Supplementary Information (SI)

Visible-Light-Responsive Polymeric Multilayers for Trapping and Release of Cargoes via Host-Guest Interactions

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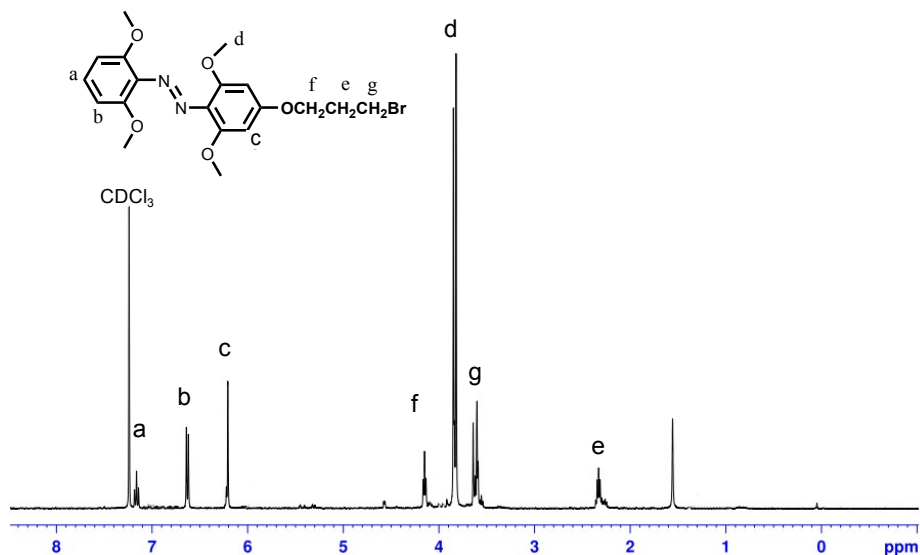## 1. ^{1}H NMR spectrum of 2,6,2',6'-tetramethoxy-(4-(6-hydroxypropoxy-bromide)) azobenzene (AzoOMeBr)

Figure S1. ^{1}H NMR spectrum of AzoOMeBr in CDCl$_3$.

2. GPC curve of poly(2-(*N, N*-dimethylaminoethyl) methacrylate) (PDMAEMA)

M_n=2.08×10^4 g/mol
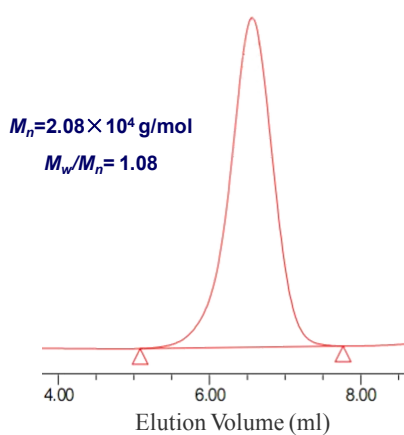
M_w/M_n= 1.08

Figure S2. GPC curve of poly(2-(*N, N*-dimethylaminoethyl) methacrylate) (PDMAEMA).

3. ^{1}H NMR spectra of mono-6-dexoy-6-(p-tolysulfonyl)-β-CD (β-CD-OTs), mono-6-dexoy-6-ethylenediamine-β-CD (NH$_2$-β-CD), and β-CD-rhodamine B (β-CD-RhB).

