

A study on the preparation and photophysical properties of an iridium(III) complexed homopolymer

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Received 4th February 2009, Accepted 1st May 2009

First published as an Advance Article on the web 1st June 2009

DOI: 10.1039/b902374g

We have prepared a poly(styrene) [poly(Irppy₂acac)] that has a bis(2-phenylpyridyl)iridium(III) acetylacetonate complex attached to every 'monomer' via a methylene unit. The polymer is solution processable and can be spin-coated to give good quality neat thin films. We show that despite the close proximity of the phosphorescent chromophores along the polymer backbone there is only a modest reduction in the solution photoluminescence quantum yield (PLQY) relative to a monomer model compound. The PLQY of the 4-ethylbenzyl substituted bis(2-phenylpyridyl)iridium(III) acetylacetonate complex was 52% while the poly(Irppy₂acac) had a PLQY of 34%. Time-resolved photoluminescence measurements showed that the photoluminescence decay of the poly(Irppy₂acac) in solution was bi-exponential indicating the presence of more than one emissive species, which was attributed to intra-polymer chromophore interactions. In contrast to the solution measurements the solid-state PLQY was very low (<1%) due to quenching arising from inter-chromophore interactions. When 6 wt% of the poly(Irppy₂acac) was blended with the small molecule host 4,4'-bis(*N*-carbazolyl)-2,2'-biphenyl (CBP), which is a ratio similar to that used for small molecule iridium(III) complexes, significant emission from the CBP was observed suggesting that there was not an even distribution of the polymer in the film. In contrast a 19 wt% blend showed almost complete energy transfer [the CBP peak was 100 times smaller than that of the poly(Irppy₂acac)] and there was an increase in the PLQY relative to the neat films.

Introduction

The heavy atom effect has been used with great success in developing materials for organic light-emitting diodes (OLEDs). Phosphorescent metal containing complexes give rise to more efficient OLEDs than devices containing fluorescent materials as they can harvest both the singlet and the triplet excitons formed during operation.^{1,2} For example, OLEDs comprising an emissive layer containing *fac*-tris(2-phenylpyridyl)iridium(III) [Ir(ppy)₃] blended with 4,4'-bis(*N*-carbazolyl)-2,2'-biphenyl (CBP) have been reported to have an external quantum efficiency of 19% (approaching the maximum 100% internal quantum efficiency).^{3,4} Phosphorescent complexes have also played an important role in the development of dye sensitized solar cells (DSSCs) with devices containing ruthenium(II) complexes still being the most efficient 'organic' excitonic solar cells.⁵ More recently it has been reported that incorporating Ir(ppy)₃ in a poly[2-(2-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene]:PCBM blended film led to more efficient bulk heterojunction solar cells.⁶ In this latter important work it was proposed that the iridium(III) complex dopant allowed tuning of the singlet to triplet ratios, which enhanced the exciton dissociation. It was also found that the incorporation of the heavy metal complex reduced the recombination of the dissociated charge carriers.

Iridium(III) complexes are therefore likely to play an important role in both OLEDs and solar cells. However, if iridium(III) complexes are to be used in large area applications such as solid-state lighting and bulk heterojunction solar cells then simple methods for their processing need to be developed. Most studies on iridium(III) complexes have focused on small molecules, which usually require high temperature/high vacuum deposition techniques.

While excellent devices can be produced by evaporation there is strong interest in having the phosphorescent complexes solution processable, thereby allowing low-cost and efficient solution processing techniques, such as spin-coating or ink-jet printing for large area device fabrication for white lighting and bulk heterojunction solar cells. The most successful approach to solution-processed phosphorescent materials thus far has been to incorporate them as the core within a dendritic structure.⁷⁻¹⁴ An alternative route to solution-processed devices is to blend small molecule emitters with a polymeric host^{6,15-19} or to have a metal complex attached to the polymer backbone.²⁰⁻⁴⁰ In the latter case the covalent attachment of the phosphorescent emitter should give rise to more morphologically stable films than the blends.

'Phosphorescent polymers' with the metal complex covalently attached to the polymer backbone fall into two classes; namely those in which the complex is connected to a conjugated polymer, such as poly(fluorene),²⁰⁻²³ poly(fluorene-carbazole),^{24,25} and poly(*p*-phenylene),²⁶ and those in which the polymer backbone is saturated,²⁷⁻⁴⁰ for example, polystyrene²⁷⁻³⁴ and poly(ϵ -caprolactone).^{35,36} In all these studies the effort has focused on copolymer structures that contain low levels of the phosphorescent emitters.

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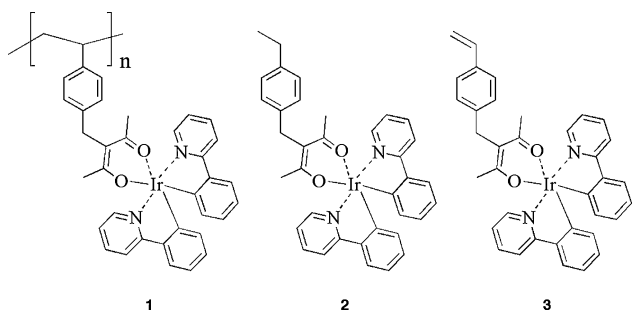


Fig. 1 Structures of poly(Irppy₂acac) **1**, the model complex **2**, and the monomer **3**.

The low number of phosphorescent emitters attached to the polymer backbone has been used to mimic the approach used for small molecule systems in which the emissive complex is diluted in the host. Interestingly, as far as we are aware there has not been a simple small-complex-containing solution processable ‘phosphorescent homopolymer’ reported. Such a material would be of interest to use as a dopant in a bulk heterojunction solar cell or potentially as an emissive material in an OLED.

