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Ferroelectric liquid crystal behavior in platinum orthometallated complexes

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Di-μ-chloro-bis[(η^3-2-methylallyl)platinum] reacts with chiral imines, p-$R^1C_6H_4CH{=}NC_6H_4OR^2$-p [HL*; with R^1, R^2, or both equal to either (*R*)- or (*S*)-1-methylheptyl], to yield the C,N-cyclometallated platinum(II) compounds [$Pt_2(\mu\text{-}Cl)_2(L^*)_2$] (**2**). Treatment of **2** with Tl[(p-$H_{21}C_{10}OC_6H_4CO)_2CH$] produces mononuclear orthoplatinated complexes (**3**) incorporating a β-diketonate. Both complexes **2** and **3** are mesomorphic materials that display smectic A (SmA) and chiral smectic C (SmC*) phases. Their mesogenic properties are compared with those of their palladium analogues, reported previously. The platinum complexes show somewhat more stable mesophases. A study of the ferroelectric properties of compounds **2** and **3** has been performed.

Introduction

During the last decade, many metal-containing liquid crystals (metallomesogens) have been reported and a number of reviews of the field have appeared.[1] Since the high transition temperatures often encountered in metallomesogens usually produce thermal decomposition, which hinders the study of the physical properties of the mesophases, not many metallomesogens where the potential ferroelectric behavior has actually been measured have been reported.[2–10] Using palladium derivatives based on orthometallated complexes, our group reported the first examples of ferroelectric metallomesogens,[2] and the improvement of their properties.[4,5] Moreover, we demonstrated the appearance of promising second-order nonlinear optical properties in the liquid crystalline state for some of these compounds.[11] In order to study the effect of the metal core on the mesogens and on the ferroelectric properties of the compounds, we have prepared monomeric and dimeric calamitic orthoplatinated complexes displaying a chiral smectic C phase (SmC*). Comparing their properties with those of their Pd analogues, we find that the nature of the metal has a significant influence. The second harmonic generation (SHG) behavior of three of these platinum-containing complexes was advanced in a previous work. Their efficiencies are rather good considering that none of the materials was specifically designed for NLO applications.[12]

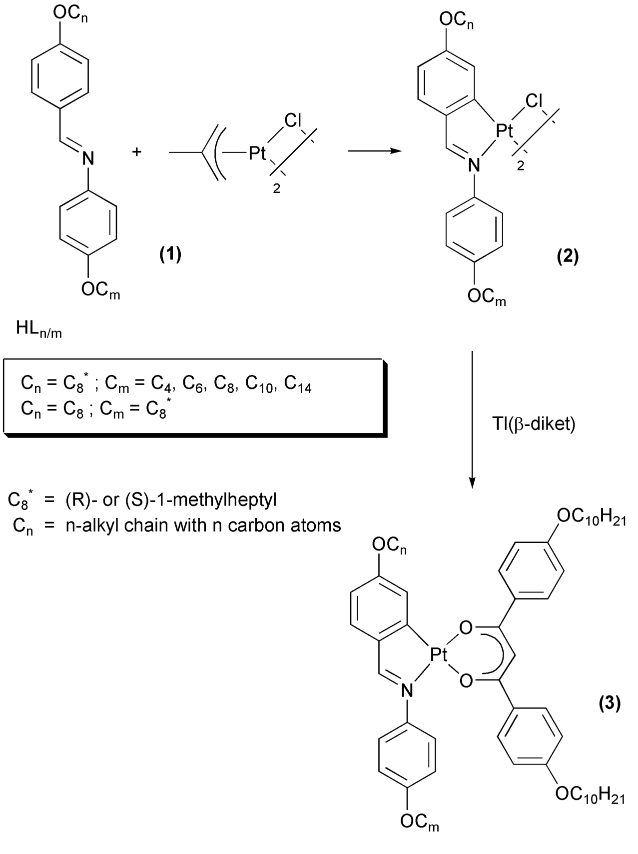
Results and discussion

Synthesis

The chiral imines with one or two chiral centers shown in Scheme 1 ($HL^*_{n/m}$ (**1**); n = number of carbons of the aldehydic chain; m = number of carbons of the anilinic chain) were obtained following literature methods.[4] The chloro-bridged complexes **2** were prepared by reaction of the corresponding imine $HL^*_{n/m}$ with [$Pt_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_4H_7)_2$] in a 2 : 1 molar ratio, in refluxing methanol for 24 h. The ^{1}H NMR spectra of the dimers **2** show that the products are inseparable mixtures of the *trans* and *cis* isomers (*ca.* 4 : 1). A similar mixture was found for the platinum compounds with achiral chains.[13] This is not the case for their palladium analogues, where only the *trans* isomers are obtained.[4] Treatment of the dimers **2** with thallium β-diketonates produces the mononuclear species [Pt(β-diket)$L^*_{n/m}$] (**3**).

