Supplementary information:
Glass formation of a DMSO-water mixture probed with a photosynthetic pigment

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S1 Sample preparations

Phyocyanobilin (purity >95%, microbial source, CAS: 20298-86-6) was purchased from Frontier Scientific as a dry powder and used without further purification. DMSO (>99.9%, anhydrous) was purchased from Sigma Aldrich and mixed with de-ionized water in a 2:1 volume ratio. A drop of the solution was placed between two 1 mm sapphire windows separated by a 180 μm Teflon spacer, and placed inside the vacuum chamber of a Janis ST-100 cryostat that was cooled down with nitrogen vapor flow. UV-vis absorption measurements at low temperature were performed with a Thorlabs stabilized fiber-coupled lamp and an Ocean Optics USB4000 spectrometer. pH-dependent spectra were taken with a 1 mm cuvette with an Ocean Optics spectrometer.

S2 Absorption spectra of PCB: cooling and heating

In Figures S1A and B, it can be seen that the UV band at ~350 nm is larger that the visible band for all temperatures. Indication that PCB remains in a helical conformation.[1] Additionally, the same visible absorption spectra are measured at each temperature during cooling and heating, showing that there is no hysteresis in the system.

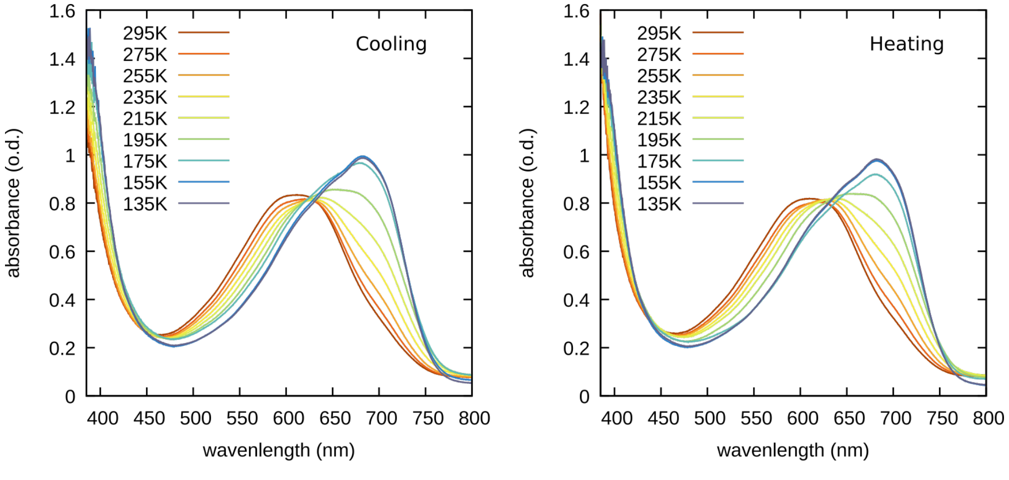

Figure S1: Absorption spectra of PCB at decreasing (cooling) and increasing (heating) temperature.

S3 Fits to visible absorption spectra

A fit was performed to the spectrum at each temperature using two Gaussian curves for the visible band, one for the wing of the UV band plus a tilted straight line as baseline.

