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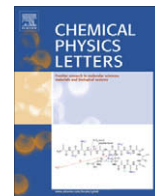


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Ultrafast excited-state dynamics of aminoperylene and of its protonated form observed by femtosecond absorption spectroscopy

Omar F. Mohammed, Eric Vauthey*

Department of Physical Chemistry, University of Geneva, 30 Quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland

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ABSTRACT

The photophysics of aminoperylene (APe) in various solvents, including a room-temperature ionic liquid, has been investigated by steady-state and femtosecond transient absorption spectroscopies. The ultrafast excited-state dynamics originates from the solvation of the polar S_1 state and not from a transition from a locally-excited to a charge-transfer state, as found with perylene-dimethylaniline. Addition of acid yields the protonated form APeH^+ , which exhibits similar photophysical properties than perylene, due to the suppression of the charge-transfer character of the S_0 – S_1 transition. However, excited-state proton transfer, resulting to the formation of APe in the S_1 state, is observed in methanol.

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1. Introduction

Addition of an amino-group to an aromatic hydrocarbon is known to substantially alter its photophysical properties. These changes arise mainly from the charge transfer (CT) character of the first electronic transition introduced by this electron-donating group [1]. Amino-aromatic compounds are generally fluorescent, with quantum yields that are often larger than those of the parent molecules. Because of this and the strong solvatochromism of their emission [2,3], these molecules have been used as fluorescent polarity probes [4,5]. The large fluorescence quantum yield implies a long-lived emitting state, typically with a nanosecond lifetime. This most probably explains why the early excited-state dynamics of these compounds has attracted little attention.

We have recently reported on the excited-state dynamics of perylene-dimethylaniline [6], and shown that, in polar solvents, the emitting state, which is characterized by a strong CT character, is not directly populated by photoexcitation but is rather populated on a picosecond time scale via a locally-excited (LE) state with a moderate CT character.

We report here on similar investigations with 3-aminoperylene (APe). A priori, a photophysics similar to that of perylene-dimethylaniline might be expected. On the other hand, the substantial coupling of the lone pair on the nitrogen atom with the π aromatic system of perylene should lead to a delocalisation of the electronic excitation and thus to direct population of the CT state from the ground-state. This agrees with previous measurements performed with aminonaphthalene, aminoanthracene and aminopyrene that suggest that the emitting state of these compounds is directly pop-

ulated upon photoexcitation [3–5,7]. However, an ultrafast transition from a LE to a CT state might have been missed because of insufficient time resolution. Although very little is known about the photophysics of APe and related derivatives [8,9], this compound has been chosen rather than another amino-aromatic molecule because of the spectral properties of the parent perylene [10–12], that should allow a clear distinction between LE and CT states by transient absorption spectroscopy.

Beside photoinduced electron transfer, excited-state proton transfer (ESPT) is another elementary process in chemistry and biology that has been recognized as a key process in several mechanistic and technological applications, such as acid–base neutralization reactions in water [13], and proton pumps through membrane protein channels [14]. The sharp increase in the acidity of photoacids by several pK_a units upon excitation is a strong driving force for ESPT during their excited-state lifetime [15]. Interestingly, water molecules are considered to be needed and to play a crucial role in ESPT by facilitating efficient charge separation when the proton leaves the photoacid [16,17], unless the acidity of the photoacid is remarkably strong to transfer its proton to nonaqueous solvents [18,19]. Such photoacids are called ‘super’ photoacids [20,21] and even larger changes in the pK_a have been observed in their excited state, making the occurrence of proton transfer to organic solvents possible [22,23]. Here, we also report on the photophysics of APe in low pH solutions and show that its protonated form, APeH^+ , is such a super photoacid.

2. Experimental

Aminoperylene (APe), was synthesized according to the procedure reported in Ref. [24] and subsequently purified by column chromatography. The protonated aminoperylene (APeH^+) was

* Corresponding author.

