Persistent π radical cations: self-association and its steric control in the condensed phase

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π Radical cations, which are highly reactive in general, can be made persistently stable by appropriate structural modification with heteroatoms, π-conjugated systems, and alkyl substituents. Many of these π radical cations undergo self-association in the condensed phase. The steric control of such self-association of stabilized π radical cations is the subject of the present article. Such an association can result in the formation of π- and/or σ-dimers. The π-dimerization in particular is now considered as an important intermolecular interaction for model studies of a charge-transport phenomenon in positively doped conducting polymers. On the other hand, the intermolecular interactions can be suppressed when the π-system is modified with sterically demanding structural units, for example, by annelation with bicycloalkene frameworks. This structural modification not only brings about unusual stabilization of the radical cations but provides valuable information on the electronic structure/properties of the positively charged π-systems in a segregated state.

1 Introduction

Radical cations are open-shell species bearing a positive charge, which are generally highly reactive in ionic reactions (nucleophilic addition, ionic cleavage, *etc.*) and/or radical reactions (radical coupling, cleavage, electron transfer, *etc.*).[1,2] At the same time, the formation, recombination and charge transport of radical cations (and anions) play essential roles in the operation mechanism of organic electronics,[3,4] which have attracted growing interest as electronic devices for the next generation.[5]

Therefore, studies on the structural characteristics of stable radical cations and their mode of intermolecular interaction, such as self-association, in the condensed phase should not only deepen understanding of the chemistry of this type of unique organic species but provide fundamental information for constructing robust and efficient organic electronic devices.

Radical cations of π-conjugated systems can be generated by chemical or electrochemical one-electron oxidation of the π-system, *i.e.*, removal of an electron from the HOMO, which is located at a relatively high energy level in the case of highly conjugated systems owing to a number of occupied π-MOs. Although the unpaired electron of such π radical cations is delocalized over the whole π-conjugated system, most π radical cations generated in solution are only of limited persistence since they are susceptible to various follow-up reactions.[1,2] However, they can become persistent in solution by extension of the π-conjugated system and/or multiple substitution with electron-donating groups at appropriate positions.

For a considerable number of persistent π radical cations, reversible dimerization in solution has been demonstrated by means of UV-vis-NIR and/or ESR spectroscopy.[4] The dimerization results in the formation of a σ-bonded dication (σ-dimer) in which a new single bond is formed between radical centers or of a cofacial π-complex (π-dimer). Although the spectroscopic studies provide information such as change in magnetic properties and thermodynamic parameters concerning the self-association in solution, the critical question of the nature of the bonding (σ or π) is sometimes difficult to solve. One approach to unambiguously clarify this problem is to determine the crystal structures of radical cation salts by X-ray

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crystallography and to compare the spectrum in the solid state with that in solution.

Among the self-association of various types of π radical cations, greater attention is currently focused on that of π-conjugated cationic oligomers. Hitherto many radical cations of π-conjugated oligomers have shown a tendency to cause self-association, which is now considered to be the most general and important intermolecular interaction in the conduction mechanism of the p-doped states of these oligomers and polymers. π-Conjugated oligomers are also of great importance as a part of molecular-scale electronics.[6] In order to deepen understanding of the behavior of the cationic states of these oligomers, it is also important to clarify the properties of the "non-associated", unimolecular structure of these oligomers, which are made possible under conditions that suppress intermolecular interaction.

In this perspective article, we will focus on the structures of persistent π radical cations which can control their intermolecular interaction, i.e., σ- and π-dimer formations, in the condensed phase. Because of space limitations, we will confine our discussion mainly to the relationship between the structure of π radical cations and their reactivity in "self-association". Apart from "self-association", the π radical cation is known to form a 1 : 1 π-complex with the corresponding neutral molecule, namely the "charge-resonance complex" or "dimer radical cation".[7–10] Although such an interaction is important as a fundamental property of radical cations, this subject will not be discussed in the present article. Furthermore, only radical cations of the stoichiometric types synthesized by chemical one-electron oxidation will be discussed here, although radical cation salts of mixed-valence types are often obtained by electrocrystallization.[11] In particular, we will place emphasis on the isolable examples analyzed with X-ray crystallography in order to avoid ambiguity concerning structural features and mode of interaction.

The reactivity of radical cations varies in a very wide range from reaction with a diffusion-controlled rate to existence as stable and isolable species. We define the "persistent radical cation" as the species stable at room temperature for at least several hours in the solution phase. In principle, radical cations with such stability should be isolable if appropriate counter anions of low nucleophilicity are used under an inert atmosphere at low temperatures with special precautions taken and special experimental techniques used.

2 Substituents that stabilize π radical cations

Among the heteroatom substituents that stabilize π radical cations, such as R_2N-, RS- and RO-groups, the amino groups are generally the most powerful and various persistent radical cations substituted with amino groups have long been known.[1] For example, radical cation salts of p-diaminobenzenes 1, known as Würster's salts, were first isolated 125 years ago[12] and those of triarylamine 2 were first prepared almost 100 years ago.[13] Their remarkable stability is apparently due to the high donor ability of nitrogen atom(s) with a high-lying n-orbital of an unshared electron-pair.


1 a: R = Me
b: R = H

2 R' = Me, Br
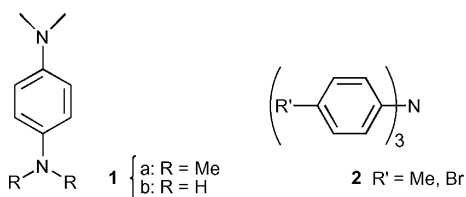
Substitution with alkylthio group(s) is also effective, but a decrease in solubility can become problematic when the number of substituents increases. The alkoxy group may be more advantageous in this regard. Various π-type substituents can stabilize π radical cations by extension of the π-conjugated systems as a matter of course.

For alkyl substituents, in addition to electron-donating inductive effects, C–C hyperconjugation (σ–π conjugation) can stabilize the positively charged π-systems although the effect is much weaker than for heteroatom substituents or π-extension. The advantage of the σ–π conjugation of alkyl groups is that the electronic perturbation in the π-system is expected to be so small that the intrinsic electronic characteristics of the stabilized π-system are not essentially altered. C–H hyperconjugation cannot be so advantageous because it can cause ready deprotonation.

Just to show some examples, full substitution with methyl groups is effective in stabilizing π-radical cations when the π-system is equal to or larger than biphenylene; the $SbCl_6^-$ salt of the radical cation of octamethyl derivative 3 has been isolated.[10] For smaller π-systems such as hexamethylbenzene 4[14] or tetramethylthiophene 5,[15] examination by means of cyclic voltammetry indicated that the life-time of the radical cations in solution is much less than a few seconds at room temperature. This instability apparently results from deprotonation of a methyl group and the following decomposition and/or polymerization. In fact, the methyl proton in π radical cations becomes extremely acidic;[2] the pK_a value of toluene is estimated to be 43 while that of the corresponding radical cation is −20 in DMSO.[16]
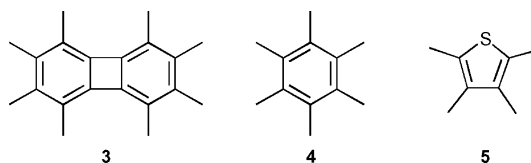
On the other hand, we found that the structural modification of various π-conjugated systems by full annelation with bicyclo[2.2.2]octene (abbreviated as BCO) units enables them to provide persistent radical cations. By the use of this method, even the simplest aromatic system, i.e., benzene 6,[17] can give the radical cation as an isolable salt, which allows an X-ray structural determination.[18] Similarly, the first successful isolation and X-ray structural determination of the radical cation salt for the non-benzenoid higher homologue, cyclooctatetraene (COT), was also accomplished using the derivative 7.[19] The extraordinary stabilizing effect of BCO units is ascribed to both thermodynamic and kinetic effects. The C–C single bond of the bicyclic framework, which is fixed at the position nearly parallel to the 2p orbital of the π-system is expected to cause effective C–C hyperconjugation (σ–π conjugation) in addition to inductive electron donation. Furthermore, the BCO units exert steric protection from nucleophiles and also the so-called "Bred's rule protection",[20] i.e., inhibition of the decomposition of the radical cation via deprotonation from the α-position (Eqn 1).

