Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supporting Information

Photographing the Synergy between Magnetic and Colour Properties in Spin Crossover Material [Fe-(NH_2trz)$_3$](BF_4)$_2$: A Temperature Sensor Perspective

Alejandro Lapresta-Fernández,*[a] Silvia Titos-Padilla,[b] Juan Manuel Herrera,[b] Alfonso Salinas-Castillo,[a] Enrique Colacio[b] and Luis Fermín Capitán Vallvey[a]

Experimental

Apparatus and Software. A Canon PowerShot G12 digital colour photographic camera with a CCD 1/1.7-inch sensor with 10.0 megapixels (Canon Europe, Amstelveen, The Netherlands) equipped with an 8 GB memory card was used to record colour images. Two ultra bright 4W lamps with 60 LED each (6500k) were used to illuminate the optical sensors (Atmoss Lighting, Alicante, Spain). To maintain a constant geometry, the camera was mounted next to a homemade chamber (see Fig S.1). Adobe Photoshop CS3 Extended ver. 10.0 (Adobe System Inc. San Jose, California, USA) was employed as software to obtain the histograms of the images. Later statistical calculations were performed with Excel software (Microsoft, Redmond, WA, USA) and OriginPro v8.0724 (Northampton, MA, USA). A controlled temperature cabinet with a (+50 to -50C) temperature range (refrigerant SUVA HP62 (R-404) A and Zerol ester oil ISO-22) from Revco (Thermo Fisher Scientific Inc. UK) were used. Magnetic measurements were carried out with a Quantum Design (SQUID) magnetometer MPMS-XL-5 with an applied field of 10000 G (0.1 T) with a heating and cooling sweep rate of 10 K mim^{-1}.

Reagents and materials. To prepare the optode films, poly(vinylchloride) (PVC; high molecular weight), polystyrene (PS, average MW 280,000, Tg: 100 ºC, GPC grade), Poly(methyl methacrylate) (PMMA, average MW 15,000, Tg: 105 ºC, GPC grade), Nafion and tetrahydrofuran (THF) were acquired from Sigma, toluene from Lab-Scan (Dublin, Ireland). A 6 % solution of D6 polyurethane hydrogel (Tyndale Plains-Hunter L.D. Lawrenceville, NJ, USA) in 90% ethanol:water mixture was used. The following octahedral coordination compound was synthesised according to reference[1]: $[Fe(NH_2\text{-}trz)_3](BF_4)_2$. Sheets of Mylar-type polyester (Goodfellow, Cambridge, UK) were used as support for the sensor membranes. The chemicals used were of analytical-reagent grade and the water used for preparing solutions was purified with a Milli-RO 12 plus Milli-Q water system (Millipore, Bedford, MA).

Test zone preparation of the temperature sensor. On a Mylar support (14 mm x 40 mm x 0.5 mm thick) we placed an array of 4 test zones (10 mm in diameter and around 5 μm in thickness each after solvent evaporation), depositing 25 μL using a dip-coating technique. Temperature-sensitive sensors were made from 2 cocktails containing: 1) 50.00 mg of PMMA, 50.00 mg of $[Fe(NH_2\text{-}trz)_3](BF_4)_2$ and 1mL of toluene, 2) 6 % solution of D6 in a mixture 9:1 ethanol:water and 50 mg of $[Fe(NH_2\text{-}trz)_3](BF_4)_2$

Imaging set-up. Parameters of the camera were set as follows: the digital camera lens with an aperture (F) 4.5; shutter speed 1/320 seconds; ISO sensitivity 100 and the white balance in the CCD chip setting was maintained constant.

Optical sensor composition: Sensors of different membrane polarities were studied containing 50.0 mg of SCO material. Thus, different mixtures of reagents (cocktails) were studied:

a) hydrophilic polymer: 6 % solution of D6 in a 9:1 ethanol:water mixture

b) mixed polarity, hydrophilic-hydrophobic nature: Nafion

c) hydrophilic polymers:

- 25.0 mg PVC in 1mL freshly prepared THF
- 60.0 mg PS in 1mL freshly prepared THF
- 50.0 mg PMMA in 1mL freshly prepared THF
- 50.0 mg PMMA in 1mL toluene.

