Unraveling *in situ* the chemical structures of polyoxomolybdate based amphiphilic nano-hybrids in aqueous solutions combining ^{31}P DOSY NMR and Molecular Mechanics as powerful tools

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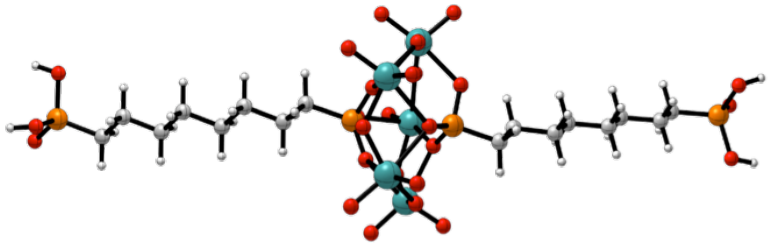
Novel hybrid organic-inorganic assemblies[1] of various sizes were generated upon reacting 1,8-octanediphosphonic acid (ODP) and $(NH_4)_6Mo_7O_{24}$ in a purely aqueous solution. The formation of rod-like hybrids with variable numbers of covalently bound ODP and polyoxomolybdate (POM) units can be tuned upon increasing $(NH_4)_6Mo_7O_{24}$ concentration at fixed ODP concentration. The chemical structure of the ODP/POM hybrids was characterized by ^{1}H, ^{31}P and ^{95}Mo NMR. Heteronuclear ^{31}P DOSY (diffusion ordered NMR spectroscopy)[2,3] and Molecular Mechanics calculations (MM)[3] were combined in order to determine the size and shape of nano-sized hybrids generated at various ODP/$(NH_4)_6Mo_7O_{24}$ ratios. For this purpose, the structures of these ODP/POM hybrids with variable number of ODP and POM units were optimized by MM and then approximated as cylindrical objects, using a recent mathematical algorithm. The cylinder length and diameter obtained in this way were further used to calculate the expected diffusion coefficients of the ODP/POM hybrids.[3] Comparison of the calculated and experimentally determined diffusion coefficients led to the most probable ODP/POM hybrid length for each sample composition. The ^{31}P DOSY results show that the length of the hybrids increases upon increase of the initial $(NH_4)_6Mo_7O_{24}$ concentration, reaching a maximum corresponding to an average of 8 ODP and 7 POM units per chain at 20 mM ODP and 14 mM $(NH_4)_6Mo_7O_{24}$ composition. At $(NH_4)_6Mo_7O_{24}$ molar excess, above the latter hinge concentration, chain hybrids terminated by Mo_7 clusters at one or both sides get shorter again upon further $(NH_4)_6Mo_7O_{24}$ concentration increase. The results demonstrate that the combination of ^{31}P DOSY and MM, although virtually unexplored in POM chemistry, represents a powerful innovative strategy for the detailed characterization of nano-sized organic-inorganic POM based hybrids in water media.



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