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Terbium(III)-thiacalix[4]arene nanosensor for highly sensitive intracellular monitoring of temperature changes within the 303–313 K range

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Abstract

© 2020, The Author(s). The work introduces hydrophilic PSS-[Tb2(TCAn)2] nanoparticles to be applied as highly sensitive intracellular temperature nanosensors. The nanoparticles are synthesized by solvent-induced nanoprecipitation of [Tb2(TCAn)2] complexes (TCAn - thiacalix[4]arenes bearing different upper-rim substituents: unsubstituted TCA1, tert-buthy--substituted TCA2, di- and tetra-brominated TCA3 and TCA4) with the use of polystyrenesulfonate (PSS) as stabilizer. The temperature responsive luminescence behavior of PSS-[Tb2(TCAn)2] within 293–333 K range in water is modulated by reversible changes derived from the back energy transfer from metal to ligand (M* → T1) correlating with the energy gap between the triplet levels of ligands and resonant 5D4 level of Tb3+ ion. The lowering of the triplet level (T1) energies going from TCA1 and TCA2 to their brominated counterparts TCA3 and TCA4 facilitates the back energy transfer. The highest ever reported temperature sensitivity for intracellular temperature nanosensors is obtained for PSS-[Tb2(TCA4)2] (SI = 5.25% K−1), while PSS-[Tb2(TCA3)2] is characterized by a moderate one (SI = 2.96% K−1). The insignificant release of toxic Tb3+ ions from PSS-[Tb2(TCAn)2] within heating/cooling cycle and the low cytotoxicity of the colloids point to their applicability in intracellular temperature monitoring. The cell internalization of PSS-[Tb2(TCAn)2] (n = 3, 4) marks the cell cytoplasm by green Tb3+-luminescence, which exhibits detectable quenching when the cell samples are heated from 303 to 313 K. The colloids hold unprecedented potential for in vivo intracellular monitoring of temperature changes induced by hyperthermia or pathological processes in narrow range of physiological temperatures.

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