Synthesis of Nonsymmetrically *N*,*N*′-Diaryl-Substituted 4,4′-Bipyridinium Salts with Redox-Tunable and Titanium Dioxide (TiO_2)-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**·PF_6^-). For the synthesis of nonsymmetric arylviologens, **1**·PF_6^- 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°(*N*,*N*′-dialkyl) < E°(*N*,*N*′-dibenzyl) < E°(*N*,*N*′-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

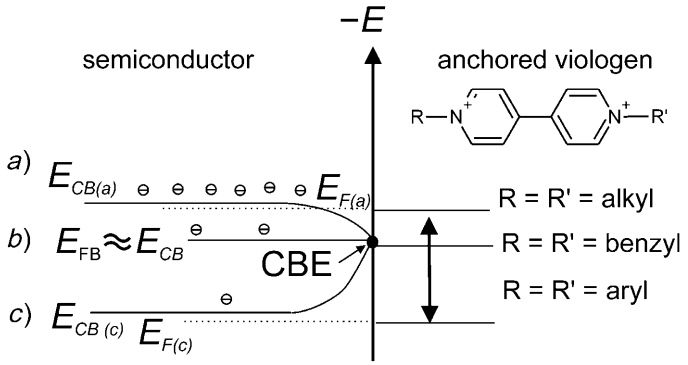
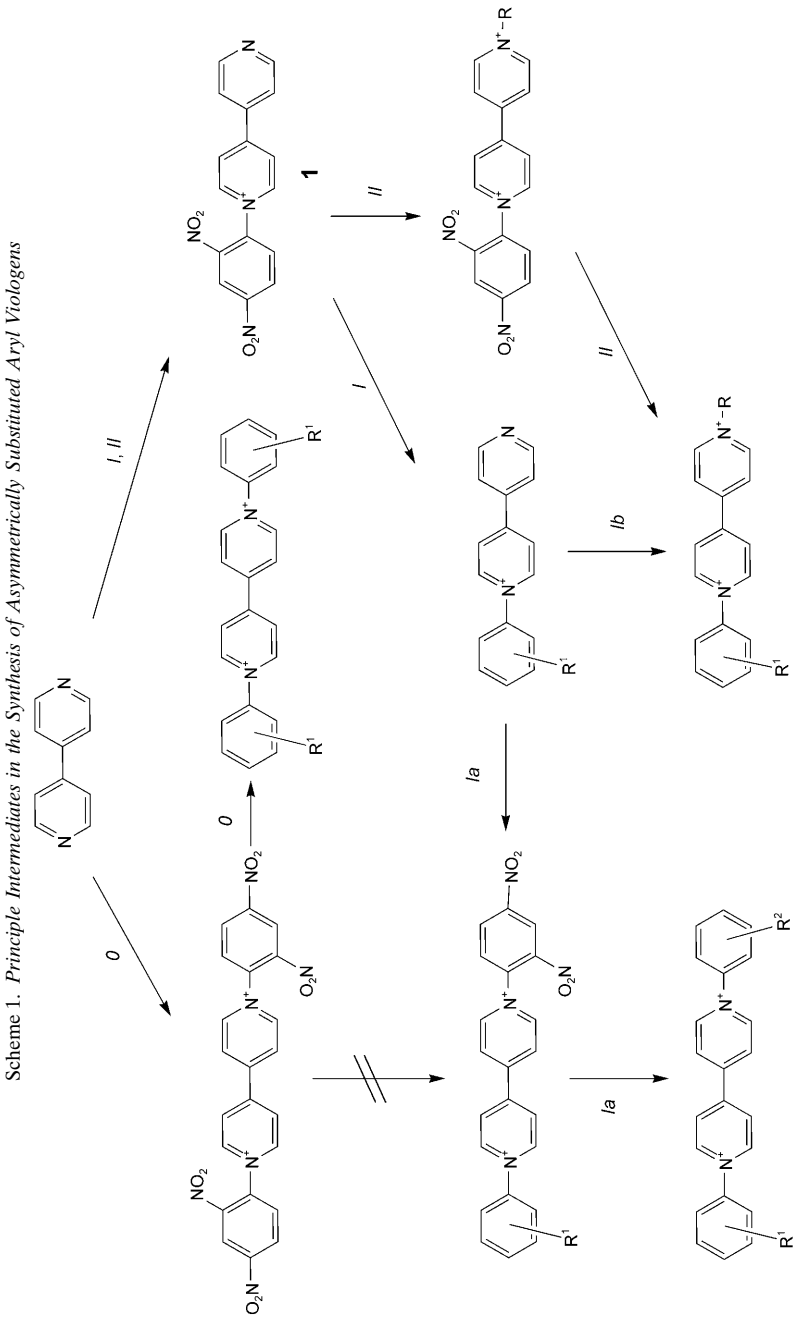


Fig. 1. *Simplified energetic situation at the TiO_2 semiconductor with anchored alkyl-, benzyl-, and phenylviologens exhibiting an increasingly positive reduction potential under different polarization*. a) *accumulation layer* ($E_{F(a)} = E^{\circ}_{(alkylviologen)}$), b) *flatband situation* ($E_{F(b)} = E_{FB(b)} = E^{\circ}_{(benzylviologen)}$), and c) *depletion layer* ($E_{F(c)} = E^{\circ}_{(phenylviologen)}$). 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 monobenzylbipyridinium 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.



