Influence of local microenvironment on the double hydrogen transfer in porphycene

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Experimental details

Preparation of polymer matrices

Poly(methyl methacrylate) – PMMA. Poly(methyl methacrylate) (Aldrich, medium molecular weight) was dissolved in toluene at 60 °C. In parallel, porphycene was dissolved in toluene following ultrasonication for 30 min. Both solutions were combined in a glass test tube with the internal diameter of approx. 20 mm. The test tube was placed in a custom built heated holder that allowed keeping the tube at an elevated, stabilized temperature, initially 60 °C. The temperature was slowly lowered, by several °C at a time. At each temperature the sample was kept for several hours. The process was finished when the sample reached the room temperature. The cylinder of solidified PMMA doped with Pc was freed from the test tube by breaking the glass. Finally, a slice approx. 2 mm thick was cut from the cylinder and polished.

Poly(vinyl alcohol) – PVA. Porphycene-doped PVA matrices were prepared by the solution-cast method[1]. PVA pellets (Sigma-Aldrich Mowiol 40-88, average molecular weight of 205000 g/mol) were added to distilled water of pH = 7.0 at the concentration of 15 wt%). The mixture was kept at 80°C and stirred with a mechanical stirrer until the polymer completely dissolved (for approx. 3 hours). The solution was then cooled down to the room temperature under continuous stirring. Solution of porphycene in ethanol (spectroscopic grade) was then added to 30 ml of the PVA solution and the mixture was continuously stirred for another hour. The resulting mixture was ultrasonically agitated for 30-45 minutes to get a homogeneous solution and remove air bubbles. Next, it was cast onto a glass Petri dish of 10 cm diameter. The liquid polymer layer was dried at 36°C for 24 h and then at 24°C for 48 h under forced air flow in a laboratory dryer (Pol-Eko SLW 32STD, 10% air flow setting was used). Finally, the dried polymer layer was peeled off from the surface of the Petri dish. The average thickness of the obtained layer was approx. 0.3 mm.

Poly(vinyl butyral) – PVB. Thin samples of Pc in PVB were prepared by evaporating the solvent (toluene, tetrahydrofuran or dichloromethane) from solutions containing poly(vinyl butyral) (POCH) and porphycene in the amounts chosen to obtain required absorbance and concentration. The latter was calculated using the thickness of a dried film, diameter of the Petri dish containing the solution and the polymer density.

Steady-state spectroscopy

Steady-state fluorescence and absorption spectra of polymer and liquid samples were measured with a HORIBA Jobin-Yvon Fluorolog (Horiba Scientific) and Lambda 35 UV–Vis spectrometer (PerkinElmer), respectively.

Time-resolved fluorescence anisotropy measurements

Time-resolved fluorescence anisotropy measurements were carried out using a home-built setup based on a Multichannel Picoseconds Event Timer and Time-Correlated Single Photon Counting module HydraHarp400 (PicoQuant, GmbH). PVB samples were excited at approx. 633 nm with a picosecond laser diode LDH-P-635 (PicoQuant, GmbH). Wavelength of the light emitted by the diode was tuned using its internal tuning mechanism based on temperature control of the junction. For excitation of other samples a white light supercontinuum laser source WhiteLase High Power Supercontinuum, WL-SC400-2 laser (NKT Photonics, Inc.) was used. Output beam of the supercontinuum laser was sent through a set of edge and bandpass interference filters (Semrock) in order to select a narrow part of the laser spectrum. The narrowest bandpass filter had a bandwidth of 2 nm FWHM and the central wavelength of 632.8 nm. Pulse repetition rate of both sources was reduced down to 5 MHz. At this repetition rate the temporal pulse separation was much longer than the excited state lifetime of porphycene (approx. 11 ns). The average power used for the excitation never exceeded 1 mW.

