SUPPORTING INFORMATION

Mechanothermally induced conformational change of a porphyrin dimer in a polymer film

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MATERIALS AND METHODS

All solvents and other materials, including polyvinyl alcohol (PVA, 130 kDa), were purchased from Sigma-Aldrich and were used as received. **PD** was prepared according to literature procedure the structure and purity were confirmed by MALDI-TOF spectrometry and HPLC.[1] A 1 mM concentration stock solution of **PD** in DMSO was prepared fresh prior to the experiments and it was used for all spectroscopic measurements, and protected from direct light exposure during storage.

PVA film preparation:

PVA films were prepared according to a modified literature procedure.[2] Briefly, doubly distilled water (170 mL) was added to a 250 mL flask containing a magnetic stirring bar, and PVA powder (30 g) was slowly added under stirring at 80-90 ^{o}C, and the stirring continued for 2 hours (bubble formation was noted during this step). The resulting homogeneous solution was allowed to cool to room temperature overnight to clear out all the bubbles.

PD solution (1-2 μL of 1 mM DMSO stock solution) was added to a freshly prepared PVA solution (6.0 mL in a 20 mL) at 40-50 ^{o}C. The mixture was thoroughly mixed using a glass pipette for 10-15 minutes to assure complete mixing, followed by sonication for 2-3 minutes to remove all bubbles that formed during the mixing. Next, the mixture was poured into a 2-inch diameter plastic petri dish on a flat balanced surface and kept in a moisture-free, dark environment for 4 to 6 days to allow the film to form.

Stretching/heating procedure:

PVA films with embedded **PD** were uniformly stretched (up to 4 times the original length) using a home-built stretching apparatus. In a typical experiment, a PVA film was mounted and a 5.0 mm distance at the center of the film was marked with two dots. The temperature was monitored using an electronic hot plate with a built-in temperature controller. In addition, a thermocouple was mounted underneath the PVA film to monitor the actual temperature of the stretched region. All measurements were performed at 70 ± 1 ^{o}C. All films were stretched at a constant rate to avoid tearing of the film.

The extent of stretching was calculated by taking the ratio of the final length of the two dots at the center relative to the original length of 5.0 mm.

The thickness of the films (both stretch and non-stretched) was measured using an electronic caliper (and with micrometer caliper). Measurements were performed at the center of the film between the two dots.

Steady-state emission measurements:

Emission spectra were obtained using an ISS K2 Multi-frequency phase fluorometer (ISS Inc) with a custom-built front-face apparatus. An ozone lamp producing white light was used as the excitation source. To select the desired excitation wavelength, light was passed through the excitation monochromator. Then, light was passed through the first Glan-Thomson polarizer, followed by the excitation of the sample. Fluorescence signal from the sample was then passed through the second Glan-Thomson polarizer before getting into the emission monochromator and finally to the detector.

The stretched **PD**-PVA films were mounted vertically along the stretching axis. VV, VH, HV and HH of emission spectra correspond to the orientation (vertical/V and horizontal/H of the two Glan-Thomson polarizers that were placed between the sample and the excitation light, and between the sample and the detector, respectively. For example, VV spectra were obtained by using excitation light through vertically (V) oriented Glan-Thomson polarizer (this gave

polarization of excitation light which was parallel to the stretching axis) and the light emitted from the **PD**-PVA film was passed through another Glan-Thomson polarizer in front of the detector that was also oriented vertically (V), thus only allowing vertical fluorescence light to come to the detector.[3]

Lifetime measurements:

Fluorescence lifetimes were measured on a FluoTime 300 fluorometer (PicoQuant, Inc.) Laser excitation was provided by a Supercontinuum WhiteLase SC-400 (Fianium, Ltd) pulsed white light laser, which was passed through a hybrid quartz prism and grading monochromator to choose an excitation light of 475 nm (± 5 nm) with resolution set to 4 ps/channel. The fluorometer was equipped with an ultrafast microchannel plate MCPPMT detector from Hamamatsu. The fluorescence lifetimes were measured in the magic angle condition (54.70) and data analyzed using FluoFit4 program from PicoQuant, Inc (Germany) using multi-exponential fitting model:

$$I(t) = \sum_i \alpha_i e^{-t/\tau_i}$$

where, α_i is the amplitude of the decay of the ith component at time t and τ_i is the lifetime of the ith component. The intensity weighted average lifetime (τ_{avg}) was calculated using following equation:

$$\tau_{avg} = \sum_i f_i \tau_i \qquad \text{where} \qquad f_i = \frac{\alpha_i \tau_i}{\sum_i \alpha_i \tau_i}$$

Percent of the planar **PD** conformation (planar PD / %) was calculated as follows:

$$\text{planar PD / \%} = (F^{max}_{planar}) / (F^{max}_{twisted} + F^{max}_{planar}) \bullet 100\%$$

where $F^{max}_{twisted}$ is the maximum fluorescence intensity of the twisted conformation; F^{max}_{planar} is the maximum fluorescence intensity of the planar conformation

FTIR measurements:

IR spectra we acquired on Jasco FT/IR-4600 equipped with ATR-PRO ONE, using the following parameters: 50 scans, 4.0 cm^{-1} resolution, background correction, H_2O & CO_2 suppression.

Measurements of the stretched and non-stretched films were taken at various points between the dots, and the crystallinity was calculated using the averages (±SD) obtained from 3-4 spectra.

**Table S1**. Lifetime measurements of **PD** in ethanol, glycerol, and isotropic PVA film.[a]

media	observation / nm	α_1	τ_1/ ns	α_2	τ_2/ ns	α_3	τ_3/ ns
ethanol	720	85820	0.077	5080	0.38	1457	1.38
	780	**−29270**	**0.02**	47351	0.37	3740	0.59
glycerol	720	23315	0.23	24403	0.59	9159	2.10
	780	16590	0.23	31294	0.50	789	1.61
PVA	720	3202	0.06	3081	0.98	9159	1.64
	780	2097	0.08	9586	0.88	3071	1.42

