

Divergent Synthesis of Amino-Functionalized Aromatic Diimides by Quantitative and Catalyst-Free Hydroamination

(¹Faculty of Pure and Applied Sciences, University of Tsukuba, ²Molecular Design and Function Group, National Institute for Materials Science: NIMS) ○Haruki Sanematsu,^{1,2} Atsuro Takai,² Masayuki Takeuchi^{1,2}

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Aromatic diimides such as naphthalenediimide (NDI) and perylenediimides (PDI) are representative π -systems having excellent optoelectronic properties and electron-accepting ability, and, as such, have been extensively studied in the fields of organic electronics, fluorescence sensors, and so forth. Functionalization of the diimide π -core is known to induce significant changes in its conformation and physicochemical properties. It often requires, however, numerous synthetic efforts and metal catalysts to attach functional groups to the π -core.¹⁾ Recently, we reported catalyst-free functionalization of an ethynyl substituted aromatic diimides with various amines that proceed almost quantitatively.²⁾ Nonetheless, the synthesis of multi-amino-functionalized π -systems and polymers has still been difficult. In this work, we designed novel aromatic diimides in which hydroamination occurs simultaneously to afford multi amine adducts and polymers.

We synthesized a series of vinyl-substituted NDIs and PDIs that reacted with amines simultaneously and quantitatively without an external catalyst (Fig.1). Hydroamination of the two vinyl groups of an aromatic diimide with a diamine and a 2 eq. of monoamine respectively afforded an amino-bridged macromolecule and an amine bisadduct. The resulting amino-functionalized aromatic diimides, especially the PDI derivative exhibited remarkable fluorescence switching by reversible interconversion between amine protonated/deprotonated forms in response to the addition of Brønsted acid/base.³⁾

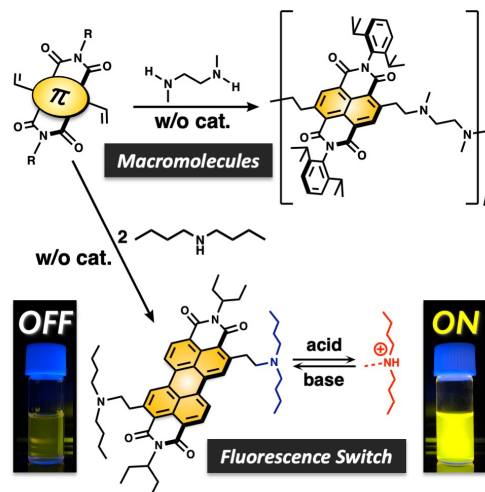


Fig.1 Catalyst-free synthesis of an amino-bridged NDI macromolecule and an acid/base responsive fluorescent PDI.

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