Electronic Supporting Information

Vapochromic and Mechanochromic Films from Square-Planar Platinum Complexes in Methacrylates

Justin R. Kumpfer,[a] Stephen D. Taylor,[b] William B. Connick,[b] and Stuart J. Rowan*[acd]

[a] *Department of Macromolecular Science & Engineering, Case Western Reserve University, 2100 Adelbert Road, Cleveland, Ohio, 44106-7202, USA. E-mail: stuart.rowan@case.edu*
[b] *Department of Chemistry, University of Cincinnati, Cincinnati, Ohio, 45221-0172, USA*
[c] *Department of Chemistry, Case Western Reserve University, Cleveland, Ohio, 44106, USA*
[d] *Department of Biomedical Engineering, Case Western Reserve University, Cleveland, Ohio, 44106, USA*

Table of Contents

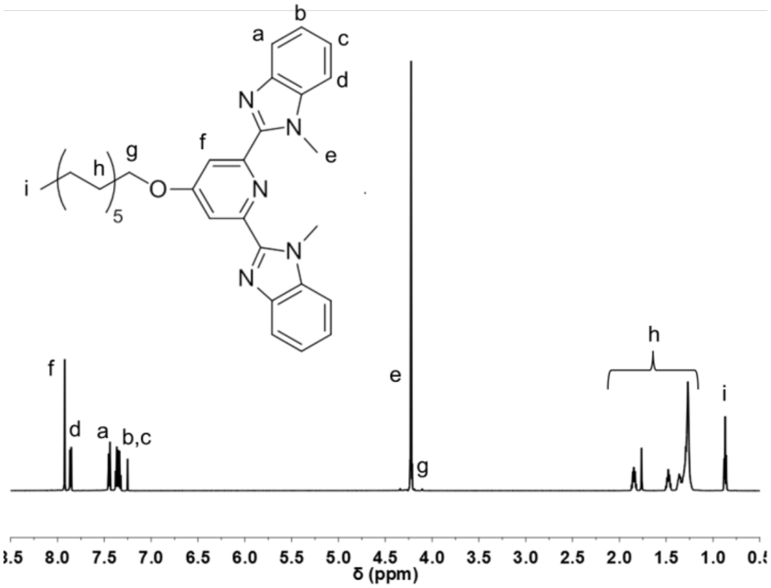

Fig. S1. ^{1}H-NMR spectrum of **1** in $CDCl_3$ (600 MHz).

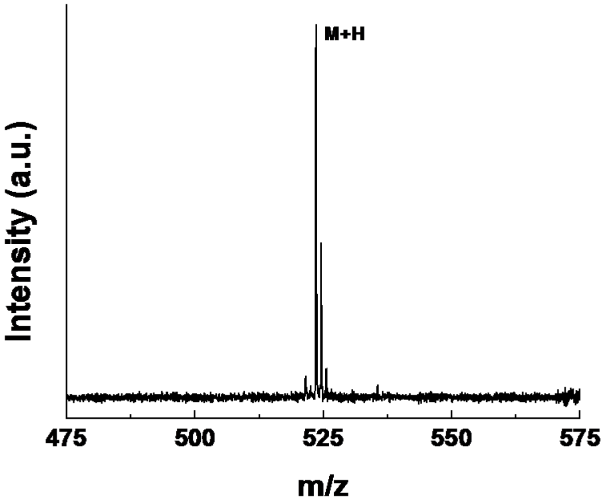

Fig. S2. Nanowire Array Laser Desorption/Ionization (NALDI) spectrum of **1** [M+H].

