The first two decades of a versatile electron acceptor building block: 11,11,12,12-tetracyano-9,10-anthraquinodimethane (TCAQ)†

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Received 7th December 2006
First published as an Advance Article on the web 26th February 2007
DOI: 10.1039/b605735g

This *critical review* surveys the development of the structural and electrochemical knowledge of the TCAQ moiety since its discovery, nearly two decades ago, until the present. Additionally, recent advances in the chemistry and functionalization of this versatile building block are highlighted, with special emphasis on the strategies devoted to the preparation of donor–acceptor molecular and polymeric materials. The applications of TCAQ-based materials in materials science as electrical conductors, molecular rectifiers, in photoinduced electron transfer processes, optoelectronic devices and as electrochiroptical materials are also reviewed (89 references).

Introduction

The tetracyano-*p*-quinodimethane (TCNQ) molecule (Fig. 1) was first reported to form semiconducting salts in 1962.[1,2] Years later, Wheland and Martin, from the DuPont Company, reported the synthesis of the first substituted TCNQ derivatives and related anion salts by following different multistep synthetic procedures.[3] Since then, many TCNQ derivatives have been synthesized including substituted derivatives, heteroquinoid analogues or π-extended derivatives.[4] Among them, the 11,11,12,12-tetracyano-9,10-anthraquinodimethane (TCAQ, Fig. 1) has attracted special attention due to its potential in areas such as photoinduced electron transfer, molecular rectifiers, transport layers in organic optoelectronic devices or electrochiroptical materials. As a consequence of its practical applications, this electron acceptor has been deeply investigated from the theoretical, structural and electrochemical points of view. Thus, in this article we will give an overview of the main theoretical, structural and electrochemical studies

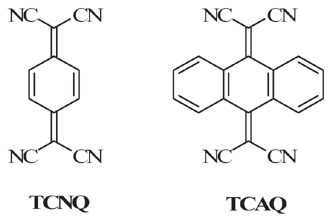

Fig. 1

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† This work is dedicated to Prof. N. Martín on the occasion of his 50th birthday.

Rafael Gómez

Rafael Gómez was born in Madrid (Spain) in 1974. After graduating in Organic Chemistry at the Universidad Complutense de Madrid (1998) he received a PhD (2001) working on the synthesis of electroactive materials (TCAQs and fullerenes) for organic solar cells. Then, he moved on to the Université Libre de Bruxelles as a post-doctoral fellow and then to industry. Since the end of 2003 he has been a "Ramón y Cajal" Researcher at the Universidad Complutense, where he works on electroactive materials based on TCAQs, perylenes, fullerenes and conjugated polymers.

Carlos Seoane

Carlos Seoane received his PhD in Chemistry at the Universidad de Santiago (Spain) in 1975. He obtained a tenured Assistant Professorship at Universidad Complutense (1978) and a Full Professorship in 1988, first at Universidad de Castilla-La Mancha and then at the Universidad Complutense, where he has been vice-rector. His research interests include heterocyclic synthesis and reactivity, industrial research projects in medicinal chemistry as well as new organic materials. He received the Research Prize of the Royal Academy of Sciences in 1981 and the Research Medal of the Spanish Royal Society of Chemistry in 2000. He was inducted to the Royal Academy in 2004. He has published some 200 scientific papers and has done joint research and publication with the University of East Anglia, Tübingen Universität, University of California, Universidad de La Habana, University of Dundee, Clemson University, Université Paris-Sud and Ber-Sheva University. He is general editor for the "Síntesis" collection of chemistry books. Besides the Academy, Professor Seoane enjoys scuba diving and soaring in his glider.

carried out on the TCAQ systems followed by a revision of the different TCAQ derivatives synthesized, including functionalized TCAQ derivatives and complex molecular and polymeric materials bearing TCAQ moieties. Finally, the main applications of this versatile electron acceptor building block will be reviewed.

Structural, electrochemical and theoretical investigations on TCAQ

The efforts to design organic conductors and superconductors were among the first goals of the emerging field of crystal engineering.[5] In this regard, crystal engineering of segregated stacked charge transfer (CT) complexes requires planar molecules with a strong tendency to stack as occurs in the classical tetrathiafulvalene (TTF)–TCNQ complex.[6–8] In order to develop new materials with enhanced conducting properties, the extension of the π system in TCNQ derivatives was thought to be of great importance to reduce the intramolecular electron repulsion and should lead to more stable radical anions. With this aim, the synthesis of the first π-extended TCNQ derivative, TCAQ, was carried out almost simultaneously by different groups.[9–13] However, after the synthesis of TCAQ, electrochemical investigations showed that the extension of the π-conjugated system does not necessarily result in an improvement of the acceptor properties and, in the particular case of TCAQ, it exhibits a more negative reduction potential compared to the parent TCNQ. Thus, in 1984 Aumüller and Hünig were the first to show that TCAQ exhibits a reversible two-electron reduction at −0.24 V *vs.* SCE in acetonitrile (Pt as working electrode)[13] and, shortly afterwards, Cowan, Gerson and co-workers performed an in-depth electrochemical investigation of the TCAQ system.[11,12] In Fig. 2, the cyclic voltammogram of TCAQ in acetonitrile, at room temperature, is depicted, as reported in 1985 by these authors.[11,12]

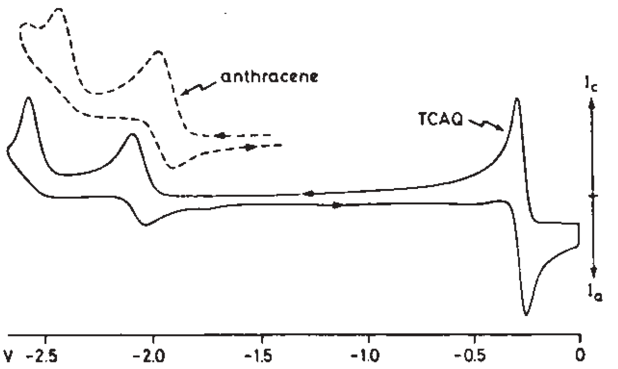


Fig. 2 Cyclic voltammetry of TCAQ and anthracene. Solvent, acetonitrile; supporting electrolyte, $Et_4N^+BF_4^-$; working electrode, hanging drop mercury, reference electrode, Ag/AgCl/3 M KCl; scan rate, 200 mV s^{-1}; I_c, cathodic current, I_a, anodic current. (Reprinted with permission from ref. 12. Copyright 1985 American Chemical Society.)

Under these conditions, two reversible redox waves were observed at $E_{1/2} = -0.285$ V and $E_{1/2} = -2.06$ V *vs.* the Ag/Ag^+ reference electrode. Interestingly, the peak intensity was twice higher for the former than for the latter wave and the separation of their anodic and cathodic peaks amounts to 0.03 and 0.06 V, respectively. This electrochemical behavior is in agreement with a two-electron process for the wave at higher potentials and a one-electron process for the other one. Additionally, an irreversible wave with a cathodic peak at −2.58 V was observed, corresponding to a one-electron process as confirmed by polarography under the same experimental conditions. The first reversible wave, in which two electrons were involved, was similar to that previously reported by Aumüller and Hünig[13] and was assigned to the reduction of the TCAQ moiety to generate the dianion:

$$\mathrm{TCAQ} + 2\,e^- \rightleftarrows \mathrm{TCAQ}^{2-}$$

On the other hand, the two redox waves at −2.06 and −2.58 V were assigned to the reduction of the anthracene moiety of $TCAQ^{2-}$, as it was further confirmed by comparison with the cyclic voltammogram of anthracene under the same conditions (Fig. 2).

The most striking fact is that, by comparison with the electrochemical behavior of the TCNQ under analogous conditions (*i.e.* two one-electron processes at $E_{1/2} = -0.09$ V and $E_{1/2} = -0.75$ V), the first and second reduction processes of the TCNQ moiety coalesce into a single wave in the case of TCAQ.

To explain this electrochemical behavior, Ortí *et al.* performed theoretical calculations at the semiempirical and *ab initio* levels.[14,15] The most stable conformation found for the neutral TCAQ corresponds to a butterfly-shaped structure in which the central TCNQ ring adopts a boat-type conformation whereas the two lateral benzene rings remain planar. This conformation lies, at the *ab initio* 6-31G* level, 33.45 kcal mol^{-1} below the fully planar conformation and is in good agreement with experimental X-ray data (Fig. 3).[16]

José L. Segura

José L. Segura obtained his PhD. in Organic Chemistry in 1994 at the Universidad Complutense de Madrid. After a short stay in the group of Professor W. Daily (University of Pennsylvania) working in the area of strained-ring organic syntheses, he performed postdoctoral stays in the group of Prof. M. Hanack (University of Tübingen) working on the syntheses of electroluminescent conjugated polymers and in the group of Professor F. Wudl (University of California at Santa Barbara), working on the functionalization of [60]fullerene. In 1995 Dr Segura joined the faculty in the Department of Organic Chemistry at the Universidad Complutense de Madrid where he is currently Professor in organic chemistry and has received the Award for Young Researchers of the Spanish Royal Society of Chemistry. His current research interests involve the synthesis and electrochemical characterization of n-type acceptor materials (TCAQ, fullerene, perylenebisimide derivatives), as well as oligomeric, dendritic and polymeric donor–acceptor π-conjugated materials for optoelectronic applications.

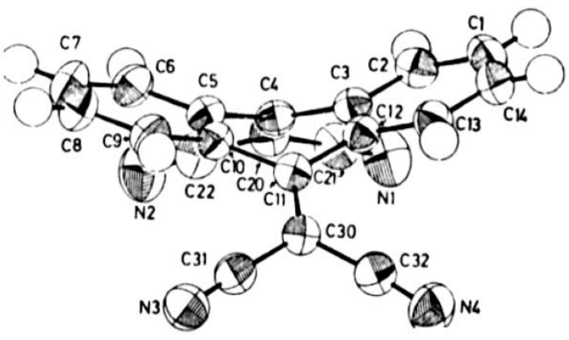


Fig. 3 X-Ray crystal structure of TCAQ. (Reprinted with permission from ref 16. Copyright 1985 Wiley-VCH.)

In order to get a deeper understanding of the TCAQ reduction processes, Ortí *et al.* also investigated the structure of the radical anion and dianions of TCNQ and TCAQ by both the PM3 method and 6-31G* calculations.[14,15] In contrast to TCNQ, in which reduction results in the aromatization of the TCNQ moiety, the radical anion of TCAQ remains non-planar. The same calculations showed that in the dianion of the TCAQ, the polycyclic skeleton is fully planar with the two dicyanomethylene ($C(CN)_2$) groups twisted out of the molecular plane. Thus, the non-planar structure obtained for $\mathrm{TCAQ}^{\bullet-}$ radical anion is destabilized by 2.78 eV when compared with the planar radical anion of TCNQ, which is in agreement with the more negative reduction potentials experimentally observed for TCAQ in comparison with TCNQ. On the other hand, the introduction of a second electron in TCAQ completes the aromatization of the TCAQ ring system, which thus becomes fully planar. In parallel to the planarization of the anthracene system, the exocyclic C=C bonds show a marked single-bond character in the dianion, thus allowing the rotation of the dicyanomethylene groups out of the molecular plane, and relieving the steric interactions between the cyano groups and the hydrogen atoms in *peri* positions (Fig. 4).

