様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

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研究課題名（和文） Reactions of Super Reductants and Oxidants Explored by Ultrafast Spectroscopy

研究課題名（英文） Reactions of Super Reductants and Oxidants Explored by Ultrafast Spectroscopy

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交付決定額（研究期間全体）：（直接経費）　　2,100,000円

研究成果の概要（和文）：　本研究の成果は、超高速分光を用いた新たな励起イオン種（励起シクロパラフェニレンジカチオン、強く相互作用する分子内の励起ナフタレンジイミドラジカルアニオン、励起フラーレンジアニオン）の励起状態ダイナミクス及び反応メカニズムの解明である。これにより、励起イオン種をさまざまな分子材料系への適用探求が可能となり、また、超還元剤と超酸化剤に関する新たな科学分野を確立・開拓する道筋を示すことができた。

研究成果の学術的意義や社会的意義
This research focuses on the excited ions as the untapped novel energy precursors instead of the traditional excited neutral species. Reactions from the excited states of ions, which act as super redox reagents, were examined to uncover new pathways for harnessing sunlight in molecular devices.

研究成果の概要（英文）：　The achievements of this research are the clarification of excited-state dynamics and reaction mechanisms of novel excited ions, and the exploration of their application for various molecular systems to establish a new scientific field of super reductants and super oxidants.

Cycloparaphenylenes (CPPs) have attracted considerable attention because of their unique properties. The excited states of CPP2+ were investigated by transient absorption measurements. Naphthalenediimide (NDI) is among the most widely explored components for n-type materials. By applying femtosecond laser flash photolysis, an investigation was conducted to exhibit the electron transfer from excited NDI radical anion in intensely interacting molecules. Fullerene anions have attracted wide interest due to their relevant performances in organic devices. Thus, femtosecond transient absorption spectroscopy was employed to directly describe the excited states and photoinduced electron transfer of fullerene dianions.

研究分野： Photochemistry

キーワード： Excited Ions　Electron Transfer　Laser Flash Photolysis　Ultrafast Spectroscopy　Molecular Materials

様　式　C－１９、F－１９－１、Z－１９（共通）

１．研究開始当初の背景

Radical ions, generated through the single electron transfer (ET) mechanism, are considered vital intermediates in various fields such as organic chemistry, photochemistry, electrochemistry, biochemistry, and radiation chemistry. On the other hand, the excitation of radical anions and cations by photoirradiation produces corresponding excited states. These excited radical ions are highly reactive intermediates, with their redox potentials amplified by the excitation energy, as demonstrated in Figure 1. Excited radial anion or cation can serve as a powerful electron or hole donor i.e., *super reductant* or *super oxidant*. Thus, excitation of radical ions should be an intriguing process, as it leads to various reactions unattainable from the corresponding ground states. Moreover, when considering the role of charge carriers upon irradiation in n-type or p-type organic semiconductors, understanding excited radical anions and cations is of paramount importance.

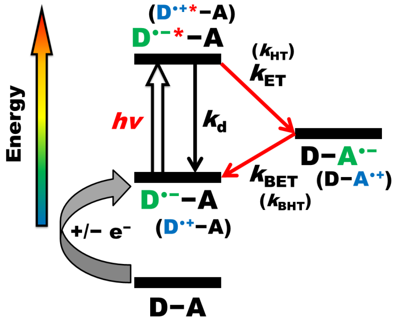

Figure 1. Schematic diagram for ET and HT from excited radical ions (D and A represent donor and acceptor, respectively; k_{d}, k_{ET}, k_{BET}, k_{HT}, and k_{BHT} represent rate constants of deactivation, ET, back ET, HT, and back HT processes, respectively).

From the 1980s, the existence of excited radical ions was first acknowledged by researchers based on product analysis and theoretical calculations. In the 1990s, nanosecond laser flash photolysis studies provided evidences for the presence of excited radical ions in reactions, and kinetic analyses revealed some of their properties, albeit indirectly. Around the year 2000, Wasielewski and his colleagues reported the first direct detection of transient absorption spectra of excited radical anions with lifetimes up to a few hundred picoseconds.[1] Following this, several research groups studied the excited-state dynamics of radical ions, primarily revealing ultrafast internal conversions. However, despite these studies, the detailed characteristics of the ET or hole transfer (HT) processes from excited radical anions or cations remain unclear due to a lack of systematic investigation. In the previous works, the applicant has developed a new methodology to study excited radical ions using femtosecond laser flash photolysis. From the series of studies, the applicant found several novel photoinduced processes which are achievable only from excited radical anions and cations. Building on these findings, in the current research, the applicant intended to explore further reactive intermediates and apply them to various reaction systems.

