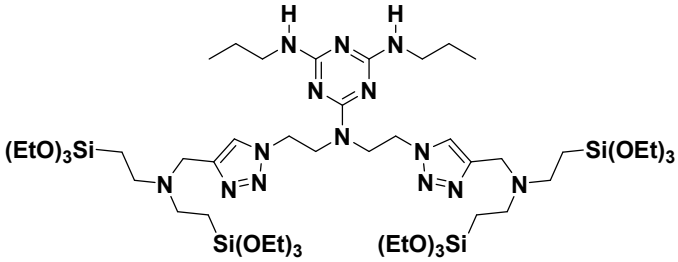
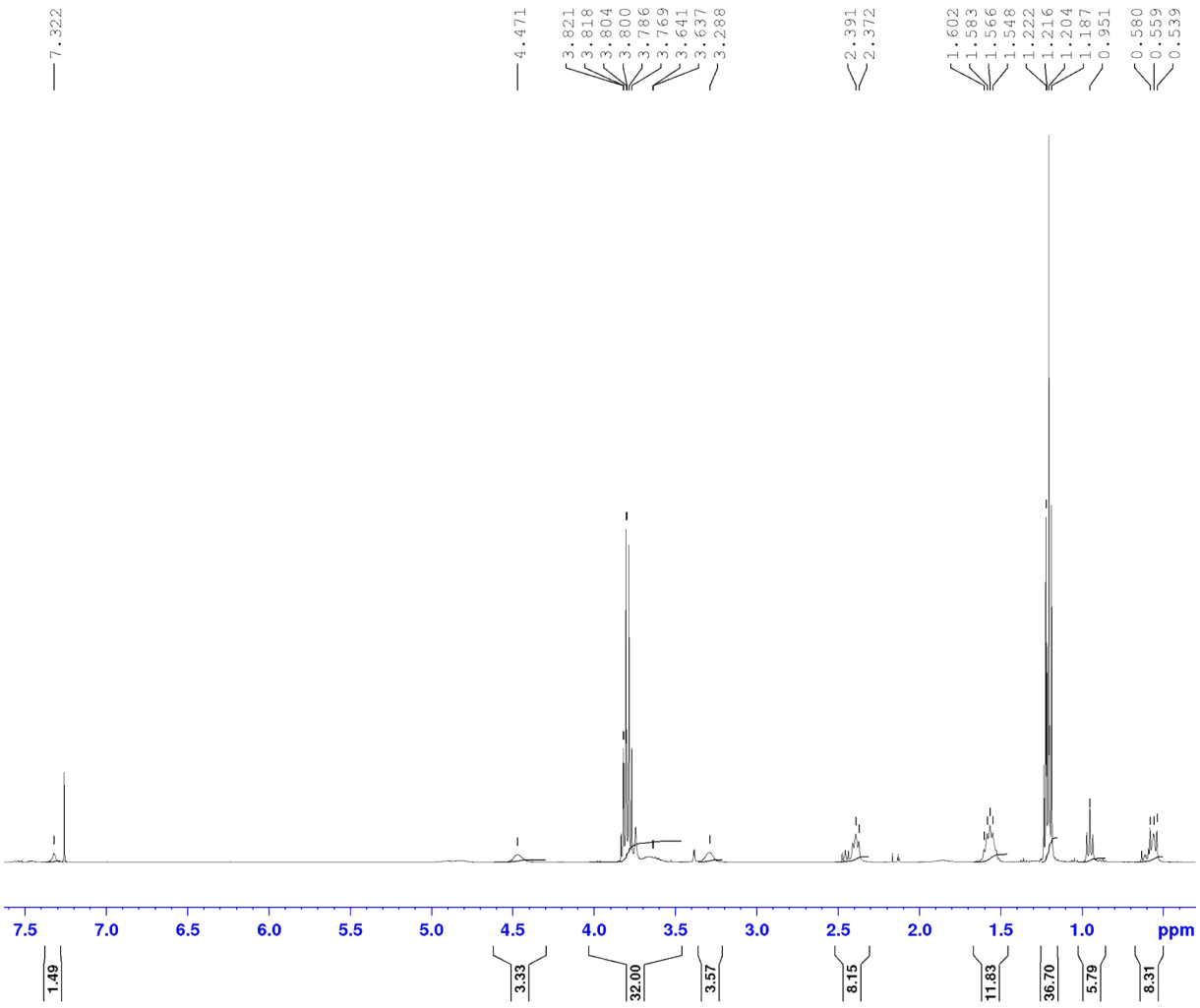
^{1}H liquid NMR spectrum of Stalk precursor





