Metal-Containing Amphiphiles: Orthometallated Iridium(III) Complexes with Substituted 6′-Phenyl-2,2′-bipyridines

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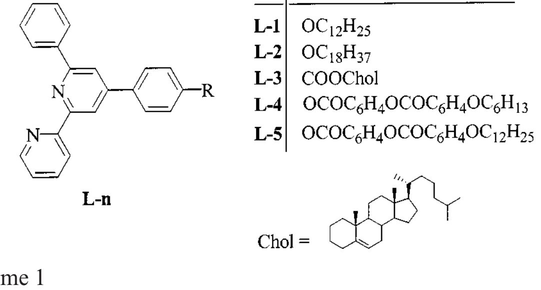
The reaction of 4′-functionalized 6′-phenyl-2,2′-bipyridine ligands (**L-*n***) with the dimer $[(ppy)_2IrCl]_2$ (ppy = 2-phenylpyridine anion) and subsequent counterion exchange affords a new series of cationic orthometallated iridium(III) complexes, $[(ppy)_2Ir(L\text{-}n)][PF_6]$ (**1**–**5**), which have been characterized by spectroscopic methods. These complexes have a large shape anisotropy and significant amphiphilic character. The crystal structure of **4** has been determined by X-ray diffraction.

Introduction

The coexistence of distinct hydrophobic and hydrophilic moieties in the same structure is the key factor inducing segregation of dissimilar parts thus generating supramolecular anisotropic assemblies. In this light amphiphilic molecules, either neutral or ionic, are known to self-organise into a great variety of supramolecular structures both in solution and in the solid state.[1,2] On the other hand, since the incorporation of a transition metal ion into the polar part may impart additional features to the resulting amphiphile, metal coordination has been considered a simple way of preparing novel classes of amphiphiles. Recently, redox-active,[3,4] photo-active[3] or simply surface-active[5] amphiphilic complexes have been prepared. In addition, liquid-crystal behaviour has also been described for both thermotropic (temperature-active)[6,7] and lyotropic (concentration-active)[8] metal-containing amphiphiles.

We recently reported the synthesis of new 6′-phenyl-2,2′-bipyridines bearing promesogenic substituents in the 4′-position.[9] Our investigation showed that strongly anisometric, photoactive complexes with square-planar geometry could be obtained with these ligands,[9,10] which eventually exhibited liquid-crystalline properties.[11] In order to prepare new amphiphilic complexes, we have focused our attention on 6′-phenyl-2,2′-bipyridine ligands that bear highly hydrophobic substituents (**L-*n*** in Scheme 1) and which, at the same time, may afford species with a high aspect ratio (i.e. width-to-length ratio). Here we report on the synthesis and structural characterization of the series of Ir^{III} cationic complexes $[(ppy)_2Ir(\mathbf{L\text{-}}n)][PF_6]$ (**1**–**5**) which are based on the ligands **L-*n*** (n = 1–5) and which also contain the orthometallated $\{(ppy)_2Ir\}$ fragment (ppy = orthometallated 2-phenylpyridine). The synthesis of ligands **L-2** and **L-3** is also reported here for the first time.



	R
L-1	$OC_{12}H_{25}$
L-2	$OC_{18}H_{37}$
L-3	COOChol
L-4	$OCOC_6H_4OCOC_6H_4OC_6H_{13}$
L-5	$OCOC_6H_4OCOC_6H_4OC_{12}H_{25}$

Scheme 1

Anisometric Ligands

The functionalized **L-*n*** ligands present either alkoxy (–OR) or ester (–COOR or –OCOR) functions in the periphery of the *N*,*N*-chelating site (Scheme 1). Such an arrangement leads to the formation of ligands with a large anisometry (i.e. shape anisotropy) provided a terminal group ensures the right content of aliphatic carbon atoms.

