

Supporting Information

Thermal control of organic semiconductors for trace detection of explosives

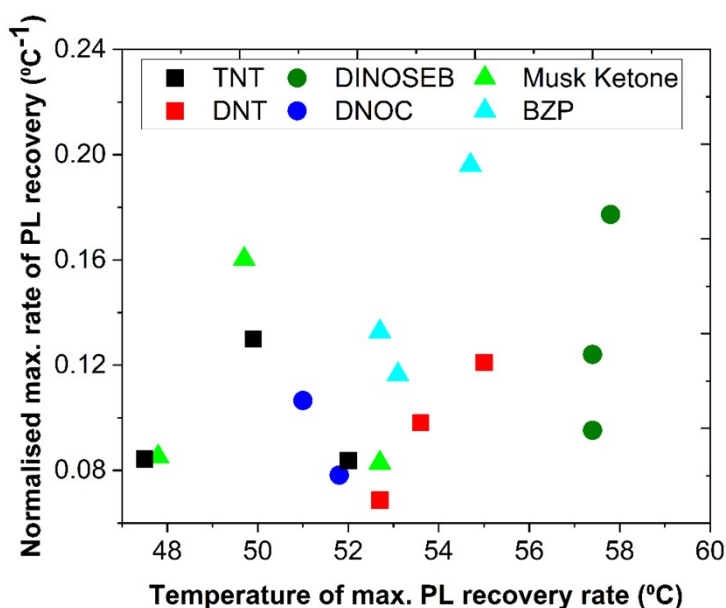
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SI1. Measurement of explosives and potential interferents

We have undertaken comparative measurements of the sensor response and recovery to a selection of analyte vapours including those of nitroaromatic explosives (DNT and TNT) and potential interferents of very similar molecular structure: agricultural pesticides 4,6-Dinitro-2-methylphenol (DNOC) and 2-*sec*-Butyl-4,6-dinitrophenol (DINOSEB), perfume musk ketone (4-*tert*-Butyl-2,6-dimethyl-3,5-dinitroacetophenone) and the non-aromatic molecule benzophenone (BZP). Following the same sensing and recovery protocol as described in the main paper, with an average temperature ramp of 1 °C/s, we measured the sensor quenching efficiency and subsequent recovery on heating. All molecules showed both a quenching of PL during vapour exposure and a subsequent recovery at elevated temperature.

Table SI1 summarises the measured quenching efficiency (expressed as a percentage of initial PL intensity), the gradient of peak recovery rate during heating (recovery rate expressed as a percentage of initial PL intensity per Kelvin); and the temperatures of the onset of PL recovery, of maximum recovery rate, and of complete PL recovery.

Figure SI1 plots the gradient of peak recovery (normalised to the room temperature quenching efficiency) against the temperature of peak recovery rate. Using this metric, we observe some discrimination between the various analytes, despite their very similar molecular structures. This indicates that the thermal release of sorbed analyte molecules has potential to be used in future to help classify/identify analyte vapours.

