Electronic Supplementary Information

Near-infrared chiro-optical effect in metallogels

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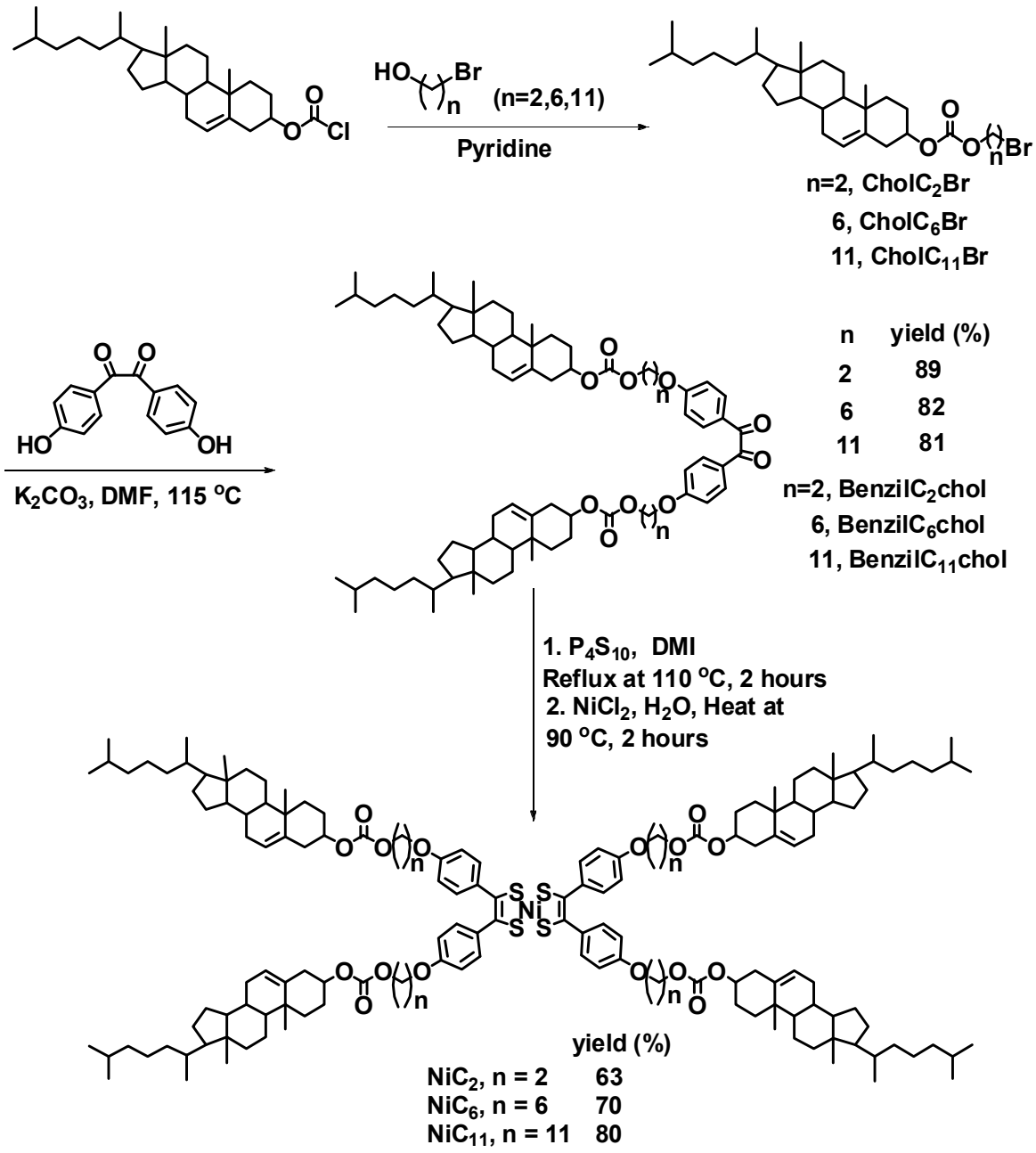
General. 300.1 (^{1}H) and 75.5 MHz (^{13}C) NMR spectra were recorded on Brucker Avance 300 spectrometer at room temperature using perdeuterated solvents as internal standards. FT-IR spectra were recorded using a Varian-640 FT-IR spectrometer. UV-Vis-NIR spectra were recorded using a Cary 5000 UV-Vis-NIR spectrophotometer (Varian, Australia). Mass spectra were recorded with a Varian MAT 311 instrument by the Centre Régional de Mesures Physiques de l'Ouest, Rennes. Elemental analysis were performed at the Centre Régional de Mesures Physiques de l'Ouest, Rennes. Cyclic voltammetry were carried out on a 10^{-3} M solution of complex in CH_2Cl_2, containing 0.2 M nBu_4NPF_6 as supporting electrolyte. Voltammograms were recorded using an Autolab electrochemical analyser (PGSTAT 30, Ecochemie BV). Voltammograms were recorded at 0.1 Vs^{-1} on a platinum disk electrode (A = 1mm^2). The potentials were measured *versus* Saturated Calomel Electrode. Circular dichroism spectra were recorded on a Jasco-815 Circular Dichroism spectrometer.

4-methoxybenzaldehyde (99%), 2-bromoethanol (95%) and cholesteryl chlorofomate (97%) were purchased from Sigma-Aldrich and used as received. 6-bromo-1-hexanol (97%), 11-bromoundecanol (97%), $NiCl_2$ (99.9 %), were purchased from Alfa Aesar and used without further purification. DMI (99%), P_4S_{10} (98%) and hydrobromic acid (48%) were purchased from Acros Organics. Anhydrous CH_2Cl_2 (Sigma-Aldrich), pyridine (Acros Organics) and triethylamine (Alfa Aesar) were obtained by distillation over P_2O_5 and KOH respectively. The reactions were followed by Thin Layer Chromatography (TLC) plates, revealed by a UV-lamp at 254 nm or phosphomolybdic acid. All other reagents and materials from commercial sources were used without further purification. Silica gel used in chromatographic separations was obtained from Acros Organics (Silica Gel, ultra pure, 40-60 μm).

