

Ruthenium(II) Dimer Capable of Reversibly Storing up to Four Electrons in a Single Acceptor Ligand upon Visible Light Irradiation.

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Ru(II) photosensitizers covalently linked to electron donor or acceptor units are frequently used in the development of artificial photosystems. One limitation of such systems has been the inability of most such photocatalysts to store multiple electrons. Current research has focused on synthesis of a new dimeric photocatalyst capable of storing up to four electrons in a single bridging ligand. This photocatalyst consists of two $[\text{Ru}(\text{phen})_3]^{2+}$ chromophores bridged by a large redox-active aromatic 9,11,20,22-tetraazatetrapyrido[3,2-a:2',3'-c:3'',2''-l:2''',3'''-n]pentacene-10,21-quinone (tatpq) ligand.

Further, it is established that, upon irradiation in the presence of triethylamine, the tatpq ligand is reduced by *four* electrons along with concomitant protonation. This process is reversible, in that, oxidation by air quantitatively reforms the initial complex. The identification of the reduction intermediates were carried out using a combination of cyclic voltammetry, differential pulse voltammetry, and spectroelectrochemistry.

Molecular orbital calculations and photophysical studies describe the tatpq ligand as compartmentalized with two low lying acceptor orbitals' one quinone-based while the other being pyrazine-based. The fact that the electrons are stored in two closely related orbitals, both spatially and energetically, suggest that this type of photocatalyst may be capable of driving reactions requiring concerted multi-electron transfer and, thus, have unique potential for photocatalysis.