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Arresting Tautomerization in a Single Molecule by the Surrounding Polymer: 2,7,12,17-Tetraphenyl Porphycene

Hubert Piwoński,^{*,†} Adam Sokołowski,[†] Michał Kijak,[†] Santi Nonell,[‡] and Jacek Waluk^{*,†}

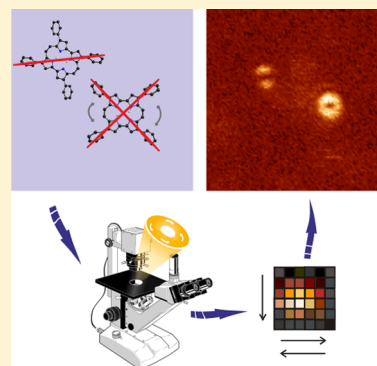
[†]Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw, Poland

[‡]Molecular Engineering Group, Institut Químic de Sarrià, Universitat Ramon Llull, Via Augusta 390, E-08017 Barcelona, Spain

S Supporting Information

ABSTRACT: 2,7,12,17-Tetraphenyl porphycene (TPPo) is known to undergo ultrafast (<1 ps) double-hydrogen transfer in solution. Fluorescence studies of single TPPo molecules embedded in a polymer matrix and excited with an azimuthally polarized laser beam reveal, for a considerable fraction of the population, double-lobe spatial emission patterns attributed to the absence of tautomerism. In consecutive image scans, these patterns change their orientation to nearly orthogonal. In some cases, switching of the orientation direction occurs through an intermediate case with a doughnut-shaped pattern, indicating the presence of fast tautomerism. These findings demonstrate that local polymer environment can drastically change the thermodynamics or kinetics of tautomerization. They also point out the contribution of the motion of peripheral substituents in the hydrogen-transfer coordinate. TPPo is proposed as a good probe for studying relaxation dynamics in thin polymer films.

SECTION: Kinetics and Dynamics



Spectral and photophysical properties of porphycenes have been drawing much attention since the first synthesis of the parent compound in 1986.¹ In particular, the interest is stimulated by possible applications in photodynamic therapy and photodiagnostics,² molecular recognition,³ and ultrafast switches.⁴ The research interest naturally encompasses intramolecular double-hydrogen transfer, a fundamental reversible chemical reaction. Tautomerization in porphycenes was studied in the last three decades by various techniques in condensed phases,^{5–13} supersonic jets,^{14,15} helium nanodroplets,¹⁶ as well as on the level of single molecules.^{17–19} This self-exchange reaction exhibits a feature that can be exploited for the determination of the tautomerization rate,^{8,12} as illustrated in Figure 1. Interconversion between two trans conformers is associated with the movement of the protons in the inner cavity of the molecule, which leads to the rotation of transition dipole moments in the molecular frame. In the case of parent porphycene, a value of $72 \pm 3^\circ$ has been determined for the angle formed by the S_1 – S_0 transition moment directions in the two trans conformers.^{8,12,13,17,20,21} Because both forms are chemically identical, monitoring of the self-exchange reaction is not trivial. Application of cylindrical vector beams in combination with confocal microscopy²² allows imaging of both the tautomerism and spatial orientation of porphycene on a single-molecule level.^{17–19} This method exploits the information about the orientation of the transition dipole moment. For porphycene, as long as the tautomerization is not frozen on the time scale of the experiment (seconds to minutes) and the molecular plane is at the right angle to the direction of observation of fluorescence, the observed spatial

pattern of fluorescence intensity distribution must reflect the presence of two transition moment directions corresponding to two tautomeric species (Figure 1).

We report an unusual new finding, obtained by using the above-mentioned methodology: reversible switching between fast and slow tautomerization regime in a single molecule. Because the phenomenon occurs only for a small fraction of the population, it can only be detected by single-molecule spectroscopy, which provides yet another demonstration of the power of this technique.

