Anion-radical conducting MeTCNQ salts with pyrazine-based cations

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Anion-radical salts (ARS) of methyl-7,7,8,8-tetracyanoquinodimethane (MeTCNQ) with simple and complex N-alkilpyrazinum cations have been first synthesized. It was shown that by the IR spectra and the results of resistive measurements in 77–300 K temperature range the ARS synthesized are characterized by two orders of magnitude greater electrical conductivity than appropriate TCNQ-based ARS. All the ARS investigated are either narrow band semiconductors (with the forbidden bandwidth <0.05 eV) or metals. ARS with small length of aliphatic radicals in the cation composition can be releted to quasi-two-dimensional conductors. Such the salts unlike the analogous ARS TCNQ exhibit the property to melt without destruction.

Впервые синтезированы анион-радикальные соли (АРС) метил-7,7,8,8-тетрацианохинодиметана (MeTCNQ) с катионами N-алкилпиразиния простого и сложного составов. Показано, что в соответствии со своими ИК спектрами и результатами резистивных измерений в интервале 77–300 K синтезированные АРС обладают на 1–2 порядка большей электропроводностью, чем аналогичные АРС на основе TCNQ. Все исследованные АРС либо узкозонные полупроводники (ширина запрещенной зоны <0.05 эВ), либо металлы. АРС с небольшой длиной алифатического радикала в составе катиона можно отнести к квазидвумерным проводникам. Такие соли, в отличие от аналогичных АРС TCNQ, обладают свойством плавиться без разложения.

Anion-radical salts (ARS) of TCNQ attracted interest of researchers in late 60th since first organic metals have been obtained in this class of organic compounds [1,2]. The interest in ARS wandered for late after further discovery of organic metals and then superconductors based on cation-radical salts (CRS). The revival of attention to ARS in late 80th caused first of all by the discovery of conductive ARS with unique ability to melt without destruction [3, 4]. The latter opens wide prospects of their practical use as materials for electronics [5]. Recently the possibility of creation of organic ferromagnets based on ARS TCNQ with Curie temperatures from 35 K up to room temperature was demonstrated [6–9]. This fact essentially increases the practical applicability of such organic materials.

Earlier we investigated the pyrazine-based ARS TCNQ of simple and complex compositon [10]. It was shown that the given salts unlike the analogous salts with isoquinoline cations were unable to melt without destruction. Nevertheless the presence of second "vacant" nitrogen atom in

the cation composition enables to use the given salts for the formation of conductive coverings at the surface of metals which are able to create donor-acceptor links with ni-trogen atoms. In accordance with our data [11] the ARS based on methyl-derivatives of TCNQ (MeTCNQ) possess lower melting tem-peratures and one order of magnitude less values of conductivity than the similar TCNQ salts. That is why the aim of this work is in investigation of possibility to create melting conductive ARS of MeTCNQ with pyrazine-based cations.

$$ARS \; (N - H_{2n+1}C_n - Pz)(MeTCNQ)_m,$$
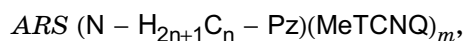
$$\text{where } 0 \leq n \leq 4, \; m = 1, 2$$

were synthesized. Pyrazine provided by Aldrich was used. MeTCNQ were purified by re-crystallization from aceton with further multi-stage zone sublimation. N-alkylpyrazi-nes were synthesized as it was described in [10]. Oxidational-reductional reaction was used for ARS synthesis:

$$1.5(N - Alk - Pz)I + mMeTCNQ \rightarrow$$
$$\rightarrow (N - Alk - Pz)(MeTCNQ)_m +$$
$$+ \; 0.5(N - Alk - Pz)(I_3),$$
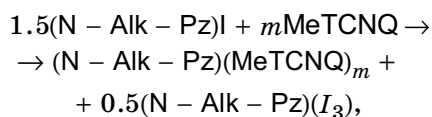
where $m = 1$ or 2. Acetonitryl was used as the solvent. Sediments of the obtained ARS were filtered, washed by hexane and ether and dried in vacuum. For further refining, double re-crystallization from acetone or methanol was performed.

The synthesized ARS composition was defined by means of spectrophotometer in similar way as it was described in [10]. The next equation was in use:

$$\frac{[MeTCNQ]}{[MeTCNQ^-]} = 0.87\frac{D_{393}}{D_{840}} - 0.46,$$

D_{393} is the value of the optical density at 393 nm, where both MeTCNQ and its anion-radical exhibit absorption; D_{840} corre-sponds to 840 nm, where anion-radical MeTCNQ$^-$ absorps only.

