Semiconducting polyfluorenes with electrophosphorescent on-chain platinum–salen chromophores†

Frank Galbrecht,[a] Xiao Hui Yang,[b] Benjamin S. Nehls,[a] Dieter Neher,[b] Tony Farrell[a] and Ullrich Scherf*[a]

Received (in Cambridge, UK) 27th January 2005, Accepted 4th March 2005
First published as an Advance Article on the web 18th March 2005
DOI: 10.1039/b501297j

The synthesis of statistical fluorene-type copolymers with on-chain Pt–salen phosphorescent units and their use in electrophosphorescent OLEDs is reported.

Recently, there has been much progress in the application of cyclometallated complexes as emitting components in electroluminescent (EL) devices.[1–3] The phosphorescent metal complexes allow for the utilization of both singlet and triplet excitons which are generated upon charge injection from the electrodes. Consequently, internal quantum efficiencies approaching 100% may be achieved. Additionally, the possibility to tune the emission color by manipulating the ligand sphere of the metal atom is a very attractive goal. Many examples of electrophosphorescent metal complexes based on iridium, osmium, platinum and rare-earth metal complexes are known.[1–3] Nonetheless, there are still relatively few examples of electrophosphorescent (co)polymers as single-component OLED materials. Examples include semiconducting polyfluorenes with side-chain or main-chain iridium complexes,[4,5] ladder poly(*para*-phenylene)s with electrophosphorescent palladium centers,[6] self-assembled Schiff-base polymers[7] and platinum-based side-chain copolymers.[8] Transition metal (Co, Ni, Zn) Schiff-base polymers have been prepared by oxidative polymerisation, transesterification and condensation of salen-type monomers but they have not been applied in OLEDs.[9,10] Remarkably, whether it is due to design or serendipidity, only a trace amount of the heavy metal atoms is necessary for efficient triplet emission.[6]

A recent paper by Che *et al.* described the utilisation of vapour-deposited Pt–salen complexes as efficient electrophosphorescent dyes in multilayer OLED devices with a maximum luminous efficiency of 31 Cd A^{-1}.[11] Recent work has intimated that higher OLED efficiencies can be achieved when the phosphorescent chromophore is molecularly dispersed within the composite material. Thus, our strategy towards main-chain electrophosphorescent copolymers involves the covalent incorporation of Pt–salen phosphors into the backbone of a solution-processable semiconducting copolymer. As proof of concept we chose to incorporate such Pt–salen phosphors into a polyfluorene (PF) backbone. We anticipated that a Ni(0)-mediated, aryl–aryl coupling protocol would best fulfil the challenge of preparing high molecular weight fluorene copolymers containing randomly incorporated platinum complexes (Table 1).[12]

Table 1 Reaction conditions and polymer analysis for the copolymerisation of 2,7-dibromo-9,9-dialkylfluorene **2** and Pt–salen monomer **1**

Sample	Solvent	Time	M_w[a]	M_n[a]	M_w/M_n
3a[b]	THF	12 min	357 400	169 500	2.11
3b[b]	DMF–toluene	12 min	65 400	24 300	2.70
PF2/6[c]	THF	3 days	22 2200	125 700	1.77

[a] After Soxhlet extraction with ethyl acetate. [b] Microwave as heat source (**3a**: T = 115 °C, **3b**: T = 220 °C). [c] Conventional heating at 80 °C.

A cyclometallated Pt(II)–salen complex suitable for the Yamamoto-type coupling procedure was prepared from the reaction of K$_2$PtCl$_4$ with bis(5-chlorosalicylidene)ethylenediamine. The chloro derivative was easily accessible from this protocol unlike the corresponding dibromo monomer. Fortunately, chloroaryl monomers readily undergo homocoupling *via* a Yamamoto-type procedure.[13] The copolymers were synthesised using feed ratios of *ca.* 0.2 mol equivalents of the Pt–salen monomer to 2,7-dibromo-9,9-bis(alkyl)fluorene. The reaction was carried out in THF using microwaves as the heat source within short reaction times of *ca.* 12 min.[13,14] A maximum temperature of 115 °C was employed which was reached in less than 30 s. The crude polymer was Soxhlet-extracted using ethyl acetate for two days to remove oligomeric by-products and yielded the yellow polymers **3a** and **3b** (Table 1). The actual percentage of the Pt(II) phosphor incorporated into the main chain of **3a** and **3b** was calculated from the relative ^{1}H NMR intensities of the ethylene bridge protons of the salen ligand at $\delta \sim 3.8$ ppm relative to the sum of the aryl protons (Scheme 1).