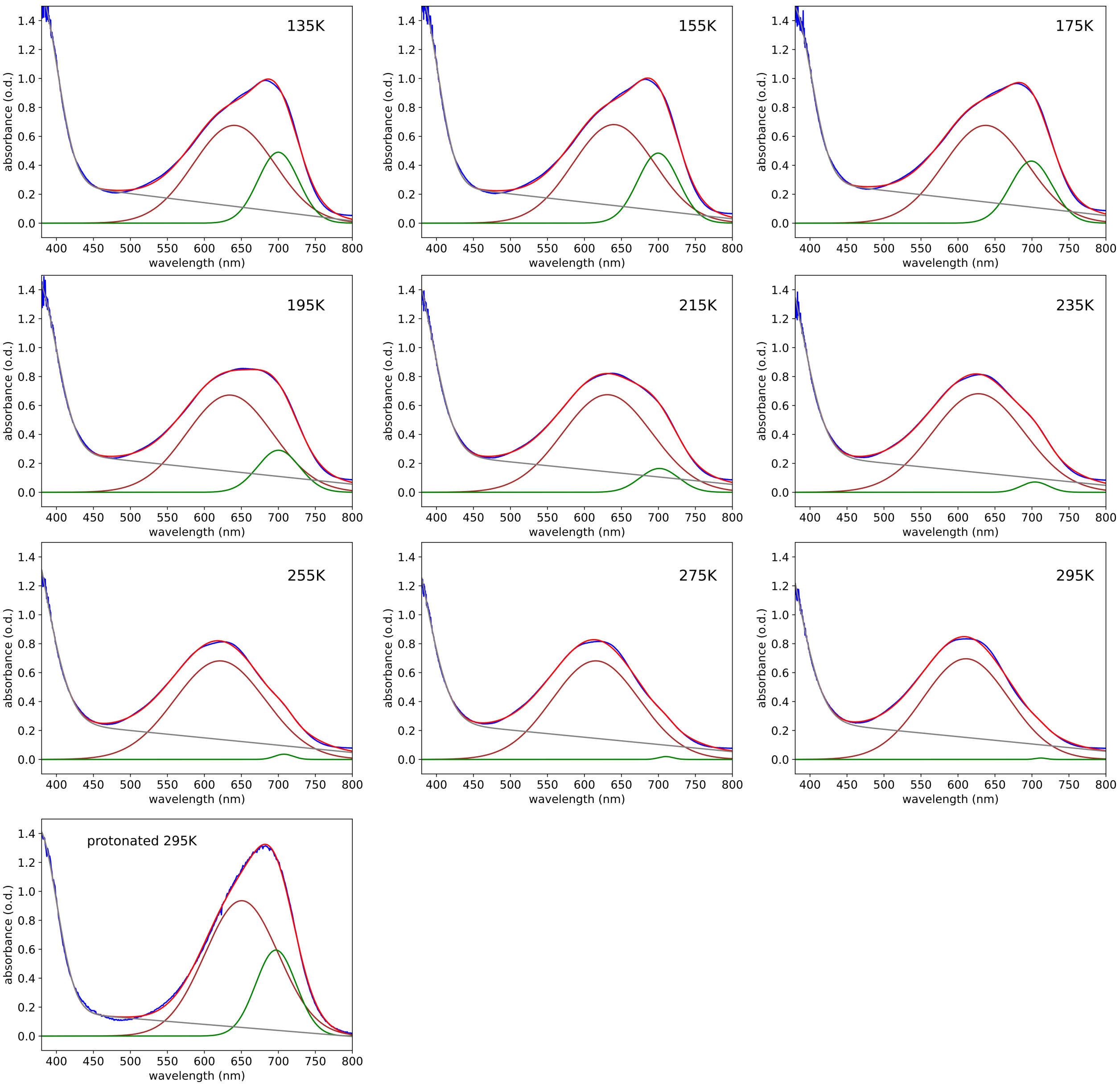

Figure S2: Fits of the absorption spectra of PCB at different temperatures and of protonated PCB at room temperature, as indicated. Plotted are the original data (blue), the result of the fit (red), the fitted Gaussian of the UV band plus the tilted baseline (gray), and the two Gaussian components of the visible band I_{600} (brown) and I_{700} (green).

S4 Absorption spectra of PCB at different pH values

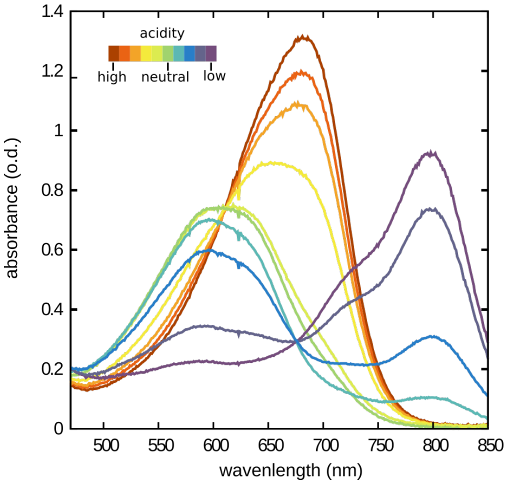

Figure S3: Room temperature absorption spectra of PCB at different acidity conditions. Small amounts of highly concentrated HCl or NaOH were added to the 2:1 DMSO:H_2O mixture with dissolved PCB, these aliquots were added until no further spectral changes were observed. The absorption of the sample without any acid or base added is in green, indicated as 'neutral' acidity. HCl was added to achieve high acidity (red), and NaOH to achieve low acidity (purple).

