

Charge-transfer complex formations of tetracyanoquinone (cyanil) and aromatic electron donors

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Single-electron oxidants are the primary reagents for investigations of the new oxidants and the development of electron-accepting materials for application in optoelectronics. Quinones are the well-known class of the neutral single-electron oxidants. Here, we present the properties of the strongest neutral electron acceptor of this class tetracyanoquinone (cyanil) and investigate its electron-accepting strength by analyzing the charge-transfer complex formations with the aromatic donor molecules. Charge-transfer complexes of tetracyanoquinone with aromatic electron donors are characterized spectroscopically in solution and isolated as the single crystals. Copyright © 2015 John Wiley & Sons, Ltd.

Keywords: acceptor; charge-transfer complex; oxidant; *p*-cyanil

INTRODUCTION

Since the first seminal work by Mulliken^[1] on the nature of charge-transfer (CT) complexes and realizing their potential as the conducting organic materials,^[2] CT complexes have witnessed continues interest in the development of novel organic electronic materials.^[3–6] CT complexes consist of an electron donors and acceptors, which with the increase in electron-donating or electron-accepting ability of the components, CT complexes could be extended to the electron-transfer (ET) salts.^[7] While the development of wide range of electron-donating materials starting from the molecular electron donors as tetrathiafulvalene (TTF)^[8] all the way to the electron-rich π -conjugated polymeric materials has been an active part of the research in organic electronics,^[9] the development of the electron-accepting counterparts is still relatively scarce.^[10] Electron-deficient alkenes and quinones are among the common molecular electron acceptors (Chart 1).^[11] [TTF⁺, TCNQ⁻] ET salt was the first molecule-based electron conductor and superconductor.^[12,13] Miller and coworkers have demonstrated the room temperature ferromagnets of ET salts between organometallic compounds and tetracyanoethylene.^[14–16]

On the other hand, electron-deficient quinones, particularly 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), which is also known as a strong hydrogen acceptor ($H^+ + e^-$) used as an oxidant for good donors and allylic arenes such as steroids.^[7] Recently, it has been used in oxidative carbon-carbon bond forming reactions via carbon-hydrogen bond activation of organic substrates.^[18–20] Often, reactions with DDQ require high-temperature regimes, which is due to the relatively low reduction potential of DDQ. From these perspectives, it was interesting for us to see the properties of better oxidant from the same class of compounds (quinones), tetracyanoquinone (cyanil, TCQ chart 1). In addition,

TCQ has a higher symmetry than DDQ, which could also be used in organic optoelectronics as a strong electron acceptor.^[21] TCQ was synthesized and characterized earlier,^[2–24] however, most of the earlier studies were focused on the reduced forms of the TCQ as hydroquinone H_2TCQ , radical anionic TCQ^- , and dianionic form TCQ^{2-} .

The objective of this work is to investigate the electron-accepting strength of TCQ by studying its CT complex formation with the various arenes that differs structurally and in their ionization potential. In particular, isolation of single crystals and spectral characterization of the CT complexes will be examined.

RESULTS AND DISCUSSION

Spectroscopy of the charge-transfer complexes of tetracyanoquinone with aromatic donors

Addition of TCQ to a solution of organic donor molecules in dichloromethane results in the appearance of an absorption band in a visible region of the spectrum. Figure 1 demonstrates the bathochromic shift of the new band appeared upon mixing of TCQ with the selected organic donor molecules. Bicyclic aromatic molecules such as naphthalene and 2,6-dimethylnaphthalene together with para-dimethoxyphenyl derivatives resulted in double absorption peaks. We correlate the lowest energy absorption

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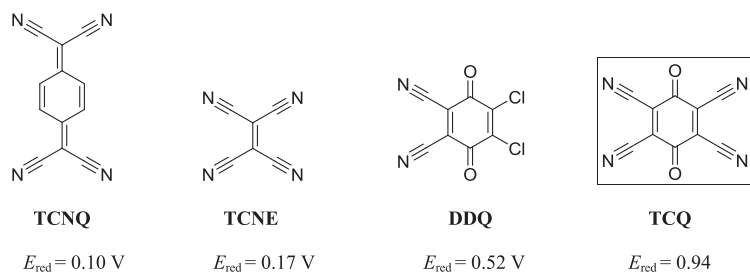


Chart 1. Typical molecular acceptors.

