

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/223173641>

Ionic Iridium(III) Complexes with Bulky Side Groups for Use in Light Emitting Cells: Reduction of Concentration Quenching

ARTICLE *in* ADVANCED FUNCTIONAL MATERIALS · JULY 2009

Impact Factor: 11.81 · DOI: 10.1002/adfm.200801767

CITATIONS

74

READS

199

9 AUTHORS, INCLUDING:



Chien-Jung Chiang

Durham University

6 PUBLICATIONS 197 CITATIONS

SEE PROFILE



Rukkiat Jitchati

Ubon Ratchathani University

24 PUBLICATIONS 346 CITATIONS

SEE PROFILE



Andy Monkman

Durham University

416 PUBLICATIONS 9,805 CITATIONS

SEE PROFILE

Ionic Iridium(III) Complexes with Bulky Side Groups for Use in Light Emitting Cells: Reduction of Concentration Quenching

By Carsten Rothe, Chien-Jung Chiang, Vygtintas Jankus, Khalid Abdullah, Xianshun Zeng, Rukkiat Jitchati, Andrei S. Batsanov, Martin R. Bryce,* and Andrew P. Monkman*

Here, the photophysics and performance of single-layer light emitting cells (LECs) based on a series of ionic cyclometalated Ir(III) complexes of formulae $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+\text{PF}_6^-$ and $[\text{Ir}(\text{ppy})_2(\text{phen})]^+\text{PF}_6^-$ where ppy, bpy, and phen are 2-phenylpyridine, substituted bipyridine and substituted phenanthroline ligands, respectively, are reported. Substitution at the N^N ligand has little effect on the emitting metal-ligand to ligand charge-transfer (MLCT) states and functionalization at this site of the complex leads to only modest changes in emission color. For the more bulky complexes the increase in intermolecular separation leads to reduced exciton migration, which in turn, by suppressing concentration quenching, significantly increases the lifetime of the excited state. On the other hand, the larger intermolecular separation induced by bulky ligands reduces the charge carrier mobility of the materials, which means that higher bias fields are needed to drive the diodes. A brightness of ca. 1000 cd m^{-2} at 3 V is obtained for complex 5, which demonstrates a beneficial effect of bulky substituents.

1. Introduction

Organic electroluminescence is currently exploited mainly in multilayer devices made of small organic molecules (organic light-emitting diodes; OLEDs) and single layer devices employing polymers (polymeric light-emitting diodes; PLEDs). OLEDs generally deliver better efficiencies compared to their polymeric counterparts but they are more complex to produce.^[1] To achieve high efficiencies in both OLEDs and PLEDs it is mandatory to use triplet emitters to exploit all the excitations generated. This requires host-matrix materials which must facilitate charge injection and transport, as well as possess a higher triplet energy compared to the guest dopant to confine the energy at the

emitter.^[2–4] For the conceptually simple PLEDs, host materials which are suitable for blue (triplet) emission are not yet available.^[5] This problem is overcome in state-of-the-art OLEDs by using a range of functionalizing layers which requires a complex evaporation sequence. However, these complex multilayer devices are far from the ideal simplicity of directly printable PLEDs in air. For efficient electron injection, the single layer diodes also require a reactive material cathode, although this is a relatively minor drawback compared to the need for thorough encapsulation of both kinds of organic diodes for stable operation.

An alternative approach to organic electroluminescence, namely single compound light emitting cells (LECs), has recently been successfully demonstrated.^[6,7] In these devices, the diode comprises only a single, spin-coated layer of an ionic transition metal

complex (iTMC) which is a heavy metal triplet emitter which harnesses all excitations created without the need for a suitable host material and is thus suitable for red, green, and blue emission.^[8] These complexes carry a positive charge which is balanced by small and mobile counter ions. The application of an external electrical field leads to ion drift through the solid film and consequently charge injection is aided by the formation of ionic layers close to the electrodes. This process results in low turn-on voltages and high power efficiencies without using reactive metals.^[9–11] The effect is similar to the concept of *p-i-n* doping the organic layer at the proximity of the metal interface with the type of charge to be injected, which, however, is a permanent doping.^[12] For LECs the time-delayed response of the luminance (due to the slow migration rate of the anions) is a consequence of their mode of operation. LECs have the potential to combine the best features of both OLEDs and PLEDs and they warrant increased research efforts in the coming years.

The performance of these single layer iTMC LECs is at first sight surprising given that organic LEDs doped with heavy metal complexes suffer from reduced emission quantum yields for guest concentrations in excess of ca. 8 wt %.^[3] These reduced PL and EL yields are commonly ascribed to excited state quenching at impurity sites, charges, or the electrodes, which is mediated by

[*] Prof. M. R. Bryce, Dr. X. Zeng, R. Jitchati, Dr. A. S. Batsanov
Department of Chemistry, Durham University
Durham, DH1 3LE (UK)
E-mail: m.r.bryce@durham.ac.uk

