Electronic supplementary information (ESI)

Lectin-gated and glycan functionalized mesoporous silica nanocontainers for targeting cancer cells overexpressing Lewis X antigen

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Materials characterization

Powder X-ray diffraction (PXRD) of as-made MSNs (see Fig. S1a) showed four low-angle peaks, corresponding to the (100), (110), (200) and (210) reflections of a hexagonal array, typical of MCM-41-type mesoporous materials. After extraction of the surfactant template, a slight shift of the main peak (assigned to the (100) Brag reflection) was observed, corresponding to a cell contraction of ca. 2 Å (Fig. S1b). PRXD pattern of all prepared solids are shown in the Fig. S1.

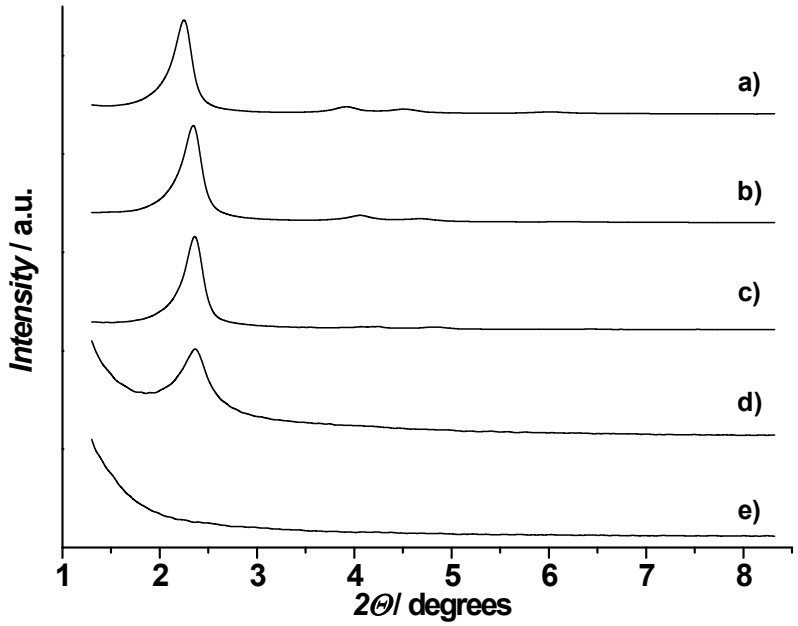

Fig. S1 PXRD patterns of as-synthesized MSNs a), extracted MSNs b), and solids **S1** c), **S2** d) and **S3** e).

Infrared spectra of all prepared solids are shown in Fig. S2.

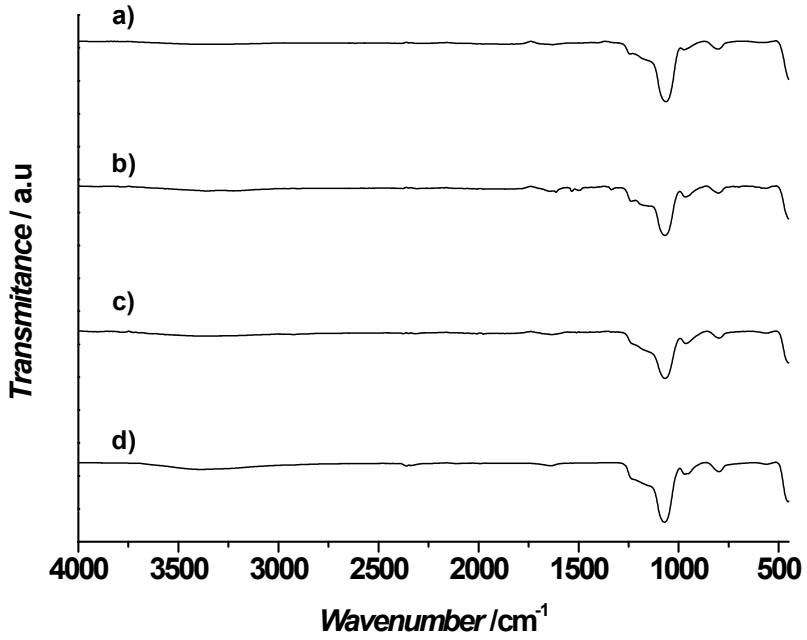

Fig. S2 Infrared spectra of MSNs a) and solids **S1** b), **S2** c) and **S3** d).