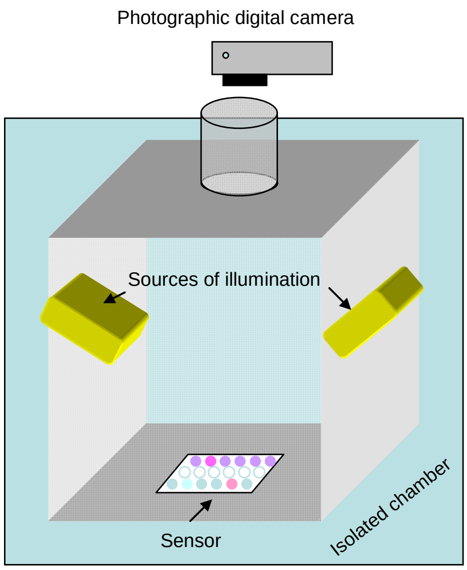

Figure S.1. Experimental arrangement for image acquisition of the optical sensors placed in an isolated box into a controlled temperature cabinet.

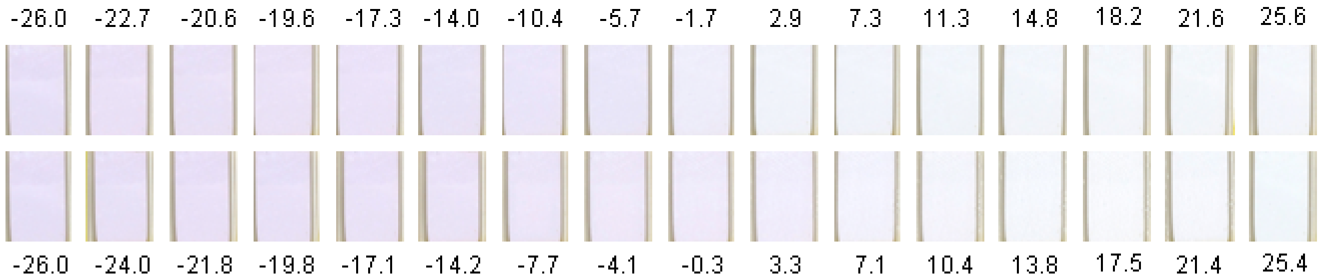

Figure S.2. Photographing the temperature response of $[Fe(NH_2\text{-trz})_3](BF_4)_2$ placed in a 1 mm optical path cuvette. Two slightly different phases (up and down) can be seen at low temperatures corresponding to: up: 1st cycle; down: 5th cycle.

