光励起とそれに続く過程の電子状態変化の実時間観測

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Real-time Observation of Electronic State Changes During Photoexcitation and Subsequent Processes

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Photoirradiation changes structures and electronic states of materials. However, these changes are so fast that direct observation of each process in a real-time manner is demanding. We have recently discovered that these processes of some material are so slow that the structural changes can be directly observed. In this study, the changes in electronic states after photoirradiation were observed by UV-Vis-NIR absorption spectra to reveal two types of charge transfer (CT) transition gradually changed in intensity and wavelengths. Density functional theory calculations based on the observed structures before and after photo-irradiation supported the interpretation of the spectral change: they demonstrated changes in energy level of the molecular orbitals associated with the CT transitions. We conclude that the gradual change in the electronic states is responsible for the shift in the absorption spectra.
Keywords : Direct observation, Real-time observation, UV-Vis-NIR absorption spectra, XPS, Metal dithiolene complex

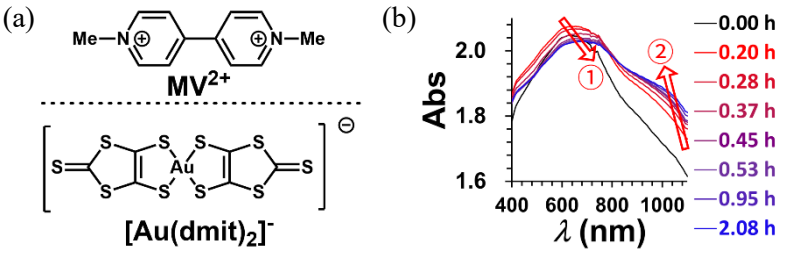

Fig. 1. (a) Molecular formulae and (b) UV-Vis-NIR absorption spectra. 0 h indicates the beginning of the first measurements of the spectra. Spectra gradually changed in the direction of red arrows (① and ②).

物質の光応答は構造や電子状態の変化を伴うが、それらの状態変化が非常に速いため変化の各過程を実時間で直接観測するには様々な制約がある。$MV[Au(dmit)_2]_2$ (Fig. 1 (a)) は光応答 (300—450 nm) が非常に遅いため、光照射後の構造変化を直接観測できる。本研究では、光照射後の電子状態の経時変化を UV-Vis-NIR 吸収スペクトルで追跡した。Fig. 1 (b)の矢印の方向に二種類のスペクトル変化が現れた。矢印に付した①は $Au(dmit)_2$ (HOMO–2)—MV (LUMO)の電荷移動遷移、②は $Au(dmit)_2$ (HOMO)—MV (LUMO)の電荷移動遷移と帰属される。①は長波長シフト、②は短波長シフトした。直接得られた光照射前後の構造に基づく第一原理計算によって、光照射後は HOMO の安定化と HOMO–2, LUMO の不安定化が示された。光照射によって各軌道間のエネルギー差が徐々に変化したことで吸収スペクトルがシフトしたと考えられる。