

# Absorption and Fluorescence Emission Attributes of a Fluorescent dye: 2,3,5,6-Tetracyano-p-Hydroquinone

Muhammad Zahid · Günter Grampp · Asim Mansha ·  
Ijaz Ahmad Bhatti · Sadia Asim

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**Abstract** Four cyano groups have been substituted on the aromatic ring of p-hydroquinone (2,3,5,6-tetracyanoquinone) in order to study the enhanced photoacidity of this molecule. The acid-base equilibria have been studied using absorption (for ground state  $pK_a$ ) and fluorescence (excited state  $pK_a$ ) spectra. Three distinct species (neutral, anionic and dianionic forms) were observed in the ground state and only two species (anionic and dianionic forms) were found in the excited state when studied at different pH/ $H_0$  in water. Absorption and emission characteristics were studied in various organic solvents, including protic and aprotic solvents. Deprotonation was also investigated using binary mixtures. It has been revealed that absorption and emission spectra are considerably changed with change in media. Proton transfer to the solvent has been observed in various solvents.

**Keywords** Photoacids · Excited state proton transfer ·  $pK_a$  ·  $pK_a^*$  · Proton transfer to the solvent · Hydroquinone

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M. Zahid (✉) · I. A. Bhatti · S. Asim  
Department of Chemistry & Biochemistry, University  
of Agriculture Faisalabad, Faisalabad, Pakistan  
e-mail: zahid595@gmail.com

M. Zahid  
e-mail: rmzahid@uaf.edu.pk

G. Grampp  
Institute of Physical and Theoretical Chemistry, Graz University  
of Technology, Graz, Austria

A. Mansha  
Department of Chemistry, GC University Faisalabad,  
Faisalabad, Pakistan

## Introduction

Proton transfer is among the most common class of reactions, which occurs in nature and excited state proton transfer (ESPT) has gained much attention. The protonation-deprotonation phenomena of Brønsted acids and bases, in their ground and excited states, are playing a key role in different elementary processes in chemistry and biochemistry. The proton transfer is extensively studied for hydroxyarenes, phenols, naphthols, hydroxystilbenes etc., which undergo enhancement of acidity upon electronic excitation, thus classified as photoacids [1–3]. Naphthols (1- and 2-) are known to undergo a strong increase in acidic character in their excited state. The  $pK_a$  value of 2-naphthol has been changed from 9.5 in ground state to 2.8 in excited state [4–7]. One of the most studied proton transfer hydroxyarene is 8-hydroxy-1,3,6-pyrenetrisulfonate (HPTS) [8–12]. Lewis and co-workers have investigated substituent and positional effect on excited state ultra fast proton transfer dynamics in hydroxystilbene photoacids [13–15]. The photoacidity has been increased many folds by the substitution of electron withdrawing groups such as cyano, perfluoroalkylsulfonyl, sulfonate etc. Aqueous medium is required for ESPT to take place in case of simple phenols and naphthols but substitution of electron withdrawing groups has greatly enhanced the photoacidity and made ESPT possible even in non aqueous solvents like alcohols and dimethylsulphoxide (DMSO) [6, 7, 16–19].

The cyano-substituted derivatives of phenols [16, 20] and naphthols [4–7] have manifested manifold increase in their acidic behavior. Schulman et al. investigated the protolytic equilibria in cyano-substituted phenols (ortho, meta and para cyanophenols) in excited states using steady state and time-resolved fluorescence measurements [20]. The extremely weak fluorescence intensities of phenoxide anions make it difficult to measure direct ESPT. Beata Szczepanik et al. studied the protolytic equilibria in monocyno- and dicyano-phenols in alcohol and water. They have shown that

p-cyanophenol is the weakest and dicyanophenol is the strongest acid among the investigated cyano-substituted phenols [21]. Hynes and coworkers have performed the theoretical investigations for excited-state acidities of hydroxyarenes [22–25].

A number of theoretical and experimental investigations have been carried out to understand the protolytic equilibria and proton transfer dynamics by taking 1- and 2-naphthols as the prototype for hydroxyaromatic compounds [26–35]. Tolbert and coworkers [4, 6, 7, 18, 19, 36] have synthesized several derivatives of naphthols aimed to study the enhancement of acidity in naphthols. Cyano-substituted derivatives of 1- and 2-naphthols are highly acidic in excited state and exhibit ESPT in non-aqueous solvents like alcohols and DMSO. Estimation of ESPT in case of cyano-substituted derivatives of 1-naphthol is problematic using fluorescence measurements due to their weak fluorescence intensity. Fortunately cyano-substituted derivatives of 2-naphthol are also strong photoacids and have better fluorescence properties. The estimated  $pK_a^*$  value for 5,8-dicyano-2-naphthol is  $-4.5$ , which is among the most acidic compounds studied to date. Agmon and coworkers [37, 38] have described a very detailed description of ESPT for various naphthols based on theoretical and experimental studies and predicted that 3,5,8-tricyano-2-naphthol might be the ultimate superphotoacid from this family. Jacquemine et al. [39] have presented a fast and reliable computational model to calculate the  $pK_a^*$  of photoacids and successfully applied to several coumarin derivatives.

