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Self-assembly of Gd^{3+}-bound keplerate polyanions into nanoparticles as a route for the synthesis of positive MRI contrast agents. Impact of the structure on the magnetic relaxivity

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Abstract

© The Royal Society of Chemistry. The present work introduces Gd3+ complexes with giant keplerate polyanions as a promising basis for MRI contrast agents. The impact of Gd3+ binding with different building blocks of keplerates on the magnetic relaxivity of the complexes is revealed by comparative study of the keplerates [{Mo6O21}12{Mo2O4(OAc)}30]42−, [{Mo6O21}12{Mo2O4(HPO4)}30]72−, and [{Mo6O21}12{Mo2O2S2(OAc)}30]42−. Unprecedentedly high longitudinal and transverse relaxivity values (up to 250 and 300 mM−1 s−1 correspondingly) are achieved for the keplerates possessing edl{Mo2O4(OAc)} and {Mo2O4(HPO42−)} moieties under their 1 : 1 complex formation with Gd3+. The transformation of the external pores from Mo9O9 to Mo9O6S3 in the {Mo2O2S2(OAc)}-keplerate and an increase in the Gd3+-to-keplerate ratio are the factors that decrease the relaxivity. The rapid degradation of the free keplerates in aqueous solutions restricts the use of the Gd3+-bound keplerates with 1 : 1 stoichiometry as MRI contrast agents. In this work, the optimized stoichiometry of the complexes, their self-assembly into ultra-small nanoparticles and their hydrophilic coating by a triblock copolymer are highlighted as tools for increasing both the colloid and chemical stability of the keplerate complexes. Optimal keplerate compositions have been identified to achieve a compromise of low cytotoxicity and high stability; these Gd3+-bound keplerates exhibit longitudinal and transverse relaxivity values (95 and 114 mM−1 s−1, respectively), well within the region of interest for MRI techniques.

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