

## **Supporting Information**

### **Molecular recognition between functionalized gold nanoparticles and healable, supramolecular polymer blends – a route to property enhancement**

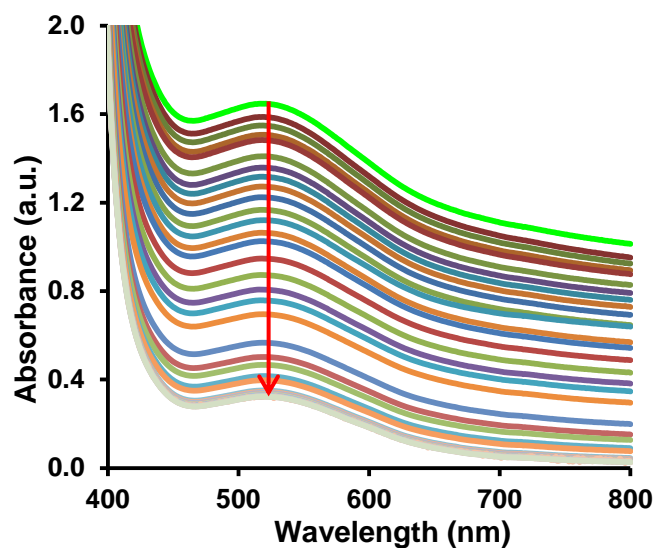
Rajendran Vaiyapuri,<sup>a</sup> Barnaby W. Greenland,<sup>b</sup> Howard M. Colquhoun,<sup>a</sup> Vitaliy V. Khutoryanskiy,<sup>b</sup> Joanne M. Elliott,<sup>a</sup> and Wayne Hayes<sup>\*,a</sup>

<sup>a</sup>Department of Chemistry, University of Reading, Whiteknights, Reading, UK, RG6 6AD.

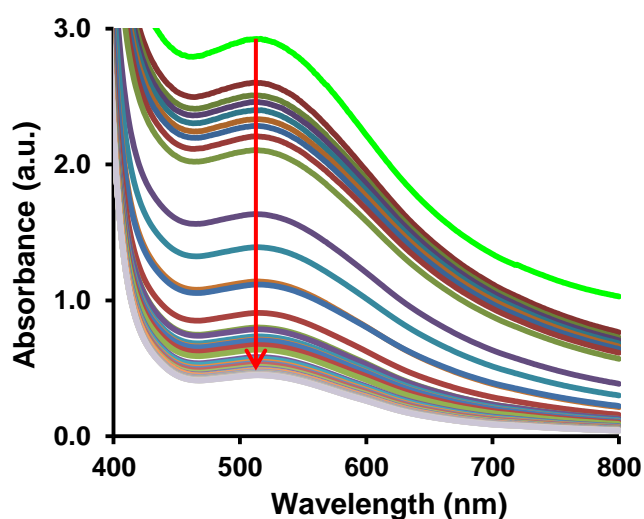
<sup>b</sup>Department of Pharmacy, University of Reading, Whiteknights, Reading, UK, RG6 6AD.

Email: [w.c.hayes@reading.ac.uk](mailto:w.c.hayes@reading.ac.uk); Fax: +44 118 3786331

- S1.** UV-visible study of supramolecular polymer nanocomposite precipitation over the period of 27 hours
- S2.** UV-visible measurement of cooling and heating cycle experimental data
- S3.** Photograph of the film cast from of polymer **1+2** (1:3, w/w ratio)
- S4. (a-c)** EDX analysis of polymer nanocomposites prepared from 1.25 - 15 wt% P-AuNPs and also 5 wt% dodecylamine-stabilized AuNPs (control experiment).
- S5.** DSC analyses of polymer nanocomposites prepared from 0 - 15 wt% P-AuNPs
- S6.** Preparation of dodecylamine-stabilized AuNPs
- S7.** Comparison of DSC thermogram of polymer nanocomposites prepared from 5 wt% P-AuNPs and 5 wt% dodecylamine-stabilized AuNPs

