

Molecular Motion Restriction of Tetraphenylethylene Enabled by a Linked Rotaxane Structure to Enhance the Robustness of Fluorescent Properties

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Keywords: Linked Rotaxane Structure; Cyclodextrins; Fluorescent Materials; Tetraphenylethylene; Aggregation-Induced Emission Enhancement

The restriction of local molecular motions is critical for improving the fluorescence quantum yields (FQYs) and the photostability of fluorescent dyes. Herein, we report a supramolecular approach to enhance the performance of fluorescent dyes by incorporating a linked rotaxane structure with permethylated α -cyclodextrins (Figure 1A). Tetraphenylethylene (TPE) derivatives generally exhibit low FQYs in solution due to the molecular motions in the excited state. We show that TPE with linked rotaxane structures on two sides displayed up to 15-fold higher FQYs (Figure 1B). Detailed investigations with variable temperature ^1H NMR, UV-Vis, and photoluminescence spectroscopy revealed that the linked rotaxane structure rigidifies the TPE moiety and thus suppresses the local molecular motions and non-radiative decay. Moreover, the linked rotaxane structure enhanced the FQY of the dye in various solvents and improved the photostability through the inhibition of local molecular motions in the excited TPE (Figure 1C).¹

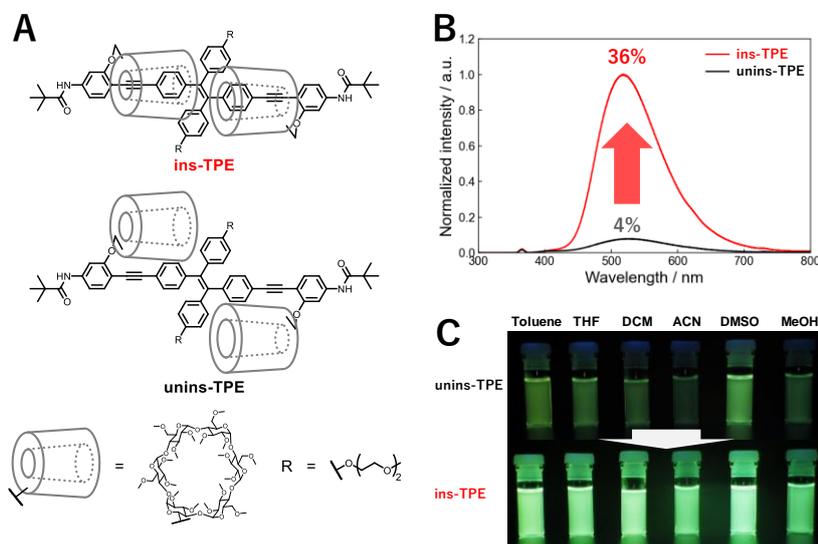


Figure 1. (A) Chemical Structures of an insulated TPE derivative with linked rotaxane structure (**ins-TPE**) and its uninsulated counterpart (**unins-TPE**). (B) Photoluminescence (PL) spectra of **ins-TPE** and **unins-TPE** ($1.0 \times 10^{-5} \text{ mol L}^{-1}$ in 1,2-dichloroethane, excited at 365 nm). The PL spectra were normalized to the same number of absorbed photons. (C) Photographs of **ins-TPE** and **unins-TPE** in various solvents ($1.0 \times 10^{-5} \text{ mol L}^{-1}$, excited at 365 nm).

1) Miyagishi, H. V.; Masai, H.; Terao, J. *Chem. Eur. J. in press*, doi: 10.1002/chem.202103175.