Radical Ion Salts Obtained from Substituted Ferrocene Cations and the Organic Acceptor TCNQ − Synthesis, Structure and Physical Properties

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The compounds $[Fe(C_5H_5)(C_5H_4CH_2NMe_3)][TCNQ]$ (**1**), $[Fe(C_5H_5)(C_5H_4CH_2NMe_3)][TCNQ]_2{\cdot}MeCN$ (**2**) and $[Fe(C_5H_5)(C_5H_4CH{=}CH\text{-}p\text{-}C_5H_4NMe)][TCNQ]$ (**3**) have been obtained from reaction of the corresponding ferrocene iodide and TCNQ or LiTCNQ. Their crystal structures have been determined, showing that **1** and **3** have only mononegative TCNQ radicals forming one-dimensional stacks. In compound **3** the pyridine substituent also overlaps with the stacked TCNQ. The formation reaction of **2** implies the reduction of neutral TCNQ by the iodide anion; in this reaction the reduction is partial and the formal charge of every TCNQ is approximately 0.5 e^- with some degree of electron delocalization. The TCNQs also overlap to form a one-dimensional stack in the solid. The three compounds are diamagnetic, indicating a strong antiferromagnetic coupling between the TCNQ spins.
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Introduction

Charge-transfer salts of substituted ferrocenes with organic polynitriles have been extensively studied following the report of the bulk ferromagnetic behavior of $[Fe(C_5Me_5)_2][TCNE]$ (TCNE= tetracyanoethylene).[1] Although this is the best known derivative several other examples show a wide range of properties and stoichiometries. For example, the previously synthesized analogue $[Fe(C_5H_5)_2][TCNE]$[2−5] has a similar crystal structure, showing 1D stacks of alternating ferrocene and TCNE units, but it is, however, diamagnetic due to the higher oxidation potential of the unsubstituted ferrocene, which can not reduce the tetracyanoethylene. Consequently, the stack should be viewed as a charge-transfer complex for $[Fe(C_5H_5)_2][TCNE]$, with essentially neutral ferrocene and TCNE molecules but as an ionic salt for $[Fe(C_5Me_5)_2][TCNE]$, with alternating ferrocenium cations and $TCNE^-$ anions.[6]

The derivative with TCNQ (7,7,8,8-tetracyanoquinodimethane), $[Fe(C_5Me_5)_2][TCNQ]$, exhibits an equivalent structure, with alternating ions along the stack, and shows metamagnetic behavior.[7−8] Another phase with the same composition shows isolated dimeric $[TCNQ]_2^{2-}$ anions, with paramagnetic behaviour,[9] and a third phase with ferromagnetic behavior has a packing similar to that of the metamagnetic phase.[10] Another derivative, of formula $[Fe(C_5Me_5)_2][TCNQ]_2$, is conducting and shows a one-dimensional stack of acceptors.[11]

This variety of structural motifs and properties shows how subtle changes in electronic density or in the interionic interactions can influence the bulk properties of the material. A degenerate ground state is a necessary but not sufficient condition to obtain cooperative magnetic properties, implying the use of symmetrical ferrocenes.[12] In this way examples of ferromagnetic coupling in the stacks but without three-dimensional ferromagnetic ordering have been found in $[Fe(C_5Me_4H)_2][TCNE]$,[13] $[Fe(C_5Me_4H)_2][TCNQ]$,[13] $[Fe(C_5Me_5)_2][TCNQI_2]$,[14] or $[Fe(C_5Et_5)_2][TCNQ]$.[15] By using the stronger acceptor perfluorotetracyanoquinodimethane ($TCNQF_4$), dimerization of the anion radical similar to that in the paramagnetic phase of $[Fe(C_5Me_5)_2][TCNQ]$[9] has been observed for $[Fe(C_5Me_5)_2][TCNQF_4]$[16] and $[Fe(C_5Et_5)_2][TCNQF_4]$.[17]

Contrarily, with less symmetrically substituted ferrocenes the steric effects and intermolecular interactions determine

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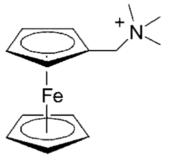
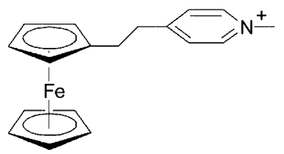
the structural motif and the crystal packing. In this way several examples of TCNQ derivatives have been obtained. The bridged ferrocenyl $[Fe(C_5H_4)_2(CH_2)_3][TCNQ]_2$ shows dimeric anions $[TCNQ]_2^-$ stacked in non-uniform columns.[18] Substituted ferrocenes having π delocalization can overlap the π system of the TCNQ, orientating the acceptor molecules in the stack. Thus, for $[Fe(C_5H_4R)_2][TCNQ]_2$, R = $CH{=}CHC_6H_4$-*p*-SMe, the crystal structure is described as an alternating stack of TCNQ and the phenyl rings of the ferrocene substituents, giving rise to an insulating, diamagnetic derivative.[19] Similar structural features are found in $[Fe(C_5H_5)(C_5H_4CH{=}CH\text{-}9\text{-}C_{16}H_9)][TCNQ]$ with pyrene acting as both a substituent on the cyclopentadienyl ring and overlapping with the TCNQ, which remains essentially neutral.[20]

