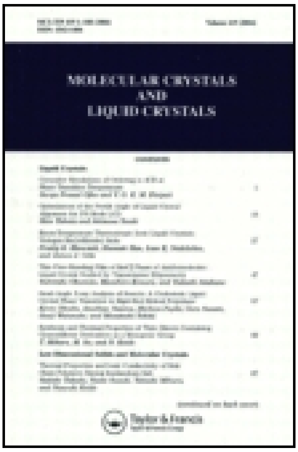

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# Neutral and Cationic Cyclopalladated Nile Red Metallomesogens: Synthesis and Characterization In Memory of Dr. Teresa Pugliese

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# Neutral and Cationic Cyclopalladated Nile Red Metallomesogens: Synthesis and Characterization

## In Memory of Dr. Teresa Pugliese

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*We present the synthesis and characterization of a series of neutral and cationic Nile Red cyclopalladated complexes, first examples of covalent coordination of Nile Red to a Pd(II) metal centre. The Pd(II) coordination sphere is completed by a series of ancillary substituted ligands (acetylacetonates or bipyridine derivatives) selected in order to tune the photophysical properties and/or to enhance the supramolecular order. Both neutral and cationic columnar rectangular metallomesogens have been obtained. Emission has been observed only for neutral complexes (both in solution and mesophase) but quenched in cationic complexes.*

**Keywords** Liquid crystals; metallomesogens; nile red; palladium (II) complexes

## Introduction

Since the last decade, metal-containing liquid crystals (metallomesogens) have been receiving particular attention due to the possibility of combining the properties of transition-metals with the self-organisation of the liquid crystalline (LC) state [1]. Lanthanidomesogens are particularly well studied and recently documented for their attractive luminescent properties in light emitting devices, although their high coordination number is often an obstacle to thermotropic behaviour on a wide temperature range [2]. Pd(II) and Pt(II) metallomesogens present the appealing square-planar geometry with a metal containing core of extendable size by using opportune flat structured ligands and therefore do not present such a geometrical handicap. Cycloplatinated metallomesogens have been studied recently for their luminescent [3] and photoconductive [4] properties. Based on the fact that their corresponding Pd(II) analogues lacked of such property, the photoconductivity of Pt(II) complexes has been attributed to possible Pt$\cdots$Pt intermolecular interactions. In this context we have recently studied a new class of Pd(II) and Pt(II) complexes comprising as a cyclometalled ligand i) azobenzene, ii) benzo[h]quinoline, iii) 2-phenylpyridine and as

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*Address correspondence to Mauro Ghedini, Centro di Eccelenza CEMIF.CAL and LaSCaMM CR-INSTM della Calabria, Dipartimento di Chimica, Università della Calabria 87036, Arcavacata di Rende (CS), Italy. E-mail: m.ghedini@unical.it ancillary ligand a Schiff base [5]. These complexes have shown excellent photorefractive properties when dispersed into a polymeric matrix [6] or in their pure amorphous state [7] correlating their excellent photogeneration-photoconduction properties to their chemical structure [8]. In addition, by grafting opportunely long alkyl chains onto both ligands, and by choosing the right chemical linker to embed these chains, we were able to induce discotic mesophases and obtain UV-Vis to near IR photoconductive cyclopalladated room temperature liquid-crystal complexes [9]. In discotic liquid crystals, the mobility of the photogenerated charges is highly increased along the column stacks due to unidirectional transport. Due to this property, discotics are regarded as a new class of organic semiconductors [8]. Our recent studies on these photoconductive cyclometallated (Pd(II) and Pt(II)) complexes, together with the possibility of inducing discotic mesophases, have led us to envisage other functional molecules to be used as cyclometallating ligands. Our attention has been focused on 9-diethylamino-5-benzo[$\alpha$]phenoxazinone, commonly known as Nile Red (or Nile blue oxazone), a highly fluorescent probe commonly used in chemistry and biology for its remarkable solvatochromism properties [9] but whose potential use as an organometallic ligand has not been yet investigated except in some few cases such as lanthanides coordination compounds [12]. The choice of such molecule has been governed by two important factors: i) its similar chemical structure to benzo[h]quinoline which should lead to comparable reactivity towards a Pd(II) metal centre ii) its high emissive properties which are expected to be transferred to the resulting Pd(II) complexes for the design of highly efficient luminescent metallomesogens.

