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New liquid crystalline materials based on *ortho*-metallated palladium(II) and platinum(II) complexes with S,O –donor CO - ligands

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In this paper we present the preparation and the mesogenic behaviour of a series of *ortho*-metallated palladium complexes with two different imine ligands carrying two or three alkoxy chains and having *N*-benzoyl thiourea derivatives as co-ligands. By choosing the appropriate imine ligand and *N*-benzoyl thiourea derivative, room temperature nematic or smectic phases can be induced in *ortho*-metallated Pt(II) and Pd(II) complexes, mesophases which are stable for hours at this temperature. First liquid crystals based on platinum complexes containing the *N*-benzoyl thiourea moiety are reported here and their mesogenic properties are compared with those of palladium analogues.

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1. Introduction

Liquid crystals containing metal ions (metallomesogens) are intensively studied due to their interesting properties which are influenced by the presence of the metal ion, such as: colour, polarizability, electrical and magnetic properties [1]. One of the most interesting and broadly studied family of metallomesogens is represented by the *ortho*-metallated platinum(II) and palladium(II) organometallic compounds with nitrogen-containing heteroaromatic ligands which form thermally stable complexes that consist of both dinuclear and mononuclear organometallic systems [2]. Amongst the heteroaromatic ligands studied, the imine ligands have been extensively used in orthometallation reactions and have shown a strong tendency to form, with palladium and platinum precursors, cyclometallated five-membered rings containing palladium(II) and platinum(II) ions in a square-planar environment [3]. These ligands were used in the preparation of di- and mononuclear species with liquid crystal properties, in particular due to the different possibilities for tuning the mesogenic properties of such compounds, as well as other physico-chemical properties [4]. A liquid crystalline material based on metallomesogens with potential application in liquid crystal displays technology should have several important features: lower transition temperatures, high thermal stability, broad mesomorphic range and good miscibility with other ingredients for its use in mixtures. A good strategy for reducing the transition temperatures and keeping a broad mesomorphic range in such systems containing the *ortho*-metallated imine fragment is to introduce various co-ligands, which lead, in most of the cases, but not always, to mononuclear compounds with more accessible and stable mesophases compare with the dinuclear parent complexes. Amongst the various co-ligands used to prepare mononuclear species with improved mesogenic properties are: β-diketones, [5] β-aminoenonates [5a, 6], α-aminoacids [7], cyclopentadienyl [8] or dialkyldithiocarbamates [9]. For example, it is well known that dimeric compounds $[(C\text{-}N)PdCl]_2$ (C-N = *ortho*-palladated imine with two long alkyl chains) form smectic A and C phases at high temperatures, while the monomeric complexes with β-diketonate ligands [(C-N)Pd(acac)] form nematic and smectic A phases at significantly lower temperatures [6a-c].

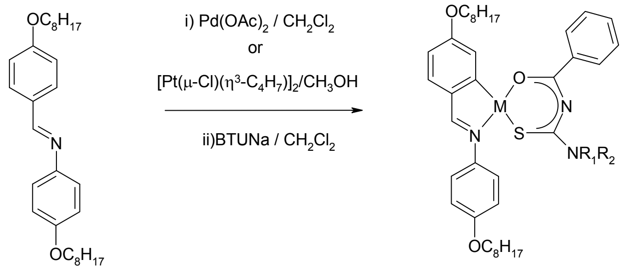
Our aim was to realize a systematic study regarding the influence of the *N*-benzoyl thiourea type co-ligands on the mesogenic behaviour of ortho-metallated imine fragment in order to prepare liquid crystalline materials with low transition temperatures and broad mesomorphic range.

N-benzoyl thiourea derivatives possess very strong donor groups (carbonyl and thioamide), which makes them very attractive for use as ligands in coordination chemistry. They react with transition metals mostly in monoanionic and bidentate form by deprotonation forming neutral complexes with *S*, *O* – coordination [10]. These derivatives have found many important applications, for example: biological activity [11], solvent extraction of metal ions [12], especially platinum group metals, and, recently, they have been used in the design of liquid crystalline materials [13-16].

In this paper we report the preparation and the mesogenic behaviour of a series of *ortho*-metallated palladium complexes with two different imine ligands carrying two or three alkoxy chains and having *N*-benzoyl thiourea derivatives as co-ligands, as well as the first examples of platinum liquid crystals bearing *N*-benzoyl thiourea moiety.

