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Fluorinated metallomesogens: lamellar *versus* columnar phase formation.

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Instrumental

The NMR spectra of the ligand semi-products and nickel(II) complexes were recorded using a Varian Unity Plus spectrometer operating at 500 MHz. For ^{1}H NMR spectra, the chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard. Results from NMR analyses of the synthesized Ni(II) complexes are consistent with the assumed molecular structures without any sign of additives or impurities. The elemental C, H and N analyses for all compounds studied were satisfactory. The mesophase identification was based on a routine microscopic examination of textures, using Zeiss Jenapol-U polarizing microscope, equipped with a Mettler FP82HT hot stage. Phase transition temperatures were determined by differential scanning calorimetry performed with a Perkin-Elmer DSC-7. The X-ray data for chosen compounds were collected with Bruker D8 Discover diffractometer (Kα line, parallel beam obtained with Gobel mirror) working in transmission geometry with setup equipped with GADDS area detector.

Synthesis

1. Synthesis of 4-octyloxy-5-perfluorooctyl-1,2-phenylenediamine (f).

1.1. N-[4-(octyloxy)phenyl]acetamide **(a)**:

To the cooled stirred mixture of N-(4-hydroxyphenyl)acetamide [151 g, 1 mol (1 equiv)] dissolved in ethanol (200 ml), a solution of potassium hydroxide [61 g, 1.1 mol (1.1 equiv)], 1-bromooctane [212 g, 1.1 mol (1.1 equiv)] and potassium iodine was added. The mixture was heated under reflux for an hour, then poured into the water, resulting in white precipitate that was filtered off and recrystallized from isooctane. Yield ~ 80%. [1]

1.2. N-[3-bromo-4-(octyloxy)phenyl]acetamide **(b)**:

To the stirred mixture of **(a)** [26.3 g, 0.1 mol (1 equiv)] and sodium acetate [10g, 0.12 mol] dissolved in acetic acid (150 ml), bromine [6 ml, 0.11 mol (1.1 equiv)] was added. During the addition the temperature was kept under 50 ^{o}C. Thereafter the addition the reaction mixture was left for an hour at room temperature and then poured into the cooled water solution of $NaHSO_3$. It resulted in a precipitate which was filtered off and recrystallized from ethanol. Yield ~ 70%, mp 88-89 ^{o}C. [2] Found: C, 56.15; H, 7.07; N, 4.09. Calc. for $C_{16}H_{24}NO_2Br$ (342.27): C, 56.44; H, 7.22; N, 4.07%. δ_H (500 MHz, $CDCl_3$, Me_4Si): 0.85 – 1.86 (15H, m, $(CH_2)_7H$); 2.14 (1H, s, $OCCH_3$); 3.97 (2H, t, J 6.5, OCH_2); 6.80 (1H, d, J 8.8, Ph); 7.39 (1H, dd, J 8.8 and 2.6, Ph); 7.57 (1H, s, NH); 7.66 (1H, d, J 2.6, Ph).

1.3. N-[5-bromo-2-nitro-4-(octyloxy)phenyl]acetamide **(c)**:

The compound **(b)** [20 g, 0.058 mol (1 equiv)] was dissolved in acetic anhydrite (80 ml). To the stirred mixture at room temperature, a 65% solution of nitric acid (8 ml, 0.11 mol, (2 equiv)] was added. During the addition the temperature was kept under 80 ^{o}C. Thereafter the addition the reaction mixture was cooled and then poured into the water resulting in precipitate which was filtered off and recrystallized from methanol. Yield ~ 85%; mp 110- 111 ^{o}C. Found: C, 49.62; H, 5.89; N, 7.23 Calc.for $C_{16}H_{23}N_2O_4Br$ (387.27): C, 49.44; H, 6.01; N, 7.11%. δ_H (500 MHz, $CDCl_3$, Me_4Si): 0.87 – 1.90 (15H, m, $(CH_2)_7H$); 2.27 (1H, s, $OCCH_3$); 4.04 (2H, t, J 6.5, OCH_2); 7.63 (1H, s, Ph); 9.05 (1H, s, Ph); 10.12 (1H, s, NH).