The linearly polarized excitation beam passed through a half-wave plate mounted in a motorized computer-controlled rotation stage (Thorlabs) in order to set its polarization to either horizontal or vertical orientation. Then the excitation light passed through a hole drilled in a silver-coated off-axis parabolic mirror used for fluorescence collection and was focused in the sample

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located inside a closed-cycle helium cryostat from Advanced Research Systems model 204 A with model ARS-4HW compressor, and an SRS 331 S temperature PID controller. The surface of the sample was perpendicular to the direction of the excitation beam (front-face detection geometry).

The emitted fluorescence light was reflected by the off-axis parabolic mirror, passed through a focusing lens and an edge absorption filter, so that the scattered excitation light was significantly attenuated. A nanowire polarizer (Meadowlark Versalight, extinction ratio 10000:1) mounted in a motorized computer-controlled rotation stage (Thorlabs) was placed in the fluorescence beam path in order to select either horizontal of vertical polarization of the detected light. The collected fluorescence light was coupled into a Czerny-Turner monochromator (SpectraPro-150, Acton Research Corporation). The central wavelength of the monochromator was set to 645 nm. The output focal-plane slit of the monochromator was imaged onto the 50 μm active area of a single photon avalanche photodiode (Micro Photon Devices) which was directly connected to the HydraHarp 400 module. The experimental apparatus was controlled by a LabVIEW application that allowed control of the cryostat and both rotation stages. For each temperature set point six fluorescence decay histograms for various excitation and detection polarizations were registered.

Four of the recorded histograms were used for calculation of the so-called *G*-factor. They were recorded for the time necessary to collect at least one thousand counts at the maximum. The *G*-factor describes the ratio of the sensitivities of the detection system for vertically and horizontally polarized light. In the front-face detection geometry the *G*-factor cannot be directly measured using only horizontally polarized excitation light, as in the case of the more commonly used L-shape detection geometry. Instead, the polarization of the excitation light also has to be changed, without changing its intensity, in order to determine the *G*-factor. At least two combinations of the excitation and detection polarization directions are necessary, but we decided to record all four of them (VV, VH, HH, HV, where „H" means horizontal and „V" – vertical polarization; the first letter refers to the excitation polarization and the second letter to polarization of the detected light) as an indicator of possible changes of polarizing properties of the polymer matrix itself. The *G*-factor value was calculated from two pairs of histograms using the formulas:

$$G_1 = \frac{\int_{t_1}^{t_2} N_{VV}(t)dt}{\int_{t_1}^{t_2} N_{HH}(t)dt} = \frac{I_{VV}}{I_{HH}}$$

$$G_2 = \frac{\int_{t_1}^{t_2} N_{VH}(t)dt}{\int_{t_1}^{t_2} N_{HV}(t)dt} = \frac{I_{VH}}{I_{HV}}$$

where $N_{XX}(t)$ denote fluorescence decay histograms after subtraction of the background (mainly dark counts of the photodiode), t_1 and t_2 were selected so that integration was over the entire meaningful fluorescence decay range and I_{XX} denote fluorescence intensities for given directions of the excitation and detection polarizations. In the course of further analysis both values of the *G*-factor were compared in order to verify if the polymer did not change the polarization of light. The mean value of the *G*-factors calculated with both equations was used in further analysis. The *G*-factor almost did not change with the temperature and was close to 0.6.

Another pair of histograms was recorded for combinations of vertically polarized excitation light with vertically and horizontally polarized detected fluorescence light. These histograms were registered until at least 20 000 counts difference between their maxima was achieved. Then the anisotropy decay was calculated using the previously determined *G*-factor according to the equation:

$$r(t) = \frac{G \cdot N_{VV}(t) - N_{VH}(t)}{G \cdot N_{VV}(t) + 2N_{VH}(t)}$$

Transient absorption anisotropy measurements

The setup used for transient absorption anisotropy measurements of the sample in PMMA was based on a Legend Elite Duo (Coherent, Inc.) Ti:Sapphire regenerative amplifier capable of delivering 800 nm pulses with 50 fs duration, 2.4 mJ pulse energy and repetition rate of 5 kHz. The output of the amplifier was divided and routed into two independent noncollinear optical parametric amplifiers (NOPAs) (TOPAS-White, Light Conversion) generating pulses tunable from 500 to 750 nm with energy in the range of 20-30 μJ. One of them generated pump pulses, the other one – probe pulses. Output pulses from the NOPAs were attenuated, to approx. 800 nJ in the case of the pump pulse, and 60 nJ in the case of the probe pulse. A mechanical chopper was placed in the excitation beam path for switching between pumped and unpumped states of the sample every other laser pulse. An achromatic half-wave plate in a rotating mount followed by a nanowire polarizer (Meadowlark Versalight) was used for control of the pump energy. Diameter of the pump beam in the sample cuvette was reduced to approx. 400 μm FWHM using a telescope.

The probe beam traversed a delay line consisting of a cube-corner retroreflector mounted on a motorized linear stage. The stage had a full-travel accuracy of 3 fs, allowed for minimal increments of 0.3 fs and provided up to 1.5 ns delay between pump and probe pulses. An achromatic half-wave plate mounted after the last routing mirror was used to rotate the polarization of the probe beam to 45° with respect to the pump polarization. A lens with 500 mm focal length focused the probe beam in the sample cuvette within the pumped area. The beam size of the probe beam in the sample was approx. 200 μm FWHM, as measured with a Spiricon LBA-USB laser beam analyzer.

The pump and probe beams formed an angle of approx. 4°. After the sample, the pump beam was blocked with an iris aperture. A second iris aperture placed at a certain distance after the first one was used to additionally isolate the probe beam from scattered excitation light and the detection system was placed inside a black enclosure. A polarizing beamsplitter (PBS), with the extinction ratio of 1000:1 for transmission and 100:1 for reflection, split the probe beam into two beams with orthogonal polarizations, which were then focused on two photodiodes. Neutral density filters were used to attenuate the intensity of the beams in order to operate within the linearity region of the detectors. One of the filters was of variable optical density so that the electrical signals from the detectors could be equalized.

The detection circuit used two photodiodes with integrated am-

plifiers. A trigger signal from the laser, after having its frequency divided by two, was used to control the mechanical chopper which blocked every other pump pulse, allowing fast switching between absorption measurements of the pumped and unpumped sample. National Instruments NI-USB 6351 data acquisition card was used to digitize the photodiodes' signals by acquiring one sample per pulse after the arrival of the trigger signal from the laser. The card also sampled the chopper output signal to differentiate between pumped and unpumped states.

In this configuration a pair of laser pulses (one with a pump pulse exciting the sample and one with the pump beam blocked) was sufficient to measure optically induced absorbance change ΔA, for mutually parallel ($\Delta A_{||}$) and perpendicular ($\Delta A_{\perp}$) pump and probe polarizations. Kinetic data were recorded by scanning the delay line. In order to reduce the influence of shot-to-shot pulse energy fluctuations, values of the absorbance change obtained from 1000 to 5000 pairs of pulses for each delay step were averaged. Long-term instabilities of the laser system were reduced by averaging 10-30 scans of the delay line to obtain mean values of $\Delta A_{||}(t)$ and $\Delta A_{\perp}(t)$ prior to computing the anisotropy using the formula:

$$r(t) = \frac{\Delta A_{||}(t) - \Delta A_{\perp}(t)}{\Delta A_{||}(t) + 2\Delta A_{\perp}(t)}$$

The sample in the form of a 2 mm-thick plate was mounted inside a closed-cycle helium cryostat, model 204 from Advanced Research Systems with an ARS-4HW compressor, and an SRS 331 S temperature PID controller (the same cryostat system as the one used in fluorescence measurements).