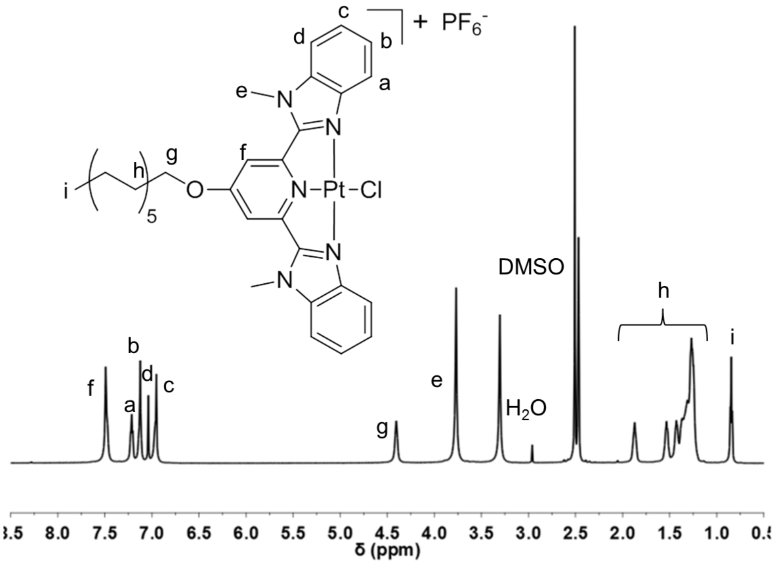

Fig. S3. ^{1}H-NMR spectrum of [Pt(**1**)Cl](PF$_6$) in DMSO-d$_6$ (600 MHz).

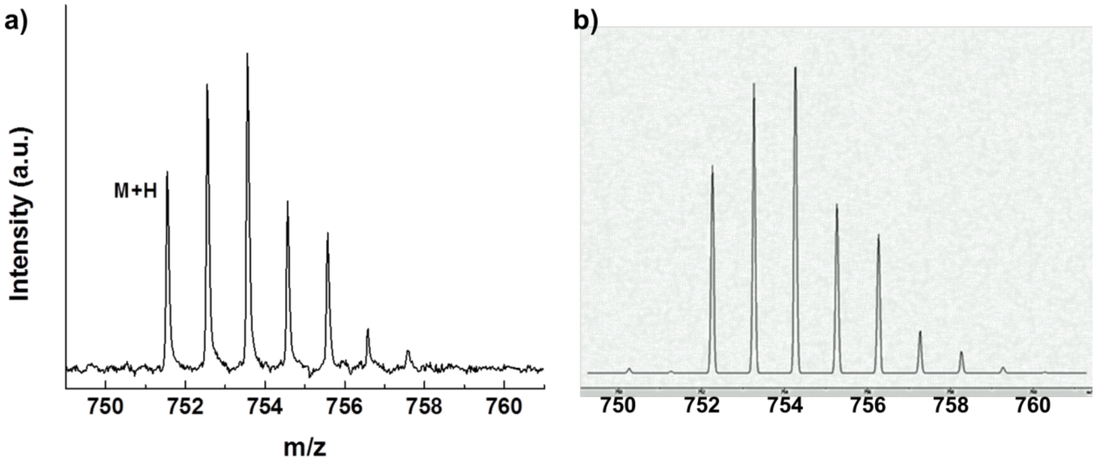

Fig. S4. (a) Nanowire Array Laser Desorption/Ionization (NALDI) spectrum of [Pt(**1**)Cl](PF$_6$) [M+H] compared with (b) the theoretical isotope pattern.

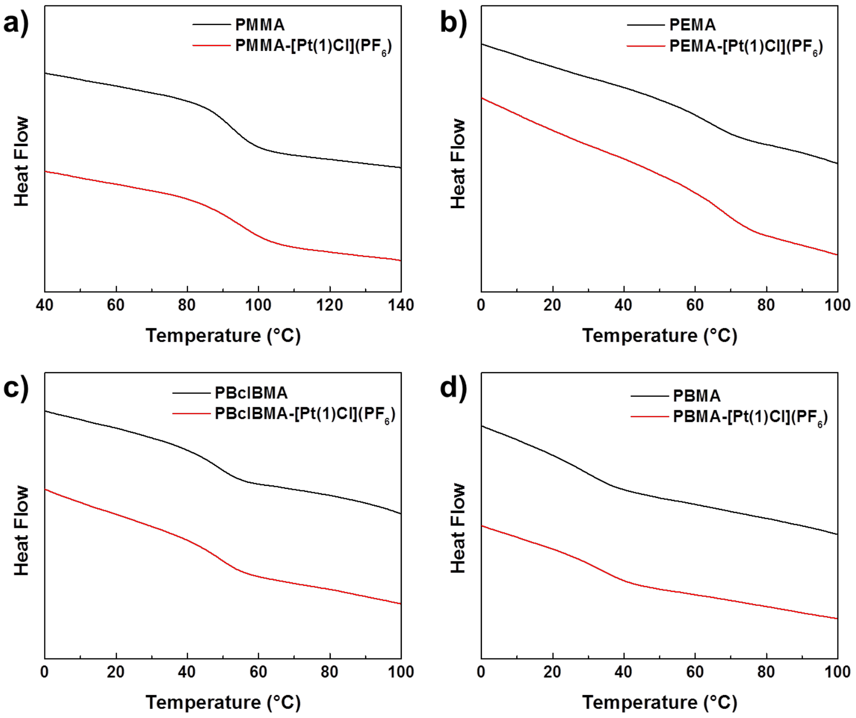

Fig. S5. DSC curves of the matrices and blends prepared with [Pt(**1**)Cl](PF_6) of a) PMMA, b) PEMA, c) PBcIBMA, and d) PBMA.