Several synthetic and natural coloring substances (dyes and pigments) are based on quinone derivatives (hydroquinone derivatives are extensively used as intermediate for the synthesis of dyes and pigments) [40, 41]. Görner has studied the photochemistry of p-benzoquinone and other quinone derivatives [42–44]. Hydroquinones are major component of photographic developers in black and white photography. The acid-base equilibria of hydroquinones in general and cyano-substituted hydroquinones, in particular, have received little attention compared to other hydroxyarenes (cyano-substituted phenol and naphthols). Sunkle et al. have studied the absorption spectra and calculated the  $pK_a$  values of different substituted hydroquinones [45, 46]. Brown et al. have described the absorption and emission characteristics of fluorescent dye, 2,3-dicyano-p-hydroquinone (DCHQ), at various pH [47]. Various studies have been accomplished to investigate the use of DCHQ as a fluorescence probe to measure intercellular pH [48, 49]. Tetracyano-p-benzoquinone (cyanil), oxidized form of TCHQ, is an exceptionally strong acceptor and has unusual redox potential. Cyanil is one of the strongest acceptor that has been isolated in the neutral form [50]. In the present study, absorption and emission characteristics have been studied for 2,3,5,6-tetracyano-p-hydroquinone (TCHQ) in aqueous and non-aqueous solvents. The absorption

and emission characteristics have also been explored in binary mixtures of water with some polar organic solvents.

## Material and Methods

The cyano-substituted derivative of p-hydroquinone, 2,3,5,6-tetracyanohydroquinone (TCHQ), was synthesized using bromanil and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) as starting materials by following the already reported methods [50, 51]. The synthesized TCHQ was purified by crystallization in acetic acid and characterized using UV/VIS, IR and NMR spectroscopy. All the solvents used were of analytical grades of highest purity (on requirement, the solvents were dried, using a molecular sieve of appropriate size, distilled and kept under Ar to avoid any contact of moisture). Doubly distilled water was used for the measurements of ground and excited state  $pK_a$  values and also when absorption/emission characteristics were investigated in binary mixtures of water and organic solvents.

Absorption and emission spectra were recorded using 1 cm quartz cuvette with the septum cap. The absorption spectra were recorded by using UV-VIS-NIR spectrophotometer (Shimadzu UV-3101PC) with a band pass of 2 nm. Steady state fluorescence measurements (corrected emission and excitation spectra) were recorded using a spectrofluorometer (Jobin–Yvon Spex FluoroMax-2) with scan range 250–900 nm and band pass 2 nm.

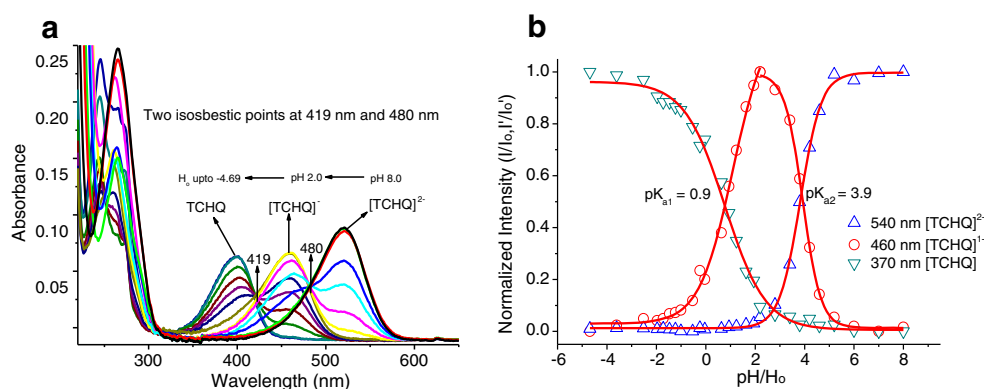
Acid dissociation constants for ground and excited states ( $pK_a$  and  $pK_a^*$ ) were determined from absorption and emission spectra of TCHQ at different pH/ $H_o$ . Buffer solutions for pH range from pH2 to 8 were prepared by using Citric acid and  $Na_2HPO_4$  [51]. Dilute aqueous solutions of  $HClO_4$  were used in order to perform measurements below pH2 [52].  $pK_a$  values were investigated by spectrophotometrically [53] and the excited state dissociation constants,  $pK_a^*$ , values were estimated from the fluorescence titration curve and Förster cycle method [54–57].