E-mail address: eric.vauthey@unige.ch (E. Vauthey).

prepared by lowering the pH to about 2 of an APe solution in methanol using concentrated HCl or HClO₄. The solvent was then evaporated, the remaining solid APeH⁺ chloride or perchlorate salt was washed several times with water to eliminate excess acid and was finally dried. Cyclohexane (CHX), acetonitrile (ACN), and methanol (MeOH, anhydrous <0.002% water) were purchased from Fluka and the room-temperature ionic liquid (RTIL), 1-ethyl-3-methylimidazolium-ethylsulfate (Ecoeng212), was from Solvent Innovation GmbH. The details of the time-correlated single photon counting experiment (TCSPC) and of the transient absorption (TA) setup are described elsewhere [25,26]. The APe solutions were adjusted to have an optical density in the range 0.05–0.1 and 0.2–0.3 on 1 mm at the excitation wavelengths, 400 and 495 nm, respectively.

Ground-state gas phase geometry optimisation was performed at the density functional level of theory (DFT) using the B3LYP functional [27], and a [3s2p1d] basis set [28]. Electronic vertical excitation energies and excited-state geometries were computed with time-dependent density functional theory (TDDFT) using the same functional and basis set [29]. The calculations were carried out using TURBOMOLE version 5.9 [30].

3. Results and discussion

3.1. Steady-state measurements

Fig. 1 shows the steady-state absorption and emission spectra of APe in various solvents. The absorption band located around 460 nm is broad and differs substantially from that of the parent molecule perylene (see Fig. 2B). This change in spectral shape is

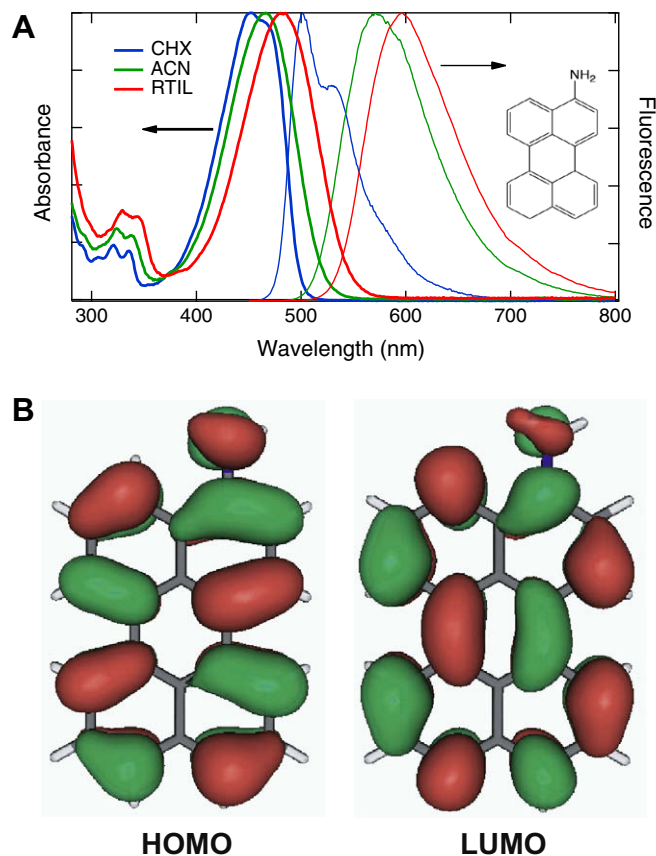


Fig. 1. Steady-state absorption and emission spectra (excitation at 440 nm) of APe in different solvents (top) and frontier molecular orbitals of APe drawn at the 0.02 a.u. level (bottom).

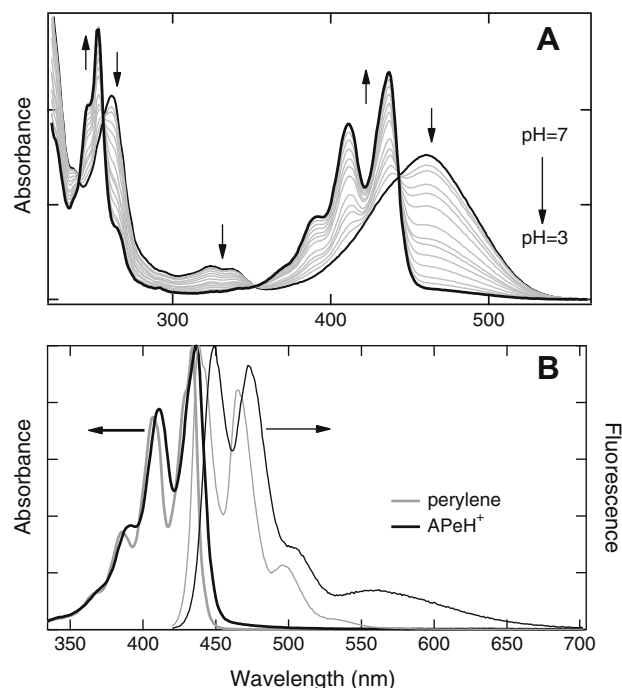


Fig. 2. (A) Steady-state absorption spectrum of APe in MeOH at different pH and (B) steady-state absorption and fluorescence spectra of APeH⁺ and perylene in MeOH.