Of more interest, structurally, are compounds obtained with octamethylferrocenyl thioethers, $[Fe(C_5Me_4SR)_2]$, R = Me, *t*Bu, and TCNQ or $TCNQF_4$,[21] of which $[Fe(C_5Me_4SMe)_2]_3[TCNQ]_7$ and $[Fe(C_5Me_4StBu)_2][TCNQ]_3$ show a TCNQ stack with electronic delocalization and semiconducting behaviour, while $[Fe(C_5Me_4SR)_2][TCNQF_4]$ derivatives consist of anionic dimers $[TCNQF_4]_2^{2-}$.

In designing molecular solids by controlling the crystal packing the distribution of electrostatic interactions is important. In this way we have studied the reactions of positively charged substituted ferrocenes with either neutral or anionic TCNQ. The cationic ferrocenes used are $[Fe(C_5H_5)(C_5H_4CH_2NMe_3)]^+$ and $[Fe(C_5H_5)(C_5H_4CH{=}CH\text{-}p\text{-}C_5H_4NMe)]^+$, both as iodide salts.





Our objective is to use these ferrocenes to build up a net of positive charges that will control the TCNQ stacking through electrostatic interactions. The size and orientation of the ferrocene cations can control the number of TCNQ units that will stack, thus inducing either the localization or the partial delocalization of electronic charges on the TCNQs. We have previously observed several examples of this modulation of charges, which gives rise to different degrees of electronic delocalization that depend on the size and packing of the counterion.[22−23]

We chose ferrocene cations as iodide salts so as to use the counterion to change the oxidation state of the TCNQ molecules involved; the half-reaction potential I_2/I^- is similar to that of TCNQ and the equilibrium $TCNQ^0 + I^- \rightleftarrows TCNQ^- + 1/2I_2$ can easily be displaced in either direction, depending on factors such as differences in solubilities of the products formed or addition of any reagents to the reaction mixture. Thus, the reaction on the right-hand side of the equilibrium is the usual method of preparing the anion radical as its lithium salt.[24] We have used the reverse reaction in forming $[Cu(cyclam)(TCNQ)_2][TCNQ]$ (cyclam: 1,4,8,11-tetraazacyclotetradecane), which has one neutral and two anionic TCNQ units, from $[Cu(cyclam)(TCNQ)_2]$ and I_2.[25]

The cationic charge in the ferrocene allows us to obtain derivatives of anionic TCNQ, either by iodide metathesis or by reduction from the neutral acceptor, but without any charge transfer that implies the iron atom.

Results and Discussion

The metathesis reaction of $[Fe(C_5H_5)(C_5H_4CH_2NMe_3)]^+I^-$ and LiTCNQ involves displacement of the iodide anion and crystallization of $[Fe(C_5H_5)(C_5H_4CH_2NMe_3)][TCNQ]$ (**1**). However, in the reaction of the same ferrocene salt with neutral TCNQ partial reduction of the organic molecule occurs and the derivative $[Fe(C_5H_5)(C_5H_4CH_2NMe_3)][TCNQ]_2\cdot MeCN$ (**2**) is formed. Since the reaction takes place in a 1:1 ratio only half of the TCNQ molecules are reduced by the iodide.

When the ferrocene salt $[Fe(C_5H_5)(C_5H_4CH{=}CH\text{-}p\text{-}C_5H_4NMe)]^+I^-$ is used $[Fe(C_5H_5)(C_5H_4CH{=}CH\text{-}p\text{-}C_5H_4NMe)][TCNQ]$ (**3**) is always obtained, either by reaction with LiTCNQ or with neutral TCNQ. In contrast to the formation of **2**, the reaction between this ferrocene salt and neutral TCNQ implies the complete reduction of the organic acceptor.

Crystal Structure Determinations

Crystal structure studies of solid compounds **1**−**3** show that they are built up of cationic ferrocene and anionic TCNQ units. Table 1 contains the more relevant bond lengths and angles.

