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$Ru_2(CO)_4(OOCR)_2L_2$ sawhorse-type complexes containing axial 5-(4-pyridyl)-10,15,20-triphenylporphyrin ligands

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A B S T R A C T

The thermal reaction of $Ru_3(CO)_{12}$ with various carboxylic acids (benzoic, 4-hydroxyphenylacetic, ferrocenic, stearic, oleic, 4-(octadecyloxy)benzoic) in refluxing tetrahydrofuran, followed by addition of 5-(4-pyridyl)-10,15,20-triphenylporphyrin (L), gives the dinuclear complexes $Ru_2(CO)_4(OOCR)_2L_2$ (**1**: R = $-C_6H_5$, **2**: R = $-CH_2$-*p*-C_6H_4OH, **3**: R = $-C_5H_4FeC_5H_5$, **4**: R = $-(CH_2)_{16}CH_3$, **5**: R = $-(CH_2)_7CH{=}CH(CH_2)_7CH_3$, **6**: R = -*p*-$C_6H_4O(CH_2)_{17}CH_3$). Complexes **1**–**6** were characterised by IR, NMR, and ESI-MS as well as by elemental analysis. The UV–Vis spectra show the Soret band centred at 417 nm and the Q bands at 515, 550, 590 and 645 nm, respectively.

Keywords

Carbonyl ligands , Carboxylato bridges, Sawhorse complexes, Dinuclear complexes, Ruthenium, Porphyrin

1. Introduction

Sawhorse-type ruthenium complexes of the type $Ru_2(CO)_4(OOCR)_2L_2$, L being a two-electron donor ligand, are well-known since 1969, when Lewis and co-workers reported their formation by refluxing $Ru_3(CO)_{12}$ in various carboxylic acids followed by depolymerisation of the obtained materials in coordinating solvents [1]. These dinuclear complexes were shown later, by a single-crystal X-ray structure analysis of $Ru_2(CO)_4(OOCBu^n)_2(PBu^t_3)_2$, to possess a $Ru_2(CO)_4$ backbone in a sawhorse-type arrangement with two μ_2-η^2-carboxylato bridges ($OOCBu^n$) and two axial two-electron donor ligands (PBu^t_3) [2]. Since their discovery, a considerable number of such sawhorse-type diruthenium complexes with carboxylato bridges have been synthesised and used for various applications ranging from catalysis to materials chemistry [3]. Recently, we found porphyrin derivatives of complexes of the type $Ru_2(CO)_4(OOCR)_2L_2$ (R = methyl, 5-(4-phenyl)-10,15,20-triphenylporphyrin; L = triphenylphosphine, 1,3,5-triaza-7-phosphatricyclo[3.3.1.1]decane, 5-(4-pyridyl)-10,15,20-triphenylporphyrin) to exhibit considerable phototoxicity specific for certain cancer cell lines [4]. Herein, we report the synthesis and characterisation of six new $Ru_2(CO)_4(OOCR)_2L_2$ sawhorse-type complexes containing 5-(4-pyridyl)-10,15,20-triphenylporphyrin as the axial ligands L.

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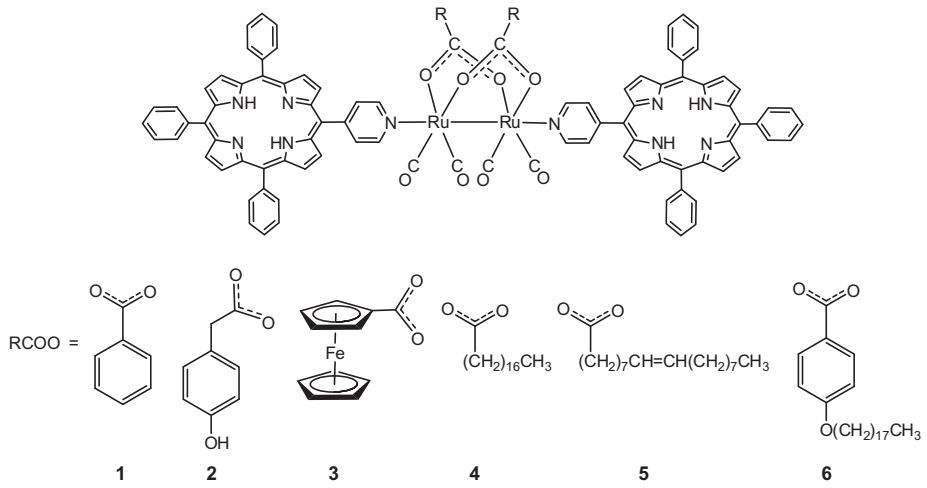
2. Results and discussion