$$\tag{1}$$
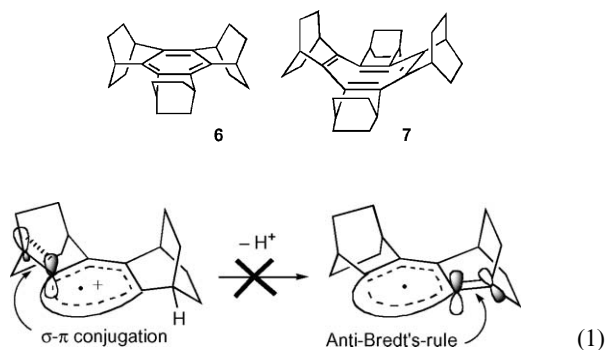
By virtue of this method, we have also isolated $SbCl_6^-$ or SbF_6^- salts of radical cations of naphthalene 8,[18,21] biphenylene 9,[18,22] fluorene 10,[23] anthracene 11,[18,24] thiophene 12,[25] 1,4-dithiin 13,[26] bithiophene 14,[27] and terthiophene 15.[27] All of their structures have been successfully determined by X-ray crystallography, except for 12.[28]

8   9   10   11

12   13   14   15
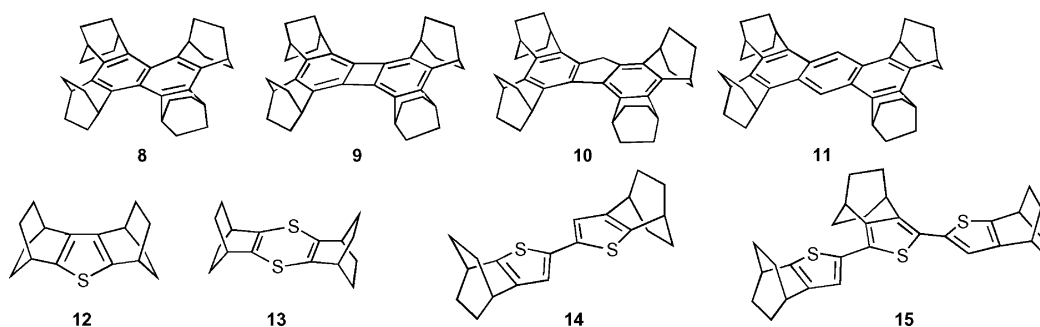
3 General properties of σ-dimers and π-dimers

As described above, the self-association of persistent radical cations can give rise to σ-dimers and π-dimers. In previous X-ray crystallographic studies, the following observation has been made concerning the structure of π radical cation salts in the solid state. While in σ-dimers, the length of a newly formed σ-bond is almost comparable to that of a normal element–element single bond, the distance between the π-planes in π-dimers is in the range 2.9–3.4 Å, which is shorter than that of normal π-stacks between neutral molecules with a van der Waals interaction. Similar σ- and π-dimerizations have been observed in the case of radical anions. For example, the radical anion of tetracyanoethylene (TCNE) can exist both as a σ-dimer and two types of π-dimers in the solid state, depending on the type of counter cation (Fig. 1).[29] Here, a favorable bond-forming interaction and repulsive electrostatic interactions are almost counterbalancing and the different packing forces derived from the different counter cations decides the structure in the solid state.[29] A similar explanation would be applicable to the self-association of radical cations.
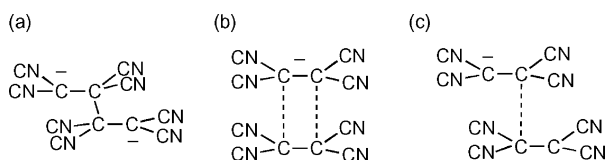

Fig. 1 Self-association modes of the TCNE radical anion: (a) σ-dimer, (b) face-to-face type π-dimer and (c) stair-like π-dimer.[29,30]

Naturally, σ-bond formation between radical centers results in the disappearance of paramagnetic properties. Combined studies of X-ray crystallography and ESR spectroscopy for many radical cations have revealed that π-dimers are also diamagnetic (*vide infra*). This can be understood when the π-dimer formation is considered as an orbital interaction between two SOMOs of an equivalent energy level (Fig. 2), resulting in a singlet electronic structure with the extensive delocalization of the interacting electrons on the whole paired molecules.[30] Thus, in the electronic spectra of π-dimers, the "π-dimer band",[31] which is not observed in the monomeric system, appears typically as the lowest-energy absorption, with a hypsochromic shift of the original band(s) of monomers due to the repulsive interaction between parallel intramolecular transition dipoles in the cofacial dimer.[32]
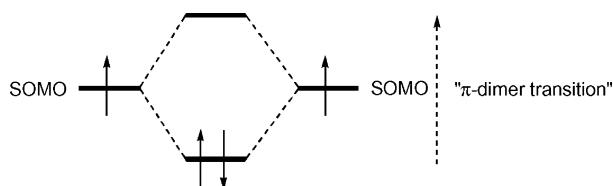

Fig. 2 Schematic orbital interaction in a π-dimer.

4 Persistent radical cations of carbon π-sytems

4.1 Benzene derivatives

As described above, Würster's salts **1** were the first isolable radical cations and their properties have been extensively investigated. The solid-state structure of perchlorate $1a^{•+}ClO_4^-$ ("Würster's blue") was determined at both room temperature and at 110 K.[33] At room temperature, each benzene plane of $1a^{•+}$ is regularly separated by a distance of 3.55 Å, while a phase transition corresponding to π-dimer formation takes place upon cooling to 110 K and the distances between benzene planes within and between the π-dimers become 3.10 and 3.62 Å, respectively. In accord with this structural change, ESR measurements revealed that $1a^{•+}ClO_4^-$ in the solid state is paramagnetic at higher temperatures and diamagnetic at lower temperatures with the transition occurring at 186 K.[34]

In the solid-state structure of bromide $1b^{•+}Br^-$ ("Würster's red"), the formation of a π-dimer was observed even at room temperature.[35] Here the radical cation stacks regularly with a distance between benzene planes of 3.105 Å and the NH_2 group is overlapped with the other benzene ring with a C–N distance of 3.20 Å (Fig. 3). In accord with this, no ESR signal was observed even at 300 K in the solid state.[36] On the other hand, variable-temperature UV-vis studies of both $1a^{•+}$ and $1b^{•+}$ in a mixed solvent of ethanol and ether (2 : 1) showed a typical spectral change corresponding to π-dimer formation, *i.e.*, appearance of a new "π-dimer band" and a hypsochromic shift of original absorption bands, upon lowering the temperature.[37] From these results, the heat of dimerization of $1a^{•+}$ ($\Delta H = -5.6$ kcal mol^{-1}) was shown to be smaller than that of $1b^{•+}$ ($\Delta H = -8.2$ kcal mol^{-1}). These solid phase and solution phase studies indicate that π-dimer formation is more facile in $1b^{•+}$ with less steric hindrance on nitrogen.
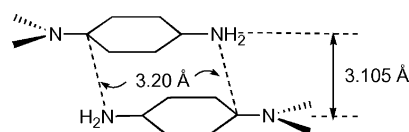

Fig. 3 Inter-plane and inter-atomic distances in the X-ray structure of $1b^{•+}Br^-$.

In contrast to these Würster's salts, the radical cation of 1,3,5-(tripyrrolidin-1-yl)benzene (**16**) generated by one-electron oxidation with AgNO₃ in acetonitrile immediately reacted to give the corresponding σ-dimer **17**, whose structure was also determined by X-ray crystallography.[38] Cyclic voltammetry showed that the oxidation potential of **16** is +0.3 V (*vs.* Ag/AgCl)[39] and an applied potential of −1.0 V is required to reductively cleave the σ-bond of dimer **17**. From these measurements, the equilibrium constant for dimerization of $16^{•+}$ to **17** is estimated to be $K_{Dimer} = 3.3 \times 10^{11}$ M^{-1}[39] and hence ΔG for the σ-dimer formation can be calculated to be −15.7 kcal mol^{-1} at 298 K.

The difference in association behavior between $1^{•+}$ and $16^{•+}$ reflects the difference in spin density on the benzene ring. The spin can delocalize to two nitrogen atoms in the quinoidal

16   **17**   **18**
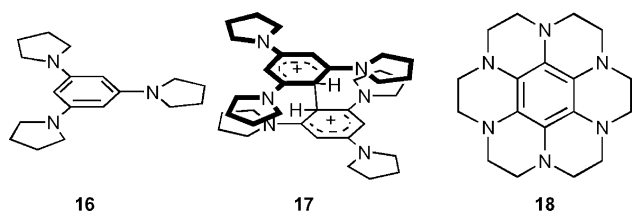
resonance structure of $1^{•+}$ while only one nitrogen atom can participate in the quinoidal structure for $16^{•+}$.