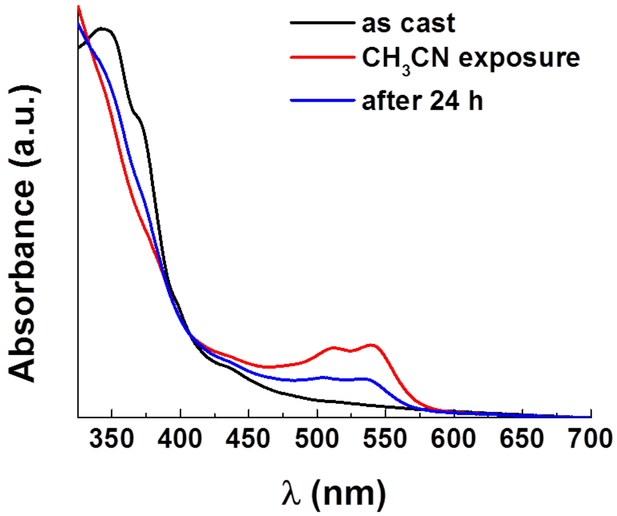

Fig. S6. UV-visible absorption spectrum of a yellow, as-cast 10 wt. % [Pt(**1**)Cl](PF_6) in PEMA film. Bands occur at 343 nm ($\pi - \pi^*$) and ~435(sh) nm (MLCT). During exposure to acetonitrile vapour, the film colour changes from yellow to red and a structured band appears with maxima at 510 and 540 nm

(MMLCT). After 24 hours in the absence of vapour, only partial colour recovery is observed (decrease in MMLCT band), which is consistent with the relatively high T_g of the polymer matrix (T_g ca. 65 °C).

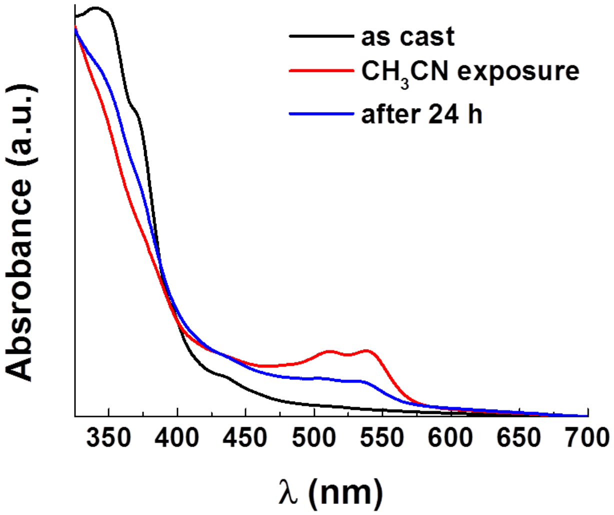

Fig. S7. UV-visible absorption spectra of a yellow, as-cast 10 wt. % [Pt(**1**)Cl](PF_6) in PBcIBMA film. Before exposure, bands are observed at 343 nm (π – π*) and ~435(sh) nm (MLCT). During exposure to acetonitrile vapour, the colour of the film changes from yellow to red, and a structured band appears at 510 and 540 nm (MMLCT). After 24 hours in the absence of vapour, only partial colour recovery is observed (decrease in MMLCT band), which is consistent with the T_g of the polymer matrix being above room temperature (T_g ca. 45 °C).