Derivatization of the 6′-phenyl-2,2′-bipyridine moiety can be accomplished following two different synthetic strategies. The build-up of the 2,2′-bipyridine skeleton through a Kröhnke-type[12] synthesis may follow (see the preparation of **L-2**) or precede the introduction of the peripheral substituent usually through condensation reactions (as for **L-3**). The latter strategy seems to be more valuable since it potentially allows a wide variety of derivatives to be prepared.[11]

Orthometallated Iridium(III) Complexes

Bridge-splitting reactions of $[(ppy)_2IrCl]_2$ with *N*,*N*-chelating ligands are commonplace when the incorporation of the orthometallated $\{(ppy)_2Ir\}$ fragment into a mononuclear[13] or multinuclear[14] species is desired. Likewise, the cationic complexes **1**–**5** were obtained in good yield upon reaction of the dimer $[(ppy)_2IrCl]_2$ with the **L-*n*** ligands under reflux conditions in a dichloromethane/methanol mixture (Scheme 2). Metathesis of the chloride counterion with excess NH_4PF_6 gave the final products $[(ppy)_2Ir(L\text{-}n)][PF_6]$.

The ^1H NMR spectroscopic characterization of **1**–**5** showed that only a single isomer resulted from the reaction. From the NMR evidence it follows that both the pyridine

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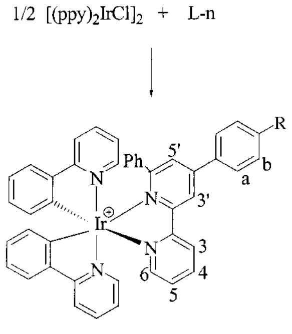

1 – 5

	R
1	$OC_{12}H_{25}$
2	$OC_{18}H_{37}$
3	COOChol
4	$OCOC_6H_4OCOC_6H_4OC_6H_{13}$
5	$OCOC_6H_4OCOC_6H_4OC_{12}H_{25}$

Scheme 2

rings of **L** are involved in the coordination and no metallation has occurred. Although no attempt was made to assign all the resonances of the spectra (e.g. the proton spectrum of **3** shows some 19 distinct signals or groups of signals in the aromatic region), it is apparent that all the complexes belong to an isostructural series, where the two metallated ppy ligands for each complex experience through-space shielding effects different from each other.

Complexes **1**–**5** are insoluble in water, but reasonably soluble in dichloromethane or chloroform (with **1** and **2** showing the best solubility) affording air-stable solutions. All complexes are also very soluble in acetonitrile and solutions of **1**–**5** in this solvent were used to measure the electronic absorption spectra. The absorption spectra of all the complexes are dominated by a broad band peaking in the UV region and extending to the visible. The maximum of this band is around 270 nm, and receives its main contribution from ligand-centred LC transitions involving the metallated phenylpyridine ligands.[15] The absorptions which appear as shoulders of the main band probably arise from spin-allowed MLCT transitions. In particular spin-allowed Ir→(**L-*n***) CT transitions probably dominate the lowest energy portion of the spectra.[13,16,17] Finally, the very weak features reaching into the visible region may correspond to formally spin-forbidden MLCT transitions. A more detailed assignment of the electronic absorption spectra of **1**–**5** is, however, beyond the scope of the present work.

Crystal Structure of 4

Despite the poor tendency to crystallize of the remaining members of the series **1**–**5**, single crystals of **4** were easily obtained at ambient temperature by slow diffusion of methanol into chloroform solutions of the complex. An X-ray analysis showed the presence in the unit cell of two crystallographically independent molecules with similar metric parameters and the same configuration at the metal (Table 1). Figure 1 shows a perspective drawing of one of the cations (cation **1**).

