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New Viologen Analogs: 1,4-Bis[2-(pyridin-4-yl)ethenyl]benzene Quaternary Salts

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Abstract—Alkylation of 1,4-bis[2-(pyridin-4-yl)ethenyl]benzene with alkyl *p*-toluenesulfonates and dimethyl sulfate gave new viologen analogs, 1-alkyl-4-(2-{4-[2-(1-alkylpyridinium-4-yl)ethenyl]phenyl}ethenyl)-pyridinium bis(*p*-toluenesulfonates) and sulfate. Their derivatives with tetrafluoroborate and tetraphenylborate ions were also obtained. Spectral properties of the synthesized compounds were examined, and their structure was determined by X-ray analysis.

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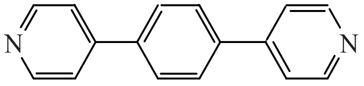
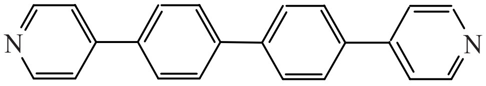
Viologens or 4,4'-bipyridine double quaternary salts have long been known, and they have found versatile applications. Viologens are used in molecular electronic devices (e.g., matrices for transistors), photochemistry (solar energy conversion, isolation of hydrogen from water), electrochromic display devices, etc. [1, 2]. Diversity of applications of viologens is determined by their unique physical and chemical properties both in solution and in crystal. First of all, this is facile one-electron reduction which generates stable radical cation [3–5].

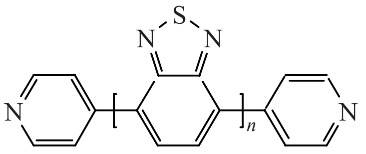
It is known that many important properties typical of viologens, such as one-electron reduction, photochromism, etc., may also be inherent to their analogs in which two pyridinium fragments are linked through a spacer [6, 7]. Moreover, variation of the spacer structure may enhance or weaken some properties.

The properties of some spacer viologen analogs derived from 1,4-bis(pyridin-4-yl)benzene and 4,4'-bis(pyridin-4-yl)biphenyl were examined previously [8].

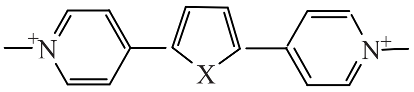




Also, viologen analogs possessing a heteroaromatic spacer were synthesized [7].



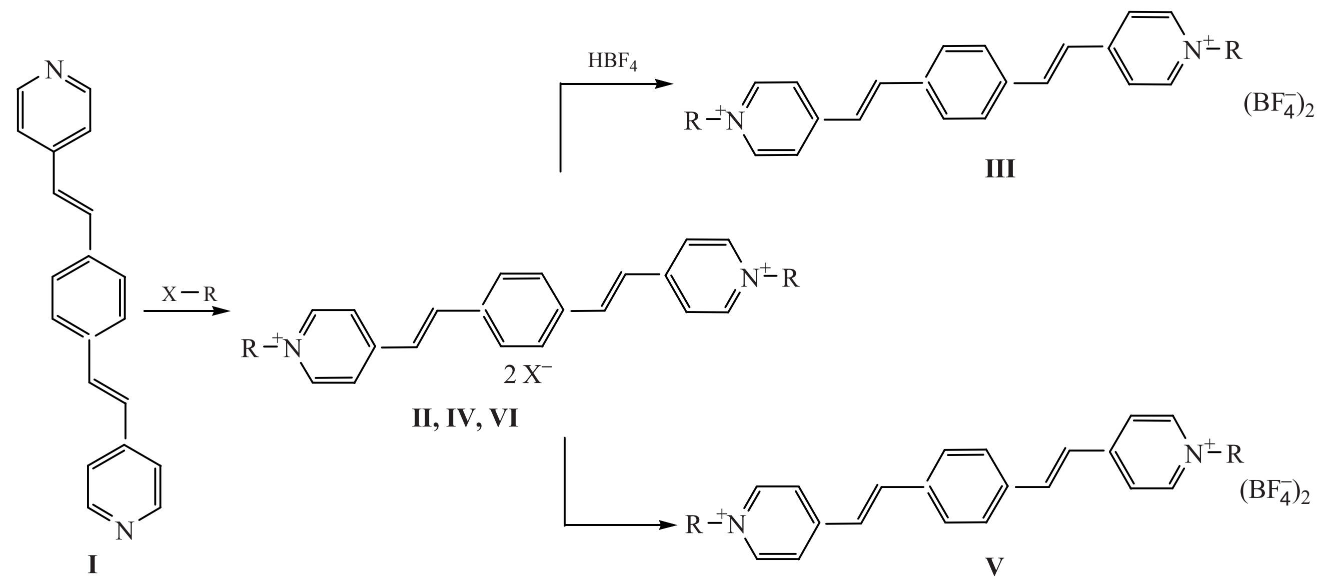
Viologens in which the pyridinium fragments are linked through a furan or thiophene fragment were reported in [6].



