

Aromatic/quinoid systems: principles and applications

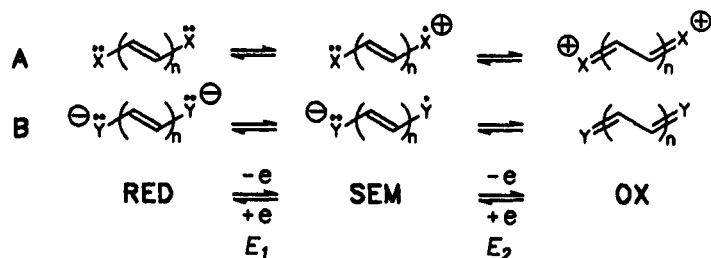
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Abstract — A general structural principle is presented for reversible two step redox systems which contain, on an intermediate oxidation level, radical ions of high thermodynamic stability. Although this principle is of much broader scope, the paper concentrates on (hetero)aromatic/quinoid Wurster and Weitz type systems and some diazolenes. These systems can be characterized in solution by their redox potentials and applied e. g. as electron transfer catalysts. In addition it is demonstrated that most organic electric conducting materials belong to these general redox systems, from which a new type of acceptor of N,N'-dicyanoquinonediimines (DCNQI's) has been developed. DCNQI's are obtained in great variety from substituted quinones in a one pot reaction. Typical examples for CT-complexes and especially radical anion salts of very high and partly metallic conductivity are discussed.

1 A STRUCTURAL PRINCIPLE FOR REVERSIBLE TWO-STEP ELECTRON TRANSFER SYSTEMS

Based on earlier suggestions of Weitz [1], Hünig [2] proposed a general structural principle for reversible organic redox systems where the redox process (i) consists of electron transfer only and (ii) occurs stepwise with an intermediate radical ion of considerable thermodynamic stability (Scheme 1). The redox steps RED/SEM and SEM/OX can normally be characterized by the potentials E_1 and E_2 from which the semiquinone formation constants K_{SEM} can be calculated.



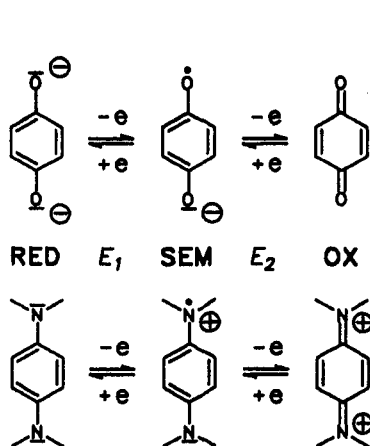
Scheme 1 General structures for reversible two step redox systems.

Systematic investigations have demonstrated that this principle is valid a very broad range of structural variations [3,4]. It can even be extended to certain polyenes. In addition, this principle explains the otherwise unexpected redox properties of many rather odd examples reported in the literature [3]. Furthermore this structural principle includes the fact that within the three oxidation stages the most delocalized system is connected with the radical ion which therefore displays the longest wavelength absorption, often shifted to the IR region.

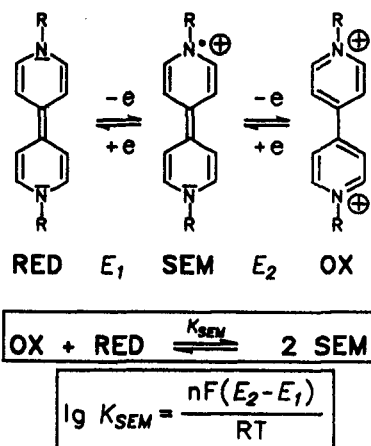
This paper, however, will be restricted to those systems, which show aromaticity in the forms RED or OX, whereas the corresponding oxidation levels OX and RED are "quinoid". By this way, two general classes can be deduced from Scheme 1 [3]:

1. *Wurster type systems*, consisting of rings, built from the vinylene groups, to which the end groups X or Y are attached and which are aromatic in the reduced form.
2. *Weitz type systems*, consisting of rings into which the end groups X and the vinylene groups (at least partly) have been incorporated and which are aromatic in the oxidized form.

Both systems are represented by the classical examples of p-phenylenediamines together with p-benzoquinone in Scheme 2 and by the quaternary salts of 4,4'-bipyridine ("viologenes" [1,5]) in Scheme 3.



Scheme 2 Examples of Wurster type redox systems.

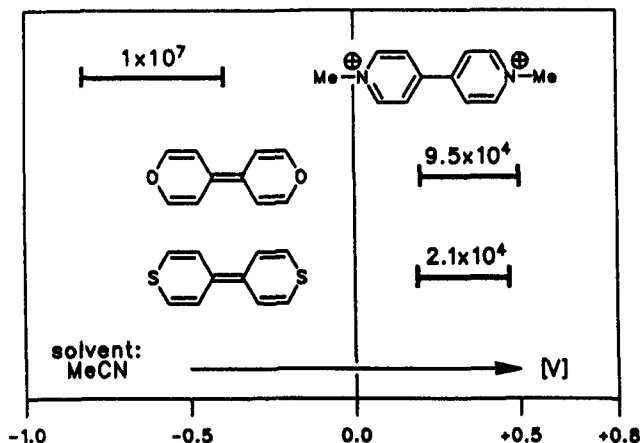


Scheme 3 Example of a Weitz type redox system.