Mesogenic properties

The thermal data for the chloro-bridged platinum complexes **2** and the β-diketonate complexes **3** are given in Table 1 and in Fig. 1.



Scheme 1

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Table 1 Optical, thermal, and thermodynamic data for the compounds $[Pt(\mu\text{-}Cl)L^*_{n/m}]_2$ (**2**) and $[Pt(\beta\text{-}diket)L^*_{n/m}]$ (**3**)[a]

Compound	$L^*_{n/m}$	Transition[b]	Temp./ °C	ΔH/ kJ mol^{-1}
2	(*S*) C8*/C4	C → I[c]	156.8	59.7
	(*R*) C8*/C6	C → SmC*	116.2	16.5
		SmC* → SmA	140.8	0.2
		SmA → I[c]	246[d]	
	(*R*) C8*/C8	C → SmC*	122.3	16.2
		SmC* → SmA	161.1	0.2
		SmA → I[c]	238.6	9.0
	(*S*) C8*/C10	C → SmC*	113.7	14.1
		SmC* → SmA	150.5	0.2
		SmA → I[c]	226.7	10.2
	(*R*) C8*/C14	C → SmA	156.9	75.9
		SmA → I[c]	210.0	9.6
	(*R*) C8/C8*	C → SmC*	114.1	4.5
		SmC* → SmA	166.7	0.2
		SmA → I[c]	238.5	12.0
	(*S*,*S*) C8*/C8*	C → SmA	120.5	24.3
		SmA → I[c]	146.3	5.0
		I → SmA	144.0	−4.9
		SmA → SmC*[e]	83.0	−0.34
3	(*R*) C8*/C6	C → SmA	98.1	14.0
		SmA → I	130.4	4.9
	(*R*) C8*/C8	C → SmC*	102.9	16.8
		SmC* → SmA	110.3	0.1
		SmA → I	127.5	4.9
	(*S*) C8*/C10	C → SmC*	100.8	14.6
		SmC* → SmA	110.3	0.2
		SmA → I	124.9	5.0
	(*R*) C8*/C14	C → SmC*	100.0	13.6
		SmC* → SmA	109.6	0.2
		SmA → I	125.1	5.4
	(*R*) C8/C8*	C → I	120.2	32.5
		I → SmC*[e]	116.4	−5.7
		SmC* → C	84.7	−16.0
	(*S*,*S*) C8*/C8*	SmC* → SmA[f]	62.2	0.1
		SmA → I	68.2	3.7

[a] DSC data obtained on 1st scan for **2** and on 2nd scan for **3**. [b] C: crystal; I: isotropic; SmA: smectic A; SmC*: chiral smectic C. [c] Transition with decomposition. [d] Observed by polarized light microscopy only. [e] Monotropic transition. [f] SmC* freezes to a glassy state on cooling.

The non-mesogenic chiral imines give rise to mesogenic orthometallated complexes. Thus, this is a new example of mesomorphic behavior induced by the introduction of a metal into a non-mesogenic organic substrate. The chiral chain used in the compounds reported here was either the (*R*)- or the (*S*)-1-methylheptoxy group. Since the transition temperatures must be identical for enantiomeric compounds,[4] the results within the series can be compared regardless of the absolute molecular configuration used.

In general, complexes **2** show wide ranges of SmC* mesophase (*ca.* 100 °C) and high transition temperatures, as is usual in this type of chloro-bridged orthometallated complex.[4,13–18] Some decomposition of the complexes was observed at the clearing point. For this reason, the data in Table 1 for the complexes **2** correspond to the first heating. Exceptions to this general mesogenic behavior of the complexes $[Pt(\mu\text{-}Cl)L^*_{n/m}]_2$ are the derivatives $[Pt(\mu\text{-}Cl)L_{8^*/4}]_2$, which is not liquid crystal, and $[Pt(\mu\text{-}Cl)L_{8^*/14}]_2$, which only shows an SmA mesophase. The position of the chiral chain, whether in the anilinic ring or in the aldehydic ring, influences the thermal properties. Comparing $[Pt(\mu\text{-}Cl)L_{8/8^*}]_2$ with $[Pt(\mu\text{-}Cl)L_{8/8^*}]_2$, the compound with the chiral chain in the anilinic ring (which can rotate quite freely) shows a somewhat larger range of SmC* mesophase.

