Photoinduced processes in functionalized and organized dye systems

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Chapter 5

Structure, Spectroscopy and Reactivity of Covalently Linked Catechol-ortho-Quinone Systems

Aviram’s Hemi-Quinones Revisited

Abstract

The structure and reactivity of a covalently linked catechol-ortho-benzoquinone (hemiquinone) is studied by UV-vis, IR absorption spectroscopy. Nanosecond transient absorption spectroscopy of the hemiquinone reveals the formation of a bi-radical state consisting of two semiquinone units. It is a long-lived state resulting from proton coupled electron transfer (PCET).

A manuscript based on this chapter has been submitted
5.1. Introduction

The great importance and the rich chemistry of catechols and quinones can be exemplified by the following facts: catechol is an important industrial chemical that is used as a precursor to pesticides, flavors and fragrances. Amino substituted catechols are present in the human body, such as dopamine, adrenaline, playing essential roles in the nerve system. The conversion of a para-quinone into a para-hydroquinone is an essential step in the generation of a transmembrane potential in photosynthesis, in which the ubiquinone is the primary electron acceptor, and after taking up two electrons, two protons are transferred over the membrane.

Beside their important industrial and biological role, the quinone-hydroquinone couple (also called quinhydrone) was one of the earliest examples of a solid-state charge transfer complex that was extensively investigated in the 1960s and 1970s. A typical model is the H-bonded charge transfer complex of 1,4-benzoquinone and 1,4-dihydroxybenzene, for which the X-ray structure and solvent dependent complex formation has been broadly studied.

It is thus not surprising that after the conceptual developments of molecular electronics in 1974, the quinone and hydroquinone couple attained attention in this field. Aviram and Ratner devised the concepts for molecular electronics, to use molecules as the smallest components in electronic devices. They envisaged the use of sigma bridged electron donor-acceptor molecules (such as the molecule 1 depicted in Figure 5.1) as molecular rectifiers, which become conductive at a certain bias (Figure 5.2).

![Figure 5.1](image-url)  
**Figure 5.1** *Examples of donor-bridge-acceptor as molecular rectifiers.*

Figure 5.2 visualizes the processes that can occur in the molecule which is sandwiched between two electrodes if a potential is applied. The conductive state of the molecule...
at forward bias Figure 5.2b) will be more easily attained than at reversed bias (Figure 5.2c). The tunneling of electrons from the cathode to the acceptor (process “A”, Figure 5.2b) and from the donor to the anode (process “C” Figure 5.2b) will be facilitated by the applied potential, and followed by intramolecular charge recombination (process “B”, Figure 5.2b) This concept has stimulated an immense amount of research and present advances go further than the early conceptions made in 1974.

**Figure 5.2** Representation of the processes occurring in a metal-molecule-metal configuration, inducing a rectifying state in a molecule. In b) and c), the labels for such as orbitals, acceptor and donor are omitted for clarity.

Recent experiments with DNA, nano-tubes, rotaxanes, substituted phenylethynyl oligomers, break-junctions and the mercury drop method go beyond the original ideas. In their seminal paper on the design and operation of molecular electronic components, Aviram and Ratner gave an example of a prototypical donor sigma acceptor system consisting of a TCNQ acceptor and a TTF type donor, coupled via a bicyclo-octane unit. Whereas this particular molecule has (so far) not been
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synthesized, other molecular systems designed as rectifiers have been realized by
Aviram et al. In the 1980s such a system (structure 2 in Figure 5.1) has been
synthesized and STM-experiments\textsuperscript{12} with I/V characteristics measured on a monolayer
have been reported. These experiments were conducted on a covalently linked
catechol-quinone (or hemiquinone)\textsuperscript{13} system with intramolecular hydrogen bonds, in
which observations were made in accordance with the induction of a highly conductive
state by using the electric field of the metal electrodes.

If we look at this system from an electron-donor-acceptor viewpoint, we can conclude
as follows: The lowering of the charge-transfer state energy by applying a voltage to
the electrodes leads to the transfer of electrons as described above. This process is
followed by a proton transfer, resulting in a biradical species with an expected high
conductivity.

In Figure 5.3 the situation is depicted where the thioether functionalized hemiquinone
system\textsuperscript{13} is attached to a gold surface, which acts as the anode. The molecule is
approached by the STM tip, which acts as the cathode. The electron transfer processes
(1) lead to the formation of the charge-separated state that consists of the radical anion
of the acceptor and the radical cation of the donor. Now proton transfer (2) is likely to
occur leading to the conductive biradical state.

