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Ionic Columnar Clustomesogens: Associations between Anionic Hexanuclear Rhenium Clusters and Liquid Crystalline Triphenylene Tethered Imidazoliums

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Supplementary information.

Characterizations.

300 (^{1}H) and 75.5 MHz (^{13}C) NMR spectra were recorded on Bruker Avance 300 spectrometer at room temperature using perdeuterated solvents as internal standards. Elemental analyses were performed by the service central d'analyses du CNRS, Vernaison, France. Mass spectra were recorded with a MALDI-TOF Microflex LT Bruker. UV-Vis spectra were recorded using a UV-3600 plus UV-Vis-NIR spectrophotometer (Shimadzu). IR spectra were recorded on a Bruker Vertex70. Absolute quantum yield were measured with a Hamamatsu C9920-03G system.

Differential scanning calorimetry (DSC) was carried out by using NETZSCH DSC 200 F3 instrument equipped with an intracooler. DSC traces were measured at 10 °C/min down to -25 °C.

Optical microscopy investigations were performed on a Nikon H600L polarizing microscope equipped with a Linkam "liquid crystal pro system" hotstage LTS420. The microscope is also equipped with a UV irradiation source (Hg Lamp, λ = 340-380 nm) and an ocean optic USB 2000+ UV-Vis-NIR spectrophotometer based on CCD detection technology.

X-ray scattering experiments (SAXS) were performed using a FR591 Bruker AXS rotating anode X-ray generator operated at 40 kV and 40 mA with monochromatic Cu Kα radiation (λ = 1.541 Å) and point collimation. The patterns were collected with a Mar345 Image-Plate detector (Marresearch, Norderstedt, Germany). The samples were held in Lindeman glass capillaries (1 mm diameter). The capillaries were placed inside a Linkam HFX350-Capillary X-Ray stage which allow measurements from -196 °C up to 350 °C with an accuracy of 0.1 °C.

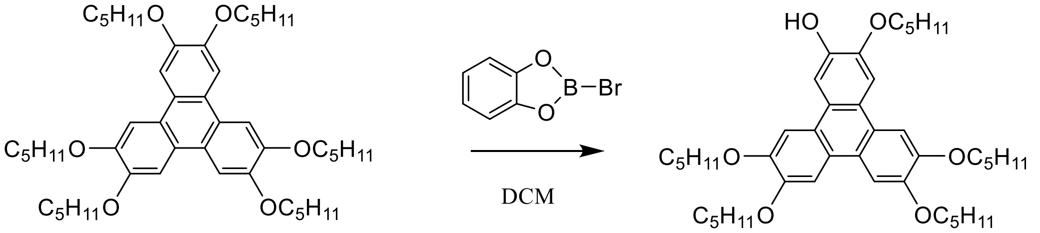
Emission measurements. Lifetime measurements and TRPL mapping were realized using a picosecond laser diode (Jobin Yvon deltadiode, 375 nm) and a Hamamatsu C10910-25 streak camera mounted with a slow single sweep unit. Signals were integrated on a 30 nm bandwidth. Fits were obtained using origin software and the goodness of fit judge by the reduced $\chi 2$ value and residual plot shape. The luminescence spectra in deaerated dichloromethane and absolute quantum yields in the solid state were measured with a C9920–03 Hamamatsu system equipped with a 150 W xenonlamp, a monochromator, an integrating sphere and a red-NIR sensitive PMA-12 detector.

SCLC Measurements. Devices were prepared by evaporating 50 nm thick gold on SU8 (epoxy photosentive commercial ink, SU8 2000.5) pre-coated glasses. Then gold was patterned by photolithography process to shape the electrodes. The distances between two electrodes, equal to 3 µm, define the semiconductor (SC) thickness of the coplanar Au-SC-Au diode. Finally, the compounds were aligned on the electrode under polarised microscope. All electrical characterizations were performed in the dark under nitrogen atmosphere using a 2636A Keithley.

Synthesis.

$K_4Re_6Se_8(CN)_6$-3.5H_2O [1] and 2,3,6,7,10,11-hexakis(pentyloxy)triphenylene[2] were synthesized as already reported.

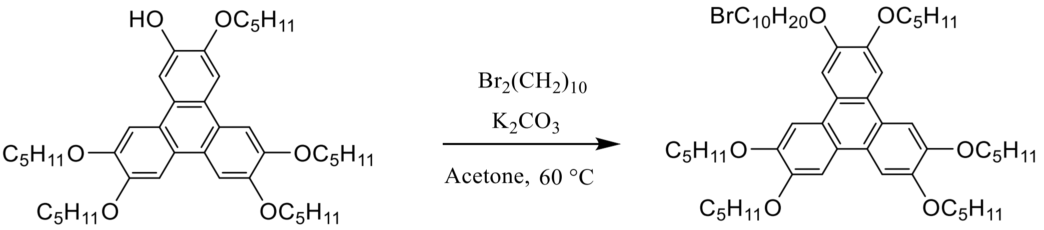
Compound 1



2,3,6,7,10,11-hexakis(pentyloxy)triphenylene (0.452 g, 0.6 mmol) was dissolved in 20 mL anhydrous dichloromethane. 1.82 mL of a 0.5M *B*-Bromocatecholborane in CH_2Cl_2 (1.5 eq) was added to the mixture. The solution was stirred under nitrogen at room temperature for 48 hours. After that, the solution was washed two times with water (50 mL) and one time with brine (50 mL) and dried over $MgSO_4$ before removal of the solvent. The compound was purified by flash chromatography on silica gel with petroleum ether/Ethyl acetate (100/0 to 95/5) as eluent. The product was isolated after removal of the solvent as a black oil (0.196 g, 48 % yield).

^{1}H NMR (300 MHz, Chloroform-d) δ 7.53-8.06 (m, CH, 6H), 5.90 (s, 1H, OH), 4.09-4.36 (m, OCH_2, 10H), 1.85-2.05 (m, CH_2, 10H), 1.34-1.67 (m, CH_2, 20H), 0.80-1.11 (m, CH_3, 15H).

Compound 2



To a solution of compound **1** (0.652 g, 0.97 mmol) and K_2CO_3 (0.877 g, 10 eq) in 30 mL acetone, 5 equivalents of 1,10-dibromodecane (1.44 g, 4.85 mmol) were added. The reaction mixture was heated at 60 °C under N_2 for 12 hours. After that, 30 mL of water was added and the solution was extracted with CH_2Cl_2 (3x30mL). The organic phase was dried over $MgSO_4$ and after removal of the solvent, the product was purified by flash chromatography on silica gel using a solvent gradient from pure petroleum ether to pure dichloromethane. The product was isolated as a black oil in 78 % yield (0.665 g).

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.85 (s, 6H, CH), 4.25 (t, $J = 6.6$ Hz, 12H, OCH_2), 3.39 (t, $J = 6.9$ Hz, 2H, CH_2Br), 1.98 (p, $J = 6.8$ Hz, 12H, CH_2), 1.72 – 1.24 (m, 34H, CH_2), 1.00 (t, $J = 7.2$ Hz, 15H,

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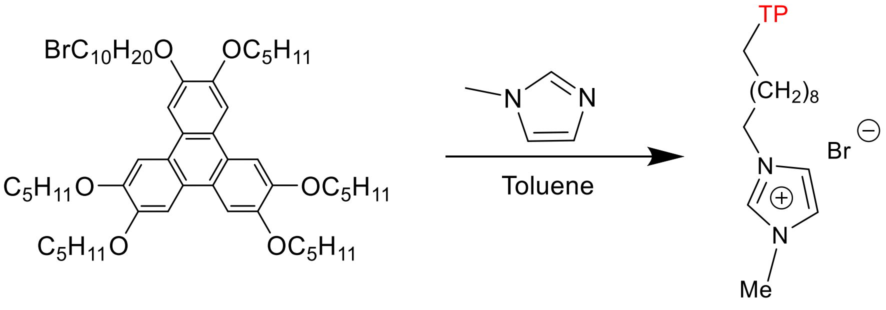
[1] N. G. Naumov, A. V. Virovets, N. V. Podberezskaya,V. E. Fedorov, *J. Struct. Chem.*, 1997, **38**, 857–862.

[2] A.N. Cammidge, H. Gopee, H. Patel, *Tetrahedron Lett.* 2009, **50**, 3513–3515

CH_3); ^{13}C NMR (75 MHz, CDCl3) δ 148.97 (Cq), 123.63 (Cq), 107.27 (CH), 69.68, 34.06, 32.90, 29.62, 29.55, 29.48, 29.23, 28.87, 28.46, 28.24, 26.26, 22.67, 14.21 (CH_3).

Compound TP1Br

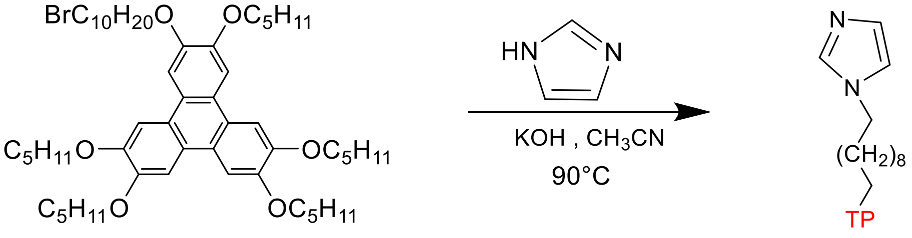


TP1

Compound **2** (0.303 g) was dissolved in 15 mL of toluene (HPLC grade) together with 3 mL of 1-methylimidazole (large excess). The reaction mixture was heated at 120 °C under N_2 for 4 days. After cooling, the solvent was removed and the product was purified by flash column chromatography on alumina gel with DCM/MeOH mixtures (100:0 to 100:10). The product was crystallized by slow evaporation of DCM from a DCM/acetonitrile mixture. Compound **TP1** was isolated as gray salt in 73 % yield after drying.

^1H NMR (300 MHz, Chloroform-d) δ 10.26 (s, 1H, CH), 7.80 (s, 6H, CH), 7.34 (d, J = 1.7 Hz, 1H, CH), 7.19 (d, J = 1.5 Hz, 1H, CH), 4.21 (q, J = 6.6, 5.6 Hz, 14H, OCH_2 + NCH_2), 4.02 (s, 3H, NCH_3), 1.99 – 1.74 (m, 12H, CH_2), 1.66 – 1.17 (m, 34H, CH_2), 1.06 – 0.78 (m, 15H, CH_3). ^{13}C NMR (75 MHz, Chloroform-d) δ 149.10 (Cq), 149.08 (Cq), 149.05 (Cq), 137.96 (CH), 123.67 (Cq), 123.64 (Cq), 123.38 (CH), 121.58 (CH), 107.52 (CH), 107.41 (CH), 69.84 (OCH_2), 69.78 (OCH_2), 50.15 (NCH_2), 36.71 (NCH_3), 30.32 (CH_2), 29.52 (CH_2), 29.48 (CH_2), 29.42 (CH_2), 29.35 (CH_2), 29.20 (CH_2), 29.03 (CH_2), 28.43 (CH_2), 26.31 (CH_2), 26.16 (CH_2), 25.89 (CH_2), 22.61 (CH_2), 14.15 (CH_3). Anal. Calcd for $C_{57}H_{87}BrN_2O_6$, H_2O: C, 68.86; H, 9.02; N, 2.82; Found C, 68.26; H, 9.12; N, 2.71. MALDI-TOF (m/z): 895.3 (100 %) $[M]^+$.

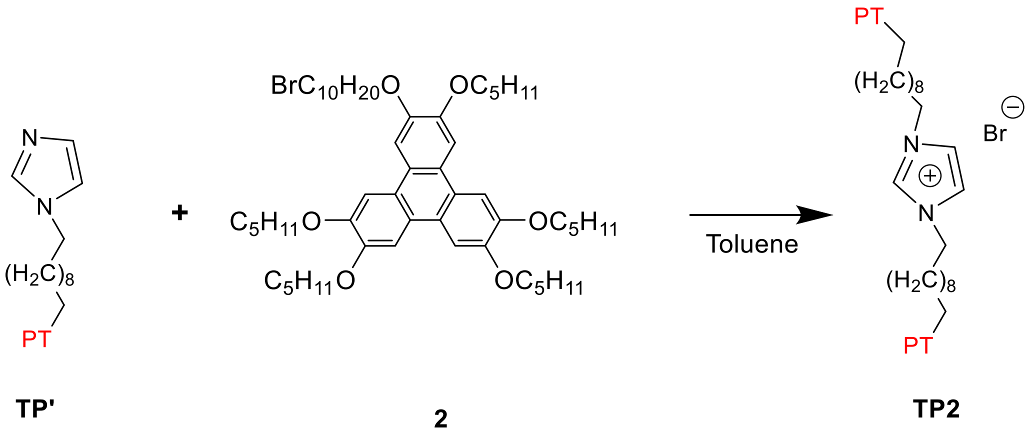
Compound TP'



Compound **2** (0.277 g, 0.3 mmol) was dissolved in acetonitrile (10 mL) together with KOH (0.035g, 2 eq) and imidazole (0.021 g, 1 eq). The reaction mixture was heated at 90°C under nitrogen for 48 hours. After cooling, acetonitrile was evaporated and the residue was dissolved in DCM (20 mL). The solution was washed with water (3x20 mL) and dried over $MgSO_4$. The compound was purified by flash chromatography on silica gel with DCM/MeOH mixtures (100:0 to 98:2). After removal of the solvent, the product was isolated as a white powder in 67 % yield (0.185 g).