2. Results and discussion

The synthetic pathway used to prepare the platinum(II) and palladium(II) complexes is presented in Scheme 1.



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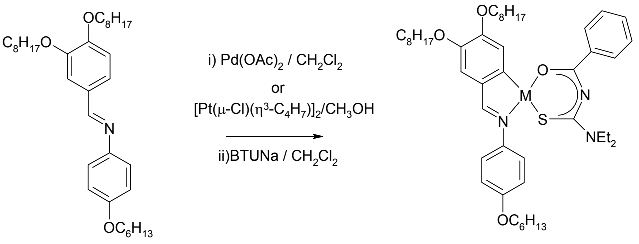
M = Pd 2 a-f
M = Pt 3a

2a: R_1= R_2=Et; **2b**: R_1= R_2=*n*-Pr; **2c**: R_1= R_2=*n*-Bu; **2d**: R_1= R_2=*n*-hexyl; **2e**: R_1= R_2=*n*-octyl; **2f**: R_1=H, R_2=2-napthyl; **3a**: R_1= R_2=Et



4

M = Pd 5a
M = Pt 6a

Scheme 1. Preparation of mononuclear Pt(II) and Pd(II) ortho-metallated complexes.

The dinuclear acetato-bridged palladium complexes, intermediates in the preparation of the corresponding palladium(II) mononuclear species, were obtained with good yield by *ortho*-palladation reaction between $Pd(OAc)_2$ and imines **1** and **4** [17]. These dinuclear complexes were used in the next step for the preparation of the mononuclear palladium(II) complexes by reacting them with a series of sodium salts of *N*-benzoyl thiourea derivatives. All the mononuclear palladium(II) complexes are microcrystalline yellow products, which are stable under atmospheric conditions. The dinuclear chloro-bridged *ortho*-platinated compounds were obtained by *ortho*-platination of the imine ligands using di-μ-chloro-bis[(η^3-2-methylallyl)platinum] as starting material [18]. They were used in the next step for the preparation of the mononuclear species without further purification. The preparation of mononuclear *ortho*-platinated complexes was carried out by ligand exchange reaction of the chloro-bridged dinuclear platinum(II) complexes using the sodium salt of the *N*,*N*-diethyl-*N'*-benzoyl thiourea. The new mononuclear complexes were obtained in moderate to good yields as orange microcrystalline solid products.

All the new products were characterized by elemental analysis, IR, ^{1}H NMR spectroscopy while the liquid crystal properties were investigated by DSC and polarizing optical microscopy.

The formation of the *ortho*-metallated mononuclear complexes with 4-octyloxybenzylidene-4'-octyloxyaniline imine (**1**) can be confirmed readily by ^{1}H-NMR spectroscopy when a pattern specific to a 1,3,4-substitution of an aromatic ring can be seen as two doublets and a doublet of doublets. The ^{1}H-NMR spectra of mononuclear palladium and platinum(II) complexes indicate the presence of only one isomer in solution (by the presence of only one set of signals in the NMR spectra), though it is possible the complexes to exist as a mixture of two isomers, with the sulfur atom of the *N*-benzoyl thiourea ligand in *trans* or *cis* position to the nitrogen atom of the imine group of the Schiff base ligand. As expected, the *N*-benzoyl thiourea derivatives are coordinated in monoanionic deprotonated form to metal center, this information is supported by ^{1}H NMR spectroscopy by the dissapearance of NH signal assigned to the aminic proton located between the carbonyl and thiocarbonyl groups which is located arround 9 ppm in the ^{1}H NMR spectra of the uncomplexed N-benzoyl thiourea ligands. This information is further confirmed by IR spectroscopy by the disappearance of ν_{NH} frequency in the IR spectra of palladium(II) and platinum(II) mononuclear complexes [19].

In the case of platinum(II) complex, another interesting feature of the ^{1}H-NMR spectra is the presence of the ^{195}Pt satellites which confirm the *ortho*-platination process. The values of $^3J_{Pt\text{-}H}$ constants were in the expected range for such compounds and are similar with those found for other *ortho*-platinated complexes [20].