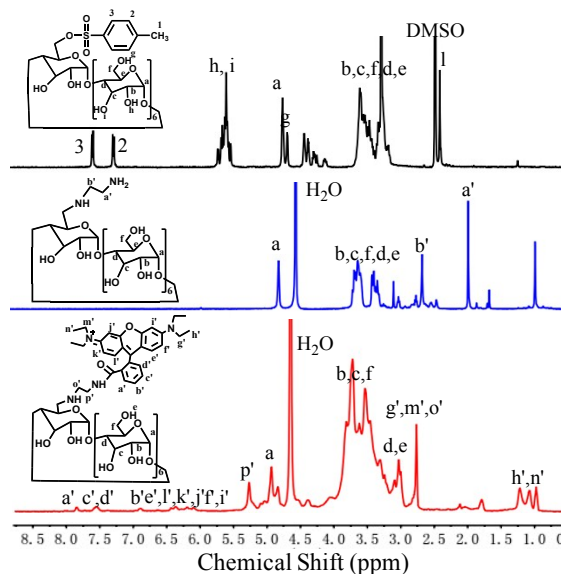**Figure S3.** ^{1}H NMR spectra of β-CD-OTs in (CD$_3$)$_2$SO, NH$_2$-β-CD in D$_2$O, and β-CD-RhB in D$_2$O, respectively.

4. Loading capacity of polymer Azo-PDMAEMA in solution.

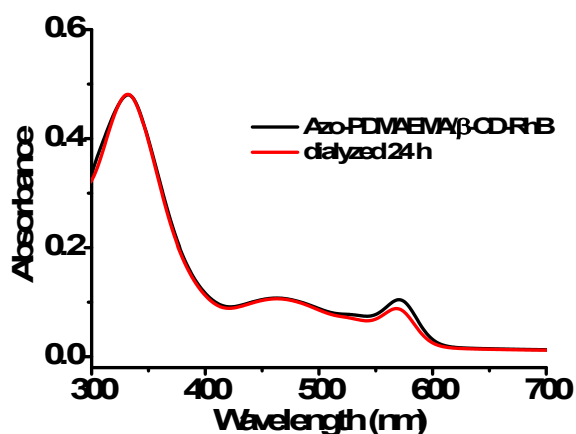**Figure S4.** UV-Vis absorption spectra of Azo-PDMAEMA/β-CD-RhB complexes before and after dialysis.

The UV-Vis absorption spectra of Azo-PDMAEMA/β-CD-RhB complexes before and after dialysis are shown in Figure S4. The azobenzene-functionalized polymer (3.665 mg, 27.96 nmol.mL^{-1} of azobenzene) was dissolved in 150 mL H$_2$O and then adjusted to pH 6.0 with 0.1 mM HCl. Subsequently, β-CD-RhB (10.14 mg, 41.93 nmol. mL^{-1}) was added and the mixture was stirred overnight at room temperature and then dialyzed (MWCO: 3500 Da) against water (30 mL) for 24 h. After dialysis, the uncomplexed β-CD-RhB could be removed and thus the absorption peak at 570 nm of β-CD-RhB decreased, while the absorption peaks at 331 nm and 470 nm of azobenzene changed little. The concentration of the complexed β-CD-RhB was determined to be 25.97 nmol.mL^{-1} by UV-Vis spectroscopy with a calibration curve shown in Figure S5. Thus the molar ratio of β-CD-RhB to the azobenzene for the complex solution was calculated to be 0.93:1.

5. Calibration curve of β-CD-RhB concentration.
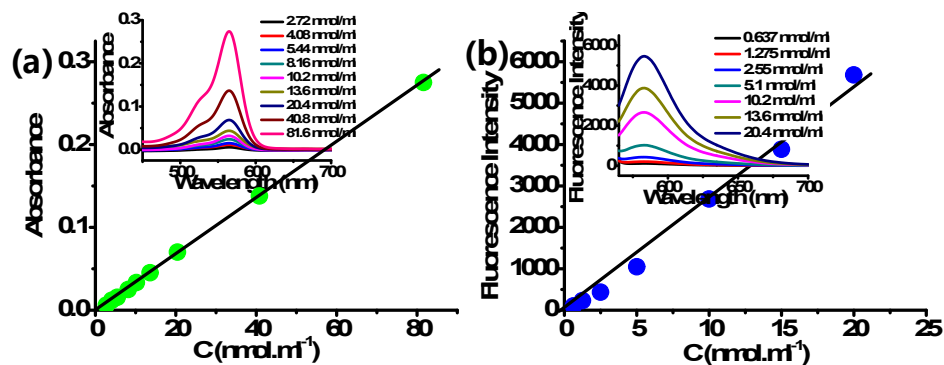

Figure S5. (a) Calibration curve of UV-Vis absorption of β-CD-RhB. Inset: UV-Vis absorption spectra of β-CD-RhB in aqueous solution with different concentrations. (b) Calibration curve of fluorescence intensity of β-CD-RhB. Inset: fluorescence spectra of β-CD-RhB in aqueous solution with different concentrations.