The introduction of a second chiral carbon in the imine produces molecules with four chiral carbons and their steric hindrance disturbs seriously the possibility of efficient inter- and intramolecular packing of the chains. This leads to a clear reduction in the range of mesogenic properties, and the SmC* mesophase of $[Pt(\mu\text{-}Cl)L_{8^*/8^*}]_2$ is only monotropic.

The mononuclear derivatives $[Pt(\beta\text{-}diket)L^*_{n/m}]$ (**3**) have clearing points about 100 °C lower than their parent complexes **2**, as expected form our previous observations in palladium or platinum when the asymmetry in molecular shape is increased.[3] Enantiotropic SmC* mesophases are observed when the chiral center is in the aldehydic chain, except for the complex with the shortest anilinic chain $[Pt(\beta\text{-}diket)L^*_{8^*/6}]$, or when the chiral center is in the anilinic chain, when the SmC* observed is only monotropic. The compound with two chiral chains $[Pt(\beta\text{-}diket)L_{8^*/8^*}]$ shows only the transition to isotropic liquid on heating, but in the cooling process, SmC* and SmA mesophases can be observed. The order of the latter is retained in the mesophase to give a glassy solid (*ca.* 30 °C). In the second heating (data in Table 1), the chiral smectic C and smectic A phases are recovered. After this second heating, the SmC* mesophase appears both in the heating and in the cooling process, near to room temperature.

Smectic A and smectic C phases were assigned based on the their optical textures.[19] The chiral smectic C phases showed a blurred *schlieren* texture, which gave rise to mielenic textures in the smectic A phase. On cooling from the isotropic liquid, the smectic A phase appears, *via bâtonnets*, as focal-conic and homeotropic textures. At the SmA → SmC* transition, broken focal-conic textures with grayish pseudo-homeotropic zones were observed.

Comparison of the thermal parameters of the platinum

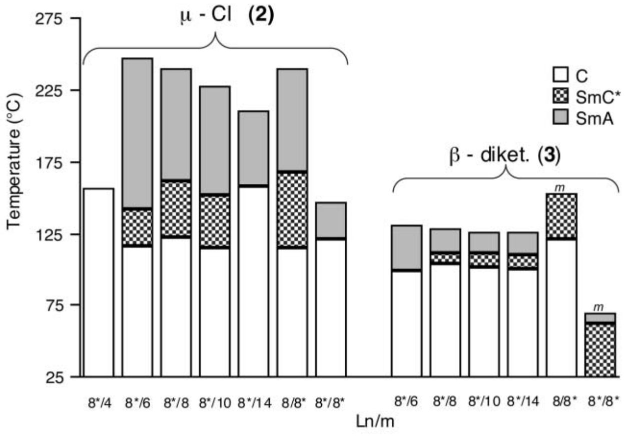

Fig. 1 Thermotropic behavior of $[Pt(\mu\text{-}Cl)L^*_{n/m}]_2$ (**2**) and $[Pt(\beta\text{-}diket)L^*_{n/m}]$ (**3**). C, crystal; SmC*, chiral smectic C; SmA, smectic A; *m*, monotropic transition. The numbers on the abscissa indicate the imine type, as defined in Scheme 1.

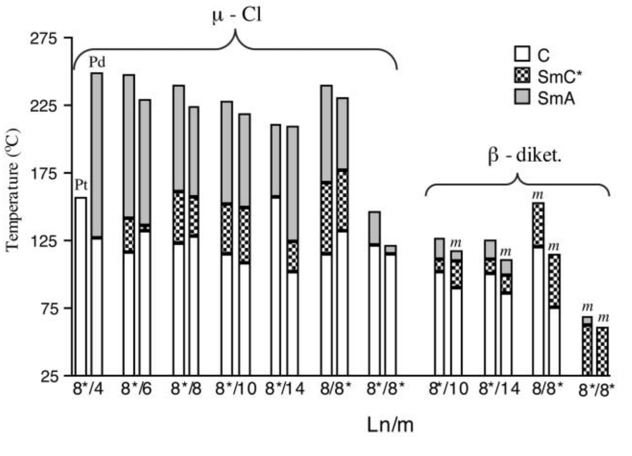

Fig. 2 Thermotropic behavior of Pt and Pd materials. On each pair, the left bar is the Pt compound. C, crystal; SmC*, chiral smectic C; SmA, smectic A; *m*, monotropic transition. The numbers on the abscissa indicate the imine type, as defined in Scheme 1.