The non-planar structure of the $\mathrm{TCAQ}^{\bullet-}$ suggests that this radical anion is less aromatic and less stable than the corresponding radical anion of TCNQ and, therefore, the first reduction potential of TCAQ is shifted to a more negative value in comparison with that of TCNQ. On the other hand, 6-31G* calculations predict that $\mathrm{TCAQ}^{\bullet-}$ is only 1.49 eV more stable than neutral TCAQ,[15] which is responsible for the collapse of the first and the second reduction potential waves under a single two-electron reduction wave as shown experimentally. Therefore, TCAQ is a good example of an electroactive system in which the gain of a second electron takes place more easily than the first one ($E_1^0 - E_2^0 < 0$). This behaviour has been normally observed in systems in which a significant structural change is associated with one or both electron-transfer steps, as is the case of TCAQ.[17] On the other hand, TCAQ^{2-} can be visualized as an anthracene molecule substituted by two negatively charged dicyanomethyl groups, and therefore, a third and even a fourth electron can be introduced during the further reduction of the anthracene central moiety to form the corresponding tri- and tetra-anions. In 2006 Macías-Ruvalcaba and Evans reported calculations to characterize the structural changes accompanying reduction to the radical anion and dianion of TCAQ.[18] So far, the cyclic voltammetry data have been interpreted in terms of two electron transfers, each with a structural change being concerted with the electron transfer. In this recent study, the authors claim that the structural change could also occur as a discrete chemical reaction either before or after the electron transfer. In an attempt to detect intermediates in the reduction, experiments at fast scan rates and low temperatures (up to 10000 V s^{-1} at 257 K and 500 V s^{-1} at 233 K) were conducted but no intermediate was found. Therefore it is still an open question whether structural change and electron transfer are concerted or occur in discrete successive steps.

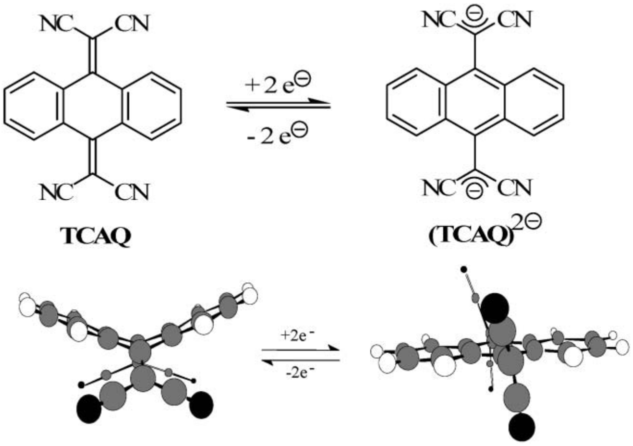


Fig. 4 PM3-optimized structure of TCAQ and TCAQ^{2-}.

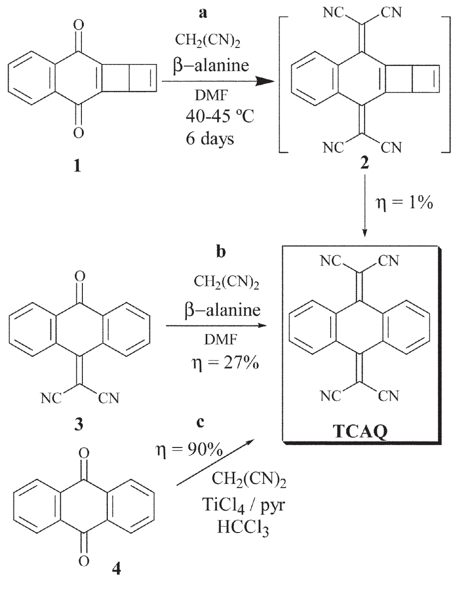
Synthesis of TCAQ and derivatives

Due to the high interest of the TCAQ system, different synthetic routes towards the preparation of TCAQ itself were developed simultaneously and independently by different research groups. Thus, the preparation of TCAQ was first reported by Misumi's group by following the synthetic route depicted in Scheme 1(a), (b).[9]

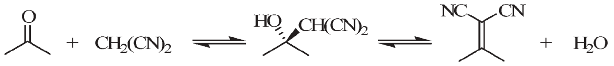
Dicyanomethylation of substituted naphthoquinone **1** was carried out with a large excess (40 eq.) of malononitrile in the presence of β-alanine as a base in DMF to give the intermediate **2**, which further gives TCAQ in 1% yield (Scheme 1(a)). Alternatively, a moderate and reproducible 27% yield of TCAQ could be obtained by dicyanomethylenation of **3** under the same conditions (Scheme 1(b)).[9]

Interestingly, although condensations between malononitrile and aromatic compounds proceed easily, its actual condensation with anthraquinones cannot be carried out under the above standard reaction conditions (b) in Scheme 1. This is due to the steric overcrowding in TCAQ, which shifts the equilibrium of condensation in favour of the reactants thus precluding the otherwise facile condensation (Scheme 2).

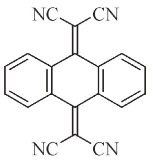
This difficulty, however, can be overcome if the tetrahedral intermediate in Scheme 2 is forced to irreversibly eliminate water. In this regard, the groups of Ong[10] and Hünig[13] reported independently on the Lewis acid titanium(IV) chloride ($TiCl_4$) as an effective reagent for the promotion of this condensation as (i) it can coordinate with oxygen atoms, thus



Scheme 1



Scheme 2



11a 2-CH_3
11b 2-C_2H_5
11c 1-Cl
11d 2-Cl
11e 2-CO_2CH_3
11f 2-CN
11g 2-NO_2
11h 2-NH-$COCH_3$
11i 2-$N(CH_3)_2$
11j 2-$NHCOC_{15}H_{31}$
11k 2-$NHCOC_{19}H_{39}$
11l 2-$CONHC_{18}H_{37}$
11m 2-$SO_2NHC_{18}H_{37}$
11n 2-$SO_2OC_{17}H_{35}$
11o 2-$CO_2C_{17}H_{35}$
11p 2-$CO_2C_{12}H_{25}$
11q 2-$CO_2C_8H_{17}$

Fig. 5 Examples of substituted TCAQ derivatives.

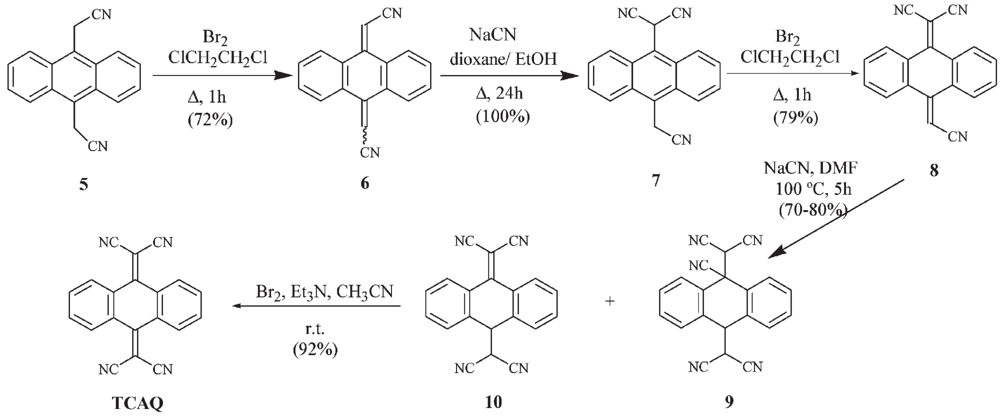
promoting the nucleophilic attack of the malononitrile to the carbonyl group and, more advantageously, (ii) it is able to irreversibly dehydrate the intermediate.

Finally in 1984, Aumüller and Hünig succeeded[13] in the direct conversion with good and reproducible yields of 9,10-anthraquinone (**4**) to TCAQ, by condensation with malononitrile in the presence of $TiCl_4$ and pyridine (Lehnert's reagent) (Scheme 1(c)).[19] In the same article, the synthesis of 2-methyl-TCAQ, 2,3-dimethyl-TCAQ and 1,5-dichloro-TCAQ was also accomplished following a similar synthetic procedure from the corresponding anthraquinone derivatives.[13] Ong and Keoshkerian described also the synthesis of TCAQ in a 87% yield and that of 2-*tert*-butyl-TCAQ in a 57% yield from the parent quinone precursors with the same procedure.[10]

In parallel to these reports, Cowan, Gerson and co-workers developed another synthetic strategy towards TCAQ starting from 9,10-bis(cyanomethyl)anthracene (Scheme 3).[11,12] Refluxing a solution of 9,10-bis(cyanomethyl)anthracene (**5**) in 1,2-dichloroethane with 2.5 eq. of bromine resulted in *ca.* 75% yield of 11,12-dicyano-9,10-anthraquinodimethane (**6**). Reaction of **6** with excess sodium cyanide in a dioxane–95% ethanol mixture, followed by acidic workup, allowed to obtain compound **7** in almost quantitative yield. Further oxidation of **7** with bromine yielded 11,11,12-tricyano-9,10-anthraquinodimethane (**8**) in 79% yield and the subsequent reaction of **8** with sodium cyanide in DMF provided a fairly labile adduct **9** which readily decomposes to give compound **10**. Finally, the reaction of either adducts **9** or **10** with bromine/triethylamine in acetonitrile at room temperature affords TCAQ in 42% overall yield.

Taking into account the multistep character of this synthetic approach and the low overall yield, the most common synthetic route for the preparation of TCAQ and its derivatives involves the condensation between malononitrile and the corresponding anthraquinone precursors with Lehnert's reagent. In this regard, a variety of substituted derivatives **11a–q**[20,21] (Fig. 5) have been synthesized following this procedure.

Special interest has been devoted during the last few years by Bryce, Martín, Panetta and others to the synthesis of new TCAQ derivatives **12**,[22] **13**,[23] **14**,[24] **15**,[25] **16**[26] and **17**[26] (Fig. 6) endowed with functional groups that have allowed their further incorporation into more complex molecular and macromolecular architectures, giving rise to a variety of



Scheme 3

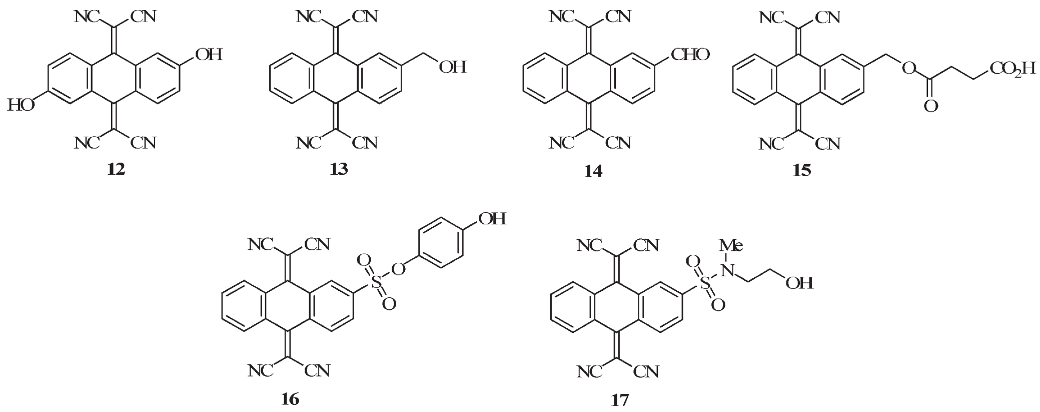


Fig. 6 TCAQ derivatives bearing chemical functionalities.

interesting electroactive materials whose properties will be discussed later on this article.