## Results and Discussion

### pH Dependant Absorption and Emission Spectra

In order to determine the acid-base equilibrium constants, for the ground and excited state proton transfer in aqueous solution, the absorption and fluorescence spectra of TCHQ were recorded at different pH/ $H_o$  values. The fluorescence quantum yields for neutral and mono-anionic forms of TCHQ is not possible due to the ESPT. The fluorescence emission from neutral TCHQ has not been observed in steady state measurements due to faster proton transfer,

**Fig. 1** **a** Absorption spectra of TCHQ measured at different pH (2–8) using buffer and pH2 to  $-4.69 H_o$  by dilution of  $HClO_4$ . **b** Normalized absorption intensity of TCHQ and its mono and dianion measured at different  $pH/H_o$  values



from TCHQ to water, compare to radiative emission of TCHQ. Pure emission of  $[TCHQ]^-$  can only be observed at  $H_o < -2$  but only neutral TCHQ (no mono-anion  $[TCHQ]^-$ ) is present in the ground state at such a high proton concentration.

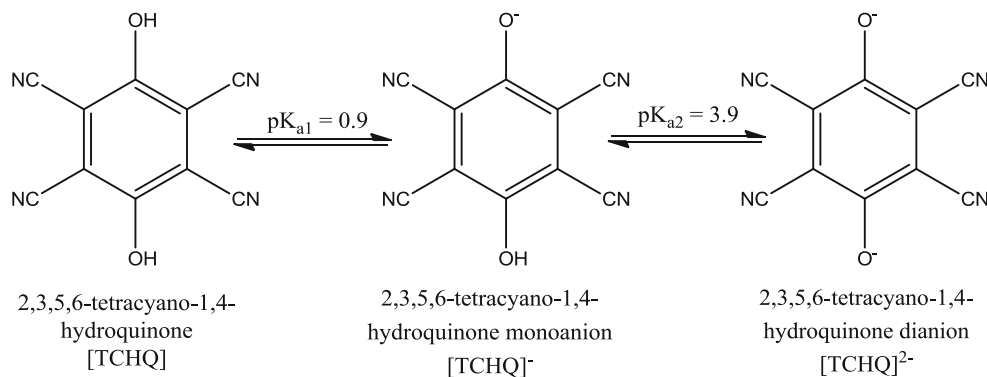
#### Ground and Excited State $pK_a$ Values

Absorption spectra of TCHQ in aqueous solution with concentration  $1 \times 10^{-5} M$  were recorded at different  $pH/H_o$  values. Three peaks ( $\lambda_{max}$  at 398 nm, 461 nm and 520 nm) and two isosbestic points (at 419 nm and 480 nm) were observed in the absorption spectra when measured at different  $pH/H_o$  values as shown in Fig. 1(a). The normalized absorption intensities at wavelengths 370 nm, 460 nm and 540 nm have been plotted against corresponding  $pH/H_o$  values to extract the  $pK_a$  values for neutral TCHQ, mono-anion  $[TCHQ]^-$  and di-anion  $[TCHQ]^{2-}$ , respectively as shown in Fig. 1(b). The maximum absorbance for wavelength 460 nm is at pH2. Therefore, the absorption intensity at 460 nm is normalized in two segments, i.e. one for data from pH8 to pH2 and the other for pH2 to  $H_o -4.7$ . The two  $pK_a$  values, i.e.  $pK_{a1} = 0.9$  (for equilibrium between neutral  $[TCHQ]$  and mono-anion species  $[TCHQ]^-$ ) and  $pK_{a2} = 3.9$  (for the equilibrium between mono-anion form  $[TCHQ]^-$  and di-anion  $[TCHQ]^{2-}$  form) were obtained as shown in Scheme 1.

