Available online at www.sciencedirect.com

ScienceDirect

Inorganic Chemistry Communications 11 (2008) 231–234

INORGANIC CHEMISTRY COMMUNICATIONS

www.elsevier.com/locate/inoche

Towards a phosphorescent cyclometalated iridium complex containing a modified polymerizable acetylacetonato ligand

Marion Graf [a], Valeria Gancheva [b,c], Manuel Thesen [b], Hartmut Krüger [b], Peter Mayer [a], Karlheinz Sünkel [a,*]

[a] *Department Chemie der Ludwig-Maximilians-Universität München, Butenandtstraße 5–13, D-81377 München, Germany*
[b] *Fraunhofer Institut für Angewandte Polymerforschung, Geiselbergstraße 69, D-14476 Potsdam-Golm, Germany*
[c] *Bulgarian Academy of Sciences, Institute of Polymers, Acad. G. Bontchev Str. 103A, BG-1113 Sofia, Bulgaria*

Received 29 June 2007; accepted 18 October 2007
Available online 15 December 2007

Abstract

A convenient synthesis of the complex [Ir(ppy)$_2$(phC6-acac)] (**1**, ppy = 2-phenylpyridyl, phC6-acac = 11-(2,5-dibromo-4-hexyloxy-phenoxy)-undecane-2,4-dione) from [{Ir(μ-Cl)(ppy)$_2$}$_2$], phC6-acacH and silver trifluoroacetate as the halide abstractor in refluxing acetone is described. The crystal and molecular structure of **1** was determined by X-ray crystallography.

Keywords: Iridium; Cyclometalated complex; Photoluminescence; Crystal structure

In the last years the photophysical and photochemical properties of cyclometalated iridium(III) complexes have been extensively investigated. Because of their high luminescence quantum yields and short phosphorescence lifetimes these compounds are suitable for various applications in photochemistry and in organic light-emitting devices (OLEDs) and exhibit still the efficient phosphorescent dyes in this field up to now, e.g. [1–16]. In this light, one of the best green-light-emitting complexes is the compound *fac*-[Ir(ppy)$_3$)] yielding a high quantum efficiency [17]. Moreover the more efficient green-light-emitting complex [Ir(ppy)$_2$(acac)] as the phosphorescent dopant was reported [18]. Therefore, complexes of the formula [Ir(ppy)$_2$(acac)] (acac = modified acetylacetonates) should obviously provide better luminescent properties. Many efforts were undertaken to chemically modify this type of complex to reach proper luminescence properties, e.g. [10] and to incorporate chemical functionalities which are useful to link these complexes covalently to phosphorescent polymer OLED materials. In this paper we report the preparation and structural characterization of a new compound in this area, [Ir(ppy)$_2$(phC6-acac)] (**1**, ppy = 2-phenylpyridyl, phC6-acac = 11-(2,5-dibromo-4-hexyloxy-phenoxy)-undecane-2,4-dione). Thus compound **1** was prepared from [{Ir(μ-Cl)(ppy)$_2$}$_2$], phC6-acacH, triethylamine as the base and silver trifluoroacetate as the halide abstractor in refluxing acetone. All manipulations were performed under a dry argon atmosphere using conventional Schlenk techniques. Solvents and reagents were used as received, [{Ir(μ-Cl)(ppy)$_2$}$_2$] was prepared according to the literature procedure [19]. The precursor of the ligand, phC6-acacH = 11-(2,5-dibromo-4-hexyloxy-phenoxy)-undecane-2,4-dione was obtained by a specially developed preparation [20]. ^{1}H NMR spectra were recorded on a Jeol EX 400 (^{1}H: 400 MHz) or a Jeol Eclipse 400 NMR spectrometer (^{1}H: 400 MHz). The spectra were referenced to external SiMe$_4$ (^{1}H). IR spectra were recorded as KBr pellets on a Mattson Perkin Elmer 983 G spectrometer. Mass spectra were obtained on a JMS-700 spectrometer from Jeol. Microanalyses (C, H, N) were performed by the University of Munich microanalytical laboratory.

