# Supporting Information

# for

# Reversible switching of structural and plasmonic properties of liquid-crystalline gold nanoparticle assemblies

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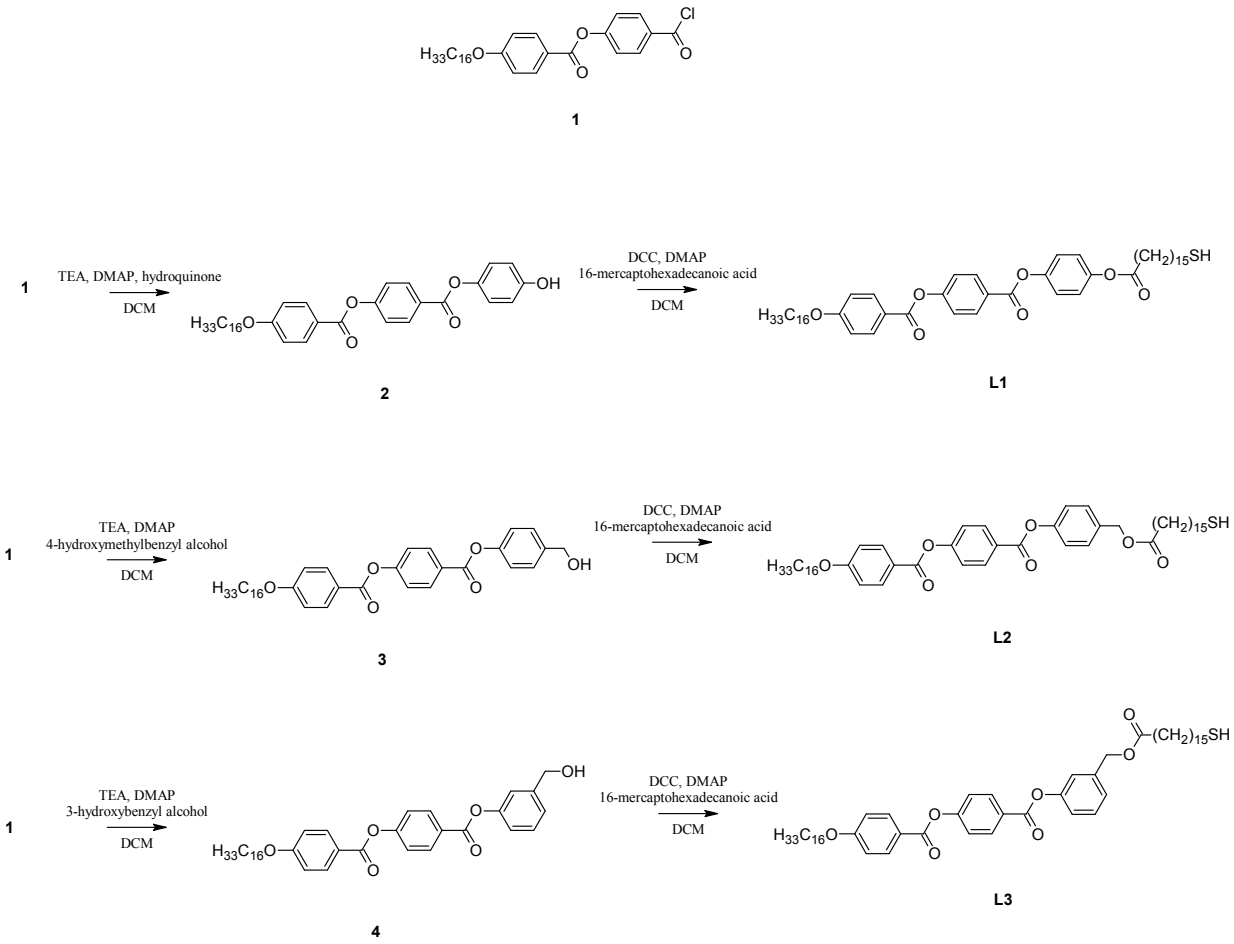


**Figure S1**. Synthetic route for the preparation of (pro)mesogenic ligands.

## Supplementary Note 1. Details of promesogenic ligand synthesis (L) and analysis

**Synthesis of 4-[(2,2,2-trichloroethoxy)carbonyl]phenyl-4-(hexadecyloxy)benzoate (1)**

4-(chlorocarbonyl)phenyl-4-(hexadecyloxy)benzoate (**1**) was synthesized as described previously [S1].