[a] – λ_{ex} = 475 nm; α_n – amplitude
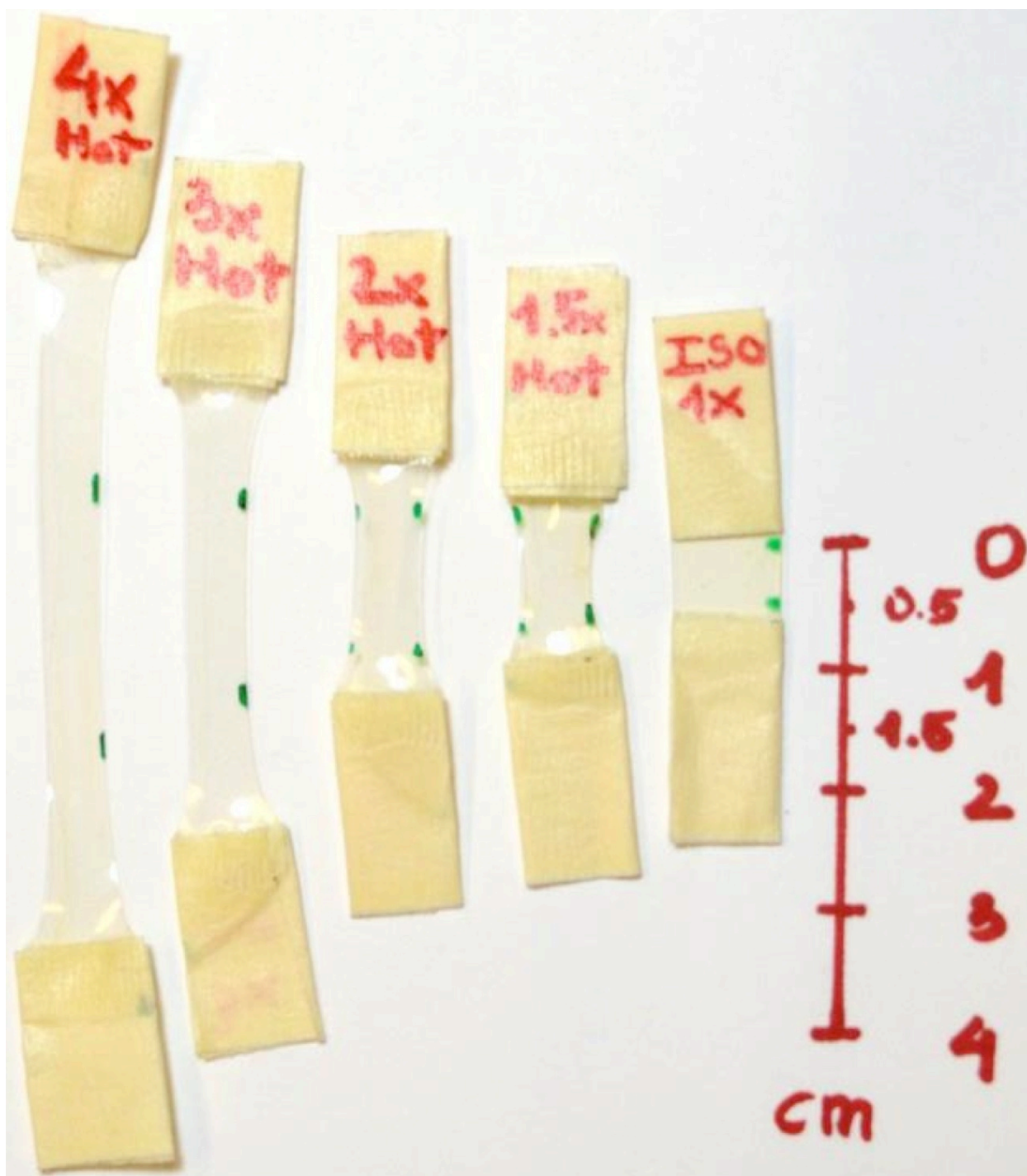
Table S2. Thickness of **PD** PVA film as a function of stretching at 70°C.

Extent of stretching	length / mm	thickness / mm
non-stretched	5	0.35
2 (200%)	10	0.21
3 (300%)	15	0.13
4 (400%)	20	0.11
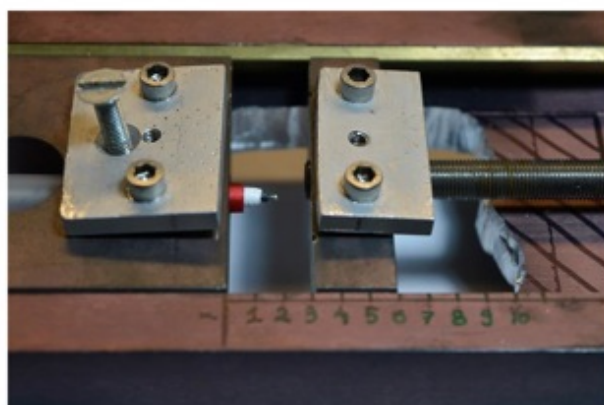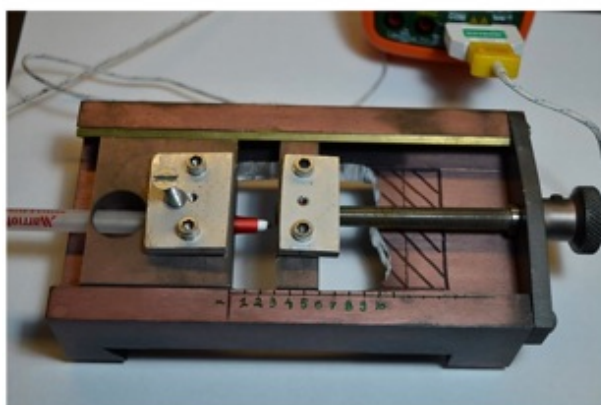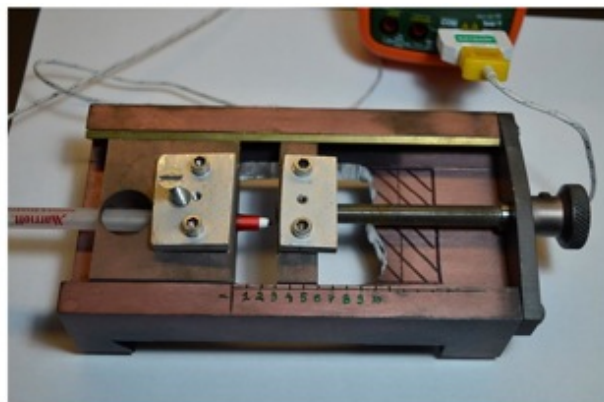
Figure S1. Photographs of the in house-built stretching/heating instrument.

