

Electrochromic Materials

Novel Bipyridinium Ionic Liquids as Liquid Electrochromic Devices

Noémi Jordão, Luis Cabrita, Fernando Pina, and Luís C. Branco^{*[a]}

Abstract: Novel mono and dialkylbipyridinium (viologens) cations combined with iodide, bromide, or bis(trifluoromethanesulfonyl)imide [NTf₂] as anions were developed. Selective alkylation synthetic methodologies were optimized in order to obtain the desired salts in moderate to high yields and higher purities. All prepared mono- and dialkylbipyridinium salts were completely characterized by ¹H, ¹³C, and ¹⁹F NMR spectroscopy, Fourier-transform IR spectroscopy, and elemental analysis (in the case of NTf₂ salts). Melting points, glass transition temperatures by differential scanning calorimetry (DSC) studies, and decomposition temperatures were also checked for different prepared organic salts. Viscosities at specific temperatures and activation energies

were determined by rheological studies (including viscosity dependence with temperature in heating and cooling processes). Electrochemical studies based on cyclic voltammetry (CV), differential pulsed voltammetry (DPV), and square-wave voltammetry (SWV) were performed in order to determine the redox potential as well as evaluate reversibility behavior of the novel bipyridinium salts. As proof of concept, we developed a reversible liquid electrochromic device in the form of a U-tube system, the most promising dialkylbipyridinium-NTf₂ ionic liquid being used as the electrochromic material and the room-temperature ionic liquid (RTIL), 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)-imide [EMIM][NTf₂], as a stable and efficient electrolyte.

Introduction

Bipyridinium (bpy) salts are prepared by mono- or diquaternization of 4,4'- and 2,2'-bipyridine scaffolds by using appropriate halide alkylating agents. The dication salts are electroactive species with relevant electrochromic properties.^[11] In general, the bipyridinium salts can be used as herbicides, redox indicators, functional organic electro-

chromic materials, or coordination polymers.^[2-4]

In general, dialkyl viologen cation salts (1,1'-dimethyl-4,4'-bipyridinium, for example) undergo two successive electrontransfer processes and thus ex-

hibit three redox states: the dication, the radical cation, and the neutral compound. Of these three redox states, it is known that the dication is the most stable; it is also a colorless species, unless optical charge transfer with the counter anion occurs.^[1] On the other hand, the radical cation is intensely colored, exhibiting high molar absorption coefficients related with an intense intramolecular optical charge transfer. The colors of radical cations are dependent of the substituents (type and length) on the nitrogen atoms.^[5] Figure 1 illustrates

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the three common redox states of disubstituted bipyridinium salts.

For example, alkyl groups can promote a blue-violet color, whereas aryl groups generally impart a variety of colors to the radical cation. The desired final color can be tuned according to the type of substituent at the N-position of the bipyridinium cation and the type of anion.^[6]



Figure 1. Three common viologen redox states.

In last years, the reported discoveries of novel and efficient electrochromic materials have been based mainly on metal oxides, polymers, viologens, among others.^[7-9] Recently, our group described the development of intrinsically electrochromic ionic liquids based on ethylenediaminotetraacetic (EDTA) metal complexes ([cation][Co(EDTA)])^[10] and vanadate oxide ([cation][VO₃]).^[11]

lonic liquids $(ILs)^{[12]}$ are salts with a melting point below 100 °C, (some are liquids at room temperature) where at least one of the elements of the salt is organic. This type of compound possesses negligible volatility combined with other peculiar properties that can be tuned by choosing the right combination of cation and anion. This possibility allowed the use of ionic liquids in a wide range of applications,^[13] such as organic reaction media,^[14,15] extractive and separation media,^[16,17]

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functional materials, $^{\rm [18,19]}$ and active pharmaceutical ingredients (APIs). $^{\rm [20]}$

Herein, we present the development of different ILs based on monoalkyl- and dialkylbipyridinium cations combined with iodide, bromide, and bis(trifluoromethanesulfonyl)imide, [NTf₂], anions (Figure 2). The thermal, physical, and electrochemical studies on these compounds have been performed in order to elucidate the potential of these salts for electrochromic applications.



Figure 2. Derivatives of mono and bipyridinium salts prepared herein.

Results and Discussion

The synthetic methodologies were optimized for the preparation of different alkyl- and dialkylbipyridinium salts. All prepared mono- and dialkylbipyridinium salts were completely characterized by ¹H, ¹³C, and ¹⁹F NMR spectroscopy, Fouriertransform IR spectroscopy, and elemental analysis (in the case of NTf₂ salts). Melting points, glass transition temperatures, and decomposition temperatures were also determined for different prepared organic salts.

