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Complexes of carboxyl-containing polymer and monosubstituted bipyridinium salts

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HIGHLIGHTS

- Monosubstituted 4,4′-bipyridinium halides form two energetically stable structures.
- We calculated the partial charge transfer system to be energetically more favorable.
- Coulomb interactions stabilize complexes between BpyR(Hal) and COOH— group.
- Water molecules play an important role in complex formation.
- The complex formation leads to change from partial charge transfer to ion pair.

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ABSTRACT

Semi-empirical PM3 method for the quantum calculations of molecular electronic structure based on NDDO integral approximation is used to investigate the complex formation of monosubstituted 4,4′-bipyridinium salts **BpyR (Hal)** containing a halide anion interacting with the quaternary nitrogen atom and carboxylic group of the two-units construct. Significant effect of the **BpyR (Hal)** electronic structure is unveiled that contributes in two different structures of these salts, namely, partial charge transfer complex and ion pair structure, both having stable energy minima. We demonstrate that (i) the structure of the N-substituent modulates the energy and electronic characteristics of monosubstituted salts **BpyR** with chlorine and bromine anions and (ii) the coulomb interactions between quaternary N-atom, halogen anion, and the proton of carboxylic group stimulate the transformation of the charge transfer complex into the ion pair structure. Results of calculations are compared with the experimental FTIR spectra of blends of **BpyR(Hal)** with Eudragit copolymer.

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1. Introduction

In order to create new electrochromic systems, the effect of non-covalent interactions between different organic species was utilized in our previous work [1]. The system studied was made of blends of carboxyl-containing copolymers and monosubstituted salt of 4,4′-bipyridinium that did not undergo any phase separation even at 1:1 mol. ratio. The above salts are described in [2]. We expected that the reason for the blend stability in our system was the formation of the complex in which carboxylic groups of methacrylic acid units in the amount of 50 mol.% (in a copolymer with ethyl acrylate) or 29 mol.% (in a triple copolymer with *tert*-butyl acrylate and ethyl acrylate) interacted with monosubstituted bipyridinium salt due to either partial or total proton transfer [3]. However the IR spectra did not provide a conclusive evidence for the proton transfer responsible for the complex formation, although the formation of the complex with high electrochromic effectiveness was proven. Possible schematics of complexes were discussed in which either quaternary or tertiary nitrogen atom of a monosubstituted bipyridyl molecule could contribute in the complex formation.

The major goal of the current research is to find the most probable structure of complexes based on monosubstituted bipyridinium salts by applying the semi-empirical PM3 method for the quantum calculation of molecular electronic structure based on NDDO (the Neglect of Differential Diatomic Overlap) integral approximation [4] and to confirm the calculated structures with the experimental FTIR spectra.

Mono-substituted halide salts of 4,4′-bipyridinium **BpyR (Hal)** having the following chemical structure were chosen as the model systems.

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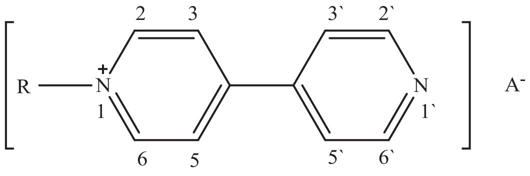
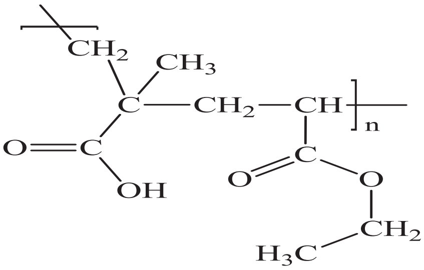


where R = CH_3 (M), $CH_2—CH{=}CH_2$ (A), $CH_2—C_6H_5$ (B).

We made a choice for Eudragit as a polymer component used in experimental studies having the following structure



It is an anionic copolymer based on methacrylic acid and ethyl acrylate. The ratio of the free carboxyl groups to the ester groups is approximately 1:1. To simulate the structure of that copolymer we have used constructs composed of methacrylic acid and ethyl acrylate units in two different conformations, namely, eclipsed (**E**) or staggered (**S**) (Fig. 1).

2. Experimental section

2.1. Materials and methods

Unless otherwise stated, all starting materials were obtained from commercial suppliers and used without further purification. Eudragit copolymer containing 50 mol.% of MAA and 50 mol.% EA monomer units (Mw = 320000) was purchased from Rohm Pharma and used as received.

^{1}H NMR spectra were recorded in D_2O using AvanceTM 600 Bruker spectrometer. Mass-spectra were run with Bruker Autoflex II.

Thermo Scientific "Nicolet" 6700 FT-IR spectrometer equipped with attenuated total reflectance device "Smart Orbit" was used to obtain FTIR spectra. The spectra were analyzed with Thermo Scientific OMNIC Array Automation software. IR spectra were run for salts, matrix polymer and their blends in the form of solid powders prepared as described below.

