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Laser triggered phase transition in photothermal liquid crystals

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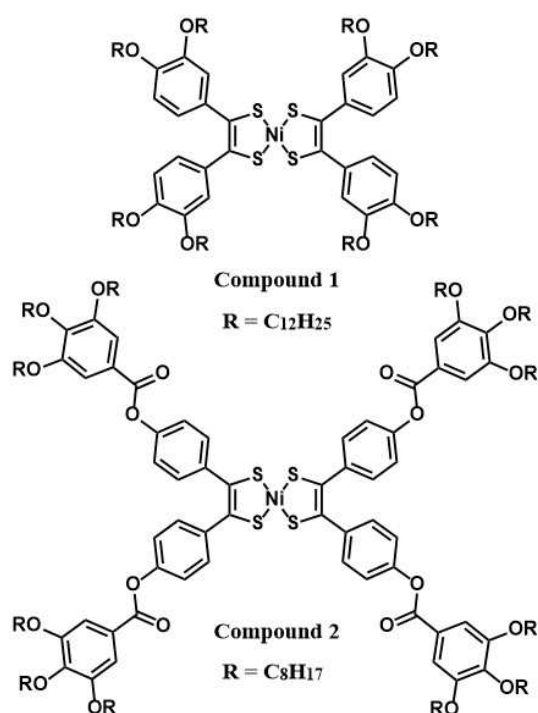
Reversible high temperature phase transitions were easily induced under laser irradiation in pure thermotropic liquid crystal built around photothermal nickel-bis(dithiolene) cores. The strong photothermal activity of nickel-bis(dithiolene) liquid crystalline thin films allows to reach temperature as high as 250 °C directly from room temperature in a few seconds with a high spatial control.

Photoresponsive materials, able to change their optical, magnetic, and electrical properties or undergo a volume phase transition in response to an external stimulus are of great interest to develop sensor and actuator materials.¹ Liquid crystalline materials which combine ordered and dynamic structures, offer opportunities to develop such photoactive materials.² Indeed, molecular orientation changes and phase transition can obviously be induced by heat but also with external stimuli such as light by developing liquid crystalline materials containing photoresponsive fragments.³ In particular, the photoisomerization ability of azobenzene has been extensively used to induce phase transitions by changing the molecular shapes of mesogens.⁴ In this way, liquid crystal to liquid crystal as well as liquid crystal to isotropic phase transitions have been achieved under UV irradiation.

Recently, it has been demonstrated that photothermal effect can also be used to induce nematic/isotropic phase transition in a liquid crystalline phase.⁵ For this purpose, functionalized photothermal gold nanoparticles have been introduced in a nematic liquid crystal. Irradiation in the near-IR region (NIR) causes a release of heat from the plasmonic nanoparticles which allows changing internally the temperature of the liquid crystalline phase. However, this system presents several drawbacks. First, the quantity of photothermal agents which can be introduced in the nematic phase without disturbing it is limited and consequently the amount of heat generated under irradiation is also limited. Second, due to this limited amount of doping agent, the nematic/isotropic transition temperature can only be reached if the temperature of the material is already set few degrees just below LC to isotropic phase transition temperature, which implies that an external source of heating is used. Besides, we have demonstrated that the photothermal properties of nickel-bis(dithiolene) based gelators can be used to tune the stability of the organogels. Under NIR irradiation, the heat released by the gelator itself induced the deconstruction of the polymeric networks at the origin of the gel stabilisation.⁶ The photothermal properties of water-soluble nickel-bis(dithiolene) were also efficiently used *in cellulo* experiments to induce cell death under laser irradiation.⁷ Several liquid crystalline systems built around metal-bis(dithiolene) core have been described in the literature.⁸ But, the photothermal properties of this class of metal complexes have never been used to induce thermal transitions. Thus, in the present paper, we demonstrate that the photothermal properties of nickel-bis(dithiolene) discotic mesogens can be used to induce phase transitions directly from room temperature up to the isotropic phase with no need for an external doping agent since the mesogen itself displays photothermal properties under NIR irradiation.