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.84 (s, CH, 6H), 7.46 (s, CH, 1H), 7.05 (s, CH, 1H), 6.88 (s, CH, 1H), 4.23 (t, OCH_2, J_{HH}= 6.6 Hz, 12H), 3.88 (t, NCH_2, 2H, J_{HH}= 7.2 Hz), 1.94 (m, CH_2, 12H), 1.19–1.69 (m, CH_2, 36H), 0.98 (m, CH_3, 15H).

Compound TP2Br



TP' (0.185 g, 0.2 mmol) and compound **2** (0.188 g, 1 eq) were dissolved in 20 mL toluene (HPLC grade). The reaction mixture was heated at 120 °C under nitrogen for 6 days. After cooling, the toluene was removed and the compound was purified by flash chromatography on alumina gel with DCM/MeOH mixtures (100:0 to 1:99). The product was crystallized by slow evaporation of DCM from a DCM/acetonitrile mixture. Compound **TP2** was isolated as dark-gray salt in 85 % yield after drying.

^{1}H NMR (300 MHz, Chloroform-d) δ 10.66 (s, 1H, CH), 7.81 (d, J = 2.9 Hz, 12H, CH), 7.11 (d, J = 1.5 Hz, 2H, CH), 4.21 (t, J = 6.6 Hz, 28H, OCH_2 + NCH_2), 1.93 (p, J = 6.8 Hz, 24H, CH_2), 1.72 – 1.11 (m, 68H, CH_2), 0.96 (t, J = 7.1 Hz, 30H, CH_3). ^{13}C NMR (75 MHz, Chloroform-d) δ 149.18 (Cq), 149.14 (Cq), 123.77 (CH), 121.19 (CH), 107.53 (CH), 69.87 (OCH_2), 50.36 (NCH_2), 30.43 (CH_2), 29.52 (CH_2), 29.40 (CH_2), 29.29 (CH_2), 29.09 (CH_2), 28.52 (CH_2), 26.40 (CH_2), 26.22 (CH_2), 22.71 (CH_2), 14.24 (CH_3). Anal. Calcd for $C_{109}H_{165}BrN_2O_{12}$, 0.5$CH_2Cl_2$: C, 72.35; H, 9.20; N, 1.54; Found C, 72.07; H, 9.47; N, 1.74. MALDI-TOF (m/z): 1695.7 (100 %) $[M]^+$.

General procedure for the synthesis of $[Re_6Se_8(CN)_6]^{4-}$ ion associates with TP1 and TP2: The cluster salt $K_4[Re_6Se_8(CN)_6,4H_2O]$) (1 equiv, 0.025 mmol) was dissolved in DMF (3 mL) and the imidazolium ion-anchored triphenylene (**TP1** or **TP2**) (4 equiv) was added. The mixture was stirred at 60 °C for one night under nitrogen atmosphere. After cooling, water (30 mL) was then added and the precipitate was filtered, washed with water and dried under vacuum. The product was finally dissolved in CH_2Cl_2 and filtered over celite and isolated after removal of the solvent as thin solid films.

Cplx1: $(TP1)_4[Re_6Se_8(CN)_6]$: 85%. ^{1}H NMR (300 MHz, Chloroform-*d*, δ ppm) 8.94 (s, $1H_{imidazolium}$), 7.80 (s, 6H, $CH_{triphenylene}$), 7.37 (s, 1H, $CH_{imidazolium}$), 7.32 (s, 1H, $CH_{imidazolium}$), 4.36 (t, J = 7.2 Hz, 2H, NCH_2), 4.20 (td, J = 6.4, 2.6 Hz, 12H, OCH_2), 4.09 (s, 3H, $CH_{3imidazolium}$), 1.99-1.87 (m, 12H, CH_2), 1.66 – 1.21 (m, 34H), 1.06 – 0.86 (m, 15H). ^{13}C NMR (75 MHz, Chloroform-*d*, δ ppm) 149.13 (Cq), 149.11 (Cq), 149.04 (Cq), 137.06 (CH), 125.90 (CH), 124.15 (Cq), 123.91 (Cq), 123.70 (Cq), 107.49 (CH), 107.43 (CH), 69.83 (OCH_2), 52.05 (NCH_2), 30.72 (CH_2), 29.73 (CH_2), 29.69 (CH_2), 29.28 (CH_2), 28.55 (CH_2), 28.50 (CH_2), 26.64 (CH_2), 26.39 (CH_2), 22.72 (CH_2), 22.69 (CH_2), 14.33 (CH_3), 14.31 (CH_3), 14.23 (CH_3). IR (ATR, powder, ν_{max}/cm^{-1}): 2110s (CN). Anal. Calcd for $C_{234}H_{348}N_{14}O_{24}Re_6Se_8$, CH_2Cl_2: C, 50.63; H, 6.33; N, 3.52; Found C, 50.31; H, 6.53; N, 3.57. EDX (atomic%): C, 87.05; O, 9,77; Se, 1.87; Re, 1.31.

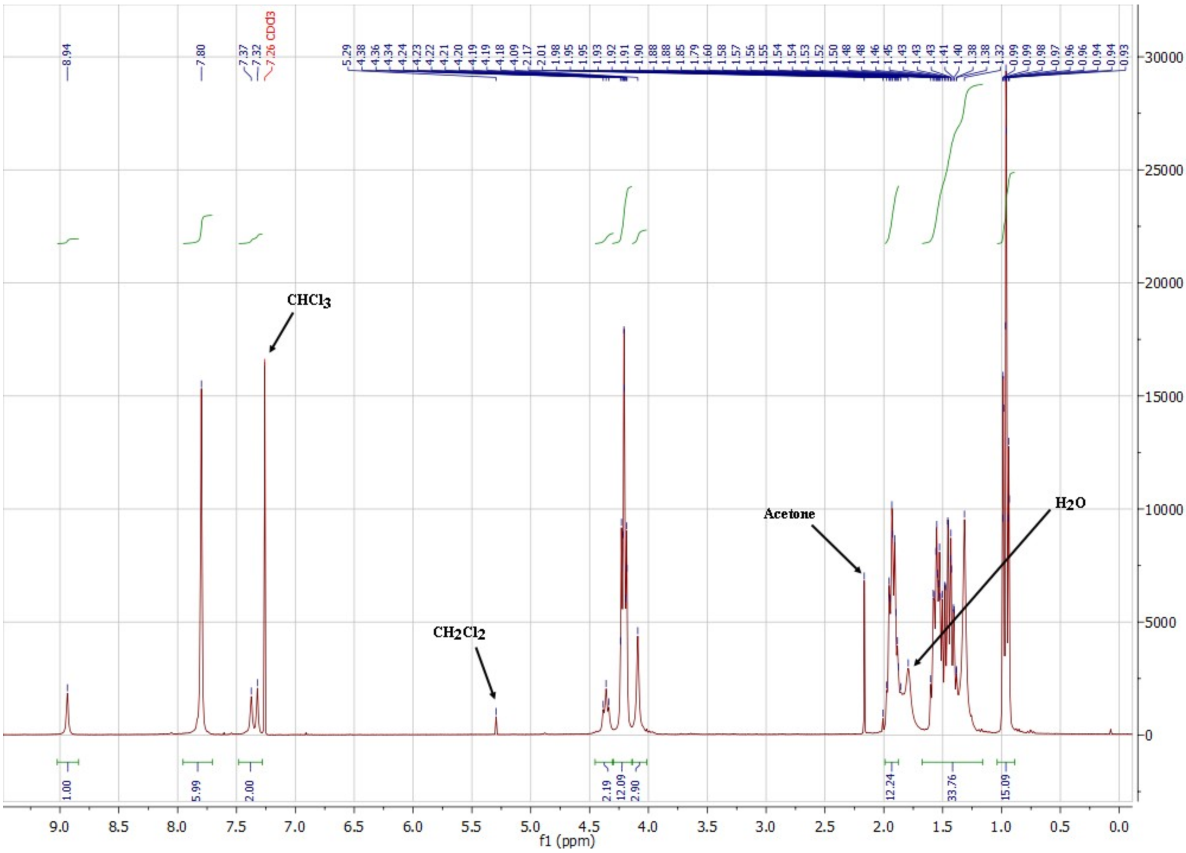


Figure A1. ^{1}H NMR spectrum of **Cplx1** (residual solvents come from the NMR tube)

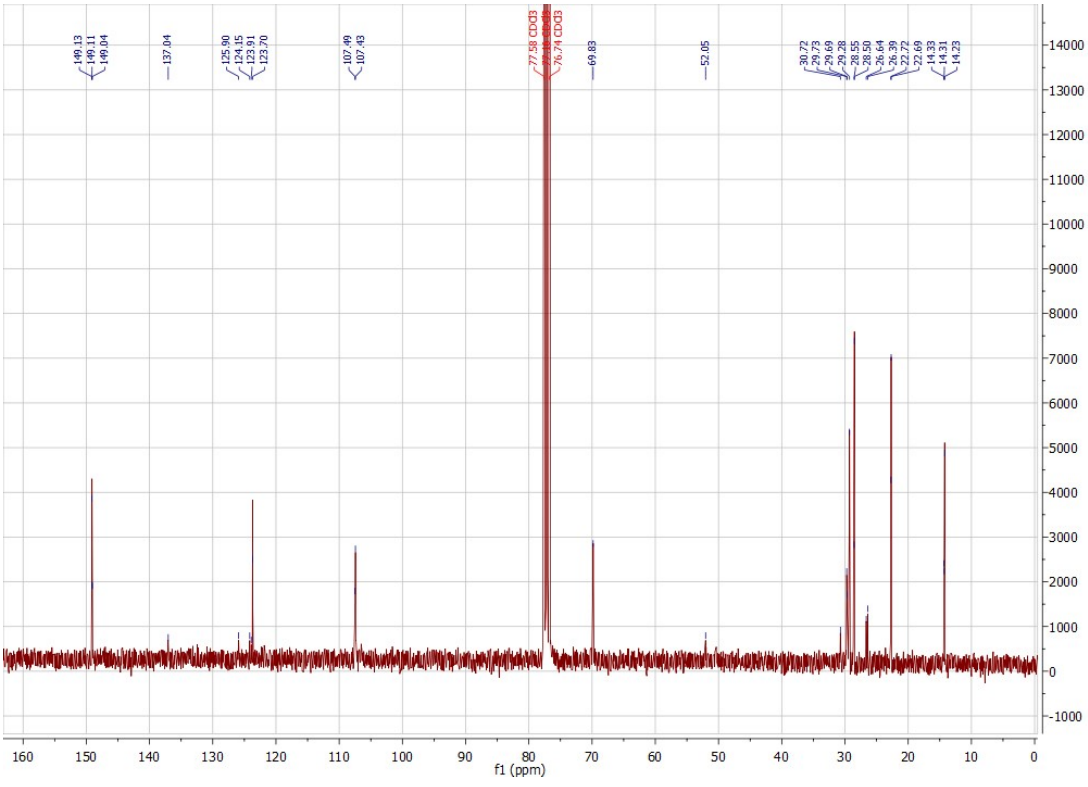


Figure A2. ^{13}C NMR spectrum of **Cplx1**

Cplx2: $(TP2)_4[Re_6Se_8(CN)_6]$: 53%. ^1H NMR (300 MHz, Chloroform-*d*, δ ppm) 9.17 (s, 1H, $CH_{imidazolium}$), 7.80 (s, 12H, $CH_{triphenylene}$), 7.28 (s, 2H, $CH_{imidazolium}$), 4.42 – 4.37 (s, 4H, NCH_2), 4.23 (t, *J* = 6.5 Hz, 24H, OCH_2), 2.04 – 1.84 (m, 24H, CH_2), 1.68 – 1.31 (m, 68H, CH_2), 1.05 – 0.89 (m, 30H, CH_3). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 149.14 (Cq), 123.74 (Cq), 118.56 (CH), 115.37 (CH), 107.51 (CH), 69.88 (OCH_2), 42.95 (NCH_2), 29.66 (CH_2), 29.30 (CH_2), 28.61 (CH_2), 28.52 (CH_2), 22.77 (CH_2), 22.71 (CH_2), 14.24 (CH_3). ^{13}C NMR (75 MHz, Chloroform-*d*, δ ppm) 149.14 (Cq), 123.74 (Cq), 107.51 (CH), 69.88 (OCH_2), 29.66 (CH_2), 29.30 (CH_2), 28.61 (CH_2), 28.52 (CH_2), 22.77 (CH_2), 22.71 (CH_2), 14.37 (CH_3), 14.24 (CH_3). IR (ATR, powder, ν_{max}/cm^{-1}): 2110s (CN). Anal. Calcd for $C_{442}H_{660}N_{14}O_{48}Re_6Se_8,\ CH_2Cl_2$: C, 60.66; H, 7.61; N, 2.24; Found C, 60.27; H, 7.77; N, 2.41. EDX (atomic%): C, 85.65; O, 12.65; Se, 1.00; Re, 0.71.