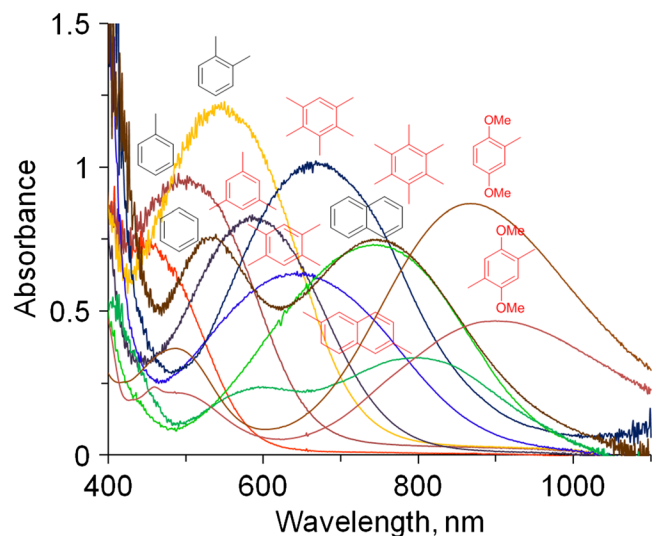


Figure 1. Bathochromic shift of the low energy band (charge transfer) with increasing donor strength in dichloromethane

band with the CT band of the electron donor–acceptor molecular complex.

It was observed that some of the CT complexes of TCQ with donor molecules with more negative oxidation potentials are not stable at room temperature. In Fig. 1, those are given in red colors.

Absorption bands of the transient CT complexes were measured at lower temperatures. Addition of the same organic

donors to the dichloromethane solution of the DDQ afforded a similar appearance of the CT bands, which are stable at room temperature. Table 1 shows the comparison of the redox potentials of the selected electron-donors and the quinones as electron acceptors. Another evidence for the CT absorptions of these lowest energy bands is presented in Fig. 2, where a clear linear relationship of the transition energies as a function of oxidation potentials of the organic donor molecules is known as a Mulliken correlation.^[25]

Recently, Kochi's group has shown that such complexes are critical precursors in intermolecular ETs,^[26–30]



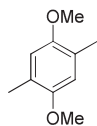
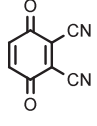
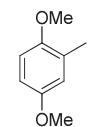
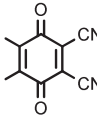
Mostly, in CT complexes, the oxidation potential of the donor is considerably higher than the reduction potential of the acceptor, which causes the thermal activation of the donor to be energetically unfavorable. TCQ has the most positive (lowest) reported reduction potential of all known quinones with $E_{\text{red}}^{\circ} = 0.94 \text{ V}$ vs. Saturated Calomel Electrode (SCE) (DDQ, $E_{\text{red}}^{\circ} = 0.52 \text{ V}$ vs. SCE).

Identification of isergonic donor/acceptor dyads is critical in order to fully understand the ET reactivity of the cyanil towards organic donors. Table 1 summarizes some potential electron donors that have low oxidation potentials (E_{ox}°). Selection of the electron donors where the ET to cyanil is in the isergonic limit ($\Delta G_{\text{ET}}^{\circ} = F(E_{\text{ox}}^{\circ} - E_{\text{red}}^{\circ}) \sim 0$) is crucial for the driving force of the ET step form CT salts.

