Novel Compounds with a Viologen Skeleton and N-Heterocycles on the Peripheries: Electrochemical and Spectroscopic Properties

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The present article deals with novel compounds comprising a redox-active group as core and a nucleobase in the peripheries, linked covalently *via* a spacer. The new derivatives 1,1′,1″-(benzene-1,3,5-triyltrimethanediyl)tris{1′-[3-(3,4-dihydro-5-methyl-2,4-dioxopyrimidin-1(2*H*)-yl)propyl]-4,4′-bipyridinium} hexafluorophosphate (**1**), 1,1′,1″-(benzene-1,3,5-triyltrimethanediyl)tris{1′-[2-(4-chloro-7*H*-pyrrolo[2,3-*d*]pyrimidine-7-yl)ethyl]-4,4′-bipyridinium} hexachloride (**2a**)[1]), and 1,1′,1″-(benzene-1,3,5-triyltrimethanediyl)tris{1′-[2-(2-amino-4-chloro-7*H*-pyrrolo[2,3-*d*]pyrimidine-7-yl)ethyl]-4,4′-bipyridinium} hexabromide (**2b**)[1]) were synthesized by nucleobase-anion alkylation and linked to the 4,4′-bipyridinium core. UV and CV analyses of these compounds were performed and revealed significantly different properties.

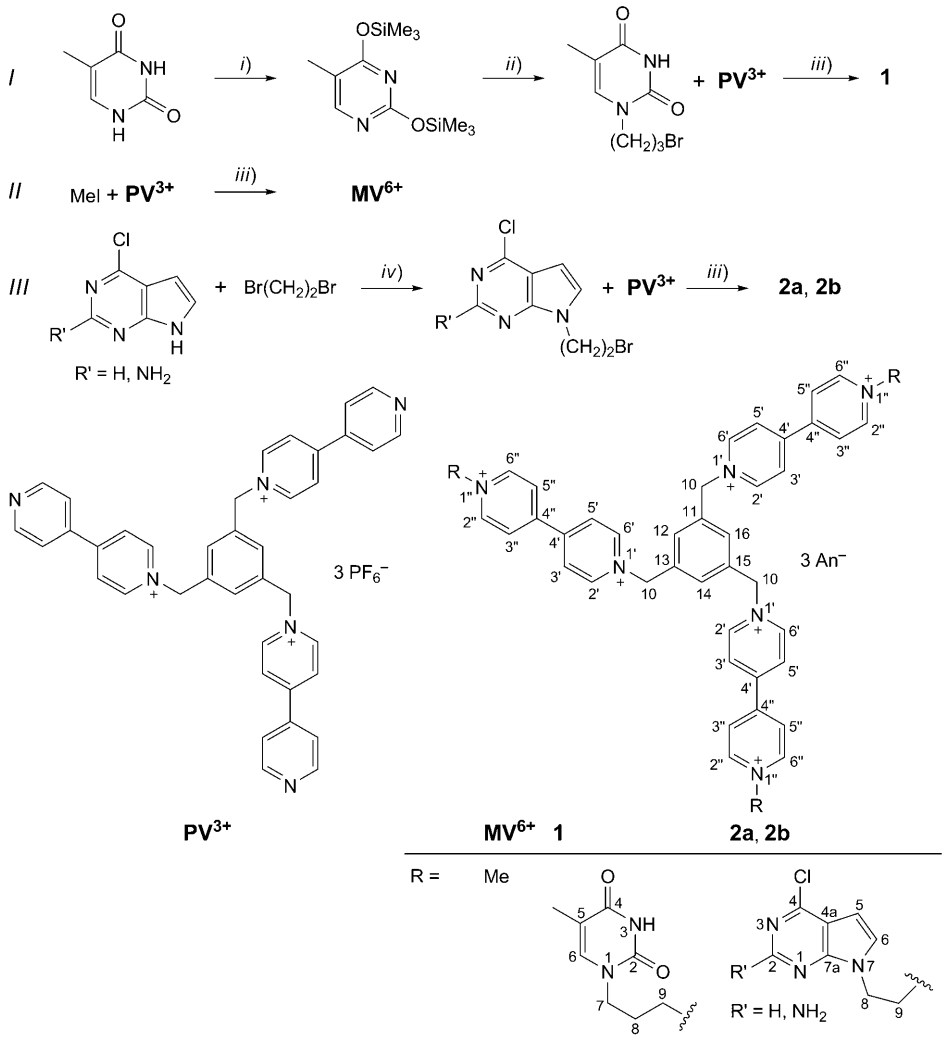
1. Introduction. – Chemical modifications play an important role in the creation of new compounds with dual functionality improving their properties. These include their hybridization abilities [1], specific recognition of biological targets [2][3], and their ability of the formation of specific H-bonds [4][5], combined with electrochemically properties [6]. These characteristics make such structures very attractive for several applications in the field of light-harvesting, electrochromics [7][8], catalysis, cellular imaging, drug delivery [9], or for the construction of complex multifunctional supramolecular systems [10][11].

The electrochromic properties of 4,4′-bipyridinium salts are well-documented, and they have received significant attention for several decades because of their wide range of potential applications [12][13]. On the other hand, dendrimers containing electroactive moieties are currently under investigation due to their useful functions, such as ion sensing with signal amplification [14][15], charge pooling [16], or as antiviral agents [17]. The present article deals with the preparation, characterization, as well as electrochemical and spectroscopic properties of a new family of compounds containing 4,4′-bipyridinium units as redox-active cores functionalized on their periphery with an N-heterocyclic nucleobase, also referred to as base. The aim was to couple a redox unit with well-known electrochemical properties with biologically active head groups. Such compounds were expected to exhibit interesting properties because the 4,4′-bipyridinium units are known as electron acceptors [12], used in electrochemical processes

[1]) The numbering of the pyrrolo[2,3-*d*]pyrimidine system follows the IUPAC rules and is different from that of the purine ring system.

