Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

XPS characterization

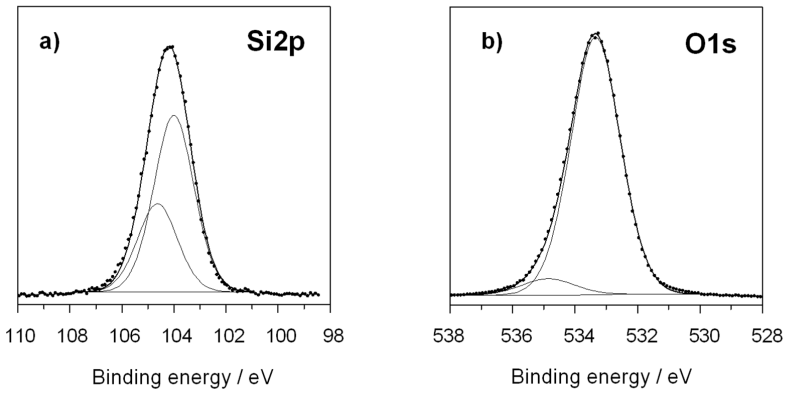

Figure S1. a) Si2p and b) O1s core peaks of stalk^{+}

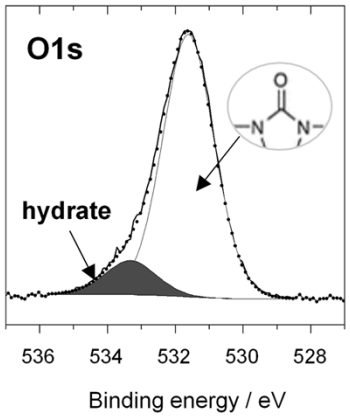

Figure S2. O1s core peak of CB6

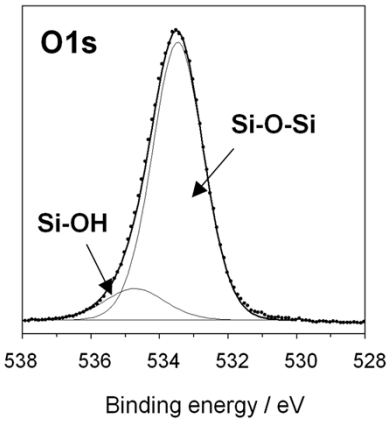

Figure S3. O1s core peak of NS@mSi

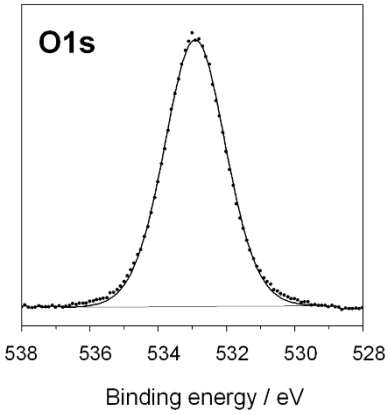

Figure S4. O1s core peak of NS@mSi-valve

NMR characterization

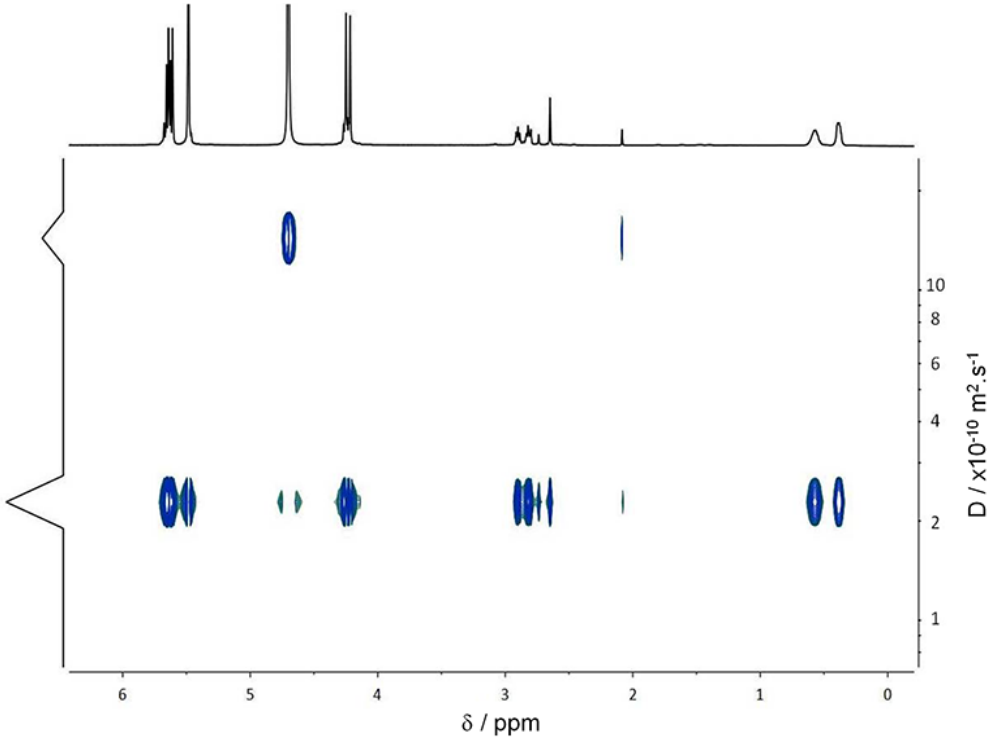

Figure S5. ^{1}H DOSY NMR spectrum in D_2O of stalk^{+}/CB6

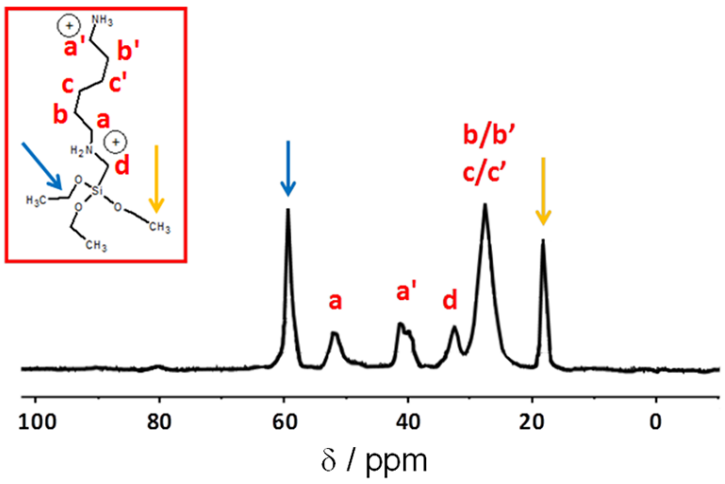

Figure S6. CP-MAS ^{13}C NMR spectrum of stalk^{+} $[(CH_3CH_2O)_3SiCH_2NH_2(CH_2)_6NH_3]Cl_2$

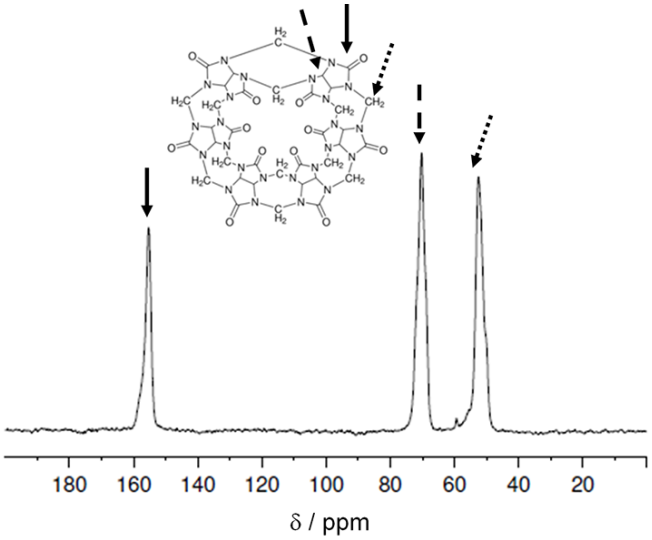

Figure S7. CP-MAS ^{13}C NMR spectrum of CB6

2D ^{1}H-^{1}H double quantum MAS experiments:

The 2D ^{1}H DQ MAS spectra of the NS@mSi-stalk, stalk^{+}/CB6, and NS@mSi-valve are shown in Figures S8-S10 and the chemical shifts together with the assignments are gathered in the Table S1.

For a proton A, the DQ coherence (AA or AB) obtained in the 2D spectrum will have the same horizontal frequency that it has in the 1D spectrum (ν_A), but its vertical coordinate will be the sum of its frequency (ν_A) and the one of the dipolar coupled proton with it ($2\nu_A$ for AA or $\nu_A+\nu_B$ for AB). The peaks located on the diagonal (dashed line) correspond to the auto-correlation peaks that result from the dipolar coupling involving equivalent protons belonging to the same groups.