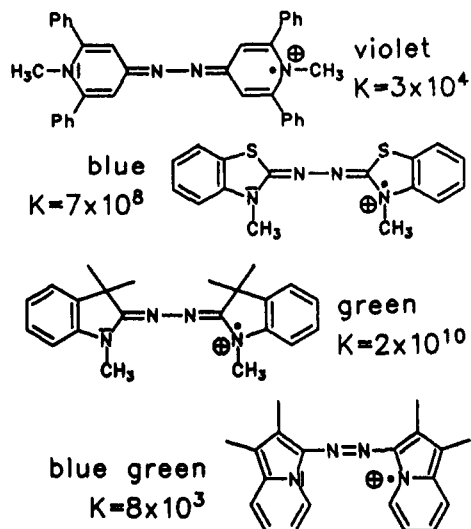
2 VARIATIONS OF THE WEITZ-TYPE REDOX SYSTEMS

Weitz type redox systems have been systematically studied over the last 25 years [2] and are still under active investigation [6]. Here the numerous variations will be demonstrated only by three typical examples.

1. Replacement of nitrogen by sulfur or oxygen in the above mentioned viologenes has two consequences as shown in Scheme 4: K_{SEM} decreases from 10^7 to 10^4 and the potentials move to the positive side of the voltage scale. This means, that the viologenes are air stable in their oxidized form whereas the corresponding pyron and thiopyron derivative are isolated in their reduced form.
2. Replacement of two central methine groups by an azo- or azino group, respectively, yields redox systems in which all three oxidation forms can easily be isolated. The wide variability of the heterocyclic end group and the high stability of the radical cations is demonstrated by Scheme 5.

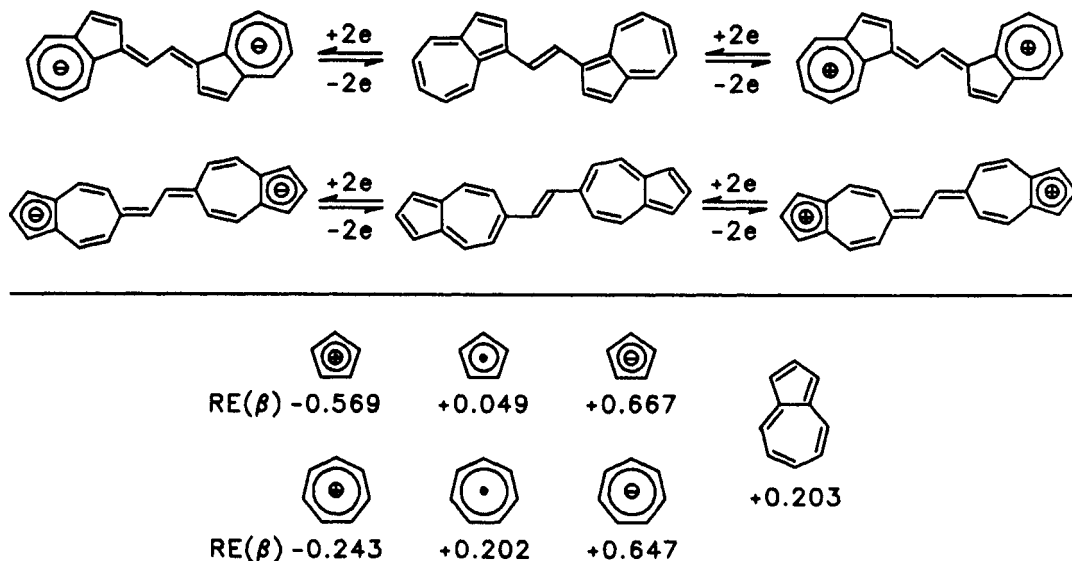


Scheme 4 Dependence of redox potentials E_1 (RED/SEM, left bar), E_2 (SEM/OX, right bar) and semiquinone formation constants K_{SEM} on different heteroatoms.



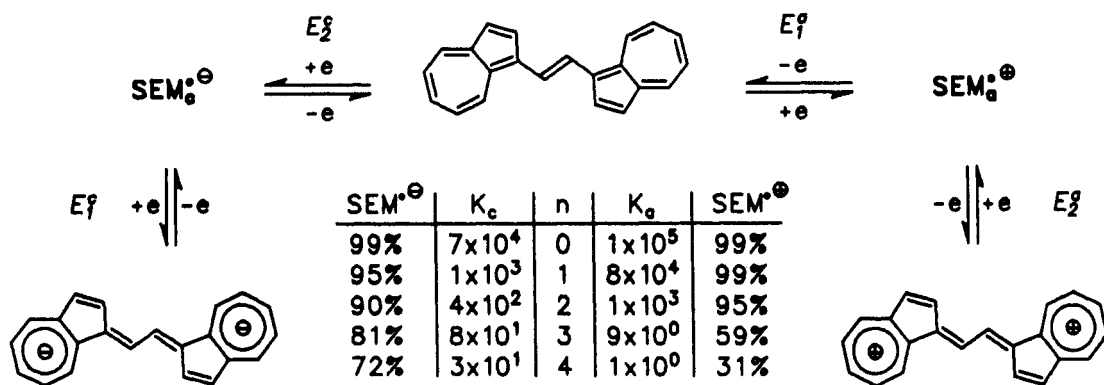
Scheme 5 Radical cations of two step redox systems with central NN-moiety and different heterocyclic end groups.

3. So far, all the end groups X and Y act by their lone pairs in the reduced form. It should be possible, however, to substitute them by certain π -systems. By this way, one might obtain unsaturated hydrocarbons, which should undergo either two step oxidation or reduction. A suitable arrangement is accomplished by two azulene moieties which are connected in positions 1,4 or 6 by vinylenes groups ($n = 0-4$). Scheme 6 demonstrates the redox situation for bisazulenes, linked by one vinylenes group in positions 1 or 6. In accordance with empirical knowledge and backed by the calculated resonance energies [7] for different oxidation levels of C_5H_5 and C_7H_7 , the redox behaviour of the bisazulenes is expected to depend strongly on the position of linkage.