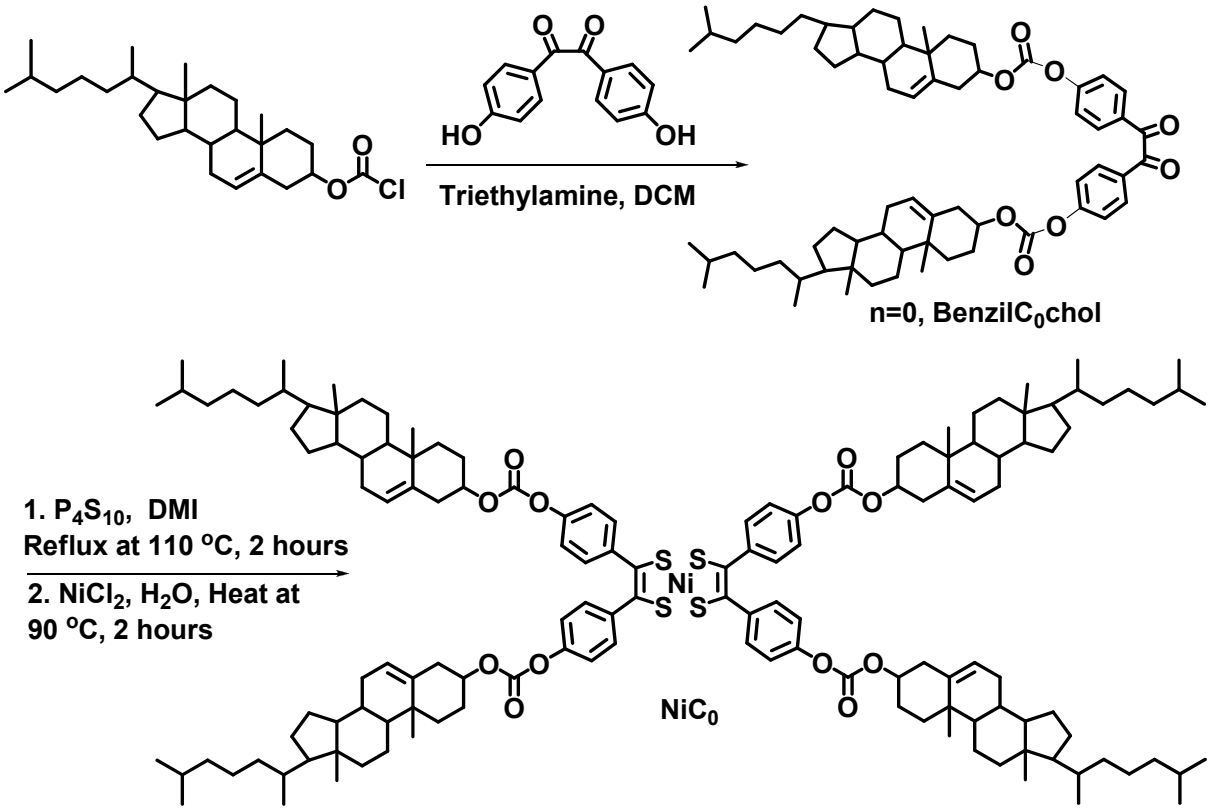
Scanning electron microscopy (SEM) measurements were performed using a JEOL-JSM6301F microscope. A piece of gel of **NiC_2** in cyclohexane at 2 mg/mL (MGC) was deposited on a silicon wafer and dried for 20 hours under vacuum before imaging.

Atomic force microscopy (AFM) measurements were performed using a PicoSPM II controller microscope. Diluted gels of compound **NiC_2** in dodecane or in cyclohexane (0.1 mg/mL) were spin-coated over highly ordered pyrolytic graphite (HOPG) or silicon wafer surfaces. The surfaces were dried for 20 hours under vacuum before imaging.

X-ray scattering experiments were performed using a FR591 Bruker AXS rotating anode X-ray generator operated at 50 kV and 50 mA with monochromatic Cu Kα radiation (λ = 1.541 Å) and point collimation. The samples were held in Lindemann glass capillaries (1 mm diameter) and heated with a variable-temperature oven. The patterns were collected with a Mar345 Image-Plate detector (Marresearch, Norderstedt, Germany).



Scheme S1. Synthetic route for the preparation of the cholesteryl based nickel-bis(dithiolene) complexes NiC_n (n = 2, 6, 11).



Scheme S2. Synthetic route for the preparation of the NiC_0.

General procedure for the synthesis of CholC$_n$Br: Cholesteryl chloroformate (2.00 g, 4.45 mmol) and bromoalcohol (4.9 mmol) were dissolved in 20 mL dry dichloromethane. 0.72 mL (8.9 mmol) of pyridine was added to this solution and the reaction mixture was stirred for overnight. After reaction, the solution was washed successively with 1 (N) hydrochloric acid (2 × 30 mL) and water (2 × 30 mL) and then dried over $MgSO_4$. After evaporation of the solvent, the compound was purified by precipitation for three times using dichloromethane and methanol solvents and used for the next reaction without further purification. Yield was reasonably good (**CholC$_2$Br:** 66 %, **CholC$_6$Br:** 76 %, **CholC$_{11}$Br:** 87 %).

Compound CholC$_2$Br: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.67-2.03 (m, 41H, CH, CH_2 and CH_3 in cholesteryl moiety), δ 2.39-2.41 (m, 2H, CH_2), 3.52 (t, 2H, ^3J = 6.3 Hz, CH_2), 4.42 (t, 2H, ^3J = 6.3 Hz, CH_2), 4.51-4.54 (m, 1H, CH), 5.39-5.4 (m, 1H, =CH).