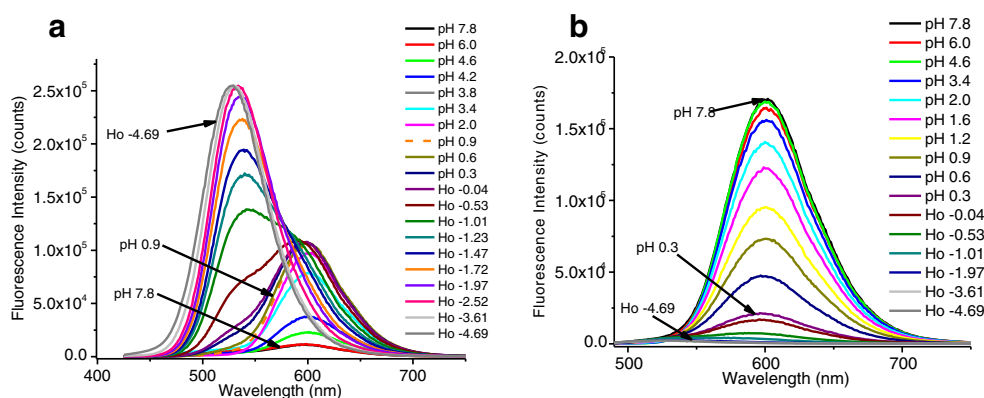
The two isosbestic points (419 nm and 480 nm) were selected as excitation wavelengths for measurements of excited state  $pK_a$ . The fluorescence spectra, after excitation at 419 nm, for different  $pH/H_o$  values of solution showed two peaks at 532 nm and 601 nm, correspond to mono-anion  $[TCHQ]^-$  and di-anion  $[TCHQ]^{2-}$  species respectively, as shown in Fig. 2(a). While exciting at 480 nm, there was only one peak at 601 nm for different pH values and the intensity of this peak was decreased with decreasing the  $pH/H_o$  value of the solution as shown in Fig. 2(b). The value for  $pK_a^*$  was determined by plotting the relative normalized fluorescence intensity of the two species as shown in Fig. 3. The curve corresponds to relative intensity at 640 nm ( $\lambda_{ext} = 419$ ) rises from  $H_o = -4.0$  to  $pH = 1$  due to new fluorescent specie (peak), and then the relative intensity is decreased for  $pH > 2$  due to decrease in absorbance at 419 nm. While exciting at 480 nm, there is only one peaks observed at all values of  $pH/H_o$ . The intensity of this peak starts decreasing ( $pH < 2$ ) merely due to decrease in absorbance at 480 nm. Thus relative fluorescence intensities also indicate the ground state  $pK_a$  values. The estimated value from fluorescence titration for  $pK_{a2}^*$  is  $-1.1$  (for the equilibrium between  $[TCHQ]^-$  and  $[TCHQ]^{2-}$ ). The absorption and emission spectra of TCHQ were also measured in basic solutions (upto 2 N NaOH) which were identical to those obtained at pH8.0.

The  $pK_a$  values for excited state equilibria ( $pK_{a1}^*$  and  $pK_{a2}^*$ ) were also estimated from Förster cycle method,

**Scheme 1** Protolytic equilibrium in the ground state among various forms of TCHQ



**Fig. 2** Fluorescence spectra of TCHQ after excitation at (a) 419 nm and (b) 480 nm for different pH/H<sub>0</sub> values



Eq. (1), using respective absorption maxima. The estimated values were found to be  $pK_{a1}^* = -3.3$  (between TCHQ and [TCHQ]<sup>-</sup>) and  $pK_{a2}^* = -1.2$  (between [TCHQ]<sup>-</sup> and [TCHQ]<sup>2-</sup>).

$$pK_a^* = pK_a - (E_{AH} - E_{A^-})/2.3RT \quad (1)$$

#### Absorption and Emission Spectra in Different Solvents

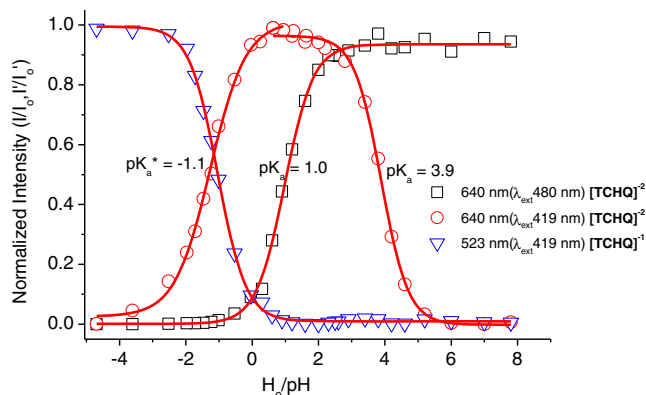
Absorption and fluorescence characteristics of TCHQ were studied in both protic and aprotic solvents. The aprotic solvents used were slightly polar (ethers), moderately polar (acetone and acetonitrile), highly polar (DMSO) and protic solvent such as ethanol and water were used. Both absorption and fluorescence spectra of TCHQ depend on the concentration of TCHQ. Non-polar solvents like cyclohexane, n-hexane, benzene, toluene etc. were also used for the measurements of absorption and emission spectra, but TCHQ showed either no or very limited solubility in these solvents.

#### Absorption Spectra

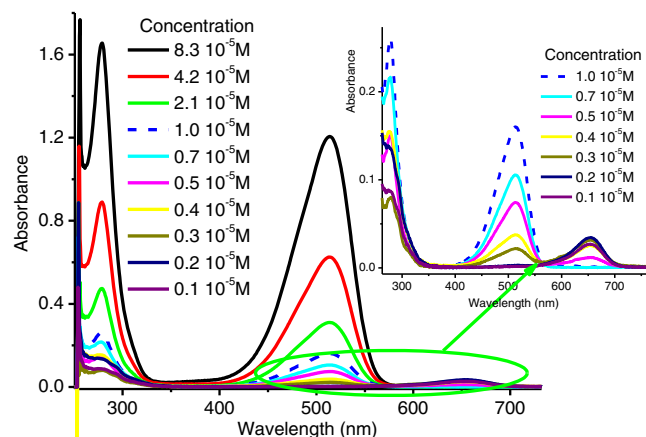
Significant changes in absorption peaks were observed with change of solvent. The absorption spectra showed only one