[18], and the nucleobases might act as electron donors, capable of fast electron-transfer reactions. For comparison, we also investigated the properties of a '*tris-viologen*' derivative 1,1′,1″-(benzene-1,3,5-triyltrimethanediyl)tris(1′-methyl-4,4′-bipyridinium) hexafluorophosphate (**MV**$^{6+}$), which contains three viologen units (*Scheme*).

Scheme. *Synthesis of compounds* **MV**$^{6+}$, **1**, **2a**, *and* **2b**



i) hexamethyldisilazane and Me_3SiCl, 21 h, reflux. *ii*) 3 equiv. of 1,3-dibromopropane (DBP) in DMF, 24 h, 80°. *iii*) MeCN, 96 h, 80°. *iv*) NaH, DMF, 72 h, 70°.

2. Results and Discussion. – 2.1. *Synthesis.* All compounds, **MV**$^{6+}$, **1**, **2a**, and **2b**, were synthesized by nucleophilic substitution reaction of alkylated nucleobase derivatives

with the corresponding 'redox matrix', 1,1′,1″-(benzene-1,3,5-triyltrimethanediyl)-tris(4-pyridin-4-ylpyridinium) trihexafluorophosphate (**PV**$^{3+}$; *Scheme*).

The well-known precursor **PV**$^{3+}$, consisting of a mesityl derivative linked to three 4,4′-bipyridine units, plays the role of the branching unit in the divergent synthesis of dendrimers. **PV**$^{3+}$ was prepared according to the procedure described in [19] by reaction of 1,3,5-tris(bromomethyl)benzene [20][21] with an excess of 4,4′-bipyridine in MeCN, followed by ion exchange with NH_4PF_6. The precursor **PV**$^{3+}$ salt with three peripheral N-atoms reacted further quantitatively with the (bromoalkyl)-pyrimidine derivative and MeI. The reference compound, 1,1′,1″-(benzene-1,3,5-triyltrimethanediyl)tris(1′-methyl-4,4′-bipyridinium) hexafluorophosphate (**MV**$^{6+}$), was obtained in 60% yield by treating the precursor **PV**$^{3+}$ with an excess of MeI in MeCN (*Scheme*, *Route II*). Compounds **1**, **2a**, and **2b** were synthesized by a divergent procedure starting from the core to the periphery. The reaction sequence was strongly determined by the stability of the redox units in alkaline medium. It is known that the 4,4′-bipyridine units are reduced irreversibly at pH of *ca.* 10. The periphery of the compounds **1**, **2a**, and **2b** consist of substituted thymine and pyrrolo[2,3-*d*]pyrimidine units, respectively. Therefore, in the first reactions step, the nucleobases were alkylated, and, in last reaction step, they were bound to the 'redox matrix' **PV**$^{3+}$. Difficulties arose during alkylation of thymine because of a lack in regioselectivity. Thymine can be alkylated at the N(1), N(3), O(2), or O(4); moreover, internal cyclization reactions were reported by *Nawrot et al.* [22]. The problem was solved by protection of the functional groups according to the reaction of *Vorbrüggen et al.* [23], which involves the conversion of pyrimidine-2,4-dione bases to their bis[trimethylsilyl]-ether derivatives by treatment with hexamethyldisilazane and Me_3SiCl. The bis(trimethylsilyl) derivative was then alkylated [24] by treatment with an excess of dibromoalkane in DMF to afford 1-(3-bromopropyl)-5-methylpyrimidine-2,4(1*H*,3*H*)-dione (*Scheme*, *Route I*) in low yield (loss during the deprotection or conversion of the raw material) [25]. 7-(2-Bromoethyl)-4-chloro-7*H*-pyrrolo[2,3-*d*]pyrimidine and 7-(bromoethyl)-4-chloro-7*H*-pyrrolo[2,3-*d*]pyrimidin-2-amine were prepared according to [26], by subsequent nucleobase-anion alkylation (NaH, DMF) with a 100-fold excess of 1,2-dibromoethane (*Scheme*, *Route III*), besides small amounts (10–15%) of the 9-vinyl derivatives, which were separated by column chromatography. Finally, the corresponding alkylated heterocycles were covalently coupled on the core by nucleophilic reaction in MeCN with a yield of more than 70%. The structures of the novel compounds were confirmed by ^{1}H- and ^{13}C-NMR as well as by UV spectroscopy, and by elemental analyses.

2.2. *Spectroelectrochemical Investigations.* The electrochemical behavior of **1**, **2a**, and **2b** was studied at glassy carbon microelectrodes in a MeCN/$NaClO_4$ electrolyte at 298 K. For comparison, the electrochemical behavior of 1,1′,1″-(benzene-1,3,5-triyltrimethanediyl)tris(1′-methyl-4,4′-bipyridinium) hexafluorophosphate (**MV**$^{6+}$) has also been investigated. The cyclic voltammetry (CV) curves obtained for compounds **1**, **2a**, and **2b** are shown in *Fig. 1*.

