Electronic Supplementary Information (ESI) for *PCCP*

Organic nanoparticles of malachite green with enhanced far-red emission: Size-dependence of particle rigidity

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Stability of MG nanoparticles.

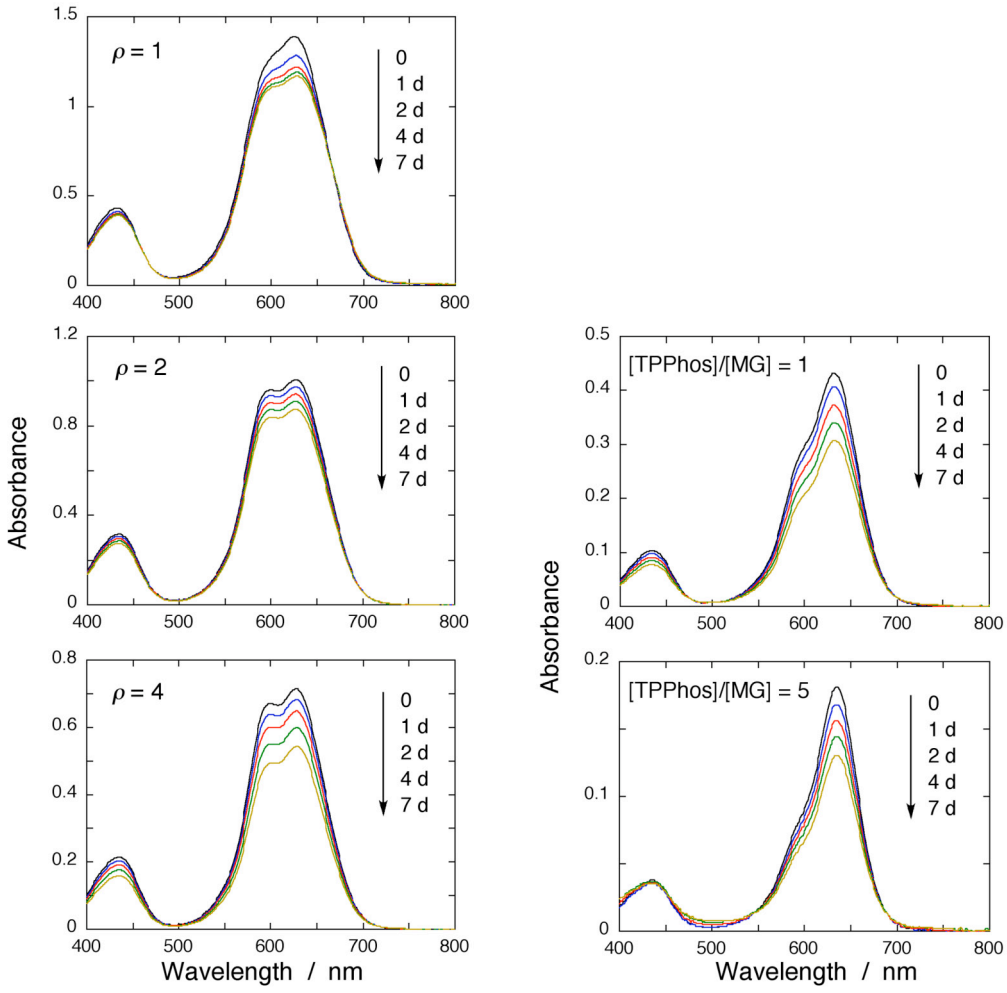

Fig. S1. Time evolution of the absorption spectra for MG nanoparticles dispersed in aqueous solution.

We examined the solution-phase stability of the prepared MG nanoparticles by conducting absorption spectral measurements as a function of time of day. The samples we chose are; MG nanoparticles prepared at ρ = 1, 2, and 4 in the presence of PVP (left column), and those prepared at ρ = 4 with TPPhos and PVP (right column). All solution samples were kept under dark at room temperature. The results are shown in Fig. S1. According to the spectra, all MG nanoparticles were considerably stable and showed almost no change in their spectral shape. Moreover, we could not observe any flocculation upon storage in the samples (for a week).

