 4.52 (t, 2H), 4.29 (t, 2H), 3.85–3.65 (m, 12H). IR (KBr pellet, cm$^{-1}$): 2917.5, 2360.5, 1725.9, 1621.1, 1538.0, 1265.6. HRMS(ESI): calcd $[M + Na]^+$ $m/z$ 512.0532; found 512.0526.

**Synthesis of Amphiphile 1.** DBU (0.76 g, 5 mmol, dissolved in 5 mL of ethyl acetate) was added to 15 mL of ethyl acetate solution of dodecanoic acid (1.0 g, 5 mmol) and compound **3** (2.45 g, 5 mmol) over 10 min. The reaction mixture was stirred at 50 °C for 1 h in a nitrogen atmosphere. The resulting solution was poured into water and extracted with $CH_2Cl_2$. The organic layer was dried over anhydrous magnesium sulfate. The solvent was removed in a rotary evaporator, and the crude product was purified by silica gel column chromatography eluting with a mixture of petroleum ether:ethyl acetate (2:1 v/v) to yield 2.2 g (72%) **1** as light yellow oil. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm), 8.73 (d, 1H), 8.31 (m, 1H), 7.69 (d, 1H), 6.43 (d, 1H), 6.15 (dd, 1H), 5.84 (d, 1H), 5.55 (s, 2H), 4.54 (t, 2H), 4.30 (t, 2H), 3.86–3.66 (m, 12H), 2.43 (t, 2H), 1.68 (m, 2H), 1.2 (m, 16H), 0.9 (t, 3H). IR (KBr pellet, cm$^{-1}$): 2924.5, 2360.6, 1728.3, 1622.7, 1538.7, 1275.6. HRMS (ESI): calcd $[M + Na]^+$ $m/z$ 632.3047, found 632.3048.

**Determination of CAC by Fluorescent Probe.** A certain amount of stock solution of Nile Red in $CH_2Cl_2$ was added in vials, and the solvent was removed by a $N_2$ stream. A series of solutions of amphiphile **1** with different concentrations were added to the vials and sonicated for 3 h. The excess Nile Red was filtered, and then the solution was examined with fluorescence spectrometer.

**Preparation of Vesicles.** 0.4 mL of amphiphile **1** chloroform solution ($10^{-2}$ M) was added to a test tube and dried in vacuum. 40 mL of water was added to the test tube and sonicated at 55 °C for 1 h. Then vesicles were formed, and the solution was stored at room temperature overnight for test.

**Polymerization of Vesicles.** An appropriate amount of stock aqueous solution of 2,2′-azobis(2-amidinopropane hydrochloride) (AAPH) was added to the vesicle sample giving an initiator/monomer mole ratio of 0.02. The vesicle solution was shaken vigorously and flushed with nitrogen for 1 h to ensure the initiator distribution uniformly. Polymerization was carried out at 60 °C for 40 h under a nitrogen atmosphere. The solution was cooled down to room temperature and ready for next experiments.

**Encapsulation of Nile Red in Vesicles.** The excess amount of Nile Red $CH_2Cl_2$ solution (0.6 mg/mL) was injected to the aqueous solution of vesicles. The mixture was sonicated for 10 min at room temperature. The organic solvent and the precipitated NR were removed by evaporation and filtration, respectively.

**Transmittance Experiment.** The solution of vesicle sample was stored in a quartz cuvette and irradiated for different times with a medium–high mercury lamp. The optical transmittances at 500 nm were recorded on a Shimadzu UV-1601PC spectrometer after different UV irradiation times.

## RESULTS AND DISCUSSION

The amphiphilic molecule **1** was synthesized through several simple reactions, such as esterification, bromination, and nucleophilic substitution, involving 4-methylbenzoic acid, tetraethylene glycol, and lauric acid which are common stuff in daily chemical industry. The *o*-nitrobenzyl group was chosen as the photocleavable unit, owing to its capabilities of controlled cleavage as a photolabile linker for solid phase synthesis[26] and caged compounds for biological applications.[27] Upon UV irradiation, the intramolecular rearrangement of *o*-nitrobenzyl leads to a cleavage of amphiphile **1** (Scheme 1).

