Light-Operated Mechanized Nanoparticles

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General. All reagents, including 4-aminoazobenzene, 3-aminopropyltriethoxysilane, azobenzene-4,4′-dicarboxylic acid, benzylamine, β-cyclodextrin (**β-CD**), 3-isocyanatopropyltriethoxysilane (**3-ICPES**), and 1-pyreneacetic acid are commercially available and were used without further purification. Mono[6-*O*-(toluene-*p*-sulfonyl)]-β-cyclodextrin[S1] and mono{6-2-[2-(2-aminoethyl-amino)ethylamino]ethylamino-6-deoxy}-β-cyclodextrin[S2] were prepared according to the previous reports in the literature. Nuclear magnetic resonance (NMR) spectra were recorded on a Brüker Avance 500 spectrometer at 25 °C. Chemical shifts were reported in parts per million (ppm) downfield from the Me_4Si resonance which was used as the internal standard when recording ^1H NMR spectra. High-resolution matrix-assisted laser desorption/ionization spectra (HR-MALDI) were measured on an AppliedBiosystems DE-STR MALDI time-of-flight mass spectrometer. The reported molecular mass (*m*/*z*) values were the most abundant monoisotopic mass. Powder X-ray diffraction (XRD) measurements were carried out using a Panalytical X'Pert Pro powder diffractometer. The radiation source was copper ($K_{\alpha1}$ and $K_{\alpha2}$ = 1.5418 Å). FT-IR spectra were recorded on a Perkin-Elmer FT-IR Paragon 500 spectrometer. Dynamic light scattering (DLS) was performed on a Beckman Coulter N4 Plus particle sizer, with a 633 nm HeNe excitation source. The controlled release profiles were obtained via luminescence spectroscopy using an Acton SpectraPro 2300i CCD, and a coherent Argon Innova 90C-5 excitation laser.

Mono[6-(1-pyreneacetamido)triethylenetriamino-6-deoxy]-β-cyclodextrin (Py-β-CD): As shown in Figure S1, the mono(6-triethylenetetramino-6-deoxy)-β-cyclodextrin (1.26 g, 1.0 mmol) and DCC (0.21 g, 1.0 mmol) were dissolved in DMF (30 mL) in the presence of a small amount of 4 Å molecular sieves under an atmosphere of Ar. A DMF solution (10 mL) of 1-pyreneacetic acid (0.26 g, 1.0 mmol) was then added dropwise. The mixture was stirred for 2 days in an ice bath and then for another 2 days at room temperature, before being left to stand for 5 h until no more

precipitate deposited. The precipitate was removed by filtration, and the filtrate was poured into Me_2CO (150 mL). The precipitate formed in Me_2CO was collected by filtration and subsequently purified on a Sephadex G-25 column with water as eluent. After the residue was dried in vacuo, a pure sample (0.72 g, 48 %) of **Py-*β*-CD** was obtained as a colorless solid. ^{1}H NMR (500 MHz, D_2O, 25 °C, TMS): δ = 2.46–2.62 (m, 12H, NCH_2CH_2N), 3.57–3.87 (m, 42H), 4.20 (s, 2H, CH_2CO), 4.94–5.06 (m, 7H), 7.84–8.13 ppm (m, 9H, Py-H); MS (HR-MALDI): Calcd for $C_{62}H_{86}N_2O_{35}$ *m*/*z* 1504.5855, found *m*/*z* 1504.5823 (*M*).

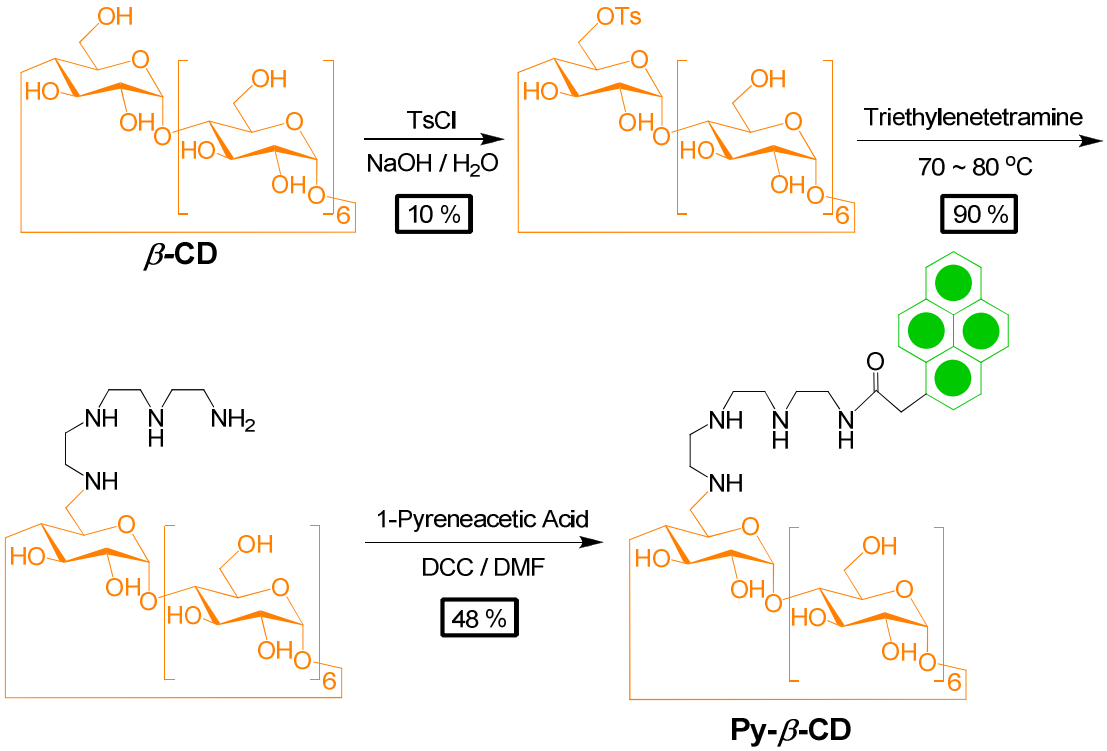

Figure S1. Schematic representation of the preparation of **Py-*β*-CD**.

