

熱活性化遅延蛍光材料 4CzIPN を用いたジアリールヘキサジエンの光増感電子移動 Cope 転位

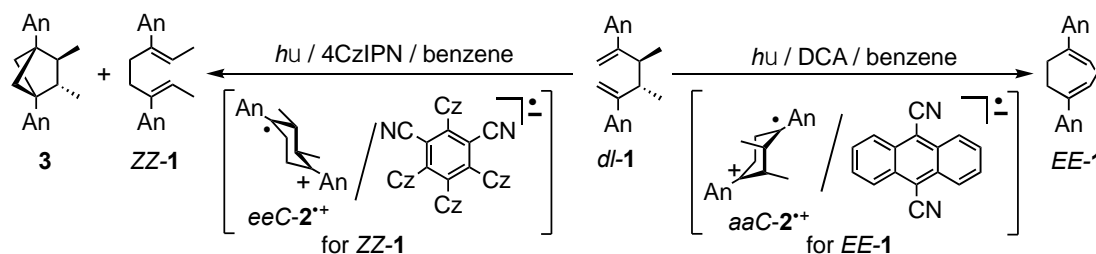
(阪公大院工¹・阪公大工²・阪公大 RIMED³)

○河岡達樹¹・秦 駿介²・大垣拓也^{1,3}・松井康哲^{1,3}・池田 浩^{1,3}

Photosensitized Electron-transfer Cope Rearrangement of Diarylhexadiene Using a Thermally Activated Delayed Fluorescence Material 4CzIPN (¹*Grad. Sch. Eng., Osaka Metro. Univ.*, ²*Col. Eng., Osaka Metro. Univ.*, ³*RIMED, Osaka Metro. Univ.*) ○Tatsuki Kawaoka,¹ Shunsuke Hata,² Takuya Ogaki,^{1,3} Yasunori Matsui,^{1,3} Hiroshi Ikeda^{1,3}

We previously reported the photosensitized electron-transfer (PET) Cope rearrangement from *dl*-**1** to *EE*-**1** (Scheme 1), using DCA as an electron-accepting photosensitizer.¹ In this electron-transfer reaction, the cyclization from [*dl*-**1**⁺/DCA^{•-}] gives [*aaC*-**2**⁺/DCA^{•-}], which is a stable six-membered chair conformation. In this study, the PET reaction of *dl*-**1** was investigated using 4CzIPN, which is known as a thermally activated delayed fluorescence material with electron-accepting ability. As a result, a triplet energy sensitization product **3** were obtained together with the Cope rearrangement product *ZZ*-**1**. The latter *ZZ*-**1** is a product via *eeC*-**2**⁺, which is less stable than *aaC*-**2**⁺. This result suggests that the conformational stability of [*aaC*-**2**⁺/4CzIPN^{•-}] and [*eeC*-**2**⁺/4CzIPN^{•-}] is remarkably affected by the bulkiness of 4CzIPN. In the presentation, we will discuss the effect of the bulkiness of the photosensitizer on the stereoselectivity of the products, based on the results of quantum chemical calculations. **Keywords** : Photoreaction; Cope Rearrangement; Electron-transfer Mechanism; Sensitizer Effect; Thermally Activated Delayed Fluorescence

我々は以前、DCA を電子受容型光増感剤とした *dl*-**1** (Scheme 1) から *EE*-**1** への光増感電子移動 (PET) Cope 転位を報告した¹。この電子移動反応では、[*dl*-**1**⁺/DCA^{•-}] の環化は、安定なす形配座である [*aaC*-**2**⁺/DCA^{•-}] を与える。本研究では、電子受容能をもち、熱活性化遅延蛍光材料としても知られる 4CzIPN を用いて、*dl*-**1** の PET 反応を検討した。その結果、三重項エネルギー増感生成物 **3** (主) と Cope 転位体 *ZZ*-**1** (副) を得た。後者の *ZZ*-**1** は、*aaC*-**2**⁺ よりも不安定な *eeC*-**2**⁺ を経由する生成物である。従ってこの結果は、[*aaC*-**2**⁺/4CzIPN^{•-}] と [*eeC*-**2**⁺/4CzIPN^{•-}] の立体配座安定性が 4CzIPN の嵩高さにより影響を受けることを示唆する。発表では、量子化学計算の結果を踏まえ、光増感剤の嵩高さが生成物の立体選択性に与える影響について議論する。



Scheme 1. PET reaction of *dl*-**1** using DCA and 4CzIPN. An = 4-MeOC₆H₄, Cz = *N*-carbazolyl.

(1) Ikeda, H.; Takasaki, T.; Konno, A.; Miyashi, T. *et al. J. Org. Chem.* **1999**, *64*, 1640–1649.