

## Photoredox reactions of naphthalimide bipyridinium conjugates

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The electron transfer is one of the most elemental chemical reactions. We investigated two dyads which are promising candidates for the study of fundamental aspects of the electron transfer reaction.

The dyads **1a** and **1b** consisting of a bipyridinium electron acceptor unit and a naphthalimide group (the electron donor in the dyad) were synthesized and their photochemical reactions were investigated. It was shown by optical spectroscopic and laser flash photolysis experiments that **1a** and **1b** formed biradicals<sup>[1]</sup> via an intramolecular photoinduced electron transfer (PET). The radical ions had a longer lifetime in the apolar solvent THF than in the polar solvent MeCN.

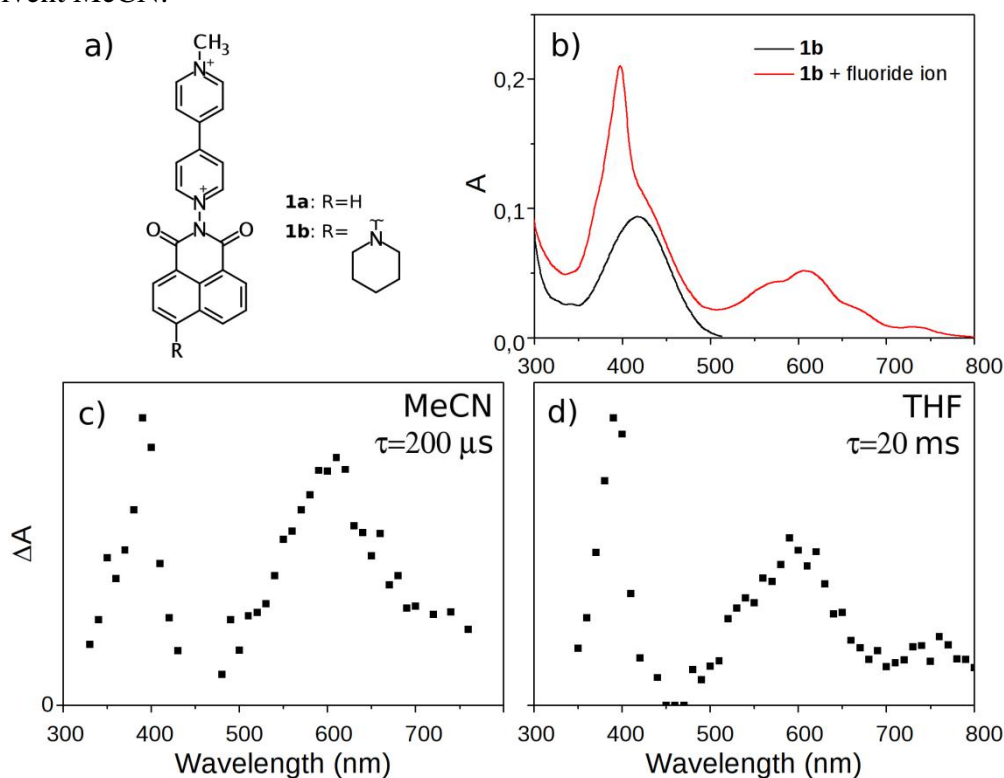


Figure 1. a) The structures of the 1,8-naphthalimide bipyridinium conjugates; b) changes in the absorption spectrum of **1b** in the presence of fluoride ions; c) and d) transient absorption spectra of conjugate **1b** in MeCN and THF,  $\tau$  is the lifetime of the biradical.

The formation of ion pair charge transfer (IPCT) complexes<sup>[2]</sup> between the dyads **1b** and halogenide ions via intermolecular PET processes were also studied. It was established by optical spectroscopic and NMR measurements that the IPCT complexes with F<sup>-</sup> ions are of radical nature. **1b** also provided IPCT complexes with the other halogenide ions, but they showed a radical character only following excitation, in their transient absorption spectra. The radical IPCT complex with fluoride proved to be stable for weeks in O<sub>2</sub>-free solutions. In the presence of dissolved oxygen the fluoride complex of **1b** underwent decomposition. The decomposition products were identified by ESI mass spectrometry.

The selective redox reaction of dyad **1b** with F<sup>-</sup> ions, resulting in a bright colored radical IPCT complex, can be utilized for the construction of colorimetric fluoride ion sensors.

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#### References:

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