6. Determination of the functionalization degree of poly{6-[(2,6 dimethoxyphenyl)azo-4-(2',6'-dimethoxy)phenoxy]propyl dimethylaminoethyl Methacrylate-random-PDMAEMA (Azo-PDMAEMA).
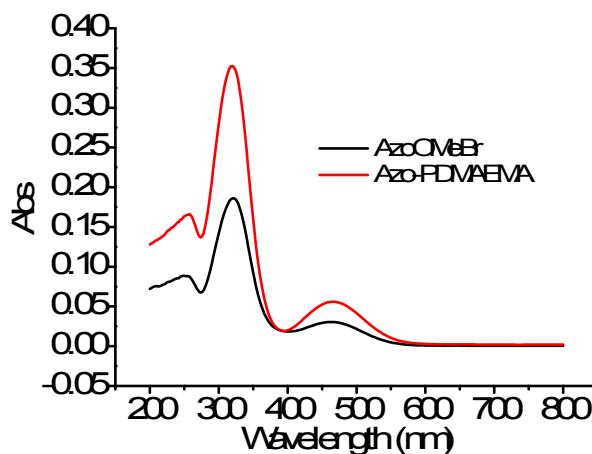

Figure S6. UV-Vis spectra of AzoOMeBr at 0.00125 mg/mL and Azo-PDMAEMA at 0.011 mg/mL in DMF.
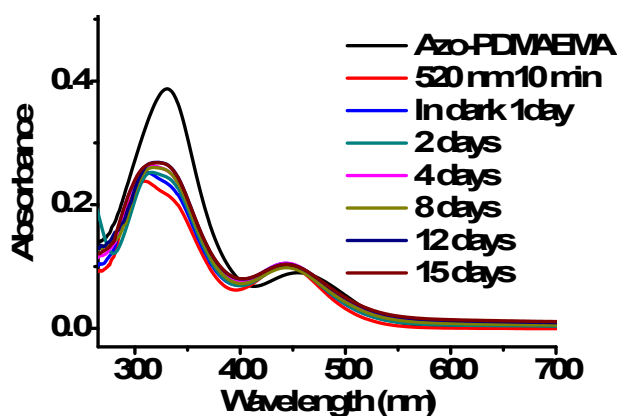
7. Measurement of the thermal half-life time.

Figure S7. UV-Vis spectra of the Azo-PDMAEMA studied in aqueous solution at room temperature, and upon green light irradiation for 10min, and then maintained in dark for different times.

8. The release and rebound ratio from the azobenzene-functionalized polymer in aqueous solution upon visible light irradiation.
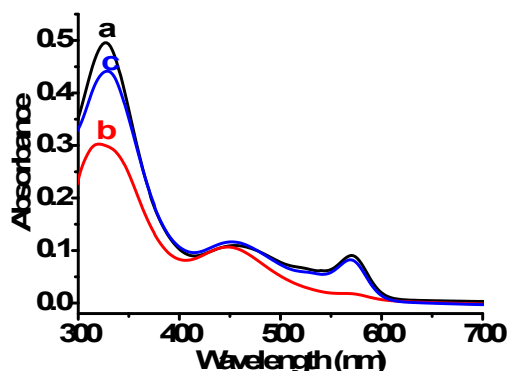

Figure S8. Absorption spectra of the complex Azo-PDMAEMA/β-CD-RhB as prepared (curve a), the complex after green light irradiation and then after dialysis (curve b), and the complex after green light irradiation and then blue light irradiation and then after dialysis (curve c).