Compound **1** crystallizes in the orthorhombic system, space group *Pna*2$_1$. An ORTEP view showing the labeling scheme is given in Figure 1. The structure consists of rows of TCNQ anions separated by the ferrocene cations. No close contacts between anions and cations were observed. Fe−C bond lengths are in the range 1.95(3)−2.06(2) Å and the Fe···Cp plane distances are 1.611(3) and 1.628(4) Å, the shorter distance corresponding to the substituted cyclopentadienyl ring. The Cp rings form an angle of 4.0(6)° and are within 6.7(6)° of the eclipsed conformation. All these features are similar to those previously reported for the $[Fe(C_5H_5)(C_5H_4CH_2NMe_3)]^+$ cation.[26−29]

All the TCNQ groups in the unit cell are crystallographically equivalent. Since they must neutralize the positive charges on the ferrocenes, all the TCNQ should be radical anions, bearing one negative charge per molecule. The charge located on every TCNQ can be related with the observed variation in the C−C bond lengths on reduction. The extra electron occupies an antibonding orbital and this is mainly reflected in a lengthening of the quinoid bond. A linear relation between the C−C bond lengths and the electronic charge held on the TCNQ has been established.[30−31] The values observed for compound **1** agree with the mononegative state expected for the TCNQ units. These radical-anions form a regular one-dimensional stack along the *c* axis (Figure 2) by overlap of the π clouds

Table 1. TCNQ bond lengths [Å] for compounds **1−3**

1		**2**		**3**	
N2−C15	1.137(8)	N2−C15	1.144(6)	N3−C37	1.143(5)
N3−C17	1.144(8)	N3−C16	1.148(6)	N4−C39	1.144(5)
N4−C25	1.149(8)	N4−C25	1.145(6)	N5−C47	1.144(5)
N5−C26	1.145(11)	N5−C26	1.150(7)	N6−C48	1.151(6)
C15−C16	1.413(9)	C15−C17	1.434(8)	C37−C38	1.420(6)
C16−C17	1.439(10)	C16−C17	1.413(7)	C38−C39	1.415(6)
C16−C18	1.416(8)	C17−C18	1.392(6)	C38−C40	1.409(5)
C18−C19	1.420(8)	C18−C19	1.438(6)	C40−C41	1.417(5)
C18−C23	1.413(10)	C18−C23	1.432(6)	C40−C45	1.415(5)
C19−C20	1.358(7)	C19−C20	1.351(6)	C41−C42	1.359(5)
C20−C21	1.414(8)	C20−C21	1.419(6)	C42−C43	1.418(5)
C21−C22	1.407(8)	C21−C22	1.433(6)	C43−C44	1.415(5)
C21−C24	1.421(9)	C21−C24	1.381(6)	C43−C46	1.418(5)
C22−C23	1.370(9)	C22−C23	1.342(6)	C44−C45	1.358(5)
C24−C25	1.413(9)	C24−C25	1.428(8)	C46−C47	1.413(6)
C24−C26	1.422(10)	C24−C26	1.434(8)	C46−C48	1.417(6)
		N6−C27	1.146(6)	N7−C49	1.124(6)
		N7−C28	1.140(6)	N8−C51	1.144(6)
		N8−C37	1.143(7)	N9−C59	1.145(6)
		N9−C38	1.136(7)	N10−C60	1.146(6)
		C27−C29	1.415(8)	C49−C50	1.421(6)
		C28−C29	1.407(8)	C50−C51	1.407(7)
		C29−C30	1.406(6)	C50−C52	1.418(6)
		C30−C31	1.430(6)	C52−C53	1.416(5)
		C30−C35	1.413(6)	C52−C57	1.415(6)
		C31−C32	1.355(6)	C53−C54	1.365(6)
		C32−C33	1.423(6)	C54−C55	1.406(6)
		C33−C34	1.427(7)	C55−C56	1.423(5)
		C33−C36	1.387(7)	C55−C58	1.407(6)
		C34−C35	1.355(6)	C56−C57	1.357(6)
		C36−C37	1.432(8)	C58−C59	1.423(6)
		C36−C38	1.446(8)	C59−C60	1.408(7)

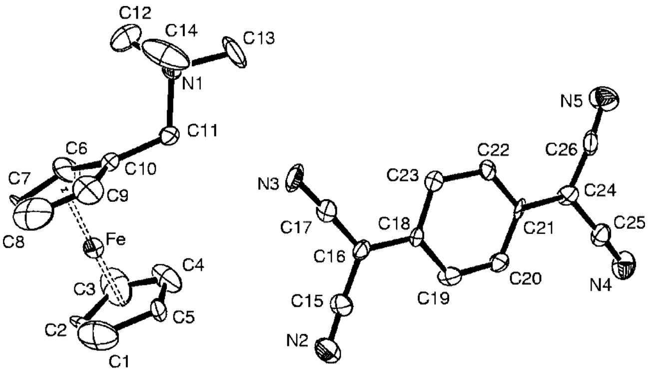


Figure 1. ORTEP view (20% probability ellipsoids) and atom labeling of compound **1**

of adjacent groups, in the ring over external bonds mode, with an intrastack separation of 3.27(1) Å. Such overlap in a regular stack of anion radicals has previously been observed;[32−33] however, dimerization is much more common, to form the dianion $[TCNQ]_2^{2-}$ which can either be isolated or form part of a non-uniform stack with alternating short and long intermolecular distances.[34−51]

Compound **2** crystallizes in the triclinic system, space group $P\bar{1}$. The asymmetric unit consists of one ferrocene cation, two TCNQ groups and one crystallization acetonitrile molecule. Figure 3 shows the numbering scheme.