## Results and Discussion

We report the synthesis of new cyclopalladated complexes of Nile Red **H(NR)**, first examples to the best of our knowledge of direct metal coordination of **H(NR)** to a metal centre, with a series of ancillary ligands allowing fine tuning of their photophysical properties and presenting enhanced supramolecular order and/or liquid crystalline phases. Also, depending on the synthetic route adopted and on the ancillary ligands used, neutral or ionic complexes have been synthesised.

Neutral cyclopalladated complexes of **H(NR)** have been synthesised through a two steps procedure in rather good overall yields (*ca.* 70 to 85%); which involves the formation of the acetato-bridged dimer **I** by reaction of **H(NR)** with $Pd(OAc)_2$ followed by its bridge splitting upon addition of the corresponding acetylacetonate bidentate ligand, as shown in Fig. 1. Following this procedure a series of acetylacetonate complexes **1–4** have been obtained.

All complexes **1–3** exhibit red emission at room temperature in solution through fluorescence process which is rarely observed for Pd (II) complexes [13]. This fluorescence can be attributed to the low-energy ligand-centred excited states. As for the parent free ligand **H(NR)**, both absorption and emission properties are solvatochromic and therefore highly dependent on the solvent polarity. In low-polar solvent such as cyclohexane, enhanced emission is observed. Compared to **H(NR)**, all complexes **1–3** have a lower fluorescence quantum yield ($\phi$). For example, complex **1** emits at room temperature in a dichloromethane solution ($\lambda_{em} = 660$ nm) with $\phi = 23\%$, while **H(NR)** emits in the same conditions ($\lambda_{em} = 602$ nm) with $\phi = 44\%$. However, by increasing the electronegativity of the substituted groups on the acetylacetonate backbone the quantum yield efficiency is enhanced, hence complex **2** in identical conditions emits ($\lambda_{em} = 670$ nm) with $\phi = 35\%$. In a low-polar solvent such as cyclohexane $\phi$ reaches a maximum value of up to 50% [14]. It is also

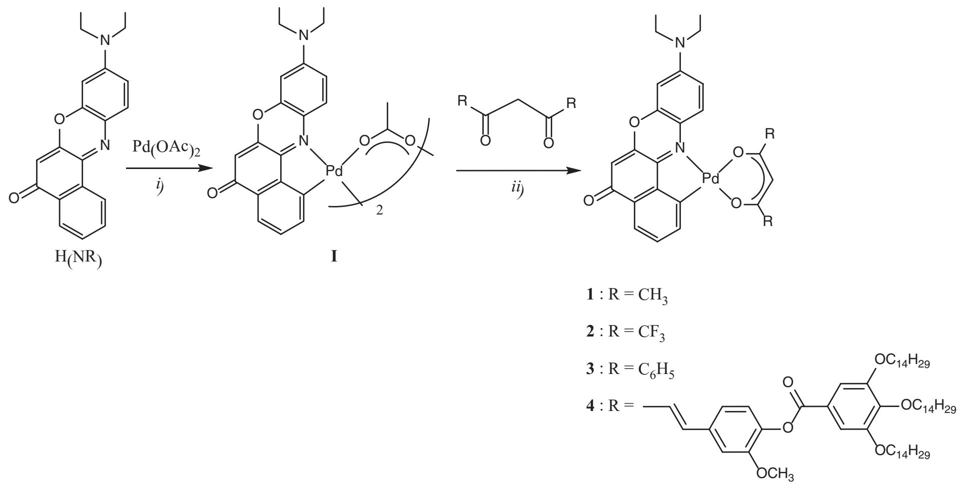

**Figure 1.** Experimental conditions: i) Acetic Acid, 55°C, 4 h; ii) Ethanol, r.t., 12 h.

worthy to note that the emission of all the complexes is slightly red shifted in comparison to **H(NR)** ligand, as a consequence of the direct cyclometallation of **H(NR)** to the Pd (II) metal centre.

Complex **4** obtained by using a polyalkylated ester derivative of curcumin as ancillary ligand shows a discotic columnar mesophase over a wide range of temperature (35–173°C) observed on a polarised microscope [15]. Temperature dependent powder X-Ray diffraction (PXRD) patterns have been recorded proving the formation of a rectangular columnar phase with cell parameters of $a = 92.5$ Å and $b = 41.5$ Å. Indexations of the PXRD spectra obtained at different temperature cycles are reported in Table 1 to show the high stability of the mesophase and the conservation of its rectangular columnar organization in the frozen room temperature state.