peak with absorption maxima at 398 nm when recorded in slightly polar solvents, e.g. diethylether as shown in Fig. S-1. In moderately polar solvents like acetone and acetonitrile, two peaks were observed for different concentrations of TCHQ as shown in Fig. S-2 and S-3 respectively. The first peak is in the range of 390–400 nm and the second peak is around 505 nm. There were two peaks at 514 nm and 657 nm in the absorption spectra of TCHQ for different concentrations in DMSO. The peak at 657 nm appeared in dilute solution (conc.  $\leq 2 \times 10^{-6}$  M) whereas the peak at 514 nm appeared in concentrated solution (conc.  $\geq 1 \times 10^{-5}$  M). There exist two peaks in between above two concentrations as shown in Fig. 4.

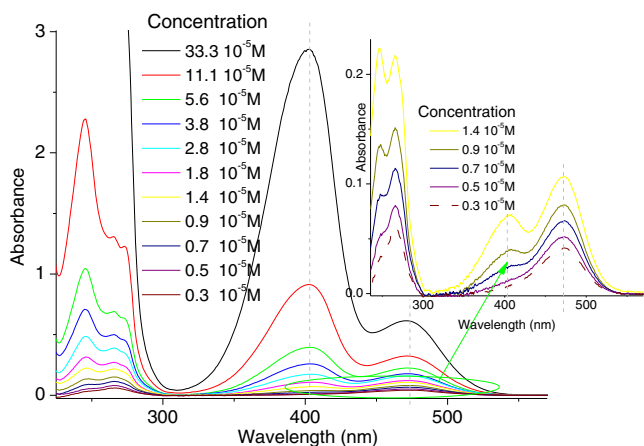
Absolute ethanol and water were also employed in order to study concentration dependence of absorption spectra in protic solvents. Two peaks (at 403 nm and 473 nm) were observed for various concentrations of TCHQ in absolute ethanol, except for the very dilute solutions (conc.  $< 5 \times 10^{-6}$  M) which showed only one peak at 473 nm as shown in Fig. 5. The TCHQ solutions in acetone (Fig. S-2) and acetonitrile (Fig. S-3 and S-4) exhibited similar concentration dependence of absorption spectra as in ethanol. An additional peak at longer wavelength (543 nm) was appeared by the addition of a small amount of water (less than 2 %)



**Fig. 3** Normalized fluorescence intensity of TCHQ mono-anion and di-anion measured at different pH/H<sub>0</sub> values



**Fig. 4** Absorption spectra of TCHQ in DMSO at different concentrations

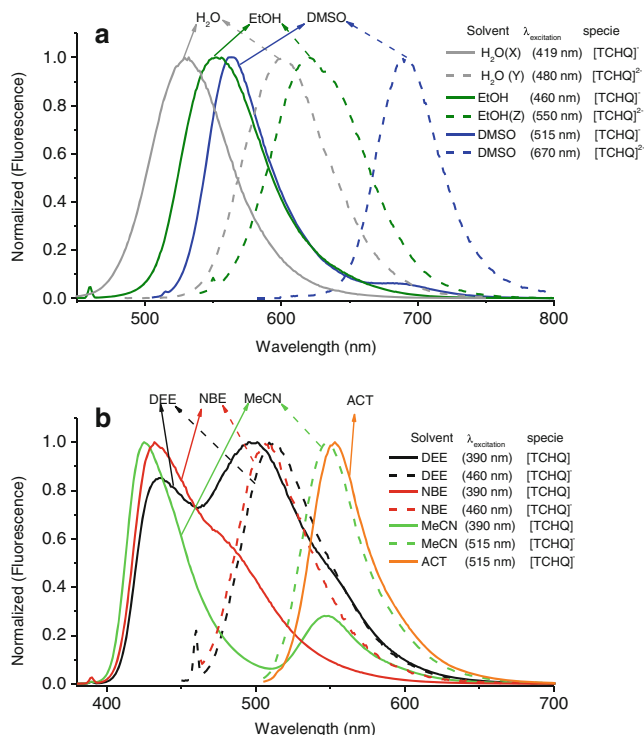


**Fig. 5** Absorption spectra of TCHQ in Ethanol at different concentrations

into the dilute solution of TCHQ in absolute ethanol as shown in Fig S-7.

Two peaks, at 461 nm and 520 nm, were observed for different concentrations of TCHQ in water as shown in Fig. S-8. Peak intensity at 461 nm decreased rapidly as compared to the one at 520 nm by decreasing the concentration of TCHQ in solution (shown in Fig. S-6). There exist only single peak in the absorption spectra in dilute solutions (conc. <math>1 \times 10^{-5}</math>M).

