## Photon upconverted emission based on dye-sensitized triplet-triplet annihilation in silica sol-gel system

## Hiromasa Nishikiori, Masahiro Takeshita, Yoshihiro Komatsu

Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan

E-mail: <u>nishiki@shinshu-u.ac.jp</u>

Energy conversion efficiency of dye-sensitized solar cells can be enhanced by utilizing a near infrared light. Photon upconverted emission based on dye-sensitized triplet-triplet annihilation (TTA-UC) was investigated in order to convert a longer wavelength light to the shorter one having twice energy.<sup>[1,2]</sup> Functional organic molecules can be encapsulated in the silica gel pores or silica network by the sol–gel method.<sup>[3]</sup> In this study, TTA-UC was observed in the sol–gel silica systems containing Pt (II) octaethylporphyrin (triplet sensitizer) and 9,10-diphenylanthracene (singlet emitter).

The triplet sensitizer was encapsulated and highly dispersed in the silica gels prepared by the sol-gel method. The singlet emitter was adsorbed from its toluene solution on the silica gel pores accessible to the outside. The emission and excitation spectra of the moderately and thoroughly dried silica gel samples were observed using a fluorescence spectrophotometer. Dependences of the emission and excitation peak intensities on the emitter concentration and irradiation light intensity were examined.



Figure 1 Stern–Volmer plot for the phosphorescence quenching in the (1) wet and (2) dry silica gel systems containing Pt (II) octaethylporphyrin (triplet sensitizer) and 9,10-diphenylanthracene (triplet quencher)

Phosphorescence of the triplet sensitizer encapsulated in the silica gels was observed at a room temperature. The phosphorescence peak was located at 645 nm. The excitation spectral peak at 535 nm originated from the sensitizer absorption. Fig. 1 shows Stern–Volmer plot for the phosphorescence quenching in the wet and dry silica gel systems. The y-axis indicates the ratio of the phosphorescence intensity observed without the singlet emitter (quencher) to that

observed with each concentration of the adsorbed quencher. The phosphorescence was gradually quenched with an increase in the concentration of the singlet emitter in the wet gel. On the other hand, the phosphorescence was slightly quenched in the dry gel. The wet gel contained a low amount of solvent and water molecules, in which the triplet sensitizer and singlet emitter should collide in the excited state lifetime of the triplet sensitizer. The phosphorescence quenching indicated that the triplet sensitizer and singlet emitter molecules were in the environment similar to solvents.

The emission peak was located at 430 nm in the wet gels. The related excitation peak at 535 nm originated from the sensitizer absorption. The singlet emission was enhanced when the phosphorescence was quenched with an increase in the concentration of singlet emitter. Fig. 2 shows the dependence of the singlet emission intensity on the irradiation power in the wet silica gel systems. The emission intensity increased proportionally to the square of the irradiation power. The energy transfer from some of the encapsulated molecules to the adsorbed molecules and TTA-UC were observed in the present silica gels.



Figure 2 Dependence of the singlet emission intensity on the irradiation power in the wet silica gel systems containing Pt (II) octaethylporphyrin (triplet sensitizer) and 9,10-diphenylanthracene (singlet emitter)

## **References:**

- [1] J. S. Lissau, J. M. Gardner, A. Morandeira, J. Phys. Chem. C, 2011, 115, 23226
- [2] H. Goudarzi, P. E. Keivanidis, J. Phys. Chem. C, 2014, 118, 14256
- [3] H. Nishikiori, N. Tanaka, K. Takagi, T. Fujii, J. Photochem. Photobiol. A, 2006, 183, 53