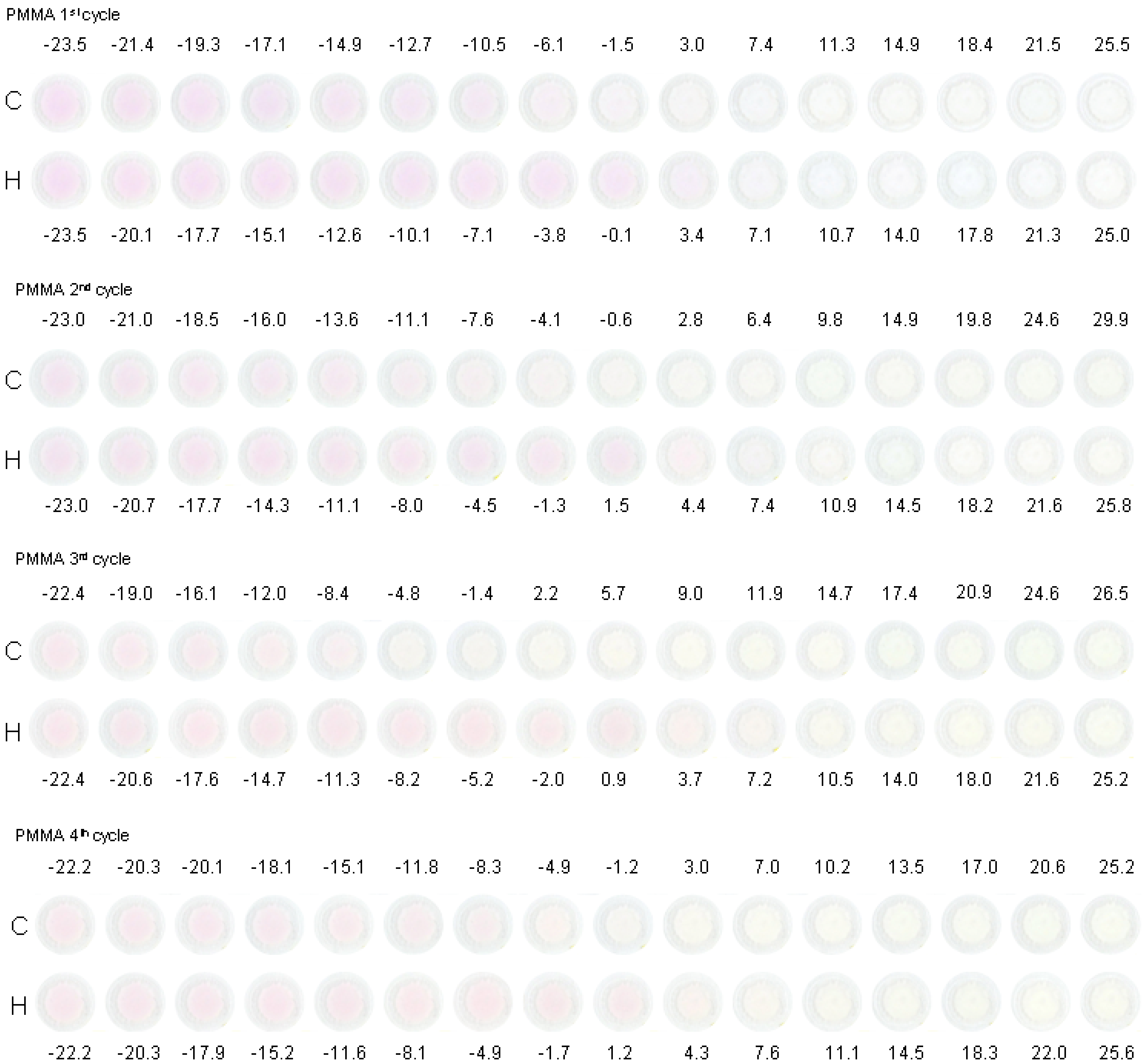

Figure S.3. Photographing the colour response of the polymer/SCO hybrid material at different temperatures in a PMMA sensor. C: cooling sequence. H: heating sequence.