^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.56 (t, 8H), 0.95 (t, 6H), 1.22 (t, 36H), 1.58 (m, 12H), 2.39 (t, 8H), 3.29 (q, 4H), 3.64 (m, 8H), 3.80 (q, 24H), 4.47 (t, 4H), and 7.32 (s, 2H) ;

Figure S1. ^{1}H NMR of the tetrasilylated **Stalk** compound

SAXS profile of NP after CTAB removal

The scattering intensity of the **CTAB-free NP** is shown in **Figure S2**. The five peaks observed at low *q* (1.59; 2.74; 3.19 ; 4.20 and 4.79 nm^{-1}) are assigned to Bragg reflections from the (100), (110), (200), (210) and (300) planes (*p6mm* symmetry), showing that the samples have pore networks exhibiting excellent long-range organisation. Furthermore, the apparent lattice parameter, a, of the *p6mm* space group is defined as $a = 2d100/\sqrt{3} = 4.5$ nm, where the d_{100} interplanar spacing corresponds to $2\pi/q = 3.9$ nm. Consequently, the SAXS analysis confirms the 2D hexagonal mesostructure of the MSNs.

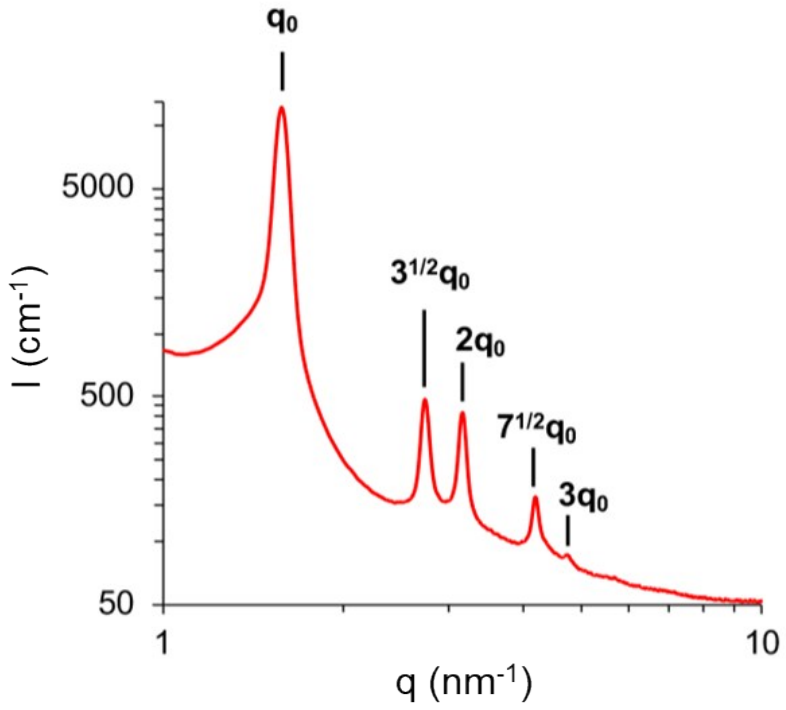


Figure S2. SAXS diffractogram of **CTAB-free NP**

Composition and thermal stability of NP3

TGA analysis of **NP3** (**Figure S3**) revealed four major weight loss events, which are attributed to the loss of pore water (1.8 % from ambient to 100 ^{o}C); decomposition and combustion of the **Stalk** (in two steps, from around 100 to 240 ^{o}C, 14.8 % weight loss and 240 to 440 ^{o}C, 8.2 % weight loss); and loss of hydroxyl species (450 to 600 ^{o}C, 3.2 % weight loss). The total weight loss associated with decomposition of the **Stalk** and dehydroxylation is 26.1 %. For comparison, the thermal behaviour of **NP** is also included in **Figure S3**.