complexes **2** with those of their palladium analogs[4,5] (Fig. 2) shows that the differences are moderate, in spite of fact that the Pt complexes are *cis*/*trans* mixtures. For compounds with chains of medium length ($L_{8*/6}$, $L_{8*/8}$, $L_{8/8*}$, and $L_{8*/8*}$), where the ranges of mesophase are larger, the Pt compounds seem to exhibit somewhat larger ranges. The differences cannot be attributed exclusively to the change of metal, since the Pt complexes are a mixture of *trans* and *cis* isomers, whereas the Pd complexes are pure *trans*. The thermal data for the chiral platinum complexes of β-diketonates **3** show that some compounds displaying only monotropic transitions in Pd give enantiotropic transitions with Pt. Thus, Pt gives rise to a moderate but noticeable stabilization of the mesophases compared to Pd. In this case, the different behavior has to be attributed to the change of metal.

Ferroelectric properties

The ferroelectric properties of the complexes showing an SmC* phase are listed in Table 2. P_s(max) and P_s at 10° below the entrance of the SmC* mesophase were determined for all the ferroelectric materials. Measurements of the tilt angle and the sign of P_s were only possible for the mononuclear compounds.

To avoid thermal decomposition, the ferroelectric switching of the Cl derivatives **2** was studied in gold–brass electrodes filled at the SmA phase. However, glass cells filled by capillarity at the isotropic phase were used with the β-diketonates. The majority of these materials exhibit response times in the range of 2 ms and rotational viscosities of 0.5 Pa s, similar to the values reported for other metallomesogens.[3–8] These values dramatically increase for the complexes with two stereogenic centers in the chiral ligand.

Fig. 3 and 4 plot the dependence of P_s *versus* temperature for the platinum chloro-bridged complexes **2** and the platinum β-diketonates **3**, respectively, showing a gradual increase in the P_s values of all the compounds when the temperature decreases.

From the point of view of the structure–ferroelectric properties relationship, several aspects are worth noting. The terminal chain length modulates the P_s value, which reaches a maximum for the hexyloxy derivatives for the chloro-bridged compounds, and for longer chains in the β-diketonate derivatives ($n = 8$ and 10).

Not unexpectedly, the spontaneous polarization increases the greater the number of stereogenic centers, but this is at the expense of a shortening of the mesophase range. No general trends concerning the influence of the metal atom on the ferroelectric behavior can be identified.

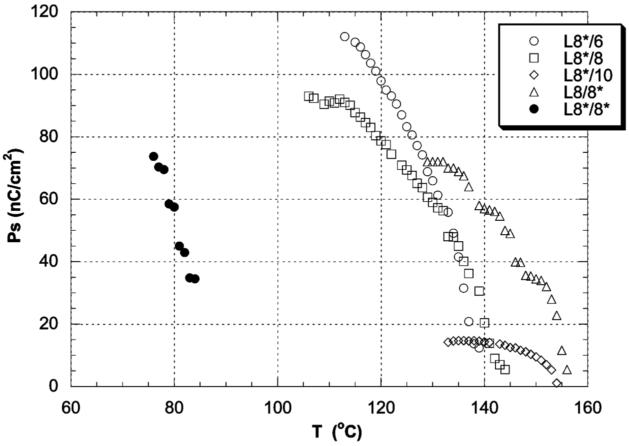

Fig. 3 Temperature dependence of the spontaneous polarization (P_s) of complexes $[Pt(\mu\text{-}Cl)L^*_{n/m}]_2$ (**2**).

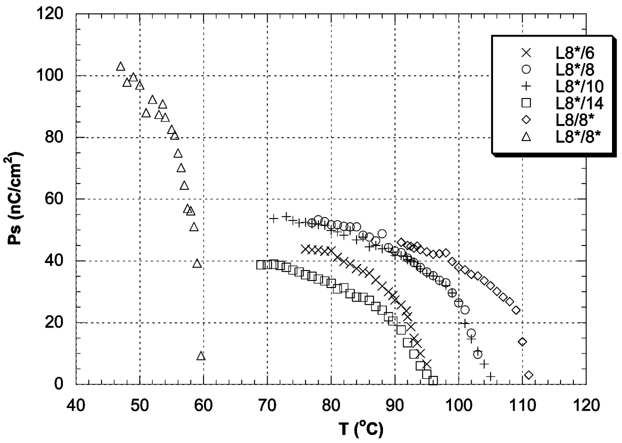

Fig. 4 Temperature dependence of the spontaneous polarization (P_s) of complexes $[Pt(\beta\text{-diket})L^*_{n/m}]$ (**3**).

