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From Fundamental interaction in Solution to the Design of Hybrid Polyoxometalate-based Materials.

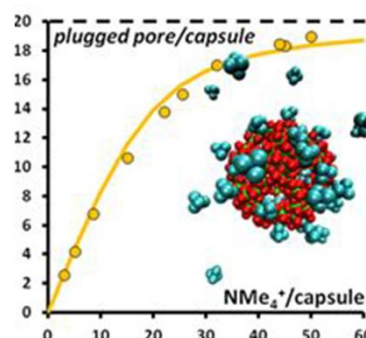
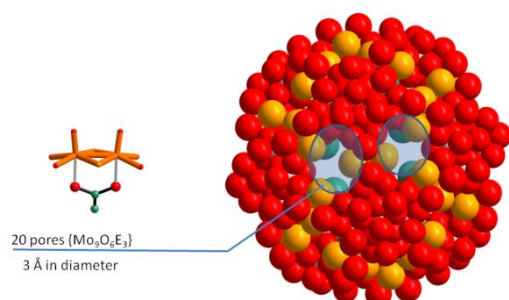
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Herein, we report the use of ¹H DOSY NMR methodology to track the interaction between an inorganic multireceptor capsule, referring to the well-defined large polyoxometalate (POM) such as the spherical Keplerate-type {Mo₁₃₂} ion and a series of organic cation (including tetraalkylammonium). The obtained results reveal a strong dependence of the self-diffusion coefficient of the cationic guests balancing from the solvated to the plugging situations. Quantitative analysis of the data based on two-site exchange regime, involving the 20 independent {Mo₉O₉} receptors of the capsule, allowed determining the stability constants associated to the plugging process of the pores. Surprisingly, the affinity of the capsule for a series of cationic guests increases continuously with its apolar character as shown from the signification change of the stability constant from 370 to 6500 for NH₄⁺ and NEt₄⁺, respectively. Such observations, supported by thermodynamic parameters, evidence that the major factor dictating selectivity in the trapping process is mainly the so-called “hydrophobic effect”.^[1] Understanding the nature of the interaction between POM and organic cation allowed us designing of POM-hybrid materials which exhibit liquid crystalline properties.^[2,3]



References:

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