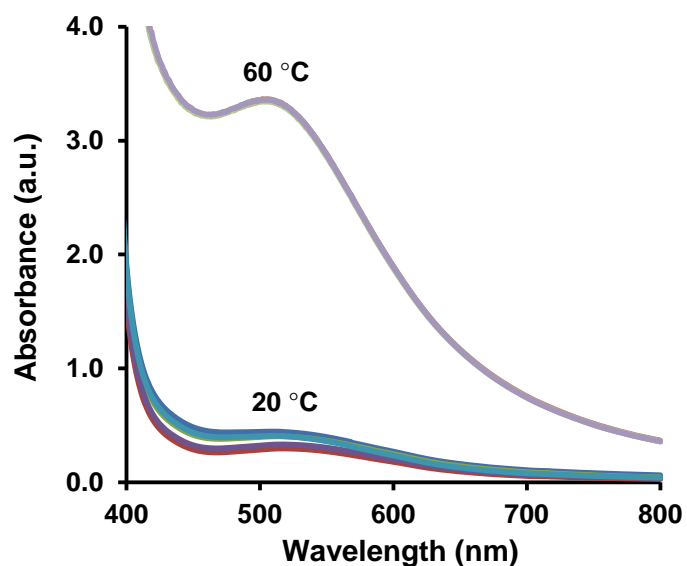


a).



b).

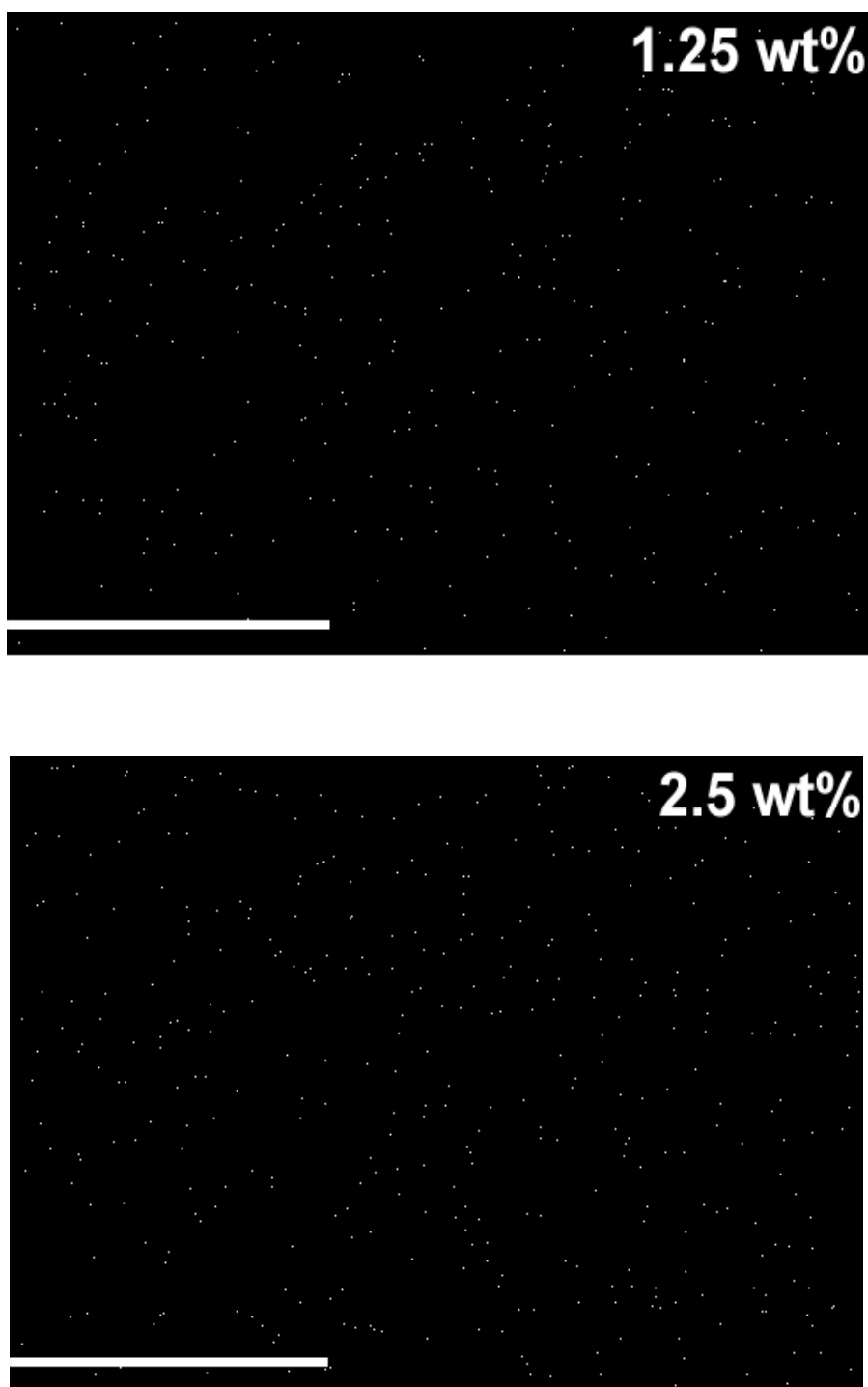
**Figure S1.** UV/visible spectroscopic analysis of supramolecular nanocomposite precipitation by UV/vis analysis of the supernatant over 27 hours. A) Absorbance change over 27 hours between 400 and 800 nm for polymer composite (polymer **1** (1 mg/mL) + polymer **2** (3 mg/mL)) precipitation; B). Absorbance change over 27 hours between 400 and 800 nm for polymer nanocomposite (polymer **1** (1 mg/mL) + polymer **2** (3 mg/mL) with 2.5 wt% P-AuNPs) precipitation. All the solutions were prepared in CHCl<sub>3</sub>/HFIP (6;1, v/v) and measurements carried at 25 °C.