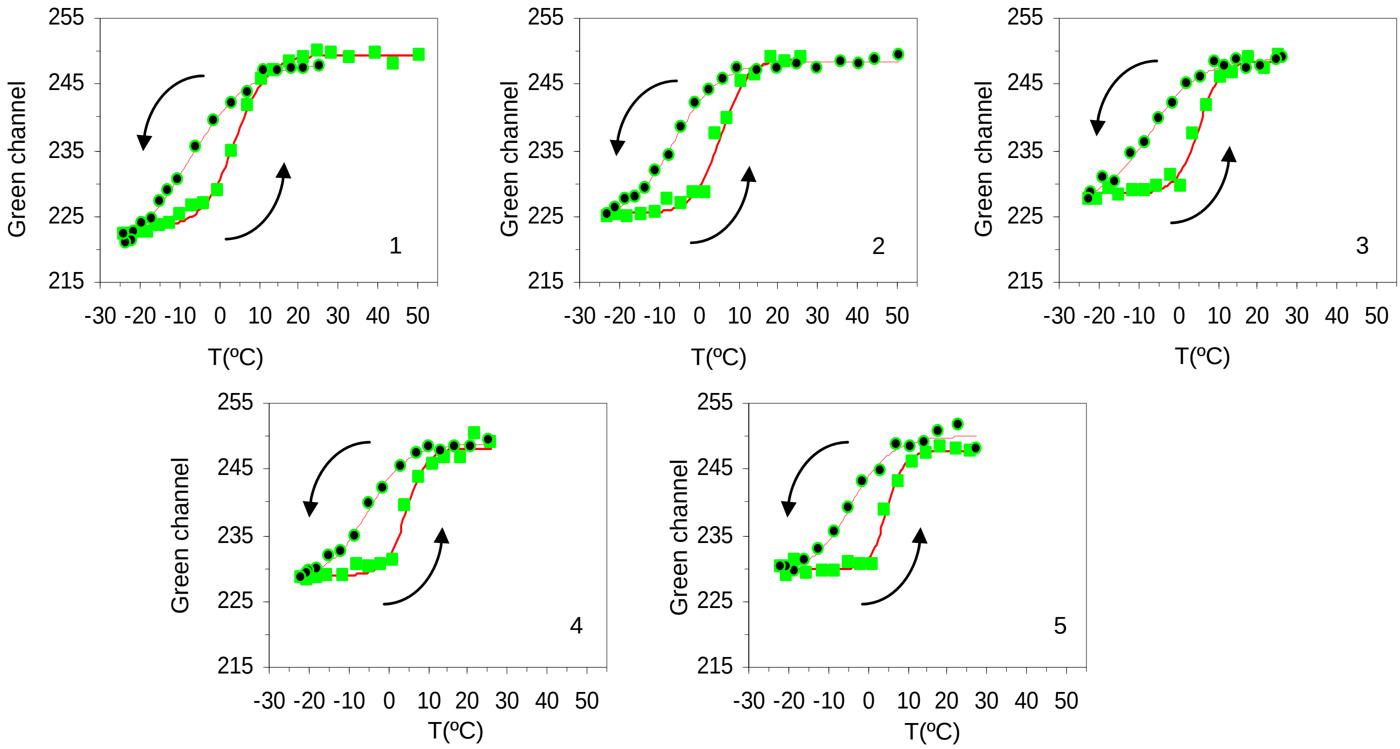

Figure S.4. Colour changes (expressed as green channel intensity modification) related to thermal variations in the heating (circles) and cooling (squares) for PMMA temperature sensors. Notice that the scale has been preserved in all graphs to appreciate the changes through each cycle. Numbers 1,2,3,4 and 5 are the corresponding temperature cycles.

