Preparation of phosphorescent crystalline tris(1-phenylisoquinoline) iridium nanobelts *via* a recrystallization method†

Debao Xiao,* Haiyan Xiao, Lili Liu and Xueling Li

Received (in Montpellier, France) 16th March 2010, Accepted 15th April 2010
First published as an Advance Article on the web 6th May 2010
DOI: 10.1039/c0nj00200c

A relatively large amount of crystalline coiled nanobelts (>6 mg per trial) of a transition metal complex, tris(1-phenylisoquinoline) iridium(III) [Ir(piq)$_3$], were prepared *via* a simple recrystallization procedure in ethyl acetate, which may offer the flexibility to process such nanobelt materials by spray coating for potential applications in functional devices.

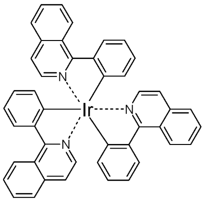
The past two decades have witnessed a rapid development of material science and technology.[1–9] During this period, inorganic nanomaterials,[1,2] as well as organic ones,[5–9] have attracted a wide range of research interest due to their theoretical interest and potential device applications arising from their optical and electrical properties. As far as the synthesis of organic nanomaterials is concerned, a wide range of methods, such as re-precipitation (or/and solvent exchange),[3–5,10] chemical vapor deposition (CVD),[6] self-assembly,[7] adsorbent-assisted physical vapor deposition (PVD),[11] laser ablation,[12] anodized aluminium oxide (AAO) nanochannel-templated growth,[13] microemulsions[14] and electrodeposition,[15] have been developed, facilitating investigations into their optoelectronic functional properties. Recently, nanowires of hexathiopentacene[8] and acid green 27 (an organic dye)[9] were successfully prepared by recrystallization, in spite of the fact that the applicability of this method to other organic functional molecules has yet to be clarified. To the best of our knowledge, a large-scale preparation of organic nanomaterials, as well as nanosized materials of transition metal complexes (*e.g.* milligram-scale for each trial), that is easy to scale up and process, remains a challenge at present.

In this work, we have conducted a series of preparations of 1-D nanowires (or nanobelts or nanotubes) *via* a recrystallization method using eight of the most frequently used organic light-emitting functional molecules, tris(2-phenylpyridine) iridium (Ir(ppy)$_3$), tris(1-phenylisoquinoline) iridium (Ir(piq)$_3$), bis(2-(2-hydroxyphenyl) benzothiazolate) zinc (Zn(ZBT)$_2$), bis(2-(2-hydroxyphenyl) benzoxazolate) zinc (Zn(BOX)$_2$), *N*,*N*′-di (naphthalene-1-yl)-*N*,*N*′-diphenyl-benzidine (NPB), tris(8-hydroxyquinoline) aluminium (AlQ$_3$), pentacene and tetracene, and ten frequently used organic solvents, as well as their mixtures. We found that successful preparation was significantly dependent on the organic molecules themselves and on the solvents used. In this scenario, only the nanomaterials of Ir(piq)$_3$ could be obtained through a recrystallization procedure, demonstrating that the applicability of this method deserves to be checked in the cases of the preparations of 1-D nanowires or nanobelts of many other organic molecules.

Iridium organometallic complexes are currently a focus of research due to their high light-emitting efficiency, arising from a strong spin–orbit coupling-induced triplet state emission,[16] in terms of both synthesizing derivatives and preparing related nanomaterials, despite the fact that iridium is one of the most expensive rare elements on the earth. Tris(1-phenylisoquinoline) iridium(III) (Ir(piq)$_3$, Scheme 1) has been extensively investigated as a predominantly-used phosphorescent red-emitting material in electroluminescent devices. We have successfully demonstrated a facile template-free route to the bulk fabrication of phosphorescent Ir(piq)$_3$ nanobelts (> 6 mg for each trial) from commercially available precursor bulk crystals by a simple recrystallization process in a relatively poor solvent for this transition metal complex, ethyl acetate, suggesting the flexibility to process as-prepared nanobelts for applications in devices.

The Ir(piq)$_3$ nanobelts were prepared *via* recrystallization of the bulk crystals in ethyl acetate. The as-fabricated nanobelts could be readily collected and transferred into a poor organic solvent for Ir(piq)$_3$, such as methanol. The nanobelts separated out of the solution within 2 h (Fig. 1A) and could be easily redispersed by mechanical agitation of the vial (Fig. 1B). It was noted that the yield of the nanobelts from the dissolved Ir(piq)$_3$ powder (6.5 mg) was higher than 95.4% (6.2 mg). This indicates that milligram-scale Ir(piq)$_3$ nanobelts could be obtained in one trial and importantly that the preparation could be easily scaled up.