4-(3-TriethoxySilylpropylUreido)Azobenzene (TSUA):[S3] As shown in Figure S2, **3-ICPES** (1.37 g, 8.5 mmol) was added to a THF solution (12 ml) of 4-aminoazobenzene (1.58 g, 8.0 mmol). The mixture was heated under reflux and an atmosphere of N_2 overnight. After removal of the solvent, the residue was recrystallized in hexane/THF. The solution was cooled to 0 °C, and

the shiny needle-like crystals which formed were filtrated and washed with hexane. The product was dried in vacuum to give **TSUA** (2.88 g, 81 %). NMR for TSUA: Solvent =^{1}H NMR (500 MHz, CD_3CN, 25 °C, TMS): δ = 0.59 (t, 2H, CH_2Si), 1.17 (t, 9H, CH_3), 1.49 (m, 2H, CCH_2C), 3.14 (m, 2H, NCH_2), 3.75(q, 6H, OCH_2), 5.40 (t, 1H, the other urea H), 7.45 (t, Ar-H, 1H), 7.46 (s, Ar-NH, 1H), 7.52 (d, Ar-H, 2H), 7.60 (t, Ar-H, 2H), 7.85 (m, Ar-H, 4H).

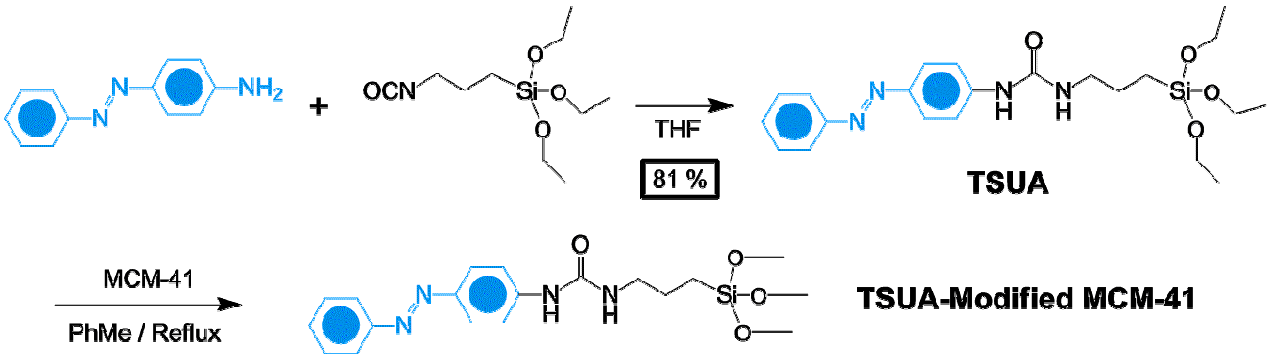

Figure S2. The preparation of **TSUA** and **TSUA**-Modified MCM-41 nanoparticles.

Preparation of MCM-41: CTAB (1.00 g, 3.0 mmol) was added to deionized H_2O (240 mL). 2 M NaOH (3.5 mL) was added to the solution causing the pH to increase to above 12 and inducing the complete dissolution of CTAB. The solution was heated to 80 °C while stirring to create a homogenous solution. Tetraethyl orthosilcate (**TEOS**, 5.0 mL, 23.0 mmol) was added to the solution dropwise over several min, resulting in the precipitation of the product. The reaction was allowed to complete over 2 h. The solution was then filtered while hot using a fritted funnel. The solid was washed with deionized H_2O and MeOH. The product was dried in oven at 80 – 100 °C. The resulting mass after reaction is approximately 2~3 g. The mesoporous structure was observed using XRD. The size of the nanoparticle was determined using dynamic light scattering.

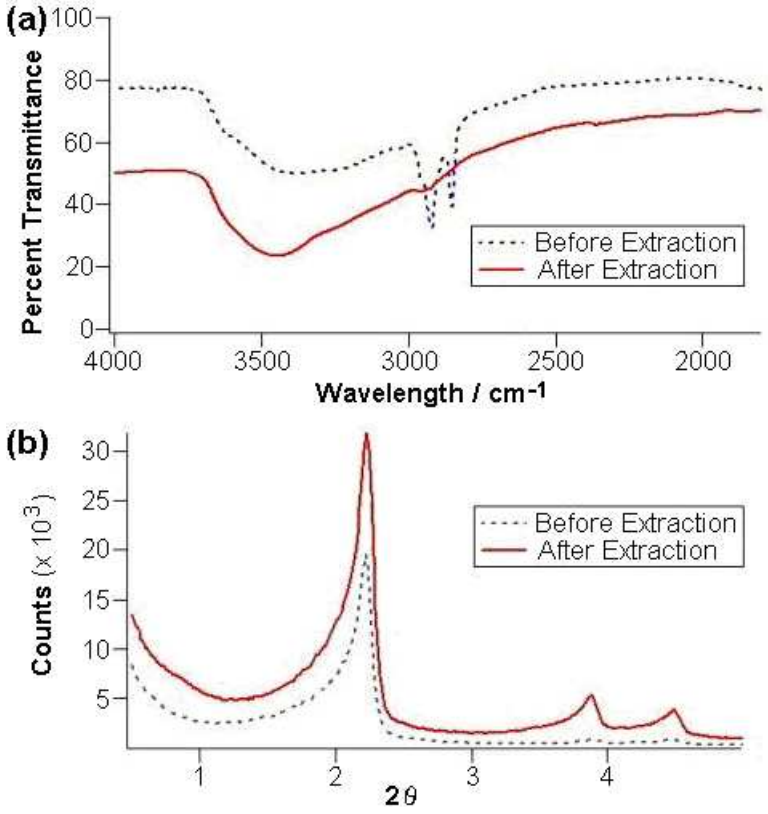

Figure S3. (a) The IR spectra of the MCM-41 nanoparticles from KBr pellets before and after extraction. The loss of the C–H peak at ~2900 cm^{-1} indicates the removal of the surfactant. (b) The XRD of the MCM-41 nanoparticles before and after extraction. The retention of the spectrum indicates that the meso-structure of the MCM-41 nanoparticles is maintained after the extraction.