Figure S2. Photographs of **PD**-PVA films.
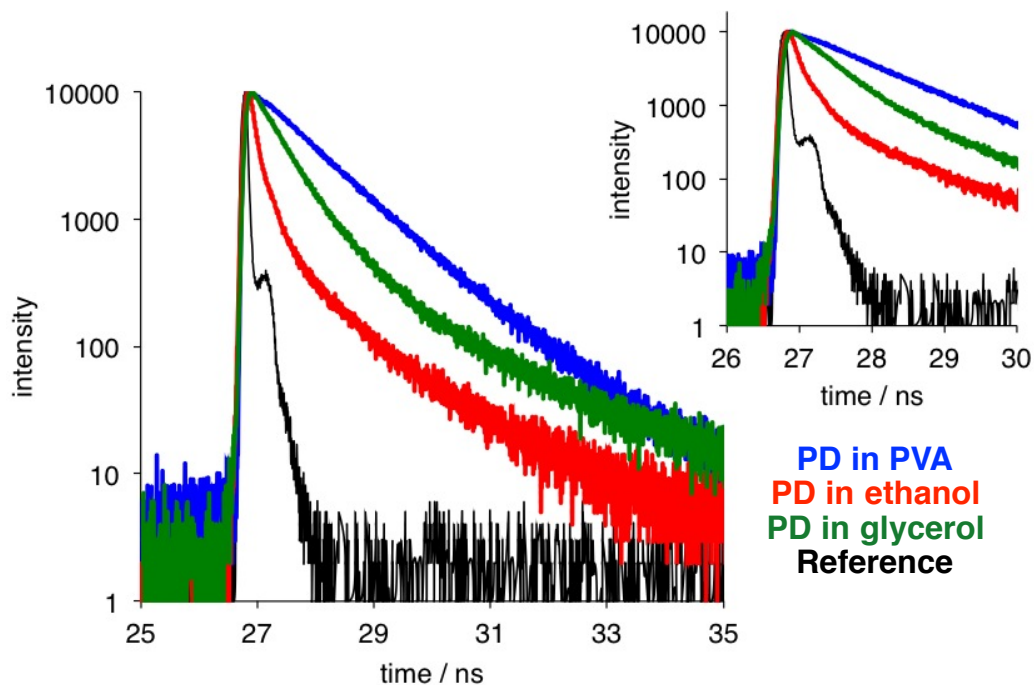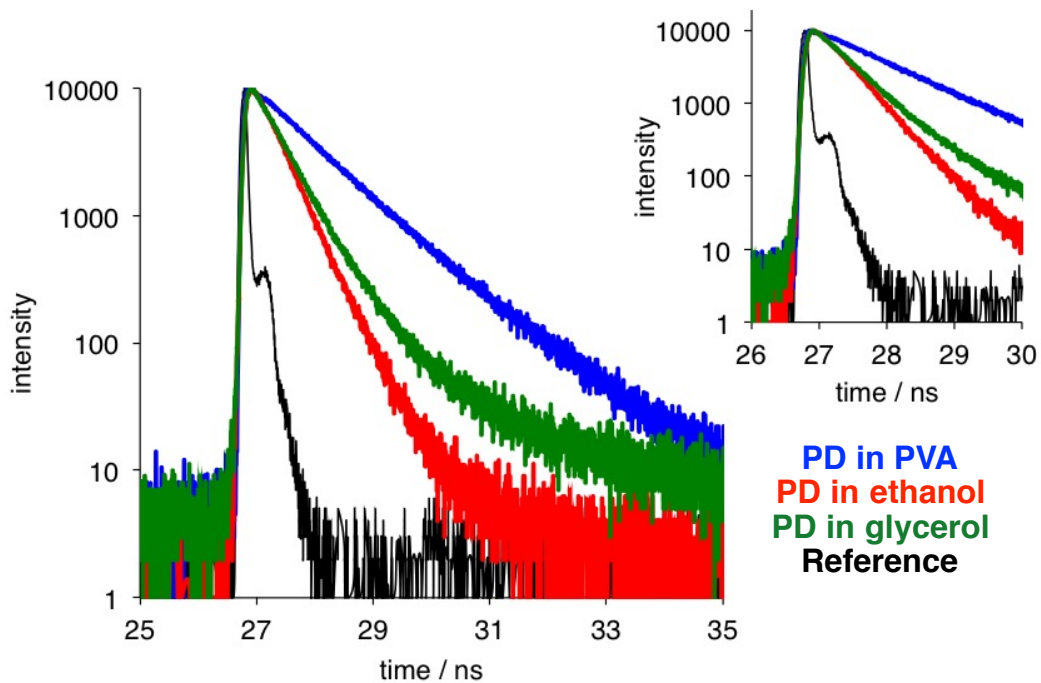
iso 1x: non-stretched (5mm);
1.5x hot: stretched to 150% –7.5mm;
2x hot: stretched to 200% – 10mm;
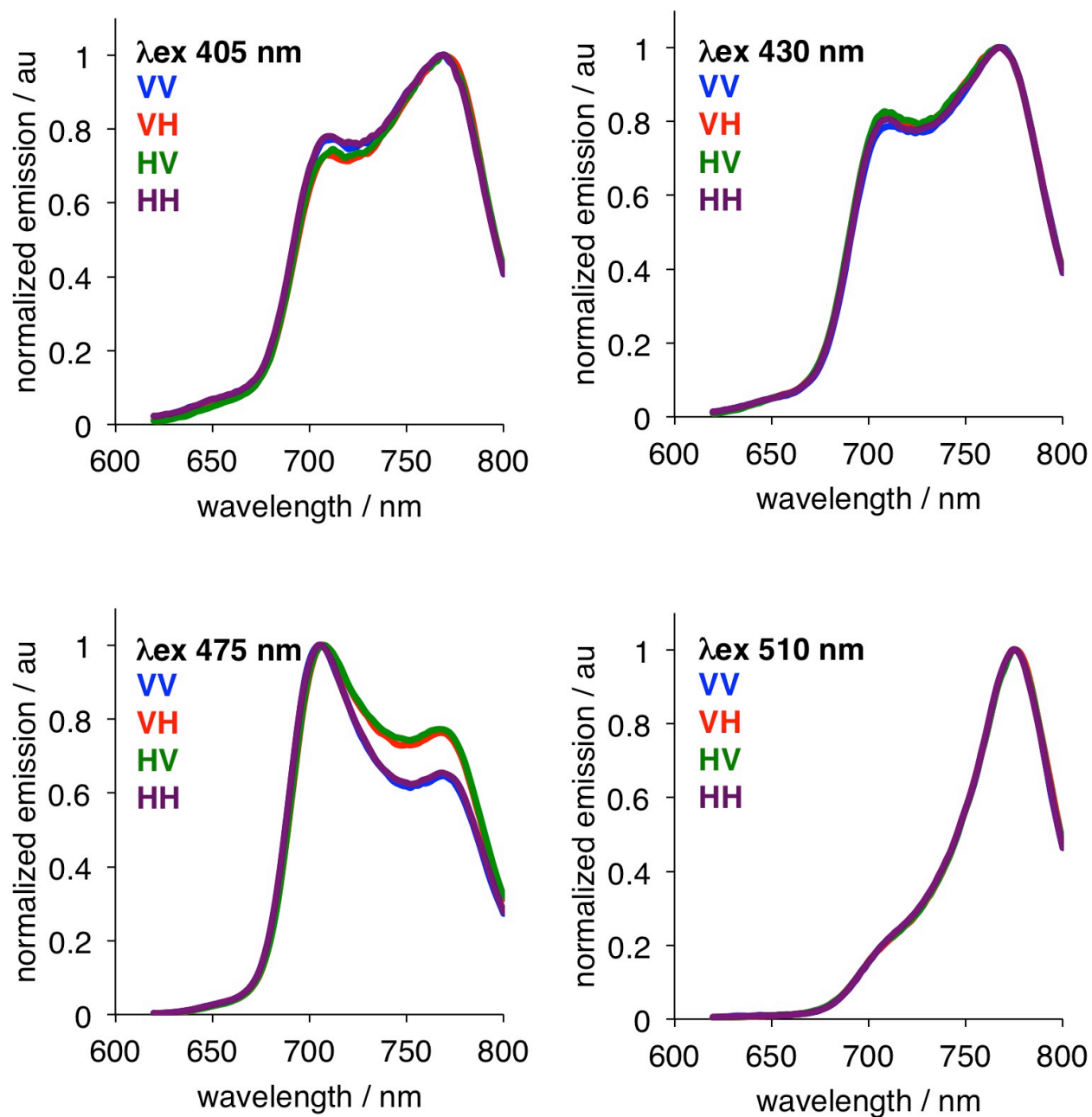3x hot: stretched to 300% – 15mm;
4x hot: stretched to 400% – 20mm.
        Hot: stretching is done at 70 ± 1 ^{o}C.

