Design and Synthesis of A–π–D-Type Fluorescent Dye and Preparation of Sensor Membranes for Water Content Sensing in Organic Solvents

([1]*Graduate School of Engineering, Osaka Metropolitan University*, [2]*PRESTO, Japan Science and Technology Agency*) ○ Ami Morimoto,[1] Kenji Sueyoshi,[1,2] Tatsuro Endo,[1] Hideaki Hisamoto[1]

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Sensing of water content is in demand for chemistry and industry, such as quality inspection of a reaction solvent and determination of fuel impurity. The commonly used Karl Fischer titration[1] could quantify the amount of water in wide range from 1 ppm to 100%.[2] However, this method needs lab equipment and could not detect water in obstructive solvents, such as methanol. To overcome these difficulties, we focused on the optical sensor membranes based on the A–π–D-type fluorescent dye bearing a betaine structure which forms intramolecular hydrogen bonds.

First, fluorescence properties in organic solvents or water-mixed solvents were investigated. The fluorescence intensity of the dye decreased as solvent polarity and/or water content in an organic solvent increased. These results indicate that the increase of polarity affected the stability of intramolecular hydrogen bonds. Then, to simplify the detection of water content in organic solvents, we prepared dye-immobilized copolymer membranes. A terminal vinyl group was introduced to the A–π–D-type dye and was copolymerized with various monomers, such as acrylamide and 2-hydroxyethyl methacrylate, on surface-modified glass by 3-(trimethoxysilyl)propyl methacrylate.[3] Prepared dye-immobilized copolymer membranes were immersed in water/organic solvent mixture, and fluorescence properties were investigated. Each membrane successfully detected water in organic solvents even in methanol and DMSO as shown in Fig. 1. In addition, the sensitivity of water content sensing could adjust by designing the composition of dye-immobilized copolymer membrane because the difference in the degree of membrane swelling affects the ease of twisting of the dye molecule, *i.e.*, stability of the intramolecular hydrogen bonds.

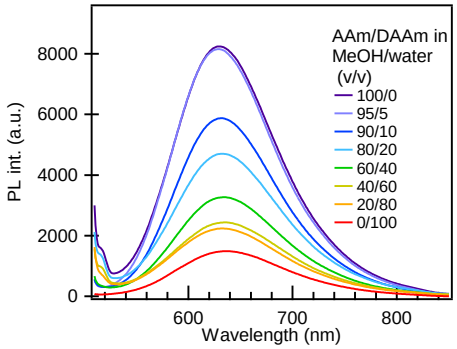

Fig. 1. Fluorescence spectra of dye-immobilized copolymer membrane with acrylamide (AAm) and dimethyl acrylamide (DAAm) in water/methanol mixture.

1) K. Fischer, *Angew. Chem*. **1935**, *48*, 394. 2) T. Osakai, *Rev. Polarogr*. **2017**, *63*, 101. 3) H. Hisamoto, *et al.*, *Anal. Chem*. **1998**, *70*, 1255.