very similar to that reported for other perylene derivatives with electron donating or accepting substituents [6,31,32], and can be attributed to the CT character of the associated transition. TDDFT calculations with APe in vacuo predict the first electronic transition at 468 nm to be associated with a one electron HOMO–LUMO transition. The density of the LUMO on the nitrogen of amino-group is substantially lower than in the HOMO (Fig. 1), supporting the CT character of this transition.

A marked solvent dependence of the position of the band maximum can be observed (Table 1). A plot of the band maximum in wavenumbers as a function of $f(\epsilon_s) - f(n^2)$ where $f(x) = 2(x - 1)/(2x + 1)$ and ϵ_s and n are the dielectric constant and the refractive index, respectively, does not exhibit a clear correlation if all the solvents listed in Table 1 are considered. However, if only solvents of similar refractive index are chosen, a reasonable linear dependence with a slope of $-1300 \pm 400 \text{ cm}^{-1}$ is obtained, suggesting a substantial dipole moment difference between the ground-state and the Franck–Condon excited state of APe.

The emission spectrum of APe exhibits large red shift with respect to the absorption band. In CHX, the fluorescence band shows

Table 1
Photophysical parameters of APe in various solvents.

Solvent	λ_{abs}^a (nm)	λ_{fl}^b (nm)	Φ_{rel}^c	τ_{fl}^d (ns)
Cyclohexane	452	500	0.55	5.3
Tetrahydrofuran	468	564	0.58	
Dichloromethane	465	543	0.47	6.8
Acetone	471	574	0.50	
Methanol	460	577	0.45	5.0
Dimethylformamide	482	588	0.56	
Acetonitrile	466	575	0.54	5.5
Ecoeng212	481	595	0.53	

^a Absorption maximum.

^b Emission maximum.

^c Relative fluorescence quantum yield compared to perylene.

^d Fluorescence lifetime.

some vibronic structure, whereas in polar solvents, it is structureless and mirror image of the absorption spectra. As indicated in Table 1, the fluorescence quantum yield of APe is smaller by a factor of about two than that of perylene. Compared to the absorption, the emission band exhibits a stronger solvatochromism (Table 1) and the plot of the emission maximum measured in all solvents listed in Table 1 vs. $f(\epsilon_s) - f(n^2)$ is linear with a slope of $-4500 \pm 600 \text{ cm}^{-1}$. According to the Onsager model [33,34], this slope, expressed in Joule, corresponds to $-\vec{\mu}_e \Delta\vec{\mu} / (4\pi\epsilon_0 a^3)$, where $\vec{\mu}_e$ is the permanent electric dipole moment of the molecule in the excited state, $\Delta\vec{\mu}$ is the dipole moment difference vector between excited and ground-states, ϵ_0 is the vacuum permittivity and a is the cavity radius. On the other hand, the slope obtained for the solvatochromism of the absorption is equal to $-\vec{\mu}_g \Delta\vec{\mu} / (4\pi\epsilon_0 a^3)$, where $\vec{\mu}_g$ is the ground-state dipole moment. Assuming a cavity radius of $3.85 \cdot 10^{-10} \text{ m}$ estimated from the Van der Waals increment method [35], these two slopes result in values for $|\vec{\mu}_g \Delta\vec{\mu}|$ and $|\vec{\mu}_e \Delta\vec{\mu}|$ of 15.2 D^2 and 51.2 D^2 , respectively. Assuming $\vec{\mu}_g$ and $\vec{\mu}_e$ to be parallel, these two values yield $\vec{\mu}_g = 2.5 \text{ D}$, $\vec{\mu}_e = 8.5 \text{ D}$ and $\Delta\vec{\mu} = 6 \text{ D}$. The ground-state dipole moment found experimentally is in excellent agreement with that of 2.7 D found from DFT calculations. A dipole moment change of 6 D corresponds to a full charge transfer over 1.25 \AA or is equivalent to a transfer of 0.25 electron from the amino nitrogen atom to the centre of the perylene unit.