Despite the variety of the known CT complexes, those that are close to the isergonic limit are interesting because of the transient nature of them and high-CT components present.^[28,31] In the series of the CT complexes with cyanil, those that are transient in nature can react through the ET step (Eqn 1) to form the hydrogen abstraction adducts as it has been shown for DDQ (Chart 2).^[32]

The CT state between neutral TCQ and its single-electron-reduced radical anionic state ($\text{TCQ}^{\cdot-}$), for which $\Delta G_{\text{ET}}^{\circ} = 0$, is also known as charge-resonance state.^[33,34] Self-exchange

Table 1. Formal potentials of some donors and acceptors

Electron donor	E_{ox}° (V versus SCE) ^a	$E_{\text{ox}}^{\text{Donor}} - E_{\text{red}}^{\text{TCQ}}$ (V)	Electron acceptor	E_{red}° (V versus SCE) ^a
 DMMB	1.10	0.16	 DCQ	0.32
 DMT	1.16	0.22	 DIQ	0.51

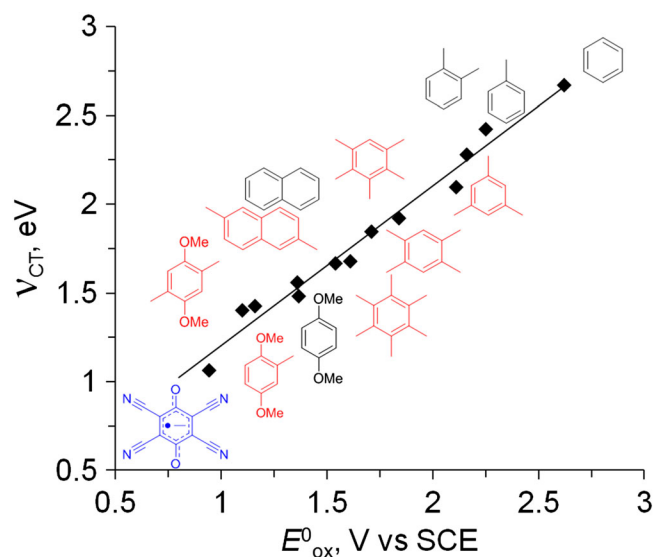
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Table 1. (Continued)

Electron donor	E_{ox}° (V versus SCE) ^a	$E_{\text{ox}}^{\text{Donor}} - E_{\text{red}}^{\text{TCQ}}$ (V)	Electron acceptor	E_{red}° (V versus SCE) ^a
	DMB	1.36		0.54
	26Naph	1.36		0.57
	Naph	1.54		0.94

DMMB, dimethoxydimethylbenzene; DMT, dimethoxytoluene; DMB, dimethoxybenzene; DCQ, 2,3-dicyanoquinone; DIQ, 2,3-diiodo-5,6-dicyano-*p*-benzoquinone; DBQ, 2,3-dibromo-5,6-dicyano-*p*-benzoquinone; DDQ, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; TCQ, tetracyanoquinone.

^aIn CH₂Cl₂ at 22 °C in the presence of supporting electrolyte 0.1-M tetrabutylammonium hexafluorophosphate (scan rate = 100 mV/s).

**Figure 2.** Mulliken correlation of the charge-transfer absorption bands ($h\nu_{\text{CT}}$) of the complexes of cyanil (tetracyanoquinone) with oxidation potentials (E_{ox}°) of various organic donors in dichloromethane

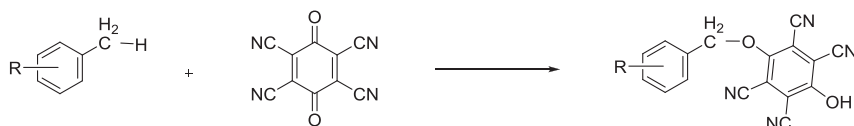
of an electron acceptor (TCQ) with its paramagnetic radical anion counterpart (TCQ^{•-}) is shown in Eqn 2.