The slight increase of the cell parameters as well as the major difference between the observed distance ($d_{obs}$) and the corresponding calculated one ($d_{calcd}$) for the room temperature PXRD spectrum can be easily attributed to the higher rigidity of the frozen columnar organisation in comparison to the corresponding values obtained in the mesophase.

Noteworthy, these cell parameters are much larger than the values of the radius of the hemi-disk like shaped complex **4** (evaluated of *ca.* 37 Å) indicating a possible association of two molecular entities assembled probably through a hydrogen bonds between the oxygen atoms and the aromatic hydrogen atoms of the NR fragment of paired molecules. This side by side interaction results in a formation of a full disk-shape like dimer which constitutes the columnar stacks as represented in Fig. 2.

Complex **4** also shows red emission ($\lambda_{em} = 660$ nm) at room temperature in a dichloromethane solution with a 23% quantum yield efficiency. Remarkably, emission is maintained in the mesophase although slightly blue shifted ($\lambda_{em} = 610$ nm), probably due to the different polar environment in which molecules are assembled in the liquid crystalline state. Moreover, this shift is indicative that the solvatochromic properties of the **H(NR)** ligand are preserved as previously observed for complexes **1–3.**

Taking advantage from the well known chemistry of the cyclopalladated compounds, [16], and in order to study the possible effects of charges and the presence of the counter anions onto the supramolecular organisation we have synthesised cationic cyclopalladated

**Table 1.** Detailed indexations of the PXRD spectra of complex **4**

| Temp. | $d_{obs}$ (Å) | *hk* | $d_{calcd}$ (Å) | Mesophase and cell parameters |
|---|---|---|---|---|
| 160°C | 46.27 | 20 | 46.27 | Col$_{r}$ |
| | 37.88 | 11 | 37.88 | $a_r = 92.5$ Å |
| On first heating | 24.79 | 31 | 24.76 | $b_r = 41.5$ Å |
| from obtained | 20.76 | 02 | 20.76 | |
| raw material | 13.89 | 03 | 13.84 | |
| | 12.64 | 33 | 12.63 | |
| | 4.56 | $h_{ch}$ | — | |
| | 3.44 | $h_0$ | — | |
| 140°C | 46.46 | 20 | 46.46 | Col$_{r}$ |
| | 38.57 | 11 | 38.57 | $a_r = 92.9$ Å |
| On second | 24.53 | 31 | 25.01 | $b_r = 42.4$ Å |
| heating cycle | 21.78 | 02 | 21.20 | |
| | 14.07 | 03 | 14.13 | |
| | 12.83 | 33 | 12.86 | |
| | 4.56 | $h_{ch}$ | — | |
| | 3.39 | $h_0$ | — | |
| Room Temp. | 48.00 | 20 | 48.00 | frozen Col$_{r}$ |
| | 39.94 | 11 | 39.94 | $a_r = 96$ Å |
| After first | 26.46 | 31 | 25.86 | $b_r = 43.9$ Å |
| heating-cooling | 20.53 | 41 | 21.06 | |
| cycle | 14.83 | 03 | 14.64 | |
| | 11.18 | 53 | 11.64 | |
| | 4.38 | $h_{ch}$ | — | |
| | 3.38 | $h_0$ | — | |

complexes of comparable structure. Two differently polyalkylated bipyridines H(C$_{n,m}$-bipy) were used as ancillary ligands to afford complexes **5** and **6** of general formula: [NRPd(C$_{n,m}$-bipy)]$^{+}$[OTf]$^{-}$ where C$_{n,m}$ represents the number and the length of the substituted alkyl chains as illustrated in Fig. 3 (for complex **5:** n = 2, m = 9; for complex **6**: n = 6, m = 12). While H(C$_{2,9}$-bipy) is commercially available, H(C$_{6,12}$-bipy) was synthesised following the previously reported procedure [14]. In particular complex **6** presents identical number of alkyl chains than its neutral parent complex **2**, with only two carbon atoms shorter, allowing structural comparison.

Complexes **5** and **6** were synthesised from the previously obtained acetato-bridge dimer **I** which was engaged in a metathesis reaction in excess of lithium chloride in ethanol/water to afford in quantitative yield the corresponding chloro-bridge dimer intermediate **II**. Bridge splitting reaction of **II** with the formation of the new ionic species were effectuated in acetone solution in the presence of quantitative amount of silver triflate, followed by addition of the corresponding H(C$_{n,m}$-bipy) bipyridine ligand after filtration of the silver chloride precipitate.

