Synthesis of amphiphilic indigoids and evaluation of their photophysical properties and electrochemical redox reaction

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Indigo changes its intra- and intermolecular hydrogen bonds in response to the redox reaction[1]. Thus indigoids are expected as redox-responsive self-assembling materials; however, its extremely low solubility limit their applications. In this research, we developed an amphiphilic indigoid by modifying oligoethylene glycol group and explore the possible applications including a redox-responsive material.

An indigoid modified with two oligoethylene glycol was synthesized (**mOEG-indigo**, Figure 1). The obtained product exhibited amphiphilicity and soluble in water, DCM and toluene.

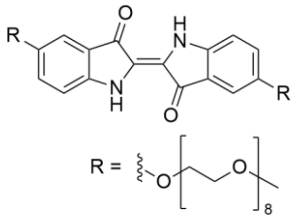

Figure 1. Structure of **mOEG-indigo**.

The emission spectra of **mOEG-indigo** in various solvents are shown in Figure 2a. In organic solvent, a couple of emission peaks at 405 nm and 500 nm were observed, which is expected to be π-π* transition and aggregation-induced emission, respectively. Besides, the peak's relative strength to the peak at 410 nm is larger in toluene than in DCM, suggesting the effect of π-π interaction. The peaks were blue-shifted in water due to be the effect of solvation by hydrogen bonds.

The reduction potential of **mOEG-indigo** was confirmed to be −0.48 V vs. Ag/AgCl by cyclic voltammetry. Then, the change of the UV-vis absorption spectrum was monitored while electrolyzing at −0.6 V (Figure 2b). The absorption peak at 655 nm decreased when electrolysis proceeded, which agreed with the color change from blue to yellow by chemical reduction.

mOEG-indigo possibly exhibits redox-responsive emission, and further exploration to confirm that is planned in addition to the measurement to reveal the association state.

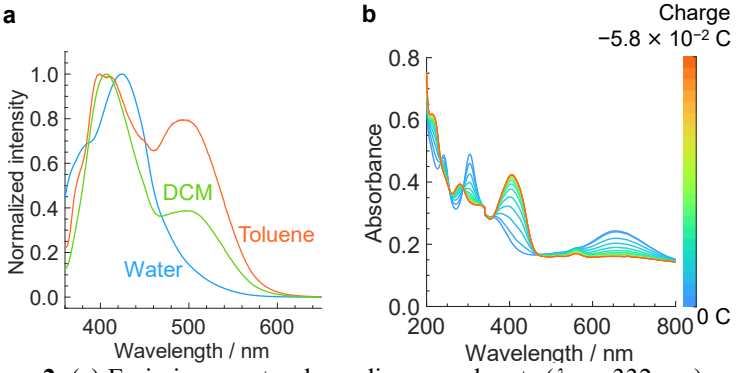

Figure 2. (a) Emission spectra depending on solvents (λ_{ex} = 332 nm) and (b) change of the absorption spectrum while electrolyzing at −0.6 V in water.

1) J. He et al., *Electrochim. Acta*, **2010**, *55*, 4845–4850.