Electronic Supplementary Information

Loading of an anti-cancer drug into mesoporous silica nano-channel and subsequent release to DNA

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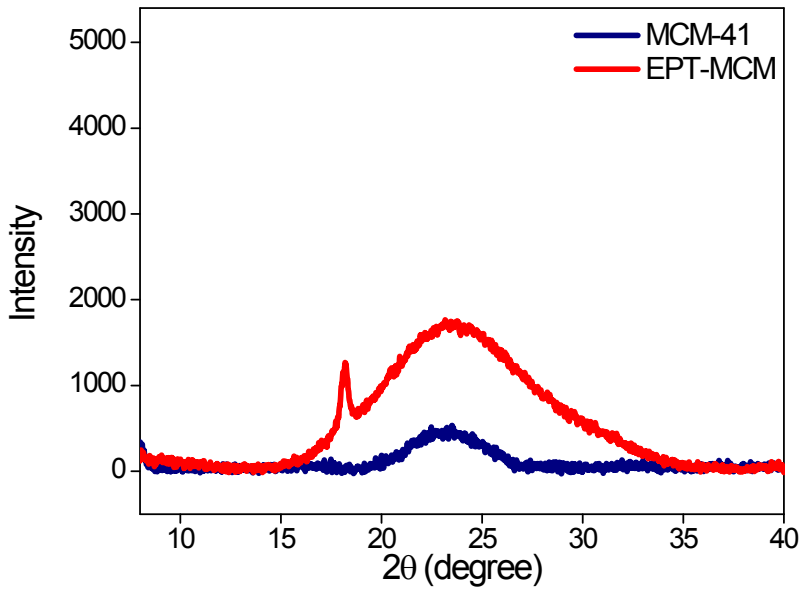

Fig. S1 Wide angle powder X-ray diffraction (PXRD) patterns of MCM-41 and EPT-MCM.

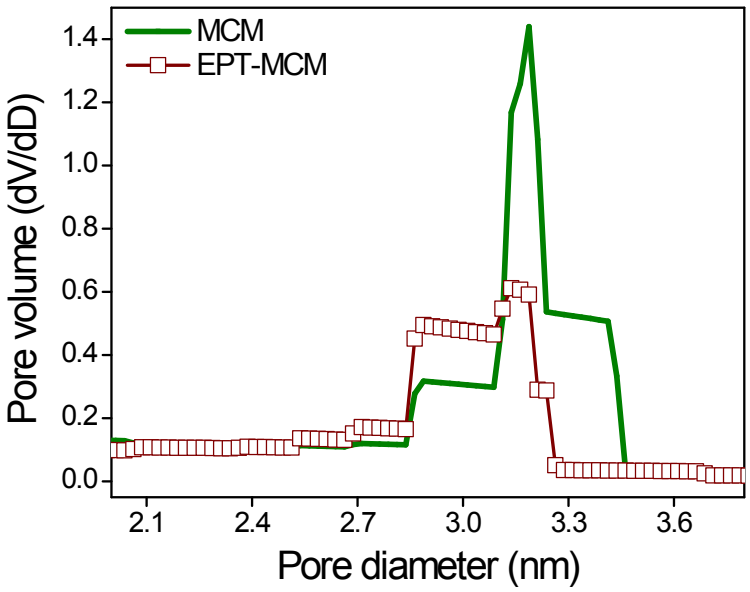

Fig. S2 Pore-size distribution of MCM-41 and EPT-MCM.

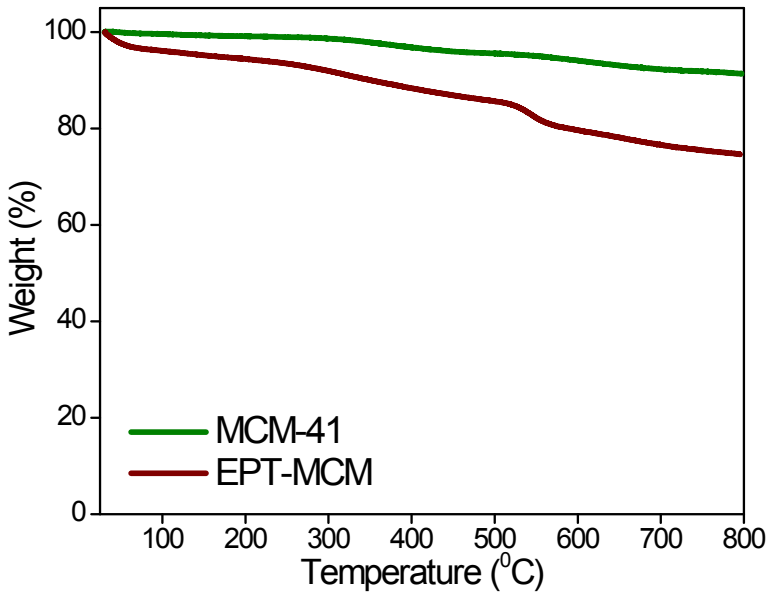

Fig. S3 Thermogravimetry analysis (TGA) of MCM-41 and EPT-MCM.