Additionally to the dipole–dipole interaction, the solvatochromism is also influenced by the occurrence of H-bonding between the lone pair on the nitrogen atom of APe and protic solvents. Indeed, the absorption maximum of APe in MeOH is blue shifted by 280 cm^{-1} compared to ACN, although both solvents have the same polarity function (Table 1). However, such shift is absent in the emission spectrum. The H-bonding interaction is stronger in the ground than in the excited state because the electronic transition involves a decrease of the electron density at the nitrogen atom.

The mirror image relationship observed in polar solvents together with the excellent consistency between the absorption and emission solvatochromism suggest that emission occurs from the state that is populated upon absorption. In this respect, APe differs substantially from perylene-dimethylaniline, for which no mirror relationship was observed and for which the absorption and fluorescence solvatochromisms did not yield a consistent set of $\vec{\mu}_g$ and $\vec{\mu}_e$ values [6]. For this compound, optical excitation was found to lead to the population of a perylene LE state, whereas emission occurs from a subsequently populated CT state.

Nevertheless, the absence of mirror relationship observed with APe in CHX is intriguing. Broad absorption and structured emission spectra are often indicative of a relatively loose structure in the ground-state and of a more rigid excited-state geometry [36]. In APe such effect could be associated with both the twist angle of the amino-group relative to the perylene plane and the pyramidalisation angle at the nitrogen atom. DFT and TDDFT calculations of APe in vacuo point to different twist (26.5° vs. 11.0°) and pyramidalisation angles (N–H out-of-plane angle: 34° vs. 15°) in the ground and excited states. As both angles are smaller in the excited state, one could conclude that there is a better conjugation of the nitrogen lone pair with the perylene aromatic system and thus a more rigid geometry. The existence of mirror relationship in more polar solvents might be indicative of smaller structural differences between the ground and the excited states due solvation that stabilises the most polar geometries. Support of this hypothesis would require intensive quantum chemistry calculations that are beyond the scope of this investigation.

The absorption spectrum of APe undergoes drastic changes upon addition of HCl (Fig. 2A). As the pH is changed from neutral to acidic, the broad absorption band around 450 nm decreases

and is progressively replaced by a new band between 360 and 440 nm with a marked vibrational progression. The absorption spectrum at shorter wavelength also undergoes substantial changes and three isosbestic points can be clearly distinguished. As illustrated in Fig. 2B, the spectrum of APe at low pH is very similar to that of perylene and therefore this spectrum is assigned to the protonated aminoperylene, APeH⁺. Protonation of APe strongly reduces the electron donating properties of the amino-group and thus the first electronic transitions are entirely localised on the perylene core. Similar spectral changes upon lowering the pH have also been reported with 2-aminoanthracene in aqueous solutions [1] and aminopyrene in various solvents [4]. Importantly, upon excitation of APeH⁺ around 400 nm , two fluorescence bands are observed (Fig. 2B): one between 425 and 525 nm that is mirror image of the absorption band and that can be ascribed to APeH⁺ fluorescence of and the other between 525 and 700 nm that is identical to the emission band of APe* in the same solvent. The presence of this band is ascribed to the formation of neutral APe upon ESPT from APeH⁺ to the solvent MeOH, reflecting a remarkably strong photoacidity of APeH⁺. This is supported by the excitation spectrum of the fluorescence in the 525 – 700 nm region that exhibits the structured APeH⁺ band only. Furthermore, in ACN where this ESPT is not operative, the fluorescence spectrum consists of the APeH⁺ band only. In this solvent, the fluorescence quantum yield of APeH⁺ is the same as that of perylene, whereas in MeOH, the relative fluorescence quantum yield amounts to 0.77 . This difference can be attributed to the occurrence of ESPT to the solvent.

3.2. Time-resolved measurements

In all solvents investigated, the fluorescence decay of APe measured by TCSPC upon 395 nm excitation can be satisfactorily reproduced using an exponential function with a time constant ranging between 5.0 and 6.8 ns (Table 1).