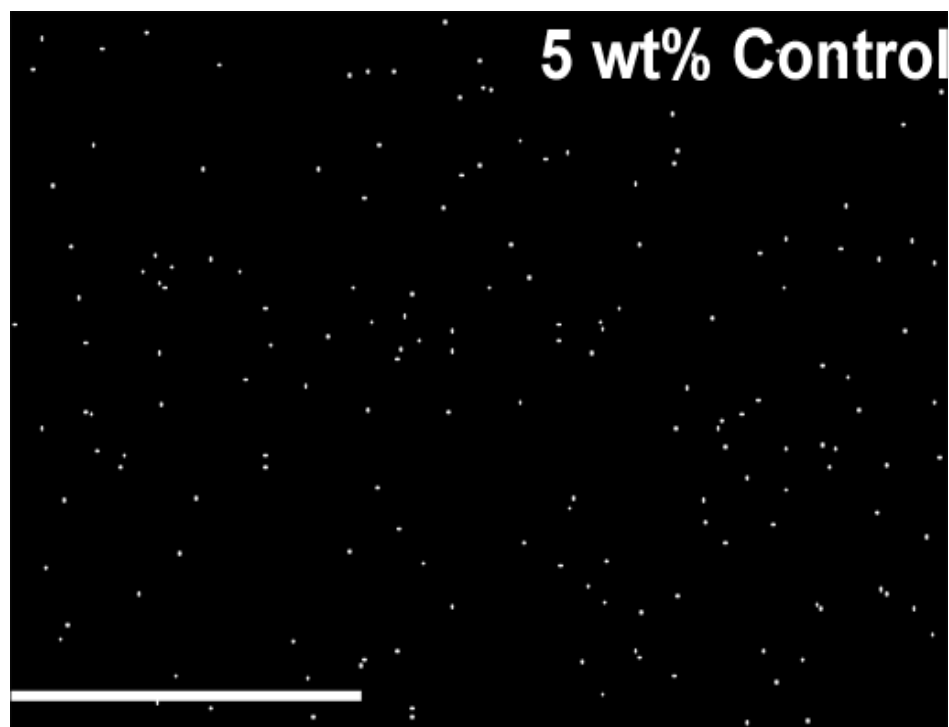
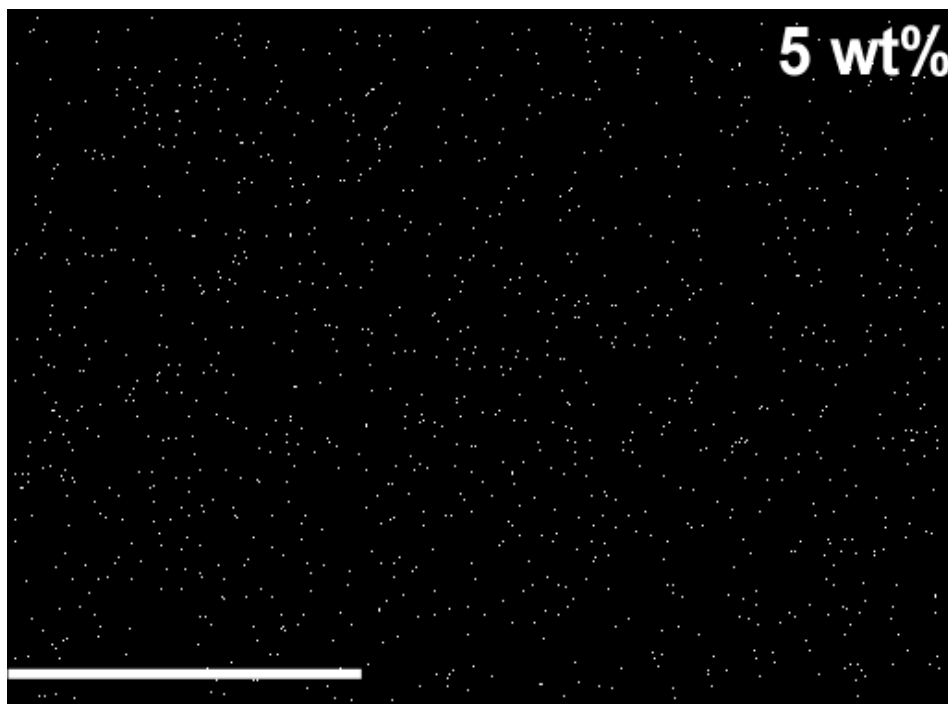
**Figure S2.** UV visible spectroscopic absorbance measurement of supramolecular polymer nanocomposite precipitation and dissolution cycling between 20 and 60 °C over 5 days. Polymers **1+2** (1:3, w/w). All the samples prepared in CHCl<sub>3</sub>/HFIP (6:1, v/v).