Among amino-substituted benzenes, hexaazaoctadecahydrocoronene **18** gives the most stable cationic species and X-ray crystal structures of not only the salts of the radical monocation ($18^{•+}X^-$; $X^- = BF_4^-$, TCNE$^{•-}$ and $CF_3SO_3^-$) but also the dication, radical trication and even tetracation have been determined.[40] Measurements of solid-state magnetic susceptibility of the radical monocation salts exhibited that they are paramagnets which obey the Curie–Weiss expression in the temperature range between 2 and 320 K, indicating no intermolecular dimerization in the solid state. Among these radical cation salts, the distance between the benzene planes of the structure of well-refined crystals of $18^{•+}$ TCNE$^{•-}$ is reported as 4.00 Å.[40] The lack of apparent intermolecular interaction is probably due to the effective spin delocalization into the six nitrogen atoms and/or the steric effects of the six ethylene units.

Other examples of isolable salts of benzene radical cations, whose structures have been determined by X-ray crystallography, include p-dimethoxybenzenes annelated with two norbornene units **19**[41] and with two bicyclo[2.2.2]octene (BCO) units **20**,[42] in addition to tris-BCO-annelated derivative **6**[18] described above in section 2. For the stabilization of salts $19^{•+}SbCl_6^-$ and $20^{•+}SbCl_6^-$, apparently both the contribution of quinoidal resonance structures (Fig. 4) and annelation of bicycloalkene units (*vide supra*) are important. When the bicycloalkene units are replaced by methyl groups as in 1,4-dimethoxy-2,3,5,6-tetramethylbenzene, the radical cation is not stable any more as indicated by an irreversible oxidation peak in cyclic voltammetry.[41] In the crystal packing of $19^{•+}SbCl_6^-$, $20^{•+}SbCl_6$ and $6^{•+}SbCl_6$, radical cation moieties are separated due to the steric repulsion of the rigid and bulky bicycloalkene frameworks.
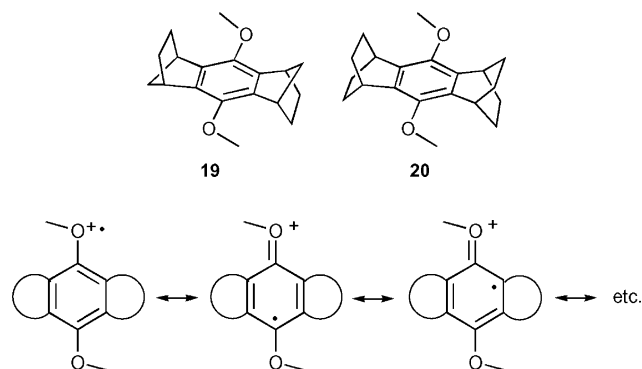

19   **20**

**Fig. 4** Quinoidal resonance structures for radical cations of dimethoxybenzene derivatives.

4.2 Polycyclic aromatic systems

Since radical cations of polycyclic aromatics tend to form π-complexes with corresponding neutral compounds, namely "charge-resonance complexes" or "dimer radical cations"[7–10] as described in the Introduction (section 1), examples of the stoichiometric formation of radical cations of these π-systems are quite limited. For example, for naphthalene derivatives, a radical cation salt of tetrakis(methylthio) derivative **21** was isolated and its X-ray structure was determined.[43] In the packing structure of $21^{•+}AsF_6^-$, a π-dimer is formed with inter-plane distances within and between the π-systems of 3.275 Å and

3.645 Å, respectively. On the other hand, in the crystal structures of radical cation salts of octadehydronaphthacene $22^{•+}SbCl_6$[10] and tetrakis-BCO-annelated derivative $8^{•+}SbCl_6$,[18] naphthalene planes are segregated from each other due to the steric effects of the substituents.

21   **22**
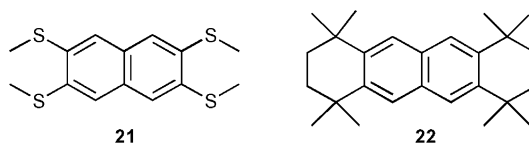
In the case of biphenylene, radical cation salts of permethyl derivative **3** and BCO-annelated derivative **9** were isolated.[10,18] While $9^{•+}SbCl_6^-$ showed a crystal structure with all the radical cation moieties totally separated as expected,[18] the crystal packing of $3^{•+}SbCl_6^-$ showed the formation of a π-dimer with a distance of 3.2 Å, each assembly being separated by two $SbCl_6^-$ anions.[10] For radical cation $3^{•+}$, the properties of the π-dimer in solution phase were investigated in detail by means of UV-vis-NIR and ESR spectroscopies[30] and were compared with those of radical anions of TCNE,[29] TCNQ (**23**),[44] DDQ (**24**),[45] and chloranil (**25**) and of the neutral radical of phenalenyl derivative **26**.[46] From this comprehensive study,[30] several important conclusions as to the energetics of dimerization of both radical cations and anions in solution were drawn. They include that "(i) the magnitudes of both the enthalpy and entropy changes in π-dimerization are relatively constant and independent of the charge on the open-shell precursor, (ii) the relatively large negative entropy change is an important contributor to the Gibbs free-energy change in π-dimerization, (iii) both ΔH_{Dimer} and ΔS_{Dimer} are singularly unaffected by changes in either the size or the nature of the counterion and (iv) large changes in the solvation of the dimeric species can occur without any detectable effect on the dimer structure."[30] The equilibrium constants K_{Dimer} for dimerization of these π radical ions in solution (0.2 to 7×10^{-4}) are much smaller than that of 1,3,5-triaminobenzene radical cation $16^{•+}$ which spontaneously forms a σ-dimer.[38,39] Thus, the ΔG_{Dimer} ($-0.8 \sim +3.4$ kcal mol^{-1} at 298 K) for the π-dimer formation is much smaller than the ΔG_{Dimer} (-15.7 kcal mol^{-1} at 298 K) for the σ-dimer formation (see section 4.1).

23   **24**   **25**   **26**
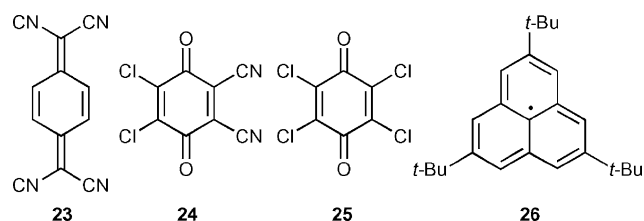
As further examples, radical cation salts of octamethylanthracene **27** were obtained upon chemical one-electron oxidation and following rearrangement of bis(pentamethylphenyl)methane (**28**).[47] Two types of crystals were obtained for $27^{•+}SbCl_6^-$: a separated stacking structure was shown in one crystal while the other demonstrated π-dimer formation with a distance between the anthracene planes of 3.42 Å. Another example of the stable radical cation salt of BCO-annelated anthracene $11^{•+}SbCl_6^-$ again exhibited a separated packing structure.[18] Similarly, the X-ray structure of the radical cation salt of fluorene $10^{•+}SbCl_6^-$ demonstrated the separated packing structure.[23,48]


27   **28**
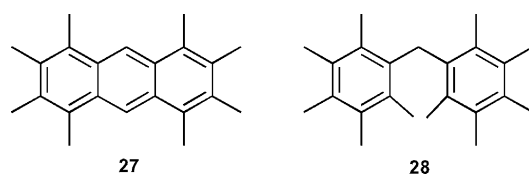
In a series of sterically segregated radical cations having aromatic rings annelated with BCO units $8^{•+}–11^{•+}$, systematic changes in π-bond lengths upon one-electron oxidation can be

observed in the X-ray structures. Since an electron is removed from the HOMO of the neutral π-system upon one-electron oxidation, it is expected that the bonds with the in-phase nature and with the out-of-phase nature in the HOMO are weakened and strengthened respectively. Accordingly, the elongation and shortening of the respective bonds in the π-systems are observed for the π-conjugated systems in **8**[.+]–**11**[.+].[18,23]

5 Persistent π-radical cations of sulfur-containing π-systems

5.1 Thiophene

The radical cation of unsubstituted thiophene is unstable and readily undergoes oxidative polymerization because of the high spin density residing mostly on the α-carbons.[49] The initial step of polymerization is the formation of σ-dimer **29** connected at the α-carbons, followed by deprotonation to give bithiophene **30** (Scheme 1).[50] Since the oxidation potential of the oligomer becomes lower in accord with the growth of the chain length, repetition of the same process becomes more facile as the oligomer becomes longer.[49]
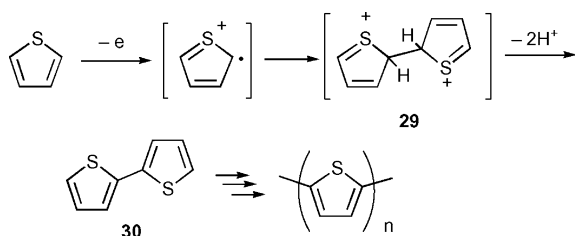
Scheme 1 Probable mechanism for oxidative polymerization of thiophene.