Prof. A. P. Monkman, Dr. C. Rothe, C.-J. Chiang, V. Jankus, K. Abdullah
Department of Physics, Durham University
Durham, DH1 3LE (UK)
E-mail: a.p.monkman@durham.ac.uk

hopping within the guest only. It could, therefore, be expected that the concentration quenching for LECs should be worse compared to OLEDs because the lifetime of the emitting species in LEDs is rather long, allowing ample time for the excitons to reach the highly charged space-charge layers at the electrodes, in turn leading to nonradiative exciton-ion quenching.^[13] For example, in doped OLEDs when buffer layers are introduced to prevent excitations from reaching the charge layers at the electrodes there is a significant increase in diode performance.^[12] Apart from such monomolecular quenching mechanisms, exciton migration is furthermore the key to understanding triplet-triplet bimolecular annihilation, which will reduce the device performance at high excitation generation rates.^[14,15] A strategy to improve further the performance of LECs is to avoid, or at least suppress, exciton migration without hampering the charge carrier mobility. Indeed, Rudmann et al. observed an increase in photoluminescence efficiency of 15–30% when a cationic complex was blended with 25% PMMA, which in effect increases the intermolecular separation leading to a reduced excited state hopping efficiency.^[11] For matrix polymer fractions in excess of this ratio, the reduced charge carrier mobility is believed to hamper the diode efficiency. Furthermore, the components in the spin-coated blends (namely, polar heavy metal complex and nonpolar matrix polymer) will tend to segregate leading to lower film quality and reduced intermolecular separation of the emitting species. Using conjugated hosts would not help matters either, as the triplet energies of most conjugated polymers lie below 2.3 eV^[16] and only in exceptional cases can this be increased to 2.5 eV^[5] which rules out their use with green and blue triplet emitters because of host quenching by the remote heavy atom effect.^[17] Another approach that has been used in guest host systems is the full substitution of the ligands in both hemispheres of the complex. This reduces guest host triplet energy transfer in such systems.^[18]

Based on this approach, we now describe studies on LECs of a series of cationic iridium complexes 1–7 (Fig. 1) which comprise two cyclometalating C^N phenylpyridine ligands and one N^N bipyridine (1 and 2) or phenanthroline ligand (3–7). Preliminary data on LECs of 6 have been reported previously.^[19] Complex 7 is the parent (unsubstituted) iTMC in this series, and was synthesized for comparative purposes.^[20] Bulky 9,9-dihexylfluorene side groups were attached to the N^N coordinating ligands of 1–6 at sites where they have little effect on the electronic properties of the complex while providing the benefit of enhanced steric hindrance which reduces concentration quenching. The pendant carbazole units of 2, 4, and 6 are hole-transporting units and they give additional steric effects while being electronically isolated by flexible hexyl spacers from the luminescent center.

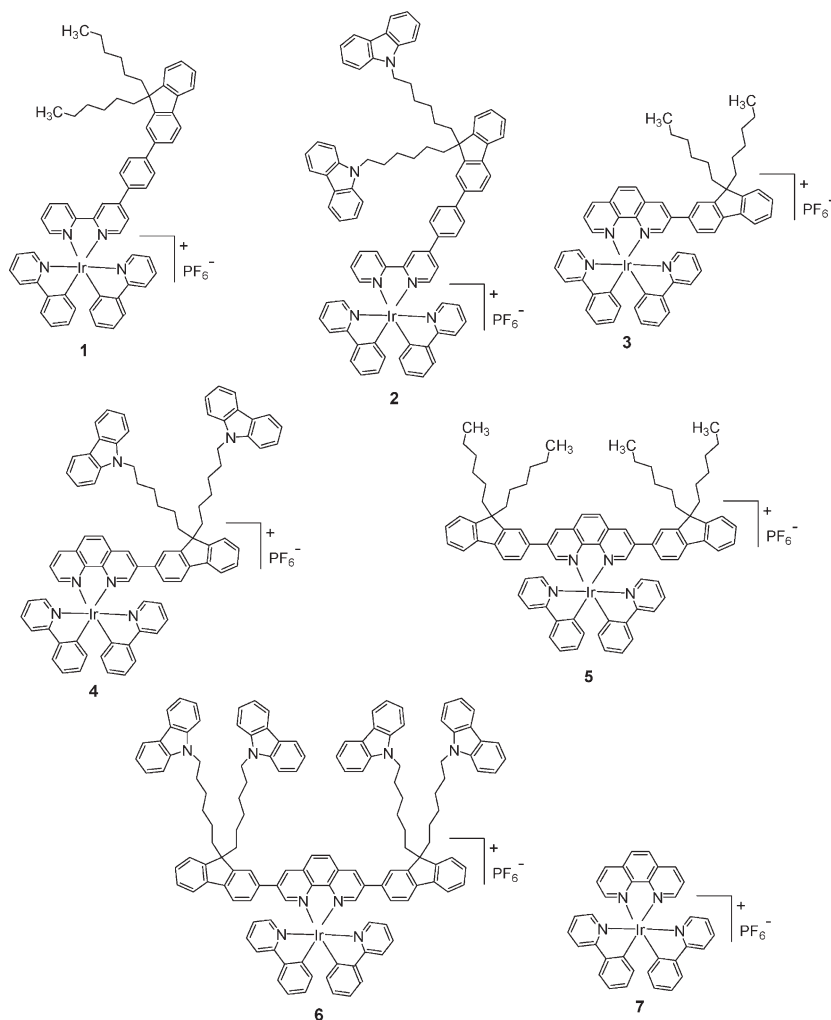


Figure 1. Chemical structures of the iTMCs investigated in this work.

Other groups have recently reported complementary strategies to probe structure–property relationships in charged Ir complexes. Su et al. have introduced sterically hindered 4,5-diaza-9,9'-spirobifluorene (sb) ligands in the complex [Ir(ppy)₂sb]PF₆ to reduce self-quenching.^[21] Bolink et al. have reported a 4,7-diphenyl-1,10-phenanthroline ligand (dpp) in the complex [Ir(ppy)₂dpp]PF₆,^[8c] and have exploited π -stacking aryl substituents on the bipyridyl ligand in [Ir(ppy)₂bipy]PF₆ to enhance stability and improve device lifetimes.^[22]

2. Results and Discussion

The photophysical and electrochemical data for the complexes are summarized in Table 1. In solution electrochemical studies all the complexes display the expected Ir-centered oxidation and reduction waves, with only a minor effect on the redox potentials from the varying substituents on the phenanthroline ligand. Additional irreversible oxidation peaks were observed for complexes 4 and 6, and were ascribed to the formation of carbazole radical cation species.