Acidic MeOH was prepared by adding 12M HCl (1.0 mL) to MeOH (100 mL) and mixed for 10 min. Acidic MeOH was added to the MCM-41 nanoparticles. The nanoparticles were sonicated and then stirred continuously for 6 h at > 60 °C. Solution is filtered through a fritted funnel and washed with MeOH. Extraction was confirmed by IR spectroscopy (see Figure S3). Loss of the C–H stretch peaks confirms removal of surfactant. The structure of the MCM-41 nanoparticles after post extraction was confirmed with XRD. The size of the nanoparticles was confirmed using dynamic light scattering (see Table 1).

Table S1. Dynamic light scattering data of the MCM-41 nanoparticles.

Rept#	Mean (nm)	Std Dev. (nm)	Baseline Error	P.I.	Counts	Diff. Coeff. (m^2/s)	Overflow
Rept.1	455.2	217.0	0.07%	−1.254	5.46e−5	1.92e−12	0
Rept.2	433.6	208.8	0.03%	−1.597	5.45e−5	2.01e−12	0
Rept.3	427.9	203.2	0.01%	−1.146	5.45e−5	2.01e−12	0
Average	438.9	209.65		−1.332			

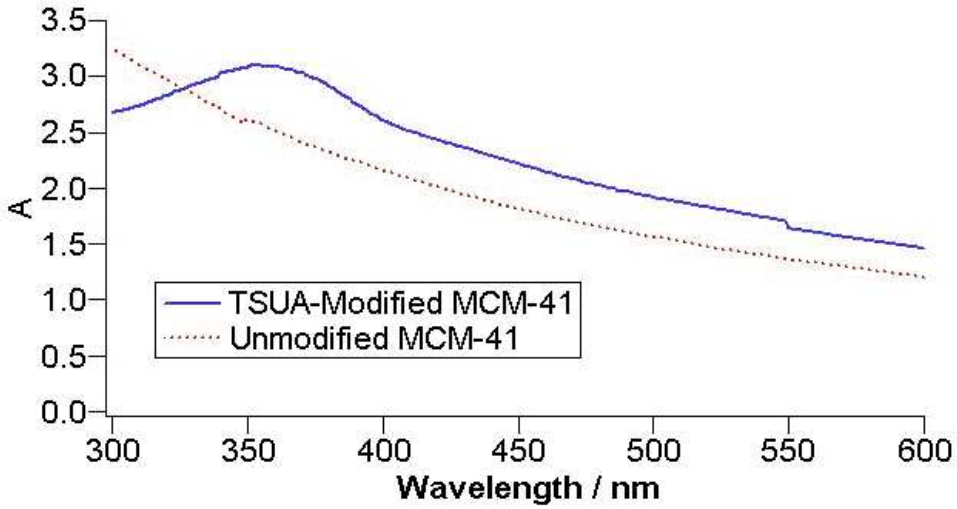

Figure S4. UV-Vis spectra of MCM-41 nanoparticles and **TSUA**-Modified MCM-41 nanoparticles. The appearance of the peak around 365 nm is indicative of the presence of the azobenzene units which leads to the conclusion that **TSUA** has reacted with the silica surface. The bright yellow color of the nanoparticles supports also the conclusion.

Attachment of TSUA to the Surface of the MCM-41 Nanoparticles (see Figure S2): A 0.1 mM solution of **TSUA** was prepared by dissolving **TSUA** (4.0 mg, 9.7 μmol) in 100 mL of dried PhMe. Unextracted MCM-41 nanoparticles (100 mg) were suspended via stirring and sonication in 0.1 mM **TSUA** solution (10 mL). The solution was refluxed under N_2 overnight. The solution was filtrated using a fritted funnel to obtain the canary yellow nanoparticles. The nanoparticles

were washed with copious amounts of PhMe, THF, and MeOH, respectively, and dried overnight under vacuum. Subsequent extraction of templating agent was performed via acidic MeOH extraction of the surfactant. Attachment of **TSUA** to the nanoparticles was confirmed by UV-vis spectroscopy. See Figure S4.

***(E)*-4-((4-(Benzylcarbamoyl)Phenyl)Diazenyl)Benzoic Acid (BPDB):** As shown in Figure S5, azobenzene-4,4′-dicarboxylic acid (0.20 g, 0.74 mmol) was stirred with thionyl chloride (0.19 g, 1.6 mmol) and pyridine (0.16 g, 2.0 mmol) in CH_2Cl_2 for 1 h followed by addition of benzylamine (0.08 g, 0.74 mmol). The mixture was stirred at room temperature until complete disappearance of starting material as verified by TLC (2~3 h). After removal of the solvent, the residue was purified by column chromatography ($CHCl_3$/MeOH 10:1) to afford pure **BPDB** as a yellow oil (0.23 g, 87%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 3.90 (s, 2H, CH_2), 7.48–7.40 (m, 5H), 7.54 (s, 1H, *J* = 7.5), 7.60 (d, 3H, *J* = 7.7), 7.93–7.88 (m, 2H), 7.99 (d, 1H, *J* = 6.4), 8.15 (d, 1H, *J* = 8.2), 8.32 (d, 1H, *J* = 7.3), 10.82 ppm (s, 1H); ^{13}C NMR (500 MHz, $CDCl_3$): δ = 169.8, 167.1, 156.0, 150.0 , 133.2, 133.1, 131.6, 131.0, 130.0, 129.9, 129.9, 128.8, 127.3, 127.1, 44.7 ppm. MS (HR-MALDI): Calcd $C_{21}H_{17}N_3O_3$ for *m/z* 359.3892, found *m/z* 359.3887.