In this manuscript we describe the synthesis of a homopolymer **1** containing a poly(styrene) backbone with one bis(2-phenylpyridyl)iridium(III) acetylacetonate complex per monomer unit (Fig. 1). We show that the polymer is solution processable and can form good quality neat thin films and can be blended with another material. The polymer structure provides a useful platform to investigate and understand how the proximity of iridium(III) complexes impacts on the associated optoelectronic properties in a controlled manner. We show that the poly(Irppy₂acac) is thermally stable and report the photophysical and electrochemical properties of the material comparing it with a model compound **2** and the monomer **3** (the structures of the materials are shown in Fig. 1).

Results and discussion

Synthesis and physical properties

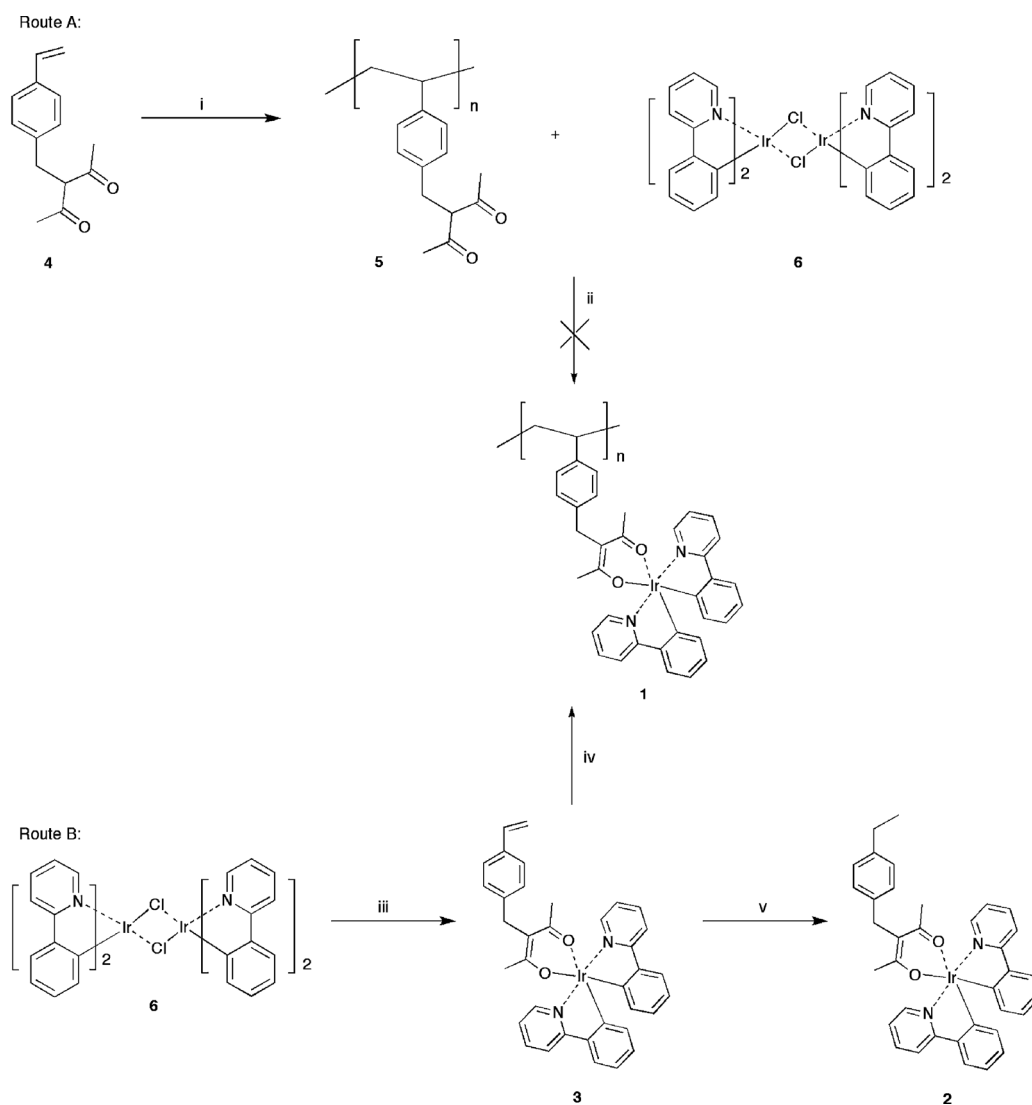
While there are several carrier polymers that could have been chosen for preparing the homopolymer we decided to use styrene monomers as they can be easily polymerized. In common with previous work on copolymeric materials we decided to utilize a heteroleptic iridium(III) complex in which the 2-phenylpyridyl ligands were responsible for the green light emission and the β -diketonate ancillary ligand was used for the connection to the styrene unit. The 3-[4-vinylbenzyl]pentane-2,4-dione ancillary ligand has been used previously in the preparation of copolymers containing iridium(III) complexes.³¹ There are two potential strategies for the formation of the homopolymer; first, the 3-[4-vinylbenzyl]pentane-2,4-dione **4** could be polymerized (**5** in Scheme 1) followed by complexation with concomitant ‘cracking’ of the bis-iridium bis-chloro dimer **6** (route A, Scheme 1). While we initially investigated this route, we found that the complexation step did not work efficiently and it was not possible to fully co-ordinate the iridium(III) to every monomer unit or form a soluble polymer. We therefore focused our efforts on the second route (route B, Scheme 1), which involved the

preparation of the styryl monomer complex for subsequent polymerization.