2.2. Synthesis of **BpyR** (**Hal**)

Monosubstituted halide salts of 4,4′-bipyridinium, namely, 1-methyl-4,4′-bipyridinium iodide (**BpyM(I)),** 1-allyl-4,4′-bipyridinium bromide (**BpyA(Br)**) and 1-benzyl-4,4′-bipyridinium chloride (**BpyB(Cl)**) were synthesized following the procedures described in [5,6] with some modification. The description of synthesis is given below.

2.2.1. ***BpyM***(***I***)

A solution of 4,4′-bipyridine (6.24 g, 40 mmol) an methyl iodide (2.73 g, 44 mmol)in dry acetone was mixed at room temperature for 24 h. The precipitated salt was collected and filtered. Recrystallisation from isopropanol/water gave the monoquaternary salt which was dried in *vacuo*. The yield of **BpyM(I)** yellow powder was 75%:8.95 (d, 2H), 8.68 (d, 2H), 8.29 (d, 2H), 7,89 (d, 2H); 4,39 (s, 3H);; m/z: 171.

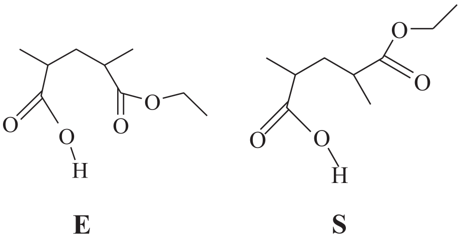


Fig. 1. Possible conformers of two units construct.

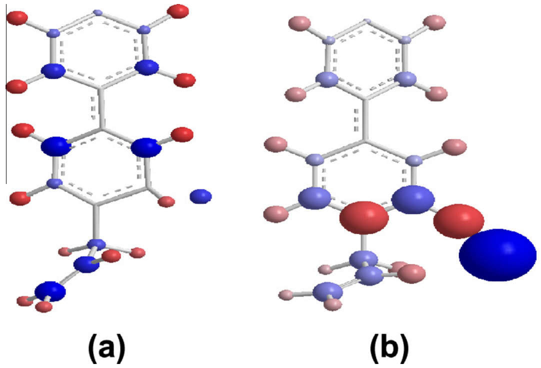


Fig. 2. The distribution of charges in structures 1 (a) and 2 (b) with A*1*(Cl) and A*2*(Cl) as examples: size of spheres (atoms) is proportional to sign value and red color indicates positive and blue – negative charges. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.2.2. ***BpyA***(***Br***)

A solution of 4,4′-bipyridine (4.68 g, 30 mmol) and allyl bromide (3.81 g, 30 mmol) in toluene was mixed at room temperature for 48 h. The precipitated salt was collected and filtered. Recrystallisation from isopropanol gave the monoquaternary salt which was dried in *vacuo*. The yield of **BpyA(Br)** pink powder was 50%. ^{1}H NMR (600 MHz, D_2O): 8,88 (d,2H); 8,65 (d,2H); (d, 2H); 8,31 (d, 2H); 7,81 (d, 2H); 6,10 (m, 1H); 5,48 (m, 2H); 5, 20 (d, 2H); m/z 197.

2.2.3. ***BpyB***(***Cl***)

A solution of 4,4′-bipyridine (4.68 g, 30 mmol) and benzyl chloride (3.81 g, 30 mmol) in toluene was heated at reflux for 4 h. Then the reaction mixture was cooled down to room temperature. The precipitated salt was collected and filtered. Recrystallisation from toluene/isopropanol gave the monoquaternary salt which was dried in *vacuo*. The yield of **BpyB(Cl)** white powder was 50%. ^{1}H NMR (600 MHz, D_2O): 9,02 (d, 2H); 8,76 (d, 2H); 8,40 (d, 2H); 7,89 (d, 2H); 7,53 (s, 5H); 5,87 (s, 2H); m/z 247.

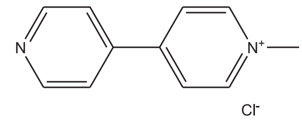
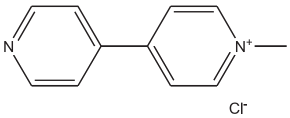
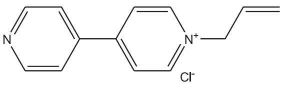
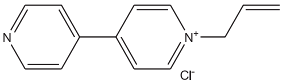
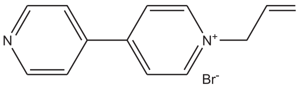
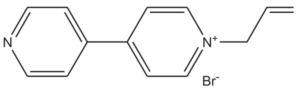
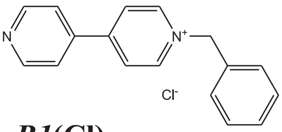
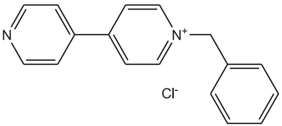
2.3. Blends preparation

BpyR(Hal) and Eudragit (1:1 mol.%) were dissolved in a common solvent, 96% ethanol, by mechanical stirring for 8 h at 40 °C until the solution became homogeneous. The solvent was vacuum-evaporated at 40 °C and the blend samples were dried under vacuum at 60 °C for 24 h to remove any residual solvent.

