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Cyclometalated palladium(II) metallomesogens with Schiff bases and *N*-benzoyl thiourea derivatives as co-ligands

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Abstract

Two series of cyclometalated palladium(II) complexes based on Schiff bases and Nbenzoylthiourea (BTU) ligands having four alkoxy groups at their periphery, with different number of carbon atoms, have been designed and prepared. The liquid crystalline behavior of these palladium(II) complexes was investigated by a combination of polarized optical microscopy (POM), differential scanning calorimetry (DSC) and powder X-ray diffraction while their thermal stability was studied by thermogravimetric analysis (TGA). The palladium(II) complexes are thermally stable on a broad temperature range up to 230° C showing, depending on the alkoxy chain length, either monotropic or, for longest alkyl chain, enantiotropic smectic A and C phases. The luminescent properties of palladium(II) complexes were reported. These complexes show a yellow-orange solid-state emission at room temperature with two emission maxima at λ_{max} around 580 and 650 nm, respectively, with a shoulder around 710 nm, when the samples are irradiated in the 330 - 380 nm range.

Introduction

The research area dealing with the design and investigation of metal-containing liquid crystals (metallomesogens) expanded considerably in the past few decades. [1,2] There is a growing interest to study the unique combination of the properties of anisotropic fluids (anisotropy of physical properties and fast orientational response to external fields) specific to liquid crystals (LC) with the particular properties of metals (geometry of coordination, electronic, magnetic or the purely structural role, depending on the metal ion). [3] The different coordination geometries adopted by metal centers enabled the rich structures and topologies of these metal complexes

and, consequently, more diversified LC properties to those found for pure organic derivatives. [4] Liquid crystalline materials have found various applications such as the manufacturing of LCD, molecular sensors and detectors, optical switches, spatial light modulator, etc. [5-7] In particular, the liquid crystalline materials based on palladium(II) complexes were given a tremendous attention. [8-18] Amongst various advantages, their square planar geometry that favors the stabilization of LC phases and their relative ease of preparation are worth to mention here. Moreover, the LC and emission properties could be controlled easier by a variety of available options to change the chemical structure around the palladium metal center. [19-23] A judicious design of the ligands coordinated to palladium(II) metal could bring improved LC properties, reflected in lower transition temperatures preventing chemical decomposition and stability of the mesophases near room temperature. [24, 25] In the past years, we have started the investigation of a new class of palladium(II) complexes with LC properties based on cyclometalated imine ligands and N-benzoylthiourea (BTU) derivatives as auxiliary ligands. The BTU compounds represent an interesting class of chelating ligands bearing two very strong donor groups (carbonyl and thioamide). In most cases they produce neutral metal complexes with S,O-coordination. [26-28] Moreover, the BTU compounds decorated with alkoxy groups show interesting mesogenic behavior. [29-32] The specific influence of the alkoxy-substituted BTU derivatives on the thermal behavior of square-planar Pd(II) and Pt(II) cyclometalated complexes together with their emissive properties were reported. [33, 34] When simple Nbenzoyl thiourea derivatives were used as co-ligands for palladium(II) metal accompanied by cyclometalated imine ligands, only monotropic nematic or smectic A phases were observed. [35-39] On the other hand, the use of BTU ligands having various number of alkoxy terminal groups, can lead to mono- or dinuclear palladium(II) complexes with lower transition temperatures and rich mesomorphic behavior ranging from calamitic to discotic materials. [34] In this work, we report the design and a systematic investigation of the LC properties of a series of palladium(II) complexes based on cyclometalated Schiff bases and BTU ligands with alkoxy groups of various chain length grafted in terminal positions. The emission properties of the palladium(II) complexes in solid state were also investigated.