２．研究の目的

The purposes of this research plan are the clarification of excited-state dynamics and reaction mechanisms of excited radical ions/excited divalent ions, and the exploration of their application for diverse molecular systems to establish a new chemistry of super reductants and super oxidants.

３．研究の方法

The steady-state absorption spectra were obtained using a UV-vis-NIR spectrometer. The transient absorption spectra were recorded during femtosecond laser flash photolysis experiments. All theoretical calculations were carried out using (time-dependent) density functional theory method.

４．研究成果

(1) Significant structural relaxations of excited [*n*]cycloparaphenylene dications (*n* = 5–9)[2]

Hoop-like macrocycles, such as cycloparaphenylenes ([*n*]CPPs, where n is the number of phenylene rings), have garnered significant attention in recent years because of their intriguing properties stemming from their highly strained aromatic structure and radially oriented p-orbitals, as illustrated in Figure 2. Although the radical cation and dication states of [*n*]CPPs have been characterized, the corresponding excited states, expected to display enhanced redox properties, remain unexplored. In this study, the S_1 state of [*n*]CPP^{2+} was investigated using transient absorption measurements in the visible and near-infrared regions. The energy of the transient absorption peak exhibited a linear relationship with the reciprocal of the repeating unit, suggesting that the distribution of the excited state broadened with increased ring size. It was also found that smaller CPP^{2+}s demonstrated longer excited state lifetimes. Theoretical calculations indicated that there was a remarkable structural relaxation in smaller CPP^{2+}s accompanying the changes in the charge distribution.

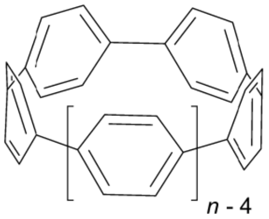

Figure 2. Molecular structures of [*n*]CPPs (*n* = 5–9).

Consequently, it was concluded that the smaller Franck-Condon factor, attributable to considerable structural changes, and the larger S_1 energy were responsible for the extended S_1 state lifetimes observed in smaller CPP^{2+}s.

(2) Electron transfer processes from excited naphthalene diimide radical anions in intensely interacting aromatic imide molecules[3]

Aromatic diimide, especially naphthalenediimide (NDI), is among the most extensively explored components for n-type semiconductor materials. Prior investigations have examined ET processes originating from excited NDI radical anion states.[4] Nevertheless, no research work has been yet reported for understanding the related photoinduced processes in polymeric and crystalline structures. Therefore, this study designed target systems aimed at revealing the ET processes of excited radical anions between molecules that have stronger interactions than conventional molecules. By using a xanthene molecule as a spacer, the interacting molecules were positioned similarly to those in organic solids (Figure 3). Due to their proximity, orientation, and stronger interactions, the dyad molecules designed in this study are expected to exhibit faster ET than traditional molecules utilizing other spacers.

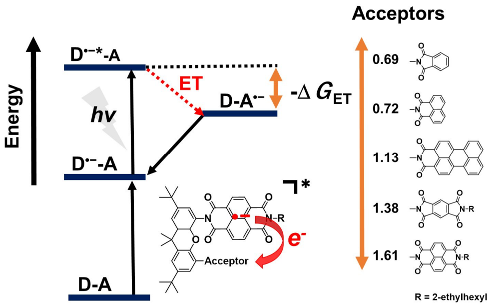

Figure 3. Molecular design for the NDI dyad systems.

In conclusion, a series of new aromatic imide dyad molecules were synthesized using xanthene molecules as spacers. Intramolecular interactions within these dyad molecules were confirmed in both the ground and excited states of the radical anions. Additionally, faster ET was observed in these xanthene-spacer dyad molecules compared to conventional dyad systems.