X = O, S.

In the present work we synthesized novel viologen analogs having a divinylphenyl spacer by alkylation of 1,4-bis[2-(pyridin-4-yl)ethenyl]benzene (**I**) with ethyl and butyl *p*-toluenesulfonates and dimethyl sulfate (Scheme 1). Compound **I** was prepared according to modified procedure [9], by condensation of terephthalaldehyde with 4-methylpyridine. Other viologen analogs were obtained by anion exchange in *p*-toluenesulfonates **II** and **IV** by tetrafluoroborate and tetraphenylborate. Compound **III** was synthesized by

Scheme 1.



II, R = Bu, X = 4-$MeC_6H_4SO_3$; **III**, R = Bu; **IV**, R = Et, X = 4-$MeC_6H_4SO_3$; **V**, R = Et; **VI**, R = Me, 2X = O_4.

treatment of **II** with tetrafluoroboric acid, while sodium tetraphenylborate was used in the synthesis of salt **VI**.

Attempts to reduce the dications in salts **II**–**VI** to the corresponding radical cations with sodium dithionite resulted in decoloration of the initial aqueous solution (in contrast to the reduction of related viologens which give rise to violet color [1]).

Numerous attempts were made to obtain crystals of salts **II**–**VI** suitable for X-ray analysis. However, we succeeded in growing single crystals only of compound **V**. Despite their poor quality and instability at room temperature on exposure to air, they were subjected to X-ray analysis. The other salts crystallized as finely dispersed powders, regardless of the solvent used and temperature conditions. According to the X-ray diffraction data, a unit cell of crystalline compound **V** includes two symmetry-independent dications **A** and **B** which differ by orientation of the terminal ethyl groups with respect to the central benzene ring. The *N*-ethyl groups in dication **VA** (Fig. 1) are oriented toward one side of the central fragment: the pseudotorsion angle $C^{22}C^{21}C^{23}C^{24}$ is 9.9°, whereas the corresponding groups in dication **VB** appear at the opposite sides of the central fragment (the pseudotorsion angle $C^{22}C^{21}C^{23}C^{24}$ is 179.1°). The C^{15} and C^{14} atoms and the C^8–C^{13} atoms in the central benzene ring in dication **VB** are statistically disordered by two positions **a** and **b** with equal populations. As a result, a superposition of two conformers **VBa** (Fig. 2) and **VBb** (Fig. 3) is observed in crystal.

