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Charge Transfer Assisted by Collective H-Bonding Network Dynamics

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Charge Transfer Assisted by Collective Hydrogen-Bonding Dynamics**

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It is widely recognized that changes of the local environment, such as solute–solvent interactions, can significantly affect excited-state properties and chemical reactivity of a variety of molecular systems.[1–7] Intermolecular hydrogen bonding (H-bonding) is a site-specific interaction between donor and acceptor molecules, and the nature of such interactions determines the properties of chemical and biological systems in the liquid phase.[2–14] Solvation dynamics, which have been studied by using ultrafast spectroscopy and theoretical simulation (see, for example, Refs. [15–18]), become critical when the timescales of bonding and solvent organization are similar to those of the processes involved, as in many charge-transfer reactions.

In protic media, relaxation of the solvent that surrounds an excited probe molecule that undergoes intramolecular charge transfer (CT) has been described to result from, in some cases, simple dielectric (nonspecific) solvation or, in other cases, from H-bonding (specific) interactions.[19,20] However, the presence of multiple binding sites[21,22] in the solute, and/or the control over solvent polarity and composition[23,24] could mask the influence of site specificity and the direct role of the solvent network. Nibbering and co-workers have shown that time-resolved IR spectroscopy of H-bonded systems has site-specific sensitivity,[7,10,12] and Phillips and co-workers recently used this technique to obtain the timescale for the H-bonding formation of solute–solvent complexes.[25,26] In a recent cogent report of CT in DNA-related systems,[27] site-specific interactions were found to be important, but the origin of the induced stabilization requires knowledge of the solvent network and its dynamics.

Herein, we examine the crucial role of H-bonding in CT by carefully designing an ideal probe molecule with one active site, and studying it in mixed solvents with different H-bonding affinities but with similar polarities. The probe, formylperylene (FPe), has a single carbonyl group, which is the unique site for specific H-bond interactions and electron-accepting character (see Scheme 1). Upon electronic excitation, the probe molecule undergoes CT with an increase in the electronic charge density (basicity) on the carbonyl group. As a result, the binding with the protic solvent molecules through
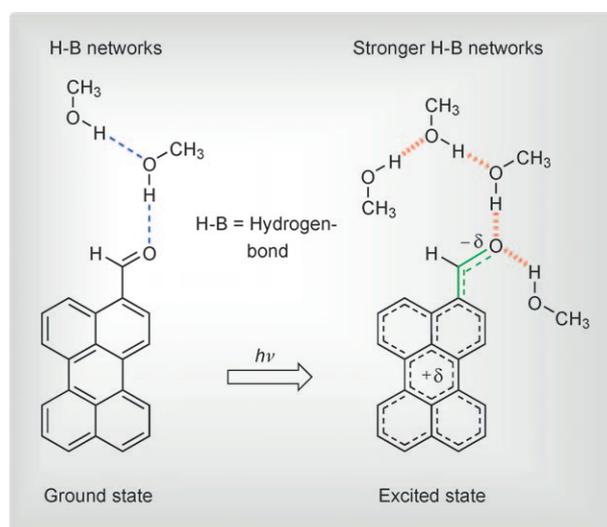
Scheme 1. Schematic representation of site-selective solvation. Ground- and excited-state hydrogen bonding (site-specific) occurs between the carbonyl oxygen atom of FPe and the protic hydrogen atom of MeOH. The network of solvent molecules is emphasized together with the charge transfer from a perylene moiety to the carbonyl group.

intermolecular H-bonds becomes stronger. To investigate the ultrafast solvation dynamics coupled to the CT of FPe, we recorded the femtosecond-resolved fluorescence Stokes shift in a series of binary mixtures of a protic solvent, methanol (MeOH), and an aprotic solvent, acetonitrile (ACN). In this way, the specific solvation dynamics of the H-bonding interaction is deciphered and distinguished from nonspecific solvation. The results allow the nature of solvent-network-assisted CT to be elucidated; this phenomenon is relevant to the issues of proton-coupled electron transfer in other systems including those of enzyme catalysis[28] and charge-transfer reactions in DNA assemblies.[29]