Experimental

Literature methods were used to prepare di-μ-chloro-bis[(η^3-2-methylallyl)platinum],[20] 1,3-bis(4′-decyloxyphenyl)-1,3-propanedionatothallium(I)[21], and the chiral imines.[4] C, H, N analyses were carried out on a Perkin-Elmer 2400 microanalyzer. All the

Table 2 Ferroelectric properties of $[Pt(\mu\text{-}Cl)L^*_{n/m}]_2$ (**2**) and $[Pt(\beta\text{-diket})L^*_{n/m}]$ (**3**)

Compound	$L^*_{n/m}$	M	P_s(max)/nC cm^{-2}	$P_s{}^a$(−10 °C)/nC cm^{-2}	θ(−10 °C)/°
2	(*R*) C8*/C6	Pt	112	69	—
		Pd	+48	+35	
	(*R*) C8*/C8	Pt	72	49	—
		Pd	+105	+54	
	(*S*) C8*/C10	Pt	92	48	—
		Pd	−69	−41	
	(*R*) C8/C8*	Pt	14	13	—
		Pd	+47	+32	
	(*S*,*S*) C8*/C8*	Pt	73	—	—
	(*R*,*R*) C8*/C8*	Pd	+206	+141	
3	(*R*) C8*/C6	Pt	+44	+37	20
	(*R*) C8*/C8	Pt	+53	+38	22
	(*S*) C8*/C10	Pt	−55	−37	29
		Pd	−29	−14	21
	(*R*) C8*/C14	Pt	+39	+28	24
	(*S*) C8*/C14	Pd	−22	−18	22
	(*R*) C8/C8*	Pt	+46	+37	33
	(*S*,*S*) C8*/C8*	Pt	−100	−98	30
	(*R*,*R*) C8*/C8*	Pd	30	30[b]	

[a] Data measured at $T_c - T = 10$ °C (T_c: SmA → SmC* transition temperature determined by DSC). [b] This property was measured at $T_c - 7$ °C.

new compounds gave satisfactory elemental analyses. IR spectra were recorded on a Perkin-Elmer FT-1720X spectrometer using Nujol mulls between polyethylene plates. ^{1}H NMR spectra were recorded on Bruker AC-300 or ARX-300 MHz spectrophotometers. The textures of the mesophases were studied with a Leitz microscope equipped with a Mettler FP82HT hot stage and a Mettler FP90 central processor and polarizers at a heating rate of approximately 10 °C min^{-1}. Transition temperatures and enthalpies were measured by differential scanning calorimetry, with a Perkin-Elmer DSC-7 operated at a scanning rate of 10 °C min^{-1} on heating. The apparatus was calibrated with indium (156.6 °C, 28.5 J g^{-1}) as standard, the samples were sealed in aluminium capsules in air and the holder atmosphere was dry nitrogen.

The spontaneous polarization and the response times were obtained simultaneously using the triangular waveform method,[22] using a field of 900 V (peak to peak) and 20 Hz for the chloro-bridged complexes (in the case of the compound with 4 chiral tails, a frequency of 2 Hz was needed) and 30–60 Vpp and 10–20 Hz for the β-diketonates. The cells used for measurements of the chloro-bridged materials were made of two gold–brass electrodes of 12 μm diameter and 100 μm thickness. The P_s signs and tilt angles were determined by the field reversal method through optical observations of the extinction direction by rotating the stage according to Lagerwall's convention.[23] For these measurements and the P_s determinations of the β-diketonates, 10 μm commercial cells with indium tin oxide (ITO) electrodes coated with polyimides were used.

Synthesis of the complexes

$[Pt_2(\mu\text{-}Cl)_2(L^*)_2]$ (2). To a suspension of di-μ-chloro-bis[(η^3-2-methylallyl)platinum] (0.53 g, 0.928 mmol) in dry MeOH (35 mL) under nitrogen, was added the imine **1** (1.90 mmol) and the mixture was refluxed for 24 h. After cooling, the dark green precipitate was collected on a frit, washed with MeOH (2 × 5 mL), dissolved in dichloromethane, and filtered through silica to remove the platinum metal. The resulting orange solution was concentrated, and addition of methanol gave an orange precipitate, which was filtered off and vacuum dried. Yields: 50–61%. IR (Nujol, cm^{-1}): $\nu_{(C=N)}$ 1607; $\nu_{(COC)}$ 1251.