Figure S3: Fluorescence lifetimes of **PD** in ethanol, glycerol and PVA.
A: λex: 475 nm, λobs: 720 nm
B: λex: 475 nm, λobs: 780 nm

Figure S4: Emission spectra of **PD** in non-stretched (5mm) PVA various excitation wavelengths (λex: 405 nm, 430 nm, 475 nm, 510 nm).
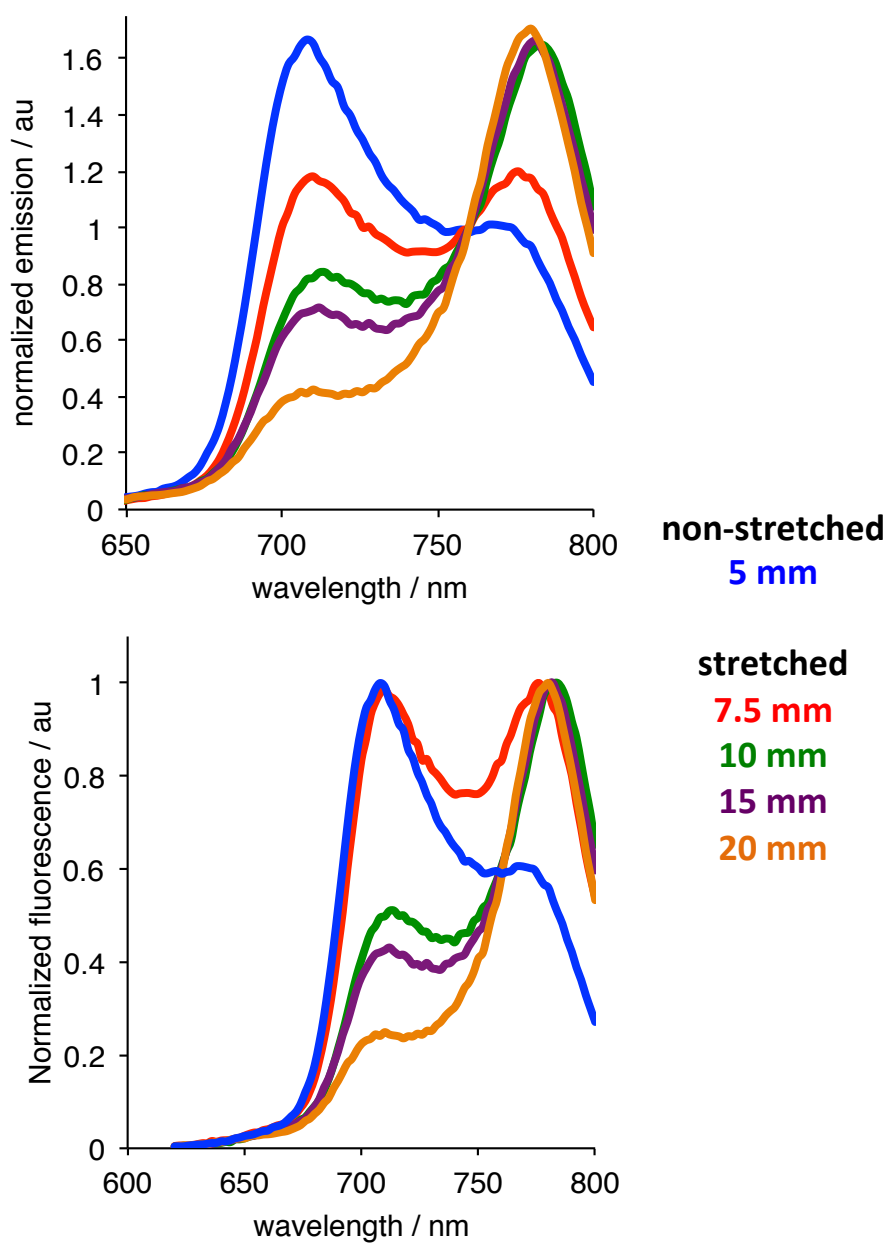
Orientation of the polarizers at excitation/detector:
VV – vertical/vertical
VH – vertical/horizontal
HV – horizontal/vertical
HH – horizontal/horizontal