The cathodic region showed two reversible one-electron transfer processes, *I* and *II*, for all compounds, being typical for viologen derivatives corresponding to the formation of a radical cation (*I*) and a neutral species (*II*) [27]. The first reduction was generally very fast, and the second was often coupled to precipitation processes due to the uncharged nature of the fully reduced species, which is insoluble in highly polar

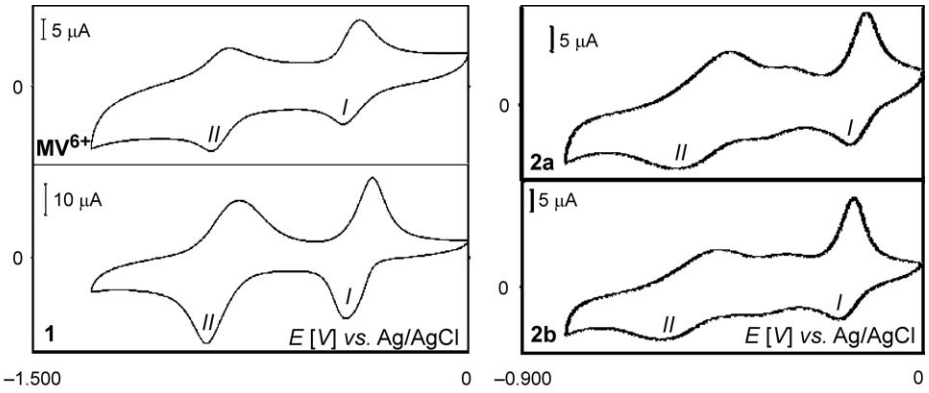


Fig. 1. *Cyclic voltammograms of compounds* $\mathbf{MV^{6+}}$, **1**, **2a**, *and* **2b** (0.1 mM) *in 0.1* M $NaClO_4$ *in MeCN at a glassy carbon electrode* (area: 0.0680 cm^2)*; scan rate* $v = 1\ Vs^{-1}$.

solvents [28]. The reduction processes of compound **1** can be directly compared with those of the model compound $\mathbf{MV^{6+}}$. A sharp positive shift of the cathodic-peak potential was observed in the case of compound **2a** and **2b**, indicating a destabilization of the redox matrix compared to compound **1** and model compound $\mathbf{MV^{6+}}$, presumably caused by folding of the pyrrolo[2,3-*d*]pyrimidine units around the 4,4′-bipyridinium units. These results point to an extension of the π-electron system, which corroborated the UV/VIS results for the chemically reduced compounds **2a** and **2b**. The reduction potential of pyrrolo[2,3-*d*]pyrimidine units measured with a glassy carbon electrode in 1 M TBABr/H_2O was highly negative (– 1.764 V; *Fig. 2*).

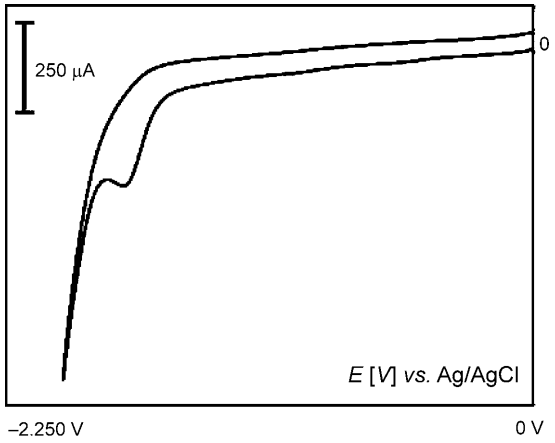


Fig. 2. *Cyclic voltammogram of 7-(2-Bromoethyl)-4-chloro-7*H*-pyrrolo[2,3-*d*]pyrimidine* (*c* = 1 mM) *recorded with a glassy carbon electrode in 1* M *TBABr/*H_2O*, scan rate* $v = 0.2\ Vs^{-1}$

The half-wave potential ($E_{1/2}$) and peak-separation data of the compounds examined are collected in the *Table.*

Table. *Electrochemical Parameters(v* in v/s^{-1} and *E* in mV) *for the Compounds* **MV**$^{6+}$, **1**, **2a**, *and* **2b**

	v	$E_{pc}1$	$E_{pa}1$	$E^{\circ}1$	$\Delta E1$	$E_{pc}2$	$E_{pa}2$	$E^{\circ}2$	$\Delta E2$
MV^{6+}	– 0.1	– 444	– 378	– 411	66	– 876	– 823	– 849	53
	– 0.3	– 435	– 371	– 403	64	– 876	– 811	843	65
	– 0.6	– 437	– 378	– 407	59	– 886	– 818	– 852	68
	– 1	– 427	– 376	– 401	51	– 879	– 828	– 853	51
1	– 0.1	– 461	– 349	– 405	112	– 886	– 779	– 832	107
	– 0.3	– 422	– 327	– 374	95	– 898	– 796	– 847	102
	– 0.6	– 427	– 332	– 379	95	– 898	– 789	– 843	109
	– 1	– 422	– 330	– 376	92	– 901	– 798	– 850	103
2a	– 0.1	– 168	– 129	– 148	39	– 560	– 420	– 238	140
	– 0.3	– 166	– 132	– 149	32	– 562	– 432	– 497	130
	– 0.6	– 166	– 129	– 147	37	– 432	– 552	– 492	120
	– 1	– 161	– 125	– 143	36	– 522	– 430	– 476	92
2b	– 0.1	– 193	– 151	– 172	39	– 583	– 449	– 516	134
	– 0.3	– 190	– 154	– 172	36	– 598	– 442	– 520	156
	– 0.6	– 186	– 154	– 170	32	– 583	– 452	– 472	131
	– 1	– 181	– 151	– 166	30	– 576	– 447	– 511	129

All electrochemical parameters were determined using a glassy carbon working electrode, *vs.* Ag/AgCl immersed in a solution of compounds **MV**$^{6+}$, **1**, **2a**, and **2b** (0.1 mM) in MeCN/0.1 M $NaClO_4$.

