ChemComm

View Article Online / Journal Homepage / Table of Contents for this issue
Dynamic Article Links

Cite this: *Chem. Commun.*, 2012, **48**, 10298–10300

www.rsc.org/chemcomm

COMMUNICATION

Polarised phosphorescent emission in an organoplatinum(II)-based liquid-crystalline polymer†

Álvaro Díez, Stephen J. Cowling and Duncan W. Bruce*

Received 16th July 2012, Accepted 30th August 2012
DOI: 10.1039/c2cc35085h

By combination of mesogenic rod-like cycloplatinated monomers based on 2,5-di(4-alkenyloxyphenyl)pyridine ligands with 1,1,3,3,5,5-tetramethyltrisiloxane, a phosphorescent, liquid-crystalline polymer was obtained, which showed polarised emission.

In recent years, Organic Light-emitting Diode materials (OLEDs) have been investigated actively, amongst other reasons, because of their potential application in lighting products[1] or backlighting of liquid crystal displays (LCD), especially where molecular orientation of the emission layer leads to a polarised output.[2] However, the external quantum efficiency of traditional OLED materials is limited by using organic chromophores where, in the majority of cases, triplet–singlet transitions are forbidden giving maximum efficiencies of 25%. The low degree of order in the molecular packing of these amorphous molecules can also compromise transport properties. By using metal complexes, the high spin–orbit coupling leads to enhanced singlet–triplet mixing and phosphorescent light emission can be achieved, increasing the optimal efficiency of the device to an ideal value of 100%.[3,4] In the case of control of molecular packing, employment of the liquid crystal state of materials gives rise to an easier alignment of the mesophase, which can lead to polarised emission,[5] and enhanced charge transport mobility in the OLED device structure.

Conventional backlit displays require a polarised source, which is achieved using a polariser at the back of the display. These can absorb up to 50% of the light and, given the need for an analyser, too, then up to 75% of the backlight intensity can be absorbed by the polarisers alone. However, if the backlight source were linearly polarised, then the need for the back polariser would disappear, doubling the brightness and halving the cost of polaroid. Consequently, polarised emission from triplet emitters is a very interesting field of research. The alignment necessary to achieve polarised alignment can be realised in different ways, but a most attractive option is to use liquid crystals, which present inherently ordered phases. With metallomesogens, this has been explored only briefly,[6] although in some cases[6b,c] it is not exactly clear that dichroism was measured on a liquid-crystalline sample. Nonetheless, Wang *et al.* reported[7] a highly dichroic system based on the columnar phase of dinuclear Pt complexes that used an extended fluorene core of the type popularised by Kelly, O'Neill and co-workers.[5,8] However, in this regard, a particular target would be liquid crystal polymers where alignment can be achieved and retained.

Within this context, most metal-containing OLED materials developed to date are based on 2-phenylpyridine complexes of iridium(III), however there are only a few cases in the literature describing liquid-crystalline analogues, all of which are columnar.[9] By using platinum(II) as the metal centre, mainly due to its geometry, mesophases are more easily realised, and for that reason, the potential of mesogenic platinum(II) derivatives in OLEDs has been investigated in the last few years.[6,7,10–12] That some of these complexes show nematic and smectic phases presents a potential advantage as it is these phases that are most easily aligned and, of the two, the SmA phase is preferred owing to its greater degree of order.

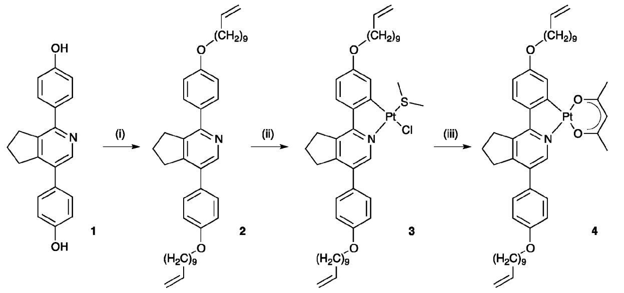
In this regard, we reported previously the synthesis and characterisation of a family of calamitic 2,5-di(4-alkoxyphenyl)pyridine-based platinum(II) luminophores, which are very efficient emitters ($\Phi_{\mathrm{lum}} \leq 70\%$) and show nematic and smectic A phases.[11,13] In these complexes, transition temperatures are controlled efficiently by the incorporation, or not, of a fused C_5 ring, which is readily introduced through synthesis of the final ligand from a 1,2,4-triazine precursor.[11] Using these as a building block, it is then possible to envisage their incorporation into a semi-flexible, main-chain polymers, which would make for materials capable of alignment leading to polarised emission.