An attempt to lower such high reactivity of the thiophene radical cation was made by placing alkylthio and alkoxyl substituents at both α- and β-positions as in **31**.[51] Even though cyclic voltammetry showed reversible oxidation waves [**31a**, +0.41 V *vs.* Fc/Fc+ (converted from the data *vs.* SCE); **31b**, +0.15 V], the chemically generated radical cations have limited persistence with a half-life of several hours for **31a**[.+] and 30 min for **31b**[.+] in 1,1,1,3,3,3-hexafluoropropan-2-ol. For alkyl-substituted derivatives, permethylated thiophene **5** and thiophenes fully annelated with cycloalkenes **32** show only an irreversible oxidation peak at around +0.8 V *vs.* Fc/Fc+ in cyclic voltammetry.[15] In contrast, the radical cation of BCO-annelated thiophene **12** can be isolated as a SbCl$_6^-$ salt, which is stable at ambient temperature, although X-ray crystallography was not successful due to severe disorder.[25]
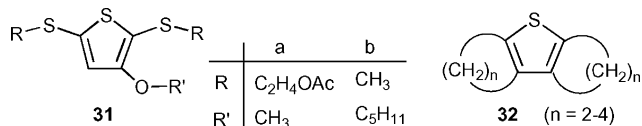
As shown by these examples, annelation with BCO units appears to be the most efficient structural modification for stabilizing π radical cations so far. However, even **12**[.+] cannot survive under air and a reaction with oxygen at the α-positions proceeds smoothly to give a novel cation of proton-chelating 2-butene-1,4-dione **33** (Scheme 2).[25] This susceptibility of the thiophene radical cation to oxygen appears to be responsible for the contamination with oxygen often observed during oxidative polymerization.[52]

5.2 Dithiins

As π-extended monocycles with one more sulfur atom inserted into the thiophene ring, both 1,2- and 1,4-dithiins are known. In the case of 1,2-dithiin, however, only a limited number of derivatives are known because of their intrinsic instability
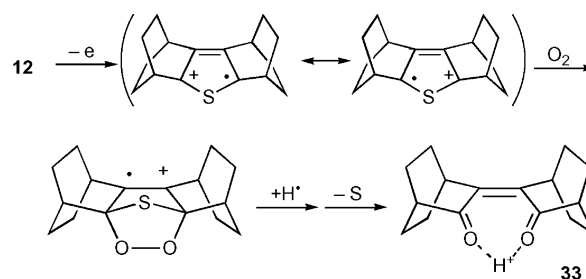
Scheme 2 Probable mechanism for the formation of **33**.

against both thermal and light stimuli,[53] and no stable radical cation has been prepared. Generation of the persistent radical cation becomes possible for the BCO-annelated derivative **34** only in a dilute solution of CH$_2$Cl$_2$ and an ESR study has been performed.[54] However upon an attempt at recrystallization of the radical cation salt **34**[.+]SbCl$_6^-$ in a more concentrated solution, a disproportionation reaction takes place to give a novel radical cation **35** stabilized by a transannular 4-center/7-electron interaction of four rigidly held sulfur atoms, probably through the self-associated state as shown in Scheme 3.[54]
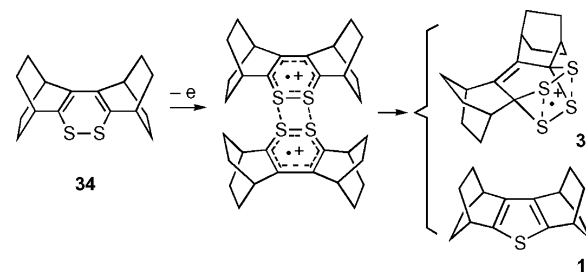
**Scheme 3** Plausible mechanism for the formation of **35**.

In contrast, 1,4-dithiin derivatives are more stable and more readily accessible.[49,55] Furthermore, unlike thiophene, the spin in their radical cations is delocalized on the sulfur atoms and hence their stability should be enhanced. Nevertheless, no example of the radical cation salt of 1,4-dithiin had been known until BCO-annelated derivative **13**[.+]SbCl$_6^-$ was prepared.[26] In its X-ray crystal structure, their is no self-association but segregated packing is observed as in the case of other π radical cation salts having BCO frameworks.

Another interesting question concerning the cationic species of dithiin as the 8 π-electron system is whether its dication has a diradical character or 6π aromatic properties. When oxidation with SbF$_5$ was conducted in CH$_2$Cl$_2$ for 1,4- and 1,2-dithiins **13** and **34**, quantitative generation of the corresponding dications was confirmed by NMR observations.[54,56] Particularly in the ^{1}H NMR spectra, signals for bridgehead protons of the BCH groups showed significant downfield shifts compared with those of neutral precursors ($\Delta\delta$ 2.0 for **13**[2+] and 1.8 for **34**[2+]) due to the diamagnetic ring current, clearly indicating the aromatic rather than diradical character of both these dithiin dications. This is also supported by values of nucleus independent chemical shift (NICS)[57] for these dications (−8.5 for **13**[2+] and −6.4 for **34**[2+] by calculations using GIAO/HF/6–31 + G*//B3LYP/6–31G*).

5.3 Thianthrene

Thianthrene **36**, which can be regarded as the dibenzo derivative of 1,4-dithiin, is readily oxidized and gives one of the oldest known radical cations.[49] The oxidation in concentrated sulfuric acid was first reported 135 years ago,[58] although the structure of the radical cation was not correctly elucidated until its ESR study in 1962.[59] The solid state structures of the radical cations were determined for the AlCl$_4^-$ salt of **36**[.+][60] and also for SbCl$_6^-$ and I$_3^-$ salts of the tetramethoxy derivative **37**[.+].[61] In the crystal packing of **36**[.+] AlCl$_4^-$ and **37**[.+]I$_3^-$, cofacial π-dimer structures

are observed with S–S contact of 3.05 and 3.11 Å for $(36^{\cdot+})_2$ and 3.16 Å for $(37^{\cdot+})_2$, whereas segregated packing is shown in the case of salt $37^{\cdot+}$ SbCl$_6^-$.

36   **37**
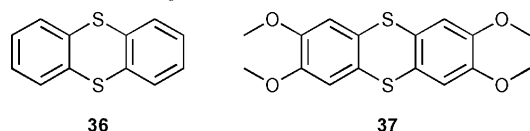
The reversible self-association of $36^{\cdot+}$ClO$_4^-$ in solution was suggested based on changes observed in the UV-vis spectrum upon changes in temperature and concentration.[62] It was assumed that the spectral change was due to the alternate sandwich-like aggregation of two units of $36^{\cdot+}$ and two ClO$_4^-$ counter anions. Recently, the reversible association process in solution was reinvestigated by fast scan cyclic voltammetry.[63] In this study, the equilibrium constant for the dimerization of the radical cation itself, K_{Dimer}, was estimated from the peak currents for the oxidation of dimer $(36^{\cdot+})_2$ and of monomer $36^{\cdot+}$, and the value was approximately in agreement with that obtained from the previous UV-vis spectral study when the previous data[62] were corrected with an assumption that only the dimerization (self-association) of radical cation $36^{\cdot+}$ is taking place, excluding interaction with the ClO$_4^-$ moiety. In another study using *in situ* ESR and UV-vis-NIR voltammetry techniques, the diamagnetic property of the dimer was confirmed.[64]

As to the structure of the self-associated dimer of $36^{\cdot+}$ in solution, the formation of the σ-dimer was once claimed based on the results of relatively simple semi-empirical MO calculations using PM3.[63] In general, sulfur-centered radical cations are known to form a σ-type 2-center/3-electron bond with a sulfur atom of another neutral compound, and the typical ΔH values for cleavage of such a bond in the gas phase are reported to be 26–28 kcal mol^{-1}.[49] Since the spin density in $36^{\cdot+}$ is relatively high on two sulfur atoms, dimerization in solution may be interpreted as the formation of two 2-center/3-electron bonds between the sulfur atoms. However, not the σ-dimer but the π-dimer was observed in the crystal structures of $36^{\cdot+}$ AlCl$_4^-$[60] and $37^{\cdot+}$I$_3^-$[61] as described above. In addition, the $-\Delta G$ values for dimerization in acetonitrile are as low as 4.6 kcal mol^{-1} for $36^{\cdot+}$ and 3.4 kcal mol^{-1} for $37^{\cdot+}$ even at 256 K,[63] and these values are too small for σ-dimer formation.[65] Thus, it is more reasonable to assume that not a σ-dimer but a π-dimer of $36^{\cdot+}$ is formed in solution as observed in the solid state.