Fig. 1D presents a typical field-emission scanning electron microscopy (FESEM) image of the as-prepared Ir(piq)$_3$



Scheme 1 The molecular structure of tris(1-phenylisoquinoline) iridium(III) (Ir(piq)$_3$).

Hebei Key Laboratory of Applied Chemistry, College of Environmental and Chemical Engineering, Yanshan University, 438 West Hebei Avenue, Qinhuangdao 066004, P. R. China. E-mail: debao.xiao@ysu.edu.cn; Fax: +86 335-8061569; Tel: +86 335-806156

† Electronic supplementary information (ESI) available: FT-IR spectrum, packing mode of the molecules, spectral evidence of resonance energy transfer and the energy level diagram. See DOI: 10.1039/c0nj00200c

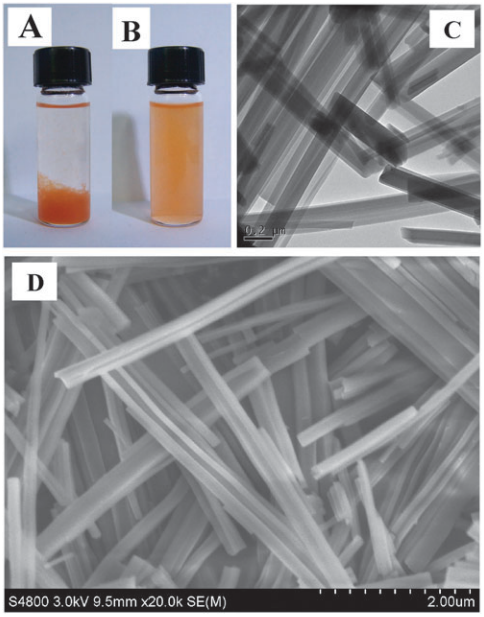


Fig. 1 (A) A digital photograph showing the cotton-like state of the Ir(piq)$_3$ nanobelts in methanol. (B) Well-suspended nanobelts after agitating the vial. (C) A TEM image of a network of Ir(piq)$_3$ nanobelts. (D) An FESEM image of a network of Ir(piq)$_3$ nanobelts.

nanobelts. It is obvious that coiled, belt-like, 1-D nanostructures are formed, which could be further proved by TEM observation (Fig. 1C). The average apparent widths of the nanobelts are 200 nm and the average length reached up to tens of microns. Note that any mechanical agitation of the cotton-like nanobelts could lead to fracturing of the nanostructures. The length of the freshly formed nanobelts could reach up to the scale of millimetres. The XRD pattern shown in Fig. 2 indicates that the nanobelts are crystalline, and the pattern could be well indexed to (1 0 0), (2 $\bar{1}$ 0), (2 0 0), (3 0 0) of the known Ir(piq)$_3$ phase,[16] suggesting that the nanobelts may potentially grow preferentially along the (1 0 0) facet (see Fig. S-2, ESI†), which is supported by the increased intensity ratio of (1 0 0) to (2 −1 3) and the emergence of two facets, (2 0 0) and (3 0 0). The FT-IR spectrum of the obtained Ir(piq)$_3$ nanobelts (see Fig. S-1, ESI†) shows the characteristic absorption peaks of the precursor molecules at 517, 630, 673, 735, 814, 1037, 1150, 1267, 1352, 1380, 1428, 1441, 1499, 1534, 1575 and 1617 cm^{-1}, indicating that no chemical modification of the Ir(piq)$_3$ molecules occurred in the as-obtained nanobelts during the recrystallization process in the hot solvent.

In this solution-phase based preparation of Ir(piq)$_3$ nanobelts, no catalyst was employed, and it is reasonable to suggest that the growth mechanism can be explained by a liquid–solid (LS) model, which is usually seen in inorganic 1-D systems.[1,2,17] After the Ir(piq)$_3$/ethyl acetate solution had been kept at 70 °C for more than 1 h and the hot filtration had been performed, the concentration of the Ir(piq)$_3$ solution was less than 5.4×10^{-5} mol L^{-1}, at which concentration molecules are usually regarded as being monomeric, indicating that this molecule is poorly soluble, even in hot ethyl acetate. The solvated Ir(piq)$_3$ molecules collide with solvent molecules and are gradually slowed down. A decrease in temperature from 70 to 20 °C leads to a low but appropriate degree of supersaturation, which in turn renders nucleation sites in solution. Driven by the low supersaturation, the nanobelts undergo a preferential growth along certain facets due to their different surface free energies. A similar mechanism induced by low supersaturation *via* a vapor–solid (VS) process can also be found in the case of the growth of other organic nanowires, such as Alq$_3$ and anthracene nanowires.[6,11] This lead us to expect that low supersaturation is the predominant factor for controlling the preferential growth of Ir(piq)$_3$ nanobelts.