Additional tables

Table S1 Fluorescence anisotropy decay times τ_1 and the excited state tautomerization rates $k_1 = 1/(2\tau_1)$ measured by the fluorescence anisotropy technique for Pc in PVB at various temperatures

Temp. (K)	τ_1 (ps)	k_1 (10^8 s^{-1})
14 ± 4	8500 ± 3100	0.59 ± 0.21
22 ± 2	7800 ± 2800	0.64 ± 0.23
31 ± 2	4900 ± 1500	1.02 ± 0.31
41 ± 2	4200 ± 1200	1.18 ± 0.33
51 ± 2	3510 ± 930	1.43 ± 0.38
61 ± 2	2350 ± 420	2.13 ± 0.38
71 ± 2	1630 ± 190	3.07 ± 0.35
81 ± 1	890 ± 130	5.62 ± 0.82

References

1 S. Sreeja, S. Sreedhanya, N. Smijesh, R. Philip and C. I. Muneera, *J. Mater. Chem. C*, 2013, **1**, 3851–3861.

2 M. Gil and J. Waluk, *J. Am. Chem. Soc.*, 2007, **129**, 1335–1341.

Additional figures

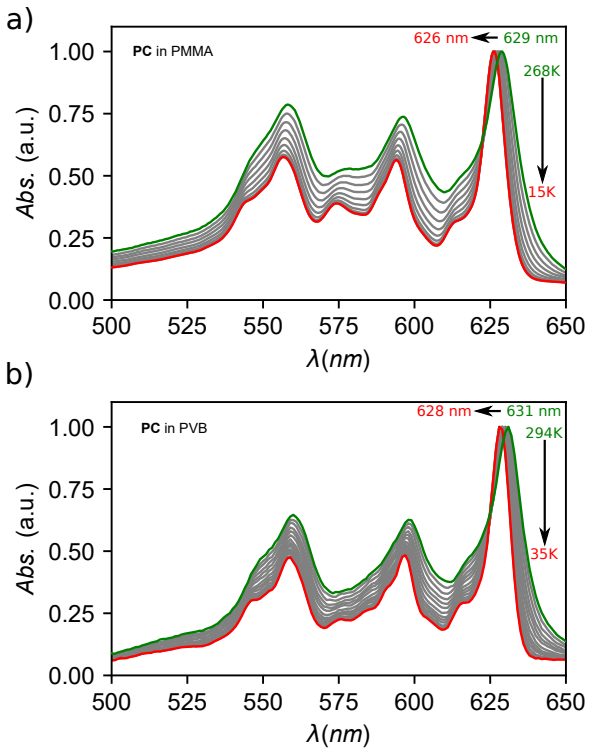

Fig. S1 Temperature dependence of absorption spectra of porphycene in a) PMMA and b) PVB.

