Nature of Large Temporal Fluctuations of Hydrogen Transfer Rates in Single Molecules

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ABSTRACT: Double hydrogen transfer was monitored in single molecules of parent porphycene and its tetra-*t*-butyl derivative using confocal fluorescence microscopy. The molecules have been embedded in a polymer matrix. Under such conditions, a significant fraction of the population reveals a huge decrease of the tautomerization rate with respect to the value obtained from ensemble studies in solution. This effect is explained by a model that assumes that the rate is determined by the reorganization coordinate that involves slow relaxation of the polymer matrix. The model provides indirect evidence for the dominant role of tunneling. It is proposed that tautomerization in single molecules of the porphycene family can be used to probe polymer relaxation dynamics on the time scale ranging from picoseconds to minutes.
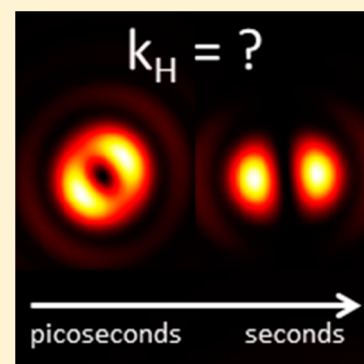

Investigation of single molecules makes it possible to observe effects that are obscured in the ensemble studies because of averaging over a large population. Monitoring single-molecule fluorescence emission in time enables observation of discrete dynamics such as blinking[1] and spectral diffusion.[2,3] Single chromophores have been widely used to probe spatial heterogeneities and local relaxation dynamics in various polymers.[4−12] Other examples include observation of variations of triplet lifetimes and intersystem crossing yields,[13] large spread in the position of fluorescence emission spectra,[14] and finding a large range of ultrafast intramolecular relaxation rates in individual molecules.[15] A less exploited subject, particularly attractive for a chemist, is a possibility to observe distributions in the rates of a chemical reaction. Such effects have been reported for phosphorescence quenching by oxygen[16] or in the study of switching between locally excited and charge transfer states.[17]

A spectacular example of such a phenomenon is a huge fluctuation of the double hydrogen transfer rate reported for 2,6,13,17-tetraphenylporphycene.[18] In solution, this reaction occurs in less than 1 ps at room temperature, as determined by transient absorption anisotropy studies.[19] However, examination of a large number of single molecules embedded in polymer films reveals that for some of them the rate fluctuates over time, sometimes so dramatically that the tautomerization becomes frozen for seconds or even longer. Such a result can be understood in view of the studies that proved that the reaction mechanism in porphycenes is governed by tunneling.[20−22] Perturbation of the symmetric double-minimum potential that describes *trans*–*trans* tautomerization can lead to localization of the inner hydrogens.

Still, the origin of such perturbation was not clear. In general, it can be due to effects of the polymer matrix and/or intramolecular properties. The presence of four phenyl substituents results in 16 possible rotameric structures because each phenyl group can be twisted in two directions from the molecular plane. Because in some of these forms the two *trans* species (Scheme 1) are no longer equivalent, slowing down of

Scheme 1. *Trans*−*Trans* Tautomerization in Porphycenes[a]

H	**1**
R = *t*Bu	**2**
Ph	**3**
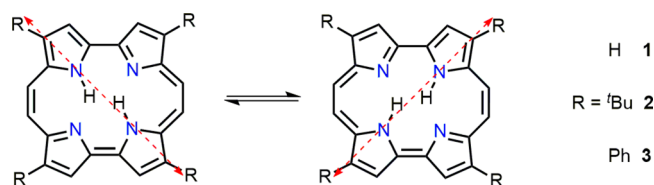
[a]The double, red arrows show the direction of the S_0−S_1 electronic transition moment.

tautomerization in some molecules could be explained as an effect of a rigid polymer matrix, which freezes the forms that lack the symmetrical double-minimum character. If bulky substituents are responsible for freezing, the effect should disappear in the parent unsubstituted porphycene.