The assembly behavior of amphiphile **1** was investigated in water by using Nile Red, a hydrophobic fluorescence dye used for probing polarity or effective dielectric constant of microenvironments.[31,32] The fluorescence emission of NR is very low in water due to the polar environment and its poor solubility. Once the Nile Red molecule is sequestered within a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hydrophobic environment, such as micelles or the membrane of vesicles, its fluorescence intensity increases dramatically and experiences a slight hypsochromic shift. The fluorescence spectra of Nile Red ($\lambda_{ex}$ = 560 nm) in aqueous solution of amphiphile **1** of different concentrations are illustrated in Figure 1. A plot of the fluorescence intensity at 625 nm versus

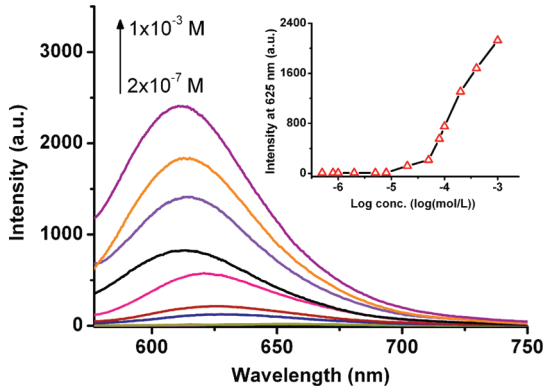


**Figure 1.** Fluorescence spectra of Nile Red ($\lambda_{ex}$ = 560 nm) in aqueous solutions with amphiphile **1** of different concentrations. Inset shows the emission intensity at 625 nm versus the logarithm of concentration of amphiphile **1**.

the logarithm of concentrations of amphiphile **1** shows a nonlinear relationship and the abrupt increase in emission at a certain concentration indicates the formation of aggregates. The critical aggregate concentration (CAC) was determined to be $3 \times 10^{-5}$ M from the extrapolated intersection of two linear regions of the plot. The dynamic light scattering result further confirmed that amphiphile **1** formed aggregates in water with an average hydrodynamic diameter ($D_h$) of ca. 258 nm (Figure S1a). SEM and TEM were also used to characterize the morphology of the aggregates derived from amphiphile **1**. As shown in Figure 2, the microscopic images reveal that the

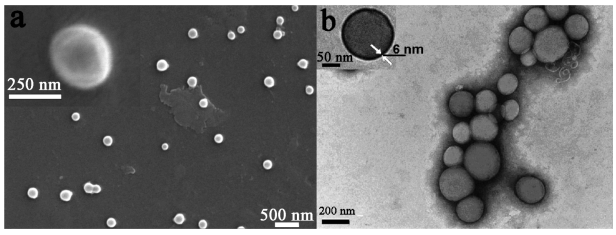


**Figure 2.** (a) SEM and (b) TEM images of the vesicles formed by amphiphile **1** in aqueous solution. Insets show the magnified photographs of the vesicle.

amphiphile **1** formed spherical aggregates in water with a diameter of about 250 nm which is consistent with the DLS result. Moreover, the TEM image shows an obvious contrast between the periphery and the central area of the sphere, indicative of the formation of vesicles in aqueous solution. The average wall thickness of vesicles obtain from the magnified TEM image is about 6 nm, which is approximately twice length of a single optimal molecule **1** (3.5 nm obtained by Hyperchem molecular model), demonstrating that the vesicle membrane is a bilayer structure.

As mentioned above, the instability of vesicles consisting of small amphiphiles can be overcome by taking the advantage of polymerization of amphiphile. In this approach, acrylate group was adopted to be the polymerizable unit and attached to the end of the hydrophilic chain of amphiphile **1**. The polymerization of the vesicle was achieved by radical polymerization using 2,2′-azobis(2-amidinopropane hydrochloride) (AAPH) as a hydrophilic thermal initiator.[28] As presented in Figure 3, the