Charge-resonance bands corresponding to the mixed-valence complex of TCQ with its single-electron-reduced radical anionic counterpart (TCQ^{•-}) appear at 1165 nm (8584 cm⁻¹) in dichloromethane. Despite the considerable work performed on mixed-valence complexes of TCQ and its radical anion in different solvents, detection of the charge-resonance bands in any other polar or protic solvents has failed. This appears to be because of the low stability of the neutral cyanil in polar and protic solvents, which are difficult to purify and dry to a reasonable extent. In the Mulliken plot (Fig. 2), the radical anion of the starting acceptor appears in far left corner.

Charge-transfer interactions of TCQ with the four organic donor molecules (naphthalene, dimethoxybenzene (DMB), dimethoxytoluene (DMT), and dimethoxydimethylbenzene (DMMB)) have the lowest oxidation potentials among the studied electron donors, which will be studied in more detail. Mixing of dichloromethane solutions of each of the donor molecules with a dichloromethane solution of an equimolar concentration of TCQ resulted in an immediate appearance of the new band in near-infrared (NIR) region of the spectra. As already mentioned previously, upon mixing of the DMT and DMMB solutions with TCQ solutions at room temperature, the new bands were not observed. However, mixing of the same solutions at lower temperatures (-60 °C for DMT and -80 °C for DMMB) resulted in new Gaussian-shaped absorption bands at 860 and 880 nm, respectively. Analogous

of an electron acceptor (TCQ) with its paramagnetic radical anion counterpart (TCQ^{•-}) is shown in Eqn 2.

**Chart 2.** Illustration of chemical reaction of arenes with TCQ through C-H activation of methyl group.

experiments of the same donor molecules with weaker electron acceptor as DDQ resulted in an appearance of the stable new absorption bands in the NIR region of the optical spectra. The Mulliken correlation of the CT absorption bands of DMT with various electron acceptors in dichloromethane is shown in Fig. 3.

The absorbance of the new Gaussian bands rose progressively as a function of the donor concentration, as shown in Fig. 4 for [DMT, TCQ]. Linear correlation of the calculated absorbance and the experimental absorbance (inset, Fig. 4) with correlation coefficients of 0.98 and the proportionality constants of 1.0 for both [DMT, TCQ] confirmed the 1:1 stoichiometry for the formation of the donor/acceptor complex according to Eqn. 3:

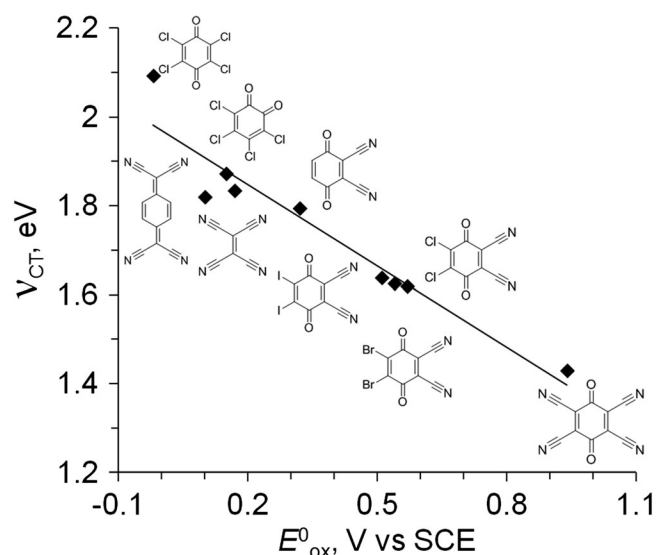


Figure 3. Mulliken correlation of the charge-transfer absorption bands ($h\nu_{\text{CT}}$) of the complexes of 2,6-dimethoxytoluene with reduction potentials (E^0_{red}) of various organic acceptors in dichloromethane