Table 1. Selected bond lengths [Å] and angles [°] for complex **4**

Cation **1**		Cation **2**	
Ir(1)–N(1)	2.06(1)	Ir(2)–N(5)	2.05(1)
Ir(1)–N(2)	1.98(1)	Ir(2)–N(6)	2.07(1)
Ir(1)–N(3)	2.14(1)	Ir(2)–N(7)	2.16(1)
Ir(1)–N(4)	2.21(1)	Ir(2)–N(8)	2.24(1)
Ir(1)–C(6)	2.03(1)	Ir(2)–C(70)	2.02(1)
Ir(1)–C(17)	2.00(1)	Ir(2)–C(81)	2.05(1)
N(1)–Ir(1)–N(4)	96.6(4)	N(5)–Ir(2)–N(8)	93.7(4)
N(1)–Ir(1)–C(6)	82.8(6)	N(5)–Ir(2)–C(70)	80.7(4)
N(1)–Ir(1)–N(3)	87.9(4)	N(5)–Ir(2)–N(7)	93.3(4)
N(2)–Ir(1)–N(1)	171.9(4)	N(6)–Ir(2)–N(5)	169.7(4)
N(2)–Ir(1)–N(3)	99.4(4)	N(6)–Ir(2)–N(7)	96.0(4)
N(2)–Ir(1)–N(4)	88.7(4)	N(6)–Ir(2)–N(8)	92.7(4)
N(2)–Ir(1)–C(6)	93.1(6)	N(6)–Ir(2)–C(70)	94.4(3)
N(3)–Ir(1)–N(4)	75.9(4)	N(7)–Ir(2)–N(8)	75.6(4)
C(6)–Ir(1)–N(3)	94.0(5)	C(70)–Ir(2)–N(7)	93.8(3)
C(6)–Ir(1)–N(4)	169.9(5)	C(70)–Ir(2)–N(8)	167.7(3)
C(17)–Ir(1)–N(1)	92.5(5)	C(81)–Ir(2)–N(5)	89.7(5)
C(17)–Ir(1)–N(2)	79.9(5)	C(81)–Ir(2)–N(6)	80.7(5)
C(17)–Ir(1)–N(3)	175.3(4)	C(81)–Ir(2)–N(7)	174.4(4)
C(17)–Ir(1)–N(4)	108.7(4)	C(81)–Ir(2)–N(8)	109.0(4)
C(17)–Ir(1)–C(6)	81.4(5)	C(81)–Ir(2)–C(70)	82.1(4)

Although the study revealed several causes of disorder which affected the general accuracy, the molecular and crystal features are well established. The metal centre displays a slightly distorted octahedral geometry with *trans* angles at the Ir^{III} centre spanning the range 167–176°. The C-donor atoms of the metallated ppy ligands adopt a *cis* configuration as in the parent dimer,[18] showing a remarkable *trans*-influence which is in good agreement with similar observations on related complexes[13b,17,19,20]. The pyridine rings of the **L-4** ligand are almost coplanar (dihedral angle between the two mean planes of 10°), whereas the rotationally free 6′-phenyl ring is found to be nearly orthogonal to the mean plane of the coordinated **L-4** ligand (tilt angle of 82°). The hexyloxy chain of cation **1** deviates from a fully *trans*-planar conformation with the C(59)–C(60) and C(62)–C(63) bonds in a *gauche* conformation (66 and 69°, respectively). The corresponding chain of cation **2** shows a slightly different sequence of conformations (i.e. *tttgg*).

The mutual orientation between the two molecules in the asymmetric unit is such that the central pyridine ring of the **L-4** ligand of one cation faces the 4′-phenyl ring of the second cation thus resulting in a slipped *head*-to-*tail* arrangement. The packing diagram shows a layered structure with layers stacking along the *b* axis (Figure 2). In particular, the alternating tilt of the hydrocarbon chain axes along *b* generates a herringbone motif.