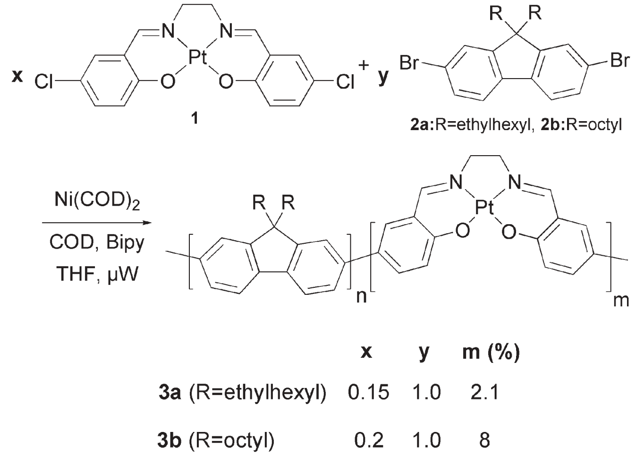
The monomeric Schiff-base Pt–salen complex **1** (Fig. 1) displays a broad absorption maximum peaking at 436 nm and a PL maximum at 563 nm in chloroform solution.† The solution UV-vis spectrum of the fluorene-based copolymer **3a** shows an intense absorption band at 383 nm due to the polyfluorene chromophore and a low intensity absorption shoulder at *ca.* 450 nm due to the incorporated Pt–salen phosphors (Fig. 2). The solution PL spectrum is dominated by the PF emission with a maximum at 413 nm.

However, the PL spectrum of copolymer **3a** in the solid state (film) displays a somewhat red-shifted PF emission (428 nm) and an additional lower energy emission with appreciable intensity peaking at 575 nm (excitation λ_{ex} = 380 nm) (Fig. 2). The lower energy peak is attributed to the phosphorescence of the Pt–salen complex and indicates considerable energy transfer from the excited PF chromophore to the green emitting Pt–salen phosphor. When the copolymer **3a** is excited directly at 450 nm *i.e.* at the

---

† Electronic supplementary information (ESI) available: Instrumental, synthesis and device fabrication. See http://www.rsc.org/suppdata/cc/b5/b501297j/

*scherf@uni-wuppertal.de



Scheme 1 Copolymer synthesis *via* microwave-assisted Yamamoto-type coupling. Molar ratio of incorporated Pt–salen units was determined from the integrated ^{1}H NMR spectra.

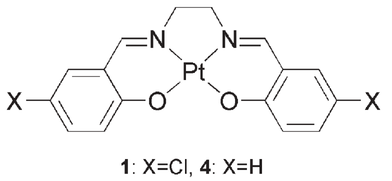


Fig. 1 Structure of Pt–salen complexes **1** and **4**.

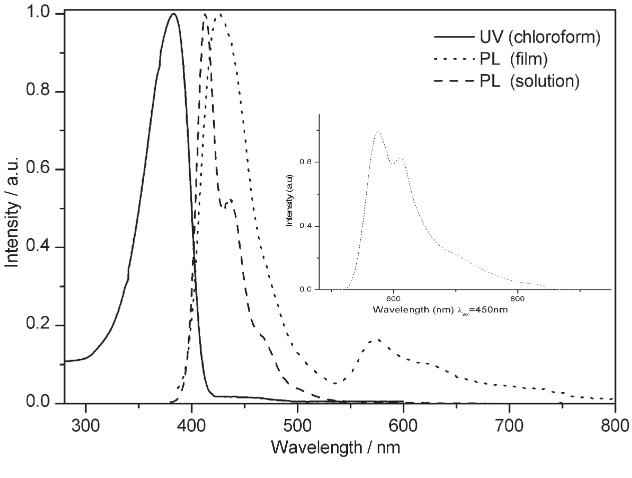


Fig. 2 Absorption and emission (λ_{ex} = 380 nm) spectra of **3a** in chloroform and of a thin spin-coated film at 298 K. The inset shows the luminescence of the film excited at 450 nm.

λ_{max} of the Pt–salen complex, the emission at 575 nm is dominant confirming the origin of the green emission since the absorption of the PF is negligible at this wavelength.