Dodecacarbonyltriruthenium reacts with the appropriate carboxylic acid (benzoic, 4-hydroxyphenylacetic, ferrocenic, stearic, oleic, 4-(octadecyloxy)benzoic) in refluxing tetrahydrofuran to give, after addition of the axial ligand 5-(4-pyridyl)-10,15,20-triphenylporphyrin (L), the dinuclear complexes $Ru_2(CO)_4(OOCR)_2L_2$ (**1** = $Ru_2(CO)_4(OOCC_6H_5)_2L_2$; **2** = $Ru_2(CO)_4(OOCCH_2$-*p*-$C_6H_4OH)_2L_2$; **3** = $Ru_2(CO)_4(OOCC_5H_4FeC_5H_5)_2L_2$; **4** = $Ru_2(CO)_4\{OOC(CH_2)_{16}CH_3\}_2L_2$; **5** = $Ru_2(CO)_4\{OOC(CH_2)_7CH{=}CH(CH_2)_7CH_3\}_2L_2$; **6** = $Ru_2(CO)_4\{OOC$-*p*-$C_6H_4O(CH_2)_{17}CH_3\}_2L_2$) in good yields (73–86%), see Scheme 1.

$$2/3Ru_3(CO)_{12} + RCOOH + 2L \rightarrow Ru_2(CO)_4(OOCR)_2L_2 + 4CO + 2H_2$$

All compounds are air-stable dark purple crystalline powders, sparingly soluble in polar organic solvents, which have been characterised by their infrared, NMR, UV–Vis and mass spectrometry as well as by their micro-analytical data. All compounds exhibit in the $\nu_{(CO)}$ region of the infrared spectrum the characteristic pattern of the $Ru_2(CO)_4$ sawhorse unit [3], which consists of three bands (very strong; medium; very strong) between 2100 and 1900 cm^{-1} (Table 1). The two carboxylato bridges give rise to two $\nu_{(OCO)}$ absorptions between 1550 and 1430 cm^{-1} that correspond to the asymmetrical and the symmetrical stretching frequencies of the three-atom oscillators. Moreover, due to the presence of the porphyrinic axial ligands, a strong absorption centred at 1595 cm^{-1} corresponding to $\nu_{(CN)}$ is observed, along with a strong absorption



Scheme 1. Synthesis of the dinuclear complexes $Ru_2(CO)_4(OOCR)_2L_2$ (**1**–**6**).

Table 1
Infrared data of complexes **1**–**6** (CH_2Cl_2).

Complex	$\nu_{(CO)}$ (cm^{-1})	$\nu_{(CN)}$ (cm^{-1})	$\nu_{(OCO)}$ (cm^{-1})
1	2026.18 vs, 1976.90 m, 1941.93 s	1598.47 s	1548.55 s, 1440.36 m
2	2026.30 vs, 1976.75 m, 1942.01 vs	1598.26 s	1547.63 s, 1439.77 m
3	2026.12 vs, 1976.77 m, 1941.53 vs	1598.43 s	1555.54 s, 1439.83 m
4	2025.14 vs, 1977.93 m, 1940.76 vs	1594.67 s	1552.05 s, 1439.75 m
5	2025.34 vs, 1977.85 m, 1940.69 vs	1594.23 s	1554.12 s, 1441.47 m
6	2025.23 vs, 1977.82 m, 1940.63 vs	1594.58 s	1555.71 s, 1438.68 m

for the in-plane N–H deformation at 1215 cm^{-1} and a medium absorption corresponding to the C–H stretching vibration at 3055 cm^{-1} [5].