Both complexes **5** and **6** were obtained as intense dark blue waxy solids, highly soluble in most organic solvents. IR spectra shown the characteristic stretching bands of the triflate (OTf) counter ion observed at 1257, 1030 and 638 cm$^{-1}$ as well as the intense stretching

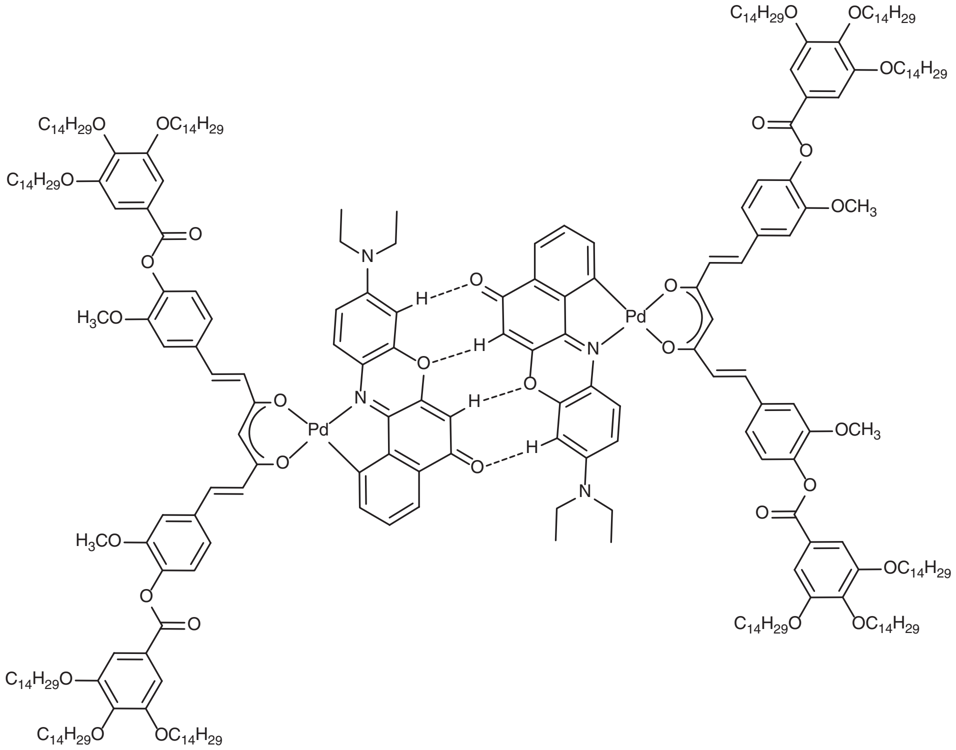

Figure 2. Sketch of the predicted disk shape-like dimer constituting the rectangular mesophase of complex **4**.

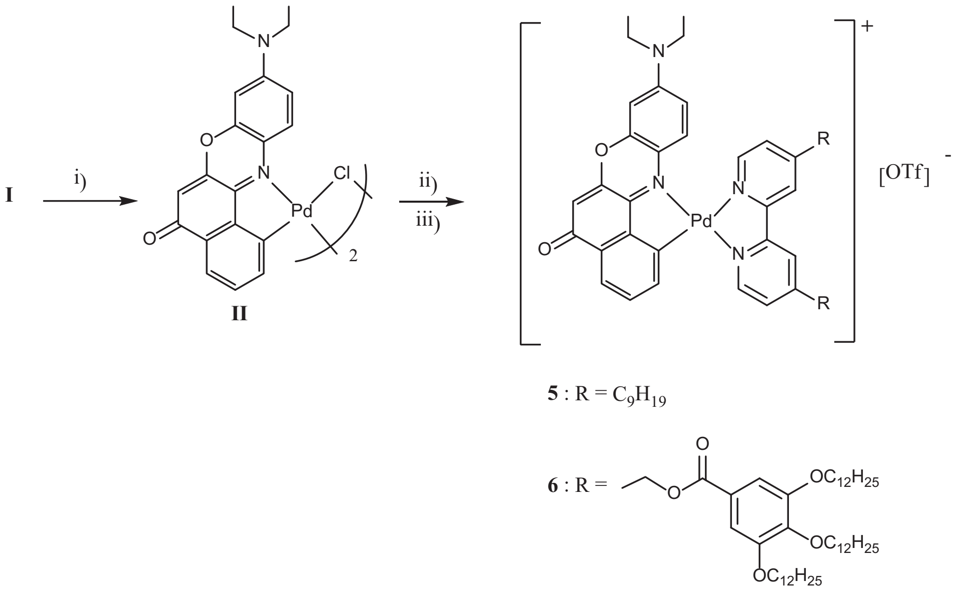

Figure 3. Reagents and conditions: i) LiCl, Ethanol/Water, r.t., 5 days; ii) $AgCF_3SO_3$, Acetone, reflux for 2 h, r.t. for 12 h; iii) H(Cn,m-bipy), Acetone, reflux for 6 h, r.t. for 12 h.

