Aligning Self-Assembled Perylene Bisimides using a Magnetic Field

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SUPPORTING INFORMATION

Contents:

Materials	S2
Instruments and Procedures	S2
Supplementary Figures	S6
References	S15

Materials

PBI-A was synthesised as reported previously.¹ All other materials were purchased from commercial sources and distilled water was used throughout.

Instruments and Procedures

Nuclear Magnetic Resonance Spectroscopy (NMR)

²³Na spectra were recorded at 105.86 MHz (²³Na) with 1024 scans, a sweep width of 10 kHz, a 33 μ s pulse (90 degrees) and a signal acquisition time of 0.3 s, giving a total acquisition time of 6 minutes. All samples were freshly pipetted from the vials into 5 mm NMR tubes and the spectra taken at 298 K, 20 minutes after magnetic field exposure. No significant changes were apparent in the spectra taken after 5 and 90 minutes magnetic field exposure, so structural alignment occurs quickly.

Preparation of Solutions

The PBI-A was added to 2 mL of water with an equimolar amount of sodium hydroxide (0.1 M, aqueous) to a concentration of 5 mg/mL. The solution was stirred until all the PBI-A was dissolved.

Preparation of samples on glass slides

Samples were prepared by dropping 20 μ L of the PBI-A solution onto a glass microscope slide and then leaving overnight to dry in air.

Rheological Measurements

Viscosity measurements were performed using an Anton Paar Physica MCR301 rheometer. with a 75 mm cone and plate measuring system. 1 mL of the solutions were transferred onto the plate for measurement. All experiments were performed at 25 °C. The viscosity of each solution was recorded under the rotation shear rate varying from 1 to 100 s⁻¹.

pH Measurements

A FC200 pH probe (HANNA instruments) with a 6 mm x 10 mm conical tip was used for pH measurements. The stated accuracy of the pH measurements is ± 0.1 . The temperature was maintained at 25 °C during the titration by using a circulating water bath.

Scanning Electron Microscopy

SEM images were obtained using a Hitachi S-4800 FE-SEM. Solutions at high pH were deposited onto glass cover slips which were stuck onto aluminum SEM stubs and left to dry for 24 hours. Image analysis used for fibre width measurements was carried out using ImageJ software. 70 images collected from SEM were collected and the average and standard deviation calculated and a histogram plotted from these measurements.

Optical Microscopy under Cross-Polarised Light

Optical microscope images were collected using a Nikon Eclipse LV100 microscope with a Nikon TU Plan ELWD 50x/0.60 lens attached to an Infinity2-1C camera, with both polarizers in place. Samples for optical microscopy were prepared on glass microscope slides and allowed to dry for 24 hours before imaging.

Photoconductivity Measurements

Photoconductivity measurements were performed using an Autolab potentiostat operating in a two-electrode configuration in the absence of a supporting electrolyte. 10 μ L of solution was placed into a mask of 3x3 mm and left to dry overnight. Once dried the mask could be removed. A 365 nm LED (LedEngin Inc, LZ1-10U600) was by a power supply with a constant current of 0.7 A. Dark experiments were performed in an enclosure in air. Linear sweep measurements were recorded from -4 V to 4 V at a scan rate Each electrochemical data set is made up of 796 data points collected at a step potential of 0.01007 V and a scan rate of 0.10003 V/s and a preconditioning step at 0.002 V for 2 seconds. No linear fit has been added to the date. The silver electrodes were made using silver paste withattached copper wires to the glass slide, shown in Fig. S1. Epoxy resin glue was placed over the silver electrodes. Again, this was left to dry overnight.



Figure S1. Experimental set up for measuring the photoconductivity of dried solutions. The counter and reference electrode clips were connected to one copper wire and the working on the other copper wire to make a two-electrode experiment.

For directional dependence measurements silver electrodes were placed 3 mm apart parallel and perpendicular (at 90° compared to the aligned samples) to the alignment of the samples. For non-aligned samples electrodes were places left and right of the sample and at the top and the bottom of the sample as shown in the Fig. S2.