Synthesis and characterization of alkylbipyridinium salts

Monocation bipyridinium salts were obtained by monoalkylation of the 4,4'-bipyridine unit by using an appropriate alkyl iodide followed by a second step based on anion ex-

change reaction by using lithium bis(trifluoromethanesulfonyl)imide (LiNTf₂) in methanol or aqueous media. Ethyl acetate or acetonitrile was used as the reaction medium, at temperatures from room temperature to 60 °C, for the monoalkylation synthetic step. Under these reaction conditions, different alkylbipyridinium iodide salts were obtained in moderate to high yields (62–89%). After recrystallization from the appropriate solvent, the salts were obtained in higher levels of purity (separation of mono from dication species). The synthesis of monocation bipyridinium salts is described in Scheme 1.

The optimized anion exchange reactions for the exchange of iodide for NTf_2 allowed a significant reduction in the final melting point of alkylbipyridinium salts. [C₁bpy][NTf₂], [C₆bpy][NTf₂], and [C₁₀bpy][NTf₂] were obtained in high-purity grade as water immiscible ionic liquids. Table 1 summarizes the different al-kylbipyridinium salts prepared herein.



Scheme 1. Preparation of monoalkylbipyridinium salts.

In the case of alkylbipyridinium cations combined with $[NTf_2]$ anion, it was observed that longer alkyl chains (hexyl and decyl) engender lower melting points and higher thermal stability.

Synthesis and characterization of dialkylbipyridinium salts

It is known that different symmetric dialkylbipyridinium salts can be prepared by dialkylation reaction by using appropriate alkyl iodide in excess. However, in our case a simple separation of mono- from dication species, as previously described, allowed the complete isolation of the desired symmetric dialkylbipyridinium salts in high purity levels.

Asymmetric dialkylbipyridinium salts were prepared by alkylation of previous prepared 1-alkyl-4,4'-bipyridinium iodides (as shown in Scheme 1) with different alkyl iodides or bromides in excess, as described in Scheme 2. Using this experimental approach, novel asymmetric dialkylbipyridinium salts were obtained in moderate to high yields (55–90%) using acetonitrile as solvent.

In order to lower the melting point of these iodide salts, [NTf₂] anion was combined with different dialkylbipyridinium cations in methanol or aqueous media, as previously described (see Scheme 2). $[C_6C_6bpy][NTf_2]_2$, $[C_1C_{10}bpy][NTf_2]_2$, and $[C_2C_6bpy][NTf_2]_2$ as electrochromic ionic liquids were obtained

Table 1. Alkylbipyri	dinium sal	ts prepared in this	s work.		
Salts	Yield [%]	Physical state	λ [nm] ^[a]	m.p. (<i>T</i> _g) [°C] ^[b]	Τ _d [°C] ^[c]
[C ₁ bpy][l]	89	orange solid	249	240	240
[C ₁ bpy][NTf ₂]	71	white solid	262	70	>210
[C ₆ bpy][I]	62	orange solid	250	190	190
[C ₆ bpy][NTf ₂]	90	brown solid	264	56 (-40.58) ^[d]	>235
[C ₁₀ bpy][I]	64	yellow solid	250	124	>155
[C ₁₀ bpy][NTf ₂] ^[e]	94	brown liquid	262	RTIL (-38.39) ^[f]	>240

[a] Maximum wavelength (λ_{max}) of each salt in acetonitrile solution (10⁻⁵ M) was determined by UV/Vis spectra at room temperature. [b] Melting point (m.p.) was measured using a melting point apparatus; glass transition temperature (T_q) measured by DSC analysis. [c] Decomposition temperature (T_d) measured by visual observation of the color change by using a melting point apparatus. [d] Melting point was determined using a melting point apparatus; glass transition temperature (T_q) was determined by DSC analysis with heating/cooling rate of 10 °C min⁻¹. [e] Density: 1.216 g cm⁻¹ (26.5 °C), measured by picnometer. [f] RTIL (room temperature ionic liquid); glass transition temperature (T_g) was determined by DSC analysis with heating/cooling of 20 °C min⁻¹.



Scheme 2. Preparation of dialkylbipyridinium salts.