$[Pt_2(\mu\text{-}Cl)_2(L_{8^*/4})_2]$. Anal. calcd for $C_{50}H_{68}Cl_2N_2O_4Pt_2$: C, 49.14; H, 5.61; N, 2.29; found: C, 48.90 H, 5.46; N, 2.20%. ^{1}H NMR (300 MHz, CDCl$_3$): *trans* isomer 0.80–0.90 (m, 6H), 1.00 (t, 6H), 1.20–1.80 (m, 28H), 3.98 (t, J = 6.5, 4H), 4.38 (m, 2H), 6.53 (dd, J = 8.3, 2.3, 2H), 6.71 (d, J = 2.3, 2H), 6.89, 7.31 (AA′BB′ system, J = 8.9, 8H), 7.21 (d, J = 8.3, 2H), 7.90 (s, 2H); *cis* isomer: 0.97 (t, 6H), 3.93 (t, J = 6.5 Hz, 4H), 4.50 (m, 2H), 7.84 (s, 2H).

$[Pt_2(\mu\text{-}Cl)_2(L_{8^*/6})_2]$. Anal. calcd for $C_{54}H_{76}Cl_2N_2O_4Pt_2$: C, 51.49; H, 6.17; N, 2.14; found: C, 51.69 H, 5.91; N, 2.17%. ^{1}H NMR (300 MHz, CDCl$_3$): *trans* isomer 0.80–1.00 (m, 12H), 1.20–1.90 (m, 42H), 3.98 (t, J = 6.5, 4H), 4.38 (m, 2H), 6.53 (dd, J = 8.3, 2.3, 2H), 6.71 (d, J = 2.2, 2H), 6.89, 7.31 (AA′BB′ system, J = 8.9, 8H), 7.21 (d, J = 8.3, 2H), 7.90 (s, 2H); *cis* isomer: 3.93 (t, J = 6.5 Hz, 4H), 4.50 (m, 2H), 7.88 (s, 2H).

$[Pt_2(\mu\text{-}Cl)_2(L_{8^*/8})_2]$. Anal. calcd for $C_{58}H_{84}Cl_2N_2O_4Pt_2$: C, 52.21; H, 6.34; N, 2.10; found: C, 52.06 H, 6.12; N, 2.30%. ^{1}H NMR (300 MHz, CDCl$_3$): *trans* isomer 0.80–1.00 (m, 12H), 1.20–1.90 (m, 50H), 3.98 (t, J = 6.5, 4H), 4.38 (m, 2H), 6.54 (dd, J = 8.3, 2.2, 2H), 6.71 (d, J = 2.2, 2H), 6.89, 7.31 (AA′BB′ system, J = 8.9, 8H), 7.22 (d, J = 8.4, 2H), 7.90 (s, 2H); *cis* isomer: 3.93 (t, J = 6.5 Hz, 4H), 4.50 (m, 2H), 7.88 (s, 2H).

$[Pt_2(\mu\text{-}Cl)_2(L_{8^*/10})_2]$. Anal. calcd for $C_{62}H_{92}Cl_2N_2O_4Pt_2$: C, 53.55; H, 6.67; N, 2.02; found: C, 53.71 H, 6.61; N, 2.03%. ^{1}H NMR (300 MHz, CDCl$_3$): *trans* isomer 0.80–1.00 (m, 12H), 1.20–1.90 (m, 56H), 3.98 (t, J = 6.5, 4H), 4.38 (m, 2H), 6.54 (dd, J = 8.3, 2.2, 2H), 6.71 (d, J = 2.2, 2H), 6.89, 7.31 (AA′BB′ system, J = 8.9, 8H), 7.22 (d, J = 8.4, 2H), 7.90 (s, 2H); *cis* isomer: 3.93 (t, J = 6.5 Hz, 4H), 4.50 (m, 2H), 7.88 (s, 2H).

$[Pt_2(\mu\text{-}Cl)_2(L_{8^*/14})_2]$. Anal. calcd for $C_{70}H_{108}Cl_2N_2O_4Pt_2$: C, 55.95; H, 7.24; N, 1.86; found: C, 55.52 H, 6.84; N, 1.95%. ^{1}H NMR (300 MHz, CDCl$_3$): *trans* isomer 0.80–1.00 (m, 12H), 1.20–1.90 (m, 66H), 3.97 (t, J = 6.5, 4H), 4.36 (m, 2H), 6.53 (dd, J = 8.5, 2.3, 2H), 6.71 (d, J = 2.2, 2H), 6.88, 7.30 (AA′BB′ system, J = 8.9, 8H), 7.21 (d, J = 8.5, 2H), 7.89 (s, 2H); *cis* isomer: 3.93 (t, J = 6.5 Hz, 4H), 4.50 (m, 2H), 7.86 (s, 2H).

