



Fig. 2. Cyclic voltammograms of 1-(2,4-dinitrophenyl)-1'-(4-ethoxyphenyl)-4,4'-bipyridinium bis(hexafluorophosphate) (**19**·2 PF₆[−]; ----) and 1-(4-ethoxyphenyl)-1'-(4-hydroxyphenyl)-4,4'-bipyridinium bis(hexafluorophosphate) (**25**·2 PF₆[−]; —). Scan rate: 0.25 V/s, 0.2M (Bu₄N)PF₆/MeCN, ref. Ag/AgCl.

1-[(4-Hydroxymethyl)phenyl]-4,4'-bipyridinium Hexafluorophosphate (**3**·PF₆[−]): Yield 83%. Dark orange powder. M.p. 188° (dec.). ¹H-NMR (250 MHz, CD₃CN): 3.48 (s, OH); 4.67 (d, ³J=5.4, CH₂); 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**·PF₆[−]): Yield 70.5%. Beige powder. M.p. 174°. ¹H-NMR (250 MHz, CD₃CN): 1.33 (t, ³J=7.6, 3 H, Me); 2.85 (q, ³J=7.6, 2 H, CH₂); 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). ¹³C-NMR (63 MHz, CD₃CN): 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**·PF₆[−]): Yield 88%. Pale yellow powder. M.p. 198°. ¹H-NMR (250 MHz, (D₆)acetone): 1.45 (t, ³J=6.9, Me); 4.25 (q, ³J=6.9, CH₂); 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**·PF₆[−]): Yield 52%. White powder. M.p. 163°. ¹H-NMR (250 MHz, CD₃CN): 1.29 (t, ³J=7.02, 2 Me); 3.38 (d, ³J=21.9, 1 CH₂); 4.10 (q, ³J=7.1, 2 CH₂); 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 Et₃N (2.5 mmol) was added prior to the addition of the 4-substituted benzenamine.

1-(4-Carboxyphenyl)-4,4'-bipyridinium Hexafluorophosphate (**4**·PF₆[−]): Yield 84%. Beige powder. M.p. 251°. ¹H-NMR (250 MHz, D₂O): 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**·PF₆[−]): Yield 62%. Ocher powder. M.p. 210°. ¹H-NMR (250 MHz, D₂O): 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, SO₃H, 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 ¹PrOH (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 H₂O/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.). ¹H-NMR (250 MHz, CD₃OD): 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 ¹PrOH (3 ml), a soln. of pyridin-4-amine (0.6 mmol, 56 mg) in ¹PrOH (1 ml) was added and refluxed for 1.5 h under Ar. ¹PrOH (3 ml) and hexane were added to induce precipitation, which was completed at 6° after 3 days.