

Supporting Information

Understanding the mechanism of nitroaromatic vapour uptake in PDMS-based pre-concentrators using 4-nitrotoluene

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Analyte Coil Calibration

The analyte coils were calibrated prior to use to determine the concentration of analyte delivered from the coil at a particular flow rate. The calibration was done using three volumetric flasks (10 mL) containing acetonitrile connected in series with Teflon tubing. The output from the analyte coil was bubbled through the acetonitrile in the first volumetric flask while the third flask was connected to the exhaust line. During the calibration, the nitrogen (at different flow rates) carrying the analyte (*p*NT) vapour was bubbled through the acetonitrile in each of the volumetric flasks for a specific duration (e.g., 3 min at 1000 mL/min). The three volumetric flasks were then topped up with pure acetonitrile to the calibration mark. The absorbance of the acetonitrile solutions was then measured. Most of the analyte was dissolved in the acetonitrile in the first volumetric flask with a negligible amount collected by the third volumetric flask, confirming the efficacy of this approach. Using the known molar extinction coefficient of the analyte, concentrations of the analyte in the acetonitrile solutions were calculated. The concentrations expressed in mol/L were then converted to mole fraction ppm. Figure S1 presents the concentration of *p*NT delivered from the coil at different flow rates. It should be noted that the amount of analyte delivered from the coil increased with flow rate, i.e., the concentration of the analyte approximately doubled when the flow rate increased from 250 mL/min to 1500 mL/min. Considering that the concentration increase was within an order of magnitude, the concentration of the analyte delivered at different flow rates were still comparable.