**Synthesis of [(4-hydroxyphenoxy)carbonyl]phenyl-4-(hexadecyloxy)benzoate (2)**

In the next step, TEA (13.8 mL) was added to the solution of hydroquinone (45.5 g, 413.5 mmol) and DMAP (catalytic amount) in 300 ml of THF. Then, 4-(chlorocarbonyl)phenyl-4-(hexadecyloxy)benzoate (13.8 g, 27.57 mmol) in 100 ml of THF was added. The reaction mixture was stirred for 8 h at reflux and evaporated to dryness. The crude product was crystallized from methanol twice and purified by column chromatography using 1% MeOH in DCM as eluent, affording pure product with 40% yield.
*Elemental analysis* Found: C, 62.95; H, 5.4. Calc. for C13H13NO4: C, 63.2; H, 5.3% for $C_{36}H_{46}O_6$ (M ~ 574.7): C 75.23, H 8.07, O 16.70 ; found C 75.00, H 8.19%
**$^1$H NMR** (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 3H, *J* = 6.0 Hz, $CH_3$); 1.24-1.50 (m, 26H); 1.83 (m, 2H); 4.05 (t, 2H, *J* = 6.6 Hz, $CH_2O$); 6.84-6.89 (m, 2H, ArH); 6.96-7.01 (m, 2H, ArH); 7.06-7.11 (m, 2H, ArH); 7.34-7.38 (m, 2H, ArH); 8.13-8.18 (m, 2H, ArH); 8.24-8.29 (m, 2H, ArH)

**Synthesis of [((4-hydroxymethyl)phenoxy)carbonyl]phenyl-4-(hexadecyloxy)benzoate (3)**

The synthesis was performed using following the recipe given for compound **2**, using 4-hydroxybenzyl alcohol in the place of hydroquinone.
*Elemental analysis* for $C_{37}H_{48}O_6$ (M ~ 588.8): calc. C 75.48, H 8.22, O 16.30; found C 75.57, H 8.19%;
**$^1$H NMR** (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 3H, J = 7.0 Hz); 1.26-1.50 (m, 22H); 1.47 (m, 2H, $\underline{CH_2}CH_2CH_2O$); 1.82 (m, 2H, $\underline{CH_2}CH_2O$); 4.04 (t, 2H, $CH_2O$); 4.72 (s, 2H, $ArCH_2O$); 6.89-6.92 (m, 2H, ArH); 7.07-7.09 (m, 2H, ArH); 7.29-7.31 (m, 2H, ArH); 7.36-7.39 (m, 2H, ArH); 8.13-8.15 (m, 2H, ArH); 8.24-8.26 (m, 2H, ArH); $^{13}$C NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 22.70, 25.98, 29.08, 29.37, 29.56, 29.60, 29.67, 29.68, 29.70, 31.93, 66.56, 68.39, 76.77, 77.03, 77.28, 114.39, 120.99, 121.89, 127.22, 127.43, 128.49, 131.30, 132.39, 132.41, 135.40, 141.01, 154.94, 163.79, 164.40, 165.75