Organic light-emitting diodes were fabricated with a ITO|PEDOT:PSS anode and an evaporated Ca|Al cathode. The EL spectrum of the device based on the pure Pt–salen copolymer **3a** is rather broad. The most prominent peak is at *ca.* 640 nm, with a shoulder at *ca.* 580 nm.† The 580 nm-band is also observed in the solid-state PL spectrum of a film of the copolymer **3a** and is attributed to the phosphorescence of the Pt–salen chromophores (Fig. 2). The additional emission peak at 640 nm can be attributed to an emission from excimers of the Pt–salen phosphors. The formation of phosphorescent excimers has also been observed in OLED devices constructed from (2-(4′,6′-difluorophenyl)-pyridinato-$N,C^{2'}$)(2,4-pentanedionato)platinum(II).[15]

The EL efficiencies of the devices based on the pure copolymer **3a** are quite low (*ca.* 0.1–0.3 cd A^{-1}), depending somewhat on the amount of Pt–salen phosphor in the copolymer and most probably influenced by the presence of aggregate quenching. In order to reduce or suppress such concentration effects, we blended the copolymer **3b** into a matrix based on poly(vinyl carbazole) (PVK) and (2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole) (PBD) with a weight ratio PVK:PBD of 4:1.† In this case, the 640 nm contribution to the EL spectrum is largely suppressed and the phosphorescence closely resembles the PL of the Pt–salen chromophore.† Interestingly, the EL spectrum of the copolymer **3b** blended into the PVK:PBD matrix is slightly red-shifted by about 0.1 eV compared to that of a device containing the monomeric Pt–salen complex **4** in the same matrix. However, the energy transfer between PVK and **3b** is rather inefficient and the EL contribution of the PVK matrix at 438 nm is dominant. Therefore we switched to a poly[9,9-bis(2-ethylhexyl)fluorene] (PF2/6) matrix. Devices based on a blend of the copolymer **3b** in PF2/6 (5 and 10 wt%) show a much more efficient energy transfer (Fig. 3). Based on recent findings for polyfluorenes with covalently attached Ir-complexes, we propose the occurrence of a mixed triplet state in our novel copolymers.[4] The efficiency of the devices were be substantially improved to *ca.* 3–6 cd A^{-1} for the copolymer **3b**–PF2/6 blends (Fig. 4). This improvement is attributed to the reduction of the electronic interaction between Pt–salen phosphors (excimer formation) in the latter device.

In summary, OLED-devices with promising performances based on novel fluorene-type copolymers with on-chain Pt–salen units have been designed with maximum luminescence efficiencies of up to 6 Cd A^{-1}. However, the EL spectra of the devices still show a minor EL contribution from the matrix polymer PF2/6. Further optimizations of our approach towards high efficiency

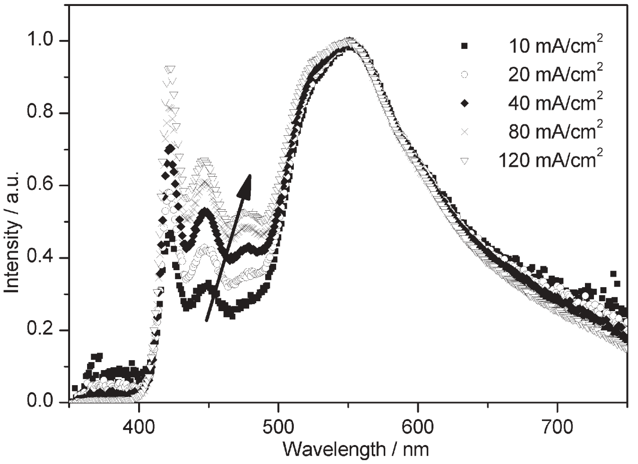


Fig. 3 EL spectra of copolymer **3b** doped into poly[9,9-bis(2-ethylhexyl)fluorene] (PF2/6) (10 wt% **3b** in PF2/6) at different current densities (device configuration: ITO|PEDT:PSS|PF2/6–**3b**|Ca|Al).

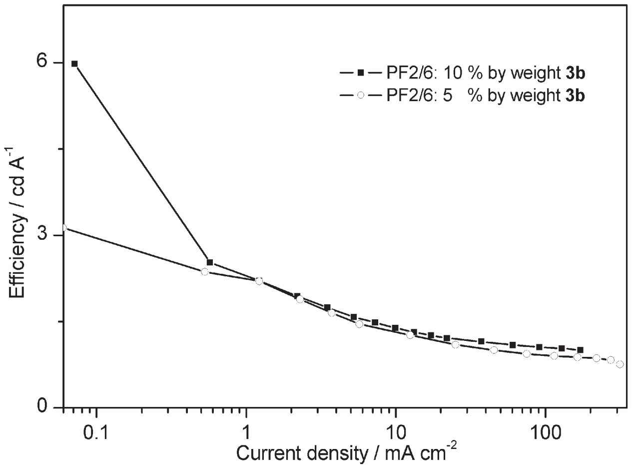


Fig. 4 Efficiency of OLED devices based on PF2/6–**3b** blends as a function of current density (device configuration: ITO|PEDT:PSS|PF2/6–**3b**|Ca|Al).

phosphorescent OLEDs will be directed towards optimising the concentration of the Pt–salen phosphor in the copolymer and of the copolymer in a suitable host polymer. Additional improvements are expected from the synthesis of related carbazole-based copolymers containing Pt–salen phosphors. The use of carbazole-based oligomers and polymers as hosts for phosphorescent guests has been described by Brunner *et al.*, wherein the fine tuning of the energy levels leads to improved energy transfer and results in higher OLED efficiencies.[16]

We thank the German Ministry of Science and Education for supporting this work (contract no. 13N8213). B. S. N. thanks the VCI foundation for financial support.