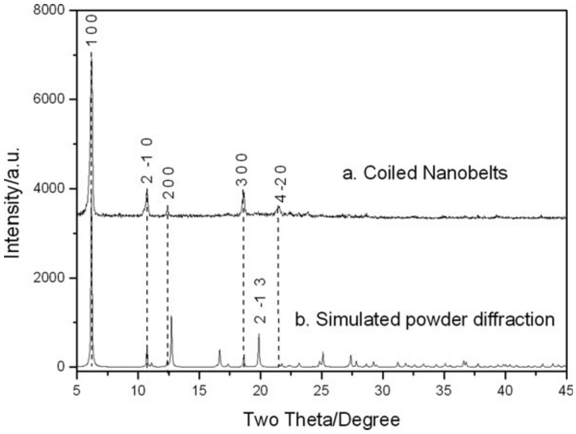


Fig. 2 XRD patterns of (a) the Ir(piq)$_3$ nanobelts and (b) the simulated powder diffraction pattern of Ir(piq)$_3$ obtained from ref. 16*a*.

The as-prepared coiled Ir(piq)$_3$ nanobelts rendered different optical properties from those of the original precursors in organic solvents. On the one hand, in the case of a dilute Ir(piq)$_3$ solution, the absorption band between 250–370 nm can be ascribed to a transition from the ground state to a locally excited state, which arises from a π–π* transition of the organic ligand (Fig. 3). The band between 370–580 nm is attributed to an overlap of the ^{1}MLCT and ^{3}MLCT states of the Ir(piq)$_3$, arising from the strong spin–orbit coupling.[16] As far as Ir(piq)$_3$ nanobelts are concerned, the π–π* transition of the organic ligand experiences a characteristic bathochromic shift up to 15 nm compared to that of the original precursor, which is due to the formation of molecular aggregates in nanobelts through a π–π interaction (see the ESI†).

On the other hand, the photoluminescence spectrum of the Ir(piq)$_3$ precursor molecule in DCM exhibits a characteristic red emission at 620 nm due to phosphorescence from the triplet excited state induced by the strong spin–orbit coupling.[16] In the case of the as-prepared Ir(piq)$_3$ nanobelts, their photoluminescence spectrum displays well-resolved vibronic progressions within three peaks, one emission peak being at 615 nm and *ca.* 40-fold lower than the emission intensity of the solution, which exhibits a slightly hypsochromic shift (*ca.* 5 nm) towards that of the precursor monomer. Interestingly, the other two emission bands at 670 and 730 nm became pronounced in comparison to that of the original precursor. It is reasonable to suggest that the decrease in the emission intensity of the nanobelts results from

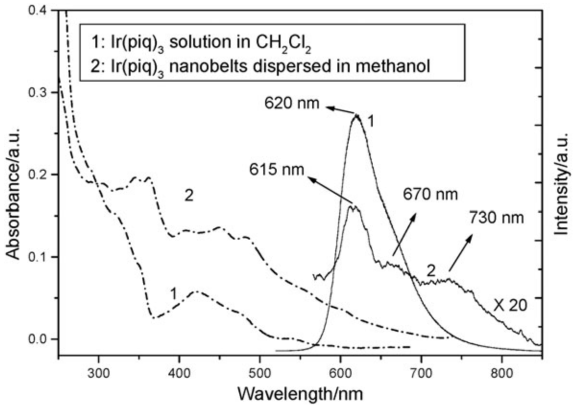


Fig. 3 UV-vis absorption (-··-) and photoluminescence (—) spectra of the original Ir(piq)$_3$ precursor in dichloromethane (DCM) and the nanobelts dispersed in methanol. Excitation wavelength: 500 nm.

triplet–triplet exciton annihilation in the molecular aggregates of the nanostructures,[18] which is usually observed in organic solids. Note that the emission intensity of the Ir(piq)$_3$ nanobelts is expected to be enhanced through resonance energy transfer by co-precipitating an energy donor, green light-emitting molecule Ir(ppy)$_3$, during the recrystallization process (see ref. 19, and ESI Fig. S-3a and also S-3b†). The band shift and the emergence of new emission bands at 670 and 730 nm are interesting in view of the point of colour modulation. The as-described band shift of the emission coupled with the emergence of the two new peaks at a longer wavelength may potentially be the result of the change in the population distribution of the phonon bands, induced by aggregation and crystal defects in the nanobelts.[18]