For this purpose, two discotic liquid crystalline nickel-bis(dithiolene) complexes have been selected, either carrying directly eight dodecyl carbon chains or substituted at both ends by

gallate derivatives carrying octyl chains through an ester linker (scheme 1). Compound **1**, which have been already extensively studied by Otha's group, form a columnar liquid crystalline phase of hexagonal symmetry (Col_h) between 70 °C and 110 °C.^{8a} The texture observed between crossed polarizers displays pseudo-fan shapes characteristic of this type of phase (Figure S1). Above 110 °C, the compound is in its isotropic phase and appears completely black under crossed polarizers. Below 70 °C, the compound is in its crystalline state and the texture observed is reminiscent of the one observed for the Col_h phase, meaning that the 2D hexagonal organization of the columns is preserved at room temperature. Compound **2** was mainly selected for its higher isotropization temperature at 142 °C.^{8b} This complex also displays a reversible transition at 89 °C which was attributed to a transition between a high-temperature Col_h phase and a columnar phase of rectangular symmetry (Col_r) at lower temperature. On very thin film, slow cooling below 142°C from the isotropic liquid reveals that a texture with homeotropic domains and pseudo-fan shapes can develop. This texture remained unchanged down to room temperature.



Scheme 1. Chemical structure of the two mesogenic nickel-bis(dithiolene) complexes investigated in this study.

Absorption spectra of the two complexes show a main absorption in the NIR region around 960 nm, extending from 700 nm up to 1200 nm in toluene (Figure S1-S2). This low-energy absorption band, with high extinction coefficients ($\epsilon \approx 30\,000\text{ M}^{-1}\cdot\text{cm}^{-1}$), is characteristic of the neutral Ni-bis(dithiolene) complexes and is attributed to an electronic transition from the HOMO ($L\pi$) to the LUMO ($L\pi^*-\alpha dxy$).⁹ The photothermal conversions efficiencies (η) of these two complexes were evaluated by monitoring the temperature profile of a toluene solution after 10 min under continuous irradiation at 940 nm with a diode laser irradiation with a power density of $5\text{ W}\cdot\text{cm}^{-2}$ followed by 10 min of relaxation with the laser being turned off (Figure S3). The η values were calculated according to the equation reported by Roper *et al.*¹⁰ The η values determined for compound **1** and **2** are respectively 40 and 39 %. Those values compare very well with those reported for other nickel-bis(dithiolene) complexes in toluene solutions.^{6,8} These two compounds were found to be highly photothermally stable in solution since no fatigue was observed after several heating and cooling cycles (Figure 2).

The photothermal activity of the two compounds were then investigated on thin films. For this purpose, powdered compounds has been melted between glass slides with a hot stage to obtained about 120 μm thick films of compound **1** and **2**. After cooling to room temperature, homogenous and birefringent thin films could have been observed by optical microscopy under crossed polarizers. The thin films were then irradiated with the 940 nm laser with a spot size of 1 cm diameter and the temperature profiles were monitored with a thermal infrared camera during 90 s under laser irradiation and for 90 s after turning off the laser. The glass slides were maintained with a thermally insulating clamp to avoid heat dissipation by the

support. The results obtained under various laser power irradiation are reported in Figure 1. Under laser irradiation, the temperature of the films drastically goes up and then reaches a maximum after irradiation. As expected, the temperature increase under laser irradiation strongly depends on the laser power used. With compound **1**, temperature increase up to 240 °C ($\Delta T = 215$ °C) can be reached by applying 2.5 W.cm⁻² laser power irradiation in 70 s. Higher laser powers have not been tested because, usually, organic molecule are not highly stable above 250 °C. To reach the isotropization temperature at 110 °C, a laser power of at least 1 W.cm⁻² should be used. The isotropization temperature is reached in 37 s ($v = 2.25$ °C/s) at 1 W.cm⁻², whereas at 2.5 W.cm⁻², the isotropic phase can be reached in less than 3.5 s ($v = 24$ °C/s). Such heating rate are hardly accessible with conventional heating stages or hot plates. It should be noticed that, in the absence of complex, only a limited temperature increase of 5 °C was observed after 90 s of irradiation at 2.5 W.cm⁻² (Figure S5). After laser irradiation, fast temperature decreases were also observed, meaning that the heat stored can rapidly be released from these thin films. The same trends were observed with compound **2**. Temperature elevations close to 250 °C can be reached under laser irradiation at 2.5 W.cm⁻² after 90 s irradiation. To reach temperature above the isotropization temperature of 142 °C, laser power densities above 1.5 W.cm⁻² should be used. The heating speeds at 1.5 and 2.5 W.cm⁻² to reach the isotropization temperature were 2.4 and 10.3 °C/s, respectively. These two compounds were also found to be highly photothermally stable in solid state and no fatigue was observed after several heating and cooling cycles (Figure 2). The maximum temperature increase (ΔT) observed after 90 s irradiation evolves linearly with the power densities (Figure S5). The slightly lower ΔT observed with compound **2** is likely attributed to a lower density of nickel-bis(dithiolene) cores inside the films, in line with its higher molecular weight.