Figure S2. Experimental set up of conductivity of non-aligned samples. Silver electrodes are placed on all sides of the sample. Arrows indicate the direction of the measurement taken.

NMR Alignment

The superconducting magnet used was a wide bore 9.4 T magnet of a Bruker Avance II spectrometer. The shim stack was removed to widen the effective bore of the magnet and allow the sample to be brought closer to the magnet centre. The cradle in which the samples were placed was a 65 mm diameter plastic lid which is suspended by nylon threads (Fig. S3a and b). A Styrofoam insert was used to provide a level base. Glass slides were cut to length and stuck onto the Styrofoam with sticky tape, typically three at a time. 10 uL of **PBI-A** solution was pipetted and dropped onto slide from height of ca. 2 cm. The sample was lowered down until it rested on the top of the NMR probe (Fig. S3c below). The samples were left to dry for at least two hours in the field. They were in the magnet within three minutes of transferring solutions to slides. There was no temperature control, so samples were dried at ambient room temperature (19 ± 1 °C).



Figure S3. Photographs of (a) cradle with samples placed on glass slides. (b) cradle attached to fishing wire (c) cradle being lowered into the spectrometer. Please note: The shim stack on the spectrometer in the photograph has not been removed.

MRI alignment

MRI alignment was achieved using Bruker 7 T Avance III instrument using a 38 mm transmit/receive quadrature volume coil. 10 μ L of the **PBI-A** solution was pipetted into the centre of a quartz bottomed cell culture dish with the lid placed on top. These were then placed on the animal holder for the MRI scanner. These were sellotaped in place and the direction of the magnetic field written on each of the dishes. The samples were then moved into the centre of the magnetic field and left overnight to dry. The room was controlled to a temperature of 25 °C. The glass bottom of the dish could then be removed from the dish and the samples measured under the microscope, SEM and electrochemically.

Small Angle Neutron Scattering in the magnetic field

SANS measurements were performed using the D33 instrument (Institut Laue Langevin, Grenoble, France).²⁶ A neutron beam, with a divergence of $\Delta\lambda/\lambda = 10.2\%$, allowed measurements over a Q-range range of 0.002 to 0.18 Å⁻¹ using three instrument configuration;

for low Q data, a wavelength of 13 Å with the detector at 12.5 m; for middle Q data, 6 Å with the detector at 12.5 m; for high Q data, 6 Å and a 2 m detector distance. The data were fitted using Sasview.³

Supplementary Figures



Figure S4. Dynamic viscosity measurements of solutions of **PBI-A** at concentrations of 5 mg/mL (orange data), 10 mg/mL (black data), 20 mg/mL (purple data), 30 mg/mL (green data), 40 mg/mL (red data) and 50 mg/mL (blue data). All show shear thinning behavior.



Figure S5. SANS data from **PBI-A** at 30 mg/mL at 0T. The fit is shown in red over the top of the data (open circles).

Table S1. Summary of fit to the SANS data for the PBI-A solution at high pH at 30 mg/mL. The data were fitted to a power law in combination with a flexible elliptical cylinder model (available in SASView).

	PBI-A ^a	PBI-A ^b
Power Law	2.52 ± 0.00	2.32 ± 0.02
Axis Ratio	1.98 ± 0.00	1.96 ± 0.01
Kuhn Length / Å	282.1 ± 1.7	280.2 ± 35.1
Length / Å	> 1000	> 1000
Radius / Å	48.2 ± 0.1	50.9 ± 0.2
χ^2	6.9695	2.2984

^a Fit to data from the solution at 30 mg/mL in this work

^b Summary of data from fit to solutions of **PBI-A** at 5 mg/mL obtained previously.²



Figure S6. Histogram showing the distribution of fibre widths from 70 measurements of SEM images of PBI-A at 10 mg/mL. Measurements were carried out using ImageJ and average width and distribution plotted using Sigmaplot. Average width was 10.8 nm \pm 0.2.