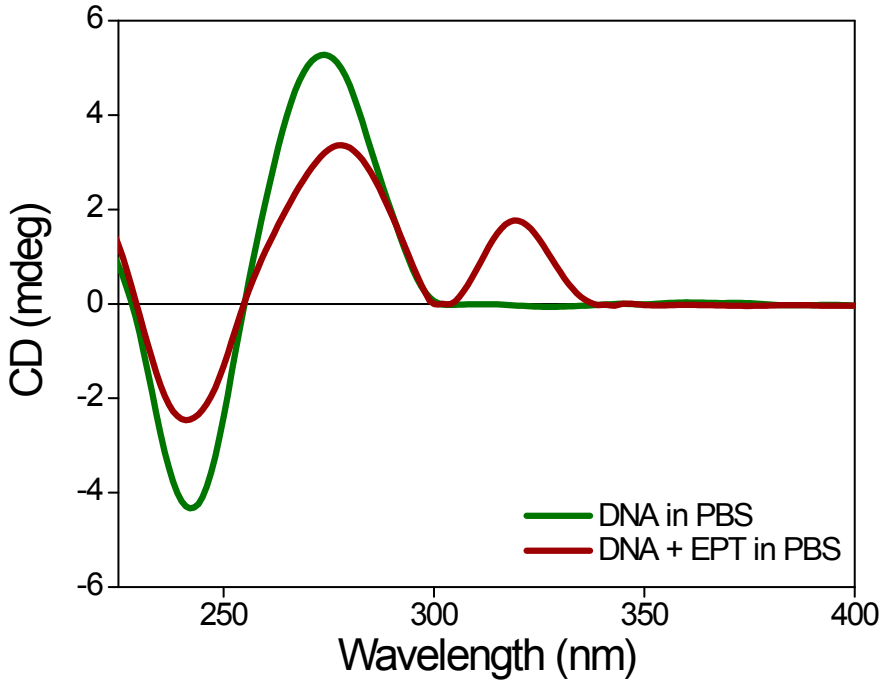

Fig. S4 Circular dichroism (CD) spectra of DNA in PBS presence and absence of EPT.

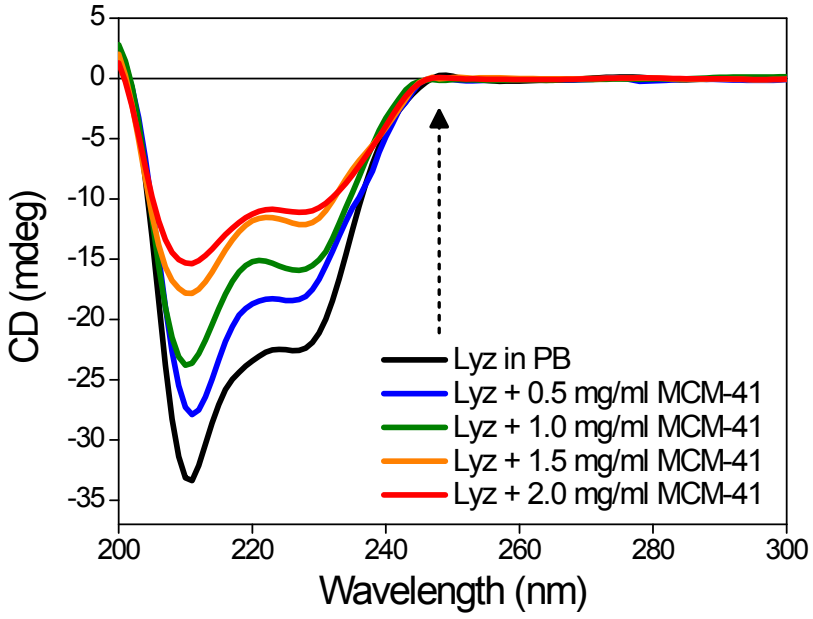

Fig. S5 CD spectra of lysozyme in presence and absence of MCM-41 in PBS solution.

