論文 / 著書情報
Article / Book Information

題目(和文)	
Title(English)	Ultrafast photoinduced dynamics of the electron donor-acceptor type metal-organic framework
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出典(和文)	学位:博士(理学), 学位授与機関:東京工業大学, 報告番号:甲第12666号, 授与年月日:2024年3月26日, 学位の種別:課程博士, 審査員:腰原 伸也,沖本 洋一,大島 康裕,河野 正規,谷口 耕治
Citation(English)	Degree:Doctor (Science), Conferring organization: Tokyo Institute of Technology, Report number:甲第12666号, Conferred date:2024/3/26, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	Chemistry 系 コース	申請学位（専攻分野）： Academic Degree Requested	博士 (Science) Doctor of
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要旨（英文 800 語程度）
Thesis Summary (approx.800 English Words)

The photo-control of macroscopic physical properties in the solid state is widely known as photoinduced phase transition (PIPT). Ultrafast switching phenomena caused by PIPT have been particularly important because of their potential applications in optical data storage, fast-switching devices, sensors, etc. (research background, **Chapter 1**). Electron donor-acceptor (DA)-type metal-organic frameworks (MOFs) with valence instability are promising molecular materials for the design of photo-responsive and electronic/magnetic functional materials. In the present study, as a target and realistic material for PIPT, we mainly focused on the DA-type (where D = donor and A = acceptor) layered MOF system, $(NPr_4)_2[Fe_2(Cl_2An)_3]$, which exhibits two-step CT phase transition (T_c = 317 and 354 K). The details of the material are discussed in **Chapter 2**. **Chapter 3** describes the experimental methodology and instruments used to conduct our desired experiments. In **Chapter 4**, the static optical spectra of $(NPr_4)_2[Fe_2(Cl_2An)_3]$ for both $E \parallel$ chain and $E \perp$ chain have been reported. Herein, we observed two absorption peaks at around 0.8 and 2.6 eV. The peak at around 0.8 eV is attributed to the CT transition between the Fe and Cl2An ions. In comparison, the peak at around 2.6 eV is attributed to an intramolecular transition in the Cl2An ions. Here, we observed highly efficient photoinduced CT dynamics in the DA-type layered MOF: $(NPr_4)_2[Fe_2(Cl_2An)_3]$ by using time-resolved spectroscopy with a pulse width of 90-fs at room temperature (RT: 300 K) discussed in **Chapter 5**. The photoinduced spectral changes are similar to the thermally induced spectral change at around 2.6 eV, suggesting photoinduced valence change of the Cl_2An ions. However, we observed a considerable difference in the spectral shapes in the CT transition and mid-IR regions. We found two unexpected new photoinduced absorption bands from the spectra analysis, one at the higher-energy side of the main CT band and the other in the mid-IR energy range—just immediately after photoexcitation. The observed spectral change strongly implies the disappearance of the local inversion center on the Cl_2An ion instantly upon photoexcitation, causing an ultrafast change in the lattice structure due to the softening of rigid bonds. This has never been realized in a thermal phase transition. These findings demonstrate that a new electronic state with a unique lattice structure—i.e., a photoinduced hidden state—appears in this MOF system at ultra-high speed (within 110 fs) upon photoexcitation at RT. Early-stage dynamics for the formation of structurally modulated photoinduced hidden state, discussed in the previous section, is still unclear, and we thought of a way to visualize them in this study. Herein, we used pump-probe spectroscopy with nearly single-cycle optical, infrared pulses (pulse width ~6 fs) to investigate early-stage dynamics for photoinduced structurally modulated state formation (details are in **Chapter 6**). After the initial large spectral change due to the photoinduced CT at Δt = 0 fs, there is an apparent spectral change in the relaxation

process (redshift of zero-crossing point) from 0 to 50 fs, suggesting sequential structural change corresponding to the ″hidden state″ we observed. Meanwhile, there is no further spectral change up to at least 500 fs. In addition, we observed coherent oscillations in the time evolution of $\Delta R/R$. According to the analysis of the coherent oscillations, we found the IR active and Raman inactive mode in the thermal equilibrium phases ~494 cm^{-1} becomes Raman active in the photoinduced state at least after 50 fs, which implies a photoinduced symmetry breaking of this material. Hence, we assumed that the formation timescale of the hidden state from the initial purely electronic excited state must be ~50 fs. In the previous chapters, we experimentally demonstrated an efficient photoinduced CT conversion between Fe and Cl_2An ions (Cl_2An^{3-} + Fe^{3+}→ Cl_2An^{2-} + Fe^{2+}) at RT. But now we intend to observe the photoinduced reverse CT (Fe^{2+} + Cl_2An^{2-}→ Fe^{3+} + Cl_2An^{3-}), i.e., conversion of HT phase to LT phase. To realize such thought, we performed a time-resolve experiment by exciting the intramolecular transition peak (~2.6 eV) with $E \parallel$ chain for pump and probe pulses in the high-temperature phase (380 K). The photoinduced $\Delta R/R$ spectra can be well reproduced by simulated ΔR/R spectrum in the CT energy range, suggesting a successful observation of photoinduced reverse CT between the Fe and Cl_2An ions. In addition to the above result, we observed a threshold behavior for realizing reverse CT for the pump excitation fluence, i.e., $I_{ex} > 1.0$ mJ/cm2, suggesting the cooperativity in reverse CT. The detailed discussion is in **Chapter 7**.

In conclusion, we can mention that the present study can be considered a first step toward developing high-speed photo-responsive MOFs with magnetic nature.