$(36^{\cdot+})_2$ (π-dimer) $(36^{\cdot+})_2$ (σ-dimer)
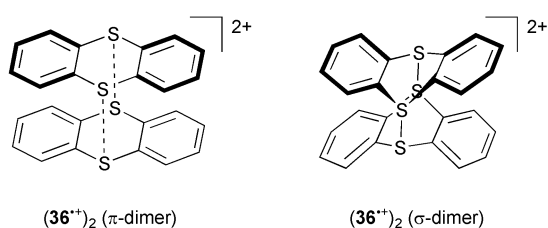
5.4 Tetrathiafulvalene

In contrast to the vast majority of mixed-valence salts of tetrathiafulvalene (TTF; **38**) and related compounds, which are prepared by electrocrystallization techniques, examples of the synthesis and isolation of the stoichiometric radical cation salts of TTFs by chemical oxidation are quite limited.[66] This situation has arisen from the fact that the nonstoichiometric salts of TTFs are usually less soluble than the stoichiometric ones and tend to separate out upon chemical and electrochemical oxidation. Thus, only a few studies concerning the dimerization of TTF radical cations have been done.

As examples of stoichiometric radical cation salts of TTF, $38^{\cdot+}$Br$^-$, $38^{\cdot+}$CF$_3$SO$_3^-$ and tetramethylthio derivative $39^{\cdot+}$CF$_3$SO$_3^-$ were prepared by chemical oxidation with bromine[32] or with (hydroxytosyloxyiodo)benzene.[66] Among them, the X-ray crystal structure of $38^{\cdot+}$Br$^-$ was reported, and it shows the cofacial π-dimer structure with an interplanar

distance of 3.34 Å.[32] A solution of $38^{\cdot+}$Br$^-$ in methanol (10^{-3} M) exhibited two bands (579, 435 nm) corresponding to the monomer radical cation at 300 K, while a new "π-dimer band" appeared at 717 nm at 225 K with a hypsochromic shift of the two original bands. The similarity between the absorption bands observed in the low-temperature solution and those in the solid state indicates that the π-dimer in the solid-state is also formed in the solution phase. ESR measurements of $38^{\cdot+}$CF$_3$SO$_3^-$ and $39^{\cdot+}$CF$_3$SO$_3^-$ in ethanol at low temperature showed that the π-dimers of $38^{\cdot+}$ and $39^{\cdot+}$ are diamagnetic.[67] Thus, the π-dimer of the TTF radical cation can exist in solution only at low temperatures.[67] On the other hand, UV-vis spectral measurements indicated that the π-dimer of the TTF radical cation at room temperature can be realized when two ethylenedithio-TTF moieties are fixed at the 1- and 8-positions of naphthalene as in **40**[68] and when TTF radical cations with penta(ethylene glycol) substituents are encapsulated in the cavity of cucurbit[8]uril as in **41** in aqueous solution.[69]


38   **39**


40   **41**
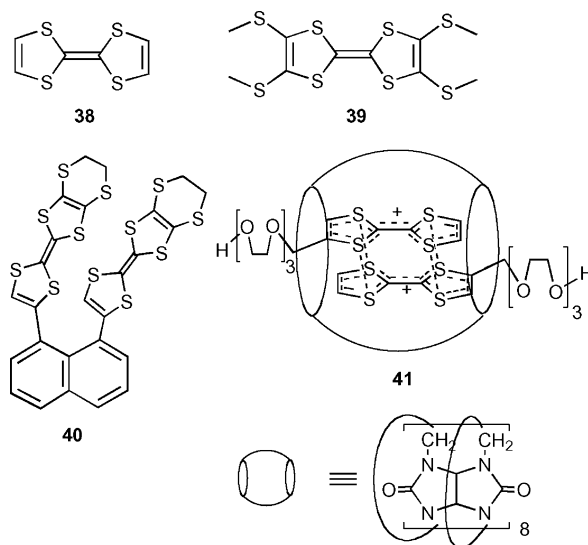
6 π-Conjugated oligomers

π-Conjugated polymers are typical examples of organic functional materials, and a variety of materials are known for this class of compounds. In this section, only some selected heterocyclic oligomers will be discussed, for which the radical cations are well characterized, since they are expected to serve as good models of the positively doped states of the corresponding conducting polymers.

In the case of cationic oligothiophenes, *i.e.*, the model of positively doped polythiophenes,[52] surprisingly there has been only one example of a radical cation salt characterized by X-ray crystallography in spite of its great significance, until our recent studies described below. This first example is a PF$_6^-$ salt of the radical cation of terthiophene derivative **42**,[70] in which the reactive α-positions of both ends are capped with phenyl groups to inhibit radical polymerization. In the crystal packing, the terthiophene moieties have a planar structure and stack in a nearly cofacial but slightly slipped manner. At 293 K, the cationic planes stack with a uniform interplanar distance of 3.47 Å, while at 106 K the distance alternates regularly between 3.36 Å and 3.42 Å. This change is accompanied by the attenuation of ESR signals in the solid state and also in solution. Accordingly, the low-temperature UV-vis-NIR spectrum in a CH$_2$Cl$_2$ solution showed a typical change corresponding to π-dimer formation, that is, the appearance of a "π-dimer band" at 1325 nm and the hypsochromic shift of the original bands. These absorption bands in solution resembled those in the solid phase except for the "π-dimer band," which became broader and more intense and extended to *ca.* 3000 nm in the solid state at room temperature presumably due to the rigid and regularly stacked

structure. At lower temperatures in the solid state, this "π-dimer band" becomes sharper with a hypsochromic shift. This widening of the band gap at low temperatures causes the conductivity of pressed pellets of the radical cation salts to decrease at lower temperatures ($2–3 \times 10^{-3}$ S cm^{-1} at room temperature and 3×10^{-5} S cm^{-1} at $-78\,°$C).[70b] Thus, the importance of the π-stacking structure of the oligothiophene radical cation for the conducting mechanism was demonstrated. The polaron/bipolaron theory cannot be adequately applied to interpret these results.

42
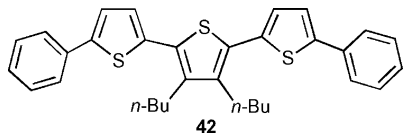
Compared to oligothiophenes, neutral species of oligopyrroles are relatively unstable and reported examples of their derivatives are quite limited. For example, the radical cation of highly substituted bipyrrole **43** was isolated as a PF$_6^-$ salt and the X-ray structure has been determined.[71] In the solid state, the radical cation was found to form π-dimers with the nearest interatomic distances of 3.23 (C–C) and 3.26 (N–N) Å. Interestingly, however, when the NMR spectrum of this radical cation was examined at low temperatures in CDCl$_3$ solution, not the formation of a π-dimer but the formation of a σ-dimer such as **44** was demonstrated.[71]


43

44
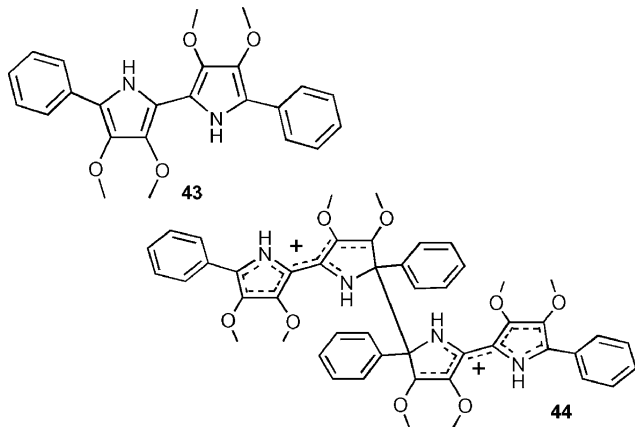
The observation of similar spectral changes in UV-vis-NIR and ESR spectra corresponding to the π-dimer formation of radical cations in solution have been claimed for various oligothiophenes[72–75] and related π-conjugated oligomers.[76–78] Among these, only one group[70,72] has demonstrated the appearance of a "π-dimer band", which is important evidence for π-dimer formation in solution. In contrast, in the case of oligomers with relatively small π-systems such as **45** and **46**, reversible formation of σ-dimers was suggested from the result that diffusion controlled radical coupling with a relatively large reaction enthalpy ($-\Delta H = 15–20$ kcal mol^{-1}) was observed by fast-scan cyclic voltammetry.[79] This seems to indicate that the higher spin-density present in smaller oligomers causes the preferential formation of a σ-dimer, as in the case of the radical cation of bipyrrole **43**$^{•+}$ in solution described above.[71]

