

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 ^1H -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 PF₆[−]) 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 PF₆[−]), 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).

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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 -0.450 | 18 ^{c)} | -0.090 -0.325 -0.961 -1.220 |
| 25 ^{c)} | -0.161 -0.464 | 19 ^{c)} | -0.072 -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 LiClO₄/MeCN. ^{c)} 0.2M (Bu₄N)PF₆/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**·PF₆[−]; 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 H₂O, the aq. soln. washed with Et₂O (3×) and evaporated, and the residue dissolved in MeOH and added to 3M NH₄PF₆. The precipitate was collected and dried *in vacuo*.

1-(4-Hydroxyphenyl)-4,4'-bipyridinium Hexafluorophosphate (2·PF₆[−]): Yield 88%. Brown powder. M.p. 245°. ^1H -NMR (250 MHz, CD₃CN): 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).