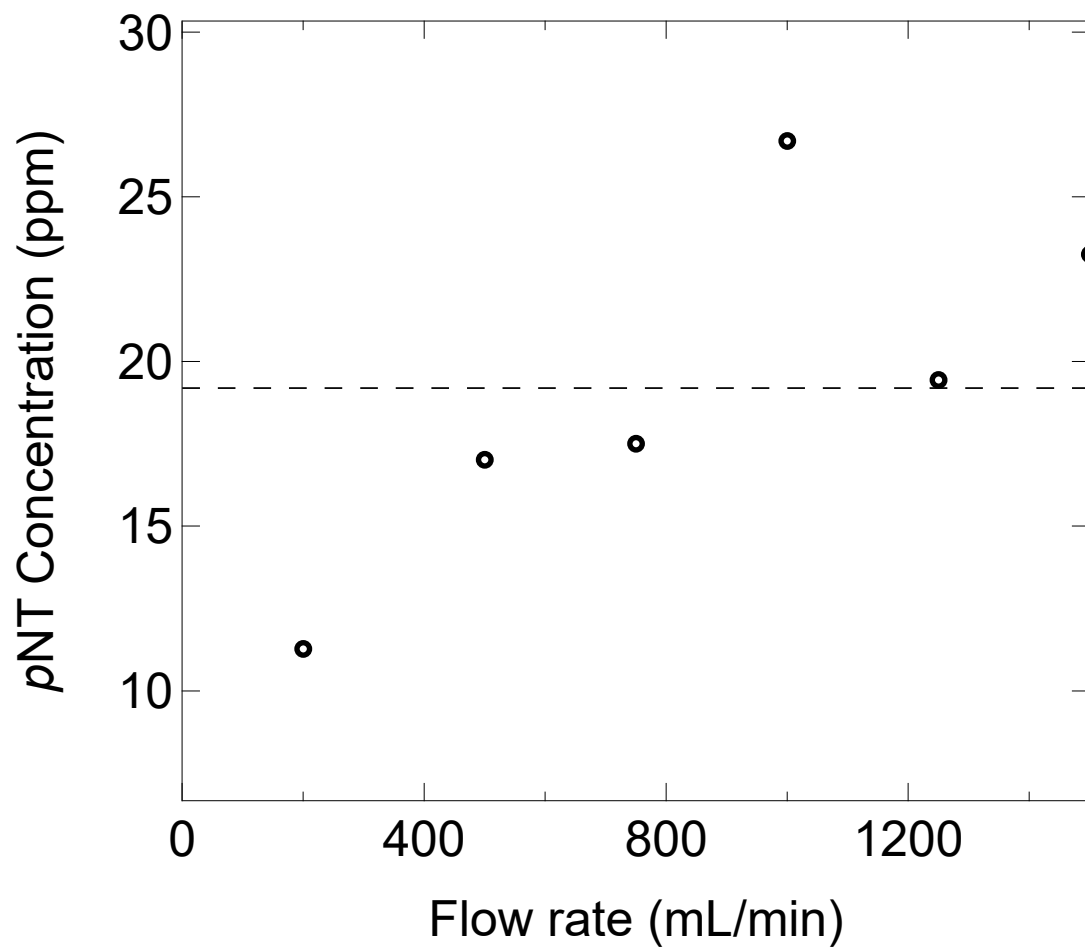


Figure S1. Concentration (mole fraction ppm) of *p*NT delivered from the coil versus the flow rate.

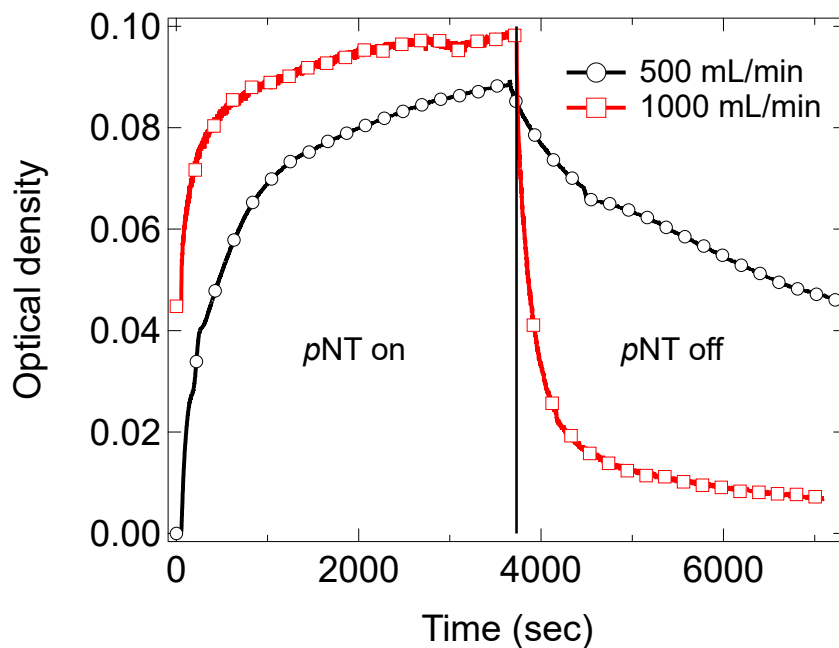


Figure S2. Measurement of the optical absorption of the *p*NT vapour in the sample chamber with no sample in place after 1 hour of analyte flow for flow rates of 500 and 1000 mL/minute. It can be seen that the flow rate of 1000 mL/minute allowed the concentration of *p*Nt in the sample chamber to reach equilibrium more rapidly. After 1 hour the MFC supplying *p*NT vapour source was turned off and only N₂ was passed through the sample chamber for 1 hour.