The first half-wave potential ($E(1)_{1/2}$) shifts for compound **1** are comparable with the reference **MV**$^{6+}$, whereas compounds **2a** and **2b** are *ca.* 260 MV more positive compared to the reference. This finding indicated that the cation state was influenced by *Coulomb* destabilization which emerged in the presence of aromatic pyrrolo[2,3-*d*]pyrimidine system with functional groups such as Cl and NH_2 with $+M$ effects on the periphery. During the voltammetry experiments, a green/blue plume for compounds **2a** and **2b** was observed in the vicinity of the electrode. The color of the electrolyzed solution indicated the formation of the radical cation dimers, as supported by the UV/VIS results for the chemically reduced compounds **2a** and **2b**. On the basis of the parameters in the *Table*, dimer formation did not appear to inhibit the reversibility of the first reductions wave. Peak-separation values indicate that this electrochemical process is reversible for compounds **2a** and **2b**, independent of the scan rate and varies from 40 to 60 mV, while that of compound **1** is strongly dependent of the scan rate (*Fig. 3*).

At a moderate scan rate, an adsorbed one-electron reduced species on the electrode surface was evident in the voltammograms for compound **1** (*Fig. 3*). At faster scan rates ($1\ V\ s^{-1}$), the voltammetric data still revealed that the first reduction was quite fast; the largest ΔE_p value measured in these experiments was 112 mV. The half-wave potentials corresponding to the second electron uptake exhibited the same trend, shifted to the less negative values for compound **1**. The ratio of the anodic and cathodic peak heights ($i_{pa}1/i_{pc}1$) provides information about the chemical reversibility of the first redox wave. The peak height ratio was calculated after base-line correction from voltammograms, and varied from 0.9 to 1.2 for all compounds at scan rates from 300 mV – 1 $V\ s^{-1}$. This indicated relatively good chemical reversibility. The kinetics of the electron-transfer

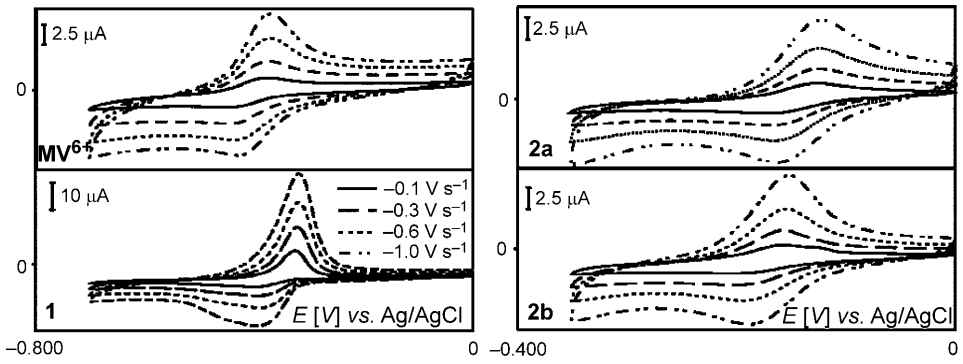


Fig. 3. *Cyclic voltammograms of compounds* $\mathbf{MV^{6+}}$, **1**, **2a**, *and* **2b** (0.1 mM) *in 0.1* M $NaClO_4$ *in MeCN at a glassy carbon electrode* (area: 0.0680 cm^2), *scan rates* v = *0.1, 0.3, 0.6, and 1 V* s^{-1}

reaction appeared to be fast, although very marked absorbed effects were observed. As was the case for the first reduction process, these effects were most pronounced for redox matrix with thymine units in the periphery (*i.e.*, **1**). Overall, the trend observed in the $E_{1/2}$ values revealed that the reduction process was thermodynamically favored, independently of the heterocycle at the periphery. The electrode response of compounds **1** and **2a**, and **2b** in the CV experiment could thus be assigned to a *quasi*-reversible case of the heterogeneous electron transfers. Further investigation of the electron transfer mechanism has not been performed because of a strong absorption of the reduced species on the electrode minigrid used as working electrode.

2.3. UV/VIS Spectroscopy. Compounds **1**, **2a**, and **2b** contain three types of chromophoric units: thymine, pyrrolo[2,3-*d*]pyrimidine units, 4,4′-bipyridine, and benzene. The absorption spectra of the alkylated thymine and pyrrolo[2,3-*d*]pyrimidine units in an EtOH solution at 298 K are shown in *Fig. 4*, and the spectra of compounds $\mathbf{MV^{3+}}$, **1**, **2a**, and **2b** in MeCN at 298 K in the oxidated states are also displayed for comparison.

The spectrum was dominated by a strong absorption of the 4,4′-bipyridine units ($\mathbf{MV^{6+}}$: $\lambda_{max} = 256$ nm, $\varepsilon = 43556$ M^{-1} cm^{-1}) with some contribution of thymine (**1**; $\lambda_{max} = 266$ nm, $\varepsilon = 59460$ M^{-1} cm^{-1}); 4-chloropyrrolo[2,3-*d*]pyrimidine (**2a**; $\lambda_{max} = 265$ nm, $\varepsilon = 83550$ M^{-1} cm^{-1}), and 4-chloropyrrolo[2,3-*d*]pyrimidin-2-amine units (**2b**; $\lambda_{max} = 235$ nm, $\varepsilon = 73200$ M^{-1} cm^{-1}, $\lambda_{max} = 262$ nm, $\varepsilon = 62700$ M^{-1} cm^{-1}). The absorbance of benzene was negligible at *ca.* 260 nm ($\lambda_{max} = 255$ nm, $\varepsilon = 250$ M^{-1} cm^{-1}) [29]. The intensity of the absorption spectrum in the UV region increased by the presence of an aromatic ring and the auxochromic groups with $+M$ effects on the periphery. The result suggests that there are interactions between the chromophoric units within the dendrimers, as confirmed by the observation that the dendrimers exhibit a broad and weak absorption peak in the visible region (**2a**: $\lambda_{max} = 384$ nm, $\varepsilon = 83550$ M^{-1} cm^{-1}; **2b**: $\lambda_{max} = 475$ nm, $\varepsilon = 7070$ M^{-1} cm^{-1}), which could not be seen in the spectrum of compound **1**, as well as of the alkylated N-heterocyclic units. The absorbance of alkylated heterocyclic units in EtOH is shown in the inset of *Fig. 4*; an absorbance maximum was present for thymine (*a*) at $\lambda_{max} = 271$ nm ($\varepsilon = 10310$ M^{-1} cm^{-1}), for 4-