Figure 1 shows the absorption and emission spectra of FPe in cyclohexane (CHx), ACN, MeOH, and ACN/MeOH binary mixtures. The absorption spectra in all solvents show vibronic structures and weak solvent dependence. The maxima of the broad absorption bands are located near 470 nm, which differs substantially from that in the parent molecule perylene (around 430 nm).[30] Although there is no perceivable spectral shift when the solvent is changed from ACN to MeOH, a systematic change in the red tail of the absorption with the increase of the MeOH concentration is observed. This change indicates the formation of a H-bonded complex between FPe and MeOH; the probability of dimer formation is very low as the concentration FPe is very low

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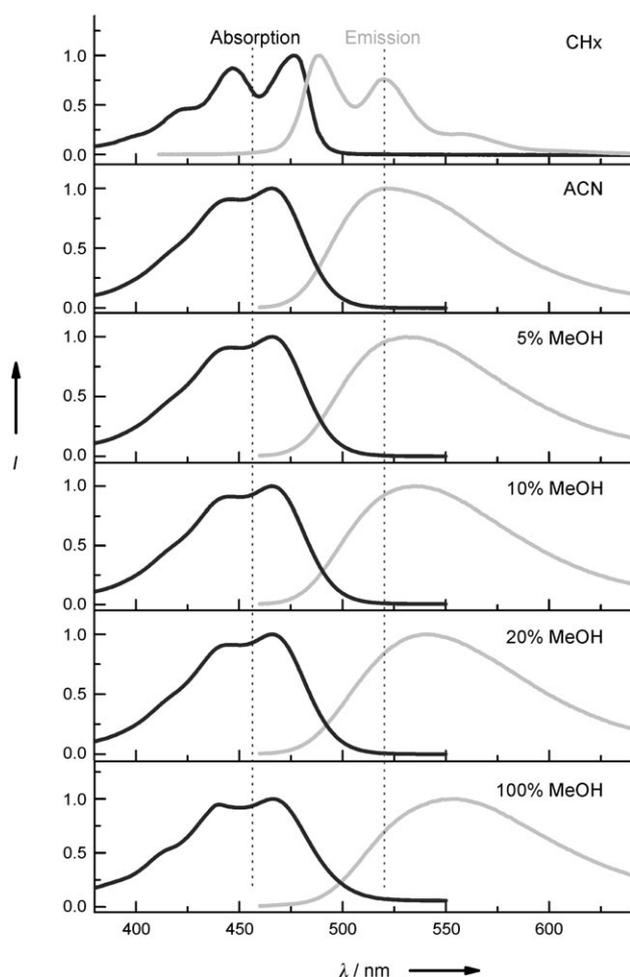   E-mail: zewail@caltech.edu

Figure 1. Steady-state absorption and fluorescence spectra. Solvent mixture compositions are given in each panel. Fluorescence spectra were obtained following excitation at 450 nm. The dotted lines are guides for the eyes to show spectral changes in absorption and emission.

(ca. 5×10^{-5} M). From the absorption spectral analysis, an equilibrium exists between the free and 1:1 H-bonded FPe with association constant of $K_{eq} = 0.5 \pm 0.2$, which indicates that more than 90% of FPe molecules are complexed in a neat MeOH solution. The existence of the ground-state H-bonding interaction between the carbonyl oxygen atom of FPe and the protic hydrogen atom of MeOH is confirmed by steady-state IR measurements. For CHx, the C=O stretch vibration is located around 1695 cm^{-1}; on the other hand, for deuterated MeOH, the C=O band is downshifted by approximately 15 cm^{-1}, and is much broader than that in CHx (data not shown), which is a signature of complexation with the solvent.