We investigate the spatial fluorescence patterns of single molecules of 2,7,12,17-tetraphenyl porphycene (TPPo)^{23,24} embedded in a thin (ca. 30 nm) poly(methyl methacrylate) (PMMA) polymer film. We repeatedly recorded and analyzed 871 fluorescence patterns corresponding to individual TPPo molecules. We found that 66% of the observed patterns correspond to a situation where the observed transition dipole moment orientation remains the same for hundreds of excitation–emission cycles. This behavior can have two origins: (i) freezing of tautomerization, which effectively locks the direction of transition dipole along one direction, or (ii) specific, vertical orientation of the molecular plane. In 29% of molecules we always found ring-shaped excitation patterns given by the superposition of two trans forms, which indicates the presence of a fast tautomerization process resulting in equal probabilities that the molecule exists in the either trans1 or

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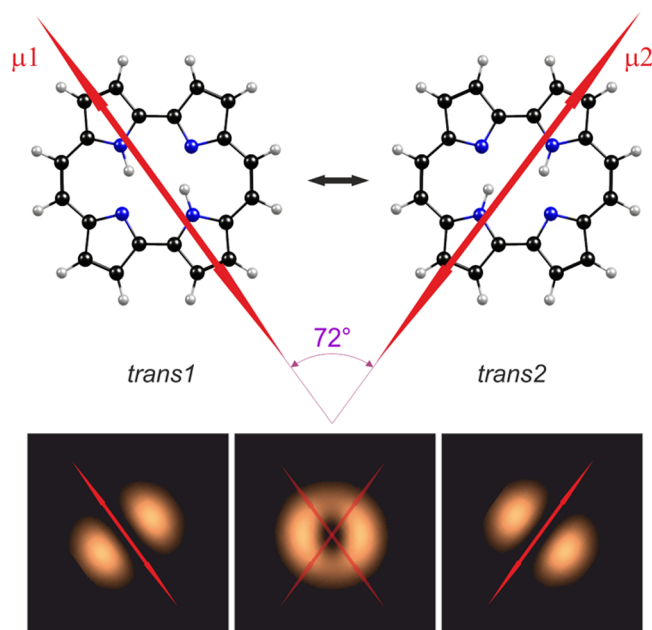


Figure 1. (Top) Tautomerization in porphycene involving rearrangement of the two inner protons, which leads to the change in the orientation of transition dipole moments. Fluorescence of a molecule undergoing trans–trans conversion can be envisaged as occurring from two oscillating dipoles that form an angle of $72 \pm 3^\circ$. (Bottom) The spatial patterns of fluorescence expected for the cases of single transition dipole (left and right) and “dual” transition dipole due to fast tautomerization (middle).

trans2 form. A strong argument indicating that the apparent “single transition dipole” behavior is not due to hindered tautomerization but rather to molecular orientation was provided by measuring fluorescence anisotropy on bulk samples. Fluorescence was found to be depolarized, indicating fast excited-state tautomerization in the majority of molecules. Indirectly, this finding also indicates a fast ground-state process because it has been demonstrated that the reaction is several times faster in S_0 than in S_1 .¹³

The most intriguing finding was the detection of switching patterns: ~5% of molecules revealed flipping of the transition dipole moment in consecutive sample scans (Figures 2 and 3). The analysis of the relative orientation of the transition dipole moments based on the generated fluorescence patterns allowed determining the reorientation angle. The value of $72 \pm 5^\circ$ has been determined for the angle formed between the axes passing through the maxima of the double-lobe patterns. This value is identical to that obtained for the angle between the S_1 – S_0 transition moment directions in parent porphycene, which strongly suggests that the observed flipping is due to trans–trans tautomerization rather than molecular rotation. Some of the observed changes in the transition moment orientation occurred through an intermediate case with a ring-shaped pattern (Figure 3), indicating that, for the time being, the switching between the trans structures occurs faster than the acquisition time; that is, the molecule obeys the regime of rapid tautomerization. Thus, for the same molecule, the tautomerization regime changes periodically with time.