In the studies of IR absorption spectra a technique of pelletting with KBr was ap-plied. IR spectra were registrated at room temperatures on the Specord-75 IR spectro-photometer with wave numbers ranging from 400 to 4000 cm^{-1}. Electrical resistiv-ity of pressed at 3 kBar powder samples of the synthesized salts was measured in the temperature interval 77−300 K using four-point contact scheme for both AC and DC. The DC conductivity turned to be equiva-lent to the AC one at audio range frequen-cies. The Table presents the obtained values of specific electrical resistivity at room temperature ρ_{RT} and resistivity activation energy Δ calculated with respect to the edge of continuous absorption in the IR spectra. The Table contains the values of melting point temperatures *mp* also. Conductivity models applied for calculation of Δ value for every particular compound are pre-sented and discussed below.

The specific peculiarities caused by elec-tron-phonon interaction are observed in IR spectra of all ASR synthesized. Fig. 1 shows the lines of vibrational structure at the background of continuous absorption (self- and inter-band conductive electron ex-citations) and also anomalous broadened lines in interval 2100−2250 cm^{-1} (ν(C≡N)-vibrations). IR spectrum of $(N - H_9C_4 - Pz)$ $(MeTCNQ)_2$ also demonstrates continuous absorption however the line broadening is substantially less, which can be explained by the lower electrical conductivity of the latter ARS. With respect to the IR spectra all synthesized ARS can be considered as metals or narrow band semiconductors with the forbidden bandwidth less than 0.05 eV (see Tabl.). By the given criterion the sim-ple ARS $(N - H_{2n+1}C_n - Pz) (MeTCNQ)$ dif-fers abruptly from both ARS of TCNQ and MeTCNQ with pyridine-, quinoline-, and iso-quinoline-based cations [5, 12], which are dielectrics. In particular the electrical con-ductivity of the simple ARS with such cat-ions is 2−3 orders of magnitude less than conductivity of corresponding complex ARS [12]. The high electrical conductivity of $(N - H_{2n+1}C_n - Pz) (MeTCNQ)$ ARS can be explained by interaction with charge trans-fer between pyrazine-based cations and anion-radicals of MeTCNQ, as it is observed in ARS NMP−TCNQ [13].

The results of resistive measurements, which were carried out in temperature in-terval 77−300 K confirms the conclusions based on optical measurements (Tabl.). The examples of the resistance temperature de-pendencies are given at Fig. 2. In previous works [5, 10] for the ARS with pyrazine-based cations the electrical conductivity re-duction was found when the replacement of TCNQ to MeTCNQ took place. This effect was explained by the crumbling action of methyl group of MeTCNQ to the heap struc-ture of ARS [12]. As one can see in the Table. the opposite type phenomenon is ob-served in our case. The electrical conductiv-

Table. Characteristics of ARS TCNQ [10] and MeTCNQ (present work)

Cation, composition	TCNQ		MeTCNQ		
	ρ_{RT}, $\Omega\cdot$cm	Δ, eV	mp, K	ρ_{RT}, $\Omega\cdot$cm	Δ, eV
N–H$_3$CPz, 1:1	100	< 0.05	455	2.63	< 0.05
N–H$_3$CPz, 1:2	66.7	0.06	440	0.72	< 0.05
N–H$_5$C$_2$Pz, 1:1	78.7	0.2	432	2.94	< 0.05
N–H$_5$C$_2$Pz, 1:2	79.4	0.2	443	0.75	< 0.05
N-iso-H$_7$C$_3$Pz, 1:1	$7.58\cdot10^3$	0.2	471	$1.75\cdot10^2$	< 0.05
N-iso-H$_7$C$_3$Pz, 1:2	$5.96\cdot10^3$	–	decomp.	$3.57\cdot10^2$	< 0.05
N–iso–H$_9$C$_4$Pz, 1:2	$2.94\cdot10^5$	–	decomp.	$7.69\cdot10^3$	< 0.05

ity of the ARS MeTCNQ is 1−2 orders of magnitude higher than for appropriate ARS of TCNQ. The abrupt conductivity increase could be associated with the supposed ste-reo-regular orientation of methyl groups of MeTCNQ in pyrazine-based cation ARS, and also with the specific influence of the latter cations. It should be expected that such ori-entation could form more ordered heap structure of MeTCNQ anion-radicals. The second atom in pyrazine cation can take part in the interaction between anion-radi-cal heaps and cations. Such type interaction can give definite quasi-two-dimensinality to the system unlike the quasi-one-dimensional-ity, which is typical for ARS of TCNQ. The results of resistive measurements are in quali-tative agreement with the above conclusions.