All materials were characterized by TEM. Fig. S3 show representative images of MSNs and solids **S1**, **S2** and **S3**.

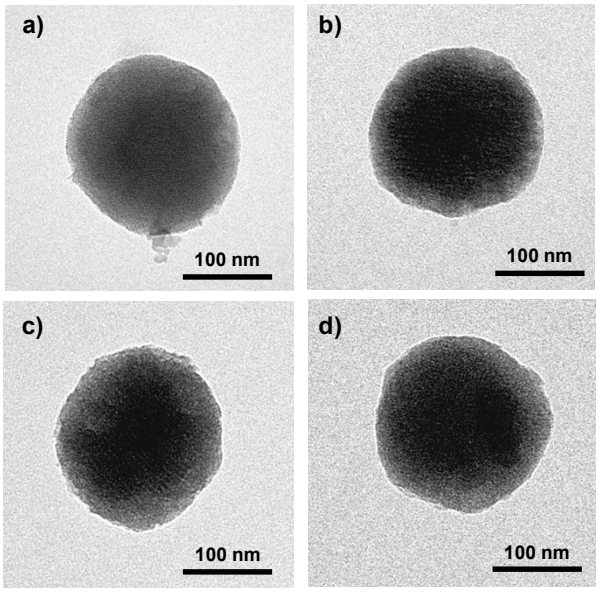

Fig. S3 Representative TEM images of MSNs a) and solids S1 b), S2 c) and S3 d).

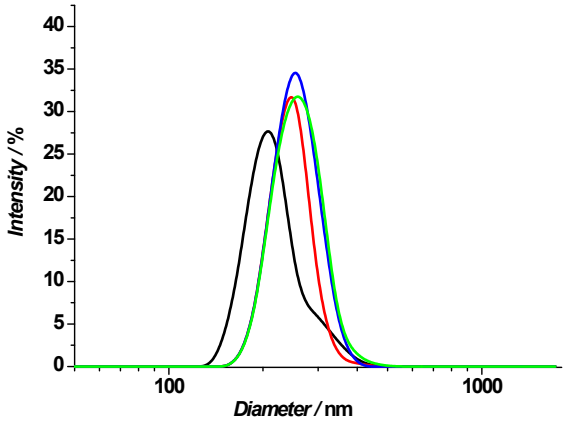

Fig. S4 Particle size distribution of MSNs (black) and solids **S1** (red), **S2** (blue) and **S3** (green).

From N_2 adsorption-desorption isotherm studies, a typical curve for mesoporous materials was observed for calcined MSNs. Application of the BET model yielded a total specific surface of 955.2 m^2/g and a pore volume of 0.75cm^3/g. The BJH model was also used at intermediate relative pressures, resulting in a narrow pore distribution centered at 2.52 nm (Fig. S5).