Experimental

Characterization methods. All the chemicals were used as supplied. C, H, N analyses were carried out with an EuroEA 3300 instrument. IR spectra were recorded on a Bruker spectrophotometer using ATR technique. ¹H and ¹³C NMR spectra were recorded on a Bruker spectrometer operating at 300 MHz, using CDCl₃ as solvent. ¹H chemical shifts were referenced to the solvent peak position, δ 7.26 ppm. The phase assignments and corresponding transition temperatures for all palladium complexes 1, 2 a-f, were evaluated by polarizing optical light microscopy (POM), placed on untreated glass slides, using a Nikon 50iPol microscope equipped with a Linkam THMS600 hot stage and TMS94 control processor. Temperatures and enthalpies of transitions were collected from their corresponding thermograms recorded by using differential scanning calorimetry (DSC) technique employing a Diamond DSC Perkin Elmer instrument. The materials were studied at 10°/min scanning rate after being encapsulated in aluminium pans. Three heating/cooling cycles were performed on each sample. The nature of LC phases was established by their optical texture and powder X-ray diffraction data. The powder X-ray diffraction measurements were made on a D8 Advance diffractometer (Bruker AXS GmbH, Germany), in parallel beam setting, with monochromatized Cu– $K_{\alpha 1}$ radiation (λ =1.5406 Å), scintillation detector, and horizontal sample stage. The measurements were performed in symmetric (θ - θ) geometry in the 2 θ range from 1.5° to 30° in steps of 0.02°, with measuring times per step in the 5-40 s range. The temperature control of the samples during measurements was achieved by adapting a home-made heating stage to the sample stage of the diffractometer. Thermogravimetric analysis was performed on a TA Q50 TGA instrument using alumina crucibles and nitrogen as purging gas. The heating rate employed was 10°C min⁻¹ from room temperature (approx. 25°C) to 1000°C. The variable-temperature emission spectra in solid state were recorded with an OceanOptics QE65PRO spectrometer attached to the microscope and using a Nikon Intensilight excitation source.

Synthesis of Pd(II) complexes 1,2a-f

Corresponding solid *N*-benzoylthiourea compound (0.30 mmol), prepared as described elsewhere [32, 54], was added to a suspension of dinuclear μ -acetato-bridged palladium complexes (0.10 mmol) and K₂CO₃ in dichloromethane (15 cm³) and the mixture stirred at room temperature for 24 hours. Evaporation of the solvent gave yellow solids, which were purified by chromatography

on silica using dichloromethane as eluant to yield the final products. They were further crystallized from a mixture of dichloromethane/ethanol (1/1) at -25° C.

Only the first compound of each series is described below as their ¹H NMR spectra are identical except for corresponding decrease in integration of the hydrogens of the alkoxy chains at δ :1.55–1.25ppm.

1a Yellow solid. Yield 76%. Calc. for C₅₁H₆₉N₃O₅PdS: %C: 64.98; %H 7.38; %N 4.46. Found: %C 64.65; %H 7.66; %N 4.32.

¹H-NMR (CDCl₃, 300 MHz): 8.13 (s, 1H), 7.90 (s, br, 1H), 7.65 (d, br, 2H), 7.49-7.33 (m, 6H), 6.98 (d, J=8.5Hz, 2H), 6.90 (d, J=8.3Hz, 2H), 6.69 (d, J=8.8Hz, 2H), 6.60 (dd, ³J=8.0Hz, ⁴J=2.1Hz, 1H), 4.06-3.92 (m, 8H), 1.90-1.82 (m, 8H), 1.55-1.25 (m, 24H), 0.95-0.90 (m, 12H). ¹³C NMR (CDCl₃, 75 MHz): 171.1, 162.3, 160.3, 158.4, 157.9, 141.6, 140.1, 132.3, 130.1, 129.8, 126.3, 124.5, 118.9, 114.7, 114.5, 113.5, 110.9, 68.6, 68.4, 68.1, 32.2, 32.1, 29.9, 29.7, 29.6, 29.5, 29.4, 29.3, 26.4, 22.9, 14.3.

IR (ATR, cm⁻¹): 3227, 2955, 2923, 2856, 1606, 1583, 1541, 1506, 1473, 1422, 1312, 1297, 1247, 1167, 1111, 1034, 915, 834, 792, 768, 669, 576, 519.

1c. Yield 84%. Yellow solid. Analytical: Calc. for C₅₉H₈₅N₃O₅PdS: %C: 67.18; %H 8.12; %N 3.98. Found: %C 66.89; %H 8.45; %N 3.81.

¹H-NMR (CDCl₃, 300 MHz): 8.13 (s, 1H), 7.91 (s, br, 1H), 7.65 (d, br, 2H), 7.50-7.32 (m, 6H), 6.98 (d, J=8.5Hz, 2H), 6.90 (d, J=8.3Hz, 2H), 6.69 (d, J=8.8Hz, 2H), 6.60 (dd, ³J=8.0Hz, ⁴J=2.1Hz, 1H), 4.06-3.92 (m, 8H), 1.90-1.82 (m, 8H), 1.55-1.25 (m, 40H), 0.95-0.90 (m, 12H). ¹³C NMR (CDCl₃, 75 MHz): 171.1, 162.3, 160.3, 158.4, 157.9, 141.5, 140.2, 132.3, 130.1, 129.8, 126.3, 124.5, 118.9, 114.7, 114.4, 113.5, 110.9, 68.7, 68.4, 68.1, 32.2, 32.1, 29.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 26.4, 22.9, 14.3.