---

[*] Corresponding author. Tel.: +49 89 2180 77773.
E-mail address: karlheinz.suenkel@cup.uni-muenchen.de (K. Sünkel).

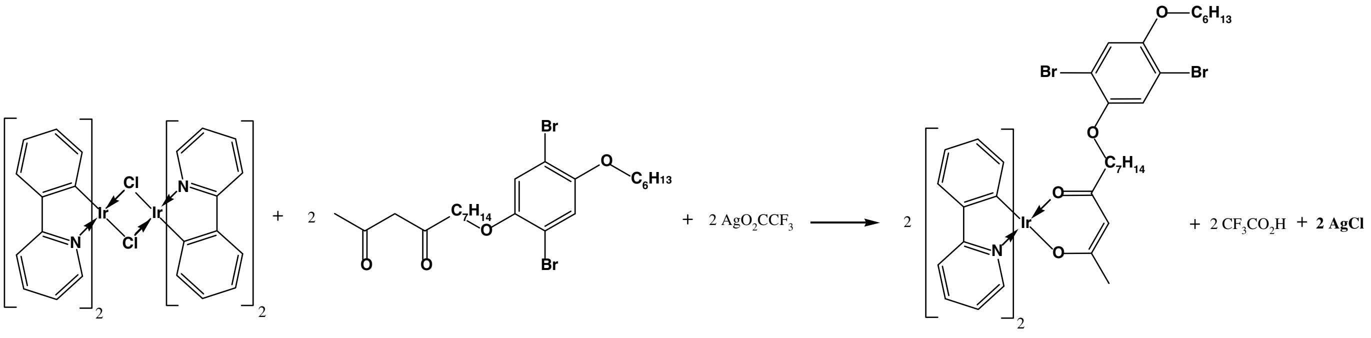
1387-7003/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.inoche.2007.10.029

A mixture of [{Ir(μ-Cl)(ppy)$_2$}$_2$] (0.500 g, 0.47 mmol), (ppy = 2-phenylpyridine), phc6-acaH = 11-(2,5-dibromo-4-hexyloxy-phenoxy)-undecane-2,4-dione (0.498 g, 0.93 mmol), and AgO_2CCF_3 (0.206 g, 0.933 mmol) were dissolved in 30 mL of acetone and refluxed under nitrogen for 3 h. The mixture was cooled to room temperature and the precipitated AgCl was separated by filtration. Then the solvent was removed in vacuo to dryness. The remaining residue was dissolved in 10 mL of dichloromethane and chromatographed over an alumina column (25 × 2 cm) with dichloromethane as the eluent. The first yellow band was collected and evaporated to dryness, dissolved in 5 mL of CH_2Cl_2 and precipitated with hexane. Crystals suitable for X-ray diffraction studies were obtained by slow diffusion of ethanol into a concentrated solution of the compound in dichloromethane. (Yield: 210 mg, 48%). Anal. Calc. for $C_{45}H_{49}Br_2IrN_2O_4$ (MW 1033.91) C, 52.28; H, 4.78; N, 2.71%. Found: C, 51.98; H, 5.00; N, 2.67%. ^1H NMR (270 MHz, $CDCl_3$): δ8.49 (dd, $J = 1.4$ Hz, $J = 1.0$ Hz, 2H), 8.47 (dd, $J = 1.41$ Hz, $J = 1.05$ Hz, 2H), 7.82 (t, $J = 8.72$ Hz, 2H), 7.70 (m, 2H), 7.52 (m, 2H), 7.02 (d, $J = 3.03$ Hz, 2H), 6.79 (m, 2H), 6.66 (m, 2H), 6.31 (m, 1H), 6.24 (m, 1H), 5.18 (s, 1H, OC–C*H*–CO), 3.92 (m, 6H), 1.97 (t, $J = 7.43$ Hz, 2H), 1.79 (s, 3H, CH_3–CO), 1.72 (m, 2H), 1.30 (m, 10H), 1.11 (m, 2H), 0.98 (m, 2H), 0.90 (t, $J = 6.98$ Hz, 3H,–CH_2–CH_3). IR (KBr): 629w, 669w, 729s, 752s, 793w, 1030s, 1062s, 1156w, 1210s, 1264s, 1302w, 1358s, 1422s, sh, 1456s, 1478s, 1492s, 1514s, 1580vs, 1605s, 2855s, 2925s, br, cm^{-1}. MS (70 eV): 1033 (M$^+$, ^{193}Ir).