2D ^{1}H-^{1}H double quantum MAS experiments typically allow to study proton proximities (within 3.5Å)[1]. However, in this case, no clear DQ correlation could be observed between the protons of the

stalk and the CB[6] molecules because of the only weak dipolar couplings between CB[6] and stalk protons (As it was observed in solution NMR with the ROESY experiment). In contrast, the strong intramolecular dipolar couplings of CB[6] and stalk protons allows the observation of the following Double Quanta Correlation (DQC).

Table S1. Chemical shifts and assignments of the 2D ^{1}H-^{1}H DQ MAS spectra of NS@mSi-stalk (a), stalk^{+}CB6 (b), and NS@mSi-valve.

	NS@mSi-stalk		stalk^{+}/CB[6]		NS@mSi-valve	
Hydrogen atom	δ(ppm)	DQC	δ(ppm)	DQC	δ(ppm)	DQC
H1-CB6	5.7		5.7	H2	5.7	H2
H2-CB6	4.3		4.3	H1	4.2	H1
H3-CB6	5.6		5.6	H3	5.5	H3
a/a'- stalk	2.8-3.1	a/a', b/b', NH_2^+/NH_3^+	2.8	a/a', b/b', NH_2^+/NH_3^+	2.9-3.0 2.8	a/a', b/b', NH_2^+/NH_3^+
b/b'- stalk	1.5	a/a', b/b', c/c'	0.4	a/a', b/b', c/c', NH_2^+/NH_3^+	1.4 0.4	a/a', b/b', c/c'
c/c'- stalk	1.3	b/b', c/c'	0.4	b/b', c/c'	1.3 0.4	b/b', c/c'
d- stalk	2.6	d	2.6	d	2.6	d
NH_2^+/NH_3^+-stalk	7.2-7.9	a/a', NH_2^+/NH_3^+	6.6	a/a', NH_2^+/NH_3^+	7.3-7.9 6.5	a/a', NH_2^+/NH_3^+

