

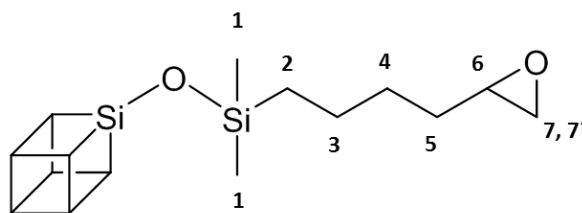
NMR POSS characterization.

POSS-8E: ^1H NMR and ^{13}C NMR spectra of 8E-POSS confirm the functionalization of the POSS cage by 8 epoxide ligands, no another species are present. Moreover the total disappearance of the ^1H NMR peak at 4.2 ppm corresponding to Si-H bond confirms the complete functionalization of the POSS cage. The ^{29}Si NMR spectrum shows 2 peaks, one at $\delta = 12.71$ ppm corresponding to the M-type silicon with the two methyl groups and the alkyl moiety and a second one at $\delta - 108.86$ ppm corresponding to the Q-type silicon of the POSS core. No cage cleavage occurs and the POSS core is still intact.

^1H NMR (CDCl_3 , ppm): 0.05 (1: Si—CH₃), 0.54 (2: Si—CH₂), 1.3 – 1.5 (3, 4, 5: CH₂—CH₂—CH₂), 2.38 and 2.68 (7, 7': O—CH₂—CH epoxy), 2.82 (6: O—CH₂—CH epoxy).

^{13}C NMR (CDCl_3 , ppm): 0.0 (1: Si—CH₃), 17.9 (2: Si—CH₂), 23.1 (3: Si—CH₂—CH₂), 29.8 (4: Si—CH₂—CH₂—CH₂), 32.5 (5: Si—CH₂—CH₂—CH₂—CH₂), 47.4 (7: O—CH₂—CH epoxy), 52.5 (6: O—CH₂—CH epoxy).

^{29}Si NMR (CDCl_3 , ppm): -100.86 (Q-type Si, POSS core), 12.71 (M-type Si, E ligands).



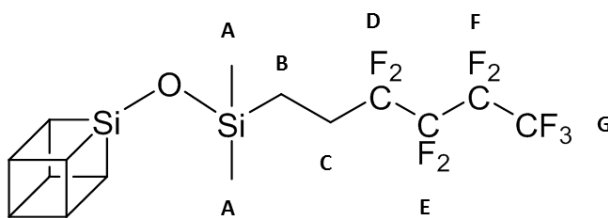
6E2F-POSS:

^1H NMR (CDCl_3 , ppm): -0.00 (1, A: Si—CH₃), 0.54 (2: Si—CH₂), 0.63 (B: Si—CH₂), 1.3 – 1.5 (3, 4, 5: CH₂—CH₂—CH₂), 1.90 (C: Si—CH₂—CH₂—CF₂), 2.38 and 2.68 (7, 7': O—CH₂—CH epoxy), 2.82 (6: O—CH₂—CH epoxy).

^{13}C NMR (CDCl_3 , ppm): -0.00 (1, A: Si—CH₃), 7.93 (B: Si—CH₂), 17.9 (2: Si—CH₂), 23.1 (3: Si—CH₂—CH₂), 25.84 (C: Si—CH₂—CH₂—CF₂), 29.8 (4: Si—CH₂—CH₂—CH₂), 32.5 (5: Si—CH₂—CH₂—CH₂—CH₂), 47.4 (7: O—CH₂—CH epoxy), 52.5 (6: O—CH₂—CH epoxy).

^{19}F NMR (CDCl_3 , ppm): -81.31 (G: CF₃—CF₂), -116.44 (F: CF₃—CF₂), -124.35 (E: CF₃—CF₂—CF₂), -126.28 (D: CF₃—CF₂—CF₂—CF₂).

^{29}Si NMR (CDCl_3 , ppm): -110.81 (Q-type Si, POSS core), 12.71 (M-type Si, E ligands), 13.44 (M-type Si, F ligands).



4E2F2Φ-POSS:

^1H NMR (CDCl_3 , ppm): -0.00 (1, A, a, a1: Si—CH₃), 0.54 (2: Si—CH₂), 0.63 (B: Si—CH₂), 0.83 (b: Si—CH₂), 1.27 (c1: Si—CH₂—CH₃), 1.3 – 1.5 (3, 4, 5: CH₂—CH₂—CH₂), 1.90 (C: Si—CH₂—CH₂—CF₂), 2.10 (b1: Si—CH₂—CH₃), 2.38 and 2.68 (7, 7': O—CH₂—CH epoxy), 2.53 (c: Si—CH₂—CH₂), 2.82 (6: O—CH₂—CH epoxy), 6.93 – 7.09 (d, e, f: multiplet Phenyl).

^{13}C NMR (CDCl_3 , ppm): -0.00 (1, A, a, a1: Si—CH₃), 7.93 (B: Si—CH₂), 14.51 (c1: Si—CH₂—CH₃), 17.9 (2: Si—CH₂), 19.60 (b: Si—CH₂), 23.1 (3: Si—CH₂—CH₂), 25.84 (C: Si—CH₂—CH₂—CF₂), 29.37 (c: Si—CH₂—CH₂), 29.8 (4: Si—CH₂—CH₂—CH₂), 31.15 (b1: Si—CH₂—CH₃), 32.5 (5: Si—CH₂—CH₂—CH₂—CH₂), 47.4 (7: O—CH₂—CH epoxy), 52.5 (6: O—CH₂—CH epoxy), 124.90 – 145.01 (d, e, f: Phenyl).

^{19}F NMR (CDCl_3 , ppm): -81.31 (G: CF₃—CF₂), -116.44 (F: CF₃—CF₂), -124.35 (E: CF₃—CF₂—CF₂), -126.28 (D: CF₃—CF₂—CF₂—CF₂).

^{29}Si NMR (CDCl_3 , ppm): -108.77 (Q-type Si, POSS core), 10.67 (M-type Si, Φ ligands), 12.54 (M-type Si, Φ_1 ligands), 12.71 (M-type Si, E ligands), 13.44 (M-type Si, F ligands).