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[1] *Bull. Soc. Chim .Fr.* 1963, p. 2141

[2] W.M Lauer, Ch. Rondesvedt, R. Arnold, N.L. Druke, J. Van Hook, J. Tinker, *J. of Am. Chem. Sc.,* 1946, **68**, p. 1545

1.4. 5-bromo-2-nitro-4-(octyloxy)aniline **(d)**:

To the stirred mixture of compound **(c)** [15.5g, 0.04 mol] dissolved in EtOH (100 ml), a solution of HCl (50 ml) was added. The reaction mixture was heated for 2 hours under reflux, then poured into the water (500 ml), resulting in precipitate that was filtered off and recrystallized from pure n-hexane. Yield ~ 100%, mp 73- 74 ^{o}C. Found: C, 47.71; H, 6.13; N, 8.11 Calc.for $C_{16}H_{21}N_2O_4Br$ (345.23): C, 47.37; H, 6.01; N, 8.31%. δ_H (500 MHz, $CDCl_3$, Me_4Si): 0.85 – 1.84 (m, 15H, $(CH_2)_7H$); 3.97 (2H, t, J 6.5, OCH_2); 5.90 (2H, s, NH_2); 7.11 (1H, s, Ph); 7.55 (1H, s, Ph).

1.5. 4-octyloxy-5-perfluorooctyl-2-nitrophenyleneamine **(e)**:

A mixture of compound **(d)** [6g, 0.017 mol (1 equiv)], copper powder [6.4g, 0.1 mol (5.6 equiv)] and perfluorooctan iodine [11g, 0.02 mol, (1.1 equiv)] was dissolved in DMSO (100 ml) boiled under reflux at 110 ^{o}C for 20 hours. Thereafter a mixture was poured into the water, resulting in precipitate that was filtered off and recrystallized from n-hexane. Yield ~ 75% mp 90- 91 ^{o}C. [3]Found: C, 38.61; H, 3.09; N, 4.09 Calc.for $C_{22}H_{21}N_2O_3F_{17}$ (684.38): C, 38.53; H, 3.14; N, 4.29%. δ_H (500 MHz, $CDCl_3$, Me_4Si): 0.80 – 1.81 (m, 15H, $(CH_2)_7H$); 3.97 (2H, t, J6.4, OCH_2); 5.88 (2H, s, NH_2); 7.05 (1H, s, Ph); 7.55 (1H, s, Ph); δ_C (125 MHz, $CDCl_3$, Me_4Si) 14.01, 22.65, 25.78, 28.94, 29.19, 29.22, 31.78, 69.61, 108.78, 111.37, 113.48, 115.55, 116.05, 117.88, 118.34, 120.56, 120.63, 120.7, 125.86, 126.04, 126.22, 133.62, 137.98, 148.44 δ_F (470 MHz, $CFCl_3$): -81.04 (3F, t, J 10, CF_3); -108.42 (2F, t, J 13, Ph-CF_2); -120.68 (2F, m, -CF_2-); -121.78- (-122.28) (6F, m, CF_2); -122.93, -126.34 (4F, 2*m, CF_2).

1.6. 4-octyloxy-5-perfluorooctyl-1,2-phenylenediamine **(f)**:

To the stirred boiling mixture of compound **(e)** [1.5g, 0.0022mol (1 equiv)] dissolved in 2-propanol (50 ml) and HCl (50 ml), a solution of $SnCl_2$ [3.4g, 0.017mol (8 equiv)] in HCl was added. The solution was evaporated under the pressure, and the residue was dissolved in sodium hydroxide solution, resulting in a precipitate that was filtered off and washed with water.