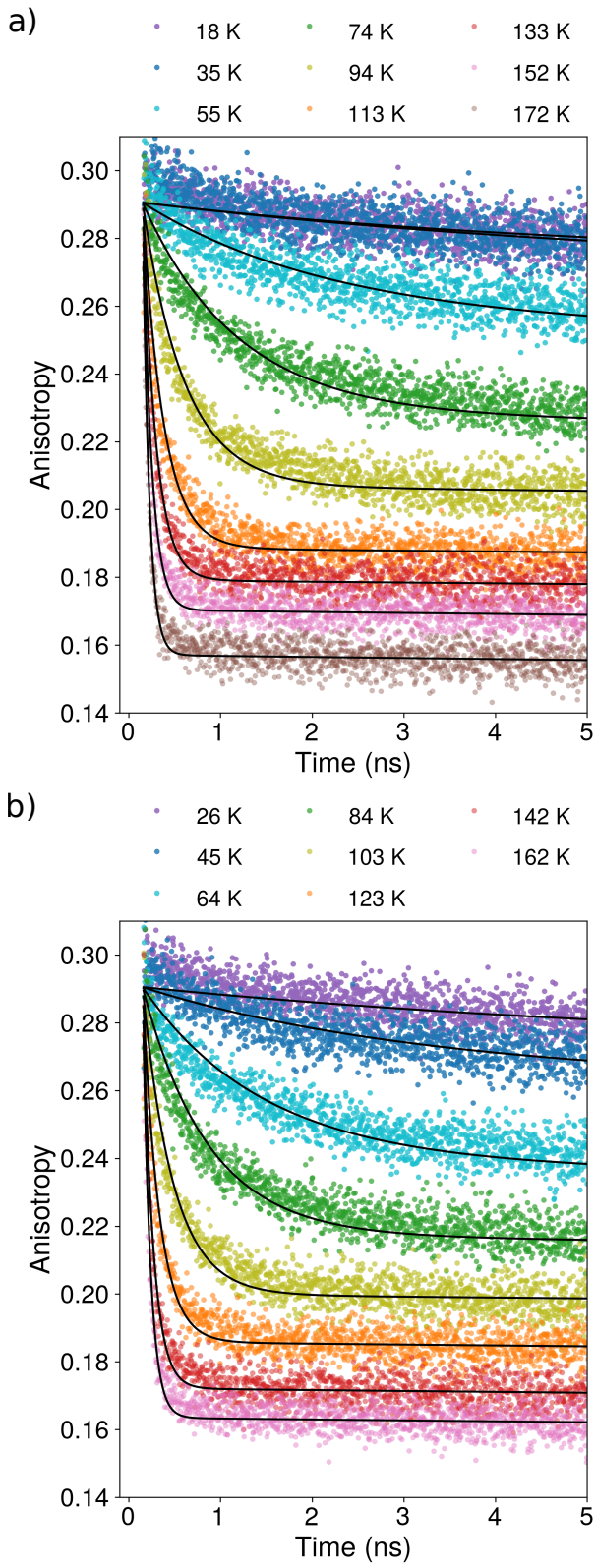

Fig. S2 Fluorescence anisotropy decays of Pc in PMMA registered at different temperatures.

