Supporting Information

Photoresponsive Real Time Monitoring Silicon Quantum Dots for Regulated Delivery of Anticancer Drug

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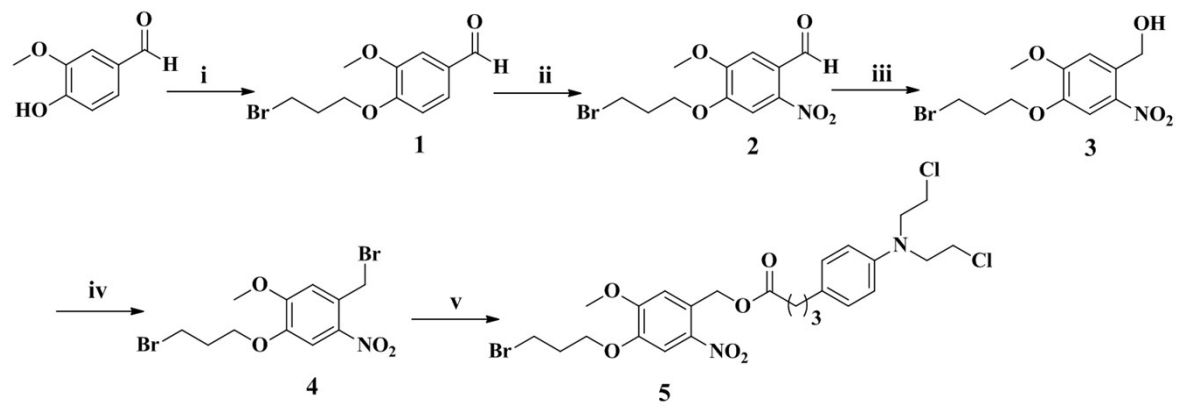
Supporting Information

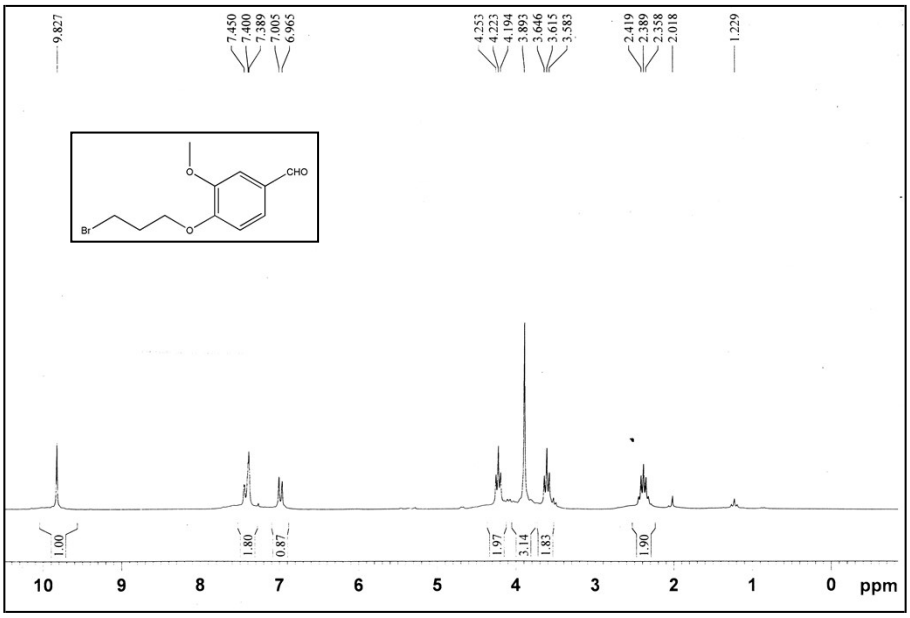
1. Synthesis of phototrigger *o*-nitrobenzyl chlorambucil conjugate:

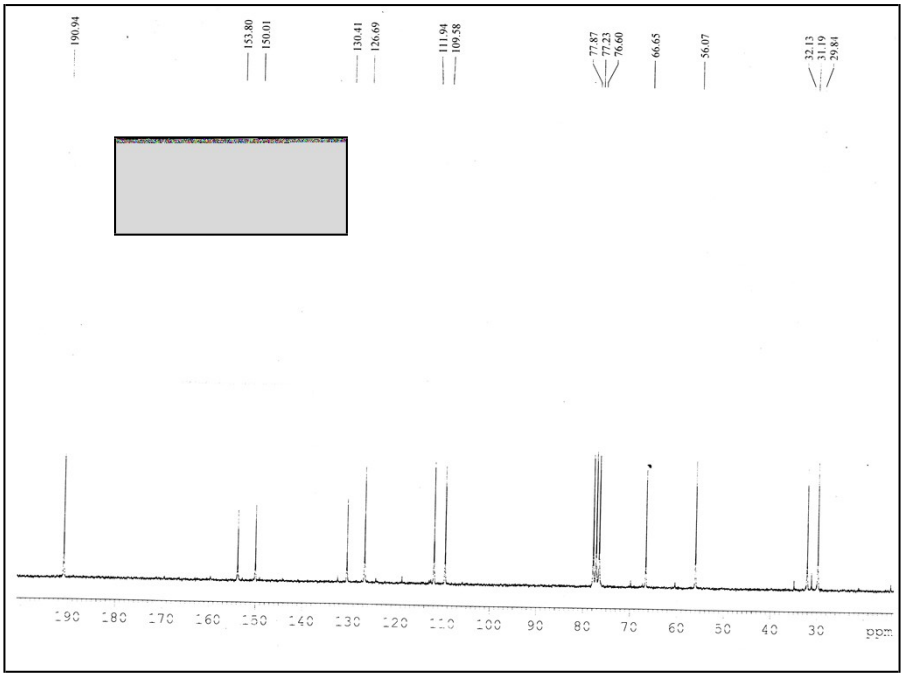


Reagents: (i) 1, 3 –Dibromopropane /K_2CO_3 /DMF at 80 °C /1 h; (ii) conc. HNO_3 at rt/1 h; (iii) $NaBH_4$/methanol at rt/1 h; (iv) PBr_3 /DCM at rt/1 h; (v) Chlorambucil/dry DMF/ K_2CO_3.

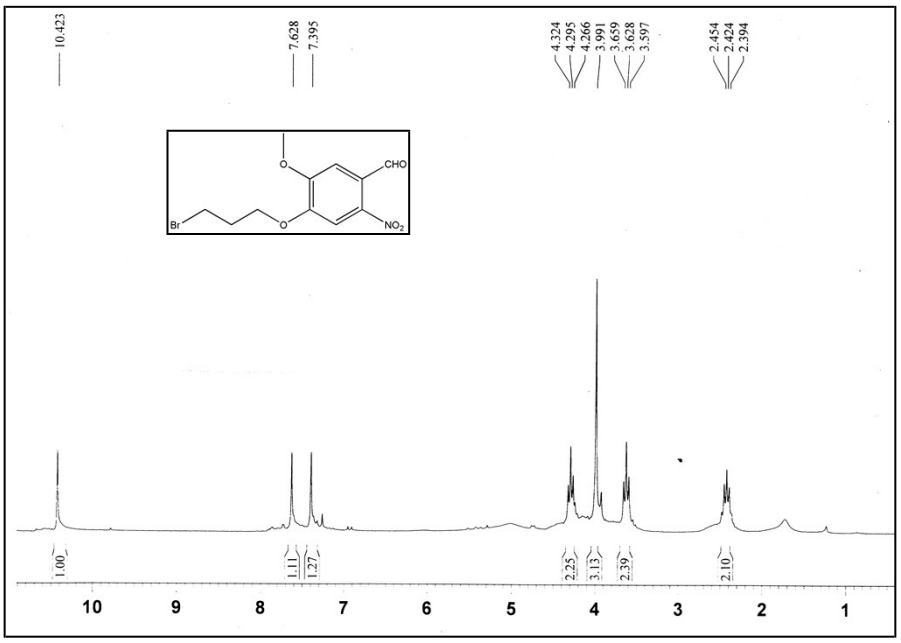
Scheme S1: Synthesis of *o*-nitrobenzyl chlorambucil conjugate.