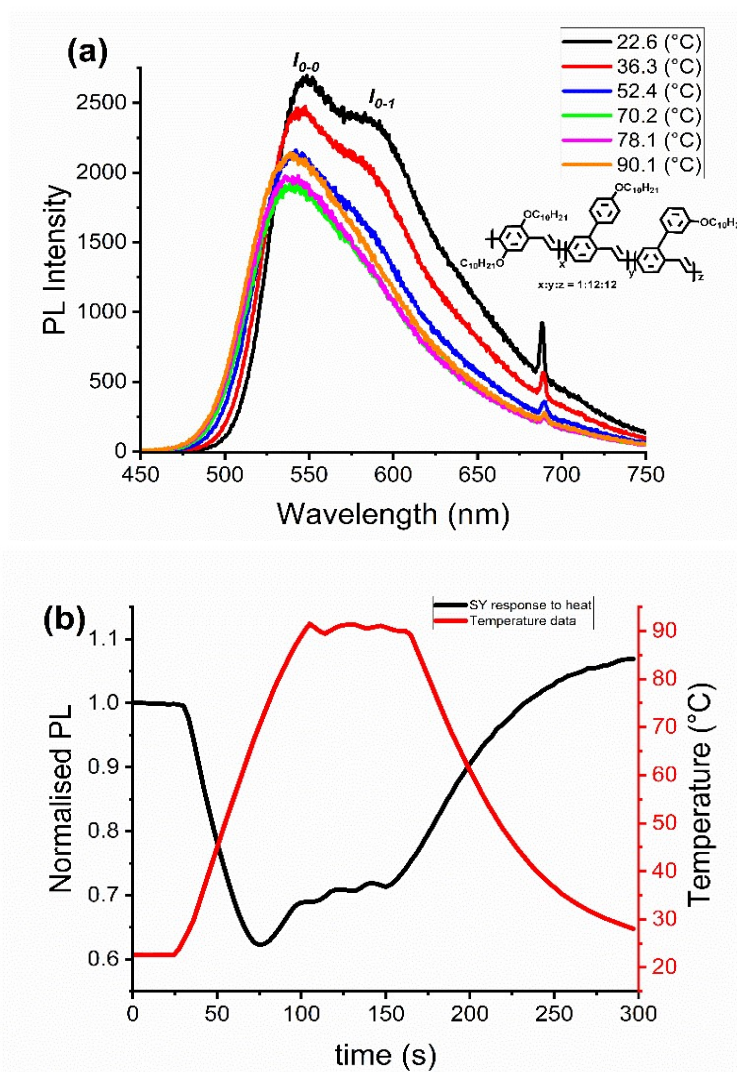


SI 1 – plot of normalised maximum rate of PL recovery vs temperature of peak PL recovery gradient for samples of average speed of 1 °C/s.

Table S11: SY sensor response to vapours of various analytes and thermal recovery

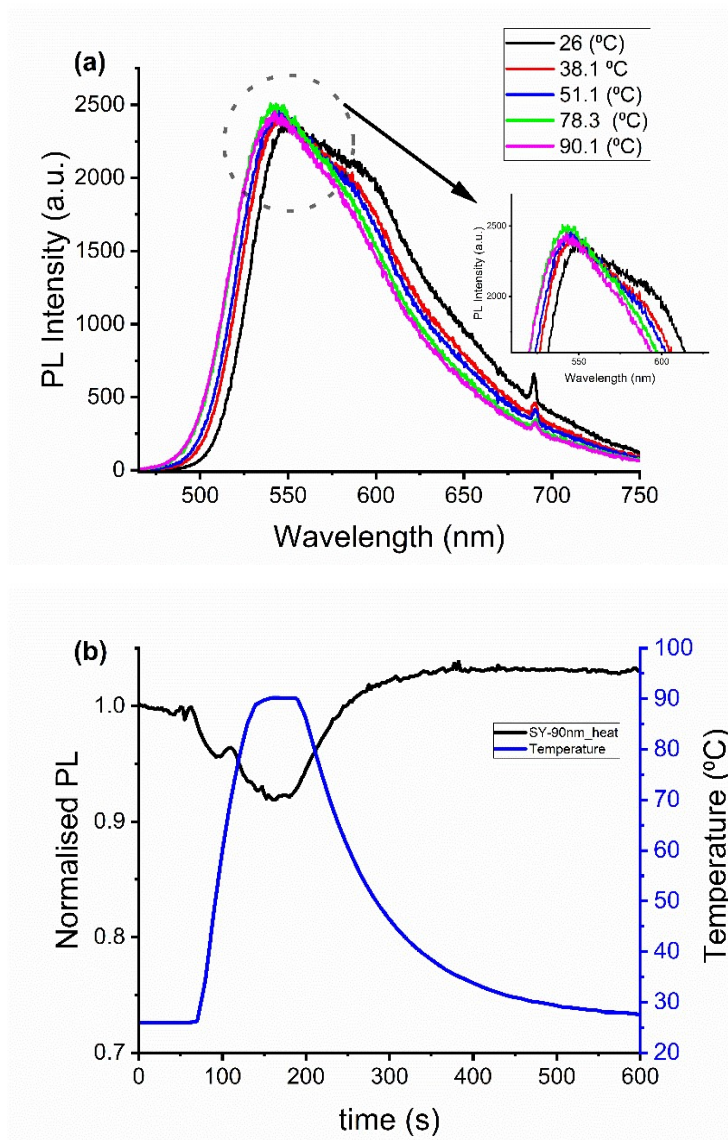
Analyte	PL quenched on exposure (%)	Temperature of recovery onset (°C)	Temperature of peak PL recovery (°C)	Maximum rate of PL recovery (%/(°C))	Temperature of peak PL recovery rate (°C)
Musk Ketone -1	8.1	41.8	57.7	0.69	47.8
Musk Ketone -2	7.8	44.0	61.7	1.25	49.7
Musk Ketone -3	6.4	44.3	62.4	0.53	52.7
DINOSEB -1	6.6	51.1	67.1	1.17	57.8
DINOSEB -2	5.4	51.3	67.3	0.67	57.4
DINOSEB -3	6.3	51.6	69.0	0.60	57.4
DNOC -1	7.6	42.0	64.0	0.81	51.0
DNOC -2	6.9	41.9	58.0	0.54	51.8
TNT -1	7.0	44.8	60.4	0.91	49.9
TNT -2	4.3	44.1	55.3	0.36	52.0
TNT -3	3.2	42.7	55.3	0.27	47.5
DNT -1	31.8	46.9	63.9	3.85	55.0
DNT -2	32.2	47.1	65.1	3.16	53.6
DNT -3	26.2	46.4	64.8	1.80	52.7
BZP -1	20.2	47.1	63.6	3.96	54.7
BZP -2	16.5	45.5	64.8	2.19	52.7
BZP -3	20.1	45.1	62.2	2.34	53.1

