



Spectral and time-resolved properties of photoinduced hydroxyquinolines doped thin polymer films

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ABSTRACT

Quinoline and its derivatives have a wide range of biological and pharmacological activities. Quinoline ring is used to design functional materials (quinoline derivatives) for OLEDs and field-induced electro-optics. It possesses antibacterial, antifungal, antimalarial, cardiotoxic, anthelmintic, anti-inflammatory, anticonvulsant and analgesic activity. Here, we have examined photoexcitation dynamics of 6-hydroxyquinoline (6-HQ) doped in polymer films of polymethyl methacrylate (PMMA), polyvinyl alcohol (PVA) and cellulose acetate (CA) at atmospheric conditions. The absorption maximum of 6-HQ in polymer films was observed at 333 ± 1 nm, whereas fluorescence (FL) maximum fell in the range of 365–371 nm. In PVA film, in addition to the typical FL, a band maximum at 432 nm appeared as a result of an excited-state intermolecular proton transfer (ESIPT) reaction facilitated in the hydrogen-bonded complex formed in the ground state between 6-HQ:PVA. The multi-exponential decay behavior of 6-HQ in all the three polymer films indicates a nanoscale heterogeneity of the polymer environments.

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1. Introduction

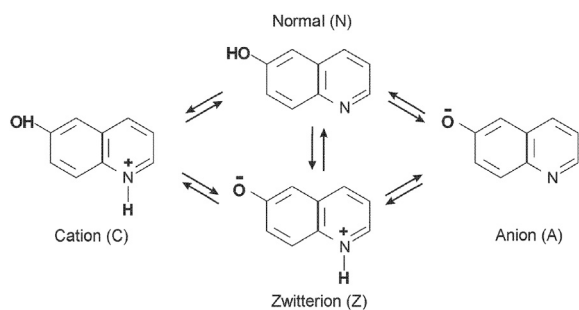
Several groups [1–29] have reported steady-state, and time-resolved fluorescence (FL) studies together with quantum chemical calculations of quinoline derivatives (hydroxy- and methoxy-quinolines) in liquid and solid phases as well as in polymeric matrices. These quinoline derivatives exist as different ionic species depending on the solvents or microenvironment used. The constants prevailing prototropic equilibrium of ionic forms (Scheme 1) of these molecules in the lowest singlet electronic excited states have been examined both theoretically and experimentally from the change in absorption and FL spectrum with hydrogen ion concentrations [1–3], as shown for 6-hydroxyquinoline (6-HQ). 6-HQ was found to be in the cationic (quinolinium) form at lower pH (<3) and the anionic (hydroxylate) form at high pH (>11). Whereas at pH ~7 it exists predominantly in the neutral form.

The 6-HQ is a bifunctional molecule which exists in different ionic forms (Scheme 1) and can act as H-atom donor at the –OH group and an acceptor at the ring >N atom [1]. Upon excitation, an excited state intermolecular proton transfer (ESIPT) takes place from 6-HQ to the solvent adiabatically in the first excited singlet state (S_1) in bulk water and also in supersonic jets [2]. The acid-base

properties of 6-HQ at both the –OH and >N positions modify actively following photoexcitation in the S_1 state and mainly making the –OH more acidic and the >N atom more basic. An excited state proton transfer to an aqueous solvent occurs due to shifting in acid-base equilibrium (pK_a value). The two ground state pK_a values of 6-HQ were found to be 5.1 and 9.2 for $>NH^+/\geq N$ and $-OH/O^-$, respectively [3]. The kinetic study of 6-HQ in acidic, basic and neutral aqueous solutions reveals exceptionally high simultaneous photoacidity and photobasicity at the two functional groups in the S_1 excited state. The deprotonation and protonation from the usual form of 6-HQ in a step-wise manner takes about 25 and 46 ps [4,5], respectively, whereas the intermediate emission decay time is found to be about 10 ps at pH 3. Further, 6-HQ can also exist as the *cis* and *trans* forms and the *cis* form is more stable and take part in the H-bonded network and subsequently in the proton transfer reaction [11,13–20].

We have studied 2-HQ to 8-HQs and 6-MQ in solvents of different polarity, hydrogen-bonding ability and doped in polymeric films, and have proposed models to demonstrate an excited state proton transfer mechanism [9–20,24–26]. The strength of hydrogen-bond, the structural arrangement of probe and solvent molecules/polymer chain have a crucial role in proton transfer process [8–20]. Our findings suggested ion pairs formation in 6HQ:TMA (1:1) system [18,20], an excited state multiple proton-transfer (PT) reaction through hydrogen-bonded molecular wire

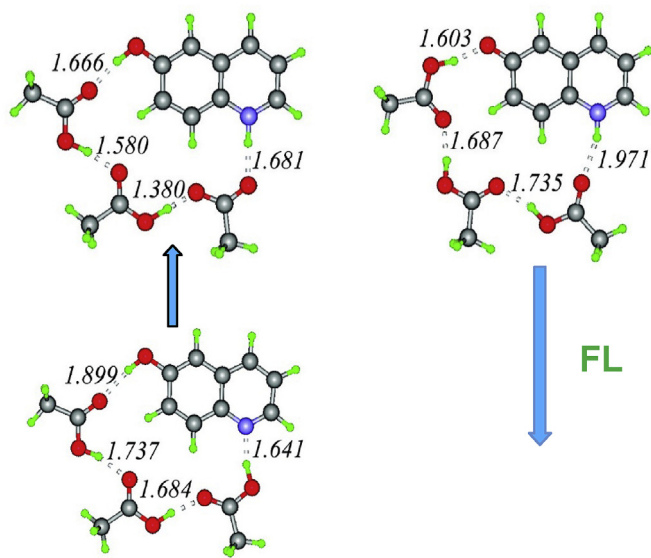
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Scheme 1. Protropic equilibrium of 6-HQ.