\textbf{Figure 5.3} Representation of the processes envisaged to occur in a metal-molecule-
metal configuration, inducing a rectifying state in a molecule.\textsuperscript{12}

These consecutive steps can in principle also occur in solution upon photo-excitation.,
and can be followed by means of time resolved spectroscopy. Thus, the study of the
photophysical properties of these systems will lead to a greater insight in the possible
mechanisms associated with and the properties of these kinds of systems.
Furthermore, interactions through hydrogen-bonded structures are in the current focus
of the scientific world.\textsuperscript{14}
Our first hypothesis is the following: Can we create and probe a potentially conductive state in a covalently bound catechol-quinone system by using a (photochemical) perturbation?

It is envisaged that the study of the photoinduced processes occurring in the catechol-quinone systems will reveal many important aspects, such as information on the electron transfer and the proton transfer, and the kinetics of the formation and the decay of the (conductive) biradical state.

Scheme 5.1 Structures of studied compounds.

5.2. Results and Discussion

Here we report the results of analysis of various types of spectroscopy (HPLC, UV-Vis, IR, nanosecond transient absorption), and calculations performed on the linked
molecules. Similar measurements for intermolecular complexes of Cat and Quin were carried out for comparison to the covalently linked system, where appropriate.

5.2.1. HPLC experiments.

The purity of the BQ and BC compounds that were synthesized in 1983 at IBM were assessed with LC-MS. For BQ, only one component eluted at 4.24 min. From this, a purity of 99.9 % was determined. The UV-Vis spectrum (corresponding to the HPLC peak at 4.24 min.) shows the typical spectrum of quinone derivatives, with a broad band centered at 405 nm and a sharp strong band at 239 nm (see also next section).

The mass spectrum (relative to the LC-peak at 4.24 min) shows four major peaks which can be assigned to BQ. The base peak at 523.31 represents the protonated molecule [BQ-H]+, whereas the ones at 540.30 and 1061.92 are assigned to the hydrated species [BQ-H2O]+ and the hydrated dimer [(BQ)2-H2O]++. The last one at 568.40 is of [BQ-HCOOH]+ due to the presence of small amount (0.1%) of HCOOH in solvent as eluent.

The HPLC measurement of BC gave two peaks at 2.35 min. and 3.85 min. and the mass spectrum shows many fragments which were the consequence of oxidation of the catechol derivatives in polar solvents (mixture of acetonitrile and water) and acidic media. Attaining oxygen free conditions was not possible. Therefore, the purity of BC could not be assessed with this technique. UV-Vis and IR spectroscopic studies indicate high purity of the compound (vide infra).

5.2.2. Steady-state UV-Vis absorption spectroscopy.

Figure 5.4 shows the UV-Vis absorption spectra of BQ and BC in methylocyclohexane (MCH). In the case of BQ, the π - π* absorption band (at 388 nm) and the n - π* transition (590 nm)15 can clearly be discerned. The solvent polarity slightly affects the absorption spectrum of BQ (not shown). For example, in acetonitrile, the maximum of π - π* band shifted 14 nm to longer wavelength while a 12 nm blue shift was observed for the n - π* band. Molar absorption coefficients of 4100 (388 nm) and 80 (590 nm) were determined for BQ in MCH. This compares reasonably well with the data
reported for Quin (1700 (390 nm); 30 (595 nm)), see Figure 5.5 also. The absorption spectrum of BC also indicates the typical absorption maximum of phenolic groups at 280 nm (4300 M\(^{-1}\) cm\(^{-1}\)).

![Absorption spectra of BQ, BC and an equimolar ratio mixture of BQ and BC (HQ) in MCH, \([BQ]_o = [BC]_o = 2 \times 10^{-4} M\); assuming that the reaction of BQ and BC completely finished.](image)

**Figure 5. 4.** Absorption spectra of BQ, BC and an equimolar ratio mixture of BQ and BC (HQ) in MCH, \([BQ]_o = [BC]_o = 2 \times 10^{-4} M\); assuming that the reaction of BQ and BC completely finished.

As reported previously, the mixing of BQ and BC leads to the generation of the hemiquione system (HQ). This proton coupled redox reaction proceeds swiftly in a non-polar solvent (vide infra).

![Scheme 5. 2. The reaction of equimolar ratio of BQ and BC in MCH leading to HQ formation.](image)

**Scheme 5. 2.** The reaction of equimolar ratio of BQ and BC in MCH leading to HQ formation.

Similar to the effects observed for BQ in acetonitrile, there were a red shift (12 nm) of the \(\pi-\pi^*\) absorption band and a blue shift of the \(n-\pi^*\) transition when BQ was mixed with BC. This agrees well with the formation of the new compound hemiquinone (HQ). Clearly, the covalent bonding between the quinone and catechol units in HQ keeps them in close proximity which is favorable for hydrogen bond formation. This
results in the significant red shift of $\pi-\pi^*$, blue shift of n-$\pi^*$ band, and increase in absorption intensity compared to BQ in the range of the n-$\pi^*$ band.

