

Light-energy harvesting and electron transfer mechanism in carbazole-dendrimers cored by a Ir-complex

Dae Won Cho

*Center for Photovoltaic materials & Department of Advanced Materials Chemistry,
Korea University (Sejong)*

In order to investigate the light-energy harvesting mechanism, a series of dendrimers with a heteroleptic iridium(III) complex core, $[\text{Ir}(\text{L})_2(\text{pic-Czn})]$ (Gn: $n = 0, 1, 2,$ and 3), with $\text{L} = 2$ -(4,6-difluorophenyl)pyridine (dfppy), 2,6-difluoro-3-(4-methylpyridin-2-yl)benzotrile (dmb), and 2-(benzo[b]thiophen-2-yl)pyridines (btp) as the cyclometallating ligands, and 3-hydroxypicolinate (pic) as the ancillary ligand, connected to carbazole-based dendrons (Czn: $n = 2, 4,$ and 8) was synthesized. The Ir centred complexes [G0] show blue, green and red emissions, which are assigned to the metal-to-ligand charge-transfer ($^3\text{MLCT}$) phosphorescence. This phosphorescence was enhanced with increasing generations due to the increase in the total absorbance of the Cz-dendron. The light-harvesting efficiencies were determined by various methods such as steady-state and time-resolved spectroscopic methods. The energy transfer efficiencies for G1–G3 from the peripheral Cz-dendron to the Ir-core complex were above 90%, determined using the reduction in the lifetime of the excited $^1\text{Cz}^*$ -dendrons or the quenching of fluorescence of Cz dendrons. In case of $[\text{Ir}(\text{dmb})_2(\text{pic-Czn})]$, G1–G3 showed a transient absorption (TA) band at 600 nm, which was attributed to the $\text{S}_n \rightarrow \text{S}_1$ transition of the Cz-dendrons. The fast decay of these TA bands was consistent with the fast emission decay times. The time-resolved TA band correlated with the core Ir-complex was observed at 500 nm, though it overlapped and interfered with the intense TA band of the Cz-dendrons. Therefore, we attempted a global analysis by singular value decomposition (SVD). The determination of the absorption spectra of the individual species participating in the energy transfer process by SVD analysis can distinguish between different mechanistic models. The analysed rate constants were consistent with the results determined by the emission decays.

In order to investigate the photoinduced electron transfer (PET) process, Cz-dendrimers with heteroleptic Ir-complex cores were synthesized. Upon excitation of the Cz dendrons, the phosphorescence of the core Ir(III) complex was quenched due to the PET process. The PET dynamics of the excited Cz-dendrons were investigated using the TA technique. A broad TA band attributed to the $\text{S}_1\text{--}\text{S}_n$ transition of the $^1\text{Cz}^*$ -dendron was observed at around 630 nm in the G1. As a result of the PET process, the Cz cationic radical species ($\text{Cz}^{+\cdot}$) was observed at around 780 nm. Interestingly, when the core Ir-complex in the dendrimer was excited with a 400 nm pulse selectively, the TA band of $\text{Cz}^{+\cdot}$ was also detected at around 780 nm. This may be due to the photoinduced hole transfer (PHT) from the highest occupied molecular orbital (HOMO) energy state of Cz to the lowest singly occupied molecular orbital (LSOMO) energy state of the excited Ir-complex. The oxidation potential of Cz is lower than that of the Ir-complex, indicating that the HOMO of the Cz-dendron is located at a higher energy state than that of the Ir-complex. The TA spectra were globally deconvoluted to generate the decay-associated spectra (DAS), from which the species-associated spectra (SAS) were calculated. The SAS can distinguish the individual intermediate species participating in the PET and PHT processes. The analysed rate constants of SAS were consistent with the results determined by the TA decays.