Figure S5. Fluorescence spectra as a function of stretching.
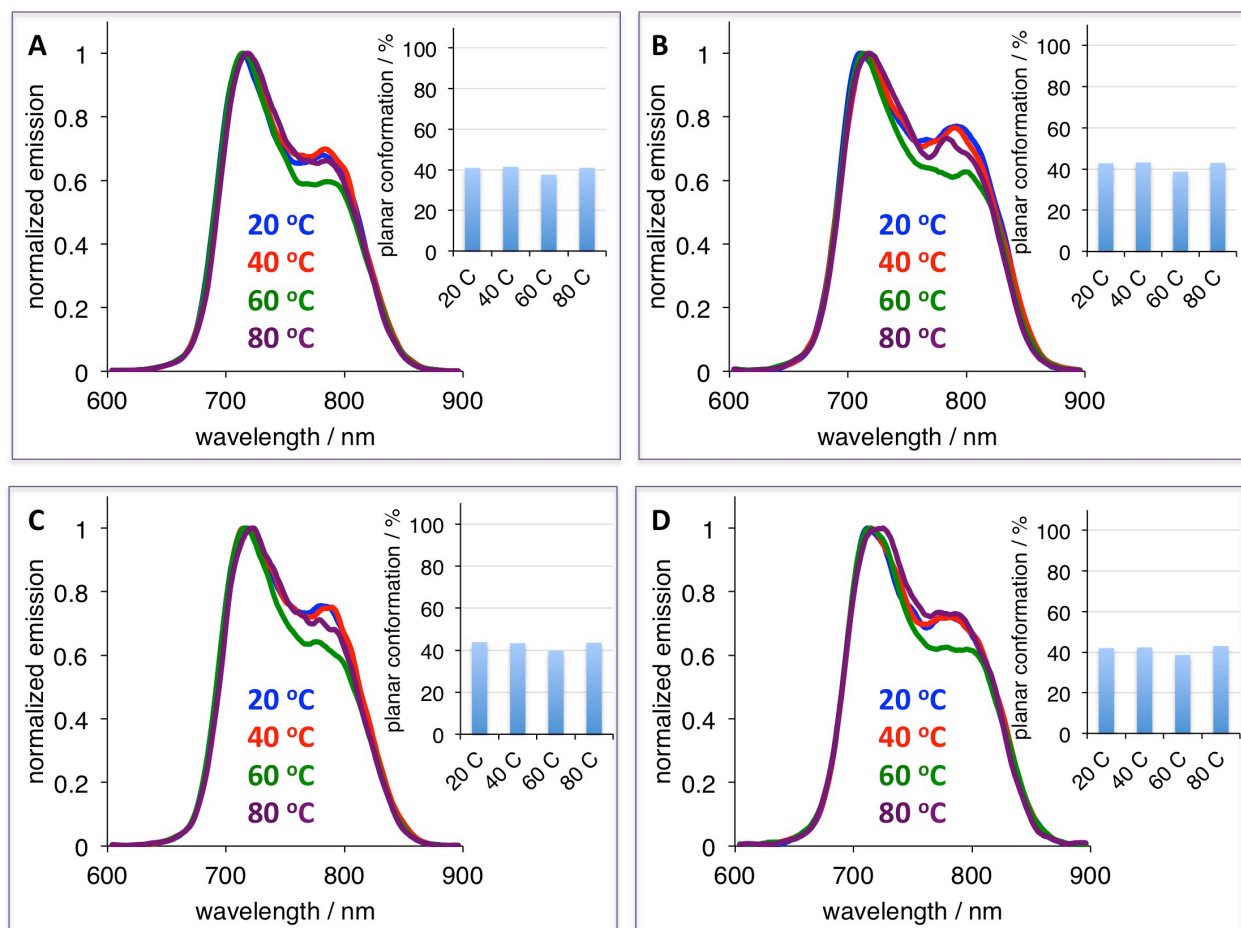
Top: normalization is done at 760 nm.
Bottom: normalization is done at the emission maximum.

λex = 475 nm;
Orientation of the polarizers at excitation/detector: VV – vertical/vertical;
Films were stretched at 70 ± 1 °C.

Figure S6. Effect of temperature on the emission spectra of **PD** in non-stretched PVA film. Insets: Percent of planar **PD** confirmation (at 780 nm) as a function of temperature (20, 40, 60 and 80 $^{\circ}$C).
A: VV; **B**: VH; **C**: HV; **D**: HH

Orientation of the polarizers at excitation/detector:
VV – vertical/vertical
VH – vertical/horizontal
HV – horizontal/vertical
HH – horizontal/horizontal

Figure S7: Emission spectra of **PD** in thermo-stretched (200%, 10 mm) PVA at various excitation wavelengths (λex : 405 nm, 430 nm, 475 nm, 510 nm).
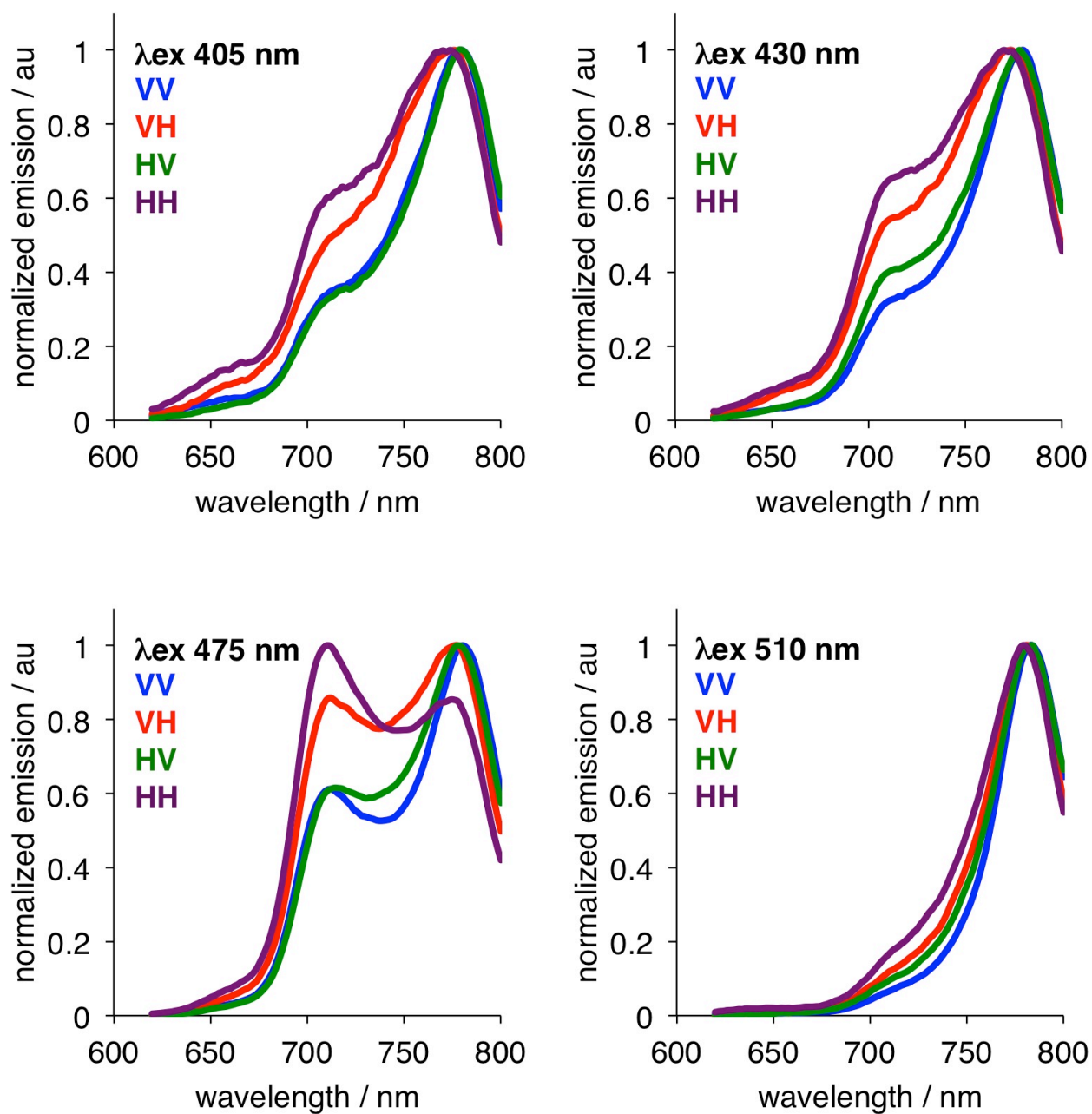Film was stretched at 70 ± 1 ^{o}C.