In 1997, Martín, Seoane and co-workers reported the synthesis of the first TCAQ dimer **18** (Fig. 7) by treatment of the corresponding 2,2′-oxydianthraquinone with malononitrile in the presence of Lehnert's reagent.[27] The electrochemical behaviour of dimer **18** corresponds to a system in which both TCAQ moieties behave independently and therefore a four-electron single reduction wave was observed indicating the simultaneous reduction of both TCAQ units to $TCAQ^{2-}$.

Dimer **19** (Fig. 7) was obtained from TCAQ derivative **13** by reaction with malonyl dichloride at 0 °C in the presence of pyridine in 69% yield.[28] This dimer represents an interesting building block, as the presence of the reactive methylene group makes it suitable for further chemical transformations, as we will see later in this section.

Efforts have been also devoted to the synthesis of TCAQ dimers with non-planar spacers in order to obtain systems with enhanced dimensionality (**20**,[25] **21**,[25] **22**,[29] Fig. 7). Due to the restricted rotation of the two naphthalene units of the binaphthyl system, the dihedral angle between naphthalene rings ranges from 60 to 120° making binaphthyl derivatives ideal candidates to be used as non-planar spacers for the connection of electroactive fragments. Thus, Martín and co-workers have synthesized TCAQ dimers **20** and **21** by esterification and Wittig–Horner reactions of TCAQ derivatives **14** and **15**, respectively, with suitably functionalized binaphthyl derivatives.[25] Whereas in dimer **21** no electronic interactions between the dodecyloxynaphthalene and TCAQ units were observed either by UV-vis or by cyclic voltammetry, a different behaviour was observed in dimer **20**, in which a charge transfer band was observed by absorption spectroscopy. Although in both cases it is clear that the binaphthyl moieties preclude any interaction between the two sides of the molecule, the conjugated spacer in **20** allows a charge transfer from the donor alkoxynaphthalene units to the acceptor

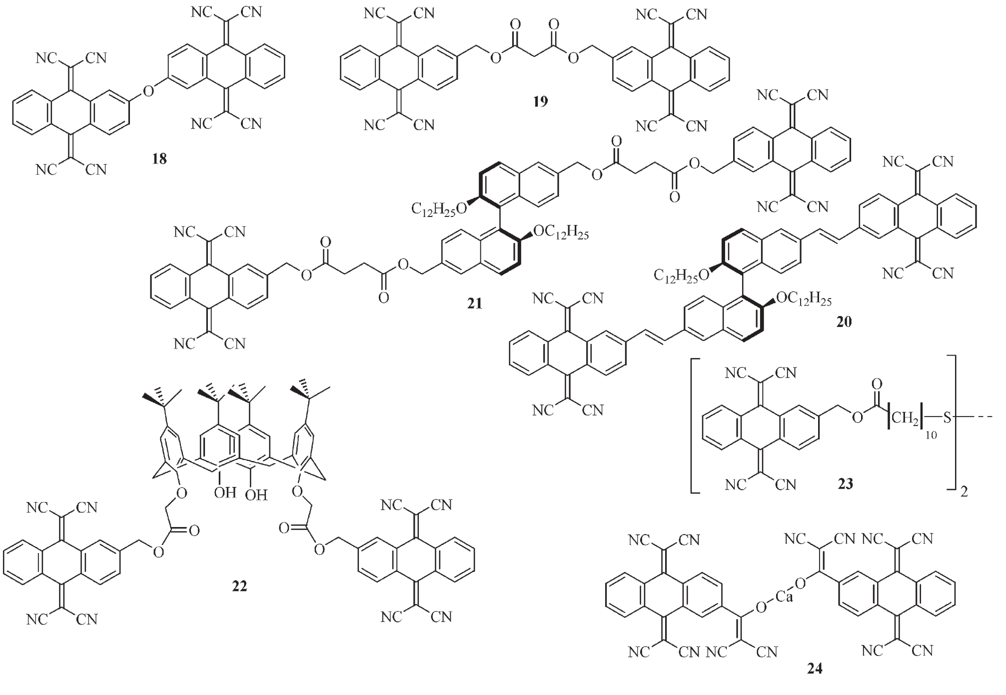


Fig. 7 Examples of TCAQ dimers.

TCAQ, which in **21** is excluded taking into account the non-conjugated nature of the spacer and the longer distance between the electroactive units. The nature of the spacer connecting the TCAQ molecule and the distance plays a key role in the charge transfer properties of TCAQ-based donor–acceptor systems, as we will see throughout this review. It is also worth mentioning that these were the first reported examples of chiral TCAQ dimers.

In 2004 Zeng and Becker reported the synthesis and electrochemical study of the novel TCAQ dimer **22** in which two TCAQ moieties were covalently linked to a calix[4]arene scaffold.[29] **22** could be obtained by reaction of TCAQ derivative **13** with a calix[4]arene derivative functionalized at the lower rim by two acid chloride groups. In this derivative, the three-dimensional structure of calix[4]arene acts as a weak electron donor, connected *via* a linear sigma spacer to two TCAQ acceptor units. Thus, due to the donor–acceptor nature of the material, the UV-vis spectrum of **22** shows an intramolecular charge transfer band in spite of the weak electron donor ability of the calix[4]arene due to the good acceptor ability of TCAQ.

In 2005 Satake and Fujihara reported the new TCAQ dimer **23**, which has been used to fabricate self-assembled monolayers on gold electrodes.[30] The TCAQ-disulfide **23** was obtained also from the versatile TCAQ derivative **13** by reaction with a suitably functionalized disulfide in the presence of diazabicyclo[5.4.0]undec-7-ene (DBU) at room temperature. The self-assembled monolayer films of TCAQ-disulfide **23** on gold electrodes were strongly stable under electrochemical recycling and showed the characteristic redox peaks of TCAQ units in cyclic voltammograms. This fact contrasts with the self-assembled monolayers of other disulfides bearing electroactive moieties, which show broad redox peaks and instability under repeated electrochemical reductions.

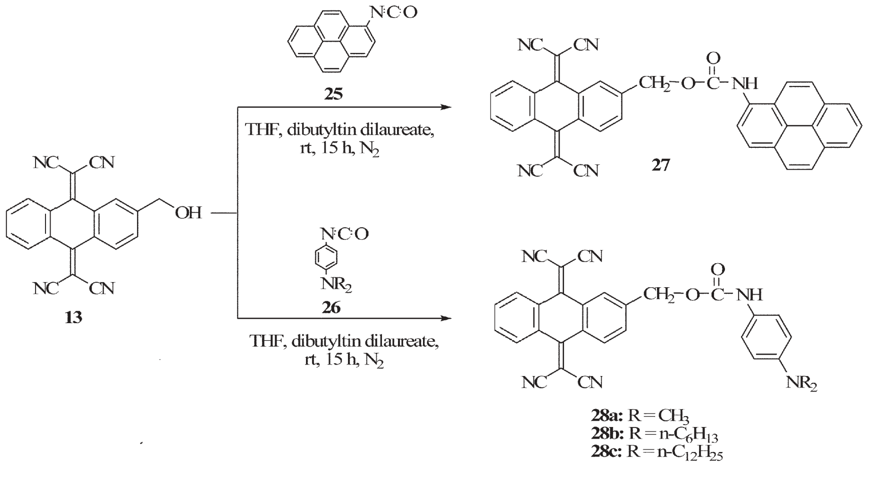
The calcium complex **24** was obtained while performing attempts to obtain TCAQ-2-carboxylic acid.[26] Thus, reaction of anthraquinone-2-carboxylic acid with malononitrile in the presence of Lehnert's reagent under standard conditions resulted in dicyanomethylation of the carboxy group to yield a product which was isolated as the calcium complex **24**. The authors claim that a possible source of calcium, leading to this lucky product, could be the distillation of dichloromethane (used in the synthesis) over CaH_2, and that some inorganic materials could have been transferred into the reaction flask.

By far, the biggest amount of TCAQ derivatives synthesized in recent years are related with donor–σ-acceptor structures for different applications, mainly in photoinduced electron transfer processes and in the search of organic rectifiers, taking advantage of the unique structural and electrochemical properties of TCAQ. The synthesis of the first TCAQ-based donor–σ-acceptor derivatives **27** and **28** was reported by Panetta and co-workers from TCAQ derivative **13**. These derivatives were prepared by the treatment of **13** with 1-pyrenyl isocyanate (**25**) and differently substituted 4-(dialkylamino)phenyl isocyanates **26**, respectively (Scheme 4).[31–34] The presence of long alkyl chains in **28b,c** allows them to form Pockels–Langmuir (PL) films at the air–water interface which can be mostly transferred as LB films onto solid substrates.[35]

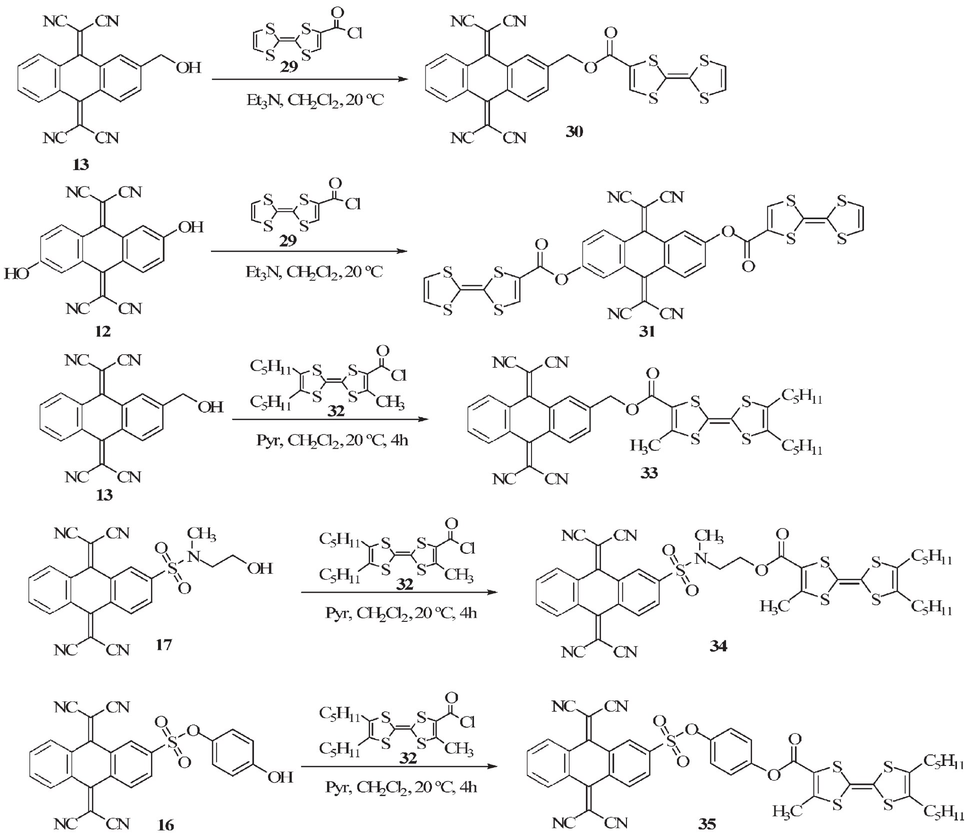
Following this seminal approach by Panetta and Metzger, other TCAQ-based donor–σ-acceptor derivatives (**30**,[22] **31**,[22] **33**,[26] **34**,[26] **35**,[26] Scheme 5) were reported by Bryce and co-workers containing stronger donor moieties such as the well known tetrathiafulvalene system.[36]

Reaction of 2-hydroxymethyl-TCAQ (**13**) with tetrathiafulvalenecarbonyl chloride (**29**) afforded the TCAQ–σ-TTF system **30** in a 30% yield. Diol **12** reacted similarly with two equivalents of TTF-carbonyl chloride to furnish the TTF–σ-TCAQ–σ-TTF assembly **31** (30%).[22] Both compounds could be isolated as very dark, colored, air-stable solids. Interestingly, their structures could be unambiguously assigned as covalent D–σ-A molecules, and not as intermolecular $D^{\cdot+}$–$A^{\cdot-}$ charge transfer complexes. Nevertheless, although compound **30** has an essentially neutral ground state, simultaneous electrochemistry and EPR experiments suggest the existence of an intramolecular interaction between the TCAQ fragment and the TTF moiety in the radical cation state.