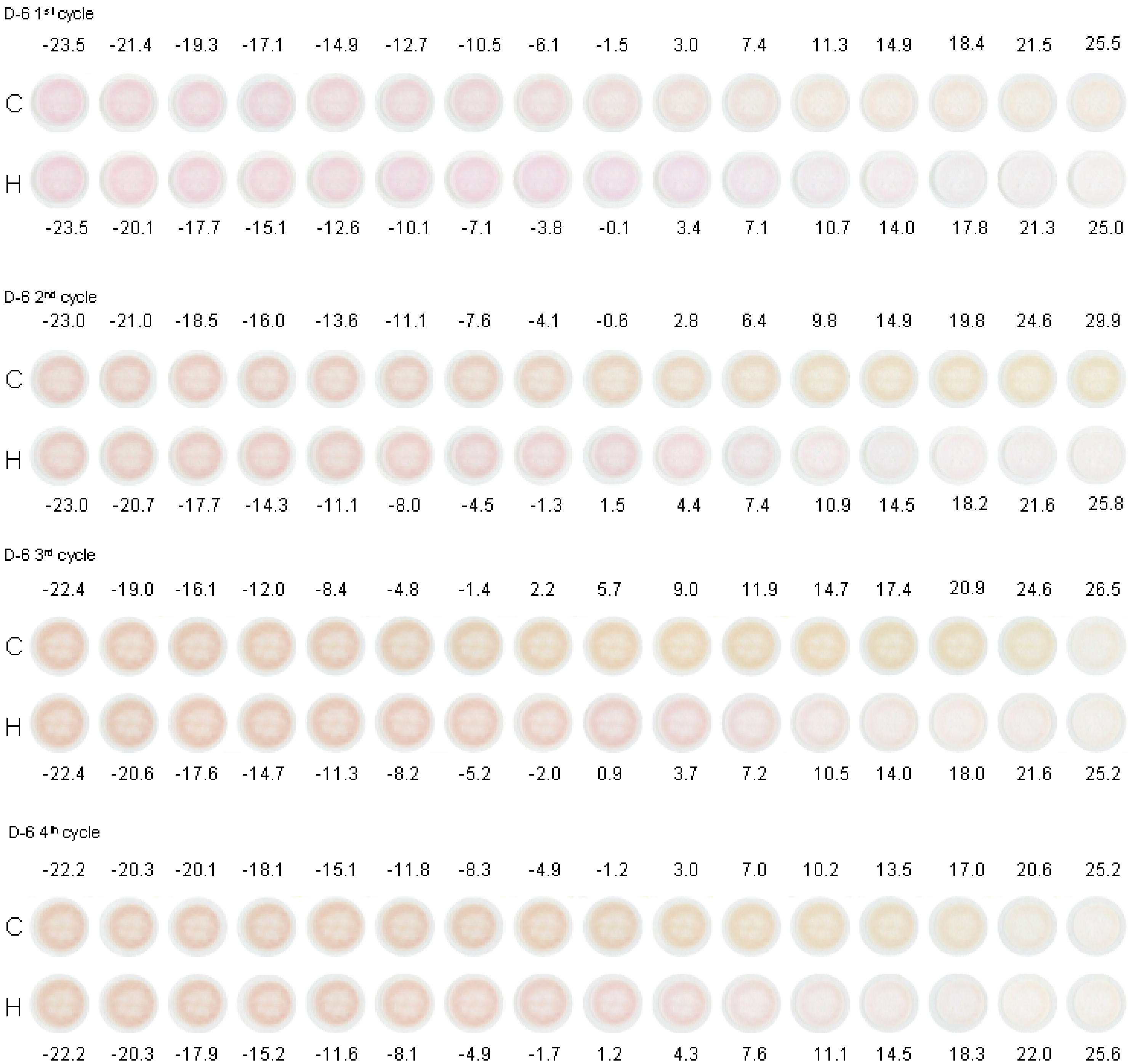

Figure S.5. Photographing the colour response of the polymer/SCO hybrid material at different temperatures in a D-6 sensor. C: cooling sequence. H: heating sequence.