Identifying main-chain polymers is important if order is to be retained, which is often not the case with side-chain analogues. As such, in order to obtain materials with moderate transition temperatures, the preparation of semi-flexible derivatives is essential. In this way, siloxane-linked materials were identified as a productive way forward as is now described.

The ligands were prepared following the method described previously, which uses the intermediacy of 1,2,4-triazines[14] that lead to the 2,5-disubstituted pyridines in an inverse electron demand Diels–Alder reaction (Scheme 1).[11] The functionalised ligand, **2**, was obtained by alkylation of the diphenolic precursor (**1**) under Williamson ether conditions, using 11-bromo-1-undecene. The final monomeric complex **4** was obtained through the preparation of the intermediate species **3**, by reaction with Na(acac). Complex **4** was obtained in moderate yield after purification *via* a short silica column using $CHCl_3$ as eluent.

Department of Chemistry, University of York, Heslington, York YO10 5DD, UK. E-mail: duncan.bruce@york.ac.uk

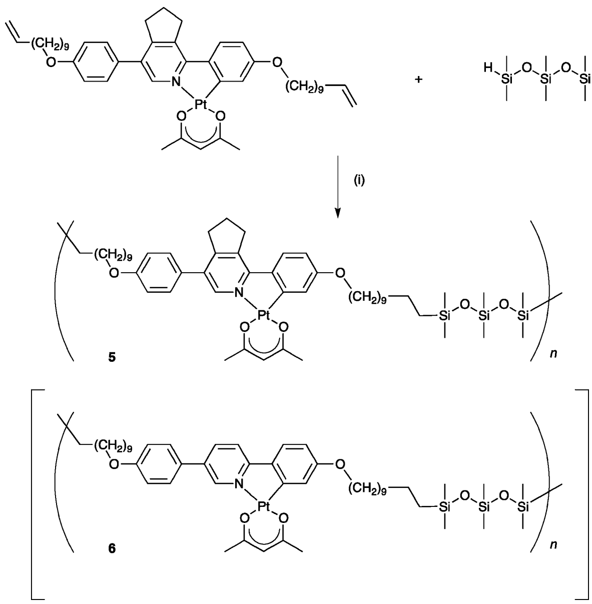
† Electronic supplementary information (ESI) available: Optical textures of ligands and details of synthesis. See DOI: 10.1039/c2cc35085h



Scheme 1 Preparation of ligands and the mesogenic monomer. Conditions: (i) $C_{11}H_{21}Br/DMF/K_2CO_3/90$ °C/12 h; (ii) *cis*-[$PtCl_2(dms)_2$]/ethoxyethanol/125 °C/12 h; (iii) Na(acac)/CH_3COCH_3 : CH_2Cl_2 (2 : 1)/rt/12 h.

The final polymer, **5**, was prepared following the method described by Donnio *et al.* (Scheme 2).[15] Polymer **5** was a pale-yellow solid and was obtained in high yield by addition of MeOH as precipitant. The precipitation was repeated several times in order to increase the purity of the final complex. Further details of these experiments are given in the ESI.† Note also that polymer **6**, in which the pyridine ring of the ligand does not bear a fused five-membered ring, was prepared in the same way starting from the analogous diphenol.

GPC was used to characterise the two polymers, but for **6** this proved unsatisfactory as a large proportion of the material was very insoluble, so that even after stirring overnight in thf, much solid remained and the resulting GPC was at best inconclusive. Thus, we believe that higher oligomers of **6** are rather insoluble and would, as such, be unsuitable for further processing. Indeed, it was the insolubility of **6** that led to the decision to prepare **5** as previous work[11] had shown that the low-molar-mass analogues with the fused ring were appreciably more soluble than those without. GPC analysis of **5** showed a weight average molecular weight was 22 180 g mol^{-1} which, with a repeat unit mass of 1128 g mol^{-1} suggested that a degree of polymerisation of just under 20 with a polydispersity of 1.2.