Table 1. Summary of the photophysical and electrochemical properties of complexes 1–7.

Compound	Half life τ_{film} [ns]	λ_{max} EL [nm]	PLQY Φ in PhMe, MeCN, film ($\pm 5\%$)	E^{ox} [V] vs. Fc/Fc ⁺ , DCM	E^{red} [V] vs. Fc/Fc ⁺ , DCM	ΔE [V][a]
1	175	621	0.06, 0.02, 0.38	0.80	−1.67	2.47
2	235	616	0.07, 0.04, 0.34	0.74 ^[b] , 0.80	−1.68	2.48
3	145	574	0.07, 0.03, 0.38	0.87	−1.60	2.47
4	250	602	0.10, 0.05, 0.34	0.75 ^[b] , 0.79	−1.68	2.47
5	205	576	0.04, 0.02, 0.36	0.88	−1.66	2.54
6	235	580	0.10, 0.02, 0.38	0.74 ^[b] , 0.78	−1.70	2.48
7	175	572	0.06, 0.01, 0.44	0.85	−1.54	2.39

[a] $\Delta E = E^{\text{ox}} - E^{\text{red}}$ for the Ir^{III}/Ir^{IV} couple. [b] Oxidation process associated with the carbazole units.

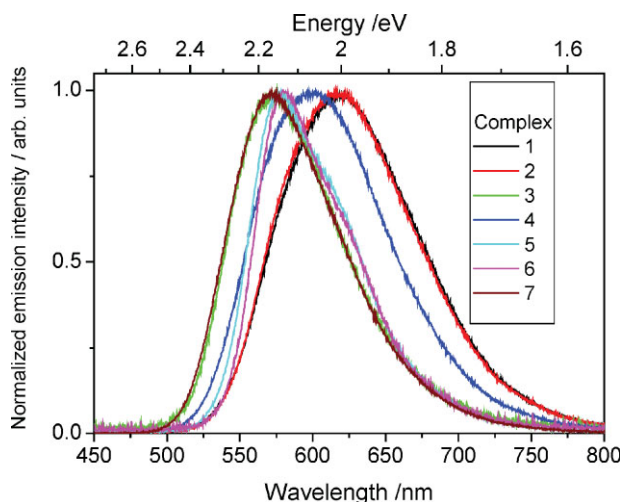


Figure 2. Normalized electroluminescent emission spectra of complexes 1–7 in the device configuration ITO/PEDOT:PSS/complex/Al.

Figure 2 shows the electroluminescence spectra of complexes 1–6. Complexes 1 (λ_{max} 621 nm) and 2 (λ_{max} 616 nm) with bipyridine ligands are slightly red shifted compared to the complexes 3–6 with the phenanthroline ligands (λ_{max} 572–602 nm). Overall, chemical substitution at the N^N coordinated ligand has relatively little impact on the emission color of the complexes, which appears in the orange spectral region (orange-red for 1 and 2). This is consistent with our recent DFT calculations^[19] and those of Tamayo et al.^[10] and Bolink et al.^[23] for other $(C^N)_2Ir(N^N)^+$ species. Thus, substitution at this site enables the introduction of further functionality into the complex, including steric bulk and increased solubility in organic solvents, without significantly influencing its electronic properties.

Figure 3 shows an AFM image of a film of complex 6 spin-coated from toluene solution rather than the more polar acetonitrile solvent which is typically used to dissolve less-soluble cationic complexes. The average surface roughness of this film is very low with only 0.7 nm deviation, which is better than typical films prepared from polymer solutions. Furthermore, Figure 3 shows regularly distributed spikes with an average height of 15 nm arising from microcrystallites of the complex.

In addition to increasing the solubility, the pendant side-groups will also increase the intermolecular separation of the complex molecules. This effect should reduce the excitation migration between neighboring emitters via Förster energy

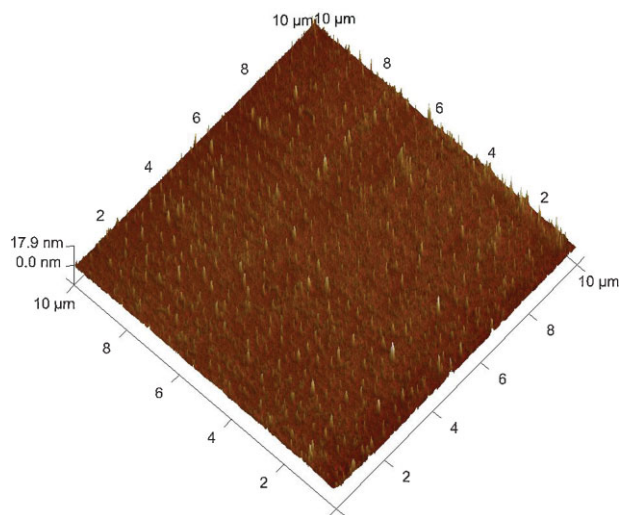


Figure 3. AFM image of complex 6 spin-coated from its toluene solution (30 mg mL^{−1}) onto a glass/ITO/PEDOT:PSS substrate.

transfer, which is expected to dominate over electron-exchange Dexter-type transfer given the non-negligible triplet absorption of the heavy metal complexes.^[24] In order to estimate the effects of the different substitution patterns on the concentration quenching the photoluminescence decay of 1–7 in the solid state was measured (Fig. 4).