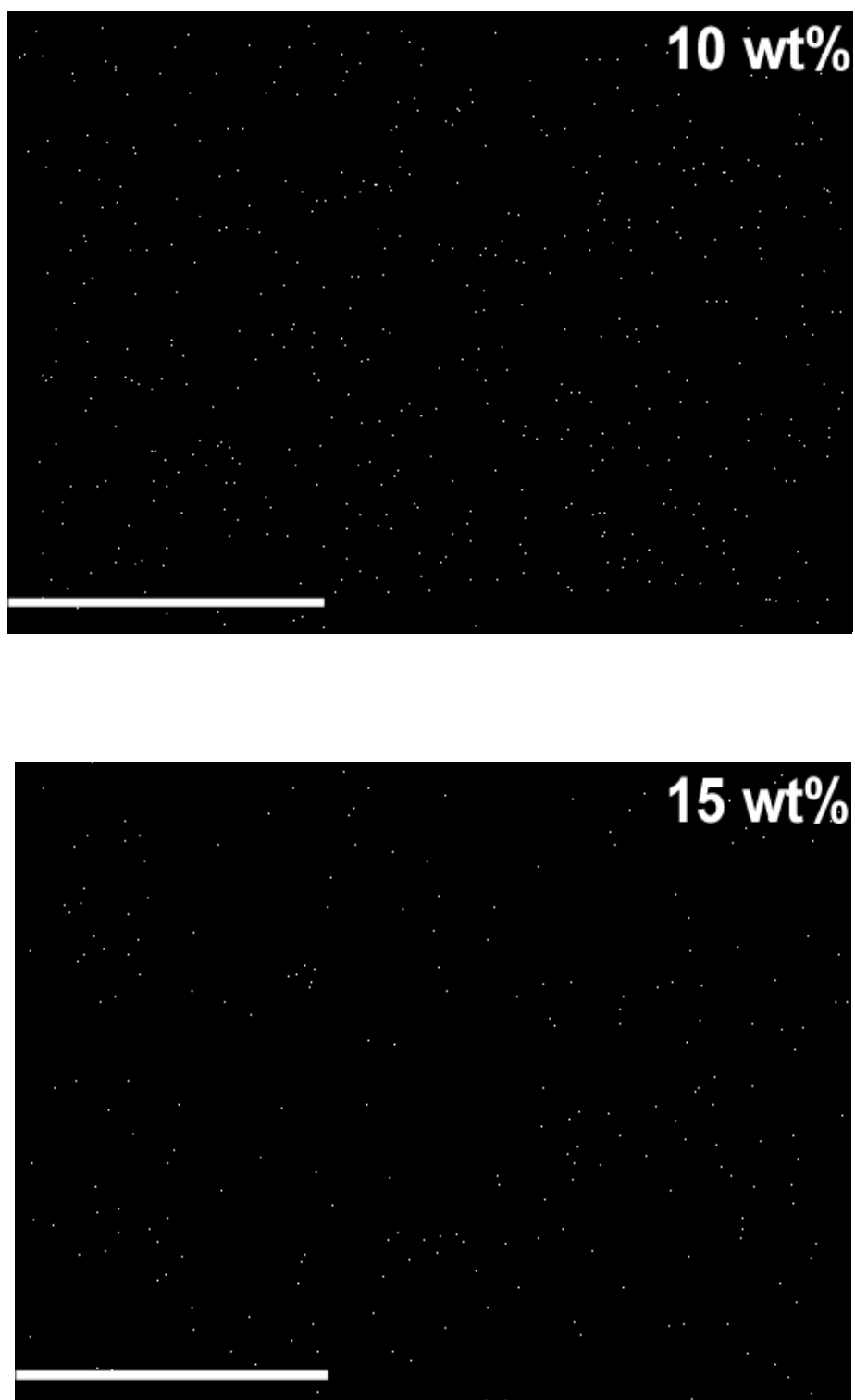
**Figure S3.** Photograph of the supramolecular polymer film prepared from polymer **1+2** (1:3, wt/wt ratio).