2. Synthesis of 4-octyloxy-5-nonyl-1,2-phenylenediamine (6a)

2.1. N-(3-hydroxy-4-nonanoylphenyl)acetamide **(g)**:

To the cooled mixture of N-(3-hydroxyphenyl)acetamide [21.8 g, 0.14 mol (1 equiv)] and nonanoyl chloride [41.9 ml, 0.25 mol (1.8 equiv)] dissolved in 1,2-dichloroethane (55 ml), a solution of anhydrous aluminium chloride (56 g, 0.42 mol) was carefully added. Thereafter the addition, the temperature was raised and kept at the boiling point. The solution was poured into the water and extracted. The residue was evaporated and the crude product was purified by repeated recrystallizations from benzene. Yield ~ 45%; mp 107 ^{o}C. Found: C, 70.07; H, 8.65; N, 4.80. Calc. for $C_{17}H_{25}NO_3$ (291.38): C, 69.97; H, 8.62; N, 4.76%. δ_H (500 MHz, $CDCl_3$, Me_4Si) 0.86 (3H, t, J 6.5 and 12, Me); 1.74 (12H, m, $(CH_2)_7H$); 2.20 (3H, s, $OCCH_3$); 2.91 (2H, t, J 7.6, CH_2CO); 7.07 (d, J 1.9, Ph); 7.18 (H, dd, J 1.9 and 8.9, Ph); 7.63 (s, H, NH); 7.71 (H, d, J 8.9, Ph); 12.64 (H, s, OH).

2.2. N-(3-octyloxy-4-nonanoylphenyl)acetamide **(h)**:

The mixture of **(g)** [10 g, 0.035 mol (1 equiv)], K_2CO_3 [5g, 0.4 mol] and 1-bromooctane [6.3 ml, 0.036 mol (1.1 equiv)] dissolved in ethanol (200 ml) was boiled under reflux for 12h. The solution was evaporated and the residue was poured into the water, resulting in precipitate that was filtered off and recrystallized from methanol. Yield ~ 90%; mp 96 ^{o}C. Found: C, 74.39; H, 10.24; N, 3.47. Calc. for $C_{25}H_{41}NO_3$ (403.60): C, 74.3; H, 10.18; N, 3.46%. δ_H (500 MHz, $CDCl_3$, Me_4Si) 0.86-1.85 (30H, m, $(CH_2)_7H$); 2.19 (3H, s, $OCCH_3$); 2.98 (2H, t, J 7.9, CH_2CO); 4.04 (2H, t, J 6.3, OCH_2); 6.75 (H, dd, J 2.0 and 8.4, Ph); 7.68 (H, d, J 8.4, Ph); 7.70 (H, d, J 2.0, Ph.); 8.07 (H, s, NH).

2.3. 3-octyloxy-4-nonylaniline **(i)**:

The compound **(h)** [9.84 g, 0.024 mol (1 equiv)] was dissolved in ethylene glycol (100 ml). To the heated mixture a solution of hydrazine [2.0 ml, 0.056 mol (2.3 equiv)] was added. Thereafter the addition, the temperature was raised and kept at 180 ^{o}C. After 2h to the yellowish cooled mixture a potassium hydroxide [10g, 0.18 mol] was added. The solution was boiled at 140 ^{o}C. After another 2h the residue was poured into the water, resulting in precipitate that was filterred off. Yield ~ 80%.

[3] N. Yoshino, A. Sasaki, T. Seto, *J. of Fluorine Chemistry,* 1995, **71**, p. 21-29

.**2.4.** N-(3-octyloxy-4-nonylphenyl)acetamide **(j)**:

To the mixture of unpurified **(i)** [8 g, 0.023 mol (1 equiv)] in laboratory distilled water (30 ml), acetic anhydride [15 ml, 0.16 mol (1.1 equiv)] was added dropwise. The solution was heated under reflux for 10 minutes. Then the mixture was cooled, resulting in precipitate that was collected by filtration and repeatedly washed with cooled water. The crude product was purified by recrystallization from methanol.Yield ~ 91%; mp 102 ^{o}C. Found: C, 77.07; H, 11.12; N, 3.59. Calc. for $C_{25}H_{43}NO_2$ (389.61): C, 77.03; H, 11.15; N, 3.61%. δ_H (500 MHz, $CDCl_3$, Me_4Si) 0.86-1.79 (32H, m, $(CH_2)_7H$, $(CH_2)_8H$); 2.14 [s, 3H, $OCCH_3$]; 2.54 (2H, t, J 7.6, CH_2); 3.90 (2H, t, J 6.3, OCH_2); 6.78 (H, dd, J 1.9, 8.1, Ph); 7.01 (d, J 8.1, H, Ph) 7.28 (d, J 1.9, H, Ph); 7.49 (H, s, NH).

2.5. N-(3-octyloxy-4-nonyl-6-nitrophenyl)acetamide **(k)**:

The compound **(j)** [5 g, 0.013 mol] was dissolved in dichloromethane (80 ml) solution of acetic acid (80 ml). To the stirred mixture at room temperature nitric acid (4 ml) was added dropwise. The solution was poured into the water, resulting in precipitate that was collected by filtration and washed with water. The crude product was recrystallized from methanol.Yield ~ 73%; mp 72 ^{o}C. Found: C, 69.09; H, 9.74; N, 6.44. Calc. for $C_{25}H_{42}N_2O_4$ (434.61): C, 69.05; H, 9.70; N, 6.44%. δ_H (500 MHz, $CDCl_3$, Me_4Si) 0.86-1.86 (32H, m, $(CH_2)_7H$, $(CH_2)_8H$); 2.29 (3H, s, $OCCH_3$); 2.57 (2H, t, J 7.6, CH_2); 4.09 (2H, t, J 6.4, OCH_2); 8.02 (H, s, Ph); 8.36 (H, s, Ph); 10.78 (H, s, NH).

2.6. 4-octyloxy-5-nonyl-1,2-phenylenediamine **(l)**:

To the stirred mixture at room temperature of compound **(k)** [1.5 g, 0.034 mol (1 equiv)], ethanol (20 ml) and 5% solution of NaOH (4 ml), a zink powder [3 g, 0.046 mol] was added. The solvent was evaporated and the residue was poured into the water, resulting in precipitate that was collected by filtration and repeatedly washed with ethanol. Yield ~ 80%.

3. Analytical data

3.1. NMR studies and C, H, N analyses for monosubstituted intermediates:

compound **(p):** m.p. 157-158 ^{0}C Found: C, 38.95; H, 2.35; N, 2.33 Calc.for $C_{39}H_{28}N_2O_2F_{34}$ (1202.59): C, 38.48; H, 2.41; N, 2.69% δ_H (500 MHz, $CDCl_3$, Me_4Si): 0.86 – 1.82 (15H, m, $(CH_2)_7H$); 3.93 (2H, t, *J* 6.4, $-OCH_2$); 4.14 (2H, s, NH_2); 6.03 (1H, d, *J*7.6, C=CH-CO); 6.35 (1H, s, Ph); 7.16 (1H, s, Ph); 7.33 (H dd, *J*7.6 and 12.0, N-CH=C); 7.68 and 8.02 (4H, AA'BB', *J*8.3, Ph); 11.94 (H, d, *J* 12, NH); δ_C (125 MHz, $CDCl_3$, Me_4Si) 13.95, 22.62, 25.83, 29.08, 29.16, 29.23, 31.77, 69.11, 93.89, 100.42, 120.04, 121.86, 127.13, 127.44, 142.46, 143.48, 150.25, 157.24, 189.44 δ_F (470 MHz, $CFCl_3$) -81.03 (6F, m, CF_3); -106.40 (2F, t, *J* 14, Ph-CF_2); -110.97 (2F, t, *J* 14, Ph-CF_2); -120.93, -121.23 (4F, 2*m, CF_2); -121.60 – (-122.10) (12F, m, CF_2); -122.78 (4F, m, CF_2); -126.18 (4F, m, CF_2).