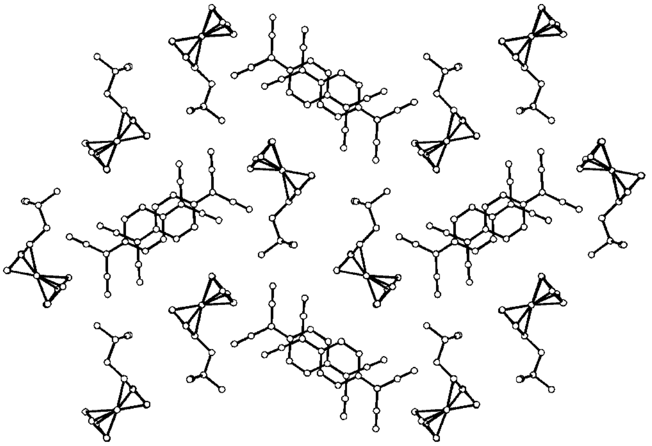


Figure 2. View of the crystal packing of compound **1** in a direction perpendicular to the *c* axis

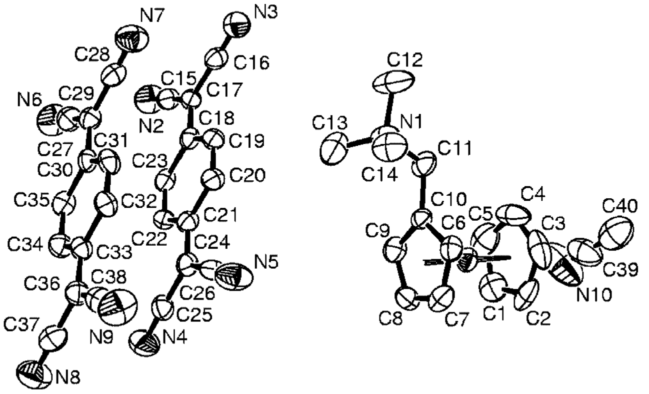


Figure 3. ORTEP view (30% probability ellipsoids) and atom labeling of compound **2**

The ferrocene cation shows similar features to those of compound **1**, with Fe−C bond lengths in the range 2.014(6)−2.048(4) Å and Fe···Cp plane distances of 1.634(6) and 1.658(5) Å − again the shortest distance corresponds to the substituted ring. The Cp rings are almost parallel, with 1.7(1)° of deviation, and are within 7.8(1)° of the eclipsed conformation.

There are two crystallographically different TCNQ molecules, types A and B. According to the Kistenmacher relation between C−C bond lengths and the negative charge located on every TCNQ,[31] we have found that TCNQ A has an approximate charge of 0.4 e^- while TCNQ B bears, approximately 0.6 e^-, i.e. two TCNQ neutralize the positive charge on the substituted ferrocene. The TCNQs are stacked in the ring over external bond mode (Figure 4) to form a one-dimensional row with the pattern ···TCNQ A···TCNQ B···TCNQ B···TCNQ A···TCNQ A···. The TCNQ As are related by inversion centers located between adjacent units. The same applies for TCNQ Bs. The angle between least-squares ring planes of TCNQ A and TCNQ B is 1.8(1)°. Thus, all the TCNQs in the stack are practically parallel since all TCNQ As are parallel, due to symmetry, as occurs with TCNQ Bs.

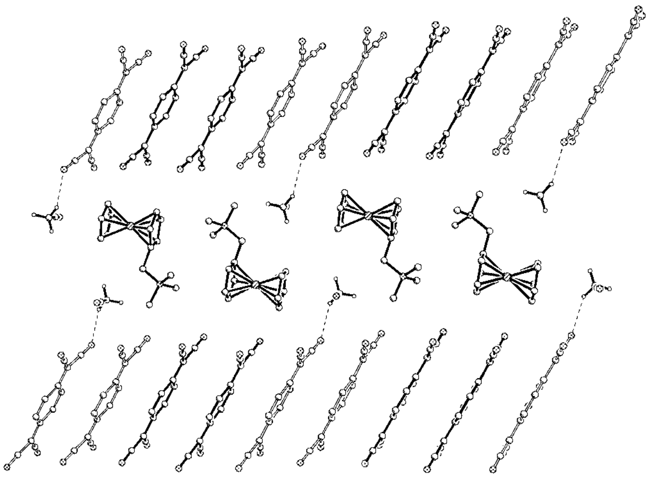


Figure 4. TCNQ stack in compound **2**; TCNQ A is depicted in black and TCNQ B in white, showing close contacts with the acetonitrile solvent molecules