For the simple ARS of MeTCNQ the tem-perature dependence of electrical resistance (Fig. 2) is best described in frames of a model, which takes into account conductive electron scattering. The latter one is possi-bly caused by the narrowness of the forbid-den electron band [14]:

$$R(T) = AT^n\exp(\Delta/2T).$$

Application of the least square fit to the experimental data in frames of the men-tioned model yields the following expres-sions for the temperature dependence of the reduced resistance R/R_{RT} of the investi-gated salts (R_{RT} is the resistivity at room temperature):

$$\ln(R/R_{RT}) = 16.34 - 3.08\ln T + 595.7/T,$$

for [N–CH$_3$–Pz](MeTCNQ) and

$$\ln(R/R_{RT}) = 17.08 - 3.36\ln T + 604.9/T,$$

for [N–C$_2$H$_5$–Pz](MeTCNQ). Here and below all the coefficients are of the corresponding dimension.

Using the obtained expressions, it is pos-sible to determine a forbidden bandwidth. In the case of [N–CH$_3$–Pz](MeTCNQ) it equals to 0.051 eV which corresponds to the edge of continuous optical absorption at 414 cm^{-1}. For [N–C$_2$H$_5$–Pz](MeTCNQ) the calculations give 0.052 eV and 419 cm^{-1}. The above estimations agree well with the results of IR absorption spectra analysis for the investigated compounds.

For adequate description of the tempera-ture behavior of electrical resistivity of complex salts [N–CH$_3$–Pz](MeTCNQ)$_2$, [N–C$_2$H$_5$–Pz](MTCNQ)$_2$ and [N–C$_3$H$_7$–Pz](MeTCNQ)$_2$, as well as of the simple salt [N–C$_3$H$_7$–Pz](MeTCNQ), we have invoked the model based on the hopping mechanism of conductivity which is possibly condi-tioned by the structural peculiarities of the listed ARS [14-16]:

$$R(T) = A\exp\left[\left(\frac{T_0}{T}\right)^{\frac{1}{\alpha+1}}\right].$$

Here α is the dimensionality of the sys-tem, T_0 and A are the parameters of the model.

For the [N–CH$_3$–Pz](MeTCNQ)$_2$ com-pound the best fit of the experimental and theoretical $R(T)$ dependencies occurs for $\alpha = 1$, which corresponds to the one-dimensional case. Logarithm of the reduced electrical re-sistivity R/R_{RT} is expressed as:

$$\ln(R/R_{RT}) = -9.32 + \frac{158.59}{\sqrt{T}}.$$

Meanwhile, fitting of the experimental $R(T)$ dependence for [N–C$_2$H$_5$–Pz](MeTCNQ)$_2$ salt by the theoretical curve with the vari-able value of α parameter allows to estimate it as $\alpha = 2$, which gives evidence for the earlier assumption of two-dimensional con-
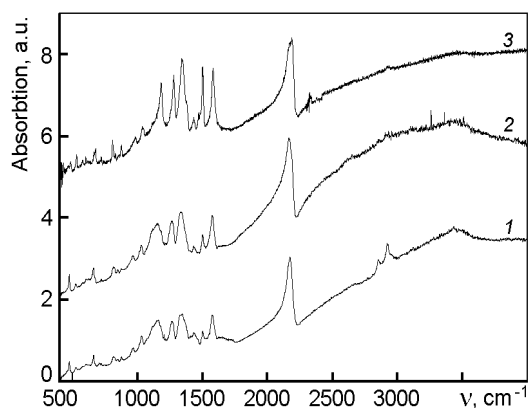
Fig. 1. IR absorption spectra of ARS:
1 — (N–CH$_3$Pz)(MeTCNQ)$_2$,
2 — (N– CH$_3$Pz)(MeTCNQ),
3 — (N-iso-C$_4$H$_9$Pz)(MeTCNQ)$_2$.