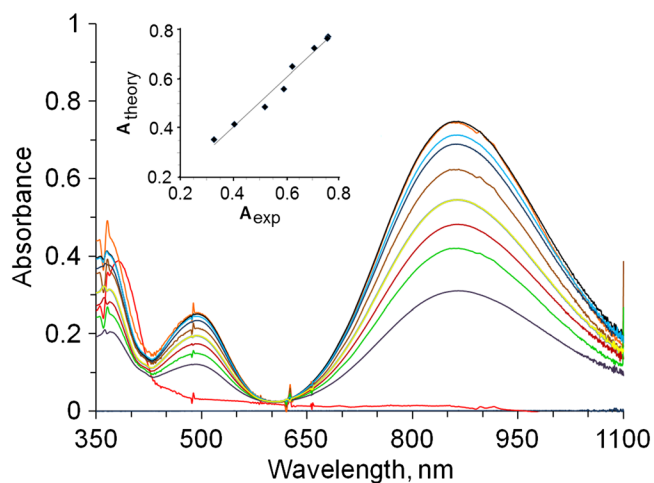


Figure 4. Optical spectra of the solution of dimethoxytoluene (donor) and tetracyanoquinone (acceptor) (1.0 mM) at different concentrations of the donor, 0, 1.7, 1.8, 2.1, 2.3, 2.5, 2.7, 2.8, and 2.9 mM in dichloromethane, at -60°C

Quantitative analysis of the concentration dependence led to the formation constants of the CT complex formation as summarized in Table 2. Determinations of the CT complex formation constants for the DMT and DMMB pairs with TCQ at low temperatures resulted in high-equilibrium constants.

Lowering the temperature of the solutions resulted in a significant increase of the absorbance of the CT bands in NIR region. Increase of the absorbance with lowering the temperature of the solution indicates a shift of the equilibrium to the right in Eqn 3. The linear dependence of $\ln K_{\text{CT}}$ with the inverse temperature afforded the thermodynamic parameters for the [DMT, TCQ] and [DMB, TCQ] complex formations as presented in Table 2. The temperature dependence of the spectrum of the dichloromethane solution containing equimolar concentrations of DMT and TCQ (3.4 mM each) show an increase of the 860-nm band upon lowering the temperature (Fig. 5).

X-ray crystallographic characterization of charge-transfer complexes of tetracyanoquinone with aromatic donors

Colored solutions of the CT complexes in dichloromethane were subjected to slow cooling and diffusion of the hexane through solution, which resulted in the precipitation of the crystalline solids. X-ray crystallographic analysis of the following crystals gives infinite π -stacked dimer pairs of 2:1 donor/acceptor complexes of toluene and mesitylene as donors and cyanil as an acceptor (Fig. 6). X-ray analysis revealed the presence of the infinite ...DDADDA... stacks. Both of the complexes show close contacts between donor molecules and the acceptor cyanil with $r_{\pi} \sim 3.17 \text{ \AA}$ in both cases and longer distances between stacks of $\sim 3.5 \text{ \AA}$.

Similar X-ray crystallographic analysis of the crystalline donor/acceptor complexes of naphthalene and DMB with TCQ gives infinite 1:1 complexes as can be seen in Fig. 7. In this case, crystallographic analysis revealed the presence of the infinite ...DADADA... stacks. Significant difference in the distances between π stacks is observed for these series of the CT complexes, which are closer to the isergonic region of the donor/acceptor dyads. π - π distances for [DMB, TCQ] and [Naph, TCQ] are $r_{\pi} \sim 2.86 \text{ \AA}$ and $r_{\pi} \sim 3.20 \text{ \AA}$, respectively (Fig. 7).

Analysis of the average bond lengths (\AA) within TCQ moieties in the various CT complexes in comparison with those in neutral and anion radical of TCQ allowed to evaluate the degree of CT in the following CT complexes. Table 3 summarizes the bond lengths of the TCQ motifs in the complexes, as well as the neutral and anion radical moieties.