Scheme 6 Possible two electron oxidations and reductions of 1,1'- and 6,6'-biazulenylenes together with calculated resonance energies of five and seven membered rings.

Indeed, the 6,6'-derivatives can only be stepwise reduced and cannot be reversibly oxidized due to strong antiaromaticity of the cyclopentadienyl cation. By contrast, the much lower antiaromaticity of the cycloheptatrienyl anion does not prevent 1,1'-linked bisazulene systems, which are easily oxidized, from also being reversibly reduced. Thus, a pure hydrocarbon can exist in five different oxidation levels, as can be seen from Scheme 7. Again the thermodynamic stabilities of both the radical cations and anions are remarkably high.

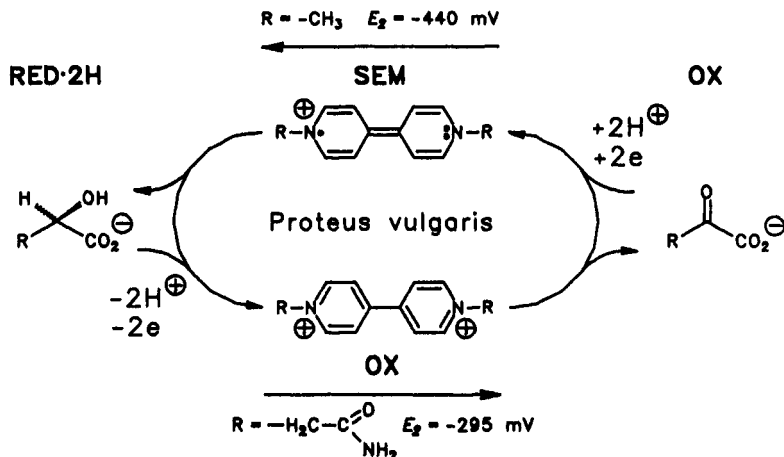


Scheme 7 Redox reactions of vinylogous 1,1'-biazulenes together with semiquinone formation constants for reduction (K_c) and oxidation (K_a).

It should be mentioned that reversible four step systems can even be derived from polyenes with crossconjugated end groups [8].

3 ELECTRON TRANSFER CATALYSIS BY REVERSIBLE TWO-STEP REDOX SYSTEMS

Since the electron transfer between the different oxidation stages of the systems under discussion occurs at nearly diffusion controlled rates [9], and because the potential can be modeled to cover a broad range, electron transfer catalysis should be possible. Indeed, important applications are found in rather different fields: E. g. unselective herbicides (Paraquat^R, Diquat^R), activation of developing agents in photography [3], and reductive debromination of 1,2-dibromides [10]. The most striking reported case is the reduction of α -ketoacids or oxidation of α -hydroxyacids with complete enantioselectivity by micro organisms [11]. According to Scheme 8, viologenes with R = Me act as mediators for reduction (electrons provided by a cathode, carbon monoxide or formic acid), whereas the more easily reducible viologenes with R = CH₂-CONH₂ mediate the enzymatic oxidation (electrons removed by an anode or dioxygen).

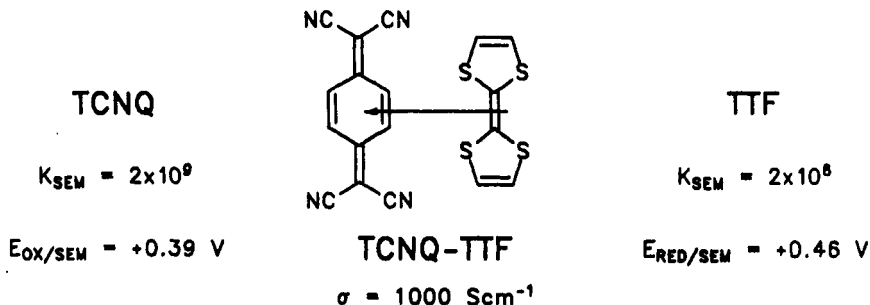


Scheme 8 Enzymatic electron transfer reactions mediated by viologenes. Reduction and oxidation depend on the potentials of the mediators.

These glimpses on a variety of two step redox systems already give a taste of their fruitful chemistry, which, however, has to be studied and applied throughout in solution. In the meantime, electron transfer reactions of these reversible redox systems in the solid state are becoming even more important, as will be demonstrated in the following chapters.

4 REVERSIBLE TWO-STEP REDOX SYSTEMS – THE BASIS FOR CONDUCTING ORGANIC MATERIALS

With very few exceptions the majority of organic materials are electric insulators. Therefore, the discovery of the CT-complex from TTF and TCNQ, which showed high metallic conductivity, rising to $\sim 10^4$ Scm⁻¹ around 60 K, at which point a metal-semiconductor transition occurred, immediately created an extremely rapid growing field of research [12].



Scheme 9 CT-complex TCNQ/TTF together with the semiquinone formation constants K_{SEM} and the corresponding redox potentials.

As expected, a plethora of similar systems has been tested for electric conductivity, but perhaps not all chemists have realized that both the powerful donors and acceptors represent examples of the general structural principle for two step redox systems: Extremely high thermodynamic stability of the radical ions — expressed by K_{SEM} — is observed for TCNQ (Wurster type — $\lg K_{SEM}$ 9.2, [13], as well as for TTF (Weitz type — $\lg K_{SEM}$ 6.2, [14]).

