Excited-multimer mediated supramolecular upconversion on multicomponent lanthanide-organic assemblies

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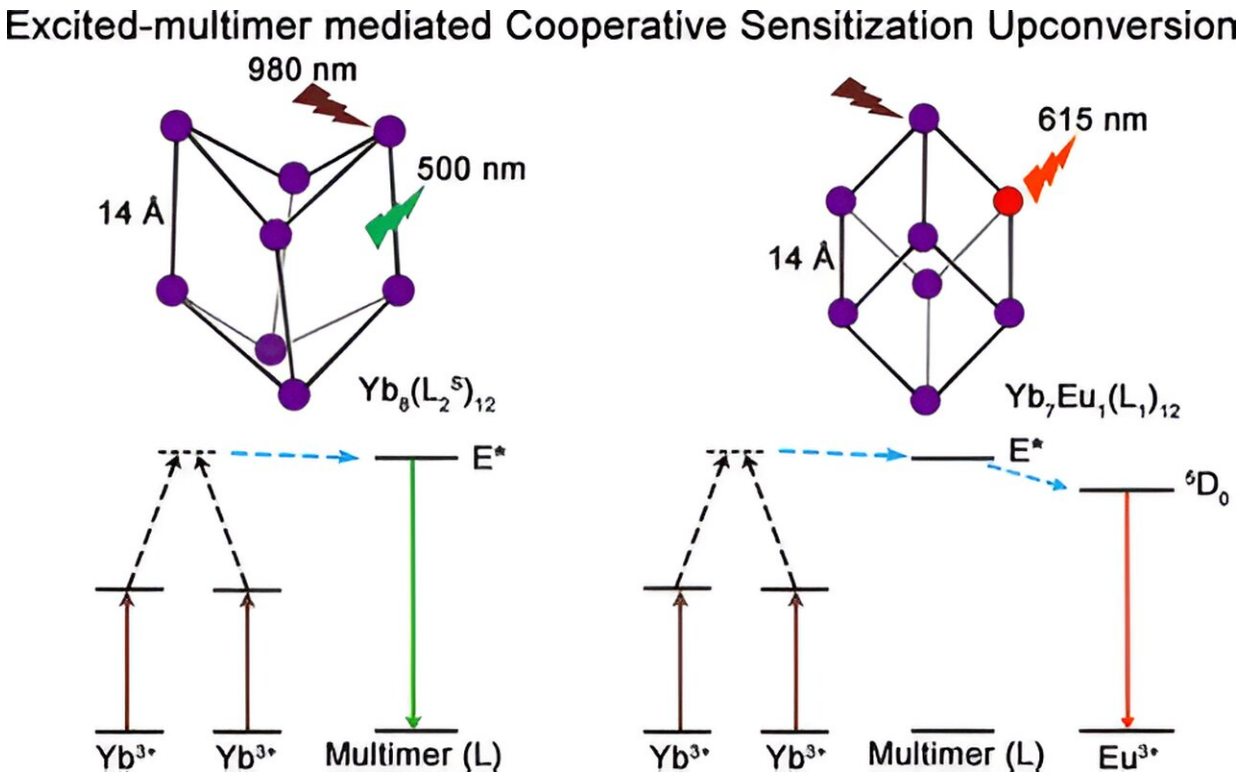

Credit: *Journal of the American Chemical Society* (2023). DOI: 10.1021/jacs.3c06775

Upconversion (UC) luminescence is a process that converts low-energy photons into higher-energy ones with promising applications in diverse

fields. However, known UC mechanisms mainly focus on the energy transfer processes between metal ions, while the role of organic ligands needs to be explored.

Lanthanide-organic assemblies constructed by coordination assembly have attracted great attention in supramolecular chemistry due to their wide applications in sensing, bioimaging, and cancer theranostics. However, limited by long-distance energy transfer of sensitizer and activator, achieving UC in multicomponent lanthanide-organic assemblies is very challenging.

In a study published in the *Journal of American Chemical Society*, the research group led by Prof. Sun Qingfu from Fujian Institute of Research on the Structure of Matter of the Chinese Academy of Sciences proposed excited-multimer mediated supramolecular UC on multicomponent lanthanide-organic assemblies.

The researchers found that subtle variation of ligand's peripheral substituents induced metal-centered stereoconfiguration control, and gave rise to two topological Ln_8L_{12}-type (Ln for lanthanide ion; L for organic ligand L_1 or $L_2^{R/S}$) lanthanide-organic complexes. Nuclear magnetic resonance, electrospray ionization time-of-flight mass spectrometry, and X-ray crystallography confirmed the formation of rhombohedral $Ln_8(L_1)_{12}$ and octahedral $Ln_8(L_2^{R/S})_{12}$.

Photophysical studies on the lanthanide-organic assemblies showed highly efficient sensitized Eu^{3+}, Sm^{3+}, and Yb^{3+} for the homometallic Ln_8L_{12} through the traditional antenna effect. Supramolecular lanthanide-organic assemblies of this pseudo-cube structure exhibited a rare example of assembly-induced excited-multimer states by suppressing intramolecular orientation and vibration.

Despite the large Ln···Ln distances (> 1.4 nm) in the complexes, the

$Yb_8(L_2)_{12}$ assembly showed unprecedented upconverted multimer green fluorescence (500 nm) under 980 nm excitation. A quadratic dependence of the UC intensity on the laser power density coincides with the expected two-photon UC mechanism. Moreover, the energies of excited-multimer states can be transferred to the partly doped Eu^{3+} ions in heterometallic $(Yb/Eu)_8L_{12}$ assemblies, realizing the upconverted red emissions of Eu^{3+} via excited-multimer-mediated cooperative sensitization UC.

The researchers observed no detectable Eu^{3+}-centered UC emission in post-assembly mixtures of 7 equiv of Yb_8L_{12} and 1 equiv of Eu_8L_{12} under 980 nm excitation, confirming that the $Yb^{3+} \rightarrow Eu^{3+}$ energy transfer is an intramolecular rather than intermolecular UC process.

This study provides a new strategy for designing UC materials, which is crucial for exploiting photofunctions of multicomponent lanthanide-organic complexes.

More information: Xiao-Fang Duan et al, Excited-Multimer Mediated Supramolecular Upconversion on Multicomponent Lanthanide-Organic Assemblies, *Journal of the American Chemical Society* (2023). DOI: 10.1021/jacs.3c06775

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