

Far-Red Fluorescent Organic Nanoparticles of Triphenylmethane Dye

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Fluorescent organic nanoparticles (FONs) have inspired growing research interests because of their variability and flexibility in materials synthesis as well as high potentials in the application of optoelectronic devices and bioassays. Among the nanoparticles, far-red to near-IR fluorescent organic nanoparticles with emission maximum wavelength >650 nm, where the influence of the main tissue absorbing components, oxy- and deoxyhemoglobin is minimal, have been dedicated immense attention for a noninvasive clinical diagnostic [1]. However, only few fluorescent organic dyes are suitable for the application, since they are frequently chemically unstable and/or highly sensitive to photobleaching.

We here demonstrate synthesis and interesting spectroscopic properties of far-red FONs with various particle sizes. A triphenylmethane dye, malachite green (MG, see Fig. 1), was chosen as the fluorophores. Syntheses of MG nanoparticles were based on the ion-association method that utilizes formation of water-insoluble ion-pair aggregates (in the presence of neutral stabilizing polymer) in water by association of the dye cation with tetrakis(4-fluorophenyl)borate (TFPB) anion. Size tuning (45 ~ 15 nm in diameter) of the dye nanoparticles was successful by varying the molar ratio (ρ) of TFPB to MG. Absorption and fluorescence spectra of MG nanoparticle samples prepared at $\rho = 1-4$ are shown in Fig. 1a. Binding of MG with TFPB resulted in the prominent appearance of a broad absorption band at ~595 nm, which can be assigned to an MG H-aggregate, and an increase in ρ caused that in the amount of the H-aggregate. However, the fluorescence quantum yield (Φ_f) in the far-red region (690-700 nm) also increased as a function of ρ , whereas the H-aggregate was almost non-fluorescent. We found that Φ_f was reached to ~1.5% when $\rho = 4$, about 200-fold larger than that of free MG in water. Time-resolved fluorescence lifetime measurements have been carried out to understand the relaxation pathways of the S_1 state of MG (Fig. 1b). In the nanoparticle samples, the fluorescence decay curves show tri-exponential behavior, so we calculated the average fluorescence lifetime $\langle\tau\rangle$ from the following equation,

$$\langle\tau\rangle = a_1\tau_1 + a_2\tau_2 + a_3\tau_3$$

where a_i and τ_i are pre-exponential factors and excited-state fluorescence lifetimes associated with the i^{th} component, respectively. Then the obtained $\langle\tau\rangle$ are 6.1, 115, and 718 ps for samples with $\rho = 1, 2,$ and 4 respectively. Note that $\langle\tau\rangle$ of MG in water was 5.8 ps. It is well known that the dynamics of the S_1 state of MG monomer shows a strong viscosity dependence, which has been ascribed to strong coupling between electronic states and the torsional degrees of freedom (or phenyl ring rotation), so the fluorescence enhancement can be due to a restriction of vibrational deexcitation of MG molecules caused by rigidization of phenyl rings in the nanoparticles.

References

- [1] K. Zhou, Y. Wang, X. Huang, K. Luby-Phelps, B. D. Sumer, J Gao, *Angew. Chem. Int. Ed.* **50** (2011) 6109.

Figures

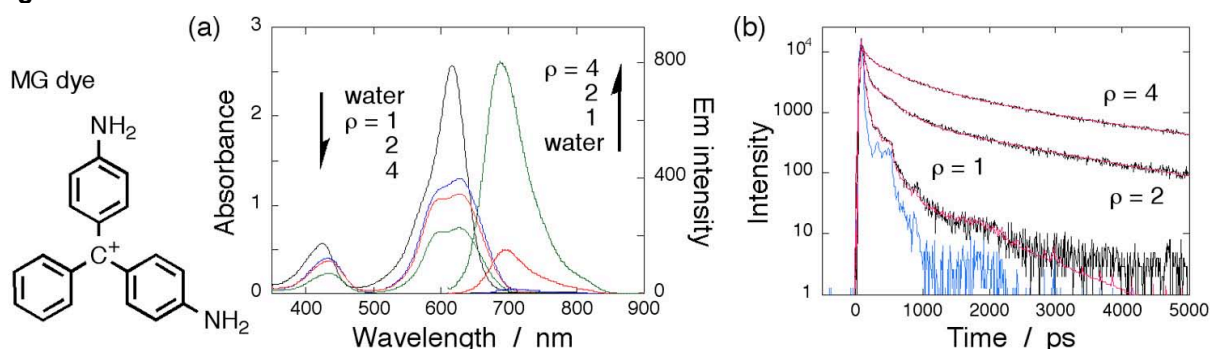


Fig. 1 (a) Absorption and fluorescence spectra of organic MG dye nanoparticle samples with $\rho = 1, 2,$ and 4 along with those of MG monomer in water. (b) The ρ dependence of the fluorescence decays of MG nanoparticles. $\lambda_{\text{ex}} = 410$ nm, $\lambda_{\text{em}} = 650$ nm.