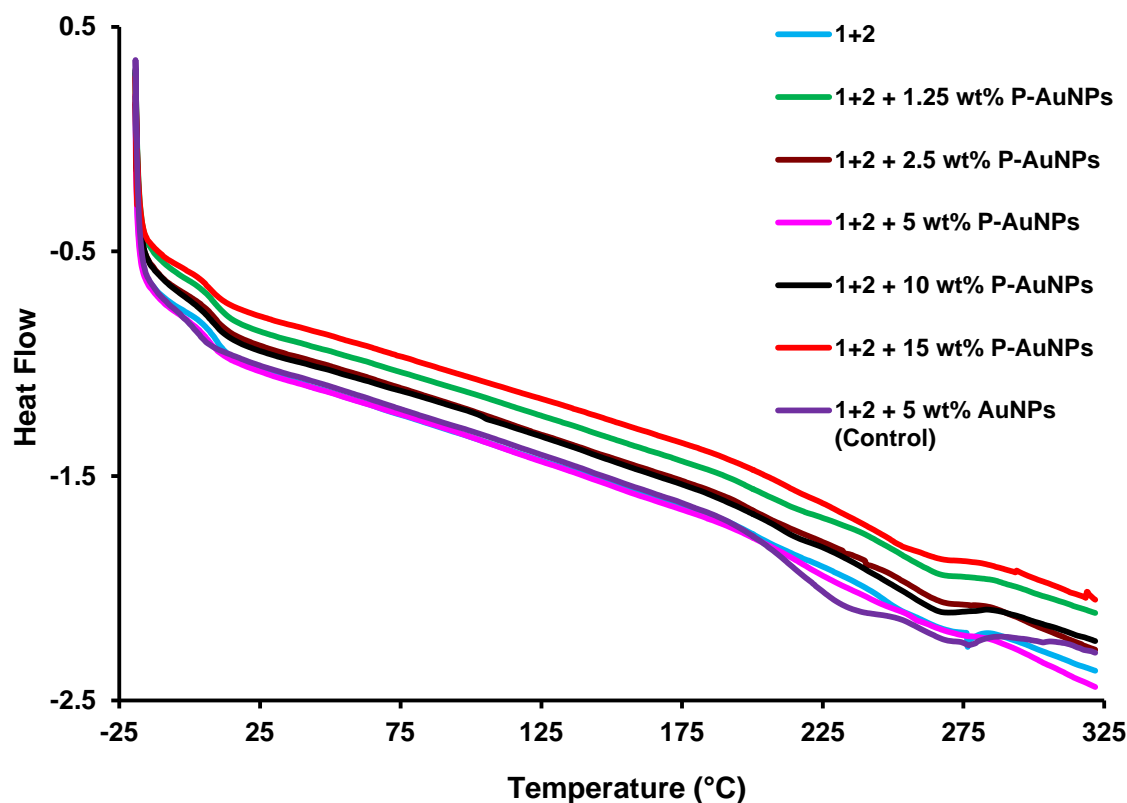
**Figure S4a.** EDX analysis of polymer nanocomposite films ( $\approx 100 \mu\text{m}$ ) prepared from 1.25 and 2.5 wt% P-AuNPs. The white dots show the presence of gold on the surface of the polymer nanocomposite films. Scale bar is  $200 \mu\text{m}$ . The calculated surface coverage of gold counts are  $1400/\text{mm}^2$  and  $1800/\text{mm}^2$  for the films containing 1.25 and 2.5 wt%, respectively.