IR (ATR, cm⁻¹): 3227, 2955, 2923, 2856, 1606, 1583, 1541, 1506, 1473, 1422, 1312, 1297, 1247, 1167, 1111, 1034, 915, 834, 792, 768, 669, 576, 519.

1d. Yield 88%. Yellow solid. Analytical: Calc. for C₆₃H₉₃N₃O₅PdS: %C: 68.11; %H 8.44; %N 3.78. Found: %C 67.87; %H 8.67; %N 3.55.

¹H-NMR (CDCl₃, 300 MHz): 8.14 (s, 1H), 7.90 (s, br, 1H), 7.65 (d, br, 2H), 7.49-7.33 (m, 6H), 6.98 (d, J=8.5Hz, 2H), 6.89 (d, J=8.3Hz, 2H), 6.69 (d, J=8.8Hz, 2H), 6.60 (dd, ³J=8.0Hz, ⁴J=2.1Hz, 1H), 4.04-3.90 (m, 8H), 1.91-1.83 (m, 8H), 1.55-1.25 (m, 48H), 0.95-0.90 (m, 12H). ¹³C NMR (CDCl₃, 75 MHz): 171.2, 162.3, 160.3, 158.5, 157.9, 141.5, 140.1, 132.3, 130.1,

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129.8, 126.3, 124.5, 118.9, 114.6, 114.5, 113.5, 110.9, 68.6, 68.4, 68.1, 32.2, 32.1, 29.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 26.4, 22.9, 14.3.

IR (ATR, cm⁻¹): 3230, 2955, 2923, 2857, 1606, 1582, 1541, 1507, 1473, 1425, 1312, 1297, 1247, 1167, 1111, 1034, 916, 834, 792, 769, 670, 576, 519.

1e. Yield 65%. Yellow solid. Analytical: Calc. for C₆₇H₁₀₁N₃O₅PdS: %C: 68.95; %H 8.72; %N 3.60. Found: %C 68.71; %H 8.97; %N 3.48.

¹H-NMR (CDCl₃, 300 MHz): 8.15 (s, 1H), 7.90 (s, br, 1H), 7.65 (d, br, 2H), 7.49-7.33 (m, 6H), 6.98 (d, J=8.5Hz, 2H), 6.90 (d, J=8.3Hz, 2H), 6.69 (d, J=8.8Hz, 2H), 6.60 (dd, ³J=8.0Hz, ⁴J=2.1Hz, 1H), 4.06-3.92 (m, 8H), 1.90-1.82 (m, 8H), 1.55-1.25 (m, 56H), 0.95-0.90 (m, 12H). ¹³C NMR (CDCl₃, 75 MHz): 171.1, 162.3, 160.3, 158.4, 157.9, 141.6, 140.1, 132.3, 130.1, 129.8, 126.3, 124.5, 118.9, 114.7, 114.5, 113.5, 110.9, 68.6, 68.4, 68.1, 32.2, 32.1, 29.9, 29.7, 29.6, 29.5, 29.4, 29.3, 26.4, 22.9, 14.3.

IR (ATR, cm⁻¹): 3227, 2952, 2924, 2856, 1608, 1583, 1544, 1506, 1473, 1421, 1312, 1297, 1247, 1167, 1113, 1035, 915, 834, 792, 768, 669, 576, 521.

1f. Yield 83%. Yellow solid. Analytical: Calc. for C₇₁H₁₀₉N₃O₅PdS: %C: 69.72; %H 8.98; %N 3.44. Found: %C 69.56; %H 9.16; %N 3.23.

