

Turning-On Fluorescence by Thiols – Diaminoterephthalates as New Tools for Life Sciences and Materials Science

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Diaminoterephthalates are bearing strong fluorescence properties and can be easily synthesized from their corresponding succinyl succinates. Using them as the scaffold, it is possible to install two different effector groups. For various applications in Biochemistry and Physics they were designed and synthesized with different residues, such as thiol, alkyne, azide, maleimide or fullerene groups.

1. Synthetic Strategy

Diaminoterephthalates with two different effector groups were prepared from succinyl succinate **1** by oxidative aminolysis (Figure 1).^[1] The orthogonal benzyl and methyl ester groups of intermediates **2** were successively cleaved and amidated with respective amines EffNH₂ and HATU, TBTU or COMU as coupling reagents.

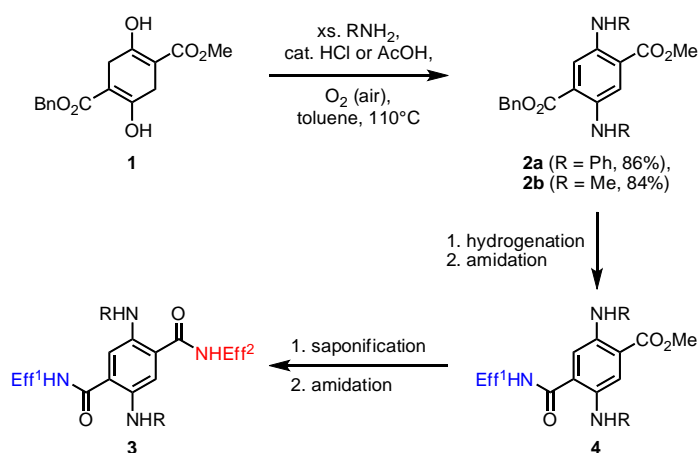


Figure 1. Synthesis of diaminoterephthalates 2–4.

2. Monofunctional Dyes

As effector groups, alkynes or azides for cycloadditions (compounds **4a** and **4b**), maleimides as thiol-reactive groups (**4c**),^[2] thiols for metal-surface binding (**4d**) or C₆₀-fullerenes as electron acceptor moiety (**4e**) were chosen; the latter furnished as a model system for light-induced electron-transfer studies (Figure 2).^[3]

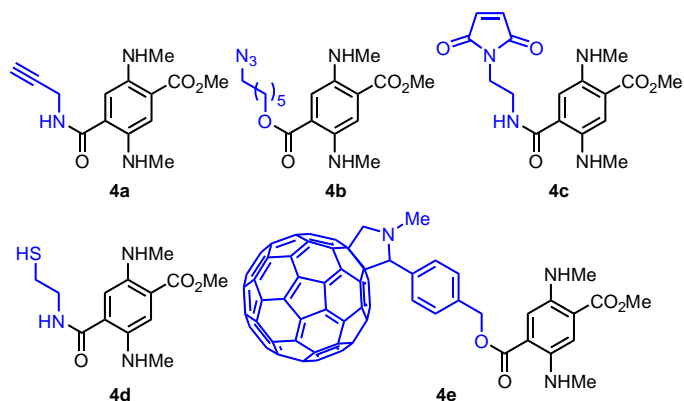


Figure 2. Monofunctionalized diaminoterephthalates 4.

3. Difunctionalized Dyes and Turn-On Probes

As examples for difunctionalized scaffolds compounds **3a** and **3b** with alkyne and maleimide moiety are shown (Figure 3). The cyclooctyne ring of **3a** is susceptible for copper-free "Click" reactions. Figure 4 shows the absorption and emission spectra of compounds **3b** and **5**.^[4] Conjugated addition of a thiol "turns on" the fluorescence of this dye: Whereas compound **3b** shows almost no emission (red graph), compound **5** gives luminescence at 560 nm (blue graph) when irradiated at its absorbance band (415 nm). The mechanism of this "turn-on" process was investigated with computational methods: It is the π*-orbital of the maleimide C=C-bond which defines the LUMO of compound **3b** and prevents relaxation by emission.^[5]

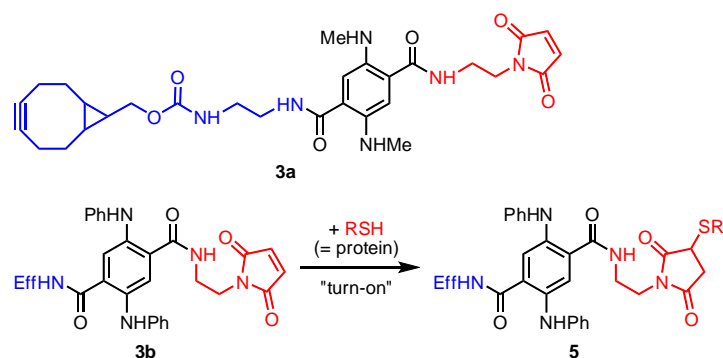


Figure 3. Difunctionalized diaminoterephthalates and "turn-on" reaction with thiol; Eff is propargyl for compounds **3b** and **5**.

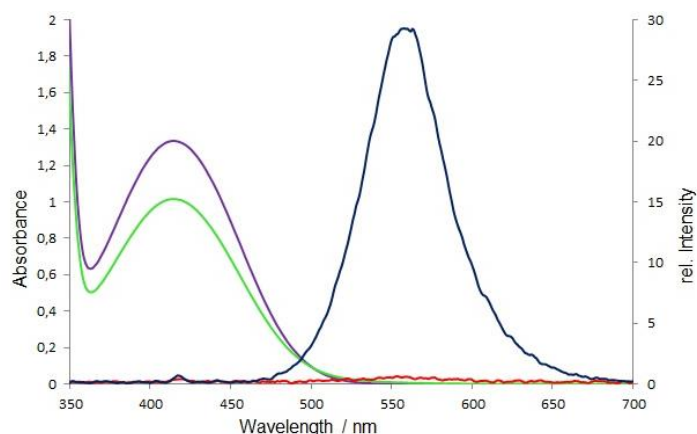


Figure 4. Spectra of compounds **3b** and **5** in CH₂Cl₂. Color code: Compound **3b**, absorbance violet, emission red; compound **5**: absorbance green, emission blue (λ_{ex} = 415 nm).

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[3] (a) L. Freimuth, C. A. Rozzi, C. Lienau, J. Christoffers, *Synthesis* **2015**, *47*, 1325–1328; (b) S. Pittalis, A. Delgado, J. Robin, L. Freimuth, J. Christoffers, C. Lienau, C. A. Rozzi, *Adv. Funct. Mater.* **2015**, *25*, 2047–2053.
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