**Figure S4b.** EDX analysis of polymer nanocomposite films ( $\approx 100 \mu\text{m}$ ) prepared from 5 wt% P-AuNPs (upper image) and 5 wt% dodecylamine stabilised AuNPs (lower image). The white dots show the presence of gold on the surface of the polymer nanocomposite films. Scale bar is  $200 \mu\text{m}$ . The calculated surface coverage of gold counts are  $5300/\text{mm}^2$  and  $750/\text{mm}^2$  for the films containing 5 wt% P-AuNPs and 5 wt% dodecylamine stabilised AuNPs, respectively. The lower gold count demonstrates the propensity of the docecylamine stabilised AuNPs to aggregate within the film.



**Figure S4c.** EDX analysis of polymer nanocomposite films ( $\approx 100 \mu\text{m}$ ) prepared from 10 and 15 wt% P-AuNPs. The white dots show the presence of gold on the surface of the polymer nanocomposite films. Scale bar is  $200 \mu\text{m}$ . The calculated surface coverage of gold counts are  $2200/\text{mm}^2$  and  $1000/\text{mm}^2$  for the films containing 10 and 15 wt%, respectively.



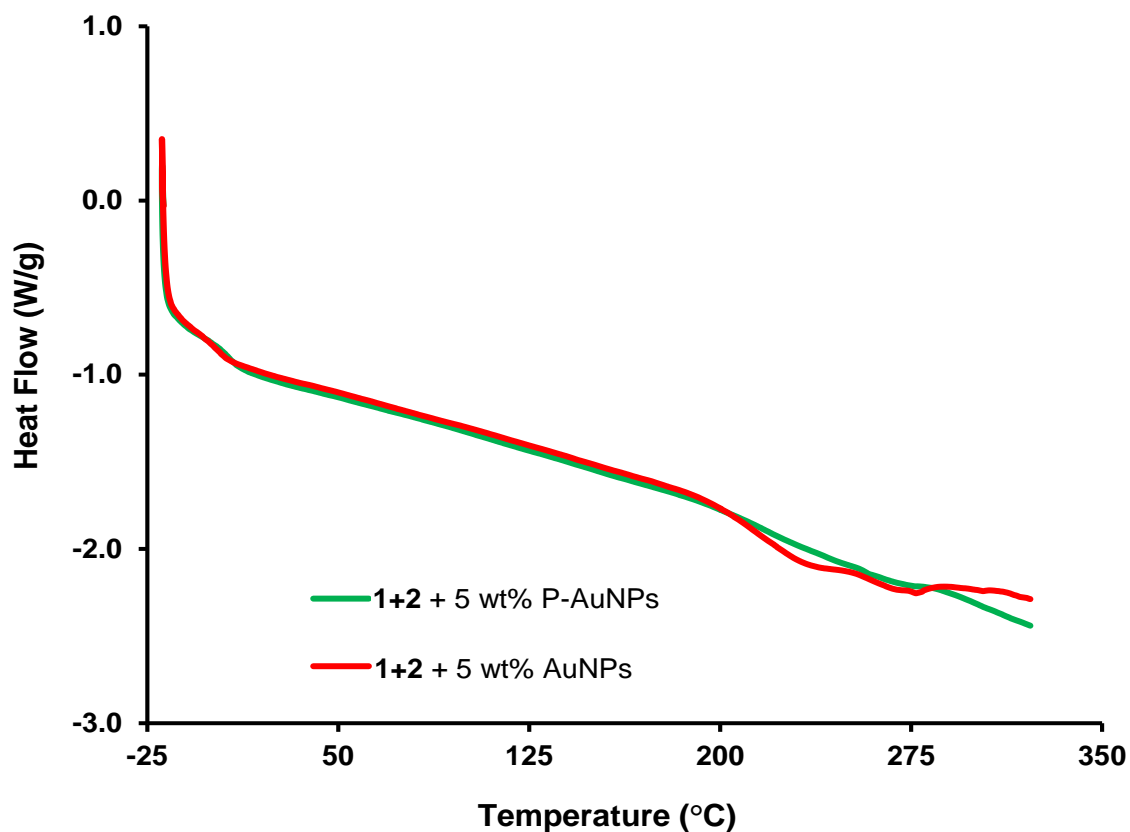
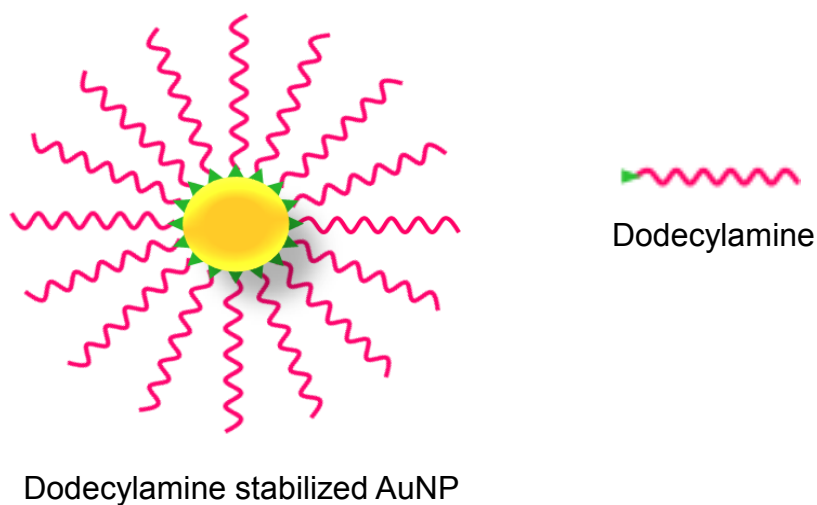