¹H-NMR (CDCl₃, 300 MHz): 8.14 (s, 1H), 7.88 (s, br, 1H), 7.65 (d, br, 2H), 7.49-7.33 (m, 6H), 6.98 (d, J=8.5Hz, 2H), 6.90 (d, J=8.3Hz, 2H), 6.67 (d, J=8.8Hz, 2H), 6.62 (dd, ³J=8.0Hz, ⁴J=2.1Hz, 1H), 4.07-3.93 (m, 8H), 1.90-1.82 (m, 8H), 1.55-1.25 (m, 64H), 0.95-0.90 (m, 12H). ¹³C NMR (CDCl₃, 75 MHz): 171.3, 162.3, 160.3, 158.4, 157.9, 141.5, 140.1, 132.3, 130.1, 129.9, 126.3, 124.5, 118.9, 114.9, 114.6, 113.5, 111, 68.6, 68.4, 68.2, 32.2, 32.1, 29.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 26.4, 22.9, 14.2.

IR (ATR, cm⁻¹): 3231, 2955, 2925, 2857, 1606, 1583, 1544, 1506, 1473, 1425, 1313, 1297, 1243, 1167, 1112, 1034, 915, 834, 792, 768, 669, 576, 519.

2a Yield 90%. Yellow solid. Analytical: Calc. for C₅₅H₇₇N₃O₅PdS: %C: 66.14; %H 7.77; %N 4.21. Found: %C 65.78; %H 7.97; %N 3.98.

¹H-NMR (CDCl₃, 300 MHz): 8.12 (s, 1H), 7.92 (s, br, 1H), 7.66 (d, br, 2H), 7.51-7.33 (m, 6H), 6.98 (d, J=8.5Hz, 2H), 6.90 (d, J=8.3Hz, 2H), 6.69 (d, J=8.8Hz, 2H), 6.61 (dd, ³J=8.0Hz, ⁴J=2.4Hz, 1H), 4.06-3.92 (m, 8H), 1.92-1.82 (m, 8H), 1.55-1.25 (m, 32H), 0.95-0.90 (m, 12H).

¹³C NMR (CDCl₃, 75 MHz): 171.1, 162.5, 160.3, 158.5, 157.9, 141.7, 140.1, 132.4, 130.1, 129.8, 126.3, 124.5, 118.9, 114.8, 114.6, 113.5, 110.9, 68.7, 68.5, 68.1, 32.2, 32.1, 29.9, 29.7, 29.6, 29.5, 29.4, 29.3, 26.4, 22.9, 14.3.

IR (ATR, cm⁻¹): 3221, 2957, 2922, 2853, 1603, 1586, 1540, 1504, 1472, 1416, 1314, 1236, 1209, 1167, 1109, 1031, 964, 910, 836, 789, 765, 724, 660, 623, 567, 519.

2c. Yield 78%. Yellow solid. Analytical: Calc. for C₆₃H₉₃N₃O₅PdS: %C: 68.11; %H 8.44; %N 3.78. Found: %C 67.88; %H 8.65; %N 3.57.

¹H-NMR (CDCl₃, 300 MHz): 8.13 (s, 1H), 7.91 (s, br, 1H), 7.67 (d, br, 2H), 7.51-7.33 (m, 6H), 6.98 (d, J=8.5Hz, 2H), 6.90 (d, J=8.3Hz, 2H), 6.70 (d, J=8.8Hz, 2H), 6.61 (dd, ³J=8.0Hz, ⁴J=2.3Hz, 1H), 4.06-3.92 (m, 8H), 1.92-1.82 (m, 8H), 1.55-1.25 (m, 48H), 0.95-0.90 (m, 12H).

¹³C NMR (CDCl₃, 75 MHz): 171.1, 162.5, 160.4, 158.5, 157.8, 141.7, 140.1, 132.4, 130.1, 129.8, 126.5, 124.6, 118.9, 114.8, 114.6, 113.5, 110.9, 68.7, 68.5, 68.2, 32.2, 32.1, 29.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 26.4, 22.9, 14.3.

IR (ATR, cm⁻¹): 3225, 2957, 2922, 2853, 1603, 1586, 1539, 1504, 1472, 1416, 1314, 1236, 1209, 1168, 1109, 1033, 964, 910, 836, 789, 765, 724, 662, 623, 567, 519.

2d. Yield 79%. Yellow solid. Analytical: Calc. for C₆₇H₁₀₁N₃O₅PdS: %C: 68.95; %H 8.72; %N 3.60. Found: %C 68.73; %H 9.03; %N 3.48.