A similar phenomenon, unusually long tautomerization times on the order of minutes, has been reported for single 2,3,7,8,12,13,17,18-octaethylporphyrin (OEP) molecules immobilized in PMMA and polystyrene films.²⁵ The authors

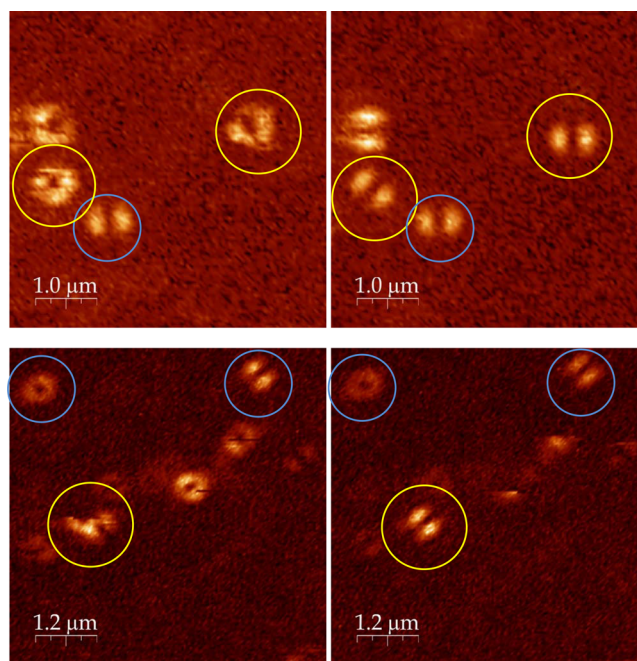


Figure 2. Two consecutive 20 min scans (left to right) of a $5 \times 5 \mu\text{m}^2$ area (top) and a $6 \times 6 \mu\text{m}^2$ area (bottom) obtained for different parts of the polymer film (top and bottom). Molecules that change their spatial emission pattern are marked with yellow circles, whereas those that do not are marked with blue ones.

interpreted this result in terms of photoinduced double-hydrogen transfer with the barrier in the excited state of OEP too high to be effectively crossed. However, it has been well-documented for various porphyrins that at room temperature the reaction occurs in the dark in the microsecond-to-millisecond regimes in both liquid and solid phases.^{5,26–28} Therefore, on the basis of these and our present results, we propose a completely different explanation involving the polymer matrix relaxation dynamics as the factor controlling tautomerization.

Arresting tautomerization may have two origins: (i) kinetic, due to increasing the barrier that separates the two isoenergetic tautomers, and (ii) thermodynamic, due to distortion of the symmetric, double-minimum potential. Switching from one long-lasting trans tautomeric form to the other indicates a slow reversal of the asymmetry of the tautomerization potential. The period during which both forms are equally probable corresponds to the symmetrical or nearly symmetrical double-minimum potential. Such situation is encountered for 95% of the probed molecules. To explain the asymmetric, slowly fluctuating potential that may be responsible for the behavior of the remaining 5%, we analyze possible deviations from molecular symmetry. B3LYP/6-31+G(d,p) geometry optimizations of TPPo yield several practically isoenergetic (within 0.2 kcal/mol) rotameric structures for which the angle between the phenyl substituent and the porphycene plane is in the range of 47 – 49° (Figure 2S in the Supporting Information). This result is in an excellent agreement with the experimental X-ray data.²⁹ One must remember, however, that for an isolated TPPo there exists $2^4 = 16$ structures with this angle value. Four pairs are equivalent, whereas, for the other eight, two trans forms are of different energies. The environment may further perturb the symmetry, even for the symmetrical pairs. The asymmetry can also be caused by polymer-induced twisting of one or more of