in 6-HQ:MeOH-water chain [17], 6-HQ:AcOH (Scheme 2) [14–16,19], 6-HQ:Nafion [10] and 7-HQ:PVA [8,9]. An efficient and fast (~ 200 ps) PT reaction takes place following photoexcitation and emits a sizeable Stokes-shifted emission [14,15]. In another report, in the presence of acceptor/donor molecule, 6-HQ form hydrogen-bonded complexes in the ground state. In the excited state, it forms the contact ion pairs and solvent separated ion pairs following proton transfer reaction [18,20]. The structural stability and the ground and excited states dipole moments of HQs critically depends on the position of $-\text{OH}$ group in the ring [11–13].

Further, quinoline ring possesses antibacterial, antifungal, anti-malarial, cardiotoxic, anthelmintic, anti-inflammatory, anticonvulsant and analgesic activity [28,29]. In addition to the wide range of biological and pharmacological activities quinoline has established protocols for the synthesis of this ring. The quinolone ring is also used for the design of ligands and functional materials (e.g., tris(8-hydroxyquinoline)aluminum) for photonic devices such as OLEDs and nonlinear effects [26,27]. The quinolone derivatives are very promising for the field-induced electrooptics, as evident by the study of optical and electric field-induced linear electrooptics effect in quinoline derivative and stilbene chromophores doped in a PMMA film [27]. The anisotropy is substantially larger for the quinoline derivative compared to the stilbene. This is because of the co-planar nitrogen atom of quinoline ring (nitrogen induced coplanarity inside the aromatic groups) plays a crucial role in the



Scheme 2. Molecular structures of 6HQ:AcOH in the ground and photoexcited states, and the excited state multiple proton transfer in the 6-HQ:AcOH complexes (in the S_1 state). The bond length is given in Å [19].

geometry of photoinduced electrooptics effects [27].

Given this, here we have demonstrated the host-guest interactions based on the spectral and transient behaviors. The 6-HQ doped in polymer films of polymethyl methacrylate (PMMA), polyvinyl alcohol (PVA) and cellulose acetate (CA) films were studied by time-resolved FL and steady-state absorption, FL, FL-excitation measurements. The possibility of an ESIPT mechanism of 6-HQ has been explored which in turn depends on the nanoscale environment around the molecule. The study not only provides information about the probe molecule but also gives information of host polymer, which has been used widely in electro-optics and polymer technology.

2. Materials and methods

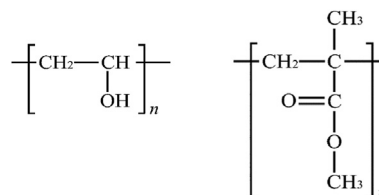
6-HQ obtained from Aldrich was purified before used and the purity of 6-HQ was checked by thin layer chromatography and the fluorescence excitation spectrum in different solvents. All the solvents used were of spectroscopic grade and used without distillation. PMMA (molecular weight 99,600) and CA (M. W. 30,000) were purchased from Aldrich and PVA (degree of polymerization is 1700–1800) from BDH was checked by fluorescence run test of the neat polymer films. 6-HQ doped films of PMMA, PVA (Scheme 3) and CA were prepared following the method described elsewhere [9,24]. All measurement were taken at room temperature and atmospheric conditions.

The absorption measurements were performed with a Jasco-V-550 spectrophotometer. FL and FL-excitation spectra were recorded with Jasco FP-777 spectrofluorometer. FL decays were recorded on an EI-199 fluorescence spectrometer using the time-correlated single-photon-counting technique [9,10].

3. Results and discussion

The absorption, FL and FL-excitation spectra of 6-HQ doped in polymer films of PVA, PMMA, and CA were measured at room temperature, and the results are shown in Table 1 and Figs. 1–3. The spectral characteristics of 6-HQ doped in PMMA and CA films are very similar. The absorption spectrum of 6-HQ in PMMA (Fig. 3) and CA films show a single band maximum in the lower energy region at around 333 nm (Table 1). However, in PVA film in addition to the 332 nm band, a small hump appears at 375 nm (Fig. 1). The absorption spectra are very similar to those observed in polar and non-polar solvents [13–17]. The difference in absorption spectrum may arise due to the difference in hydrogen bonding ability and polarity of the polymers. Out of these three polymers, PVA has most robust H-bonding ability whereas PMMA and CA show weaker hydrogen bonding ability concerning to the PVA [9–12,24].

Figs. 2 and 3 show the fluorescence (FL) spectra of 6-HQ doped in films of PVA and PMMA. The FL spectrum shows a band at around 371 nm and 364 nm in PVA and PMMA, respectively, which has been assigned to the usual FL of 6-HQ. In PVA polymers, in addition to the typical FL, a relatively weaker emission band is appeared at ~ 432 nm (Fig. 2 and Table 1). By increasing the wavelength of



Scheme 3. Molecular structure of PVA (left) and PMMA (right) polymers.

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