In the meantime well established rules [15] have provided guidelines for the design of organic metals: E. g. the organic components should be planar π -systems which in CT-complexes crystallize in segregated stacks. Electric conductivity along these stacks is rendered by partial electron transfer, provided by a difference of 0.25 to 0.34 V [16,17,18] between the potentials OX/SEM of the acceptor and RED/SEM of the donor.

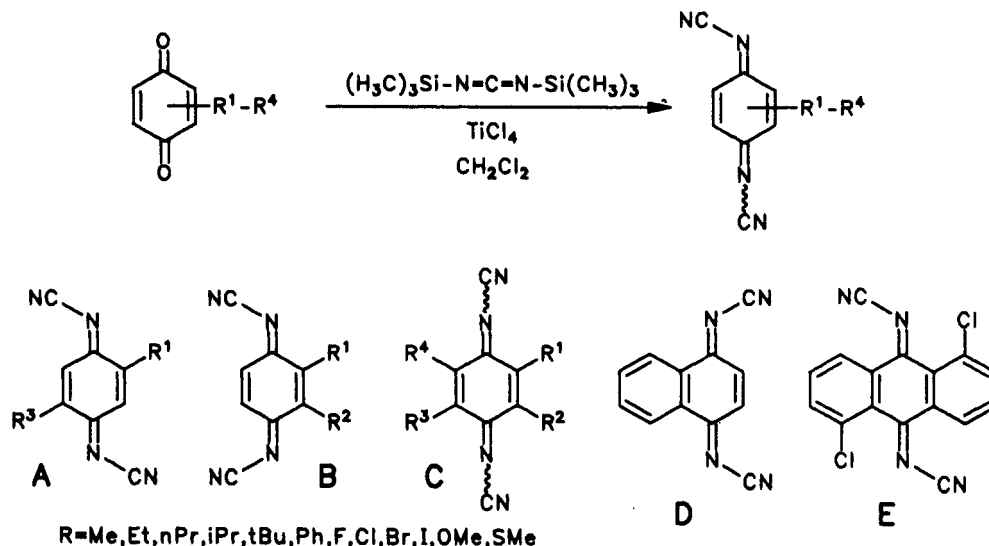
Most of the variations reported in the literature concern the donor TTF (substituents, Se and Te instead of S) from which even superconducting radical cation salts [19] with T_c up to 11 K ([20]) have been isolated. By contrast, very few substituted TCNQ's were checked, presumably for the following reasons: (i) The Y-shaped and rigid $=C(CN)_2$ group tolerates only very small substituents to preserve the planarity of the molecule; (ii) interstack interactions which are prerequisite for the striking properties of radical salts based on TTF-derivatives (e. g. BEDT-TTF, [21,22]) were not expected for TCNQ's.

Nevertheless, we think that still larger variations of the acceptor are highly desirable and may even lead to radical anion salts of outstanding properties.

5 DCNQI's — A NEW CLASS OF ACCEPTORS

Since we already knew that a certain analogy between the groups $=C(CN)_2$ and $=N-CN$ had been proposed [23,24], we set out to create the so far unknown class of N,N'-dicyanoquinonediimines (DCNQI's, [25]) which, for the following reasons, immediately caught the interest of several groups:

1. The possibility of a one pot synthesis starting from 1,4-benzo- and naphthoquinones as well as 9,10-anthraquinones and bis(trimethylsilyl)carbodiimide in the presence of titanium-tetrachloride produces DCNQI's in good to excellent yield [26,27,28]. By this route a broad spectrum of DCNQI's can easily be obtained.



Scheme 10 General synthesis of DCNQI's and typical examples A - E

2. Since the $=N-CN$ group is no longer Y-shaped and its bond angle is somewhat flexible, planarity is even preserved on tetrasubstitution (C, E, [29]). Disubstitution as in A, B and D gives rise to definite anti and syn configuration, respectively, of the CN groups, whereas on tetrasubstitution (e. g. C) a low energy conversion between the two configurations (ca. 13 kcal/mol) [30] occurs in solution.
3. Because of this variability, the acceptor strength for the unsubstituted DCNQI which is similar to TCNQ can be modified between ca. -0.1 V to $+0.8$ V (Ag/AgCl, CH_2Cl_2) [31].

From these DCNQI's many CT-complexes and especially radical anion salts have been prepared whose conducting properties equal or even surpass those of the corresponding TCNQ derivatives.

6 CT-COMPLEXES FROM DCNQI'S AND TTF

So far more than two dozens of DCNQI-TTF-complexes have been obtained. Most of them show powder conductivities of $10^{-2} - 10^{-1} \text{ Scm}^{-1}$ ([28]). The segregated stacks are arranged in two different patterns as demonstrated by the following two examples (Figs. 1, 2). In Fig. 1 a chess board like arrangement [32] is realized in which the water molecules seem to occupy the place of a cyano group in the corresponding TCNQ-TTF complex.