The high field region of the ^{1}H NMR spectra of mononuclear complexes reveals two sets of signals at least for one group of protons belonging to the alkyl chain of dialkylamino group as a consequence of partially double bond character of –C(S)-N that makes the two alkyl chains magnetically non-equivalents.

3. Thermal behaviour

The thermal and liquid crystal properties were investigated by a combination of differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The DSC data and the type of mesophases observed by microscopy are presented in Table 1.

It is worth noting that the Schiff base with three alkoxy chains used as ligand is not a liquid crystal (**4**: Cr – I, 70ºC).

Table 1 Thermal data for platinum and palladium (II) complexes.

Compound	**Transition**	***T*/°C**	**ΔH/kJ mol^{-1}**
2a	Cr – I	81	24.5
	(N – I)[b]	(64)[a]	(0.4)
2b	Cr – I	106	31.8
	(I - N)[c]	(67)[a]	(21.7)
	(N – Cr)		
2c	Cr – I	107	35.6
2d	Cr – I	101	37.4
2e	Cr – I	83	32.5
	(I – N)[c]	(60)	(0.3)
3a	Cr – I	93	37.0
	(N – I)[b]	(68)	(0.6)
5a	Cr – I	64	44.0
	(N – I)[b]	(41)	(0.6)
	(SmA - N)	(27)	(0.2)
6a	Cr – I	66	45.5
	(N – I)[b]	(48)	(0.8)
	(SmA - N)	(43)	(0.3)

[a] These values represents the temperatures taken from microscopy

[b] In this case $T_{(N-I)}$ is quoted as the sample was cooled from isotropic to nematic and then re-heated back to the isotropic

[c] The two transition could not be isolated on the DSC's, the values represent the combined enthalpies

It is very clear that the mesogenic behaviour of the platinum(II) and palladium(II) complexes is strongly influenced by the *ortho*-metallated imine fragment, but the nature of the *N*-benzoyl thiourea, more specific the R_1 and R_2 substituents, can significantly influence the mesogenic behaviour of these complexes (Table 1). Thus, the lack of mesogenic properties for the complex bearing *N*-benzoyl-*N*'-naphtyl thiourea derivative (R_1 = H, R_2 = naphtyl) (**2f**) could be assigned to the structure of this type of ligand. On one hand the aromatic group linked to the nitrogen atom, which imposes a less favourable molecular shape and, on the other hand, the intramolecular hydrogen bonds N-H···S, that could be formed between the S atom of the thiocarbonyl group and the hydrogen atom of the amino group of the *N*-benzoyl thiourea ligand. This type of N-H···S hydrogen bonds is very often found for uncomplexed *N*-benzoyl thiourea derivatives [21]. All the mononuclear prepared complexes show mesomorphic properties, except compounds **2c** and **2d**, with $R_1 = R_2$ = butyl or hexyl. Now, if we look at the first series of complexes having the 4-octyloxybenzylidene-4'-octyloxyaniline imine ligand, **2a-e** and **3a**, the most striking feature is that both the melting points and the nematic phase stability (T_{N-I}) show an increasing trend on going from ethyl to butyl after which these two values start to decrease up to octyl substituents. Obviously, increasing the length of the alkyl chain of the N-benzoyl thiourea derivative, considerably increases the melting points due to the excessive van der Waals intermolecular forces of attraction, up to a maximum point represented by butyl fragments, after which they start to decrease with increasing the length, probably because of increased flexibility that disrupt the packing forces [22]. Another way of regarding this behaviour is to discuss the molecular anisotropy of these complexes. Increasing the length of the alkyl chain of the *N*-benzoyl thiourea derivative leads to the increase of the molecule breadth with strong influences on the mesogenic behaviour (figure 1). In this way, one can assume that the minimum length-to-breadth ratio is reached for $R_1 = R_2$ = butyl, when the mesogenic behaviour is being totally suppressed.