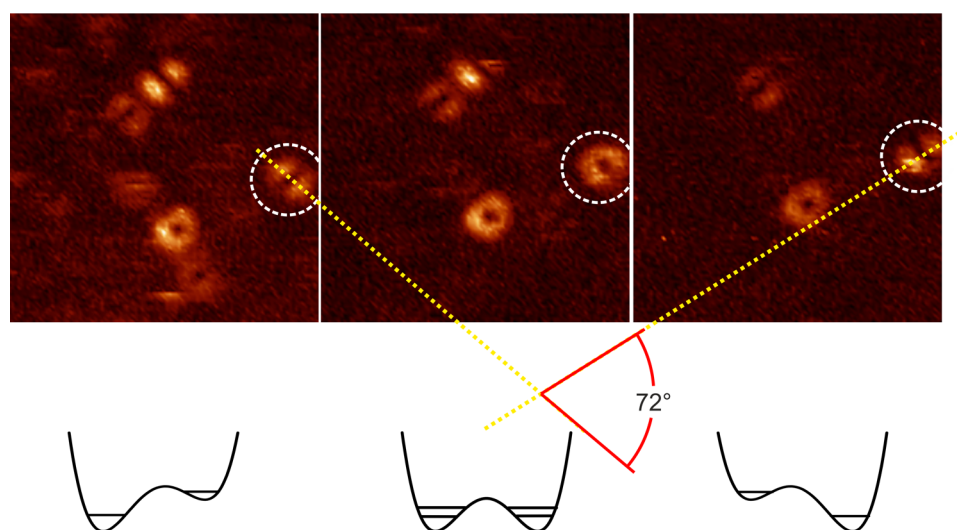


Figure 3. Three consecutive images of single TPPo molecules embedded in a PMMA matrix, showing switching between double-lobe patterns, which can be attributed to the absence of fast tautomerism. For the indicated molecule, flipping occurs via a ring-shaped pattern, suggesting the presence of fast tautomerism. (In the case of molecules excited with azimuthally polarized doughnut mode, the absorption transition dipole moments are oriented orthogonally to the direction of the two lobe patterns). Bottom: schematic representation of changes in the double-minimum potential.

the phenyl substituents. The energy profiles calculated along the twisting coordinate (Figure S3 in the Supporting Information) reveal a low barrier (<1.5 kcal/mol and <3 kcal/mol for twisting of one and two phenyl groups, respectively). It is evident that the structural relaxation accompanying tautomerization is in many cases accompanied by the phenyl group twisting, which can be controlled by changes in the local polymer structure. It has been demonstrated that the relaxation processes in thin polymer films are very heterogeneous and occur on a slow time scale.^{30–33} For PMMA, the rate of structural relaxation is smaller by a factor of 15 at the interface to a silica substrate with respect to the bulk value, which means that the relaxation is practically stopped.³⁰ Heterogeneity of the polymer matrix has also been demonstrated for studies of tautomerism in glassy polystyrene.³⁴ We therefore propose that the time-dependent behavior of tautomerization observed for TPPo in PMMA reflects the local dynamics of the polymer matrix. Such hypothesis could also explain the unexpected behavior of 2,3,7,8,12,13,17,18-octaethylporphyrin:²⁵ in this case, the reason for the slowing down of hydrogen transfer would be the inability of the ethyl groups to assume the conformation for which the energies of both tautomeric forms would be equal. It should be recalled that the parent, unsubstituted porphyrin undergoes very fast tautomerization even in the crystalline phase at room temperature.⁵

Our results confirm a multidimensional character of tautomerization, pointing to the important role of motions of peripheral substituents in gating the reaction. A related case we have discussed recently, for both solutions¹⁰ and supersonic jet-isolated molecules¹⁵ is the coupling between torsional motions of alkyl groups and tautomerization in meso-substituted porphycenes.

Tautomerization in porphyrins can be described by a model of stepwise, thermally activated tunneling.²⁸ In the case of TPPo, the experimental evidence favors the synchronous transfer of both hydrogens.¹³ As for tunneling, its importance, even at room temperature, has been suggested based on (i) a huge dependence of tautomerization rates on the NH...N distance in differently substituted porphycenes and (ii) large

kinetic isotope effects.¹² A Marcus-type model, in which the reorganization energy would mainly involve twisting of phenyl groups, seems compatible with present findings, but further studies (temperature dependence) seem mandatory.

In summary, single-molecule studies of a tautomerizing system have provided an insight into the reaction mechanism and demonstrated the role of the environment in modifying the reaction profile. The possibility of gating the chemical transformation via substituents remote from the reaction center can be explored in the design of molecular switches. Actually, a very recent work demonstrated that tautomerism in a single porphycene molecule can be controlled by moving a single copper atom toward or away from the molecule.³⁵ Finally, single TPPo molecules turned out to be good probes for investigating the relaxation dynamics in thin polymer films.