The ^1H NMR spectra of **1**–**6** in CD_2Cl_2 at 23 °C display a similar signal pattern for the protons of the coordinated 5-(4-pyridyl)-10,15,20-triphenylporphyrin units (L). The N–H protons of the L axial ligands are observed at $\delta = -2.78$ ppm, while two multiplets at 7.84 and 8.26 ppm are found in the aromatic region corresponding to the protons of the phenyl rings. In addition, two broad unresolved singlets of equal intensity for the pyrrole protons ($\delta = 8.9$ and 9.0 ppm) and two doublets for the pyridyl group ($\delta = 8.4$ and 9.5 ppm) are observed. These signals are in agreement with those found in the mononuclear arene ruthenium porphyrin complexes, [(η^6-arene)$RuCl_2$L] (arene = *p*-cymene, toluene) [6]. In the ^{13}C {^1H} NMR spectra, the peaks of the terminal carbonyl groups and of the carboxylato bridges are found around 180 and 205 ppm, respectively, in agreement with those reported in the literature [7–9].

The complexes were characterised by electrospray ionisation mass spectroscopy in positive mode. In all cases, a major peak at *m*/*z* = 1789.36 for **1**, 1849.37 for **2**, 1876.21 for **3**, 2113.82 for **4**, 2109.79 for **5** and 2325.90 for **6**, corresponding to $[M+H]^+$ have been assigned unambiguously on the basis of their characteristic Ru_2 isotope pattern.

Optical absorption spectra of **1**–**6** as well as the porphyrin ligand (L) were acquired in dichloromethane at 10^{-5} M concentration in the range 250–800 nm (Fig. 1). The UV–Vis spectra of all compounds are characterised by intense absorptions due to the porphyrin ligands, including the Soret band at around 420 nm and a series of Q bands between 500 and 700 nm. The four Q bands are labelled I, II, III and IV on going from longer to shorter wavelength (Table 2). The data in Table 2 show that the absorption bands of the uncoordinated 5-(4-pyridyl)-10,15,20-triphenylporphyrin compound remain unchanged upon coordination to the dinuclear sawhorse unit, thus suggesting no perturbation of the porphyrin π-orbitals upon coordination.

The fluorescence spectra of L and **1**–**6** are presented in Fig. 2. Their fluorescence spectra show after excitation at 350 nm two red shifted emission peaks, a strong peak at 650 nm and a weak one at about 705 nm which is the mirror image of the absorption band. These spectral properties are in good agreement with those reported for 5-(4-pyridyl)-10,15,20-triphenylporphyrin [10].

In conclusion, we have synthesised and characterised six new sawhorse-type complexes containing various carboxylato bridging ligands and the 5-(4-pyridyl)-10,15,20-triphenylporphyrin axial ligands. However, possible biological applications are limited due to the low solubility of these compounds.

3. Experimental

3.1. General

All manipulations were carried out by routine under nitrogen atmosphere. Organic solvents were degassed and saturated with nitrogen prior to use. All carboxylic acids (benzoic, 4-hydroxyphenylacetic, ferrocenic, stearic, oleic and 4-(octadecyloxy)benzoic acid) were purchased either from Aldrich or Fluka and used as received, while 5-(4-pyridyl)-10,15,20-triphenylporphyrin was purchased from TriPorTech GmbH, Germany. Dodecacarbonyltriruthenium was prepared according to published methods [11]. NMR spectra were recorded on a Bruker AvanceII 400 MHz spectrometer. IR spectra were recorded on a Perkin-Elmer 1720X FT-IR spectrometer (4000–400 cm^{-1}). UV–Vis absorption spectra were recorded on an Uvikon 930 spectrophotometer using precision cells made of quartz (1 cm). Fluorescence spectra were recorded on a Luminescence Spectrometer Perkin-Elmer LS50B using precision cells made of quartz (1 cm). Mass spectra were obtained in positive-ion mode with a Bruker FTMS 4.7T BioAPEX II mass spectrometer, University of Fribourg, Switzerland. Elemental analyses were performed by the Mikroelementarisches Laboratorium, ETH Zürich or the Laboratory of Pharmaceutical Chemistry, University of Geneva, Switzerland.