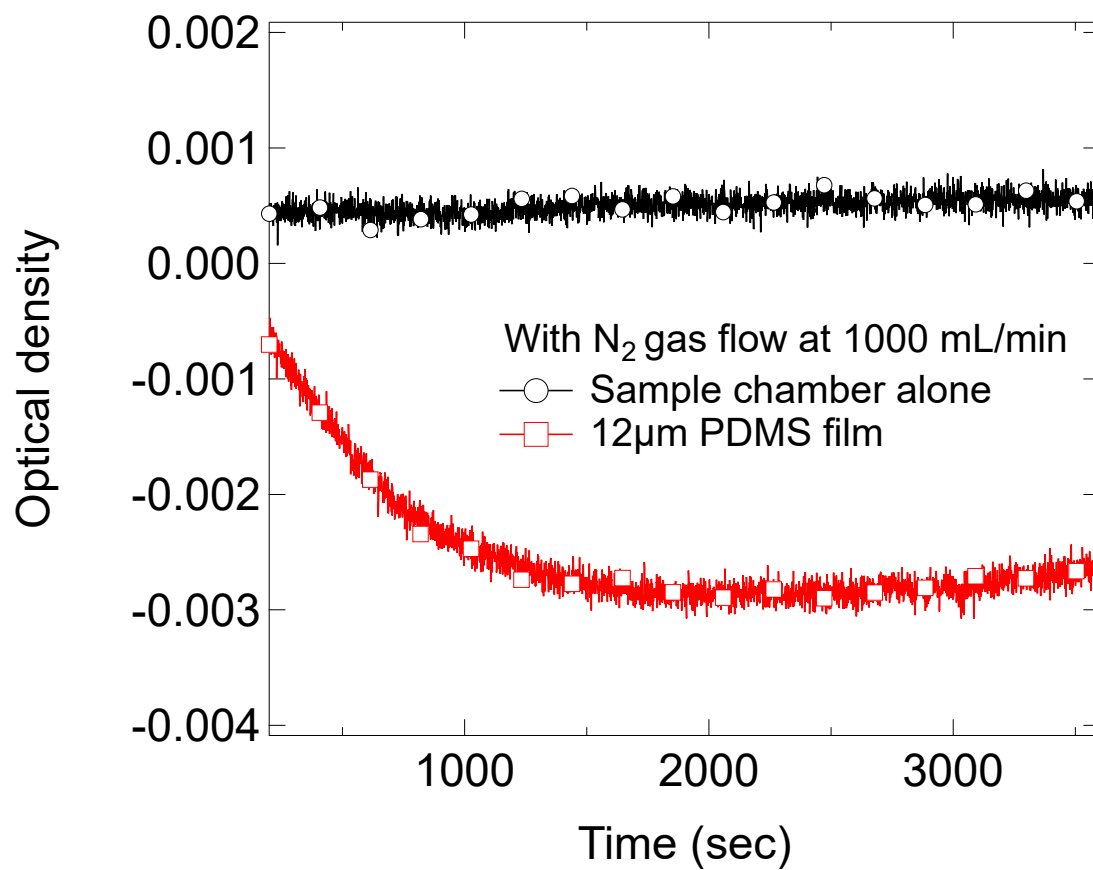


Figure S3. The optical density changes of the chamber alone and with a 12µm PDMS film over 1 h under a N₂ flow (1000 mL/min). The optical density was measured at 269 nm every second.