It is clear from the semilogarithmical presentation in Figure 4 that none of the complexes 1–7 exhibits an exponential decay profile. Instead, the decay rate proceeds faster initially and slows

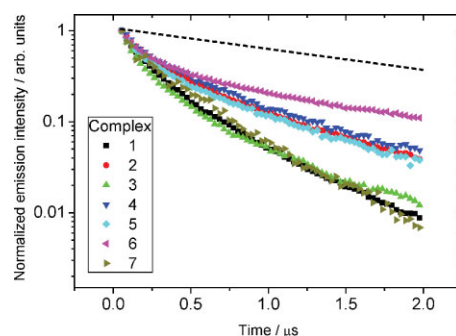


Figure 4. Solid state photoluminescence decays of 1–7 shown as a semi-logarithmical plot. The dashed line indicates an exponential decay with 2.0 μs lifetime, i.e., without any concentration quenching.

down at longer times, i.e., the decay is dispersive.^[25] The half lives fall in the range of ca. 150–250 ns (Table 1) which is a timescale consistent with phosphorescence associated with mixed ³MLCT–³LLCT states of the complexes. These nonexponential decay kinetics indicate that the excited state itself does not necessarily have a low radiative quantum yield but does suffer a lifetime quenching mechanism whose quenching efficiency slows down with time. These decay patterns are typical of an excited state prone to quenching which is activated by migration within an energetically distributed environment.^[15,26] During their energetical relaxation within the density of states (DOS), states of relatively high energy migrate quickly, thereby sampling a lot of sites, including potential quencher sites. Once relaxed, i.e., at lower energy, the migration, and thus the quenching, slows down and the excited states decay with their natural lifetimes; see complex **6**, Figure 4, for example. At this point the excitations become trapped within the DOS at relatively low energy sites, whereby the trapping efficiency depends on the available thermal activation energy and the site density, i.e., the intermolecular separation. In this situation the emission spectrum will exhibit a continuous red shift with time. For example, within the initial 5 μ s the emission spectrum of complex **6** monotonically shifts by 9.3 nm (38 meV) (Fig. 5). During the same time frame the spectrum also undergoes a small redistribution from what appears as the first vibronic mode at 600 nm towards the leading mode at 579 nm. Most likely, the low energy, longer lived sites possess a slightly different electronic configuration, potentially including different molecular conformations (relaxed), compared to the average DOS, which in turn may be the reason for their lower energy.

In the framework of energetic relaxation by excitation migration, the differences in the decays of Figure 4 can be qualitatively explained as follows. Complexes **1**, **3**, and **7**, which are the least substituted complexes, can pack relatively closely and therefore suffer most from migration activated quenching, which translates into the fastest observed decays within this group of materials. The complex which is most heavily substituted, i.e., complex **6**, consistently shows the longest decay time, whereas

complexes **2**, **4**, and **5**, with their medium-sized substituents, exhibit intermediate decay times compared to the above extremes. At long times the decay of **6** becomes nondispersive as it asymptotically approaches an exponential lifetime of $\sim 2 \mu$ s. Assuming this to be the unquenched radiative lifetime of all the complexes then the emission quantum yields in the solid state relative to the radiative yield would be 21, 32, 19, 35, 30, 43, and 20% for complexes **1**–**7**, respectively. These results clearly demonstrate a beneficial effect of increasing the length and number of the linear side-chains which leads to a reduction of concentration quenching and an approximate doubling in the PL yield, although it is known that larger ligands reduce spin-orbit coupling in Ir complexes.^[27] Even for the best complex, **6**, as much as ca. 60% of the emission is lost by concentration quenching. Therefore, there is still a significant potential to increase further the emission yield of cationic iridium complexes by judicious choice of ligands.

It should be noted that measuring the emission decay of these heavy metal complexes in solution (including deaerated solution) is not a convincing alternative method to obtain the exact decay lifetime, since excited state relaxation may lead to lower quantum yields. Indeed, in spite of concentration quenching many of these complexes **1**–**7** show longer lifetimes in the solid state compared to their dilute solutions.^[21] In solution the excited state of the complex, with its charge transfer character, can potentially be stabilized by polar solvents, leading to broader and typically red shifted spectra, with longer lifetimes observed in more polar solvents.^[28] This solvatochromic effect is observed for the materials studied here. In degassed solutions the typical lifetime is about ten times longer than in the solid state, but the solution PLQY values in acetonitrile are low for all the complexes ($\Phi = 1$ –5%). In a nonpolar solvent (toluene) the values were raised to 4–10%, which provides further evidence that because the emitters are ionic their photophysical properties are significantly modified by solute–solvent interactions in polar solvents, allowing nonradiative deactivation pathways. A general trend is that higher PLQY values in solution were obtained for the more highly substituted complexes. However, in spin-coated neat films PLQY values for all the complexes are raised significantly to ca. 40% ($\pm 5\%$), e.g., $\Phi = 0.36$ and 0.44, for compounds **5** and **7**, respectively. Low PLQY values for iridium-based LECs have recently been concluded from an analysis of diode performance by Lowry et al.^[29] Therefore, solution data cannot be used to predict solid state PL yields as a function of the corresponding PL lifetime.