The 3-[4-vinylbenzyl]pentane-2,4-dione **4**³¹ and bis-iridium bis-chloro dimer **6**⁴¹ were synthesized following literature procedures. To form the monomer the bis-iridium bis-chloro dimer was first treated with silver triflate in acetone heated at reflux. The cloudy yellow solution was gravity-filtered before 3-[4-vinylbenzyl]pentane-2,4-dione and triethylamine were added sequentially. The chelation proceeded very quickly at room temperature and strong green luminescence could be observed immediately on addition of the triethylamine under long-wave UV radiation. The monomer was purified by column chromatography over neutral alumina, followed by precipitation by pouring a dichloromethane solution into hexane to afford **3** in a good yield of 71%. Monomer **3** was air-stable, although it was found to be somewhat sensitive to acidic environments, and was found to decompose on silica and as a solution in chloroform in the presence of light. In addition, it was determined that the best way to dry the monomer was under a flow of nitrogen.

With the monomer **3** in hand the next step was to carry out its polymerization using 1,1-azobis(cyclohexanecarbonitrile) as the initiator. The polymerizations were carried out at concentrations in the range of 0.35–0.40 M in tetrahydrofuran, 1,4-dioxane, or *N*-methylpyrrolidinone. In each case the polymer was purified by precipitation into acetone. It was found that when the polymerization was carried out in tetrahydrofuran there was a significant amount of low molecular weight material, which was absent from the reaction that was carried out in *N*-methylpyrrolidinone. Analysis of the polymer molecular weights by gel permeation chromatography against polystyrene standards was hampered by the fact that after drying even the polymer that was formed in tetrahydrofuran had a portion that was insoluble in the tetrahydrofuran used for the analysis. Therefore, the analysis of the molecular weights was based on the fraction soluble in tetrahydrofuran after drying. It was found that when the polymer was synthesized in tetrahydrofuran it could be isolated in a 53% yield and the soluble fraction had a bimodal molecular weight distribution with the higher molecular weight component having an \overline{M}_w of 5.0×10^3 and polydispersity of 1.4. The higher boiling point 1,4-dioxane gave similar results to the tetrahydrofuran. The proportion of the different molecular weights in the bimodal distribution varied a little between experiments, which was probably due to the efficiency of mixing on the small scales used. In contrast, *N*-methylpyrrolidinone consistently gave polymer with the soluble fraction having a higher molecular weight ($\overline{M}_w = 8.3 \times 10^3$, polydispersity = 1.8) and higher yields (of order 71%). The solubility of the monomer, polymer, and model compound will be commented on further shortly.

A key aspect of this work is understanding the effect of placing the iridium(III) complexes in close proximity along the polymer backbone. While in principle a comparison between the photophysical properties of the poly(Irppy₂acac) **1** and monomer **3** could be made, a better model of the effect of incorporating the complexes into the polymer would be to have an ethylene unit attached to the ‘monomer’ unit rather than the vinyl moiety so as to mimic the complex in the polymer. We therefore prepared the model compound **2** whereby the vinyl group was converted to an ethylene moiety. Hydrogenation of monomer **3** with a palladium on carbon catalyst gave the model compound **2** in a yield of 76%.



Scheme 1 Reagents and conditions: (i) THF, 1,1-azobis(cyclohexanecarbonitrile), 80 °C, sealed tube; (ii) Na₂CO₃, 50 : 50 2-ethoxyethanol–anisole, 80 °C, sealed tube; (iii) AgOTf, acetone, Δ then **4**, Et₃N, r.t.; (iv) *N*-methylpyrrolidinone, 1,1-azobis(cyclohexanecarbonitrile), 80 °C, sealed tube; (v) H₂, Pd/C, THF, r.t.

Both the monomer **3** and model compound **2** were soluble in organic solvents such as dichloromethane, chloroform, and tetrahydrofuran. The poly(Irppy₂acac) **1** was found to be completely soluble in dichloromethane and 1,2-dichloroethane, but only partly soluble in chloroform, tetrahydrofuran, toluene, and xylene. The reason for the specific solubility of the poly(Irppy₂acac) in the two solvents that have similar polarities to the other solvents is unclear. However, the good solubility in dichloromethane and 1,2-dichloroethane enabled the spin-coating of the polymer to form good quality thin films. For example, a neat film with thickness of the order of ~120 nm was obtained by spin-coating a 1,2-dichloroethane solution of poly(Irppy₂acac) **1** at a concentration of 20 mg mL⁻¹. The fact that the poly(Irppy₂acac) could be solution-processed is remarkable given the lack of solubilizing groups and solution processibility of the parent complex.

The thermal stability of poly(Irppy₂acac) **1** under nitrogen was evaluated using thermal gravimetric analysis. The poly-

(Irppy₂acac) was found to be thermally stable with the onset of weight loss at a temperature higher than 335 °C. The polymer had a weight loss of 5% at around 347 °C. Between 335 °C and 520 °C the polymer was found to lose around 23% of its weight. The 23% weight loss is similar to the mass associated with the 2-phenylpyridyl ligands (22%) or the polymer backbone with the acetoacetonate ligand (30%). Given that the acetoacetonate ligand binding constant is smaller than that of the 2-phenylpyridyl ligands it is likely that this weight loss is due to the latter. Differential scanning calorimetry showed that the polymer did not have a glass transition temperature or melting point in the range of -20 °C to 280 °C.