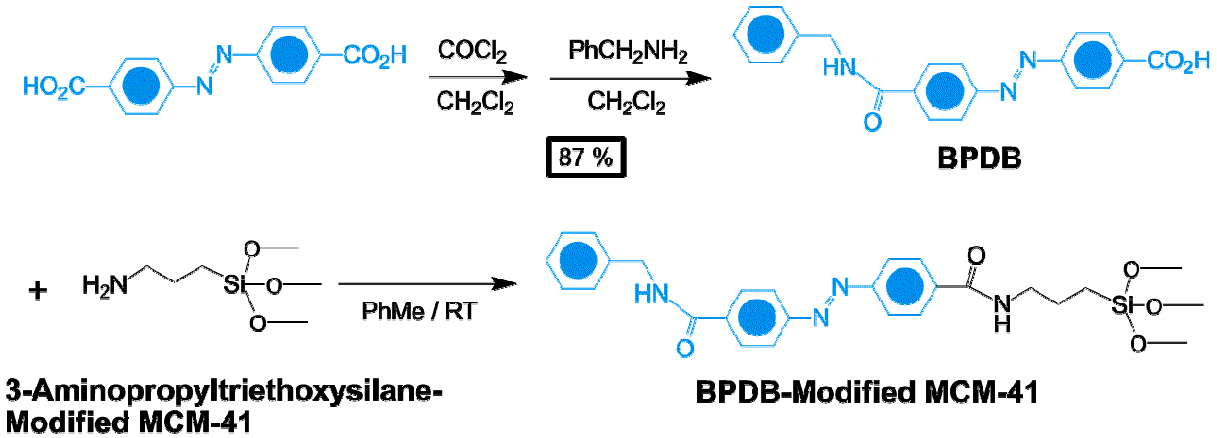

Figure S5. The preparation of **BPDB** and **BPDB**-Modified MCM-41 nanoparticles.

Attachment of 3-Aminopropyltriethoxysilane to Surface of MCM-41 Nanoparticles: Extracted MCM-41 nanoparticles (100 mg) were added to dried PhMe (10 mL) and suspended via stirring and sonication. 3-Aminopropyltriethoxysilane (25 μL, 0.1 μmol) was added to the mixture using a micropipette. The solution was placed under N_2 and heated under reflux overnight. The nanoparticles were removed from solution via filtration using a fritted funnel and washed with PhMe, THF, and MeOH, respectively. The material was dried overnight using vacuum. The presence of amine group was confirmed by IR spectroscopy (see Figure S6) using KBr pellet method.

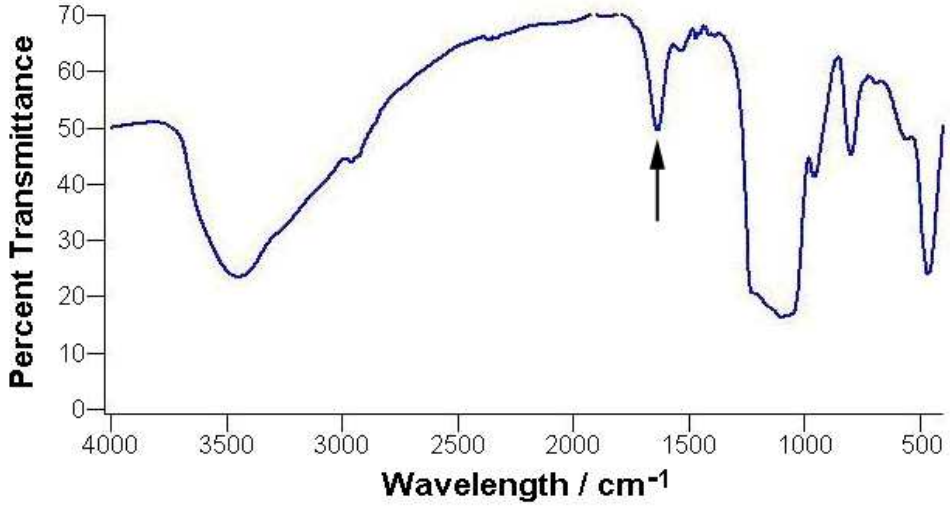

Figure S6. IR spectrum of the MCM-41 nanoparticles after extraction and subsequent modification using 3-aminopropyltriethoxysilane. The spectrum was generated using a KBr pellet. The growth of the peak at 1465 cm^{-1} is indicative of the presence of a primary amine group, which leads to the conclusion that the amine modification has taken place.

BPDB-Modified MCM-41 Nanoparticles (see Figure S5): BPDB (4 mg, 10 μmol) was dissolved in dried PhMe (5 mL). The solution was added to flask containing 3-aminopropyltriethoxysilane coated MCM-41 nanoparticles (50 mg). The solution was mixed and sonicated to disperse nanoparticles. The solution was then allowed to stir under room temperature

for > 24 h. The nanoparticles were separated from solution by filtration and washed with PhMe, THF, and MeOH, respectively. The particles were dried under vacuum overnight.

Loading Nanoparticles with Rhodamine B: Rhodamine B (0.48 g, 1 mM) solution (100 mL) was prepared using volumetric equipment. Rhodamine B solution (10 mL, 1 mM) was added to a reaction flask containing nanoparticles (100 mg). The nanoparticles were stirred and sonicated in solution to maximize dispersion. The solution was then stirred overnight to allow Rhodamine B to diffuse into the nanopores.