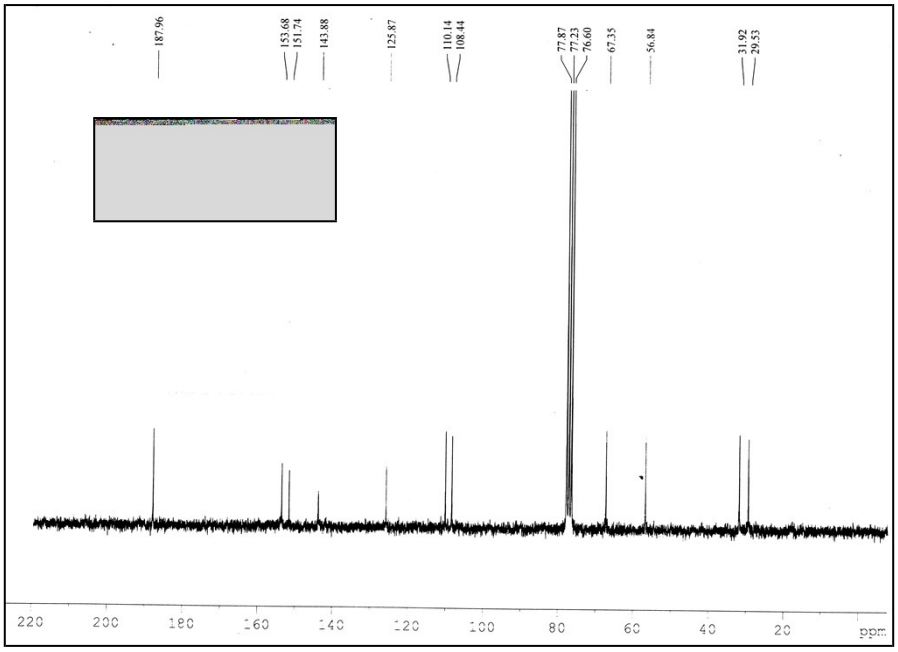
2.1. ^{1}H NMR ($CDCl_3$, 200 MHz) and ^{13}C NMR (50 MHz, $CDCl_3$) of 4-(3-bromopropoxy)5-methoxy-nitrobenzaldehyde (1)



