光励起後の特異的に遅い状態変化における電子状態と結晶構造の追跡

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Electronic states and crystal structures in uniquely slow changes after photoexcitation ([1] *Faculty of Science, Ehime University*, [2] *Graduate School of Science and Engineering, Ehime University,* [3] *Geodynamics Research Center, Ehime University*, [4] *Research Unit for Materials Development for Efficient Utilization and Storage of Energy (E-USE), Ehime University*) ○ Harune Nishida,[1] Mika Kabumoto,[1] Minaho Nakaie,[2] Toshio Naito[2,3,4]

As photoexcitation and subsequent relaxation processes proceed rapidly, it was difficult to observe them directly. However, by using the material exhibiting uniquely slow processes after photoirradiation, the processes can be observed as if they are in steady states. Then the mechanisms of various photochemical processes can be elucidated. $BPY[Au(dmit)_2]_2$ [1] and $MV[Au(dmit)_2]_2$ [2] are reported as such materials. In this study, we observed the electronic states and crystal structures of an additional example of such materials, $MV[Ni(dmit)_2]_2$ [3]. Observation of the core electronic states using X-ray photoelectron spectroscopy, they achieved steady states different from that before irradiation (Fig. 1, $t \geq 400$ h). The crystal structure exhibited changes in the lattice constants and volume (Fig. 2, $t \geq 534$ h). By slightly making unstable their energy levels and structures, a part of the photon energy received is retained in the molecular crystals.

Keywords : real-time observation; XPS; single-crystal X-ray structure analysis; DFT; metal-dithiolene complexes

光励起とその後の緩和過程は通常迅速に進行するため、直接観測するのは困難だった。しかし、光応答が特異的に遅い物質を用いれば、その過程を定常状態の様に観測することが可能になり、様々な光化学過程の機構を明らかにできる。このような物質として、$BPY[Au(dmit)_2]_2$ [1]や $MV[Au(dmit)_2]_2$ [2]が報告されている。本研究では、同様の応答が期待できる $MV[Ni(dmit)_2]_2$ [3]を用いて、光照射後の電子状態と結晶構造を観測した。X 線光電子分光で内殻の電子状態を観測すると、約 400 時間後に照射前の状態とは別の定常状態を示し、照射前の状態には戻らなかった (Fig. 1)。結晶構造に関しては、格子定数や体積が 534 時間以降で明確に変化した (Fig. 2)。エネルギー準位や構造をわずかに不安定化させ、そのまま準安定状態として留まることで、受光したエネルギーの一部を保持していると考えられる。

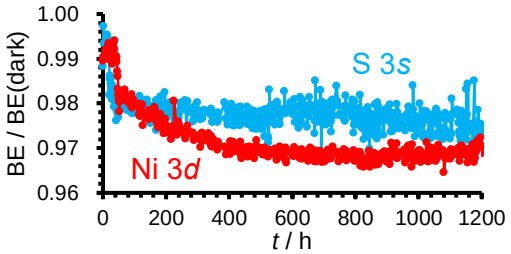

Fig. 1: Changes in the binding energy of Ni 3*d* and S 3*s* orbitals after UV irradiation for 162 min. The values of BE are normalized by the values before UV irradiation (dark). The time when irradiation was stopped was defined as 0 h.

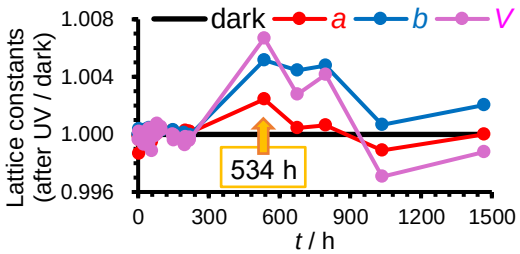

Fig. 2: Changes in the lattice constants and volume after UV irradiation for 142 min. The values are normalized by the values before UV irradiation (dark). The time when irradiation was stopped was defined as 0 h.

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