

論文の内容の要旨

論文題目 Studies on Photoinduced Electron Transfer Based on Carbon-Bridged Oligo(phenylenevinylene)s

(炭素架橋オリゴフェニレンビニレンに基づく光誘起電子移動の研究)

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Introduction

Understanding of the factors that control the nonadiabatic electron transfer (ET) in the donor-bridge-acceptor (DBA) system is essential to develop the molecular device and the artificial photosynthetic model. The ET rate (k_{ET}) can be described by the semi-classical Marcus equation:

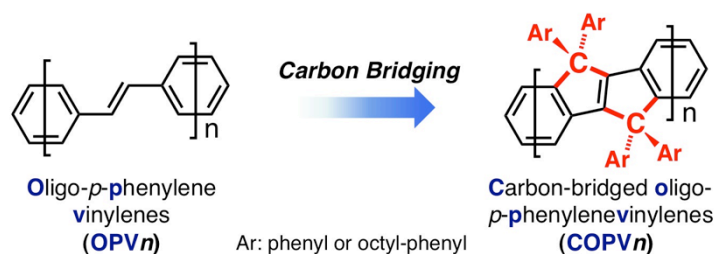
$$k_{\text{ET}} = \sqrt{\frac{\pi}{\hbar^2 \lambda_{\text{S}} k_{\text{B}} T}} |V|^2 \sum_n \frac{e^{-S} S^n}{n!} \exp\left(-\frac{(\Delta G_{\text{ET}}^0 + \lambda_{\text{S}} + n\hbar\omega)^2}{4\lambda_{\text{S}} k_{\text{B}} T}\right)$$

Here, λ_{S} is the solvent reorganization energy, λ_{V} is the vibrational reorganization energy, V is the donor-acceptor electronic coupling, $S = \lambda_{\text{V}}/\hbar\omega$ is the electron-vibration (e-v) coupling, ω is the averaged frequency of the coupled quantum mechanical vibrational mode, and n denotes to the vibrational quantum number.

The electronic factor V largely depends on the degree of the overlap between the bridge π -orbitals. Thus the conventional flexible bridges suffer from torsional motions, resulting in an attenuated electronic coupling. On the other hand, the electron-nuclear factor S depends on the degree of the overlap between the electron density difference upon the ionization and the derivative of the nuclear-electronic potential, which is not significant for flexible bridges except for certain conditions such as cryogenic temperatures.

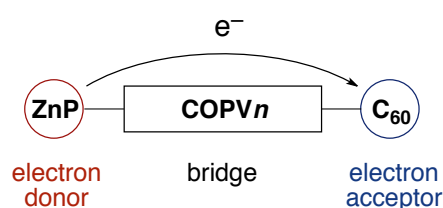
In light of the aforementioned, the author envisioned that planarization and rigidification of the bridge would maximize not only the electronic coupling but also the e-v coupling, which is prerequisite for the molecular electronics. With this hypothesis in mind, the DBA systems having a

carbon-bridged oligo-*p*-phenylenevinylene (COPV) bridge, a rigid and planar π -conjugated framework, were designed and synthesized to investigate the effects of the bridge planarization and rigidification on electronic coupling and e–v coupling in comparison with the DBA systems having a flexible oligo-*p*-phenylenevinylene (OPV) bridge.



Synthesis and Photophysical Properties of Zinc Porphyrin–Fullerene Conjugates Bridged by Carbon-Bridged Oligo(Phenylenevinylene)s

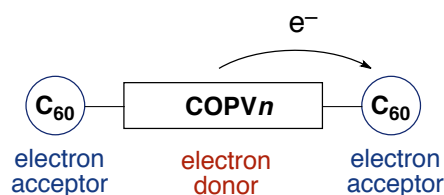
A series of zinc porphyrin–fullerene conjugates bridged by COPVs has been synthesized and photochemical properties were studied. It was found that a rigid and flat COPV exhibited 650-fold increase in ET rate compared with the conventional organic wires in the Marcus inverted region, where the e–v coupling affects ET greatly. The rigidity caused an unusually strong e–v coupling and accounted for the 50-fold rate enhancement, which was caused by inelastic electron tunneling. The flatness enhanced electronic coupling and accounted for the remaining amplification. This ET pathway emerged in solution at room temperatures, suggesting the practical utility of COPVs as molecular devices. The COPV wire is unique among organic and carbon nanotube nanowires regarding the diversity of molecular designs, stability, solubility, and processability.



Synthesis and Photophysical Properties of Carbon-Bridged Oligo(Phenylenevinylene)s–Fullerene Conjugates

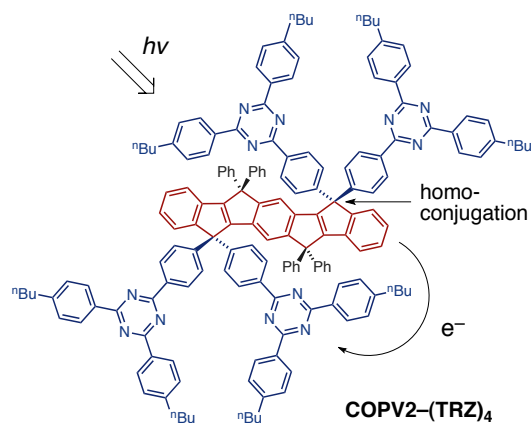
A series of COPV n –fullerene dyads has been synthesized and the photochemical properties were studied. For $n = 2$ and 3, the charge separation occurred to provide the charge separated state from the singlet excited state of C₆₀ produced after the ultrafast energy transfer from COPV n to C₆₀. The semiclassical Marcus analysis indicated the significant e–v couplings caused by COPV n moiety as well as the strong electronic couplings. These observations are contrastive to the

OPV–fullerene dyads, in which the photoinduced ET does not occur due to the higher oxidation potentials arising from the flexibility of OPVs.



Large Electronic Coupling in a Homoconjugated Donor–Acceptor System Involving Carbon-Bridged Oligo-*p*-Phenylenevinylene and Triazine

The COPV2 possessing triazine (TRZ) substituents, which is a new class of homoconjugated D–A system, was synthesized and the photophysical properties were studied. Efficient charge separation (CS) from COPV2 to TRZ moieties (98%) was observed in polar solvent, which can be ascribed to the short D–A distance and the multiple acceptors. The charge recombination (CR) process is successfully located in the Marcus inverted region, which is a key phenomenon to produce a long-lived charge separated state. Thus the CR rate was 100-times slower than CS rate. The electronic coupling via homoconjugation was one of the largest values among reported interactions such as π conjugation and π – π stacking.



Conclusion

The author has demonstrated the significance of bridge rigidification and planarization on the electronic coupling and the e – ν coupling in the photoinduced electron transfer in DBA systems, where an electron travels through a planar fused π -conjugated molecule over tens of angstrom in a single step. The enhancement of the e – ν coupling opened the channels of inelastic tunneling, which is unprecedented in well-defined organic molecular wires. In addition, the author has successfully developed a new donor-acceptor system featuring homoconjugation in the COPV skeleton. These results provide the deeper insight into the electron transfer, which must be beneficial to create efficient molecular electronic systems as well as light-to-energy conversion systems.