The very similar intermolecular distances give rise to a quasi-uniform stack; with the shortest distance being between least-squares ring planes of TCNQ A and TCNQ B, 3.27(1) Å, followed by the separation between adjacent TCNQ As, 3.32(1) Å, and that between two TCNQ Bs, 3.34(1) Å. We can reconcile this stack with several reported examples of regularly spaced TCNQ$^{0.5-}$.[52−56]

The ferrocene cations and the acetonitrile molecules are located between the parallel rows of TCNQ. The acetonitrile molecule binds TCNQ A and B that belong to neighboring rows at the distances 3.268(9) and 3.445(8) Å

The (ethylenepyridinium)ferrocene **3** crystallizes in the triclinic system, space group $P\bar{1}$. The asymmetric unit is composed by two crystallographically independent ferrocene cations and two independent TCNQ anions. The numbering scheme is shown in Figure 5.

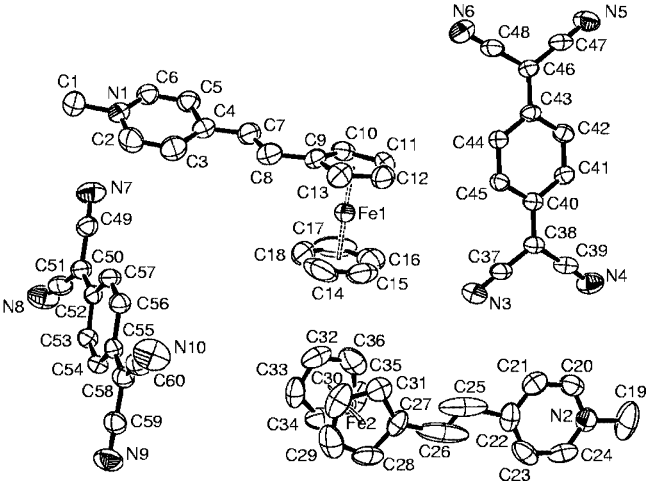


Figure 5. ORTEP view (30% probability ellipsoids) and atom labeling of compound **3**

Both ferrocene units show equivalent features and, in general terms, are similar to the trimethylammoniummethyl derivatives in **1** and **2**. For the two ferrocene units the Fe−C bond lengths are in the range 1.997(6)−2.039(4) and 2.016(5)−2.028(5) Å, respectively, with Fe···Cp plane distances of 1.630(6) and 1.647(5) Å for the first ferrocene (labeled A) and 1.642(5) and 1.649(5) Å for the second (labeled B); in both cases the shortest distance corresponds to the substituted ring. The Cp rings are almost parallel, deviating by 1.1(1)° in ferrocene A and 2.9(1)° in ferrocene B, and are, respectively, within 9.2(1)° and 22.3(1)° of the eclipsed conformation. Both ferrocene cations are almost perpendicular, forming an angle of 84(1)° between them.

There are also two crystallographically different TCNQ molecules (A and B) in the crystal; both are negatively charged to neutralize the ferrocene cations and thus bear one electron per molecule, as the C−C distances confirm.

The TCNQ As are dimerized by a ring over external bond overlap, with a distance between mean planes of 3.12(1) Å. These dimers are stacked to form a non-uniform one-dimensional chain (Figure 6) by overlap of the exocyclic dicyanomethyl groups of one end of the molecule, with a shortest distance of 3.35(1) Å. The other extreme of each TCNQ overlaps with the pyridine ring of the ferrocene B cations, showing a shortest contact of 3.33(2) Å. Overlap with the substituent π systems has been observed in other ferrocene derivatives, but only for neutral TCNQ[19,20] or isolated radical anions,[57] leading in all cases to alternated stacks of donors and acceptors. In our case, such overlap occurs at one end only of each TCNQ, thus allowing the formation of the TCNQ stack.

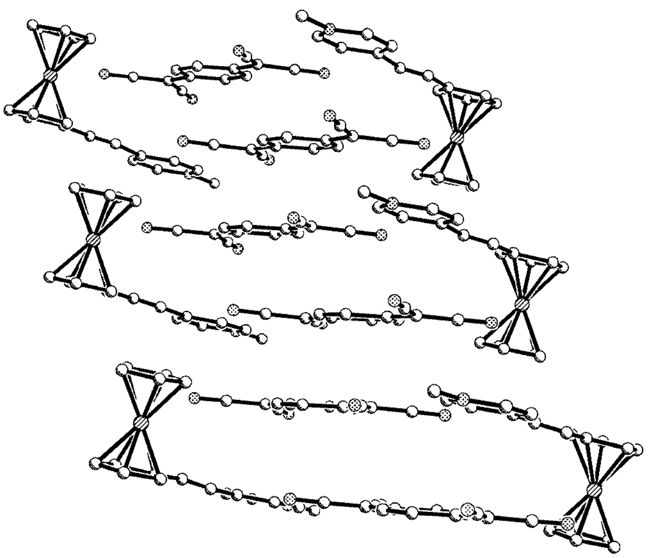


Figure 6. View of the stack of TCNQ A in compound **3** showing the overlap with the pyridine rings (see text)