Note S1

Calculation of the free-energy change of photo-induced electron transfer (PET)

To realizing feasibility of electron transfer process between aromatic amino acids and ellipticine, the free energy of PET (ΔG_{PET}) process was calculating by using the redox potentials of EPT and amino acids. The following equation (**Eqn. S1**) was used to obtain free energy,

$$\Delta G_{PET} = E_{D/D^+} - E_{A/A^-} - E_{0,0} \quad \text{(S1)}$$

where $E_{D+/D}$ is the redox potential of the donor (aromatic amino acids), $E_{A/A-}$ is the redox potential of the acceptor (EPT), and $E_{0,0}$ is the energy S_1 excitation energy of EPT. The $E_{0,0}$ value for EPT was estimated from the intersection point of the absorption and emission spectra of EPT. $E_{D+/D}$ values were obtained from literature reports.[1-4] $E_{A/A-}$ value of EPT was reported -1.35 V (Vs SCE).[3] Then the free-energy change of the PET (ΔG_{PET}) was calculated, and the value of ΔG_{PET} was negative in all cases, which explains the feasibility of PET in the various aromatic amino acids−EPT donor−acceptor systems (**Table S1**).

Table S1 Thermodynamic Parameters of PET between Different Aromatic Amino Acids and Ellipticine.

Donor	E_{D/D^+} (V)	ΔG_{PET} (eV)	ΔG_{PET} (kcal/mol^{-1})
Tryptophan	1.02	-0.343	-7.91
Tyrosine	0.93	-0.433	-9.98
Histidine	1.17	-0.193	-7.45

Note S2

Release kinetics

The drug release from the EPT-MCM and EPT-MCM-Lyz were performed at pH 7.4 (physiological pH). EPT loaded MCM-41 (EPT-MCM) was taken in a dialysis bag (in 1 mL), and immersed in a 20 mL of same phosphate buffer solution (pH 7.4) in a beaker and dialyzed at 37°C (physiological temperature) with constant stirring condition. In the case of EPT-MCM-Lyz, first lysozyme solution (60 μM) was prepared in 1 ml PBS, and then EPT-MCM was added to this solution. After that whole mixture was taken in a dialysis bag immersed in 20 mL of phosphate buffer solution (pH 7.4) in a beaker. For both EPT-MCM and EPT-MCM-Lyz systems, after each time intervals (0.5, 1, 2, 3, 5, 6, 10, 12, 18, 20, 24 and 32 hrs) 1 ml of dialysis medium was withdrawn and replaced with an equal volume of fresh buffer solution. The absorbance of each aliquot was determined at 300 nm using UV-Vis absorption spectrophotometer. The amount of EPT released was calculated using molar absorption coefficient as 39000 $M^{-1}cm^{-1}$ at 300 nm.[5] We found that there was 7% of drug released within the 1 hr duration. After that there was no significant drug release. In presence of lysozyme, there was only <3% of drug released within the duration of 1 hr. After that no release was found. This clearly indicates that Lyz acting as a pore blocker to prevent premature drug release form MCM-41.

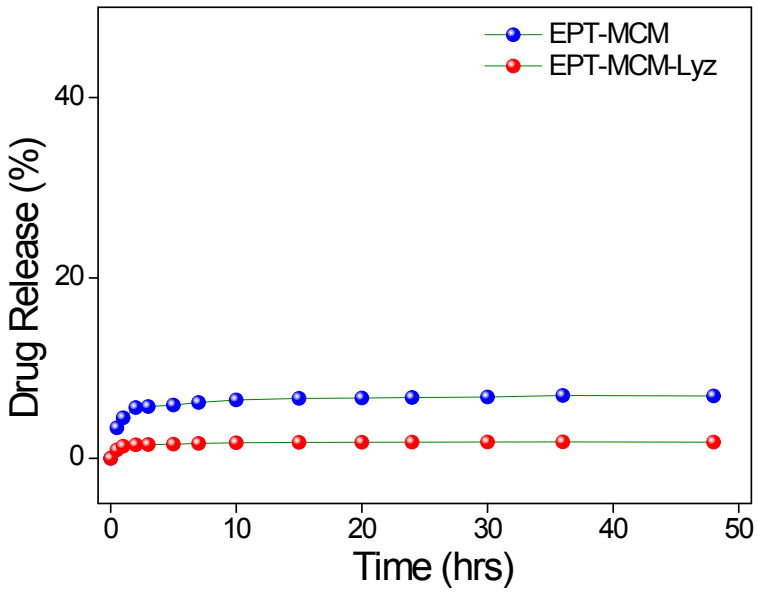

Fig. S6 Release profile of drug from EPT-MCM and EPT-MCM-Lyz systems at pH 7.4.