To assess the effective steric hindrance due to the fluorenyl substituents, the X-ray crystal structure of **5** was obtained. The Ir atom has a distorted octahedral geometry (Fig. 6). The two Ir–C bonds are situated *cis* to each other and *trans* to the Ir–N(phen) bonds, which are 0.1 Å longer than the Ir–N(ppp) bonds due to a *trans*-influence. The planar fluorene moieties *A* and *B* are inclined to the central phenanthroline plane by 9 and 43°, respectively, and to each other by 51°. The alkyl substituents of moiety *A* are in the *syn*-orientation with respect to the metal center, and those of moiety *B* are close to the anti-orientation. Three out of four hexyl chains are disordered, while large atomic displacement parameters of the anion and the DCM molecule also imply disorder which we could not rationalize. The cations related via an inversion center ($0 \frac{1}{2} \frac{1}{2}$) have substantial overlap

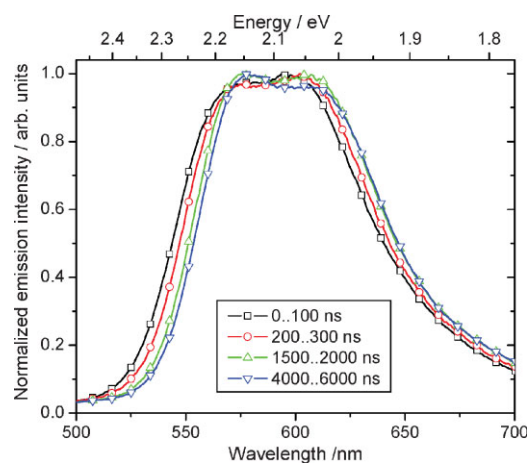


Figure 5. Normalized emission spectra as a function of time of a spin-coated thin film of complex **6** with light integration settings as indicated.

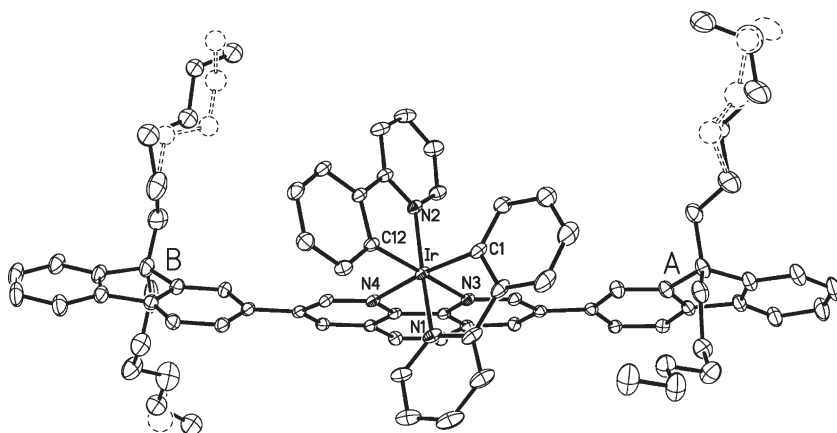


Figure 6. Cation in the crystal of $5 \cdot \text{CH}_2\text{Cl}_2$ showing the disorder of hexyl chains. Thermal ellipsoids are drawn at the 30% probability level, hydrogen atoms are omitted. Bond distances (Å): Ir–N(1) 2.049(3), Ir–N(2) 2.052(3), Ir–N(3) 2.143(3), Ir–N(4) 2.163(3), Ir–C(1) 2.003(4), Ir–C(2) 2.011(4).

between their near-planar cores (comprising phenanthroline and fluorene A moieties), the interplanar separation between which (3.49 Å) is close to the normal van der Waals contact distance. However, these dimers are interspersed with anions and DCM molecules and do not form any continuous stacking motif (Fig. 7). The shortest Ir...Ir distances in the structure (9.08 and 8.94 Å) are similar to those observed in a sterically hindered 4,5-diaza-9,9'-spirobifluorene (sb) complex $[\text{Ir}(\text{ppy})_2\text{sb}]\text{PF}_6$ (9.21 and 8.62 Å).^[21] They occur between molecules which are related via inversion centers (0 0 1/2) and (0 1/2 1/2) and form a chain parallel to the crystallographic y-axis.

After charging, the LECs of complexes 1–6 reached a luminous efficiency of ca. 7 cd A^{-1} when using air-stable aluminum cathodes; typical data for 6 are shown in Figure 8, which shows that a brightness value as high as 7000 cd m^{-2} was obtained, albeit at a high driving voltage of 16 V. This is among the highest reported brightness for an iTMC device.^[22] The luminous efficiency of the 6 device was further increased to ca. 10 cd A^{-1}

by using barium capped with aluminum as the cathode, which shows that the electron injection is not ohmic, as observed recently for other iridium(III) complexes.^[10,30] Luminous efficiency data as a function of time are shown in the Supporting Information (Figs. S1 and S2).

Red-emitting single-layer LECs are typically driven at 3 V, which results in very high luminous power efficiencies.^[9,10] Compared to these precedents, our devices require higher bias and no emission was observed even after applying 4 V for several hours. A significant result is that the bias needed to charge and drive our LECs increased with the size and the number of the side chains. Figure 9 compares the charging time and brightness for complexes 3, 5, and 7 showing the effect of one, two, and no fluorene units, respectively.

