

## Ultrafast dynamics of photoinduced neutral-ionic phase transitions in charge transfer compounds with quantum paraelectricity

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In this paper, we report photoinduced neutral to ionic (NI) transitions in DMTTF-QBr<sub>n</sub>Cl<sub>4-n</sub> (DMTTF=4,4'-dimethyltetrathiafulvalene, QBr<sub>n</sub>Cl<sub>4-n</sub>=tetrahalo-*p*-benzoquinones) studied by fs pump-probe (PP) reflection spectroscopy. In this series of the compounds, the NI transition temperature decreases with increase of the number (n) of Br in an acceptor molecule, QBr<sub>n</sub>Cl<sub>4-n</sub> [1]. DMTTF-QCl<sub>4</sub> (n=0) shows the NI transition at 65 K, which is more continuous than that in the most typical NI transition material of TTF-CA. DMTTF-QBr<sub>2</sub>Cl<sub>2</sub> (n=2) does not show the NI transition but shows quantum paraelectricity at low temperatures. We can expect that dynamical aspects of photoinduced NI transitions in DMTTF-QBr<sub>n</sub>Cl<sub>4-n</sub> will be largely different from that in TTF-CA.

The results of the fs PP reflection spectroscopy have revealed that DMTTF-QCl<sub>4</sub> shows both photoinduced NI and IN transitions, which are similar to those of TTF-CA except for the nature of the coherent oscillations observed on the photoinduced reflectivity changes in the intramolecular transition region; in TTF-CA, only one oscillation mode (the LO mode) is observed [2], while in DMTTF-QCl<sub>4</sub>, two modes attributable to the LO and TO modes are detected. The results suggest that the two kinds of the molecular displacements contribute to the stabilization of the I phase in DMTTF-QCl<sub>4</sub>. In DMTTF-QBr<sub>2</sub>Cl<sub>2</sub>, on the other hand, the dynamical behavior of the photoinduced NI transition is considerably modified. The efficiency of the photoinduced NI transition shows strongly nonlinear behavior against the excitation density. In addition, gigantic amplitude of a coherent oscillation with low frequency (~28 cm<sup>-1</sup>) is generated. The analyses of the signals revealed that the coherent oscillations of molecules are produced not only in photogenerated I domains but also in the neighboring wide neutral regions including more than 100 donor-acceptor pairs. We will discuss such an anomalous behavior in the photoinduced NI transition by taking account of the quantum paraelectricity in DMTTF-QBr<sub>2</sub>Cl<sub>2</sub>.

[1] S. Horiuchi *et al.*, J. Am. Chem. Soc. 123 (2001) 665.

[2] H. Okamoto *et al.*, Phys. Rev. B 70 (2004) 165202.