Molecular geometries of the corresponding cyanil or the donor molecules are considerably different within different CT complexes. In particular, C=O bond length is the longest in radical anion moiety ($^{\ominus}\text{C}=\text{O}^{\cdot}$) and the shortest in the neutral cyanil moiety, mostly resembling the (C=O) carbonyl double bond. All of the C=O bond lengths from the CT complexes are neither shorter nor longer than those in the neutral or anion radical moieties, respectively. This finding leads us to consider the CT complexes as being intermediate partial CT species between neutral and fully reduced radical anion form of the cyanil. By the analysis of the C=O bond length differences, one can easily estimate the transferred charge (q). For the [Naph, TCQ] complex moiety based on the crystallographic data, it was estimated as $q = 0.3$ and almost close to zero for both [Toluene, TCQ] and [Mesitylene, TCQ]. Similar analysis for the [DMB, TCQ] failed to give

Table 2. Properties and thermodynamic characteristics of the charge-transfer complexes of TCQ with donors near the isergonic region

Complex	Solvent	ν_{CT} , 10^3 cm^{-1}	K_{CT} , M^{-1}	ϵ_{CT} , $10^3 \text{ M}^{-1} \text{ cm}^{-1}$	ΔH_{CT} , kcal/mol	ΔS_{CT} , $\text{cal M}^{-1} \text{ K}^{-1}$ (e.u.)
[TCQ, Naph]	CH_2Cl_2	13.4	13	1154	c	c
[TCQ, DMB]	CH_2Cl_2	11.9	30	4000	-5.3	-10.9
[TCQ, DMT]	CH_2Cl_2	11.7	500 ^a	12,980 ^a	-7.9	-19.8
[TCQ, DMMB]	CH_2Cl_2	11.4	550 ^b	14,570 ^b	—	—

TCQ, tetracyanoquinone; DMB, dimethoxybenzene; DMT, dimethoxytoluene; DMMB, dimethoxydimethylbenzene.

^aAt -60°C .

^bAt -82°C .

^cBecause of the precipitation of the charge-transfer complexes at low-temperatures, thermodynamic parameters were not calculated.

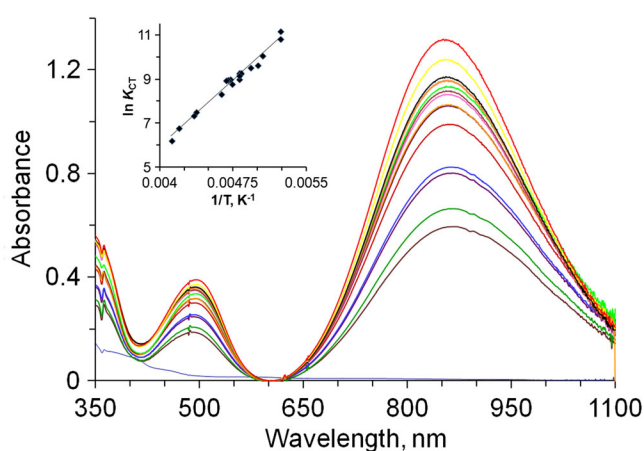


Figure 5. Optical spectra of the dichloromethane solution of tetracyanoquinone and dimethoxytoluene at variable temperatures (between -30 and -82°C)