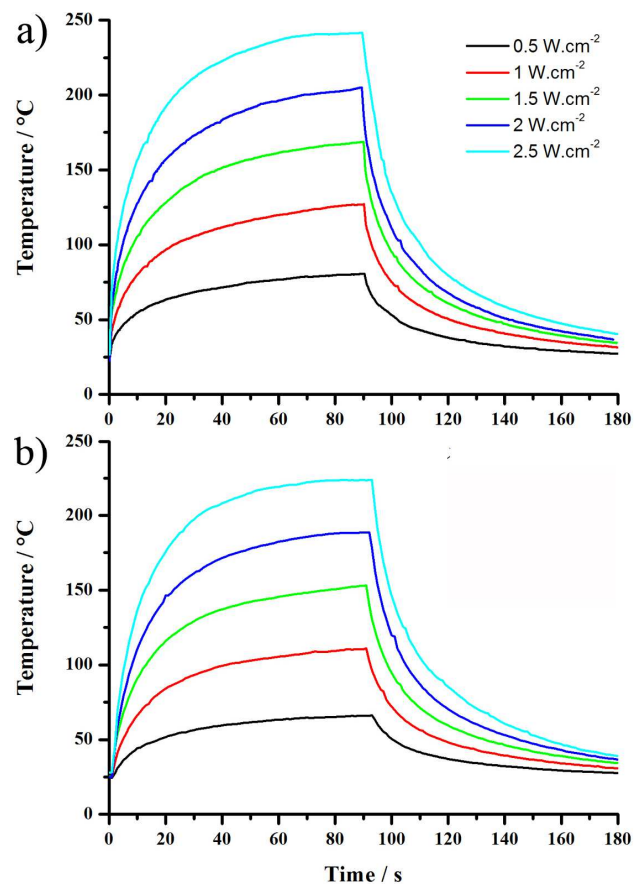


Figure 1. Temperature elevation of a thin films of compound 1 (Top) and compound 2 (bottom) under 940 nm wavelength laser irradiation at various laser powers (both films have been irradiated on the same area in all the measurements).

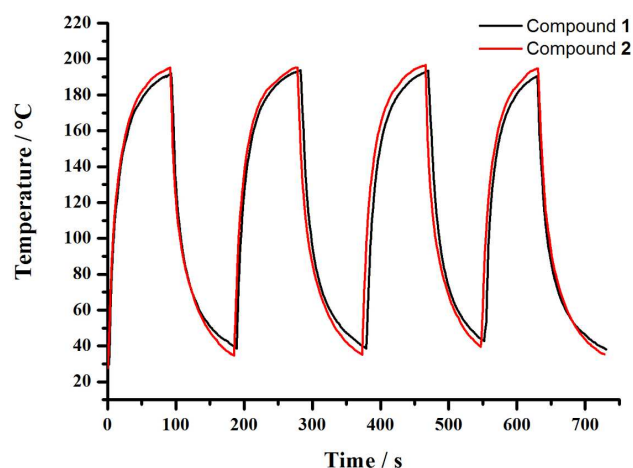


Figure 2. Stability measurement of compound **1** and **2** as thin films by four heating cycles under 940 nm laser irradiation (2.5 W.cm^{-2}).