Photophysical and electrochemical properties

The first step in the analysis of the photophysical properties of the materials was the measurement of the UV-visible absorption spectra of the monomer **3**, model compound **2**, and

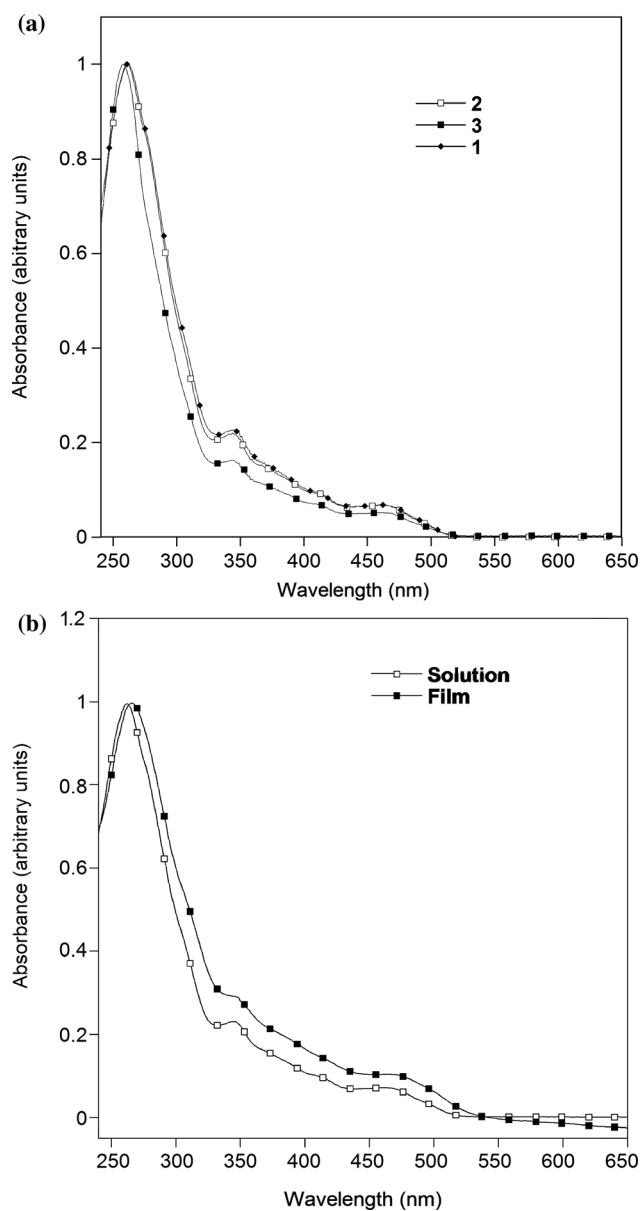


Fig. 2 (a) Normalized UV-visible solution absorption spectra of the monomer **3**, model complex **2**, and poly(Irppy₂acac) **1** in dichloromethane. (b) Comparison of the solution (dichloromethane) and film UV-visible absorption of poly(Irppy₂acac) **1**.

poly(Irppy₂acac) **1**, and these are shown in Fig. 2. The absorption spectra of the three compounds in solution (Fig. 2a) are similar indicating that the polymerization to a first approximation has not changed the optical transition energies of the iridium(III) complex chromophore. In common with other simple iridium(III) complexes the spectra can be divided into two regions; the short and strong absorptions at wavelengths less than 320 nm are primarily due to the $\pi-\pi^*$ transitions associated with the 2-phenylpyridyl ligands and in this case the acetylacetonate ancillary ligand, while the weaker multiple overlapping absorptions extending to around 520 nm are typical of the ‘metal-to-ligand charge-transfer’ transitions of iridium(III) complexes. The film UV-visible absorption spectrum of the poly(Irppy₂acac) is similar to that of the solution (Fig. 2b)

indicating that there are not strongly aggregating species formed on moving to the solid-state.

We next investigated the photoluminescence (PL) properties of the materials in solution with the PL spectra of **1** and **3** shown in Fig. 3a. The monomer **3** had a peak at 524 nm and shoulder at 553 nm while the poly(Irppy₂acac) **1** had a peak at 527 nm and shoulder at 556 nm. One of the interesting observations of the PL spectra is that the poly(Irppy₂acac) does not have a broad and red-shifted spectrum that would be associated with intermolecular interactions of the iridium(III) complexes along the polymer backbone, that is, intra-polymer chromophore interactions. To understand the effect of structure on the photophysical properties we determined the PL quantum yields (PLQYs) and undertook time-resolved PL (TRPL) measurements. Monomer **3** had