Our future plans include separating the contributions from ground and excited state tautomerization in single molecules. Depending on the substitution pattern, various scenarios are possible in porphycenes. In some cases, the correspondence between absorption and emission dipoles should be preserved, but, especially for nonsymmetrical substitution, one can also expect a situation where the chromophore behaves as a single dipole in emission but a dual dipole in absorption. To disentangle these effects, one could combine the technique of cylindrical vector beams with procedures that use defocused single-molecule imaging.³⁶

■ ASSOCIATED CONTENT

● Supporting Information

Experimental procedures, data, computational methods, and predicted structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hpiwonski@ichf.edu.pl, waluk@ichf.edu.pl.

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Vogel, E.; Köcher, M.; Schmickler, H.; Lex, J. Porphycene - a Novel Porphin Isomer. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 257–259.
- (2) Stockert, J. C.; Cañete, M.; Juarraz, A.; Villanueva, A.; Horobin, R. W.; Borrell, J.; Teixidó, J.; Nonell, S. Porphycenes: Facts and Prospects in Photodynamic Therapy of Cancer. *Curr. Med. Chem.* **2007**, *14*, 997–1026.
- (3) Matsuo, T.; Ikegami, T.; Sato, H.; Hisaeda, Y.; Hayashi, T. Ligand Binding Properties of Two Kinds of Reconstituted Myoglobins with Iron Porphycene Having Propionates: Effect of β -Pyrrolic Position of Two Propionate Side Chains in Porphycene Framework. *J. Inorg. Biochem.* **2006**, *100*, 1265–1271.
- (4) Abdel-Latif, M. K.; Kühn, O. Laser Control of Double Proton Transfer in Porphycenes: Towards an Ultrafast Switch for Photonic Molecular Wires. *Theor. Chem. Acc.* **2011**, *128*, 307–316.
- (5) Wehrle, B.; Limbach, H. H.; Köcher, M.; Ermer, O.; Vogel, E. ^{15}N -CPMAS-NMR Study of the Problem of NH Tautomerism in Crystalline Porphine and Porphycene. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 934–936.
- (6) Lopez del Amo, J.; Langer, U.; Torres, V.; Pietrzak, M.; Buntkowsky, G.; Vieth, H. M.; Shibl, M. F.; Kühn, O.; Bröring, M.; Limbach, H. H. Isotope and Phase Effects on the Proton Tautomerism in Polycrystalline Porphycene Revealed by NMR. *J. Phys. Chem. A* **2009**, *113*, 2193–2206.
- (7) Waluk, J. Ground- and Excited-State Tautomerism in Porphycenes. *Acc. Chem. Res.* **2006**, *39*, 945–952.
- (8) Gil, M.; Waluk, J. Vibrational Gating of Double Hydrogen Tunneling in Porphycene. *J. Am. Chem. Soc.* **2007**, *129*, 1335–1341.
- (9) Waluk, J. Tautomerization in Porphycenes. In *Hydrogen-Transfer Reactions*; Hynes, J. T., Klinman, J. P., Limbach, H. H., Schowen, R. L., Eds.; Wiley-VCH: Weinheim, Germany, 2007; Vol. 1, pp 245–271.
- (10) Gil, M.; Dobkowski, J.; Wiosna-Salyga, G.; Urbańska, N.; Fita, P.; Radzewicz, C.; Pietraszkiewicz, M.; Borowicz, P.; Marks, D.; Glasbeek, M.; Waluk, J. Unusual, Solvent Viscosity-Controlled Tautomerism and Photophysics: Meso-Alkylated Porphycenes. *J. Am. Chem. Soc.* **2010**, *132*, 13472–13485.