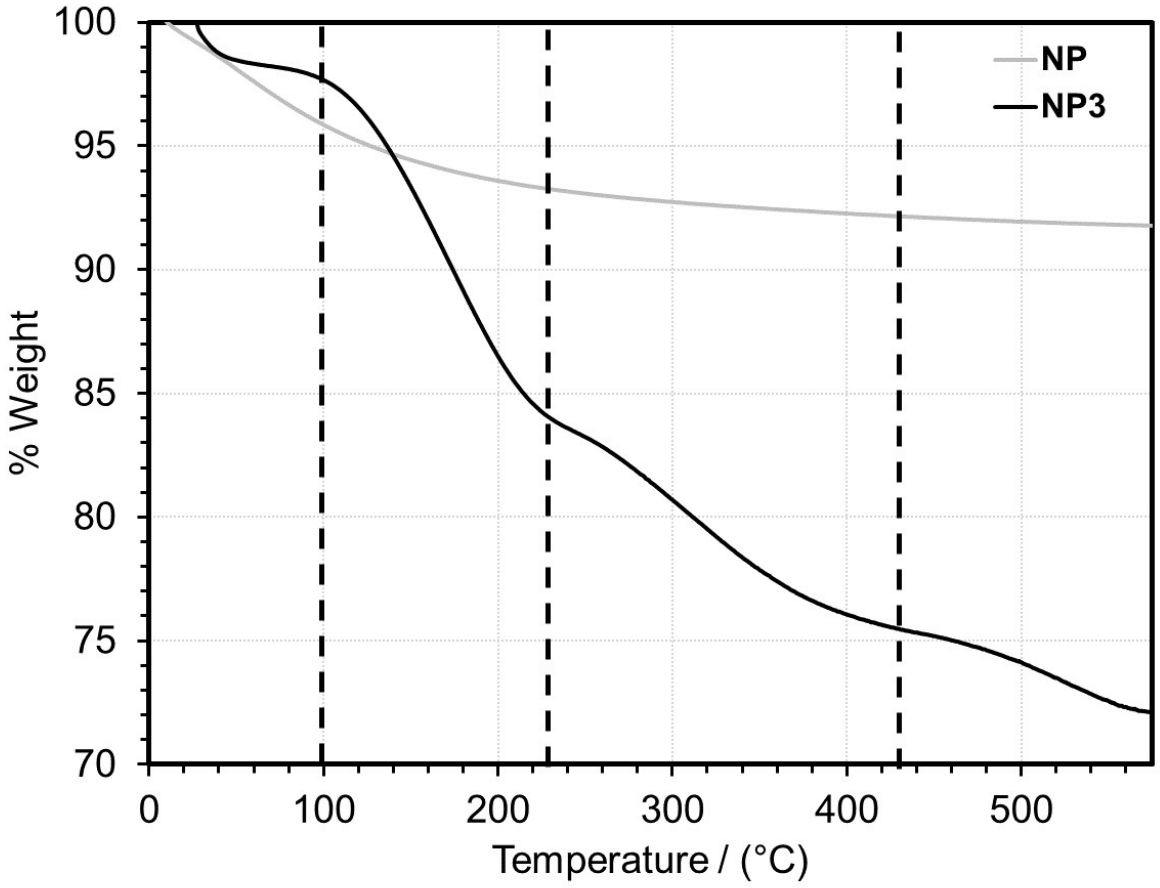


Figure S3. Thermogravimetric analysis of **NP** and **NP3**

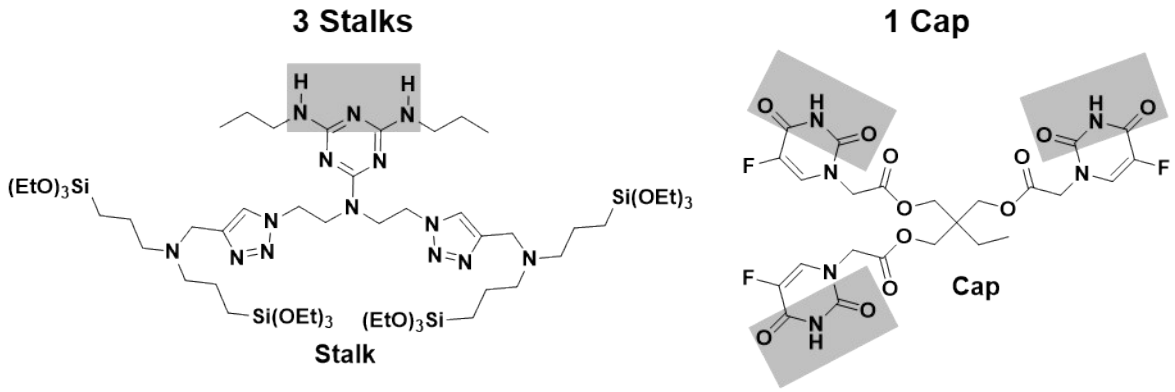
Quantities of Stalk and Cap in NP3 – verifying the 3:1 Stalk:Cap Mole Ratio

The semi-quantitative EDX-TEM analysis of **NP3CPT** in **Figure S4** reveals a nitrogen/fluorine atomic ratio *R* = N/F of ~18. The fluorine content in the material arises from **Cap**, while **Cap**, **Stalk** and **CPT** all contain nitrogen. Hence, the value of *R* should reflect the relative quantities of these three components in **NP3CPT**. In the absence of any **CPT** loaded into the pores, the expected ratio, based on the stoichiometry of **Cap** and **Stalk**, together with the nominal **Stalk**:**Cap** ratio of 3:1, is 16.0.

The thermal analysis data in **Figure S3** reveal that the SiO_2:**Stalk** mass ratio is 73.9:23.0, corresponding to a mole ratio of 1.23:0.0369 (1.00:0.0300; assuming that the stoichiometry of the organic component of **Stalk** condensed onto the NP surface is $C_{31}H_{54}N_{14}$, with a corresponding formula weight of 622.87). This indicates that there are three molecules of **Stalk** for every 100 Si in **NP3**. Based on the typical **CPT** content after loading (4 wt %), each 1.23 moles of Si (73.9 wt% SiO_2 in 100 g **NP3CPT**, based on the TGA data) are associated with 0.011 moles of **CPT** ($C_{20}H_{16}N_2O_4$, formula weight 348.36) or 0.023 moles of N (corresponding to 0.019 moles N per mole Si).