Scheme 1. *Principle Intermediates in the Synthesis of Asymmetrically Substituted Aryl Viologens*

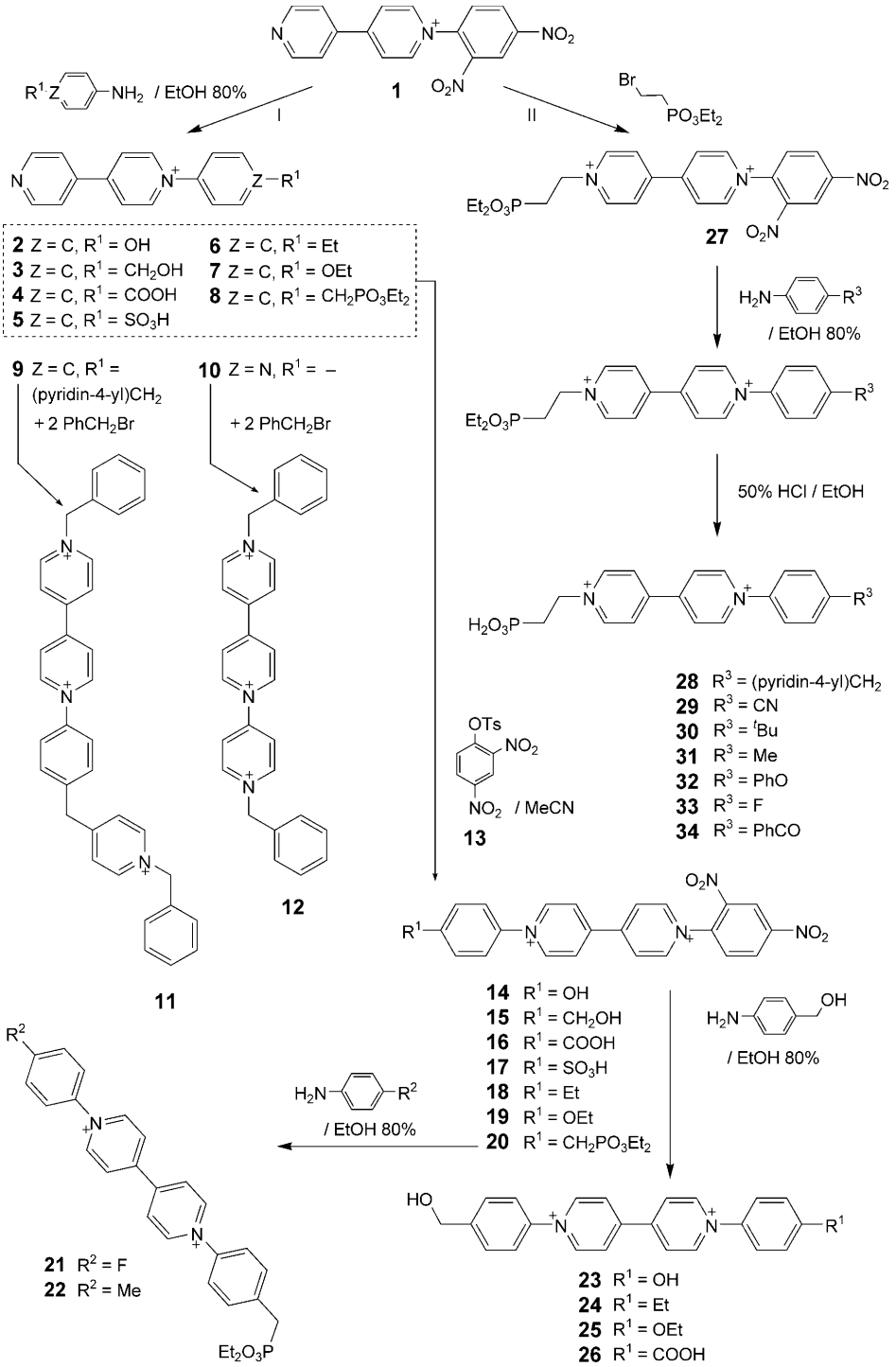
Results and Discussion. – The general route for the synthesis of nonsymmetrically substituted mixed aryl-aryl′-, aryl-benzyl-, and alkyl-aryl viologens is depicted in *Scheme 1*, *Route I* and *II*. Double activation of 4,4′-bipyridine *via N,N′*-bis(2,4-dinitrophenyl)-4,4′-bipyridinium (*Route 0* in *Scheme 1*, corresponding to the traditional route for symmetrically substituted arylviologens) is not suitable, because the conversion of bis(2,4-dinitrophenyl)bipyridinium with a stoichiometric amount of a benzenamine derivative yielded always mixtures in our hands. However, the introduction of nonsymmetry is possible by *Route I* and *II via* mono(2,4-dinitrophenyl)bipyridinium **1**, a compound described earlier by *Hünig* [17]. Thus, all the syntheses described in the following start from the key intermediate **1**. According to *Route II*, this compound is first alkylated or benzylated at the free N-atom and then treated with benzenamine derivative. Alternatively, **1** is benzenamine-exchanged according to *Route I* and then either alkylated/benzylated (*Route Ib*) or phenylated and benzenamine-exchanged (*Route Ia*). The latter route opens a way to nonsymmetric diaryl-substituted viologens.