Scheme 2 Preparation of the polymers **5** and **6**; (i) toluene, 50 °C, 12 h, [$PtCl_2$(COD)] (1 wt%).

The mesomorphism of the ligands, monomers and polymers was investigated by polarising optical microscopy. Thus, in common with the related ligand with a saturated terminal chain, the analogue of **2** *without* the fused C_5 ring (Fig. S1, ESI†) was polymesomorphic showing the following phase sequence, in which the complexes were identified by their characteristic textures (examples as Fig. S2, ESI†):

Cr · 111 · SmF · 155.5 · SmI · 176.5 · SmC · 205 · Iso

This is similar to that shown by the longer-chain, saturated homologues except that a SmF phase appears below the SmI. Compound **2** itself showed a less rich mesomorphism (suppressed by the lateral fused ring) and an enantiotropic SmA phase was found [Cr · 91.5 · SmA · 114 · Iso]. Complex **4** showed a monotropic SmA phase [Cr · 105 · Iso · 101 · SmA], while its analogue in which the ligand did not possess fused the C_5 ring (Fig. S1, ESI†) showed an enantiotropic SmA phase with signs of decomposition on reaching the isotropic phase [Cr · 149 · SmA · 230 · Iso/dec].

In characterising polymer **6** by optical microscopy, the sample was heated until what appeared to be its clearing point at 200 °C, after which it was held just below that temperature in order to develop a useful optical texture. However, prolonged holding at this temperature led to decomposition of the material and we were not able to determine its mesomorphism. Given the high thermal stability of the monomeric analogues,[11] we attribute the instability to the siloxane fragment.

Polymer **5**, however, was much better behaved and was observed to melt at 64 °C, clearing at 150 °C; the mesophase was readily identified as SmA (Fig. 1) from a texture developed after holding just below the clearing point for 30 minutes.

In the literature, different methodologies describe how linearly polarised luminescence may be induced in emitters.[16] Here, nylon-6,6 was spin-coated onto two glass coverslip substrates, which were dried at 100 °C and then rubbed uniaxially with a dust-free cloth. A solid sample of **5** was then deposited between the coverslips. After reaching the desired phase at 149 °C, the phase was quenched to room temperature. The temperature was then increased to 120 °C, the coverslip on top was slid uniaxially over the one on the bottom and the texture quenched again in a cold surface. As is illustrated in Fig. 2, the optical properties of the aligned sample are different depending on the degree of rotation of the microscope polarisers. Samples were also prepared by filling pre-assembled cells (5 μm thickness, homogeneous (planar) alignment) with molten polymer, but it was evident from both microscopy and polarised fluorescence

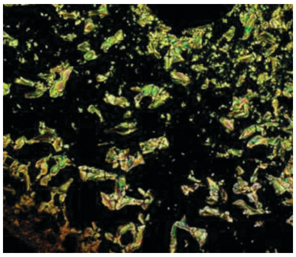
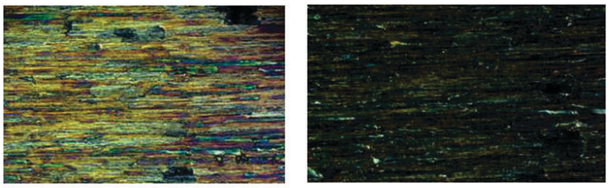


Fig. 1 Optical micrograph (on cooling) of the SmA phase of polymer **5** at 149 °C.



(a) (b)

Fig. 2 Optical micrograph of the aligned sample: (a) polariser at 0°; (b) polariser rotated 90°.