In order to separate the effects of hydrogen bonding and ground state charge transfer between o-quinone and catechol moieties in the HQ system, different donors which have a very similar structure to the catechol unit were used in combination with Quin. The results are shown in Figure 5.5, displaying the charge transfer absorption characteristics of Quin in different media.

![Absorption spectra of Quin in MCH (solid line), toluene (TOL; dotted line), anisole (dashed line) and veratrole (dash-dot-dot line), and of the of Cat and Quin mixture (molar ratio 1:40) in MCH (solid bold line)](image)

**Figure 5.5** Absorption spectra of Quin in MCH (solid line), toluene (TOL; dotted line), anisole (dashed line) and veratrole (dash-dot-dot line), and of the of Cat and Quin mixture (molar ratio 1:40) in MCH (solid bold line)

Either a red-shift in the $\pi-\pi^*$ band or a blue shift in the n-$\pi^*$ band was observed in TOL, anisole and veratrole in comparison with the case of Quin in MCH. The red-shift could be due to i) the $\pi-\pi$ interaction between Quin and these solvents and ii) the higher polarity of these solvents. A detailed consideration on the n-$\pi^*$ transition, the 500 – 600 band (insert figure), show the noticeably different behavior of Quin in veratrole and catechol which have similar donor strengths. This band is broader and has higher intensity in the case of Cat-Quin solution in MCH, giving an evidence for the complexation between Cat and Quin favorable by hydrogen bonding.17
Previous works\textsuperscript{16,17} stated that the molar ratio between the two components was 1:1 and there were two possible complexes, a sandwich and a coplanar form (see the structures in Figure 5.6). In the sandwich complex (SC), two rings are in two parallel planes whereas in the co-planar one (CC), these rings are in one plane so that the two carbonyl and hydroxyl groups are opposite in pair. However, Lazarev \textit{et al.} concluded that the sandwich complex was not as favorable as the other because of the repulsion between the two oxygen atoms in carboxyl and in the hydroxyl groups. Also, the intermolecular complex formed by only one hydrogen bond could be neglected because it was extremely weak.\textsuperscript{16,17}

\textbf{Figure 5.6} Two possible complexes of Quin-Cat mixture, (A) sandwich complex (SC) and (B) co-planar complex (CC).

Nevertheless, the complexes formed by the two intermolecular hydrogen bonds were reported to be rather weak. The change in the band at the region 500 – 600 nm is only apparent when the ratio between \textit{Cat} and \textit{Quin} is adequate as shown in Figure 5.7.

\textbf{Figure 5.7} The normalized UV-vis absorption spectra (A) and the difference absorption (B) of the different ratio mixtures \textit{Cat} – \textit{Quin} MCH, $[\textit{Quin}] = 5 \times 10^{-4}$ M.
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The red shift at \( o \)-benzoquinone band \((i.e. \ 385 \ nm)\) becomes more obvious when the ratio \([\text{Cat}]:[\text{Quin}]\) increases significantly. At higher \text{Cat} \ concentration the equilibrium is pushed more towards the complex. Figure 5.7B demonstrates an increase of magnitude of \( \Delta A \) as the ratio of \text{Cat} and \text{Quin} concentrations was increased.

Beside the hydrogen bonds, the complex can also be stabilized by the charge transfer interaction between the electron donor molecule (catechol) and the electron acceptor (\( o \)-quinone).\(^{20}\) When we compare the spectra of the covalently linked system (HQ), \text{Cat-Quin} in MCH, and \text{Quin} in veratrole and in TOL at the 500-700 nm region three aspects can be noticed: 1) charge transfer interaction of \text{Quin} with veratrole results in relatively small changes; 2) the absorption of \text{Cat-Quin} is broader and more intense than that of HQ; 3) the range of complex structures present in the \text{Cat-Quin} mixture (from CC to SC) is larger than for HQ.