Nonsymmetric Diaryl Viologens via Route Ia. Using the key intermediate mono-(2,4-dinitrophenyl)bipyridinium **1** as a common starting material, we prepared the monoarylbipyridinium salts **2**–**10** (*Scheme 2*). The exchange of the 2,4-dinitroaniline moiety by the corresponding aromatic amines occurred smoothly under standard conditions (aq. EtOH at 80°, 24 h) in 52–88% yield, except for the preparation of **4** and **5** with 4-aminobenzoic acid and 4-aminobenzenesulfonic acid in which case a stoichiometric amount of Et_3N was used to prevent protonation of the aromatic-amine moiety. For the preparation of nonsymmetric diarylviologens **14**–**20**, we tried the traditional reagent 2,4-dinitrophenyl chloride, but only minor yields (*ca.* 20–30%) were obtained. The same unsatisfactory yields were observed with the corresponding fluorides and bromides, but using 2,4-dinitrophenyl 4-methylbenzenesulfonate, we found acceptable yields in the range of 30–60% [18][19]. Purification of the products was crucial and most easily performed by counter-ion-induced precipitation, making use of the fact that the dicationic viologens are H_2O-soluble and insoluble in organic solvents in the presence of halide counterions, but insoluble in H_2O and soluble in certain organic solvents as hexafluorophosphates. The exchange of the dinitrophenyl substituent was then achieved with a series of aromatic amines yielding the products **21**–**26** in yields of 50–80%.

Nonsymmetric Aryl-benzylviologens via Route Ib. In two exemplary reactions, we prepared compounds **11** and **12**, *i.e.*, asymmetrically aryl-benzyl-substituted viologens in yields of 50–70%. The synthetic route diverges from *Route Ia* after introduction of the first aryl group. The nucleophilicity of the second N-atom in **9** and **10** is sufficient for the complete conversion with benzyl bromides. The same *Route Ib* is probably also applicable to the synthesis of mixed alkyl-aryl-viologens; however, this class of compounds were prepared according to *Route II* in this work.

Nonsymmetric Alkyl-arylviologens via Route II. This route was followed mainly for the preparation of aryl-(phosphonoalkyl)viologens which were synthesized because of their excellent coordinating abilities towards mesoporous TiO_2 electrodes [13]. The synthesis started with the key intermediate. The monocationic bipyridinium salt reacted smoothly with diethyl (1-bromoethyl)phosphonate. After exchange of the 2,4-dinitrophenyl group by a series of *p*-substituted anilines in aq. EtOH, followed by hydrolysis in 50% HCl/EtOH, **28**–**34** were obtained. The synthesis is exemplified

Scheme 2. *Aryl Viologens Prepared According to* Routes I *and* II



here with *p*-substituted aromatic amines, but it worked as well with *o*- and *m*-substituted arenamines (not shown).

The purity of all compounds was checked by ^{1}H-NMR, in some cases additionally by ^{13}C-NMR and by mass spectroscopy (see *Exper. Part*). An unusual electrochemical technique was used to monitor the progress of the exchange reaction of the (dinitrophenyl)bipyridinium salts reacting with the arenamine compounds, *e.g.*, **14**–**20** being transformed to **21**–**26**. The 1,3-dinitrobenzene is electroactive and shows two reduction processes at −0.92 and −1.25 V *vs.* SCE in MeCN [20]. *Fig. 2* shows the cyclic voltammograms of 1-(2,4-dinitrophenyl)-1′-(4-ethoxyphenyl)-4,4′-bipyridinium bis(hexafluorophosphate) (**19**·2 PF_6^-) and that of the corresponding product after reaction with 4-aminobenzenemethanol, *i.e.*, 1-(4-ethoxyphenyl)-1′-[(4-hydroxymethyl)phenyl]-4,4′-bipyridinium bis(hexafluorophosphate) (**25**·2 PF_6^-), the two waves corresponding to the dinitrophenyl moiety having disappeared in the product. Preliminary electrochemical studies with the products reveal that tuning of the first reduction potential is possible over a broad range from −0.04 to −0.300 V *vs.* Ag/AgCl (*cf. Table*).

D. B. thanks the Interdisciplinary Graduate College 612 of the University of Osnabrück for financial support.

Table. *Selected Half-Wave Potentials*

Final product	$E_{1/2}$ [V][a])	Dinitrophenyl intermediate	$E_{1/2}$ [V][a])
12[b])	−0.044		
	−0.261		
24[c])	−0.223	**18**[c])	−0.090
	−0.450		−0.325
			−0.961
			−1.220
25[c])	−0.161	**19**[c])	−0.072
	−0.464		−0.238
			−0.892
			−1.180
11[b])	−0.334		
	−0.689		

[a]) Measured on glassy carbon *vs.* Ag/AgCl at 25°. [b]) 0.2M $LiClO_4$/MeCN. [c]) 0.2M $(Bu_4N)PF_6$/MeCN.

Experimental Part

General. Compound **1** [17] and 2,4-dinitrophenyl 4-methylbenzenesulfonate (**13**) [18][19] were prepared according to published procedures. Pyridine-4-amine was from *Sigma-Aldrich*, and the preparation of 4-(pyridin-4-ylmethyl)benzenamine for the synthesis of **28** is described in [21]. Electrochemical measurements: three-electrode systems under Ar with a potentiostat *PGSTAT-20* from *AUTOLAB*. NMR Spectra: *Bruker-Avance-250* (250 MHz) spectrometer; δ in ppm, J in Hz. MS: *Agilent-HP-1100* spectrometer operating in the API-ES mode; in m/z (rel. %).