45

46
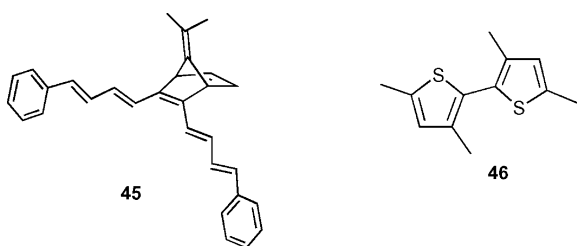
From these results it may be concluded that π-dimer formation from radical cations in solution becomes more favorable when the oligomer chain becomes longer. However, there appears to be a limitation to the extension of π-systems to give stable

radical cations in solution. For example, crystals with a π-dimer structure are obtained from radical cation salts of π-expanded TTF **47** by electrocrystallization, but in solution this radical cation is not stable and undergoes disproportionation into a neutral molecule and a dication.[80]

47
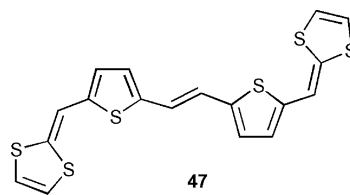
On the other hand, we designed and synthesized a series of oligothiophenes annelated with BCO units in order to generate and examine the properties of cationic oligothiophenes, which are expected to be greatly stabilized and have a segregated crystal structure due to steric effects.[27] It is considered to be similarly important to examine the electronic structure of non-dimerizable cationic oligomers for clarification of their characteristics in the unimolecular state, and structural modification with BCO frameworks is ideal for this purpose as has been shown in section 2.

As expected, one-electron oxidation of oligothiophenes **14** and **15** readily afforded the radical cation salts of bithiophene **14**$^{•+}$ SbF$_6^-$ and terthiophene **15**$^{•+}$ SbF$_6^-$, which are isolable and remarkably stable at room temperature even under air. X-Ray crystallography revealed that these cationic π-systems are segregated by bulky BCO frameworks in the solid state. Accordingly, the formation of π-dimer was not observed by UV-vis-NIR spectroscopy in CH$_2$Cl$_2$ solutions even at 180 K with relatively high concentration (1×10^{-3} M) for both of these radical cation salts.[27b]

In the case of quaterthiophene **48** and sexithiophene **49**, even treatment with one equivalent of oxidant NO$^+$SbF$_6^-$ afforded salts of not the radical cations but dications, *i.e.*, **48**$^{2+}$ 2SbF$_6^-$ and **49**$^{2+}$ 2SbF$_6^-$ also as stable salts.[27b] X-Ray crystallography was conducted for these two salts, and indicated that the counter anions are located above and below the planar dication moiety in the solid-state structure of **48**$^{2+}$ 2SbF$_6^-$. In the case of **49**$^{2+}$ 2SbF$_6^-$, two dicationic moieties are paired and the pairs stack regularly as shown in Fig. 5a. However the π-systems are separated considerably with an intermolecular distance between the sp^2 carbons of 3.9–4.9 Å. Because of a totally segregated structure in these cationic π-systems, some information as to the inherent electronic structure of cationic oligothiophenes can be deduced. Upon going from a neutral to a cationic system, the importance of the quinoidal resonance structure is shown to increase with apparent shortening of the inter-ring bonds according to the increase in net positive charge per one thiophene ring. In the case of dication salt **49**$^{2+}$ 2SbF$_6^-$, it appears that the positive charge density is higher in the four central units of thiophene rings than in the two terminal rings, in which the contribution of the quinoidal structure is barely observable.
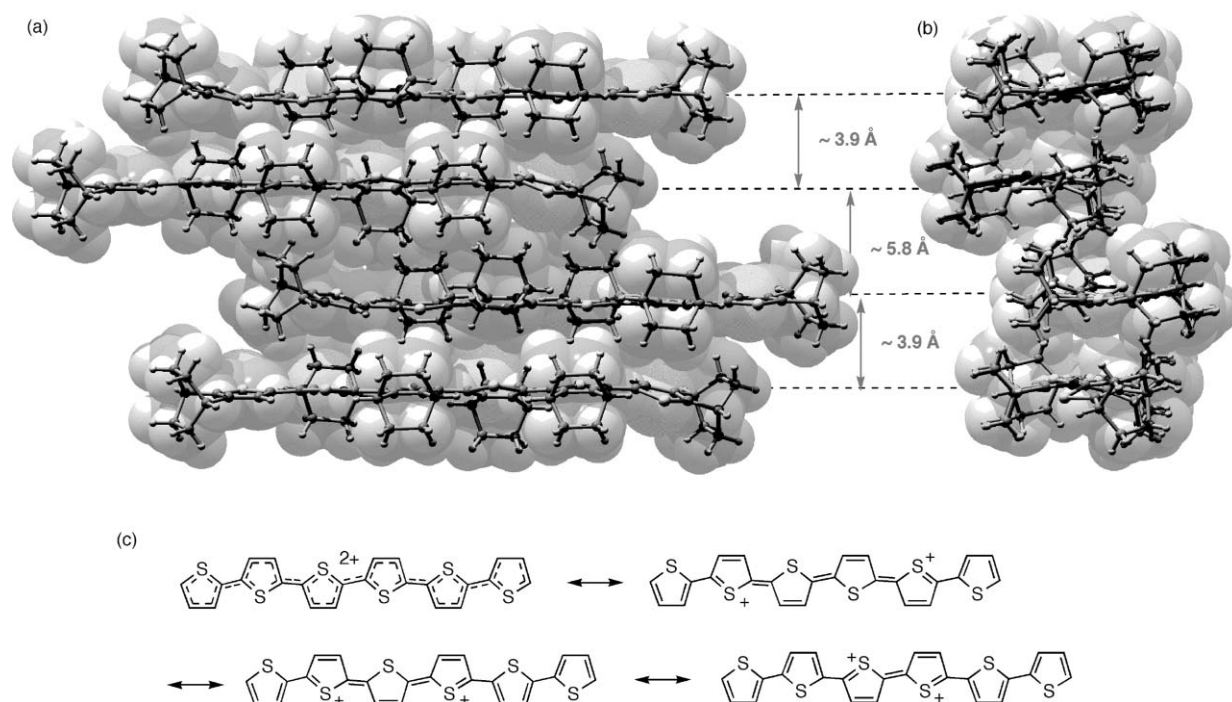

48

49
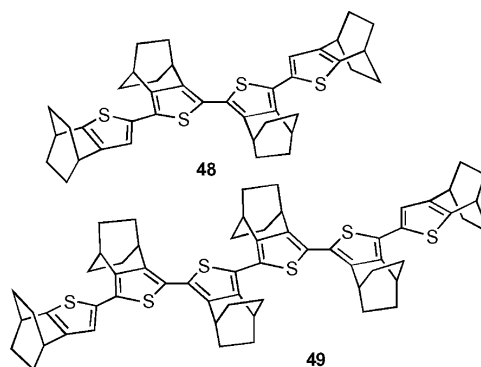
Fig. 5 (a) Side and (b) front views of packing structure of $49^{2+}(SbF_6^-)_2 \cdot CH_2Cl_2$ and (c) quinoidal resonance structures operating in dication 49^{2+}.

7 Conclusion and perspectives

In this article, we surveyed the structural and spectroscopic properties of persistent π radical cations both in solution and in the solid state. Despite the intrinsic instability of π radical cations, multiple substitution with alkylamino, alkoxy, alkylthio, and alkyl groups can make them persistent in solution, for example, for several hours at room temperature. In particular, annelation with bicyclic frameworks such as BCO units has been shown to be one of the most efficient methods to afford persistent π radical cations owing to both thermodynamic and kinetic stabilization effects.