In order to get more visual insight on the effect of the laser irradiation on the thin films, irradiation have directly been performed in an optical microscope equipped with crossed polarizers. Here, the spot size was more difficult to evaluate. Consequently the laser power is given in ampere only. 120 μm -thick films of compound **1** and **2** have been freshly prepared by a first heating and cooling between glass slides with a hot stage ($10 \text{ }^\circ\text{C/min}$). Compound **1** forms an homogenous thin film displaying a texture with large homeotropic domains and birefringent pseudo-fan shapes (Figure 3a). Application of a laser irradiation with sufficient power to reach the phase transition temperature at $110 \text{ }^\circ\text{C}$ allows to observe the direct melting of the liquid crystalline phase into the isotropic one. At the laser impact, the film appears completely dark under the crossed polarizers (Figure 3b). At a fixed power, the size of the melted areas remains stable. The extent of the area, in which the product has melted, can directly and finely be controlled with the laser power density. Above the isotropization temperature, the compounds are in a highly fluid phase while under this temperature, the compounds are in a highly viscous state. Thus, the isotropic fluid formed under laser

irradiation can be confined into the solid and cold bulk phase. More interestingly, when the laser irradiation is removed, the irradiated area rapidly cools and the fast recovery of the organized phase leads to the formation of a texture with optical properties drastically different from the one of the bulk obtained by slow cooling (Figure 3c). Indeed, in the bulk, the homogenous texture with large homeotropic domains and pseudo fan-shapes is preserved whereas in the irradiated area, a non-characteristic texture of higher birefringence is formed, leading to marked birefringence contrast between the irradiated and the non-irradiated areas. Such thin films can be good candidate for optical data storage. Indeed, upon further irradiation and non-irradiation cycles, the exposed area can be remelted and reorganized in a reproducible way with the same lateral extent.

With compound **2**, only uncharacteristic texture with very small birefringent domains have been obtained by slow cooling from the isotropic phase (Figure 4a). The absence of well-defined textural features is attributed here to the high thickness of the film (120 μm). After irradiation and fast cooling from the isotropic phase, the same texture has always been observed at room temperature. However, it has been possible to demonstrate that the extent of the black areas observed under crossed polarizers, in which the product has melted, can directly and finely be controlled with the laser power density. In fact, depending on the power density and the spot size, the diameter of the areas can be controlled from hundreds of micrometers to several millimeters (Figure 4b, 4c and 4d). Surely, lower irradiation spot size can be obtained with a better control of the laser collimation.