Femtosecond transient absorption (TA) measurements reveal the occurrence of faster dynamics that clearly depends on the solvent. Fig. 3 displays TA spectra recorded at different time delays after 400 nm excitation of APe in three solvents. In CHX, the spec-

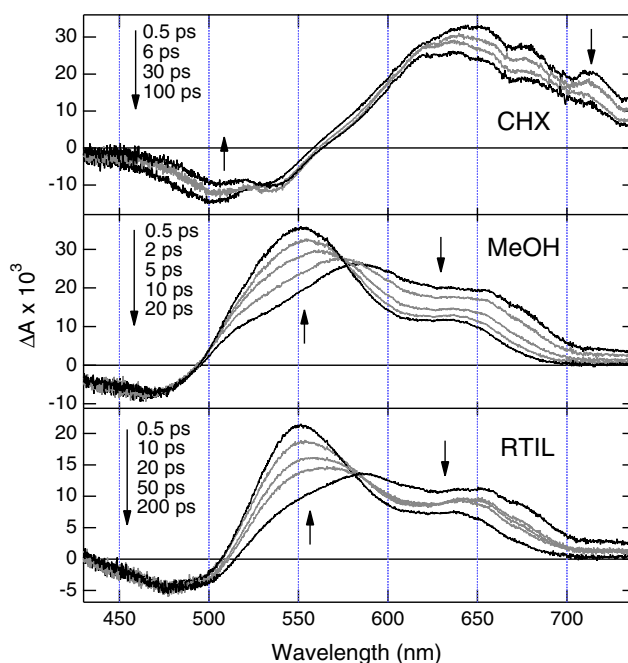


Fig. 3. Transient absorption spectra recorded at different time delays after 400 nm excitation of APe in CHX, MeOH and RTIL.

tra consist of a negative band between 450 and 550 nm, that can be assigned to the bleach of the ground-state absorption and to stimulated emission, and of a broad positive band centred around 640 nm, which can be ascribed to excited-state absorption (ESA). Apart from a small shift and narrowing taking place during the first tens of picoseconds, these bands go to zero on a nanosecond timescale, in agreement with the excited-state lifetime deduced from time-resolved fluorescence measurements. As excitation is performed at 400 nm, i.e. with about 0.5 eV excess energy, the early spectral dynamics is ascribed to vibrational relaxation [37,38].

In polar solvents, the TA spectra measured at long time delays differ considerably from those in CHX. They are dominated by a broad positive band peaking at ~ 550 nm with a shoulder around 640 nm. A negative band due mainly to the bleach of the ground-state absorption is also visible. These bands decay on the nanosecond timescale in agreement with the fluorescence lifetime. At early time however, the positive TA band culminates at longer wavelength, i.e. at about 585 nm, and the relative intensity of the shoulder is substantially larger. As time goes, the whole band shifts to shorter wavelengths and narrows, but its area remains essentially unchanged. Meanwhile, the intensity of the negative band stays constant, indicating that this spectral dynamics is not accompanied by a recovery of the ground-state population. The dynamics of these changes depends strongly on the solvent, as illustrated by the time profiles of the TA intensity at 550 and 650 nm (Fig. 4). In a given solvent, these profiles can be analysed globally using a multiexponential function with the time constants listed in Table 2. Those obtained in ACN and MeOH agree very well with the solvation times reported in the literature [39].

In principle, this spectral dynamics observed in polar solvents could be interpreted in two different ways: (1) a transition from a LE to a CT state or (2) the relaxation of an electronic excited state with a substantial CT character. As discussed above, the steady-state measurements do not support the first hypothesis. If the initially populated state were a LE state, the early TA spectra in polar solvents should be essentially identical to those in non-polar solvents. This has been very clearly observed with perylene-dimethylaniline [6], but this is not the case here with APe, even in RTIL, where the dynamics is the slowest. Moreover, the absorption spectrum of the LE state should resemble the ESA spectrum of perylene, which exhibits an intense band at 700 nm. This is again not the

Table 2

Time constants obtained from the global analysis of the TA profiles of APe in polar solvents at 550 and 650 nm (limit of error $\pm 20\%$). The values in parentheses are solvation times taken from Ref. [39].