Orientation of the polarizers at excitation/detector:
VV – vertical/vertical
VH – vertical/horizontal
HV – horizontal/vertical
HH – horizontal/horizontal

Figure S8: Emission spectra of **PD** in thermo-stretched (300%, 15 mm) PVA at various excitation wavelengths (λex : 405 nm, 430 nm, 475 nm, 510 nm).
Film was stretched at 70 ± 1 °C.

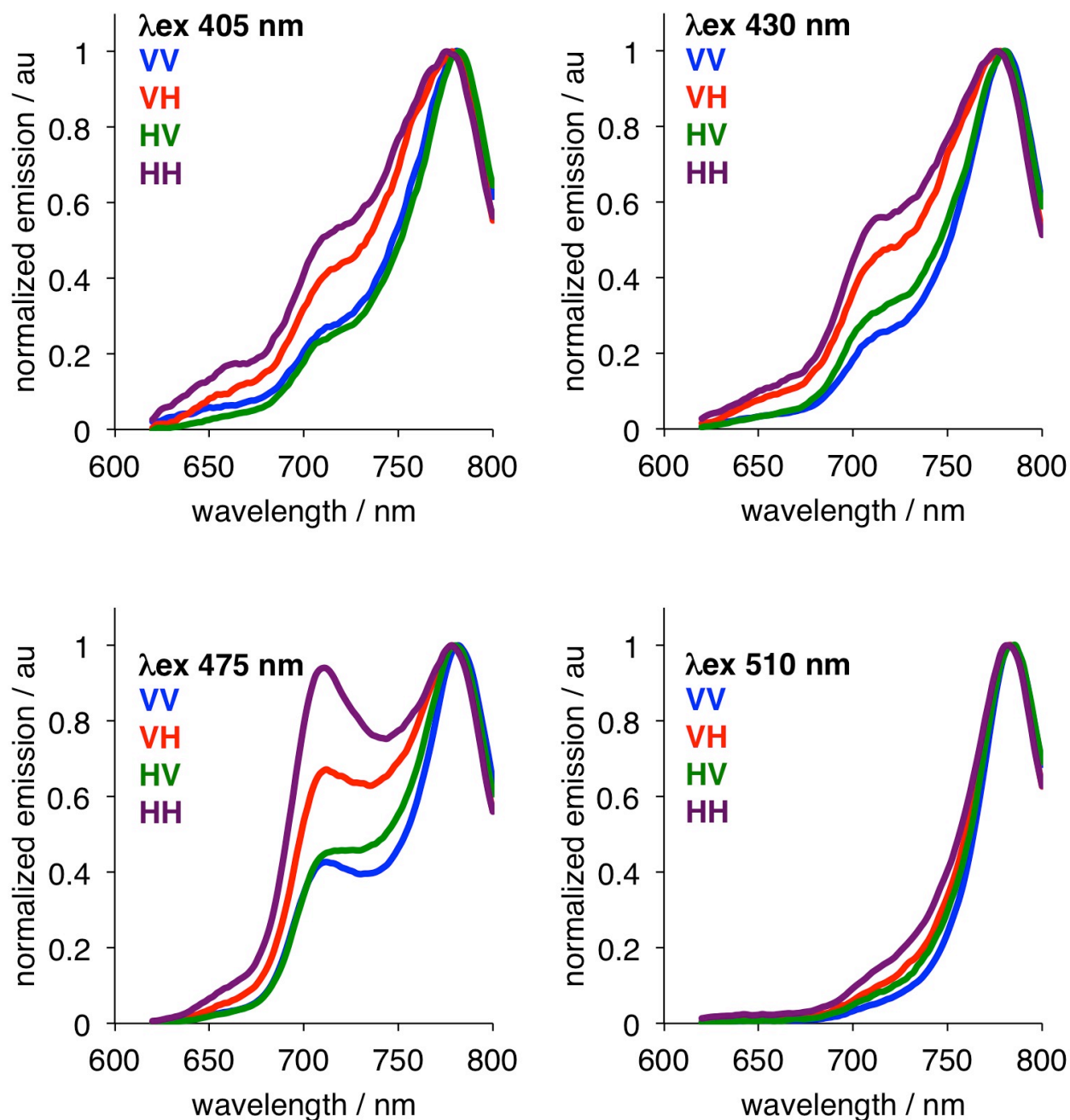Orientation of the polarizers at excitation/detector:
VV – vertical/vertical
VH – vertical/horizontal
HV – horizontal/vertical
HH – horizontal/horizontal

Figure S9: Emission spectra of **PD** in thermo-stretched (400%, 20 mm) PVA at various excitation wavelengths (λex : 405 nm, 430 nm, 475 nm, 510 nm).

