Study of Excited States Dynamics of Expanded Porphyrin Complexes using Time-resolved Degenerate Four-Wave Mixing

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Asymmetric pentaazadentate porphyrin-like metal complexes, [(*R*-APPC)M]Cl_n, are a new class of optical power limiting (OPL) materials.[1] These complexes have two-dimensional delocalized conjugated π-electron systems and exhibit strong third-order nonlinearities just like metallophthalocyanines and regular metalloporphyrins.[2] However, unlike metallophthalocyanines and regular metalloporphyrins, the conjugated ring structures of these complexes can be readily modified opening the possibility of structural optimization for better OPL performance.

The main mechanism contributing to OPL in these complexes is excited state absorption (ESA), or sometimes called reverse saturable absoption (RSA), in which the molecules are excited to the higher excited states by absorption of additional photons (ESA) after the initial excitation from the ground state to the first excited state (linear absorption). In order to understand how nonlinear optical properties and photophysical characteristics are related to the OPL performance, the dynamic characterization of these complexes is essential. The time-resolved degenerate four-wave mixing (TRDFWM) is one of the methods for such characterization. The regular DFWM method measures the bulk static third-order nonlinearity, $\chi^{(3)}$, by monitoring the phase conjugate signal of the probe beam in the presence of two pump beams. The TRDFWM method works in much the same way except addition of the optical delay in one of the pump beams. In TRDFWM, the time evolution of the phase conjugate signal as a function of the temporal delay is measured providing the information how the phase conjugate signal from the transient grating formed by nonlinear wave mixing process changes in time comparable to the excitation pulsewidth.

The TRDFWM experiments for a series of [(*R*-APPC)M]Cl_n complexes were performed using a Q-switched Nd:YAG mode-locked laser with 40 ps pulsewidth and 10 Hz repetition rate, (see Fig. 1.) and the results revealed a faster process, indicated by the autocorrelation of the excitation pulse, and a relatively slower process, indicated by

a slowly decaying tail (see Fig. 2.). The results also showed that the triplet quantum yield close to 0.9 or above has a very strong correlation to the slowly decaying tail of the phase conjugate signal after the excitation. All other fast nonlinear processes such as singlet ESA to the higher excited states, which is faster than the excitation pulsewidth (~40 ps), were hidden under the autocorrelation profile of the excitation pulsewidth. The complex with the fastest inter-system crossing rate showed fluence-dependent dynamics.

To understand the mechanism further, the lifetimes of the singlet excited states for some APPCs were measured using the time-correlated single photon counting method (TCSPC). The TCSPC results showed the singlet excited lifetimes shorter than 1 ns for all the complexes in the series that we measured.

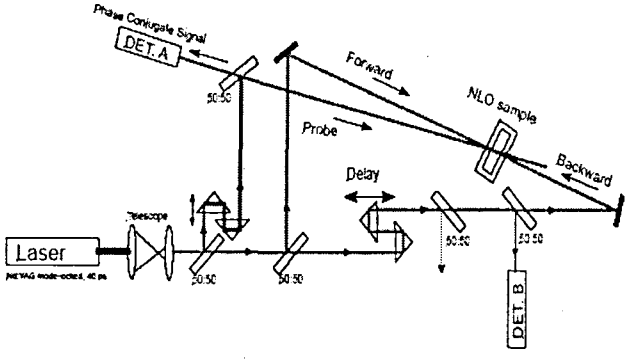

Fig. 1. TRDFWM experimental configuration. The pulse width is ~40 ps, and the repetition rate is 10 Hz. The actual beam splitting ratio of Forward: Probe: Backward:Monitor is 67:61:14:11.

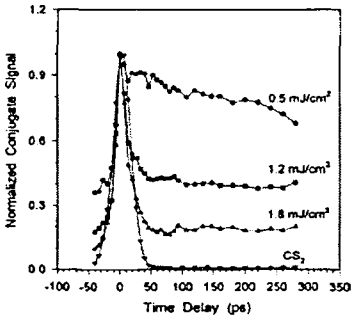

Fig. 2. Conjugate signal as a function of the delay of the backward pump beam for 4.42 x 10^{-5} mol/L [(DBP-APPC)Cd]Cl solution in a 1 mm cell. Fluence labeled for each plot is the backward pump beam fluence. Solid line in each plot is used for eye guided.

References

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2. W. Sun, Clare C. Byeon, C. M. Lawson, G. M. Gray, and D. Wang, Appl. Phys. Lett. **74**(22), 3254 (1999).