Table 2. Dialkylbi	oyridiniu	um salts prepa	red in th	is work.	
Salts	Yield [%]	Physical state	λ [nm] ^[a]	m.p. (<i>T</i> _g) [°C] ^[b]	T _d [°C] ^[c]
[C ₁ C ₁ bpy][I] ₂	n.d. ^[d]	orange solid	247	> 290	>290
$[C_1C_1bpy][NTf_2]_2$	68	white solid	257	130	>250
[C ₆ C ₆ bpy][I] ₂	n.d.	red solid	248	256	256
[C ₆ C ₆ bpy][NTf ₂] ₂	86	yellow solid	261	75	>250
[C ₁₀ C ₁₀ bpy][l] ₂	n.d.	red solid	247	290	290
$[C_{10}C_{10}bpy][NTf_2]_2$	95	yellow solid	262	161	230
[C ₁ C ₁₀ bpy][I] ₂	90	red solid	248	225	225
[C ₁ C ₁₀ bpy][NTf ₂] ₂	83	brown solid	259	46 (-26.45) ^[e]	>250
[C ₂ C ₆ bpy][I][Br]	55	red solid	253	241	241
[C ₂ C ₆ bpy][NTf ₂] ₂	97	brown solid	259	48 (-28.27) ^[f]	>250

[a] Maximum wavelength (λ_{max}) in acetonitrile solution (10^{-5} M) was determined by UV/Vis at room temperature. [b] Melting point (m.p.) was measured by using a melting point apparatus; glass transition temperature (T_g) determined by DSC analysis. [c] Decomposition temperature (T_d) determined by visual observation of the color change by using a melting point apparatus. [d] Not determined (n.d.); these salts were obtained by recrystallization of monocation. [e] Melting point and glass transition temperature (T_g) were determined by DSC analysis with heating/cooling rate of 5 °C min⁻¹. [f] Melting point and glass transition temperature were determined by DSC analysis with heating/cooling rate of 10 °C min⁻¹.

in high yields. Table 2 summarizes the different dialkylbipyridinium salts prepared in this work.

Asymmetric dialkylbipyridinium salts showed lower melting points but higher levels of thermal stability than symmetric salts, as indicated in Table 2.

Our approach to obtain electrochromic ionic liquids by using a significant difference in the alkyl chain units was successfully achieved. In particular, $[C_1C_{10}bpy][NTf_2]_2$ and $[C_2C_6bpy][NTf_2]_2$ are examples of ionic liquids with lower melting points (46 °C and 48 °C) as well as characteristic glass transition temperatures (-26.45 °C and -28.27 °C). In general, all halide salts (iodide and bromide) are water miscible, whereas the corresponding NTf₂ salts are not. The final salts were tested for the presence of halides by using AgNO₃ aqueous solution and the results were negative.

Absorbance measurements were performed for all salts, in acetonitrile solutions at the same concentrations (10^{-5} M) , to determine the wavelength of maximum absorbance. The exchange of iodide for NTf₂ for a particular cation leads to a red shift in the wavelength of maximum absorbance (a shift varying from 10 to 15 nm).

Additional experimental details are included in the Experimental Section and the Supporting Information. Detailed rheological studies for ionic liquids $[C_{10}bpy][NTf_2]$ and $[C_1C_{10}bpy][NTf_2]_2$ were performed. These studies allowed the evaluation of their Newtonian fluid behavior, as well as the determination of both their viscosity at specific temperatures and viscosity dependence with temperature (heating and cooling processes). Viscosities were measured at 25 °C ($[C_{10}bpy][NTf_2]$) and 60 °C ($[C_1C_{10}bpy][NTf_2]_2$) to ensure that both salts are in the liquid state. From the steady-state flow measurements of both salts analyzed under a wide range of shear conditions, Newtonian behavior was observed.

Table 3 summarizes the viscosity values at different temperatures as well as the activation energy obtained from the fitting of the heating and cooling profiles.

Table 3. Rheological properties of $[C_{10}bpy][NTf_2]$ and $[C_1C_{10}bpy][NTf_2]_2$.							
Salts	25 °C	Viscosity [Pa. s ⁻¹] ^[a] $60 ^{\circ}C^{[c]}$	80 °C ^[c]	Activatic [kJ m E _h	on energy ol ⁻¹] ^[b] E _c		
$[C_{10}bpy][NTf_2]$ $[C_1C_{10}bpy][NTf_2]_2$	0.118 ^[d] n.d. ^[g]	0.027 0.625 ^[d]	0.012 0.194	45.96 ^[e] 58.35 ^[h]	51.50 ^[f] 59.34 ^[i]		