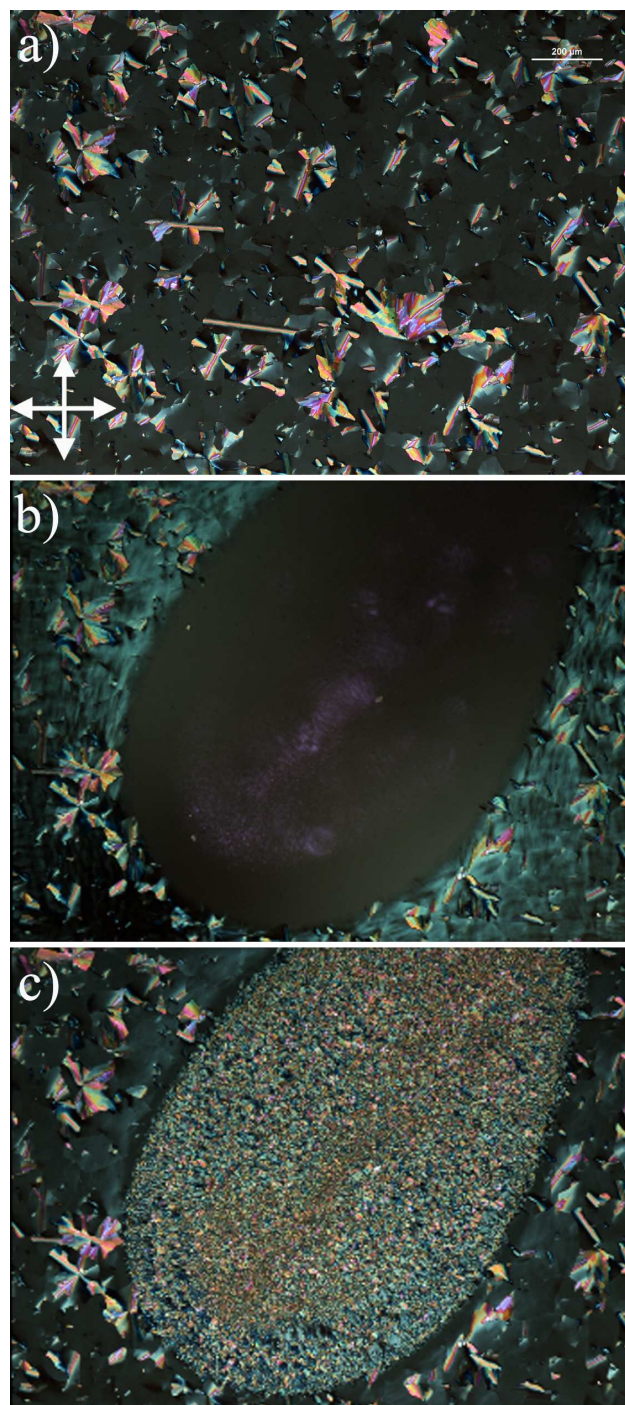


Figure 3. POM images of a thin film of compound **1**: a) before irradiation, b) under a laser irradiation that allows to reach the isotropization temperature (laser on) and c) after removal

of the laser irradiation (laser off) (crossed-polarizers symbolized by the white cross in the corner of the picture).

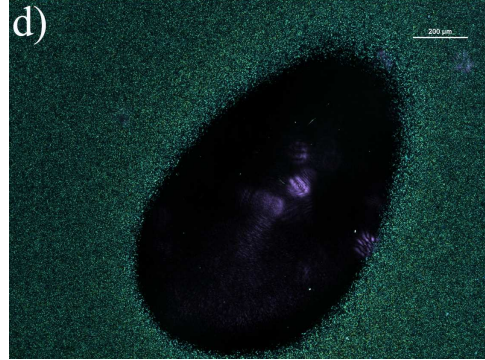
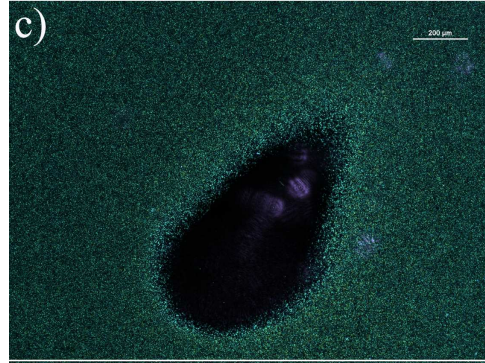
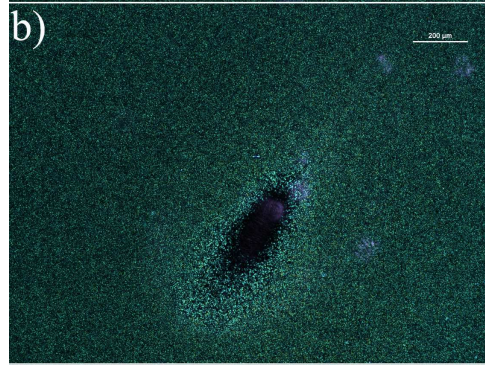
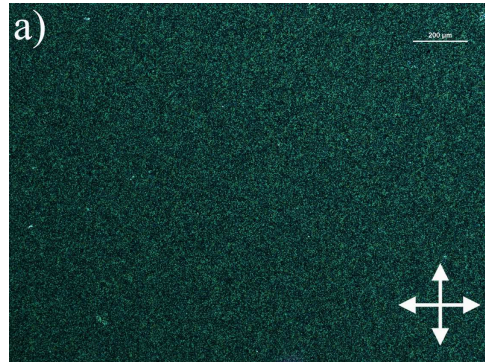


Figure 4. POM images of a thin film of compound **2** under various 940 nm laser powers: a) 0 W, b) 1.23 W, c) 1.37 W, d) 1.56 W. In the black areas, the temperature of the thin film is above the isotropization temperature of 142 °C.

The present work demonstrated that phase transitions can easily be induced with light by using liquid crystalline materials directly built around photothermally active cores. The use of photothermal mesogens prevent the use of doping agents which can disturb the molecular organization. In addition, high temperature phase transition can quickly be reached, even starting from room temperature. Discotic mesogens forming columnar liquid crystalline phase have been studied in the present work but the concept demonstrated here should easily be transferred to others type of liquid crystalline phases such as nematic phase.¹¹ Such photothermally active liquid crystals expressing thermal transitions, associated to changes in total excluded volume fraction, local orientational order and viscosity, which can be induced by light allowing fast response and spatial control, are of particular interest when considering the development of new light sensitive actuators and sensors as well as thin films for data storage.¹² Works along these lines are currently under investigations in our Laboratory.