Complex **1** was prepared from the reaction of [{Ir(μ-Cl)(ppy)$_2$}$_2$] with 2 equiv. of silver trifluoroacetate, 1 equiv. of the diketone, and triethylamine as the base in refluxing acetone (Scheme 1). The new compound was separated by column chromatography and purified by crystallization from ethanol/dichloromethane. Elemental analysis, mass spectrum, and the ^1H NMR spectroscopic data confirmed the constitution of compound **1**. Crystals for the X-ray diffraction study were selected by means of a polarization microscope, mounted on the tip of a glass fiber, and investigated on a Nonius KappaCCD diffractometer using graphite-monochromated Mo$_K\alpha$ radiation ($\lambda =$ 0.71073 Å). The structure was solved by direct methods (SIR 97) [21] and refined by full-matrix least-squares calculations on F^2 (SHELXL-97) [22]. Anisotropic displacement parameters were refined for all non-hydrogen atoms. *Crystal data*: $C_{45}H_{49}Br_2IrN_2O_4$ $F_W = 1033.91$, triclinic, space group $P\bar{1}$, $a = 7.5953(2)$, $b = 13.8109(3)$, $c = 19.9793(5)$ Å, $\alpha = 84.3394(12)$, $\beta = 79.3392(14)$, $g = 89.2467(13)°$, $V = 2049.54(9)$ Å^3, $Z = 2$, $D_{calc} = 1.675$ g cm^{-3}, $T = 200(2)$ K, 37,708 reflections were collected, of which 7721 ($R_{int} = 0.045$ [$I > 2\sigma(I)$] were unique.

The molecular structure of **1** is illustrated in Fig. 1 including important bond lengths and angles in the caption. The iridium complex exhibits two cyclometalated phenylpyridine ligands and the diketonate ligand in a pseudooctahedral coordination sphere at the metal center. The Ir–C bond lengths, ranging from 1.983(6) to 1.987(6) Å, are within the range reported for other mononuclear complexes containing the Ir(ppy)$_2$ moiety [10]. The Ir–N bond lengths are in the range of 2.033(6)–2.036(6) Å. Furthermore, the C–C and C–N bond lengths and angles are within normal ranges and in accordance with corresponding parameters described for other similarly constituted complexes [14]. The Ir–O bond lengths are 2.151(4) and 2.164(5) Å, respectively. Furthermore, the C–O bond lengths are in agreement with the literature reports, e.g. [12].

The absorption and room-temperature emission spectrum of **1** recorded in dichloromethane is shown in Fig. 2. In the absorption spectrum the intense bands around 300 nm can be assigned to spin-allowed $^1(\pi–\pi^*)$ transitions, and bands at 339, 365, and 406 nm correspond to spin-allowed ^{1}MLCT bands. The two bands at 457 and 485 nm can be assigned to the formally spin-forbidden ^{3}MLCT transition as reported for [Ir(ppy)$_2$(acac)] [15]. The peak wavelength of phosphorescent emission of compound **1** was observed at 520 nm and is comparable to similar constituted cyclometalated iridium complexes containing the acetylacetonate ligand, e.g. [4,15]. The new green-emitting complex [Ir(ppy)$_2$(phC6-acac)] (**1**) will be used now in applications for phosphorescent polymer OLED systems. By the hexyloxy-spacer the phosphores-



(1)

Scheme 1.