[a] Viscosity values were measured by using a rheometer with control of temperature ± 0.5 °C. [b] Activation energy calculated with Arrhenius model, with $r^2 > 0.999$. [c] Viscosity values were determined by single point of temperature profile. [d] Newtonian fluid. [e] Heating profile (25 °C to 80 °C) with heating rate of $0.9 \,^{\circ}$ Cmin⁻¹. [f] Cooling profile (80 °C to 25 °C) with cooling rate of $0.9 \,^{\circ}$ Cmin⁻¹. [g] Not determined. [h] Heating profile (60 °C to 80 °C), with heating rate of $1.0 \,^{\circ}$ Cmin⁻¹. [j] Cooling profile (80 °C to 60 °C), with cooling rate of $1.0 \,^{\circ}$ Cmin⁻¹.

As expected, $[C_1C_{10}bpy][NTf_2]_2$ is significantly more viscous than $[C_{10}bpy][NTf_2]$ at 60 °C and 80 °C (Table 3). It is known that the incorporation of NTf₂ tends to reduce viscosity owing to the presence of fluorine atoms. However, the stronger hydrophobic nature of $[C_1C_{10}bpy][NTf_2]_2$ may justify its higher viscosity. Consequently, for $[C_1C_{10}bpy][NTf_2]_2$, the activation energies for the heating and cooling processes (E_h and E_c) are higher than those for $[C_{10}bpy][NTf_2]$. Figure 3 illustrates the dependence of viscosity with temperature through heating and cooling processes. In the case of $[C_1C_{10}bpy][NTf_2]_2$, both processes follow the same profile and the fluid returns to its initial state. On the other hand, the levels of viscosity of $[C_{10}bpy]$ - $[NTf_2]$ during the cooling process are higher than those found in the heating process.

Electrochemical properties

The electrochemical behavior of the mono- and dialkylbipyridinium salts combined with iodide [I], bromide [Br] and $[NTf_2]$ anions was studied by cyclic voltammetry (CV), differential pulsed voltammetry (DPV) and square-wave voltammetry (SWV). Table 4 summarizes the redox potentials of mono- and dialkylbipyridinium salts.

In general, the reduction potentials were more negative in the case of monoalkyl cations (-1.68/-0.98 V) than for the cor-

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Figure 3. Profile of the dependence of viscosity with temperature: (a) Heating and cooling profiles of $[C_1C_{10}bpy][NTf_2]_2$ from 60 °C to 80 °C (1.0 °C min⁻¹) (b) Cooling profile of $[C_1C_{10}bpy][NTf_2]_2$ from 60 °C to 25 °C (5.0 °C min⁻¹). (c) Heating and cooling profile of $[C_{10}bpy][NTf_2]$ from 25 °C to 60 °C (0.9 °C min⁻¹).

responding dialkyl dications, as expected. Dialkylbipyridinium salts were studied in more detail in accordance with their higher electrochemical stability as well as their potential electrochromic applications.

Figure 4 shows the two well-defined redox waves (-0.86 V/-0.44 V vs SCE) upon reduction of the 4,4'-bipyridinium moiety in the dialkylpyridinium salt.

The first reduction wave of the dialkylbipyridinium salt was studied in detail and it was shown to be fully reversible, as shown in Figure 5.

According to the electrochemical data, symmetrical and asymmetrical dialkylbipyridinium cations combined with $[NTf_2]$ anion can be used for electrochromic cell devices operating at potentials close to the first reduction wave (-0.5 V). Our results are comparable with some voltammetry studies already reported in the literature regarding the use of methyl viologen dissolved in methylimidazolium ionic liquids.^[21]

Table 4. Electrochemical propertie salts. ^[a]	s of mono	and dialkylbipyridinium
Salts	E_{p1} [V]	E _{p2} [V]
[C ₆ bpy][I]	-0.86	-
[C ₆ bpy][NTf ₂]	-0.98	-
[C ₁₀ bpy][l]	-0.96	-
[C ₁₀ bpy][NTf ₂]	-0.98	-
[C ₁ C ₁ bpy][I] ₂	-0.44	-0.85
[C ₁ C ₁ bpy][NTf ₂] ₂	-0.44	-0.85
[C ₂ C ₆ bpy][I][Br]	-0.47	-0.89
[C ₂ C ₆ bpy][NTf ₂] ₂	-0.40	-0.84
$[C_1C_{10}bpy][I]_2$	-0.43	-0.86
[C ₁ C ₁₀ bpy][NTf ₂] ₂	-0.44	-0.86

[a] Square-wave voltammetry (SWV) and cyclic voltammetry (CV) studies were performed in order to check the redox peaks of mono and dialkylbipyridinium salt in dry acetonitrile (1 mM) with 0.1 m TBAP. Acquisition parameters: SWV at 20 Hz, CV at 200 mV s⁻¹ scan rate; working, auxiliary, and reference electrodes of Pt, Pt wire, and SCE, respectively.