Keywords

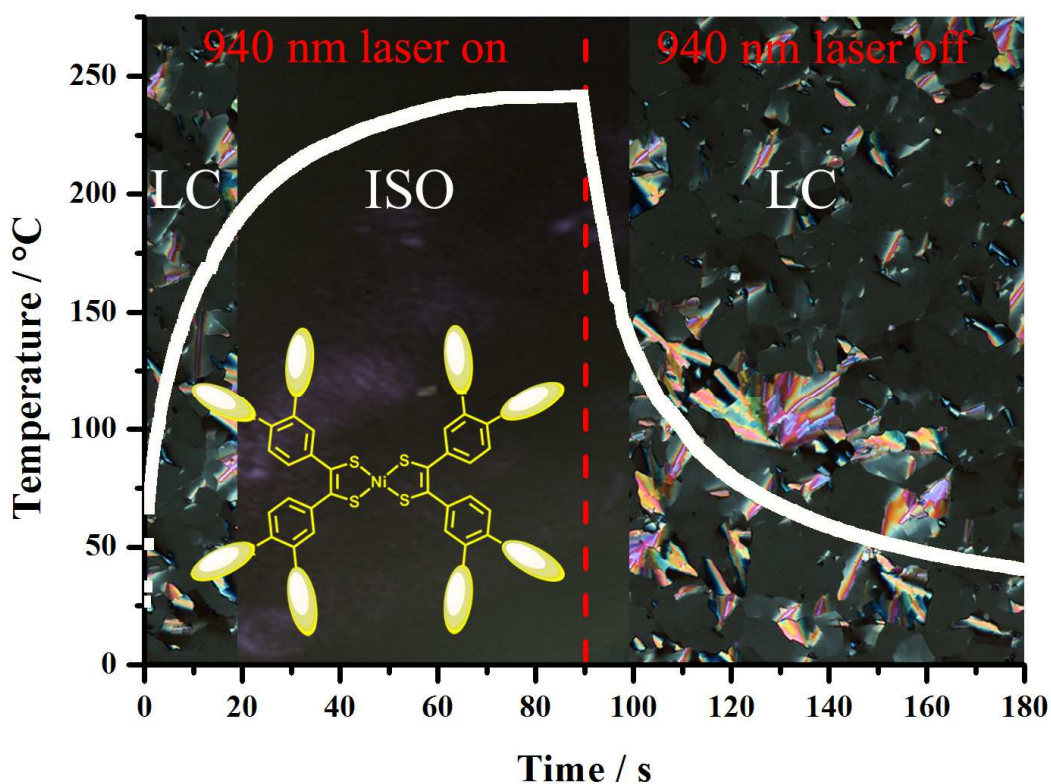
Photothermal, Thermotropic liquid crystal, Phase transition, Laser, Dithiolene complexes

Acknowledgments

The CNRS and the University of Rennes 1 are gratefully acknowledged for financial support.

Electronic Supplementary Information (ESI) available: Experimental details, UV-vis-NIR absorption spectra and temperature profiles with time constants for heat transfer determined on solutions of compound **1** and **2** in toluene, temperature profile of the glass support and evolution of the maximum temperature increase as a function of the power density for compound **1** and **2** as thin films. See DOI: 10.1039/c000000x/

TOC



Laser irradiation allows rapid high temperature phase transition directly from room temperature in pure liquid crystalline materials built around photothermal cores with a high spatial control and responsiveness.

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Supporting information

Laser triggered phase transition in photothermal liquid crystals

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Compound **1**¹ and compound **2**² were synthesized as previously described. Optical microscopy investigations were performed on a Nikon H600L polarising microscope equipped with a Linkam “liquid crystal pro system” hotstage. Laser irradiation on solution or on thin films were performed with a 940 nm-wavelength semiconductor laser (BWT Beijing LTD). The power intensity of the laser could be adjusted externally (0-10 W). The output power was independently calibrated using an optical power meter. In solution, the temperature profiles were recorded thank to a thermocouple with an accuracy of ± 0.1 °C connected to an Agilent U1253B multimeter. The thermocouple was inserted into the solution at such a position that the direct irradiation of the laser was avoided. The temperature was measured every 1s. Temperature elevations on thin films were directly recorded with a thermal infrared camera (OPTRIS PI400) and the PI Connect software. UV-Vis-NIR absorption spectra in solution were recorded on a Shimadzu UV3600 Plus spectrophotometer. Samples were placed in 1 cm path length quartz cuvettes. The thickness of the films have been determined with a Taylor-Hobson Talystep surface profilometer after gentle removing of the cover-glass slide at room temperature.