Thermal Behaviour of Complexes 1–5

Since some of the free **L-*n*** ligands are thermotropic liquid crystals,[11] we tried to ascertain whether complexes **1**–**5** displayed a thermotropic phase behaviour using thermal polarizing optical microscopy and differential scanning calorimetry (DSC) techniques. Although some notable differ-

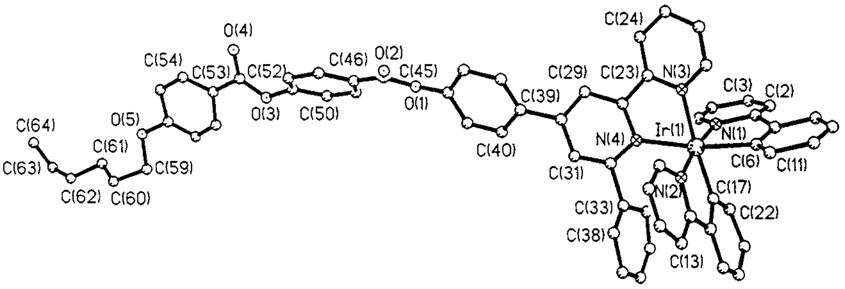

Figure 1. A perspective view and numbering scheme of cation **1** of complex **4**; all atoms are shown as arbitrarily sized circles; H atoms omitted for clarity

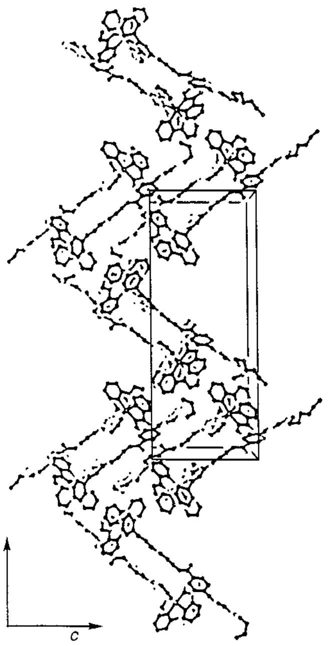

Figure 2. Packing diagram of **4** viewed down the *a* axis

ences were observed, both techniques confirmed the absence of liquid-crystalline behaviour along the whole series of complexes. Thus, while **1** and **4** clearly melt to an isotropic liquid, compounds **2** and **5** very smoothly become plastic solids on heating (above 140 and 170 °C, respectively) with fading birefringence. No clearing (or decomposition) is then observed till ca. 300°C, and cooling affords only glassy solids. The behaviour of **3** is even less clear, roughly matching that of **2**.

The above observations show that, whereas the cations $[(ppy)_2Ir(L\text{-}n)]^+$ possess a suitable polar/apolar ratio of their molecular parts which may guarantee phase separation, the bulkiness of the six-coordinate head-group in **1**–**5** somewhat reduces the structural anisotropy of the **L-*n*** ligands and no compensation for such a reduction is available from dipolar and/or dispersive interactions in the melt. In conclusion, we have prepared ionic metal-containing amphiphiles which failed to display mesogenic properties as pure species. Other properties are more predictable (e.g. photoluminescence) although unexplored. Attempts are in progress to design materials with improved properties.

Experimental Section

Materials and Methods: Ammonium acetate (Lancaster), 1-[2-oxo-2-(phenyl)ethyl]pyridinium bromide [hereafter *N*-(phenacyl)pyridinium bromide] (Lancaster), cholesterol (Lancaster), 1,3-dicyclohexylcarbodiimide (Aldrich) and 4-(pyrrolidino)pyridine (Aldrich) were used as received. The complex $[(ppy)_2IrCl]_2$ was prepared as described in the literature.[16a] The diester ligands 4′-{4-[4-(hexyloxybenzoyloxy)benzoyloxy]phenyl}-6′-phenyl-2,2′-bipyridine (**L-4**) and 4′-{4-[4-(dodecyloxybenzoyloxy)benzoyloxy]phenyl}-6′-phenyl-2,2′-bipyridine (**L-5**) were obtained according to a method recently devised in our laboratory.[11] The synthesis of 4′-(4′′-carboxyphenyl)-6′-phenyl-2,2′-bipyridine to be used as starting material in the preparation of the ligand **L-3** has been reported elsewhere.[20] All reactions and manipulations of the complexes were performed in air. – ^{1}H NMR spectra were recorded at room temperature on a 300-MHz Bruker AC300 spectrometer. Chemical shifts are reported relative to internal TMS. – IR spectra were obtained as nujol mulls or KBr pellets on a Perkin–Elmer System-2000 FT-IR spectrophotometer. – Optical observations were carried out with a Zeiss Axioskop polarizing microscope equipped with a Linkam CO 600 heating stage and a temperature control unit. – Melting temperatures were measured by differential scanning calorimetry (DSC) with a Perkin–Elmer DSC-7. – Elemental analyses of the new complexes were performed by the Microanalytical Service of our department.

