Aggregation behavior of perylenediimide carboxylic acid derivatives in solutions.

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Background. Perylenediimide derivatives are organic dyes which are used in a wide range of applications, including photooxidation of water[1]. One promising approach towards photooxidation of water is a solution-phase photochemistry with CoOx nanoparticles as a water oxidation catalyst[2]. The challenge in this approach is that CoOx nanoparticles aggregate over time and stop working as a catalyst. Such aggregation behavior may be suppressed by constructing supramolecular composites of CoOx nanoparticles with organic dye molecules. In this study, we synthesized perylenediimide carboxylic acid derivatives and investigated their aggregation behavior in water/DMSO solutions and assembly with CoOx nanoparticles.

Preparation. Perylenediimide carboxylic acid derivatives PDI-$(Ala)_2$, PDI-$(Phe)_2$, and PDI-$(Tyr)_2$ were synthesized according to reference 3. These compounds were dissolved in the water/DMSO mixtures (volume % of DMSO = 25, 50, 75, and 100%). We investigated their aggregation behavior in solutions.

Results and discussion. The changes in the UV-vis absorption spectra and emission spectra of PDI-$(Ala)_2$ for different solvent compositions are shown in Figures 1 and 2, respectively. When the percentage of DMSO in mixtures is 25% and 50%, the UV-vis absorption spectra become broadened, which suggests aggregation behavior in solutions. On the other hand, the shapes of the emission spectra did not change. It is likely that the emission mainly originates from the monomer molecules in the solution. Similar spectral changes were observed for PDI-$(Phe)_2$ and PDI-$(Tyr)_2$. We will also discuss dependence of aggregation behavior on substituents and formation of complexes with CoOx nanoparticles.

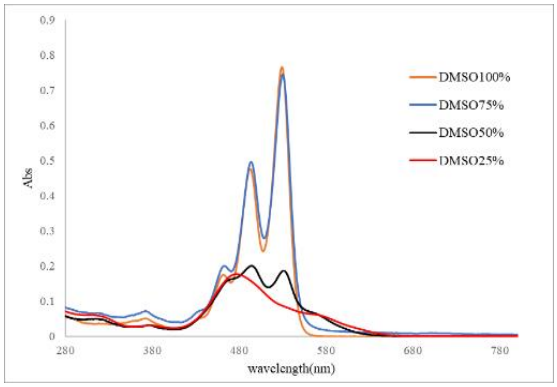

Fig.1 UV-vis absorption spectra of PDI-$(Ala)_2$

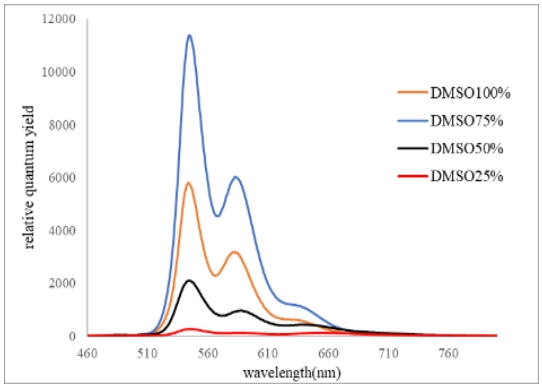

Fig.2 Emission spectra of PDI-$(Ala)_2$

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2) M. Grzelczak et al., *ACS Catal.*, **2013**, *3*, 383-388.
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