2.4. Calculations

Geometries as well as energies were calculated with Chem3D Ultra 8.0 package and MOPAC2000 software. After optimization and analysis of electronic, structural and energy characteristics of

Table 1
Energy and electronic characteristics of monosubstituted salts **BpyR**.

BpyR (Hal) R – Structure	ΔE (kJ/mol)	Charge (e)			Distance (Å) **N^+–Hal^-**
		N	**N^+**	**Hal^-**	
 M*1*(Cl)	**−17.50**	−0.10	0.02	−0.20	2.73
 M*2*(Cl)		−0.08	0.49	−0.73	3.57
 A*1*(Cl)	**−9.02**	−0.10	0.02	−0.21	2.75
 A*2*(Cl)		−0.08	0.48	−0.76	3.52
 A*1*(Br)	**−12.22**	−0.09	0.13	−0.41	2.81
 A*2*(Br)		−0.08	0.48	−0.81	3.63
 *B1*(Cl)	**−5.07**	−0.10	0.04	−0.22	2.73
 B*2*(Cl)		−0.08	0.48	−0.76	3.56
M*2*(I)	–	−0.08	0.51	−0.80	2.90
A*2*(I)	–	−0.08	0.50	−0.81	2.91
B2(I)	–	−0.08	0.51	−0.80	2.90

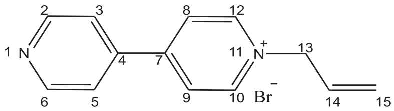
BpyR(Hal), the semi-empirical method PM3 based on NDDO integral approximation was used to explore the complex formation.

3. Results and discussion

3.1. Structure of monosubstituted bipyridinium salts **BpyR (Hal)**

The PM3 calculations applied to monosubstituted bipyridinium salts containing R substituents (M, A and B groups) and chloride (or bromide) anion show two local minima of the total energy. **BpyR (Hal)** may exist as two different structures that have stable energy minima. Fig. 2 presents the images of these two structures (***1*** and ***2***) in which the atoms are shown as spheres. Structure ***1*** are characterized by low charges on N^+ and Hal^- and a small distance between Hal^- and N^+ whereas structure ***2*** represent N^+ and Hal^- atoms with high charges and a bigger distance between them (Table 1). Thus, structure ***1*** may be considered as a complex with a partial charge transfer whereas structure ***2*** is an ion pair. It can be frequently seen when organic and inorganic moeties interact [7,8]. The characteristic electronic density distribution in both structures of **BpyR(Hal)** is given in Table 2 with R = A***1*** and A***2*** as examples. There is an effect of the strong delocalization of electron density across the aromatic part of the molecules, although it depends on the specific structure (A***1*** or A***2***). When comparing two pyridinium cores, the major contrast between ***1*** and ***2*** is seen in the N^+-substituted pyridinium core, whereas it is much less visible in the non-substituted one. As one can see, structures ***1*** are more energetically favorable in comparison with structures ***2*** although relatively low ΔE value between structures ***1*** and ***2*** particularly for benzyl (B) and allyl (A) substituents show that ion pairs may also exist. The charge distribution in both bipyridinium core and allyl substituent essentially depends on the counterion (anion).

Table 2
The distribution of charges in structures ***1*** and ***2***.



Atoms	**A(Cl) (e)**		**A(Br) (e)**	
	A*1*	**A2**	**A*1***	**A2**
N	−0.10	−0.08	−0.09	−0.08
2 C	−0.14	−0.13	−0.14	−0.13
3 C	−0.24	−0.23	−0.23	−0.23
4 C	−0.01	−0.04	−0.02	−0.05
5 C	−0.24	−0.22	−0.24	−0.22
6 C	−0.14	−0.13	−0.14	−0.13
7 C	0.03	0.00	0.04	0.01
8 C	−0.30	−0.17	−0.27	−0.18
9 C	−0.29	−0.18	−0.28	−0.18
10 C	−0.16	−0.33	−0.18	−0.35
11 N	0.02	0.48	0.13	0.48
12 C	0.00	−0.42	−0.01	−0.32
13 C	−0.17	−0.28	−0.20	−0.28
14 C	−0.29	−0.33	−0.27	−0.34
15 C	−0.30	−0.25	−0.29	−0.23
Hal	−0.21	−0.76	−0.41	−0.81

The use of the iodine anion changes the picture described above because the calculated energies give just one minimum which can be interpreted as related to the ion pair structure ***2*** in accordance with high charges on N^+ and Hal^- atoms. However contrary to cloride and bromide salt structures in the form of ion pair ***2*** the distance between N^+ and I^- atoms is more comparable with that of the form ***1*** (Table 1).