The central $N^1N^2C^1$–C^{20} fragment in all three conformers is almost planar: deviations of atoms from the mean-square plane do not exceed 0.06 Å in **VA**, 0.33 Å in **VBa**, and 0.31 Å in **VBb**. Such geometry implies partial conjugation of the pyridinium rings

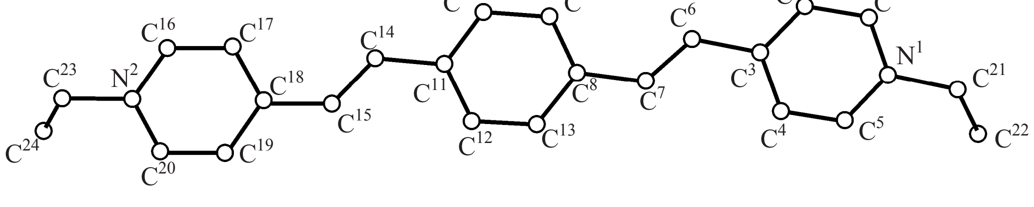


Fig. 1. Structure of dication **VA** according to the X-ray diffraction data. Principal bond lengths (Å) and bond and torsion angles (deg): C^1–N^1 1.348(2), C^5–N^1 1.350(2), C^{21}–N^1 1.485(2), C^{16}–N^2 1.348(2), C^{20}–N^2 1.350(2), C^{23}–N^2 1.485(2), C^6–C^7 1.325(3), C^{14}–C^{15} 1.330(3); $C^7C^6C^3$ 123.62(19), $C^6C^7C^8$ 127.98(19), $C^{11}C^{14}C^{15}$ 125.14(18), $C^{14}C^{15}C^{18}$ 126.93(18); $C^3C^6C^7C^8$ 179.4, $C^{11}C^{14}C^{15}C^{18}$ –178.5.

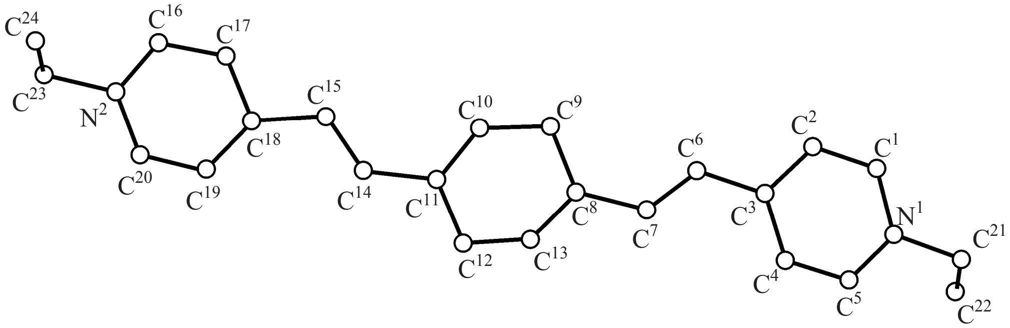


Fig. 2. Structure of dication **VBa** according to the X-ray diffraction data. Principal bond lengths (Å) and bond and torsion angles (deg): $C^1–N^1$ 1.351(2), $C^5–N^1$ 1.347(2), $C^{21}–N^1$ 1.485(2), $C^{16}–N^2$ 1.342(2), $C^{20}–N^2$ 1.343(2), $C^{23}–N^2$ 1.488(2), $C^6–C^7$ 1.336(4), $C^{14}–C^{15}$ 1.323(8); $C^7C^6C^3$ 124.98(19), $C^6C^7C^8$ 127.48(2), $C^{11}C^{14}C^{15}$ 126.6 (5), $C^{14}C^{15}C^{18}$ 117.0(4); $C^3C^6C^7C^8$ –174.8, $C^{11}C^{14}C^{15}C^{18}$ 178.6.