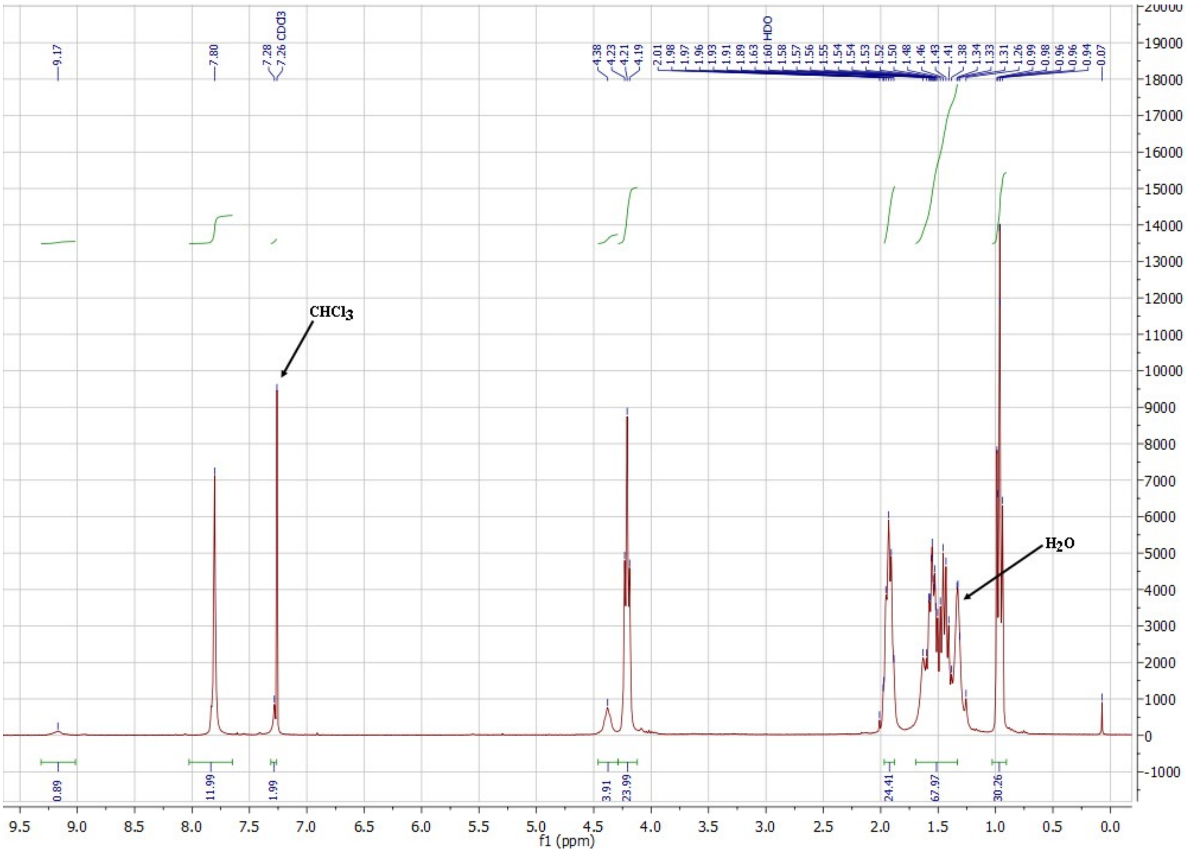


Figure A3. ^1H NMR spectrum of **Cplx2** (H_2O comes from the NMR tube)

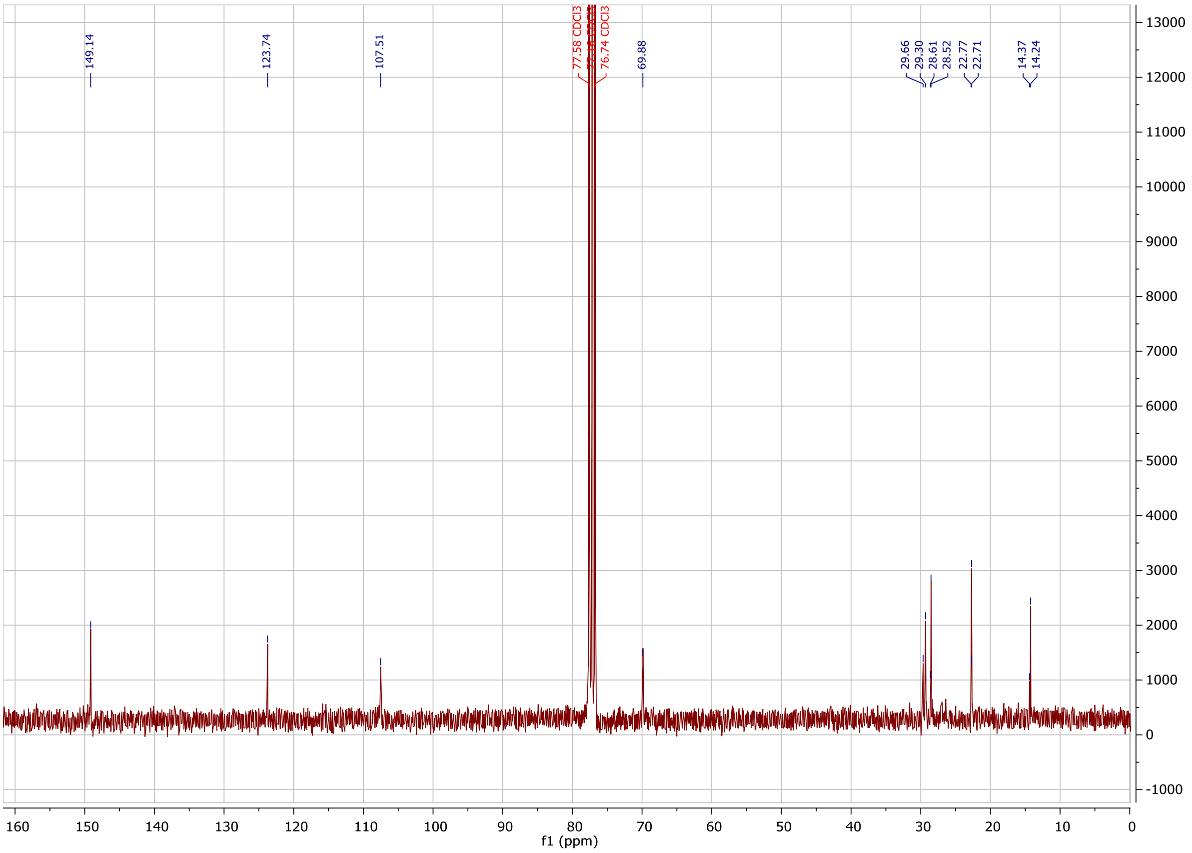


Figure A4. ^{13}C NMR spectrum of **Cplx2** (The imidazolium fragment is hardly visible on the ^{13}C NMR spectrum)

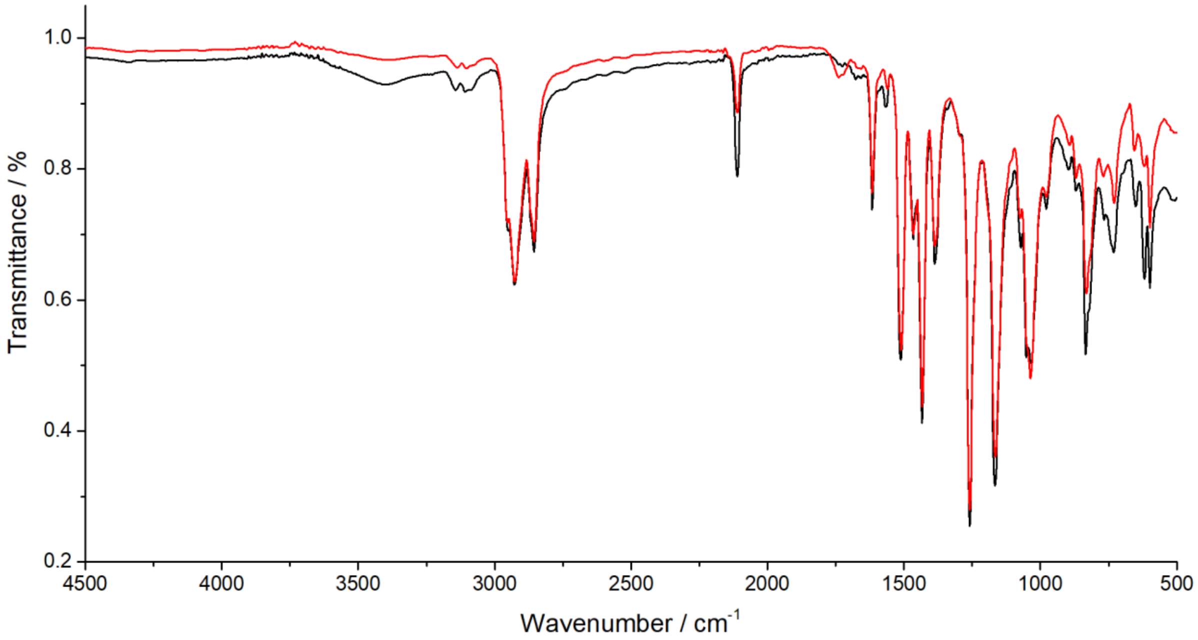


Figure A5. IR spectra of **Cplx1** (black line) and **Cplx2** (red line)

Supplementary figures

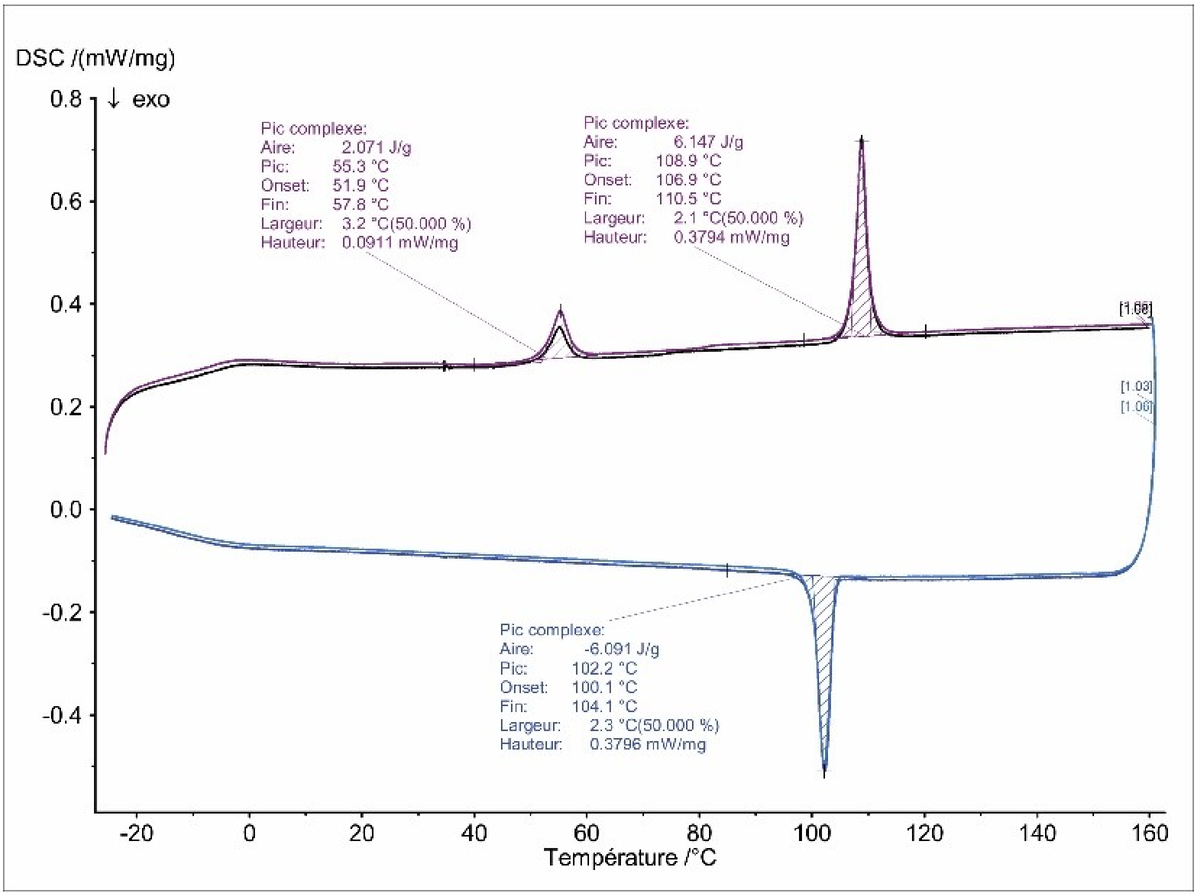


Figure S1. DSC traces of **TP1Br** (Top: 2nd and 3rd heating curves, bottom: 1st and 2nd cooling curves, scan rate: 10°C/min).

