Enhanced visible photoluminescence in ultrathin poly(3-hexylthiophene) films by incorporation of Au nanoparticles†

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Incorporation of non-luminescent dodecanethiolate-protected gold clusters into regioregular poly(3-hexylthiophene) films results in a 6-fold increase in the visible photoluminescence (PL) of the polymer, which arises predominantly from NP-induced structural changes in the composite films.

There is increasing interest in the optical properties of nanoparticle (NP)/π-conjugated polymer (CP) composite films in view of their applications in photovoltaic cells[1] and light-emitting diodes[2] *inter alia*. The inclusion of nanostructures in the form of multiwall carbon nanotubes,[3,4] fullerenes[5] and metallofullerenes[6] into luminescent CPs has been reported to quench the PL of the polymer. This occurs due to an increase in exciton dissociation resulting from photoinduced electron transfer from the photoexcited CP to the dopant, which competes with radiative exciton recombination in the CP. This effect has been used to improve the efficiency of CP photovoltaic devices.[6] Blends of luminescent CPs and NPs have also been extensively studied[7,8] as a means of retarding photo-oxidation of the polymer. For these applications it is advantageous to have a uniform dispersion of NPs within the host polymer matrix. Thus, substantial synthetic effort has gone into varying the NP protective ligand in order to prevent NP aggregation.[9–11]

Here we report the first observation of an increase in the solid state PL of a CP ultrathin film due to the incorporation of metallic NPs into the matrix. We demonstrate that very uniform films with well-dispersed Au NPs (5.4 ± 0.3 nm) can be obtained simply by spin casting chloroform solutions of P3HT and NPs onto glass. The polymer-to-nanoparticle ratio (which we will define in terms of mass) has proved to be a crucial factor determining the extent of NP dispersion and enhancement in PL.

Composite films were made by spin casting (1000 rpm, 40 s; Cookson Electronics, SCS, G3-8 spincoat, USA) chloroform solutions of P3HT (Aldrich) and Au NPs onto cleaned glass slides. The concentration of CP was 1 mg mL^{-1} for all solutions, with various amounts of Au NPs added to give the desired ratios. The Au NPs were synthesised according to the two-phase Brust method[12] and then thermally annealed using the method reported by Shimizu *et al.*[13] to obtain highly monodisperse (5% dispersity) Au NPs with a 5.4 ± 0.3 nm core diameter,[14] as determined from TEM images of drop cast films on carbon-coated copper grids (see supporting information).

The optical properties of the resulting composite films were investigated with steady-state visible absorption and PL techniques. Fig. 1 shows representative absorption and PL spectra. The absorption spectrum of the Au NP film shows a broad band centred at 560 nm due to plasmon resonance. P3HT exhibits a characteristic broad band due to a $\pi \rightarrow \pi^*$ transition (with the maximum at 555 nm) and two shoulders corresponding to the vibronic fine structure. The absorption spectrum of the composite film appears to have the characteristics of the two components from which it was made.

Steady-state PL was recorded (Renishaw, inVia Raman Microscope, UK) after exciting the composite films with a 514 nm laser. Fig. 1b shows the PL signature for the P3HT film, the 1 : 1 composite film and two extreme P3HT : Au NP ratios: 1 : 10 and 10 : 1, each being the average of three measurements in different areas of the film. Note that the composite films do not show any substantial peak shift (except a small *ca.* 15 nm red-shift). This indicates that the effective conjugation length in the polymer has not been significantly altered by addition of the particles. P3HT luminescence is clearly enhanced by the addition of NPs, with the 1 : 1 film showing *ca.* 6-fold increase with respect to the native P3HT. It is also noteworthy that even the 10 : 1 composite (which corresponds to a molar ratio of 6×10^4 : 1 hexylthiophene monomer units to Au NPs) still exhibits *ca.* 3-fold increase in the PL. The dip in the spectra at 880 nm is an artefact due to background correction. Although strong emission has been reported for smaller[15,16] and similar-sized Au NPs[17] in aqueous solutions, spin cast films of only the Au NPs used in this study and the Au NPs embedded in an inert polymer (polymethylmethacrylate) did not exhibit perceivable luminescence at the excitation wavelength employed.

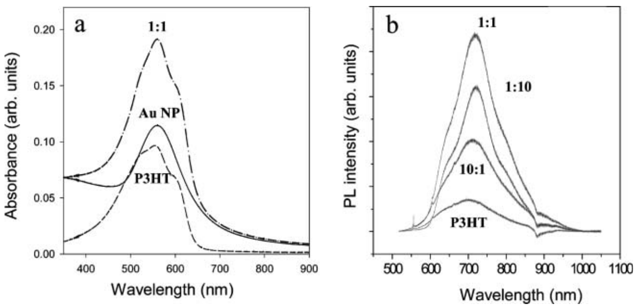

Fig. 1 (a) Visible absorption and (b) photoluminescence spectra for P3HT/Au NPs composite films. The labels refer to the P3HT : Au mass ratios.

