

Time-resolved luminescence and transient absorption measurements of chiral azo-salen Mn(II) and Zn(II) complexes in combination with silver nanoparticles

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[Abstract] As an approach to improve dyes' performance and mechanism of dye-sensitized solar cells (DSSC) [1-3], we have originally developed chiral azo-salen metal complexes (Fig. 1) for inducing localized surface plasmon resonance (LSPR) caused by incorporating silver nanoparticles (AgNPs) [4]. In this context, understanding excited state and reaction intermediate during light irradiation to return to ground state may be important. Therefore, we investigated such systems using time-resolved luminescence and transient absorption measurements.

[Experimental] Metal complexes were synthesized and characterized (including X-ray crystal structure analysis based on powder XRD) according to similar procedures to previous ones [2,3]. Induced CD bands from chiral complexes could be observed in the plasmon region of AgNPs. DMSO solutions of four complexes (MMn, MZn, CMn, and CZn) and ethanol solutions of composite materials of each complexes with AgNPs were also prepared. The time-correlated single photon counting (TCSPC), the streak camera which is much shorter period of time than TCSPC and transient absorption measurement was performed for eight samples.

[Results & Discussion] The fluorescence lifetime of the sole complex and the composite materials with AgNPs was derived from curve-fitting analysis of luminescence decay curves of TCSPC (Figs. 2 and 3). Lifetime of all three components (t_1 , t_2 , and t_3) of the composite with AgNPs was longer than that of the corresponding sole metal complexes. During relaxation from excited state to ground state, composite systems may go through three reaction intermediates.

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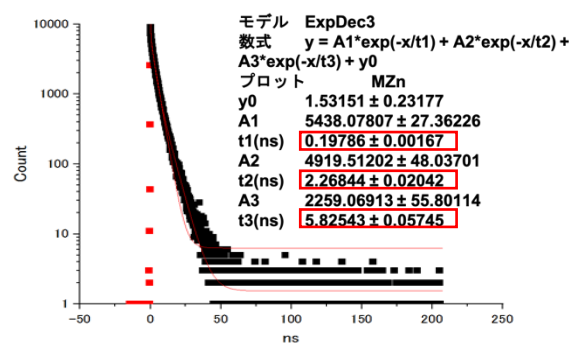
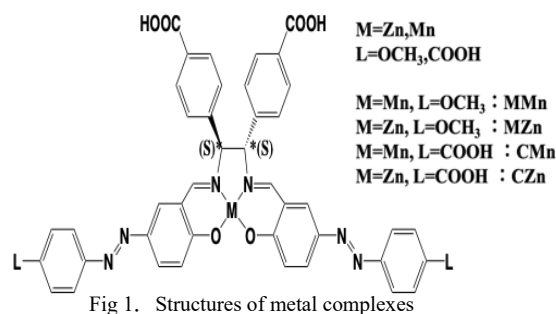


Fig 2. Fluorescence decay curve of MZn complex

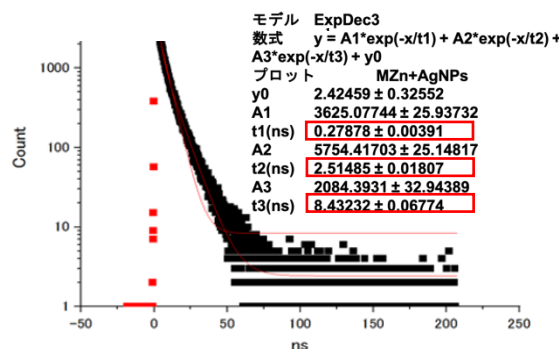


Fig 3. Fluorescence decay curve of composite of MZn complex and silver nanoparticles