Compound CholC$_6$Br: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.67-2.03 (m, 49H, CH, CH_2 and CH_3 in cholesteryl moiety and CH_2 of the C_6 chain), δ 2.36-2.42 (m, 2H, CH_2), 3.4 (t, 2H, ^3J = 6.6 Hz, CH_2), 4.1 (t, 2H, ^3J = 6.6 Hz, CH_2), 4.41-4.51 (m, 1H, CH), 5.37-5.9 (m, 1H, =CH).

Compound CholC$_{11}$Br: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.67-2.03 (m, 59H, CH, CH_2 and CH_3 in cholesteryl moiety and CH_2 of the C_{11} chain), δ 2.36-2.42 (m, 2H, CH_2), 3.4 (t, 2H, ^3J = 6.6 Hz, CH_2), 4.1 (t, 2H, ^3J = 6.6 Hz, CH_2), 4.41-4.51 (m, 1H, CH), 5.37-5.9 (m, 1H, =CH).

Compound BenzilC$_0$chol: Cholesteryl chloroformate (2.00 g, 4.45 mmol) and 4,4′dihydroxy benzil (0.54 g, 2.22 mmol) were dissolved in 20 mL dry dichloromethane. 1.25 mL (8.9 mmol) of triethylamine was added to this solution and the reaction mixture was stirred for overnight. After reaction, the solution was washed with 1 (N) hydrochloric acid and water (2 × 30 mL) and water (2 × 30 mL). After drying over $MgSO_4$ and evaporation of the solvent, the compound was purified by column chromatography on silica gel using dichloromethane as eluent and recristallized from a CH_2Cl_2/MeOH mixture by slow evaporation of the dichloromethane (1.62 g, 68 %).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.68-2.03 (m, 82H, CH, CH_2 and CH_3 in cholesteryl moiety), δ 2.47-2.49 (m, 4H, CH_2), 4.54-4.65 (m, 2H, CH), 5.41-5.43 (m, 2H, =CH), 7.35 (d, 4H, ^3J = 9.0 Hz), 8.18 (d, 4H, ^3J = 9.0 Hz). ^{13}C{^{1}H} DEPT NMR (75.5 MHz, $CDCl_3$) 11.99 (CH_3), 18.85 (CH_3), 19.4 (CH_3), 21.17 (CH_2), 22.70 (CH_3), 22.95 (CH_3), 23.95 (CH_2), 24.4 (CH_2), 27.71 (CH_2), 28.1 (CH), 28.35 (CH_2), 31.94 (CH), 32.0 (CH_2), 35.91 (CH), 36.3 (CH_2), 36.65 (Cq), 36.91 (CH_2), 37.98 (CH_2), 39.63 (CH_2), 39.8 (CH_2), 42.42 (Cq), 50.08 (CH), 56.24 (CH), 56.77 (CH), 79.62 (CH), 121.85 (CH), 123.54 (CH), 130.46 (Cq), 131.89 (CH), 139.02 (Cq), 152.01 (Cq), 156.15 (Cq), 192.75 (C=O). UV-vis (CH_2Cl_2, 23 °C): λmax (ε, $M^{-1}cm^{-1}$) = 269 (25700). IR (KBr): 2948, 2867, 1764, 1671, 1598, 1504, 1467, 1440, 1413, 1375, 1353,

1319, 1305, 1257, 1216, 1160, 1085, 1045, 1010, 993, 943, 883, 846, 800 cm^{-1}. EI-MS: *m/z* (%) = 1089.7155 (100) $[M+Na]^+$. Anal. Calcd for $C_{70}H_{98}O_8$: C, 78.76; H, 9.25; Found C, 78.59; H, 9.42.

General procedure for the synthesis of BenzilC$_n$chol: CholC_nBr compound (1.03 mmol) and 4,4′ dihydroxy benzil (0.10 g, 0.413 mmol) were mixed together in 20 mL of *N,N* dimethylformamide (DMF). K_2CO_3 (0.12 g, 0.83 mmol) was added to this solution and the solution was heated at 110 °C for 16 hours. After the reaction, the DMF was evaporated and the solid mass was dissolved in DCM and washed with water. After drying over $MgSO_4$ and evaporation of the solvent, the compound was purified by column chromatography on silica gel using dichloromethane/petroleum ether mixture (75/25 %v/v) as eluent. The yield was reasonably good (**BenzilC$_2$chol:** 89 %, **BenzilC$_6$chol:** 82 %, **BenzilC$_{11}$chol:** 81%).

Compound BenzilC$_2$chol: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.67-2.02 (m, 82H, CH, CH_2 and CH_3 in cholesteryl moiety), δ 2.37-2.4 (m, 4H, CH_2), 4.26 (t, 4H, ^3J = 4.2 Hz), 4.47-4.5 (m, 6H, OCH_2 and OCH), 5.38-5.39 (m, 2H, =CH), 6.97 (d, 4H, ^3J = 9.0 Hz), 7.93 (d, 4H, ^3J = 9.0 Hz). $^{13}C\{^1H\}$ DEPT NMR (75.5 MHz, $CDCl_3$) 11.97 (CH_3), 18.82 (CH_3), 19.36 (CH_3), 21.14 (CH_2), 22.68 (CH_3), 22.94 (CH_3), 23.93 (CH_2), 24.39 (CH_2), 27.75 (CH_2), 28.12 (CH), 28.35 (CH_2), 31.92 (CH), 32.0 (CH_2), 35.88 (CH), 36.28 (CH_2), 36.63 (Cq), 36.92 (CH_2), 38.07 (CH_2), 39.62 (CH_2), 39.81 (CH_2), 42.41 (Cq), 50.08 (CH), 56.22 (CH), 56.78 (CH), 65.4 (OCH_2), 66.18 (OCH_2), 78.48 (CH), 114.88 (CH), 123.2 (CH), 126.73 (CH), 132.5 (CH), 139.31 (Cq), 154.44 (Cq), 163.69 (Cq), 193.39 (C=O). UV-vis (CH_2Cl_2, 23 °C): λmax (ε, $M^{-1}cm^{-1}$) = 298 (30900). IR (KBr): 2948, 2867, 1745, 1666, 1598, 1575, 1509, 1465, 1421, 1376, 1315, 1249, 1162, 1064, 1027, 1008, 993, 973, 946, 883, 842, 790 cm^{-1}. EI-MS: *m/z*