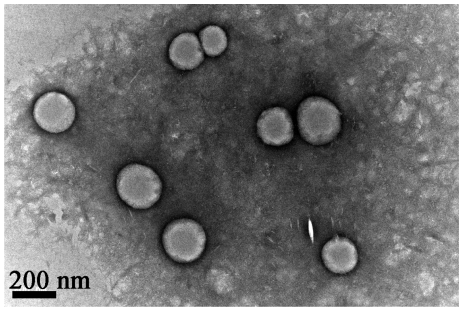


**Figure 3.** TEM image of the vesicles after polymerization.

TEM image shows that the aggregate of amphiphile **1** remained vesicular structure after polymerization, and only the diameter of the vesicle decreased slightly (ca. 236 nm by DLS, Figure S1b), which can be attributed to the closer stacking of polymerized bilayer. The stability of polymeric vesicles was tested by simply diluting the vesicle solution to the concentration below CAC or adding tetrahydrofuran (50% THF in volume) to the aqueous solution. The unpolymerized vesicles dissociated immediately once THF was added, while the polymeric vesicles existed stably without significant diameter change at the beginning (Figure S1c) and then swelled gradually and dissolved completely in about 1 h, suggesting that the stability of vesicles has been dramatically improved by the polymerization.

The photoinduced cleavage of amphiphile **1** in polymeric vesicles exposed to UV irradiation ($\lambda$ > 315 nm) was monitored by observing the absorption changes of the vesicle solution. As shown in Figure 4a, irradiation of the polymeric vesicle solution

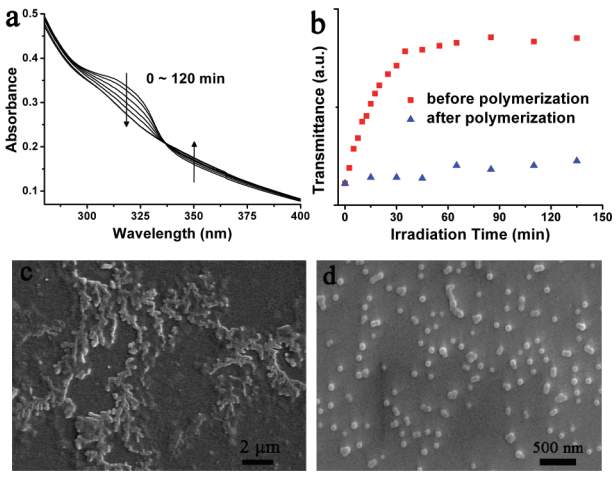


**Figure 4.** (a) Absorption spectra of polymeric vesicles upon UV irradiation. (b) Optical transmittance of different vesicle solutions as a function of UV irradiation time. SEM images of (c) unpolymerized vesicles and (d) polymeric vesicles after UV irradiation for 60 min.

with UV light resulted in a continuous drop of the absorption at ~315 nm and a slight increase ~350 nm, which originate from the formation of 2-nitrosobenzaldehyde, a byproduct of the


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cleavage reaction. This result gives the evidence that the photocleavage of amphiphile **1** occurs effectively in the polymeric vesicle, indicative of the application potential of the vesicle for photocontrolled release.[13,29] Furthermore, the stability of unpolymerized/polymeric vesicles during the UV irradiation was also examined. The optical transmittance at 500 nm of the polymerized and the unpolymerized vesicle solutions was monitored at various irradiation times (Figure 4b). The transmittance of the unpolymerized vesicle solution increased rapidly within the first 30 min of irradiation and reached a plateau when prolonging the irradiation time, suggesting the dissociation of unpolymerized vesicles due to the photocleavage of amphiphile **1**. By contrast, the transmittance of the polymeric vesicle solution only showed slight increase upon sufficient UV light exposure, implying an evident stability enhancement of vesicles due to the polymerization of acrylate. SEM images were also obtained to reveal the different appearances of the two kinds of vesicles after UV irradiation (Figure 4c,d). The unpolymerized vesicles were entirely destroyed by UV exposure, while the polymeric one retained the shape integrity according to the TEM image (Figure S3) although the amphiphilic structure of amphiphile **1** was broken by UV irradiation, which were consistent with the optical transmittance measurements.