$[Pt_2(\mu\text{-}Cl)_2(L_{8/8^*})_2]$. Anal. calcd for $C_{58}H_{84}Cl_2N_2O_4Pt_2$: C, 52.21; H, 6.34; N, 2.10; found: C, 52.22 H, 6.07; N, 2.09%. ^{1}H NMR (300 MHz, CDCl$_3$): *trans* isomer 0.80–1.00 (m, 12H), 1.20–1.90 (m, 50H), 3.95 (t, J = 6.5, 4H), 4.37 (m, 2H), 6.55 (dd, J = 8.3, 2.3, 2H), 6.72 (d, J = 2.3, 2H), 6.87, 7.29 (AA′BB′ system, J = 8.9, 8H), 7.22 (d, J = 8.3, 2H), 7.91 (s, 2H); *cis* isomer: 4.05 (t, J = 6.5 Hz, 4H), 4.29 (m, 2H), 7.88 (s, 2H).

$[Pt_2(\mu\text{-}Cl)_2(L_{8^*/8^*})_2]$. Anal. calcd for $C_{58}H_{84}Cl_2N_2O_4Pt_2$: C, 52.21; H, 6.34; N, 2.10; found: C, 52.50 H, 6.14; N, 2.06%. ^{1}H NMR (300 MHz, CDCl$_3$): *trans* isomer 0.80–1.00 (m, 12H), 1.20–1.90 (m, 52H), 4.37 (q, J = 6.0, 2H), 4.38 (m, 2H), 6.52 (dd, J = 8.3, 2.3, 2H), 6.72 (d, J = 2.3, 2H), 6.88, 7.30 (AA′BB′ system, J = 8.9, 8H), 7.21 (d, J = 8.3, 2H), 7.89 (s, 2H); *cis* isomer: 4.30 (q, J = 6.0 Hz, 2H), 4.50 (m, 2H), 7.87 (s, 2H).

$[Pt(\beta\text{-diket})L^*]$ (3). To a stirred solution of $[Pt_2(\mu\text{-}Cl)_2(L^*)_2]$ (0.072 mmol) in 5 mL of dichloromethane and 20 mL of acetone was added the corresponding thallium diketonate (0.122 g, 0.165 mmol). After 4 h stirring, the white precipitate of TlCl was filtered off and the solution was evaporated to dryness. The crude product was purified by column chromatography (silica gel, dichloromethane–hexane 1 : 1). Evaporation of the solvent afforded an orange solid, which was filtered off and washed with 2 × 5 mL of methanol. Yields: 50–65%. IR (Nujol, cm^{-1}): $\nu_{(C=N)}$ 1603; $\nu_{(COC)}$ 1251.

$[Pt(\beta\text{-diket})L_{(8^*/6)}]$. Anal. calcd for $C_{62}H_{89}NO_6Pt$: C, 65.35; H, 7.87; N, 1.23; found: C, 65.23 H, 7.64; N, 1.47%. ^{1}H NMR (300 MHz, CDCl$_3$): 0.80–1.00 (m, 12H), 1.20–1.75 (m, 45H), 1.79 (m, 8H), 3.95–4.07 (m, 6H), 4.62 (m, 1H), 6.61 (dd, J = 8.3, 2.3, 2H), 6.67 (s, 1H) 7.32 (d, J = 2.3, 1H), 7.37 (d, J = 8.3, 1H), 6.80, 7.72 (AA′BB′ system, J = 8.9, 4H), 6.92, 8.02 (AA′BB′ system, J = 8.9, 4H), 6.97, 7.45 (AA′BB′ system, J = 8.9 Hz, 2H), 8.18 (s, 4H).

$[Pt(\beta\text{-diket})L_{(8^*/8)}]$. Anal. calcd for $C_{64}H_{93}NO_6Pt$: C, 65.84; H, 8.03; N, 1.20; found: C, 65.70 H, 7.74; N, 1.49%. ^{1}H NMR (300 MHz, CDCl$_3$): 0.80–1.00 (m, 12H), 1.20–1.70 (m, 49H), 1.79 (m, 8H), 3.96–4.07 (m, 6H), 4.62 (m, 1H), 6.61 (dd, J = 8.3, 2.3, 2H), 6.67 (s, 1H) 7.32 (d, J = 2.3, 1H), 7.36 (d, J = 8.3, 1H), 6.80, 7.72 (AA′BB′ system, J = 8.8, 4H), 6.92, 8.02 (AA′BB′ system, J = 8.8, 4H), 6.96, 7.46 (AA′BB′ system, J = 8.9 Hz, 2H), 8.18 (s, 4H).

