Self-assembled Multidyes-Sensitized Erbium Single Molecules for Boosting Energy Transfer Light-Upconversion in Solution

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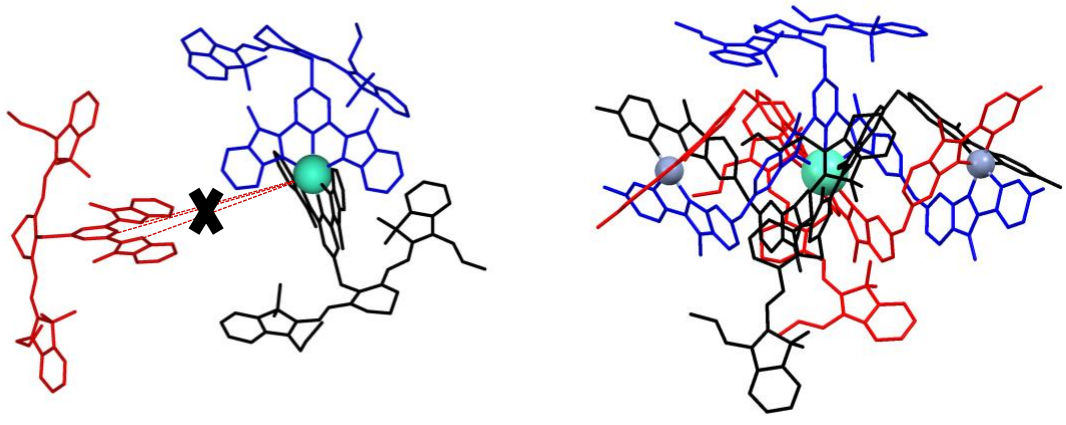
Upconversion is the process of transforming two or more low-energy photons into one higher-energy photon.[1] The challenge of implementing upconversion using linear optics in molecular complexes mainly relies on two mechanisms: Excited State Absorption (ESA) and Energy Transfer Upconversion (ETU). ETU efficiency could be recently boosted by attaching a single cyanine dye to a ligand $[\mathbf{L1}]^+$ coordinated to $Er(hfac)_3$, which increased the upconversion brightness without affecting the quantum yield.[2] Extending this strategy to Er(III) sources that could host three $[\mathbf{L1}]^+$ units to give $[Er(\mathbf{L1})_3]^{6+}$ proved unsuccessful due to electrostatic repulsion between the cationic components (Figure, left).

To overcome this limitation, we designed a new ligand, $[\mathbf{L2}]^+$, featuring two additional bidentate sites at its extremities capable of binding d-metals. This modification leveraged the thermodynamic advantage of strict self-assembly, enabling the formation of stable trinuclear $[ZnErZn(\mathbf{L2})_3]^{10+}$ triple-stranded helicate, where the three cationic dyes are arranged around a single Er(III) activator (Figure, right). While the standard coordination approach failed to assemble the desired complex, the new supramolecular strategy proved beneficial and led to the exclusive formation of the targeted species in solution. Upon NIR excitation of $[ZnErZn(\mathbf{L2})_3]^{10+}$, an unprecedented upconversion emission and brightness was detected.[3]



$[Ln\mathbf{L1}_3]^{6+}$ is not formed

$[MLnM\mathbf{L2}_3]^{10+}$ is formed

References:

[1] A. M. Nonat, L. J. Charbonnière, *Coord. Chem. Rev.* **2020**, *409*, 213192.
[2] I. Taarit, F. Alves, A. Benchohra, L. Guénée, B. Golesorkhi, A. Rosspeintner, A. Fürstenberg, C. Piguet, *J. Am. Chem. Soc.* **2023**, *145*, 8621–8633.
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