Figure S7. Scattering patterns of a 30 mg/mL solution of **PBI-A** at different strength of magnetic field, from 0T to 8T. The scattering pattern elongate in the horizontal field direction, indicating alignment is occurring.



Figure S8. Scattering patterns of a 50 mg/mL solution of **PBI-A** at different strength of magnetic field, from 0T to 8T (magnetic field in the horizontal).



Figure S9. Scattering patterns of a 10 mg/mL solution of **PBI-A** at different strength of magnetic field, from 0T to 8T (magnetic field in the horizontal).



Figure S10. Graphs showing the degree of alignment vs. the magnetic field strength for 10 mg/mL (black data), 30 mg/mL (blue data) and 50 mg/mL (red data). Data shows the more concentrated the system the more alignment is achieved.



Figure S11. Overlay of SANS data from a solution of **PBI-A** at 30 mg/mL at 0T initially (black), after one cycle to 8T and back to 0T (red), and after two cycles to 8T and back to 0T (green). The data are so close as to make the overlays difficult to distinguish.



Figure S12. Optical microscope images of field-dried solution of **PBI-A** under cross-polarised showing magnetic alignment. Dried solutions from a concentration of (a) 10 mg/mL (b) 20 mg/mL (c) 30 mg/mL and (d) 50 mg/mL. Scale bar represents 50 µm.



Figure S13. (a) and (b) SEM images of a solution of **PBI-A** (prepared at 50 mg/mL) after drying not in a magnetic field. (c) and (d) SEM images of a solution of **PBI-A** (prepared at 50 mg/mL) after drying under a magnetic field. Scale bar for (a) and (c) represents 500 nm. Scale bar for (b) and (d) represents 2.5 µm.



Figure S14. Photoresponse of magnetic field dried solutions of **PBI-A** at (a) 5 mg/mL (b) 10 mg/mL, (c) 30 mg/mL and (d) 50 mg/mL. Black data is without light exposure and red data is under 365 nm light. Solid red data is perpendicular to and red dashed data is with alignment direction. In (c) the dark data cannot be seen as the red solid data is very similar and over the top of the black data.



Figure S15. (a) and (b) Optical microscope images under cross-polarised light of two different solutions of **PBI-A** at 5 mg/mL dried under a magnetic field with no or reduced alignement, respectively. Scale bar represents 50 μ m. (c) and (d) Photoresponse of the different samples dried under a magnetic field of a solution of **PBI-A** at 30 mg/mL with low or high degree of directional photoresistance, respectively. Black data is in the dark and red data is under 365 nm light. Solid red data is perpendicular and red dashed data is with alignment direction. In (d) the dark data cannot be seen as the red solid data is very similar and over the top of the black data.



Figure S16. The MRI scanner alignment process. (a) A sample of **PBI-A** is pipetted into the centre of a cell culture dish (b) the direction of the magnetic field is drawn on the sample dish and (c) placed into the MRI machine with the arrow in the direction of the magnetic field. (d) the sample is allowed to dry in the magnetic field overnight. Please note no mice were used or harmed in these alignment experiments.



Figure S17. (a) SEM image of a MR aligned film of **PBI-A** at 30 mg/mL. Scale bar represents 1 μ m. (b) Photoresponse of the different samples dried in MRI machine of a dried solution of **PBI-A** at 30 mg/mL. Black data is in the dark and red data is under 365 nm light. Solid red data is perpendicular and red dashed data is parallel to the alignment direction, respectively. In (b) the dark data cannot be seen as the red solid data is very similar and over the top of the black data.



Figure S18. Optical microscope images of dried solution of **PBI-A** under cross-polarised showing magnetic alignment. Dried solutions from a concentration of (a) 10 mg/mL (b) 50 mg/mL (c) 30 mg/mL and (d) 20 mg/mL. Scale bar represents 50 μ m.

References

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