3.2. Conformation of the model two-units construct

To make the choice for the most probable conformation of the model copolymer structure we have calculated the ΔE between the total energy of **E** and **S** conformers (Fig. 1, Table 3). The energy gain is in favor of **S** conformer ($\Delta E_{\mathbf{S-E}}$ = −10.62 kJ/mol). However, according to our previous experimental observations [1] that water also plays an important role in the complex formation, the comparison between the energies of (**E** + $\mathbf{H_2O}$) and (**S** + $\mathbf{H_2O}$) systems is carried out. Fig. 2 shows the structure images of (**E** + $\mathbf{H_2O}$) and (**S** + $\mathbf{H_2O}$). The calculations show that if water is involved in the formation of (**E** + $\mathbf{H_2O}$), the system becomes energetically more favorable (−25.29 kJ/mol) than the formation of (**S** + $\mathbf{H_2O}$) (−14.18 kJ/mol). Nevertheless, the difference between the energy levels of these two constructs with water is negligible (0.5 kJ/mol) which means that both conformers could be taken in consideration for the simulation of salt–polymer interactions. Interestingly, the formation of both conformers containing water is accompanied by a very short distance between hydrogen atoms of water and carbonyl groups in carboxylic and/or ester groups (Table 3). It also proves the strong interaction between the construct and water molecules (Fig. 3).

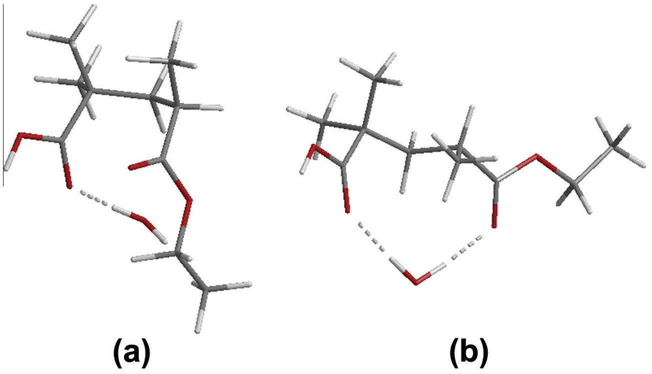


Fig. 3. The images of conformers E (a) and S (b) when water molecule is included.

3.3. Complex formation

The next step is to make a choice for the construct which provides the most energetically favorable complex with **BpyR(Hal).** We have run the calculations of energy of the formation of **E** and **S** complexes with **BpyR**. Taking into account the prevailing energetic role of structures ***1*** (**BpyR*1***) in the form of the charge transfer structure shown in Table 1, the first simulations of complexes have been done with structures **BpyR*1***. We have analyzed the probability of the contribution of both N atoms, the tertial and quaternary ones, in **BpyR(Hal)** interaction with the carboxylic group of a model construct. The designation (Table 4) of **R*1*-I** complexes is related to the complexes in which just tertiary N-atom has contributed (Fig. 4a), whereas **R*1*-II** corresponds to the formation of complexes in which the quaternary N-atom is involved (Fig. 4b). As it comes from Table 4, the interaction of (**E** + $\mathbf{H_2O}$) with **BpyR*1*(Hal)** gives very ambiguous results and the formation of **BpyR*1*(Hal)-I** does not seem to be preferable, whereas the interaction **S** + $\mathbf{H_2O}$ with **BpyR*1*(Hal)** resulting in the formation of **BpyR*1*(Hal)-II** complexes

Table 3
Model conformation of the two units construct.

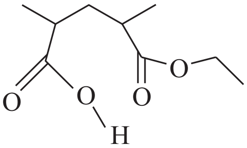
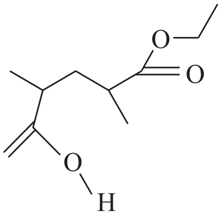
Abbreviation	Construct	ΔE (kJ/mol)	$\Delta E_{\mathbf{S-E}}$ (kJ/mol)	$\Delta E_{(\mathbf{S+H2O})-(\mathbf{E+H2O})}$ (kJ/mol)	Distance (**Å**) (**CO**···$\mathbf{H_2O}$)
E **E** + $\mathbf{H_2O}$		−25.29	−10.62	+0.5	1.81
S **S** + $\mathbf{H_2O}$		−14.18			1.85 1.85

Table 4
Energy change (kJ/mol) **R*1*-I** and **R*1*-II** complexes formation for **E** and **S** conformers with water.