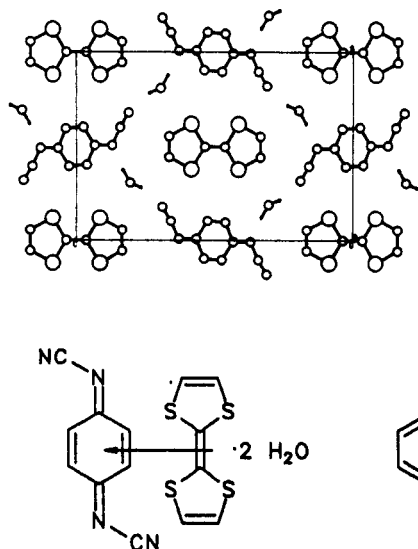


Fig. 1: DCNQI·TTF·2H₂O space group P2₁/c; b,c-projection ($\sigma=10 \text{ Scm}^{-1}$)

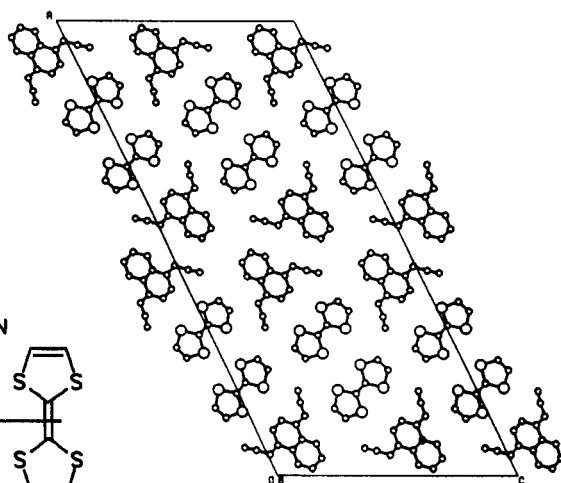


Fig. 2: DCNNQ·TTF space group C2/c; a,c-projection ($\sigma=26 \text{ Scm}^{-1}$)

By contrast, the DCNNQ·TTF complex [33] is composed of two parallel rows of both DCNNQ and TTF molecules. Both stacks are skewed in the same direction, but with a slightly different angle, thereby allowing two sulfur atoms of one TTF molecule to approach the CN groups of two stacked DCNNQ molecules as close as 318 and 323 pm, respectively. The conductivity of the complex increases down to $T_c = 140 \text{ K}$, below which it drops sharply due to a phase transition.

7 DCNQI RADICAL ANION SALTS WITH ORGANIC CATIONS

Both sp^3 -nitrogen (N^+Me_4) and sp^2 -nitrogen (N-methylquinolinium ion (NMQ)) can serve as counter ions in conducting DCNQI-radical anion salts with stoichiometries 2:1 and 3:2. Fig. 3 presents the crystal packing of $[2,5-Cl_2-DCNQI]_2[NMe_4]$ which shows zig zag stacks of equidistant acceptor molecules [34]. The cations appear to be situated in the holes of the crystal lattice without any specific interaction with the radical anions.

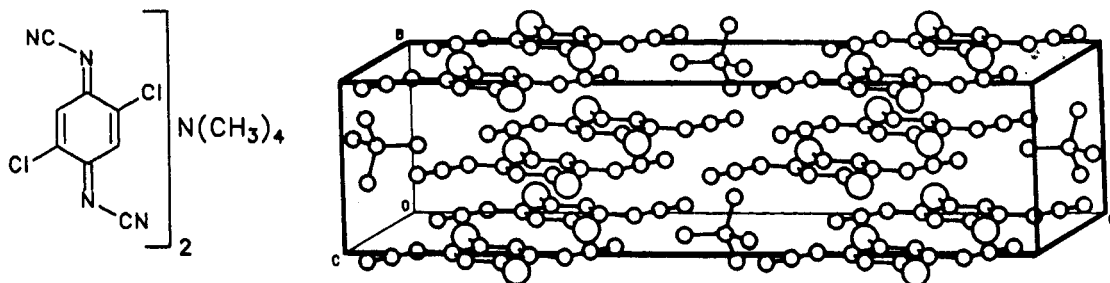


Fig. 3: Crystal packing of $[2,5-Cl_2-DCNQI]_2[NMe_4]$ space group C 2/m; ($\sigma = 10^{-2} \text{ Scm}^{-1}$)

A different pattern is observed with $[2,5-Br_2-DCNQI]_3[NMQ]_2$ according to Fig. 4 [35]. Slightly shifted trimers of DCNQI's form stacks which are separated by stacks of equidistant N-methylquinolinium (NMQ) cations.

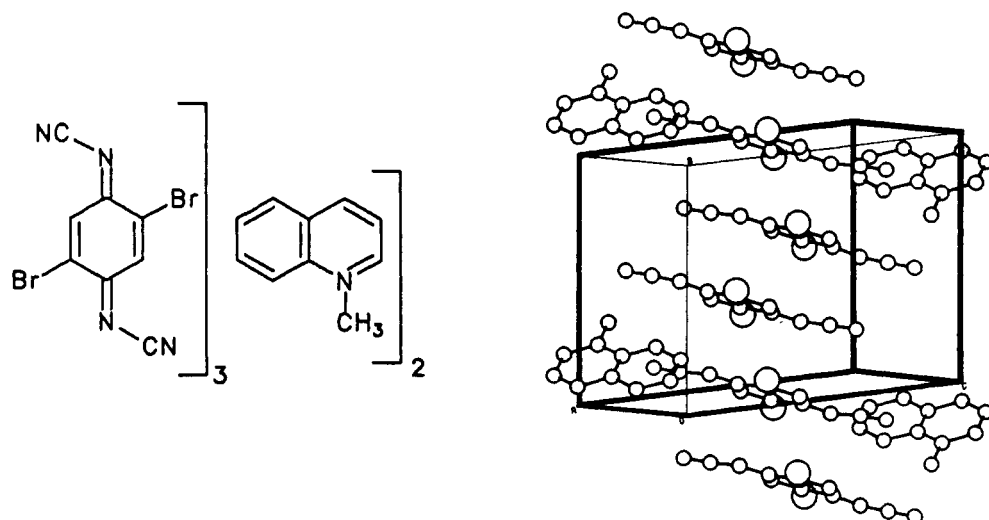


Fig. 4: Crystal packing of $[2,5\text{-Br}_2\text{-DCNQI}]_3[\text{NMQ}]_2$ space group $P\bar{1}$ ($\sigma = 0.1 \text{ Scm}^{-1}$ (powder))