(3) Direct investigation of excited C_{60} dianion and its intramolecular electron transfer behaviors[5]

Fullerenes serve as crucial organic functional materials in a wide array of fields, such as organic field-effect transistors (OFETs), organic solar cells (OSCs), and organic light-emitting diodes (OLEDs), due to their high electron affinities and exceptional electron transport properties. Moreover, fullerene anions have drawn considerable interest because of their implications in performances such as the superconductivity of doped semiconducting materials and the ferromagnetism of fullerene-inclusive devices, etc. Thus, in this study, C_{60}, its derivative pyrrolidino[60]fullerene ($C_{60}H$), and C_{60}-containing dyads such as C_{60}-NDI and C_{60}-pyromellitimide (PI) were prepared as target compounds, as shown in Figure 4. For the first time, femtosecond transient absorption spectroscopy was utilized as a primary tool to directly characterize the excited states and photoinduced ET properties of fullerene dianions.

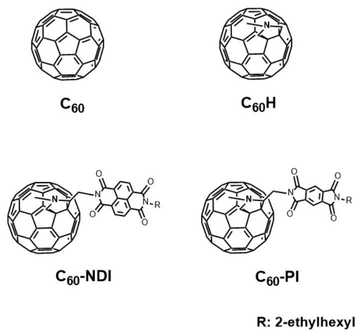

Figure 4. Chemical structures of C_{60}, $C_{60}H$, C_{60}-NDI, and C_{60}-PI.

Upon near-infrared laser excitation, the excited dianion of either C_{60} or $C_{60}H$ displayed two states with lifetimes of less than 1 ps and several tens of ps, respectively, due to the internal conversion from the theoretically predicted S_n state (Figure 5). Furthermore, ET processes from the excited C_{60}^{2-} in dyad molecules, including C_{60}^{2-}-NDI$^{\bullet-}$ and C_{60}^{2-}-PI$^{\bullet-}$, were confirmed. These ET processes exhibited varying ET rate constants, attributable to the differences in their driving forces.

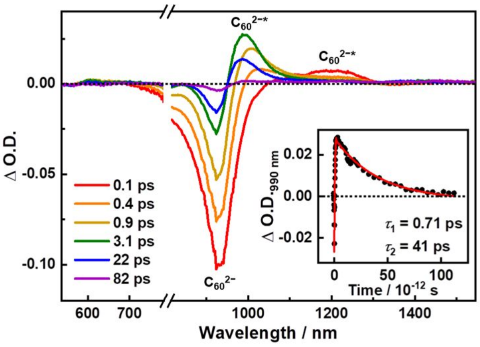

Figure 5. Transient absorption spectra of C_{60}^{2-}. Inset: kinetic trace of ΔO.D. at 990 nm.

The current findings have provided a clear description of the previously uncharted excited-state characteristics of fullerene dianions for further exploration in the photochemistry study of excited multi-ions (excited multi-polarons) and their potential applications in organic semiconducting materials.

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５．主な発表論文等

〔雑誌論文〕　計2件（うち査読付論文　2件／うち国際共著　0件／うちオープンアクセス　0件）

１．著者名 Fujitsuka Mamoru、Lu Chao、Zhuang Bo、Kayahara Eiichi、Yamago Shigeru、Majima Tetsuro	４．巻 123
２．論文標題 Size-Dependent Relaxation Processes of Photoexcited [n]Cycloparaphenylenes (n = 5-12): Significant Contribution of Internal Conversion in Smaller Rings	５．発行年 2019年
３．雑誌名 The Journal of Physical Chemistry A	６．最初と最後の頁 4737～4742
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acs.jpca.9b03334	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

１．著者名 Fujitsuka Mamoru、Kayahara Eiichi、Lu Chao、Yamago Shigeru、Majima Tetsuro	４．巻 20
２．論文標題 Significant Structural Relaxations of Excited [n]Cycloparaphenylene Dications (n = 5-9)	５．発行年 2018年
３．雑誌名 Physical Chemistry Chemical Physics	６．最初と最後の頁 29207～29211
掲載論文のDOI（デジタルオブジェクト識別子） 10.1039/c8cp04860f	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

〔学会発表〕　計1件（うち招待講演　0件／うち国際学会　0件）

１．発表者名 Fujitsuka Mamoru、Kawakami Hiroki、Lu Chao、Majima Tetsuro
２．発表標題 Electron Transfer Processes from Excited Naphthalene Diimide Radical Anions in Intensely Interacting Aromatic Imide Molecules
３．学会等名 Annual Meeting on Photochemistry 2019
４．発表年 2019年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

－

６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関