Capping Nanoparticles with *β*-CD: ***β*-CD** (40 mg, 35.2 μmol) was added to an aqueous solution containing the Rhodamine B-loaded nanoparticles (100 mg). The mixture was then stirred and sonicated. After complete dessolvation of ***β*-CD**, the solution was allowed to stir on ice for > 12 h to maximize the association of ***β*-CD** and the formation of the pseudorotaxanes. The nanoparticles were separated from solution via centrifugation and were then washed using a 2 mM ***β*-CD** solution. The product was separated from washing solution by centrifugation. The nanoparticles were subsequently dried via vacuum overnight for analysis.

Capping with *β*-CD and Py-*β*-CD Mixture: In order to examine the function of ***β*-CD** as a gatekeeper on the surfaces of the MCM-41 nanoparticles, the release of ***β*-CD** into solution as a time function needs to be monitored. Therefore, **Py-*β*-CD** as a fluorescence probe was mixed with ***β*-CD** to monitor by fluorescence.

Extracted surface-modified nanoparticles (100 mg), ***β*-CD** (35 mg, 30.1 μmol), and **Py-*β*-CD** (3 mg, 2 μmol) were mixed together and dissolved in deionized H_2O (10 mL) via sonication. The

solution was then cooled to 0 °C and stirred overnight. The nanoparticles were collected by centrifugation, washed with 2 mM aqueous solution of **β-CD**, and dried overnight under vacuum.

Rhodamine B-Loaded, Py-β-CD-Associated Nanoparticles (Preparation for Dual Release): The dye was loaded into the nanopores of the extracted MCM-41 nanoparticles by mixing and diffusion. The nanoparticles (100 mg) were added to a Rhodamine B solution (10 mL, 1 mM), the solution was sonicated to disperse the nanoparticles, and the mixture was left to stir for > 12 h. **β-CD** (35 mg, 30.1 μmol) before **Py-β-CD** (3 mg, 2 μmol) was then added to the solution. The solution was stirred and sonicated in order to insure both the complete redispersion of the nanoparticles and the solubilization of the CDs. The solution was cooled on ice and stirred overnight. The nanoparticles were then removed from solution by centrifugation and washed with 2 mM **β-CD** aqueous solution.

Release Analysis of Nanoparticles (Experimental Set-Up): Capped and dried nanoparticles were examined in the same spectroscopic set-up (see Figure S7). The nanoparticles were placed in the side of a glass container that has a dimension with a 1 cm × 2 cm base and 6 cm height. Deionized H_2O was added to the solution in a dropwise fashion in order to keep the nanoparticles from dispersing into the liquid. The deionized H_2O was then removed in order to abstract any nanoparticles that may have been dispersed into the deionized H_2O. Additional deionized H_2O was added to the flask to fill the container about 4 cm in height. A 1 mm stirring bar was added to the glass container. This container is then stirred at about 100 rpms. The solution was monitored by a CCD, which collects the emission spectrum from the solution. Emission from the solution was stimulated by a diode laser (0.4 W cm^{-2} at 377 nm) which focused ~3 cm above the base of the glass vessel. Excitation of the nanoparticles was induced by an Ar/Kr^+ ion gas laser at 351 nm

with variable outputs depending on the experiment. The majority of the emission from the nanoparticle as well as the scattered light from the excitation beam were removed by masking the nanoparticles with a 1.5 cm high black stopper. Data was collected both in emission spectra as well as in integration of wavelengths corresponding with fluorescence (λ_{max}) of the species being monitored versus time.

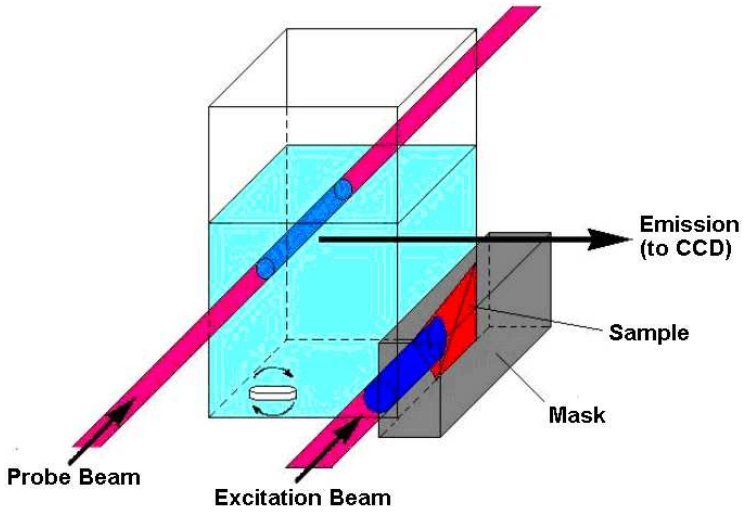

Figure S7. General set-up for probing the release from the MCM-41 nanoparticles. The probe beam is generated from a diode laser (0.4 W cm^{-2} at 377 nm) while the excitation beam (0.3 W cm^{-2} at 351 nm) is generated from an Ar/Kr^{+} ion laser. A mask is used to reduce the emission from the nanoparticles and the scattering of the excitation beam. The sample of the nanoparticles is placed into the cuvette and the solution is added to the nanoparticles to fill the chamber. The emission from the nanoparticles is collected 90° from the probe beam using a N_2 Cooled CCD.

Red Light Stimulation: **TSUA**-Modified MCM-41 nanoparticles with **Py-*β*-CD** associated to the azobenzene unit of TSUA were prepared using the aforementioned methods. An Ar/Kr^{+} laser light (0.8 W cm^{-2} at 647 nm) came from a diode laser (0.4 W cm^{-2} at 377 nm) was employed as the excitation source for monitoring (see Figure S8).

