

Synthesis of Nonsymmetrically *N,N'*-Diaryl-Substituted 4,4'-Bipyridinium Salts with Redox-Tunable and Titanium Dioxide (TiO₂)-Anchoring Properties

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A general method for the synthesis of so far unknown nonsymmetrically substituted *N*-aryl-*N'*-aryl'-4,4'-bipyridinium salts is presented (*Scheme 1*). The common intermediate in all procedures is *N*-(2,4-dinitrophenyl)-4,4'-bipyridinium hexafluorophosphate (**1**·PF₆[−]). For the synthesis of nonsymmetric arylviologens, **1**·PF₆[−] was arenamine-exchanged by the *Zincke* reaction, and then activated at the second bipyridine N-atom with 2,4-dinitrophenyl 4-methylbenzenesulfonate. The detailed preparation of the six *N*-aryl-*N'*-aryl'-viologens **21–26** is discussed (*Scheme 2*). The generality of the procedure is further exemplified by the synthesis of two nonsymmetrically substituted *N*-aryl-*N'*-benzyl- (see **11** and **12**), and seven *N*-aryl-*N'*-alkyl-4,4'-bipyridinium salts (see **28–34**) including substituents with metal oxide anchoring and redox tuning properties. The need for these compounds and their usage as electrochromic materials, in dendrimer synthesis, in molecular electronics, and in tunable-redox mediators is briefly discussed. The latter adjustable property is demonstrated by the reduction potential measured by cyclic voltammetry on selected compounds (*Table*).

Introduction. – Viologens, *i.e.*, 4,4'-bipyridinium salts with two alkyl, two benzyl, or two aryl substituents (*R*) at both N-atoms are well known reversible redox compounds. One-electron reduction is fast, and the resulting monocationic radicals exhibit good stability and large absorptions coefficients in the VIS range, rendering these compounds excellent candidates for redox mediators in amperometric sensors [1], molecular electronics [2–5], switchable electrochromic filters [6], and electrochromic displays (ECDs) [7].

The *R* groups influence strongly the absorption spectrum (ϵ_{\max} , λ_{\max}), the reduction potential (E°), the solubility, and the surface-anchoring properties. The colors of the radicals can be tuned from blue (typical for the dialkyl- or dibenzylviologens [8]) over violet (typical for the same substituents but for pimerized radicals [9]) to green (typical for aryl substituents [10]). The reduction potentials of 4,4'-viologens follow generally the trend $E^\circ(N,N'\text{-dialkyl}) < E^\circ(N,N'\text{-dibenzyl}) < E^\circ(N,N'\text{-diphenyl})$, but additional substituents at the aromatic system or at *R* (if conjugated with the chromophore), can further influence E° [11]. Further fine tuning of the reduction potential can be achieved by a nonsymmetric substitution pattern, as well known for alkyl- and benzylviologens but not for arylviologens [11]. Such redox tuning can be crucial to adjust the rate of electron transfer between a redox species in solution and the band edge potential of a semiconducting metal oxide (*cf. Fig. 1*) [12].

Furthermore, surface-confined viologens necessitate generally a nonsymmetric substitution pattern with different alkyl, benzyl, or aryl groups at the two N-atoms, one of them being equipped with a surface-anchoring group to guarantee a well-defined