One strategy followed to enhance the intramolecular charge transfer in these D–σ-A molecules involves the reduction of the oxidation potential of the TTF moiety and/or the increase of the electron affinity of the TCAQ moiety. With this aim, the novel TCAQ-σ-TTF derivatives **33–35** were synthesized.[26]



Scheme 4

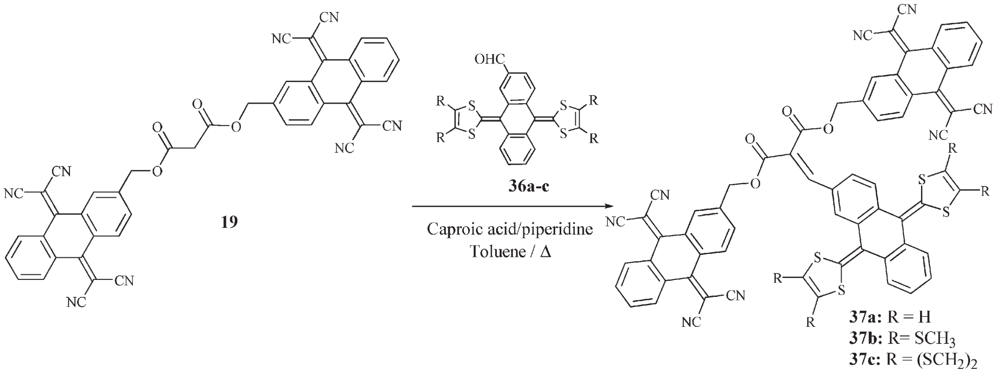


Scheme 5

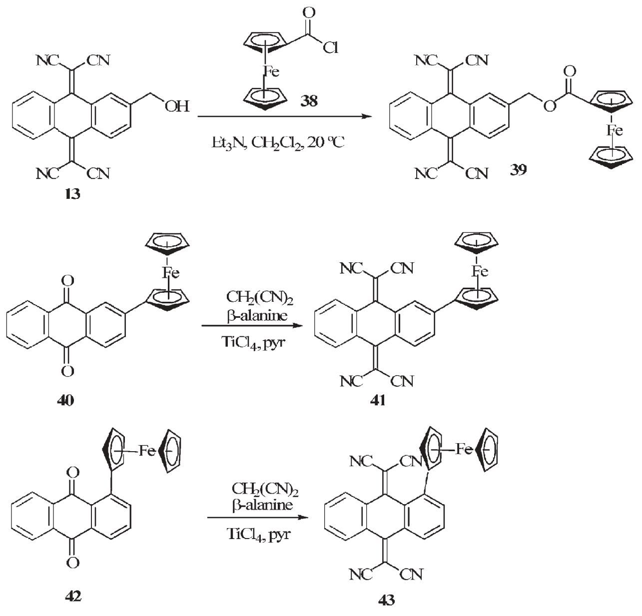
4,5-dipentyl-4′-methyl-TTF was used instead of TTF as it is known that alkyl substitution reduces significantly the oxidation potential of TTF.[37,38] On the other hand, the acceptor properties of the TCAQ moiety could be enhanced with the substitution of the TCAQ moiety with electron withdrawing sulfonamide and sulfonic ester groups. The beneficial effect of this new substitution pattern was manifested by the presence of broad absorption bands in the 400–550 nm region of their electronic spectra, which could be assigned to intramolecular charge transfer.

The π-extended tetrathiafulvalene unit has been also used as donor in TCAQ-based donor–σ-acceptor systems (**37**, Scheme 6).[28] TCAQ derivatives **37a–c** were prepared from TCAQ dimer **19** by Knoevenagel condensation between the acidic methylene groups of **19** and the formyl-substituted π-extended tetrathiafulvalene derivatives **36a–c**, using caproic acid/piperidine as catalyst in refluxing toluene with azeotropic distillation (Dean–Stark) of the water generated during the condensation reaction. Cyclic voltammetry measurements revealed no significant electronic interactions between the redox active units. Nevertheless, the electronic spectra of the triads showed intramolecular charge transfer bands from the strong donor π-extended tetrathiafulvalene to the conjugated carbonyl groups. Once again, the importance of the nature of the spacer on the degree of interaction between the electroactive units is made evident.

Ferrocene (Fc) moieties have been also used as donors in donor–acceptor ensembles together with TCAQ. Thus,



Scheme 6



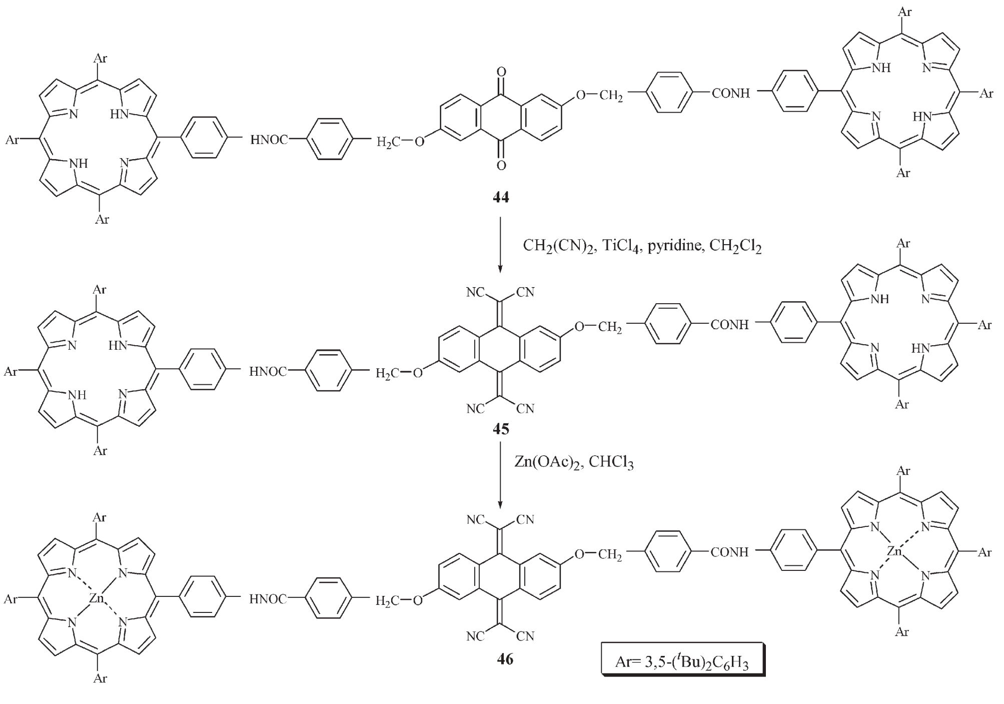
Scheme 7

reaction of TCAQ derivative **13** with ferrocene carbonyl chloride (**38**) afforded the TCAQ–σ-Fc system **39** (Scheme 7) in 40% yield.[22] Cyclic voltammetry measurements revealed that clean oxidation of the ferrocene moiety and reduction of the TCAQ processes take place in solution similarly to what is observed for TTF analogues. A very weak band in the 420–660 nm region was observed in this case and it was assigned to a charge transfer from the donor ferrocene fragment to the acceptor TCAQ moiety.

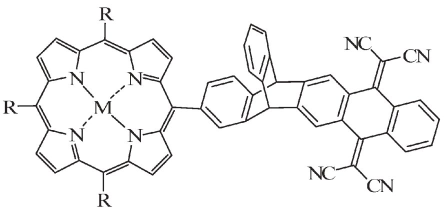
Butler and co-workers have recently synthesized novel donor–acceptor assembles containing ferrocene and TCAQ, in which the donor ferrocene moieties are linked to different positions of the TCAQ acceptor system by a direct covalent link (**41**, **43**, Scheme 7).[39] These new donor–acceptor systems were obtained from the appropriate quinoid precursors (**40**, **42**) by reaction with malononitrile in the presence of β-alanine and titanium tetrachloride. In contrast to the previous examples, in which donor and acceptors are linked through saturated spacers, in **41** and **43** both moieties are directly linked. Thus, structural, electrochemical and spectroscopic investigation performed in these systems showed a comparatively stronger interaction between the two units and shifts in the redox potentials could be also observed. Furthermore, low energy transitions above 600 nm were observed in the electronic spectra of **41** and **43**, which were assigned to intramolecular charge transfer processes. Interestingly, the position of the charge transfer band and the electrochemical behaviour differed significantly between **41** and **43**. A smaller separation between the oxidation and reduction processes was observed for **41**, which is consistent with the lower energy observed for the charge transfer transition.

Imahori, Okada, Sakata and co-workers have investigated the photophysical behaviour of the porphyrin–TCAQ–porphyrin triad **46** (Scheme 8).[40] **46** was obtained from the precursor quinone **44** by the typical TiCl$_4$ catalyzed condensation with malononitrile in dichloromethane followed by metallation of the porphyrin unit with Zn(OAc)$_2$ in 31% yield. This system exhibits photon-dependent molecular switching using two different excitation wavelengths. Thus, successive two-photon excitation with different wavelengths produces TCAQ^{2-} as output, whereas one-photon excitation generates TCAQ$^{\bullet-}$.