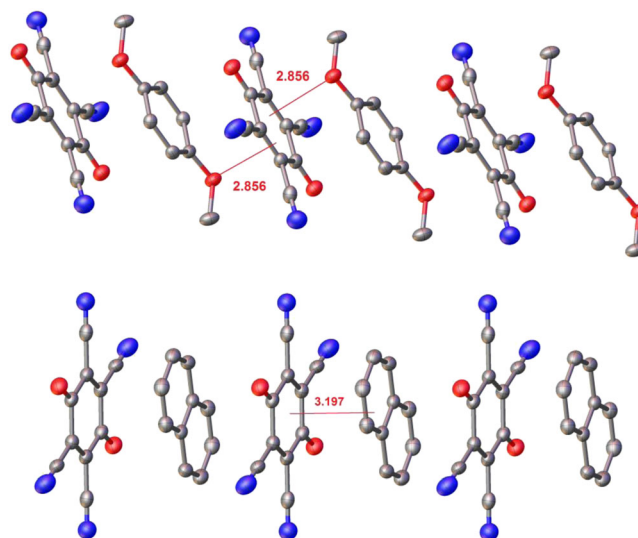


Figure 7. X-ray structure of the 1:1 charge-transfer complexes of [TCQ, Naph] and [TCQ, DMB]. Molecular diagrams are drawn with 50% probability ellipsoids

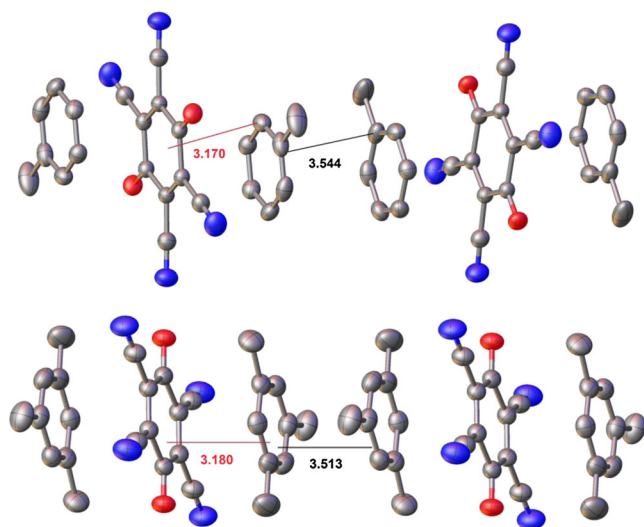


Figure 6. X-ray structure of the 2:1 charge-transfer complexes of [TCQ, Toluene] and [TCQ, Mesitylene]. Molecular diagrams are drawn with 50% probability ellipsoids

Table 3. Bond length characteristics of the TCQ moiety in the neutral, radical anionic, and charge-transfer complexes with various donor molecules

Structure	a	b	c	d	e
TCQ ^a	1.204(3)	1.487(5)	1.338(3)	1.437(7)	1.132(2)
[TCQ] ^{-a}	1.229(3)	1.463(7)	1.372(5)	1.439(7)	1.137(6)
TCQ-Toluene	1.207(2)	1.492(2)	1.344(1)	1.442(2)	1.133(2)
TCQ-Mesitylene	1.209(4)	1.477(3)	1.357(1)	1.413(6)	1.099(4)
TCQ-Naph	1.212(2)	1.494(8)	1.357(4)	1.467(3)	1.090(2)
TCQ-DMB	1.206(2)	1.484(2)	1.355(1)	1.450(5)	1.081(1)

^aFrom the work of Vazquez *et al.*^[24]

Table 4. Crystallographic parameters

Compound	[Toluene, TCQ]	[Mesitylene, TCQ]	[Naph, TCQ]	[DMB, TCQ]
Color	Brown blue	Plum	Brown	Green
Formula	C ₁₇ H ₈ N ₄ O ₂	C ₁₉ H ₁₂ N ₄ O ₂	C ₂₀ H ₈ N ₄ O ₂	C ₁₈ H ₁₀ N ₄ O ₄
<i>M_r</i>	300.27	328.32	336.30	346.30
Space group	C2/c	P-1	P-1	P-1
<i>a</i> /Å	8.559(4)	8.22(3)	6.96(3)	7.292(4)
<i>b</i> /Å	12.895(5)	8.98(4)	7.78(2)	7.412(4)
<i>c</i> /Å	18.697(9)	9.90(2)	8.24(2)	8.571(5)
<i>α</i> /°	90.00	102.35(14)	111.70(13)	75.988(12)
<i>β</i> /°	90.731(8)	106.99(19)	102.44(17)	66.966(11)
<i>γ</i> /°	90.00	113.54(10)	94.62(19)	77.099(12)
<i>V</i> /Å ³	2063.4(16)	593(3)	398(2)	409.4(4)
<i>Z</i>	8	2	1	1
<i>ρ</i> /g cm ⁻³	1.263	1.256	1.402	1.405
Refls	7601	7428	5159	6224
Indpndt	2985	3463	2253	2400
Obsd (<i>F</i> > 4σ)	1836	2175	1212	1342
<i>R</i> ₁ (<i>F</i> > 4σ)	0.0553	0.0673	0.0553	0.0638
<i>wR</i> ₂	0.1298	0.1701	0.1163	0.1444