$[Pt(\beta\text{-diket})L_{(8^*/10)}]$. Anal. calcd for $C_{66}H_{97}NO_6Pt$: C, 66.30; H, 8.17; N, 1.17; found: C, 66.23 H, 8.01; N, 0.95%. ^{1}H NMR (300 MHz, CDCl$_3$): 0.80–1.00 (m, 12H), 1.20–1.70 (m, 53H), 1.79 (m, 8H), 3.96–4.07 (m, 6H), 4.61 (m, 1H), 6.61 (dd, J = 8.3, 2.3, 2H), 6.67 (s, 1H) 7.32 (d, J = 2.3, 1H), 7.37 (d, J = 8.3, 1H), 6.80, 7.72 (AA′BB′ system, J = 8.8, 4H), 6.92, 8.02 (AA′BB′ system, J = 8.9, 4H), 6.96, 7.46 (AA′BB′ system, J = 8.8 Hz, 2H), 8.18 (s, 4H).

$[Pt(\beta\text{-diket})L_{(8^*/14)}]$. Anal. calcd for $C_{70}H_{105}NO_6Pt$: C, 67.17; H, 8.45; N, 1.12; found: C, 66.89 H, 8.29; N, 1.04%. ^{1}H

NMR (300 MHz, CDCl$_3$): 0.80–1.00 (m, 12H), 1.20–1.70 (m, 61H), 1.79 (m, 8H), 3.95–4.04 (m, 6H), 4.62 (m, 1H), 6.61 (dd, J = 8.3, 2.3, 2H), 6.67 (s, 1H) 7.32 (d, J = 2.3, 1H), 7.36 (d, J = 8.3, 1H), 6.80, 7.72 (AA′BB′ system, J = 8.8, 4H), 6.92, 8.02 (AA′BB′ system, J = 8.8, 4H), 6.96, 7.46 (AA′BB′ system, J = 8.8 Hz, 2H), 8.18 (s, 4H).

[Pt(β-diket)L$_{(8/8*)}$*].* Anal. calcd for $C_{64}H_{93}NO_6Pt$: C, 65.84; H, 8.03; N, 1.20; found: C, 65.78 H, 7.66; N, 1.38%. ^{1}H NMR (300 MHz, CDCl$_3$): 0.80–1.00 (m, 12H), 1.20–1.70 (m, 42H), 1.79 (m, 6H), 3.97 (t, J = 6.6, 2H), 4.02 (t, J = 6.5, 2H), 4.15 (t, J = 6.7, 2H), 4.41 (m, 1H), 6.64 (dd, J = 8.3, 2.4, 2H), 6.68 (s, 1H) 7.33 (d, J = 2.4, 1H), 7.37 (d, J = 8.3, 1H), 6.80, 7.72 (AA′BB′ system, J = 8.9, 4H), 6.93, 8.03 (AA′BB′ system, J = 8.9, 4H), 6.95, 7.45 (AA′BB′ system, J = 8.9 Hz, 2H), 8.19 (s, 4H).

[Pt(β-diket)L$_{(8*/8*)}$*].* Anal. calcd for $C_{64}H_{93}NO_6Pt$: C, 65.84; H, 8.03; N, 1.20; found: C, 65.68 H, 7.85; N, 1.07%. ^{1}H NMR (300 MHz, CDCl$_3$): 0.80–1.00 (m, 12H), 1.20–1.70 (m, 42H), 1.79 (m, 6H), 3.96 (t, J = 6.6, H), 4.02 (t, J = 6.5, H), 4.41 (m, 1H), 4.61 (m, 1H), 6.61 (dd, J = 8.3, 2.3, 2H), 6.67 (s, 1H) 7.32 (d, J = 2.3, 1H), 7.37 (d, J = 8.3, 1H), 6.86, 7.72 (AA′BB′ system, J = 8.9, 4H), 6.93, 8.03 (AA′BB′ system, J = 8.9, 4H), 6.95, 7.45 (AA′BB′ system, J = 8.9 Hz, 2H), 8.18 (s, 4H).

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