It can be clearly seen that the mirror symmetry between absorption and emission spectra is broken for FPe in polar solvents, unlike the case in CHx solution (see Figure 1), and the emission shows featureless broad spectra that are substantially red-shifted relative to their absorption spectra. As with nitroperylene and substituted vinyltetrahydropyrenes,[5,31] the emission is that of the CT state, as evidenced by

the magnitude of the large red-shift and the fact that transient absorption of the perylene cation near 555 nm has been observed.[32] The CT involves the perylene moiety and the carbonyl group as an electron donor and acceptor, respectively. As the emission maximum of FPe in MeOH solution is red-shifted by approximately 1000 cm^{-1} compared to that in ACN solution, the emissive state (CT state) must be more stable in the protic solvent, even though both ACN and MeOH are of similar polarity: $\varepsilon_{20°C} = 33.0$ for MeOH and 36.6 for ACN.

The additional shift in MeOH is, therefore, attributable to the site-specific H-bonding interaction of the carbonyl group of FPe with the hydroxy group of MeOH. It is noteworthy that the emission spectrum of FPe in ethanol is more bathochromically shifted than that in ACN (data not shown), despite the fact that ethanol ($\varepsilon_{20°C} = 25.3$) is less polar than ACN. This observation is again consistent with this selective binding, beyond the dielectric continuum effect of solvation. The extent of selectivity becomes clear from studies in ACN/MeOH mixtures. The emission maxima red-shift from 529.3 to 541.4 nm when the MeOH content in ACN was increased from 5 to 20%, and begins to reach an asymptotic value at an MeOH content of approximately 50% (see Figures 1 and 5).

The dynamics were investigated by recording the time-dependent fluorescence spectral shift, which is a consequence of energy relaxation. Time-resolved fluorescence spectra were reconstructed with a series of kinetic profiles measured at ten different emission wavelengths that cover the blue and the red envelopes of fluorescence, as described elsewhere.[9,33] As an example, Figure 2 displays several representative femtosecond-resolved fluorescence transients in a binary MeOH/ACN (20:80) mixture. The fluorescence transients display a multiple exponential decay (the blue region) and rise (in the red region) with time constants that span a few hundred femtoseconds to several tens of picoseconds, which is a signature of an ultrafast solvation process. By fitting the reconstructed spectra to lognormal shapes (Figure 3), we can correlate the time-dependent peak fluorescence wavenumber $\bar{\nu}_{max}(t)$ to the solvation-energy change ΔE_s. The transient behavior shows very different timescales, and typically can be fitted well to three exponential decays. Details of the results for all solvents are presented in Figure 4 and Table 1.

The magnitude of the total Stokes shift strongly depends on the proportion of MeOH in the solvent mixture. The steady-state spectral behavior indicates that the H-bonding interaction between the carbonyl group of FPe and MeOH is stronger in the excited state than that in the ground state. Upon excitation, FPe undergoes ultrafast CT, which gives rise to a sudden increase in the electron density on the carbonyl group as well as a large change in the dipole moment. The spectral dynamics observed for FPe in neat ACN result from "nonspecific solvation", for which no specific chemical bonds are formed or broken, because ACN does not possess any H-bond-donating ability. The obtained time constants of 90 and 530 fs agree well with those reported for inertial librational motion (≤ 100 fs) and the rotational and translational diffusive motion (ca. 0.5 ps) in ACN.[19] Time constants of 1.6 and 13.4 ps were obtained for FPe in neat MeOH solution. The
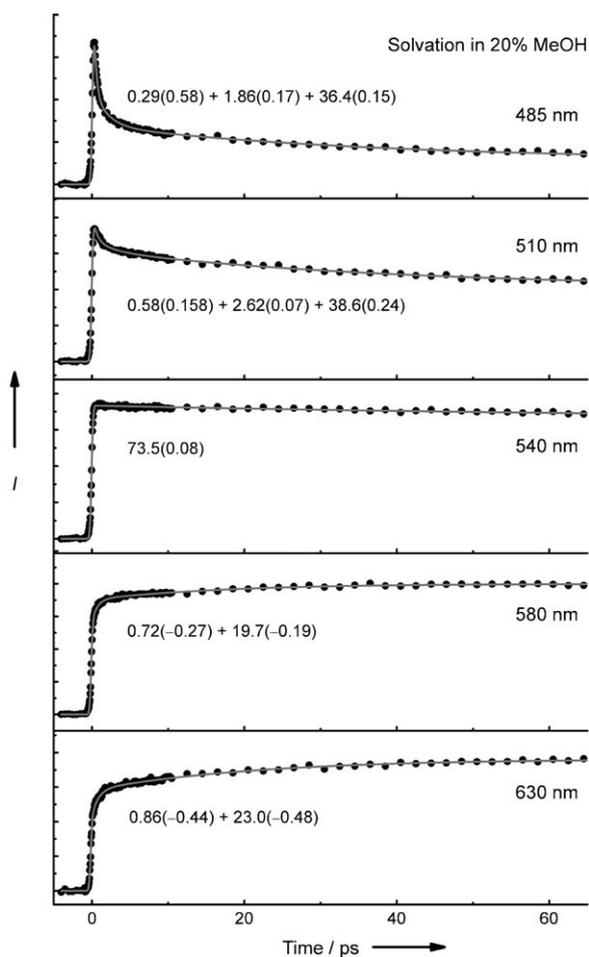
Figure 2. Transient fluorescence spectra. Representative femtosecond time-resolved upconversion signals were obtained following excitation at 448 nm in ACN with 20% MeOH. The monitored wavelengths are indicated in each panel. Time constants in picoseconds as well as their fractions (in parenthesis) from the multiexponential fits are also given in the panels. The long lifetime component of 5 ns was included in the analysis but not given in the panels for simplicity, as it represents the lifetime of the state.