Solvent	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)
Methanol	0.7 (0.67)	6.5 (3.2, 15)	
Acetonitrile	~ 0.15 (0.12)	0.75 (0.63)	
Ecoeng212	2.0	15	150

case here with APe. Because of this and of the close similarity of the measured and the solvation time constants, the spectral dynamics observed in polar solvents is ascribed to the solvation of the S_1 state of APe. The blue shift of the ESA band upon solvent relaxation can be accounted for by a final state of the ESA transition less polar than the S_1 CT state.

It should also be remembered that in polar solvents, the contribution of stimulated emission to the TA spectrum overlaps with that of the ESA. The early stimulated emission spectrum should be centred around 530 nm and, as dynamic Stokes shift takes place, it should move to about 580–600 nm. Therefore, the observed changes in the TA spectrum do not only arise from a change of the ESA spectrum but are also due to the overlapping dynamic Stokes shift of the stimulated emission.

Consequently, the time constants found for the spectral dynamics in RTIL can be considered as good estimates of the solvation time constants in this solvent. To our knowledge, the solvation dynamics of this RTIL (Ecoeng212) has not been investigated before. However, 2.4 and 14.9 ps components have been observed in the spectral dynamics of nitroperylene in this liquid, in excellent agreement with the two shortest time constant found here [31]. Furthermore, the dynamics of intramolecular charge separation in perylene-dimethylaniline was found to be close to the solvation dynamics and to be biphasic in this RTIL with 15.7 and 197 ps time constants [6].

Measurements with sufficient time resolution in other ionic liquids reveal a multiphasic dynamics with a subpicosecond component and components going from a few tens to several hundreds of picoseconds [40,41]. The number of TA spectra recorded here at very early time is not enough to resolve a subpicosecond component, but its presence cannot be excluded. On the other hand, by comparing the two observed time constants with those reported for other ionic liquids, one can conclude that Ecoeng212 should be considered as a RTIL with a fast response.

TA measurements in polar solvents have been repeated upon 495 nm excitation, i.e. on the red side of the absorption band. Both the TA spectra and the dynamics were the same than upon 400 nm excitation (data not shown). This indicates that, in polar solvents, the S_0 – S_1 absorption band of APe is homogeneously broadened, unlike that of nitroperylene where a distribution of twist angles of the nitro group relative to the aromatic plane contributes to the broadening of the absorption band [31].

Fig. 5A shows the TA spectra measured upon excitation of a solution of $APeH^+$ salt in anhydrous MeOH. At early time, the spectrum consists of a negative and structured band below 530 nm, due mostly to stimulated emission, and of an intense positive band with a maximum at 690 nm that can be assigned to the S_1 state absorption of $APeH^+$. This spectrum is very similar to that measured with the parent perylene. As time goes, the intensity of the 690 nm band and of the stimulated emission band decrease and a new positive band centred around 550 nm rises. The latter is very similar to that observed with APe at neutral pH and can be ascribed to APe in the S_1 state (see Fig. 3). Thus, the spectral changes illustrated in Fig. 5A can be interpreted as ESPT from $APeH^+ (S_1)$ to MeOH to yield $APe^* (S_1)$. The time window of the experiment is

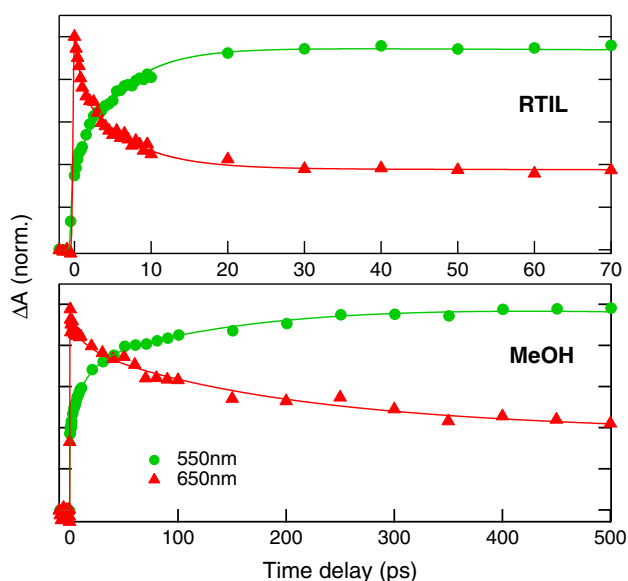


Fig. 4. Temporal evolution of the transient absorption at 550 and 650 nm in MeOH and RTIL and best multiexponential global fit.