The reactivity of BQ was studied by an addition of thiol compounds to the quinone units. We used two thiols with different acidic properties, mercaptopropionic acid (MPA) and \( n \)-propyl-mercaptan (NPM). Similar experiments for \text{Quin} were also performed, and considered as reference data. When a molar equivalent of MPA was added into the BQ solution (Figure 5.8A), the decrease in the quinone absorption band \((i.e. \ 388 \ nm)\) was observed immediately (within 30 seconds). From 5 to 30 minutes, only minor changes could be observed indicating completion of the reaction. The increase of a new band at 300 nm (shoulder) and two isosbestic points (280 and 310 nm) were observed. This implies a formation of a new compound which has a typical absorption band of catechol derivatives. A shift of 20 nm to longer wavelengths (compared to the band of BC as seen in Figure 5.4) is assigned to the influence of the thiol. It also causes a less sharp peak than in the case of BC. A similar phenomenon is observed for the combination of \text{Quin} with MPA (or with NPM). Changes in UV-vis absorption of Quin and NPM are much slower, presented in Figure 5.8C. The data of \text{Quin} and MPA are not displayed.
Figure 5. 8. (A) The reactivity of BQ and of Quin with thiol compounds in MCH. (A) BQ with MPA. \([BQ]_0 = [MPA]_0 = 1 \times 10^{-4} \text{ M}\), spectrum of BC were used for comparison, \([BC] = 1 \times 10^{-4} \text{ M}\); (B) BQ and MPA with different molar ratios, \([BQ]_0 = 1.5 \times 10^{-4} \text{ M}\). Absorption spectra were recorded 5 hours after two solutions were mixed; (C) Quin with NPM, \([Quin]_0 = [NPM]_0 = 5 \times 10^{-4} \text{ M}\).
As reported, the addition reaction of thiols (RSH) into Quin was more favorable to position 6 than position 4 to form a substitution product with SR next to the OH group. We assume that the reaction of the BQ with thiols results in an asymmetric hemiquinone system (AHQ) as expressed in the following reaction (Scheme 5.3).

![Scheme 5.3 Reaction of BQ with thiol compounds with equimolar ratio.](image)

In summary, the UV-Vis absorption studies give details about the electronic structure and reactivity of the hemiquinone systems. However, probing the specific hydrogen bonding requires additional techniques.

### 5.2.3. IR-spectroscopy

Figure 5.9A displays the IR spectra of BC and the mixture of BC and BQ. Measurements of Cat-Quin mixtures were also performed for comparison.

![Figure 5.9 The FT-IR spectra of the OH stretching vibrations of the studied compounds.](image)

**Figure 5.9** The FT-IR spectra of the OH stretching vibrations of the studied compounds. (A) \([\text{BC}] = [\text{BQ}] = 2 \times 10^{-3} \text{ M}\); (B) Cat – Quin systems \([\text{Cat}] = 5 \times 10^{-3} \text{ M}, [\text{Quin}] = 25 \times 10^{-3} \text{ M}\) (b) in CCl₄, 1 mm cell thickness.
The peaks at 3617 cm\(^{-1}\) and 3554 cm\(^{-1}\) of the BC compound (at 3618 cm\(^{-1}\) and 3556 cm\(^{-1}\) in the case of Cat) are attributed to \(v_{\text{OH}}\) vibrations. The former is of a free O-H vibration, and the latter is due to the intramolecular hydrogen bonded O-H vibration of the two OH groups in the same unit. The positions of these peaks were characterized for phenol derivatives in non-polar solvent.\(^{22,23}\) The small hump at 3425 cm\(^{-1}\) is assigned to an intramolecular hydrogen-bonded OH stretching vibration between two OH groups of different phenol units (Figure 5.10).

The hydrogen bond between two BC molecules is insignificant in dilute solution (2 \(\times\) 10\(^{-3}\) M). This conclusion is deduced from IR measurements of Cat solutions at 3 different concentrations (60 \(\times\) 10\(^{-3}\) M, 5 \(\times\) 10\(^{-3}\) M and 0.5 \(\times\) 10\(^{-3}\) M, the data are not presented here). The shapes and positions of \(v_{\text{OH}}\) vibration peaks did not depend on concentration. It implies that intermolecular hydrogen bonds are insignificant.\(^{22}\)

When the BC and BQ solutions were mixed together, there was an apparent change in O-H stretching bands in position, shape and in intensity of the peaks. Stretching modes of the free OH and the intramolecular hydrogen-bonded OH(s) are reduced in intensity. In addition, the peak at 3452 cm\(^{-1}\) disappears. They are accompanied by the appearance of a new broad peak at 3469 cm\(^{-1}\) which is assigned to the OH stretching vibration of the hydrogen-bond(s) O-H\(\cdots\)O=C.\(^{22}\) These demonstrate the reaction between BC and BQ to form the hemiquinone (HQ) compound (Scheme 5.2). Therefore, the OH and O=C groups are close enough in space to favor the intramolecular hydrogen bondings between the two units.
Notice that the absorbance for free $\nu_{OH}$ does not completely reduce to zero which can be explained by a distribution of the molecules which have a different number of hydrogen bonds between OH and C=O groups (i.e. one or two hydrogen bonds in one molecule). As calculated in the modeling part (see below), there are likely to be two major groups of conformations, one consists of the molecules which have one OH···C=O hydrogen bond, and the other contains two OH···C=O hydrogen-bonded molecules.