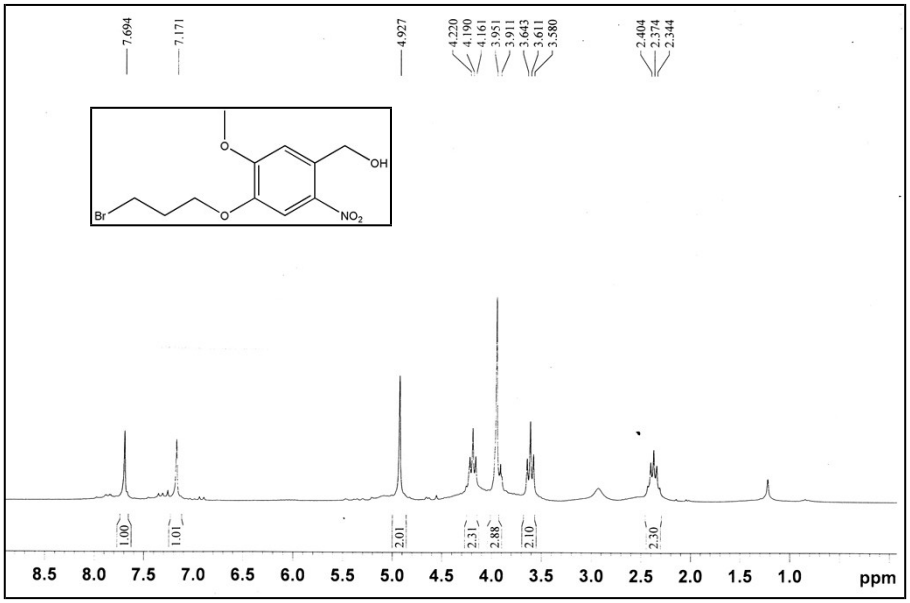


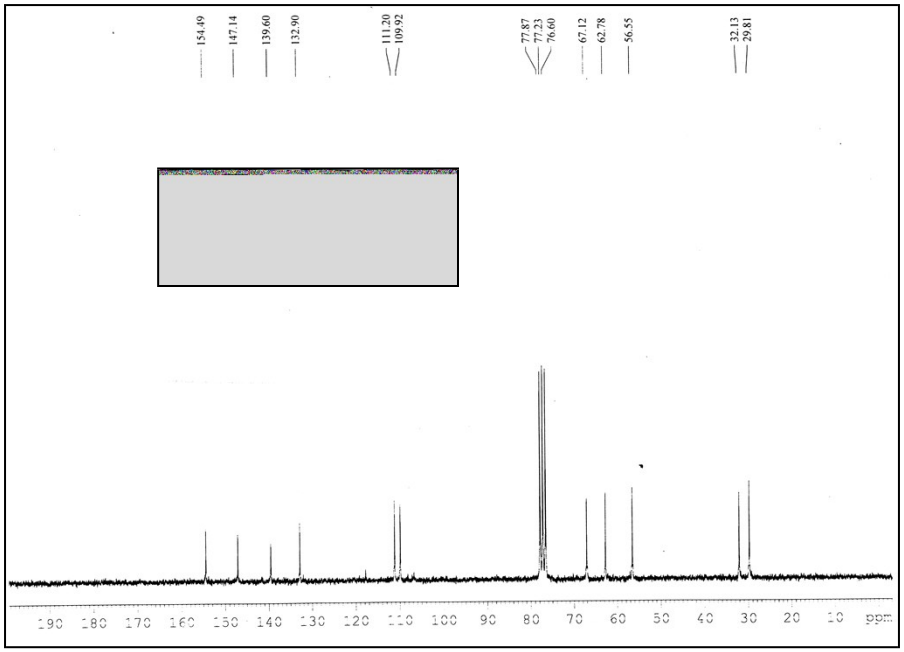
2.2. ^{1}H NMR (200 MHz, $CDCl_3$) and ^{13}C NMR (50 MHz, $CDCl_3$) spectra of 4-(3-bromopropoxy)-5-methoxy-2-nitrobenzaldehyde (2)