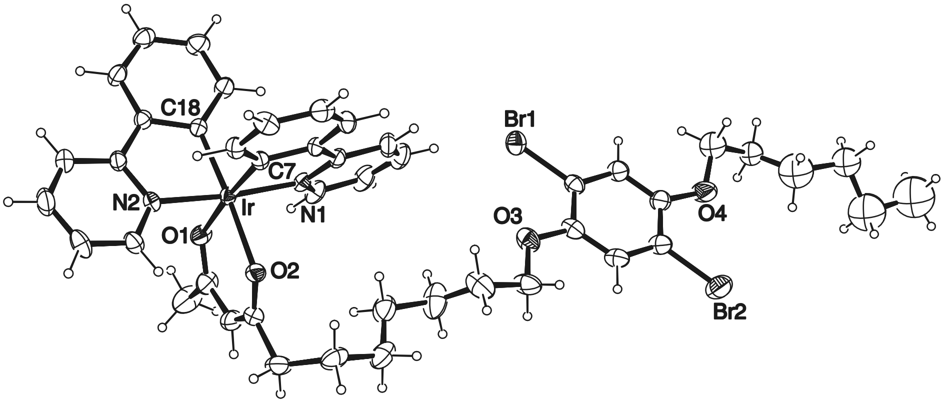


Fig. 1. ORTEP view of **1** with thermal ellipsoids are drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Ir(1)–N(1) 2.033(6), Ir(1)–N(2) 2.036(6), Ir(1)–C(7) 1.987(6), Ir(1)–C(18) 1.983(6), Ir(1)–O(1) 2.164(5), Ir(1)–O(2) 2.151(4) Å; O(1)–Ir–O(2) 88.21(18), O(1)–Ir–N(1) 94.5(2), O(1)–Ir–N(2) 89.2(2), O(1)–Ir–C(7) 175.0(2), O(1)–Ir–C(18) 90.6(2), O(2)–Ir–N(1) 88.70(19), O(2)–Ir–N(2) 95.97(19), O(2)–Ir–C(7) 89.5(2), O(2)–Ir–C(18) 176.4(2), N(1)–Ir–N(2) 174.1(2), N(1)–Ir–C(7) 81.0(2), N(1)–Ir–C(18) 94.8.(2), N(2)–Ir–C(7) 95.5(2), N(2)–Ir–C(18) 80.6(2), C(7)–Ir–C(18) 91.9(3)°.

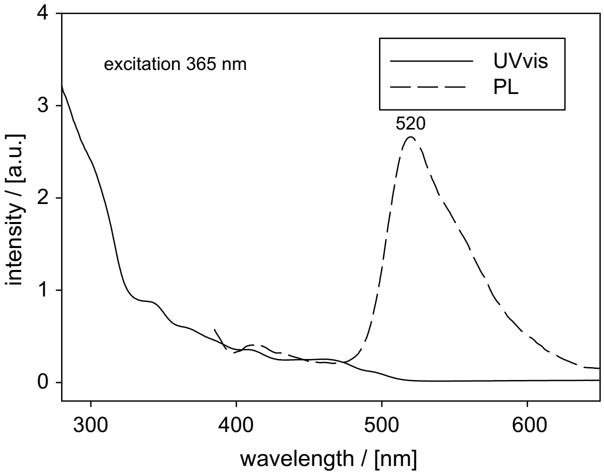


Fig. 2. Absorption spectrum and photoluminescence for [Ir(ppy)$_2$(phC6-acac)] (**1**) in dichloromethane at room temperature.

cent complex will be covalently, but non-conjugatedly linked to the polymer backbone.

Supplementary material

CCDC 650267 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

The authors are grateful to the BMBF for funding within the CARO-Project (01 BD 0685) and to the Department of Chemistry and Biochemistry of the Ludwig Maximilians University Munich for supporting these investigations. V.G. and H.K. thank the NATO for funding a part of the work at Fraunhofer IAP within the CLG-Project (CBP.EAP.CLG 981997).

References

[1] X. Li, Z. Chen, Q. Zhao, L. Shen, F. Li, T. Yi, Y. Cao, C. Huang, Inorg. Chem. 46 (2007) 5518.