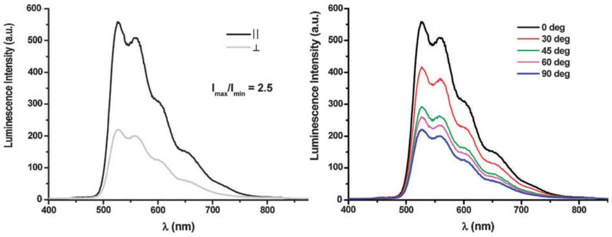


Fig. 3 PL spectra of the aligned sample at different degrees of polarisation (λ_{ex} = 360 nm).

measurements that this method of alignment was much less successful and negligible dichroism was observed in these cases.

The polarised photoluminescence of the aligned sample was recorded on a Hitachi F-4500 instrument with a polariser inserted between the sample and the spectrograph, which could be rotated to different angles. When the polariser was perpendicular (⊥) to the rubbing direction, the PL intensity was much higher than in the case of the polariser located parallel (‖) (Fig. 3a). The PL dichroic ratio $PL_{\perp}/PL_{\parallel}$ is 2.5 at 528 nm (emission maximum). Fig. 3b shows the dependence of the PL when rotating the polariser different angles and the maximum dichroism was found with an angle of 90°.

While it is understood that dichroic ratios well in excess of 2.5 will be required for application, this is nonetheless an important proof of concept. Thus for the first time, a metallomesogenic triplet emitter has been fabricated as a semi-flexible, main-chain polymer and it is demonstrated that the polymer may be aligned mechanically to give polarised emission. Given the higher maximum efficiencies of metal-containing systems and the ability to process and align liquid crystal polymers and to retain that alignment, then the observations reported here are an important step forward notwithstanding the modest dichroism observed.

We thank the White Rose Consortium for funding (AD), Johnson Matthey for generous loans of $K_2[PtCl_4]$, Dr Laurence Abbott (York) for assistance in collecting fluorescence data and Dr Abdel Belaissaoui (York) for assistance with GPC measurements.