Optimized structures of MG and 1:1 ion-pair adduct of MG–TFPB calculated at the DFT level.

We made a simple structural model of 1:1 ion-pair adduct of MG-TFPB to estimate its size and thereby how many chromophores are present in a single nanoparticle. We optimized the ground-state geometry of the adduct with the Gaussian 09 program at the density functional theory (DFT) level using B3LYP functional and a 6-31G* basis set for all atoms.[1] Fig. S2 displays the optimized structures of MG alone and MG-TFPB ion-pair adduct. The typical dimension of the adduct as well as the pure MG molecule is also shown in the figure.

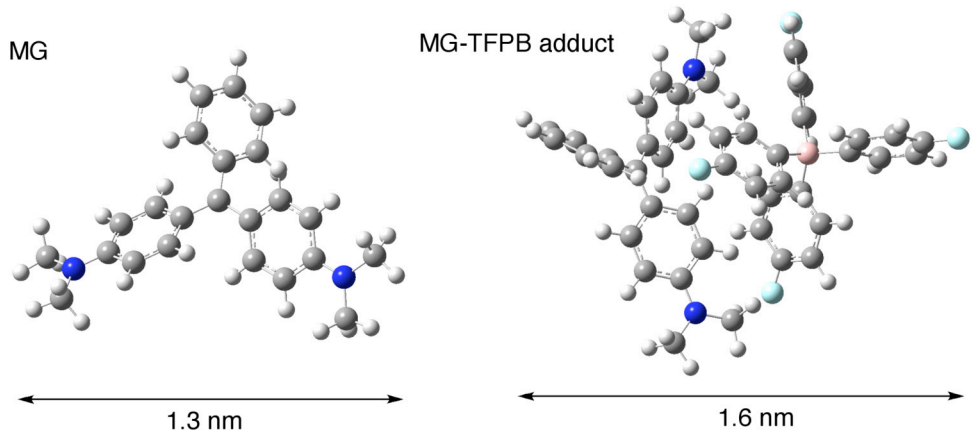

Fig. S2. Optimized structures of MG and 1:1 ion-pair adduct of MG–TFPB calculated at the DFT level.

When we assume that the MG-TFPB adduct is a sphere with the diameter of ~1.6 nm, the mean number of chromophore MG molecules in a nanoparticle could be estimated as ~2900, ~400, or ~90 for the sample prepared at ρ = 1, 2, or 4, since the mean diameter of each nanoparticle sample was 45.6, 23.6, or 14.3 nm, respectively.

Fluorescence decay curve of MG in water.

Fig. S3 shows the fluorescence decay curve (black curve) of MG in aqueous solution. Excitation wavelength was tuned to 410 nm. Fluorescence emission was collected at 700 nm. Blue dot expresses an instrument response function (IRF) recorded via scattering at the excitation wavelength (410 nm).

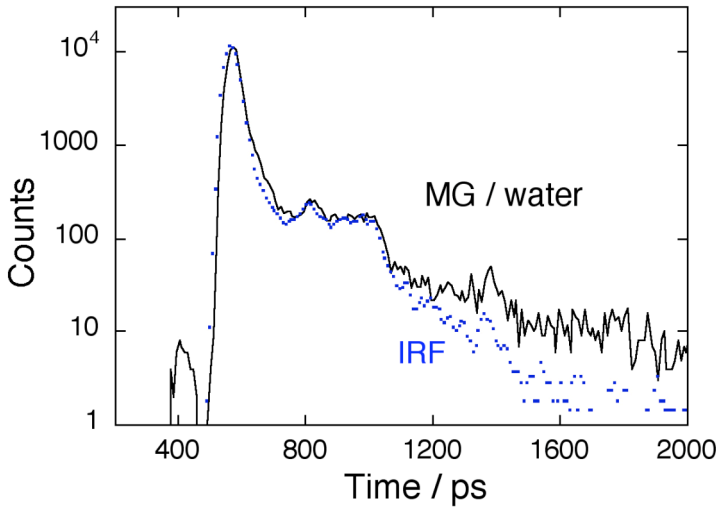

Fig. S3. Fluorescence decay curve of MG in water.

References

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