8 DCNQI RADICAL ANION SALTS WITH METAL CATIONS

This class of compounds is the most interesting one, especially salts of 2,5-disubstituted DCNQI's to which this report will be restricted [34,36,37]. As one can judge from Table 1, high conductivities are achieved with a variety of metal monocations culminating at 1000 Scm^{-1} for copper salts. It is worthwhile to note that high conductivity is not restricted to cations which strongly coordinate with cyano groups (Cu^+ , Ag^+). Furthermore, the 2,5-substituents can be varied within wide limits. Even disorder by two different 2,5-substituents is tolerated and only bulky substituents, e. g. iodine, seem to reduce the conductivity.

Table 1: Room Temperature Powder Conductivities of $(2\text{-R}^1, 5\text{-R}^3\text{-DCNQI})_2\text{M}$ Anion Radical Salts (*Single Crystal, +for similar results see [36,37])

R ¹	Me	Me	Me	Me	Me	Me	Me	Me	Cl
R ³	Me	Me	Me	Me	Me	Me	Me	Me	Me
Metal	Cu	Ag	Tl	Li	Na	K	Rb	NH ₄	Cu
σ [Scm^{-1}]	1000**	100**	>20*	100**	0.05	0.03	0.1	0.1 ⁺	300**
R ¹	Cl	Cl	Cl	Br	Br	Br	Br	Br	I
R ³	Me	Me	Me	Me	Me	Me	Me	Me	Me
Metal	Ag	Li	Na	Cu	Ag	Li	Na	NH ₄	Cu
σ [Scm^{-1}]	100**	0.06 ⁺	0.02	1000**	100	0.1	0.001	0.02	200*
R ¹	I	I	I	I	I	Cl	Cl	Br	Br
R ³	Me	Me	Me	Me	Me	Cl	Cl	Br	Br
Metal	Ag	Li	Na	K	NH ₄	Cu	Ag	Cu	Ag
σ [Scm^{-1}]	20*	0.07	0.1	0.07	0.04	0.4 ⁺	0.02	0.1 ⁺	0.01
R ¹	Br	Br	OMe	OMe	OMe	Et	Br	I	Br
R ³	Cl	Cl	OMe	OMe	Me	Me	I	I	OMe
Metal	Cu	Ag	Cu	Na	Cu	K	Cu	Cu	Cu
σ [Scm^{-1}]	600*	0.02	0.1 ⁺	0.05	0.1	0.1	0.01	0.02	0.02

It turns out that all salts possess the same crystal structure ($I4_1/a$ or a closely related space group), allowing for the first time to study a series of the radical salts with the same crystal lattice and to correlate the observed effects with the structural variations. These salts introduce a new stacking motif into organic conducting materials as one can see from Figs. 5 and 6.

According to Fig. 6, the cations are arranged like a string of pearls, being surrounded by four stacks of DCNQI ligands in such a way that tetrahedral coordination is allowed at each cation. The distances between the cations (378–397 pm) do not correlate with the nature of the metal since they are dictated by the thickness and the skew angle of the organic ligands. This distance is much too large for electron transport along the metal ion stack. Therefore one dimensional conductivity occurs through the DCNQI stacks only and not through the metal ions.

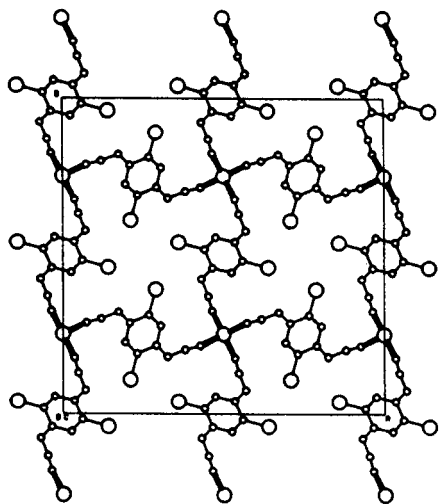


Fig. 5: a,b-projection;