Synthesis of **2**, **3**, *and* **6**–**8**: *General Procedure A*. To 1-(2,4-dinitrophenyl)-4,4′-bipyridinium hexafluorophosphate (**1**·PF_6^-; 2 mmol) dissolved in 80% EtOH (50 ml), the corresponding 4-substituted benzenamine (3 mmol) was added, and the mixture was stirred for 24 h at 90°. The mixture was evaporated, the residue dissolved in H_2O, the aq. soln. washed with Et_2O (3×) and evaporated, and the residue dissolved in MeOH and added to 3M NH_4PF_6. The precipitate was collected and dried *in vacuo*.

1-(4-Hydroxyphenyl)-4,4′-bipyridinium Hexafluorophosphate (**2**·PF_6^-): Yield 88%. Brown powder. M.p. 245°. ^{1}H-NMR (250 MHz, CD_3CN): 7.15 (*d*, ^3J=8.9, arom. H); 7.61 (*d*, ^3J=8.9, arom. H); 7.89 (*d*, ^3J=6.1, Vio); 8.46 (*d*, ^3J=6.8, Vio); 8.91 (*d*, ^3J=6.1, Vio); 8.98 (*d*, ^3J=6.9, Vio). API-ES-MS: 249.3 (100), 250.2 (18).

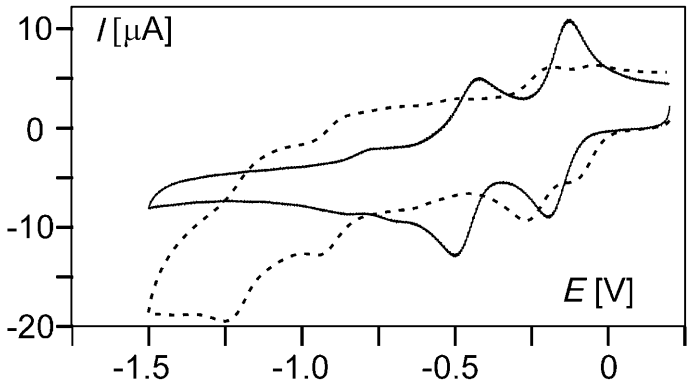


Fig. 2. *Cyclic voltammograms of 1-(2,4-dinitrophenyl-)-1′-(4-ethoxyphenyl)-4,4′-bipyridinium bis(hexafluorophosphate)* (**19**·2 PF_6^-; ----) *and 1-(4-ethoxyphenyl)-1′-(4-hydroxyphenyl)-4,4′-bipyridinium bis(hexafluorophosphate)* (**25**·2 PF_6^-; —). Scan rate: 0.25 V/s, 0.2M $(Bu_4N)PF_6$/MeCN, ref. Ag/AgCl.

1-[(4-Hydroxymethyl)phenyl]-4,4′-bipyridinium Hexafluorophosphate (**3**·PF_6^-): Yield 83%. Dark orange powder. M.p. 188° (dec.). ^{1}H-NMR (250 MHz, CD_3CN): 3.48 (*s*, OH); 4.67 (*d*, ^3J=5.4, CH_2); 7.62 (*s*, 4 arom. H); 8.39 (*d*, ^3J=7.0, 2 H, Vio); 8.81 (*d*, ^3J=6.2, Vio); 8.94 (*d*, ^3J=7.1, 2 H, Vio). API-ES-MS: 263.3 (100), 264.2 (15).

1-(4-Ethylphenyl)-4,4′-bipyridinium Hexafluorophosphate (**6**·PF_6^-): Yield 70.5%. Beige powder. M.p. 174°. ^{1}H-NMR (250 MHz, CD_3CN): 1.33 (*t*, ^3J=7.6, 3 H, Me); 2.85 (*q*, ^3J=7.6, 2 H, CH_2); 7.62 (*d*, ^3J=8.7, 2 arom. H); 7.70 (*d*, ^3J=8.75, 2 arom. H); 8.02 (*d*, ^3J=6.3, 2 H, Vio); 8.51 (*d*, ^3J=6.9, 2 H, Vio); 8.94 (*d*, ^3J=6.2, 2 H, Vio); 9.06 (*d*, ^3J=7.0, 2 H, Vio). ^{13}C-NMR (63 MHz, CD_3CN): 14.4; 27.7; 117.0; 121.6; 123.9; 125.6; 129.6; 139.9; 140.6; 144.5; 148.4; 150.9; 154.4. API-ES-MS: 261.2 (100), 262.2 (20).

1-(4-Ethoxyphenyl)-4,4′-bipyridinium Hexafluorophosphate (**7**·PF_6^-): Yield 88%. Pale yellow powder. M.p. 198°. ^{1}H-NMR (250 MHz, (D_6)acetone): 1.45 (*t*, ^3J=6.9, Me); 4.25 (*q*, ^3J=6.9, CH_2); 7.32 (*d*, ^3J=9.0, 2 arom. H); 7.96 (*d*, ^3J=9.0, 2 arom. H); 8.11 (*d*, ^3J=6.0, 2 H, Vio); 8.82 (*d*, ^3J=6.8, 2 H, Vio); 8.94 (*d*, ^3J=5.64, 2 H, Vio); 9.5 (*d*, ^3J=6.86, 2 H, Vio). API-ES-MS: 277.1 (100), 278.1 (38).