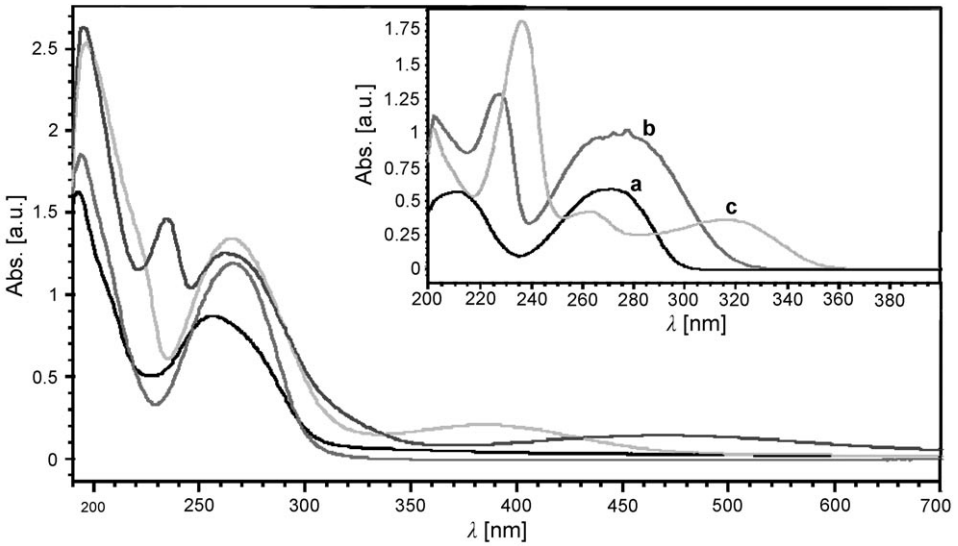


Fig. 4. *Adsorption spectra of* $\mathbf{MV}^{6+}$ (black line), **1** (medium grey line), **2a** (light grey line), *and* **2b** (dark grey line) *in oxidated state, 0.1 m* M *in 0.1* M $NaClO_4$ *in MeCN. Inset:* Adsorption spectra of 1-(3-bromopropyl)-5-methylpyrimidine-2,4(1*H*,3*H*)-dione (*a*), 7-(2-bromoethyl)-4-chloro-7*H*-pyrrolo[2,3-*d*]pyrimidine (*b*) and 7-(bromoethyl)-4-chloro-7*H*-pyrrolo[2,3-*d*]pyrimidin-2-amine (*c*) in EtOH solution.

chloropyrrolo[*2,3-d*]pyrimidine (*b*) at $\lambda_{max} = 227$ nm ($\varepsilon = 27690$ ‰M^{-1} cm^{-1}) and $\lambda_{max} = 277$ nm ($\varepsilon = 21980$ M^{-1} cm^{-1}), and for 4-chloropyrrolo[*2,3-d*]pyrimidin-2-amine- (*c*) at $\lambda_{max} = 236$ nm ($\varepsilon = 36170$ M^{-1} cm^{-1}) and $\lambda_{max} = 263$ nm ($\varepsilon = 8350$ M^{-1} cm^{-1}). In the case of *c*, a pronounced bathochromic shift was also observed in the long-wavelength range at $\lambda_{max} = 316$ nm ($\varepsilon = 7230$ M^{-1} cm^{-1}).

Due to their redox properties, the 4,4′-bipyridinium units can be examined by spectroelectrochemical properties, because they change their color depending on their redox status. The monomeric viologens exhibit absorption maxima in the range of 300 – 750 nm. Benzyl-substituted viologens have typical absorption maxima at 401 ($\varepsilon =$ 28900 $M^{-1}cm^{-1}$) and 608 nm ($\varepsilon = 11700$ $M^{-1}cm^{-1}$), phenyl-substituted viologens typically show absorption maxima at 446 ($\varepsilon = 29000$ M^{-1} cm^{-1}) and 714 nm ($\varepsilon = 15600$ M^{-1} cm^{-1}), and Me-substituted viologens show absorption maxima at 400 ($\varepsilon = 18860$ M^{-1} cm^{-1}) and 600 nm ($\varepsilon = 7084$ M^{-1} cm^{-1}). In case of dimers, the maxima are shifted to *ca.* 370 and 550 nm. In addition, in the long-wavelength range at *ca.* 900 nm, a new band appears which seems to be due to charge-transfer (CT) complexes of the mentioned compounds [30].