SI 2. Thermal response of a SY film prepared in air.



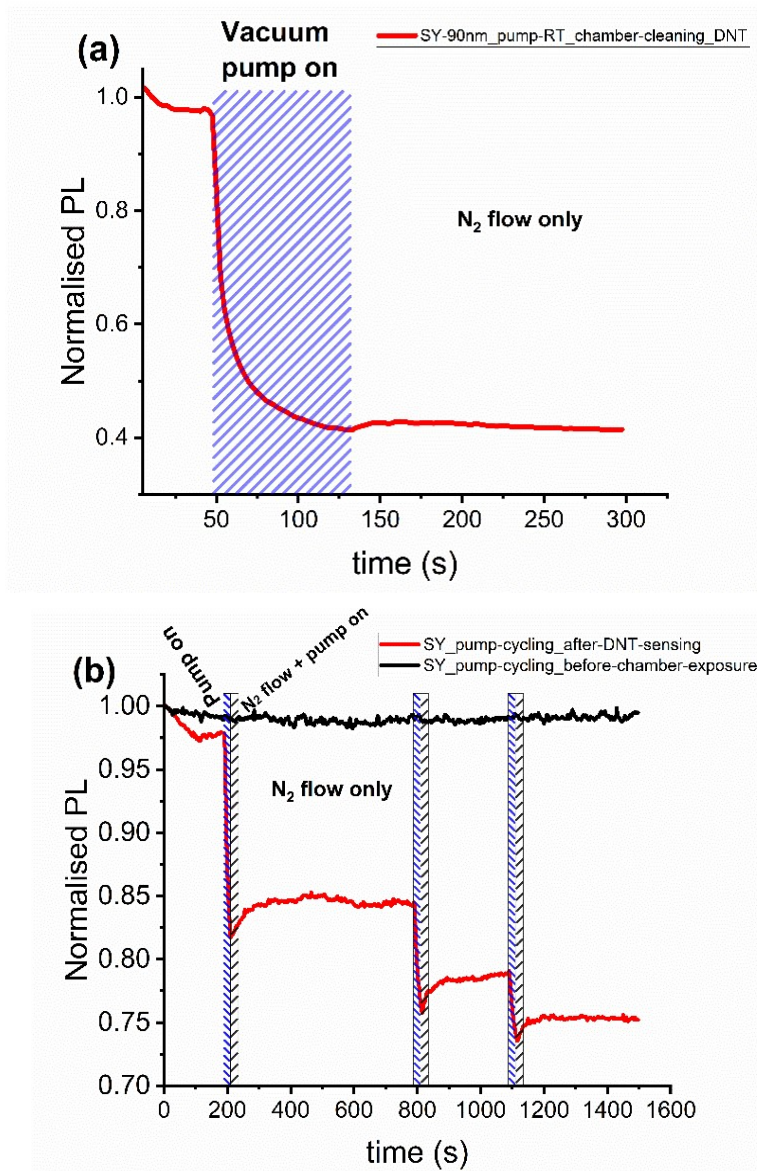
SI 2. (a) PL of 90nm SY film at a range of temperatures. The film was prepared in air without pre-annealing. (b) Normalised, spectrally integrated PL of SY data in (a), showing PL reduction due to heat and full PL recovery on cooling. There is an increase of 6% in the PL on cooling, which may be attributed to the SY chains reorganising their morphology and becoming more emissive, or the release of contaminants which was absorbed during storage of the film. Note that the films were stored in a nitrogen filled glovebox until usage.