1-[4-[(Diethoxyphosphinyl)methyl]phenyl]-4,4′-bipyridinium Hexafluorophosphate (**8**·PF_6^-): Yield 52%. White powder. M.p. 163°. ^{1}H-NMR (250 MHz, CD_3CN): 1.29 (*t*, ^3J=7.02, 2 Me); 3.38 (*d*, ^3J=21.9, 1 CH_2); 4.10 (*q*, ^3J=7.1, 2 CH_2); 7.68 (*d*, ^3J=8.9, 2 arom. H); 7.74 (*d*, ^3J=8.75, 2 arom. H); 7.91 (*d*, ^3J=5.7, 2 H, Vio); 8.51 (*d*, ^3J=6.6, 2 H, Vio); 8.92 (*d*, ^3J=5.5, 2 H, Vio); 9.06 (*d*, ^3J=6.6, 2 H, Vio).

Preparation of **4** *and* **5**: *General Procedure B.* According to the *General Procedure A*, but Et_3N (2.5 mmol) was added prior to the addition of the 4-substituted benzenamine.

1-(4-Carboxyphenyl)-4,4′-bipyridinium Hexafluorophosphate (**4**·PF_6^-): Yield 84%. Beige powder. M.p. 251°. ^{1}H-NMR (250 MHz, D_2O): 7.73 (*d*, ^3J=8.6, 2 arom. H); 7.91 (*d*, ^3J=6.2, 2 H, Vio); 8.04 (*d*, ^3J=8.6, 2 arom. H); 8.49 (*d*, ^3J=6.9, 2 H, Vio); 8.71 (*d*, ^3J=5.8, 2 H, Vio); 9.16 (*d*, ^3J=6.87, 2 H, Vio). API-ES-MS: 277.1.

1-(4-Sulfophenyl)-4,4′-bipyridinium Hexafluorophosphate (**5**·PF_6^-): Yield 62%. Ocher powder. M.p. 210°. ^{1}H-NMR (250 MHz, D_2O): 7.92 (*d*, ^3J=8.4, 2 arom. H); 8.03 (*d*, ^3J=4.5, 2 H, Vio); 8.12 (*d*, ^3J=8.5, 2 arom. H); 8.60 (*d*, ^3J=6.3, 2 H, Vio); 8.83 (br., 3 H, SO_3H, Vio); 9.25 (*d*, ^3J=6.6, 2 H, Vio). API-ES-MS: 311.2 (100), 312.1 (20%).

1-[4-(Pyridin-4-ylmethyl)phenyl]-4,4′-bipyridinium Chloride (**9**·Cl^-): To a suspension of **1**·Cl^- (1 mmol, 0.359 g) in ^{i}PrOH (7 ml), a suspension of 4-(pyridin-4-ylmethyl)benzenamine (1.5 mmol, 0.276 g) was added and refluxed for 1 h. The solvent was evaporated, the residue extracted with H_2O/AcOEt 1:1 (30 ml), the aq. phase washed with AcOEt and evaporated, and the beige residue dried *in vacuo*; 0.337 g (94%) of **9**·Cl^-. Beige powder. M.p. 250° (dec.). ^{1}H-NMR (250 MHz, CD_3OD): 7.41 (*d*, ^3J=6.0, 2 H); 7.70 (*d*, ^3J=8.8, 2 H); 7.87 (*d*, ^3J=8.5, 2 H); 8.10 (*dd*, ^3J=4.8, ^4J=1.5, 2 H); 8.50 (*d*, ^3J=5.8, 2 H); 8.70 (*d*, ^3J=7.0, 2 H); 8.90 (*dd*, ^3J=4.8, ^4J=1.5, 2 H); 9.37 (*d*, ^3J=7.0, 2 H).

1-(Pyridin-4-yl)-4,4′-bipyridinium Chloride (**10**·Cl^-). To a soln. of **1**·Cl^- (0.4 mmol, 0.144 g) in ^{i}PrOH (3 ml), a soln. of pyridin-4-amine (0.6 mmol, 56 mg) in ^{i}PrOH (1 ml) was added and refluxed for 1.5 h under Ar. ^{i}PrOH (3 ml) and hexane were added to induce precipitation, which was completed at 6° after 3 days.

The brown precipitate was washed with ^{i}PrOH/hexane 1:4 and dried *in vacuo* to give **10**·Cl$^-$ (136 mg, 89%) as a reddish brown powder. M.p. >264° (dec.). ^{1}H-NMR (250 MHz, CD_3OD): 8.03 (*dd*, ^3J=4.8, ^4J=1.5, 2 H); 8.13 (*dd*, ^3J=4.6, ^4J=1.5, 2 H); 8.79 (*d*, ^3J=6.9, 2 H); 8.92 (*dd*, ^3J=4.7, ^4J=1.5, 2 H); 9.03 (*dd*, ^3J=4.7, ^4J=1.5, 2 H); 9.50 (*d*, ^3J=6.9, 2 H). API-ES-MS (pos.): 234.2 (M^+), 235.3.