Fig. 5 shows UV/VIS spectra of **1**, **2a**, and **2b** (0.1 m M) in 0.1 M $NaClO_4$ in MeCN after chemical reduction, in a three-electrode system *vs.* Ag/AgCl at several potentials. All compounds showed the typical absortion maxima as other viologenated dendrimers at 400 ($\varepsilon(\mathbf{1}) = 8450$, $\varepsilon(\mathbf{2a}) = 47860$, $\varepsilon(\mathbf{2b}) = 13934$ M^{-1} cm^{-1}) and 600 nm (($\varepsilon(\mathbf{1}) = 4460$, $\varepsilon(\mathbf{2a}) = 46045$, $\varepsilon(\mathbf{2b}) = 10990$ M^{-1} cm^{-1}). We observed the same behavior as in the cyclovoltammetry experiments for **2a** and **2b** which exhibit a maximum concentration of

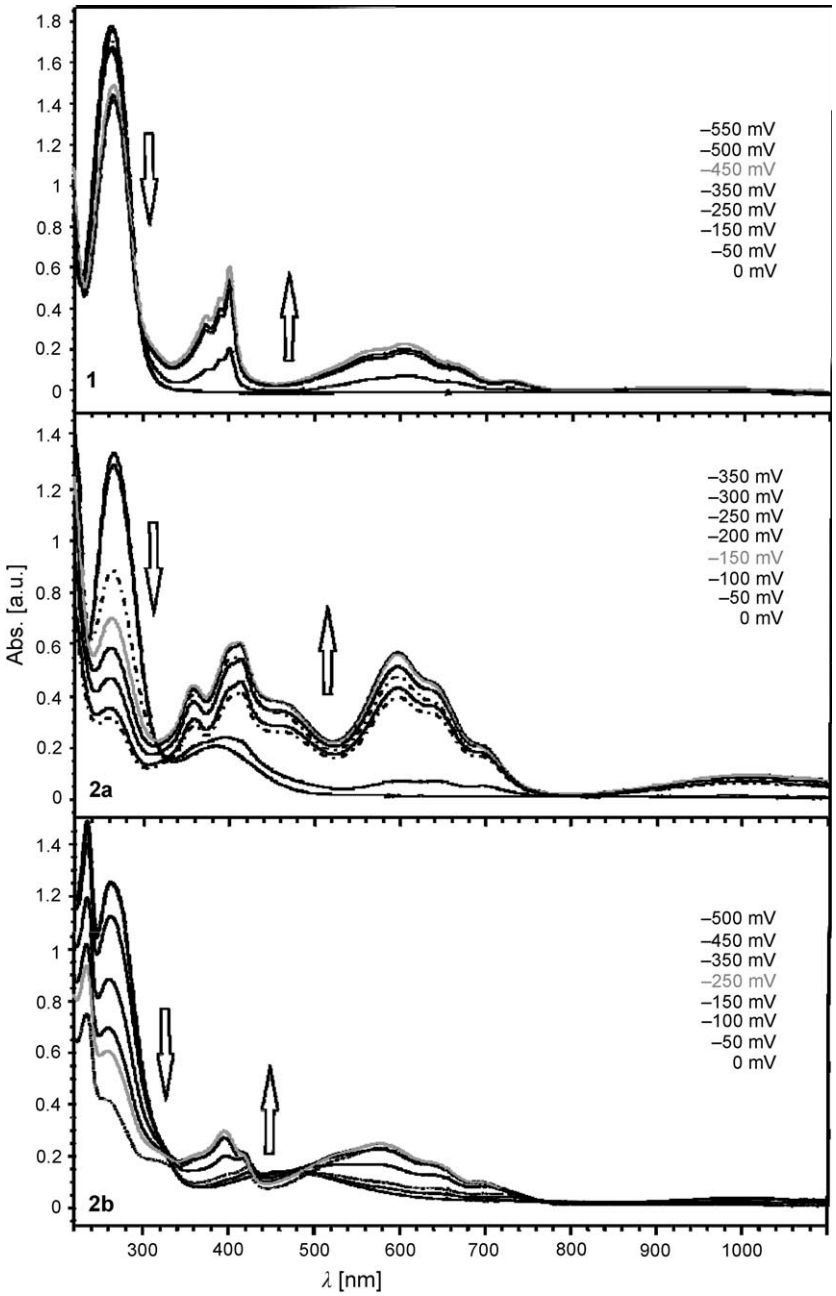


Fig. 5. *Absorption spectra of* **1**, **2a**, *and* **2b** *in the reduced state, 0.1 mM in 0.1 M $NaClO_4$ in MeCN at several potentials*

radical cation species at -150 mV for **2a** and at -250 mV for **2b**, respectively. Maximum concentration of radical cation species is found at -450 mV for compound **1** and reference $\mathbf{MV}^{6+}$. The colors of the reduced solutions were deep green for the first, deep purple for the second reduction step for compound **2a**, and deep blue for the first and deep violet for the second reduction step for compound **2b**, with absorbance peaks at 400, 595, and 950 nm. This indicates dimer formation [30]. Such an absorption tail can be assigned to a CT transition from electron-donor units on the periphery to the 4,4′-bipyridinium electron-acceptor core.

In conclusion, a series of electroactive, functionalized dendrimers with interesting properties were prepared by using a simple synthetic procedure. The 4,4′-bipyridinium units undergo two distinct and fast one-electron transfer processes at *ca.* -150 mV and -250 mV, respectively. This might be useful in photochemical energy-conversion schemes as well as for information processing.