compound **(q):** m.p 138-139 ^{0}C Found: C, 51.31; H, 4.97; N, 3.07 Calc.for $C_{39}H_{45}N_2O_3F_{17}$ (912.76): C, 51.47; H, 5.01; N, 3.12%: δ_H (500 MHz, $CDCl_3$, Me_4Si): 0.89 – 1.84 (30H, m, $(CH_2)_7H$); 3.91 (2H, t, *J* 6.3, $-OCH_2$); 4.02 (2H, t, *J* 6.6, $-OCH_2$); 4.18 (2H, s, NH_2); 6.01 (d, *J* 7.8, H, C=CH-CO); 6.33 (1H, s, Ph); 6.93 and 7.91 (4H, AA'BB', *J* 8.8, Ph); 7.12 (1H, s, Ph); 7.23 (H, dd, *J* 7.8 and 11.7, N-CH=C); 11.78 (H, d, *J* 11.7); δ_C (125 MHz, $CDCl_3$, Me_4Si) 13.98, 14.08, 22.62, 22.66, 25.78, 25.99, 26.03, 29.06, 29.17, 29.18, 29.23, 29.24, 29.35, 31.76, 31.82, 68.27, 68.91, 93.63, 97.72, 100.21, 100.76, 106.95, 107.13, 111.28, 114.18, 114.49, 116.52, 120.54, 121.18, 121.26, 121.33, 129.29, 129.62, 131.62, 143.33, 148.54, 156.66, 162.16, 176.54, 190.19 δ_F (470 MHz, $CFCl_3$) 81.02 (3F, t, *J* 10, CF_3); -106.45 (2F, t, *J* 14, Ph-CF_2); -121.10 (2F, m, CF_2); -121.75- (-122.20) (6F, m, CF_2); -122.91, -126.32 (4F, 2*m, CF_2)

compound **(r):** Found: C, 79.56; H, 10.75; N, 4.52. Calc. for $C_{41}H_{66}N_2O_2$ (618.97): C, 79.55; H, 10.70; N, 4.50%. δ_H (500 MHz, $CDCl_3$, Me_4Si): 0.85-1.79 (49H, m, $(CH_2)_8H$, $(CH_2)_7H$); 2.51 (2H, t, J 7.6, $ArCH_2$); 2.65 (2H, t, J 7.6, $ArCH_2$); 3.67 (2H, s, NH_2); 3.87 (2H, t, J 6.2 and 12.0, OCH_2); 5.98 (H, d, J 7.6, N-CH=C); 6.29 (H, s, Ph); 6,83 (H, s, Ph); 7.25 and 7.86 (4H, AA'BB', J 8.1, Ph); 7.34 (H, dd, J 7.6 and 12.2, C=CH); 11.96 (H, d, J 12.2, NH).

compound **(s):** Found: C, 77.37; H, 10.39; N, 4.51. Calc. for $C_{40}H_{64}N_2O_3$ (620.95): C, 77.39; H, 10.40; N, 4.52%. δ_H (500 MHz, $CDCl_3$, Me_4Si): 0.86-1.85 (47H, m, $(CH_2)_8H$, $(CH_2)_7H$); 2.51 (2H, t, J 7.7, $ArCH_2$); 3.67 (2H, s, NH_2); 3.87 (2H, t, J 6.3, OCH_2); 4.00 (2H, t, J 7.1, OCH_2); 5.95 (H, d, J 7.6, N-CH=C); 6.29 (H, s, Ph); 6.82 (H, s, Ph); 6.92 and 7.92 (4H, AA'BB', J 8.8, Ph); 7.31 (dd, J 7.6 and 11.9, H, C=CH); 11.89 (H, d, J 11.9, NH).