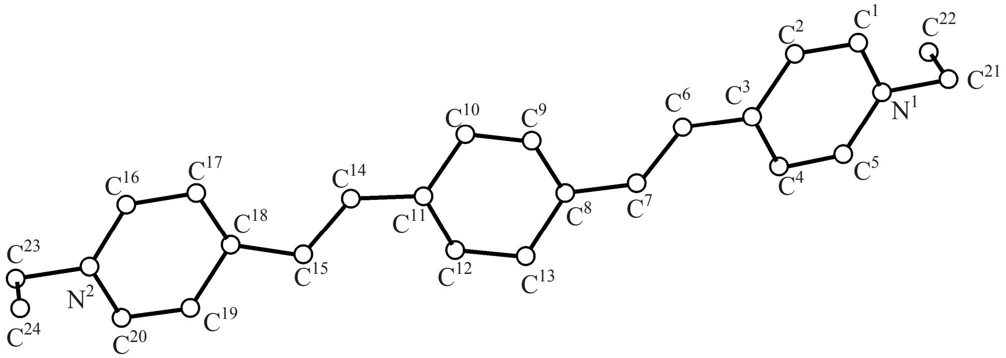


Fig. 3. Structure of dication **VBb** according to the X-ray diffraction data. Principal bond lengths (Å) and bond and torsion angles (deg): $C^1–N^1$ 1.351(2), $C^5–N^1$ 1.347(2), $C^{21}–N^1$ 1.485(2), $C^{16}–N^2$ 1.342(2), $C^{20}–N^2$ 1.343(2), $C^{23}–N^2$ 1.488(2), $C^6–C^7$ 1.336(3), $C^{14}–C^{15}$ 1.340(8); $C^7C^6C^3$ 124.98(19), $C^6C^7C^8$ 127.48(19), $C^{11}C^{14}C^{15}$ 125.87 (5), $C^{14}C^{15}C^{18}$ 117.41(4); $C^3C^6C^7C^8$ –174.8, $C^{11}C^{14}C^{15}C^{18}$ –177.1.

through the π-system formed by double bonds and benzene ring. The dihedral angles between the central benzene ring ($C^8–C^{13}$) and pyridine rings $N^1C^1–C^5$ and $N^2C^{16}–C^{20}$ are, respectively, 2.3 and 2.5° in **VA**, 7.5 and 2.9° in **VBa**, and 8.7 and 0.4° in **VBb**). It should be noted that the double bonds $C^6–C^7$ and $C^{14}–C^{15}$ in dication **VA** are oriented *trans* relative to the central benzene ring (the pseudotorsion angle $C^6C^7C^{14}C^{15}$ is– 175.9°). Analogous conformation of the central fragment is typical of dication **VBb** where the corresponding torsion angle is –176.0°. On the other hand, the double bonds $C^6–C^7$ and $C^{14}–C^{15}$ in **VBa** are oriented *cis* with respect to the $C^8–C^{13}$ fragment (pseudotorsion angle $C^6C^7C^{14}C^{15}$ 11.9°). The bond lengths and bond angles in the pyridinium rings do not differ significantly from those typical of viologens [1–4].

Dications **VA** and **VB** in crystal are arranged almost parallel to each other, the corresponding dihedral angle being 12.0°. No shortened intermolecular contacts like cation–cation, cation–anion, cation–solvent molecule, etc., were observed in the crystalline structure of compound **V** since the dications are spatially separated by large tetraphenylborate anions and solvate dimethylformamide molecules (Fig. 4).

The luminescence spectra of crystalline compounds **III** and **VI** showed single structureless bands with their maxima at λ 490 (**III**) and 545 nm (**VI**), while compound **IV** displayed at least two bands at λ 490 and 514 nm. Interestingly, the luminescence intensity of compound **IV** was greater by more than an order of magnitude than the intensity of luminescence of related viologens. This may be due to different properties of the anion and specificity of crystal packing.

To conclude, we have synthesized new spacer viologen analogs extended by a stilbene fragment. According to the X-ray diffraction data, these compounds in crystal may exist as at least three conformers. The examined salts exhibit luminescence in the crystalline state, and its intensity strongly depends on the anion nature and alkyl groups on the nitrogen atoms.