Experimental Part

General. All chemicals were purchased from *Merck* (D-*Hohenbrunn*), *Sigma–Aldrich*, or from *Fluka.* Solvents were of laboratory grade. TLC: aluminium sheets, silica gel *60 F_{254}*, 0.2-mm layer (*Merck*, Germany). M.p.: *Advanced SMP3*; uncorrected. UV Spectra: *8453* UV-visible spectrophotometer (*Agilent*, Germany); λ_{max} in nm (ε in $M^{-1}\,cm^{-1}$). NMR Spectra: *Bruker* AMX-500 spectrometer; ^{1}H: 500.13, ^{13}C: 125.7 MHz; chemical shifts δ in ppm rel. to Me_4Si as internal standard for ^{1}H and ^{13}C. Elemental analyses: *VarioMICRO cube.*

Electrochemistry and Spectroelectrochemistry. MeCN and $NaClO_4$ (*puriss.*, electrochem. grade) were purchased from *Sigma–Aldrich* and *Acros Organics* for cyclic voltammetry and spectroelectrochemical studies. CVs were measured under Ar with the potentiostat *PGSTAT 302N* from *AUTOLAB*, controlled by a PC running under GPES from *Windows*, version 4.9 (*ECO Chemie B. V.*); a glassy carbon electrode (GCE) from *Metrohm* (Germany) with an active electrode surface of $A = 0.07$ cm^2 was used for CV. The electrode surface was polished with Al_2O_3. The reference electrode was Ag/AgCl/KCl (3 M in H_2O), and the counter electrode was a Pt wire.

The spectroelectrochemical cell used for measurements of the dendrimers in soln. was a H-Type spectroelectrochemical bulk electrolysis cell. The reference electrode was Ag/AgCl immersed in an electrolyte vessel filled with LiCl (2 M in EtOH), separated from the cell by a glass frit, and the counter electrode was a Pt foil. The working electrode was 0.039 g of graphitized carbon felt *GFA-5* of *ca.* 0.021 m^2 BET area from SGL carbon, the electrochemically active area of which is not known. Absorbance changes were recorded with a *Hewlett-Packard 8453* spectrophotometer.

The UV/VIS spectra of the dendrimers in their oxidized and reduced state have been recorded spectroelectrochemically in MeCN/$NaLiO_4$ (0.1 M), and the corresponding λ_{max} values and extinction coefficients (ε) are reported. The reference for UV/VIS spectra of dendrimers was the pure solvent/electrolyte.

*1-(3-Bromopropyl)-5-methylpyrimidine-2,4(1*H*,3*H*)-dione* [25]. To a soln. of thymine (2.24 g, 17.6 mmol) in hexamethyldisilazane (HMDS; 11.4 ml, 54 mmol) under Ar was added a cat. amount of trimethylchlorosilane (1.08 ml, 8.54 mmol), and the mixture was stirred for 21 h under reflux. Excess HMDS was then removed under reduced pressure to afford crude *O*-silylated thymine. The crude material was taken up in DMF (10 ml), 1,3-dibromopropane (4.6 ml) was added, and the mixture was stirred at 80° for 24 h. H_2O (150 ml) was then added, and, after stirring for 10 min, the mixture was filtered, and the aq. filtrate was extracted with CH_2Cl_2. The combined extracts were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Crystallization of the residue from abs. EtOH gave white crystals of *1-(3-bromopropyl)-5-methylpyrimidine-2,4(1*H*,3*H*)-dione* (1.5 g, 6.07 mmol, 34.4%). M.p. 140°. ^{1}H-NMR ((D$_6$)DMSO): 11.17 (*s*, H–N(3)); 7.48 (*s*, H–C(6)); 3.73 (*t*, $J = 7.0$, H–C(9)); 3.51 (*t*, $J = 6.5$, H–C(7)), 2.13 (*q*, $J = 6.7$, H–C(8)); 1.74 (*s*, H–C(5)). ^{13}C-NMR ((D$_6$)DMSO): 164.19 (C(4));

151.17 (C(2)); 140.38 (C(6)); 110.46 (C(5)); 47.26 (C(7)); 31.29 (C(8)); 29.76 (C(9)); 12.60 (*Me*–C(5)). Anal. calc. for $C_8H_{11}BrN_2O_2$ (247.09): C 38.89, H 4.49, N 11.34; found: C 39.32, H 4.73, N 11.47.

*1,1′,1″-(Benzene-1,3,5-triyltrimethanediyl)tris{1′-[3-(3,4-dihydro-5-methyl-2,4-dioxopyrimidin-1(2*H*)-yl)propyl]-4,4′-bipyridinium} Hexafluorophosphate* (**1**). A soln. of 1,1′,1″-(benzene-1,3,5-triyltrimethanediyl)tris[4-(pyridin-4-yl)pyridinium] trihexafluorophosphate (214 mg, 0.20 mmol) in MeCN (10 ml) were added to a stirred soln. of 1-(3-bromopropyl)-5-methyl-1*H*-pyrimidine-2,4-dione (1,570 g, 1.61 mmol) in MeCN (45 ml). The mixture was refluxed for 4 d at 85°. The cooled mixture was added dropwise to 30 ml of a stirred tetrabutylammonium chloride soln. (Bu_4NCl; 5% in MeCN). The yellowish precipitate was filtered off and washed three times with MeCN (10 ml each) and three times with CH_2Cl_2 (10 ml each). After drying for 24 h *in vacuo*, the resulting powder was dissolved in H_2O (20 ml) and precipitated with a NH_4PF_6 soln. (10% in H_2O). The residue was washed several times with H_2O and dried *in vacuo* for 24 h to yield 285 mg of **1** (0.14 mmol, 70%). ^{1}H-NMR (CD_3CN): 9.34 (*s*, H–N(3)); 8.98 (*d*, *J* = 6.5, H–C(5″,3″)); 8.93 (*d*, *J* = 7.0, H–C(5′,3′)); 8.43 – 8.34 (*m*, H–C(2′,6′,2″,6″); 7.68 (*s*, H–C(12,14,16)); 7.24 (*s*, H–C(6)); 5.86 (*s*, H–C(10)); 4.68 (*t*, *J* = 7.2, H–C(9)); 3.80 (*t*, *J* = 6.2, H–C(7)); 2.39 (*q*, *J* = 6.7, H–C(8)); 1.85 (*s*, H–C(5)). ^{13}C-NMR (CD_3CN): 165.4 (C(4)); 152.7 (C(4″)); 151.7 (C(4″)); 151.1 (C(2)); 146.8 (C(3′,5′,3″,5″)); 141.7 (C(6)); 136.1 (C(13,15,11)); 132.8 (C(12,14,16)); 128.5 (C(2′,6′,2″,6″)); 111,6 (C(5)); 64.8 (C(10)); 60.4 (C(9)); 45.3 (C(7)); 31.4 (C(8)); 12.4 (Me–C(5)).