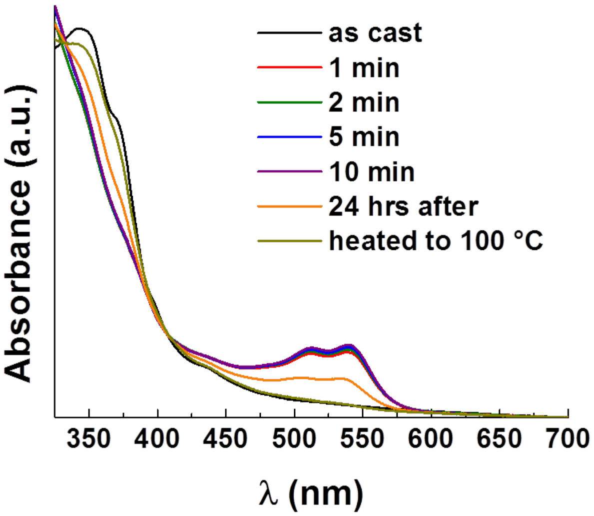

Fig. S8. Absorption spectra of an as-cast 10 wt. % [Pt(**1**)Cl](PF_6) blend in PEMA film while exposed to CH_3CN vapour. Changes are essentially complete within the first minute of exposure. After 24 hours in the absence of vapour, only partial recovery is observed (orange). Full recovery is observed after heating to 100 °C for 10 minutes.

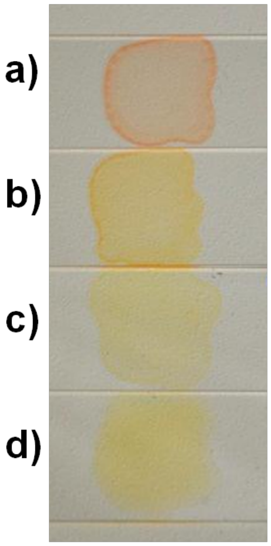

Fig. S9. Images of the color recovery after 24 hrs for drop-cast films 10 wt. % [Pt(**1**)Cl](PF_6) in a) PMMA, b) PEMA, c) PBcIBMA, and d) PBMA.

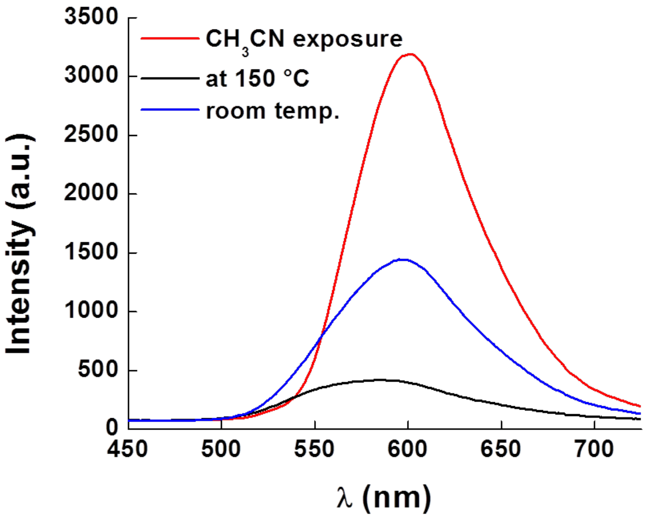

Fig. S10. Emission spectrum of a 10 wt. % [Pt(**1**)Cl](PF_6) blend in PMMA after exposure to acetonitrile vapour (red). Upon heating to 150 °C, the emission intensity decreased and the maximum shifted to the blue (black). Cooling the film to room temperature yielded an emission profile (blue) with the same maximum as the original vapour-exposed film, but with decreased intensity.

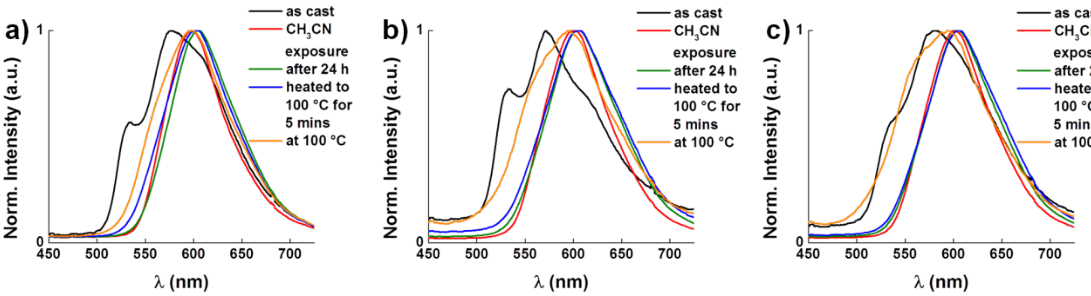

Fig. S11. Normalized emission spectra of 10 wt. % [Pt(**1**)Cl](PF_6) in (a) PMMA, (b) PBcIBMA, and (c) PBMA. Exposure to acetonitrile vapour results in a red-shift and narrowing of the emission band. The emission profile also becomes increasingly symmetric. The change is not reversible, and heating only results in decreased intensity and a slight broadening.