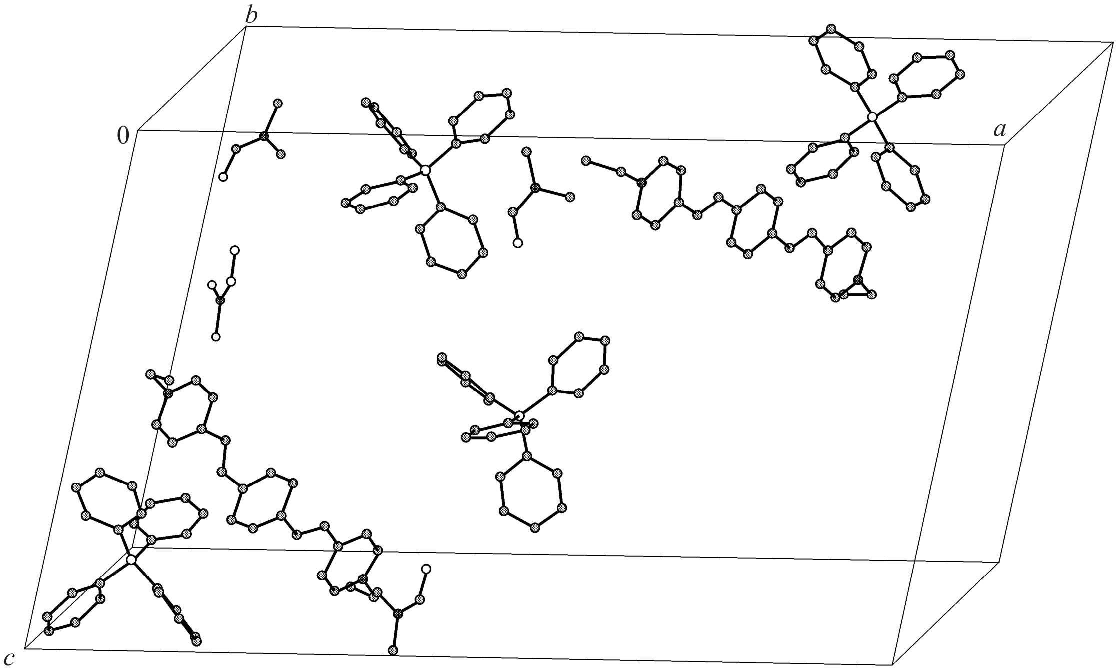


Fig. 4. A fragment of crystal packing of compound **V**.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker spectrometer at 282.2 MHz using DMSO-d_6 as solvent and tetramethylsilane as internal reference. The electronic absorption spectra were measured on a Shimadzu UV-3100 spectrophotometer from solutions in methanol. Luminescence studies were performed on a Coderg T-800 automated spectrometer (excitation at λ_{excit} 280 nm with a UV light-emitting diode).

The X-ray diffraction data for a single crystal of compound **V** as solvate with DMF, **V**·2DMF, were acquired on a Bruker Smart Apex II CCD diffractometer (MoK_α irradiation, $\lambda = 0.71069$ Å) at 88 K; $\theta_{max} = 25.58$, spherical segment$-35 \leq h \leq 42$, $-16 \leq k \leq 21$, $-26 \leq l \leq 26$. Total of 70269 reflection intensities were measured, 24033 of which were independent. Monoclinic crystals with the following unit cell parameters: $a = 34.9368(14)$, $b = 17.5556(6)$, $c = 21.6119(8)$ Å; $\beta = 104.451(1)°$; $V = 12877.6(8)$ Å^3; $Z = 8$; $d_{calc} = 1.16$ g/cm^3; $\mu = 0.069$ cm^{-1}; $F(000) = 4816$; space group $P2_1/c$. The structure was solved by the direct method and was refined by the least-squares procedure in full-matrix anisotropic approximation using SHELX software package. The refinement was performed with 15624 reflections with $I > 2\sigma(I)$ (1602 refined parameters, 9.75 reflections per parameter). The positions of hydrogen atoms were calculated on the basis of geometry considerations and were refined with fixed thermal and positional factors. The following weight scheme was applied: $w = 1/[s^2(Fo^2) + (0.0458P)^2 + 2.6973P]$ where $P = (Fo^2 + 2Fc^2)/3$. The final divergence factors were $R_1 = 0.051$ and $wR_2 = 0.1023$; goodness of fit 1.007. The residual electron density from the Fourier difference series was –0.430 and 0.326 e Å^{-3}. The complete set of crystallographic data for compound **V** was deposited to the Cambridge Crystallographic Data Centre (entry no. CCDC 653127).