On-Off Experiments: **TSUA**-Modified nanoparticles with associated **Py-*β*-CD** were produced by aforementioned methods. The nanoparticles (15 mg) were placed into the glass cuvette for analysis. For this experiment, the excitation beam was blocked at certain times with a beam stop and allowed to irradiate the nanoparticles at other times. Excitation was induced with an Ar/Kr^+ ion laser (0.3 W cm^{-2} at 351 nm). The experimental results are shown in Figure S8.

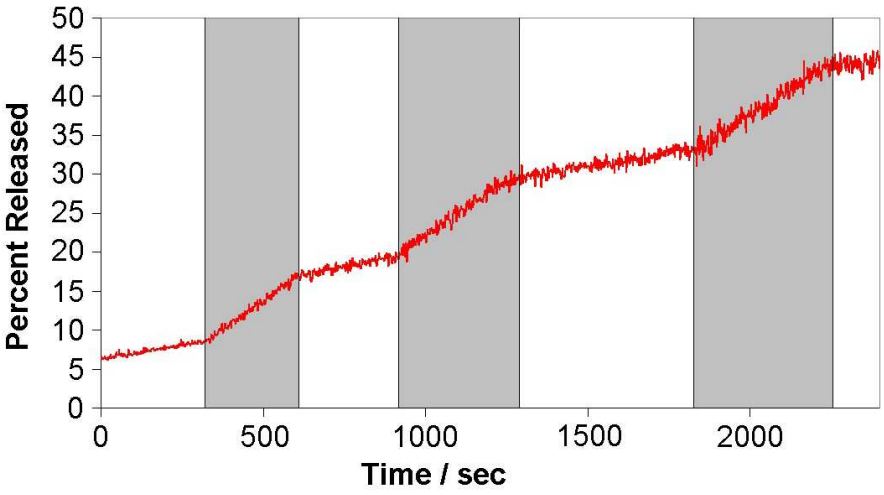

Figure S8. Demonstration of the UV-light effect has on the release of **Py-*β*-CD** when exposed to radiation (dark regions) and when left exposed only to the probe beam (light regions). In comparison, the regions where the nanoparticles are irradiated have a much greater rate of release than the regions where only the probe beam is blocked. This observation indicates that the release of the **Py-*β*-CD** capping group is stimulated by the UV radiation. Note that 100% is determined by allowing the sample to be irradiated for 400 min.

Power Dependence Investigation: **TSUA**-Modified MCM-41 nanoparticles with **Py-*β*-CD** associated to the azobenzene units of **TSUA** were prepared via aforementioned methods. The investigation was conducted by running two sets of sample independently with different powers from the laser. The nanoparticles (15 mg) were placed in a glass cuvette and exposed to an excitation beam (0.2 W cm^{-2} at 351 nm) for 30 min. Subsequently, the nanoparticles (15 mg) from

the same batch of prepared nanoparticles were placed into a glass cuvette and exposed to an excitation beam (0.7 W cm^{-2} at 351 nm) for 30 min. The experimental results are displayed in Figure S9 with the red analysis, as well as compared to the baseline. Note that the nanoparticles were exposed only to continuous probe beam.

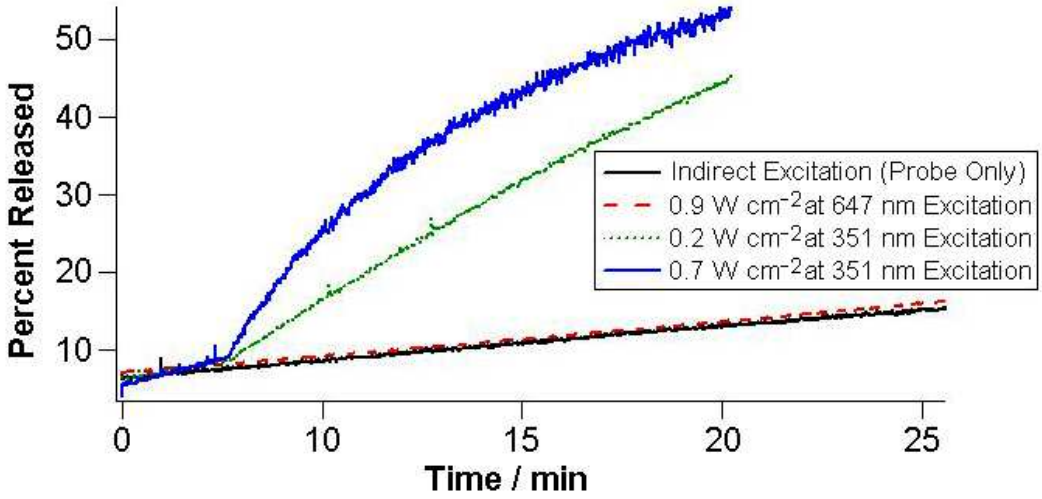

Figure S9. Release of **Py-*β*-CD** from the **TSUA**-Modified MCM-41 nanoparticles when monitored at 488 nm. The bottom trace is the "baseline" for all the experiments. It indicates the release of **Py-*β*-CD** under stimulation by the probe beam. It can be seen that the release under 647 nm light follows the exact slope of the baseline, indicating that light (no absorption by the azobenzene unit) does not induce release from the nanoparticles. The top two traces show the power dependence of the release mechanism as more power causes a greater rate of release. Note that 100 % release was determined by allowing the sample to be irradiated for 400 min.

The power dependence experiment was performed by increasing the power of the laser on the same sample to observe a change in rate of release. The **Py-*β*-CD**-capped nanoparticles (15 mg) were prepared by aforementioned methods and placed into a glass cuvette. The excitation beam (351 nm) was started at a 0.02 W cm^{-2} of power and then it was ramped up to 0.09 W cm^{-2} and

later to 0.4 W cm^{-2}. The sample was exposed to the probe beam only part of the time so that the effect of only the excitation beam can be monitored (see Figure S10).

