

Synthetic Routes to Core-fluorinated Perylene Bisimide Dyes and their Properties

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Dedicated to Professor Gerhard Maas on the occasion of his 60th birthday

Numerous core-fluorinated perylene bisimide (PBI) dyes with various substituents at the imide positions have been synthesized by different methods. Core-difluorinated PBIs **4a–f** are obtained by imidization of difluoro-substituted perylene bisanhydride **1** with appropriate primary amines or, alternatively, by nucleophilic halogen exchange reactions (Halex process) of the corresponding dibromo-substituted PBIs **2a–d,f** with potassium fluoride. Core-tetrafluorinated PBIs **5a–c** could also be synthesized by halogen exchange reactions of the respective tetrachlorinated PBIs **3a–c**. In particular, core-fluorinated perylene bisimide pigments **4h**, **5h** containing hydrogen atoms in the imide positions could be obtained for the first time by deprotection of α -methylbenzyl-substituted precursors. Compared with core-unsubstituted perylene bisimides, these fluorinated dyes display hypsochromically shifted absorption and fluorescence spectra, and they exhibit fluorescence quantum yields up to unity, enabling bright yellow emission. The electrochemical properties of these electron-poor perylene bisimides have been studied. Furthermore, the packing features of a tetrafluorinated PBI derivative in the solid state have been discussed.

Key words: Dyes and Pigments, Fluorination, n-Type Semiconductors, Perylene Bisimides