[2] C.-H. Yang, K.-H. Fang, W.-L. Su, S.-P. Wang, S.-K. Su, I.-W. Sun, J. Organomet. Chem. 691 (2006) 2767.

[3] I.R. Laskar, S.-F. Hsu, T.-M. Chen, Polyhedron 24 (2005) 189.

[4] M.-L. Xu, W.-L. Li, Z.-W. An, Q. Zhou, G.-Y. Wang, Appl. Organometal. Chem. 19 (2005) 1225.

[5] K.K.-W. Lo, J.S.-W. Chan, C.-K. Chung, V.W.-H. Tsang, N. Zhu, Inorg. Chim. Acta 357 (2004) 3109.

[6] P. Coppo, E.A. Plummer, L. De Cola, J. Chem. Soc., Chem. Commun. (2004) 1774.

[7] A. Tsuboyama, T. Takiguchi, S. Okada, M. Osawa, M. Hoshino, K. Ueno, J. Chem. Soc., Dalton Trans. (2004) 1115.

[8] J.D. Slinker, A.A. Gorodetsky, M.S. Lowry, J. Wang, S. Parker, R. Rohl, S. Bernhard, G.G. Malliaras, J. Am. Chem. Soc. 126 (2004) 2763.

[9] M.-K. Lau, K.-M. Cheung, Q.-F. Zhang, Y. Song, W.-T. Wong, I.D. Williams, W.-H. Leung, J. Organomet. Chem. 689 (2004) 2401.

[10] S. Jung, Y. Kang, H.-S. Kim, Y.-H. Kim, C.-L. Lee, J.-J. Kim, S.-K. Lee, S.-K. Kwon, Eur. J. Inorg. Chem. (2004) 3415.

[11] A.J. Sandee, C.K. Williams, N.R. Evans, J.E. Davies, C.E. Boothby, A. Köhler, R.H. Friend, A.B. Holmes, J. Am. Chem. Soc. 126 (2004) 7041.

[12] M.C. DeRosa, D.J. Hodgson, G.D. Enright, B. Dawson, C.E.B. Evans, R.J. Crutchley, J. Am. Chem. Soc. 126 (2004) 7619.

[13] A. Beeby, S. Bettington, I.D.W. Samuel, Z. Wang, J. Mater. Chem. 13 (2003) 80.

[14] A.B. Tamayo, B.D. Alleyne, P.I. Djurovich, S. Lamansky, I. Tsyba, N.N. Ho, R. Bau, M.E. Thompson, J. Am. Chem. Soc. 125 (2003) 7377.

[15] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R. Kwong, I. Tsyba, M. Brotz, B. Mui, R. Bau, M.E. Thompson, Inorg. Chem. 40 (2001) 1704.

[16] V.V. Grushin, N. Herron, D.D. LeCloux, W.J. Marshall, V.A. Petrov, Y. Wang, J. Chem. Soc., Chem. Commun. (2001) 1494.

[17] M.A. Baldo, S. Lamansky, P.E. Burrows, M.E. Thompson, Appl. Phys. Lett. 75 (1999) 4.

[18] C. Adachi, M.A. Baldo, M.E. Thompson, S. Forrest, J. Appl. Phys. 90 (2001) 5048.

[19] S. Sprouse, K.A. King, P.J. Spellane, R.J. Watts, J. Am. Chem. Soc. 106 (1984) 6647.

[20] *Synthesis of PhC6-acacH*: (a) *2,5-Dibromo-4-hexyloxy-phenol*: In a 100-mL-3-necked round bottom flask were placed 1.00 g (3.73 mmol) 2,5-dibromohydrochinone and 20 mL of ethanol. Then 0.84 g of KOH pellets (14.9 mmol) and hexylbromide (1.86 mmole) were