The TCHQ was found in three different forms (neutral TCHQ, mono anion  $[TCHQ]^-$  and dianion  $[TCHQ]^{2-}$ ) in the absorption spectra in different solvents at various concentrations. The absorption maxima of different forms of TCHQ were in the following order;  $\lambda_{max, [TCHQ]} < \lambda_{max, [TCHQ]^-} < \lambda_{max, [TCHQ]^{2-}}$ . In ethers (diethylether and n-butylether), TCHQ was present in the neutral form only ( $\lambda_{max}$  398 nm) which was also observed in the absorption spectra of TCHQ in very acidic medium ( $H_0 < -1$ ). In moderately polar solvent (acetone, acetonitrile and ethanol), the absorption spectra showed two peaks (for TCHQ and  $[TCHQ]^-$ ) in concentrated solutions (absorbance >0.1) and only one peak in very dilute



**Fig. 6 a, b** Fluorescence spectra of TCHQ in different solvents: DEE (diethylether), NBE (n-butylether), MeCN (acetonitrile), ACT (acetone), EtOH (ethanol), DMSO (dimethylsulfoxide). X  $H_2O$  at  $-3.6H_0$ ; Y  $H_2O$  at pH 7.8 and Z (add <math>2\%</math>  $H_2O$ ) in EtOH

solution (for  $[TCHQ]^-$ ). TCHQ showed two peaks (due to presence of mono anionic and dianionic forms of TCHQ) for various concentrations of TCHQ in polar solvents like DMSO and neutral water. Only one peak was observed due to  $[TCHQ]^{2-}$  in very dilute solutions, and no neutral form of TCHQ was observed for all concentrations of TCHQ. For aqueous solutions, similar peaks were also observed between the pH range 0–8. The peak positions of absorption bands in different solvents are summarized in Table 1. The reason for such concentration dependence is deprotonation of neural TCHQ and/or mono-anionic  $[TCHQ]^-$  on dilution. The extent

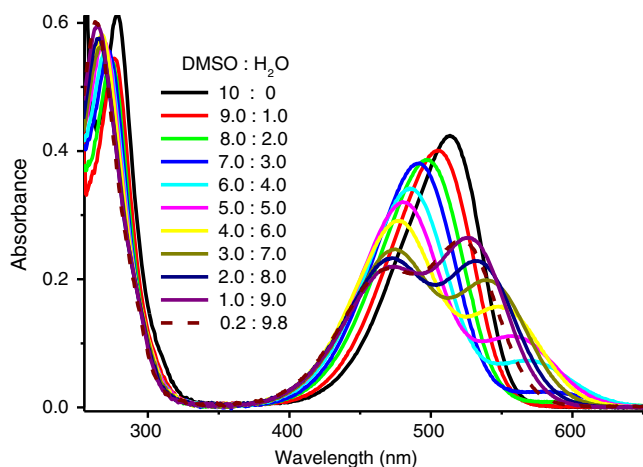
**Table 1** Absorption and fluorescence maxima of TCHQ,  $[TCHQ]^-$  and  $[TCHQ]^{2-}$  in different solvents

Solvents	$\lambda_{abs}$ [TCHQ] (nm)	$\lambda_{abs}$ $[TCHQ]^-$ (nm)	$\lambda_{abs}$ $[TCHQ]^{2-}$ (nm)	$\lambda_{flu}$ ( $\lambda_{ext}$ ) [TCHQ] (nm)	$\lambda_{flu}$ ( $\lambda_{ext}$ ) $[TCHQ]^-$ (nm)	$\lambda_{flu}$ ( $\lambda_{ext}$ ) $[TCHQ]^{2-}$ (nm)
DEE	398	.....	.....	436,500(390)	511(460)	...
NBE	398	.....	.....	433(390)	507(460)	...
MeCN	392	502	.....	425(390)	548(515)	...
ACT	396	508	.....	...	553(515)	...
EtOH	403	473	543 <sup>a</sup>	...	553(460)	621(550) <sup>a</sup>
$H_2O$	398 <sup>b</sup>	461	520	...	532(419) <sup>c</sup>	532(419) <sup>c</sup>
DMSO	.....	513.5	654	...	563(515)	692(670)

DEE diethylether, NBE n-butylether, MeCN acetonitrile, ACT acetone, EtOH ethanol, DMSO dimethylsulfoxide

<sup>a</sup>EtOH +  $H_2O$  (less than 2 %);