The IR spectroscopy of the reference systems, the Cat and the mixture of Cat and Quin, presented very similar phenomena, indicating the complex formation between Cat and Quin (Figure 5.9B). These results relate very well to previous work\textsuperscript{16,24} After the addition of the Quin solution, a new peak appeared at 3456 cm\textsuperscript{-1} attributed to the stretching vibration of O-H group which is bound by the C=O group of the benzoquinone compound. When the ratio [Quin] : [Cat] increases, the intensity of the bound OH group increase whereas that of the free OH group decreases indicating the interaction between Cat and Quin. The peak at 3326 cm\textsuperscript{-1} in Figures 5.9A and 5.9B is of overtone of C=O stretch which is at 1663 cm\textsuperscript{-1}. The changes in C=O stretching frequencies due to the hydrogen bonding are much less pronounced than that of the O-H stretching modes and therefore are not presented here. Even in protic solvents such as alcohols, the change in $\nu_{C=O}$ modes of ketones were reported to be insignificant\textsuperscript{22}

In summary, the covalent linkage between the catechol and the quinone units in hemiquinone compound makes the hydrogen bond more favorable in comparison to the Cat and Quin mixture (i.e. high local concentration). Clear signatures for hydrogen bond formation can be obtained but still some free OH is present.

The reaction between Quin and thiol compounds could also be detected with IR spectroscopy. The reactivity of Quin with thiols was probed by mixing the solutions of Quin and thiols (MPA and NPM) in a 1:1 molar ratio.

For pristine MPA, the spectrum showed the typical monomer peak at 3530 cm\textsuperscript{-1} of the OH vibration of the acid group (Figure 5.11A). A characteristic broad band in the range of 3300 – 2500 cm\textsuperscript{-1} is assigned as O–H stretching absorption of a dimeric
carboxylic acid. This vibration frequency strongly overlaps with the C – H stretching ones.\textsuperscript{22} The bands at 1760 cm\textsuperscript{-1} and 1714 cm\textsuperscript{-1} (Figure 5.11B) are corresponding to the monomer and dimer C=O stretching modes,\textsuperscript{22} respectively, of the acid group in MPA.

![FT-IR spectra of the mixture of MPA and Quin versus time](image)

**Figure 5.11** FT-IR spectra of the mixture of MPA and Quin versus time A) OH vibration band region, B) CO vibration band region; [MPA]\textsubscript{o} = [Quin]\textsubscript{o} = 5 \times 10\textsuperscript{-3} M. The cell thickness is 1 mm. CCl\textsubscript{4} was used as solvent. The IR spectrum of Cat is for comparison.

When Quin was added, the bands at 3547 cm\textsuperscript{-1} and at 3371 cm\textsuperscript{-1} (Figure 5.11A) immediately appeared, indicating the fast reaction of Quin with MPA. They are of two different intramolecular hydrogen-bonded OH stretch vibrations of a catechol product (Possible hydrogen bonds in the adduct molecule are presented in Scheme 5.4A). A
small red shift in position of the peak at 3547 cm\(^{-1}\) is observed (that position in the case of Cat is 3556 cm\(^{-1}\)). It can be explained by the effect of the sulfur atom and oxygen atom of acid group on the O\(^1\)H\(^1\) vibration (Scheme 5.4A). The other peak at 3371 cm\(^{-1}\) is attributed by the stretch vibration of the O\(^2\)H\(^2\) group which is bound with sulfur atom by an intramolecular hydrogen bond (OH⋯S-R).\(^{22}\) This band is also evidence for the addition of the thiols to the position 6 (not position 4) in the Quin. There is no evidence of “free”OH which has frequency at 3617 cm\(^{-1}\) as seen in the spectrum of Cat. Beside these changes in the OH region, the exhibition of the band in C=O stretching region indicates the reaction of Quin with MPA. The peaks at 1666 cm\(^{-1}\) and 1690 cm\(^{-1}\) which are assigned to the symmetric and asymmetric C = O stretch vibrations of Quin (Figure 5.11B) vanish with the addition of MPA. The very little change in the bands of the C=O of the carboxylic MPA (at 1761 cm\(^{-1}\) and 1714 cm\(^{-1}\)) shows that the C=O stretching of carboxylic acid dimers still remains after the addition reaction of MPA to Quin. Moreover, the broad band in the region 3300 – 2500 cm\(^{-1}\) remains almost unchanged, indicating that the addition of the aromatic group did not influence the formation of the carboxylic acid dimers.