The percentage of released and rebound β-CD-RhB from the azobenzene-functionalized polymer in the solution was determined by the absorption changes of RhB shown in Figure S8. To investigate the percentage of released β-CD-RhB from the azobenzene-functionalized polymer in the solution, the complex was irradiated by green light for 10 min and dialyzed against water to remove the released β-CD-RhB. The percentage of released β-CD-RhB was determined to be 80.1% by the equation Υ = 1-(A/A_0), where A_0 is the initial absorbance value of RhB at 570 nm in the complex as prepared (shown in curve a) and A is the absorbance value after green light irradiation and then after dialysis (shown in curve b). To investigate percentage of rebound β-CD-RhB from the azobenzene-functionalized polymer in the solution, the complex was irradiated by green light for 10 min and subsequently irradiated by blue light for 5 min, then dialyzed against water to remove the uncomplexed β-CD-RhB. The percentage of rebound β-CD-RhB was determined to be 90.6%.

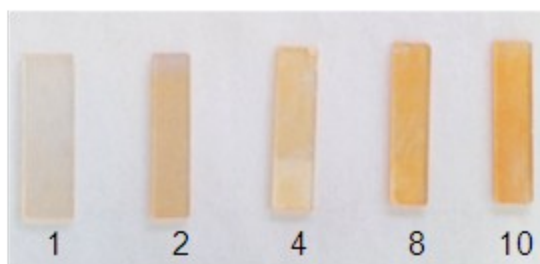## 9. Photographs of multilayers assembled on quartz substrates.

Figure S9. The photographs of multilayers assembled on quartz substrates. (1, 2,…represent the number of multilayers.).

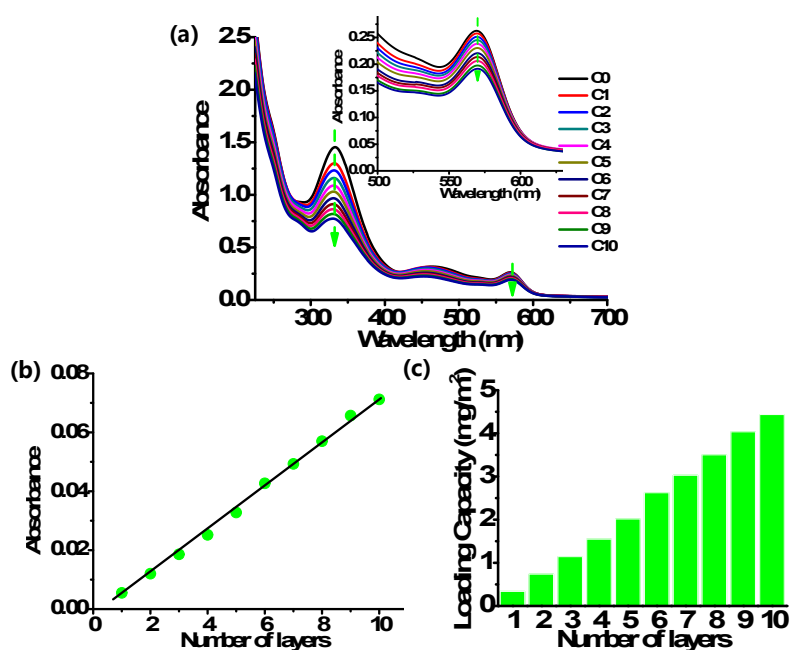## 10. Loading capacity of multilayers.

Figure S10. (a) Absorption spectra of the complex Azo-PDMAEMA/β-CD-RhB solution after each layer formation (C0, C1,…represent the number of layers; Inset: a magnified view in the range of 500-600 nm.). (b) UV-Vis inferred loading capacity of multilayer films. (c) Loading capacity of multilayer films.