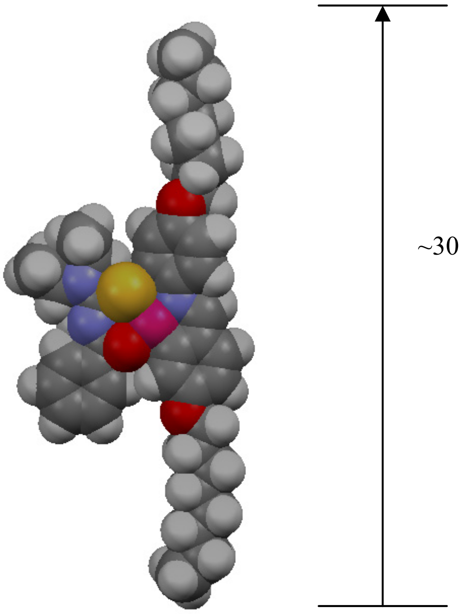


*Fig. 1. The space-filling diagram of complex **2a** (the alkoxy and alkyl chains are considered in their trans extended conformation).*

The mononuclear palladium(II) complexes **2a** and **2e**, with *N*,*N*-diethyl- or *N*,*N*-dioctyl-*N'*-benzoyl thiourea complementary ligands were the only compounds of palladium(II) with 4-octyloxybenzylidene-4'-octyloxyaniline imine ligand for which it was possible to extract the enthalpy parameter associated with the isotropic to nematic phase transition because the other palladium mononuclear complexes of this series either do not exhibit liquid crystals properties or have the isotropic to nematic transition very close to the crystallization temperature and even at lower cooling rates (5ºC/min) these two transitions could not be separated (**2e**). Interestingly, the nematic phase of complexes **2a** and **3a** is stable up to room temperature for several hours after which a slow crystallization process occurs.

Complexes having the imine ligand with three alkoxy chains, **5a** and **6a**, show an additional smectic phase which is stable for hours at room temperature (figure 2 and 3).

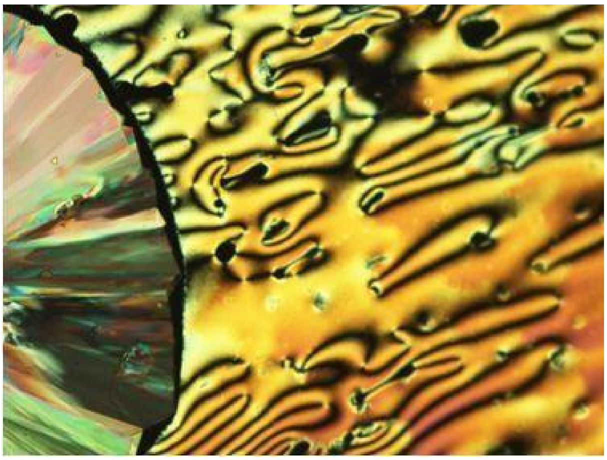


*Fig. 2. Polarized light optical microphotograph of the nematic phase of compound **5a** as observed by annealing the sample for 4 hours at 39ºC (slight crystallisation can be seen on the left side, 200X).*

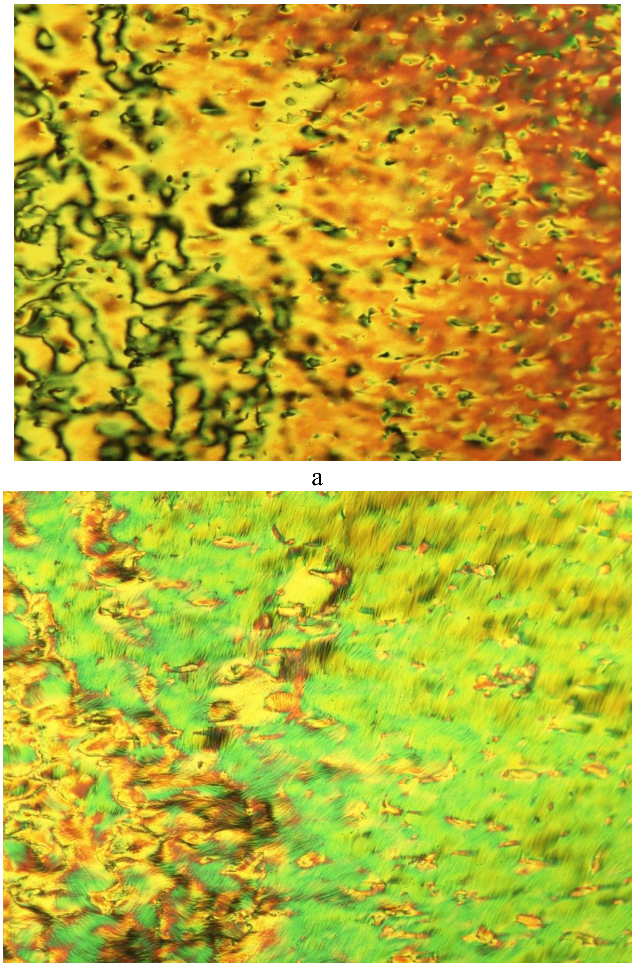
If the mesogenic properties of the palladium complexes are compared with those of platinum complexes which present the same structure then the same type of mesophases is seen but with higher transition temperatures in the case of platinum complexes, as a result of substitution of palladium with the heavier platinum metal which brings an enhancement in polarization. The stability of the nematic phase increased for both platinum(II) complexes, **3a** and **6a**, but in the later case this stability is accompanied by a reduction of the nematic range, from 14ºC for palladium analogue complex (**5a**) to about 5ºC for platinum complex (**6a**). A similar change in mesogenic properties, when replacing palladium with platinum, was reported for other *ortho*-metallated imine complexes [23].