![Scheme 5.4](image)

**Scheme 5.4** The possible hydrogen bonds in the thiol-ethers, adducts of Quin with (A) MPA and (B) NPM.

Figure 5.12 shows that the reaction of Quin with NPM was slower than with MPA owing to the lower acidity of NPM. Notice, the features of the peaks of the OH vibrations are very similar to the case of the reaction with MPA. The two bands (Figure 5.12A) at 3551 cm\(^{-1}\) and 3336 cm\(^{-1}\) appear and increase in time after Quin is added. The introduced thiol substituent on the phenyl ring also slightly influence on the hydrogen bond of the OH (that is O\(^1\)H\(^1\)) bound with oxygen atom of the other OH
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group (O\(^2\)H\(^2\)) (Scheme 5.4B), resulting a minor shift of the position (i.e. 3551 cm\(^{-1}\)). The bands at 1690 cm\(^{-1}\) and 1667 cm\(^{-1}\) (Figure 5.12B) decreased showing the reduction of Quin.

Figure 5.12 The FT-IR spectra of the mixture Quin and NPM versus time (A) in the OH vibration region and (B) in the CO vibration region, \([\text{Quin}]_0 = [\text{NMP}]_0 = 5 \times 10^{-3} \text{ M}\), 1 mm cell thickness, CCl\(_4\) was used as solvent. The IR spectrum of Cat is as a reference.

Thus, in both cases the reaction between Quin and the thiols formed the phenolic compounds with the –SR substituent at position 6. As derived from the OH vibration, the difference in the reaction rate is due to the acidity of the thiol compounds.
5.2.4. Molecular modeling

Calculation of the Boltzmann conformational distribution of the symmetric hemiquinone (Figure 5.13) was performed, using molecular mechanics (MMFF)\textsuperscript{25}. Conformations that are more 3 kcal/mol higher in energy than the lowest one were disregarded.

![A) B)](image)

**Figure 5.13** Two representative structures for the Boltzmann conformational distributions of HQ based on the number of hydrogen bonds, (A) one hydrogen bond conformation population; (B) two hydrogen bond conformation population. The hydrogen atoms in the alkyl chain were omitted for clarity.

The conformers were simply classified into groups based on the number of hydrogen bonds, one-hydrogen-bond conformations (ca. 60%), two-hydrogen-bond conformations (ca. 39%) and conformers without any hydrogen bond (ca. 1%). The calculation is correlated to the IR spectroscopy of the mixture of BC and BQ (see above) at the OH stretching vibrations, in which the absorbance of free OH stretching mode decreased only ca. 50% when an equimolar amount of BQ was added to BC solution. Therefore, the symmetric hemiquinone molecules could occur either in one hydrogen bond conformer or in two hydrogen bond conformer. The hydrogen bonding keeps the donor unit (i.e. catechol) and the acceptor unit (i.e. o-quinone) at such a distance that makes charge transfer more favourable.
5.2.5. Nanosecond transient absorption (ns-TA) spectroscopy

In order to detect photoinduced processes occurring in the covalently linked catechol-ortho-benzoquinone system (HQ), transient absorption spectroscopy on the nanosecond timescale was performed. Spectral details of each case are discussed below, and kinetic data are listed in Table 5.1.

Photoexcitation of Quin and of BQ in MCH leads to the population of their triplet excited states because of efficient and rapid intersystem crossing processes. Figure 5.14 shows the transient absorption spectra and kinetic traces of Quin and BQ on the nanosecond time scale. The obtained spectra of Quin and BQ are virtually identical, presenting a band centered at 523 nm, which is characteristic of the triplet absorption of o-benzoquinone derivatives with a long lifetime (≈ 280 ns for BQ and ≈ 300 ns for Quin).

\[ \bullet \]

Figure 5.14 ns-TA spectra (\( \lambda_{ex} = 440 \) nm) of (A) BQ (1 x 10^{-3} M), (B) Quin (5 x 10^{-3} M) in MCH, and (C, D) corresponding decays; the solutions were de-aerated by Ar bubbling for 20 minutes; laser power after sample holder was \( \approx 1.2 \) mJ/pulse for BQ and \( \approx 0.5 \) mJ/pulse for Quin; 40 ns incremental time delay.
The ns-TA spectra (Figure 5.15) of the hemiquinone (HQ) and of the Cat-Quin mixture show different features, as compared to BQ or Quin. The 500 – 600 nm band attributed to the triplet excited state of the o-quinone derivatives is absent. A new band is observed centered at 740 nm, which is in the area of the semiquinone radical28 and the radical anion18, 29 bands of o-quinone. For the linked system (HQ), the decay of the signal is bi-exponential with time constants of 300 ns and 18 μs. These values can be ascribed to the intramolecular radical recombination of two-hydrogen-bonded and one-hydrogen-bonded conformations.