considerable correlation with the other three CT complexes. This could be understandable with a close look to the [DMB, TCQ] complex, which differs with its closer π - π distances and lack of planarity of the *p*-methoxyphenyl moiety.

Details of the crystallographic analysis are summarized in Table 4.

Unfortunately, despite the relative persistency and observation of the CT absorption bands of [DMT, TCQ] and [DMMB, TCQ] complexes at low temperatures, we were unable to grow single crystals of them that were suitable for X-ray crystallographic analysis.

CONCLUSIONS

Interaction of the strongest neutral organic π -electron acceptor TCQ with various aromatic electron donor molecules was investigated. Single crystals of four CT complexes of TCQ with aromatic donor molecules were isolated and analyzed by X-ray crystallography. Two types of π -associations were observed in solid state, one with the infinite ...DDADDA... stacks with the weaker donor molecules and one with the infinite ...DADADA... stacks with the stronger donor molecules, which potentially could be extended to ...DD⁺A⁻DD⁺A⁻... and ...D⁺A⁻D⁺A⁻D⁺A⁻... CT salts, respectively. Transient CT complexes of TCQ with strong aromatic donor molecules at the isergonic limit were observed spectroscopically at low temperatures, and thermodynamic parameters for π -associations were estimated experimentally.

EXPERIMENTAL SECTION

Materials and methods

Ortho-Xylene, mesitylene, durene, pentamethylbenzene, hexamethylbenzene, naphthalene, 2,6-dimethylnaphthalene, and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) are from commercial sources. TCQ,^[24] 2,3-dibromo-5,6-dicyano-*p*-benzoquinone,^[22] 2,3-diiodo-5,6-dicyano-*p*-benzoquinone,^[22] 2,3-dicyanoquinone,^[24] DMB,^[34] DMMB,^[35] and DMT^[36] were

synthesized according to the reported procedures. Single crystals of the 1:1 [TCQ, DMB] and [TCQ, DMB] and 1:2 [TCQ, Toluene] and [TCQ, Mesitylene] complexes were prepared by slow diffusion of hexane into the dichloromethane solutions containing the TCQ acceptor and a large excess of DMB donor at -60 °C.

Electronic absorption spectra were recorded on a UV-Vis-NIR (200–3000 nm) spectrometer in Teflon-capped quartz cuvettes under an argon atmosphere. The measurement of the newly formed NIR bands was carried out by addition of the donor to the solution of acceptor. Low-temperature measurements were carried out with the aid of a Dewar equipped with quartz windows. Formation of the transient CT complexes of various donor/acceptor dyads was studied under an argon atmosphere in dichloromethane. The quantitative analysis of the NIR intensities was carried out with the aid of Benesi-Hildebrand as described earlier.^[28,31,37]

Electrochemical measurements (cyclic voltammetry) were performed on a potentiostat in dichloromethane in the presence of tetrabutylammonium hexafluorophosphate as the supporting electrolyte and ferrocene with $E^{\circ} = 0.475$ V vs SCE as the internal standard, as described previously.^[33,36b]

Acknowledgements

A. S. J. thanks Prof. Stephen F. Nelsen and Prof. Sergiy V. Rosokha for many helpful discussions. This work was financially supported by Robert A. Welch Foundation.

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