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Review

Photochemical and photophysical properties of ion-pair charge transfer complexes for all-optical information processing

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Abstract

The photochemical and photophysical properties of ion-pair charge transfer (IPCT) complexes comprising of 4,4′-bipyridinium and various counter ions have been reviewed. Quantum chemical and thermodynamic properties of IPCT complexes are summarized. IPCT complexes of 4,4′-bipyridinium with tetraphenylborate derivatives showed specific absorption and fluorescence properties. The photoinduced electron transfer from a counter anion to 4,4′-bipyridinium cation occurred within less than 100 fs upon excitation of IPCT complexes. The back electron transfer was controlled by changing counter anions and/or microenvironments. The transient absorption spectroscopy showed the ultrafast back electron transfer between 4,4′-bipyridinium and iodide in less than 2 ps. The absorption spectra of reduced 4,4′-bipyridinium derivatives were controlled over a broad range covering from visible to optical telecommunication wavelength. This phenomenon was applied to all-optical light modulation based on the guided wave mode devices composed of a photoresponsive polymer layer and a low-refractive-index polymer layer.

Keywords: Ion-pair charge transfer (IPCT) complex; 4,4’-bipyridinium derivatives; Photoinduced electrochromism; Counter anion effect; Transient absorption spectroscopy; Photoresponsive polymer; All-optical light modulation; Guided wave mode device

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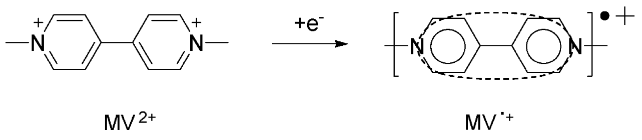
Fuyuki Ito was born in 1977 in Nagano Prefecture, Japan. He received his BS in Education and MS in Engineering from Shinshu University in 1999 and 2001, respectively. He received a PhD in Chemistry from Tohoku University in 2004 under the direction of Prof. Shozo Tero-Kubota. He worked as a postdoctoral fellow in the Center for Advanced Science and Innovation, Osaka University with Prof. Hiroshi Miyasaka. He moved to Kyushu University in 2005 as a research associate and became an assistant professor in 2007, working with Prof. Toshihiko Nagamura. His current research is photoexcitation dynamics of molecular-assembly and polymer related to energy or electron transfer.

Toshihiko Nagamura was born in 1946 in Iki Island, Nagasaki Prefecture. He received his Bachelor (1969), Master (1971), and Doctor (1974) degrees of Engineering from Kyushu University. After staying 3 years in USA as a postdoc, he joined Department of Organic Synthesis, Faculty of Engineering, Kyushu University as a research associate in 1978. He was promoted to a lecturer in 1978 and to an associate professor in 1980. He moved to Interdisciplinary Graduate School of Engineering Sciences, Kyushu University in 1983 as an associate professor. He was promoted to a full professor in 1990 at Research Institute of Electronics, Shizuoka University. He moved to the present place as a full professor in 2003. His current research is related to molecular photonics, ultrafast dynamics of molecular assemblies, chemistry and physics of advanced polymers, characterization of ultrathin polymer films, and high performance chemical sensing by evanescent light.

1. Introduction

Viologens such as 1,1′-dimethyl-4,4′-bipyridinium dication, methylviologen (MV^{2+}), and their alkyl derivatives attract a great deal of interests in basic researches and applications [1–3]. Solar energy conversion and electrochromic display are among typical applications. MV^{2+} is a good electron acceptor to form very stable radical cation ($MV^{\bullet+}$) in an inert atmosphere as shown in Scheme 1 [2,4–8]. Electrochemically reduced species has a characteristic absorption spectrum in the visible region with two maxima at 396 and 606 nm [9], which shows blue color. The reduced species, $MV^{\bullet+}$, reversibly generate MV^{2+} by oxidation, which shows no absorption in visible wavelength region. Such behavior is widely known as "electrochromism" [3]. The bipyridinium radical cation is one of the most stable redox-active organic compounds. The stability and absorption spectra of radical cations is attributed to the delocalization of unpaired electron throughout a π-framework of the bipyridyl group and central conjugated units, if any, connecting two pyridyl groups. Therefore, the viologens have a great potential for display based on the electrochromism or ultrafast switching in the optical telecommunication system.



Scheme 1.

Nagamura et al. first reported that the bipyridinium salts with specific tetraphenylborate derivative, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (abbreviated as $TFPB^-$), show reversible color change upon photoirradiation due to the electron transfer between counter anion and bipyridinium cation in various microenvironments including Langmuir Blodgett (LB) films, solutions, polymer films and microcrystals [10,11]. They named it as "photoinduced electrochromism". It was due only to the single electron transfer reaction via the excited state of specific ion-pair charge transfer (IPCT). Charge transfer (CT) complexes are generally formed between neutral molecules, ion and neutral species, and two ions with opposite charges and redox activities [12]. CT complexes have attracted interests in not only fundamental chemistry, photochemistry and electron transfer dynamics [13], but also information processing such as optical memory [14,15], solar energy conversion and storage [16]. The formation of IPCT complexes are characterized by their specific absorption spectra usually in the visible region which are absent in both parent ions. At the ground state of CT or IPCT complexes only a small fraction of electrons is transferred from a donor to an acceptor. A complete single electron transfer occurs at the excited state of CT or IPCT complexes. So if an acceptor showing electrochromism such as viologens is employed, color or absorption spectral changes in IPCT complexes can also be optically driven.

In this review, we describe the photochemical and photophysical properties of IPCT complexes of which fundamental aspect will be described based on the quantum chemical and thermochemical properties. This review also shows application to the all-optical information processing using IPCT complexes as a light modulation material in broad time and wavelength domains based on the photoinduced electrochromism.

2. Fundamental aspect of ion-pair charge transfer complexes

2.1. Summary of charge transfer theory

Before mentioning about IPCT complexes, the fundamental aspect of CT complexes generated by neutral species is described. CT complexes are formed between two neutral molecules or two ions with opposite charges. In 1952, Mulliken reported the quantum chemical treatment for molecular complex formation [12,17]. The 1:1 complex, the most simplified case, is formed by weak interaction of electron donor (D) and acceptor (A). According to Mulliken's valence-bond (resonance) treatment, the ground and excited states of weak complexes formed