**Figure 5.15** The nanosecond transient absorption of HQ (A) with its time profile (C) and mixture of Cat and Quin (B), and its time profile (D) upon 440 nm excitation, laser power was ca. 1.2 mJ/pulse; degassed by Ar bubbling in 20 minutes; the incremental delay was 40 ns for HQ and 2000 ns for the Cat-Quin mixture; [HQ] = (1 \times 10^{-3} M), [Quin] = 2.5 \times 10^{-3} M and [Cat] = 1 \times 10^{-1} M.
For the case of the **Cat-Quin** mixture, the hydrogen bonds result in a complex formation. Upon the excitation of the **Quin** molecules, an electron and a proton transfer from **Cat** to triplet state **Quin** to produce semiquinones.

\[
[\text{Cat} + \text{Quin}]_{\text{complex}} \xrightarrow{h\nu} [\text{Cat} + \overset{1}{\text{Quin}}^*]_{\text{complex}} \xrightarrow{\text{ISC}} [\text{Cat} + \overset{3}{\text{Quin}}^*]_{\text{complex}}
\]

\[
[\text{Cat} + \overset{3}{\text{Quin}}^*]_{\text{complex}} \xrightarrow{\text{PCET}} [\text{semiquinones}]_{\text{solvent cage}}
\]

The formed semiquinones then can escape from the solvent cage. This process competes with the radical recombination, which leads to the **Cat-Quin** complex.

\[
[\text{semiquinones}]_{\text{solvent cage}} \xrightarrow{\text{escape}} \xrightarrow{\text{diffusion}} [\text{semiquinones}]_{\text{solvent cage}} \xrightarrow{\text{radical recombination}} [\text{Cat} - \text{Quin}]_{\text{complex}}
\]

The time profile (Figure 5.15D) should contain second order decay kinetics as well as mono-exponential decay. These are due to the radical recombination of attained semiquinones in solvent cage and the recombination process controlled by the diffusion of escaped products. It is not easy to separate these two components, so this time profile was fitted with a bi-exponential model, giving two lifetimes for comparison.

To get more information about the formation of \(o\)-quinone radical anion and its absorption band, ns-TA spectra of **Quin** in two electron donating solvents, anisole and veratrole, were carried out. The results are shown in Figure 5.16.

For anisole, the typical triplet state absorption of \(o\)-benzoquinone in the region 400 – 600 nm with a life time of ca. 300 ns was observed, the same as the life time of **Quin** in MCH. With a stronger electron donor, \(i. e.\) veratrole, the charge transfer process could be observed clearly, characterized by the decay of the band at 500 nm and the rise of the broad band, centered at 700 nm which is of the \(o\)-quinone radical anion species.
Figure 5.16 ns-TA spectroscopy of Quin \( (5 \times 10^{-3} \text{ M}) \) in A) anisole, and B) veratrole, upon 440 nm excitation wavelength, 1.2 mJ laser power after sample holder, 40 ns incremental time delay, degassed by Ar-bubbling in 30 minutes.

Table 5.1 The triplet state lifetimes (top) and CT-lifetimes (lower part) with relative amplitude, obtained with ns-TA of Quin with different donors and of BQ and HQ

<table>
<thead>
<tr>
<th></th>
<th>( \tau_T ) (ns)</th>
<th>( \tau_3 ) (( \mu )s)</th>
<th>( \tau_4 ) (( \mu )s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quin in MCH</td>
<td>310</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quin in Tol</td>
<td>330</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quin in anisole</td>
<td>320</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BQ in MCH</td>
<td>300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quin in veratrole</td>
<td>127 (87%)</td>
<td>1.7 (13%)</td>
<td></td>
</tr>
<tr>
<td>Cat – Quin in MCH</td>
<td>6.1 (51%)</td>
<td>91 (49%)</td>
<td></td>
</tr>
<tr>
<td>HQ in MCH</td>
<td>0.3 (81%)</td>
<td>18 (19%)</td>
<td></td>
</tr>
</tbody>
</table>

If we now make a spectral and kinetic comparison of the various ns-TA experiments (Table 5.1 and Figure 5.17) the following can be observed:
Figure 5.17 The comparison of spectral traces of HQ in MCH, Cat-Quin in MCH, and Quin in veratrole at certain time delay.

1) The spectra of HQ and Cat-Quin are rather similar indicating similar excited state species with a ground state bleaching at around 450 nm and a broad absorption band centered at 740 nm.

2) The transient spectra of Quin in veratrole are different from those of HQ and Cat-Quin in MCH. The latter shows a red shift of 40 nm on the red edge and no bleaching at 450 nm.

3) If we assume that Quin in veratrole only results in electron transfer products (e.g. quinone radical anion), then it implies that the excited state species of HQ is different. It is most likely the semi-quinone radical, the product of proton coupled electron transfer (PCET). For Cat-Quin, there is more evidence for this assignment.

4) The very long lifetime of the excited state indicates triplet character, also for the PCET products.