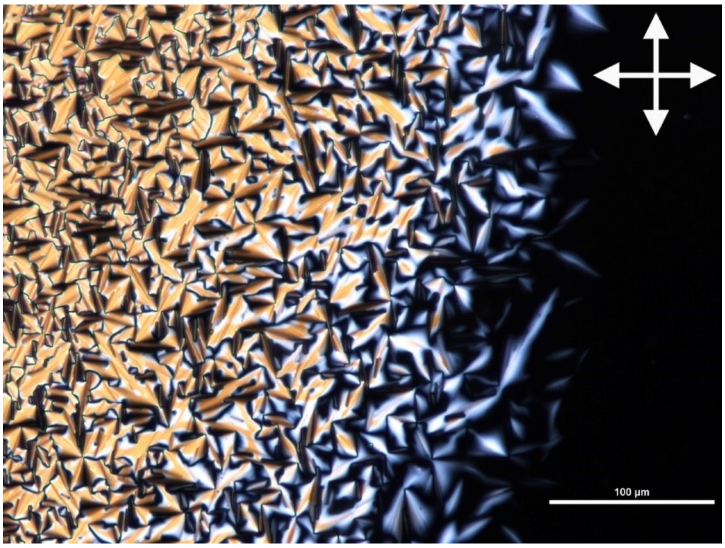


Figure S2. TP1Br compound observed by optical microscopy between crossed-polarizers at 95 °C upon cooling from the isotropic state (crossed-polarizers symbolized by the white cross in the corner of the picture).

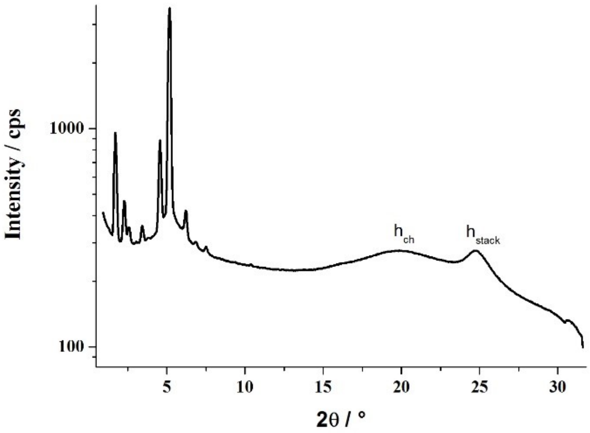


Figure S3. SAXS pattern of **TP1Br** compound recorded at 100 °C (2nd heating curve).

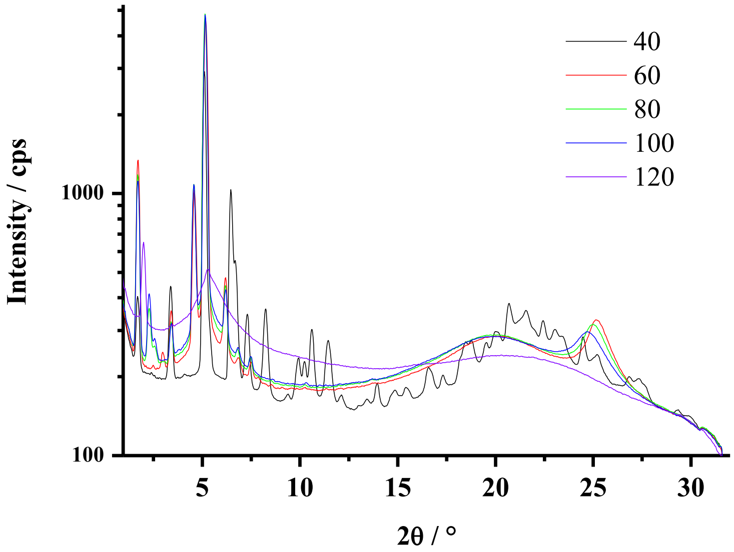


Figure S4. Temperature-dependent SAXS patterns of **TP1Br**.

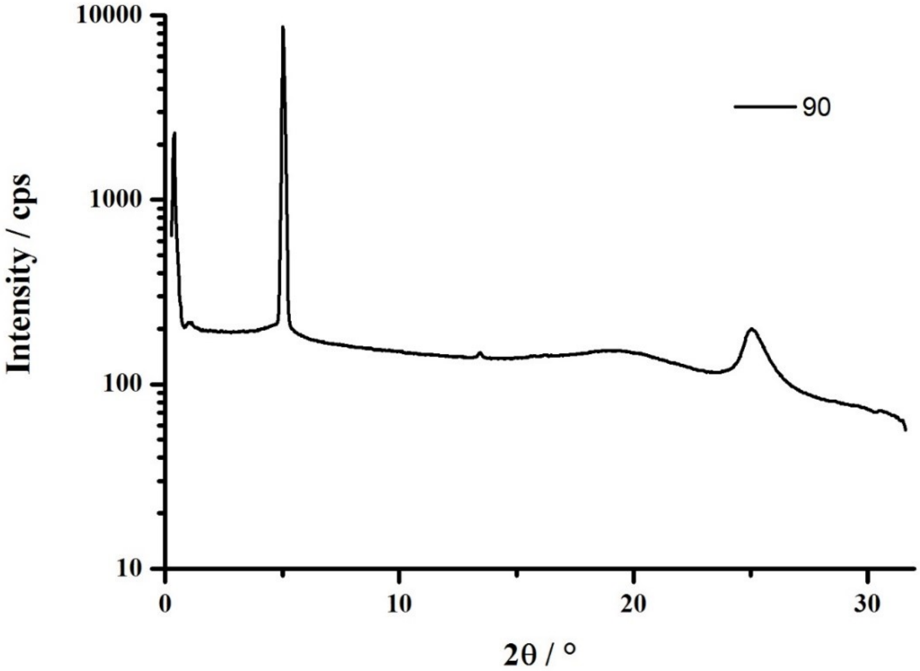


Figure S5. SAXS pattern of 2,3,6,7,10,11-hexakis(pentyloxy)triphenylene compound at 90 °C.

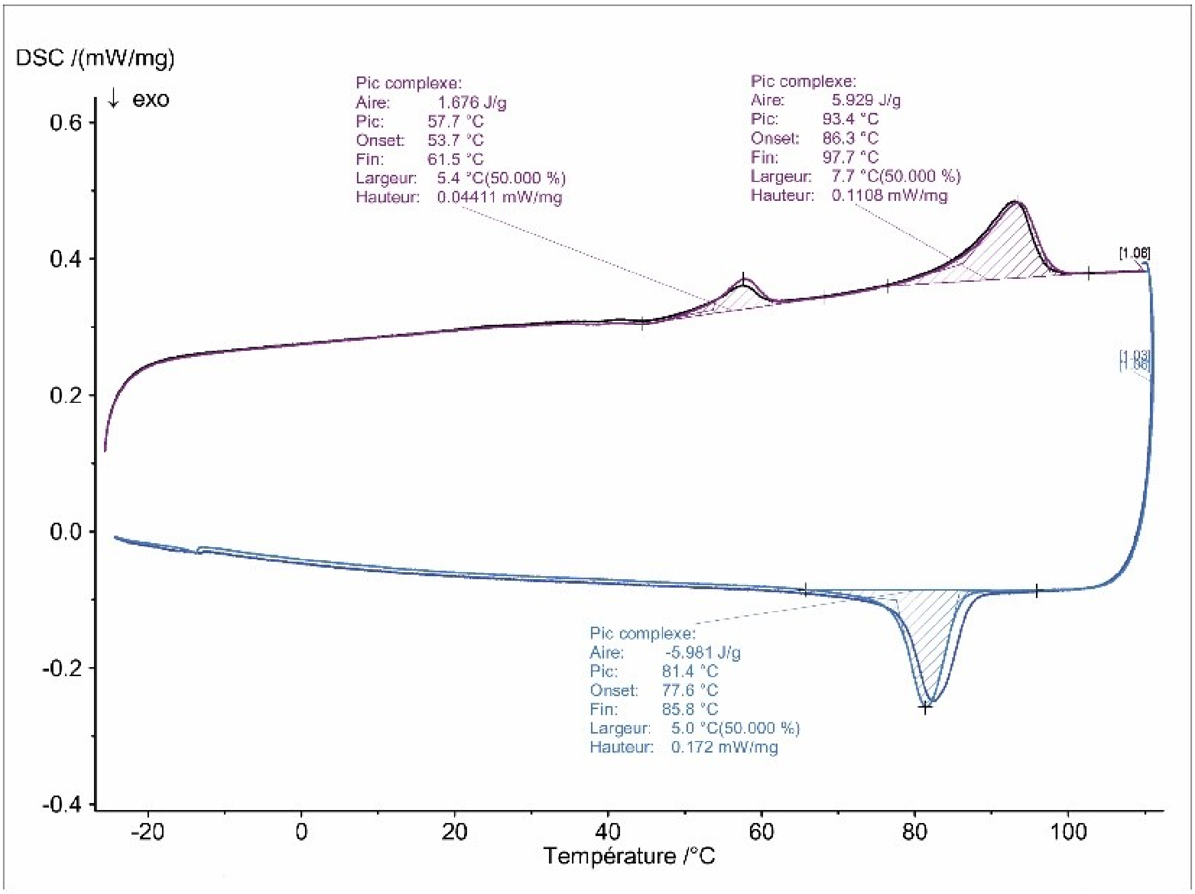


Figure S6. DSC traces of **TP2Br** (Top: 2nd and 3rd heating curves, bottom: 1st and 2nd cooling curves, scan rate: 10°C/min).

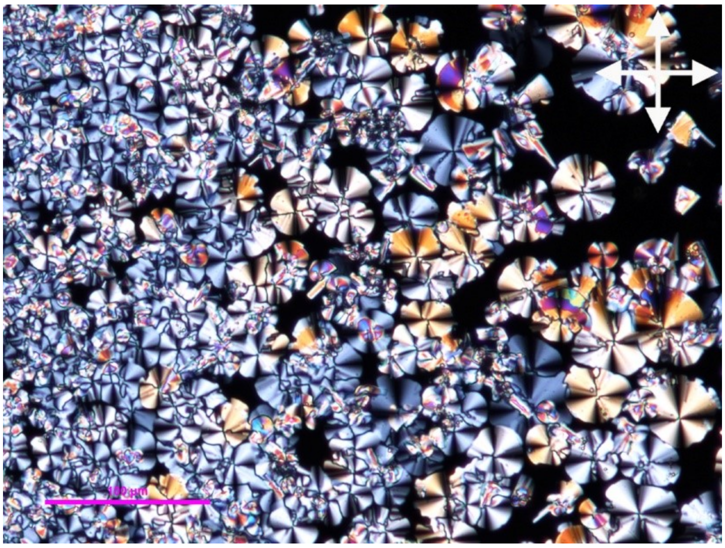


Figure S7. Optical photomicrograph of **TP2Br** obtained with a polarizing microscope on cooling from the isotropic liquid at 80 °C (crossed-polarizers symbolized by the white cross in the corner of the picture).

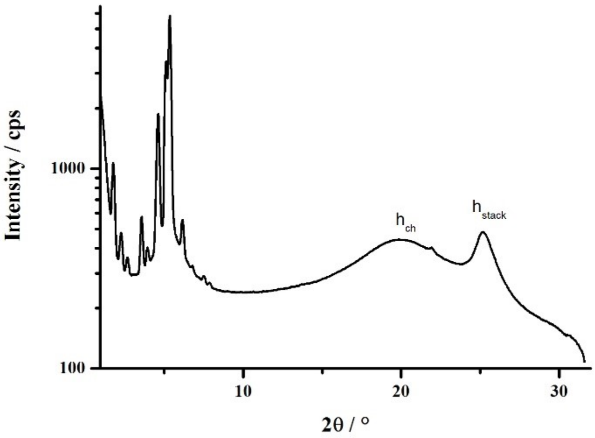


Figure S8. SAXS pattern of **TP2Br** compound recorded at 70 °C (2nd heating curve).