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† Electronic supplementary information (ESI) available: TEM image of the Au NPs. See http://www.rsc.org/suppdata/cc/b4/b416107f/

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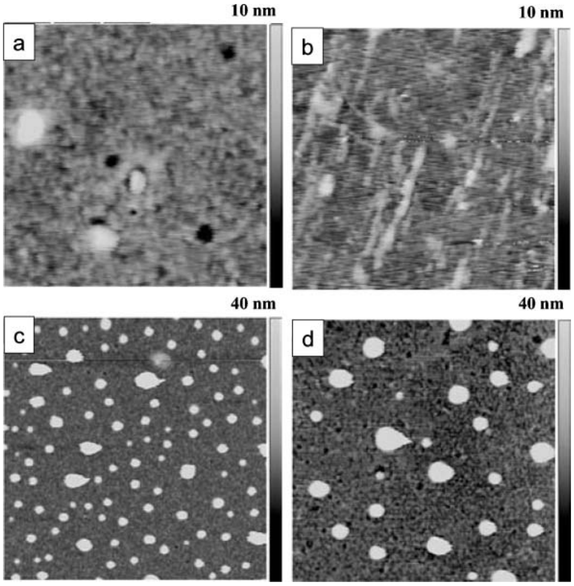

Fig. 2 TM-AFM height images. P3HT (a), 1 : 1 (b), 10 : 1 (c) and 1 : 10 (d) (P3HT : Au NPs) films. (a–b): 1 × 1 μm, (c–d): 3 × 3 μm.

Morphology studies of the composite films were carried out with atomic force microscopy (AFM) and field emission scanning electron microscopy (FE-SEM). Fig. 2 shows tapping-mode (TM)-AFM images (DI Multimode AFM, Digital Instruments, Veeco, USA) of native P3HT (2a), 1 : 1 (2b), 10 : 1 (2c) and 1 : 10 (2d) (P3HT : Au NPs) spin-coated films. The native P3HT films were uniform and flat. Film thickness was measured to be 7–8 nm (as determined by height profile analysis of a scalpel made scratch), which is reasonably close to the value expected for a lamella (bilayer) structure.[18] In contrast, the 10 : 1 and 1 : 10 (P3HT : Au NPs) films showed clumps of the order of 30–40 nm and 40–90 nm (vertical dimension) respectively, suggesting P3HT and Au NP aggregation. Interestingly, the 1 : 1 film showed very good uniformity with a thickness of 15–16 nm, *i.e.* an increase of 8 nm with respect to P3HT. We tentatively suggest that this is most likely due to the insertion of a layer of Au NPs into the film. In order to further probe the arrangement of Au NPs within the composite films, we used FE-SEM (Zeiss, Supra 55 VP, USA) with typical results shown in Fig. 3. In the 10 : 1 film (3a) the Au NPs showed a layered arrangement (as evident from the difference in brightness) with aggregates apparent. In the 1 : 10 composite (3b), the film was overloaded with NPs and multiple cracks in the NP network were evident. In contrast, the 1 : 1 film (3c–d) exhibited a well dispersed, ordered monolayer of NPs. The higher magnification image shows that the NP domains were in close-packed hexagonal arrays.

As shown above, the enhancement of PL intensity in the films is clearly linked to the inclusion of Au NPs into the P3HT matrix. The addition of Au NPs is expected to increase the amount of incident light absorbed by the composite film, effectively leading to an increase in the CP exciton population.[19] Moreover, the nanoparticle nature of the Au dopant is significant to the results presented herein: spin cast films of P3HT onto an underlying Au surface (Cr/Au 10/200 nm film) only showed *ca.* 2-fold increase in the PL.

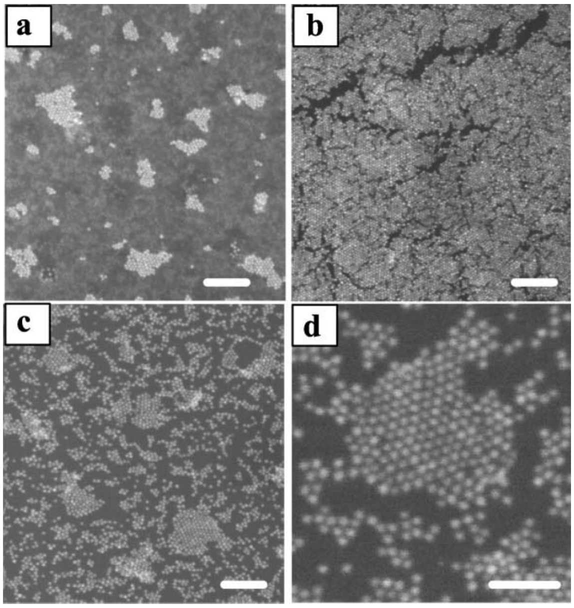

Fig. 3 FE-SEM images of composite films (P3HT : Au NPs): 10 : 1 (a), 1 : 10 (b), 1 : 1 (c and d). Scale bars: (a–c) 100 nm, (d) 50 nm.

However, the increase of PL is not proportional to the concentration of Au NPs. We thus propose that the main effect of Au NPs is to act as a spacer between P3HT chains. An increase in chain separation will result in enhanced intrachain character of the photogenerated singlet excitons (with a stronger optical coupling to the ground state[20]) and consequently an increase in the PL. This "chain separation" effect is greatest in the 1 : 1 films as a uniform, aggregrate-free, monolayer of NPs is more efficient at separating the polymer chains. The 1 : 10 and 10 : 1 films will have more interchain (non-radiative) interactions arising from the aggregates. Thus, the incorporation of Au NPs results in a similar effect as seen from the introduction of long alkyl side groups in the P3HT conjugated backbone.[21]

In addition, inclusion of Au NPs does not induce significant loss of order in the polymer, as evidenced from the lack of significant shift in the PL spectra. As previously reported,[21–23] chain separation can occur without reducing the effective conjugation length of a CP, as long as the planarity in the conjugated backbone is not substantially altered.

In summary, we have presented a simple method for fabricating well-dispersed, uniform Au NPs/P3HT composite films by controlling the ratio of the dopant NP and the host polymer matrix. The morphological changes induced by the NPs correlate well with the steady-state PL, which may increase 6-fold under optimal conditions. This is most likely due to an increase in the intrachain *versus* interchain exciton character of the primary photoexcitations.

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