**Figure S5.** DSC analyses of polymer nanocomposites prepared from 0-15 wt% P-AuNPs.

### S6. Preparation of dodecylamine stabilized AuNPs

Dodecylamine stabilized AuNPs were prepared according to previously reported method;<sup>1</sup> in brief, 100 mM DDAB stock solution was prepared in toluene. Gold(III) chloride (7.5 mg) was dissolved in DDAB (2.5 mL) solution with sonication, giving a deep reddish orange colour. After that, DDA (90 mg) was added with sonication, the solution colour changing to faint yellow. Finally, 25 mg of TBAB was dissolved in DDAB (1 mL) solution and added to the gold salt solution with vigorous stirring. The solution colour change to deep reddish brown as a result of AuNPs formation.

In order to remove toluene and excess ligand from the AuNPs, MeOH (1 mL) was added to a solution of AuNPs (2 mL, toluene). After 1 h, a further aliquot of MeOH (2 mL) was added and the AuNPs precipitated after a further period of approximately 1 h. The supernatant was separated and allowed to stand, providing a further crop of AuNPs. The

resulting combined precipitates were washed with 2 mL of MeOH and separated from the supernatant. This precipitate was dissolved in  $\text{CHCl}_3$  to obtain a 10 mM solution of AuNPs.



**Figure S7.** DSC analyses of polymer nanocomposites prepared from 5 wt% P-AuNPs (green) and 5 wt% dodecylamine stabilized AuNPs (red).

## References

1. N. R. Jana and X. G. Peng, *J. Am. Chem. Soc.*, 2003, **125**, 14280-14281.