Sample	**R*1*-I**			**R*1*-II**				
R (Hal)	ΔE_{S+H20}	ΔE_{E+H20}	$\Delta E_{S+H20} - \Delta E_{E+H20}$	ΔE_{S}	ΔE_{S+H20}	$\Delta E_{S+H20} - \Delta E_{S}$	ΔE_{E+H20}	$\Delta E_{S+H20} - \Delta E_{E+H20}$
M*1*(Cl)	−40.41	−51.48	11.07	−32.63	−86.86	−54.23	−61.40	−25.46
A*1*(Cl)	−34.14	−29.41	−4.73	−57.29	−92.00	−34.71	−55.55	−36.45
B*1*(Cl)	−28.33	−35.85	7.52	−64.38	−96.11	−31.73	−86.46	−9.65
A*1*(Br)	−32.87	−37.75	4.88	−32.02	−70.76	−38.74	−58.60	−12.16

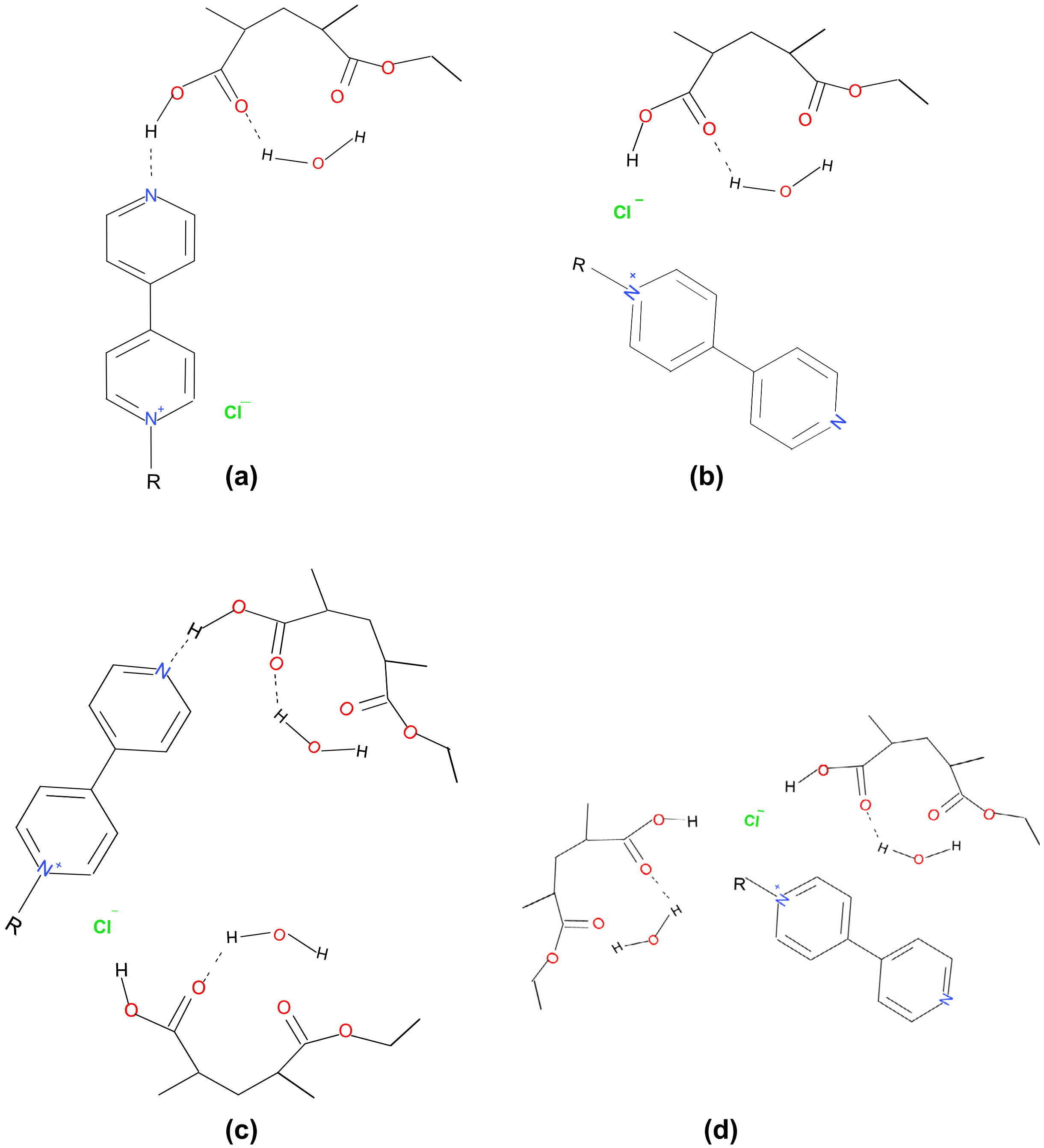


Fig. 4. Model images of complexes based on R(Cl):R*1*-I (a), R*1*-II (b), R*1*-III (c), R*1*-IV (d).

is energetically more favorable. That is why in our further calculations and data analysis we have used just **S** + **H$_2$O** to contribute in complex formation.

In addition to **R*1*-I** and **R*1*-II** complexes already mentioned in Table 4, we have also considered the case when both N atoms contribute in the complex formation resulting in the complex of 1 salt molecule per 2 molecules of the construct (**R*1*-III**) (Table 5). As it is seen, the formation of complexes of all types (when either tertiary or quaternary or both N atoms are involved) (Fig. 4a–c) is an energetically favorable process.

Table 5
Energy of the complex formation between monosubstituted salts **BpyR*1*(Cl)** and **S + H_2O** construct.