Wasielewski and co-workers investigated the electron transfer rate in several porphyrin–triptycene–acceptor molecules including TCAQ derivatives **47** (Fig. 8). These systems



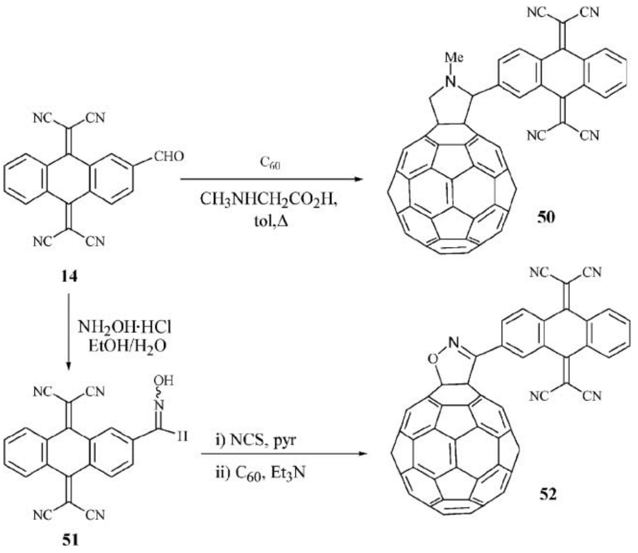
Scheme 8



47

R = C_5H_{11}, C_6H_5
M = 2H, Zn

Fig. 8



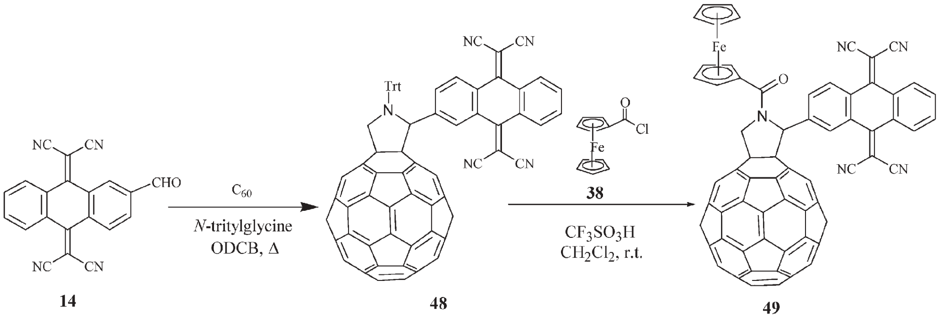
Scheme 10

possess ion-pair states whose energies (determined electrochemically) are destabilized by 0.8 eV in rigid glasses in comparison to polar liquids. Moreover, this value was proven to be dependent on the spacer structure. This observation was then used to design multistep electron transfer molecules to separate charge efficiently in the solid state.[41]

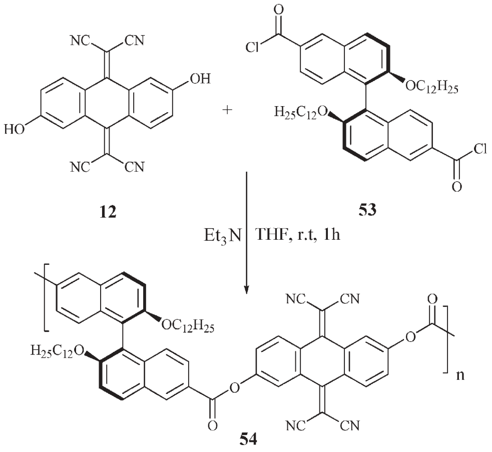
The covalent linkage of the electron acceptor fullerenes to electron donor fragments has been considered thoroughly in recent years to investigate photoinduced electron transfer processes.[42–45] One strategy to improve the stability of the charge separated state in donor–acceptor arrays involves the design of well-defined redox gradients along multiple redox centers, in order to gain control over the unidirectional electron transfer. In this regard, TCAQ has been incorporated in triad **49** (Scheme 9), together with [60]fullerene as an additional electron acceptor and a ferrocene unit as electron donor.[46] Triad **49** could be obtained in two steps from 2-formyl-TCAQ (**14**). Thus, 1,3-dipolar cycloaddition reaction of the *in situ* generated azomethine ylide upon treatment of 2-formyl-TCAQ (**14**) with *N*-tritylglycine to [60]fullerene, afforded the corresponding N-trityl-protected fulleropyrrolidine **48** in 27% yield. Subsequent deprotection of **48** with CF_3SO_3H followed by reaction with ferrocene carbonyl chloride (**38**) afforded the trichromophoric system **49** in a 36% yield. Cyclic voltammetry measurements of triad **49** exhibited three one-electron reduction steps corresponding to the [60]fullerene reduction together with a two-electron reduction wave from the TCAQ reduction and an oxidation wave corresponding to the formation of the radical cation of the ferrocene moiety. It is worth mentioning that some degree of interaction was observed between the TCAQ and the [60]fullerene unit, as can be inferred by the anodic shift of the [60]fullerene reduction potentials. Concerning the photophysical properties of this compound, an electron transfer in which ferrocene acts as the donor and the [60]fullerene as the acceptor is observed, the participation of TCAQ being excluded of the process.[46]

This interaction between the TCAQ moiety and the [60]fullerene system has been also used to prepare [60]fullerene derivatives with enhanced electron acceptor ability (**50**,[24,47] **52**,[47] Scheme 10). This fact is of major importance if it is taken into account that most of the [60]fullerene derivatives present weaker electron acceptor properties than the parent unsubstituted [60]fullerene due to the saturation of one double bond during the addition process to the [60]fullerene sphere, which raises the LUMO energy.[48]

Thus, Martín, Seoane and co-workers carried out the synthesis of **50**[24] by reaction of *N*-methylglycine with aldehyde **14** in the presence of [60]fullerene by a 1,3-dipolar cycloaddition reaction, similarly to that previously shown for **48**. On the other hand, reaction of aldehyde **14** with hydroxylamine hydrochloride afforded the corresponding oxime **51** which, upon further chlorination with *N*-chlorosuccinimide (NCS) and subsequent dehydrochlorination of the resulting hydroxymoyl chloride, yielded a nitrile oxide which undergoes a [3 + 2] cycloaddition reaction to the [60]fullerene moiety to afford compound **52** in a 16% yield.



Scheme 9



Scheme 11

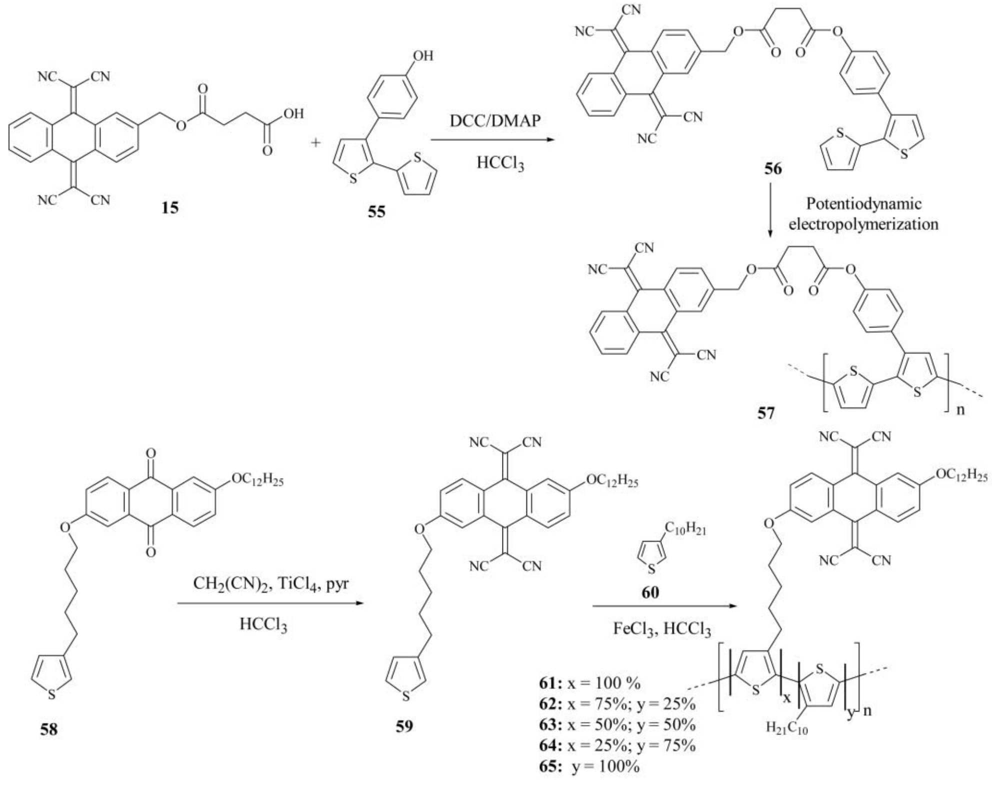
A remarkable difference can be observed when the reduction potential of the fulleropyrrolidine derivative **50** and the isoxazolofullerene derivative **52** are compared. Whereas **50** shows reduction waves at nearly the same reduction potentials as unsubstituted [60]fullerene, isoxazolofullerene derivative **52** exhibits reduction potentials which are anodically shifted (*ca.* 70 mV) in comparison with the parent [60]fullerene. This fact indicates that **52** is a stronger electron acceptor than the [60]fullerene itself, in spite of the saturation of one double bond. Moreover, it is remarkable that the presence of TCAQ in combination with [60]fullerene makes these systems truly "electron sponges" that are able to accept up to eight electrons in solution.

In order to enhance the miscibility of TCAQ with conjugated polymers in optoelectronic applications, Segura, Martín and co-workers have synthesized the first copolymer containing TCAQ moieties in the main chain together with enantiomerically pure binaphthyl units to increase dimensionality (**54**, Scheme 11).[49]

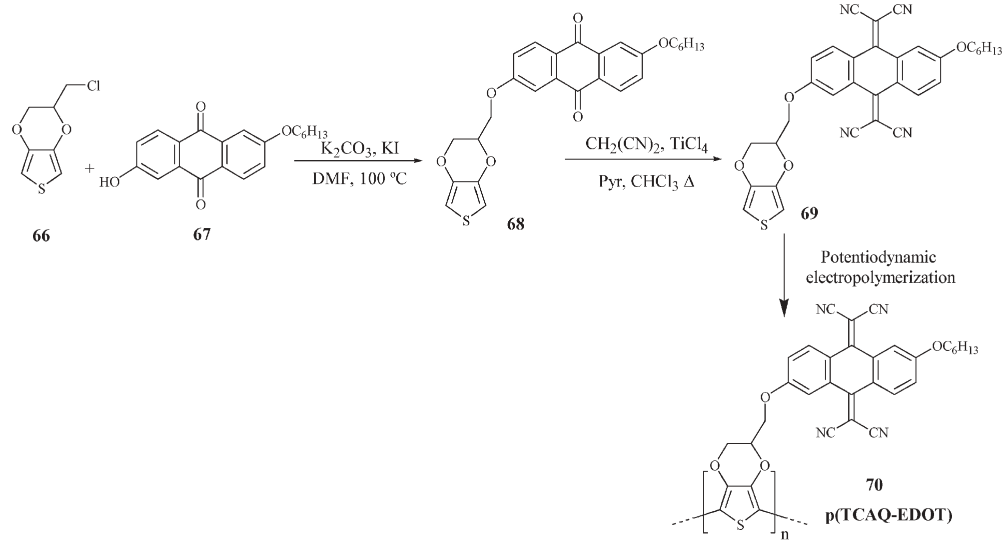
Polymer **54** was obtained by polycondensation reaction between 2,6-dihydroxy-TCAQ (**12**) and the acid chloride **53** in almost quantitative yield. The presence of alkyl chains in the 1,1′-binaphthyl moieties endowed the polymer with good solubility in common organic solvents, thus allowing its complete characterization despite its high molecular weight (M_n = 12000, M_w = 21000, polydispersity = 1.75). Similarly to the parent TCAQ, polymer **54** shows a single-wave, two-electron reduction. As in dimer **21**, no interaction between TCAQ and naphthalene units was observed.

The synthesis of donor–acceptor polymers consisting of polythiophenes bearing TCAQ as pendant groups have been also carried out by the groups of Bäuerle, Martín and Segura (**57**,[50] **61–64**,[51,52] **70**[53] Schemes 12 and 13). These types of materials are known as "double-cable" polymers,[54,55] as they consist of a hole-conducting conjugated polymer chain carrying pendant electron-conducting moieties.