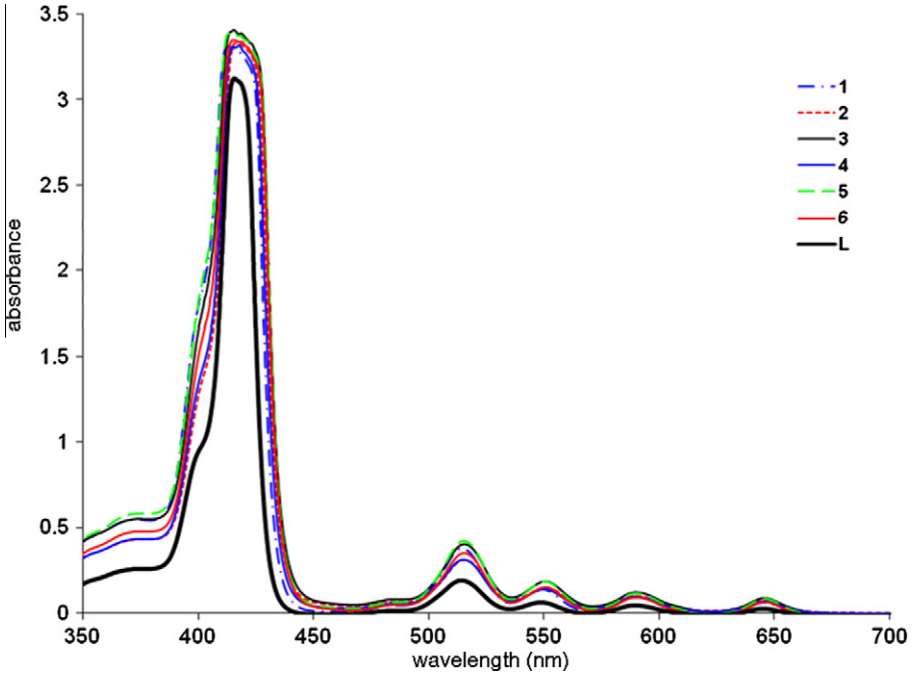


Fig. 1. Optical spectra of L and complexes **1**–**6** at 10^{-5} M concentration in CH_2Cl_2 solution at room temperature.

Table 2
UV–Vis data for L and complexes **1**–**6** at 10^{-5} M concentration in CH_2Cl_2 solution at room temperature[a].

Compound	Soret	Visible IV	Visible III	Visible II	Visible I
1	413 (331)	514 (37.7)	549 (13.7)	589 (9.6)	645 (6.0)
2	416 (333)	515 (21.2)	550 (15.1)	590 (10.2)	645 (7.6)
3	415 (341)	515 (40.1)	550 (18.2)	590 (11.9)	645 (8.5)
4	417 (332)	515 (31.4)	550 (14.1)	590 (9.6)	645 (7.1)
5	414 (340)	515 (41.9)	550 (18.1)	590 (11.3)	645 (8.0)
6	416 (335)	515 (35.2)	550 (15.2)	590 (9.2)	645 (6.6)
L	415 (313)	514 (19.0)	548 (6.1)	589 (4.4)	645 (2.5)

[a] λ_{max} (extinction coefficient ($\varepsilon \times 10^{-3}$, $M^{-1}\,cm^{-1}$)).