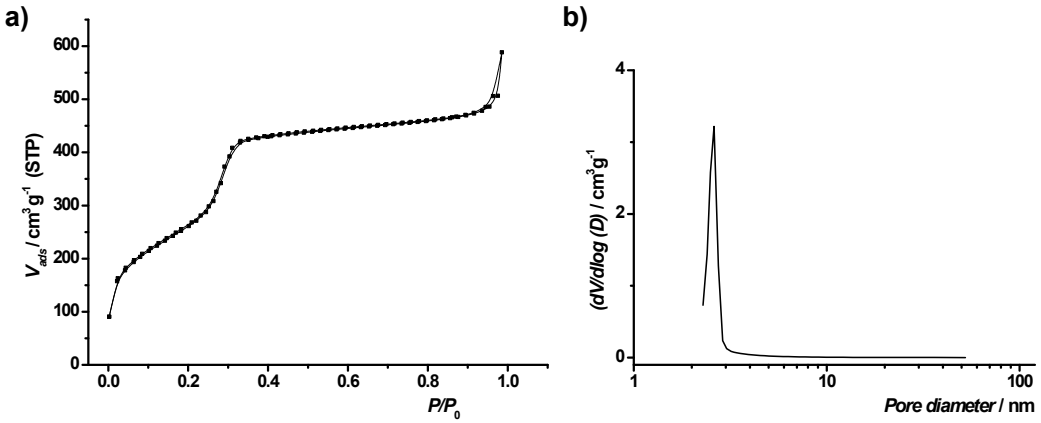

Fig. S5. a) Nitrogen adsorption-desorption isotherms for MSNs and b) pore size distribution.

NMR characterization of the trisaccharide Le^x derivative

Le^x derivative was obtained following the established procedure described in the literature. The obtained trisaccharide was deprotected, purified and characterized by ^{1}H-NMR. ^{1}H-NMR (500 MHz, D_2O, 300 K). 1D proton spectrum and 2D homo (COSY) and heteronuclear correlation (^{1}H ^{13}C HSQC) were acquired. The 1D and 2D experiments are shown in the figures S6, S7 and S8. The signals were overlapped in some regions of 1D and cosy spectra. Hsqc spectrum enabled the assignment of the ^{1}H and ^{13}C signals. The chemical shifts for the molecule were very similar to those already published in the literature.[1]

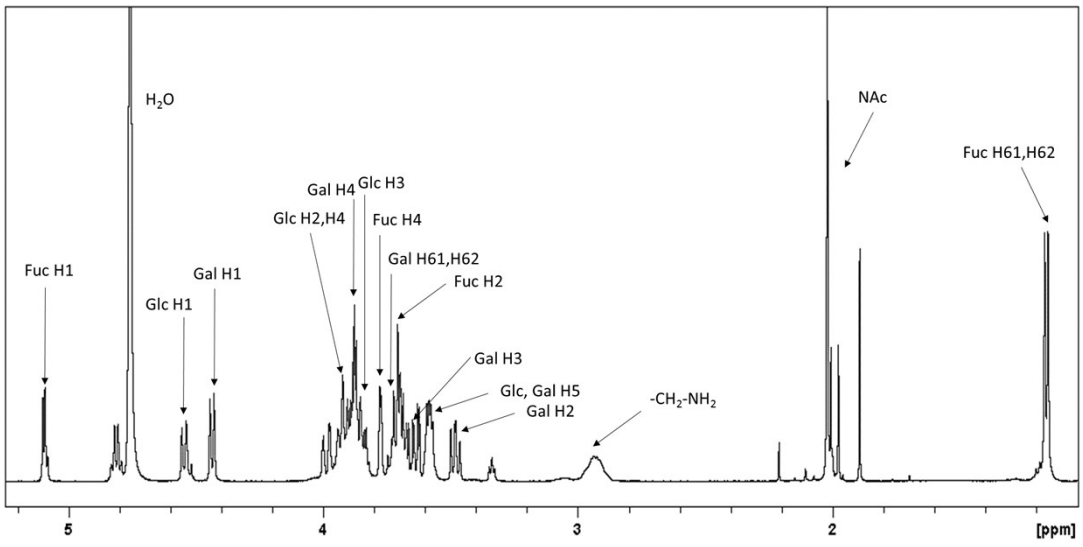

Fig. S6 ^{1}H-NMR spectrum of amino-functionalized Le^x antigen derivative 1 (D_2O, 500 MHz).