Figure 3. Time-dependent spectral evolution. Solvent mixture compositions and delay times are given in each panel, which show the spectral shift that arises from the solvent response. Spectral intensities are normalized.

former value is similarly ascribed to rotational and translational motions in MeOH,[19,34] whereas the latter is unique to the specific interactions through H-bonding, and the timescale for the solvent network around the probe is determined by the solvent binding and reorganization. We note that the 13.4 ps component is absent in the transient spectra of nitroperylene in MeOH, where the specific interaction is effectively weakened; only two time constants of 150 fs and 1.7 ps were reported.[5] A time constant of 15 ps, which arises from H-bonding interactions, has also been observed in the bulk solvent of MeOH (with coumarin 153).[19] However, experiments in mixed solvents are essential in order to establish its origin.

In a binary mixture, free FPe and H-bonded FPe–MeOH coexist in their ground states. From the value of K_{eq} (0.5), it can be calculated that 70% of the FPe molecules form 1:1 ground-state H-bonded complexes when the MeOH content is 20%. In the mixture, solvent molecules have to diffuse from
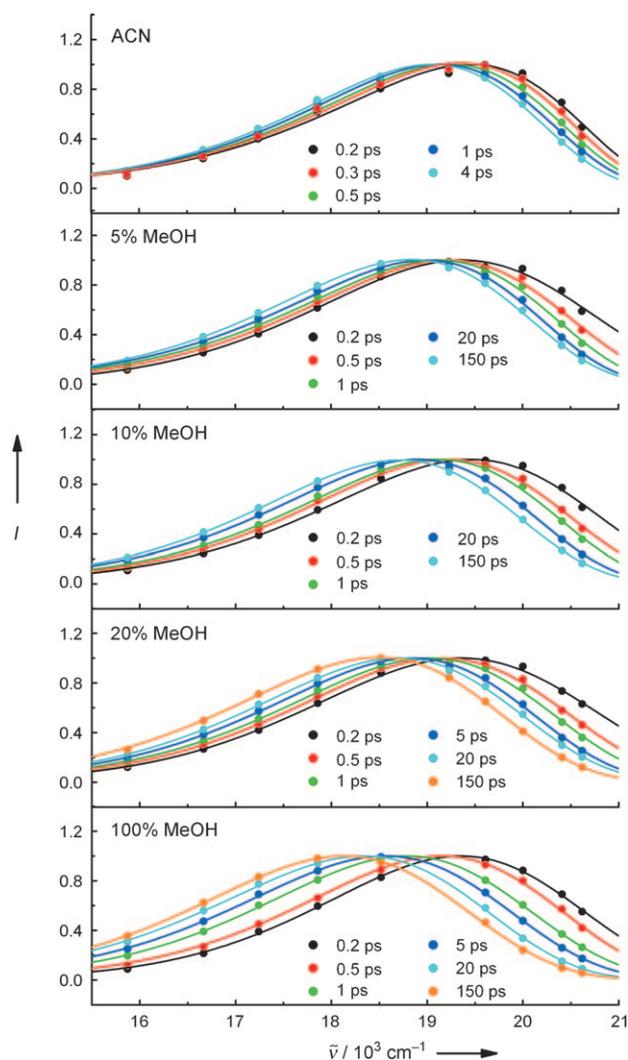