Similarly, each mole of Si is associated with 0.0300 moles of **Stalk**, corresponding to 0.420 moles of N (since each **Stalk** contains 14 N). Assuming a **Stalk**:**Cap** mole ratio of 3:1, the further contribution of **Cap** to the quantity of N per mole Si would be 0.0300/3x6=0.060.

Hence, the total moles of N per mole of Si is 0.019+0.420+0.060=0.499 (**CPT**+**Stalk**+**Cap**, respectively). The number of moles of F associated with this quantity of **Cap** (assuming 3:1 **Stalk**:**Cap** and 0.0300 moles **Stalk**) is (0.0300/3)x3=0.0300. Thus, the expected N:F mole ratio, assuming 4 wt % CPT and a **Stalk**:**Cap** mole ratio of 3:1 is 0.499/0.0300~17, which is in reasonable agreement with the measured value of ~18. Accordingly, it is concluded that the TGA, EDX-TEM and CPT analyses are internally consistent and that the **Stalk**:**Cap** mole ratio is ~3, in accord with the design of the **Stalk:Cap** complex.



Theoretical mole ratio between N:F ~ 17

Elements	Energy (keV)	Atoms %
C	0.277	60.27
N	0.392	**6.86**
O	0.525	21.64
F	0.677	**0.39**
Si	1.739	10.84
Total		**100**

Ratio between N:F from semi-quantitative EDX = 17.6

Figure S4. Elemental composition of **NP3CPT** by EDX-TEM.