1,4-Bis[2-(pyridin-4-yl)ethenyl]benzene (I). Powdered anhydrous zinc chloride, 13.64 g, was added to a solution of 13.7 g of 4-methylpyridine and 6.7 g of terephthalaldehyde in 40 ml of acetic anhydride, and the mixture was heated for 24 h under reflux, cooled to 70°C, and filtered. The precipitate was washed with acetic anhydride and alcohol to obtain 11 g of the crude product which was recrystallized from pyridine.

Yield 6.6 g (46%), yellowish powder. ^{1}H NMR spectrum, δ, ppm: 7.2 d (2H, J = 16.2 Hz), 7.592 s (4H), 7.65 d (2H, J = 16.2 Hz), 7.92 d (4H, J = 6.6 Hz), 8.426 d (4H, J = 7.2 Hz).

1-Butyl-4-(2-{4-[2-(1-butylpyridinium-4-yl)ethenyl]-phenyl}ethenyl)pyridinium bis(4-methylbenzenesulfonate) (II). A mixture of 1.4 g of compound **I** and 4.6 g (excess) of butyl *p*-toluenesulfonate was fused at 200°C on heating on an oil bath over a period of 1.5 h. The hot melt was treated with 20 ml of diisobutyl ketone, and the precipitate was filtered off, washed with acetone, and recrystallized from ethanol. Yield 2.76 g (76%), yellow powder. ^{1}H NMR spectrum, δ, ppm: 0.9 t (6H), 1.3 m (4H), 1.9 m (4H), 2.3 s (6H), 4.5 q (4H), 7.1 d (4H, J = 7.5 Hz), 7.5 d (4H, J = 8.1 Hz), 7.64 d (2H, J = 16.2 Hz), 7.9 s (4H), 8.07 d (2H, J = 16.5 Hz), 8.27 d (4H, J = 6.6 Hz), 9 d (4H, J = 6.9 Hz). Electronic absorption spectrum, λ_{max}, nm ($\varepsilon\times10^{-4}$, l mol^{-1} cm^{-1}): 251 (0.9), 384 (4.29). Found, %: C 67.94, 67.95; H 6.27, 6.28; S 8.69, 8.73. $C_{42}H_{48}N_2O_6S_2$. Calculated, %: C 68.08; H 6.53; S 8.65.

1-Butyl-4-(2-{4-[2-(1-butylpyridinium-4-yl)ethenyl]-phenyl}ethenyl)pyridinium bis(tetrafluoroborate) (III). Quaternary salt **II**, 0.5 g, was dissolved in 30 ml of water on heating to the boiling point, and 2 ml (excess) of tetrafluoroboric acid was added. After 5 h, the precipitate was filtered off, dried, and recrystallized from 6 ml of acetonitrile. Yield 0.16 g (42%), white powder. ^{1}H NMR spectrum, δ, ppm: 0.94 t (6H), 1.32 m (4H), 1.92 m (4H), 4.53 q (4H), 7.64 d (2H, J = 16.2 Hz), 7.9 s (4H), 8.05 d (2H, J = 15.9 Hz), 8.27 d (4H, J = 6.6 Hz), 9 d (4H, J = 6.3 Hz). Electronic absorption spectrum, λ_{max}, nm ($\varepsilon\times10^{-4}$, l mol^{-1} cm^{-1}): 251 (0.69), 382 (2.6). Found, %: C 58.73, 58.75; H 5.71, 5.78; N 5.15, 5.16. $C_{28}H_{34}B_2N_2F_8$. Calculated, %: C 58.77; H 5.98; N 4.89.