In the crystal packing, zig-zagged TCNQ chains are stacked parallel to each other, leaving holes that are occupied by the ferrocene cations. The other TCNQs, type B, form isolated dimers $[TCNQ]_2^{2-}$, with an interplanar spacing of 3.05(1) Å, and ring over external bond overlap. These dimers are oriented almost perpendicularly to the TCNQ A chains, forming an angle of 88.4° between the respective molecular planes (Figure 7).

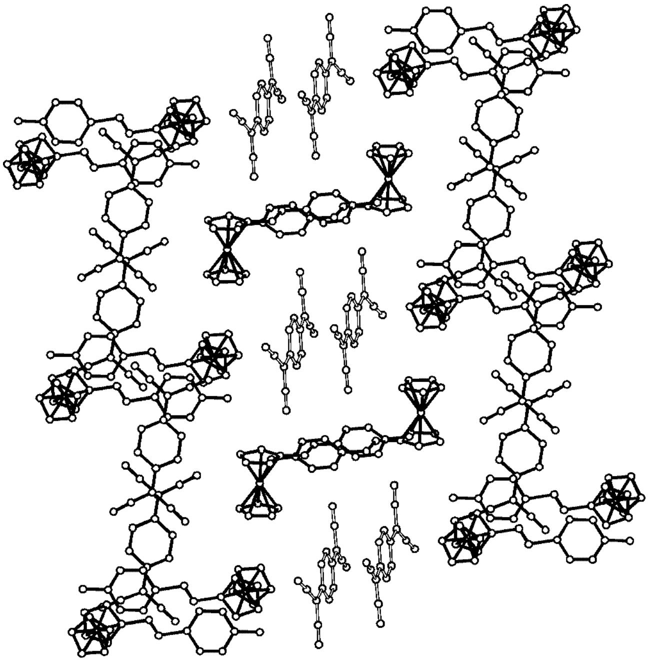


Figure 7. Crystal packing in compound **3**; TCNQ A is in black and TCNQ B in white

Finally the ferrocene A cations are located in the channels left by the stacks of TCNQ A and the dimers of TCNQ B (Figure 7). This ferrocene is perpendicular to all of the TCNQs and no π interactions are found.

Spectroscopic Studies

IR spectra are a very useful source of information about the formal oxidation state of the TCNQ molecules. The most characteristic bands[58−60] are ν(CN), which appears at 2228 cm^{-1} in neutral TCNQ and is shifted to lower frequencies and split (2194/2177 cm^{-1}) in the radical anion, the $\nu_{20}(b_{1u})$ and the $\nu_4(a_g)$ bands assignable to C−C stretching modes and which appear at 1530 and 1424 cm^{-1} in the neutral TCNQ and are shifted to 1507 and 1386 cm^{-1} in the anionic TCNQ. The last significant band is $\nu_{50}(b_{3u})$, an out-of-plane bending mode appearing at 860 cm^{-1} in neutral and 824 cm^{-1} in anionic TCNQ. The last three vibration modes are shifted almost linearly to lower frequencies with increasing negative charge on the TCNQ and are, thus, a good indication of its oxidation state.[60]

In compound **1** these bands appear at 2188, 2173, 2161, 2149, 1508, 1356 and 821 cm^{-1} respectively, clearly indicating the mononegative nature of TCNQ suggested by the crystal structure. The large split of the ν(CN) bands can be attributed to the non-equivalence of the TCNQ nitrile groups that are crystallographically different. Similar features are observed in the IR spectrum of compound **3**, with bands at 2184, 2168, 2146, 1506, 1350 and 823 cm^{-1}.

In contrast, the IR spectrum of compound **2** is dominated by the tail of an electronic absorption with broad vibrational bands superimposed on it − a typical feature of derivatives with a degree of electronic delocalization along the TCNQ stacks.[61−62] This electronic absorption is observed in the Vis/NIR spectrum centered at 4500 cm^{-1} and can be assigned to the low energy charge-transfer transition, CT_2, between radical-anion and neutral TCNQ.[63] The most significant TCNQ IR bands appear at 2197, 2156, 1519, 1410 and 833 cm^{-1}. Assuming a linear relation between the electronic charge in the TCNQ and the frequency shift of ν_{20} we can attribute a formal charge of 0.5 e^- per TCNQ, in agreement with the assignation made by crystallographic means. The other bands, ν_4 and ν_{50}, do not show this linear shift although their intermediate values clearly indicate that the TCNQ are in an intermediate oxidation state.[22−23]

Due to the partial electronic delocalization compound **2** is weakly semiconducting, with a room temperature conductivity of 10^{-4} S cm^{-1} (measured in a powder pressed sample). Conversely, compounds **1** and **3**, with only the mononegative radical anion present, have conductivities below 10^{-6} S cm^{-1} at room temperature.