Here, complex 3 (one fluorene substituent) initially exhibits a higher current which relatively slowly increases with time. In contrast, the current of the bulkier complex 5 starts from a lower value but increases more steeply. For the parent complex 7 (no fluorenes) the charging time is reduced. Compared to these three complexes, the largest complex in our series, 6, required 6 V for 2 h before any emission was detected. Thus, using exactly the same device structure, the more bulky complexes require higher driving voltages. However, it is noteworthy that the maximum brightness (ca. 1000 cd m^{-2} at 3 V) was obtained for complex 5 which demonstrates a beneficial effect of bulky substituents. From these observations, we conclude that the diffusion of the counter ions is reduced with increasing size of the side-groups, which is consistent with findings by Handy et al.^[31] Additionally, an LEC made from complex 6 cannot be driven at 3–4 V even after charging at sufficiently high bias (6 V). This can be observed by extrapolating the semilogarithmic brightness versus bias curve in Figure 8. Thus, the charge carrier mobility is also reduced for the larger iridium complexes leading to stronger space-charge

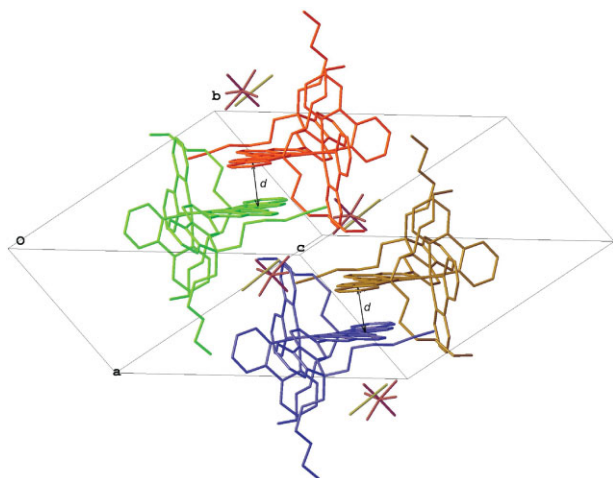


Figure 7. Crystal packing of $5 \cdot \text{CH}_2\text{Cl}_2$. Note the overlap between planar molecular cores ($d = 3.49 \text{ Å}$).

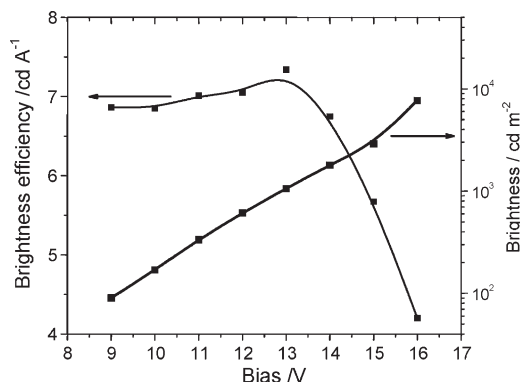


Figure 8. Brightness (semilogarithmic plot) and brightness efficiency as a function of bias of the LEC made of complex 6 with an aluminum cathode. Device configuration: ITO/PEDOT:PSS/complex 6/Al. The data shown were recorded after charging the LEC for 30 min at 9 V at which point the time-dependent performance saturated.

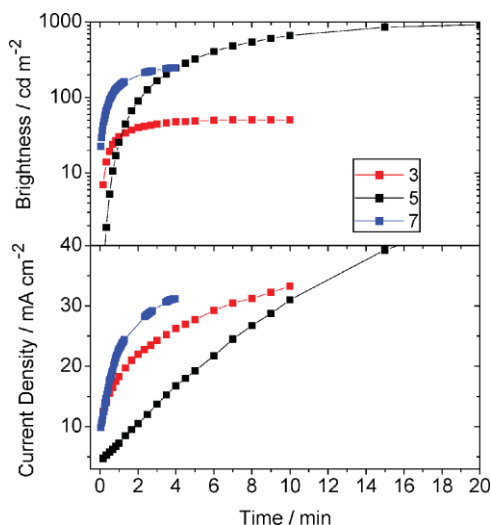


Figure 9. Linear logarithmical presentation of the brightness and current density as a function of time for LECs of complexes **3**, **5**, and **7** driven at an applied bias of 3 V: device architecture ITO/PEDOT:PSS/complex/Al.

effects inside the diode accompanied by a corresponding drop in applied electric field. In this context, the pendant carbazole side-groups are not conjugated to the core of the iridium complex and as such they possess an independent electronic structure of significantly higher energy compared to the heavy metal complex on its own. Consequently, the charge carriers will only hop between the iridium cores with the side-groups acting like an inert matrix. Larger side groups then correspond to larger intermolecular separations, which are reflected by higher driving fields, as observed. At present, we cannot judge whether the mobilities of both carriers are reduced.

The lifetimes of the devices, defined as the time after which the brightness decayed to half-maximum ($t_{1/2}$) under a constant bias of 6 V, were in the range of 6–20 h for the complexes **1**–**5**. The unsubstituted complex **7** could be driven at 3 V and this could explain the longer lifetime ($t_{1/2}$ 48 h) for the device using this complex. These lifetime data are comparable to those of LECs of $[\text{Ir}(\text{ppy})_2\text{sb}]\text{PF}_6$ with a bulky 4,5-diaza-9,9'-spirofluorene (sb) ($N^{\wedge}N$) ligand studied by Su et al. ($t_{1/2}$ ca. 26–54 h)^[21] and a complex with a bulky 4,7-diphenyl-1,10-phenanthroline (dpp) ligand $[\text{Ir}(\text{ppy})_2\text{dpp}]\text{PF}_6$ studied by Bolink et al. ($t_{1/2}$ ca. 65 h).^[8c] Dramatically enhanced lifetimes (thousands of hours) have been reported very recently by Bolink et al. for devices of complexes which are stabilized by intramolecular π – π stacking.^[22] The very high driving voltage (>12 V) required for devices of **6** are clearly detrimental to stability leading to $t_{1/2}$ of <30 min due to accelerated degradation of the complex.