- (11) Waluk, J. Structure, Spectroscopy, Photophysics, and Tautomerism of Free-Base Porphycenes and Other Porphyrin Isomers. In *Handbook of Porphyrin Science*; Smith, K., Kadish, K., Guillard, R., Eds.; World Scientific: Singapore, 2010; Vol. 7, p 359.
- (12) Fita, P.; Urbańska, N.; Radzewicz, C.; Waluk, J. Ground and Excited State Tautomerization Rates in Porphycenes. *Chem.—Eur. J.* **2009**, *15*, 4851–4856.
- (13) Fita, P.; Pszona, M.; Orzanowska, G.; Sánchez-García, D.; Nonell, S.; Vauthey, E.; Waluk, J. Tautomerization in 2,7,12,17-Tetraphenylporphycene and 9-Amino-2,7,12,17-tetraphenylporphycene: Influence of Asymmetry on the Transition Moment Directions. *Chem.—Eur. J.* **2012**, *18*, 13160–13167.
- (14) Sepiól, J.; Stepanenko, Y.; Vdovin, A.; Mordziński, A.; Vogel, E.; Waluk, J. Proton Tunneling in Porphycene Seeded in a Supersonic Jet. *Chem. Phys. Lett.* **1998**, *296*, 549–556.
- (15) Vdovin, A.; Sepiól, J.; Urbańska, N.; Pietraszkiewicz, M.; Mordziński, A.; Waluk, J. Evidence for Two Forms, Double Hydrogen Tunneling, and Proximity of Excited States in Bridge-Substituted Porphycenes: Supersonic Jet Studies. *J. Am. Chem. Soc.* **2006**, *128*, 2577–2586.
- (16) Vdovin, A.; Waluk, J.; Dick, B.; Slenczka, A. Mode-Selective Promotion and Isotope Effects of Concerted Double-Hydrogen Tunneling in Porphycene Embedded in Superfluid Helium Nanodroplets. *ChemPhysChem* **2009**, *10*, 761–765.
- (17) Piwoński, H.; Stupperich, C.; Hartschuh, A.; Sepiól, J.; Meixner, A.; Waluk, J. Imaging of Tautomerism in a Single Molecule. *J. Am. Chem. Soc.* **2005**, *127*, 5302–5303.
- (18) Piwoński, H.; Hartschuh, A.; Urbańska, N.; Pietraszkiewicz, M.; Sepiól, J.; Meixner, A.; Waluk, J. Polarized Spectroscopy Studies of Single Molecules of Porphycenes: Tautomerism and Orientation. *J. Phys. Chem. C* **2009**, *113*, 11514–11519.
- (19) Czerski, I.; Listkowski, A.; Nawrocki, J.; Urbańska, N.; Piwoński, H.; Sokołowski, A.; Pietraszkiewicz, O.; Pietraszkiewicz, M.; Waluk, J. The Long and Winding Road to New Porphycenes. *J. Porphyrins Phthalocyanines* **2012**, *16*, 589–602.
- (20) Waluk, J.; Vogel, E. Distance Dependence of Excited-State Double Proton Transfer in Porphycenes Studied by Fluorescence Polarization. *J. Phys. Chem.* **1994**, *98*, 4530–4535.
- (21) Fita, P.; Urbańska, N.; Radzewicz, C.; Waluk, J. Unusually Slow Intermolecular Proton-Deuteron Exchange in Porphycene. *Z. Phys. Chem.* **2008**, *222*, 1165–1173.
- (22) Züchner, T.; Failla, A. V.; Meixner, A. J. Light Microscopy with Doughnut Modes: A Concept to Detect, Characterize, and Manipulate Individual Nanoobjects. *Angew. Chem., Int. Ed.* **2011**, *50*, 5274–5293.
- (23) Nonell, S.; Bou, N.; Borrell, J. I.; Teixidó, J.; Villanueva, A.; Juarraz, A.; Cañete, M. Synthesis of 2,7,12,17-Tetraphenylporphycene (TPPo). First Aryl-Substituted Porphycene for the Photodynamic Therapy of Tumors. *Tetrahedron Lett.* **1995**, *36*, 3405–3408.
- (24) Rubio, N.; Prat, F.; Bou, N.; Borrell, J. I.; Teixidó, J.; Villanueva, A.; Juarraz, A.; Cañete, M.; Stockert, J. C.; Nonell, S. A Comparison between the Photophysical and Photosensitizing Properties of Tetraphenyl Porphycenes and Porphyrins. *New J. Chem.* **2005**, *29*, 378–384.