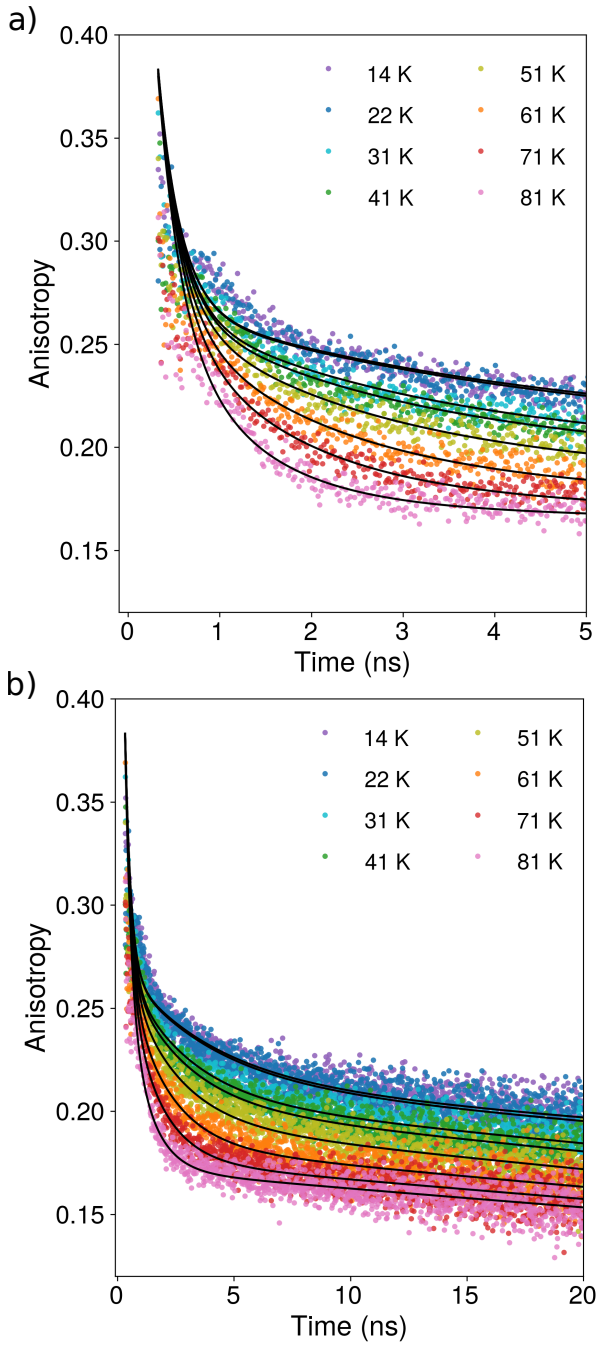

Fig. S3 Fluorescence anisotropy decays of Pc in PVB registered at different temperatures. Panel a) shows the same data as panel b) but in a limited time range.

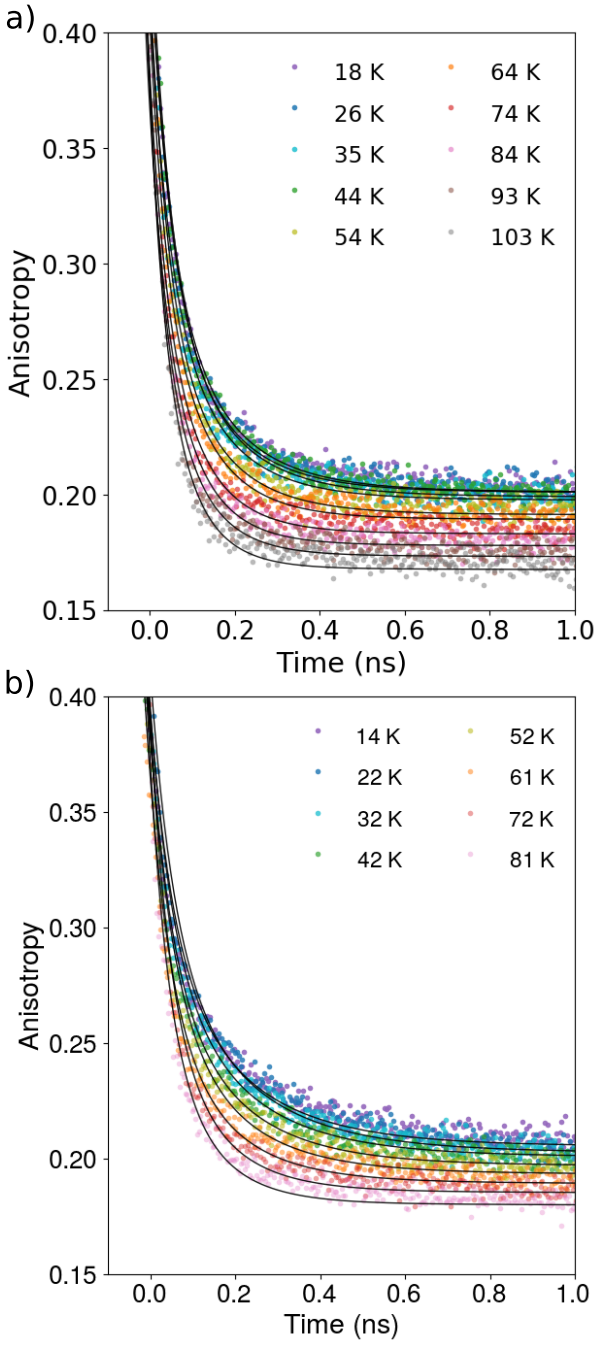

Fig. S4 Fluorescence anisotropy decays of Pc in PVA registered for two separate fragments of the same sample (**sample 1**) at different temperatures. The first fragment (a) was measured with temperature step of approx. 10 K and the second one (b) with the step of 5 K but only half of the collected data is shown for clarity.

