

ARTIFICIAL PHOTOSYNTHESIS WITH ELECTRON ACCEPTOR/PHOTOSENSITIZER-APTAMER CONJUGATES

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Our recent efforts to artificial photosynthesis [1] centered on the use of photosensitizer-modified aptamer conjugates as functional scaffolds to organize supramolecular diads, mimicking photosynthesis by guiding photo-sensitized electron transfer to drive catalytic and biocatalytic transformations. We describe the synthesis of Ru(II)-*tris*-bipyridine (Ru(bpy)₃)²⁺-anti-tyrosinamide aptamer conjugates as functional supramolecular scaffolds for controlling photo-induced electron transfer (ET) processes that are coupled to the light-induced biocatalyzed generation of NADPH or to the photochemically-induced evolution of hydrogen (H₂). Prof. Willner's recently reported method to design "nucleocapzymes" [2] can be adapted to introduce a versatile paradigm to assemble artificial photosynthetic model systems. Supramolecular complexes consisting of the photosensitizer, Ru(II)-*tris*-bipyridine, conjugated to the anti-tyrosinamide aptamer, and N-methyl-N'-propyl-(amino)tyrosinamide)-4,4'-bipyridinium, TA-MV2+, an electron acceptor ligand provide artificial photosynthetic model systems. Four different photosensitizer-aptamer conjugates are described and these include the photosensitizer linked to the 5'- or 3'-end of the aptamer, and conjugates that include the photosensitizer tethered to the 5'- or 3'-end of the aptamer through four-thymidine bridges. The photosensitizer-aptamer/electron acceptor complexes stimulate the photosensitized ferredoxin-NADP⁺ reductase, FNR, catalyzed synthesis of the NADPH cofactor or the photosensitized hydrogen evolution in the presence of Pt nanoparticle catalysts. The yields of the H₂-evolution processes depend on the complex configuration. Steady-state fluorescence and life-time quenching experiments reveal that static intra-complex electron transfer quenching of the Ru(II)-*tris*-bipyridine photosensitizer within the photosensitizer-aptamer/TA-MV2+ complexes control the photocatalyzed biotransformation and the light-induced H₂-evolution processes.

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Various carotenoids play a number of important roles in photosynthesis including absorption of light in blue range of visible spectrum followed by excitation energy transfer to chlorophylls and dissipation of excessive energy which prevents photodamage of photosynthetic apparatus caused by highly reactive species formed under excessive light illumination. Two excited states of carotenoids are most likely responsible for these processes: the optically bright $1B_u$ state and the dark $2A_g$ state, respectively. Adiabatic relaxation of both excited states is accompanied with a significant change of bond length alternation (BLA) in the conjugated π -system which is responsible for pronounced vibrational structure in absorption spectra and impedes assessment of quality of computational results usually relying on vertical transitions for rather large molecules.

Excitation energies of adiabatic and vertical transitions from a series of polyenes with the number of conjugated double bonds ranging from 8 to 13 which corresponds to the majority of natural carotenoids. Excited state geometries were optimized using TDDFT/CAMB3LYP for $1B_u$ and MCSCF in the entire space of π -orbitals, energies of excited states were computed using DMRGSCF with NEVPT2 correction accounting for dynamic correlation. This approach provided qualitative agreement with experimental data for $1A_g \rightarrow 2A_g^+$ excitation energies and good agreement for $1A_g^- \rightarrow 2A_g^-$ transition is approximate -1.1 eV which is due to the strong impact of BLA on energy levels of vertical and adiabatic excitation energies for $1A_g^- \rightarrow 2A_g^-$. The difference between DFT/MRCI and AM1/CASCI methods widely used for modeling of non-photo-carotenoids. The aforementioned agreement with experimental data shows that geometry optimization of the $2A_g^-$ state requiring semi-numerical MCSCF gradient geometry optimization of the $2A_g^-$ state requires current implementation.

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