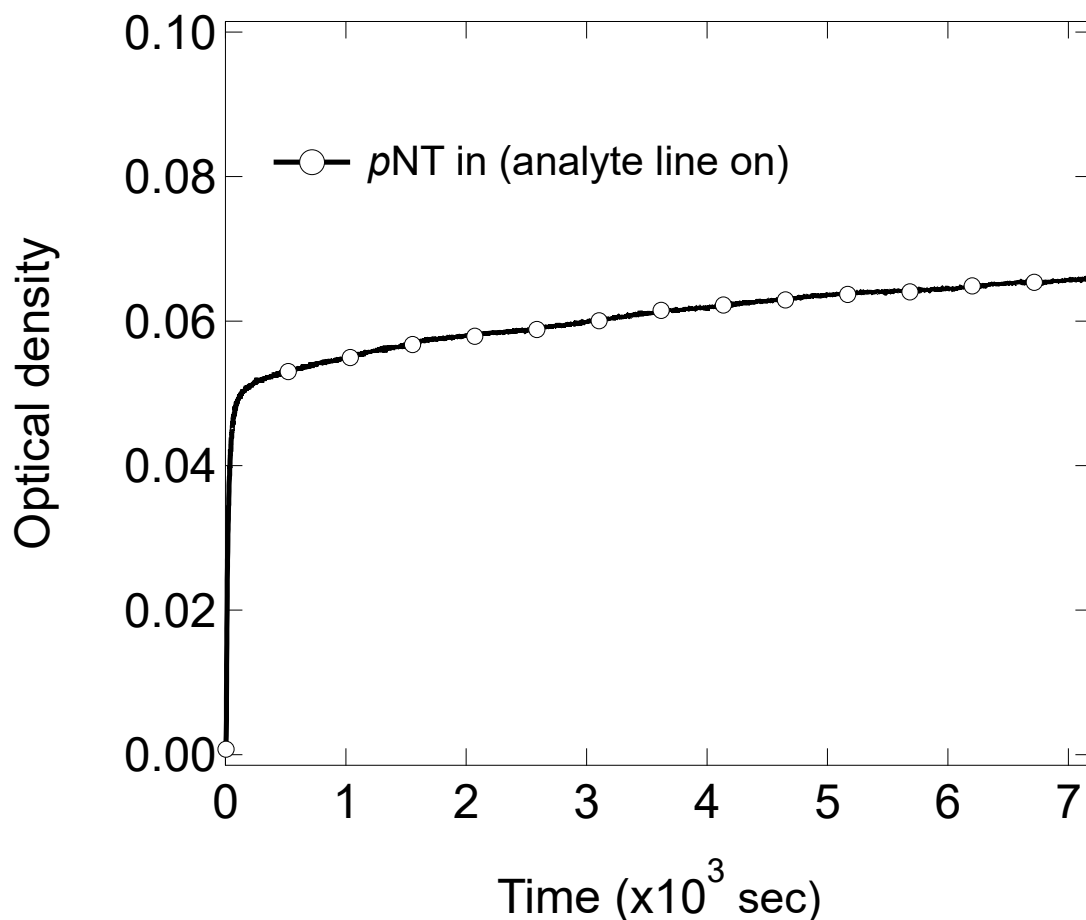


Figure S4. The optical density changes of the chamber alone over 2 h under a *p*NT vapour flow (1000 mL/min). The optical density was measured at 269 nm every second.

Supplementary Table 1. The *n* values of *p*NT sorption kinetics in PDMS, PDMS:DVB and PDM-co-DV film determined from fitting. The uncertainty of the average *n* value reflects the standard deviation.

	PDMS	PDMS:DVB	PDMS-co-DVB
<i>n</i> values	0.993 ± 0.002	0.993 ± 0.001	0.865 ± 0.004
	1.013 ± 0.006	1.073 ± 0.001	0.890 ± 0.002
	0.984 ± 0.001	0.910 ± 0.001	0.993 ± 0.002
	0.985 ± 0.001		
Average <i>n</i>	0.99 ± 0.01	0.99 ± 0.08	0.92 ± 0.07