For most persistent radical cations, self-association, *i.e.*, formation of the σ- or π-dimer, can take place in the condensed phase. In order to characterize the properties of these dimers in detail, combined studies including UV-vis-NIR, ESR, NMR, cyclic voltammetry, and X-ray crystallography are desirable. X-Ray crystallography in particular provides the most direct and informative structural data for the dimers, although examples of stoichiometric radical cation salts are quite limited. From the results obtained so far, all the dimerized structures of *persistent* radical cations observed *in the solid phase* are π-dimers probably because spin delocalization is the most important factor in these structures. *In the solution phase*, however, some of these π-dimers become equilibrated with σ-dimers. On the other hand, sterically demanding substituents like BCO units have been shown to prohibit the formation of any dimerized structure in both the solid and solution phases.

A typical example of a persistent radical cation forming a π-dimer is $42^{\bullet+}$ PF_6^-, for which the cumulative weak π-stacks were shown to cause a new "semiconductor band structure" with absorption extending over an NIR region in the solid state.[70] This stacking is considered to be the origin of the conductivity in this radical cation salt. This notion appears to be generally applicable to the radical cations of relatively short π-conjugated oligomers from similarities to the other conducting organic salts.[4] However, the electronic structure of positively charged oligomers with longer chain lengths is still controversial; one example is the issue of spin multiplicity in the dication of the thiophene dodecamer.[74a] The clarification of the electronic structure of the radical cation of a non-dimerizable, unimolecular π-conjugated oligomer is therefore important not only for understanding the conduction mechanism of π-conjugated polymer but also for the design of molecular-scale electronics. As an example of the realization of such a structure, the utilization of π-segregated oligothiophenes surrounded by BCO units was demonstrated. While the π-dimer formation of cation radicals in a π-conjugated molecular wire may be envisaged as a "short-circuit," the BCO units are considered as effective molecular insulators. A fundamental study of this kind would be as important as an applied study, such as the direct exploitation of conductive materials, in order to deepen understanding of the basic principles of π-conjugated functional materials.

Acknowledgements

References

1 N. L. Bauld, *Radicals, Ion Radicals, and Triplets*, Wiley-VCH, New York, 1997, 141.
2 M. Schmittel and A. Burghart, *Angew. Chem., Int. Ed.*, 1997, **36**, 2550.
3 M. Baumgarten and K. Müllen, *Top. Curr. Chem.*, 1994, **169**, 1.
4 L. L. Miller and K. R. Mann, *Acc. Chem. Res.*, 1996, **29**, 417.
5 For example, S. R. Forrest, *Nature*, 2004, **428**, 911.
6 (*a*) J. M. Tour, *Acc. Chem. Res.*, 2000, **33**, 791; (*b*) C. Joachim, J. K. Gimzewski and A. Aviram, *Nature*, 2000, **408**, 541; (*c*) A. Nitzan and M. A. Ratner, *Science*, 2003, **300**, 1384.
7 L. C. Lewis and L. S. Singer, *Chem. Phys.*, 1965, **43**, 2712.
8 (*a*) B. Badger and B. Brocklehurst, *Nature (London)*, 1968, **219**, 263; (*b*) B. Badger and B. Brocklehurst, *Trans. Faraday Soc.*, 1969, **65**, 2582 and 2588; (*c*) B. Badger and B. Brocklehurst, *Trans. Faraday Soc.*, 1970, **66**, 2939.
9 M. A. Rodgers, *J. Chem. Soc., Faraday Trans.*, 1972, **68**, 1278.
10 J. K. Kochi, R. Rathore and P. L. Magueres, *J. Org. Chem.*, 2000, **65**, 6826.
11 For example, P. Batail, K. Boubekeur, M. Fourmigué and J.-C. P. Gabriel, *Chem. Mater.*, 1998, **10**, 3005.
12 C. Wurster and R. Sendtner, *Chem. Ber.*, 1879, **12**, 1803; C. Wurster and R. Sendtner, *Chem. Ber.*, 1879, **12**, 2071.
13 H. Wieland, *Chem. Ber.*, 1907, **40**, 4260.
14 J. O. Howell, J. M. Goncalves, C. Amatore, L. Klasinc, R. M. Wightman and J. K. Kochi, *J. Am. Chem. Soc.*, 1984, **106**, 3968.
15 J. Nakayama and K. Kuroda, *J. Am. Chem. Soc.*, 1993, **115**, 4612.

16 F. G. Bordwell and J.-P. Cheng, *J. Am. Chem. Soc.*, 1989, **111**, 1792.

17 (*a*) K. Komatsu, H. Akamatsu, Y. Jinbu and K. Okamoto, *J. Am. Chem. Soc.*, 1988, **110**, 633; (*b*) K. Komatsu, S. Aonuma, Y. Jinbu, R. Tsuji, C. Hirosawa and K. Takeuchi, *J. Org. Chem.*, 1991, **56**, 195.

18 A. Matsuura, T. Nishinaga and K. Komatsu, *J. Am. Chem. Soc.*, 2000, **122**, 10007.

19 T. Nishinaga, K. Komatsu, N. Sugita, H. J. Lindner and J. Richter, *J. Am. Chem. Soc.*, 1993, **115**, 11642.

20 (*a*) F. Gerson, J. Lopez, R. Akaba and S. F. Nelsen, *J. Am. Chem. Soc.*, 1981, **103**, 6716; (*b*) T. Clark, M. F. Teasley, S. F. Nelsen and H. Wynberg, *J. Am. Chem. Soc.*, 1987, **109**, 5719.

21 A. Matsuura, T. Nishinaga and K. Komatsu, *Tetrahedron Lett.*, 1999, **40**, 123.

22 A. Matsuura, T. Nishinaga and K. Komatsu, *Tetrahedron Lett.*, 1997, **38**, 4125.

23 T. Nishinaga, R. Inoue, A. Matsuura and K. Komatsu, *Org. Lett.*, 2002, **4**, 4117.

24 A. Matsuura, T. Nishinaga and K. Komatsu, *Tetrahedron Lett.*, 1997, **38**, 3427.

25 A. Wakamiya, T. Nishinaga and K. Komatsu, *Chem. Commun.*, 2002, 1192.

26 T. Nishinaga, A. Wakamiya and K. Komatsu, *Tetrahedron Lett.*, 1999, **40**, 4375.

27 (*a*) A. Wakamiya, D. Yamazaki, T. Nishinaga, T. Kitagawa and K. Komatsu, *J. Org. Chem.*, 2003, **68**, 8305; (*b*) T. Nishinaga, A. Wakamiya, D. Yamazaki and K. Komatsu, *J. Am. Chem. Soc.*, 2004, **126**, 3163.

28 Although a single crystal of **12**·⁺SbCl₆⁻ was isolated and was subjected to X-ray crystallography, there was too much disorder around the BCO frameworks.

29 R. E. Del Sesto, J. S. Miller, P. Lafuente and J. J. Novoa, *Chem. Eur. J.*, 2002, **8**, 4894.

30 J.-M. Lü, S. V. Rosokha and J. K. Kochi, *J. Am. Chem. Soc.*, 2003, **125**, 12161.

31 Because of the similarity between the π-dimer and charge-transfer complex, the transition is occasionally referred to as a "charge-transfer band".

32 J. B. Torrance, B. A. Scott, B. Welber, F. B. Kaufman and P. E. Seiden, *Phys. Rev. B: Condens. Matter*, 1979, **19**, 730.

33 J. L. de Boer and A. Vos, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1972, **28**, 835; J. L. de Boer and A. Vos, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1972, **28**, 839.

34 C. T. Pott, C. F. van Bruggen and J. Kommandeur, *J. Chem. Phys.*, 1967, **47**, 408.

35 J. Tanaka and N. Sakabe, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1968, **24**, 1345.

36 J. Tanaka, M. Inoue, M. Mizuno and K. Horai, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 1998.

37 S. Nakayama and K. Suzuki, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 3694.

38 F. Effenberger, K.-E. Mack, R. Niess, F. Reisinger, A. Steinbach, W.-D. Stohrer, J. J. Stezowski, I. Rommel and A. Maier, *J. Org. Chem.*, 1988, **53**, 4379.

39 J. Heinze, C. Willmann and P. Bäuerle, *Angew. Chem. Int. Ed.*, 2001, **40**, 2861.

40 J. S. Miller, D. A. Dixon, J. C. Calabrese, C. Vazquez, P. J. Krusic, M. D. Ward, E. Wasserman and R. L. Harlow, *J. Am. Chem. Soc.*, 1990, **112**, 381.

