



Fig. 1. Simplified energetic situation at the  $\text{TiO}_2$  semiconductor with anchored alkyl-, benzyl-, and phenylviologens exhibiting an increasingly positive reduction potential under different polarization. a) accumulation layer ( $E_{F(a)} = E_{(\text{alkylviologen})}^*$ ), b) flatband situation ( $E_{F(b)} = E_{FB(b)} = E_{(\text{benzylviologen})}^*$ ), and c) depletion layer ( $E_{F(c)} = E_{(\text{phenylviologen})}^*$ ). Electron transfer is slow in situation c) due to the activation barrier.

'head-on' fixation. In a previously reported study, the synthesis and use of nonsymmetrical alkyl-arylviologens, *i.e.*, of (*N*-aryl-*N'*-(2-phosphonoethyl)-4,4'-bipyridinium salts, was described [13]. The viologen substituted at one of the *N*-alkyl chains with a phosphonic acid residue exhibit an interesting range of reduction potential and optimized electrochromic-device performance with respect to switching speed, change in absorbance, and coloration efficiency. Another reason for a nonsymmetrical substitution pattern can be the fine tuning of spectral properties. Moreover, the controlled synthesis of oligomeric linear or dendritic compounds consisting of viologen units often requires nonsymmetrically substituted bipyridinium precursors.

The synthesis of symmetrical alkyl- or benzyl-substituted viologens is straightforward. Bipyridine is refluxed in presence of the corresponding electrophiles (alkyl or benzyl halides, in excess or stoichiometrically) in a solvent that dissolves the starting materials and the intermediate monosubstituted bipyridinium salt. For the preparation of symmetrically substituted diarylviologens, the reaction is conducted *via* the intermediate *N,N'*-bis(2,4-dinitrophenyl)-4,4'-bipyridinium salt introduced by Zincke (*Path 0* in *Scheme 1*) [5][11][13–16]. For the synthesis of nonsymmetrically substituted monoalkyl- or monobenzylobipyridinium salts, a solvent is used in which the monocations precipitate. These are then reacted with a second alkylating or benzylating agent in a more polar solvent. Using this technique, viologens with two different alkyl or benzyl groups or mixed *N*-alkyl-*N'*-benzyl viologens are accessible in good yields. Viologens with a mixed aryl-aryl, alkyl-aryl-, or aryl-benzyl substitution pattern have not been described, except for the alkyl-aryl substitution pattern in a recent publication by one of us [13].

In this study, we have extended the scope of the nonsymmetrically aryl-substituted viologens. We describe for the first time the synthesis of mixed *N*-aryl-*N'*-aryl'-viologens, some electrochemical properties of these compounds, as well as new nonsymmetrically *N*-aryl-*N'*-benzyl- and *N*-alkyl-*N'*-aryl substituted viologens obtained from the same intermediate compound.