

## Photochemistry of Pyromellitimides: Stable Radical Anions in Aqueous Solution

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Pyromellitimide (1,2,4,5-Benzenetetracarboxylic acid diimide) is widely used in polymeric films (Kapton) due to its high thermal stability, good mechanical properties, low dielectric constant, low coefficient of thermal expansion and high radiation resistance. Additionally, the characteristic absorption of the radical anion at 720 nm makes pyromellitimide an attractive component of electron-transfer cascade systems.<sup>[1]</sup>

Aromatic imides such as phthalimide undergo the decarboxylative photocyclization, which yields medium to large ring structures, tolerating several functional groups and giving excellent yields.<sup>[2]</sup> The reduction potential of pyromellitimide identifies it as a potential chromophore for this photochemical transformation.

The photochemical starting materials were synthesized by simple condensation reactions yielding pyromellitimide  $\omega$ -carboxylic acids. Irradiation in basic aqueous solution led to the formation of a stable radical species, which was identified by ESR, UV/Vis and NMR as the radical anion of pyromellitimide. The radical anion concentration, characterized by the absorption at 720 nm and the reported extinction coefficient,<sup>[1]</sup> was largest after about 100 minutes. It disappeared completely after 200 to 400 minutes, Fig. 1, depending on the spacer length of the carboxylic acid substituent. Interestingly, the radical anion has a lifetime of several days in deoxygenated solution.

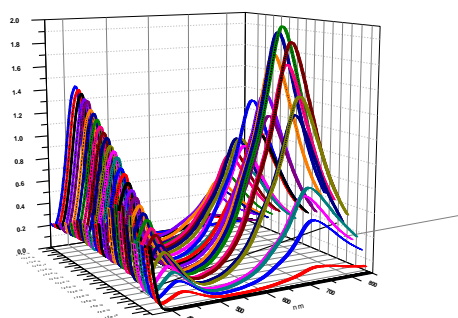


Figure 1. UV/Vis time-course analysis of the irradiation of a pyromellitimide  $\omega$ -carboxylic acid. Characteristic absorptions at 720 nm and 420 nm appear during the 6 hour irradiation.

Photocyclization products were isolated for carboxylic acids with 3, 4 and 5 methylen spacers. The complex product mixture, containing multiple regio- and stereoisomers, did not allow an exact characterization of the products. 2D-NMR confirmed the formation of dicyclization products as well as monocyclization products. For the shorter carboxylic acids, simple

decarboxylation products as well as a complex polymeric product were isolated.

The solution turned from colorless to green (720 nm absorption of the radical anion) to yellow (420 nm absorption) during the course of the irradiation. The 420 nm absorption is due to the monoprotonated dianion of pyromellitimide, which might have applications as an excellent reductant.

This is the first time pyromellitimides have been shown to exhibit synthetic photochemical potential.

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