*1,1′,1″-(Benzene-1,3,5-triyltrimethanediyl)tris{1′-[2-(4-chloro-7*H*-pyrrolo[2,3-*d*]pyrimidin-7-yl)ethyl]-4,4′-bipyridinium} Hexachloride* (**2a**). A soln. of 1,1′,1″-(benzene-1,3,5-triyltrimethanediyl)tris[4-(pyridin-4-yl)pyridinium] trihexafluorophosphate (81 mg, 0.08 mmol) in MeCN (16 ml) were added in portions of 1 ml within 4 h to a stirred soln. of 7-(2-bromoethyl)-4-chloro-7H-pyrrolo[2,3-*d*]pyrimidine (104 mg, 0.4 mmol) in MeCN (10 ml). The mixture was refluxed for three d at 70°. The cooled mixture was added dropwise to 15 ml of a stirred Bu_4NCl soln. (5% in MeCN). The yellowish precipitate was filtered off and washed three times with MeCN (10 ml each) and three times with CH_2Cl_2 (10 ml each). After drying for 24 h *in vacuo*, 87 mg of **2a** (0.067 mmol, 84%) were obtained as a brown powder. ^{1}H-NMR (D_2O): 10.0 (*d*, *J* = 6.5, H–C(6″,2″)); 9.45 (*d*, *J* = 6.0, H–C(6′,2′)); 9.15 (*d*, *J* = 6.5, H–C(5″,3″)); 8,95 (*d*, *J* = 7.0, H–C(5′,3′)); 8.22 (*s*, H–C(12,14,16)); 8.02 (*s*, H–C(2)); 7.85 (*d*, *J* = 3.0, H–C(6)); 7.10 (*d*, *J* = 4.0, H–C(5)); 5.99 (*s*, H–C(10)); 4.89 (*t*, *J* = 11.5, H–C(8)); 4.06 (*t*, *J* = 11.5, H–C(9)). ^{13}C-NMR (D_2O): 153.8 (C(4′)); 151.5 (C(4)); 150.9 (C(4″)); 150.1 (C(6″,2″)); 149.3 (C(7a)); 146.0 (C(6′,2′)); 144.6 (C(5″,3″)); 135.4 (C(11,13,15)); 134.6 (C(12,14,16)); 130.6 (C(6)); 127.2 (C(5′,3′)); 121.8 (C(2)); 110.1 (C(4a)); 98.0 (C(5)); 62.8 (C(10)); 46.3 (C(8)); 31.5 (C(9)).

*1,1′,1″-(Benzene-1,3,5-triyltrimethanediyl)tris{1′-[2-(2-amino-4-chloro-7*H*-pyrrolo[2,3-*d*]pyrimidin-7-yl)ethyl]-4,4′-bipyridinium} Hexabromide* (**2b**). A soln. of 1,1′,1″-(benzene-1,3,5-triyltrimethanediyl)-tris[4-(pyridin-4-yl)pyridinium] trihexafluorophosphate (81 mg, 0.08 mmol) in MeCN (16 ml) were added dropwise in portions of 1 ml within 4 h to a soln. of 7-(bromomethyl)-4-chloro-7*H*-pyrrolo[2,3-*d*]pyrimidin-2-amine (110 mg, 0.4 mmol) in MeCN (16 ml). The mixture was refluxed for 3 h at 70°. The cooled mixture was filtered, and washed three times with MeCN and Et_2O, resp., and dried. The mother liquor was evaporated, and the residue was dried. The combined solids were resuspended in H_2O (15 ml) and precipitated with 6 ml of a NH_4PF_6 soln. (10% in H_2O). The residue was washed several times with H_2O and dried *in vacuo* for 48 h. Subsequently, anion-exchange chromatography was applied with 103 mg of a Br^-/PF_6^- mixed salt of the crude product and a 5% Bu_4NBr soln. (8 ml) to afford 96 mg of **2b** (0.058 mmol, 72%). Pink powder. ^{1}H-NMR (D_2O): 9.85 (*d*, *J* = 5.0, H–C(6″,2″)); 9.36 (*d*, *J* = 6.0, H–C(6′,2′)); 8.91 (*d*, *J* = 6.0, H–C(5″,3″)); 8.81 (*d*, *J* = 5.0, H–C(5′,3′)); 7.78 (*s*, H–C(12,14,16)); 7.58 (*d*, *J* = 3.5, H–C(10)); 6.78 (*d*, *J* = 3.5, H–C(11)); 6.15 (*s*, H–C(10)); 4.64 (*t*, *J* = 11.0, H–C(8)); 3.98 (*t*, *J* = 11.0, H–C(9)). ^{13}C-NMR (D_2O): 157.1 (C(2)); 153.1 (C(4′)); 153.9 (C(7a)); 150.6 (C(4″)); 149.5 (C(4)); 144.9 (C(6″,2″)); 144.4 (C(6′,2′)); 136.1 (C(11,13,15,)); 131,3 (C(12,14,16)); 126.9 (C(5″,3″)); 123.8 (C(5′,3′)); 116.7 (C (4a)); 98.2 (C(6)); 97.8 (C(5)); 62.6 (C(10)); 58.9 (C(8)); 45.1 (C(9)).

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