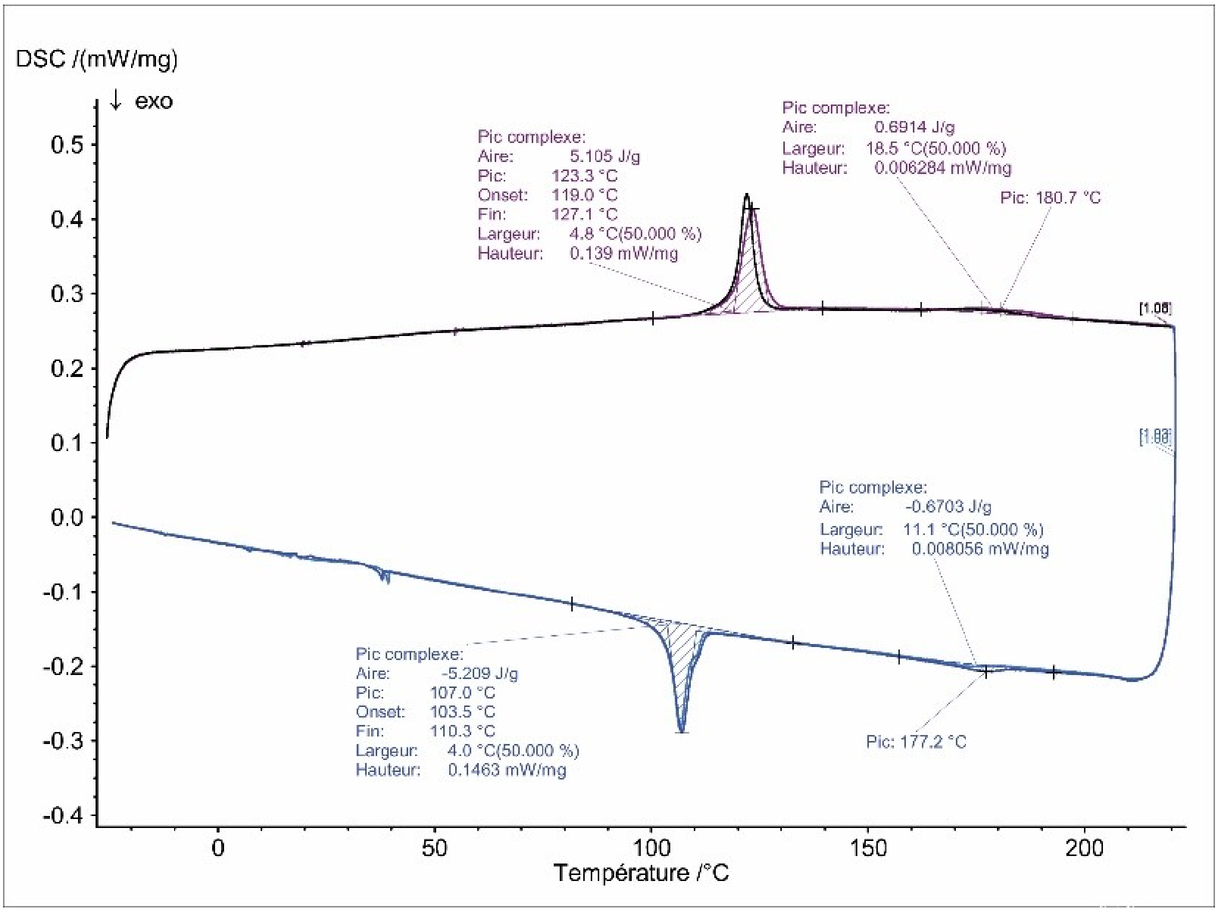


Figure S9. DSC traces of **Cplx1** compound (Top: 2nd and 3rd heating curves, bottom: 1st and 2nd cooling curves, scan rate: 10°C/min).

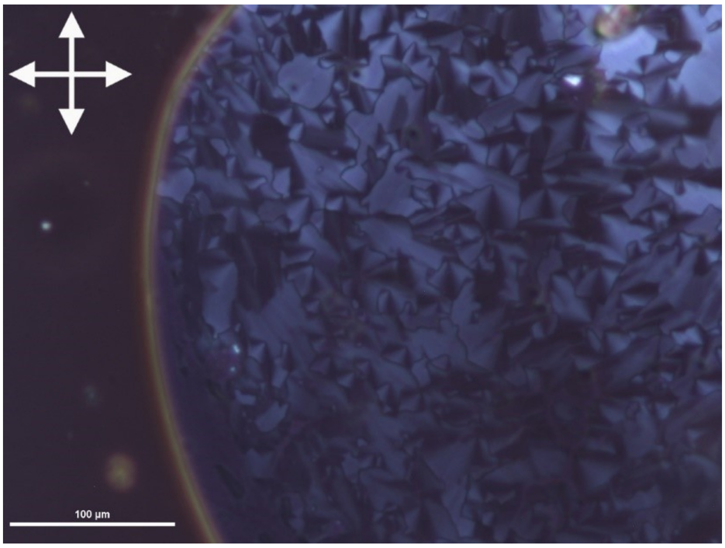


Figure S10. POM images of **Cplx1** compound obtained at 191 °C upon cooling from the isotropic state (crossed-polarizers symbolized by the white cross in the corner of the picture).

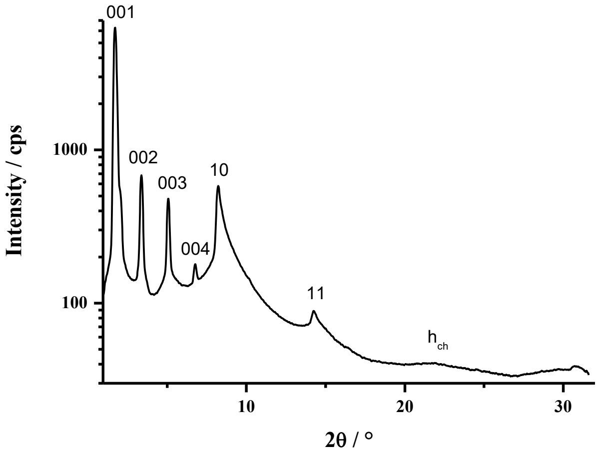


Figure S11. SAXS pattern of **Cplx1** recorded at 140 °C (2nd heating curve).

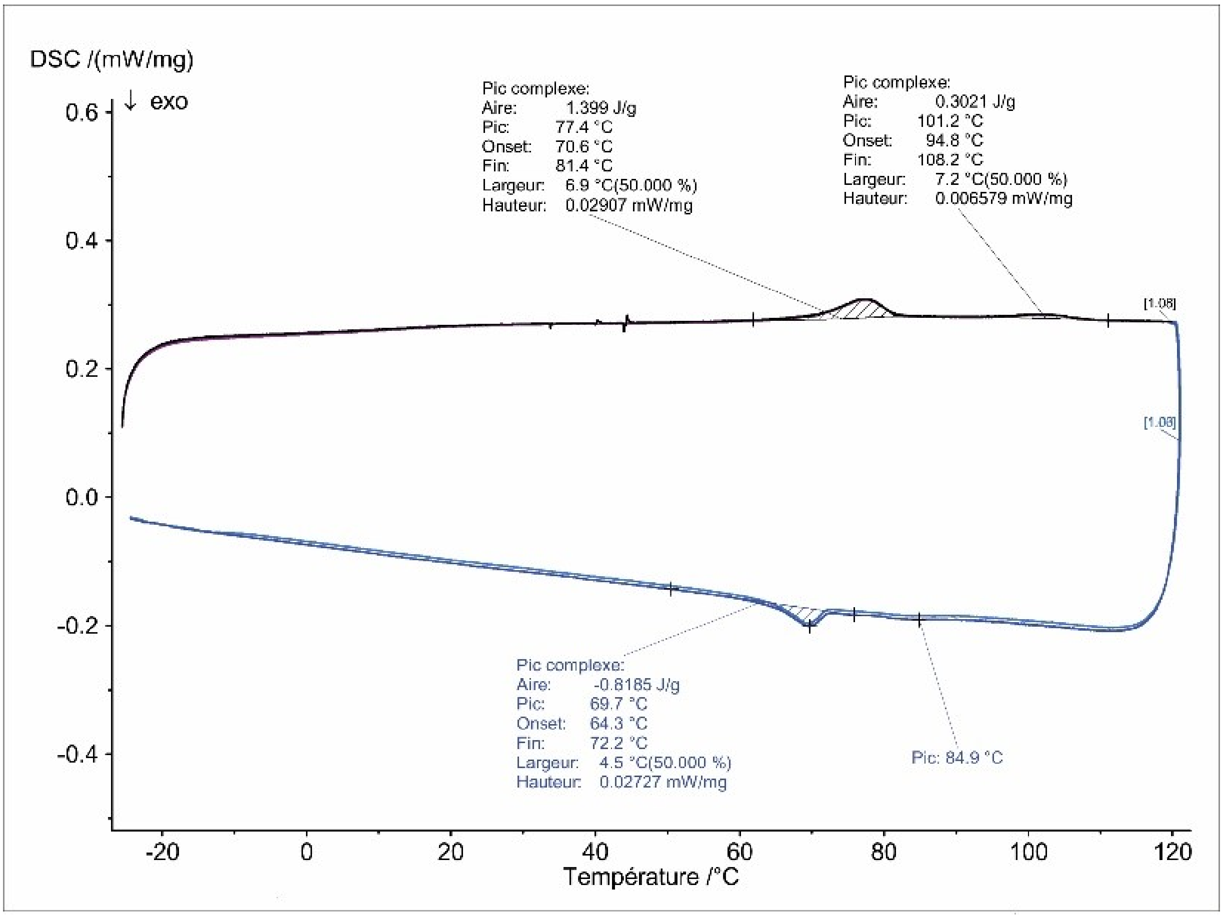


Figure S12. DSC traces of **Cplx2** compound (Top: 2nd and 3rd heating curves, bottom: 1st and 2nd cooling curves, scan rate: 10°C/min).

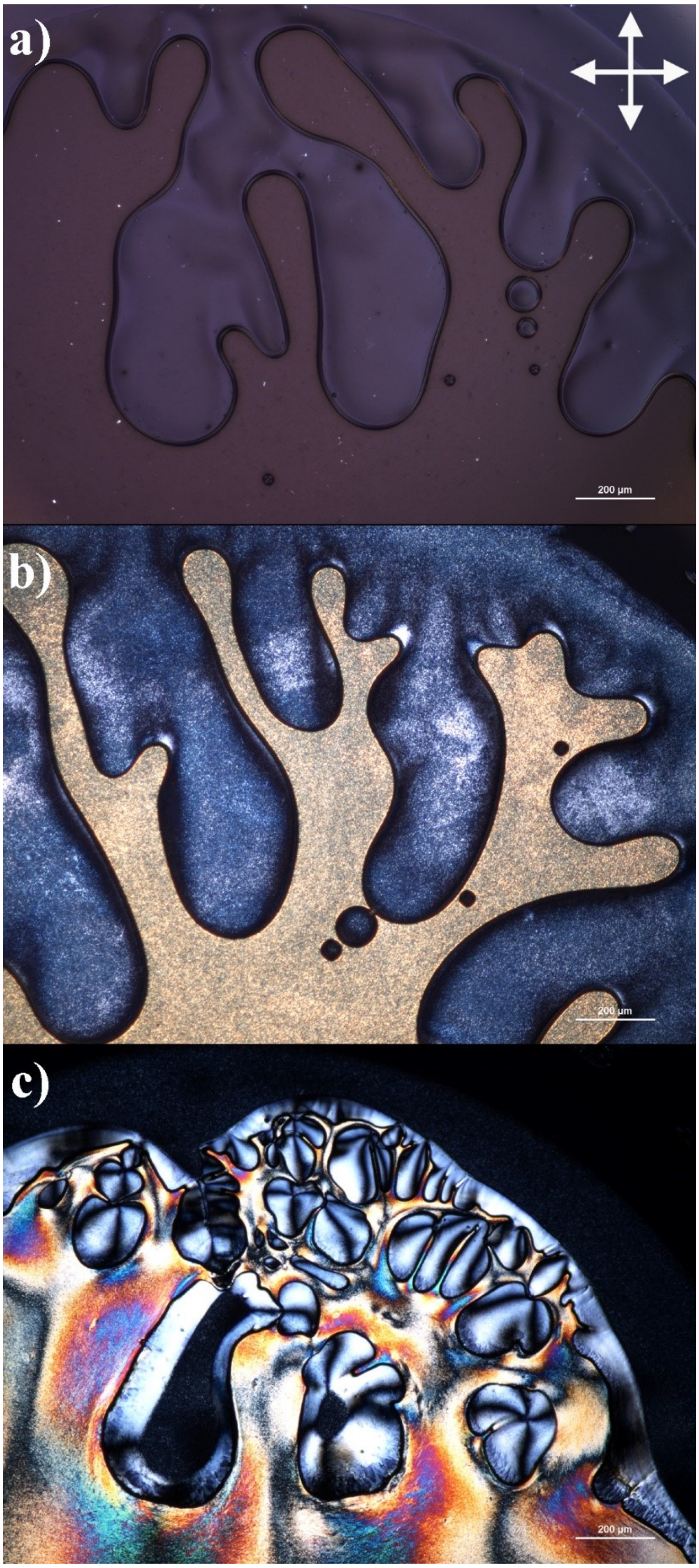


Figure S13. Optical photomicrograph of **Cplx2** obtained with a polarizing microscope at: a) 120 °C in the isotropic phase, b) 84 °C upon slow cooling from the isotropic phase and c) 84 °C after gentle pressure on the glass slide (crossed-polarizers symbolized by the white cross in the corner of the picture).