To investigate how much β-CD-RhB was encapsulated in the monolayer and the multilayer films, the concentration changes of the complex Azo-PDMAEMA/β-CD-RhB solution were recorded by UV-Vis spectroscopy when the films were fabricated. The absorption spectra of the complex solution after each layer formation are shown in Figure S10a. β-CD-RhB loading experiments were conducted on 4.0×1.0 cm^2 quartz slides. The loading capacity of ((Azo-PDMAEMA/β-CD-RhB)/PAA)$_n$ multilayer films increased with the increase of number of layers, shown in Figure S10 b and c. The amount of encapsulated β-CD-RhB from monolayer to ten-layers were 0.33 mg/m^2, 0.74 mg/m^2, 1.14 mg/m^2, 1.55 mg/m^2, 2.02 mg/m^2, 2.62 mg/m^2, 3.02 mg/m^2, 3.50 mg/m^2, 4.03 mg/m^2, 4.48 mg/m^2, respectively.

11. Photoresponsive behaviors of Azo-PDMAEMA/PAA monolayer and ten-layers revealed by UV-Vis spectroscopy.
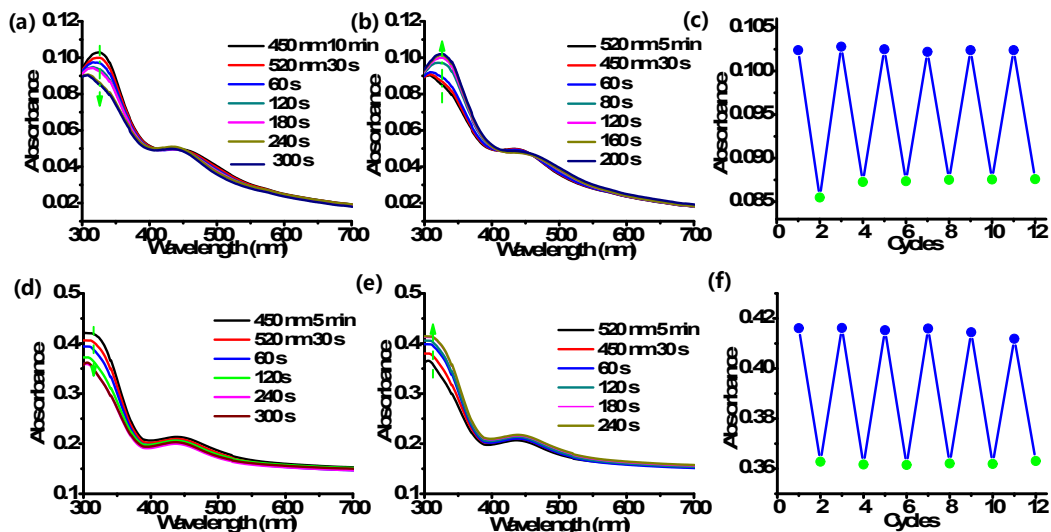

Figure S11. (a) and (b) UV-Vis absorption spectra of Azo-PDMAEMA/PAA monolayer under irradiation of 520 nm and 450 nm, respectively. (c) Reversible absorbance changes of monolayer under the alternative green light irradiation for 10 min and blue light irradiation for 5 min (d) and (e) UV-Vis absorption spectra of ten-layers under irradiation of 520 nm and 450 nm, respectively. (f) Reversible

absorbance changes of ten-layers under the alternative green light irradiation for 10 min and blue light irradiation for 5 min.

Azo-PDMAEMA/PAA multilayers were prepared by the electrostatic layer-by-layer assembly method onto the pretreated substrates at room temperature. Briefly, the pretreated anionic-modified substrates were immersed in a solution of Azo-PDMAEMA (1.25×10^{-4} M) for 10 min and washed with deionized water for 2 min, and then dried under nitrogen stream. Then the cationic-modified substrates were immersed in a PAA solution (1×10^{-4} M) for 10 min and washed with deionized water for 2 min, and dried under nitrogen stream. The sequential deposition operations for Azo-PDMAEMA and PAA were repeated several times to produce multilayers.