S5 Stimulated Raman measurements

An 800 nm beam from an amplified titanium:sapphire laser system (50 fs pulse duration, 1 kHz repetition rate) is split into two beams with a beam splitter. The first part (most of the power) is used to generate a narrow-band Raman pump pulse by means of an 4f-filter in which a grating-dispersed and focused beam is frequency trimmed with two parallel razor blades and later re-collimated. The razor blades' separation is adjusted to lead a 1.5 nm bandwidth at 792 nm (0.6 ps transform limited pulse duration). The second part of the amplifier output is used to generate a white light continuum probe by focusing the beam into a sapphire plate. The 850-920 nm frequency range from the white light continuum is used to detect Stokes gain features, and residual 800 nm is removed with a long-pass filter. The Raman pump and white-light probe are focused and overlapped at the sample with a parabolic mirror, and in time by changing the beam path of the Raman-pump with perpendicular mirrors mounted on a translation stage. Before the sample, the Raman-pump repetition rate is halved to 500 Hz with an optical chopper. After the sample, the Raman pump is dumped, and the white-light probe re-collimated with a parabolic mirror and directed to a spectrograph for frequency-resolved detection with a CCD array. The intensity of the probe is adjusted with a neutral density filter (ND). Raman spectra are calculated by dividing the white-light spectrum with Raman pump unblocked by the one with Raman pump blocked. The Raman-shift axis is calibrated with cyclohexane lines taken from the literature.[2] Baseline subtraction was done using and asymmetric least square fitting.[3]

S6 Pump-probe measurements

An 800 nm beam from an amplified titanium:sapphire laser system (140 fs pulse duration, 1 kHz repetition rate) is split into two beams with a beam splitter (BS). Most of the power is used to pump a non-collinear optical parametric amplifier to generate pump pulses centered at either 700 nm or 600 nm. The bandwidth of the pump spectra is narrowed with an acousto-optic programmable dispersive filter (AOPDF) pulse shaper that is also used to compress the pulses, resulting in $\sim$15 nm bandwidth and $<$200 fs pulse length at the sample. From the second part of the 800 nm beam, a white light continuum is generated on a 2 mm sapphire plate and used as probe. Residual 800 nm is removed with a short-pass filter, and a pair of chirped mirrors are used to compress the probe pulses. Pump and probe pulses are focused and overlapped on the sample with a parabolic mirror, and probe pulses are time-delayed with respect to the pump with a mechanical translation stage. The polarization of the pump beam was set to parallel with respect to the probe using a $\lambda/2$ plate and a polarizer. After the sample the pump pulses are dumped, and the probe is recollimated with a second parabolic mirror and directed to a spectrograph for frequency-resolved detection on a CCD detector

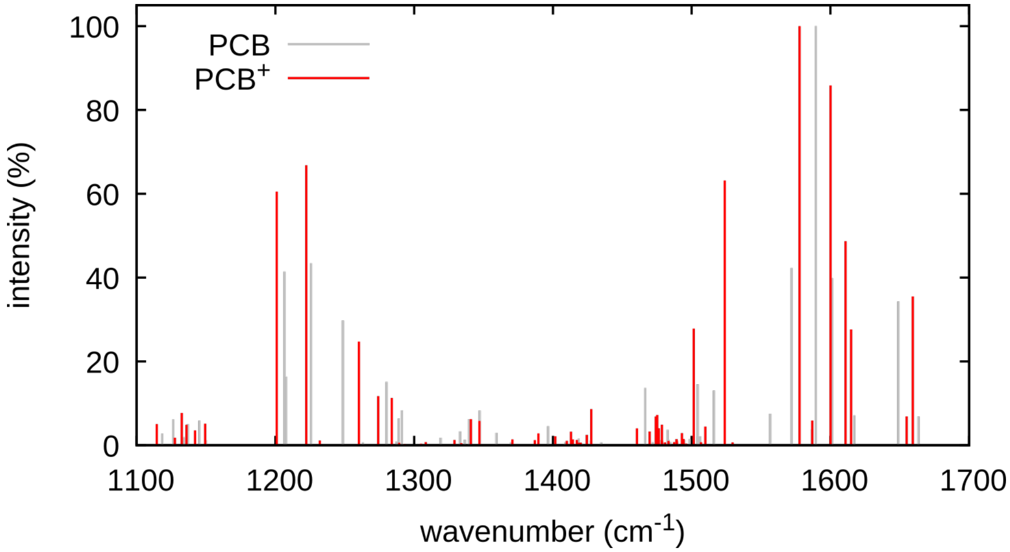

Figure S4: Calculated Raman spectra using Gaussian at the BLYP/6-31G* level of theory and CPCM solvent=H2O. Note the change in relative intensity of the bands around 1200 cm^{-1}, and an overall red-shift and increased in absorbance of the bands at around 1600 cm^{-1}.