Frank Galbrecht,[a] Xiao Hui Yang,[b] Benjamin S. Nehls,[a] Dieter Neher,[b] Tony Farrell[a] and Ullrich Scherf*[a]
[a]*Bergische Universität Wuppertal, Makromolekulare Chemie,*
Gauss-Str. 20, D-42097 Wuppertal, Germany.
E-mail: scherf@uni-wuppertal.de; Fax: 49 202 439 3880;
Tel: 49 202 439 2493
[b]*Universität Potsdam, Institut für Physik, Am Neuen Palais 10, D-14471*
Potsdam, Germany. E-mail: neher@rz.uni-potsdam.de;
Fax: 49 331 977 1290; Tel: 49 331 977 1265

Notes and references

1 (*a*) M. A. Baldo, M. E. Thompson and S. R. Forrest, *Pure Appl. Chem.*, 1999, **71**, 2098; (*b*) X. Gong, J. C. Ostrowski, G. C. Bazan, D. Moses, A. J. Heeger, M. S. Liu and A. K. Y. Jen, *Adv. Mater.*, 2003, **15**, 45.
2 (*a*) S. A. Bagnich, C. Im, H. Bässler, D. Neher and U. Scherf, *Chem. Phys.*, 2004, **299**, 11; (*b*) M. D. McGehee, T. Bergstedt, C. Zhang, A. P. Saab, M. B. O'Regan, G. C. Bazan, V. I. Srdanov and A. J. Heeger, *Adv. Mater.*, 1999, **11**, 1349.
3 (*a*) X. H. Yang and D. Neher, *Appl. Phys. Lett.*, 2004, **84**, 2476; (*b*) C.-L. Lee, K. B. Lee and J. J. Kim, *Appl. Phys. Lett*, 2000, **77**, 2280; (*c*) Y.-L. Tung, S.-W. Lee, Y. Chi, Y.-T- Tao, C.-H. Chien, Y.-M. Cheng, P.-T. Chou, S.-M. Peng and C.-S. Liu, *J. Mater. Chem.*, 2005, **4**, 460.
4 A. J. Sandee, C. K. Williams, N. R. Evans, J. E. Davies, C. E. Boothby, A. Köhler, R. H. Friend and A. B. Holmes, *J. Am. Chem. Soc.*, 2004, **126**, 7041.
5 X. Chen, J.-L. Liao, Y. Liang, M. O. Ahmed, H.-E. Tseng and S.-A. Chen, *J. Am. Chem. Soc.*, 2003, **125**, 636.
6 J. M. Lupton, A. Pogantsch, T. Piok, E. J. W. List, S. Patil and U. Scherf, *Phys. Rev. Lett.*, 2002, **89**, 167401.
7 C.-C. Kwok, S.-C. Yu, I. H. T. Sham and C.-M. Che, *Chem. Commun.*, 2004, 2758.
8 P. T. Furuta, L. Deng, S. Garon, M. E. Thompson and J. M. Fréchet, *J. Am. Chem. Soc.*, 2004, **126**, 15388.
9 R. P. Kingsborough and T. M. Swager, *Adv. Mater.*, 1998, **10**, 1100.
10 D. Wöhrle and A. D. Pomogailo, *Metal Complexes and Metals in Macrocycles*, Wiley-VCH, Weinheim, 2003, p. 230.
11 C.-M. Che, S.-C. Chan, H. F. Xiang, M. C. W. Chan, Y. Liu and Y. Wang, *Chem. Commun.*, 2004, 1484.
12 K. R. Carter, *Macromolecules*, 2002, **35**, 6757.
13 E. C. Hagberg, D. A. Olson and V. V. Sheares, *Macromolecules*, 2004, **37**, 4748.
14 B. S. Nehls, U. Asawapirom, S. Füldner, E. Preis, T. Farrell and U. Scherf, *Adv. Funct. Mater.*, 2004, **14**, 352.
15 W. D'Andrade, J. Brooks, V. Adamovich, M. E. Thompson and S. R. Forrest, *Adv. Mater.*, 2002, **14**, 1032.
16 K. Brunner, A. van Dijken, H. Börner, J. J. A. M. Bastiaansen, N. M. M. Kiggen and B. M. W. Langeveld, *J. Am. Chem. Soc.*, 2004, **126**, 6035.