Monomer **56** was synthesized by reaction of TCAQ derivative **15** with the phenol functionalised bithiophene **55** in dichloromethane in the presence of 1,3-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) in 88% yield. Thin polymer films were electrodeposited anodically, by sweeping the potential between 0 and +1.3 V with a rate of 100 mV s^{-1}, at 0 °C under argon atmosphere. Photoinduced



Scheme 12



Scheme 13

charge transfer was observed in the polymer as revealed by the features of polymer polarons and TCAQ anion radicals observed by photoinduced absorption spectroscopy and light induced ESR.[50]

On the other hand, random copolymers **61–65** were synthesized *via* chemical oxidation with $FeCl_3$ in chloroform starting from mixtures of monomers **59** and **60** in well-defined molar ratios.[51] The polymers were obtained with yields between 80 and 90 wt% with respect to the monomers after thorough washing with methanol to remove excess oxidant. It was shown that the electronic properties of the polymers could be modulated by tuning the amount of TCAQ-containing monomer **59** in the initial feed. In the electronic spectrum, the intensity of the band corresponding to the conjugated backbone increases with the decrease of the TCAQ content in the copolymers. This can be explained by the steric hindrance induced by the bulky TCAQ system, which produces more distortions of the conjugated backbone as the amount of the TCAQ-containing monomer increases. An efficient quenching of the characteristic fluorescence of the polythiophene system was also observed, the quenching being more efficient as the amount of TCAQ monomer in the polymer increases.

Bäuerle, Segura and co-workers have also recently synthesized a donor–acceptor poly(3,4-ethylenedioxythiophene) (PEDOT) derivative with pendant TCAQ moieties (**70**, Scheme 13).[53] By adapting a synthetic route developed to synthesize functionalized PEDOT derivatives,[56] we have covalently linked a 9,10-anthraquinone moiety to the EDOT core (**68**). Further reaction of **68** with malononitrile in the presence of Lehnert's reagent afforded the TCAQ-EDOT derivative **69**. Potentiodynamic electropolymerization of **69** yielded polymer p(TCAQ-EDOT) **70** as thin films on Pt electrodes. The electrochemical characterization of this polymer shows the presence of characteristic waves of solid-state "charge trapping" phenomena, where charge is released at over potential.[57] This may be due to the close vicinity of the TCAQ moieties in the solid state, which may allow the formation of weak σ bonds by the coupling of the radicals located on the nitrile-bearing carbons.

To conclude with this synthetic part, it is worth mentioning how the first two decades after the initial synthesis of 11,11,12,12-tetracyano-9,10-anthraquinodimethane (TCAQ) in 1983 have witnessed an impressive development of the TCAQ chemistry, which has shown this molecule as a versatile electron acceptor building block. In the next section we will focus on some of the applications found for compounds built with the TCAQ moiety.

Applications of TCAQ and derivatives

Electrical conductivity

Since high electrical conductivity was discovered in the charge-transfer (CT) complex between tetracyano-*p*-quinodimethane (TCNQ) and tetrathiafulvalene (TTF), much attention has been devoted to CT complexes of electron donors and acceptors. Thus, in order to develop new materials with enhanced conducting properties, as we have previously mentioned, the extension of the π system in TCNQ derivatives was thought to be of great importance to reduce the intramolecular electron repulsion and thereby should lead to more stable radical anions. It is in this context that the first synthesis of TCAQ was developed. Soon after its synthesis, it was suggested that TCAQ would fail to form charge transfer complexes[9,10] because of its lack of planarity and the lower acceptor ability in comparison with the parent TCNQ, commonly used as CT component at that time. However, a different scenario was depicted when in 1985 Mukai and co-workers reported that TCAQ could form CT complexes not only in solution but also in the solid state. It could form stable molecular complexes in combination with organic donors such as pyrene, anthracene, perylene or TTF, in spite of its non-planar structure.[20] Nevertheless, the high electrical resistivities of TCAQ complexes, which were mainly attributed to the non-planar structure of TCAQ, makes them behave as insulators.

Other attempts to form CT complexes with TCAQ derivatives have been carried out,[27,58,59] and although evidences of complexation in solution have been observed in the UV-vis spectra, no conducting CT-complexes based on TCAQ have been reported so far.

A different strategy to achieve electrical conductivity involves the use of Langmuir–Blodgett films.[21,60–65] Conducting Langmuir–Blodgett films with high quality morphology and with reproducible and stable properties are interesting in view of the development of molecular electronics. It was shown that the use of surfactant TCNQ derivatives with long-chain alkylic substituents could be successfully used for the preparation of conducting films when used in combination with tetrathiafulvalene derivatives.[66] Although the electron affinity of TCAQ is lower than that of TCNQ, the stability of TCAQ is higher and the presence of electron withdrawing groups such as sulfonyl or carbonyl at the head of these substituents efficiently increases the electron affinity of the molecule. The introduction of hydrophilic groups such as amino, sulfonyl or carbonyl at the head of a long-chain substituted TCAQ has been used to improve the molecular spreading on water subphases. With this aim, Vorobyova and Berzina have investigated the possibility to prepare highly conducting LB films from mixtures of surfactant TCAQ derivatives (**11l**, **11m**, **11o**, Fig. 5) and surfactant tetrathiafulvalenes.[21] It was shown that compound **11l** in a mixture with tetrathiafulvalene derivatives gives LB films with homogeneous morphology and a conductivity of *ca.* 0.1–0.5 S cm^{-1} which are stable for more than three months. Compounds **11m,o** yielded LB films of excellent quality having a stable conductivity of 1–5 S cm^{-1} from a mixture with tetrathiafulvalene derivatives. The higher electron affinity of acceptors **11m,o** in comparison with **11l** may be responsible for the higher conductivity of the films fabricated with **11m,o**. This study shows how the presence of the electron-accepting carbonyl or sulfonyl groups improves the ability of TCAQ derivatives to form conducting films in combination with donor counterparts.

Molecular rectification in donor–σ-TCAQ materials

In 1974 Aviram and Ratner proposed rectification of electrical current through a single D–σ–A molecule, in which a strong donor moiety was covalently attached to a strong acceptor moiety through a covalent, saturated σ bridge.[67] Molecule **71** (Fig. 9(a)) was chosen as a prototype material because of the excellent acceptor and donor properties of TCNQ and TTF, respectively. In order to achieve molecular rectification, the molecule should exhibit anisotropic electrical properties. Thus, these materials should be aligned uniformly between two electrodes (M_1 and M_2) so that they would allow electrons to flow from the cathode (M_2) to the acceptor end, from there to the donor through the σ bridge *via* electron tunneling, and then from the donor terminus to the anode (M_1). Fig. 9(b) shows that such a device is asymmetric, because the HOMO of the donor (D) is relatively low whereas the LUMO of the acceptor (A) is relatively high. The device will work if the inelastic through-bond tunneling is more likely than the elastic through-space tunneling, which is unaffected by molecular orbitals.[68]

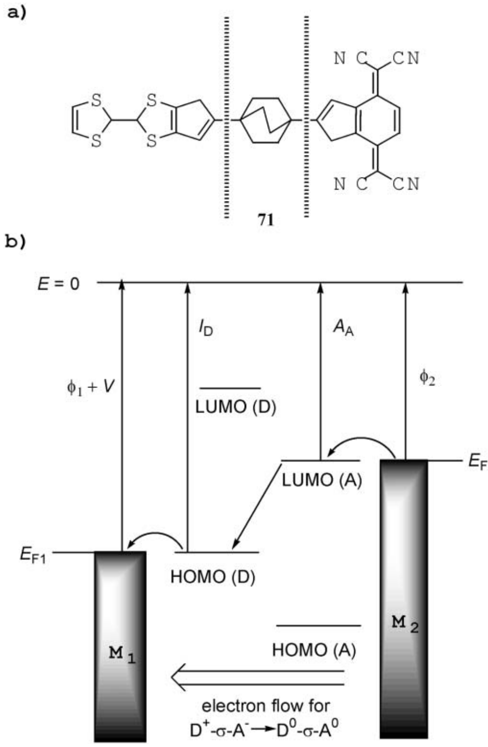


Fig. 9 (a) Original D–σ–A structure **71** proposed by Aviram and Ratner for a molecular rectifier. (b) The Aviram–Ratner mechanism, showing the through-molecule electron flow from the excited zwitterion state D^+–σ–A^- to the ground state D^0–σ–A^0.

TCAQ-based carbamates **28b** and **28c** (Scheme 4) were proposed as potential candidates for unimolecular electrical rectifiers.[35] They showed an amphoteric redox donor–acceptor behavior and were designed to include appropriate terminations to enable the molecule to assemble between metal electrodes for electrical measurements. Both molecules formed Pockel–Langmuir monolayers at the air–water interface and LB films on a solid substrate. However, the methods of testing for rectification used by the Metzger group in the period 1983–1990 were too crude in words of the authors, and no rectification was found in spite of the smart design.[69] Since the theoretical seminal idea by Aviram and Ratner, numerous experimental strategies to achieve rectification in donor–acceptor molecules have been attempted.[70–74]

Although the covalent linkage of TTF and TCNQ moieties has received special attention to be used in rectifiers since the proposal of molecular rectification of Aviram and Ratner,[67] a major drawback for the synthesis of such a system arises from the often observed irreversible formation of intermolecular TTF·TCNQ charge transfer complexes instead of the desired covalently linked molecule. In fact, electron paramagnetic resonance (EPR) and IR data of the first donor–acceptor system containing a TCNQ molecule covalently attached to a TTF unit suggested an ionic ground state, *i.e.* the formation of a CT complex.[75] Furthermore, difficulties with its purification precluded a detailed characterization. As an alternative to overcome this difficulty, in 1998 Bryce and co-workers reported on the synthesis and study of **30** (Scheme 5) and a related TTF–σ-TCAQ–σ-TTF triad (**31**, Scheme 5) in which the strong donor TTF was covalently attached to the acceptor TCAQ moiety.[22] These were the first readily available, analytically pure and stable TTF–spacer–TCAQ derivatives. In contrast to the previous TTF–TCNQ system, EPR (no signal) and IR data on powdered samples of **30** suggested a neutral ground state. Moreover, simultaneous electrochemical and EPR experiments provided evidence that the spin density distribution in the radical cation of **30** was modulated intramolecularly by the adjacent TCAQ moiety. This behavior was significantly different to that observed in a mixture of model TTF and TCAQ derivatives which did not interact in solution when mixed under the same experimental conditions.

Other D–σ–A dyads **31–34** (Scheme 5) where the D and the A are, respectively, TTF and TCAQ units substituted with electron donating and electron withdrawing substituents have been also synthesized.[26] As in the case of **30**, these systems are essentially neutral and there are no significant interactions between donor and acceptor moieties in the solid state. Therefore, these derivatives would be good candidates to prepare macroscopic films in order to study their behavior as bulk rectifiers in devices. However, to the best of our knowledge, the achievement of rectification by these systems has not been reported so far.

TCAQ derivatives and photoinduced electron transfer

Since photoinduced energy and electron transfer processes within a molecule can occur in an ultrafast time scale, *e.g.* femto- and picoseconds, it is possible to develop efficient optoelectronic devices which respond quickly and reversibly. The first investigations of photoinduced electron transfer processes in a TCAQ-based system were reported by Wasielewski and co-workers[41] Thus, it was shown that the porphyrin–triptycene–TCAQ system **47** (Fig. 8) had a sufficiently large and negative free energy for charge separation to allow electron transfer to compete with excited singlet state decay. This result, together with those of a series of 13 porpyrin–tryptycene–acceptor molecules allowed to design multistep electron transfer molecules to efficiently separate charge transfer in the solid state.