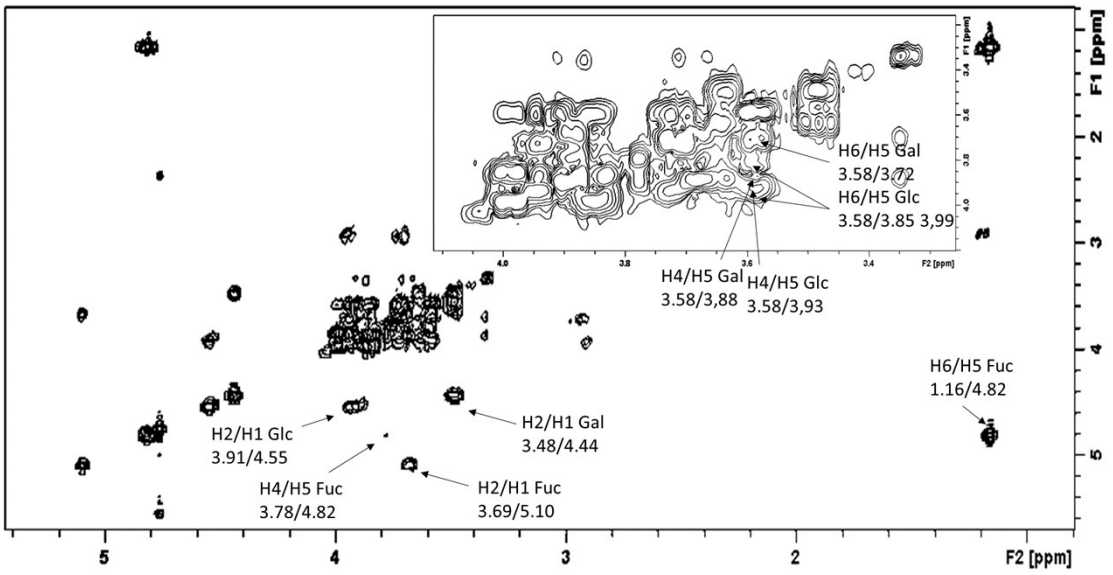

Fig. S7. COSY spectrum of amino-functionalized Le^x antigen derivative 1 (D_2O, 500 MHz).

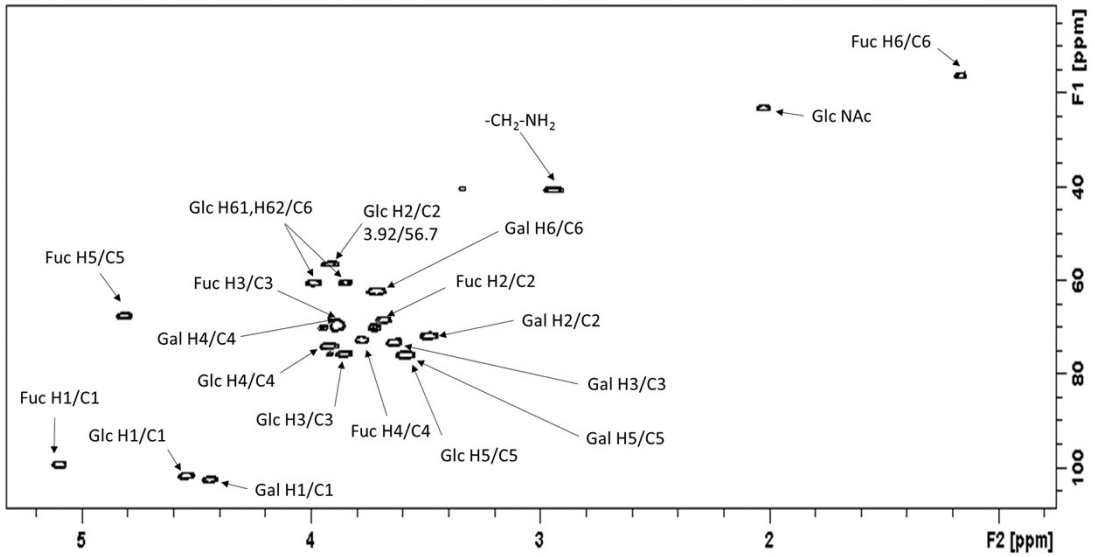

Fig. S8. HSQC spectrum of amino-functionalized Le^x antigen derivative 1 (D_2O, 500 MHz).

