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Review

Charge-separated excited states in platinum(II) chromophores: Photophysics, formation, stabilization and utilization in solar energy conversion

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Contents

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ABSTRACT

This review discusses photophysical properties and application of diverse and broadly tuneable Pt(II) based chromophoric systems for solar energy conversion. Firstly, we outline photophysical properties of the prevailing classes of Pt(II) compounds, as classified by the donor ligand(s). A brief review of the multicomponent electron transfer cascade systems follows. The trends in the photophysical properties – the lifetime of the charge-separated state, emission yields, etc. – as a function of the electronic and steric

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properties of the ligands are analysed. The final part considers emerging exciting applications of Pt(II) compounds in dye-sensitized solar cells and dihydrogen production.

1. Introduction

The fascinating world of research into "solar energy conversion" stems from our understanding that the energy of sunlight could satisfy all worlds' energy demand, providing it is harnessed efficiently. There is a diversity of approaches to solar energy conversion, ranging from reproducing natural systems, designing hybrid natural–artificial systems where natural enzymes are performing part of the task, or creating fully artificial systems. Such a chemical approach holds much promise, and primarily embraces solar-to-electrical power conversion in photovoltaics, dye-sensitized solar cells, and photocatalysis. Their general principles and practical realization have been comprehensively reviewed previously [1–6].

The key photophysical steps of solar energy harnessing in a fully artificial, "chemical" system are the same as in a natural one. They involve (i) absorption of light which drives an initial electron–hole separation; (ii) cascade electron/hole transfer to the periphery of the system creating an independently reactive electron/hole pair (a long-distant charge separated state which stores part of the absorbed light energy); and (iii) independent redox reactions at each site. The most desired reductive processes are the production of hydrogen from water and reduction of CO_2, the most desired oxidation process is water oxidation.

The fundamental process of photoinduced charge separation lies at the heart of the natural and artificial systems, regardless of what the end use of the power would be [3,4,7–11].

A practical system should include a chromophore (C) that absorbs sunlight, and electron donor (D) and electron acceptor (A) moieties, which are pre-organized in a way that permits the control of their electronic and steric interactions and therefore the rates and yields of electron transfer [10,12,13]. A sequence of basic processes in such D–C–A light-harvesting photocatalytic systems (Fig. 1) involves:

1. Light absorption by the chromophore to form an initial excited state D–C*–A. The initial excited state of the chromophore is frequently charge-transfer in nature.
2. Electron transfer quenching of the chromophore by either the donor (reductive quenching, forming $D^+–C^-–A$) or by the acceptor (oxidative quenching, forming $D–C^+–A^-$).
3. Charge separation from either of the states above to form a long-distant charge separated state, $D^+–C–A^-$, which in the case of multiple donors and acceptors involves cascade process of "dark" electron/hole transfer steps.
4. Electron transfer from A^- to the reduction catalyst and from the oxidation catalyst to D^+.
5. Multiple electron transfer by repetition of steps 1–4 to give the required number of electrons at the catalytic sites for the redox process in question.
6. Reaction of the activated catalysts, completing the electrochemical half-reaction and returning the system to the initial state.

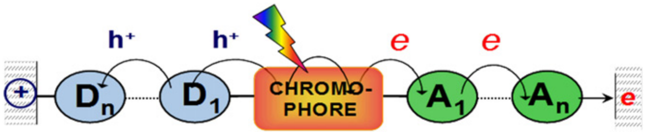

Fig. 1. General outline of a D–C–A (donor–chromophore–acceptor) photochemical device for solar energy conversion involving multiple electron donors and acceptors.

Notably, the sequence above is based on electron transfer cascades (not dissimilar to the electron transport chain in photosynthesis), to which we will return later in the text. A large variety of chemical systems have been developed and built around this general principle, from transition metal complexes [14–16] and porphyrins [17], to bio-inspired systems such as metal complex sensitized hydrogenase [18–21] and semiconductor based systems [22,23].

From the basic process described above, in order to catalyse photochemical reactions, D–C–A complexes should possess the following properties: (i) efficient absorption of visible light; (ii) long lived charge separated excited state; and (iii) sufficient energy to catalyse the specific reaction in question.

Transition metal complexes are most promising for such applications as they intensely absorb visible light, producing a charge-transfer lowest excited state, thus they are capable of acting as chromophores. They are also capable of being electron relays and catalysts, and hence can potentially perform multiple functions within an integrated photocatalytic system.

The main types of charge-transfer excited states in transition metal complexes include metal-to-ligand charge transfer (MLCT), interligand charge transfer (LL'CT), and mixed MLCT/LLCT (also denoted MLL'CT or MMLL'CT), where the frontier orbitals are considerably delocalized over both the ligand(s) and the metal centre. More detailed descriptions of the photophysical properties and applications of transition metal complexes can be found in many comprehensive reviews [24,25].

An overwhelming volume of research exists on the use of octahedral d^6 metal complexes in a variety of "solar driven" applications, starting from the archetypal dication $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) [3,5,16,26,27] and expanding to many of its derivatives. This complex efficiently absorbs light in the visible region (λ_{max} = 452 nm, ε = 13,000 M^{-1} cm^{-1} in acetonitrile) [8], forming an MLCT excited state, which due to strong spin–orbit coupling induced by the heavy atom, relaxes on the ultrafast time scale into the lowest triplet (^{3}MLCT) state. The ^{3}MLCT state of $[Ru(bpy)_3]^{2+}$ has a relatively long lifetime (~600 ns in deoxygenated solutions), and a high energy content, of 2.1 eV, sufficient for oxidation of water [8]. The design principles developed on the example of Ru(II) compounds for solar applications have been translated to other octahedral metal centres, notably Os(II) or Ir(III).