the bulk for network formation. For example, at the concentration of 20%, the density d of MeOH is 3×10^{27} m^{-3} and the average distance between MeOH molecules is given by $\bar{x} = d^{-1/3}$.[35] With a diffusion coefficient of approximately 3×10^{-9} m^{2}s^{-1}, the time constant $(\bar{x}^2/6D)$ is deduced to be approximately 30 ps, which is remarkably close to the value obtained for the solvation time at the same concentration. The slowest time constant (τ_3) in binary mixtures follows this trend of diffusion quite well (Table 1). As the rotational time, which partly contributes to the solvation in MeOH, is an order of magnitude faster (1–2 ps) than τ_3, the observed slowest solvation component represents the translational diffusion of MeOH to replace some of ACN molecules in the first solvation shell of FPe. This diffusion is followed by rapid H-bonding formation (see below); the local H-bonding dynamics are reported to occur on a timescale of 100 fs or less.[3,10] The τ_2 value of around 1 ps in mixed solvents reflects the convolution of diffusive motion of ACN and MeOH, and
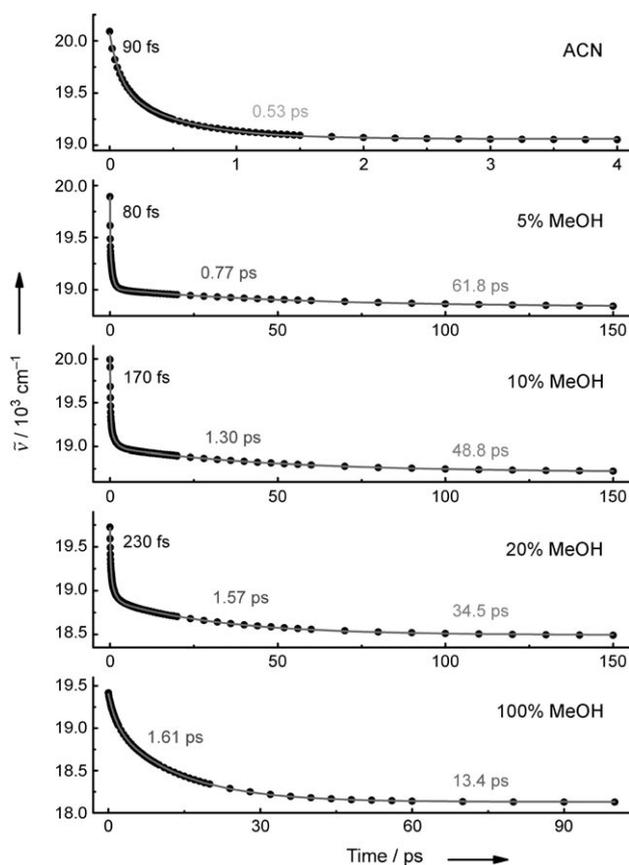
Figure 4. Solvation-energy change. Solvation time constants in the bi- or tri-exponential fits are given in each panel for each solvent mixture composition. Detailed parameters of the multiexponenial fits are summarized in Table 1.