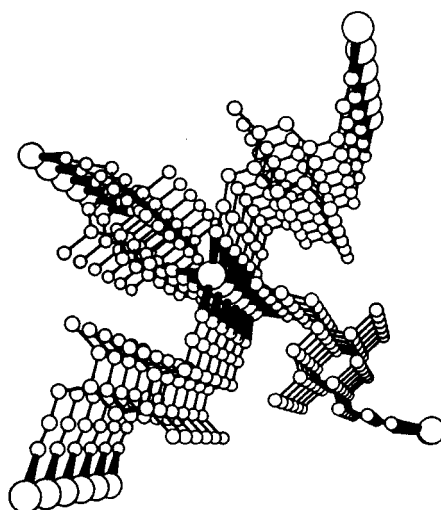
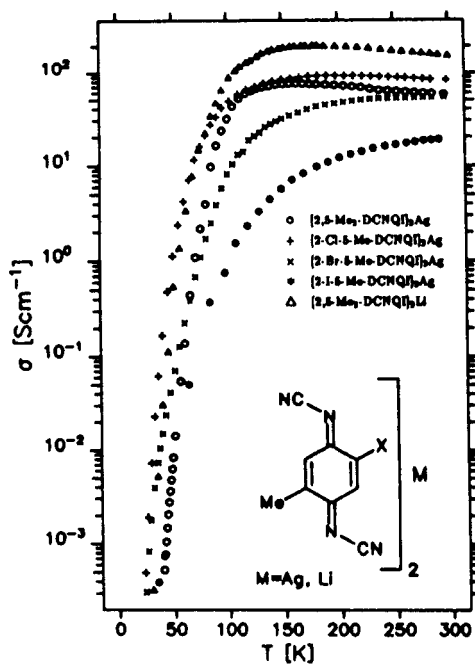
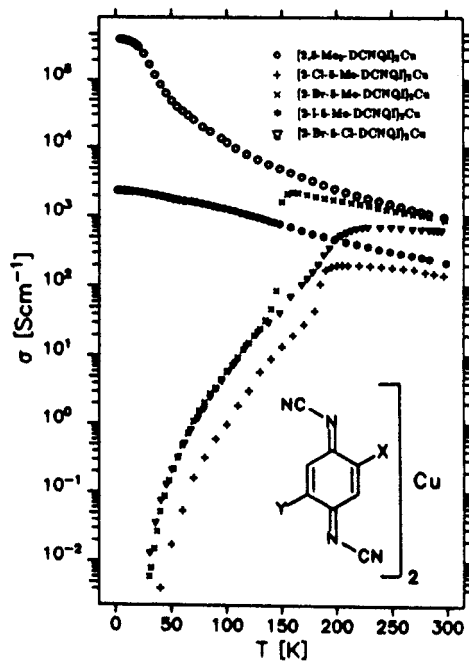
[2,5-Me₂-DCNQI]₂Cu, space group I4₁/a

Fig. 6: perspective view of one stack of copper ions surrounded by four stacks of DCNQI's

As can be seen from Fig. 5, however, due to the bifunctionality and the special geometry of the DCNQI units, each ligand column is connected to two cation columns, thereby creating a network of parallel stacks of radical anions and cations. The very special but still general arrangement may even allow conductivity perpendicular to the axis of stacking, if the metal ions can easily change their oxidation levels at the appropriate potentials. This rather unique feature has indeed been observed, but with copper salts only. The radical salts [2-R¹,5-R³-DCNQI]₂M are therefore discussed in two separate groups.

1. DCNQI-Non-Copper Radical Anion Salts

All non-copper salts investigated so far [38,39,37] are "metal like semiconductors" [40] as can be judged from the temperature dependence of their electrical conductivity. This is exemplified by the behaviour of differently substituted silver salts shown in Fig. 7. The rather high conductivities at room temperature drop slowly but steadily until they are reduced by ca. 10⁵ Scm⁻¹ at ca. 50 K.

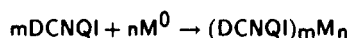
Fig. 7: [2-X,5-Me-DCNQI]₂M Temperature dependence of conductivityFig. 8: [2-X,5-Y-DCNQI]₂Cu Temperature dependence of conductivity

2. DCNQI-Copper Radical Anion Salts

All copper salts so far investigated clearly show metallic conductivity. As it is well known from other metallic organic conductors, on cooling at a certain temperature, the conductivity sharply drops, because of a phase transition (Peierls distortion) which produces a semiconductor. This behaviour is demonstrated in Fig. 8 and has also been proven by temperature dependent X-ray analysis [36]. But some of the copper salts exhibit extraordinary and unprecedented features: In salts with certain substituents metal conductivity is prevailed down to < 1 K without any phase transitions: $[2,5\text{-Me}_2\text{-DCNQI}]_2\text{Cu}$ $\sigma \sim 500,000$ Scm^{-1} at $T \leq 10$ K (Fig. 8, [41]), $[2\text{-I,5-Me-DCNQI}]_2\text{Cu}$ $\sigma \sim 2,500$ Scm^{-1} at $T \leq 1.2$ K (Fig. 8, [42]), $[2,5(\text{MeO})_2\text{-DCNQI}]_2\text{Cu}$ ($\sigma \sim 100,000$ Scm^{-1} at $T < 10$ K [43]. With $500,000$ Scm^{-1} the conductivity of copper is already approached if one counts the number of movable electrons per volume unit.

The metallic behaviour of DCNQI copper salts is connected to pseudo three-dimensional conductivity, which has been measured to be 100 Scm^{-1} perpendicular to the crystal axis of $[2,5\text{-Me}_2\text{-DCNQI}]_2\text{Cu}$ [44]. The special role of copper has been substantiated by other methods [45,46,47], although the interpretation of the results seems still to be controversial. Short bond distances, (Cu-N 199 pm) cannot be the only reason for the specific behaviour of the DCNQI-copper salts, because the short Ag-N distance of 230 pm also indicates strong coordination [32] similar to $[\text{M}(\text{MeCN})_4]\text{ClO}_4, d(\text{M-N}): \text{Cu}: 195\text{-}202$ pm [48], Ag: 218-233 pm [49].