(%) = 1177.7679 (100) $[M+Na]^+$. Anal. Calcd for $C_{74}H_{106}O_{10}$: C, 76.91; H, 9.25; Found C, 76.61; H, 9.24.

Compound BenzilC$_6$chol: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.66-2.02 (m, 98H, CH, CH_2 and CH_3 in cholesteryl moiety and CH_2 of the linker), δ 2.35-2.41 (m, 4H, CH_2), 4.01 (t, 4H, ^3J = 6.3 Hz), 4.12 (t, 4H, ^3J = 6.3 Hz), 4.4-4.51 (m, 2H, CH), 5.36-5.38 (m, 2H, =CH), 6.93 (d, 4H, ^3J = 9.0 Hz), 7.91 (d, 4H, ^3J = 9.0 Hz). $^{13}C\{^1H\}$ DEPT NMR (75.5 MHz, $CDCl_3$) 11.95 (CH_3), 18.8 (CH_3), 19.35 (CH_3), 21.11 (CH_2), 22.66 (CH_3), 22.92 (CH_3), 23.91 (CH_2), 24.36 (CH_2), 25.6 (CH_2), 25.71 (CH_2), 27.78 (CH_2), 28.1 (CH), 28.31 (CH_2), 28.67 (CH_2), 28.96 (CH_2), 31.9 (CH), 31.97 (CH_2), 35.87 (CH), 36.26 (CH_2), 36.6 (Cq), 36.93 (CH_2), 38.13 (CH_2), 39.59 (CH_2), 39.78 (CH_2), 42.37 (Cq), 50.05 (CH), 56.19 (CH), 56.75 (CH), 67.66 (OCH_2), 68.27 (OCH_2), 77.17 (CH), 114.76 (CH), 123.0 (CH), 126.19 (CH), 132.44 (CH), 139.42 (Cq), 154.72 (Cq), 164.44 (Cq), 193.58 (C=O). UV-vis (CH_2Cl_2, 23 °C): λmax (ε, $M^{-1}cm^{-1}$) = 301 (29600). IR (KBr): 2948, 2867, 1741, 1666, 1598, 1573, 1508, 1467, 1376, 1255, 1160, 1120, 1056, 997, 973, 879, 840, 808, 792 cm^{-1}. EI-MS: *m/z* (%) = 1289.8929 (100) $[M+Na]^+$. Anal. Calcd for $C_{82}H_{122}O_{10}$: C, 77.68; H, 9.7; Found C, 78.38; H, 9.76.

Compound BenzilC$_{11}$chol: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.66-2.02 (m, 118H, CH, CH_2 and CH_3 in cholesteryl moiety and CH_2 of the linker), δ 2.35-2.4 (m, 4H, CH_2), 4.0 (t, 4H, ^3J = 6.6 Hz), 4.1 (t, 4H, ^3J = 6.6 Hz), 4.41-4.51 (m, 2H, CH), 5.37-5.39 (m, 2H, =CH), 6.93 (d, 4H, ^3J = 9.0 Hz), 7.91 (d, 4H, ^3J = 9.0 Hz). $^{13}C\{^1H\}$ DEPT NMR (75.5 MHz, $CDCl_3$) 11.95 (CH_3), 18.81 (CH_3), 19.36 (CH_3), 21.12 (CH_2), 22.67 (CH_3), 22.93 (CH_3), 23.92 (CH_2), 24.37 (CH_2), 25.82 (CH_2), 26.02 (CH_2), 27.8 (CH_2), 28.1 (CH), 28.32 (CH_2), 28.75 (CH_2), 29.1 (CH_2), 29.3 (CH2), 29.41 (CH2), 29.54 (CH2), 29.57 (CH2), 31.92 (CH), 31.99 (CH_2), 35.88 (CH), 36.27 (CH_2), 36.63 (Cq), 36.95 (CH_2), 38.14 (CH_2), 39.6 (CH_2), 39.8 (CH_2), 42.39

(Cq), 50.1 (CH), 56.2 (CH), 56.77 (CH), 67.95 (OCH_2), 68.53 (OCH_2), 77.71 (CH), 114.78 (CH), 122.98 (CH), 126.15 (CH), 132.45 (CH), 139.48 (Cq), 154.77 (Cq), 164.57 (Cq), 193.63 (C=O). UV-vis (CH_2Cl_2, 23 °C): λmax (ε, $M^{-1}cm^{-1}$) = 301 (30500). IR (KBr): 2948, 2852, 1737, 1654, 1592, 1508, 1467, 1398, 1369, 1309, 1268, 1251, 1157, 1027, 1010, 993, 840, 792 cm^{-1}. EI-MS: *m/z* (%) = 1430.0496 (100) $[M+Na]^+$. Anal. Calcd for $C_{92}H_{142}O_{10}$: C, 77.47; H, 10.16; Found C, 77.27; H, 10.19.