*3.2. General method for the preparation of complexes **1**–**6***

A solution of $Ru_3(CO)_{12}$ (50 mg, 0.07 mmol) and the appropriate carboxylic acid (0.22 mmol: 28 mg, **1**; 34 mg, **2**; 52 mg, **3**; 62 mg, **4**; 62 mg, **5**; 86 mg, **6**) in dry tetrahydrofuran (25 ml) was heated at 120 °C in a pressure Schlenk tube for 18 h. Then the solvent was evaporated to give a purple or brown residue which was dissolved in tetrahydrofuran and 3 equiv. of 5-(4-pyridyl)-10,15,20-triphenylporphyrin (0.22 mmol, 135 mg) was added. The solution was stirred at room temperature for 3 h, and the product was isolated by precipitation upon addition of diethyl ether. The precipi-

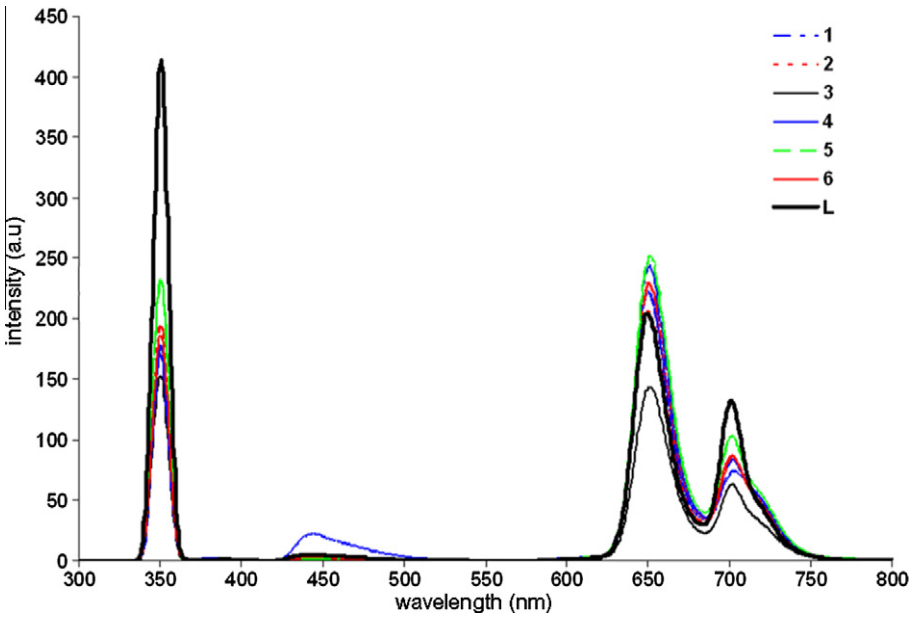


Fig. 2. Fluorescence emission spectra of L and complexes **1**–**6** at 10^{-5} M concentration in CH_2Cl_2 solution upon excitation at 350 nm at room temperature.

tate was filtered and dried under vacuum to give air-stable purple crystalline powders.

3.2.1. $Ru_2(CO)_4(OOCC_6H_5)_2(L)_2$: ***1***

Yield: 339 mg (86%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = −2.76 (s, 4H, N*H*), 7.43–7.50 (m, 10H, C_6H_5), 7.82–7.85 (m, 18H, C_6H_5), 8.26–8.30 (m, 12H, C_6H_5), 8.54 (d, 4H, NC_5H_4, $^3J_{H-H}$ = 6 Hz), 8.93 (br s, 8H, C*H*$_{porph}$), 9.11 (br s, 8H, C*H*$_{porph}$), 9.47 ppm (d, 4H, NC_5H_4, $^3J_{H-H}$ = 6 Hz). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 120.95, 126.89, 128.18, 129.94, 130.73, 130.98, 133.56, 134.75, 142.05, 152.43, 179.33, 197.60, 204.77 ppm. IR (CH_2Cl_2): $\nu_{(porphyrin\ N-H)}$ 1214.19 s, $\nu_{(OCO)}$ 1440.36 m, $\nu_{(OCO)}$ 1548.55 s, $\nu_{(CN)}$ 1598.47 s, $\nu_{(CO)}$ 1941.93 vs, $\nu_{(CO)}$ 1976.90 m, $\nu_{(CO)}$ 2026.18 vs, $\nu_{(aromatic\ C-H)}$ 3052.34 m, cm^{-1}. ESI-MS: *m*/*z* = 1789.36 [M+H$^+$]. *Anal.* Calc. for $C_{104}H_{68}N_{10}O_8Ru_2$: C, 69.87; H, 3.83; N, 7.83. Found: C, 69.66; H, 3.95; N, 7.72%.