4. Conclusions

A series of organometallic platinum(II) and palladium(II) complexes bearing imine ligands, carrying two or three alkoxy chains, and different types of *N*-benzoyl thiourea derivatives as co-ligands were prepared and investigated for their liquid crystal properties. First liquid crystals based on platinum complexes containing the *N*-benzoyl thiourea moiety are reported here and their mesogenic properties are compared with those of palladium analogues.

By a judicious choice of the imine ligand and *N*-benzoyl thiourea derivative, room temperature nematic or smectic phases can be induced in *ortho*-metallated platinum(II) and palladium(II) complexes, mesophases which are stable for hours at this temperature, after which slow crystallization occurs.

We appreciate that the *N*-benzoyl thiourea derivatives can be used in the design of new liquid crystalline materials capable to exhibit tunable mesogenic properties and further studies will be carried on this direction.



a

b

*Fig. 3. Polarized light optical microphotograph of the nematic phase of compound **6a** at 43ºC (a) and of the smectic A phase at 35ºC (200X) (b).*

5. Experimental

Dichloromethane was distilled from phosphorus pentaoxide while acetone was distilled from calcium chloride; other chemicals were used as supplied.

Proton and carbon NMR spectra were recorded on a Varian Gemini 300 BB spectrometer operating at 300 MHz, using $CDCl_3$ as solvent. ^1H chemical shifts were referenced to the solvent peak position, δ 7.26 ppm.

Transition temperatures were measured using a Linkam THMS600 hot stage and a TMS94 temperature controller attached to a Nikon 50i Pol polarising microscope. These temperatures were confirmed by differential scanning calorimetry (Perkin-Elmer Diamond instrument using 10ºC/min heating rate). Two or more heating/cooling cycles were performed on each sample. Mesophases were assigned by their optical texture [24].

6. Synthesis of imine ligands

The imine ligands were prepared by the condensation reaction between the corresponding aldehydes and anilines, catalyzed by glacial acetic acid, in absolute ethanol, as described elsewhere [25]. Below is presented the preparation of **4**. To a solution of *p*-hexyloxyaniline (0.193 g, 1 mmol) in ethanol (10 cm^3), 3,4-dioctyloxybenzaldehyde (0.362 g, 1 mmol) followed by few drops of glacial acetic acid were added. The mixture was heated under reflux for 2 h and then cooled to –25 ºC to give the crude product. Recrystallisation from hot ethanol gave the analytically pure product as off-white crystals.

7. Synthesis of dinuclear platinum(II) and palladium(II) complexes

The following is the typical procedure for acetato-bridged palladium dinuclear complexes [16]. The imine ligand (2.5 mmol) was dissolved in dichloromethane (30 cm^3) and palladium acetate (2.5 mmol) was added. The resulting mixture was stirred at room temperature for 18h after which the solvent was removed *in vacuo*. The residue was crystallized from a mixture dichloromethane – ethanol to give the yellow – brown crystalline products, which were washed with cold ethanol and dried under *vacuum*.