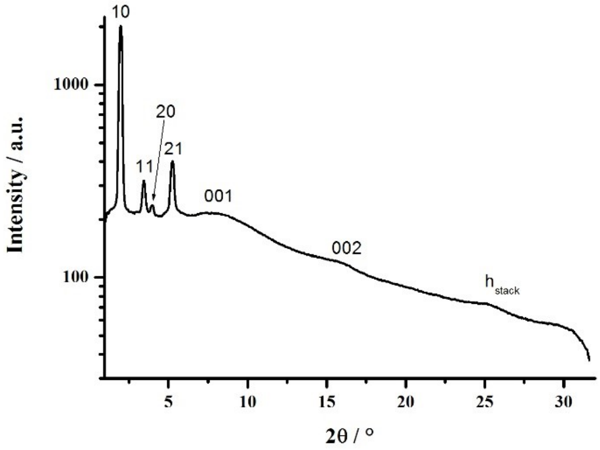


Figure S14. SAXS patterns of **Cplx2** recorded at 80 °C.

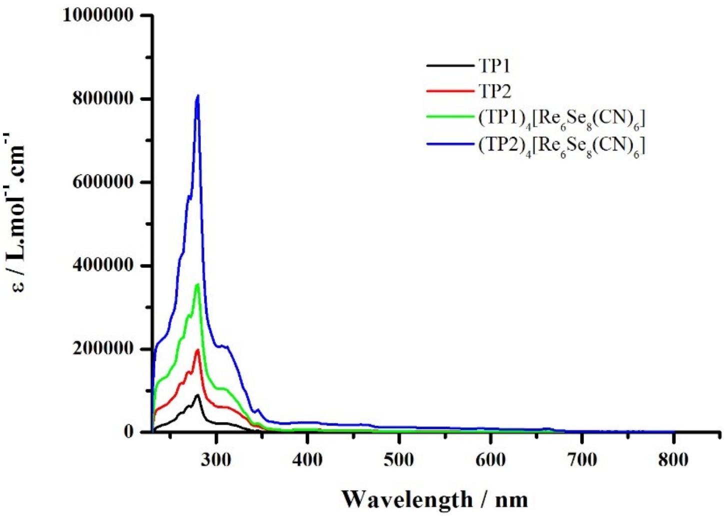


Figure S15. Absorption spectra of **TP1Br**, **TP2Br**, **Cplx1** and **Cplx2** in dichloromethane (c ~ 10^{-6} M)

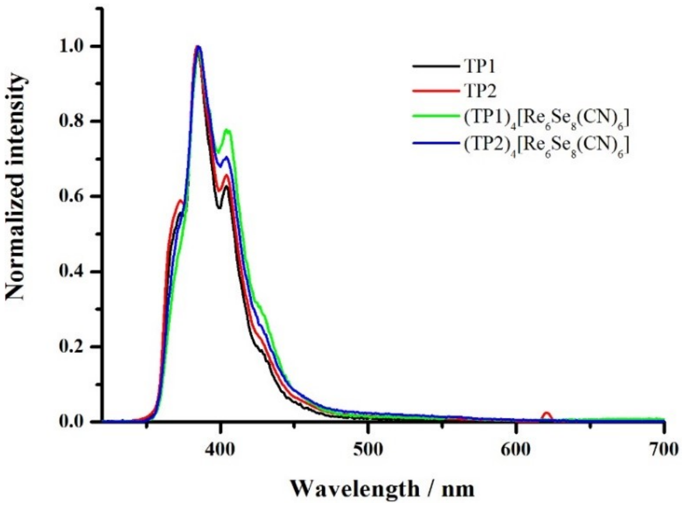


Figure S16. Normalized emission spectra in aerated dichloromethane of **TP1Br**, **TP2Br**, **Cplx1** and **Cplx2** upon excitation at 310 nm.

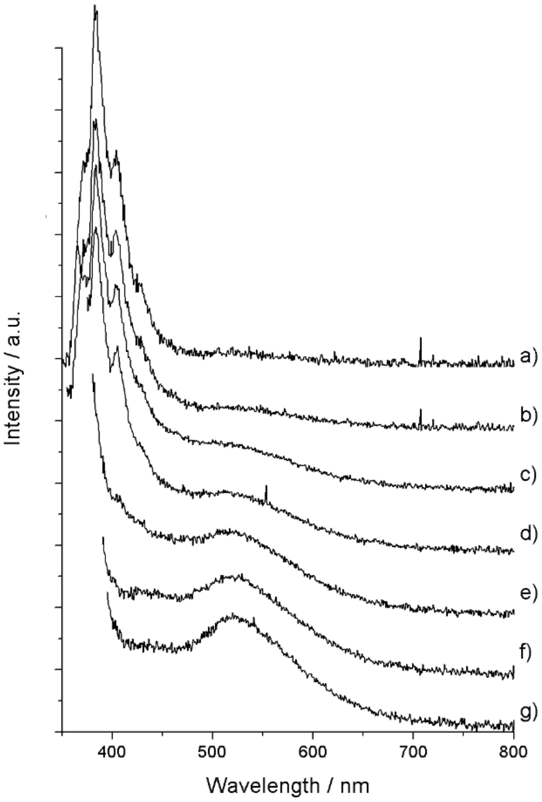


Figure S17. Emission spectra in deaerated dichloromethane of **TP1Br**, upon excitation at a) 320 nm, b) 350 nm, c) 360 nm, d) 365 nm, e) 370 nm, f) 375 nm and g) 380 nm.

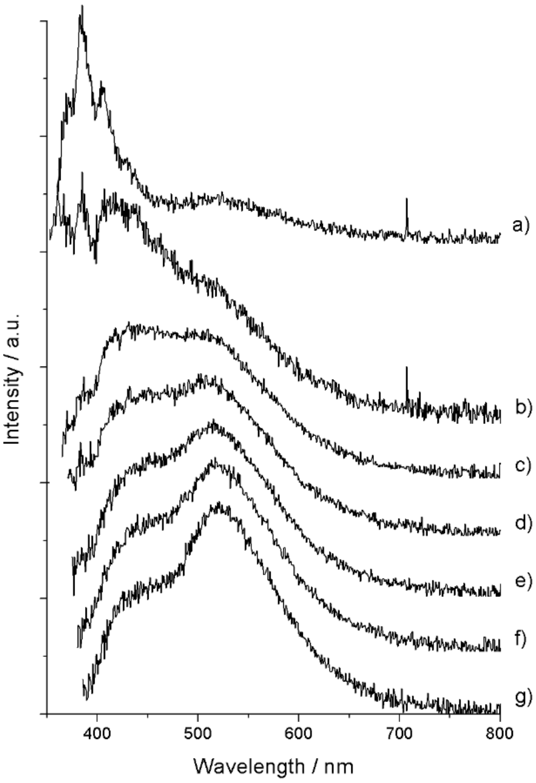


Figure S18. Emission spectra in deaerated dichloromethane of **TP2Br**, upon excitation at a) 320 nm, b) 350 nm, c) 360 nm, d) 365 nm, e) 370 nm, f) 375 nm and g) 380 nm.

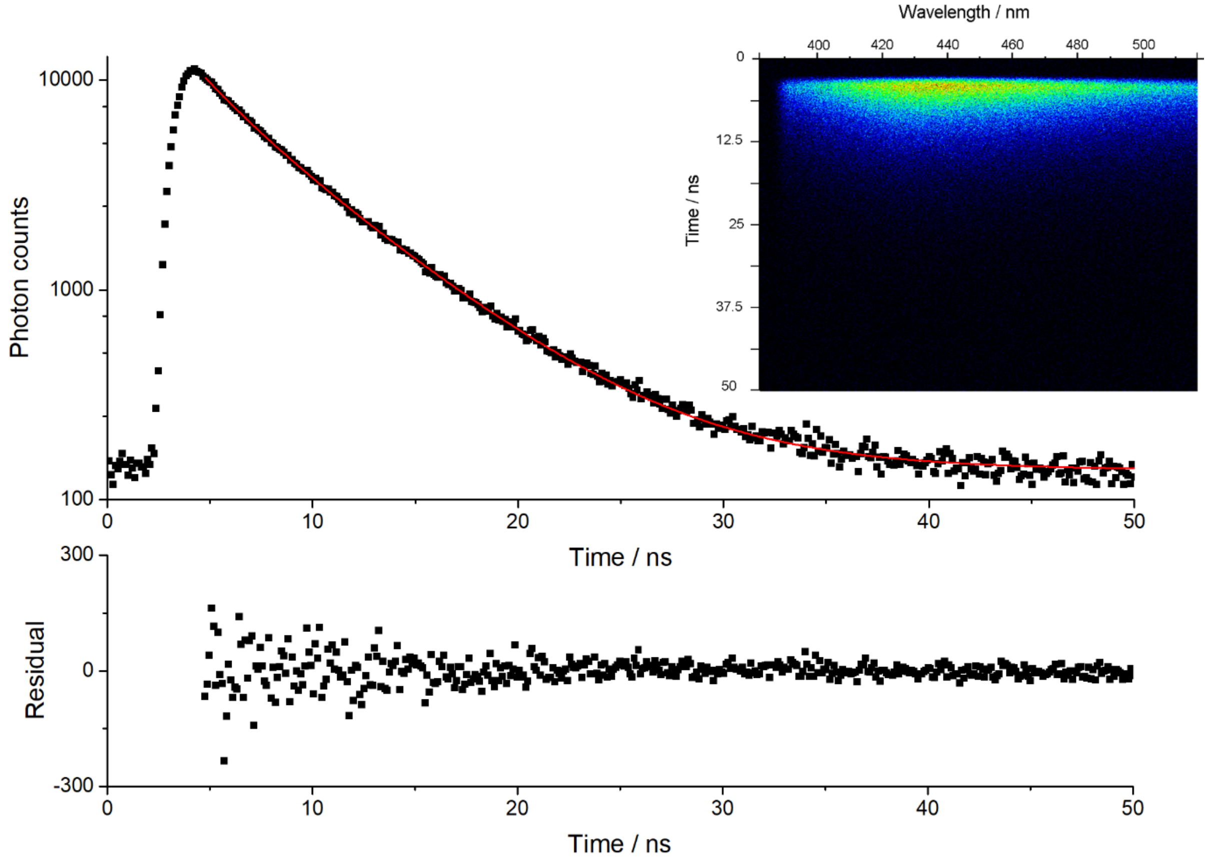


Figure S19. Integrated luminescence decay profile of **TP1Br** in dichloromethane; inset: corresponding emission decay map.

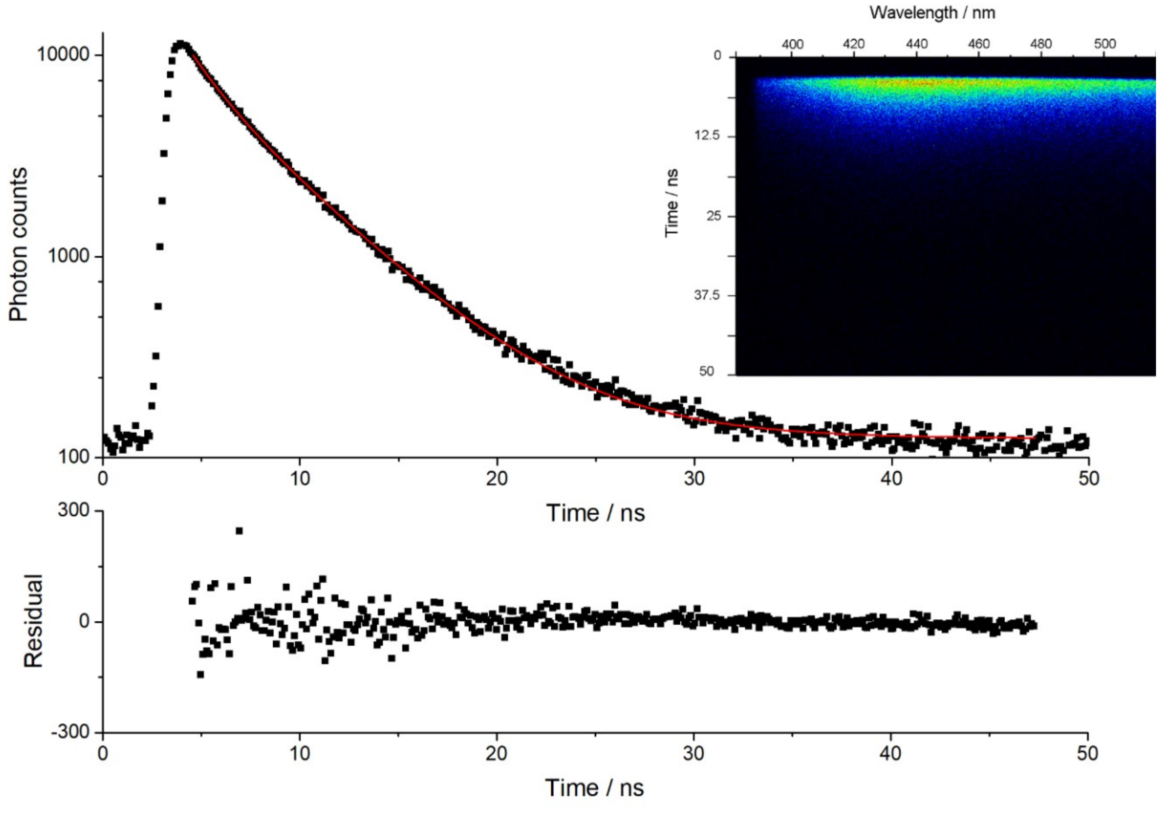


Figure S20. Integrated luminescence decay profile of **TP2Br** in dichloromethane; inset: corresponding emission decay map.