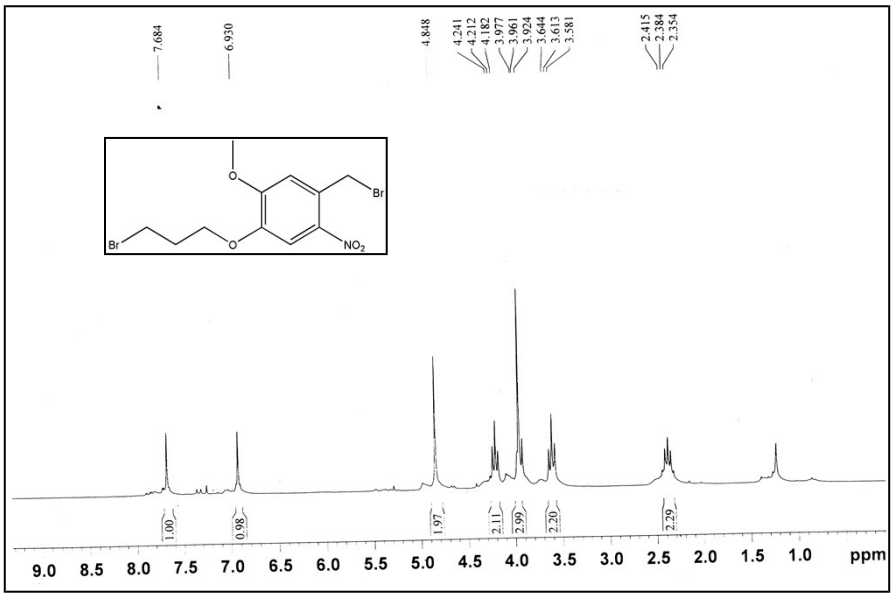


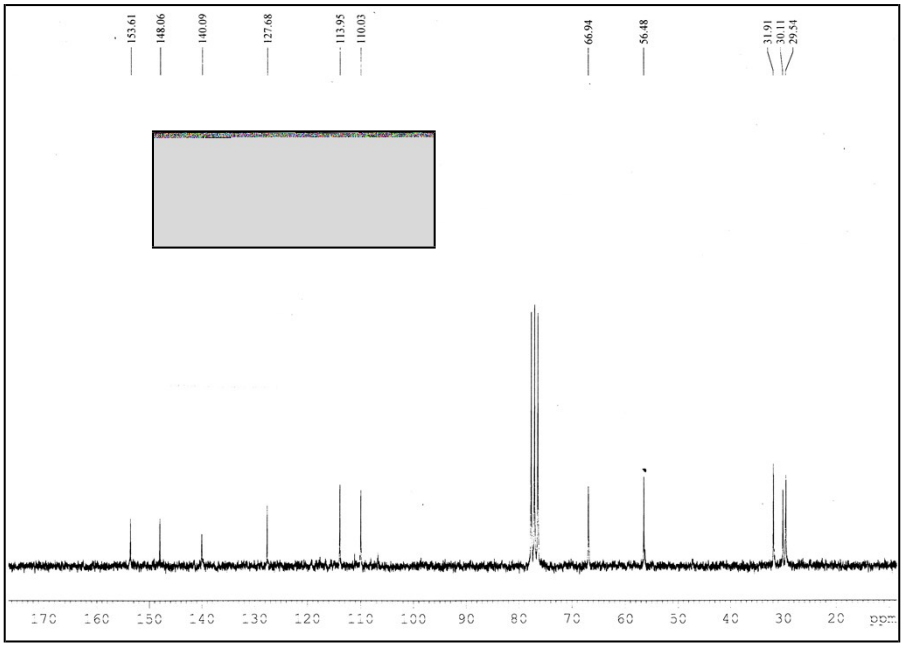
2.3. ^{1}H NMR ($CDCl_3$, 200 MHz) ^{13}C NMR (50 MHz, $CDCl_3$) spectra of 4-(3-bromopropoxy)-5-methoxy-2-nitrophenyl)methanol (3)