4′-(4′′-Octadecyloxyphenyl)-6′-phenyl-2,2′-bipyridine (L-2): The ligand **L-2** was prepared in a way similar to that for the previously reported **L-1**.[10] A solution of *N*-(phenacyl)pyridinium bromide (0.52 g, 1.88 mmol), 1-(2-pyridyl)-3-[4-(octadecyloxy)phenyl]propen-1-one (0.90 g, 1.88 mmol), and ammonium acetate (1.45 g, 18.8 mmol) in methanol (25 mL) was heated to reflux for 8 h. A brown precipitate was obtained after cooling the reaction mixture to 0 °C. Purification of the crude solid by column chromatography on SiO_2 (CH_2Cl_2 and diethyl ether as consecutive eluents) yielded the product after workup as a pinkish-brown flaky solid in low yield (18%). M.p. 92 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.72$ (br d, 1 H), 8.69 (d, $J = 8.1$ Hz, 1 H), 8.62 (d, $J = 1.4$ Hz, 1 H), 8.20 (m, 2 H), 7.96 (d, $J = 1.4$ Hz, 1 H), 7.86 (t d, $J = 7.6$ Hz, $J = 5.0$ Hz, $J = 1.7$ Hz, 1 H), 7.79 (d, $J = 8.6$ Hz, 2 H), 7.52 (m, 3 H), 7.34 (m, 1 H), 4.03 (t, 2 H, OCH_2), 1.80 (m, 2 H, OCH_2CH_2), 1.49–1.20 [m, 30 H, $(CH_2)_{15}$], 0.88 (t, 3 H, CH_3).

4′-[(Cholesteryloxycarbonyl)phenyl]-6′-phenyl-2,2′-bipyridine (L-3): Cholesterol (0.08 g, 0.2 mmol), 4′-(4′′-carboxyphenyl)-6′-phenyl-2,2′-bipyridine (0.07 g, 0.2 mmol), 1,3-dicyclohexylcarbodiimide (0.04 g, 0.2 mmol) and 4-(pyrrolidino)pyridine (0.004 g, 0.03 mmol) were suspended in degassed CH_2Cl_2 (30 mL) and stirred under a dry nitrogen atmosphere for 24 h. A white precipitate was removed by filtration, and the colourless filtrate was consecutively washed with 5% acetic acid (20 mL) and water (2 × 20 mL). The organic phase was dried over sodium sulfate and rotary-evaporated to dryness. The desired product was obtained as a white solid after purification of the solid residue by column chromatography (SiO_2, CH_2Cl_2/3% MeOH). Yield: 31%. – IR (KBr): $\tilde{\nu}$ = 1716 cm^{-1} (CO). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.74–8.69 (m, 2 H), 8.66 (br s, 1 H), 8.23–8.17 (m, 4 H), 8.00 (br s, 1 H), 7.90–7.86 (m, 3 H), 7.57–7.45 (m, 3 H), 7.36 (m, 1 H), 5.44 (br d, 1 H, chol.), 4.92 (m, 1 H, chol.), 2.53–0.68 (m, 43 H, chol.).

