Experimental Section

Reagents and solvents were commercially available and were used as received. [Ru(bpy)$_2$(PPh$_3$)$_2$Cl]Cl was synthesized according to the literature.[1]

Instrumental Methods, Conditions and Parameters for Structural Characterization

Powder XRD diffraction data were collected on a Scintag XRD 2000 X-ray diffractometer using Cu (Kα) radiation. Nitrogen adsorption and desorption isotherms, surface areas, and median pore diameters were measured using a Micromeritics Tristar 3000 surface area and porosity analyzer. Sample preparation included degassing at 100 °C for 5 h. Specific surface areas and pore size distributions were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) method, respectively. Particle morphology of the material was determined by SEM using a JEOL 840A scanning electron microscope. TEM images were taken on FEI-Tecnai G2-F20 transmission electron microscope.
Synthesis of mercaptopropyl-functionalized MSN material (MP-MSN)

\( n\)-Cetyltrimethylammoniumbromide (CTAB, 1.00 g, \(2.74 \times 10^{-3}\) mol) was first dissolved in 480 mL of Nanopure water. NaOH(aq) (2.00 M, 3.50 mL) was added to the CTAB solution, followed by adjusting the solution temperature to 353 K. TEOS (5.00 mL, \(2.57 \times 10^{-2}\) mol) was first introduced dropwise to the surfactant solution, followed by dropwise addition of 3-mercaptopropyltrimethoxysilane (MP-TMS) (0.97 mL, \(5.13 \times 10^{-3}\) mol). The mixture was allowed to stir for 2 h to give rise to a white precipitate (as-synthesized MP-MSN). The solid product was filtered, washed with copious amount of deionized water and methanol, and dried for 12 h under high vacuum at 353 K in order to stabilize the mesoporous structure. Final mercaptopropyl-MSN material was obtained upon removal of the CTAB surfactant template by stirring in a solution of conc. HCl in methanol (1%, v:v) for 6 h at 60ºC. Material was then additionally washed with copious amount of deionized water and methanol, and it was again placed under high vacuum at 353 K to remove the remaining solvent from the mesopores.

Loading of sulforhodamine 101 into the mesopores of MP-MSN and capping with \([\text{Ru(bpy)}_2(\text{PPh}_3)\text{Cl}]\text{Cl}\)

MP-MSN (100 mg) was added to an aqueous solution (3.0 mL) of sulforhodamine 101 (1.0 mg mL\(^{-1}\)) and the suspension was stirred for 24 h at RT. A separate solution (2.0 mL) of sulforhodamine 101 (1.0 mg mL\(^{-1}\)) was prepared containing \([\text{Ru(bpy)}_2(\text{PPh}_3)\text{Cl}]\text{Cl}\) (100 mg) and the solution was degassed with Ar prior to heating at 80 ºC for 1 h. After this time the solution containing \([\text{Ru(bpy)}_2(\text{PPh}_3)\text{Cl}]\text{Cl}\) and Sr101 was added to the
suspension containing MP-MSN and Sr101, which was previously degassed with Ar. Combined solution was protected from light and was heated at 80 °C for 24 h under argon. As-synthesized material (SR101@[Ru]-MP-MSN) was filtered, washed with copious amounts of PBS buffer (pH 7.4, I = 154 M), water and methanol and finally dried in lyophilizer. The filtrate was collected and the loading of SR101 was determined from the difference in UV-VIS absorption of the filtrate in PBS solution vs. starting concentration.

**Release kinetics measurements**

Suspensions of the cargo loaded material (1 mg mL⁻¹) were prepared in PBS solution and the drug release was measured for sulforhodamine 101 by fluorescence emission at 595 nm (exc. 568 nm) and by UV-VIS spectroscopy (maximum at 568 nm); and for the release of capping ruthenium complex by measuring UV-VIS absorbance at 288 nm. After initial stirring for a prolonged time while protected from light, the suspensions were subjected to visible light irradiation with a photoreactor equipped with 3 serially connected LEDs (Luxeon III Star LED - Royal Blue Lambertian, 340 mW, 700mA, emission maximum at 455 nm, I = 1500 lux). Other suspensions of the same concentration were used for testing the influence of ligand substitution on cargo release or were not subjected to any stimuli and were stirred in dark (control samples). For ligand induced release, after 21 h of initial stirring in dark, solid KCN, histidine or imidazole were added into the stirred suspension of Sr101@[Ru]-MP-MSN in phosphate buffer (100 mM) to form 50 mM ligand total concentration. The release of the dye was monitored by fluorescence spectroscopy.
Figure 1. a) BET nitrogen adsorption/desorption isotherms and b) BJH average pore diameters for MP-MSN, Sr101@[Ru]-MP-MSN and [Ru]-MP-MSN.

Table S1. Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) data for MP-MSN, Sr101@[Ru]-MP-MSN and [Ru]-MP-MSN.

<table>
<thead>
<tr>
<th></th>
<th>MP-MSN</th>
<th>[Ru]-MP-MSN</th>
<th>Sr101@[Ru]-MP-MSN</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET Surface area</td>
<td>1082</td>
<td>610</td>
<td>522</td>
</tr>
<tr>
<td>(m² g⁻¹)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BJH pore diameter</td>
<td>2.3</td>
<td>≤2</td>
<td>≤2</td>
</tr>
<tr>
<td>(nm)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Figure S2.** Comparison of UV-VIS spectra of Sr101 before and after addition of [Ru(bpy)$_2$(PPh$_3$)Cl]Cl ([Ru]Cl) and MP-MSN.

**Scheme S3.** Schematic representation of visible light induced release of caps and cargo molecules from mercaptopropyl-functionalized MSN.