Figure 4. Square Wave Voltammetry (SWV) of 1 mm solutions of ILs based on bipyridine salts with NTf₂ anions, in acetonitrile containing 0.1 m TBAP, at a platinum working electrode vs SCE, 6 mV step potential, 60 mV pulse amplitude, 20 Hz.



Figure 5. Cyclic voltammetry (CV) of 1 mm solutions of ILs based on bipyridinium salts with NTf₂ anions in acetonitrile containing 0.1 m TBAP, at a platinum working electrode vs SCE, at 200 mV s⁻¹, showing the reversibility of first reduction process (dication \rightarrow radical cation) in detail.

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Detailed electrochemical data can be found in the Supporting Information in the form of additional CV and SWV figures.

Electrochromic applications

After electrochemical studies, $[C_1C_{10}bpy][NTf_2]_2$ and $[C_2C_6bpy]$ - $[NTf_2]_2$ were selected for application as liquid electrochromic devices in the form of a U-tube system. These ionic liquids were tested as novel electrochromic materials dissolved in dry acetonitrile (0.025 M) or conventional RTIL [EMIM][NTf_2] (0.01 M with w/w 5 and 34% of acetonitrile). In the acetonitrile system, the dialkylbipyridinium salt is working as the electrochromic species and the electrolyte simultaneously, whereas, in the case of the RTIL [EMIM][NTf_2] system, [EMIM][NTf_2] is working as the electrolyte. Two-sides of a U-tube were filled with the reported mixtures and platinum wires placed at each side were connected to a commercial battery (potential > \pm 0.5 V).

Figure 6 illustrates a reversible liquid electrochromic device by using $[C_2C_6bpy][NTf_2]_2$ as electrochromic ionic liquid dissolved in conventional RTIL [EMIM][NTf_2] as electrolyte. This



Figure 6. A liquid electrochromic cell containing $[C_2C_6bpy][NTf_2]_2$ in [EMIM]-[NTf_2] (0.01 m) (with w/w 34% CH_3CN). Two-sides of U-tube were submitted to $>\pm0.5$ V potential using two platinum wires connected to a commercial battery. Reversible switch between a transparent or pale-yellow-colored solution to a blue-colored solution.

device can reversibly switch between being transparent or as a pale yellow solution to a blue solution, a process that can be tuned by varying the viscosity of the media and applied redox potential (the time taken for the initial color switch can be varied from an order of seconds to a few minutes).

Conclusion

Novel mono- and dialkylbipyridinium cations combined with iodide, bromide, and bis(trifluoromethanesulfonyl)imide [NTf₂] as anions were developed. These salts were obtained in moderate to high yields and higher purities by using optimized synthetic methodology. Longer alkyl chains (hexyl and decyl) in the case of monoalkylbipyridinium salts and asymmetric (instead of symmetric) alkyl chains in the case of dialkylbipyridinium salts lead to lower final melting points as well as the observation of glass transition temperatures. Six bipyridinium salts based on the NTf₂ anion were obtained as novel electro-

chromic ionic liquids. Dialkylbipyridinium salts exhibited higher viscosities and were more electrochemically reversible in comparison to the corresponding monoalkyl salts. In this context, we developed a reversible liquid electrochromic device composed of dialkylbipyridinium NTf₂ salts as the electrochromic material and another conventional RTIL as a stable and efficient electrolyte.

The thermal, physical, and electrochromic properties of the salts could be tuned by varying the *N*-alkyl groups of the bipyridinium cation and the anion.