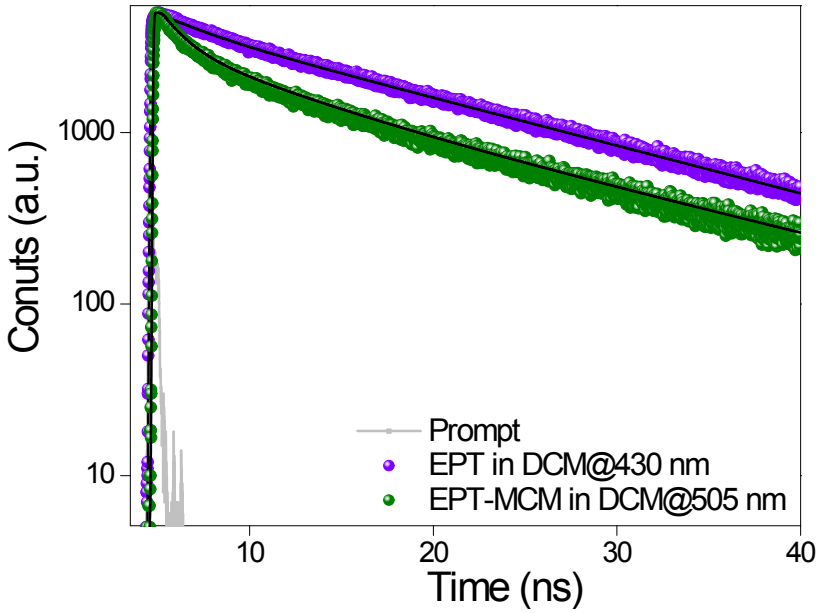

Fig. S7 Fluorescence transients of EPT (λ_{ex} = 375 nm) in DCM solvent decay collected at 430 nm (violate color decay) and fluorescence decay of EPT-MCM (λ_{ex} = 375 nm) in DCM solvent collected at 505 nm (green color decay).

Table S2 Fluorescence transient fittings of EPT (10 μM) in absence and presence of MCM-41 in DCM solvent, collected at respective emission maximum.

Sample	a_1	a_2	a_3	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	$^{\#}\tau_{avg}$ (ns)	χ^2
EPT in DCM at 430 nm	-	0.18	0.82	-	2.74	16.07	13.67	1.05
EPT-MCM in DCM at 505 nm	0.48	0.15	0.36	1.19	5.74	19.75	8.62	1.02

$^{\#}\tau_{avg} = (a_1\tau_1 + a_2\tau_2 + a_3\tau_3)$

Table S3 Fluorescence transient fittings of EPT (10 μM) in PBS; EPT-MCM in absence and presence of lysozyme (Lyz); EPT-MCM-Lyz system in presence of DNA, all decays are excited at 375 nm and collected at respective emission maximum.

Sample	a_1	a_2	a_3	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	$^{\#}\tau_{avg}$ (ns)	χ^2
EPT in PBS at 530 nm	0.87	0.13	-	1.91	5.74	-	2.41	1.08
EPT-MCM in PBS at 515 nm	0.34	0.43	0.23	0.59	3.314	13.48	4.74	0.99
E-MCM + DNA at 525 nm	-	0.17	0.83	-	5.035	15.78	13.96	1.04
E-MCM + Lyz at 515 nm	0.49	0.39	0.12	0.550	3.10	14.87	3.22	1.10
E-MCM + Lyz + DNA at 525 nm	0.30	0.23	0.47	0.157	2.54	15.1	7.75	1.02