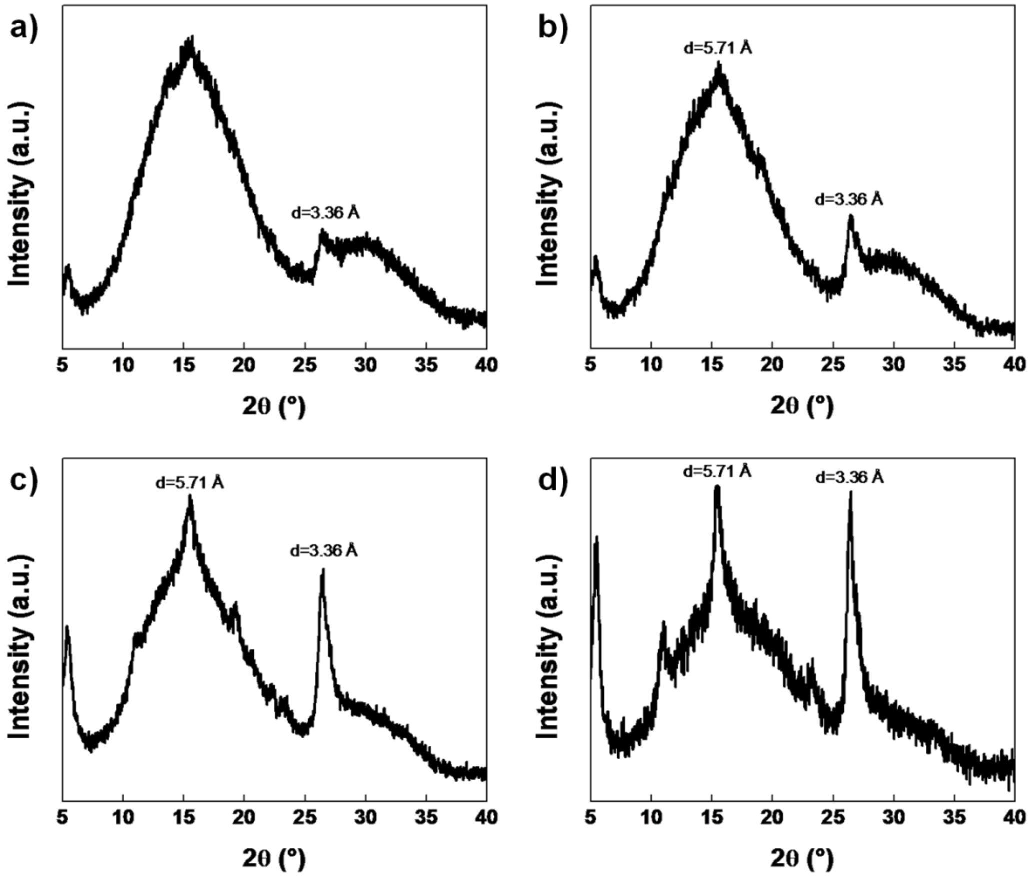

Fig. S12. WAXS of (a) 2.5, (b) 5, (c) 10, and (d) 20 wt. % [Pt(**1**)Cl](PF_6) in PMMA after compression. At 2.5 wt. % loading the scattering from the platinum complexes is mostly obscured by that of the polymer matrix. However as the loading increases peaks at 2θ = 15.5° and 26.5° (d = 5.71 and 3.36 Å respectively) can be seen.