To check this hypothesis and to explain the origin of the unusual tautomerization "freezing effect", we have compared

the behavior of two porphycenes, the parent unsubstituted molecule (**1**) and 2,6,13,17-tetra-*t*-butylporphycene (**2**). In analogy with the previously studied tetraphenyl derivative (**3**), two possible orientations of each *t*-butyl substituent can lead to a nonsymmetrical double minimum on the tautomerization potential energy surface. Moreover, while the electronic spectra of **1** and **3** differ considerably, this is not the case for **1** and **2** (Figure 1), which makes **2** a better candidate for comparison with the parent porphycene **1**.
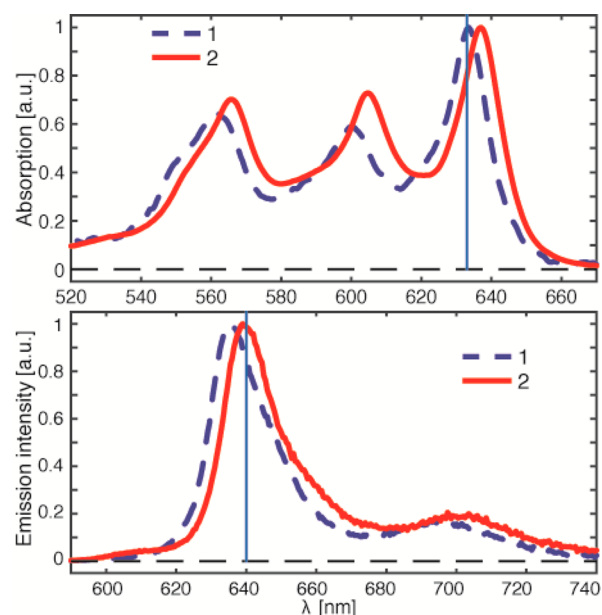
Our experimental technique of monitoring tautomerization in single molecules is based on fluorescence imaging using azimuthally (APM) and radially (RPM) polarized laser beams for excitation.[23−26] These polarization modes have been used to determine the dipole moment orientation of single nanoparticles or the dimensionality of single quantum dots.[27−29] Different spatial patterns of fluorescence intensity are expected for porphycene molecules that undergo tautomerization and those that do not. The latter correspond to a "normal" chromophore with a well-defined fixed transition moment direction, whereas a tautomerizing molecule can be treated as a superposition of two emitters, equal in magnitude, forming an angle of ca. 70° (Scheme 1).[25,30] Fast tautomerization (compared to the time scale of the experiment) leads to spatial patterns impossible to obtain from a single transition dipole, such as a ring-like shape observed for excitation with azimuthal polarization. The observation of a double lobe requires more careful analysis because such a pattern may correspond either to a nontautomerizing molecule (single dipole) or to a dual emitter of which the molecular plane is oriented perpendicular to the sample plane. To distinguish between these two cases, we use subsequently APM and RPM for excitation of the same molecule. Such a procedure also allows one to minimize the effects due to possible rotation of the molecule in the polymer matrix. For instance, the observation of a double-lobe pattern of which the axis changes the direction can be interpreted either as switching from one *trans* tautomer to the other or by assuming that a (nontautomerizing) molecule changed its orientation by a certain angle. A molecule could in principle change its orientation by any angle, leading to a respective change of the dipole moment orientation. However, finding a particular angle of ∼70° between the axes of two double lobes is a strong argument for switching.