It is also interesting to note that the as-prepared Ir(piq)$_3$ nanobelts' suspension in methanol is facile and flexible for processing into a film by spray coating (Fig. 4). The processing of the phosphorescent nanobelts by this simple method is interesting in terms of their applications in devices. It is rationally expected that the nanobelts can be employed as the functional component of device arrays by processing them, such as by spray-coating and drop coating, onto nano-/microelectrode arrays prefabricated onto silicon wafers by photolithography.[8]

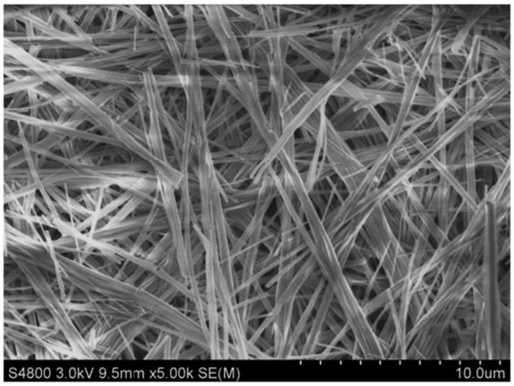


Fig. 4 An FESEM image of the as-prepared Ir(piq)$_3$ nanobelt bundles on a quartz surface processed by spray coating followed by solvent evaporation.

In summary, a large quantity (>6.0 mg for each trial) of coiled tris(1-phenylisoquinoline) iridium(III) nanobelts were successfully prepared for the first time by a facile solution-based recrystallization process in ethyl acetate. The as-obtained crystalline 1-D Ir(piq)$_3$ nanobelts exhibited a classical phosphorescent red emission due to the strong spin–obit coupling, with two additional emission bands at 670 and 730 nm that will be beneficial to colour modulation. The preparation can be easy scaled up, and the as-prepared organic nanomaterial is ready to be further processed to obtain thin films on substrates by a facile spray coating technique. Such a simple preparation technique, accompanied by processing, provides an alternative route for the fabrication of large amounts of 1-D organic optoelectronic functional materials, which may find applications in molecular electronic devices and large-area flat panel displays.

This work was financially supported by the National Natural Science Foundation of China (NSFC, no. 20973150) and Yanshan University. The authors would also like to thank Anshan Municipal Commission of Science and Technology for minor support.

Experimental

Precursor bulk crystals of tris(1-phenylisoquinoline) iridium(III) (Ir(piq)$_3$ (sublimated, >99.0 examined by HPLC)) were used as purchased from Nichem Fine Technology Co. Ltd. Taiwan. Ethyl acetate was purchased from ACROS, and was dried and distilled prior to use for recrystallization.

The Ir(piq)$_3$ nanobelts were prepared as follows: 6.5 mg of Ir(piq)$_3$ powder was loaded into 150 mL of freshly distilled ethyl acetate hosted in a 250 mL round-bottomed flask. The mixture was subsequently heated and kept at 70 °C for 1 h under magnetic stirring. After this time, both magnetic stirring and heating were turned off, and a hot filtration was immediately performed using a 0.22 μm GV type filter membrane (Millipore) to remove all the possible powders that were not dissolved. The filtrate solution was slowly cooled down to induce supersaturation and crystallization. After 48 h, orange Ir(piq)$_3$ nanobelts in a cotton-like state were observed floating in the ethyl acetate. Note that it is necessary to keep the solution mixture below 70 °C during the preparation process. Manipulation at temperatures higher than this, *e.g.* at the boiling point of ethyl acetate (78 °C), will not yield Ir(piq)$_3$ nanobelts but instead microstructures. The as-fabricated nanobelts were readily collected (6.2 mg, yield = 95.4%) and transferred into a poor organic solvent for Ir(piq)$_3$, such as methanol. SEM and TEM images were collected on a Hitachi S-4800 field emission scanning electron microscope operating at 3 kV and a JEOL TEC 2010 transmission electron microscope operating at 20 kV, respectively. The X-ray diffraction of the Ir(piq)$_3$ nanobelts was recorded on a D/max-2400 X-ray diffractometer with a Cu-Kα X-ray source operating at 40 kV and 120 mA. UV-vis absorption spectra of the Ir(piq)$_3$ molecules in solution and the nanobelt suspension in methanol were measured on a Shimadzu UV-2500 double beam spectrophotometer and a Jobin Yvon Inc. FL3-11 fluorescence spectrometer, respectively.