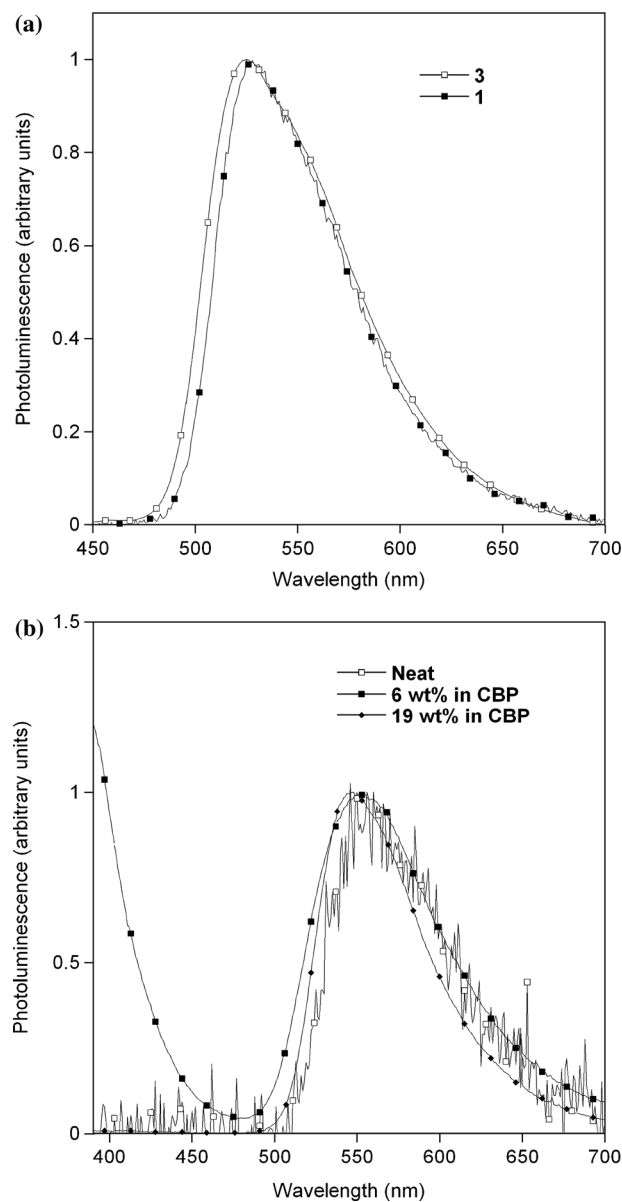


Fig. 3 (a) Normalized PL spectra of polymer **1** and monomer **3**. (b) Film PL spectra of neat **1**, and 6 wt% and 19 wt% in CBP. Excitation wavelength = 360 nm.

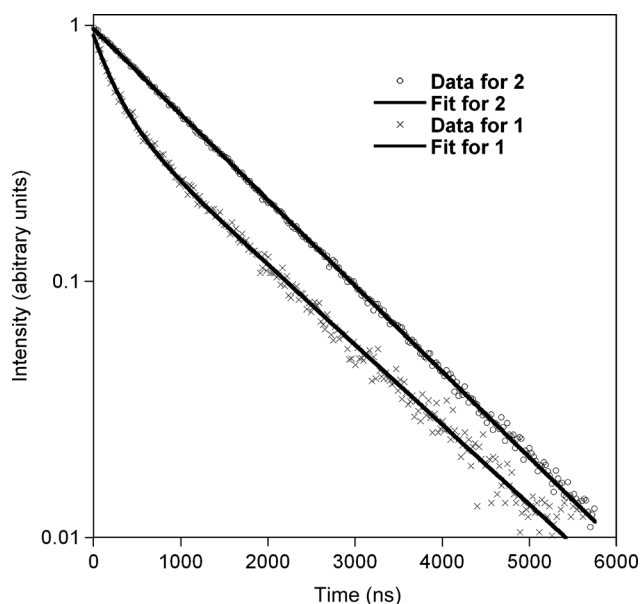


Fig. 4 Time-resolved lifetime decay curves of polymer **1** and the model compound **2**, following excitation at 355 nm.

a PLQY of 42% and the TRPL measurement showed a mono-exponential decay with a lifetime of 670 ns. A mono-exponential decay indicates that there is only one emissive species present. Model compound **2** in which the double bond of **3** has been converted to an ethyl moiety was found to have a PLQY of 52% and the TRPL gave a lifetime of 1.3 μ s. Again the decay was mono-exponential (Fig. 4), which is expected for a dilute solution of identical non-interacting chromophores. The higher PLQY and longer PL lifetime of **2** when compared to **3** imply that the presence of the vinyl group leads to a more efficient non-radiative pathway for the excited state in the latter. Finally, the PLQY of the poly(Irppy₂acac) **1** was 34% and the TRPL (Fig. 4) showed a bi-exponential decay with an initial fast component with a lifetime of 255 ns and a second longer component with a lifetime of 1.4 μ s. The long component closely matches the 1.3 μ s mono-exponential lifetime for model compound **2**. The good PLQY of **1** is an important result for materials design as it shows that iridium(III) complexes can be held close together without severe detrimental effects to their PL properties, at least in solution. If there were strong intra-polymer chromophore interactions then the PLQY of the poly(Irppy₂acac) would be expected to be quenched in a similar manner to neat thin films of the simple iridium(III) complexes.⁴² The two-component decay profile arises from there being more than one emissive species. That is, both time-resolved PL and PLQY measurements show that there are interactions between the intra-polymer chromophores of **1** but they are not sufficient to quench the luminescence strongly.

Differences were observed in the photophysical properties on moving from solution to the solid-state. Neat films of the poly(Irppy₂acac) **1** were spin-coated from 1,2-dichloroethane and the PL spectrum is shown in Fig. 3b. The first detail to note is that the emission is weak, leading to a spectrum with a poor signal to noise ratio. This is confirmed by the solid-state PLQY, which was found to be <1%. The decrease in PLQY in the solid-

state is similar to that seen for neat films of simple iridium(III) complexes and is likely to arise from inter-polymer chromophore interactions. Such intermolecular interactions could lead to the red-shifted emission (peak at 557 nm) seen for the poly(Irppy₂acac) **1** in the film. However, it is important to note that in spite of the interactions that lead to the quenching of the luminescence the films were clear and showed no signs of crystallite formation. Atomic force microscopy (AFM) showed that the films were uniform (Fig. 5a) and the average roughness (Ra) of the 45 nm thick film shown in Fig. 5a was <0.5 nm. To test whether inter-polymer chromophore interactions were the dominant cause for the decrease in PLQY we blended the material with a host to see whether there would be an increase in the PLQY. The poly(Irppy₂acac) **1** was therefore blended with CBP, which is commonly used as a host for small molecule iridium(III) complexes, at two different concentrations. When the poly(Irppy₂acac):CBP weight ratio was 19 wt% the emission maximum was blue-shifted (peak at 546 nm) slightly and the PLQY was increased to 7%. This shows that inter-polymer chromophore interactions had been decreased although not