Figure 2 shows an example of a series of consecutive confocal fluorescence images obtained for **2** as a function of time. The
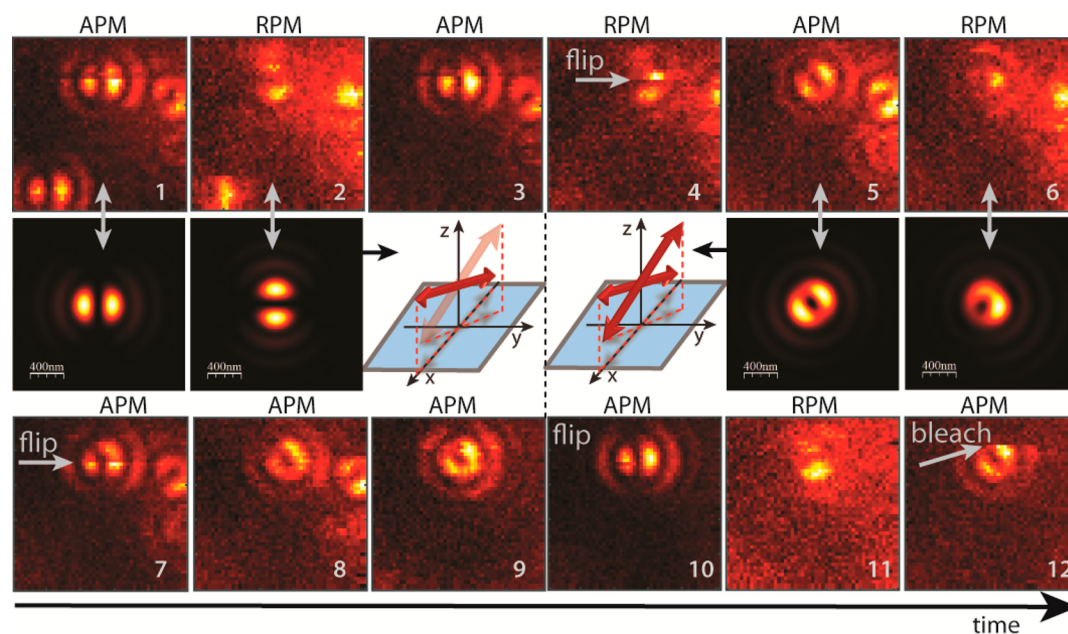
Figure 1. Absorption (top) and fluorescence (bottom) of **1** and **2** in toluene at 293 K.

Figure 2. Exemplary series of confocal fluorescence images of **2** acquired with azimuthal (APM) and radial (RPM) polarization. Twelve consecutive images: zoomed-in view on a 50 × 50 pixels area around the molecule of interest. The molecule flips between fast and slow tautomerization three times (marked) and bleaches during acquisition of image 12. The middle row shows simulation of the fluorescence pattern corresponding to images 1−2 and 5−6.

molecule of interest is in the upper part of the image and switched, before bleaching, three times between the fast (ring-like pattern) and the slow (double-lobe pattern) tautomerization regime. The statistical analysis allows one to divide the observed single chromophores into three classes: (i) those that exhibit only fast tautomerization; (ii) the ones that behave as single emitters all the time (i.e., nontautomerizing ones), and (iii) molecules that switch between the two regimes during the experiment.

The histogram showing the relative contributions of these three classes in **1** and **2** is presented in Figure 3. As previously
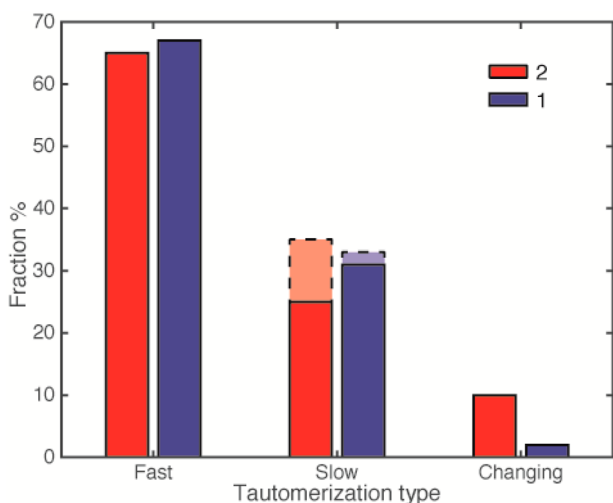

Figure 3. Fraction of molecules that showed fast/slow tautomerization and fraction of molecules that, within the experimental time window, exhibited changes between slow and fast tautomerization regimes. The dashed fraction for the "slow" molecules is the addition of the changing fraction.

reported for **3**, the "fast" fraction is dominant for both chromophores. Most importantly, **1** and **2** exhibit similar behavior: for about 70% of the total number of observed molecules, rapid tautomerization is observed. The rest is due to tautomers that remain "frozen", either during the whole experiment or at least for some part of it.