R	ΔE (kJ/mol)			
	R*1*(Cl)-I	**R*1* (Cl)-II**	**R*1* (Cl)-III**	**R*1* (Cl)-IV**
M	−40.41	−86.86	−118.33	−168.02
A	−34.14	−92.00	−125.05	−186.95
B	−28.33	−96.11	−120.28	−180.55

Table 6
Interatomic distances calculated for complexes **BpyR** (**Hal**).

Complexes R*1*(Hal)	**Distance (Å) $N\cdots H_{poly}$**	**Distance (Å) $Hal^-\cdots H_{construct}$**	**Distance (Å) $Hal^-\cdots N^+$**
M*1*(Cl)-I	1.78	–	2.74
M*1*(Cl)-II	–	1.70	2.87
M*1*(Cl)-III	1.79	1.73	3.58
M*1*(Cl)-IV	–	1.76 1.77	3.59
A*1*(Cl)-I	1.79	–	2.73
A*1*(Cl)-II	–	1.73	3.57
A*1*Cl)-III	1.79	1.73	3.57
A1(Cl)–IV	–	1.77 1.77	3.61
B1(Cl)-I	1.78	–	2.74
B1(Cl)-II	–	1.73	3.57
B1(Cl)-III	1.79	1.74	3.57
B1(Cl)–IV	–	1.76 1.76	3.62

Table 7
Electronic characteristics calculated for **BpyA*1*(Cl)** and **BpyA*1*(Br)** structures in complexes with **S + H_2O** construct.

Atoms	**A*1*(Cl)_I**	**A*1*(Cl)_II**	**A*1*(Cl)_III**	**A*1*(Cl)_IV**	**A*1*(Br)_II**	**A*1*(Br)_IV**
1 N	−0.12	−0.08	−0.12	−0.08	−0.08	−0.09
2 C	−0.14	−0.13	−0.14	−0.14	−0.13	−0.14
3 C	−0.23	−0.23	−0.23	−0.23	−0.22	−0.23
4 C	0.00	−0.04	−0.03	−0.06	−0.04	−0.05
5 C	−0.24	−0.23	−0.22	−0.22	−0.23	−0.22
6 C	−0.14	−0.13	−0.13	−0.13	−0.13	−0.14
7 C	0.03	0.01	0.00	0.03	0.03	0.04
8 C	−0.30	−0.19	−0.18	−0.18	−0.19	−0.17
9 C	−0.29	−0.17	−0.17	−0.15	−0.19	−0.18
10 C	−0.16	−0.39	−0.39	−0.35	−0.20	−0.22
11 N	0.03	0.52	0.52	0.50	0.55	0.55
12 C	−0.01	−0.29	−0.29	−0.32	−0.32	−0.31
13 C	−0.18	−0.31	−0.31	−0.30	−0.31	−0.31
14 C	−0.25	−0.32	−0.32	−0.29	−0.29	−0.30
15 C	−0.30	−0.26	−0.26	−0.28	−0.28	−0.27
Hal	−0.21	−0.83	−0.82	−0.86	−0.93	−0.97

Table 8
Energy of the complexes II and IV formation between monosubstituted salts **BpyR** (**Hal**) and **S + H_2O** construct.

R	Energy change, (kJ/mol)					
	R*1*(Cl)-II	**R*1*(Cl)-IV**	**R*1*(Br)-II**	**R*1*(Br)-IV**	**R*2*(I)-II**	**R2(I)-IV**
M	−86.86	−168.02	−79.92	−135.02	−51.49	−91.05
A	−92.00	−186.95	−70.76	−143.53	−54.38	−99.67
B	−96.11	−180.55	−67.20	−145.75	−64.98	−82.03

The total energy change under complex formation shows the increase in the complex stability in the following range: **R*1*-I** < **R*1*-II** < **R*1*-III**. However the simulation of the structure of **R*1*-III** complex during the optimization of **N···H** distance shows that **R*1*-III** cannot be stabilized and it undergoes a transformation into **R*1*-IV** complex structure (Fig. 4d). This **R1-IV** complex shows the highest energy gain and complex stability among all complexes under consideration. Moreover, it means that the most energetically favorable complex involves primarily the N^+ side of a monosubstituted salt of **BpyR** together with an Hal^- anion interacting with 2 carboxylic groups (equal to 2 construct molecules), whereas nonsubstituted N atom in **BpyR(Hal)** molecule is not directly involved in the complex formation. The latter is clearly seen with the important interatomic distances summarized in Table 6. Energetically favorable **R*1*-II** and **R*1*-IV** are characterized by two (or three) interatomic distances that have to be analyzed, namely, one or two $\mathbf{Hal^-\cdots H_{construct}}$ distances (1.70–1.77 Å) and one $\mathbf{Hal^-\cdots N^+}$ distance (2.87–3.62 Å). It means that COOH group (or two of them) of the construct is located in a close proximity of the Hal anion indicating the strong interaction of the construct molecule (molecules) with the **BpyR(Hal)** via anion. If we now compare the electronic characteristics using as an example complexes based on **A*1*(Hal)** (Table 7) with original structures ***A1*** and ***A2*** structures (Tables 1 and 2) then one can conclude that upon **A1(Hal)-II** and **A1(Hal)-IV** complexes formation the electronic density in the whole **BpyR (Hal)** molecule changes and the charge distribution in **BpyR*1*(Hal)** molecule becomes very similar to that in **BpyR*2*(Hal).** The charge values on N^+ and Hal^- become much higher indicating the formation of the structure which is much similar to an ion pair. This conclusion is also proved by the increase in the $\mathbf{Hal^-\cdots N^+}$ distance in **BpyR*1*(Hal)** complexes with (**S + H_2O**) **II** and **IV** which also becomes similar to that in **BpyR2(Hal)**. This is confirmed for all R-systems studied. One more detail to point out is the change in the energy of complex IV formation with the variation of the **R** structure. The major energy gain is calculated for the **BpyA*1*(Hal) IV** (−186.95 kJ/mol).

