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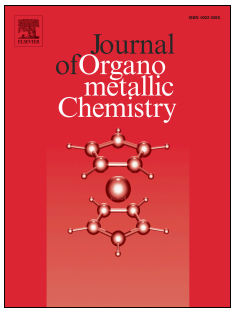

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Luminescence Differences between Two Complexes of Divalent Europium

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Abstract

We report a computational study of the photophysical properties of two divalent europium cryptates. Our calculations provide an explanation for the bright yellow luminescence of the Eu^{II}-containing octaaza-cryptate compared to the less intense blue luminescence of the structurally similar Eu^{II}-containing 222-cryptate. Calculations using time-dependent density functional theory with the B3PW91 functional, the Stuttgardt–Dresden relativistic core potential basis for europium, and SMD implicit solvation are used to compute the excitation and emission spectra of both complexes. Emission is also calculated with state-specific solvation. The results are compared with experimental luminescence data acquired in methanol. Natural-transition orbitals reveal similar spin-allowed transitions between the 4f and 5d orbitals on the europium ion in both complexes. For the 222-cryptate, the emissive state is hidden underneath the broad ultraviolet absorption; therefore, the state is not experimentally differentiated in the spectra, despite being present in the calculated spectra. For the octaaza-cryptate, the emissive state is observed as a separate band, shifted to lower energy than the broad ultraviolet absorption. Using ligand-field arguments, sharp differences in luminescence and the bathochromic shift of the