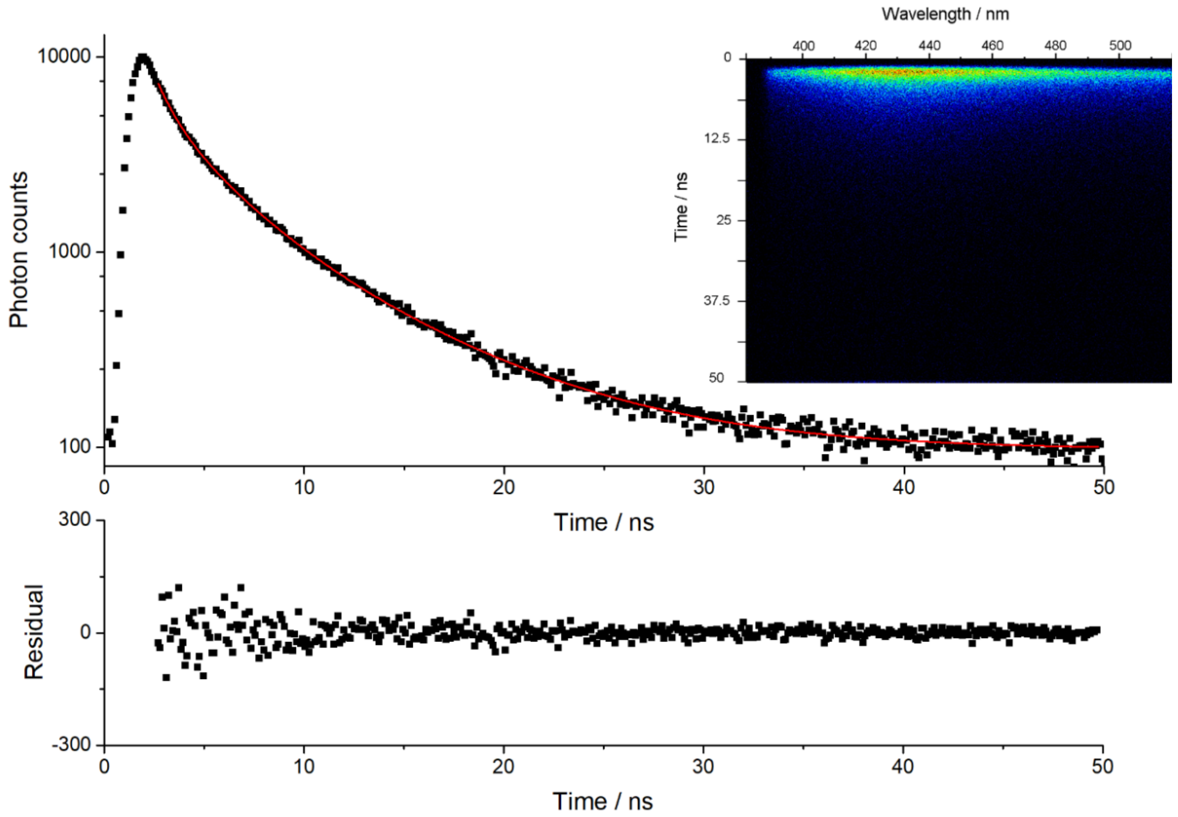


Figure S21. Integrated luminescence decay profiles of **Cplx1** in deaerated dichloromethane; inset: corresponding emission decay map between 382 and 518 nm.

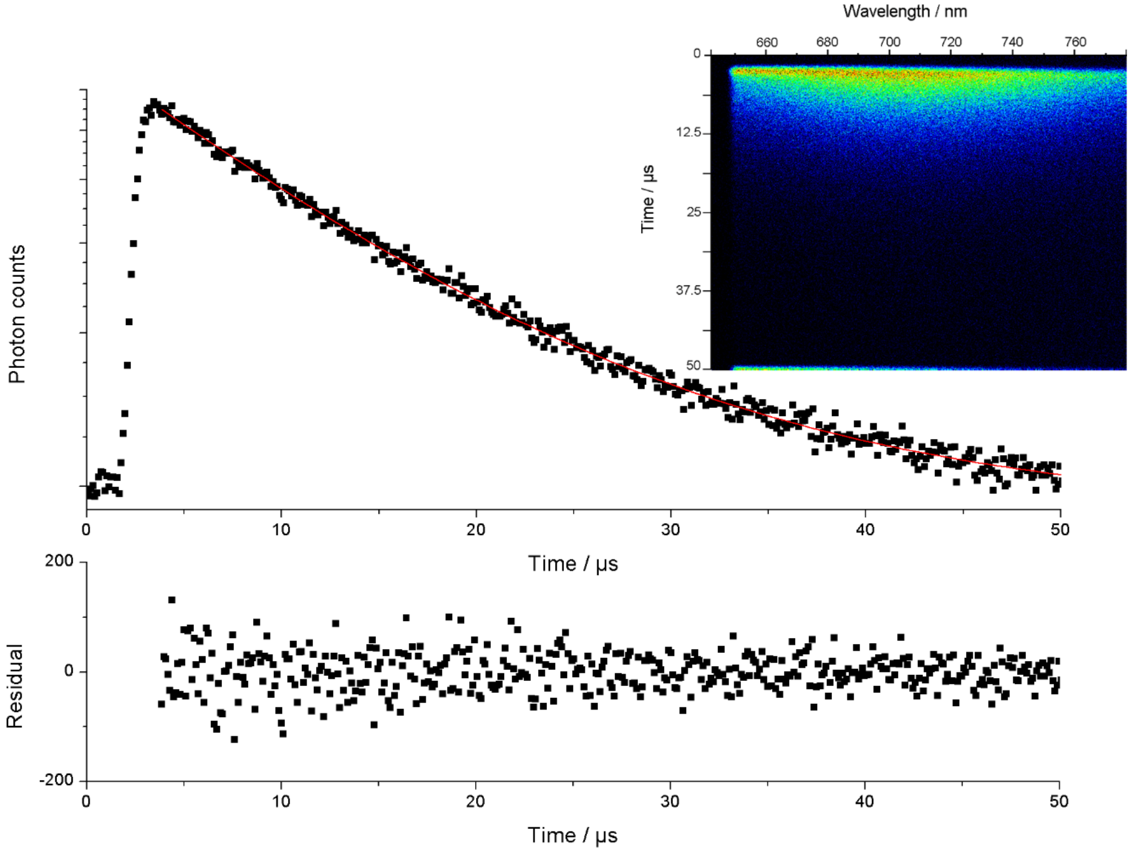


Figure S22. Integrated luminescence decay profiles of **Cplx1** in deaerated dichloromethane; inset: corresponding emission decay map between 642 and 778 nm.

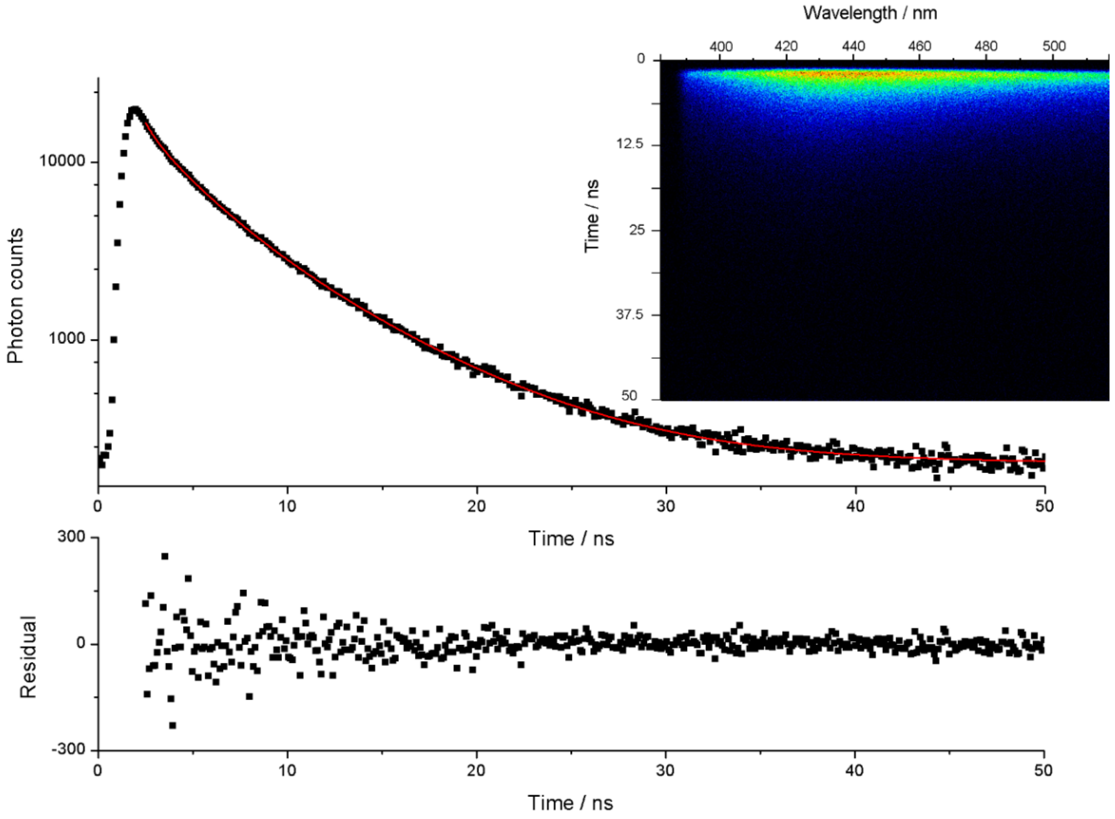


Figure S23. Integrated luminescence decay profiles of **Cplx2** in deaerated dichloromethane; inset: corresponding emission decay map between 382 and 518 nm.

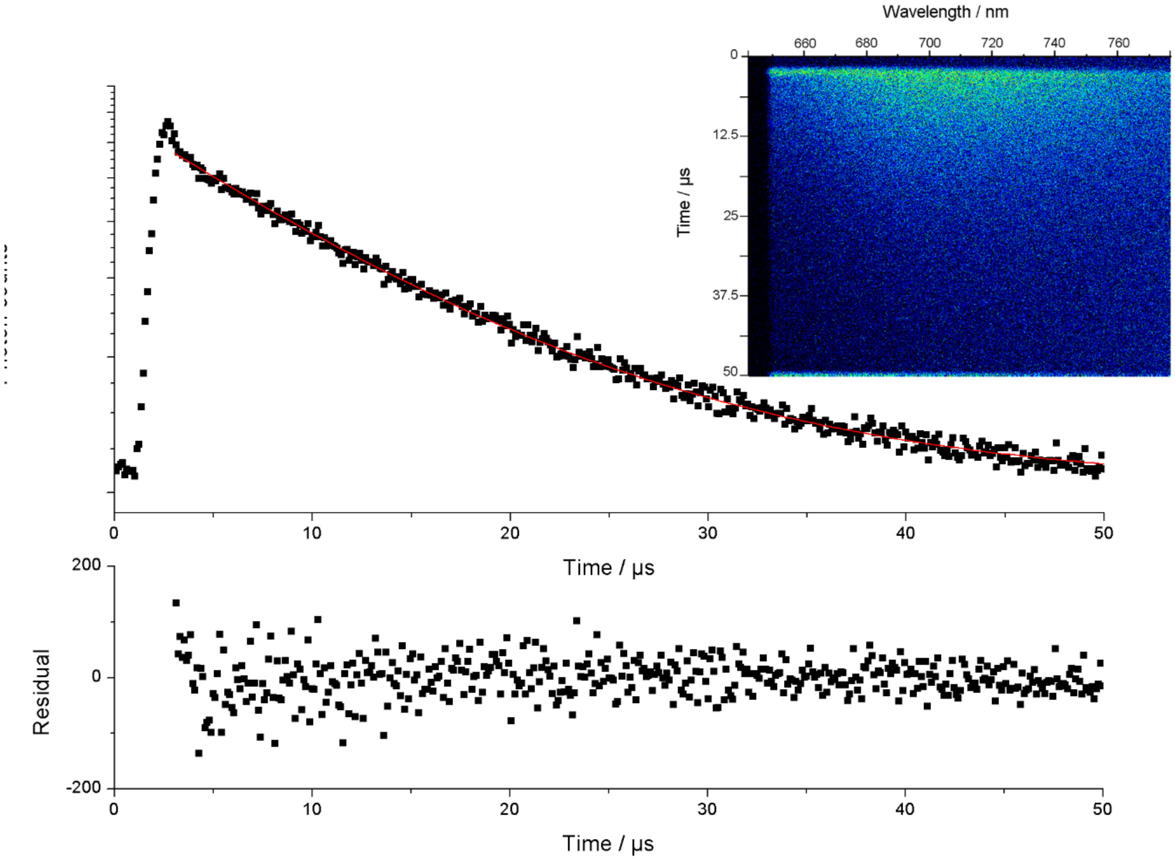


Figure S24. Integrated luminescence decay profiles of **Cplx2** in deaerated dichloromethane; inset: corresponding emission decay map between 642 and 778 nm.