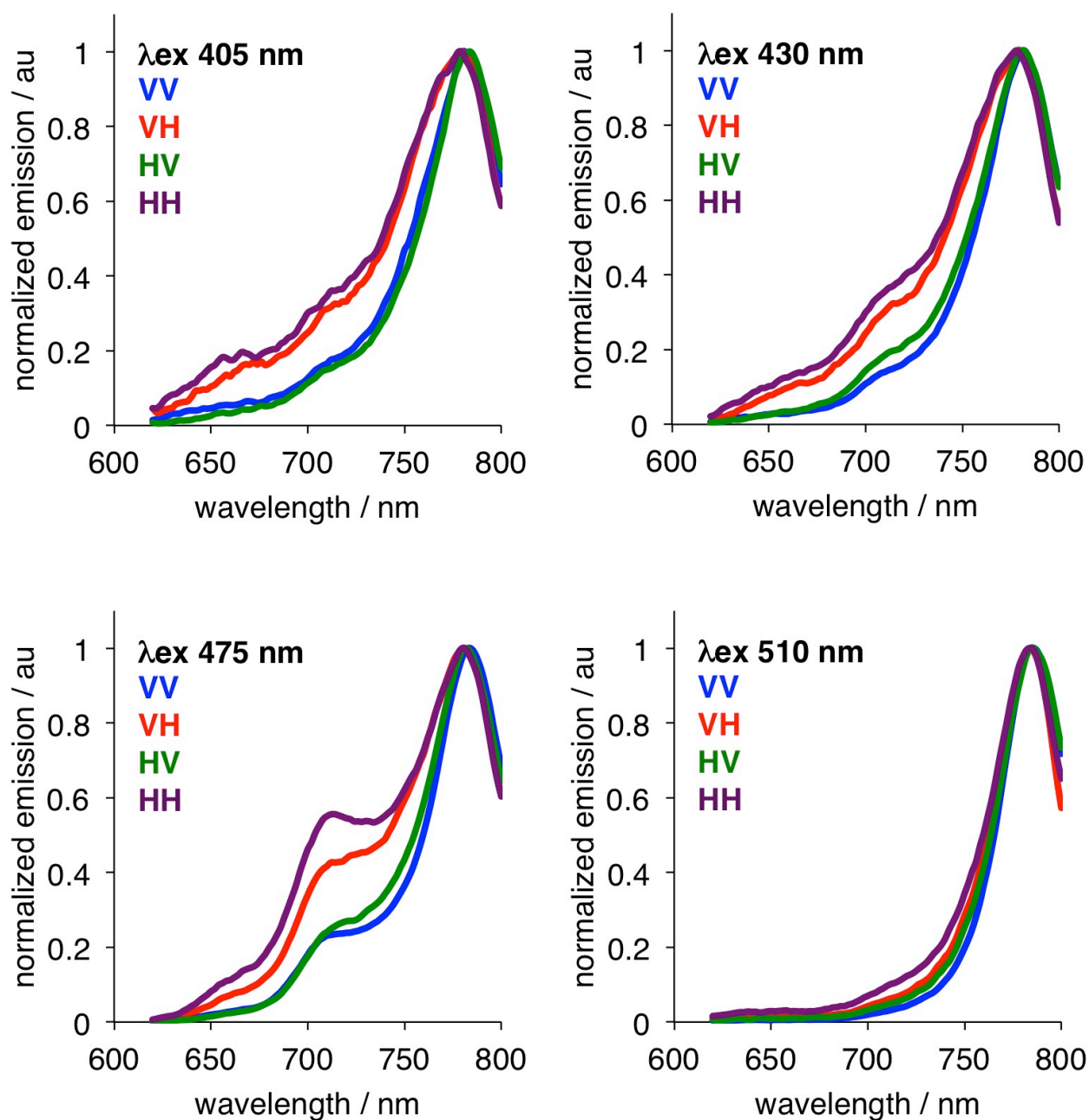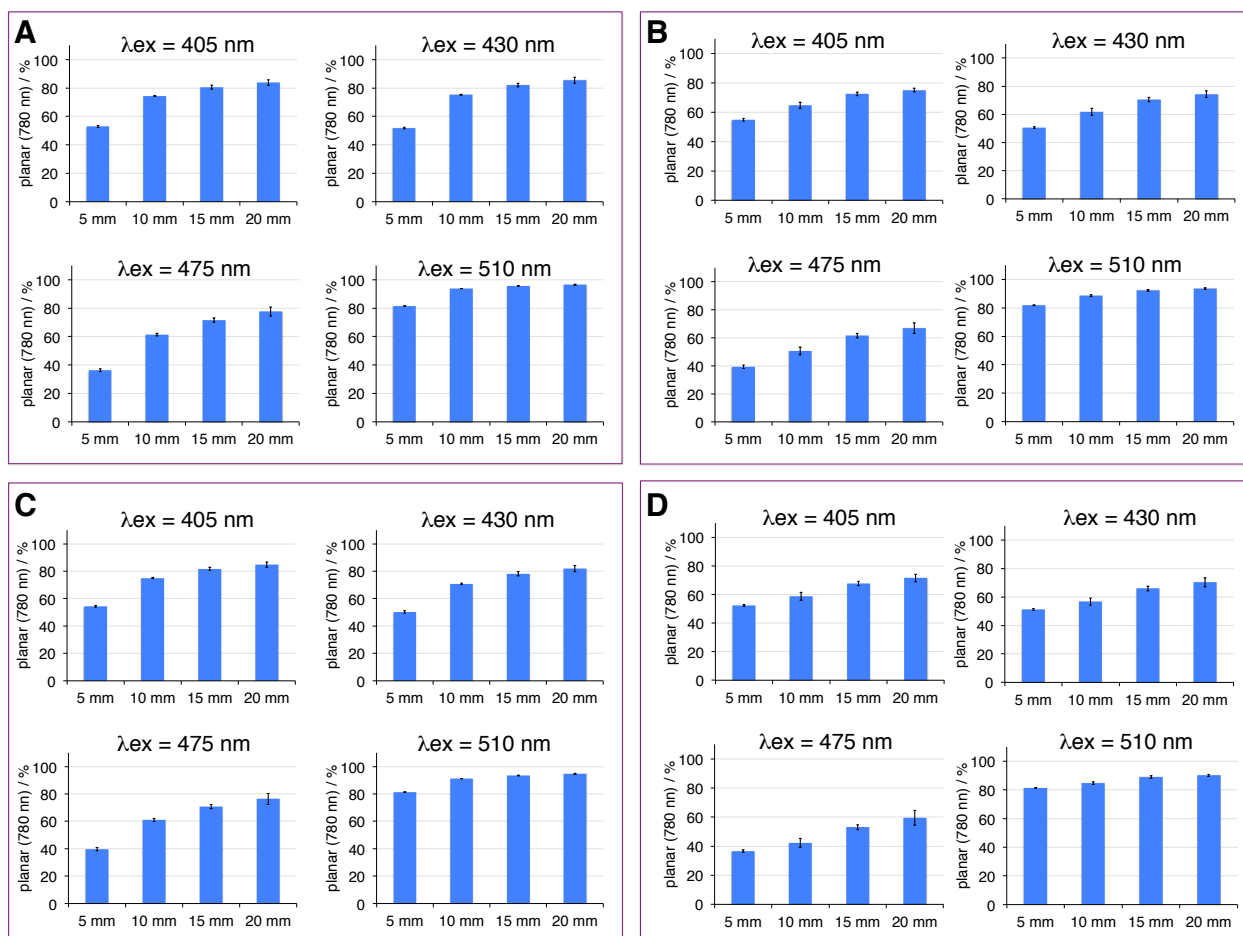Film was stretched at 70 ± 1 $^{\circ}$C.
Orientation of the polarizers at excitation/detector:
VV – vertical/vertical
VH – vertical/horizontal
HV – horizontal/vertical
HH – horizontal/horizontal