**Synthesis of [((3-hydroxymethyl)phenoxy)carbonyl]phenyl-4-(hexadecyloxy)benzoate (4)**

The synthesis was performed using following the recipe given for compound **3**, using 3-hydroxybenzyl alcohol in the place of hydroquinone.
*Elemental analysis* for $C_{37}H_{48}O_6$ (M ~ 588.8): calc. C 75.48, H 8.22, O 16.30; found C 75.47, H 8.25%;
**$^1$H NMR** (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 3H, *J* = 7.0 Hz, $CH_3$); 1,26-1,40 (m, 24H); 1,45-1.51 (m, 2H, $\underline{CH_2}CH_2CH_2O$); 1.80-1.85 (m, 2H, $\underline{CH_2}CH_2O$); 4.05 (t, 2H, *J* = 6.5 Hz, $\underline{CH_2}O$); 4.75 (s, 2H, $ArCH_2O$); 6.97-7.00 (m, 2H, ArH); 7.14-7.17 (m, 1H, ArH); 7.28-7.29 (m, 1H, ArH); 7.36-7.38 (m, 2H, ArH), 7.41-7.45 (m, 2H, ArH); 8.13-8.17 (m, 2H, ArH), 8.26-8.29 (m, 2H, ArH), **$^{13}$C NMR** (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.13, ,22.70, 25.98, 29.09, 29.37, 29.57, 29.60, 29.67, 29.71, 31.93, 64.72, 68.40, 76.78, 77.03, 114.42, 120.09, 120.80, 120.92, 122.12, 122.25, 124.27, 126.82, 129.64, 131.80, 132.42, 142.86, 151.08, 155.40, 163.83, 164.35, 164.55

**Synthesis of 4-({4-[(16-sulfanylhexadecanoyl)oxy]phenoxy}carbonyl)phenyl-4-(hexadecyloxy)benzoate (L1)**

DCC (206 mg, 1.05 mmol) was added to the solution of **2** (575 mg, 1.0 mmol), 16-mercaptohexadecanoic acid (303 mg, 1.05 mmol), DMAP (catalytic amount) in 20 mL of dichloromethane at room temperature and stirred for 12h. A white precipitate formed which was fileterd out. The crude product was chromatographed twice on silica gel eluted with toluene affording pure product with 15% yield.
*Elemental analysis* for $C_{52}H_{76}O_7S$ (M ~ 845.2): calc. C 73.89, H 9.06, O 13.25, S 3.79; found C 73.77,
H 8.99, S 3.87;
**$^1$H NMR** (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 3H, J = 7 Hz, $CH_3$); 1.26-1.53 (m, 53H); 1.81 - 1.88 (m, 2H; $\underline{CH_2}CH_2O$); 2.51 (q, 2H, *J* = 7.0 Hz, $CH_2S$); 2.56 (t, 2H, J = 7.5 Hz, $CH_2COO$); 4.05 (t, 2H, *J* = 6.5 Hz; $CH_2O$); 6.97-6.99 (m, 2H, ArH); 7.13-7.16 (m, 2H, ArH); 7.22-7.24 (m, 2H, ArH); 7.35-7.38 (m, 2H, ArH); 8.14-8.16 (m, 2H, ArH); 8.25-8.27 (m, 2H, ArH); **$^{13}$C NMR** (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.13, 28.79, 29.10, 29.12, 29.27, 29.37, 29.45, 29.47, 29.55, 29.57, 29.62, 29.64, 29.67, 29.69, 29.70, 29.71, 31.94, 32.86, 34.05, 34.38, 68.41, 114.44, 120.95, 122.13, 122.53, 126.73, 131.82, 132.43,148.19, 148.30, 155.46, 163.85, 164.32, 164.36, 172.19