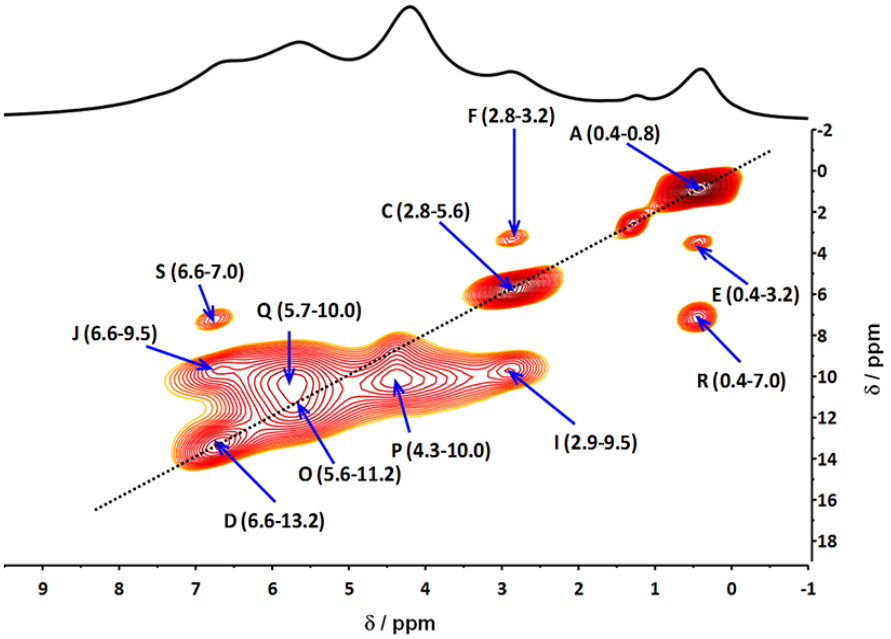

Figure S8. 2D ^{1}H-^{1}H DQ MAS spectrum of stalk^{+}/CB6

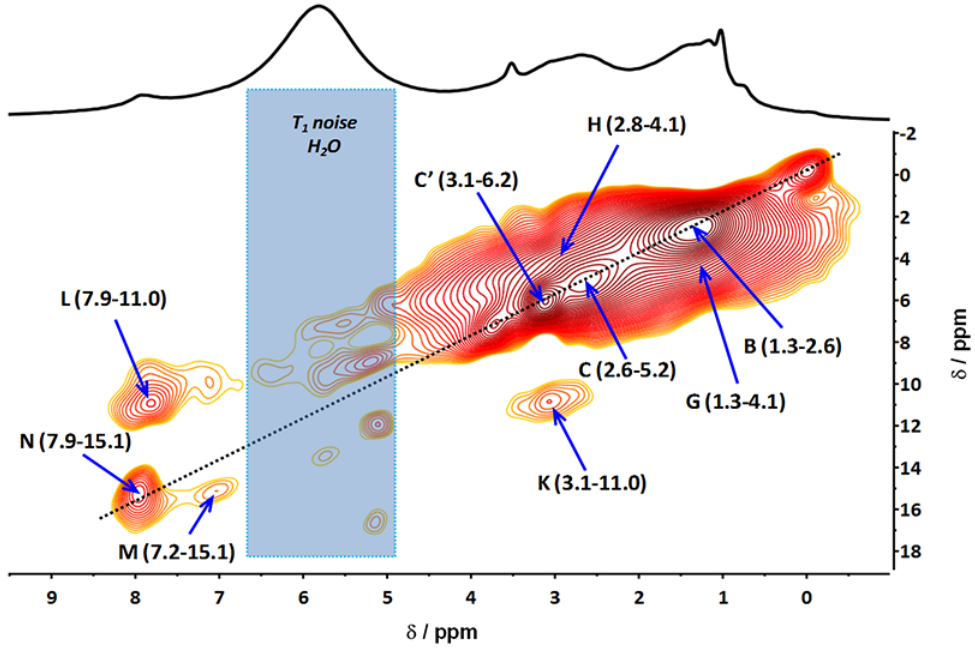

Figure S9. 2D ^{1}H-^{1}H DQ MAS spectrum of NS@mSi-stalk

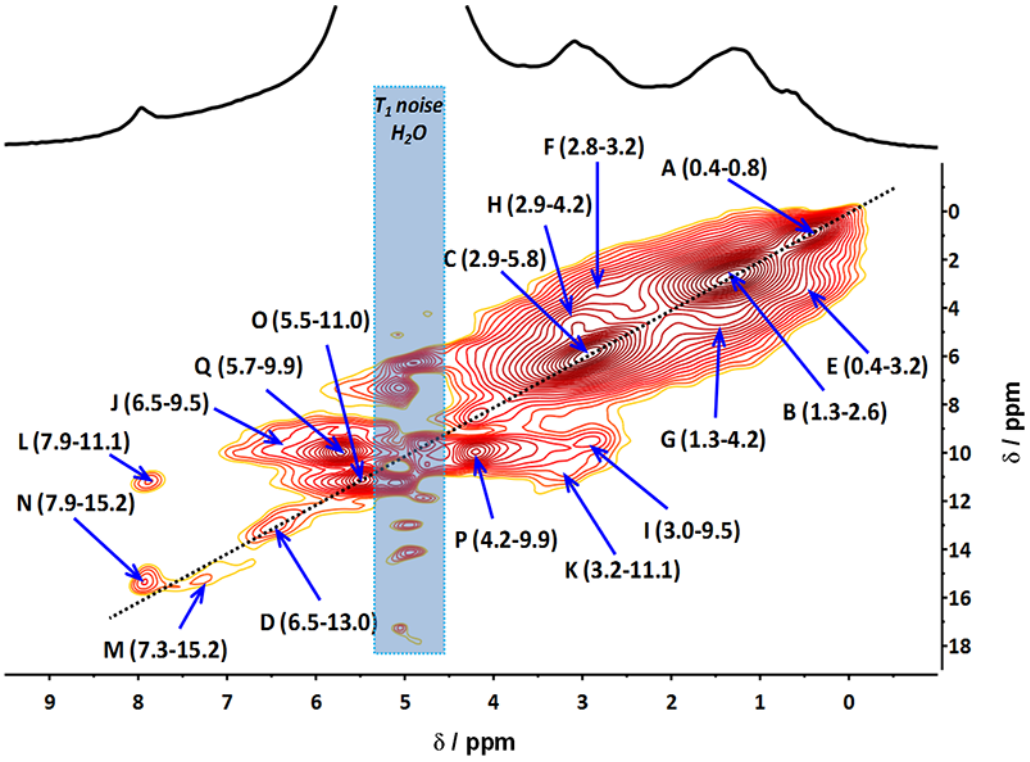

Figure S10. 2D ^{1}H-^{1}H DQ MAS spectrum of NS@mSi-valve

1 S. P. Brown, *Macromol. Rapid Commun.*, 2009, **30**, 688–716.