<sup>b</sup>at  $H_0 < -1$ ; <sup>c</sup>at pH >2



**Fig. 7** Absorption spectra of TCHQ (conc.  $2.8 \times 10^{-5}$  M) in DMSO-water mixture

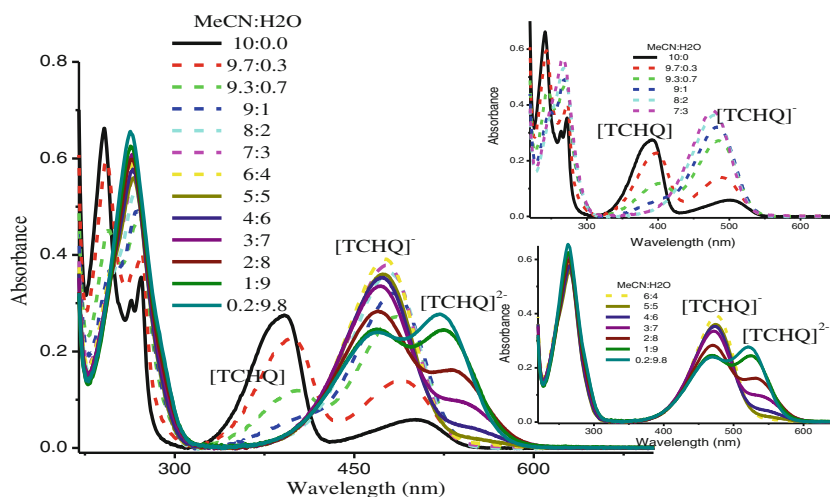
of deprotonation depends on the type solvents as well as on concentration of solute in the solution. Solvents like water, DMSO, alcohol (containing very small amount of water) etc. have high tendency to accept protons from the hydroxyl groups of TCHQ thus producing majorly deprotonated species ( $[\text{TCHQ}]^-$  and/or  $[\text{TCHQ}]^{2-}$ ) in these solvents. On the other hand, ethers have minimum (no) affinity for protons, so only neutral TCHQ is observed in absorption spectra in ethers. The concentration of TCHQ also affects the equilibrium between the protonated-deprotonated forms because of solvent limited ability to accept protons. Therefore, in very dilute solutions of TCHQ in water and DMSO, the only species is doubly deprotonated TCHQ ( $[\text{TCHQ}]^{2-}$ ). Addition of TCHQ in solvent (or increasing concentration of TCHQ) shifts the equilibrium toward the protonated species (neutral TCHQ and/or  $[\text{TCHQ}]^-$ ). The deprotonation of TCHQ forms  $[\text{TCHQ}]^-$  and that of  $[\text{TCHQ}]^-$  produces  $[\text{TCHQ}]^{2-}$ . So the concentrations (hence absorption peak intensities) of the two species in the solution are not equally decreased on dilution. The protonated species ( $[\text{TCHQ}]$  or  $[\text{TCHQ}]^-$ ) were observed in concentrated

solutions and deprotonated species ( $[\text{TCHQ}]^-$  or  $[\text{TCHQ}]^{2-}$ ) were majorly present in dilute solutions.

### Fluorescence Spectra

There exist three species of TCHQ in the solution as was observed in the absorption spectra in various solvents. The normalized fluorescence spectra for the various forms of TCHQ in different solvents were shown in Fig. 6. All the three forms of TCHQ ( $[\text{TCHQ}]$ ,  $[\text{TCHQ}]^-$  and  $[\text{TCHQ}]^{2-}$ ) demonstrated fluorescence emission over a wide range (400 nm to 750 nm) of the visible region of the light spectra. Fluorescence emissions by two species were observed either in the form of additional peak (DEE and MeCN) or in the form of shoulder of the already existed peak (NBE, DMSO) in most of the emission spectra. Only neutral TCHQ was observed in the ground state when studied in diethyl ether (as depicted in the absorption spectra) but emission from two different species suggests excited state proton transfer to the solvent. No neutral form of TCHQ was observed in the excited state when investigated in protic solvents such as water and alcohols. So a more rigorous work is required to calculate the quantum yields of each species (TCHQ,  $[\text{TCHQ}]^-$  and  $[\text{TCHQ}]^{2-}$ ). The fluorescence maxima for these species are summarized in Table 1. Fluorescence emission spectra of TCHQ in individual solvents excited at various wavelengths have been shown from Fig. S-8 to Fig. S-13. Polarity of solvent is one of the parameters that influence the shift in both absorption and emission spectra. There are other solvent parameters like solvent hydrogen bond donating ability (solvent acidity), solvent hydrogen bond accepting ability (solvent basicity) etc. that are responsible for peak shift in various solvents. A detailed solvatochromism study (which is beyond the scope of current paper) based on linear solvation energy relationship (LSER), using Kamlet-Taft and/or Javier Catalán parameters for various solvents, is required for quantitative correlation of solvent-solute interaction.