Notes and references

1 Y. Sun, N. C. Giebink, H. Kanno, B. Ma, M. E. Thompson and S. R. Forrest, *Nature*, 2006, **440**, 908; B. W. D'Andrade and S. R. Forrest, *Adv. Mater.*, 2004, **16**, 1585; A. R. Duggal, D. F. Foust, W. F. Nealon and C. M. Heller, *Proc. SPIE*, 2004, **5214**, 241; H. Kanno, R. J. Holmes, Y. Sun, S. Kena-Cohen and S. R. Forrest, *Adv. Mater.*, 2006, **18**, 339.
2 K. S. Whitehead, M. Grell, D. D. C. Bradley, M. Jandke and P. Strohriegl, *Appl. Phys. Lett.*, 2000, **76**, 2946; C. M. vanHeesch, H. Jagt, C. Sánchez, H. J. Cornelissen, D. J. Broer and C. W. M. Bastiaansen, *Chem. Rec.*, 2005, **5**, 59; A. Montali, C. Bastiaansen, P. Smith and C. Weder, *Nature*, 1998, **392**, 261; M. Grell and D. D. C. Bradley, *Adv. Mater.*, 1999, **11**, 895.
3 M. A. Baldo, D. F. O'Brien, M. E. Thompson and S. R. Forrest, *Phys. Rev. B*, 1999, **60**, 14422; R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Lögdlund and W. R. Salaneck, *Nature*, 1999, **397**, 121.
4 H. Yersin, *Highly Efficient OLEDs with Phosphorescent Materials*, Wiley-VCH, Weinheim, Germany, 2008.
5 M. O'Neill and S. M. Kelly, *Adv. Mater.*, 2011, **23**, 566.
6 (*a*) S. H. Liu, M. S. Lin, L. Y. Chen, Y. H. Hong, C. H. Tsai, C. C. Wu, A. Poloek, C. A. Chen, S. H. Chen and H. F. Hsu, *Org. Electron.*, 2011, **12**, 15; (*b*) S. P. Jiang, K. J. Luo, Y. H. Wang, X. Wang, Y. Jiang and Y. Y. Wei, *Chin. Chem. Lett.*, 2011, **22**, 1005; (*c*) Y. F. Wang, Y. Liu, J. Luo, H. R. Qi, X. S. Li, M. J. Ni, M. Liu, M. X. Zhu, W. G. Zhu and Y. Cao, *Dalton Trans.*, 2011, **40**, 5046.
7 Y. F. Wang, Q. Chen, Y. Li, Y. Liu, H. Tan, J. Yu, M. Zhu, H. Wu, W. Zhu and Y. Cao, *J. Phys. Chem. C*, 2012, **116**, 5908.
8 See *e.g.* M. R. Billa, K. Kassireddy, M. Haro, M. S. Al-Kalifah, S. M. Kelly, S. P. Kitney and M. O'Neill, *Liq. Cryst.*, 2011, **38**, 813.
9 A. Santoro, A. M. Prokhorov, V. N. Kozhevnikov, A. C. Whitwood, B. Donnio, J. A. G. Williams and D. W. Bruce, *J. Am. Chem. Soc.*, 2011, **133**, 5248; A. M. Prokhorov, A. Santoro, J. A. G. Williams and D. W. Bruce, *Angew. Chem., Int. Ed.*, 2012, **51**, 95; E. L. Szerb, A. M. Talarico, I. Aiello, A. Crispini, N. Godbert, D. Pucci, T. Pugliese and M. Ghedini, *Eur. J. Inorg. Chem.*, 2010, 3270.
10 K. Binnemans, *J. Mater. Chem.*, 2009, **19**, 448; K. Binnemans, in *Molecular Materials*, ed. D. W. Bruce, D. O'Hare and R. I. Walton, Wiley, Chichester, 2010, pp 61–141; C. Damm, G. Israel, T. Hegmann and C. Tschierske, *J. Mater. Chem.*, 2006, **16**, 1808; K. Venkatesan, P. H. J. Kouwer, S. Yagi, P. Müller and T. M. Swager, *J. Mater. Chem.*, 2008, **18**, 400; F. Camerel, R. Ziessel, B. Donnio, C. Bourgogne, D. Guillon, M. Schmutz, C. Iacovita and J. P. Bucher, *Angew. Chem., Int. Ed.*, 2007, **46**, 2659; V. N. Kozhevnikov, B. Donnio and D. W. Bruce, *Angew. Chem., Int. Ed.*, 2008, **47**, 6286.
11 A. Santoro, A. C. Whitwood, J. A. G. Williams, V. N. Kozhevnikov and D. W. Bruce, *Chem. Mater.*, 2009, **21**, 3871.
12 C. T. Liao, H. H. Chen, H. F. Hsu, A. Poloek, H. H. Yeh, Y. Chi, K. W. Wang, C. H. Lai, G. H. Lee, C. W. Shih and P. T. Chou, *Chem.–Eur. J.*, 2010, **17**, 546.
13 M. Spencer, A. Santoro, G. R. Freeman, A. Díez, P. R. Murray, J. Torroba, A. C. Whitwood, L. J. Yellowlees, J. A. G. Williams and D. W. Bruce, *Dalton Trans.*, DOI: 10.1039/c2dt31525d.
14 V. N. Kozhevnikov, D. N. Kozhevnikov, O. V. Shabunina, V. L. Rusinov and O. N. Chupakhin, *Tetrahedron Lett.*, 2005, **46**, 1791; V. N. Kozhevnikov, D. N. Kozhevnikov, T. V. Nikitina, V. L. Rusinov, O. N. Chupakhin, M. Zabel and B. König, *J. Org. Chem.*, 2003, **68**, 2882; V. N. Kozhevnikov, D. N. Kozhevnikov, O. V. Shabunina, V. L. Rusinov and O. N. Chupakhin, *Tetrahedron Lett.*, 2005, **46**, 1521.
15 B. Donnio, H. Wermter and H. Finkelmann, *Macromolecules*, 2000, **33**, 7724.
16 V. Cimrova, M. Remmers, D. Neher and G. Wegner, *Adv. Mater.*, 1996, **8**, 146; J. C. Wittmann and P. Smith, *Nature*, 1991, **352**, 414; Y. Yoshida, N. Tanigaki, K. Yase and S. Hotta, *Adv. Mater.*, 2000, **12**, 1587; N. S. Sariciftci, U. Lemmer, D. Vacar, A. J. Heeger and A. J. Janssen, *Adv. Mater.*, 1996, **8**, 651.