¹H-NMR (CDCl₃, 300 MHz): 8.14 (s, 1H), 7.92 (s, br, 1H), 7.66 (d, br, 2H), 7.51-7.33 (m, 6H), 6.98 (d, J=8.5Hz, 2H), 6.90 (d, J=8.3Hz, 2H), 6.69 (d, J=8.8Hz, 2H), 6.60 (dd, ³J=7.9Hz, ⁴J=2.4Hz, 1H), 4.06-3.92 (m, 8H), 1.92-1.82 (m, 8H), 1.55-1.25 (m, 56H), 0.95-0.90 (m, 12H).

¹³C NMR (CDCl₃, 75 MHz): 171.2, 162.5, 160.3, 158.5, 157.9, 141.7, 140.1, 132.4, 130.1, 129.8, 126.3, 124.3, 118.9, 114.8, 114.5, 113.5, 110.9, 68.7, 68.5, 68.1, 32.2, 32.1, 29.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 26.4, 22.9, 14.3.

IR (ATR, cm⁻¹): 3224, 2955, 2924, 2853, 1603, 1586, 1540, 1504, 1472, 1416, 1314, 1237, 1209, 1167, 1110, 1031, 965, 910, 836, 789, 765, 724, 660, 623, 568, 520.

2e. Yield 86%. Yellow solid. Analytical: Calc. for C₇₁H₁₀₉N₃O₅PdS: %C: 69.72; %H 8.98; %N 3.44. Found: %C 69.53; %H 9.15; %N 3.27.

¹H-NMR (CDCl₃, 300 MHz): 8.13 (s, 1H), 7.92 (s, br, 1H), 7.67 (d, br, 2H), 7.52-7.34 (m, 6H), 6.98 (d, J=8.5Hz, 2H), 6.91 (d, J=8.3Hz, 2H), 6.69 (d, J=8.8Hz, 2H), 6.61 (dd, ³J=8.0Hz, ⁴J=2.4Hz, 1H), 4.06-3.92 (m, 8H), 1.92-1.82 (m, 8H), 1.55-1.25 (m, 64H), 0.95-0.90 (m, 12H).

¹³C NMR (CDCl₃, 75 MHz): 171.1, 162.5, 160.3, 158.5, 157.9, 141.7, 140.1, 132.4, 130.1, 129.8, 126.3, 124.5, 118.9, 114.8, 114.6, 113.5, 110.9, 68.7, 68.5, 68.1, 32.2, 32.1, 29.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 26.4, 22.9, 14.3.

IR (ATR, cm⁻¹): 3225, 2956, 2921, 2853, 1603, 1589, 1540, 1504, 1473, 1416, 1314, 1236, 1209, 1165, 1112, 1031, 964, 912, 838, 789, 765, 724, 660, 623, 567, 519.

2f. Yield 77%. Yellow solid. Analytical: Calc. for C₇₅H₁₁₇N₃O₅PdS: %C: 70.42; %H 9.22; %N 3.28. Found: %C 70.19; %H 9.51; %N 3.07.

¹H-NMR (CDCl₃, 300 MHz): 8.11 (s, 1H), 7.92 (s, br, 1H), 7.65 (d, br, 2H), 7.51-7.33 (m, 6H), 6.98 (d, J=8.5Hz, 2H), 6.90 (d, J=8.3Hz, 2H), 6.70 (d, J=8.7Hz, 2H), 6.60 (dd, ³J=8.0Hz, ⁴J=2.4Hz, 1H), 4.05-3.91 (m, 8H), 1.92-1.82 (m, 8H), 1.55-1.25 (m, 72H), 0.95-0.90 (m, 12H).

¹³C NMR (CDCl₃, 75 MHz): 171.3, 162.5, 160.2, 158.5, 157.9, 141.7, 140.1, 132.4, 130.1, 129.7, 126.3, 124.6, 118.9, 114.8, 114.6, 113.5, 111, 68.7, 68.5, 68.1, 32.2, 32.1, 29.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 26.4, 22.9, 14.3.

IR (ATR, cm⁻¹): 3225, 2957, 2926, 2853, 1605, 1586, 1540, 1504, 1472, 1416, 1314, 1236, 1209, 1167, 1112, 1034, 964, 910, 836, 789, 765, 725, 660, 624, 567, 517.