Experimental Section

General remarks

All solvents were used as supplied; acetonitrile was purchased from J.T. Baker; methanol and ethyl acetate were purchased from Carlo Erba Reagents; dichloromethane and acetone were purchased from Sigma-Aldrich; 4,4'-bipyridine was purchased from Alfa Aesar (98%); iodomethane was purchased from B.D.H laboratory reagent; iododecane, bromoethane, iodohexane were purchased from Sigma-Aldrich (98%); lithium bis(trifluoromethanesulfonyl)imide was purchased from Sigma-Aldrich. RTIL [EMIM][NTf₂] was used as purchased from Solchemar. For electrochemical studies, acetonitrile (J.T.Baker) and methanol (Carlo Erba) were of gradient-HPLC grade and acetonitrile was dried over CaH₂ and distilled under Argon. Electrochemical-grade tetrabutylammonium perchlorate (TBAP) was purchased from Fluka, and was dried overnight at 80 °C before use. Type I water was obtained from a Watermax purification station (Diwer Technologies). All glassware was cleaned with a mixture of concentrated H₂SO₄/H₂O₂ (1:1), thoroughly rinsed, oven dried, and cooled in a desiccator prior to use. NMR spectra were obtained by using a Bruker AMX 400 instrument operating at 400.13 MHz (¹H), 100.61 MHz (¹³C), and 376.50 MHz (¹⁹F). Elemental analysis was carried out by using a Thermofinnigan Flash EA 1112 Series instrument and was performed by the Laboratório de Análises at REQUIMTE. UV/Vis spectroscopy was carried out by using a Varian Cary 100 Bio spectrophotometer. Melting points were determined by using capillaries in an Electrothermal melting point apparatus (uncorrected). DSC analysis was carried out by using a TA Instruments Q-series TM Q200 DSC with a refrigerated cooling system. The sample is continuously purged with 50 mLmin⁻¹ nitrogen gas. About 5–10 mg of salt was crimped into an aluminum standard sample pan with lid. And the melting point and glass transition temperature were determinate in the second heating. The density measurement was obtained by using a micropycnometer. The density of [C10bpy][NTf2] was measured by an indirect method in the presence of *n*-heptane to complete the volume of the micropycnometer. IR spectra were recorded on a Buker Tensor 27, by using a KBr pellet for the solids and NaCl cells for the liquids. The viscosity measurements were done using a Rheometer (RS-300, Haake, Germany). Steady-state flow measurements were carried out by using a controlled-stress rheometer fitted with a PP20 sensor. The torque amplitude was imposed by using a logarithmic ramp of shear stress increasing in 30 min from 0.01 to 1000 Pa. The temperature of [C₁₀bpy][NTf₂] and [C₁C₁₀bpy]- $[NTf_2]_2$ were maintained at 25 \pm 0.5 °C and 60 \pm 0.5 °C, respectively, by using a circulating water bath. Another study made was the temperature dependence of viscosity. [C10 bpy][NTf2] and $[C_1C_{10}bpy][NTf_2]_2$ were heated from 25 to 80 °C (0.91 °C min⁻¹) and 60 to 80 $^{\circ}\text{C}$ (1.00 $^{\circ}\text{C}\,\text{min}^{-1}\text{)},$ respectively, by using a constant shear stress of 20 Pa. All the measurements were performed in duplicate

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and the viscosity values were determinate based on the average of these two measurements.

Additional experimental details can be found in the Supporting Information.

General procedure for synthesis of monoalkylbipyridinium salts

To a solution of 4,4'-bipyridine in acetonitrile (or ethyl acetate), was added slowly the appropriate iodoalkane in excess (1–5 equiv). The reaction mixture was stirred (25–80 °C) for 15–72 h. After this period of time, the crude product was precipitated and washed with diethyl ether (3×15 mL). After purification by recrystallization from acetone (or ethanol), the desired product was isolated and dried in vacuum.

[C₁₀**bpy]I**: 1-decyl-4,4'-bipyridinium iodide was obtained as yellow solid (0.877 g, 64%). M.p. 124°C; ¹H NMR (400.13 MHz, MeOD, 25°C): δ = 9.15 (d, *J* = 6.6 Hz, 2H), 8.82 (d, *J* = 6.1 Hz, 2H), 8.53 (d, *J* = 6.4 Hz, 2H), 8.01 (d, *J* = 6.1 Hz, 2H), 4.70 (t, *J* = 7.6 Hz, 2H), 2.16–2.00 (m, 2H), 1.50–1.20 (m, 14 H), 0.88 ppm (t, *J* = 6.5 Hz, 3 H); ¹³C NMR (100.61 MHz, MeOD, 25°C) δ = 155.50, 151.79, 146.54, 143.66, 127.20, 123.61, 62.80, 33.03, 32.49, 30.59, 30.50, 30.39, 30.14, 27.21, 23.71, 14.43 ppm; FTIR (KBr): ν = 3038, 2920, 2853, 1641, 1543, 1462, 1412, 1217, 1178, 812, 727 cm⁻¹.