The full assignment for Le^x derivative 1 is in the Table S1 (^{1}H chemical shifts) and Table S2 (^{13}C chemical shifts):

Table S1: ^{1}H chemical shifts for Le^{x} antigen derivative 1.

Residue	**H1**	**H2**	**H3**	**H4**	**H5**	**H61 H62**	**NAc**
Glc NAc	4.55	3.92	3.85	3.93	3.58	3.85 3.99	2.02
Fuc	5.10	3.69	3.90	3.78	4.82	1.16	
Gal	4.44	3.49	3.64	3.88	3.58	3.72	

Table S2: ^{13}C chemical shifts for Le^{x} antigen derivative 1.

Residue	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**NAc**
Glc NAc	101.9	56.7	75.8	74.0	76.0	60.6	23.13
Fuc	99.5	68.4	69.7	72.8	67.3	16.33	
Gal	102.7	71.9	73.3	69.5	76.0	62.3	

Delivery experiments in competitive media

To assess the performance of **S3** in competitive media, delivery experiments were carried out in cell culture medium, in the presence and in the absence of L-fucose (Figure S9).

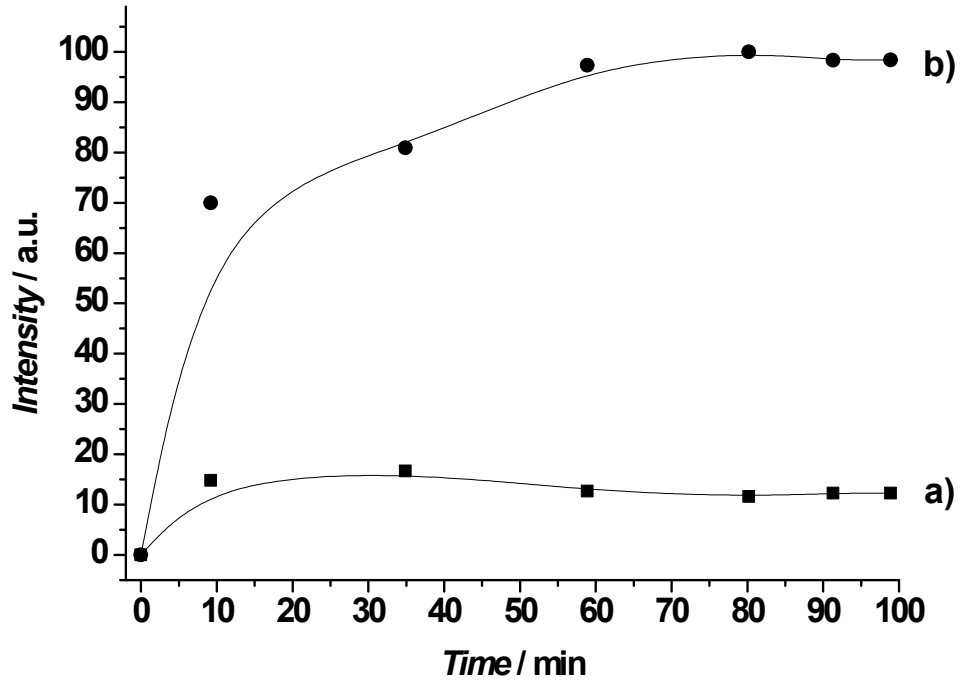

Fig. S9 Release profile of ATTO 430LS dye from solid **S3** in the absence a) and in the presence b) of L-fucose, in cellular medium.

References

1 K. E. Miller, C. Mukhopadhyay, P. Cagas and C. A. Bush, *Biochemistry*, 1992, **31**, 6703–6709.