3.2. NMR studies and C, H, N analyzes for Ni(II) complexes studied:

complex **(I-1):** Found: C, 54.78; H, 5.33; N, 2.28 Calc.for $C_{56}H_{65}N_2O_5F_{17}Ni$ (1227.79): C, 54.38; H, 5.71; N, 2.42%: δ_H (500 MHz, $CDCl_3$, Me_4Si): 0.86 – 1.84 (45H, m, $(CH_2)_7H$); 3.88 (2H, t, *J* 6.5, OCH_2); 3.98 – 4.22 (4H, m, OCH_2); 6.09 i 7.37 (2H, *J* 6.7, C=CH); 6.15 and 7.47 (2H, *J* 7.0, N-CH=C); 6.86 – 6.90 (4H, m, Ph); 6.92 (H, s, Ph); 7.44 (H, s, Ph); 7.82 – 7.88 (4H, m, Ph) δ_C (125 MHz, $CDCl_3$, Me_4Si) 13.99, 14.09, 22.64, 22.67, 25.80, 26.05, 29.09, 29.19, 29.26, 29.29, 29.39, 31.77, 31.84 68.15, 68.19, 69.06, 94.75, 95.77, 97.55, 111.47, 112.64, 112.72, 114.13, 114.18, 128.75, 128.98, 129.06, 129.18, 135.81, 146.52, 146.68, 147.16, 155.16, 161.35, 161.75, 174.17, 176.48 δ_F (470 MHz, $CFCl_3$) -81.00 (3F, t, *J* 10 Hz, CF_3); -106.60 (2F, t, *J* 10, PhCF_2); -120.65 (2F, m, CF_2); -121.65 – (-122.20) (6F, m, CF_2); -122.90, -126.29 (4F, 2m, CF_2).

complex **(I-2):** Found: C, 44.32; H, 3.19; N, 1.84 Calc.for $C_{56}H_{48}N_2O_4F_{34}Ni$ (1517,63): C, 44.08; H, 3.26; N, 1.52%: δ_H (500 MHz, $CDCl_3$, Me_4Si): 0.86 – 1.56 (30H, m, $(CH_2)_7H$); 3.99 (2H, t, *J* 6.3, OCH_2); 4.03 (2H, t, *J* 6.6, OCH_2); 6.26 i 7.53 (2H, *J* 6.9, C=CH); 6.26 and 7.63 (2H, *J* 6.6, N-CH=C); 6.94 and 7.90 (4H, *J* 9.0, Ph); 7.01 (H, s, Ph); 7.60 (H, s, Ph); 7.66 and 8.04 (4H, *J* 8.5, Ph) δ_C (125 MHz, $CDCl_3$, Me_4Si) 13.97, 14.06, 22.63, 22.67, 25.78, 26.03, 29.05, 29.19, 29.23, 29.26, 29.32, 29.39, 31.78, 31.84, 68.25, 69.03, 95.84, 96.03, 97.41, 114.16, 114.26, 126.88, 127.01, 127.16, 129.13, 130.46, 135.17, 140.03, 147.08, 155.81, 162.01, 171.89, 176.76; δ_F (470 MHz, $CFCl_3$) -81.96 (6F, m, CF_3); -106.77 (2F, t, *J*13.7 Hz, $PhCF_2$); -111.06 (2F, t, *J*14.6 Hz, $PhCF_2$); -120.70, -121.35 (4F, 2*m, CF_2); -121.85 –(-122.09) (12F, m, CF_2); -122.88 (4F, m, CF_2); -126.28 (4F, m, CF_2).