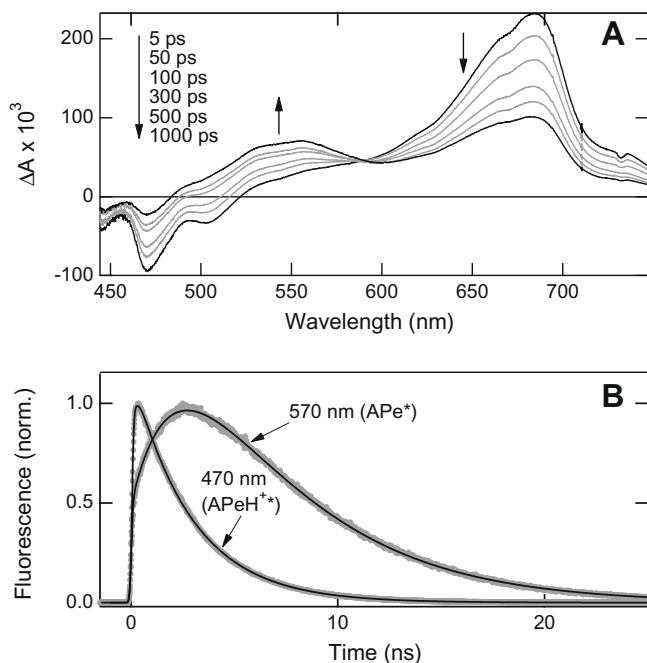


Fig. 5. (A) Transient absorption spectra measured at different time delays after excitation of a solution of APeH⁺ chloride salt in anhydrous MeOH. (B) Time profiles of the fluorescence intensity measured upon 395 nm excitation of the same solution.

too narrow to allow a reliable determination of the ESPT time constant. TCSPC measurements have therefore been carried out to completely resolve this dynamics. Fig. 5B shows the fluorescence decay of APeH⁺ (*S*₁) at 470 nm together with the rise and decay of APe* (*S*₁) emission at 570 nm. The first one can be reproduced using a single exponential function with a 2.9 ns lifetime, whereas the second requires a biexponential function with a 2.9 ns rise time and a 5.0 ns decay time. The latter time constant is identical with the fluorescence lifetime of APe in MeOH at neutral pH (Table 1). These data together with the TA spectra are unambiguous evidence of ESPT. Assuming that the difference in the fluorescence quantum yields of APeH⁺ in ACN and MeOH is due to this process, the ESPT time constant can be estimated to about 2 ns. It can be compared with those found with other ‘super’ photoacids, like monocyano- and dicyano-naphthol, that are capable of transferring protons to a wide range of organic solvents within their excited-state lifetime [42]. On the other hand, APeH⁺ differs from a structurally very similar acid, protonated aminopyrene, APyH⁺, which only undergoes ESPT when water is present as a cosolvent [43]. In the present case, the water concentration in the methanolic APeH⁺ solutions should not exceed $5 \cdot 10^{-4}$ M, and is thus far below that required for APyH⁺ to undergo ESPT. This difference in photoacidity may stem from the superior electron accepting properties of perylene ($E_{\text{red}} = -1.66$ V vs. SCE) compared to pyrene ($E_{\text{red}} = -2.04$ V vs. SCE) [44].

4. Conclusions

We have reported here on the ultrafast excited-state dynamics of APe and of its protonated form. Although important solvent dependences of the stationary spectra as well as of the transient absorption spectra are observed, the photophysics of APe can be well accounted for with a single excited state having a substantial CT character and directly populated upon optical excitation. In this respect, APe is similar to nitroperylene [31], except that the perylene moiety acts as electron acceptor.

On the other hand, APe differs from perylene-dimethylaniline [6] where the CT state is populated via a LE state. This difference arises from the coupling of the nitrogen atom lone pair with the perylene π electronic system. In perylene-dimethylaniline, such coupling occurs with the phenyl group and, as the dimethylaniline moiety is twisted relatively to the perylene plane, the first electronic transition is mainly localised on the perylene unit.

Finally, this investigation shows that APe can be used as a very efficient fluorescent pH probe and that its protonated form, APeH⁺, exhibits strong photoacid properties that are comparable to those of cyano- and dicyano-naphthol ‘super’ photoacids.

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