1-Ethyl-4-(2-{4-[2-(1-ethylpyridinium-4-yl)ethenyl]-phenyl}ethenyl)pyridinium bis(4-methylbenzolsulfonate) (IV). A mixture of 0.85 g of compound **I** and 2.4 g of ethyl *p*-toluenesulfonate was fused at 175°C (oil bath) over a period of 1.5 h. The melt was cooled, 20 ml of anhydrous acetone was added, the mixture was heated for 1 h under reflux and filtered while hot, and the precipitate was washed with anhydrous acetone on a filter. Recrystallization from 12 ml of ethanol gave 1.46 g (71%) of salt **IV** as a bright yellow powder. ^{1}H NMR spectrum, δ, ppm: 1.54 t (6H), 2.3 s (6H), 4.55 q (4H), 7.1 d (4H, J = 7.8 Hz), 7.5 d (4H, J = 7.8 Hz), 7.64 d (2H, J = 16.5), 7.9 s (4H), 8.05 d (2H, J = 16.2 Hz), 8.27 d (4H, J = 6.9 Hz), 9 d (4H, J = 6.6 Hz). Electronic absorption spectrum, λ_{max}, nm ($\varepsilon\times10^{-4}$, l mol^{-1} cm^{-1}): 251 (0.76), 384 (3.86). Found, %: C 66.29, 66.49; H 5.92, 6.06, S 9.04, 9.24. $C_{38}H_{40}N_2O_6S_2$. Calculated, %: C 66.29; H 5.88; S 9.36.

1-Ethyl-4-(2-{4-[2-(1-ethylpyridinium-4-yl)ethenyl]-phenyl}ethenyl)pyridinium bis(tetraphenylborate) (V). Quaternary salt **IV**, 0.68 g, was dissolved in 20 ml of hot water, and a solution of 0.75 g of sodium tetraphenylborate in 15 ml of hot water was added in one portion. A yellow solid separated. The mixture was shaken, heated for 5 min at 70°C (oil bath), and left to stand for 1 h at room temperature. The precipitate was filtered off, washed with warm water, and dried. The crude product, 0.95 g, was dissolved in 4 ml of DMF on heating, the solution was filtered, and 17 ml of hot alcohol was added. After 2 h, the precipitate was filtered off and washed with alcohol. Yield 0.78 g (76%). ^{1}H NMR spectrum, δ, ppm: 1.54 t (6H), 4.54 q (4H), 6.75 t (8H), 6.9 t (16H), 7.2 m (16H), 7.54 d (2H, J = 16.4 Hz), 7.8 s (4H), 7.96 d (2H, J = 16.4 Hz), 8.2 d (4H, J = 6 Hz), 8.9 d (4H, J = 6 Hz). Electronic absorption spectrum: λ_{max} 382 nm. Found, %: C 87.89, 88.09; H 7.98, 7.18. $C_{72}H_{66}B_2N_2$. Calculated, %: C 88.15; H 6.79.

1-Methyl-4-(2-{4-[2-(1-methylpyridinium-4-yl)-ethenyl]phenyl}ethenyl)pyridinium sulfate (VI). A mixture of 0.8 g of compound **I** and 1.4 g of dimethyl sulfate was heated for 4 h at 180°C on an oil bath. The mixture was cooled to 100°C, 3 ml of water was added, the mixture was heated for 10 min at the boiling point and allowed to cool down, and the precipitate was filtered off, washed with acetone, and recrystallized from aqueous ethanol. Yield 1.01 g (88%), yellow powder. Found, %: C 64.74, 64.69; H 4.91, 4.95; S 7.49, 7.53. $C_{22}H_{20}N_2O_4S$. Calculated, %: C 64.31; H 4.87; S 7.80.

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