Energy-Transfer Quenching of $[Ru(bpy)_3]^{2+}$ in Ionic Nanosphere

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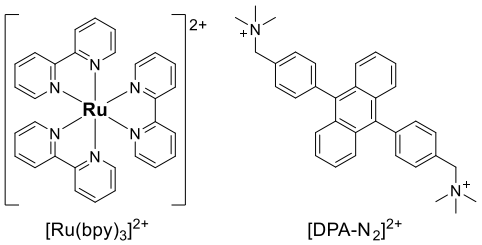
Photoinduced energy- and electron-transfer reactions are primary processes in the solar–energy conversion system such as artificial photosynthesis and solar photovoltaics. Therefore, constructing an efficient photoinduced-reaction system is one of the most important research topics. In this study, we demonstrated energy-transfer quenching of $[Ru(bpy)_3]^{2+}$ by a 9,10-diphenylanthracene derivative ($[DPA\text{-}N_2]^{2+}$) by codoping in ionic nanospheres,[1] a class of cationic exchange resins with a diameter of <300 nm.

$[Ru(bpy)_3]^{2+}$/$[DPA\text{-}N_2]^{2+}$-codoped nanospheres ($[Ru(bpy)_3]^{2+}$: 50 nmol/mg, $[DPA\text{-}N_2]^{2+}$: 0–10 nmol/mg) were prepared by soaking the ionic nanosphere with a poly(styrenesulfonate-*co*-divinylbenzene) structure in aqueous solutions of $[Ru(bpy)_3]Cl_2$ and $[DPA\text{-}N_2]Cl_2$ at room temperature. $[Ru(bpy)_3]^{2+}$ doped in the nanosphere exhibited emission from the triplet metal-to-ligand charge transfer excited state with a quantum yield (Φ_{em}) being 0.105, which was higher than that of the aqueous solution (Φ_{em} = 0.063). The emission quantum yield of $[Ru(bpy)_3]^{2+}$ decreased even by codoping 10-nmol/mg $[DPA\text{-}N_2]^{2+}$ and, furthermore, an excitation band similar to the absorption band of $[DPA\text{-}N_2]^{2+}$ was observed by monitoring at 620 nm. These results are explainable by the excited-state energy transfer between $[Ru(bpy)_3]^{2+}$ and $[DPA\text{-}N_2]^{2+}$. The emission from the $[Ru(bpy)_3]^{2+}$/$[DPA\text{-}N_2]^{2+}$-codoped nanosphere was responsive to the presence of the molecular oxygen as shown in Fig. 1. Upon an increase in an oxygen concentration, the emission from $[Ru(bpy)_3]^{2+}$ was reduced. Since the emission lifetime of $[Ru(bpy)_3]^{2+}$ was also shortened ($<\tau_{em}>$ = 910, 770 and 560 ns under argon, air and oxygen atmospheres, respectively), energy-transfer quenching of $[Ru(bpy)_3]^{2+}$ by oxygen occurred by a dynamic process.



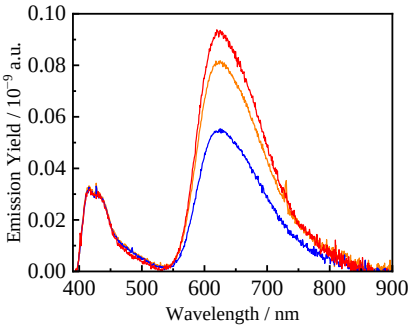


Fig. 1: Emission spectra of the ionic nanosphere containing 50-nmol/mg $[Ru(bpy)_3]^{2+}$ and 10-nmol/mg $[DPA\text{-}N_2]^{2+}$ (λ_{ex} = 375 nm) under argon (red), air (orange) and oxygen atmospheres (blue).

1) H. Yamamoto, M. Taomoto, A. Ito, D. Kosumi, *J. Photochem. Photobiol. A: Chem.* **2020**, *401*, 112771.