3.2.2. $Ru_2(CO)_4(OOCCH_2$-p-$C_6H_4OH)_2(L)_2$: ***2***

Yield: 349 mg (85%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = −2.79 (s, 4H, N*H*), 3.62 (s, 4H, −C*H*$_2$-*p*-C_6H_4–OH), 6.57 (d, 4H, C_6H_4), 7.02 (d, 4H, C_6H_4), 7.77–7.83 (m, 18H, C_6H_5), 8.21–8.26 (m, 12H, C_6H_5), 8.88 (br s, 8H, C*H*$_{porph}$), 8.92 (br s, 8H, C*H*$_{porph}$), 8.94 (d, 4H, NC_5H_4, $^3J_{H-H}$ = 6 Hz), 9.40 ppm (d, 4H, NC_5H_4, $^3J_{H-H}$ = 6 Hz). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 42.92, 53.93, 114.95, 115.41, 120.94, 121.45, 126.94, 128.02, 128.82, 130.58, 130.68, 130.72, 134.65, 134.68, 141.92, 150.24, 152.04, 154.33, 185.49, 204.70 ppm. IR (CH_2Cl_2): $\nu_{(porphyrin\ N-H)}$ 1214.55 s, $\nu_{(OCO)}$ 1439.77 m, $\nu_{(OCO)}$ 1547.63 s, $\nu_{(CN)}$ 1598.26 s, $\nu_{(CO)}$ 1942.01 vs, $\nu_{(CO)}$ 1976.75 m, $\nu_{(CO)}$ 2026.30 vs, $\nu_{(aromatic\ C-H)}$ 3055.74 m, cm^{-1}. ESI-MS: *m*/*z* = 1849.37 [M+H$^+$]. *Anal.* Calc. for $C_{106}H_{72}N_{10}O_{10}Ru_2$: C, 68.90; H, 3.93; N, 7.58. Found: C, 68.74; H, 4.06; N, 7.43%.

3.2.3. $Ru_2(CO)_4(OOCC_5H_4FeC_5H_5)_2(L)_2$: ***3***

Yield: 342 mg (77%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = −2.76 (s, 4H, N*H*), 4.27 (s, 10H, C*H*$_{Fc}$), 4.33 (d, 4H, C*H*$_{Fc}$), 4.92 (t, 4H, C*H*$_{Fc}$), 7.81–7.87 (m, 18H, C_6H_5), 8.26–8.30 (m, 12H, C_6H_5), 8.52 (d, 4H, NC_5H_4, $^3J_{H-H}$ = 6 Hz), 8.93 (br s, 8H, C*H*$_{porph}$), 9.06 (br s, 8H, C*H*$_{porph}$), 9.43 ppm (d, 4H, NC_5H_4, $^3J_{H-H}$ = 6 Hz). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 29.77, 69.86, 70.54, 70.76, 120.95, 121.45, 126.89, 126.94, 128.03, 130.79, 134.66, 134.67, 141.94, 150.34, 186.29, 204.43 ppm. IR (CH_2Cl_2): $\nu_{(porphyrin\ N-H)}$ 1214.23 s, $\nu_{(OCO)}$ 1439.83 m, $\nu_{(OCO)}$ 1555.54 s, $\nu_{(CN)}$ 1598.43 s, $\nu_{(CO)}$ 1941.53 vs, $\nu_{(CO)}$ 1976.77 m, $\nu_{(CO)}$ 2026.12 vs, $\nu_{(aromatic\ C-H)}$ 3053.61 m, cm^{-1}. ESI-MS: *m*/*z* = 1876.21 [M+H$^+$]. *Anal.* Calc. for $C_{102}H_{67}Fe_2N_{10}O_8Ru_2$: C, 65.36; H, 3.60; N, 7.47. Found: C, 65.35; H, 3.66; N, 7.33%.