**Synthesis of 4-({4-[(16-sulfanylhexadecanoyl)methyloxy]phenoxy}carbonyl)phenyl-4-(hexadecyloxy)benzoate (L2)**

The synthesis was performed using following the recipe given for compound **L1** using compound **3** in the place of **2**.
**$^{1}$H NMR** (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 3H, $CH_3$); 1.26-1.70 (m, 52H); 1.83 (m, 2H, $\underline{CH_2}CH_2O$), 2.35 (t, 2H, J = 7.0 Hz, $OOC\underline{CH_2}$); 2.51 (q, 2H, *J* = 7.5 Hz, $\underline{CH_2}SH$); 4.04 (t, 2H, *J* = 7.0, $\underline{CH_2}$ OAr); 5.37 (s, 2H; $Ar\underline{CH_2}OOC$), 6.98-7.01 (m, 2H; ArH), 7.07-7.09 (m, 2H, ArH); 7.07-7.09 (m, 2H, ArH); 7.38-7.40 (d, 2H; ArH), 8.13-8.15 (d, 2H, ArH), 8.24-8.26 (d, 2H, ArH); **$^{13}$C NMR** (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 173.68, 165.70, 164.38, 163.80, 154.97, 136.28, 135.97, 132.39, 131.31, 128.43, 128.39, 127.43, 121.91, 121.00, 114.40, 77.28, 77.23, 77.03, 76.77, 68.39, 66.44, 34.33, 34.07, 31.94, 29.71, 29.67, 29.66, 29.64, 29.60, 29.57, 29.53, 29.46, 29.37, 29.26, 29.15, 29.09, 28.97, 28.83, 28.40, 25.99, 25.73, 24.96, 24.67, 22.71, 14.14

**Synthesis of 4-({3-[(16-sulfanylhexadecanoyl)methyloxy]phenoxy}carbonyl)phenyl-4-(hexadecyloxy)benzoate (L3)**

The synthesis was performed using following the recipe given for compound **L1** using compound **4** in the place of **2**.
*Elemental analysis* for $C_{52}H_{76}O_7S$ (M ~ 845.2): calc. C 73.89, H 9.06, O 13.25, S 3.79; found C 73.96,
H 9.15, S 3.70; **$^{1}$H NMR** (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (m, 3H, $CH_3$); 1.24-1.70 (m, 54H); 1.80-1.86 (m, 2H, $\underline{CH_2}CH_2O$); 2.37 (t, 2H, *J* = 7.5 Hz, $OOC\underline{CH_2}$ ), 2.52 (q, 2H, J = 7.0 Hz, $\underline{CH_2}SH$), 4.06 (t, 2H, *J* = 6.5 Hz, $CH_2OAr$), 5.15 (s, 2H, $Ar\underline{CH_2}OOC$), 6.98-7.00 (m, 2H, ArH); 7.18-7.27 (m, 2H, ArH); 7.36-7.38 (m, 2H, ArH); 7.41-7.44 (m, 1H, ArH); 8.14-8.16 (m, 2H, ArH); 8.26-8.28 (m, 2H, ArH); **$^{13}$C NMR** (500 MHz, $CDCl_3$, 25 °C, TMS): δ =14.14, 22.71, 24.68, 24.96, 26.00, 28.41, 29.10, 29.16, 29.27, 29.38, 29.47, 29.52, 29.54, 29.57, 29.61, 29.65, 29.66, 29.68, 29.69, 29.73, 31.95, 34.08, 34.30, 65.38, 68.42, 76.78, 77.03, 114.44, 120.94, 121.31, 121.49, 122.14, 125.52, 126.78, 129.66, 131.83, 132.44, 137.98, 151.03, 155.45, 163.86, 164.34, 164.42, 173.62

