

Dual Emission of a Cyclic Hexanuclear Gold(I) Complex. Interplay between Au₃ and Au₂ Ligand-Supported Luminophores

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Finding diverse and tunable molecular structures is relevant toward the design of functional nanostructures. The photoluminescence of complex [Au₂Cl(η -P-C- η P, η C, η N)]₃ (1), featuring a ligand-supported hexanuclear Au(I) framework comprising a triangular Au₃ core of which each apex is connected to an external Au(I) center, has revealed a remarkable dual emission at room temperature. The emission bands display maxima centered at λ_{em} = 512 and 694 nm with Stokes shifts of 19 530 and 14 410 cm⁻¹ and are attributed to the radiative relaxation of two excited-states centered on the central Au₆ skeleton arising from 5d \rightarrow 6p \rightarrow excitation. As suggested by the strikingly different dioxygen dependency of the relative intensity of the two emission bands, the observed dual emission can be tentatively attributed to the incomplete equilibration between two close-lying-emissive excited states with singlet and triplet characters, most likely because of the slow intersystem crossing process, yielding green fluorescence and red phosphorescence, respectively; this phenomenon is rarely observed in heavy element compounds. Based on theoretical calculations, these excited states originated from two different substructure luminophores of the molecular skeleton, mainly (i) the Au₃ core and (ii) one specific Au₂ unit. Thus, the dual luminescence of 1 originates from the noteworthy inclusion of two luminophores within the overall molecular structure. Both solution and solid-state emission spectra show similar characteristics owing to the intramolecular nature of the suggested luminescence mechanism. Such luminophores can be envisaged as novel metalloligands to be incorporated in larger gold nanoclusters toward the development of intense luminescent molecular devices. Copyright © 2018 American Chemical

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