General procedure for synthesis of symmetric dialkylbipyridinium salts

Symmetric dialkylbipyridinium salts were recovered from the crude mixture by recrystallization of the monocation salt from acetone or ethanol, the desired product was isolated and dried in vacuum.

[C₁₀**C**₁₀**bpy]I**₂: 1,1′-didecyl-4,4′-bipyridinium diiodide was obtained as red solid. M.p. 290 °C (dec.); ¹H NMR (400.13 MHz, MeOD, 25 °C): δ=9.29 (d, J=5.7 Hz, 4H), 8.69 (d, J=5.2 Hz, 4H), 4.75 (t, J= 7.4 Hz, 4H), 2.15–2.03 (m, 4H), 1.51–1.22 (m, 28H), 0.88 ppm (t, J= 6.8 Hz, 3H); ¹³C NMR (100.61 MHz, MeOD, 25 °C): δ=151.23, 147.27, 128.29, 128.29, 63.33, 33.03, 32.57, 30.61, 30.52, 30.41, 30.15, 27.24, 23.72, 14.44 ppm; FTIR (KBr): $\tilde{\nu}$ =3011, 2920, 2853, 1634, 1555, 1454, 1371, 1230, 1175, 831, 723 cm⁻¹.

General procedure for synthesis of asymmetric dialkylbipyridinium salts

The prepared monocation salts were dissolved in dried acetonitrile, and the appropriate haloalkane (iodide or bromide) was slowly added to the mixture. The reaction mixture was vigorously stirring at 25-60 °C for a period of 44–144 h under an argon atmosphere. Upon completion of the reaction, the product was precipitated from acetonitrile media, filtered, washed with diethyl ether, and dried in vacuum.

[**C**₁**C**₁₀**bpy**]**I**₂: 1'-methyl-1-decyl-4,4'- bipyridinium diiodide was obtained as red solid (1.030 g, 90%). M.p. 225 °C (dec.); ¹H NMR (400.13 MHz, DMSO, 25 °C): δ = 9.40 (d, *J* = 6.6 Hz, 2 H), 9.30 (d, *J* = 6.6 Hz, 2 H), 8.79 (dd, *J* = 6.7 Hz, 4 H), 4.69 (t, *J* = 7.3 Hz, 2 H), 4.44 (s, 3 H), 2.03–1.89 (m, 2 H), 1.39–1.13 (m, 14 H), 0.85–0.82 ppm (m, 3 H); ¹³C NMR (100.61 MHz, DMSO, 25 °C): δ = 148.43, 148.08, 146.56, 145.70, 126.52, 126.06, 60.81, 48.05, 31.23, 30.71, 28.84, 28.77, 28.61, 28.37, 25.38, 22.05, 13.94 ppm; FTIR (KBr): $\tilde{\nu}$ = 3015, 2922, 2853, 1637, 1555, 1456, 1364, 1273, 1178, 829, 719 cm⁻¹.

General procedure for the anion exchange of monocation salts

Monocation salts were dissolved in water (or methanol) and lithium bis(trifluoromethanesulfonyl)imide, LiNTf_2 (1.2 equiv) was added. After addition, the reaction was stirred for 24 h at room temperature. The product was recovered by filtration (precipitate) or extraction (biphasic solution) with water/dichloromethane. In the case of extracted product, the organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated to give the desired product. In order to eliminate residual inorganic salts, all final NTf₂ salts were completely washed with water. The presence of halides was tested by the addition of an aqueous solution of AqNO₃.

[C₁₀**bpy][NTf**₂]: 1-decyl-4,4'-bipyridinium bis(trifluoromethanesulfonyl)imide was obtained as a brown liquid (0.582 g, 94%); *T*_g -38.39 °C; ¹H NMR (400.13 MHz, DMSO): δ = 9.24 (d, *J* = 6.5 Hz, 2 H), 8.88 (d, *J* = 5.7 Hz, 2 H), 8.65 (d, *J* = 6.5 Hz, 2 H), 8.05 (d, *J* = 5.9 Hz, 2 H), 4.63 (t, *J* = 7.3 Hz, 2 H), 2.03–1.90 (m, 2 H), 1.38–1.15 (m, 14 H), 0.85 ppm (t, *J* = 6.5 Hz, 3 H); ¹³C NMR (100.61 MHz, DMSO): δ = 152.72, 151.45, 145.76, 141.36, 125.87, 122.38, 60.89, 31.74, 31.15, 29.33, 29.25, 29.11, 28.86, 25.89, 22.55, 14.41 ppm; ¹⁹F NMR (376.50 MHz, MeOD): δ = −80.64 ppm; FTIR (NaCl): ψ = 3072, 2928, 2856, 1643, 1607, 1549, 1524, 1464, 1348, 1188, 1055, 816, 789, 741 cm⁻¹; elemental analysis calcd (%) for C₂₂H₂₉F₆N₃O₄S₂: C 45.75, H 5.07, N 7.27; found: C 45.52, H 4.50, N 6.99.