Results and Discussion

The preparation of cyclometalated palladium(II) complexes along with their numbering scheme is presented in Scheme 1. Their synthesis has been achieved by treatment of the corresponding dinuclear μ-acetato-bridged species with BTU derivatives in dichloromethane, in the presence of potassium carbonate at room temperature. The final mononuclear complexes were purified on silica by using dichloromethane as eluant, followed by repeated recrystallization from a mixture of dichloromethane and ethanol, to give the desired compounds in good yields as yellow to yellow-brown solid products. The new mononuclear palladium(II) complexes were characterized by using several techniques: elemental analysis, IR, ¹H and ¹³C NMR spectroscopy and, to evaluate the potential LC properties, a combination of differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and powder X-ray diffraction were employed.



Scheme 1. Preparation of mononuclear palladium(II) complexes

Several features in the ¹H NMR and IR spectra of palladium(II) complexes confirm the coordination of the *N*-benzovlthiourea derivatives in the chelating deprotonated form to the metal center. While the ¹H NMR spectra of the BTU derivatives contains two singlets, one in the range 12.48–12.37 ppm and a second one in the range 9.02– 8.98 ppm, which were assigned to the two existing NH groups, the ¹H-NMR spectra of the corresponding palladium(II) complexes show no presence of these two signals as a consequence of ligand coordination.[32, 33] The other signals, sometimes overlapped as multiplets, assigned to aromatic protons show the normal splitting pattern of a 1,4-or 1,3,4-substitution of the aromatic rings. These data suggest the absence of the NH hydrogen atom located between the thiocarbonyl and carbonyl groups belonging to the Nbenzoylthiourea unit. Moreover, there are no absorption bands in the range between 1610 and 1690 cm⁻¹ in the infrared spectra of all palladium(II) complexes, which is the normal range for $v_{C=0}$ stretches in the spectra of the free BTU ligands. [40] Such a large shift of more than 200 cm⁻¹ to lower wavenumbers indicates chelate formation with a high degree of electron delocalization within the chelate rings; this behavior has been observed previously for other chelate complexes of BTU derivatives with various metals. [41, 42] Still, the IR spectrum of the palladium(II) compounds exhibit a sharp, medium absorption around 3225 cm⁻¹ assigned to the NH vibration of the remaining NH-R group. These BTU derivatives are asymmetric and they can lead to mixture of *cis* and *trans* isomers for mononuclear palladium(II) complexes. The signal assigned to H-C=N- iminic hydrogen atom appears as a singlet around 8.10 ppm in ¹H NMR spectra of palladium(II) complexes, well apart from the other aromatic signals, and, for this reason it could be useful to evaluate the presence of cis and trans isomers mixture in final products.[25] Thus, the presence of one signal in the region, together with the presence of only

one set of other signals, led to the conclusion that the products contain mainly one of the two possible isomers with respect to the positions of sulfur atom of the BTU ligand and nitrogen atom of the cyclometalated imine ligand.

Liquid crystals properties

The thermal data for all palladium(II) complexes are presented in Table 1. The LC phase assignment was done based on their optical texture and X-ray measurements. [43, 44] Several typical features for SmA and SmC features were observed by POM. For instance, the SmA phase was assigned based on its characteristic focal fan shape texture with several homeotropic regions when developed from the isotropic state. The SmC phase was assigned based on its broken fan shape texture which was developed from the previous SmA phase (Figure 2). We were interested to employ BTU derivatives containing different numbers of carbon atoms in the alkoxy mesogenic group in order to establish a correlation structure - mesomorphic behavior for such mononuclear cyclopalladated complexes. Two different approaches were undertaken: varying the number of carbon atoms of the alkoxy groups of Schiff base (6 or 8 carbon atoms), on one hand, and, on the other hand, change of chain length of the terminal alkoxy groups (6, 8, 10, 12, 14 and 16 carbon atoms) attached to the BTU derivatives while keeping unchanged the Schiff base ligand. In this respect, the length of alkyl chains onto the BTU auxiliary ligands was progressively increased by taking advantage of our previous synthetic strategy to attach long alkyl chains in para position of the benzoyl moiety of these ligands.[32] Indeed, these palladium(II) complexes display, depending on the alkoxy chain length, either monotropic or, for longest alkyl chain, enantiotropic smectic A and C phases. For example, the first series of palladium(II) complexes, having two hexyloxy in terminal position of the Schiff bases and different chain length on the BTU ligand, **1a-f**, can be divided in two groups. The palladium(II) complexes with shorter chain length (6 to 12, 1a-d) display monotropic SmA and SmC phases on cooling from the liquid state. Complexes with longer alkyl chain (14 or 16 carbon atoms) 1e and 1f, exhibit an enatiotropic SmA phase and an additional monotropic SmC on the cooling run. For both groups, the SmA phase was stable on a short thermal range, up to 6°C, and the two thermal events could not be well separated on the DSC trace.