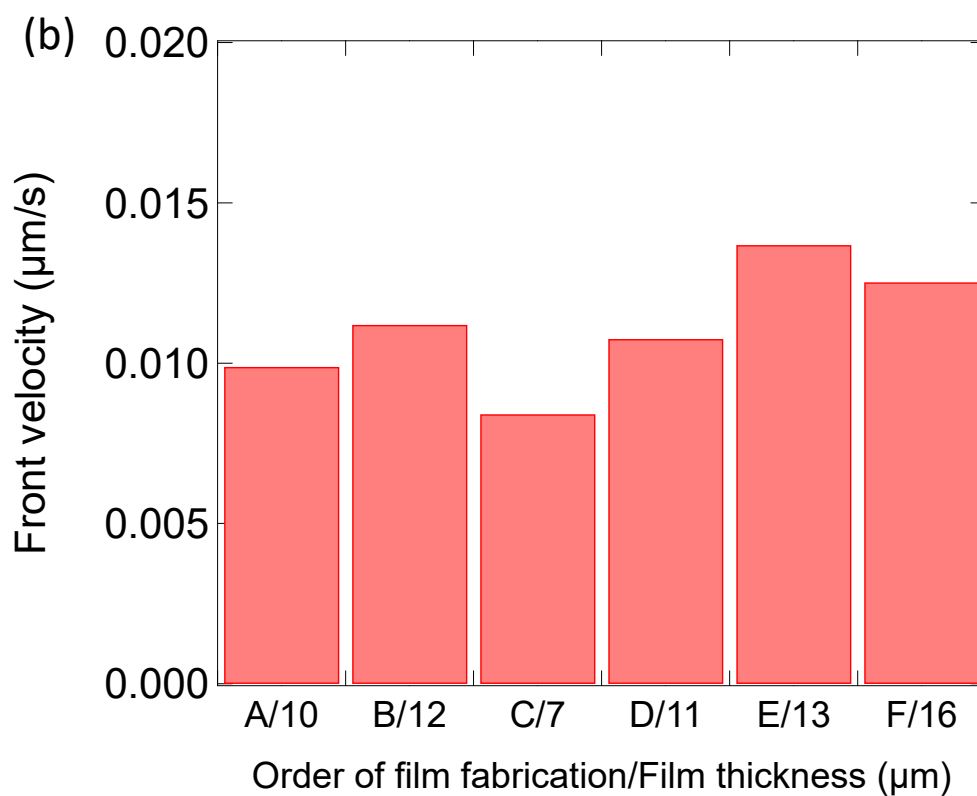
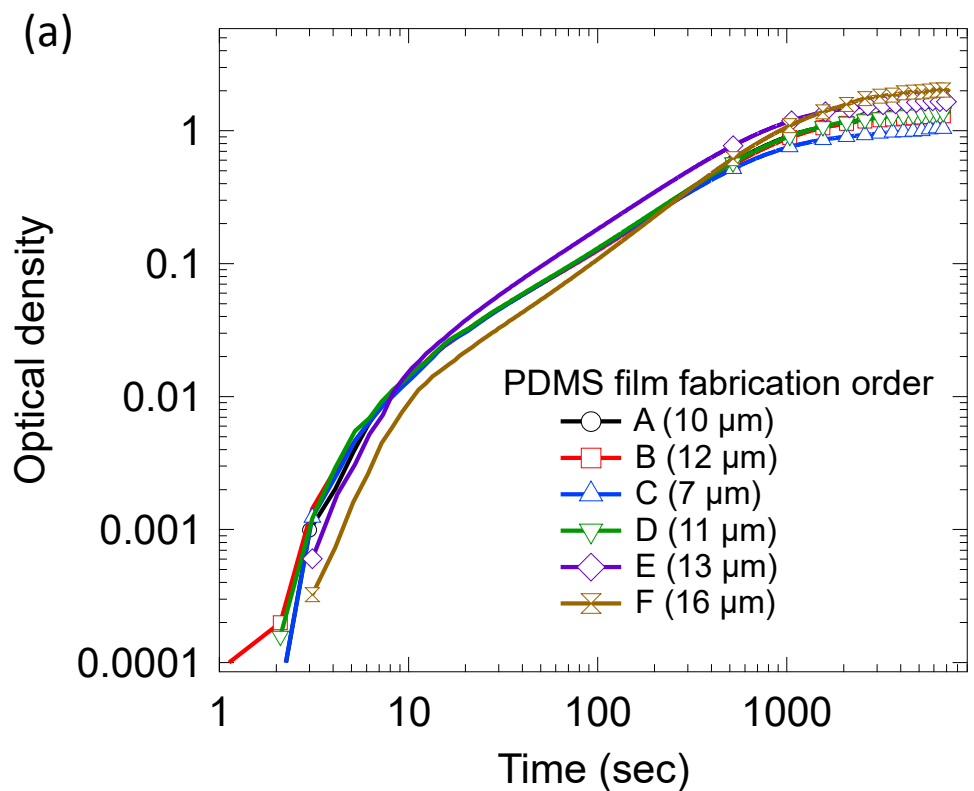


Figure S5. (a) Change in the optical density of the PDMS films of different film thickness upon *p*NT sorption over 2 hours measured every second and plotted in log scale; (b) Velocity of the *p*NT front in PDMS films arranged according to order of film fabrication.