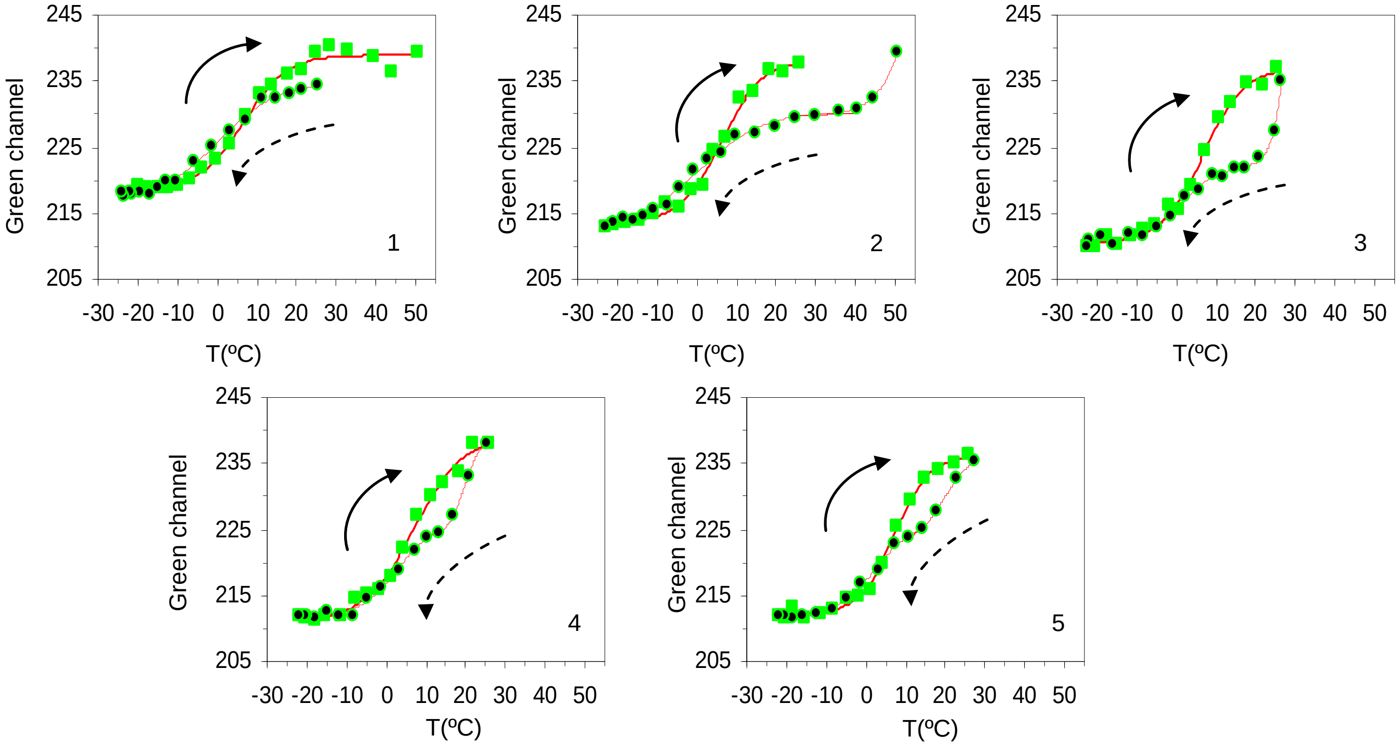

Figure S.6. Colour changes (expressed as green channel intensity modification) related to thermal variations in the heating (circles) and cooling (squares) for D-6 temperature sensors. Notice that the scale has been preserved in all graphs to appreciate the changes through each cycle. Numbers 1,2,3,4 and 5 are the corresponding temperature cycles.

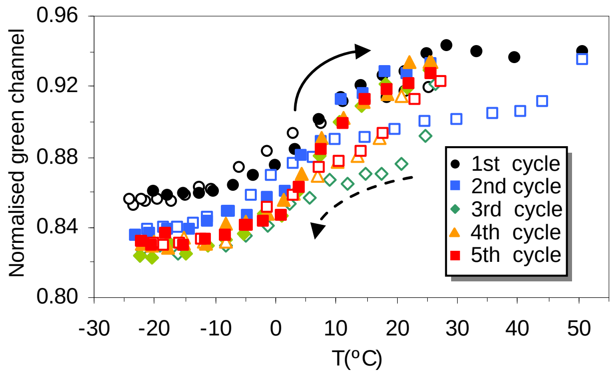

Figure S.7. All temperature cycles from 1 to 5 for D-6 optical sensor. Heating (filled symbols), cooling (open symbols).

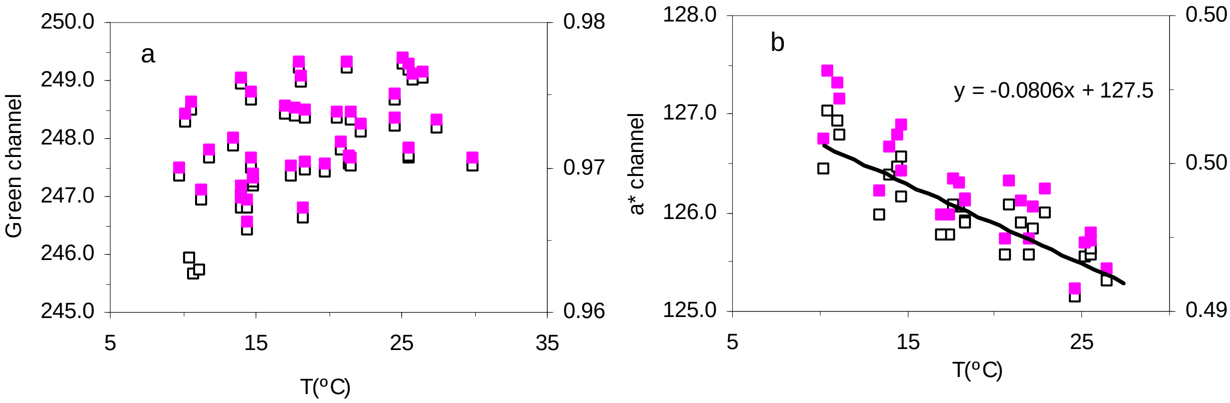

Figure S.8. Calibration Curve for PMMA sensor at high temperatures. a) Green channel trend. b) a* channel trend. While in the green channel random data is shown, for the a* channel it is clear that the data follow a linear trend. Colour coordinate (open symbols), normalised colour coordinate (filled symbols).

References

1 J. Kroeber, J. P. Audiere, R. Claude, E. Codjovi, O. Kahn, J. G. Haasnoot, F. Groliere, C. Jay and A. Bousseksou, *Chem. Mater.*, 1994, **6** (8), 1404-1412.