added. The reaction mixture was refluxed for 24 h, filtered hot, and cooled to room temperature. Subsequently it was diluted with dichloromethane and washed several times with water. The organic layer was dried over Na_2SO_4. After removing the solvent, the compound was purified by column chromatography on SiO_2 using hexane/ethyl acetate (4:1) as the eluant. The procedure yields the pure product as a white powder. (Yield 62%) Anal. Calc. for $C_{12}H_{16}Br_2O_2$ (MW 352.07): C, 40.94; H, 4.58; Br, 45.39%. Found: C, 41.06; H, 4.65%. ^1H NMR (500 MHz, $CDCl_3$) δ7.24 (s, 1H); 6.98 (s, 1H); 5.20 (s, 1H); 3.93 (t, 2H); 1.80 (m, 2H); 1.48 (m, 2H); 1.34 (m, 4H); 0.91 (t, 3H). (b) *1,4-Dibromo-2-(6-bromo-hexyloxy)-5-hexyloxy-benzene*: In a 100-mL-3-necked-round bottom flask with nitrogen inlet 1.10 g (3.13 mmol) 2,5-dibromo-4-hexyloxy-phenol and 30 mL of cyclohexanone were placed. Subsequently 1.30 g (9.40 mmol) of potassium carbonate, a catalytic amount of potassium iodide, and 31.3 mmol of 1,6-dibromohexane were added. The reaction mixture was refluxed for 3 h. Then the mixture was filtered hot. After distillation of spare 1,6-dibromohexane crystallisation (at least twice) from hexane gave the pure product as slight yellow powder. (Yield 61%) Anal. Calc. for $C_{19}H_{28}Br_3O_2$ (MW 528.14): C, 41.97; H, 5.28; Br, 46.53% Found: C, 42.23; H, 5.42%. ^1H NMR (500 MHz, $CDCl_3$) δ 7.08 (s, 2H); 3.95 (tt, 4H); 3.43 (t, 2H); 1.80 (m, 8H); 1.53 (m, 2H); 1.48 (m, 2H); 1.35 (m, 4H); 0.91 (t, 3H). (c) *11-(2,5-Dibromo-4-hexyloxy-phenoxy)-undecane-2,4-dione*: In a 25-mL-3-necked-round bottom flask with septum 64 mg (2.67 mmol) of sodium hydride were placed. The equipment was evacuated and flushed with argon. 5 mL of dry THF and 50 μL of hexamethylphosphamide were added by syringe. The reaction mixture was cooled to 0 °C and 0.13 g (1.30 mmol) of acetylacetone were injected. After 20 min 0.91 mL (1.46 mmol) 1.6 M butyllithium-solution in hexane were added slowly and the mixture stirred for another 20 min at 0 °C. Then 0.7 g (1.37 mmol) of 1,4-dibromo-2-(6-bromo-hexyloxy)-5-hexyloxy-benzene solved in 2 mL of dry THF were injected. The reaction mixture was stirred for 20 h at room temperature and after acidification it was solved in ethyl acetate. The organic layer was washed with sodium bicarbonate solution and water and finally dried over Na_2SO_4. After removal of the solvent, the pure product was obtained by column chromatography using petrol ether/ethyl acetate (10:1) as the eluent. The product was obtained as a white powder. (Yield 56%) Anal. Calc. for $C_{23}H_{34}Br_2O_4$(MW 543.33): C, 51.70; H, 6.41; Br, 29.91% Found: C, 53.29; H, 6.46%. ^1H NMR (500 MHz, $CDCl_3$) (a) keto-form (12%) δ 7.08 (ss, 2H); 3.94 (tt, 4H); 3.57 (s, 2H); 2.51 (t, 2H); 2.24 (s, 3H); 1.80 (m, 4H); 1.62 (m, 2H); 1.48 (m, 4H); 1.35 (m, 8H); 0.91 (t, 3H). (b) enol-form (88%) δ 7.08 (ss, 2H); 5.49 (s, 1H); 3.94 (tt, 4H); 2.27 (t, 2H); 2.05 (s, 3H); 1.80 (m, 4H); 1.62 (m, 2H); 1.48 (m, 4H); 1.35 (m, 8H); 0.91 (t, 3H).

[21] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidore, R. Spagna, SIR97: a new tool for crystal structure determination and refinement, J. Appl. Crystallogr. 32 (1999) 115.

[22] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.