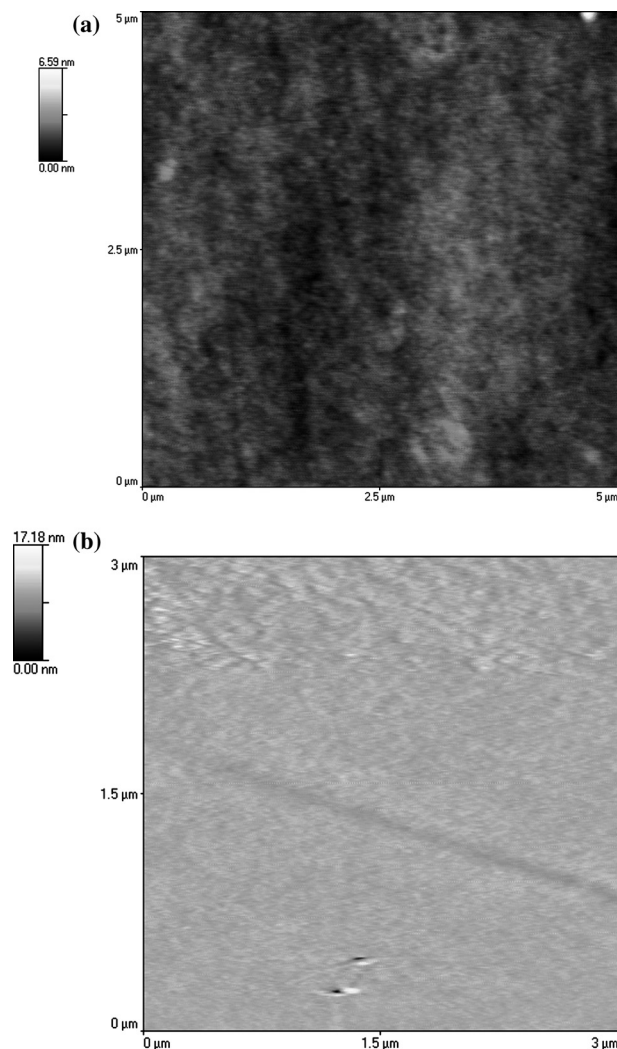


Fig. 5 AFM scans of: (a) a neat film of **1** and (b) a film of 6 wt% of **1** blended in CBP.

completely eliminated due to the fact that the PLQY is still significantly below that of the solution measurement. Decreasing the poly(Irppy₂acac):CBP ratio to 6 wt% was expected to decrease the inter-polymer chromophore interactions further. However, while the PL spectrum of the 19 wt% poly(Irppy₂acac):CBP film showed emission from the poly(Irppy₂acac) the 6 wt% film showed emission from both the CBP and the poly(Irppy₂acac) (Fig. 3b). For small molecule iridium(III) complexes blended with CBP at a concentration of 6 wt% it is assumed that the complex is evenly distributed throughout the film because only emission from the complex is observed. However, in our system, the Irppy₂acac chromophores are attached to the polymer chains, and so are unable to be uniformly distributed throughout the film as individual chromophores. This means that there are some CBP molecules that are far from the Irppy₂acac chromophores, which leads to incomplete energy transfer at this concentration in our system. Nevertheless the lower PLQY in the solid-state indicates that there are inter-chromophore interactions, which may be intra- and inter-polymer in nature. It is important to note that even though there was not complete energy transfer from the host to the guest in the 6 wt% film, the film is uniform with no significant phase separation observed by AFM (Fig. 5b). The Ra of the film that was 110 nm thick was determined to be around 0.4 nm.

Finally, cyclic voltammetry (CV) experiments were carried out to investigate the electronic properties of the iridium(III) complexes, **2** and **3**, and the poly(Irppy₂acac) **1**. It has been reported that the parent complex [bis(2-phenylpyridinato-*N,C'*)acetylacetonate]iridium(III) undergoes one chemically reversible oxidation.⁴¹ The oxidation cyclic voltammograms were measured in dichloromethane and **3**, **2**, and **1** had chemically reversible oxidations at 0.24 V, 0.23 V, and 0.23 V, respectively. That is, the first oxidation of all three compounds occurs at the same potential showing that the methylene unit between the acetylacetonate co-ligand and the phenyl of the 'styrene' breaks the conjugation and hence the energy of the highest occupied molecular orbital (HOMO) is not affected.

Conclusion

We have demonstrated an efficient approach to the synthesis of a homopolymer in which iridium(III) complexes are attached to every monomer unit. The homopolymer was found to be sufficiently soluble to allow solution processing in spite of there being no solubilizing groups attached to the complex. The solution photophysical measurements show that even when the iridium(III) complexes are held close together, efficient PL is still obtained. Solid-state measurements show that inter-polymer chromophore interactions lead to strong quenching of the luminescence, and that the normal strategy to overcome this of blending the material with a simple host is only partially successful due to the clustering of the complexes on the polymer chain.