By changing the chain length of alkoxy group on the Schiff base from 6 to 8, complexes **2a-f**, now both SmA and SmC phases were enantiotropic for the longest chain (14 and 16, complexes

2e and **2f**, respectively), while the SmA phase shows an enantiotropic character starting with shorter alkoxy groups on the BTU derivative, only ten carbon atoms, complex **2c**. Obviously, there is a very fine balance between these two competing structural features (the number of carbon atoms of either alkoxy groups of the Schiff base or BTU derivative) that lead to the SmA and SmC phase stabilization for these palladium(II) complexes. Their melting points slightly depend on the chain length of the BTU ligand, with lower transition temperatures recorded for higher number of carbon atoms on the BTU ligand. The SmC phase of complexes **2d-f** was stable down to room temperature on the cooling run and the subsequent heating run exhibit a cold crystallization step preceding the normal crystal-mesophase and isotropisation transitions.

For each of the above-mentioned complexes, three consecutive heating–cooling cycles were recorded by DSC. It is important to mention here that, with several exceptions, complexes with the longest chain length, the transition temperatures recorded both on heating and cooling the samples are slightly shifted (one or two degrees between consecutive cycles) towards lower values on subsequent heating-cooling cycles. Such behavior could indicate a possible partial decomposition of the complexes. Their thermal behavior was investigated by TG analysis, in the 25 – 1000°C temperature range, and the decomposition curves of selected samples are presented in Figure 3. It was found that these palladium(II) complexes show a small weight loss, less than 3%, around 150°C, slightly above the clearing points. The poorer thermal stability, also found for other palladium(II) complexes with mixed ligands, Schiff bases and BTU derivatives, could account for the observed shifting of the transition temperatures recorded by DSC.

Compound	Transitions, T/°C (ΔH/kJ [·] mol ⁻¹)
1a	Cr 147 (44.8) Iso 138 (9.9) ^b SmA 134 SmC 106 (11.5) Cr
1b ^c	Cr 143 (46.1) Iso 136 (10.8) ^b SmA 132 SmC 114 (17.9) Cr
1c	Cr 141(51.7) Iso 137 (11.8) ^b SmA 134 SmC 86 (10.2) Cr
1d	Cr 135 (48.3) Iso 137 (10.9) ^b SmA 132 SmC 81 (3.6) Cr
1e	Cr 63(19.2) Cr' 129 (48.0) SmA 135 Iso 133(12.3) ^b SmA 127 SmC 81(9.7) Cr
1f	Cr 82 (28.5) Cr' 126 (32.6) SmA 132 (10.2) Iso 132(12.4) ^b SmA 129 SmC 77 (8.9) Cr
2a	Cr 138 Iso 137 (10.7) ^b SmA 124 SmC
2b ^c	Cr 137 (62.3) Iso 136 (14.0) ^b SmA 133 SmC 63 (2.7) Cr
2c	Cr 132 (59.2) SmA 136 Iso 135(12.4) ^b SmA 132 SmC 110 (18.3) Cr
2d	Cr 125 (54.6) SmA 132 Iso 131(9.1) ^b SmA 126 SmC
2e	Cr 118 (25.7) SmC 128(0.4) SmA 132 (4.4) Iso 132(7.4) ^b SmA 128 SmC
2f	Cr 54 (13.5) Cr' 113 (27.6) SmC 124 (0.3) SmA 127 (3.4) Iso 127(5.7) ^b SmA 123 SmC

Table 1. Thermal	parameters	for	palladium(II) complexes

^aCr, Cr' = crystalline phases, Iso=isotropic phase, SmA = smectic A phase, SmC = smectic C phase; ^bCombined enthalpy of the two transitions Iso-SmA and SmA-SmC; ^cdata reported in ref [33].



Figure 1. The DSC traces of compounds 1c (a) and 1f (b), corresponding to the first heatingcooling cycle.







Figure 2. POM pictures (x200) of complex 2c on cooling at 135°C (a), 132°C (b) and at 125°C (c).

Figure 3. The TG curves for complexes 1d(a), 1f (b), 2d(c) and 2f(d).