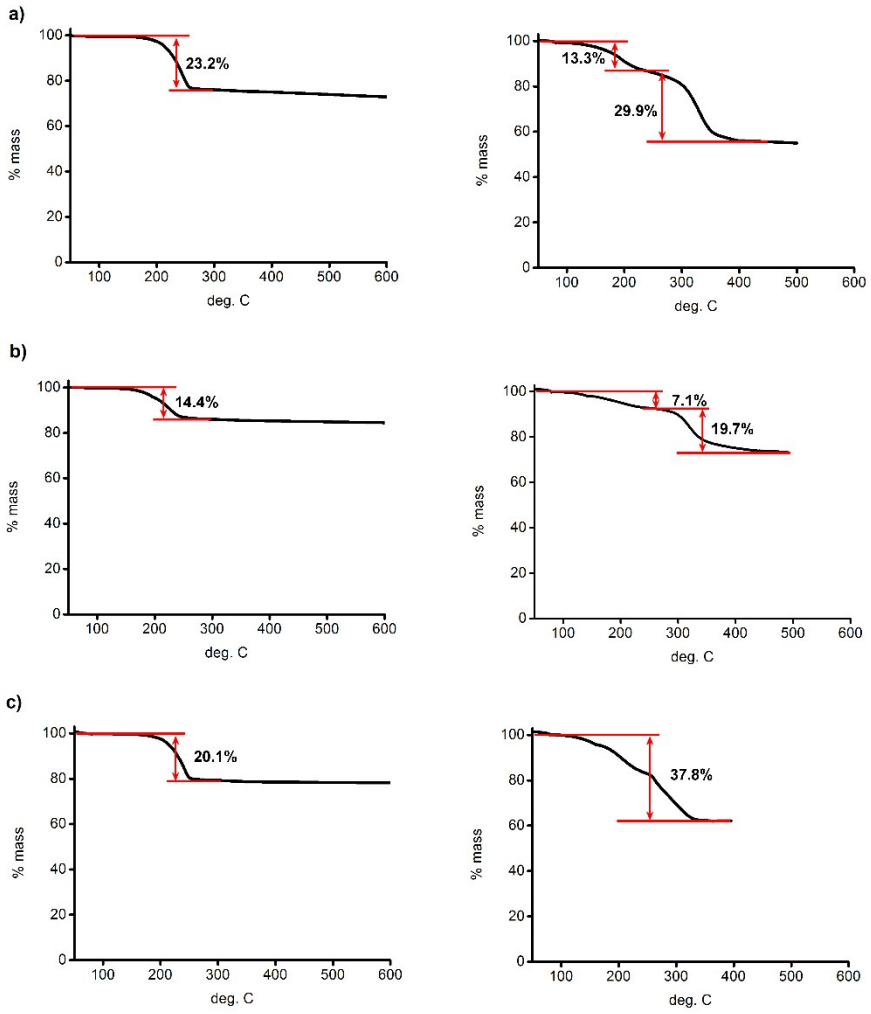


**Figure S2.** Thermogravimetric analysis of nanoparticles. TGA analysis of dodecanethiol coated nanoparticles (on the left) and hybrid materials (on the right); **a) G2** and **L3_G2**; **b) G4**, **L3_G4**, **c) S5**, **L3_L3**; % of mass drops are given in pictures.