$^{\#}\tau_{avg} = (a_1\tau_1 + a_2\tau_2 + a_3\tau_3)$

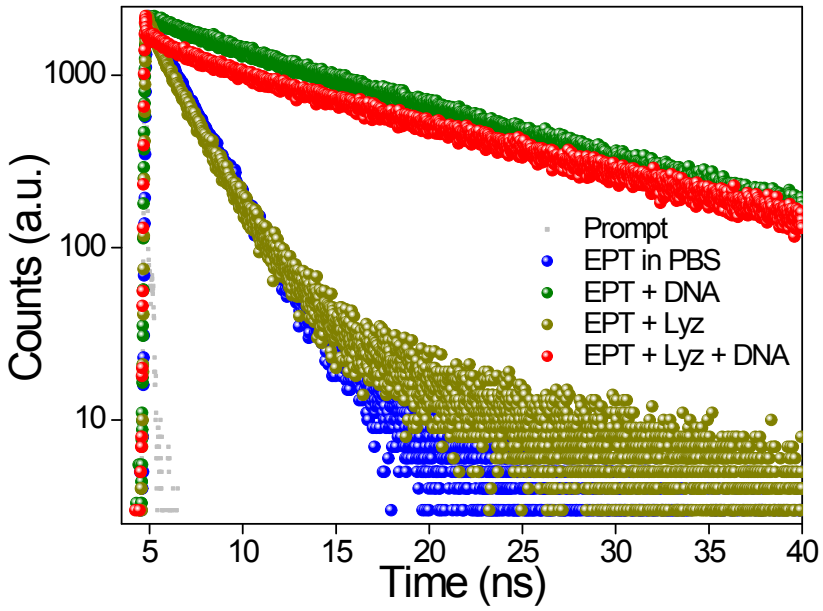

Fig. S8 Fluorescence transients of EPT (λ_{ex} = 375 nm) in presence of Lyz, DNA and Lyz-DNA.

Table S4 Fluorescence transient fittings of EPT (10 μM) in PBS, in presence of 100 μM DNA, in presence of 60 μM of lysozyme (Lyz) and EPT-Lyz system in presence of 90 μM DNA, all decays are excited at 375 nm and collected at respective emission maximum.

Sample	a_1	a_2	a_3	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	$^{\#}\tau_{avg}$ (ns)	χ^2
EPT in PBS at 530 nm	-	0.87	0.13	-	1.91	5.74	2.41	1.08
EPT + 100 μM DNA at 525 nm	-	0.15	0.85	-	2.02	16.01	13.91	1.04
EPT + 60 μM Lyz at 530 nm	0.30	0.62	0.08	0.50	2.06	9.02	2.15	1.03
EPT-Lyz + 100 μM DNA at 525 nm	0.29	0.30	0.41	0.50	2.41	16.34	7.56	1.02

$^{\#}\tau_{avg} = (a_1\tau_1 + a_2\tau_2 + a_3\tau_3)$

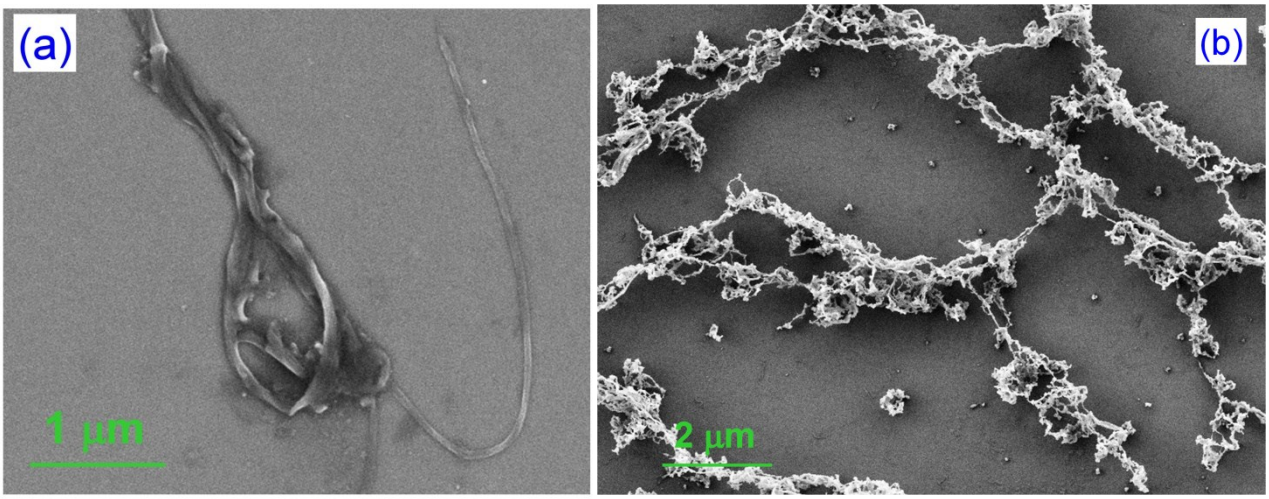

Fig. S9 FE-SEM image of (a) DNA and (b) lysozyme.