General procedure for the synthesis of Nickel complexes: The benzil derivatives (0.35 mmol) were refluxed with P_4S_{10} (0.390 gm, 0.875 mmol) in 5 mL of 1,3-dimethyl-2-imidazolidione (DMI) for two hours under an inert Argon atmosphere at 110 °C. After that, the temperature of the reaction mixture was lowered down to 60 °C followed by 0.0415 gm (0.175 mmol) $NiCl_2$, $6H_2O$ in 1 mL of water was added. After refluxing for 2 hours at 90 °C, the reaction mixture was cooled and equal amount of water was added. A black precipitate was found which was collected by filtration. The pure dark green complexes were purified by column chromatography on silica gel using dichloromethane as eluent and the products were recrystallized from CH_2Cl_2/MeOH mixtures by slow evaporation of the dichloromethane. The products were isolated in good yields (**NiC_0:** 28 %, **NiC_2:** 63 %, **NiC_6:** 70 %, **NiC_{11}:** 80 %.)

Compound NiC_0: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.69-2.04 (m, 164H, CH, CH_2 and CH_3 in cholesteryl moiety), δ 2.46-2.5 (m, 8H, CH_2), 4.55-4.62 (m, 4H, CH), 5.42-5.44 (m, 4H, =CH), 7.14 (d, 8H, ^3J = 9.0 Hz), 7.38 (d, 8H, ^3J = 9.0 Hz). $^{13}C\{^1H\}$ DEPT NMR (75.5 MHz, $CDCl_3$) 12.0 (CH_3), 18.85 (CH_3), 19.42 (CH_3), 21.19 (CH_2), 22.7 (CH_3), 22.95 (CH_3), 23.97 (CH_2), 24.42 (CH_2), 27.75 (CH_2), 28.1 (CH), 28.35 (CH_2), 31.97 (CH), 32.05 (CH_2), 35.93 (CH), 36.31 (CH_2), 36.68 (Cq), 36.97 (CH_2), 38.05 (CH_2), 39.65 (CH_2), 39.84 (CH_2), 42.45 (Cq), 50.19 (CH), 56.27 (CH), 56.81 (CH), 79.23 (CH), 121.31 (CH),

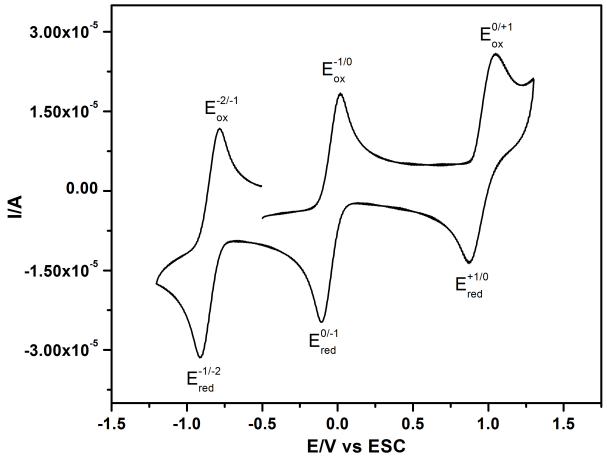
123.41 (CH), 130.28 (Cq), 138.6 (Cq), 139.21 (Cq), 151.81 (Cq), 152.5 (Cq), 180.44 (Cq). UV-vis-NIR ($CHCl_3$, 23 °C): λmax (ε, $M^{-1}cm^{-1}$) = 273 (35400), 317 (39300), 866 (24400). IR (KBr): 2948, 2865, 1762, 1596, 1504, 1467, 1440, 1411, 1355, 1317, 1251, 1216, 1170, 1139, 1085, 991, 970, 946, 889, 836, 802 cm^{-1}. EI-MS: *m/z* (%) =2278.2835 (100) $[M+Na]^+$. Anal. Calcd for $C_{140}H_{196}NiO_{12}S_4$: C, 74.47; H, 8.75; S, 5.68; Found C, 74.50; H, 8.88; S, 5.34.

Compound NiC_2: ^1H NMR ($CDCl_3$, 300 MHz) δ 0.67-2.03 (m, 164H, CH, CH_2 and CH_3 in cholesteryl moiety), δ 2.38-2.42 (m, 8H, CH_2), 4.2 (t, 8H, ^3J = 4.5 Hz), 4.45-4.55 (m, 12H, OCH_2 and OCH), 5.39-5.41 (m, 4H, =CH), 6.81 (d, 8H, ^3J = 9.0 Hz), 7.31 (d, 8H, ^3J = 9.0 Hz). $^{13}C\{^1H\}$ DEPT NMR (75.5 MHz, $CDCl_3$) 11.99 (CH_3), 18.84 (CH_3), 19.4 (CH_3), 21.17 (CH_2), 22.69 (CH_3), 22.95 (CH_3), 23.96 (CH_2), 24.41 (CH_2), 27.79 (CH_2), 28.13 (CH), 28.35 (CH_2), 31.95 (CH), 32.03 (CH_2), 35.91 (CH), 36.3 (CH_2), 36.66 (Cq), 36.97 (CH_2), 38.12 (CH_2), 39.63 (CH_2), 39.85 (CH_2), 42.43 (Cq), 50.11 (CH), 56.25 (CH), 56.8 (CH), 65.77 (OCH_2), 65.83 (OCH_2), 78.37 (CH), 114.56 (CH), 123.17 (CH), 130.52 (CH), 134.84 (CH), 139.78 (Cq), 154.52 (Cq), 159.15 (Cq), 180.5 (Cq). UV-vis-NIR ($CHCl_3$, 23 °C): λmax (ε, $M^{-1}cm^{-1}$) = 301 (40050), 920 (29600). IR (KBr): 2946, 2867, 1743, 1598, 1508, 1465, 1417, 1353, 1268, 1240, 1176, 1141, 1110, 1066, 1027, 1008, 993, 973, 946, 885, 823, 793 cm^{-1}. EI-MS: *m/z* (%) = 2454.3908 (100) $[M+Na]^+$. Anal. Calcd for $C_{148}H_{212}NiO_{16}S_4$: C, 73.03; H, 8.78; S, 5.27; Found C, 72.78; H, 8.85; S, 5.11.

