Femtosecond time-resolved emission measurements of prompt fluorescence of luminescent halogeno copper(I) coordination polymers

(*University of Toyama*) ○Taishi Kobayashi, Kosuke Miura, Munetaka Iwamura, and Koichi Nozaki

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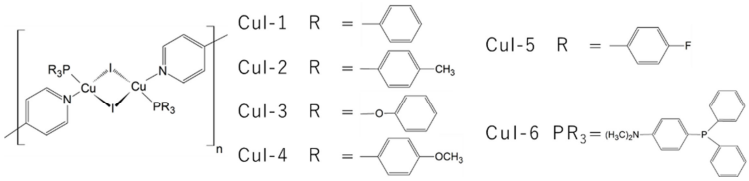
While halogeno copper(I) coordination polymers with intense thermally activated delayed fluorescence have been extensively studied recently, photorelaxation dynamics such as intersystem crossing or structural relaxation processes is still unclear. In this work, we carried out femtosecond time-resolved fluorescence up-conversion measurements for thin films of a series of halogeno copper(I) coordination polymers (CuI-1~6 in Scheme) to investigate the photorelaxation processes in Cu(I) coordination polymers.



Scheme Structures of halogeno copper(I) coordination polymers

Thin films were prepared by spraying suspension of a coordination polymer on to a glass substrate. Sprayed films of the Cu(I) complexes exhibited intense emission (Fig. 1) and the emission maxima varied with the substituent of the phosphine (PR_3). In time-resolved emission spectra for CuI-1 (Fig. 2), an emission band was observed at around 500 nm after the 405 nm exaction, which was rapidly red-shifted to 550nm within 0.3 ps. The 550nm-emission then decayed biexponentially with time constants of 3 ps and >200ns which are assignable to the lifetime of prompt and delayed fluorescence, respectively. The lifetime of the prompt fluorescence were dependent on the substituent on PR_3 : 1ps (CuI-3), 2.5-3ps (CuI-4, CuI-5), 3ps (Cu-1), 10ps (CuI-2, CuI-6). It is worth noting that these lifetimes of prompt fluorescence are much shorter than those for the Cu(I) complexes reported so far.

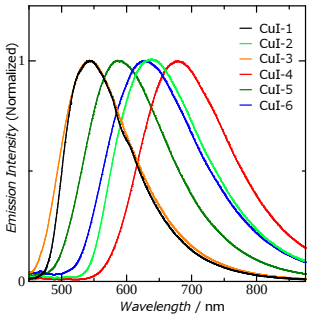


Figure 1. Emission spectra for CuI-1~CuI-6 films.

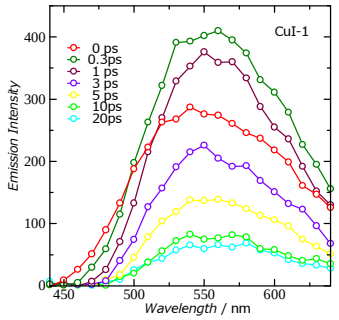


Figure 2. Time-resolved emission spectra for CuI-1 films (Ex 405 nm).