The photoisomerization properties of Azo-PDMAEMA/PAA monolayer and ten-layers under light stimulation were demonstrated by UV-Vis spectroscopy. Upon green light irradiation, the intensity of π-π^* transition bands at 330 nm decreased and reached a photostationary state after 4 min, shown in Figure S11a. After blue light irradiation, the cis form recovered to the trans and the transition reached a photostationary state after 3 min, shown in Figure S11b. This reversible photoisomerization process could be recycled many times by alternative irradiation of 520 nm and 450 nm respectively, shown in Figure S11c. The similar photoisomerization properties of the ten-layers are shown in Figure S11d, e and f.

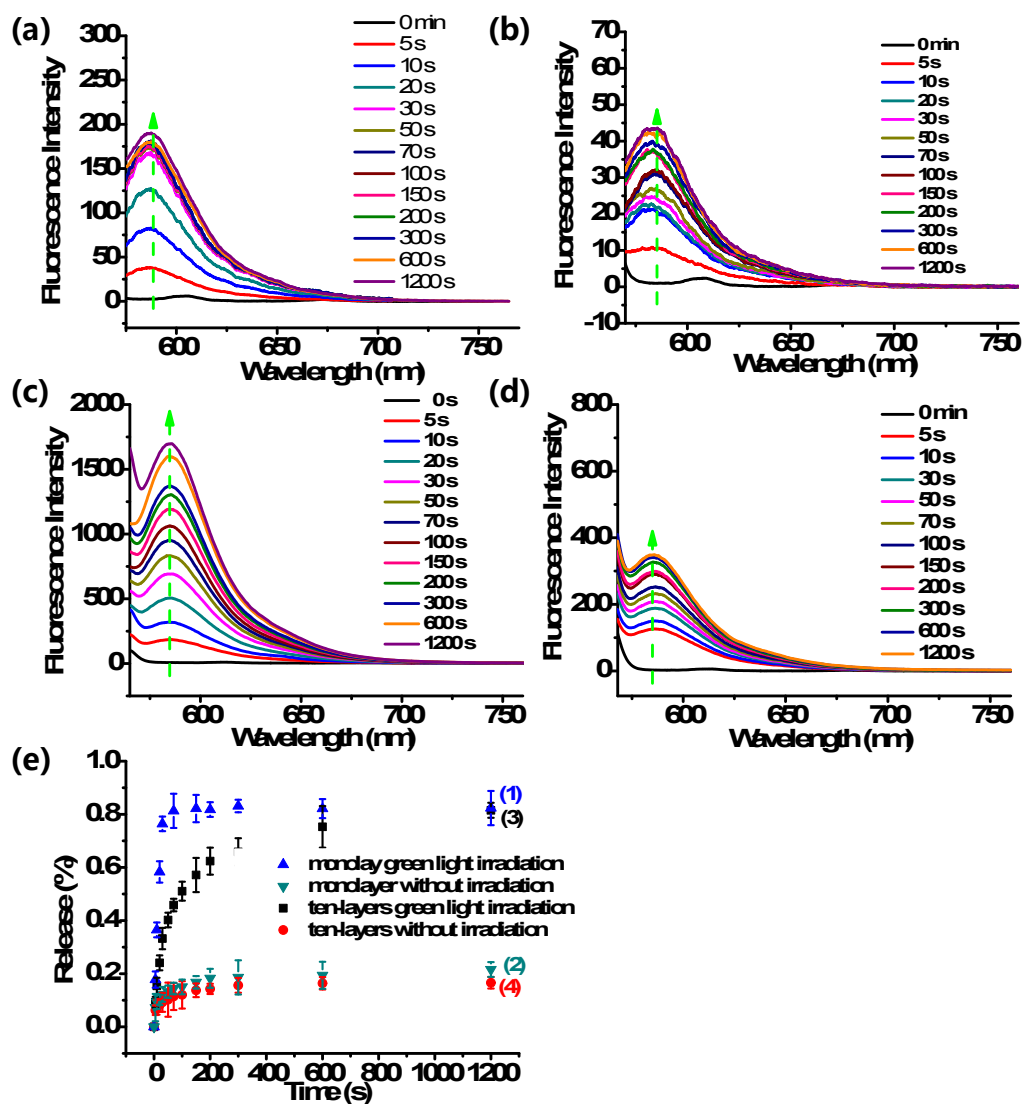## 12. Release ratio of cargoes from the monolayer and ten-layers.