To interpret the results, we apply a model reminiscent of the Marcus theory approach to proton transfer. This model is useful to explain low reaction rates in such systems, as e.g., enzymes, where the intrinsic proton transfer step is preceded by reorganization of the reactants and the environment.[31] We assume that the tautomerization occurs most efficiently once the potential energy surface system achieves a symmetric double-minimum character along the hydrogen transfer coordinate (see Figure 4). This assumption has been verified by comparison of double hydrogen transfer rates in porphycenes with symmetric and asymmetric potentials.[32] The fluctuations in the potential, which may lead to localization of the internal hydrogens, are described by the reorganization coordinate. It can include both intramolecular and external contributions. The former are environmentally insensitive, whereas the latter strongly depend on the local environment of the molecule. This has a crucial impact on the tautomerization rate, which may depend on the time scale of the dynamics of the reorganization coordinate. When the reorganization is slow in comparison with the time required for hydrogen transfer in the symmetric double-minimum potential, the rate of
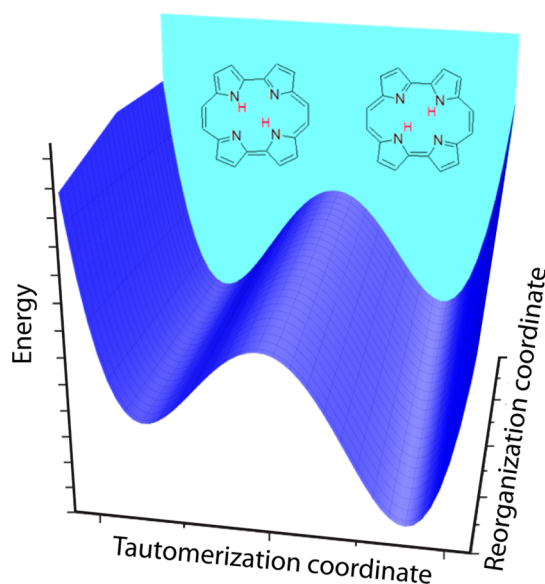

Figure 4. Scheme of the potential energy surface depicting tautomerization in porphycenes.

tautomerization will not be determined by the barrier along the tautomerization coordinate but by the relaxation of the matrix. Slow relaxation times, on the order of 1 s, have been reported, e.g., for poly(methyl acrylate).[5] On the contrary, in nonviscous solutions, the time scale of motion of solvent molecules can be shorter than the intrinsic tautomerization time. Under these conditions, the observed hydrogen transfer rate will reflect the "real" value due to the molecular structure. We recall that the rates measured in solutions for differently substituted porphycenes span nearly 4 orders of magnitude,[33] reflecting the strength of intramolecular hydrogen bonds. The tautomerization times in solutions vary between several tens of femtoseconds and hundreds of picoseconds, never approaching the regime of seconds.

The above model explains the similar behavior observed for three different porphycenes in polymer matrices, in particular, the finding that the bulky *t*-butyl or phenyl substituents are not responsible for slowing down tautomerization in porphycene and its derivatives. However, there remains one particular result that requires discussion. The fraction of molecules that switch between the regimes of slow and fast tautomerization is definitely higher for **2**, i.e., the substituted molecule (Figure 3). We tentatively propose that such behavior is due to more efficient coupling between the tautomerization and reorganization coordinates, owing to the presence of low-frequency torsional modes in **2** (and **3**) but not in the parent unsubstituted molecule.

The model can also help in rationalizing the results obtained by ensemble studies. The analysis of fluorescence anisotropy of **1** in low-temperature alcohol glasses and polymers suggested a tautomerization rate of about 10^9 s^{-1}.[34] Interestingly, recent, unpublished experiments with better time resolution revealed anisotropy decays on the picosecond scale. These seemingly divergent results can be understood assuming that different subpopulations are probed by the two experimental regimes.

Yet another observation can be understood using the concept of reorganization coordinate. Studies of *meso*-substituted porphycenes demonstrated a huge viscosity dependence of fluorescence quantum yields and lifetimes.[35] This was explained by the presence of the S_1–S_0 conical intersection along the path

of a *trans−cis* single hydrogen transfer, involving distortion from planarity.[36] In the parlance of the present model, such distortion and the solvent viscosity-dependent potential belong to the reorganization coordinate.