1-Benzyl-1′-{4-[[1-benzypyridinium-4-yl]methyl]phenyl}-4,4′-bipyridinium Tris(hexafluorophosphate) (**11**·3 PF_6^-). Benzyl bromide (5 mmol, 0.855 g) was added to a soln. of **9**·Cl$^-$ (0.5 mmol, 0.180 g) in ^{i}PrOH (5 ml) and refluxed for 18 h to yield a yellow precipitate. The latter was isolated, dissolved in H_2O and precipitated with 10% aq. NH_4PF_6 soln. The white product was isolated and dried *in vacuo*: 0.341 g (72%) of **11**·3 PF_6^-. White powder. M.p. 221°. ^{1}H-NMR (250 MHz, CD_3OD): 4.58 (*s*, 2 H); 5.83 (*s*, 2 H); 6.03 (*s*, 2 H); 7.67–7.50 (*m*, 10 H); 7.78 (*d*, ^3J=8.8, 2 H); 7.94 (*d*, ^3J=8.5, 2 H); 8.05 (*d*, ^3J=7.0, 2 H); 8.74 (*d*, ^3J=7.0, 2 H); 8.80 (*d*, ^3J=7.0, 2 H); 8.98 (*d*, ^3J=7.0, 2 H); 9.38 (*d*, ^3J=7.3, 2 H); 9.48 (*d*, ^3J=7.0, 2H).

1-Benzyl-1′-(1-benzylpyridinium-4-yl)-4,4′-bipyridinium Tris(hexafluorophosphate) (**12**·3 PF_6^-). Benzyl bromide (0.2 mmol, 342 mg) and **10**·Cl$^-$ (0.2 mmol, 54 mg) were refluxed in ^{i}PrOH (3 ml) for 20 h. The precipitate was isolated, dissolved in H_2O and filtered to eliminate a brown by-product. The product was then precipitated with 10% aq. NH_4PF_6 soln. (3 ml), isolated, and dried *in vacuo*: 56.5 mg (33%) of **12**·3 PF_6^-. Beige powder. M.p. >205° (dec.).

Synthesis of **14**–**20**. *General Procedure C*. The monoaryl compound (0.01 mol) was treated with tosylate **13** (0.015 mol) in MeCN and stirred under reflux for 48 h. The solvent was evaporated and the residue dissolved in a few ml of H_2O, washed with Et_2O (4×50 ml), and evaporated. The solids were dissolved in MeOH, and the soln. was added dropwise to 3M aq. NH_4PF_6.

1-(2,4-Dinitrophenyl)-1′-(4-hydroxyphenyl)-4,4′-bipyridinium Bis(hexafluorophosphate) (**14**·2 PF_6^-): Yield 26%. Yellowish powder. M.p. 212°. ^{1}H-NMR (250 MHz, CD_3CN): 7.08 (*d*, ^3J=8.8, 2 arom. H); 7.57 (*d*, ^3J=8.8, 2 arom. H); 8.09 (*d*, ^3J=8.6, 1 arom. H); 8.54 (*d*, ^3J=6.5, 2 H, Vio); 8.62 (*d*, ^3J=6.7, 2 H, Vio); 8.79 (*d*, ^3J=8.5, 1 arom. H); 9.08 (*d*, ^3J=6.5, 4 H, Vio); 9.13 (*s*, 1 arom. H).

1-(2,4-Dinitrophenyl)-1′-[4-(hydroxymethyl)phenyl]-4,4′-bipyridinium Bis(hexafluorophosphate) (**15**·2 PF_6^-): Yield 43%. Ochre. M.p. 241°. ^{1}H-NMR (250 MHz, D_2O): 7.65 (*d*, ^3J=8.6, 2 arom. H); 7.73 (*d*, ^3J=8.7, 2 arom. H); 8.19 (*d*, ^3J=8.5, 1 arom. H); 8.71 (*d*, ^3J=6.1, 2 H, Vio); 8.78 (*d*, ^3J=3.6, 2 H, Vio); 8.84 (*d*, ^3J=8.2, 1 arom. H); 9.33 (*d*, ^3J=5.2, 5 H, arom. H, Vio).

1-(4-Carboxyphenyl)-1′-(2,4-dinitrophenyl)-4,4′-bipyridinium Bis(hexafluorophosphate) (**16**·2 PF_6^-): Yield 58%. Beige powder. M.p. 222°. ^{1}H-NMR (250 MHz, D_2O): 7.8 (*d*, ^3J=8.5, 2 arom. H); 8.05 (*d*, ^3J=8.4, 2 arom. H); 8.19 (*d*, ^3J=8.7, 1 arom. H); 8.85–8.71 (*m*, 5 H, arom. H, Vio); 9.38–9.31 (*m*, 5 H, arom. H, Vio).

1-(2,4-Dinitrophenyl)-1′-(4-sulfophenyl)-4,4′-bipyridinium Bis(hexafluorophosphate) (**17**·2 PF_6^-): Yield 40.5%. Orange powder. M.p. >270° (dec.). ^{1}H-NMR (250 MHz, D_2O): 7.09 (*d*, ^3J=8.6, 2 arom. H); 7.65 (*d*, ^3J=8.1, 2 arom. H); 7.87 (br., arom. H); 8.05 (br., arom. H); 8.18 (*d*, arom. H); 8.57 (*d*, arom. H); 8.83 (br., arom. H); 9.20 (*d*, arom. H); 9.30–9.38 (br., arom. H).