Experimental

General methods

All commercial reagents were used as received unless otherwise noted. Tetrahydrofuran was distilled from sodium and benzophenone under a nitrogen atmosphere before use. ¹H and ¹³C

NMR spectra were recorded using a 300 MHz or 400 MHz Bruker spectrometer, in deuterated chloroform or dichloromethane solution; LPH = ligand phenyl H, pyH = pyridyl H, styrylPH = protons of the phenyl ring attached to the vinyl moiety, ethylPH = protons of the phenyl ring attached to the ethyl moiety. Coupling constants are quoted to the nearest 0.5 Hz. Gel permeation chromatography was carried out on a Polymer Laboratories PL-GPC 50 using PLgel Mixed-A columns (600 mm + 300 mm lengths, 7.5 mm diameter) from Polymer Laboratories calibrated with polystyrene narrow standards ($M_p = 162-6.035 \times 10^6$) in tetrahydrofuran with toluene as the flow marker. The tetrahydrofuran was pumped at a rate of 1 cm³ min⁻¹ at 40.0 °C. Microanalyses were carried out in Microanalysis Laboratory of the School of Chemistry and Molecular Biosciences, The University of Queensland. UV-visible absorption measurements were recorded with a Cary Varian 5000 UV-Vis-NIR spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. A polymer film of thickness 120 nm was spin-coated onto a quartz substrate from a 1,2-dichloroethane solution of polymer at a concentration of 20 mg mL⁻¹ at a spin rate of 1500 rpm. Melting points were measured in a glass capillary on a BUCHI Melting Point B-545 and are uncorrected. Thermogravimetric analysis (TGA) was carried out on a Perkin Elmer STA6000 and the Differential scanning calorimetry was performed using a Perkin Elmer Diamond DSC. Mass spectra were recorded on an Applied Biosystems Voyager matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) from 2-[(2-*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) in positive reflection mode.

Electrochemistry was performed using a BAS Epsilon electrochemistry station using a glassy carbon working, 0.1 M AgNO₃ in acetonitrile reference, and platinum counter electrodes, and a 100 mV s⁻¹ scan rate. All measurements were made at room temperature on samples at a 1 mM concentration in dichloromethane (HPLC grade), with 0.1 M tetra-*n*-butylammonium tetrafluoroborate as the electrolyte. The solutions were deoxygenated with argon and the ferricenium/ferrocene couple was used as standard.⁴³ The scan rate was 100 mV s⁻¹ and in all cases several scans were carried out to confirm the chemical reversibility of the redox processes.

AFM measurements were made using a Veeco diCaliber AFM operating in contact mode. The scans were made at a scan rate of one line per second.

Solution PLQYs were measured by a relative method using quinine sulfate in 0.5 M sulfuric acid, which has a PLQY of 0.546, as the standard.⁴⁴ The materials were dissolved in dichloromethane and freeze-thaw degassed. Photoluminescence spectra were recorded in a JY Horiba Fluoromax 2 fluorimeter, with the solutions excited at 360 nm. The optical densities of the standard and sample were similar and small (~0.1). The accuracy of these measurements is estimated to be ±10% of the stated value. The time-resolved luminescence measurements were performed using the time-correlated single photon counting technique, with excitation at 355 nm from a pulsed Nd:YAG microchip laser and an instrument response of ~1 ns. For the solid-state PLQY measurements the sample was placed in an integrating sphere under a nitrogen purge and excited with the 325 nm line of a He-Cd laser at a power of ~0.3 mW. The

luminescence was detected from a calibrated photodiode behind a UV filter and the PLQY was calculated in accordance with the method of Greenham *et al.*⁴⁵

Bis(2-phenylpyridyl)iridium(III) [3-(4-vinylbenzyl)acetylacetonate] 3

6 (700 mg, 0.65 mmol) and silver triflate (334 mg, 1.31 mmol) were dissolved in acetone (55.5 cm³). The solution was deoxygenated with argon before being heated at reflux for 24 h. The cloudy yellow solution was cooled and gravity-filtered to remove silver chloride. 3-[4-Vinylbenzyl]pentane-2,4-dione **4**³¹ (611 mg, 2.82 mmol) and triethylamine (1.3 cm³) were added to the filtrate. The solution was deoxygenated with argon and was then stirred at room temperature in the absence of light for 24 h. The solvent was removed and the dark yellow solid was purified by column chromatography over alumina using dichloromethane as the eluent. The bright yellow band was collected and the solvent was removed. The residue was redissolved in dichloromethane (60 cm³), and the complex was precipitated by pouring into hexane (200 cm³). The precipitate was collected at the filter and dried under flow of nitrogen at room temperature, yielding a bright yellow powder of **3** (665 mg, 71%), mp ≥ 284 °C (decomp.). Found: C, 60.1; H, 4.1; N, 3.9. C₃₆H₃₁IrN₂O₂ requires C, 60.4; H, 4.4; N, 3.9%. ν_{\max} (solid)/cm⁻¹ 1567 (C=O); λ_{\max} (CH₂Cl₂)/nm 258 [log ϵ /dm³ mol⁻¹ cm⁻¹ (4.73)], 343 (3.94), 368sh (3.78), 387sh (3.67), 410sh (3.56), 460 (3.42), 492sh (3.63); δ_{H} (300 MHz, CDCl₃) 1.81 (6H, s, CH₃), 3.71 (2H, m, CH₂), 5.22 (1H, d, $J = 11$, vinyl H), 5.72 (1H, d, $J = 17.5$, vinyl H), 6.29 (2H, d, $J = 7.5$, LPH), 6.67–6.73 (3H, m, vinyl H and LPH), 6.82 (2H, m, LPH), 7.08 and 7.31 (4H, AA'BB', styrylPH), 7.18 (2H, m, pyH), 7.57 (2H, d, $J = 8$, LPH), 7.78 (2H, m, pyH), 7.89 (2H, m, pyH), 8.60 (2H, m, pyH); δ_{C} (75 MHz, CDCl₃) 28.4, 36.4, 107.0, 113.0, 118.4, 120.5, 121.2, 123.8, 126.1, 127.6, 129.0, 133.1, 135.2, 136.6, 136.8, 142.3, 144.6, 148.1, 168.7, 184.7. m/z (MALDI: DCTB) found: 714.2 (54%), 715.2 (20%), 716.2 (100%), 717.2 (39%), 718.2 (8%). C₃₆H₃₁IrN₂O₂ requires 714.2 (58%), 715.2 (25%), 716.2 (100%), 717.2 (40%), 718.2 (8%).