3.2.4. $Ru_2(CO)_4(OOC(CH_2)_{16}CH_3)_2(L)_2$: ***4***

Yield: 342 mg (73%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = −2.78 (s, 4H, N*H*), 0.75 (t, 6H, −(CH$_2$)$_{16}$–C*H*$_3$), 0.85–1.46 (m, 56H, −(CH$_2$)$_2$–(C*H*$_2$)$_{14}$–CH$_3$), 1.79 (q, 4H, −CH$_2$–C*H*$_2$–(CH$_2$)$_{14}$–CH$_3$), 2.56 (t, 4H, −C*H*$_2$–CH$_2$–(CH$_2$)$_{14}$–CH$_3$), 7.80–7.86 (m, 18H, C_6H_5), 8.25–8.28 (m, 12H, C_6H_5), 8.40 (d, 4H, NC_5H_4, $^3J_{H-H}$ = 6 Hz), 8.92 (br s, 8H, C*H*$_{porph}$), 9.01 (br s, 8H, C*H*$_{porph}$), 9.26 ppm (d, 4H, NC_5H_4, $^3J_{H-H}$ = 6 Hz). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 13.85, 22.62, 26.58, 29.18, 29.44, 29.47, 29.52, 29.54, 29.61, 29.73, 29.82, 31.81, 37.21, 120.92, 126.88, 126.92, 128.02, 130.78, 134.66, 141.96, 150.26, 187.52, 204.86 ppm. IR (CH_2Cl_2): $\nu_{(porphyrin\ N-H)}$ 1214.30 s, $\nu_{(OCO)}$ 1439.75 m, $\nu_{(OCO)}$ 1552.05 s, $\nu_{(CN)}$ 1594.67 s, $\nu_{(CO)}$ 1940.76 vs, $\nu_{(CO)}$ 1977.93 m, $\nu_{(CO)}$ 2025.14 vs, $\nu_{(aromatic\ C-H)}$ 3054.37 m, cm^{-1}. ESI-MS: *m*/*z* = 2113.82 [M+H$^+$]. *Anal.* Calc. for $C_{126}H_{128}N_{10}O_8Ru_2$: C, 71.64; H, 6.11; N, 6.63. Found: C, 71.36; H, 5.94; N, 6.55%.