array. The AOPDF filter is used to half the repetition rate of the pump pulses, so transient absorption spectra are collected by dividing probe spectra with pump on and pump off. The energy of the pump pulses was adjusted to avoid photo-bleaching of the sample; larger photo-bleaching was observed for 600 nm pump, so smaller energies were used accordingly. For 700 nm pump-probe data, pump energies were 20 nJ (295 K), 10 nJ (255 K), 5.5 nJ (215, 175 and 135 K). For 600 nm pump-probe data, pump energies were 10 nJ (295, 255, 215 K), 5 nJ (175 and 135 K). Transient absorption spectra were collected for pump-probe delays from 0.5 ps to 500 ps.

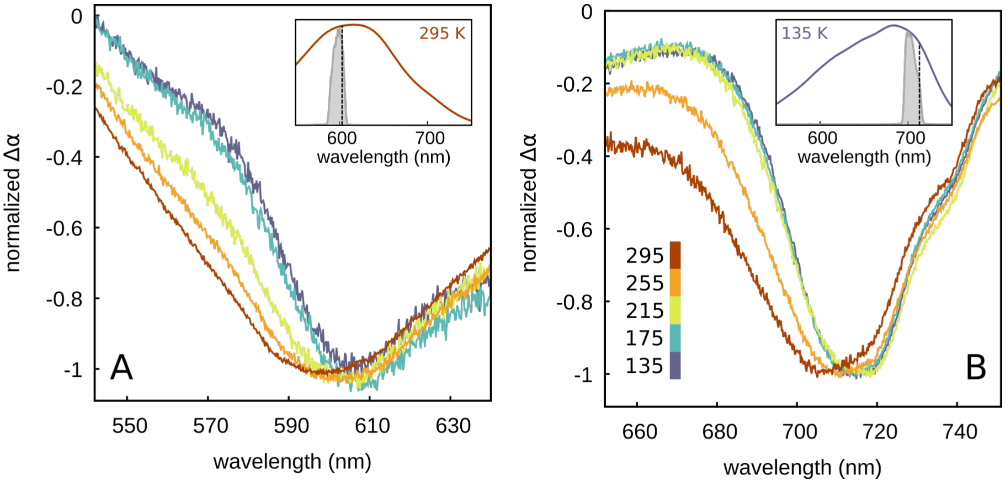

Figure S5: Transient absorption spectra of PCB at 0.5 ps for the indicated temperature. (A) Pump-probe at 600 nm. (B) Pump-probe at 700 nm.

Figures S5A and B show the transient absorption at 0.5 ps for decreasing temperatures for 600 nm and 700 nm pump, respectively. Spectra were normalized to their minimum value. The insets show the pump spectra relative to the absorption when the maximum of absorption is at either ∼600 nm or ∼700 nm. The vertical dashed line indicates the probe wavelengths used for the pump-probe traces in Figure 4 of the main text. These traces were fit with the sum of two exponential functions, and the resulting fit parameters are shown in Tables S1 and S2. In the 600 nm pump-probe data, the slow component remains of a similar relative amplitude for all temperatures. In the 700 nm pump-probe data, the slow component becomes dominant at lower temperatures, and at 175 K, both components have a longer time constant.

Table S1: Parameters resulting from fits with two exponential functions to the 600 nm pump-probe data

Temperature (K)	τ_1 (ps)	τ_2 (ps)	A2/A1
135	2.8	471	1.9
175	4.2	413	1.6
215	3.9	224	1.9
255	10	128	1.6
295	5.7	60	2.0

Table S2: Parameters resulting from fits with two exponential functions to the 700 nm pump-probe data

Temperature (K)	τ_1 (ps)	τ_2 (ps)	A2/A1
135	7.8	470	5.9
175	65	513	6.5
215	8.7	309	4.5
255	7.6	149	2.0
295	3.3	65	1.0

References

[1] H. Falk, N. Müller, and S. Wansch, “Zur chemie der pyrrolpigmente, 63. mitt,” *Monatsh. Chem.*, vol. 116, p. 1087, 1985.

[2] McCreery research group, http://www.chem.ualberta.ca/ mccreery/ramanmaterials.html#cyclohexane.

[3] P. H. C. Eilers and H. F. M. Boelens, “Baseline correction with asymmetric least squares smoothing,” *Leiden University Medical Centre Report*, vol. 1, no. 1, p. 5, 2005.