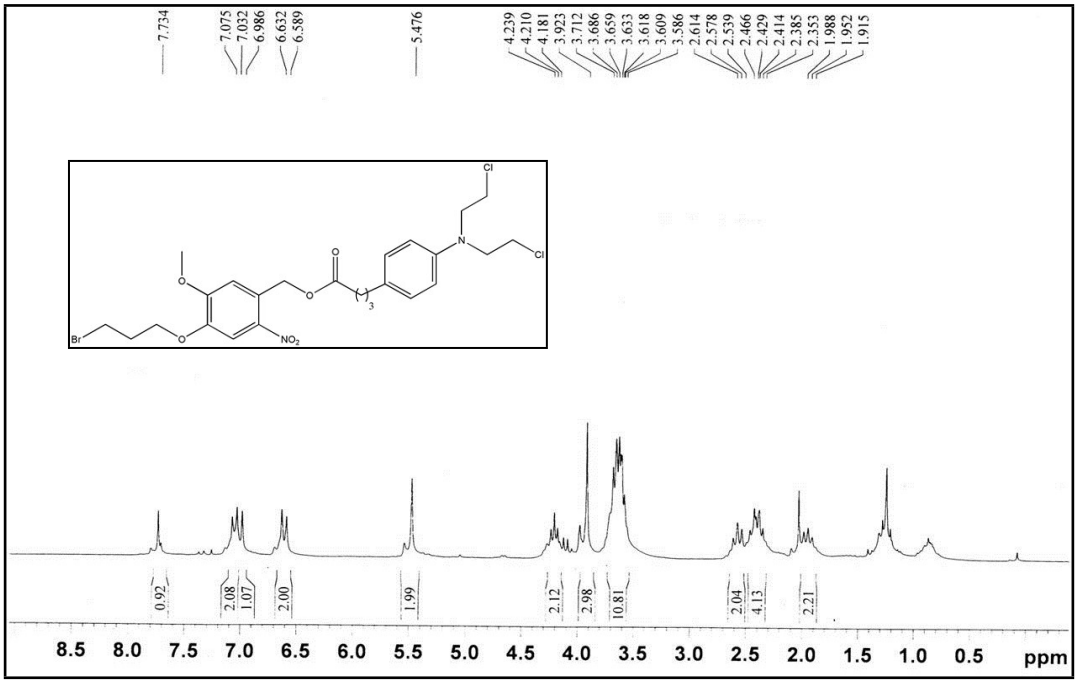


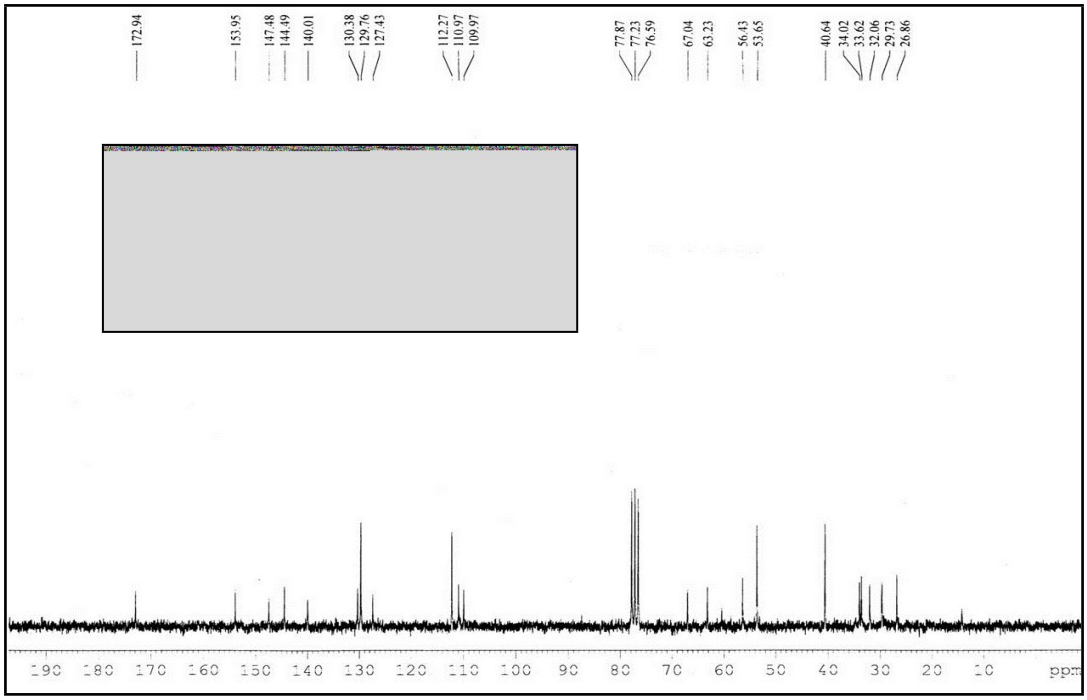
2.4. ^{1}H NMR ($CDCl_3$, 200 MHz) and ^{13}C NMR ($CDCl_3$, 50 MHz) spectra of 1-(bromoethyl)-4-(3-bromopropoxy)-5-methoxy-2-nitrobenzene (4)





2.5. ^{1}H NMR ($CDCl_3$, 200 MHz) and ^{13}C NMR ($CDCl_3$, 50MHz) spectra of 4-(3-bromopropoxy)-5-methoxy-2-nitrobenzyl chlorambucil (ONBCbl) (5)