Compound NiC_6: ^1H NMR ($CDCl_3$, 300 MHz) δ 0.66-2.02 (m, 196H, CH, CH_2 and CH_3 in cholesteryl moiety and CH_2 of the linker), δ 2.37-2.41 (m, 8H, CH_2), 3.95 (t, 8H, ^3J = 6.3 Hz), 4.14 (t, 8H, ^3J = 6.3 Hz), 4.41-4.52 (m, 4H, CH), 5.37-5.39 (m, 4H, =CH), 6.78 (d, 8H, ^3J = 9.0 Hz), 7.32 (d, 8H, ^3J = 9.0 Hz). $^{13}C\{^1H\}$ DEPT NMR (75.5 MHz, $CDCl_3$)

11.97 (CH_3), 18.83 (CH_3), 19.38 (CH_3), 21.15 (CH_2), 22.69 (CH_3), 22.95 (CH_3), 23.95 (CH_2), 24.39 (CH_2), 25.67 (CH_2), 25.84 (CH_2), 27.82 (CH_2), 28.13 (CH), 28.34 (CH_2), 28.75 (CH_2), 29.19 (CH_2), 31.94 (CH), 32.01 (CH_2), 35.90 (CH), 36.29 (CH_2), 36.65 (Cq), 36.97 (CH_2), 38.16 (CH_2), 39.62 (CH_2), 39.81 (CH_2), 42.41 (Cq), 50.07 (CH), 56.22 (CH), 56.77 (CH), 67.75 (OCH_2), 67.93 (OCH_2), 77.8 (CH), 114.4 (CH), 123.04 (CH), 130.47 (CH), 134.39 (CH), 139.48 (Cq), 154.77 (Cq), 159.88 (Cq), 180.52 (Cq). UV-vis-NIR ($CHCl_3$, 23 °C): λmax (ε, $M^{-1}cm^{-1}$) = 301 (46100), 932 (33400). IR (KBr): 2939, 2865, 1739, 1598, 1569, 1508, 1467, 1417, 1353, 1249, 1172, 1141, 1110, 1025, 1008, 993, 882, 827, 792 cm^{-1}. EI-MS: *m/z* (%) = 2678.6405 (100) $[M+Na]^+$. Anal. Calcd for $C_{164}H_{244}NiO_{16}S_4$: C, 74.09; H, 9.25; S, 4.82; Found C, 73.94; H, 8.95; S, 4.54.

Compound NiC_{11}: ^1H NMR ($CDCl_3$, 300 MHz) δ 0.67-2.02 (m, 236H, CH, CH_2 and CH_3 in cholesteryl moiety and CH_2 of the linker), δ 2.37-2.41 (m, 8H, CH_2), 3.95 (t, 8H, ^3J = 6.6 Hz), 4.1 (t, 8H, ^3J = 6.6 Hz), 4.41-4.52 (m, 4H, CH), 5.37-5.4 (m, 4H, =CH), 6.79 (d, 8H, ^3J = 9.0 Hz), 7.32 (d, 8H, ^3J = 9.0 Hz). $^{13}C\{^1H\}$ DEPT NMR (75.5 MHz, $CDCl_3$) 11.98 (CH_3), 18.82 (CH_3), 19.38 (CH_3), 21.14 (CH_2), 22.68 (CH_3), 22.95 (CH_3), 23.94 (CH_2), 24.38 (CH_2), 25.84 (CH_2), 26.15 (CH_2), 27.81 (CH_2), 28.12 (CH), 28.34 (CH_2), 28.79 (CH_2), 29.33 (CH_2), 29.5 (CH_2), 29.57 (CH_2), 29.62 (CH_2), 31.93 (CH), 32.0 (CH_2), 35.89 (CH), 36.28 (CH_2), 36.63 (Cq), 36.97 (CH_2), 38.16 (CH_2), 39.62 (CH_2), 39.8 (CH_2), 42.4 (Cq), 50.07 (CH), 56.2 (CH), 56.77 (CH), 67.96 (OCH_2), 68.17 (OCH_2), 77.7 (CH), 114.4 (CH), 123.01 (CH), 130.46 (CH), 134.3 (CH), 139.48 (Cq), 154.77 (Cq), 159.93 (Cq), 180.47 (Cq). UV-vis-NIR ($CHCl_3$, 23 °C): λmax (ε, $M^{-1}cm^{-1}$) = 301 (48100), 933 (32800). IR (KBr): 2931, 2852, 1741, 1598, 1508, 1467, 1353, 1249, 1172, 1143, 1110, 1025, 1008, 993, 993, 946, 825, 794 cm^{-1}. EI-MS: *m/z* (%) = 2958.9541 (100) $[M+Na]^+$. Anal. Calcd for $C_{184}H_{284}NiO_{16}S_4$: C, 75.19; H, 9.74; S, 4.36; Found C, 74.83; H, 9.79; S, 4.13.



Cyclic voltammograms of complex **NiC_2** in dichloromethane (vs SCE, v = 100 $mV.s^{-1}$, electrolyte = 0.2M $n$$Bu_4NPF_6$).

Electrochemical data for complexes **NiC_n** (n = 2, 6, 11).

Complex	$E^{1/2}$(-2/-1)	$E^{1/2}$(-1/0)	$E^{1/2}$(0/+1)
NiC_2	-0.847	-0.044	0.956
NiC_6	-0.87	-0.069	0.931
NiC_{11}	-0.86	-0.06	0.926

0.2M $n$$Bu_4NPF_6$ in dichloromethane at room temperature; scan rate, 100 mVs^{-1}. $E^{1/2}$ = $(E_{pa}+E_{pc})/2$; E_{pa} and E_{pc} are the anodic peak and the cathodic peak potentials, respectively.