**Table 2.** Detailed indexation of the PXRD spectra of complex **5** obtained by annealing from the melt (160°C) for 24 h at 100°C followed by 5 h at 50°C

| T (°C) | $d_{obs}$ (Å) | *hk* | $d_{calcd}$ (Å) | Mesophase and cell parameters |
|---|---|---|---|---|
| 50°C | 36.48 | 20 | 36.48 | $Col_r$ |
|  | 21.22 | 11 | 21.22 | $a_r = 72.96$ Å |
| After annealing | 18.94 | 21 | 18.95 | $b_r = 22.18$ Å |
| at 100°C for 24 h | 16.67 | 31 | 16.39 |  |
| and at 50°C for 5 h | 4.46 | $h_{ch}$ | — |  |

band at 1635 $cm^{-1}$ characteristic of NR fragment carbonyl group. The intensity of the dark colour of both complexes and the high viscosity of the samples prevented a constructive observation through POM microscopy and lead to a high difficulty in the phase transition temperature determination. Nonetheless, on the basis of the increased fluidity observed during heating, a melting temperature of ca. 180°C and ca. 160°C for complexes **5** and **6** respectively can be attributed. The thermal behavior of these complexes was investigated by thermogravimetric analysis (TGA) showing that both complexes are stable up to ca. 200°C. Differential scanning calorimetry (DSC) run at 5°C/min and 2°C/min scan rates did not present for both complexes any visible thermal transitions indicating a complete amorphous/glassy state. However, under PXRD analysis, while complex **5** showed typical broad patterns of a glassy state morphology independently on the temperature/time chosen, complex **6** upon annealing from the melt (160°C) at 100°C for 24 h and further 5 h at 50°C presented a PXRD pattern characteristic of a columnar organization, which indexation is reported in Table 2.

As for its parent neutral complex **4**, the high cell parameter obtained for complex **6** ($a = 72.96$ Å) is indicative of the presence of a similar dimeric association of molecules, leading to a full disk-shape like structure.

The long time required for the development of the columnar texture of complex **6** and the low resolution of its PXRD spectrum (in terms of peak numbers and intensity) compared with the PXRD spectrum obtained for complex **4** is indicative of a higher disorder. This latter could be easily attributed to both the presence of the triflate counter ion as well as the electrostatic repulsions that seem to hinder the stacking efficiency within the columns more than the formation of the hydrogen bonding network within the dimer. The lower number of alkyl chains results in absence of thermotropic behaviour for complex **5** which remains in its glassy state until its thermal decomposition at ca. 200°C.

Unfortunately for both complexes, light emission was not observed in solution nor in the solid state most likely due to the quenching of the bipyridine ancillary ligands by electronic effects.

## Conclusions

Through the synthesis of complexes **1–6**, we have shown the possibility of using Nile Red as a cyclometallated ligand obtaining either neutral or cationic cyclopalladated complexes. When acetylacetonate is used as ancillary ligands, neutral complexes **1–4** are obtained, which maintain both the emission and solvatochromic properties of Nile Red. By opportune functionalisations such as the introduction of long alkyl chains into the acetylacetonate backbone, it has been possible to obtain a highly ordered discotic metallomesogen on a wide temperature range, showing red emission both in solution and in the mesophase. Furthermore, cationic cyclopalladated complexes **5** and **6** have been obtained presenting, in the case of 12 alkyl chains, a disordered columnar liquid-crystal organisation. As a result of the structural similarities between metallomesogens **4** and **6**, it has been possible to observe the influence of charges onto the columnar supramolecular organisation of the mesophase. Electrostatic interactions generated by the ionic nature of complex **6** do not prevent the formation of the dimers that constitute the building blocks of the mesophase, but increase the intracolumnar disorder, hindering the mesophase induction upon cooling. The emission quenching observed for the cationic complexes **5** and **6** could be most likely attributed to the presence of the bipyridine ancillary ligand. Further studies are currently under working progress to investigate the effect of different ancillary ligands with the intention to prevent emission quenching effects.