- (25) Chizhik, A. M.; Jäger, R.; Chizhik, A. I.; Bär, S.; Mack, H. G.; Sackrow, M.; Stanciu, C.; Lyubimov, A.; Hanack, M.; Meixner, A. J. Optical Imaging of Excited-State Tautomerization in Single Molecules. *Phys. Chem. Chem. Phys.* **2011**, *13*, 1722–1733.
- (26) Eaton, S. S.; Eaton, G. R. Kinetic Isotope Effect on Proton Tautomerism in Tetraarylporphyrins. *J. Am. Chem. Soc.* **1977**, *99*, 1601–1604.
- (27) Crossley, M. J.; Field, L. D.; Harding, M. M.; Sternhell, S. Kinetics of Tautomerism in 2-Substituted 5,10,15,20-Tetraphenylporphyrins: Directionality of Proton Transfer between the Inner Nitrogens. *J. Am. Chem. Soc.* **1987**, *109*, 2335–2341.
- (28) Braun, J.; Schlabach, M.; Wehrle, B.; Köcher, M.; Vogel, E.; Limbach, H. H. NMR Study of the Tautomerism of Porphyrin Including the Kinetic HH/HD Isotope Effects in the Liquid and the Solid State. *J. Am. Chem. Soc.* **1994**, *116*, 6593–6604.
- (29) Hennig, W. Neuartige Pyrrolische Porphyrinoide und Ihre Metallkomplexe. Ph.D. Thesis, University of Cologne, 1992.
- (30) Priestley, R. D.; Ellison, C. J.; Broadbelt, L. J.; Torkelson, J. M. Structural Relaxation of Polymer Glasses at Surfaces, Interfaces, and In Between. *Science* **2005**, *309*, 456–459.
- (31) Oba, T.; Vacha, M. Relaxation in Thin Polymer Films Mapped across the Film Thickness by Astigmatic Single-Molecule Imaging. *ACS Macro Lett.* **2012**, *1*, 784–788.
- (32) Wöll, D.; Braeken, E.; Deres, A.; De Schryver, F. C.; Uji-i, H.; Hofkens, J. Polymers and Single Molecule Fluorescence Spectroscopy, What Can We Learn? *Chem. Soc. Rev.* **2009**, *38*, 313–328.
- (33) Flier, B. M. I.; Baier, M. C.; Huber, J.; Müllen, K.; Mecking, S.; Zumbusch, A.; Wöll, D. Heterogeneous Diffusion in Thin Polymer Films As Observed by High-Temperature Single-Molecule Fluorescence Microscopy. *J. Am. Chem. Soc.* **2011**, *134*, 480–486.
- (34) Wehrle, B.; Zimmerman, H.; Limbach, H. H. A Solid-state ^{15}N CPMAS NMR Study of Dye Tautomerism in Glassy Polystyrene: Site Dependence of Double Minimum Potentials and their Motional Averaging. *J. Am. Chem. Soc.* **1988**, *110*, 7014–7024.
- (35) Kumagai, T.; Hanke, F.; Gawinkowski, S.; Sharp, J.; Kotsis, K.; Waluk, J.; Persson, M.; Grill, L. Controlling Intramolecular Hydrogen Transfer in a Porphycene Molecule with single Atoms or Molecules Located Nearby. *Nat. Chem.* **2013**, in press.

(36) (a) Jasny, J.; Sepiol, J. Single Molecules Observed by Immersion Mirror Objective. A Novel Method of Finding the Orientation of a Radiating Dipole. *Chem. Phys. Lett.* **1997**, *273*, 439–443. (b) Uji-i, H.; Deres, A.; Muls, B.; Melnikov, S.; Enderlein, J.; Hofkens, J. Defocused Imaging in Wide-field Fluorescence Microscopy. *Springer Ser. Fluoresc.* **2008**, *4*, 257–284. (c) Habuchi, S.; Oba, T.; Vacha, M. Multi-beam single-molecule defocused fluorescence imaging reveals local anisotropic nature of polymer thin films. *Phys. Chem. Chem. Phys.* **2011**, *13*, 7001–7007.