The idea of matrix-induced perturbation of a symmetric double-minimum potential has been discussed by Limbach and co-workers in the NMR studies of tautomerism of dibenzotetraaza[14]annulenes, molecules structurally related to porphyrins.[37] In a glassy polystyrene, a broad distribution of different microenvironments (sites) has been postulated, based on the analysis of line shapes. Our present studies not only confirm this picture but, due to single-molecule resolution, allow observation of individual sites and their temporal evolution.

We should stress that the proposed model is based on the assumption of tunneling along the tautomerization coordinate. Recent works on porphycenes demonstrated the importance of tunneling, in both single molecules[21] and ensembles.[20,22] The present results indirectly confirm the dominant role of the tunneling mechanism. The role of tunneling and its extreme sensitivity to molecular environment have also been discussed in an earlier work on polycrystalline porphycene studied by high-resolution solid-state NMR spectroscopy and longitudal relaxometry.[38] These experiments indicated a phase transition at around 225 K. Tunneling was postulated for the lower-temperature phase, whereas at higher temperatures, the lack of kinetic hydrogen/deuterium isotope effect suggested an overbarrier mechanism.

Studies of tautomerization in single molecules embedded in a rigid environment allow observation of "snapshots" along the trajectory corresponding to the slowly fluctuating reorganization coordinate. Such experiments provide information about the relaxation processes occurring in polymers, implying that porphycenes can be used as probes of polymer relaxation dynamics, thus joining other techniques based on a single-molecule approach.[4−12] Our ongoing single-molecule studies on tautomerization in hemiporphycene,[39] another porphyrin isomer, reveal a behavior similar to the one described in this work: freezing the hydrogen transfer rate by several orders of magnitude. This could suggest using other isomers in the studies of matrix relaxation dynamics. The advantage of porphycenes, however, is that, among all isomers, they exhibit the fastest tautomerization, thus providing the largest range for the time scales to be probed.

In the present work, the border between the slow and fast regime was dictated by the experimental conditions, which, in fact, did not include any time-resolved measurements. One can envisage, however, a procedure of recording time profiles of the anisotropy of fluorescence from single molecules. The time range of such experiments could span many orders of magnitude, starting from the time periods similar to those required for hydrogen transfer in solution (down to the femtosecond regime) and with the upper limit being dictated only by photostability. Taking the latter into account, the longest time scale can be estimated as minutes.

■ EXPERIMENTAL SECTION

Parent porphycene (Pc) and tetra-*t*-butylporphycene were synthesized in our group using procedures reported previously.[40] For single-molecule studies, porphycene molecules were embedded in a polymer matrix. Poly(methyl methacrylate) (PMMA, MW = 94600) was purchased, and used as is, from Acros Organics. PMMA was not cross-linked, and no plasticizer was added. Microscope cover slides were cleaned with piranha solution and rinsed with deionized water and high-purity methanol. A cosolution of PMMA (1% w/v or ∼10 mg/mL) and porphycenes (∼10^{-9} M) in toluene was spin-coated on the cleaned microscope cover slides at speeds in the range of 2000−3000 rpm. This procedure yields samples with porphycene density of less than 1 molecule per μm^2 in an approximately 30 nm thick polymer film, as measured with AFM.

An excitation beam at 633 nm was delivered by a HeNe laser. The laser beam was propagated through a mode converter (Arcoptix). Azimuthally and radially polarized light was produced by precise adjustment of the voltage applied to the mode converter. The laser beam was then propagated through a spatial filter to suppress higher-order spatial modes and into a home-built inverted confocal microscope optimized for single-molecule detection. The collimated beam was reflected from a nonpolarizing 50/50 beam splitter and focused onto the sample with a high numerical aperture objective (NA = 1.46). Fluorescence images were acquired by raster-scanning of the sample in the *xy* plane using a feedback-controlled piezo stage (Physics Instruments). The collected fluorescence signal was separated from the reflected laser light by two long-pass filters (633 nm RazorEdge long pass, AHF) and detected using a single-photon counting module (Count-blue, Laser Components).

Images were typically acquired with a size of 5 μm × 5 μm, with 100 × 100 pixels and pixel dwell time of 10 ms. The total image acquisition time was approximately 3.5 min. Typically, we used 20 μW excitation power, measured before the microscope objective (∼10 μW at the sample plane).

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Notes
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