In the case of chloro-bridged dinuclear platinum(II) complexes, the starting material was $[Pt(\mu\text{-}Cl)(\eta^3\text{-}C_4H_7)]_2$, which was prepared according to literature data [18]. Thus, the mixture of the corresponding imine ligand and $[Pt(\mu\text{-}Cl)(\eta^3\text{-}C_4H_7)]_2$ in methanol, in molar ratio 2:1, was stirred for 1 day at room temperature. The resulting brown precipitate was filtered and washed several times with cold methanol. The preparation of the dinuclear platinum(II) complexes followed the one described in literature [26]. These crude products were used in the next step, for the preparation of mononuclear species, without further purification.

8. Synthesis of mononuclear complexes 2 (a-f), 3a, 5a and 6a

The procedure used in the preparation of **2a** is described here. The other mononuclear complexes were prepared in the same manner using binuclear palladium or platinum complex / sodium salt of *N*-benzoyl thiourea molar ratio of 1:3.

Solid sodium salt of *N,N*-diethyl-*N'*-benzoyl thiourea (0.0715 g, 0.27 mmol) was added to a solution of binuclear palladium complex (0.075 g, 0.09 mmol) in dichloromethane (15 cm^3) and the mixture stirred at room temperature for 24 hours. Evaporation of the solvent gave a yellow solid, which was purified by chromatography on silica using dichloromethane as eluent to give a yellow solid. This was recrystallised from a mixture of dichloromethane / ethanol (1/1) at –25ºC.

The platinum(II) complexes were recrystallized from a mixture of acetone / methanol (1/1) at -25 ºC.

The yields, elemental analysis results as well as ^1H NMR data are presented below:

2a. Yield 89%, yellow crystals, m.p. 81ºC. Anal. Calcd for $C_{41}H_{57}N_3O_3PdS$: C, 63.3; H, 7.4; N, 5.4; Found: C, 62.9; H, 7.7; N, 5.1.

^1H NMR (300 MHz, $CDCl_3$): 8.13 (s, 1H), 7.74 (m, 2H), 7.41 – 7.21 (m, 6H), 7.00 (d, ^4J = 2.3 Hz, 1H), 6.97 (AA'BB' system, ^3J = 8.9 Hz, 2H), 6.59 (dd, ^3J = 8.3 Hz, ^4J = 2.3 Hz, 1H), 4.02 (m, 6H), 3.86 (q, ^3J = 7.1 Hz, 2H), 1.90 – 1.24 (m, 30H), 0.90 (m, 6H).

IR (cm^{-1}): 1580s($\nu_{C=N}$); 1520s(δ_{NH}); 1419vs(ν_{CN+CS}).

2b. Yield 52%, yellow crystals, m.p. 106ºC. Anal. Calcd for $C_{43}H_{61}N_3O_3PdS$: C, 64.0; H, 7.6; N, 5.2; Found: C, 63.7; H, 8.0; N, 5.0.

^1H NMR (300 MHz, $CDCl_3$): 8.21 (s, 1H), 7.73 (m, 2H), 7.40 – 7.19 (m, 6H), 7.03 (d, ^4J = 2.4 Hz, 1H), 6.96 (AA'BB' system, ^3J = 8.9 Hz, 2H), 6.59 (dd, ^3J = 8.4 Hz, ^4J = 2.5 Hz, 1H), 4.03 (m, 4H), 3.90 – 3.74 (m, 4H), 1.95 – 1.31 (m, 28H), 1.04 (t, ^3J = 7.4 Hz, 3H), 0.95 (m, 9H).

IR (cm^{-1}): 1582s($\nu_{C=N}$); 1540s(δ_{NH}); 1420vs(ν_{CN+CS}).

2c. Yield 75%, yellow crystals, m.p. 106 - 107ºC. Anal. Calcd for $C_{45}H_{65}N_3O_3PdS$: C, 64.8; H, 7.9; N, 5.0; Found: C, 64.3; H, 8.3; N, 4.7.