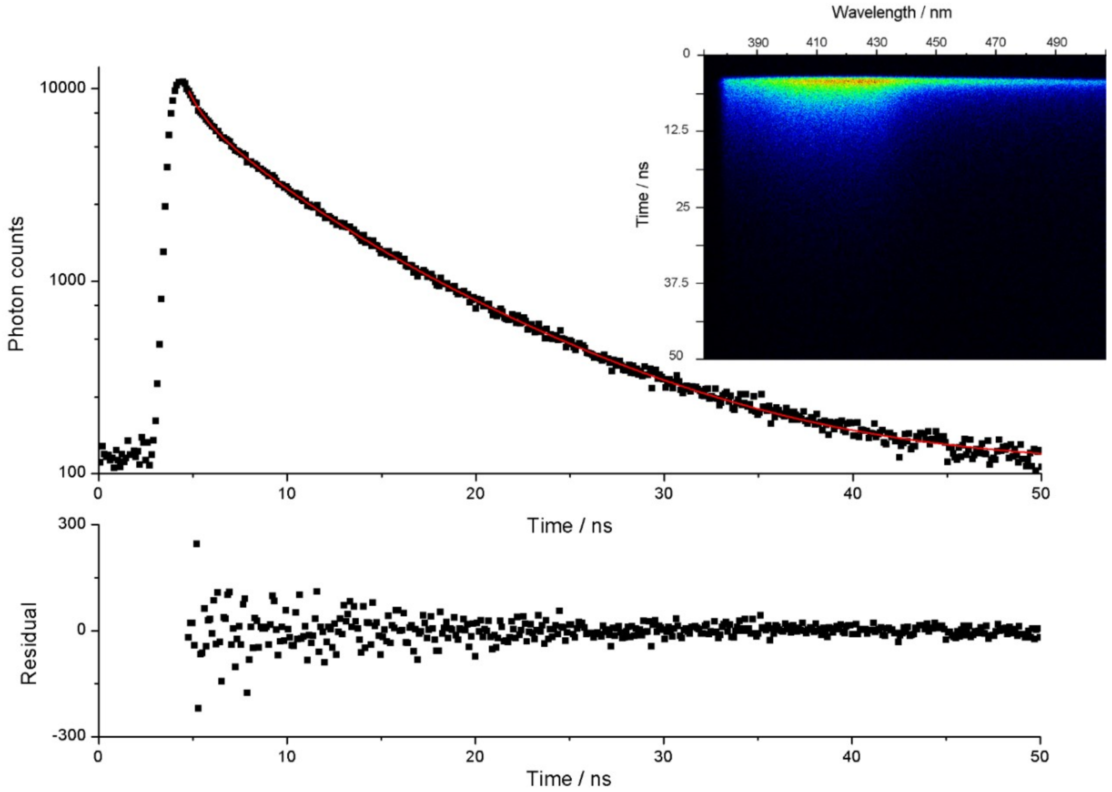


Figure S25. Solid state integrated luminescence decay profile of **TP1Br**; inset: corresponding emission decay map.

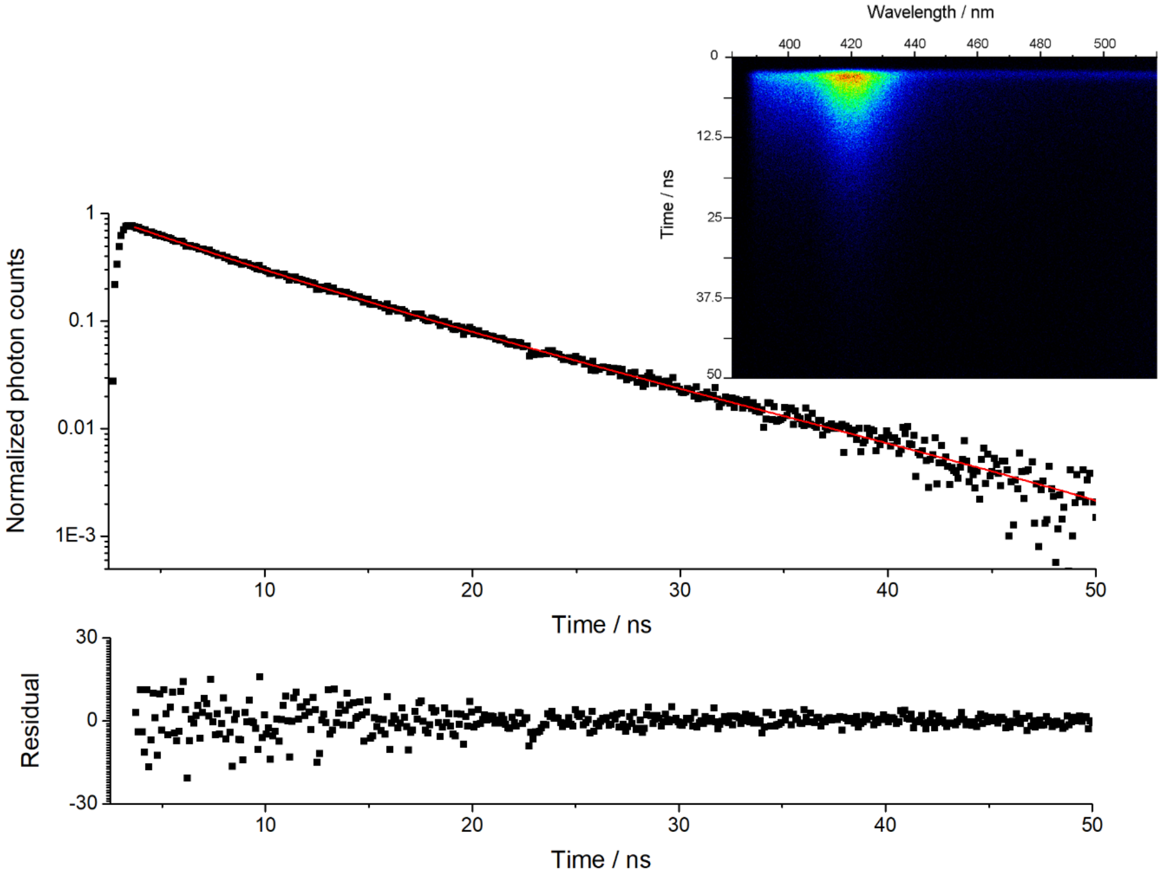


Figure S26. Solid state integrated luminescence decay profile of **TP2Br**; inset: corresponding emission decay map.

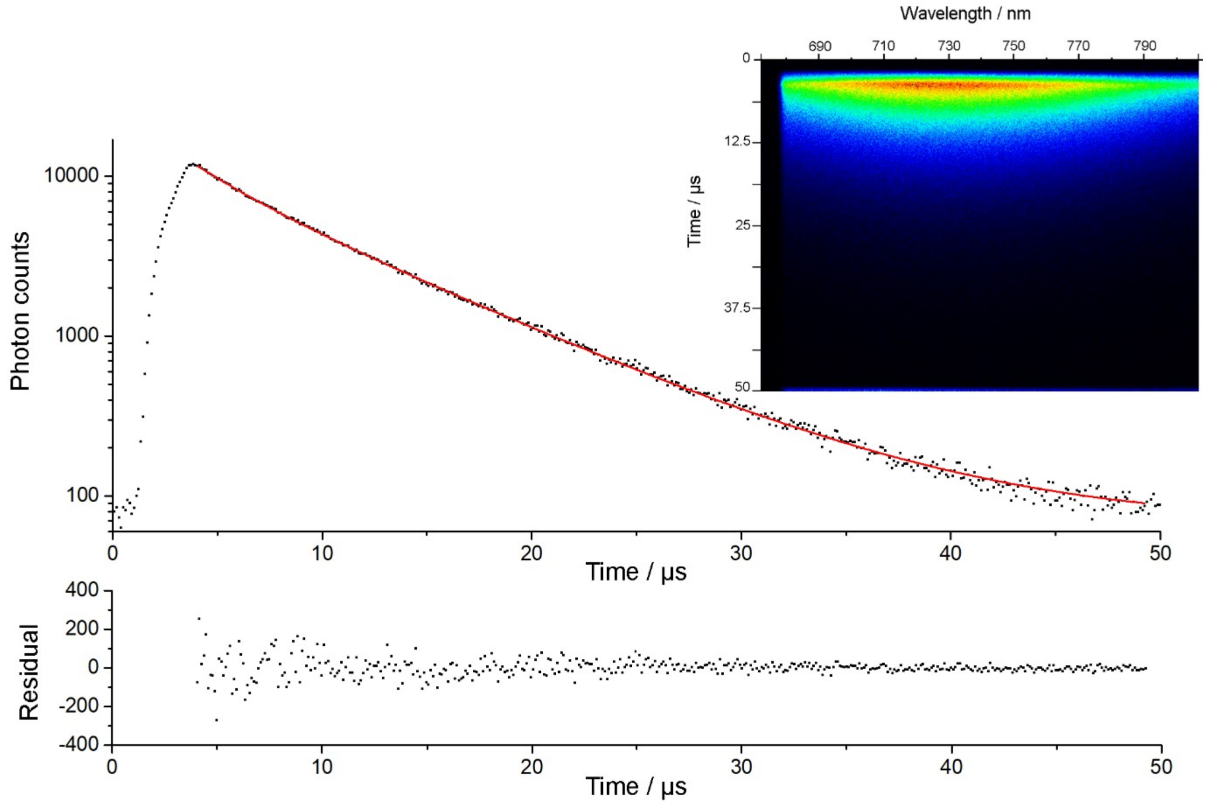


Figure S27. Solid state integrated luminescence decay profile of **Cplx1**; inset: corresponding emission decay map.

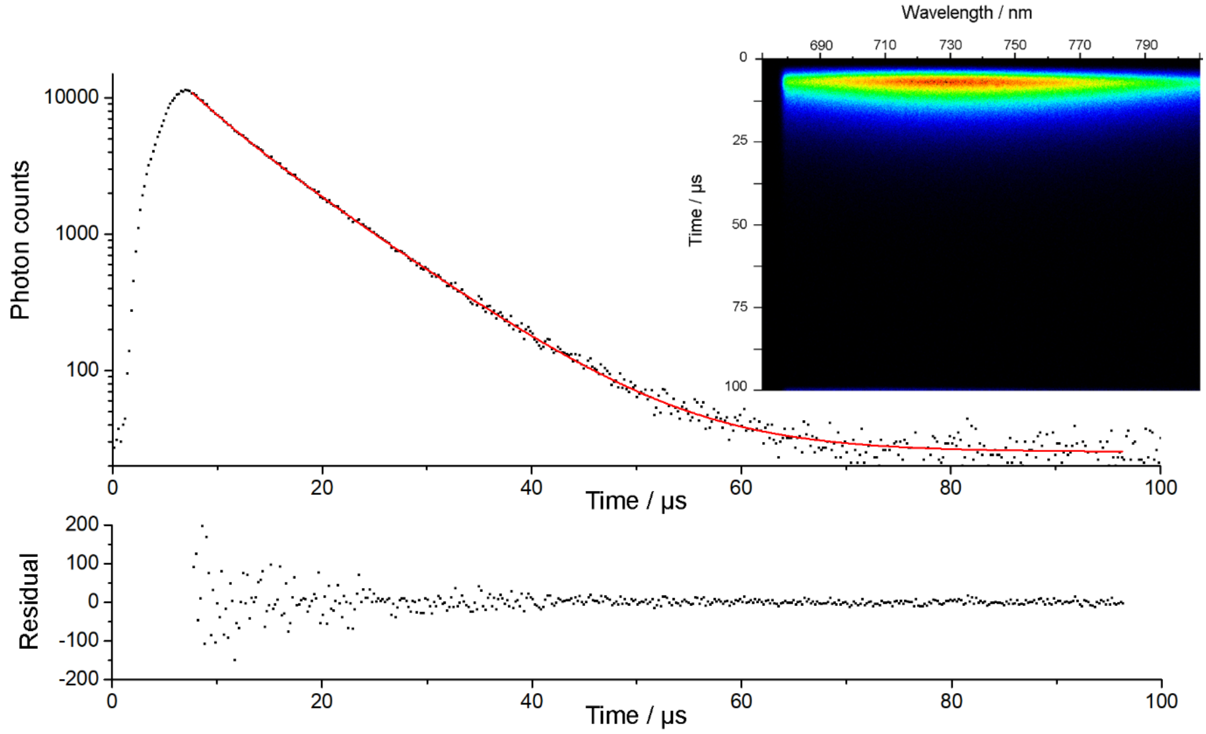


Figure S28. Solid state integrated luminescence decay profile of **Cplx2**; inset: corresponding emission decay map.