Figure S10. Percent of planar conformation of **PD** as a function of stretching at various λex.
Orientation of the polarizers at excitation/detector:
A: VV – vertical/vertical
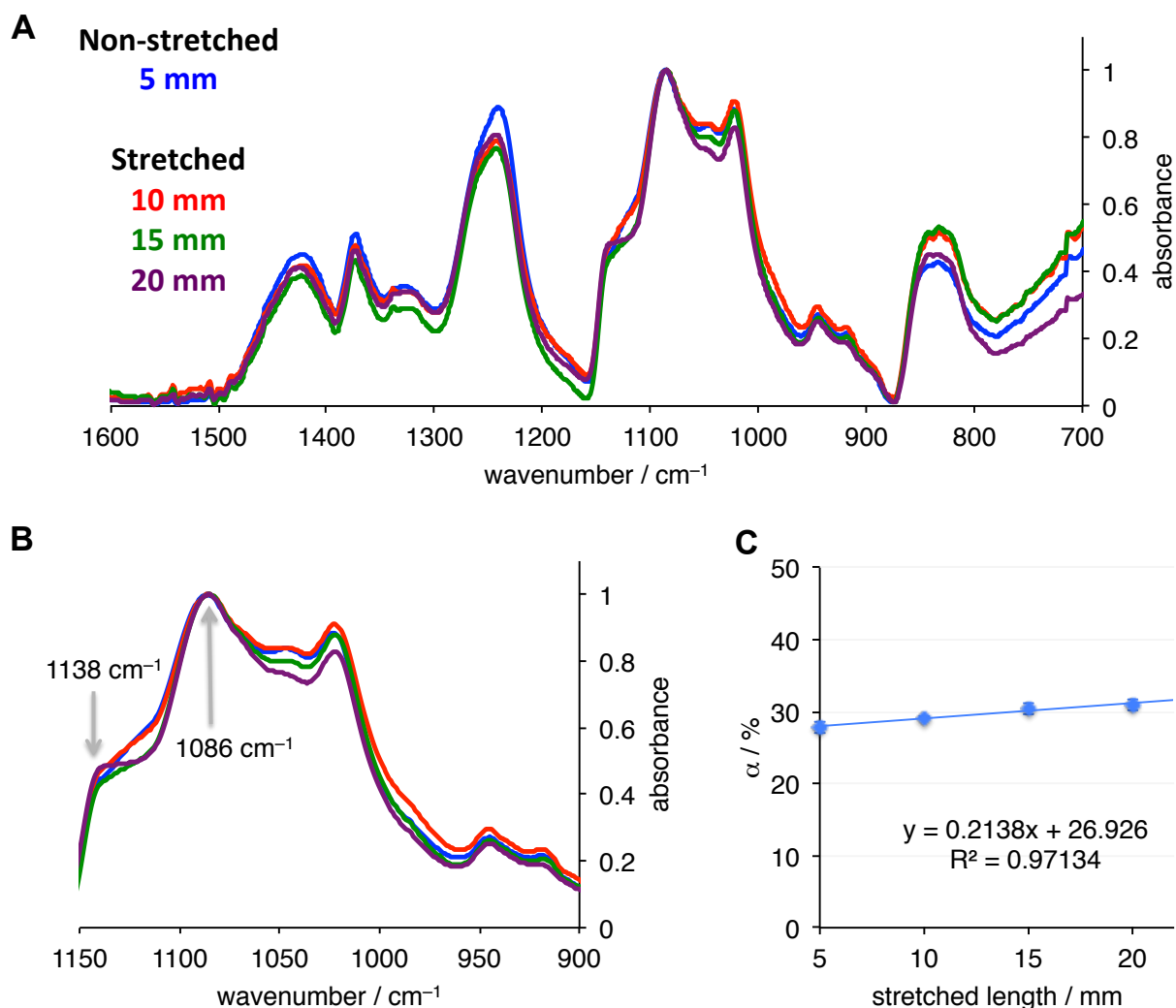**B**: VH – vertical/horizontal
C: HV – horizontal/vertical
D: HH – horizontal/horizontal

Non-stretched: 5 mm film; thermo-stretched**:** 10, 15, 20 mm film.
Data presented as the average of two independent measurement (*i.e.*, two preparations of the **PD**/PVA films) ± SD. Stretching was done at 70 ± 1 °C.

Percent of planar conformation is calculated as described in materials and methods.

Figure S11. ATR-FTIR spectra of PVA films and estimated crystallinity.

Non-stretched (5 mm) and stretched (10, 15, 20 mm corresponding to 200, 300 and 400%, respectively) films.

A: FTIR spectra of non-stretched and stretched PVA films. The spectra were normalized to the intensity at 1086 cm^{-1}.

B: Expanded region of the FTIR spectra with the labeled peaks used for the determination of crystallinity.

C: Crystallinity as a function of stretching; crystallinity was calculated using the equation provided in ref. 4: α % = −13.1 + 89.5 * (A_{1138}/A_{1086}); where α is the crystallinity content, A_{1138} and A_{1084} are the intensities at 1138 and 1084 cm^{-1}, respectively. A_{1138} and A_{1084} were used here, although A_{1141} and A_{1094} were used in ref. 4. A_{1138} and A_{1086} are the most prominent peaks. Notably, using A_{1141} and A_{1094} gave similar results in regard to the crystallinity content.

References

1. (a) M. Balaz, H. A. Collins, E. Dahlstedt and H. L. Anderson, *Org. Biomol. Chem.* 2009, **7**, 874; (b) L. P. Jameson, J. D. Kimball, Z. Gryczynski, M. Balaz and S. V. Dzyuba, *RSC Adv.* 2013, **3**, 18300.

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