complex **(I-3):** Found: C, 44.32; H, 3.19; N, 1.84 Calc.for $C_{56}H_{48}N_2O_4F_{34}Ni$ (1517,63): C, 44.78; H, 3.50; N, 1.57%: δ_H (500 MHz, $CDCl_3$, Me_4Si): 0.86 – 1.85 (30H, m, $(CH_2)_7H$); 3.96 (2H, t, *J* 6.3, OCH_2); 4.02 (2H, t, *J* 6.9, OCH_2); 6.18 and 7.47 (2H, *J* 6.6, olefin); 6.30 and 7.68 (2H, *J* 6.6, olefin); 6.92 and 7.87 (4H, *J* 8.9, Ph); 7.03 (H, s, Ph); 7.55 (H, s, Ph); 7.66 and 8.04 (4H, *J* 8.4, Ph). δ_C (125 MHz, $CDCl_3$, Me_4Si): 13.97, 14.06, 22.63, 22.67, 25.78, 26.03, 29.05, 29.19, 29.23, 29.26, 29.32, 29.39, 31.78, 31.84, 68.25, 69.03, 95.84, 96.03, 97.41, 114.16, 114.26, 126.88, 127.01, 127.16, 129.13, 130.46, 135.17, 140.03, 147.08, 155.81, 162.01, 171.89, 176.76; 80.97. δ_F (470 MHz, $CFCl_3$): (3F, m, CF_3); -106.87 (2F, t, *J* 13.7, $PhCF_2$); -111.13 (2F, t, *J* 14.1, $PhCF_2$); -120.69,-121,36 (4F, 2*m, CF_2); -121,75 – (-122.20) (12F, m, CF_2); -122.90 (4F, m, CF_2);-126.29 (4F, m, CF_2).

complex **(I-4):** Found: C, 38.54; H, 1.72; N, 1.55 Calc.for $C_{56}H_{31}N_2O_3F_{51}Ni$ (1807,47): C, 38.65; H, 2.00; N, 1.54%: δ_H (500 MHz, d_8 toluene, Me_4Si) 0.86 – 1.78 (15H, m, $(CH_2)_7H$); 3.72 (2H, t, *J* 6.2, OCH_2); 5.81 and 7.25 (2H, AB, *J* 6.3, olefin); 5.94 and 7.17 (2H, *J* 6.7, olefin); 6.71 (H, s, Ph); 7.46 – 7.50 (4H, m, Ph); 7.55 (H, s, Ph); 7.88 – 7.92 (4H, m, Ph). δ_F (470 MHz, d_8 toluene): -76.10 – (-76.62) (9F, m, CF_3); -105.16 (4F, m, CF_2); -114.56 (2F, m, CF_2); -115.04 – (- 116.60) (24F, m, CF_2); -117.26 (6F, m, CF_2); -120.74 (6F, m, CF_2)

complex **(II-1):** Found: C, 73.14; H, 9.04; N, 2.99. Calc. for $C_{57}H_{84}N_2O_5Ni$ (935.98): C, 73.16; H, 9.07; N, 2.96%. δ_H (500 MHz, $CDCl_3$, Me_4Si): 0.86-1.83 (62H, m, $(CH_2)_8H$ i $(CH_2)_7H$); 2.54 (2H, t, J 7.6, $ArCH_2$); 3.88 (2H, t, J 6.3, OCH_2); 3.99 (4H, t, J 6.6, OCH_2); 6.04-6.08 (2H, m, N-CH=C); 6.82 (H, s, Ph); 6.88 and 7.86 (8H, AA'BB', J 9.0, Ph); 7.13 (H, s, Ph); 7.42 (H, d, J 6.8, C=CH); 7.45 (H, d, J 6.8, C=CH).

complex **(II-2):** Found: C, 74.58; H, 9.28; N, 1.50. Calc. for $C_{58}H_{86}N_2O_4Ni$ (934.01): C, 74.56; H, 9.27; N, 1.46%. δ_H (500 MHz, $CDCl_3$, Me_4Si): 0.86-1.84 (m, 64H, $(CH_2)_8H$ I $(CH_2)_7H$); 2.55 (2H, t, J 7.8, $ArCH_2$); 2.64 (2H, t, J 7.7, $ArCH_2$); 3.91 (2H, t, J 6.8, OCH_2); 4.00 (2H, t, J 6.6, OCH_2); 6.11 (H, d, J 6.6, N-CH=C); 6.14 (H, d, J 6.4, N-CH=C); 6.86 (s, H, Ph.); 6.90 i 7.00 (4H, AA'BB', J 9.0, Ph); 7.19 (s, H, Ph); 7.21 and 7.84 (4H, AA'BB', J 8.5, Ph); 7.48-7.52 (2H, m, C=CH).