SI 3. Thermal response of a SY film prepared in a nitrogen filled glovebox.



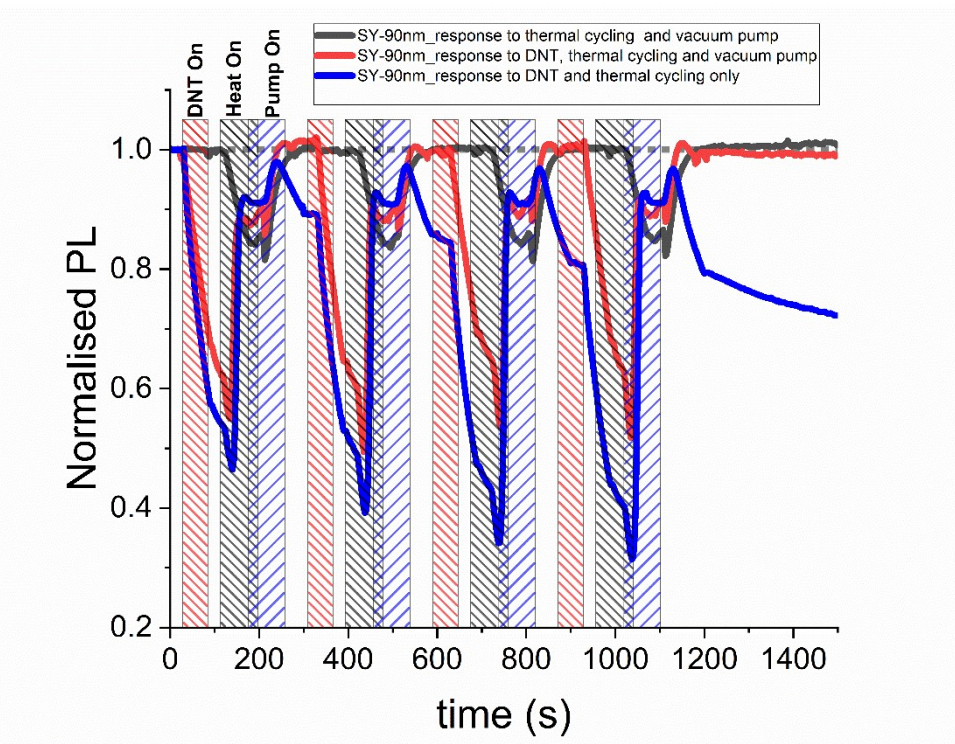
SI 3. (a) PL of 90nm SY film with respect to temperature. The film was prepared and pre-annealed in a nitrogen-filled glovebox. (b) Normalised integrated PL of SY data in (a), showing PL reduction due to heat and full PL recovery on cooling. There is an increase of 3% in the PL on cooling, which can also be attributed to the SY chains organising its morphology and becoming more emissive, or the release of contaminants which was absorbed during storage of the film. The contaminants may be degradation products of the solvents present in the glovebox.

SI 4. SY response to vacuum pumping of sensing chamber before and after sensing experiments.



SI 4. (a) Evacuating sensing chamber after experiment. Fluorescence quenching of SY film show that DNT molecules stuck on the inner walls of the pipe and chamber are desorbed at vacuum of $\sim 10^{-2}$ to 10^{-3} mbar. (b) SY response to vacuum pumping of the chamber in a clean nitrogen flow (black curve), the sensor is unaffected by the vacuum, indicating no adsorption of explosives on the walls of the tube and chamber. However, the response of SY to vacuum pumping in a post-sensing experiment (red curve), shows a drop in the PL when the chamber was pumped down to $\sim 10^{-2}$ mbar at 200, 800, and 1100 seconds respectively.

SI 5. Multiple uses of the SY sensors for DNT sensing using thermal control and with and without a vacuum pump



SI 5. Multiple uses of the SY sensors for DNT sensing using thermal control and a vacuum pump (red curve). The multiple uses of the SY sensor without a vacuum pump (blue curve) results in DNT poisoning of the SY film after each exposure and desorption cycle. The black curve shows the response of pristine SY film to multiple thermal and vacuum cycling.

References¹⁻⁶

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