## Experimental

The acetato-bridged dimer **I** and complexes **1–4** were synthesised following previously described procedures [13–15].

The chloro-bridged dimer **II** was synthesised as followed:

To a suspension of **I** (246 mg, 0.255 mmol) in 22 ml ethanol/water: (10/1 v/v) were added 20 eq. of LiCl (216 mg, 5.096 mmol) and the obtained solution was stirred at room temperature and dark conditions for 5 days. The precipitate was filtered, washed with water and dichloromethane, and dried under vacuum.

Black solid, yield 96%, m.p. >250 °C, FT-IR (KBr, $cm^{-1}$): 3069, 2972, 2937, 2904, 2866, 2689, 1776, 1636 (Nile Red CO), 1617, 1575, 1544, 1524, 1490, 1403, 1352, 1305, 1279, 1352, 1305, 1279, 1247, 1183, 1123, 1091, 1075, 1019, 953, 853, 797, 769, 716, 697, 650, 517, 507, elemental analysis: calcd (%) for $C_{40}O_4N_4H_{34}PdCl_2$ (918.48): C 52.31, H 3.73, N 6.10, found C 52.33, H 3.70, N 6.12.

Complex **5** was synthesised through the following procedure:

To a suspension of **II** (55 mg, 0.05 mmol) in 10 mL of acetone were added 2 eq. (31 mg, 0.10 mmol) of AgOTf. The blue solution obtained was stirred at reflux for 2 h and at room temperature overnight. The AgCl precipitated was filtered off and to the resulting solution 2 eq. (50 mg, 0.11 mmol) of H($C_{2,9}$-bipy) were added. The mixture was stirred at reflux for 6 hours and at room temperature overnight. The solvent was evaporated under reduced pressure and the final complex was recrystallized from dichloromethane/heptane to yield a dark solid.

Dark-blue solid, yield 40%, m.p.: 180 °C, FT-IR (KBr, $cm^{-1}$): 3059, 2926 (alifatic CH), 1635 (Nile Red CO), 1615, 1581, 1493, 1462, 1409, 1379, 1355, 1276, 1257 (OTf), 1221, 1158, 1120, 1030 (OTf), 803, 716, 638 (OTf), 589, 573, 519, 491, 450; $^1$H-NMR (300 MHz, $CDCl_3$, 25°C, TMS, ppm): 8.6–8.5 (m, 2H), 8.30 (s, 1H), 8.15 (s, 1H), 7.77–7.75 (m, 1H), 7.65–7.48 (m, 4H), 7.42–7.39 (m, 1H), 6.75–6.71 (m, 1H), 6.55 (s, 1H), 6.19 (s, 1H), 3.53 (q, 6.6 Hz, 4H), 2.86 (m, 4H), 1.72 (m, 4H), 1.26 (m, 30 H), 0.87 (t, 6.24 Hz, 6H); elemental analysis: calcd (%) for $C_{49}N_4O_5H_{61}PdF_3S$ (981.63): C 59.96, H 6.26, N 5.71, F 5.81, found C 59.90, H 6.30, N 5.73, F 5.78.

Complex **6** was similarly synthesised using the corresponding H($C_{6,12}$-bipy) bipyridine ligand [17]:

Purification of the crude solid was performed by successive precipitations in acetone/methanol solutions (freezer) and filtrations of the non reacted bipyridine ligand to obtain **6** as a waxy solid.

Blue solid, yield 40%, m.p.: 160°C, FT-IR (KBr, $cm^{-1}$): 2924, 2853 (alifatic CH), 1718 (CO), 1635, 1615, 1583, 1495, 1466, 1429, 1335, 1256 (OTf), 1160, 1118, 1030 (OTf), 848, 765, 720, 638 (OTf); $^1$H-NMR (300 MHz, $CDCl_3$, 25°C, TMS, ppm): 8.9–8.7 (m, 2H), 8.45 (s, 1H), 8.35 (s, 1H), 8.0–7.9 (m, 1H), 7.8–7.5 (m, 4H), 7.4–7.3 (m, 6H), 6.75 (s, 1H), 6.55 (s, 1H), 5.6 (s, 4H), 4.05 (m, 16H), 3.65 (m, 4H), 1.8 (m, 12H), 1.4–0.9 (m, 114 H), 0.9–0.5 (m, 18H); elemental analysis: calcd (%) for $C_{75}N_4O_8H_{102}PdF_3S$ (1899.89): C 47.41, H 5.41, N 2.95, F 2.99, found C 47.43, H 5.39, N 2.97, F 3.0.

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