In 1998, Imahori, Okada, Sakata and co-workers reported photon-dependent molecular switching in the porphyrin–TCAQ–porphyrin triad **46** (Scheme 8).[40] As it was already mentioned, the structure of $TCAQ^{2-}$ dianion species is quite different from the neutral one with the two negatively charged dicyanomethylene $[C(CN)_2]^-$ groups rotated around the single bond that connects these $C(CN)_2$ groups with the anthracene ring. As a consequence, the dianion structure is stabilized in comparison to that of the monoanion, where the steric interactions are not fully relieved. Thus, it was expected that two-photon excitation in **46** led to the formation of a long-lived charge-separated state as output, while one-photon excitation would result in the formation of the short-lived charge-separated state if the rotational rate of $C(CN)_2$ is faster than that for charge recombination.[40] It was observed experimentally that one-photon excitation of one of the two porphyrins within triad **46** with a picosecond laser led to a single reduction of the acceptor by intramolecular electron transfer, whereas an additional delayed excitation of the non-excited porphyrin resulted in double reduction of the acceptor (Fig. 10).

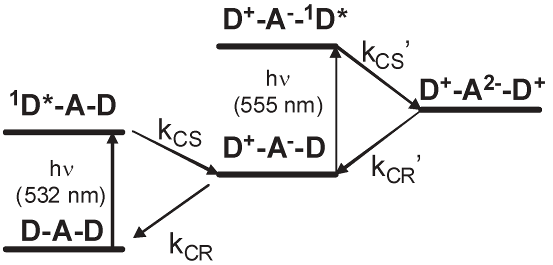


Fig. 10 Energy level diagram of **46** in dioxane. K_{CS}: charge separation constants; K_{CR}: charge recombination constants. (Redrawn from ref. 40.)

The photophysics of the triad [60]fullerene–TCAQ–ferrocene **49** (Scheme 9) have been also investigated in detail by means of fluorescence spectroscopy and time-resolved transient absorption spectroscopy.[46] It was observed that the singlet lifetimes in triad **49** were nearly identical to that of a reference [60]fullerene–ferrocene dyad, which is in agreement with an intramolecular electron transfer from the donor ferrocene (Fc) to the acceptor [60]fullerene. In principle, taking into account the reduction potentials, a secondary electron transfer between the reduced fullerene ($E_{1/2}(C_{60}/C_{60}^{\bullet -}) = -0.60$ V *vs.* SCE in **49**) and TCAQ ($E_{1/2}(TCAQ/TCAQ^{\bullet -}) = -0.34$ V *vs.* SCE in **49**), in a thermodynamic sense, might take place. However, when the large free energy changes for charge recombination within the $C_{60}^{\bullet -}$–TCAQ–$Fc^{\bullet +}$ couple are compared to the small free energy changes for a subsequent electron transfer to yield C_{60}–$TCAQ^{\bullet -}$–$Fc^{\bullet +}$, the second electron transfer can be ruled out and thus the overall photophysical processes that take place are:

$$C_{60}\text{–TCAQ–Fc} \rightarrow {}^1C_{60}^*\text{–TCAQ–Fc} \rightarrow C_{60}^{\bullet -}\text{–TCAQ–Fc}^{\bullet +}$$

On the other hand, it is worth mentioning that, since the discovery of efficient photoinduced charge separation between semiconducting polymers, acting as donors, and [60]fullerene and its derivatives, as acceptors,[76,77] the possibility to use conjugated polymers to fabricate inexpensive and flexible large areas solar cells and photodetectors has been intensively investigated.[78,79] Although different types of π-conjugated polymers have been tested as donors, which exhibit electron transfer to [60]fullerene upon photoexcitation, the acceptor side has received less attention.[80] In this regard, Janssen *et al.* reported in 1995 photoinduced electron transfer processes in composite films of π-conjugated polymers and a homologous series of tetracyano-*p*-quinodimethane derivatives **72–75** (for molecular structures, see Fig. 11).[81,82] This paved the way to the extensive work by Martín and co-workers on photoinduced electron transfer of TCAQ derivatives.[46,47,50–52] Near-steady-state photoinduced absorption (PIA) spectroscopy investigation demonstrated that photoinduced electron transfer occurs from poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and poly[3-(2-(3-methylbutoxy)ethyl)thiophene] (P3MBET) to various aromatic-fused tetracyano-*p*-quinodimethane derivatives with different

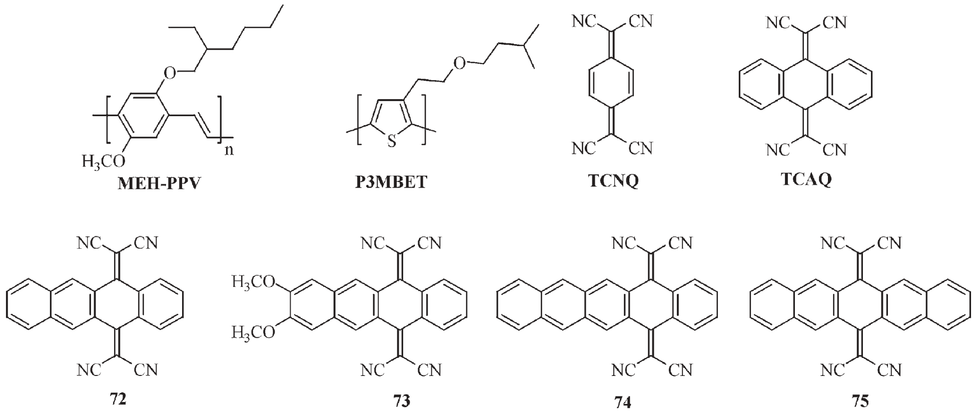


Fig. 11 Molecular structures of MEH-PPV, P3MBET and aromatic-fused tetracyano-*p*-quinodimethane derivatives used in mixed films to investigate photoinduced electron transfer processes.

efficiencies. Two factors were found to affect the electron transfer rate: (i) differences in electron affinity and (ii) phase segregation and solubility of the acceptor molecules within the conjugated polymer matrix.[81] Surprisingly, TCAQ was found to be a more efficient electron acceptor than TCNQ in these photoinduced electron transfer processes, despite its lower reduction potential. It is worth mentioning that the different solubilities of the donor and acceptor components used for the film preparation and their limited miscibility caused morphological problems, such as the mentioned phase separation, which in turn influenced the photoinduced charge generation.

One way to circumvent the problem of phase separation is given by the concept of donor–acceptor "double cables". As previously mentioned, this kind of materials consists of a hole-conducting conjugated polymer chain carrying pendant electron-conducting moieties. In this way, electron-acceptor and donor units are forced from the primary structure to form a p- and n-conducting network with well-defined links.[54]

In 2001 Sariciftci, Martín and co-workers reported the first example of a TCAQ-based double-cable polymer (**57**, Scheme 12), which was investigated by time-resolved photoinduced absorption spectroscopy (PIA) and light-induced electron spin resonance (LESR).[50]

The PIA spectrum of **57** displayed additional bands together with the TCAQ radical anion features already observed in the monomer **56** (Scheme 12). These new absorptions were assigned to charged excitations on the thiophene backbone of **57** by comparison with pristine unsubstituted polythiophene. Furthermore, the LESR signal was the result of an overlap of the two neighbouring lines from the TCAQ anion and polymer radical cation generated during a photoinduced charge transfer.

One important issue in the design of "double-cable" polymers is to improve the processability in order to obtain soluble materials with a high content of acceptor moieties. For example, soluble conjugated polymers containing [60]fullerene exhibit a content of acceptors not exceeding 20%, which greatly restrains its application in devices.[83] A series of donor–acceptor polythiophene copolymers containing TCAQ electron acceptors as pendant groups (**61–64**, Scheme 12) aimed to obtain processable photoactive materials with a tunable D/A content have been prepared as an alternative to fullerenes.[51] The most outstanding feature of this approach is that the content of acceptor can be easily tailored within the 0–100% range, giving soluble and processable materials even in the case of a 100% substitution of acceptor on the backbone. For this copolymer series, the photoluminescence (PL) of chloroform solutions is quenched by one or two orders of magnitude with respect to a reference polythiophene without TCAQ units (**65**, Scheme 12) after photoexcitation at 450 nm. The quenching increases with the TCAQ content suggesting a photoinduced charge transfer from the conjugated backbone to the acceptor.[52] Photoluminescence intensities of these copolymers were compared with that of mixtures of the homopolymers **61** and **65**. In these mixtures, the PL quenching was less efficient than in the donor–acceptor copolymers, which indicates that when the electron donor backbone and the acceptor molecules are covalently linked, their proximity leads to a more efficient photoinduced electron transfer than in mixtures.

Martín and Sariciftci have also investigated TCAQ derivatives with an alkyl side-chain substitution pattern (**76a,b**, **77**), one of them attached to a [60]fullerene molecule forming the dyad **77**, shown in Fig. 12(a).[84] Alkyl side substitution was chosen as a way to provide better solubility in organic solvents and also to improve the miscibility with conjugated polymers, thus increasing photoinduced electron transfer.

Photoinduced electron transfer was observed in composite films of the electron acceptor TCAQ derivatives (**76a,b** and **77**) with the electron donor poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV, Fig. 12) by light induced ESR and photoinduced absorption spectroscopy. After the addition of 0.1 mol% of TCAQ derivatives **76** to the MDMO-PPV a luminescence quenching by a factor of 3 was observed. In the case of the electron acceptor dyad **77**, composed of a [60]fullerene and a TCAQ unit, there is some evidence for an additional influence of the [60]fullerene unit on the electron accepting properties of the whole compound.[84] Nevertheless, a change of morphology and phase separation of the sample when passing from a TCAQ-type to a [60]fullerene-type electron acceptor may also strongly influence the amount of luminescence quenching, which could explain the different behavior. Following the LESR investigation of dyad **77**, the dominant final state of the electron transferred from the polymer to the electron acceptor dyad seems to be the TCAQ

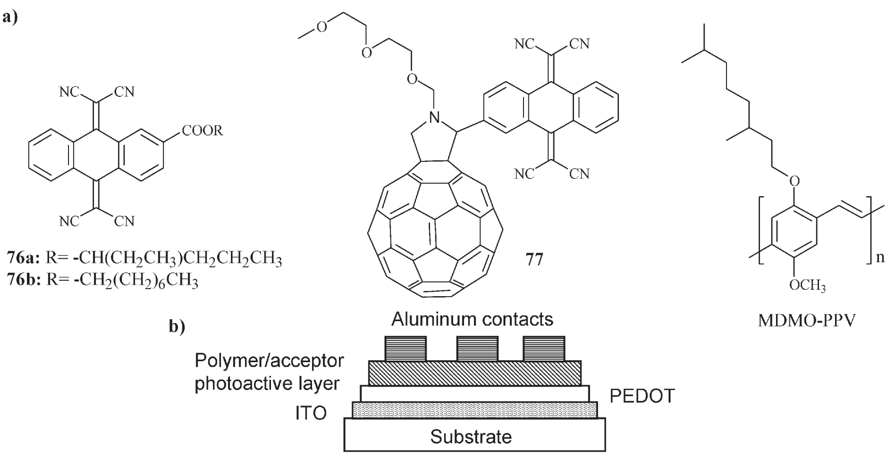


Fig. 12 (a) Chemical structures of the highly soluble TCAQ derivatives **76a,b** and **77** together with that of MDMO-PPV used in the fabrication of organic photovoltaic devices. (b) Schematic setup of a plastic solar cell device. ITO: indium tin oxide, PEDOT: poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate).

unit (dominant LESR line), with a small [60]fullerene anion formation (weak LESR shoulder). From these results, it can be inferred that both parts of the acceptor dyad are involved in the charge transfer.