Bis(2-phenylpyridyl)iridium(III) [3-(4-ethylbenzyl)acetylacetonate] 2

A solution of **3** (200 mg, 0.28 mmol) in tetrahydrofuran (16 cm³) was deoxygenated with argon. Palladium on carbon (10 wt%, 16.9 mg) was added and the mixture was deoxygenated with argon. A hydrogen balloon was attached and the reaction mixture was stirred at room temperature under a positive pressure of hydrogen for 24 h. The reaction mixture was loaded onto a short alumina plug and the product was washed through using dichloromethane as the eluent. The bright green band was collected and the solvent removed. The residue was further purified by dissolution in dichloromethane (10 cm³) and precipitation by pouring into hexane (40 cm³). The precipitate was collected at the filter and dried under a flow of nitrogen at room temperature, yielding a bright yellow powder of **2** (151 mg, 76%), mp ≥ 292 °C (decomp.). Found: C, 60.0; H, 4.5; N, 3.9. C₃₆H₃₃IrN₂O₂ requires C, 60.2; H, 4.6; N, 3.9%. ν_{\max} (solid)/cm⁻¹ 1567 (C=O); λ_{\max} (CH₂Cl₂)/nm 261 [log ϵ /dm³ mol⁻¹ cm⁻¹ (4.55)], 276sh (4.48), 310sh (4.11), 343 (3.90), 369sh (3.73), 388sh (3.63), 410sh (3.52), 461 (3.39), 492sh (3.07); δ_{H} (300 MHz, CDCl₃) 1.25 (3H, t, $J = 7.5$, CH₂CH₃), 1.81 (6H, s, CH₃), 2.64

(2H, q, $J = 7.5$, CH₂CH₃), 3.68 (2H, m, CH₂), 6.29 (2H, d, $J = 7.5$, LPH), 6.69 (2H, dd, $J = 7.5$, 7.5, LPH), 6.82 (2H, dd, $J = 7.5$, 7.5, LPH), 7.02 and 7.09 (4H, AA'BB', ethylPH), 7.18 (2H, m, pyH), 7.58 (2H, d, $J = 8$, LPH), 7.77 (2H, m, pyH), 7.89 (2H, d, $J = 8$, pyH), 8.60 (2H, d, $J = 6$, pyH); δ_{C} (75 MHz, CDCl₃) 15.6, 28.4, 36.2, 107.4, 118.4, 120.5, 121.2, 123.8, 127.4, 127.7, 129.1, 133.1, 136.8, 139.5, 141.5, 144.7, 148.1, 148.6, 168.7, 184.7. m/z (MALDI: DCTB) found: 716.2 (50%), 717.2 (20%), 718.2 (100%), 719.2 (33%), 720.2 (6%). C₃₆H₃₃IrN₂O₂ requires 716.2 (56%), 717.2 (24%), 718.2 (100%), 719.2 (40%), 720.2 (9%).

Synthesis of poly(Irppy₂acac) 1

A Schlenk tube was charged with **3** (400 mg, 0.56 mmol), 1,1-azobis(cyclohexanecarbonitrile) (6.83 mg, 0.028 mmol), and 1-methyl-2-pyrrolidinone (1.2 cm³). The solution was deoxygenated by cooling with dry ice and placing under vacuum and backfilling with argon three times before it was heated at 80 °C for 24 h. Upon completion, it was allowed to cool to room temperature. The reaction mixture was then poured into a stirred acetone (40 cm³) solution and the precipitate was collected at the filter. The residue was dissolved in dichloromethane (3 cm³) before being precipitated by pouring into a stirred acetone (40 cm³) solution. The precipitate was collected at the filter and then dried under a flow of nitrogen to give a yellow powder of **1** (284 mg, 71%). mp ≥ 344 °C (decomp.); TGA (5%) 347 °C. Found: C, 59.7; H, 4.4; N, 3.9. (C₃₆H₃₁IrN₂O₂)_n requires C, 60.2; H, 4.4; N, 3.9%. ν_{\max} (solid)/cm⁻¹ 1564 (C=O); λ_{\max} (CH₂Cl₂)/nm: 262, 277sh, 308sh, 346, 370sh, 388sh, 413sh, 465, 492sh; δ_{H} (400 MHz, CD₂Cl₂) 1.22–2.14 (br m, CH₂CH₃, CH₃, and CH₂CH₃), 3.27–3.77 (br s, CH₂), 6.16–7.19 (br m, LPH, pyH, and/or ethylPH), 7.41–7.94 (br m, LPH, pyH, and/or ethylPH), 8.37–8.65 (br s, pyH); GPC: $\overline{M}_w = 8.3 \times 10^3$, $\overline{M}_n = 4.6 \times 10^3$, PD = 1.8.

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