The three compounds are diamagnetic, implying that the radical anions formed must interact antiferromagnetically with adjacent molecules in order to pair their spins. This is common for TCNQ derivatives that form the dimeric dianion $[TCNQ]_2^{2-}$.[25,48] The diamagnetism of compound **2** is surprising since the electronic delocalization is usually reflected in the magnetic susceptibility, either as a weak Pauli paramagnetism[64] or as the contribution of an $S = 1/2$ spin 1D system with antiferromagnetic coupling.[23,65] The unexpected diamagnetism of **2** could suggest a higher localization of the TCNQ unpaired electrons, giving rise to a stronger antiferromagnetic coupling in the bulk.

Conclusion

Cationic ferrocenium salts react with LiTCNQ by a metathesis process to form the corresponding [Ferrocene][TCNQ] derivatives **1** and **3**, which behave as typical salts of the anion radical $TCNQ^-$, forming dimeric anions, $[TCNQ]_2^{2-}$, that overlap with neighbouring dimers to give a non-uniform one-dimensional stack. A typical stack is found in **1**, but that of **3** is highly unusual as the TCNQ radical anions also overlap with the π-delocalized system of the pyridinium substituent. Such overlap is common in integrated systems of neutral TCNQ but extremely rare with anionic TCNQ, and in the reported cases the integrated stack is formed by dimeric $[TCNQ]_2^{2-}$ [66] or trimeric $[TCNQ]_3^{2-}$ [67] overlapping with the cationic donor. To the best of our knowledge there are no previous reports of overlap between 1D-stacked TCNQ and the counterion.

Compound **2** is also formed by rows of stacked TCNQ separated by the cationic ferrocenes, with only electrostatic interactions between them. The TCNQ are, however, partially reduced as a consequence of the crystal packing conditions, which will probably determine the equilibrium between the TCNQ and the iodide anion. Figure 4 shows that the TCNQ stack leaves space for two ferrocene cations and two acetonitrile molecules. If these solvent molecules were removed the ferrocene could be closely packed, occupying the space equivalent to three TCNQ. The resulting stoichiometry [ferrocene]$_2$[TCNQ]$_3$ is also well known,[22,51] with structures described as trimeric dianions [TCNQ]$_3^{2-}$ stacked in infinite rows. Inside the trimer every TCNQ bears approximately $^2/_3$ of an electron and the difference between this oxidation state and that found on our compound (0.5 of an electron) is small and would not determine the extent of TCNQ reduction. Therefore, we attribute the partial reduction to the need to accommodate two TCNQ groups in the stack per ferrocene and acetonitrile molecules.

The complete displacement of the reaction with iodide in the formation of **3** by either metathesis with LiTCNQ or by reduction of neutral TCNQ supports the influence of the crystal structure on the TCNQ reduction. The driving force here is the overlap between the TCNQ anions and the pyridinium substituent in the ferrocenes. Figure 6 shows that TCNQ and pyridinium alternate along the stack and that consecutive TCNQ anions overlap with ferrocenes of different rows. This packing does not allow room for extra TCNQ molecules and thus the reduction with iodide must be complete since there is only now one TCNQ per ferrocenium cation. The remaining cations and TCNQ anions in this structure are oriented perpendicularly relative to the stacks, forcing the isolation of both the anions as dimeric [TCNQ]$_2^{2-}$ and the cations, and leaving electrostatic interactions as the only force that holds them together.

Experimental Section

General Remarks: All reactions were carried out under an inert gas. LiTCNQ was obtained according to a published method[24] and its purity checked by elemental analysis. Elemental analyses were carried out by the Servicio de Microanálisis of the Universidad Complutense de Madrid. Infrared spectra were recorded as KBr pellets with a Nicolet Magna-550 FT-IR spectrophotometer. Magnetic susceptibility experiments were made on polycrystalline samples using a Quantum Design SQUID magnetometer, Model MPMS-5S in the temperature range 2−250 K and at constant field of 0.5 T. Electrical conductivity measurements at room temperature were performed by the two points method in pressed powdered samples.[68]

[Fe(C$_5$H$_5$)(C$_5$H$_4$CH$_2$NMe$_3$)][TCNQ] (1): [Fe(C$_5$H$_5$)(C$_5$H$_4$CH$_2$NMe$_3$)](I) (135 mg; 0.35 mmol) was dissolved in methanol/water (20 mL of 3:1 mixture) and then LiTCNQ (148 mg; 0.70 mmol), dissolved in methanol (35 mL), was slowly added to the double layer. After 3 d, dark blue crystals of the title compound appeared, which were filtered off and washed with methanol. The crystals were suitable for X-ray analysis. Yield: 104 mg, 64%. IR (KBr): $\tilde{\nu}$ = 2188, 2173, 2161, 2149, 1582, 1508, 1485, 1369, 1356, 1324, 1179, 881, 843, 821, 480 cm^{-1}. $C_{26}H_{24}FeN_5$ (462.3): calcd. C 67.6, H 5.2, N 15.1; found C 67.4, H 5.1, N 14.9.