General procedure for the anion exchange of dication salts

Dication salts were dissolved in water (or methanol) and lithium bis(trifluoromethanesulfonyl)imide (2.3 equiv) was added. After addition, the reaction was stirred for 24 h at room temperature. The product was recovered by filtration (precipitate) or extraction (biphasic solution) with water/dichloromethane. In the case of extracted product, the organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated to give the desired product. In order to eliminate residual inorganic salts, all final NTf₂ salts were completely washed with water. The presence of halides was tested by the addition of an aqueous solution of AgNO₃.

1'-methyl-1-decyl-4,4'-bipyridinium [C₁C₁₀bpy][NTf₂]₂: di-[bis(trifluoromethanesulfonyl)imide] was obtained as brown solid (0.195 g, 83%); M.p. 46 °C; $T_{\rm g}$ –26.45 °C; $^1{\rm H}$ NMR (400 MHz, DMSO, 25 °C): δ = 9.36 (d, J = 6.8 Hz, 2 H), 9.27 (d, J = 6.7 Hz, 2 H), 8.75 (dd, J=6.8 Hz, J=6.9 Hz, 4 H), 4.66 (t, J=7.4 Hz, 2 H), 4.43 (s,3 H), 2.05-1.90 (m, 2 H), 1.38–1.15 (m, 14 H), 0.84 ppm (t, J=6.7 Hz, 3 H); ¹³C NMR (100.61 MHz, MeOD, 25 °C) $\delta =$ 148.59, 148.23, 146.63, 145.75, 126.54, 126.08, 121.06, 117.86, 60.94, 48.01, 31.26, 30.76, 28.87, 28.79, 28.64, 28.39, 25.43, 22.08, 13.90 ppm; ¹⁹F NMR (376.50 MHz, DMSO, 25 °C): $\delta = -78.75$ ppm; FTIR (NaCl) $\tilde{\nu} = 3128$, 3070, 2930, 2860, 1641, 1564, 1508, 1456, 1350, 1192, 1140, 1057, 831, 793, 735 cm⁻¹; elemental analysis calcd (%) for $C_{25}H_{32}F_{12}N_4O_8S_4$: C 34.40, H 3.70, N 6.42; found: C 35.20, H 3.26, N 6.18.

Electrochemical studies

General remarks: Cyclic voltammetry (CV), differential pulse voltammetry (DPV), and squared-wave voltammetry (SWV) measurements were performed on an Autolab PGSTAT 12 potentiostat/galvanostat, controlled with GPES software version 4.9 (Eco-Chemie), by using a cylindrical three-electrode cell of 10 mL. A platinum electrode (MF-2013, $\phi = 1.6$ mm, BAS inc.) was used as the working electrode and a Pt wire as the auxiliary electrode. All potentials refer to a SCE (3 m KCl) reference electrode (Metrohm). Prior to use,

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the working electrode was polished in aqueous suspensions of 1.0 and 0.3 μ m alumina (Beuhler) over 2–7/8" micro-cloth (Beuhler) polishing pads, then rinsed with water and methanol. Subsequently, the electrode was sonicated in acetonitrile for 1 min. This cleaning procedure was always applied before any electrochemical measurement. Electrochemical cleaning was also employed by submitting the electrode to -1/+1 V currents for 60 s.

Electrochemical procedure: Cyclic voltammetry (CV) at a scan rate of 25–250 mV s⁻¹ was used to characterize the electrochemical responses between +0.2 and -2.0 V, starting at the OCP (open-circuit potential) as initial potential scanning. Differential pulse voltammetry (DPV) was performed between +0.2 and -2.0 V by using 6 mV step potential, 60 mV pulse amplitude, and 20 Hz excitation frequency for square-wave voltammetry (SWV).

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Keywords: bipyridinium salts · electrochemistry · ionic liquids · liquid electrochromic devices · rheology

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