After the stabilized vesicle was obtained, the light-triggered release properties of the polymeric vesicles were investigated by using hydrophobic dye NR as a model payload. The encapsulation and the release process can be explored by monitoring the NR absorption of the vesicle solution because NR is solubilized in vesicles and the solubility of NR in water is negligible. After the solution of polymerized vesicles was treated with NR, the solution showed a typical absorption of NR with maximum at ~550 nm, indicating the loading of NR into the hydrophobic interior of vesicle membranes. Irradiation of the vesicle solution with $\lambda > 315$ nm UV light led to a gradual drop in the absorption spectra of solution as depicted in Figure S4a, which indicated that NR was being released out of the vesicle. During the photocleavage, the amphiphilic structure of amphiphile **1** is split and lauric acid is possibly expelled out of the vesicle membrane because of its higher CAC in water (~0.025 M),[30] while the vesicular structure still retains. The release of hydrophobic guest is rationalized to the lower accommodative capability due to the loss of hydrocarbon components. In addition, the release of NR in unpolymerized vesicles and the control experiment were carried out as comparison. The absorption change of the polymeric vesicle solution showed a smooth style over time of irradiation, while the release process in unpolymerized vesicle was much faster and reached a plateau in about 10 min, and the absorption almost kept constant for the polymeric vesicle in the absence of UV irradiation (Figure S4b). These results clearly substantiate that the polymeric vesicle can release hydrophobic molecules effectively and sustainedly as a consequence of splitting the amphiphilic structure with UV light stimulus. Because the photolysis amount of *o*-nitrobenzyl group is dependent on the UV light dosage, the release of NR can be easily tuned and controlled by adjusting the UV irradiation within a wide time range.

To further evaluate the temporal controlled release of the polymeric vesicle, the photorelease was investigated by periodically turning on and off the UV illumination. A series of evident drop of absorbance were generated due to the release of encapsulated NR by each UV irradiation, and once the UV light was shut down the release process was ceased with no significant leakage of dye, showing a stepwise-release fashion as demonstrated in Figure S5. The stair height of the curve denoted the amount of NR expelled out of the vesicle which was dependent on the irradiation time. This result reveals that the polymerization makes vesicles not only shape-persistent but also guest molecule-sequestered even when part of the amphiphile structure has already been broken by UV irradiation. In contrast, the absorption of NR in the unpolymerized vesicle solution showed a steep decrease at the first irradiation period and reached a plateau only after three irradiation periods, and its release profile is shown in Figure S5. This phenomenon is understandable that the vesicles underwent the dissociation when the amphiphile was cleaved by UV irradiation, resulting in a NR abrupt release and much fewer stimuli-responsive cycles. Apparently, the temporal controlled-release performance of the polymeric vesicle is much better than the unpolymerized one according to the data above. Therefore, a stepwise release of hydrophobic guests from the polymeric vesicle can be easily achieved by splitting demanded amount of amphiphilic parts through repeating the UV exposure and the subsequent dark condition, implying the application potential of polymeric vesicle for a dose control carrier. A visual expression of the photocontrolled release process of the stabilized vesicle is shown in Figure 5.

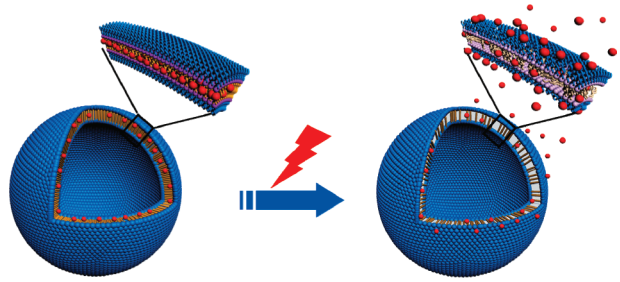

**Figure 5.** Visual expression of the photocontrolled release process of the stabilized vesicle.

## CONCLUSION

A novel amphiphile with an acrylate tail and nitrobenzyl unit in the middle, which is capable of polymerizing and photocleavage, was designed and synthesized. The nanosized vesicles formed by the synthesized amphiphile in water can be stabilized by in-situ polymerization of the peripheral acrylate groups. The polymeric vesicle with high stability can encapsulate hydrophobic guests within its membrane and release the cargo through splitting the amphiphilic structure of the amphiphile by UV irradiation. The release process from the polymeric vesicle was smoother than that form the unpolymerized one and a stepwise controlled-release profile was presented by simply turning on/off the UV illumination, implying that a better sustained controlled release of guests from the polymeric vesicle. Such a promising approach provides potential applications in stimuli-responsive and dose-controlled release systems for drug delivery and other biological investigations. We are currently studying new controlled-release assemblies containing two-photon sensitive groups, which are more appropriate for the applications in living systems.


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## ■ ASSOCIATED CONTENT

### Supporting Information

Characterization data of amphiphile **1**, DLS data, TEM image, and photorelease data. This material is available free of charge via the Internet at http://pubs.acs.org.

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