General Procedure for the Synthesis of the Complexes 1–5: A stirred suspension of the appropriate ligand (0.06 mmol) and [(ppy)$_2$IrCl]$_2$ (0.03 mmol) in CH_2Cl_2/MeOH (10 ml; 6:4) was heated to reflux. Clear orange or brown solutions were observed within 10 min. After 2 h, the solution was allowed to cool to ambient temperature. Then, a saturated solution of a five-fold excess (based on the ligand) of NH_4PF_6 in MeOH was added and stirring was continued for a further 30 min. The products were isolated after partial evaporation of the solvents under reduced pressure, washed with methanol and diethyl ether, and dried in vacuo.

[(ppy)$_2$Ir(L-1)][PF$_6$] (1): Yield: 65%, brown powder. – M.p. (DSC) 187 °C. – IR (KBr): $\tilde{\nu}$ = 842 cm^{-1} (PF) cm^{-1}. – UV/Vis (acetonitrile): λ_{max} (log ε) = 271 nm (4.64), 315sh (4.52), 383sh (4.02). – ^{1}H NMR (300 MHz, CD_3CN): δ = 8.88 (d, J = 8.2 Hz, 1 H, 3-H), 8.83 (br s, 1 H, 3′-H), 8.19 (br t, 1 H, 4-H), 7.92 (d, J = 8.6 Hz, 2 H, a-H), 7.81–7.69 (m, 6 H), 7.54 (br s, 1 H, 5′-H), 7.48 (d, J = 7.5 Hz, 1 H), 7.31 (br m, 1 H, 5-H), 7.20 (d, J = 7.6 Hz, 1 H), 7.10–7.05 (m, 3 H), 6.95–6.88 (m, 2 H), 6.81–6.70 (m, 3 H), 6.59–6.54 (m, 2 H), 6.36 (br t, 1 H), 5.93 (d, J = 7.5 Hz, 1 H), 5.57 (d, J = 7.5 Hz, 1 H), 4.03 (t, 2 H, OCH_2), 1.80 (m, 2 H, $OCH_2\mathit{CH_2}$), 1.46–1.27 (m, 18 H, $(CH_2)_9$), 0.88 (t, 3 H, CH_3). – $C_{56}H_{56}F_6IrN_4OP$ (1138): calcd. C 59.09, H 4.92, N 4.92; found C 58.72, H 5.23, N 5.10.

[(ppy)$_2$Ir(L-2)][PF$_6$] (2): Yield (after chromatography on silica gel with CH_2Cl_2/5% MeOH as eluent): 24%, orange-brown powder. – IR (KBr): $\tilde{\nu}$ = 843 cm^{-1} (PF). – UV/Vis (acetonitrile): λ_{max} (log ε) = 272 nm (4.63), 314sh (4.49), 377sh (4.01). – ^{1}H NMR ($CDCl_3$): δ = 8.86 (d, J = 7.9 Hz, 1 H, 3-H), 8.81 (d, J = 2.0 Hz, 1 H, 3′-H), 8.17 (br t, 1 H, 4-H), 7.91 (d, J = 8.8 Hz, 2 H, a-H), 7.85–7.67 (m, 6 H), 7.54 (br s, 1 H, 5′-H), 7.47 (d, J = 7.0 Hz, 1 H), 7.30 (br m, 1 H, 5-H), 7.19 (d, J = 7.0 Hz, 1 H), 7.07–7.04 (m, 3 H), 6.94–6.87 (m, 2 H), 6.80–6.70 (m, 3 H), 6.58–6.53 (m, 2 H), 6.35 (br t, 1 H), 5.92 (d, J = 7.9 Hz, 1 H), 5.57 (d, J = 7.9 Hz, 1 H), 4.01 (t, 2 H, OCH_2), 1.79 (m, 2 H, $OCH_2\mathit{CH_2}$), 1.45–1.25 [m, 30 H, $(CH_2)_{15}$], 0.87 (t, 3 H, CH_3). – $C_{62}H_{68}F_6IrN_4OP$ (1222): calcd. C 60.92, H 5.61, N 4.58; found C 61.08, H 5.78, N 4.34.