Fig. 2. Temperature dependence of electrical resistivity for ARS:
1 — (N–CH$_3$Pz)(MeTCNQ)$_2$,
2 — (N–C$_2$H$_5$Pz)(MeTCNQ),
3 — (N–C$_2$H$_5$Pz)(MeTCNQ)$_2$,
4 — (N-iso-C$_4$H$_9$Pz)(MeTCNQ)$_2$.

ductivity of the studied compound. In this case for $\ln(R/R_{RT})$ we have:

$$\ln(R/R_{RT}) = -21.44 + \frac{143.48}{T^{1/3}}.$$

For the simple and complex ARS ([N–C$_3$H$_7$–Pz](MeTCNQ) and [N–C$_3$H$_7$–Pz](MeTCNQ)$_2$) we can get respectively:

$$\ln(R/R_{RT}) = -26.65 + \frac{178.36}{T^{1/3}}$$

and

$$\ln(R/R_{RT}) = -25.02 + \frac{165.08}{T^{1/3}}.$$

Direct verification of the assumption of quasi-two-dimensional character of electrical conductivity which is rather unusual for TCNQ-based ARS may be performed through the studies of the anisotropy of electrical resistance of [N–C$_2$H$_5$–Pz](MeTCNQ)$_2$ single crystals.

The temperature dependence of ARS [N–C$_4$H$_9$–Pz](MeTCNQ)$_2$ electrical resistivity can be described in terms of simple activation model:

$$\ln(R/R_{RT}) = -7.12 + \frac{2088}{T}.$$

Hence for the given salt the value of activation energy is equal to 0.36 eV. Inconsistency in results of resistivity measurements and IR spectral data can be explained in the following way. For all ARS synthesized by us the MeTCNQ heap structure is of the same type, as it is seen from their IR spectra, which are characterized by the continuous absorption in the whole
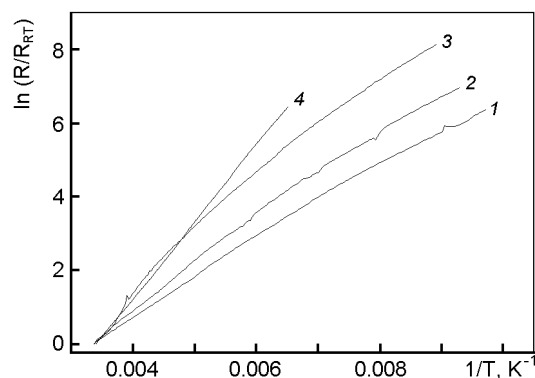
wave number interval. ARS with smaller size cations (up to the N–C$_3$H$_7$–Pz) possess noticeable quasi-two-dimensional electronic structure. That is why the results of resistivity measurements performed on pelleted samples agree qualitatively with the optical data. Larger N-butylpyrazine cations, which are situated between anion-radical heaps, prevent the inter-heap links formation. Therefore ARS MeTCNQ with big-size cations exhibit quasi-one-dimensional character of conductivity. The latter was the condition of high activation energy values obtained in resistivity measurements on pelleted samples (high conductivity along the stacks and dielectrical behavior in other two directions).

One more characteristic peculiarity of the (N – H$_{2n+1}$C$_n$ – Pz) (MeTCNQ)$_m$ ARS, which differs it from analogous TCNQ salts, is in its ability to melt without destruction (Table.). It gives us a reason to confirm the tendency, which was detected earlier [11]. In accordance with it ARS MeTCNQ melting temperatures are 40−50 K lower than appropriate ones for ARS TCNQ. As it can be seen from Table. the melting temperatures of the given ARS are rather low. This circumstance makes it possible to create definite microelectronic constructive elements directly from the liquid phase. Besides they have an advantage over the known ARS of TCNQ and MeTCNQ, which is in their greater adgesion to metal surfaces due to ability to coordination (i.e. formation of coordinated links Me–N). That is why the ARS are promising for use in electronics and microelectronics.

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Провідні аніон-радикальні солі **МеTCNQ** з катіонами на основі піразину

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Вперше синтезовано аніон-радикальні солі (АРС) метил− 7,7,8,8-тетрацианохіноди-метану (МеTCNQ) з катіонами N-алкілпіразінію простого та складного складу. Показано, що відповідно своїм IЧ спектрам і результатам резистивних вимірювань в інтервалі 77−300 К синтезовані АРС мають на 1−2 порядки більшу електропровідність, ніж аналогічні АРС на основі TCNQ. Всі досліджені АРС або вузькозонні напівпровідники (ширина забороненої зони <0.05 еВ), або метали. АРС з малою довжиною аліфатичного радикалу у складі катіону можна віднести до квазідвомірних провідників. Такі солі, на відміну від аналогічних АРС TCNQ, здатні плавитись без розкладу.