1-(2,4-Dinitrophenyl)-1′-(4-ethylphenyl)-4,4′-bipyridinium Bis(hexafluorophosphate) (**18**·2 PF_6^-): Yield 58.5%. White powder. M.p. 255°. ^{1}H-NMR (250 MHz, CD_3CN): 7.56 (br., 2 arom. H); 7.63 (br., 2 arom. H); 8.13 (*d*, ^3J=7.0, 1 arom. H); 8.64 (br., 4 H, Vio); 8.79 (*d*, ^3J=7.07, 1 arom. H); 9.13 (br., 5 H, arom. H, Vio). ^{13}C-NMR (63 MHz, (D_6)DMSO): 16.3; 28.7; 122.4; 125.5; 127.5; 127.7; 130.4; 131.2; 132.8; 146.7; 148.1; 148.6; 149.0; 150.2.

1-(2,4-Dinitrophenyl)-1′-(4-ethoxyphenyl)-4,4′-bipyridinium Bis(hexafluorophosphate) (**19**·2 PF_6^-): Yield 35%. Yellow. M.p. 254°. ^{1}H-NMR (250 MHz, CD_3CN): 1.36 (*t*, ^3J=6.5, 3 H, Me); 4.12 (*q*, ^3J=6.8, 2 H, CH_2); 7.17 (*d*, ^3J=8.1, 2 arom. H); 7.64 (*d*, ^3J=7.0, 2 arom. H); 8.08 (*d*, ^3J=7.2, 1 arom. H); 8.58 (*d*, ^3J=20.5, 4 H, Vio); 8.79 (*d*, ^3J=7.1, 1 arom. H); 9.08 (br., 5 H, Vio, arom. H).

1-{4-[(Diethoxyphosphinyl)methyl]phenyl}-1′-(2,4-dinitrophenyl)-4,4′-bipyridinium Bis(hexafluorophosphate) (**20**·2 PF_6^-): Yield 25%. White powder. M.p. 209°. ^{1}H-NMR (250 MHz, CD_3CN): 1.30 (*t*, ^3J=7.1, 2 Me); 3.40 (*d*, ^3J=22.0, 1 CH_2); 4.08 (*q*, ^3J=7.3, 2 CH_2); 7.77 (*m*, 4 arom. H); 8.20 (*d*, ^3J=8.8, 1 arom. H); 8.73 (*m*, 4 H, Vio); 8.90 (*d*, ^3J=8.4, 1 arom. H); 9.24–9.17 (*m*, 5 H, Vio, arom. H).

1-{4-[(Diethoxyphosphinyl)methyl]-phenyl}-1′-(4-fluorophenyl)-4,4′-bipyridinium Bis(hexafluorophosphate) (**21**·2 PF_6^-). Bis(hexafluorophosphate) **20** (5 mmol) was treated with 4-fluorobenzenamine (7.5 mmol) in 80% EtOH under reflux for 24 h. The mixture was evaporated, the residue dissolved in H_2O, and the soln. washed with Et_2O (4×). After anion exchange with aq. 3M NH_4PF_6, the precipitate was filtered and dried *in vacuo*. ^{1}H-NMR (D_2O): 3.15 (*d*, 2 H); 7.1–7.7 (*m*, 8 H); 8.6–9.3 (*m*, 8 H).

1-{4-[(Diethoxyphosphinyl)methyl]phenyl}-1′-(4-methylphenyl)-4,4′-bipyridinium Bis(hexafluorophosphate) (**22**·2 PF_6^-): As described for **21**, with 4-methylbenzenamine. ^{1}H-NMR (D_2O): 2.33 (*s*, 3 H); 3.25 (*d*, 2 H); 7.35–7.8 (*m*, 8 H); 8.7–9.3 (*m*, 8 H).

Synthesis of **23**–**26**: *General Procedure D.* The 1-aryl-substituted 1′-(2,4-dinitrophenyl)-4,4′-bipyridinium precursor (5 mmol) was treated with 4-aminobenzenmethanol (7.5 mmol) in 80% aq. EtOH under reflux for 24 h. The soln. was evaporated, and the residue dissolved in H_2O (50 ml), the soln. washed with Et_2O (4×30 ml) and evaporated, and the residue dissolved in MeOH (3 ml) and ion-exchanged with aq. 3M NH_4PF_6.

1′-[4-(Hydroxymethyl)phenyl]-1-(4-hydroxyphenyl)-4,4′-bipyridinium Bis(hexafluorophosphate) (**23**·2 PF_6^-): Yield 57%. Reddish-brown powder. M.p. >265° (dec.). ^{1}H-NMR (250 MHz, CD_3CN): 4.80 (*s*, 2 H, CH_2); 7.19 (*d*, ^3J=8.82, 2 arom. H); 7.67 (*d*, ^3J=8.57, 2 arom. H); 7.78 (*s*, 4 arom. H); 8.65 (*t*, ^3J=6.95, 4 H, Vio); 9.16 (*d*, ^3J=6.7, 2 H, Vio); 9.22 (*d*, ^3J=6.82, 2 H, Vio).

1-(4-Ethylphenyl)-1′-[4-(hydroxymethyl)phenyl]-4,4′-bipyridinium Bis(hexafluorophosphate) (**24**·2 PF_6^-): Yield 53%. Pale yellow powder. M.p. 230°. ^{1}H-NMR (250 MHz, CD_3CN): 1.23 (*t*, ^3J=7.5, Me); 2.76 (*q*, ^3J=7.5, 1 CH_2); 4.68 (*s*, 1 CH_2); 7.54 (*d*, ^3J=8.4, 2 arom. H); 7.66–7.61 (*m*, 6 arom. H); 8.55 (*d*, ^3J=5.5, 4 H, Vio); 9.10 (*d*, ^3J=4.1, 4 H, Vio).