Figure 5. Role of the collective H-bonding network in the charge-transfer process. a) Representation of solvation in our charge-transfer system. Pe and CH-O represent the perylene moiety and the formyl group, respectively, of formylperylene. Whereas a probe dipole is stabilized by dielectric solvation in the non-H-bonding solvent ACN, the charge transfer is further facilitated by collective H-bonding network formation around the specific site of the probe in the protic solvent MeOH. The enhanced charge separation is highlighted using large circles of charges, and the charge-conducting network is regarded as a part of the chemical system. b) Steady-state fluorescence spectral shift. In the presence of MeOH, an additional Stokes shift, which arises from the H-bond network formation in the protic solvent, is evident compared to the shift in aprotic ACN with a similar polarity. c) Ultrafast solvation dynamics for two extremes of solvent composition (MeOH and ACN; for all other mixtures, see Figure 4); however, the former (MeOH) clearly displays the additional site-specific interactions, as evidenced by the 13 ps component (see text).

the inertial dynamics (τ_1) contributed by ACN is observed on the timescale of 0.1–0.2 ps (Figure 4 and Table 1).

A significant observation in the transient behavior shown in Figure 4 is the absence of the 13 ps component for FPe in ACN solution and in mixed solvents. This observation is consistent with the steady-state spectra shown in Figure 1, in which an asymptotic value is reached nearly at the 50 % range (see also Figure 5). If such slow dynamics (13 ps component) were present in the H-bonding interaction with a single MeOH molecule, these would have also appeared in binary mixtures because of the appreciable fraction of ground-state FPe–MeOH complexes, whose solvation processes are not governed by slow diffusion. Accordingly, in neat MeOH a
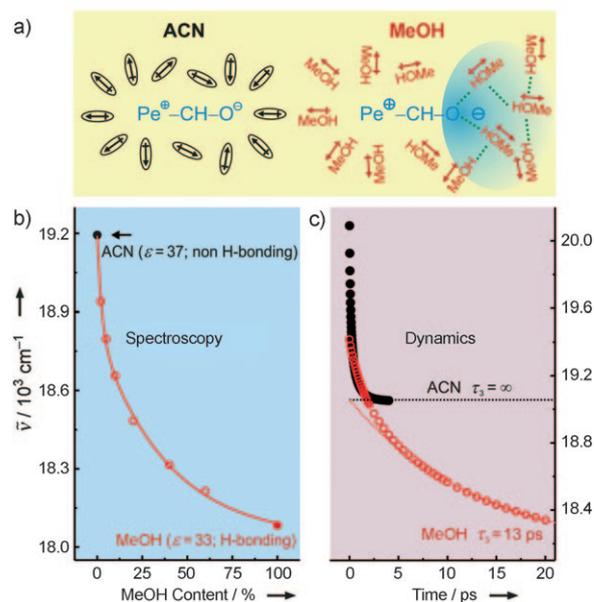
collective solvation process is involved, and cooperatively defines the network around the site. Beyond the range of approximately 50 %, the critical size of the effective network is expected to be established (Figure 5).

When a steady state is reached in solvation (Figure 3) and a fully relaxed excited CT state is formed, the transient fluorescence spectra show the dependence of the shift on solvent composition. The maximum of the spectra at long times ($\bar{\nu}_\infty$) is located at 19 100 cm^{-1} and 18 100 cm^{-1} for FPe in ACN and MeOH, respectively, and somewhere between these

Table 1: Parameters obtained for solvation dynamics.[a]

MeOH content [%]	ΔE_1 [cm^{-1}]	τ_1 [ps]	ΔE_2 [cm^{-1}]	τ_2 [ps]	ΔE_3 [cm^{-1}]	τ_3 [ps]	$\bar{\nu}_0$ [cm^{-1}]	$\bar{\nu}_\infty$ [cm^{-1}]
0	514±43	0.09±0.01	490±41	0.53±0.05			20 090±129	19 060±8
5	453±119	0.08±0.03	419±70	0.77±0.14	174±14	61.8±15.8	19 892±120	18 829±16
10	769±83	0.17±0.03	284±63	1.30±0.33	279±9	48.8±4.7	19 994±90	18 711±8
20	531±77	0.23±0.06	294±75	1.57±0.49	392±11	34.5±2.2	19 724±62	18 488±5
100			348±28	1.61±0.21	926±27	13.4±0.7	19 417±24	18 130±7