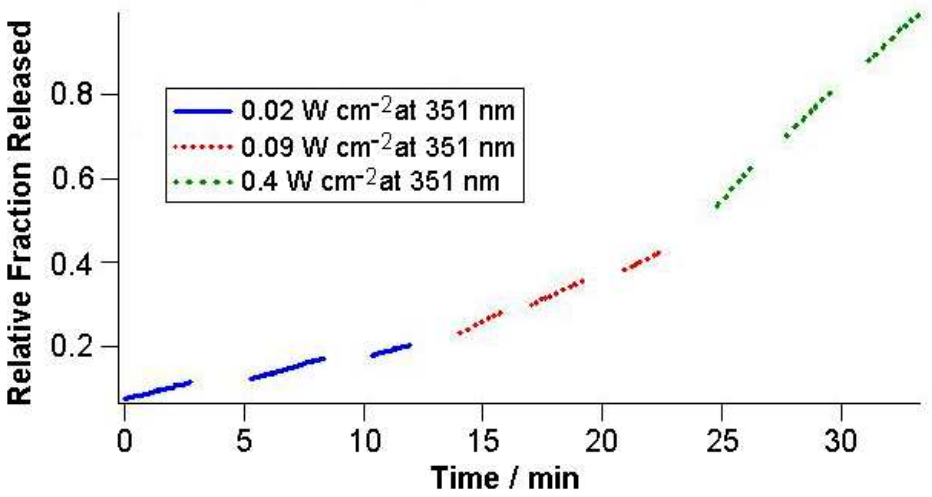

Figure S10. When the nanoparticles were exposed to a 0.02 W cm^{-2} of power, very little release was observed. As the power was increased to 0.09 and 0.4 W cm^{-2} over time, the slope noticeably increases. It is important to note that the nanoparticles did not change in this experiment, so when the nanoparticles were exposed to a 0.09 W cm^{-2} of power and later to a 0.4 W cm^{-2}, the nanoparticles have already released some of **Py-*β*-CD**. This observation means that the initial rates of release under these powers would be of even greater slope.

Stability of TSUA-Modified MCM-41 Nanoparticles: **TSUA**-Modified MCM-41 nanoparticles were prepared using aforementioned methods. The nanoparticles (15 mg) were placed in two glass cuvettes with THF (3 mL). THF was employed because **TSUA** and any other potential decomposition products are highly soluble in this solvent. One set of the **TSUA**-Modified MCM-41 nanoparticles was exposed to a light (0.3 W cm^{-2} at 351 nm) for 1 h while the other was kept in the dark for the same duration. The UV-Vis spectra of the two samples were identical and displayed no release of the azobenzene fragments into solution, indicating that there is no degradation of the TSUA-derived stalks under the experimental conditions. Figure S11 shows the UV-Vis spectra of **TSUA** and 4-aminoazobenzene for comparison.

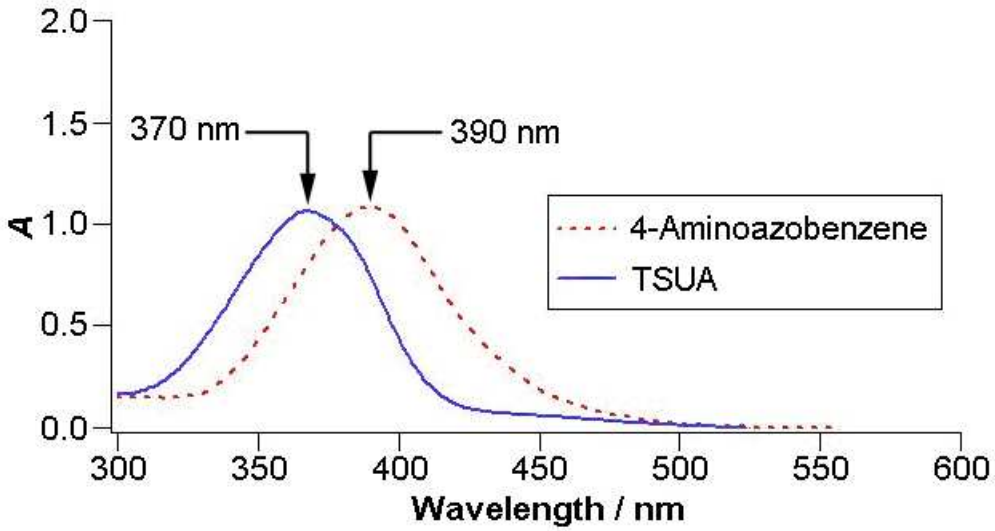

Figure S11. UV-Vis spectra of **TSUA** and 4-aminoazobenzene taken in THF. If the **TSUA**-Modified MCM-41 nanoparticles were decomposed to release the **TSUA** and/or 4-aminoazobenzene fragments under the current experimental conditions, either the peak of the **TSUA** units would grow in (if cleaved from the silica) or the 4-aminoazobenzene would be created by the photo-cleavage of the carbamide bond. The resulting UV-Vis spectrum (not shown here) of the **TSUA**-Modified MCM-41 nanoparticles displayed neither peak, leading to the conclusion that the **TSUA**-Modified MCM-41 nanoparticles are not photo-cleaved under the current experimental conditions.

Probe Beam Excitation (Dark Investigation): **TSUA**-Modified MCM-41 nanoparticles with **Py-*β*-CD** associated to the azobenzene unit of **TSUA** were prepared using aforementioned methods. No excitation beam was utilized during this portion of the experiment. A light line (0.4 W cm^{-2} at 351 nm) from a diode laser was employed to monitor the solution. For the experiment, the laser was blocked from the sample for 5 min and then exposed to the sample for 10 s. The control was exposed continuously to the light (0.4 W cm^{-2} at 351 nm). The experimental results are shown in Figure S12 and Figure 3 in the Manuscript.