5) The different kinetics of HQ and Cat-Quin are a consequence of the covalent linker in HQ. The linker prevents solvent separation of the two semiquinone radicals. For the Cat-Quin second order decay kinetics (fitted here as bi-exponential) can be explained by the escape of photoproducts form the initial solvent cage, followed by diffusion controlled recombination processes.
5.3. Conclusions

UV-Vis absorption spectroscopy shows the interaction of BQ and BC to generate HQ, containing catechol and o-quinone units. The decrease of the o-quinone bands observed by means of UV-Vis absorption shows the reactivity of o-quinone derivatives with thiols.

Steady-state IR spectroscopy strongly demonstrated the formation of HQ with the appearance of the new band in the region of the stretch OH vibration (3469 cm⁻¹) and the reduction in intensity of the band of free OH stretching vibration (3617 cm⁻¹) and of intramolecular-hydrogen OH vibration stretch (3554 cm⁻¹) when the BQ and the BC was mixed together in equal amounts. Also, the addition of thiols to the 3, 5-di-tert-butyl o-benzoquinone at substitution position 6 was confirmed by the appearance of a new band at 3371 cm⁻¹ (in the reaction with MPA) or at 3337 cm⁻¹ (in the reaction with NPM). These peaks are assigned to the frequency of hydrogen-bonded OH-stretching vibration (O-H···S-R). There is very little contribution of the free OH vibration whose frequency is at 3618 cm⁻¹, together with the disappearance of C=O stretching vibration band at 1667 cm⁻¹ and 1690 cm⁻¹.
The Boltzmann conformation distribution calculation of HQ, which is in good agreement with the IR measurements, gave two major types of conformations, i.e. groups of one-hydrogen-bond (ca. 60%) and two-hydrogen-bond (ca. 39%) conformers.

Nanosecond transient absorption spectroscopy shows that the process occurring in the mixture of o-quinone with veratrole is photoinduced electron transfer (ET), whereas proton-coupled electron transfer (PCET) is advantageous in HQ and Quin-Cat. The PCET process was confirmed by evidence for the formation of a biradical with an absorption band in the 750-800 nm region and a very long lifetime.

Upon photo-excitation, a bi-radical state in covalently linked hydrogen bonding catechol-quinone system was generated by an electron transfer from catechol to triplet-excited-state quinone coupled to a proton transfer.

5.4. Experimental part

All the solvents were purchased from Aldrich with spectroscopic or HPLC grade and were used as received. The 3,5-di-tert-butyl o-benzoquinone (Quin), 3,5-di-tert butyl catechol (Cat), mercaptopropionic (MPA) and n-propyl mercaptane (NPM) were purchased from Aldrich and used as received without further purification.

The infrared (IR) spectra were obtained using Bruker Vertex 70 FTIR spectrometers with a resolution of 1 cm⁻¹. All samples were recorded in solution using spectroscopic grade CCl₄ as a solvent.

In nanosecond pump-probe experiments, for excitation a (Coherent) Infinity Nd:YAG-XPO laser was used. The laser illuminated a slit of 10 × 2 mm. Perpendicular to this, the probe light was provided by an EG&G (FX504) low pressure Xenon lamp, which irradiated the sample through a 1 mm pinhole. The overlap of the two beams falls within the first two millimeter of the cell, after the slit. The probe light from both the signal and the reference channels is then collected in optical fibers which are connected to an Acton SpectraPro-150 spectrograph which is coupled to a Princeton
Instruments ICCD-576-G/RB-EM gated intensified CCD camera. Using a 5 ns gate this camera simultaneously records the spectrally dispersed light from both optical fibers on separate stripes of the CCD. De-eration was performed by bubbling with Ar for 30 minutes.

The UV-Vis absorption spectra of the samples were measured before and after the laser experiments to find out any possible degradation or chemical change of the samples. All photophysical data reported here have a 5 to 10% error limit, unless indicated otherwise. All experiments were performed at room temperature.

The LC-MS experiments were carried out with a Finnigan LXQ Ion Trap Mass Spectrometer coupled with a Finnigan Surveyor Plus HPLC system equipped with a Xterra-C18 column (50 mm × 2.1 mm; 3.5μm particle size). A gradient between solvent A (H₂O/0.1% HCOOH) and solvent B (CH₃CN/0.1% HCOOH) was used as eluent. The electrospray ionization mass spectra (ESI) were scanned in a full range (m/z = 100.00 – 2000.00). The detection range for HPLC-UV/Vis determination was between 200 and 600 nm.

5.5. References


26. Various attempts were made to obtain spectral and kinetic information on the sub-nanosecond timescale. However, femtosecond transient absorption (fs-TA) spectroscopy experiments led us to conclude that the excited state species present on the short timescale all have extremely low molar absorption coefficients, as all signals obtained under various conditions were at the intrinsic noise level.