^1H NMR (300 MHz, $CDCl_3$): 8.03 (s, 1H), 7.66 (m, 2H), 7.30 (AA'BB' system, ^3J = 8.9 Hz, 2H), 7.24 (d, ^3J=8.4 Hz, 1H), 7.12 (m, 3H), 6.92 (d, ^4J = 2.5 Hz, 1H), 6.87 (AA'BB' system, ^3J = 8.8 Hz, 2H), 6.50 (dd, ^3J = 8.4 Hz, ^4J = 2.5 Hz, 1H), 3.93 (m, 4H), 3.85 – 3.78 (m, 2H), 3.75 – 3.69 (m, 2H), 1.82 – 1.15 (m, 32H), 0.95, (t, ^3J = 7.3 Hz, 3H), 0.85 – 0.77 (m, 9H).

IR (cm^{-1}): 1575s($\nu_{C=N}$); 1510s(δ_{NH}); 1410vs(ν_{CN+CS}).

2d. Yield 86%, yellow crystals, m.p. 101ºC. Anal. Calcd for $C_{49}H_{73}N_3O_3PdS$: C, 66.1; H, 8.3; N, 4.7; Found: C, 65.7; H, 8.5; N, 4.3.

^1H NMR (300 MHz, $CDCl_3$): 8.02 (s, 1H), 7.65 (m, 2H), 7.30 (AA'BB' system, ^3J = 8.8 Hz, 2H), 7.25 (d, ^3J=8.2 Hz, 1H), 7.11 (m, 3H), 6.92 (d, ^4J = 2.4 Hz, 1H), 6.87 (AA'BB' system, ^3J = 8.9 Hz, 2H), 6.49 (dd, ^3J = 8.2 Hz, ^4J = 2.5 Hz, 1H), 3.93 (m, 4H), 3.81 – 3.78 (m, 2H), 3.72 – 3.67 (m, 2H), 1.82 – 1.15 (m, 40H), 0.88 – 0.75 (m, 12H).

IR (cm^{-1}): 1582s($\nu_{C=N}$); 1516s(δ_{NH}); 1420vs(ν_{CN+CS}).

2e. Yield 85%, yellow crystals, m.p. 83ºC. Anal. Calcd for $C_{53}H_{81}N_3O_3PdS$: C, 67.2; H, 8.6; N, 4.4; Found: C, 66.9; H, 9.0; N, 4.1.

^{1}H NMR (300 MHz, $CDCl_3$): 8.02 (s, 1H), 7.66 (m, 2H), 7.30 (AA'BB' system, ^3J = 8.9 Hz, 2H), 7.24 (d, ^3J=8.4 Hz, 1H), 7.12 (m, 3H), 6.92 (d, ^4J = 2.4 Hz, 1H), 6.87 (AA'BB' system, ^3J = 8.8 Hz, 2H), 6.50 (dd, ^3J = 8.4 Hz, ^4J = 2.4 Hz, 1H), 3.94 (m, 4H), 3.82 – 3.78 (m, 2H), 3.71 – 3.67 (m, 2H), 1.82 – 1.15 (m, 48H), 0.85 – 0.75 (m, 12H).

IR (cm^{-1}): 1582s($\nu_{C=N}$); 1516s(δ_{NH}); 1418vs(ν_{CN+CS}).

2f. Yield 40%, yellow crystals, m.p. 160ºC with dec. Anal. Calcd for $C_{47}H_{55}N_3O_3PdS$: C, 66.5; H, 6.5; N, 5.0; Found: C, 66.0; H, 6.9; N, 4.7.

^{1}H NMR (300 MHz, $CDCl_3$): 8.12 (s, 1H), 8.09 – 8.06 (m, 2H, naphtyl), 7.93 – 7.90 (m, 3H, naphtyl), 7.84 – 7.78 (m, 2H), 7.56 – 7.49 (m, 6H), 7.38 (AA'BB' system, ^3J = 8.9 Hz, 2H), 7.34 (d, ^3J=8.9 Hz, 1H), 6.96 (AA'BB' system, ^3J = 8.9 Hz, 2H), 6.59 (dd broad, 1H), 4.01 (t, ^3J = 6.6 Hz, 4H), 1.87 – 1.25 (m, 24H), 0.92 – 0.87 (m, 6H).

IR (cm^{-1}): 1582s($\nu_{C=N}$); 1540s(δ_{NH}); 1405vs(ν_{CN+CS}).

3a. Yield 59%, orange crystals, m.p. 93º. Anal. Calcd for $C_{41}H_{57}N_3O_3PtS$: C, 56.8; H, 6.6; N, 4.8; Found: C, 56.3; H, 7.1; N, 4.5.