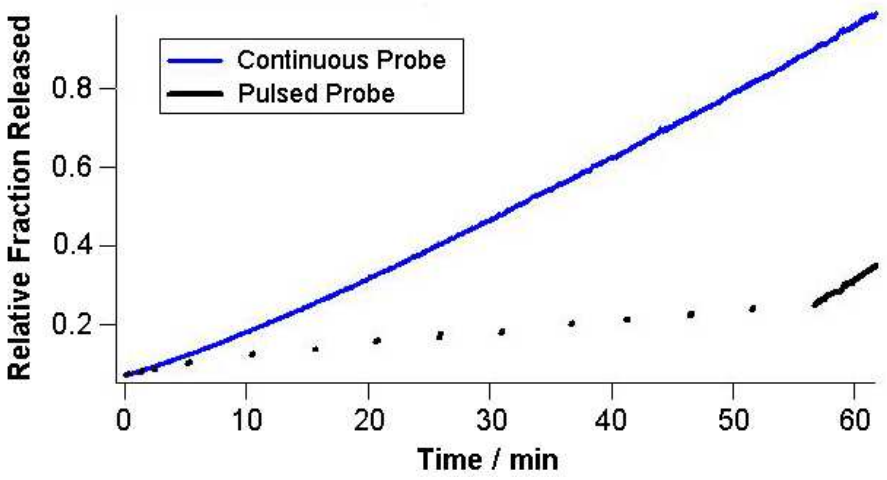

Figure S12. The light effect for the release of **Py-*β*-CD** from the nanoparticles with and without UV exposure. Under the conditions of limited UV exposure, the slope of the traces indicates the release of **Py-*β*-CD** because of non-light stimulated dissociation, or slippage from the thread. When the probe beam is exposed to the sample just long enough to get an absorbance reading (the bottom trace), it can be seen that the slope is dramatically less than when the probe beam is allowed to irradiate the sample continuously. It is also important to note that the slopes of both traces match each other when probed continuously – namely, from 55 min to 60 min in the figure. This observation indicates that all samples that are exposed continuously to light will have a slope that is a product of the probe beam excitation and not a product of the instability of the system.

Effect of pH on the Release of Rhodamine B: The pH of solution before release of Rhodamine B was determined to be 7.02 by using an Accumet 915 pH meter. After the release of the dye, the pH of the solution was determined to be 7.41. As the isoelectric point of silica has a pH of about 2, the change from 7.02 to 7.41 would induce very little change in the silica surface charge. Therefore, the change in pH in the solution would not explain the release profiles observed during experimentation.

It is important to note that the Rhodamine B is not completely removed from the silica during the release process. Some of the dye remains on the particle surface. For this reason, the data collected

is done in terms of Rhodamine B that is released, not the total amount of Rhodamine B present on and inside of the MCM-41 matrix.

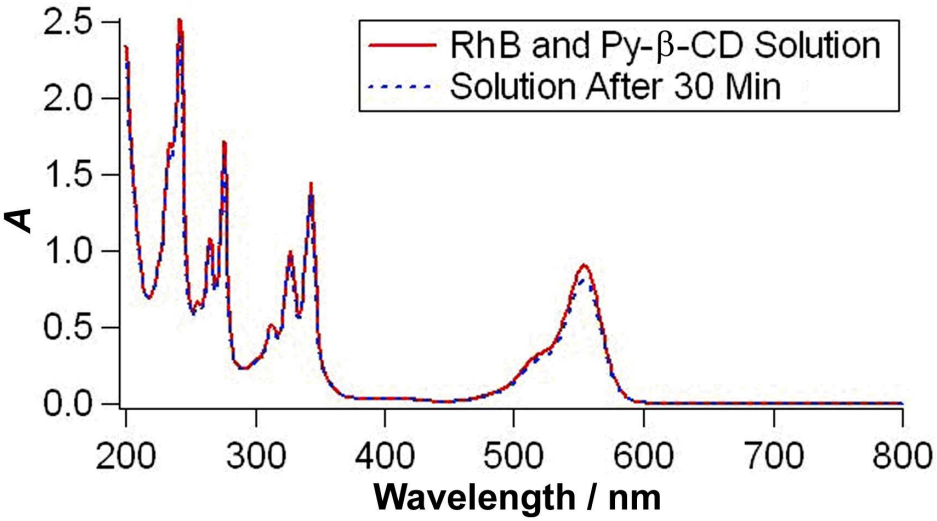

Figure S13. A spectrum of an aqueous solution containing both Rhodamine B (λ_{max} = 565 nm) and **Py-*β*-CD** (peak from 220~350 nm). Mixing of the two fluorescent molecules causes no shifts in the peak maxims as compared to solutions that contain only one of the fluorescent molecules (not shown). This indicates that there is no reaction between the two fluorescent molecules during the release of Rhodamine B from the MCM-41 nanoparticles. Interaction between the molecules is limited as Rhodamine B is cationic and *β*-CD cavity is hydrophobic.

References

[S1] Petter, R. C.; Salek, J. S.; Sikorski, C. T.; Kumaravel, G.; Lin, F.-T. *J. Am. Chem. Soc.* **1990**, *112*, 3860–3868.

[S2] May, B. L.; Kean, S. D.; Easton, C. J.; Lincoln, S. F. *J. Chem. Soc., Perkin Trans. 1* **1997**, 3157–3160.

[S3] (a) Liu, N.; Yu, K.; Smarsly, B.; Dunphy, D. R.; Jiang, Y.-B.; Brinker, C. J. *J. Am. Chem. Soc.* **2002,** *124*, 14540–14541. (b) Liu, N.; Dunphy, D. R.; Rodriguez, M. A.; Singer, S.; Brinker, C. J. *Chem. Comm.* **2003,** 1144–1145.