41 R. Rathore and J. K. Kochi, *J. Org. Chem.*, 1995, **60**, 4399.

42 R. Rathore, A. S. Kumar, S. V. Lindeman and J. K. Kochi, *J. Org. Chem.*, 1998, **63**, 5847.

43 J. Noreland, G. Olovsson and I. Olovsson, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1993, **49**, 168.

44 M. C. Grossel and S. C. Weston, *Chem. Mater.*, 1996, **8**, 977.

45 J. S. Miller, P. J. Krusic, D. A. Dixon, W. M. Reiff, J. H. Zhang, E. C. Anderson and A. J. Epstein, *J. Am. Chem. Soc.*, 1986, **108**, 4459.

46 K. Goto, T. Kubo, K. Yamamoto, K. Nakasuji, K. Sato, D. Shiomi, T. Takui, M. Kubota, T. Kobayashi, K. Yakushi and J. Ouyang, *J. Am. Chem. Soc.*, 1999, **121**, 1619.

47 R. Sebastiano, J. D. Korp and J. K. Kochi, *J. Chem. Soc., Chem. Commun.*, 1991, 1481.

48 Deprotonation at the 9-position to give the neutral fluorenyl radical, as observed for many fluorenes (F. G. Bordwell, J.-P. Cheng and M. J. Bausch, *J. Am. Chem. Soc.*, 1988, **110**, 2867) was not observed.

49 R. S. Glass, *Top. Curr. Chem.*, 1999, **205**, 1.

50 There is mechanistic uncertainty as to whether radical–radical coupling or coupling between the radical cation and neutral precursor is operative. See ref. 2.

51 I. Tabakovic, T. Maki, L. L. Miller and Y. Yu, *Chem. Commun.*, 1996, 1911.

52 P. Bäuerle, in *Electronic Materials: The Oligomer Approach*, ed. K. Müllen and G. Wegner, Wiley, Weinheim, 1998, p. 105.

53 H. Viola and R. Winkler, in *Houben veyl: Methoden Organische Chemie*, ed. E. Schaumann, Thieme, Stuttgart, 1997, vol. E9a, p. 209.

54 A. Wakamiya, T. Nishinaga and K. Komatsu, *J. Am. Chem. Soc.*, 2002, **124**, 15038.

55 G. Klar, in *Houben Veyl: Methoden Organische Chemie*, ed. E. Schaumann, Thieme, Stuttgart, 1997, vol. E9a, p. 250.

56 T. Nishinaga, A. Wakamiya and K. Komatsu, *Chem. Commun.*, 1999, 777.

57 P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. v. E. Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317.

58 J. Stenhouse, *Liebigs Ann. Chem.*, 1869, **149**, 247.

59 (*a*) H. J. Shine and L. Piette, *J. Am. Chem. Soc.*, 1962, **84**, 4798; (*b*) M. Kinoshita and H. Akamatsu, *Bull. Chem. Soc. Jpn.*, 1962, **35**, 1040; (*c*) E. A. C. Lucken, *J. Chem. Soc.*, 1962, 4963.

60 H. Bock, A. Rauschenbach, C. Näther, M. Kleine and Z. Havlas, *Chem. Ber.*, 1994, **127**, 2043.

61 W. Hinrichs, P. Berges and G. Klar, *Z. Naturforsch., B: Chem. Sci.*, 1987, **42**, 169.

62 M. de Sorgo, B. Wasserman and M. Szwarc, *J. Phys. Chem.*, 1972, **76**, 3468.

63 P. Hübler and J. Heinze, *Ber. Bunsen-Ges. Phys. Chem.*, 1998, **102**, 1506.

64 P. Rapta, L. Kress, P. Hapiot and L. Dunsch, *Phys. Chem. Chem. Phys.*, 2002, **4**, 4181.

65 These values decrease further at 293 K due to the large negative ΔS_D,⁶² whereas the $-\Delta G$ for σ-dimer formation in the case of **16**·⁺ is reported to be much larger, *i.e.*, 15.7 kcal mol⁻¹ at 293 K (See section 4.1.).

66 M. Giffard, G. Mabon, E. Leclair, N. Mercier, M. Allain, A. Gorgues, P. Molinié, O. Neilands, P. Krief and V. Khodorkovsky, *J. Am. Chem. Soc.*, 2001, **123**, 3852.

67 V. Khodorkovsky, L. Shapiro, P. Krief, A. Shames, G. Mabon, A. Gorgues and M. Giffard, *Chem. Commun.*, 2001, 2736.

68 M. Iyoda, M. Hasegawa, Y. Kuwatani, H. Nishikawa, K. Fukami, S. Nagase and G. Yamamoto, *Chem. Lett.*, 2001, 1146.

69 A. Y. Ziganshina, Y. H. Ko, W. S. Jeon and K. Kim, *Chem. Commun.*, 2004, 806.

70 (*a*) D. D. Graf, J. P. Campbell, L. L. Miller and K. R. Mann, *J. Am. Chem. Soc.*, 1996, **118**, 5480; (*b*) D. D. Graf, R. G. Duan, J. P. Campbell, L. L. Miller and K. R. Mann, *J. Am. Chem. Soc.*, 1997, **119**, 5888.

71 A. Merz, J. Kronberger, L. Dunsch, A. Neudeck, A. Petr and L. Parkanyi, *Angew. Chem. Int. Ed.*, 1999, **38**, 1442.

72 (*a*) M. G. Hill, K. R. Mann, L. L. Miller and J.-F. Penneau, *J. Am. Chem. Soc.*, 1992, **114**, 2728; (*b*) M. G. Hill, J.-F. Penneau, B. Zinger, K. R. Mann and L. L. Miller, *Chem. Mater.*, 1992, **4**, 1106; (*c*) Y. Yu, E. Gunic, B. Zinger and L. L. Miller, *J. Am. Chem. Soc.*, 1996, **118**, 1013.

73 (*a*) P. Bäuerle, U. Segelbacher, K.-U. Gaudl, D. Huttenlocher and M. Mehring, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 76; (*b*) P. Bäuerle, U. Segelbacher, A. Maier and M. Mehring, *J. Am. Chem. Soc.*, 1993, **115**, 10217; (*c*) P. Bäuerle, T. Fisher, B. Bidlingmeier, A. Stabel and J. Rabe, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 303.

74 (*a*) J. A. E. H. van Haare, E. E. Havinga, J. L. J. van Dongen, R. A. J. Janssen, J. Cornil and J.-L. Brédas, *Chem. Eur. J.*, 1998, **4**, 1509; (*b*) J. J. Apperloo, R. A. J. Janssen, P. R. L. Malenfant, L. Groenendaal and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2000, **122**, 7042; (*c*) J. J. Apperloo, L. Groenendaal, H. Verheyen, M. Jayakannan, R. A. J. Janssen, A. Dkhissi, D. Beljonne, R. Lazzaroni and J.-L. Brédas, *Chem. Eur. J.*, 2002, **8**, 2384.

75 (*a*) H. Nakanishi, N. Sumi, S. Ueno, K. Takimiya, Y. Aso, T. Otsubo, K. Komaguchi, M. Shiotani and N. Ohta, *Synth. Met.*, 2001, **119**, 413; (*b*) T. Satou, T. Sakai, T. Kaikawa, K. Takimiya, T. Otsubo and Y. Aso, *Org. Lett.*, 2004, **6**, 997.

76 (*a*) J. A. E. H. van Haare, L. Groenendaal, E. E. Havinga, R. A. J. Janssen and E. W. Meijer, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 638; (*b*) J. A. E. H. van Haare, L. Groenendaal, E. E. Havinga, E. W. Meijer and R. A. J. Janssen, *Synth. Met.*, 1997, **85**, 1091; (*c*) J. A. E. H. van Haare, M. van Boxtel and R. A. J. Janssen, *Chem. Mater.*, 1998, **10**, 1166.

77 A. Sakamoto, Y. Furukawa and M. Tasumi, *J. Phys. Chem. B*, 1997, **101**, 1726.

78 E. Levillain and J. Roncali, *J. Am. Chem. Soc.*, 1999, **121**, 8760.

79 (*a*) A. Smie and J. Heinze, *Angew. Chem., Int. Ed.*, 1997, **36**, 363; (*b*) P. Tschuncky, J. Heinze, A. Smie, G. Engelmann and G. Kossmehl, *J. Electroanal. Chem.*, 1997, **433**, 223; (*c*) J. Heinze, P. Tschuncky and A. Smie, *J. Solid State Electrochem.*, 1998, **2**, 102.

80 P. Frere, M. Allain, E. H. Elandaloussi, E. Levillain, F.-X. Sauvage, A. Riou and J. Roncali, *Chem. Eur. J.*, 2002, **8**, 784.