**Fig. 8** Absorption spectra of TCHQ ( $3.0 \times 10^{-5}$  M) in acetonitrile water mixture



**Table 2** pK<sub>a</sub> and pK<sub>a</sub><sup>\*</sup> values of hydroquinone and cyano-substituted hydroquinone

	Hydroquinone (HQ)	2,3-dicyano-p-hydroquinone (DCHQ) <sup>a</sup>	2,3,5,6-tetracyano-p-hydroquinone (TCHQ)
pK <sub>a1</sub>	10 <sup>b</sup> , 9.85 <sup>c</sup>	5.5	0.9 <sup>d</sup> , 1.0 <sup>e</sup>
pK <sub>a2</sub>	11.4 <sup>c</sup>	8.0	3.9 <sup>d,e</sup>
pK <sub>a1</sub> <sup>*</sup>	3.1 <sup>b</sup>	0.04, -0.3	-3.3 <sup>f</sup>
pK <sub>a2</sub> <sup>*</sup>	–	4.8	-1.1 <sup>e</sup> , -1.2 <sup>f</sup>

<sup>a</sup> From reference [47]; <sup>b</sup> From reference [58]; <sup>c</sup> From reference [59]; <sup>d</sup> from absorption titration; <sup>e</sup> from fluorescence titration; <sup>f</sup> Calculated using Förster method, Eq. (1)

### Absorption Spectra in Binary Mixtures

In order to know more about the absorption characteristics of TCHQ, the absorption spectra of TCHQ were measured in two different solvent binary mixtures. In these binary mixtures, one part is chosen as H<sub>2</sub>O (has high ability to accept and donate proton) where as the second partner was either acetonitrile or DMSO. The concentration of TCHQ was essentially the same while varying the volume ratio of water in the binary mixture.

In case of water and DMSO solvent mixture, the concentration of the TCHQ was  $2.8 \times 10^{-5}$  M. The absorption spectra at various volume ratios of the binary mixture are shown in Fig. 7. There was only one peak at 514 nm in pure DMSO and the intensity of this peak decreased with the increase in the water volume ratio. A new peak appeared at longer wavelength with the further increase in water contents (more than 20 %) in the solvent mixture. Two peaks, at 521 nm and 469 nm, were observed in the mixture that contains only 2 % of DMSO.

In acetonitrile-water mixture, three different peaks were observed by changing the volume ratio of the two solvents. The concentration of TCHQ for this solvent mixture was  $1 \times 10^{-5}$  M. Two peaks were observed at 392 nm and 502 nm in pure acetonitrile. A small red shift in the peak at 392 nm and a blue shift in the second peak were observed with a little addition of water. The peak at 392 nm was vanished at about 10 % of water contents (V/V) in the solvent mixture, as shown by Fig. 8. From about 15 % to 50 % of water contents there was only one peak, which underwent a hypsochromic shift by increasing the aqueous component of mixture. Further increase of water contents (more than 50 %), a new peak appeared at the longer wavelength of already existed peaks and shifted hypsochromically.

### Conclusion

The substitution of cyano-groups has enhanced the acidic properties of the parent hydroquinone many folds as can be

seen by comparing pK<sub>a</sub> and pK<sub>a</sub><sup>\*</sup> values for hydroquinone and cyano-substituted hydroquinones (see Table 2). In aqueous solution, neutral form of TCHQ was only observed at lower pH (highly acidic). TCHQ behaves as an extremely strong acid in electronically excited state that makes it impossible to observe the steady state emission spectra of the neutral TCHQ in highly acidic water. Absorption spectra in different organic solvents showed that TCHQ was present in one form (neutral TCHQ) in solvents with very little polarity like ethers (DEE and NBE) and two forms of TCHQ (neutral and mono anionic) were detected in moderately polar solvents such as acetone and acetonitrile. In strongly polar solvent like water and DMSO, no neutral TCHQ was observed. Only dianionic form, [TCHQ]<sup>2-</sup>, was present in the very dilute solutions in DMSO and water. Ethers are the only solvents that contain just the neutral TCHQ in the ground state. TCHQ behaves like such a strong acid in the excited state that it donates the proton in ethers as is seen in the fluorescence spectra of TCHQ in ethers. Investigations performed in binary mixture has further has strengthened the idea of the existence of three different species of TCHQ in various solvents. The addition of water led to the formation of mono-anion and/or di-anion of TCHQ by giving an opportunity to donate the proton(s) to water molecules.

Fluorescence emission spectra in various solvents suggested a fast excited state proton transfer to solvents. Present findings about absorption and fluorescence emission TCHQ will provide a strong base for the investigation of proton transfer kinetics in various solvents.

All the three forms of TCHQ (neutral TCHQ, TCHQ<sup>-1</sup> and TCHQ<sup>2-</sup>) are fluorescent. Both absorption and emission characteristics of TCHQ and its deprotonated forms (TCHQ<sup>-1</sup> and TCHQ<sup>2-</sup>) depend on the medium in which these are studied. TCHQ can be used as a fluorescence probe for the presence of trace amount of moisture due to high sensitivity of water contents. It can also be used as pH probe because of its sensitivity towards pH of the medium under investigation and has an advantage of being characterized through absorption and/or emission characteristics.

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