3. Conclusions

New cationic iridium complexes substituted with bulky side-chains have been investigated for applications in single-layer electroluminescent LECs. In these complexes the side units are attached to bipyridine or phenanthroline ligands where they exert little influence on the electronic structure of the emitting MLLCT

state. These complexes possess very good solubility and film forming properties even in nonpolar solvents such as toluene. Analysis of the solid state photoluminescence decays establishes that concentration quenching is significantly reduced for the more bulky complexes, which should lead to better diode performance. A brightness of ca. 1000 cd m^{-2} at 3 V was obtained for complex **5** which demonstrates a beneficial effect of bulky substituents. These findings are consistent with the work of Bernhard et al. on ruthenium complexes.^[32] However, the trade-off is that the higher drive voltages are required for the complexes with bulkier ligands and charge carrier mobility is reduced as a consequence of the larger intermolecular separation which lowers the luminous power efficiencies. Future work will involve further optimization of ligand design and will address ways to increase the carrier mobility while also maintaining the large intermolecular separation required for suppression of concentration quenching. A possible strategy is to modify the complexes by attaching side-groups with low LUMO or high HOMO levels. Simultaneously, the electronic structure of these side-groups should possess high triplet levels to ensure that the excitation is confined at the heavy metal MLLCT state. These are challenging targets with potentially high rewards in electroluminescent device technology.

4. Experimental

Representative syntheses of complexes **1**, **2**, and **7** are detailed in the Supporting Information. Cyclic voltammograms of the complexes were recorded using a BAS CV50W electrochemical analyzer fitted with a three-electrode system consisting of a Pt disk ($\varnothing = 1.8$ mm) as the working electrode, a Pt wire as an auxiliary electrode and an Ag/Ag^+ (0.01 M AgNO_3 in CH_3CN) as the reference electrode. Experiments were carried out in dichloromethane solution with 0.1 M tetra(*n*-butyl)ammonium hexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte, at a scan rate of 100 mV s^{-1} . For device studies the complexes were dissolved in either toluene or acetonitrile at a concentration of 30 mg mL^{-1} . These solutions were filtered using a 200 nm syringe filter and subsequently spin-coated onto pre-patterned ITO glass substrates, which had been thoroughly cleaned, treated with ozone and coated with poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonic acid) (PEDOT:PSS). After baking the substrates for 1 h at 80°C , aluminum or barium capped with aluminum cathodes were applied using an evaporation system in a glove box. A Keithley 2400 source meter in conjunction with a photodiode was used to measure the I – V – L characteristics. The luminescence intensity was calibrated by measuring the absolute brightness using a Minolta LS110 luminance meter. The radiative photoluminescence decay of the complexes was measured at room temperature using gated spectroscopy, where the sample was excited at 355 nm, the emission was passed through a spectrograph and monitored by a gated CCD camera as a function of delay and integration time [15]. Photoluminescence quantum yields (PLQY) were measured in degassed acetonitrile and toluene solutions with 9,10-diphenylanthracene in cyclohexane as a standard ($\Phi = 0.9$) at a range of concentrations to give absorbances of 0–1 OD. Thin films were obtained by spin-casting from acetonitrile solutions of the complex (6 mg in 0.5 mL) and measurements were made using a calibrated integrating sphere system.

Acknowledgements

The authors thank Durham County Council (Project SP/082), CENAMPS, and the University of Durham Photonic Materials Institute for funding this

work. R. J. thanks the Royal Thai Government for a scholarship. Supporting Information is available online from Wiley InterScience or from the author.