Donor/acceptor interpenetrating network photovoltaic devices have been also fabricated with compounds **76** and **77** with the setup depicted in Fig. 12(b).[84] A power conversion efficiency of 0.03% was observed under 60 mW cm^{-2} white light illumination when using **77** as the acceptor. Interestingly, the dark and illuminated I/V curves of the device are rather symmetric around 0 V and V_{oc} respectively. This symmetry typically indicates an ohmic contribution to the diode, probably due to small shunts as a consequence of the immiscibility between **77** and MDMO-PPV in spite of the long oligoether solubilizing chains. Finally, atomic force microscopy (AFM) studies have given evidence of phase separation between MDMO-PPV and **77**.

For mixtures of **76** and MDMO-PPV, although an efficient photoinduced electron transfer was observed, only weak photovoltaic performance was obtained, which can be explained by poor charge carrier transport of the electrons *via* the TCAQ derivative.

A different approach in order to enhance the miscibility between the donor and the acceptors involves the incorporation of TCAQ moieties in copolymers such as **54** (Scheme 11).[49] Again, efficient photoinduced electron transfer has been observed in blends composed of MDMO-PPV and **54**, but only poor performances have been achieved in photovoltaic devices.

From all of the above it can be concluded that TCAQ is a good candidate to be used as model compound to investigate photoinduced electron transfer processes. Nevertheless, its application in photovoltaic devices seems to be limited so far by the poor charge carrier transport in the amorphous blend.

TCAQ as sublayers in optoelectronic devices

Cao *et al.* have used TCAQ as hole transport layer in electroluminescent devices (Fig. 13).[85,86] In this application, while the metal electrode injects electrons into the electroluminescent material, the TCAQ layer injects holes into the conduction band of the electroluminescent material, which hardly meet any energy barriers. Therefore, the driving voltage of the device is lower than that of a similar device without the TCAQ layer.

On the other hand, as the field of organic electronics is an emerging field, there is an increasing need for fine-tuning the energy level alignment between conjugated organic materials and metal electrodes. One interesting approach in this regard involves the absorption of a monolayer of TCAQ on a metal surface.[87] It has been recently demonstrated that the insertion of a TCAQ monolayer at organic/metal interfaces enables the systematic tuning of the hole injection barrier height. Thus, the hole injection barrier height at the interface between α-sexithiophene and Ag(111) can be reduced by 0.3 eV by insertion of a monolayer of TCAQ. This is possible due to a charge transfer type interaction between the electron acceptor TCAQ and the silver. This strategy shows that by choosing appropriate material combinations it is possible to fine-tune the hole injection barrier height at organic/metal interfaces.

Applications of chiral TCAQ derivatives

Electrochiroptical materials are a novel class of multi-output response systems, in which the electrochemical input is transduced into two types of spectral outputs, *e.g.* UV-vis

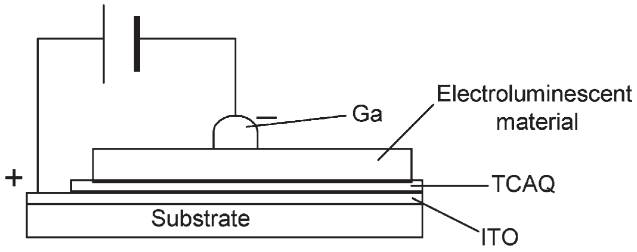
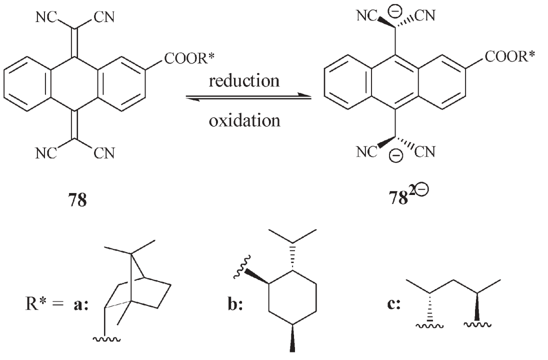


Fig. 13 Schematic setup of a light emitting diode with a TCAQ-based hole conducting layer.



Scheme 14

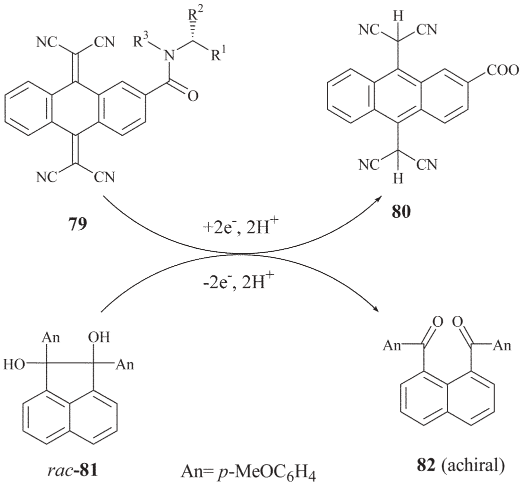
and circular dichroism. Suzuki and co-workers have recently shown that chiral TCAQ derivatives **78** (Scheme 14) can serve as unprecedented molecular response systems, by which an electrochemical input is transduced into three-way spectral outputs (UV-vis, fluorescence and circular dichroism).[88] **78** was designed taking into account the following considerations: (i) the TCAQ moiety must act as a strong chromophore, what induces UV-vis spectral change upon electrolysis, (ii) a chiroptical output must be obtained when the chromophore is attached with an asymmetric element like a chiral ester group and (iii) the non-fluorescent TCAQ must become fluorescent upon reduction thanks to the anthracene skeleton generated in the reduced state.

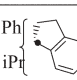
Thus, the electrochemical reduction of **78a,b** caused continuous UV-vis spectral changes with a vivid colour change to violet characteristic of the TCAQ dianion. Furthermore, after the electrolysis, the solution became fluorescent but, unfortunately, the circular dichroism (CD) signals of **78a,b** were too weak to be used as spectral outputs.

On the contrary, the twin compound **78c** is much more CD active. Thus, following the electrochemical reduction of **78c**, together with the change in the UV-vis spectrum and the increase in the fluorescence intensity, a drastic change was also observed by CD spectroscopy. This was the first example of an electrical input that is transduced into three independent spectral outputs.

In 2005, Suzuki *et al.* have also shown that TCAQ derivatives with a chiral amide group can be involved in reactions that can serve as a novel prototype of photochirogenesis.[89]

They have found that TCAQ derivatives with a chiral amide auxiliary (**79**, Scheme 15) can act as stereodifferentiating oxidants under charge transfer excitation conditions. Thus, the photochemical reaction of TCAQ derivatives **79** with *rac*-1,2-dianisylacenaphthene-1,2-diol (**81**) provides the dihydro-TCAQ **80** together with achiral 1,8-dianisoylnaphthalene **82** (Scheme 15).



	a	b	c	d	e	f
R^1	Ph	Ph	Ph		Ph	cHex
R^2	Me	Et	iPr		Me	Me
R^3	H	H	H	H	Me	H

Scheme 15

Upon irradiation of a solution of TCAQ derivative **79a** and racemic pinacol **81** with a 500 W Xe lamp at 0 °C, **79** and **81** were consumed with the concomitant formation of dihydro-TCAQ **80a** and the diketone **82**. Interestingly, the enantiomeric excess (*ee*) of the recovered **81** could be determined by chiral HPLC, which gave a value of 12.3% *ee* [*i.e.* rich in (*S*,*S*)-(+)-**81**] at 54% conversion. A higher value of 21.5% *ee* was obtained at 70% conversion upon prolonged irradiation (3 h). The same results were obtained for derivatives **79b,c,f** whereas neither bicyclic amide **79d** nor *tert*-amide **79e** induced more than 1% *ee* for the recovered pinacol. The different behavior is probably due to the different geometrical difference around the chiral amide groups. However, although the observed photo-differentiation is not very high, this reaction provides a rare example of asymmetric photoreactions under charge transfer excitation conditions.

Summary

The first two decades after the synthesis of TCAQ have witnessed a great interest on this system from the synthetic, theoretical and applications point of view.

The structural behavior of TCAQ has been investigated showing that in the neutral form it adopts a folded boat-type structure as shown by X-ray crystallography and theoretical calculations. Upon reduction, the dicyanomethylene units in TCAQ can rotate freely allowing the anthracene core to become planar. From the electrochemical point of view, whether structural change and electron transfer are concerted or occur in discrete steps is still an open question.

Despite the several synthetic approaches developed for its synthesis, the direct conversion of anthraquinone derivatives to TCAQ analogues by condensation with malononitrile in the presence of $TiCl_4$ and pyridine remains as the most efficient and versatile. This approach has made possible the synthesis of functionalised TCAQ derivatives whose reactive groups have allowed its incorporation into complex architectures by a variety of reactions (Wittig–Horner, esterification, …).

Thus, the understanding of the particular structural and, moreover, electrochemical characteristics as well as the establishment of an accessible method for the synthesis of this unique molecule has allowed the smart design of materials with tailored properties.

In the search of electrically conducting materials, the most promising strategy involves the development of highly conducting LB films from mixtures of surfactant substituted TCAQ derivatives and surfactant tetrathiafulvalenes.

Many efforts have been devoted to the synthesis of TCAQ-based donor–acceptor systems towards unimolecular rectifiers, which allowed the synthesis of the first TTF–spacer–TCNQ derivative **30** and other substituted analogues **31–34**. Some of these derivatives are good candidates to prepare macroscopic films in order to study their potential behavior as bulk rectifiers in suitable devices.

TCAQ derivatives have proven to be very important materials to be used in the investigation of both inter- and intramolecular photoinduced electron transfer processes. However, despite the presence of efficient photoinduced electron transfer processes in blends of TCAQ derivatives and conjugated polymers, the application of TCAQ derivatives in photovoltaic devices seems to be limited by the poor charge carrier transport in the amorphous blends.

Other important applications of TCAQ have evolved in 2005. The first one involves the use of TCAQ to fine-tune the hole injection barrier of metal electrodes in optoelectronic devices which is fundamental to improve performances of the devices. A second and interesting one is concerned with the development of multi-output response system by which an electrochemical input is transduced into three-way spectral outputs (UV-vis, fluorescence and circular dichroism). Finally, TCAQ has been recently found to offer exciting possibilities in reactions that can serve as a novel prototype of photochirogenesis.

In summary, TCAQ is a molecule whose interesting electronic properties have challenged the creativity and inventiveness of chemists in areas such as organic, polymer, supramolecular and materials chemistry. The knowledge accumulated during this twenty years paves the way for the development of novel applications for this unique molecule.

Acknowledgements

We thank the Comunidad de Madrid (PR45/05-14167) and MCyT (Ref. CTQ2004-03760) for financial support. R. G. is indebted to the "Programa Ramón y Cajal". The authors wish to give credit to the scientists who have participated in the development of this chemistry whose names are cited in the references.

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