In order to confirm the smectic nature of the LC phases displayed by these palladium(II) complexes, compound **1c** was selected for X-ray powder diffraction studies. Thus, the X-ray pattern of **1c**, recorded on cooling from the isotropic state, after a previous heating run above clearing temperature, contains a series of four Bragg diffraction peaks in the low angle region with their ratio 1:2:3:4, which is typical to a layered phase, with layer periodicity in the SmC phase of 59.5Å (Figure 4). Such an observation indicates a lamellar structure, whereby the

calculated interlayer spacing is comparable to the molecular length derived from molecular modelling in an all-trans conformation, by considering the X-ray single-crystal structures for similar palladium(II) complexes previously reported by us.[33, 38] Along with these reflections, a broad peak around 4.6 Å, corresponding to the molten state of the chains, was also observed in the X-ray pattern of complex **1c**, supporting the presence of an LC phase.



Figure 4. XRD powder pattern for compound **1c** recorded at 95°C on cooling from the isotropic state.

Emission properties

Luminescent metallomesogens are of great interest for their application in electrooptical devices, especially, for display applications based on liquid crystals or organic light-emitting diode (OLED) technology. [45-48] The emissive Pd(II) complexes at room temperature are very rare when compared to their Pt(II) analogues, in particular because of the presence of low-lying metal-centered excited states which deactivate the potentially luminescent metal-to-ligand charge transfer (MLCT) and ligand-centered (LC) levels through thermally activated processes.[49-53] Therefore, the prepared palladium(II) complexes were investigated for their emission properties in solid state at room temperature and on heating to isotropic phase. These palladium(II) complexes were almost non-emissive in dichloromethane solution at room temperature. The emission spectrum of a selected complex **1c**, recorded in solid-state at room temperature, is

shown in Figure 5. The emission spectra of all reported palladium(II) complexes show two maxima at λ_{max} around 580 and 650 nm, respectively, with a shoulder around 710 nm when the samples are irradiated in the 330 - 380 nm range. No significant change of position of the maxima emission was observed on changing the carbon chain length of alkoxy groups. The intensity of this yellow-orange emission varies amongst the different palladium(II) complexes, but no correlation with their mesogenic groups could be made.

Recording the emission signal on heating the sample to reach the liquid crystalline state, revealed that the emission is rapidly quenched, which could be explained both by the influence of temperature and self-assembly in the mesophase. By cooling back to room temperature, the emission signal is restored slowly, once the crystallization process developed.



Figure 5. The variable-temperature solid-state emission spectrum of complex **1c** when irradiated in the 330-380 nm region. Inset: microscope pictures taken at room temperature in normal light (top) and under UV light irradiation (bottom).

Conclusions

Yellow-orange-emissive palladium(II)-containing liquid crystalline materials with SmA and SmC mesophases were prepared by using the alkoxy-substituted N-benzoyl thiourea derivatives as auxilliary ligands into the cyclopalladated Schiff base system. The number of carbon atoms of long flexible alkyl tails on the ancillary BTU derivatives as well as on the Schiff base ligands has significant effects on the LC phase character (either monotropic or enantiotropic), thermal ranges of SmA and SmC phases and the corresponding transition temperatures, assigned to different ways of packing inside the LC phases. For the first series **1a-f**, palladium(II) complexes with Schiff base having two hexyloxy terminal groups, there is a minimum chain length of 14 carbon atoms on the BTU ligand for complexes to display enantiotropic SmA phase. In contrast, for the second series 2a-f, complexes with Schiff base having octyloxy terminal groups, the minimum chain length required for changing the monotropic to enatiotropic character of SmA phase decreased significantly to only ten carbon atoms. The thermal stability of these palladium(II) metallomesogens is limited by a slight decomposition on heating above the clearing points. The complexes show interesting luminescent properties with two emission maxima at λ_{max} around 580 and 650 nm, respectively, with a shoulder around 710 nm, when the samples are irradiated in the 330 - 380 nm range.

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Cyclometalated palladium(II) metallomesogens with Schiff bases and *N*-benzoyl thiourea derivatives as co-ligands

Graphical abstract



Highlights

- Cyclometalated palladium(II) metallomesogens with N-benzoyl thiourea ancillary ligands were prepared and studied.
- Palladium(II) metallomesogens display either monotropic or enantiotropic SmA and SmC phases.
- Longer alkyl chains leads to SmA and SmC phase stabilization.
- Palladium(II) metallomesogens show yellow-orange emission in solid-state.

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