If we apply the similar approach to iodide salts **BpyR (I)** which are forming just ion pair type of structure ***2*** (Table 1) one can see the formation of complexes of the same type. As an example the comparison of the values of energy of the formation of complexes of type II and IV is given in Table 8. The energy gain of complex formation by **BpyR (I)** is always lower than that of complexes formed with chloride and bromide salts which may be resulted from the much bigger size of I^- anion.

3.4. Experimental FTIR spectra and comparison with PM3 results

The next step is to compare PM3 calculations of **BpyR(Hal)** and their complexes with a two-unit construct with the experimental FTIR spectra obtained for salts and their complexes with Eudragit copolymer. As an example, FTIR spectra of **BpyM**(**I**) and **BpyA**(**Br**), the Eudragit copolymer and their 1:1 blends are presented in Fig. 5.

First of all, note that there is an intense ν(OH) band at 3437 cm^{-1} in the spectra of the blends (Fig. 5c and d) that confirms the presence of coordinated water which is considered in PM3 calculations as a necessary tool for the complexes formation. The spectra of initial components contain fairly broad bands in that spectral range. However, the spectral bands of the blends are characterized by the strong increase in the relative intensity and a slight shift of ν_{OH} to the longer wavelength. It serves as a direct indication of the additional association of —OH bonds of water, and this is in good agreement with the results of quantum-chemical calculations. The experimental IR spectrum of Eudragit copolymer contains an intense spectral band at 1695 cm^{-1} and a shoulder at 1725 cm^{-1} (Fig. 5). Both of them correspond to the $\nu_{C=O}$ of the carboxylic (1695 cm^{-1}) and ester (1725 cm^{-1}) groups [9]. The spectral band at 1725 cm^{-1} remains practically unchanged in the spectra of 1:1 copolymer blends with mono-N-substituted 4,4′-bipyridinium halogenated salts indicating that ester groups are not involved in any interaction with salts studied. As for $\nu_{C=O}$ at 1695 cm^{-1} corresponding to the carboxylic group, it either nearly disappears in spectra of blends with M and A – substituted