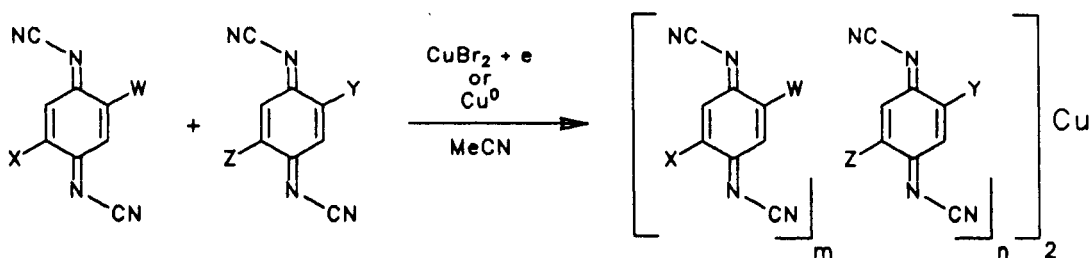
Single crystals of DCNQI salts can be grown by electrocrystallisation [41], a well developed technique, which has already been used with TCNQ salts. For DCNQI copper salts, an extremely simple and useful method was found, which is also applicable to silver salts [50]. Instead of slowly reducing the DCNQI's electrochemically, the metal itself serves as the reducing agent:



Indeed, on reaction of acetonitrile solutions of substituted DCNQI's with wires of copper or silver, the sparingly soluble anion radical salts deposit as crystals of 1-30 mm length in many cases. These salts have been shown to be identical with those grown by electroreduction.

9 ALLOYS FROM DCNQI RADICAL ANION SALTS

Since the space group $I4_1/a$ is preferred for the DCNQI-metal salts discussed so far, despite of a broad variety of 2,5-substituents, one may anticipate that alloys of DCNQI salts should exist. Indeed, numerous alloys from two different DCNQI's with copper as cation [51] can be synthesized either by electrocrystallisation or by the metal wire approach.

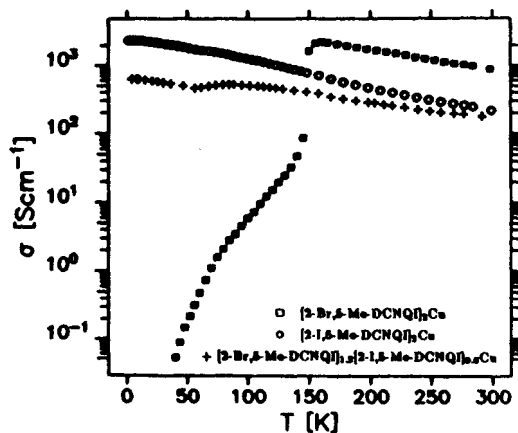
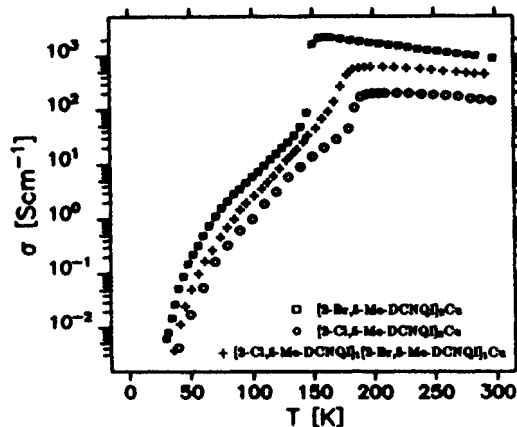


The ratio of the two components may vary from 1:1 to 1:3, very often being independent of the stoichiometry of the two DCNQI's employed. This ratio certainly does not depend directly on the difference of the reduction potentials; e. g. for $2,5\text{-Me}_2\text{-DCNQI}$ and 2-Me,5-Br-DCNQI ΔE amounts to 0.21 V = 4.8 kcal/mol. If only thermodynamic factors govern the composition of the alloy, a ratio of 1:3000 would be expected and not 1:3 as observed.

It is not yet clear if the two different DCNQI's are statistically ordered or occur in clusters within the stacks.

Alloying of two (or more) DCNQI's to one radical salt allows the manipulation of the temperature dependence of the electric conductivities together with the phase transitions as demonstrated by the two following extreme examples. As pictured in Fig. 9, the alloys can behave as a mixture of the two components.

The temperature dependence of conductivity is unchanged and the conductivity lies between those of the components [52]. By contrast, according to Fig. 10, the sharp phase transition with drastic loss of conductivity of $[2,5\text{-Br,Me-DCNQI}]_2\text{Cu}$ at 150 K is completely eliminated by alloying with $[2,5\text{-I,Me-DCNQI}]_2\text{Cu}$ (1.2 : 0.8). In this alloy the conductivity remains nearly constant down to 3 K [52]. In addition, alloys from three and even four DCNQI's have also been obtained.



Temperature dependent conductivities of alloys and their components.

Fig. 9: $[2,5\text{-Br,Me-DCNQI}]_1[2,5\text{-Cl,Me-DCNQI}]_1\text{Cu}$. Fig. 10: $[2,5\text{-Br,Me-DCNQI}]_{1.2}[2,5\text{-I-Me-DCNQI}]_{0.8}\text{Cu}$.

10 CONCLUSIONS

The scope of the general structural principle for two step redox systems outlined here is remarkable broad. It covers i. a. aromatic/quinoid Wurster and Weitz type systems. From the examples shown it is evident that redox potentials and molecular geometry, including substituents with ligand properties, can be varied within very wide limits. Within the high range of thermodynamic stability of the intermediate radical ion stage (SEM) systems can be tailored to meet specific needs. In this way, in addition to the discussed examples, new applications may be found in the areas of chemical and biochemical electron transfer catalysis as well as in the field of organic conducting materials.

Acknowledgements

I am very grateful to a great number of enthusiastic coworkers who developed this chemistry over the last 25 years, including the electrochemical investigations and the growing of numerous single crystals. Physical and structural data for the conducting organic materials were provided through excellent cooperation of physicists and crystallographers. All their names are given in the cited literature.

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