3.2.5. $Ru_2(CO)_4(OOC(CH_2)_7CH{=}CH(CH_2)_7CH_3)_2(L)_2$: ***5***

Yield: 386 mg (83%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = −2.79 (s, 4H, N*H*), 0.75 (t, 6H, −(CH$_2$)$_7$–CH=CH–(CH$_2$)$_7$–C*H*$_3$), 0.85–1.43 (m, 44H, −CH$_2$–(C*H*$_2$)$_5$–CH$_2$–CH=CH–CH$_2$–(C*H*$_2$)$_6$–CH$_3$), 1.77 (m, 8H, −(CH$_2$)$_6$–C*H*$_2$–CH=CH–C*H*$_2$–(CH$_2$)$_6$–CH$_3$), 2.54 (t, 4H, −C*H*$_2$–(CH$_2$)$_6$–CH=CH–(CH$_2$)$_7$–CH$_3$), 4.99 (m, 4H, −CH$_2$–(CH$_2$)$_6$–C*H*=C*H*–(CH$_2$)$_7$–CH$_3$), 7.81–7.86 (m, 18H, C_6H_5), 8.25–8.28 (m, 12H, C_6H_5), 8.39 (d, 4H, NC_5H_4, $^3J_{H-H}$ = 6 Hz), 8.92 (br s, 8H, C*H*$_{porph}$), 9.01 (br s, 8H, C*H*$_{porph}$), 9.25 ppm (d, 4H, NC_5H_4, $^3J_{H-H}$ = 6 Hz). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 22.63, 26.57, 29.29, 29.42, 29.51, 29.64, 29.75, 29.80, 31.82, 37.21, 115.38, 120.92, 121.43, 126.88, 126.93, 128.02, 130.10, 131.51, 131.62, 134.66, 141.96, 150.26, 187.55, 204.83 ppm. IR (CH_2Cl_2): $\nu_{(porphyrin\ N-H)}$ 1214.25 s, $\nu_{(OCO)}$ 1441.47 m, $\nu_{(OCO)}$ 1554.12 s, $\nu_{(CN)}$ 1594.23 s, $\nu_{(CO)}$ 1940.69 vs, $\nu_{(CO)}$ 1977.85 m, $\nu_{(CO)}$ 2025.34 vs, $\nu_{(aromatic\ C-H)}$ 3055.32 m, cm^{-1}. ESI-MS: *m*/*z* = 2109.79 [M+H$^+$]. *Anal.* Calc. for $C_{126}H_{124}N_{10}O_8Ru_2$: C, 71.77; H, 5.93; N, 6.64. Found: C, 71.54; H, 5.97; N, 6.49%.

3.2.6. $Ru_2(CO)_4(OOC$-p-$C_6H_4O(CH_2)_{17}CH_3)_2(L)_2$: ***6***

Yield: 432 mg (84%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = −2.77 (s, 4H, N*H*), 0.82 (t, 6H, −*p*-C_6H_4–O–(CH$_2$)$_{17}$–C*H*$_3$), 1.21 (m, 56H, −*p*-C_6H_4–O–(CH$_2$)$_3$–(C*H*$_2$)$_{14}$–CH$_3$), 1.40 (q, 4H, −*p*-C_6H_4–O–CH$_2$–CH$_2$–C*H*$_2$–), 1.73 (q, 4H, −*p*-C_6H_4–O–CH$_2$–C*H*$_2$–), 3.95 (t, 4H, −*p*-C_6H_4–O–C*H*$_2$–CH$_2$–), 6.89 (d, 4H, C_6H_4), 7.82–7.85 (m, 18H, C_6H_5), 8.18 (d, 4H, C_6H_4), 8.26–8.30 (m, 12H, C_6H_5), 8.51 (d, 4H, NC_5H_4, $^3J_{H-H}$ = 6 Hz), 8.93 (br s, 8H, C*H*$_{porph}$), 9.06 (br s, 8H, C*H*$_{porph}$), 9.45 ppm (d, 4H, NC_5H_4, $^3J_{H-H}$ = 6 Hz). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 22.72, 26.02, 29.63, 29.65, 29.68, 29.72, 31.95, 113.81, 120.67, 126.90, 126.94, 128.04, 134.68, 150.43, 187.56, 204.64 ppm. IR (CH_2Cl_2): $\nu_{(porphyrin\ N-H)}$ 1214.29 s, $\nu_{(OCO)}$ 1438.68 m, $\nu_{(OCO)}$ 1555.71 s, $\nu_{(CN)}$ 1594.58 s, $\nu_{(CO)}$ 1940.63 vs, $\nu_{(CO)}$ 1977.82 m, $\nu_{(CO)}$ 2025.23 vs, $\nu_{(aromatic\ C-H)}$ 3055.42 m, cm^{-1}. ESI-MS: *m*/*z* = 2325.90 [M+H$^+$]. *Anal.* Calc. for $C_{140}H_{140}N_{10}O_{10}Ru_2$: C, 72.33; H, 6.07; N, 6.02. Found: C, 72.26; H, 5.88; N, 5.94%.

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