3. Energy Dispersion X-Ray (EDX) pattern of ONBCbl-SiQDs

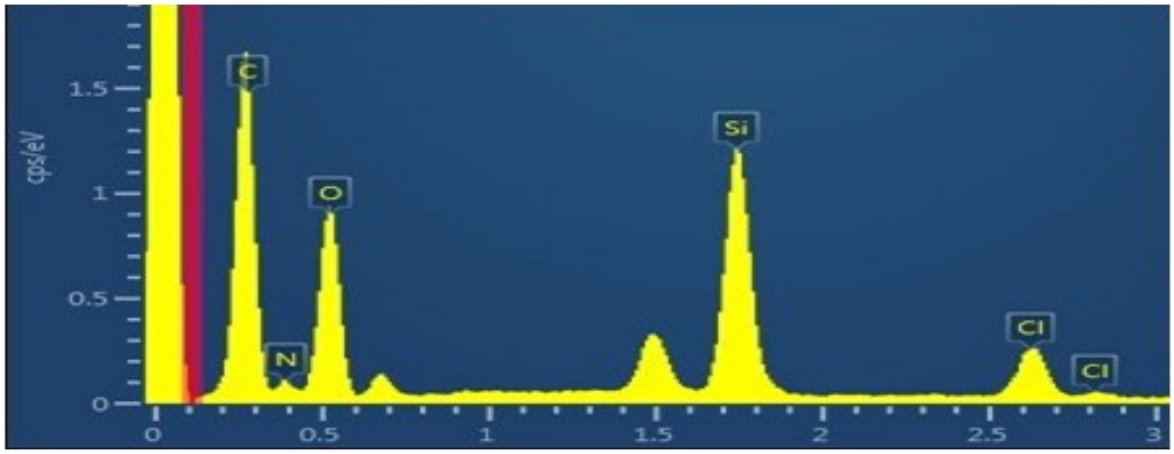


Figure S1: EDX pattern of ONBCbl-SiQDs showing the presence of constituent elements.

4. Loading of *o*-nitrobenzyl chlorambucil on SiQDs by absorption spectra.

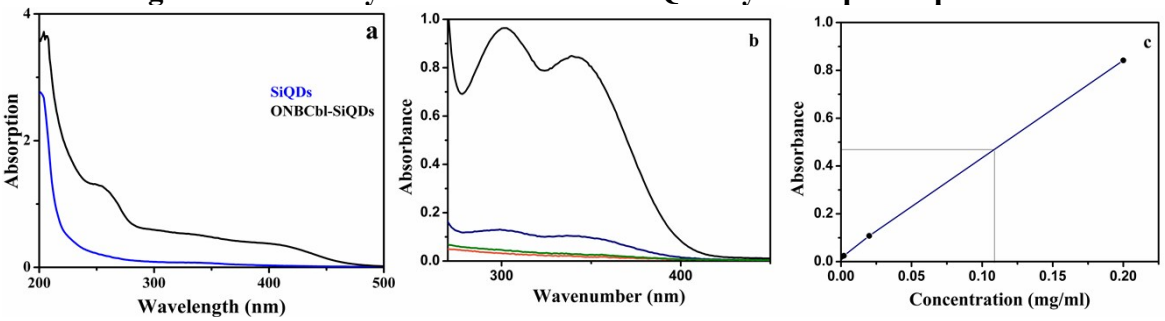


Figure S2: (a) UV-vis absorption spectra of silicon quantum dots and *o*-nitrobenzyl chlorambucil loaded silicon quantum dots, (b) standard UV-vis absorption spectra of *o*-

nitrobenzyl, (c) calibration curve for the concentration of ONBCbl-SiQDs in the reaction mixture.

The concentration of ONBCbl-SiQDs in the reaction mixture after 24 h obtained from the absorption spectra (x)= 0.114 mg/ml

Concentration of ONBCbl-SiQDs at 0 min obtained from absorption spectra (y) = 0.005 mg/ml

ONBCbl loaded on SiQDs

= x-y

= (0.114 - 0.005) mg/ml

= 0.109 mg/ml

= 0.109 mg of ONBCbl in 5 mg of SiQDs

= 0.0218 mg in 1mg of SiQDs

~ 22 μg/mg of ONBCbl was loaded on the SiQDs.

The amount of drug loaded on the nanoparticles was measured with UV–vis spectroscopy by dissolving drug-loaded nanoparticles in methanol. UV absorbance was monitored at a wavelength of 410 nm. The amount of the drug loaded was determined by calibration with a series of standards of known concentrations of drugs in the same solvent.

5. Measurement of fluorescence quantum yields[1]

The fluorescence quantum yield (QY) of the silicon quantum dots (SiQDs) was determined by the reference point method.[1] Quinine sulfate in 0.1 M H_2SO_4 (literature quantum yield: 54 %) was used as a standard sample to calculate the QY of SiQDs and ONBCbl-SiQDs, which were dissolved in acetonitrile. The absorbance values of the solutions at the excitation wavelength were measured by UV–Vis spectrophotometer. Photoluminescence (PL) emission spectra of all the sample solutions were recorded by Hitachi F-7000 fluorescence spectrophotometer at an excitation wavelength of 410 nm.

$$\frac{\Phi_S}{\Phi_R} = \frac{A_S}{A_R}\,\frac{(Abs)_R}{(Abs)_S}\,\frac{\eta_s^2}{\eta_R^2}$$

Where **Φ** represents quantum yield, **Abs** represents absorbance, **A** represents the area under the fluorescence curve, and **η** is the refractive index of the medium. The subscripts **S** and **R** denote the corresponding parameters for the sample and reference, respectively.