Notes and references

1 (*a*) W. U. Huynh, J. J. Dittmer and A. P. Alivisatos, *Science*, 2002, **295**, 2425; (*b*) X. Duan, Y. Huang, Y. Cui, J. Wang and C. M. Lieber, *Nature*, 2001, **409**, 66.
2 (*a*) Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim and H. Yan, *Adv. Mater.*, 2003, **15**, 353; (*b*) Z. W. Pan, Z. R. Dai and Z. L. Wang, *Science*, 2001, **291**, 1947.
3 B. K. An, S. K. Kwon, S. D. Jung and S. Y. Park, *J. Am. Chem. Soc.*, 2002, **124**, 14410.
4 S. R. Forrest, *Chem. Rev.*, 1997, **97**, 1793.
5 (*a*) D. Xiao, L. Xi, W. Yang, H. Fu, Z. Shuai, Y. Fang and J. Yao, *J. Am. Chem. Soc.*, 2003, **125**, 6740; (*b*) D. Xiao, W. Yang, J. Yao, L. Xi and Z. Shuai, *J. Am. Chem. Soc.*, 2004, **126**, 15439.
6 H. Liu, Q. Zhao, Y. Li, Y. Liu, F. Lu, J. Zhuang, S. Wang, L. Jiang, D. Zhu, D. Yu and L. Chi, *J. Am. Chem. Soc.*, 2005, **127**, 1120.
7 J. P. Hill, W. Jin, A. Kosaka, T. Fukushima, H. Ichihara, T. Shimomura, K. Ito, T. Hashizume, N. Ishii and T. Aida, *Science*, 2004, **304**, 1481.
8 A. L. Briseno, S. C. B. Mannsfeld, X. Lu, Y. Xiong, S. A. Jenekhe, Z. Bao and Y. Xia, *Nano Lett.*, 2007, **7**, 668.
9 H.-P. Cong and S.-H. Yu, *Chem.–Eur. J.*, 2007, **13**, 1533.
10 C. Szymanski, C. Wu, J. Hooper, M. A. Salazar, A. Perdomo and A. Dukes, *J. Phys. Chem. B*, 2005, **109**, 8543.
11 Y. S. Zhao, C. Di, W. Yang, G. Yu, Y. Liu and J. Yao, *Adv. Funct. Mater.*, 2006, **16**, 1985.
12 Y. Tamaki, T. Asahi and H. Masuhara, *J. Phys. Chem. A*, 2002, **106**, 2135.
13 L. Zhao, W. Yang, Y. Ma, J. Yao, Y. Li and H. Liu, *Chem. Commun.*, 2003, 2442.
14 (*a*) F. Debuigne, L. Jeunieau, M. Wiame and J. B. Nagy, *Langmuir*, 2000, **16**, 7605; (*b*) J. Jang and J. H. Oh, *Adv. Mater.*, 2003, **15**, 977.
15 (*a*) M. Mas-Torrent and P. Hadley, *Small*, 2005, **1**, 806; (*b*) A. Nafady, A. M. Bond, A. Bilyk, A. R. Harris, A. I. Bhatt, A. P. O'Mullane and R. D. Marco, *J. Am. Chem. Soc.*, 2007, **129**, 2369–2382.
16 (*a*) Tsuboyama, H. Iwawaki, M. Furugori, T. Mukaide, J. Kamatani, S. Igawa, T. Moriyama, S. Miura, T. Takiguchi, S. Okada, M. Hoshino and K. Ueno, *J. Am. Chem. Soc.*, 2003, **125**, 12971; (*b*) S. Lamansky, P. Djurovich, D. Murphy, F. Abde-Razzaq, H. Lee, C. Adachi, P. E. Burrows, S. R. Forrest and M. E. Thompson, *J. Am. Chem. Soc.*, 2001, **123**, 4304.
17 K. Balakrishnan, A. Datar, R. Oitker, H. Chen, J. Zuo and L. Zang, *J. Am. Chem. Soc.*, 2005, **127**, 10496.
18 H. Wang, Q. Liao, H. Fu, Y. Zeng, Z. Jiang, J. Ma and J. Yao, *J. Mater. Chem.*, 2009, **19**, 89.
19 S. H. Kim, J. Jang and J. Y. Lee, *Synth. Met.*, 2007, **157**, 228.