^{1}H NMR (300 MHz, $CDCl_3$): 8.38 (s, 1H, $^3J_{Pt-H}$=115Hz), 7.63 (m, 2H), 7.38 (m, 4H), 7.19 (m, 2H), 7.07 (d, ^4J = 2.5 Hz, 1H), 6.98 (AA'BB' system, ^3J = 9.1 Hz, 2H), 6.58 (dd, ^3J = 8.2 Hz, ^4J = 2.5 Hz, 1H), 4.04 (q, ^3J = 6.5 Hz, 4H), 3.95 (q, ^3J = 6.9 Hz, 2H), 3.84 (q, ^3J = 6.9 Hz, 2H), 1.90 – 1.25 (m, 30H), 0.90 (m, 6H).

IR (cm^{-1}): 1580s($\nu_{C=N}$); 1520s(δ_{NH}); 1419vs(ν_{CN+CS}).

4. Yield 45%, off white crystals, m.p. 70ºC. Anal. Calcd for $C_{35}H_{55}NO_3$: C, 78.2; H, 10.3; N, 2.6; Found: C, 78.0; H, 10.6; N, 2.3.

^{1}H NMR (300 MHz, $CDCl_3$): 8.36 (s, 1H, CH=N), 7.60 (s, broad, 1H), 7.27 (dd, J = 1.8 Hz and J = 8.4 Hz, 1H), 7.21 (AA'BB' system, J = 8.5 Hz, 2H aniline ring), 6.92 (d, J = 8.6 Hz, 3H), 4.12 – 4.03 (m, 4H, 2OCH_2 groups), 3.97 (t, J = 6.5 Hz, 2H, OCH_2), 1.90 – 1.25 (m, 32H, CH_2 groups), 0.95 – 0.85 (m, 9H, CH_3 groups).

IR (cm^{-1}): 1574m($\nu_{C=N}$); 1511s(δ_{NH}).

5a. Yield 74%, yellow crystals. Anal. Calcd for $C_{47}H_{69}N_3O_4PdS$: C, 64.3; H, 7.9; N, 4.8; Found: C, 64.0; H, 8.2; N, 4.5.

^{1}H NMR (300 MHz, $CDCl_3$): 8.08 (s, 1H), 7.76 (m, 2H), 7.40 – 7.34 (m, 3H), 7.22 (m, 2H), 7.01 (s, 1H), 6.99 (s, 1H), 6.97 (AA'BB' system, ^3J = 8.8 Hz, 2H), 4.15 (t, ^3J = 6.6 Hz, 2H), 4.04 - 3.99 (m, 4H), 3.94 (t, ^3J = 6.7 Hz, 2H), 3.86 (q, ^3J = 7.0 Hz, 2H), 1.90 – 1.75 (m, 6H), 1.53 – 1.25 (m, 32H), 0.95 – 0.86 (m, 9H).

IR (cm^{-1}): 1587m($\nu_{C=N}$); 1521s(δ_{NH}); 1412vs(ν_{CN+CS}).

6a. Yield 55%, orange-brown crystals. Anal. Calcd for $C_{47}H_{69}N_3O_4PtS$: C, 58.4; H, 7.2; N, 4.3; Found: C, 58.0; H, 7.6; N, 4.1.

^{1}H NMR (300 MHz, $CDCl_3$): 8.33 (s, $^3J_{Pt-H}$=109Hz, 1H), 7.64 (m, 2H), 7.41 – 7.36 (m, 3H), 7.19 (m, 2H), 7.03 (s, 1H), 7.02 (s, 1H), 6.98 (AA'BB' system, ^3J = 8.8 Hz, 2H), 4.15 (t, ^3J = 6.6 Hz, 2H), 4.03 (t, ^3J = 6.6 Hz, 2H), 3.94 (m, 4H), 3.84 (q, ^3J = 7.1 Hz, 2H), 1.90 – 1.77 (m, 6H), 1.50 – 1.25 (m, 32H), 0.95 – 0.80 (m, 9H).

IR (cm^{-1}): 1585m($\nu_{C=N}$); 1520s(δ_{NH}); 1415vs(ν_{CN+CS}).

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