1-(4-Ethoxyphenyl)-1′-[4-(hydroxymethyl)phenyl]-4,4′-bipyridinium Bis(hexafluorophosphate) (**25**·2 PF_6^-): Yield 84%. Yellow powder. M.p. 265°. ^{1}H-NMR (250 MHz, CD_3CN): 1.35 (*t*, ^3J=7.3, Me); 4.11 (*q*, ^3J=7.1, 1 CH_2); 4.65 (*s*, 1 CH_2); 7.16 (*d*, ^3J=9.4, 2 arom. H); 7.63 (*d*, ^3J=9.3, 2 arom. H); 7.76–7.66 (*m*, 4 arom. H); 8.54 (*m*, 4 H, Vio); 9.11–9.05 (*m*, 4 H, Vio).

1-(4-Carboxyphenyl)-1′-[4-(hydroxymethyl)phenyl]-4,4′-bipyridinium Bis(hexafluorophosphate) (**26**·2 PF_6^-): Yield 65.5%. Dark yellow powder. M.p. >270° (dec.). ^{1}H-NMR (250 MHz, CD_3CN): 4.64 (*d*, ^3J=27.1, 1 CH_2); 7.82 (*d*, ^3J=8.5, 2 arom. H); 8.29 (*d*, ^3J=8.5, 2 arom. H); 8.59 (*d*, ^3J=6.3, 4 H, Vio); 9.13 (*m*, 4 H, Vio).

Synthesis of the Phosphonic Acids **28**–**34**: *General Procedure E. 1-[2-(Diethoxyphosphinyl)ethyl]-1′-(2,4-dinitrophenyl)-4,4′-bipyridinium* (**27**; 0.005 mol) prepared according to [13], was added to the appropriately substituted aromatic amine (0.075 mol) in EtOH (60 ml). The solvent was evaporated, and H_2O (80 ml) was added. The suspension was stirred and filtered, and the filtrate decolorized with charcoal and then evaporated. The resulting product was dissolved in MeCN and the solid filtered and dried *in vacuo* to yield the phosphonate ester derivative. The latter was refluxed in 50% HCl soln. (60 ml) for 24 h. Then, the solvent was evaporated and the residue dried *in vacuo*: phosphonic acid derivative. For spectroscopic data for **28**–**34**, see also [22].

1-(2-Phosphonoethyl)-1′-[4-(pyridine-4-ylmethyl)phenyl]-4,4′-bipyridinium Hexafluorophosphate (**28**·PF_6^-): Yield 95%. White powder. M.p. 211°. ^{1}H-NMR (250 MHz,D_2O): 2.32 (br., 1 CH_2); 4.35 (*s*, 1 CH_2); 7.57 (*d*, 2 arom. H); 7.71 (*m*, 4 arom. H); 8.59 (*d*, 2 H, Vio); 9.08 (*d*, 2 H, Vio); 9.25 (*d*, 2 H, Vio).

1-(4-Cyanophenyl)-1′-(2-phosphonoethyl)-4,4′-bipyridinium Dichloride (**29**·2 Cl^-): ^{1}H-NMR (D_2O): 2.3 (*m*, 2 H); 4.8 (*m*, 2 H); 7.8 (*d*, 2 H); 8.16 (*d*, 2 H); 8.4–9.2 (*m*, 8 H).

*1-[4-(*tert*-Butyl)phenyl]-1′-(2-phosphonoethyl)-4,4′-bipyridinium Dichloride* (**30**·2 Cl^-): ^{1}H-NMR (D_2O): 1.29 (*s*, 9 H); 2.31 (*m*, 2 H); 4.78 (*m*, 2 H); 7.60 (*d*, 2 H); 7.68 (*d*, 2 H); 8.56–9.2 (*m*, 8 H).

1-(4-Methylphenyl)-1′-(2-phosphonoethyl)-4,4′-bipyridinium Dichloride (**31**·2 Cl^-): ^{1}H-NMR (D_2O): 2.32 (*s*, 3 H); 2.4–2.52 (*m*, 2 H); 4.75 (*m*, 2 H); 7.42 (*d*, 2 H); 7.53 (*d*, 2 H); 8.48–9.19 (*m*, 8 H).

1-(4-Phenoxyphenyl)-1′-(2-phosphonoethyl)-4,4′-bipyridinium Dichloride (**32**·2 Cl^-): ^{1}H-NMR (CD_3CN, PF_6): 2.36 (*m*, 2 H); 4.88 (*m*, 2 H); 7.1–7.45 (*m*, 5 H); 7.44–7.74 (*m*, 4 H); 8.49–9.11 (*m*, 8 H).

1-(4-Fluorophenyl)-1′-(2-phosphonoethyl)-4,4′-bipyridinium Dichloride (**33**·2 Cl^-): ^{1}H-NMR (D_2O): 2.33 (*m*, 2 H); 4.81 (*m*, 2 H); 7.35 (*d*, 2 H); 7.71 (*d*, 2 H); 8.58–9.22 (*m*, 8 H).

1-(4-Benzoylphenyl)-1′-(2-phosphonoethyl)-4,4′-bipyridinium Dichloride (**34**·2 Cl^-): ^{1}H-NMR (D_2O): 2.32 (*m*, 2 H); 4.8 (*m*, 2 H); 7.4–8.2 (*m*, 9 H); 8.40–9.33 (*m*, 8 H).

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Received June 27, 2005