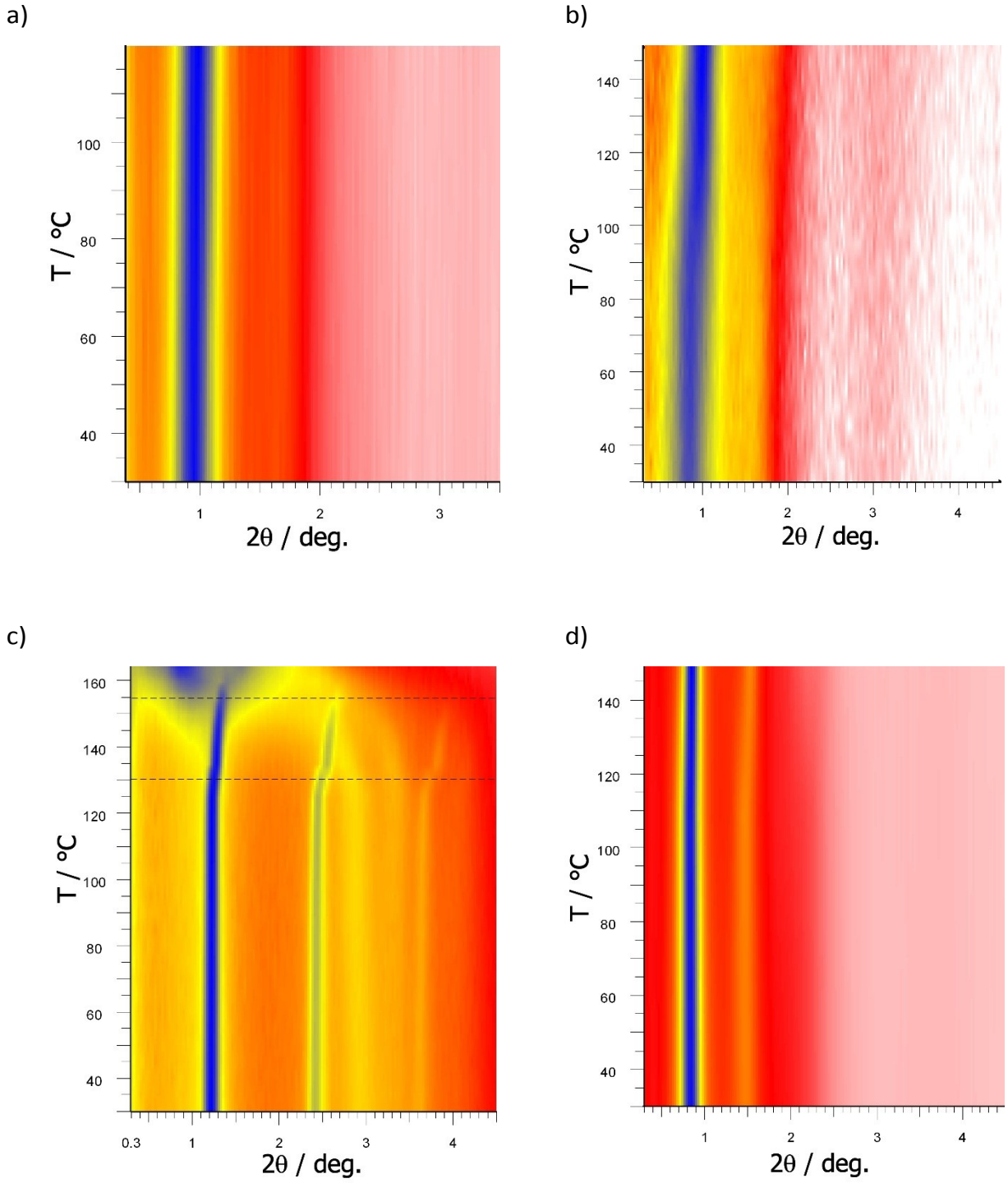


**Figure S3.** Temperature dependent SAXRD reflections of aligned samples of hybrid materials: a) **L1_G4**, b) **L1_S5**, c) **L2_G2** and d) **L2_G4**.

**Table S1.** Mass losses and number of ligands calculated from TGA measurements.

| | Mass loss [%] | Mass loss [%] | Number of alkyl ligands | Number of (pro)mesogenic ligands | % L |
|---|---|---|---|---|---|
| **G2** | 23.2 | - | 100 | - | - |
| **G4** | 13.4 | - | 400 | - | - |
| **S5** | 20.1 | - | 460 | - | - |
| **G2_L3** | 13.3 | 29.9 | 75 | 40 | 35 |
| **G4_L3** | 7.1 | 19.7 | 250 | 160 | 39 |
| **S5_L3** | | | 260 | 200 | 43 |

**Table S2.** Positions of XRD signals for **L3_G4** material at low temperatures (tetragonal symmetry).

| Signals indexing | Signals positions from measurements [Å] | Signals positions from modelling [Å] |
|---|---|---|
| **002** | 75.1 | 75.0 |
| **011** | 53.5 | 53.5 |
| **110** | 40.3 | 40.5 |
| **004** | 37.7 | 37.5 |
| **112** | 35.8 | 35.6 |