[(ppy)$_2$Ir(L-3)][PF$_6$] (3): Yield: 81%, orange powder. – IR (KBr): $\tilde{\nu}$ = 1716 cm^{-1} (CO), 842 (PF). – UV/Vis (acetonitrile): λ_{max} (log ε) = 270 nm (4.44), 317sh (4.08), 386sh (3.57). – ^{1}H NMR (300 MHz, CD_3CN): δ = 8.82 (d, J = 2.0 Hz, 1 H, 3′-H), 8.74 (d, J = 7.8 Hz, 1 H, 3-H), 8.20 (d, J = 8.9 Hz, 2 H, b-H), 8.16 (t, J = 7.8 Hz, 1 H, 4-H), 8.08 (d, J = 8.9 Hz, 2 H, a-H), 7.96–7.89 (m, 4 H), 7.84 (d, J = 6.0 Hz, 2 H), 7.79 (d, J = 2.0 Hz, 1 H, 5′-H), 7.69 (d, J = 5.9 Hz, 1 H), 7.61 (d, J = 7.8 Hz, 1 H), 7.13–7.07 (m, 2 H), 6.98–6.92 (m, 2 H), 6.82 (t, J = 7.0 Hz, 1 H), 6.77 (t, J = 7.8 Hz, 2 H), 6.65 (br s, 2 H), 6.57 (t, J = 7.0 Hz, 1 H), 6.37 (d, J = 7.4 Hz, 1 H), 5.96 (d, J = 7.0 Hz, 1 H), 5.57 (d, J = 7.0 Hz, 1 H), 5.45 (d, J = 4.9 Hz, 1 H, chol.), 4.81 (m, 1 H, chol.), 2.5–0.7 (m, 43 H, chol.). – $C_{72}H_{76}F_6IrN_4O_2P$ (1366): calcd. C 63.28, H 5.61, N 4.10; found C 63.02, H 5.62, N 4.12.

[(ppy)$_2$Ir(L-4)][PF$_6$] (4): Yield: 80%, bright yellow powder. – M.p. (DSC) 288 °C. – IR (KBr): $\tilde{\nu}$ = 1740, 1733 cm^{-1} (CO), 840 (PF). – UV/Vis (acetonitrile): λ_{max} (log ε) = 270 nm (4.61), 320sh (4.14), 380sh (3.60). – ^{1}H NMR (300 MHz, CD_3CN): δ = 8.83 (br s, 1 H, 3′-H), 8.74 (d, J = 8.2 Hz, 1 H, 3-H), 8.31 (d, J = 8.5 Hz, 2 H), 8.22–8.02 (m, 5 H), 7.98–7.83 (m, 6 H), 7.80 (br s, 1 H, 5-H), 7.68 (d, J = 5.7 Hz, 1 H), 7.61 (d, J = 7.6 Hz, 1 H), 7.54–7.44 (m, 5 H), 7.31 (d, J = 7.8 Hz, 1 H), 7.17–7.06 (m, 4 H), 6.95 (m, 2 H), 6.83 (br t, 1 H), 6.77 (t, J = 7.8 Hz, 2 H), 6.66 (v br s, 2 H), 6.58 (t, J = 7.4 Hz, 1 H), 6.38 (t, J = 7.4 Hz, 1 H), 5.97 (d, J = 7.7 Hz, 1 H), 5.58 (d, J = 7.7 Hz, 1 H), 4.12 (t, 2 H, OCH_2), 1.80 (m, 2 H, $OCH_2\mathit{CH_2}$), 1.41–1.36 [m, 6 H, $(CH_2)_3$], 0.94 (t, 3 H, CH_3). – $C_{64}H_{52}F_6IrN_4O_5P$ (1294): calcd. C 59.39, H 4.05, N 4.33; found C 59.30, H 4.17, N 4.21.