Cyclic voltammetry of the neutral complexes in CH_2Cl_2 shows one reversible oxidation process centered at 0.90 V (*vs*. SCE), corresponding to the formation of the monocationic species and two reversible reduction processes centered at –0.06 V and –0.80 V, corresponding to the formation of the monoanionic and dianionic species, respectively as shown above. The redox potentials are weakly affected by the variation of the chain length of the spacer and are closely related to those of monosubstituted analogous complexes with linear alkyl chains.[S1]

[S1] a) R. Perochon, L. Piekara-Sady, W. Jurga, R. Clérac, M. Fourmigué, *Dalton Trans.* **2009**, *16*, 3052-3061; b) R. Perochon, C. Poriel, O. Jeannin, L. Piekara-Sady and M. Fourmigué, *Eur J. Inorg. Chem.* **2009**, 5413-5421.

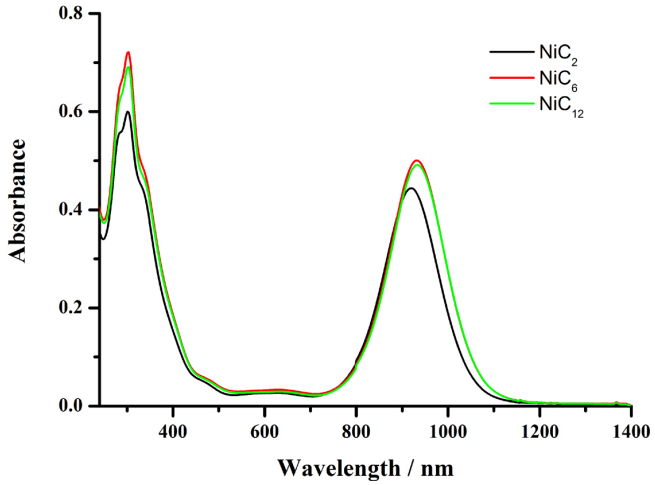


Figure S1. UV/Vis/NIR absorption spectra of NiC_n complexes in chloroform at room temperature ($C \approx 1.5 \times 10^{-5}$ mol.L^{-1}).

Table S1. Optical properties of complexes **NiC_n** (n = 2, 6, 11).

Complex	λ/nm	ε/M^{-1}.cm^{-1}
NiC_2	919	29600
NiC_6	932	33400
NiC_{12}	933	32800

Table S2. Solvents tested for gelation with compounds **NiC_n** (n = 0, 2, 6, 11).

Solvents	Status of compounds[a] (MGC) [mg.mL^{-1} / mM]			
	NiC_2	**NiC_6**	**NiC_{11}**	**NiC_0**
Dodecane	G (0.7 / 0.3)	G (12 / 4.5)	P	I
Decane	G (0.8 / 0.3)	G (15 / 5.6)	P	I
Heptane	G (2.0 / 0.8)	G (16 / 6.0)	P	I
Hexane	I	I	P	I
Cyclohexane	G (2.0 / 0.8)	G (8.0/ 3.0)	P	I
Petrolium ether	I	I	P	I
THF	S	S	S	I
DMF	P	Ins	P	I
Toluene	S	S	S	I
Ethyl acetate	FG (3.0 / 1.2)	Ins	P	I
Dioxane	S	S	S	I
DCM	S	S	S	P
Chloroform	S	S	S	S

[a] G, gel; FG; fragile gel; I, insoluble; S, soluble; P, precipitate.

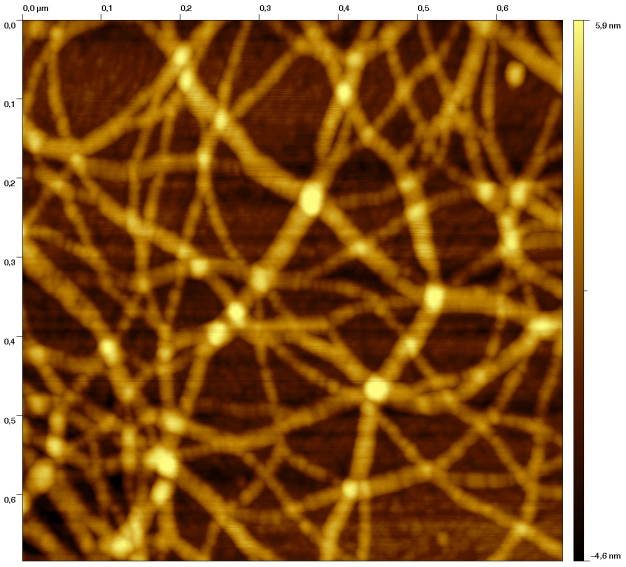


Figure S2. a) AFM tapping mode image (0.7 µm × 0.7 µm) of a dried diluted gel of **NiC_2** in cyclohexane (C = 0.2 mg.L^{-1}) deposited on HOPG.