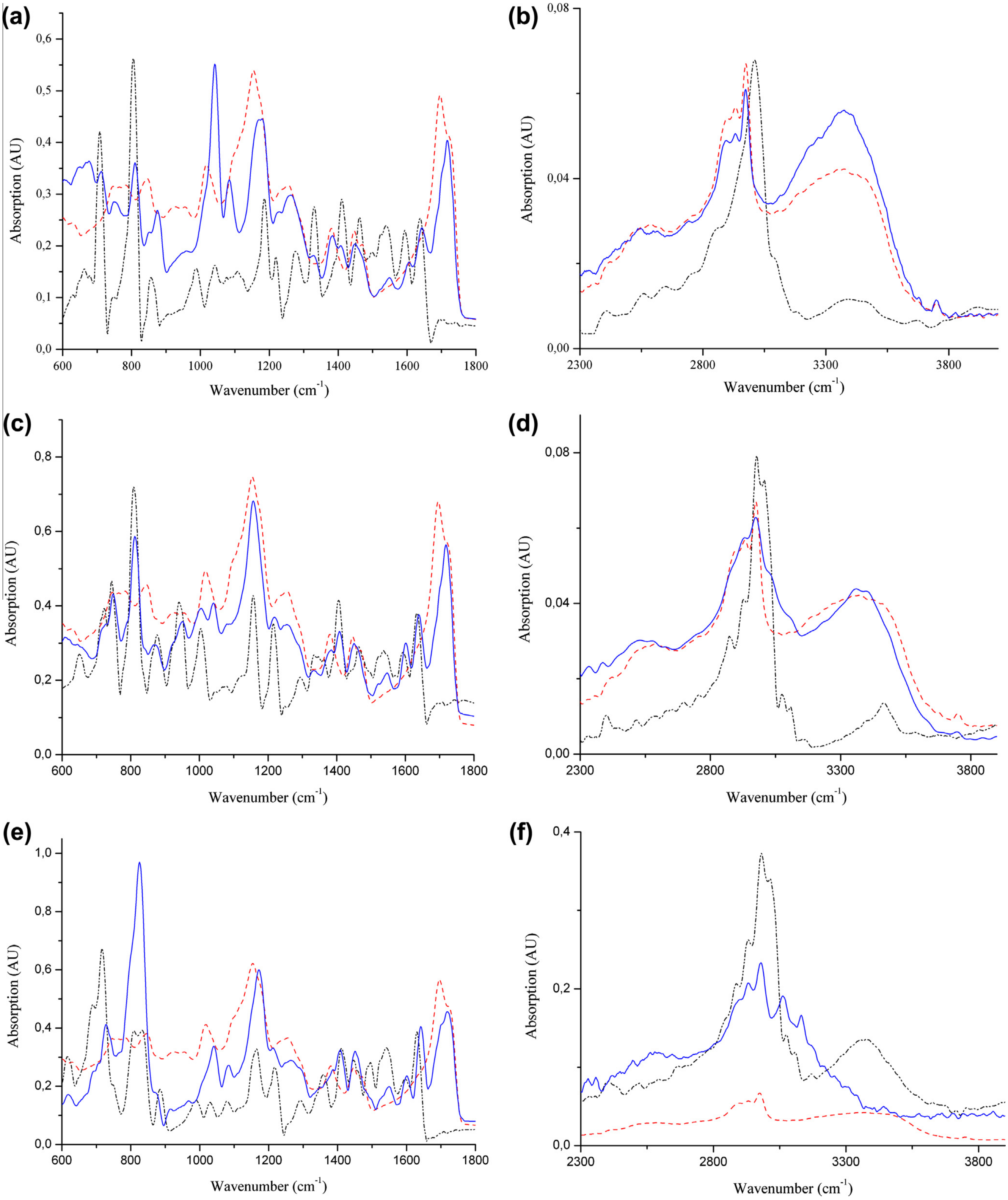


Fig. 5. FTIR spectra of 4,4′-bipyridinium salts (-..-): M (I) – (a and b), A(Br) – (c and d) and B(Cl) (e and f); Eudragit copolymer (···) and their 1:1 complexes (—).

salts (Fig. 4a and b) or its intensity decreases in the spectrum of the blend with a B-substituted salt. These data prove the participation of COOH-groups of the copolymer in a complex formation. In addition to the changes in the carboxylic group bands, there are some changes in the spectra of monosubstituted 4,4′-bipyridinium salts. By comparison of FTIR spectra of free salts and 1:1 blends with Eudragit one can see that the prominent aromatic core skeletal band ν_{as} at 1630 cm^{-1} shifts to 1637 cm^{-1} and ν_s at1595 cm^{-1} moves up to 1601 cm^{-1} due to the interaction. The spectral change can be also seen in the spectral range of the pyridine core (1300 and 880 cm^{-1}): $\delta_{C\text{—}H}$ stretching mode at 809 cm^{-1} shifts up to 815 cm^{-1}.

It means that the whole system of conjugated bonds in the salts molecules rearranges its structure due to an interaction with copolymer molecules which results in the formation of polymer–bipyridilium salt complex. The fact of the experimentally observed change of the distribution of electron density along the whole salt molecule is in good agreement with the calculated distribution of electron density that strongly changes when **BpyR*1*(Hal)-II** complexes are formed. On the other hand, FTIR spectra do not show any sign of the COOH-group proton transfer and carboxylate anion formation.

4. Conclusions

PM3 calculations show that monosubstituted 4,4′-bipyridinium halides exist in two different energetically favorable structures: the first structure is a partial charge transfer complex **BpyR*1* (Hal)** that includes both organic and inorganic (halogen) moieties and the second one is an ion pair **BpyR*2* (Hal)**. The charge transfer system is energetically more favorable. The additive character of energy values given in Table 5 allows to hypothesize the coulomb mechanism of interactions between the halogenated monosubstituted 4,4′-bipyridinium salts and COOH-containing polymers leading to a complex formation.

However, it is much different from the idea about proton transfer and contribution of the tertiary nitrogen in the process of the complex formation. The basic role is played by the interaction between proton of the carboxylic group and halogen anion. Due to a much higher electrophilicity of the proton in comparison with the quaternary nitrogen atom, the electron density distribution in the initial partial charge transfer complex **BpyR*1*(Hal)** changes. The halogen anion acquires a high negative charge, whereas its interaction with proton provides the energy gain and Hal···HOOC distance becomes close to that of a strong hydrogen bond (Table 6). During the formation of that complex **BpyR*1*(Hal)-II** the interaction $N^{+}\cdots Hal^{-}$ reaches the level of coulomb interaction in such a way that halogen anion ends up in an electrostatic trap comprised of two (complex II) or three atoms (complex IV). In addition, water molecules play an essential role in stabilization of complexes considered in this study. The results of calculations are in a very good agreement with experimental FTIR spectra data.

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