[Fe(C$_5$H$_5$)(C$_5$H$_4$CH$_2$NMe$_3$)][TCNQ]$_2$·MeCN (2): A solution of TCNQ (79 mg; 0.39 mmol) in acetonitrile (40 mL) was mixed with a solution of [Fe(C$_5$H$_5$)(C$_5$H$_4$CH$_2$NMe$_3$)](I) (150 mg; 0.39 mmol) in acetonitrile/water (15 mL of a 2:1 mixture). The resulting green solution was concentrated to half of its original volume and cooled to −20 °C. Dark-violet platelets then appeared after 2 d. Yield: 48 mg, 35%. IR (KBr): $\tilde{\nu}$ = 2197, 2156, 1558, 1519, 1469, 1410, 1298, 1104, 1045, 870, 833, 683, 593, 480 cm^{-1}. $C_{40}H_{31}FeN_{10}$ (707.6): calcd. C 67.9, H 4.4, N 19.8; found C 67.8, H 4.4, N 19.6.

[Fe(C$_5$H$_5$)(C$_5$H$_4$CH=CH-*p*-C$_5$H$_4$NMe)][TCNQ] (3): This was obtained by reaction in a double layer of [Fe(C$_5$H$_5$)(C$_5$H$_4$CH=CH-*p*-C$_5$H$_4$NMe)](I) (150 mg; 0.35 mmol) in methanol (15 mL) with either an acetonitrile (20 mL) solution of TCNQ (71 mg; 0.35 mmol) or a methanolic (30 mL) solution of LiTCNQ (147 mg; 0.70 mmol). In both cases dark red prismatic crystals suitable for X-ray were obtained after 1 week. Yield: 55 mg, 31%. IR (KBr): $\tilde{\nu}$ = 2184, 2168, 2146, 1646, 1607, 1577, 1506, 1475, 1458, 1370, 1350, 1195, 1180, 950, 879, 823, 716, 475 cm^{-1}. $C_{30}H_{22}FeN_5$ (508.4): calcd. C 70.9, H 4.4, N 13.8; found C 70.6, H 4.4, N 13.4.

X-ray Crystallographic Studies: A summary of the relevant data collection parameters is given in Table 2. Data were collected with a Bruker AXS-CCD, Enraf−Nonius CAD-4, and Nonius CCD[69] for **1**, **2** and **3**, respectively, by using graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å) at room temperature. The structures were solved by Patterson or direct methods and refined by full-matrix least squares on F^2 with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were included with fixed isotropic contributions at their calculated positions determined by molecular geometry. The calculations were carried out with SHELX-97 software package.[70] CCDC-201484 (**1**), -201485 (**2**), -201486 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Crystal and refinement data for compounds **1−3**

	1	**2**	**3**
Empirical formula	$C_{26}H_{24}FeN_5$	$C_{40}H_{31}FeN_{10}$	$C_{30}H_{22}FeN_5$
Formula mass	462.3	707.6	508.3
Crystal system	orthorhombic	triclinic	triclinic
Space group	$Pna2_1$ (no. 33)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a [Å]	16.909(1)	10.562(2)	7.516(2)
b [Å]	20.748(1)	11.277(2)	14.913(3)
c [Å]	6.541(1)	15.328(3)	22.561(5)
α [°]	90	101.09(3)	100.23(3)
β [°]	90	100.74(3)	98.40(3)
γ [°]	90	91.25(3)	94.88(3)
Z	4	2	4
V [Å^3]	2294.7(4)	1757.1(6)	2445.8(10)
$D_{\text{calcd.}}$ [Mg·m^{-3}]	1.338	1.337	1.381
μ [cm^{-1}]	6.80	4.74	6.45
θ range [°]	1.55−24.97	1.84−20.95	1.52−24.97
Reflections collected	4082	7084	4480
Independent reflections	2041	3711	4105
Refined parameters	289	461	649
Goodness of fit	1.037	1.077	1.055
Absolute structure parameter	0.04(11)		
$R1$[a] [$I > 2\sigma(I)$]	0.0404	0.063	0.0359
$wR2$[b] [$I > 2\sigma(I)$]	0.0812	0.1083	0.095

[a] $R1 = \Sigma(|F_o| - |F_c|)^2/\Sigma F_o^2$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

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