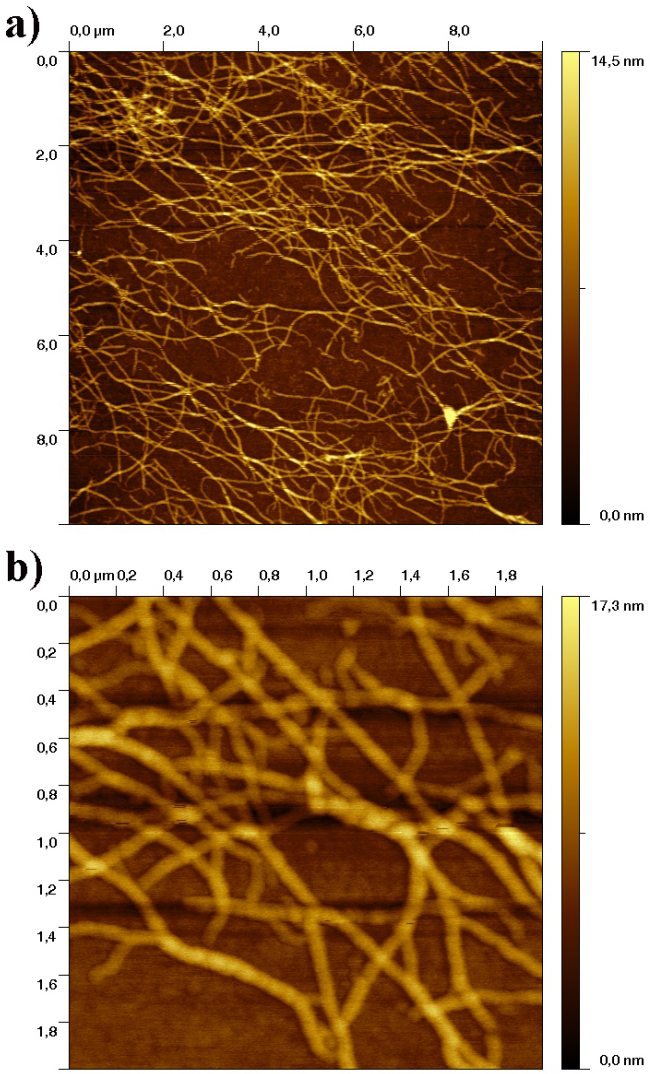


Figure S3. a) AFM tapping mode image (10 µm × 10 µm) of a dried diluted gel of **NiC_2** in dodecane (C = 0.1 mg.mL^{-1}) deposited on Silicon wafer. b) Zoomed area 2 µm × 2 µm.

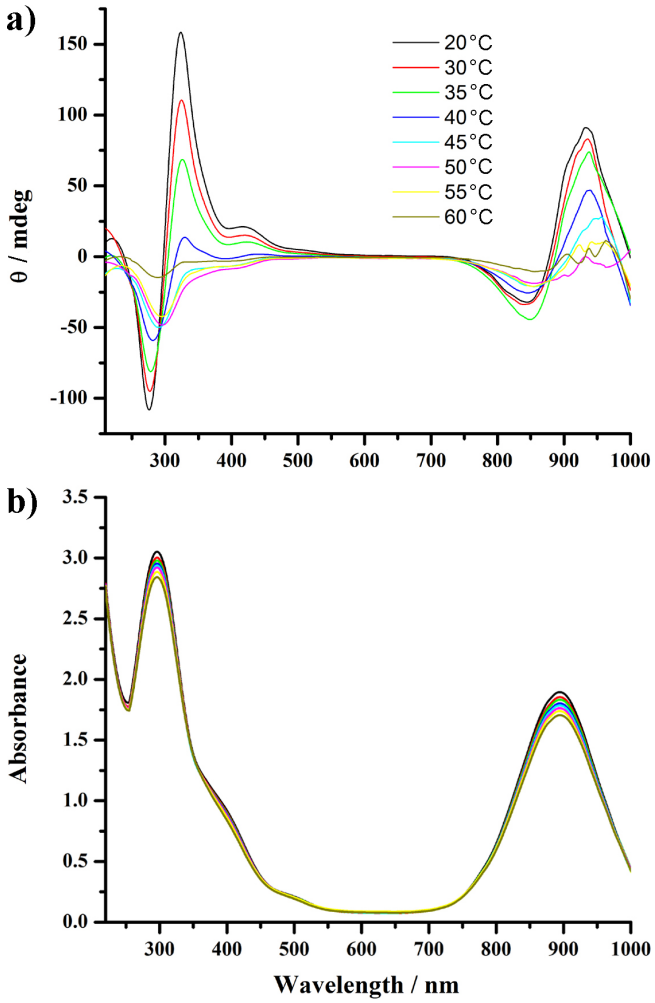


Figure S4. a) Temperature dependence of the CD signal of **NiC_2** in a diluted cyclohexane gel (C = 0.7 mg/mL, l = 2 mm); b) Temperature dependence of the UV/Vis/NIR absorption.

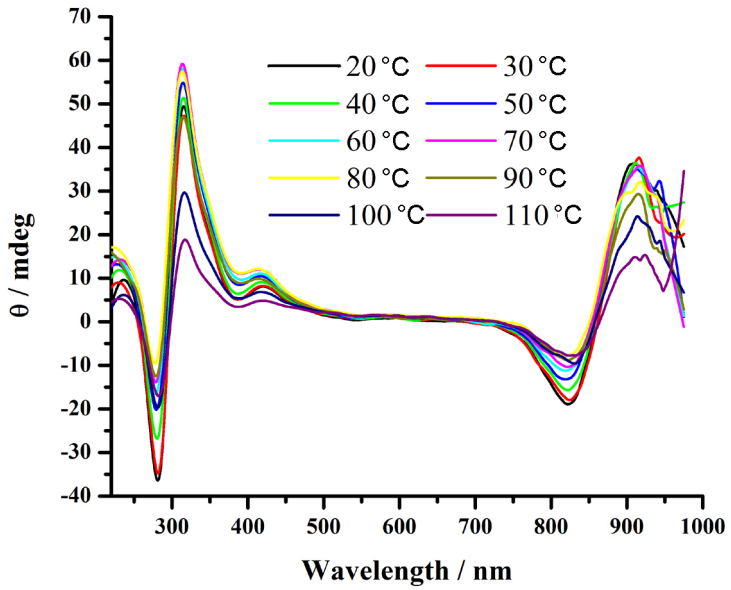


Figure S5. a) Temperature dependence of the CD signal of **NiC_2** in a diluted dodecane gel (C = 0.5 mg/mL, l = 2 mm).