Table S1: Quantum yield of the fluorescent SiQDs and ONBCbl-SiQDs

Sample	Intergrated Emission Intensity (I)	Abs.	Refractive Index of Solvent (η)	Fluorescence Quantum Yield (QY)
Quinine sulfate	35605.59	0.058	1.33	54 % (known)
SiQDs	4268.27	0.035	1.327	18.8 %
ONBCbl-SiQDs	2345.49	0.043	1.327	4.2 %

Fluorescence quantum yield (excitation wavelength 410 nm, error limit within ± 5 %).

6. HPLC profile of chlorambucil release from ONBCbl-SiQDs:

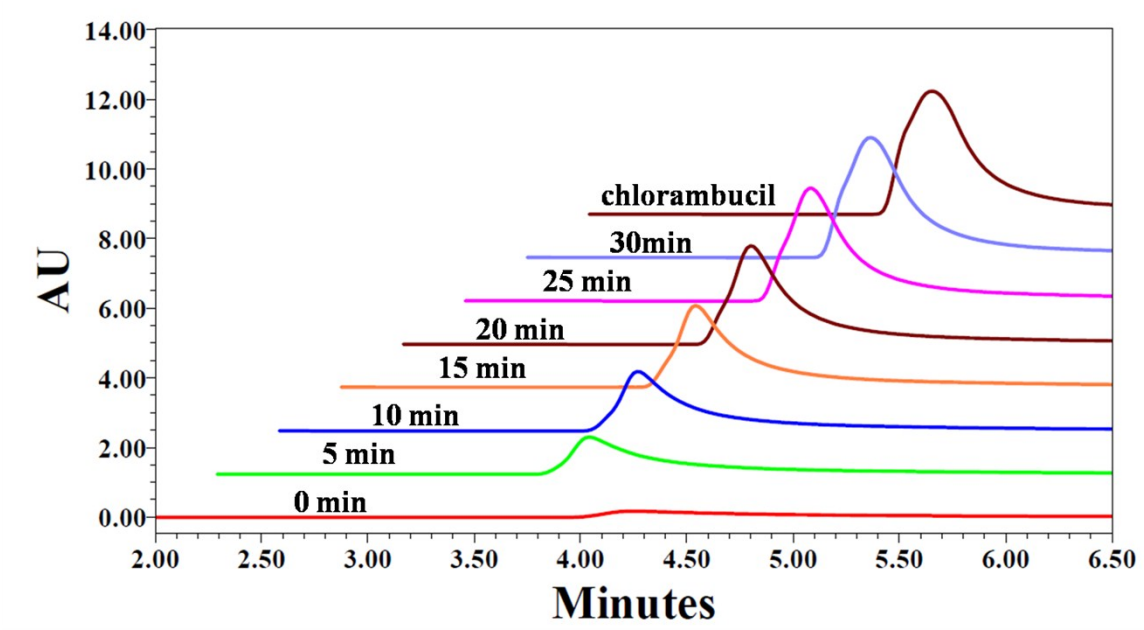


Figure S3: HPLC profile of chlorambucil release from ONBCbl-SiQDs upon irradiating with visible light (≥410 nm).) at regular intervals (0-30 min, time interval of 5 min). The *x-axes* was offset by 30 s, to facilitate better visualization.

References:

1. a) S. Mandal, C. Ghatak, V. G. Rao, S. Ghosh, N. Sarkar. *J. Phys. Chem. C* **2012**, 116, 5585−5597. S. Zhu; b) Q. Meng; L. Wang; J. Zhang; Y. Song; H. Jin; K. Zhang; H. Sun; H. Wang; B.Yang. *Angew. Chem. Int. Ed*. **2013**, 52, 3953 –3957.