Received: November 28, 2008
Published online: April 14, 2009

- [1] Reviews: a) (Ed.: Z. H. Kakafi), *Organic Electroluminescence*, CRC Press, Boca Raton **2005**. b) A. P. Kulkarni, C. J. Tonzola, A. Babel, S. A. Jenekhe, *Chem. Mater.* **2004**, *16*, 4556. c) G. Hughes, M. R. Bryce, *J. Mater. Chem.* **2005**, *15*, 94.
- [2] M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, *Nature* **1998**, *395*, 151.
- [3] C. Rothe, S. King, A. P. Monkman, *Phys. Rev. B* **2006**, *73*, art no. 245208.
- [4] E. Holder, B. M. W. Langeveld, U. S. Schubert, *Adv. Mater.* **2005**, *17*, 1109.
- [5] A. van Dijken, J. J. A. M. Bastiaansen, N. M. M. Kiggen, B. M. W. Langeveld-Voss, C. Rothe, A. P. Monkman, I. Bach, P. Stöbel, K. Brunner, *J. Am. Chem. Soc.* **2004**, *126*, 7718.
- [6] J. K. Lee, D. S. Yoo, E. S. Handy, M. F. Rubner, *Appl. Phys. Lett.* **1996**, *69*, 1686.
- [7] a) J. Slinker, D. Bernards, P. L. Houston, H. D. Arbruña, S. Bernhard, G. G. Malliaras, *Chem. Commun.* **2003**, 2392. b) Review: J. D. Slinker, J. Rivnay, J. S. Moskowitz, J. B. Parker, S. Bernhard, H. D. Arbruña, G. G. Malliaras, *J. Mater. Chem.* **2007**, *17*, 2976.
- [8] a) F. De Angelis, S. Fantacci, N. Evans, C. Klein, S. M. Zakeeruddin, J.-E. Moser, K. Kalyanasundaram, H. J. Bolink, M. Grätzel, M. K. Nazeeruddin, *Inorg. Chem.* **2007**, *46*, 5989. b) H. J. Bolink, L. Cappelli, S. Cheylan, E. Coronado, R. D. Costa, N. Lardiés, M. K. Nazeeruddin, E. Ortí, *J. Mater. Chem.* **2007**, *17*, 5032. c) H. J. Bolink, L. Cappelli, E. Coronado, M. Grätzel, E. Ortí, R. D. Costa, P. M. Viruela, M. K. Nazeeruddin, *J. Am. Chem. Soc.* **2006**, *128*, 14786.
- [9] M. K. Nazeeruddin, R. T. Wegh, Z. Zhou, C. Klein, Q. Wang, F. De Angelis, S. Fantacci, M. Grätzel, *Inorg. Chem.* **2006**, *45*, 9245.
- [10] A. B. Tamayo, S. Garon, T. Sajoto, P. I. Djurovich, I. M. Tsyba, R. Bau, M. E. Thompson, *Inorg. Chem.* **2005**, *44*, 8723.
- [11] H. Rudmann, S. Shimada, M. F. Rubner, *J. Am. Chem. Soc.* **2002**, *124*, 4918.
- [12] G. F. He, M. Pfeiffer, K. Leo, M. Hofmann, J. Birnstock, R. Pudzych, J. Salbeck, *Appl. Phys. Lett.* **2004**, *85*, 3911.
- [13] S. Sinha, C. Rothe, R. Güntner, U. Scherf, A. P. Monkman, *Phys. Rev. Lett.* **2003**, *90*, 127402.
- [14] C. Rothe, R. Güntner, U. Scherf, A. P. Monkman, *J. Chem. Phys.* **2001**, *115*, 9557.
- [15] C. Rothe, A. P. Monkman, *Phys. Rev. B* **2003**, *68*, 075208.
- [16] A. P. Monkman, H. D. Burrows, L. J. Hartwell, L. E. Horsburgh, I. Hamblett, S. Navaratnam, *Phys. Rev. Lett.* **2001**, *86*, 1358.
- [17] C. Rothe, S. King, A. Monkman, *Nat. Mater.* **2006**, *5*, 463.
- [18] S. M. King, H. A. Al-Attar, R. J. Evans, A. Congreve, A. Beeby, A. P. Monkman, *Adv. Funct. Mater.* **2006**, *16*, 1043.
- [19] X. Zeng, M. Tavasli, I. F. Perepichka, A. S. Batsanov, M. R. Bryce, C.-J. Chiang, C. Rothe, A. P. Monkman, *Chem. Eur. J.* **2008**, *14*, 933.
- [20] During the course of our work complex 7 was synthesized by other workers for studies on chemosensing of anions: Q. Zhao, S. Liu, M. Shi, F. Li, H. Jing, T. Yi, C. Huang, *Organometallics* **2007**, *26*, 5922.
- [21] H.-C. Su, F.-C. Fang, T.-Y. Hwu, H.-H. Hsieh, H.-F. Chen, G.-H. Lee, S.-M. Peng, K.-T. Wong, C.-C. Wu, *Adv. Funct. Mater.* **2007**, *17*, 1019.
- [22] a) H. J. Bolink, E. Coronado, R. D. Costa, E. Ortí, M. Sessolo, S. Graber, K. Doyle, M. Neuburger, C. E. Housecroft, E. C. Constable, *Adv. Mater.* **2008**, *20*, 3910. b) S. Graber, K. Doyle, M. Neuburger, C. E. Housecroft, E. C. Constable, R. D. Costa, E. Ortí, D. Repetto, H. J. Bolink, *J. Am. Chem. Soc.* **2008**, *130*, 14944.
- [23] H. J. Bolink, L. Cappelli, E. Coronado, M. Grätzel, E. Ortí, R. D. Costa, P. M. Viruela, Md, K. Nazeeruddin, *J. Am. Chem. Soc.* **2006**, *128*, 14786.
- [24] R. W. T. Higgins, A. P. Monkman, H. G. Nothofer, U. Scherf, *J. Appl. Phys.* **2001**, *91*, 99.
- [25] C. Rothe, S. King, A. P. Monkman, *Phys. Rev. B* **2006**, *73*, 245208.
- [26] a) S. C. J. Meskers, J. Hubner, M. Oestreich, H. Bassler, *Chem. Phys. Lett.* **2001**, *339*, 223. b) R. Richert, H. Bassler, *Chem. Phys. Lett.* **1985**, *118*, 235. c) R. Richert, H. Bassler, *J. Chem. Phys.* **1986**, *84*, 3567.
- [27] M. Tavasli, S. Bettington, M. R. Bryce, H. A. Al Attar, F. B. Dias, S. King, A. P. Monkman, *J. Mater. Chem.* **2005**, *15*, 4963.
- [28] F. B. Dias, S. Pollock, G. Hedley, L. O. Pålsson, A. Monkman, I. I. Perepichka, I. F. Perepichka, M. Tavasli, M. R. Bryce, *J. Phys. Chem. B* **2006**, *110*, 19329.
- [29] M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal, G. G. Malliaras, S. Bernhard, *Chem. Mater.* **2005**, *17*, 5712.
- [30] J. D. Slinker, C. Y. Koh, G. G. Malliaras, M. S. Lowry, S. Bernhard, *Appl. Phys. Lett.* **2005**, *86*, 173506.
- [31] E. S. Handy, A. J. Pal, M. F. Rubner, *J. Am. Chem. Soc.* **1999**, *121*, 3525.
- [32] S. Bernhard, J. A. Barron, P. L. Houston, H. D. Arbruña, J. L. Ruglovsky, X. C. Gao, G. G. Malliaras, *J. Am. Chem. Soc.* **2002**, *124*, 13624.