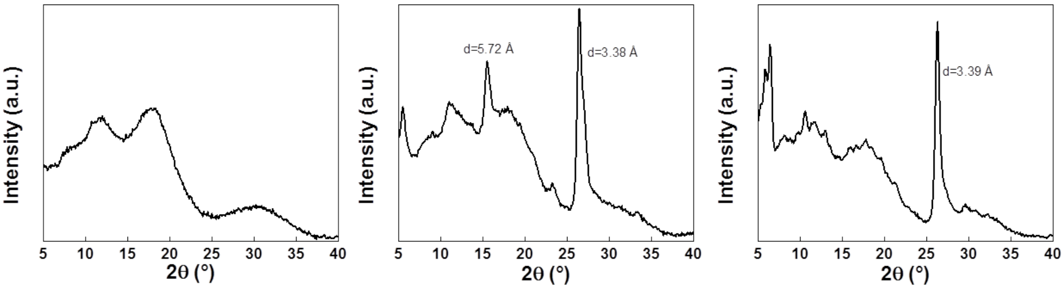

Fig. S13. WAXS of neat PEMA (left) and as-cast, yellow 10 wt. % [Pt(**1**)Cl](PF_6) in PEMA (middle). The latter shows two dominant peaks at 2θ = 15.5 and 26.4 (d = 5.72 and 3.38 Å respectively). After exposure to acetonitrile (right), only the "short" Pt – Pt interaction is observed (d = 3.39 Å) indicating significant structural rearrangement. The peak at low 2θ is tentatively assigned to longer Pt – Pt distances.

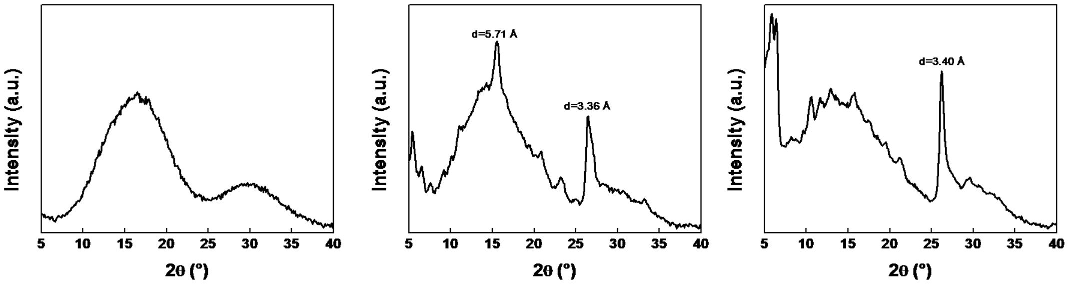

Fig. S14. WAXS of neat PMMA (left) and as-cast, yellow 10 wt. % [Pt(**1**)Cl](PF_6) in PMMA (middle). The latter shows two dominant peaks at 2θ = 15.5 and 26.5 (d = 5.71 and 3.36 Å respectively). After exposure to acetonitrile (right), only the "short" Pt – Pt interaction is observed (d = 3.40 Å) indicating significant structural rearrangement. The peak at low 2θ is tentatively assigned to longer Pt – Pt distances.

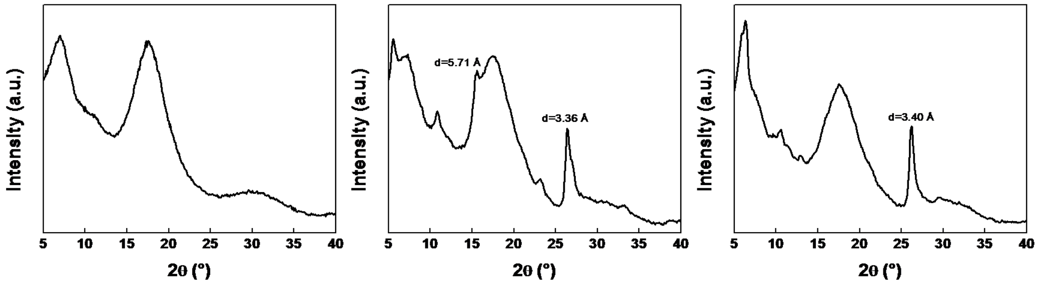

Fig. S15. WAXS of neat PBcIBMA (left) and as-cast, yellow 10 wt. % [Pt(**1**)Cl](PF$_6$) in PBcIBMA (middle). The latter shows two dominant peaks at 2θ = 15.6 and 26.4 (d = 5.68 and 3.37 Å respectively). After exposure to acetonitrile (right), only the "short" Pt – Pt interaction is observed (d = 3.40 Å) indicating significant structural rearrangement. The peak at low 2θ is tentatively assigned to longer Pt – Pt distances.