[(ppy)$_2$Ir(L-5)][PF$_6$] (5): Yield: 75%, brownish orange powder. – IR (KBr): $\tilde{\nu}$ = 1736 cm^{-1} (CO), 842 (PF). – UV/Vis (acetonitrile): λ_{max} (log ε) = 270 nm (4.71), 321sh (4.27), 381sh (3.72). – ^{1}H NMR (300 MHz, CD_3CN): δ = 8.83 (br s, 1 H, 3′-H), 8.74 (d, J = 8.2 Hz, 1 H, 3-H), 8.31 (d, J = 8.5 Hz, 2 H), 8.18–8.02 (m, 5 H), 7.98–7.83 (m, 6 H), 7.80 (d, J = 1.8 Hz, 1 H, 5′-H), 7.66 (d, J = 5.8 Hz, 1 H), 7.63 (d, J = 8.0 Hz, 1 H), 7.53–7.43 (m, 5 H), 7.30 (d, J = 8.0 Hz, 1 H), 7.17–7.06 (m, 4 H), 6.95 (m, 2 H), 6.83 (t, J = 7.7 Hz, 1 H), 6.76 (t, J = 7.8 Hz, 2 H), 6.65 (v br s, 2 H), 6.57 (t, J = 7.6 Hz, 1 H), 6.37 (t, J = 7.4 Hz, 1 H), 5.96 (d, J = 7.7 Hz, 1 H), 5.58 (d, J = 7.5 Hz, 1 H), 4.07 (t, 2 H, OCH_2), 1.81 (m, 2 H, $OCH_2\mathit{CH_2}$), 1.45–1.28 [m, 18 H, $(CH_2)_9$], 0.89 (t, 3 H, CH_3). – $C_{70}H_{64}F_6IrN_4O_5P$ (1378): calcd. C 60.99, H 4.68, N 4.06; found C 60.56, H 4.57, N 4.27.

Crystal Structure Determination: Diffraction data for complex **4** were collected on a Siemens (Bruker) SMART area detector diffractometer by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) with the ω-2θ method (T = 163 K). Data were corrected for absorption (SADABS)[21] and Lorentz-polarization effects. The structure was solved by direct methods using SHELXS-97[22] and refined by full-matrix least-squares on F^2 (SHELXL-97).[22] Crystal data and structure refinements parameters are given in Table 2. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions with fixed contri-

Table 2. Crystal data, data collection parameters, solution and refinement for complex **4**

Empirical formula	$C_{64}H_{52}F_6IrN_4O_5P$
Formula weight	1294
Crystal system	monoclinic
Space group	$P2_1/c$
a [Å]	22.037(11)
b [Å]	34.821(22)
c [Å]	13.987(6)
α [°]	90
β [°]	90.38(4)
γ [°]	90
V [Å^3]	10733(10)
Z	8
$d_{calcd.}$ [g cm^{-3}]	1.602
Crystal size [mm]	0.19 × 0.15 × 0.08
μ [mm^{-1}]	2.596
Transmission (min/max)	0.701/0.928
2θ range [°]	3.0–50
Index range (h, k, l)	–26 26, –41 41, –16 16
Reflections collected	93561
Independent reflections	18890
Observed reflections [$I > 2\sigma(I)$]	11149
Parameters	1368
Final R indices	$R1 = 0.0903$, $wR2 = 0.1631$
R indices (all data)	$R1 = 0.1569$, $wR2 = 0.1760$
Goodness-of-fit on F^2	1.562

butions (U = 0.08 Å^2). The two sets of C atoms [C(33) through C(38)] and [C(97) through C(102)] have been refined as rigid regular hexagons with default C–C bond lengths of 1.39 Å.

Crystallographic data (excluding structure factors) for the structure included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-112438. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

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