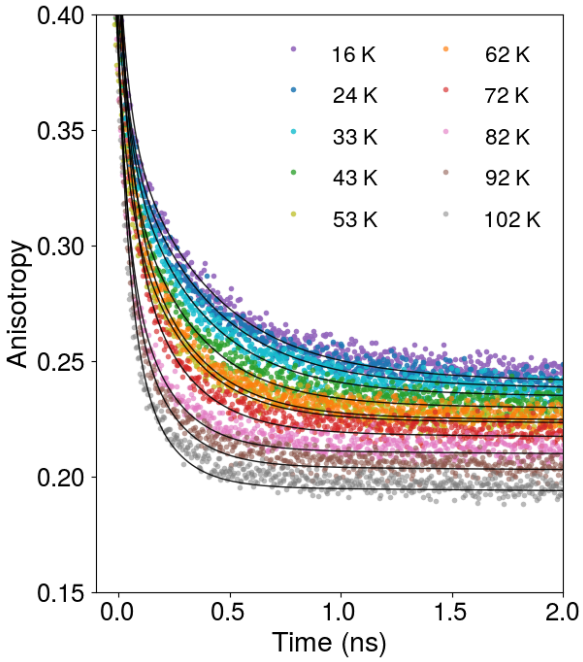

Fig. S5 Fluorescence anisotropy decays of Pc in PVA registered for **sample 2** at different temperatures. This sample was prepared separately from **sample 1**.

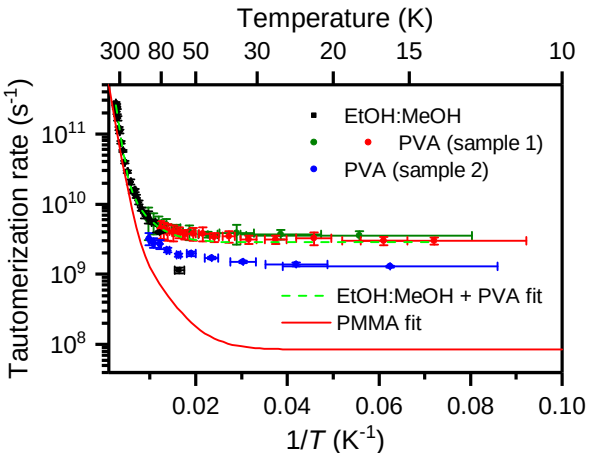

Fig. S6 Temperature dependence of S_1 state tautomerization rates for Pc in PVA and in the alcohols mixture. Results for two different PVA samples are shown, two fragments cut out of the first sample were independently measured. The green dashed line represents a fit of the three-component Arrhenius-like function to the merged data sets for the sample 1 in PVA and in the alcohols mixture. The red solid line shows a fit of the data measured in PMMA.

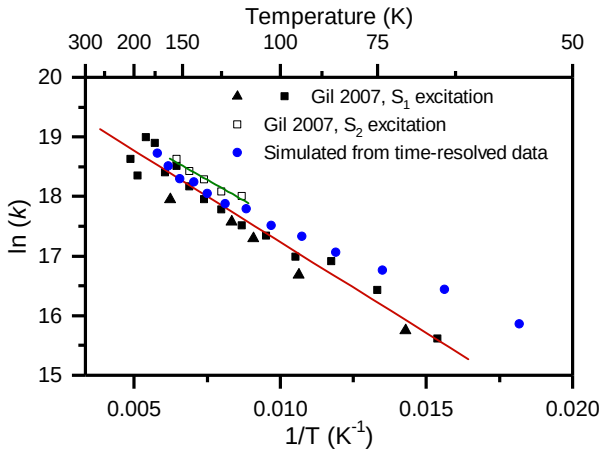

Fig. S7 Comparison of tautomerization rates in the S_1 state reported in Ref.[2] (Gil 2007) and simulated results obtained by application of the data analysis procedure used in Ref.[2] to steady state fluorescence anisotropy calculated from time-resolved data obtained in this work.