Note S3

EDAX Analysis

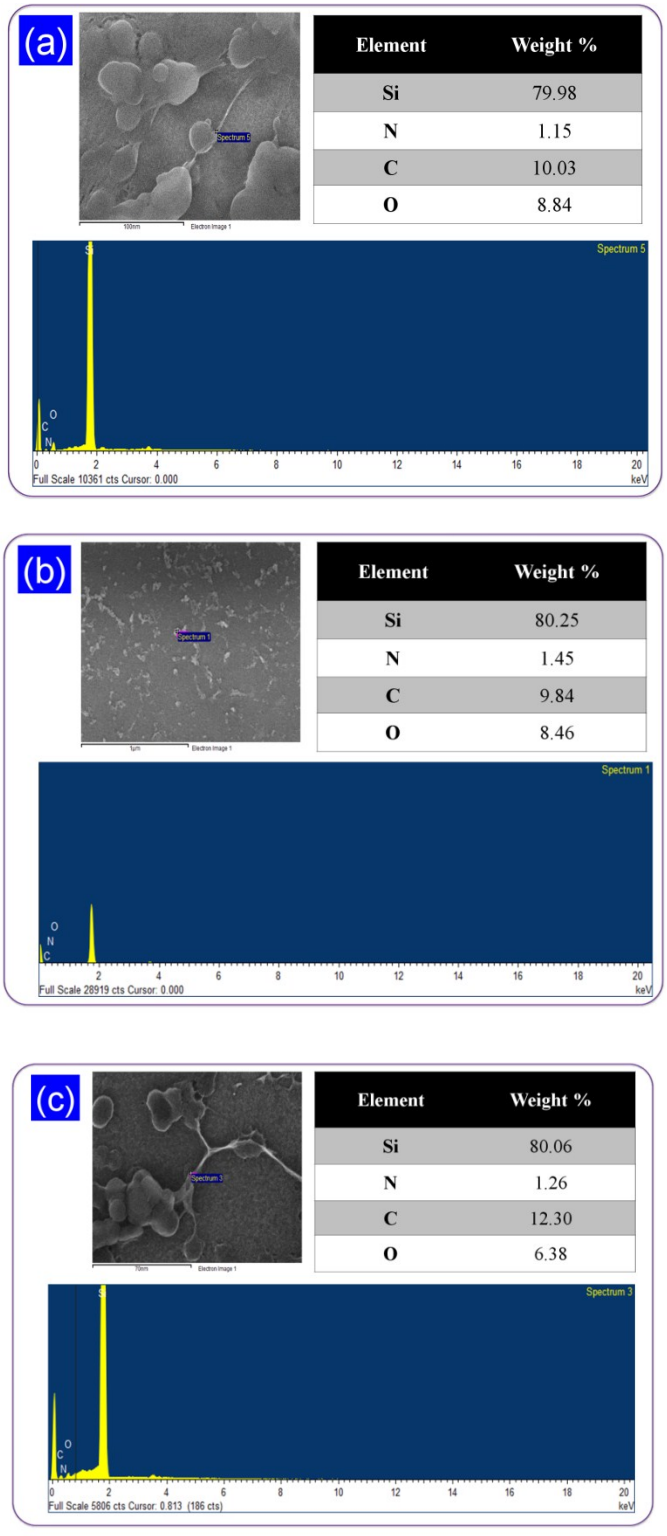

Fig. S10 EDAX analysis of (a) MCM-DNA, (b) MCM-Lyz, and (c) MCM-Lyz-DNA.

References

1. J. Moiroux and A. M. Armbruster, *J. Electroanal. Chem.*, 1984, **165**, 231-240.
2. J. Moiroux and A. M. Armbruster, *J. Electroanal. Chem.*, 1980, **114**, 139-146.
3. A. Anne and J. Moiroux, *J. Electroanal. Chem.*, 1982, **137**, 293-306.
4. T. Katerina, K. Ludmila, H. David, A. Vojtech, B. Petr, T. Libuse, S. Marie, E. Tomas and K. Rene, *Anticancer Agents Med Chem.*, 2014, **14**, 331-340.
5. F. Zsila, J. Kaman, B. Boganyi and D. Jozsvai, *Org. Biomol. Chem.*, 2011, **9**, 4127-4137.