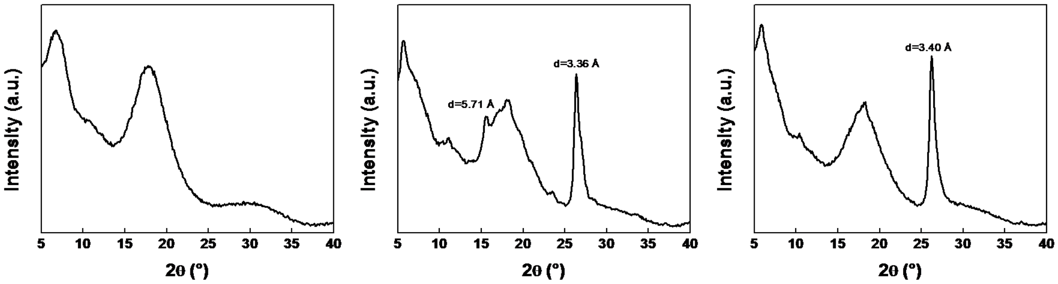

Fig. S16. WAXS of neat PBMA (left) and as-cast, yellow 10 wt. % [Pt(**1**)Cl](PF$_6$) in PBMA (middle). The latter shows two dominant peaks at 2θ = 15.5 and 26.4 (d = 5.71 and 3.37 Å respectively). After exposure to acetonitrile (right), only the "short" Pt – Pt interaction is observed (d = 3.40 Å) indicating significant structural rearrangement. The peak at low 2θ is tentatively assigned to longer Pt – Pt distances.

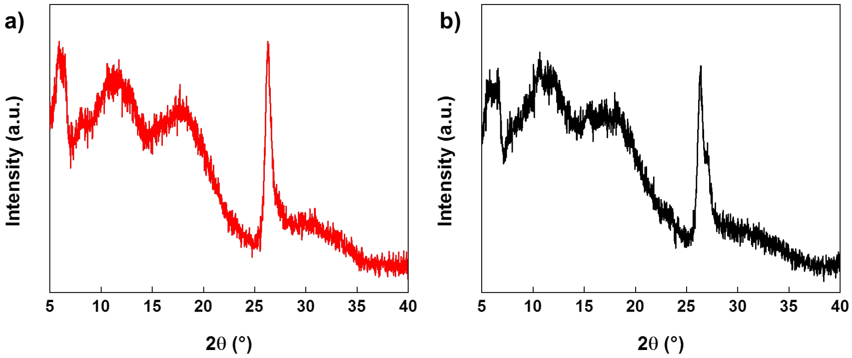

Fig. S17. WAXS of 10 wt. % [Pt(**1**)Cl](PF$_6$) in PEMA (a) after exposure to acetonitrile and (b) after heating at 100 °C for 1 hour. The exposed film has a dominant peak at 2θ = 26.3 (d = 3.39 Å) and after heating an increase in the form of a shoulder at 2θ = 26.4 (d = 3.38) is observed which matches with the distance seen in the unexposed sample.

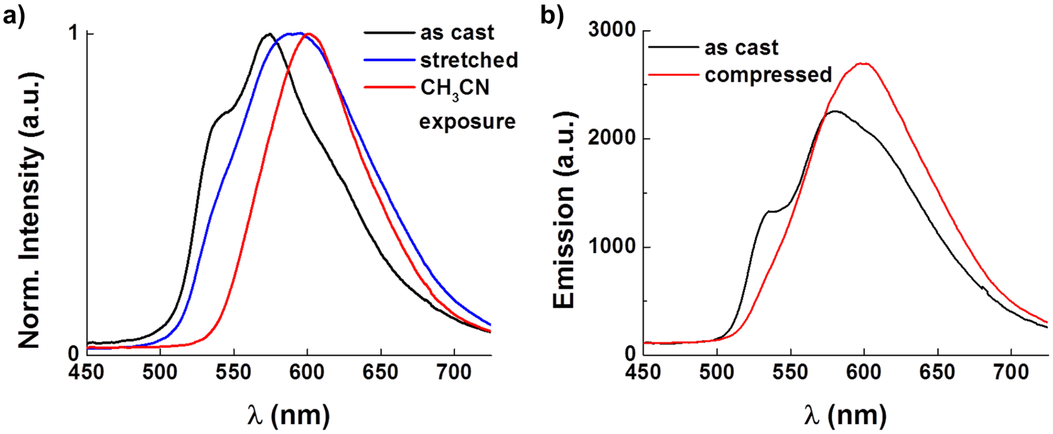

Fig. S18. a) Normalized emission spectra of samples of 10 wt. % [Pt(**1**)Cl](PF$_6$) in PBMA film as cast and after either stretching or exposure to acetonitrile vapor, and b) unnormalized emission spectra of a 10 wt. % [Pt(**1**)Cl](PF$_6$) in PEMA film before (as cast) and after compression.