[a] Solvation energy change is fitted to $\Delta E_s = \sum_i \Delta E_i \exp(-t/\tau_i) + \bar{\nu}_\infty$. Error bars are determined from the standard deviation in the fits of reconstructed spectra to a lognormal function.

values in ACN/MeOH mixtures. This observation reflects the stabilization of the CT state, which increases with the content of MeOH. The approximate total Stokes shift in ACN and in neat MeOH is 1500 and 2500 cm^{-1}, respectively. Upon excitation of FPe, the strong negative charge on the C=O group can be delocalized along new H-bond networks and the CT state can be consequently further stabilized. In this case, the H-bond reformation, which is indispensible for the efficient charge-flow through H-bond networks, is expected to govern the rate of the overall specific solvation. We note that the transient absorption spectra of FPe in MeOH[32] is close to that of a perylene cation radical produced by bimolecular electron quenching.[36,37] This observation gives additional support to a substantial charge transfer from the perylene moiety to the carbonyl group in the protic solvent MeOH; no evidence for electron solvation by MeOH molecules was observed. Finally, this component has been shown to exist in neat MeOH on the timescale of 10–20 ps,[38,39] which is consistent with the site binding time being faster than the observed 13 ps process, and again supports the significance of network reorganization (see Figure 5).

In conclusion, these first observations of charge transfer assisted by solvent dynamics for formylperylene in protic solvents indicate the direct role of the collective solvent network at a single molecular site. The systematic variation of composition for the two solvents studied, methanol and acetonitrile, which are of similar polarities but different hydrogen-bonding affinities, allowed us to decipher the contribution of specific hydrogen-bonding interaction to the overall solvation. The timescales involved are generally of two types: those involved directly in site binding through solvent reorganization (13 ps for neat methanol), and the longer one, which is controlled by solvent bulk diffusion and ranges here from 35–60 ps, depending on the mole fraction of methanol in the mixture. The results reported in this study can explain features of solvation that are not understood within the framework of the dielectric continuum model and those involved in charge transfer, as, for example, in the case when such binding drives the transfer from the donor to the acceptor sites in a pyrene-labeled DNA base.[27] The notion that the charge transfer is assisted by collective solvent interactions and the delocalization of charges through the network, have important implications not only to solvation but also to local chemical reactions such as those of enzyme catalysis.

Experimental Section

FPe was synthesized according to the procedure previously reported[40] and purified twice by column chromatography. The solvents, ACN and MeOH, were purchased from Sigma–Aldrich and used without further purification. The experimental apparatus is detailed elsewhere.[4]

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[34] The ultrafast solvent inertial relaxation (librational motion) is faster than ca. 100 fs in MeOH and is not fully resolved in our measurements because of the limited instrumental response function of 250 fs; the fractional amplitude of the inertial motion of ACN in this study is appreciably smaller than that reported with a better time resolution.[19] We can estimate the missing component in the solvation dynamics that arises from the inaccessibility of the ultrafast inertial component (≤ 100 fs) by following a method proposed by Fee and Maroncelli (see R. S. Fee, M. Maroncelli, *Chem. Phys.* **1994**, *183*, 235). Using an approximation, $\bar{\nu}_p(0) \approx \bar{\nu}_p(abs) - [\bar{\nu}_{np}(abs) - \bar{\nu}_{np}(em)]$, where the subscripts "p" and "np" denote polar and nonpolar reference spectra, $\bar{\nu}(0)$ for ACN and MeOH were deduced to be (20600 ± 150) cm^{-1}. With this value, the fractional amplitudes for ultrafast inertial motions (τ_1) in ACN and MeOH were calculated to be 0.68 and 0.48, respectively, which are satisfactorily similar to the corresponding values (0.69 and 0.44) reported by Horng et al.[19] with the time resolution of ca. 100 fs.

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