Figure S12. (a) and (b) Fluorescence spectra of released β-CD-RhB in water at different time for the monolayer with and without green light irradiation. (c) and (d) Fluorescence spectra of released β-CD-RhB in water at different time for the ten-layers with and without green light irradiation. (e) Release profiles of β-CD-RhB from the monolayer and ten-layers with (1,3) and without green light irradiation (2,4).

To determine the released amount upon visible light irradiation, the fluorescence spectra of released β-CD-RhB in water at different time for the monolayer and ten-layers with and without light irradiation were recorded, shown in Figure S12a, b, c,

S10

and d. The release ratios of β-CD-RhB were calculated by M/M_0, where M_0 is the initial amount of β-CD-RhB loaded into the film (shown in Figure S10) and M is the released amount of β-CD-RhB from the film after green light irradiation. The release profiles of β-CD-RhB are shown in Figure S12d. The release ratios for the monolayer and ten-layers after green light irradiation for 10 min were measured to be 77.0 % and 73.5 % respectively, while the release ratios for the monolayer and ten-layers without green light irradiation were only 21.7 % and 15.7 % respectively.
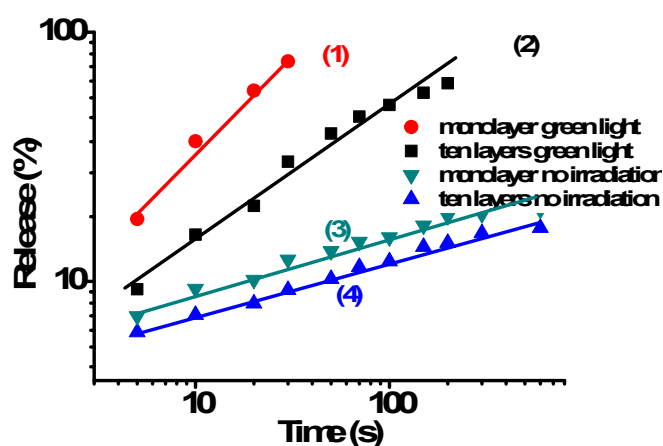
13. Release kinetics.

Figure S13. Log-log plots of kinetics of β-CD-RhB release from the monolayer and ten-layers with (line 1 and 2) and without (line 3 and 4) green light irradiation.

The release kinetics can be analyzed using the equation $\log M(t)/M(\infty)=k*\log t$, where M is the released amount of β-CD-RhB, $M(t)/M(\infty)$ is the fraction of β-CD-RhB released at time t, and $M(\infty)$ is the total amount of β-CD-RhB in loaded film. The log-log plots of kinetics of β-CD-RhB release from the monolayer and ten-layers upon green light irradiation are shown in Figure S13. Upon green light irradiation, the calculated slopes for the monolayer and ten-layers were 0.80 and 0.65 respectively, while the slopes for the monolayer and ten-layers without light irradiation were 0.22 and 0.21 respectively. These values show that without green light irradiation, the

cargo is released from the film by Fickian diffusion (n<0.5), while upon green light irradiation, the release becomes non-Fickian (0.5<n<1) as the host-guest interaction between azobenzene and β-CD is disrupted.[1,2]

Reference

1. I. Lynch, P. Gregorio, K. A. Dawson, J. Phys. Chem. B, 2005, 109, 6257-6261.

2. Z. Zhu, S. A. Sukhishvili, ACS Nano 2009, 3, 3595-3605.