complex **(II-3):** Found: C, 74.58; H, 9.28; N, 1.50. Calc. for $C_{58}H_{86}N_2O_4Ni$ (934.01): C, 74.56; H, 9.27; N, 1.46%. δ_H (500 MHz, $CDCl_3$, Me_4Si): 0.86-1.85 (64H, m, $(CH_2)_8H$, $(CH_2)_7H$); 2.55 (2H, t, J 7.7, $ArCH_2$); 2.64 (2H, t, J 7.7, $ArCH_2$); 3.90 (2H, t, J 6.4, OCH_2); 4.00 (2H, t, J 6.6, OCH_2); 6.09 (H, d, J 6.7, N-CH=C); 6.15 (H, d, J 6.7, N-CH=C); 6.86 (H, s, Ph); 6.90 and 7.88 (4H, AA'BB', J 8.9, Ph); 7.18 (H, s, Ph); 7.22 i 7.84 (4H, AA'BB', J 8.3, Ph); 7.47 (H, d, J 6.7, C=CH); 7.53 (H, d, J 6.7, C=CH).

complex **(II-4):** Found: C, 76.03; H, 9.51; N, 3,00. Calc. for $C_{59}H_{88}N_2O_3Ni$ (935.98): C, 76.06; H, 9.50; N, 3.02%. δ_H (500 MHz, $CDCl_3$, Me_4Si): 0.85-1.79 (66H, m, $(CH_2)_8H$, $(CH_2)_7H$); 2.54 (2H, t, J 7.7, $ArCH_2$); 2.63 (4H, t, J 7.6, $ArCH_2$); 3.90 (2H, t, J 6.3, OCH_2); 6.10-6.16 (H, m, N-CH=C); 6.85 (H, s, Ph); 7.17 (H, s, Ph); 7.20 i 7.83 (8H, AA'BB', J 8.3, Ph); 7.47 (H, d, J 6.6, C=CH); 7.50 (H, d, J 6.6, C=CH).

3.3. C, H, N analyzes for Cu(II) complexes studied:

complex **(I –1):** Found: C, 54.56; H, 5.31; N, 2.27 Calc.for $C_{56}H_{65}N_2O_5F_{17}Cu$ (1232,64): C, 54.29; H, 5.19; N, 2.44%

complex **(I – 2):** Found: C, 44.17; H, 3.17; N, 1.84 Calc.for $C_{56}H_{48}N_2O_4F_{34}Cu$ (1522,48): C, 47.27; H, 3.15; N, 1.74%

complex **(I – 3):** Found: C, 44.17; H, 3.17; N, 1.84 Calc.for $C_{56}H_{48}N_2O_4F_{34}Cu$ (1522,48): C, 47.25; H, 3.22; N, 1.69%

complex **(I– 4):** Found: C, 37.11; H, 1.71; N, 1.54 Calc.for $C_{56}H_{31}N_2O_3F_{51}Cu$ (1812,32): C, 37.00; H, 1.70; N, 1.58%

complex **(II–1):** Found: C, 72.77; H, 8.99; N, 2.97 Calc.for $C_{57}H_{84}N_2O_5Cu$ (940.83): C, 73.01; H, 9.09; N, 2.98%

complex **(II–2):** Found: C, 74.19; H, 9.23; N, 2.98 Calc.for $C_{58}H_{86}N_2O_4Cu$ (938.86): C, 73.97; H, 9.05; N, 2.54%

complex **(II–3):** Found: C, 74.19; H, 9.23; N, 2.98 Calc.for $C_{58}H_{86}N_2O_4Cu$ (938.86): C, 74.08; H, 9.35; N, 3.03%

complex **(II–4):** Found: C, 75.63; H, 9.47; N, 2.99 Calc.for $C_{59}H_{88}N_2O_3Cu$ (936.88): C, 76.07; H, 9.68; N, 3.14%