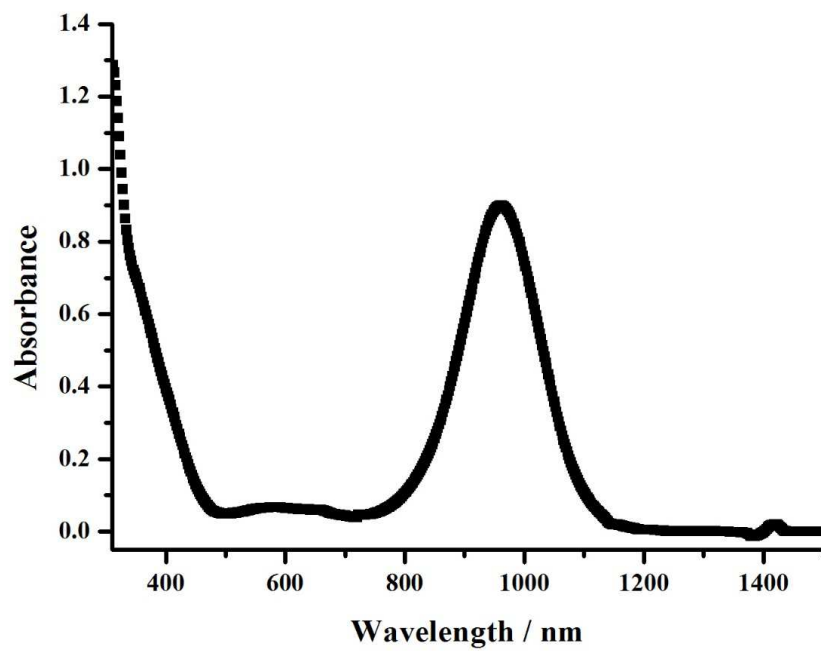


Figure S1. UV-vis-NIR absorption spectrum of compound 1 in toluene ($C = 2.5 \times 10^{-5} \text{ mol.L}^{-1}$)

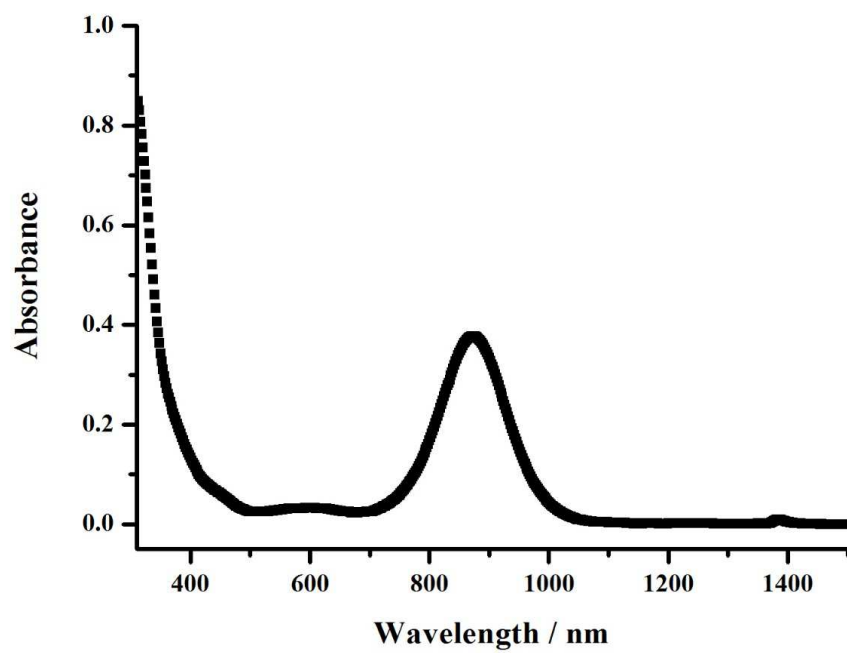


Figure S2. UV-vis-NIR absorption spectrum of compound 2 in toluene ($C = 1.2 \times 10^{-5} \text{ mol.L}^{-1}$)

1)

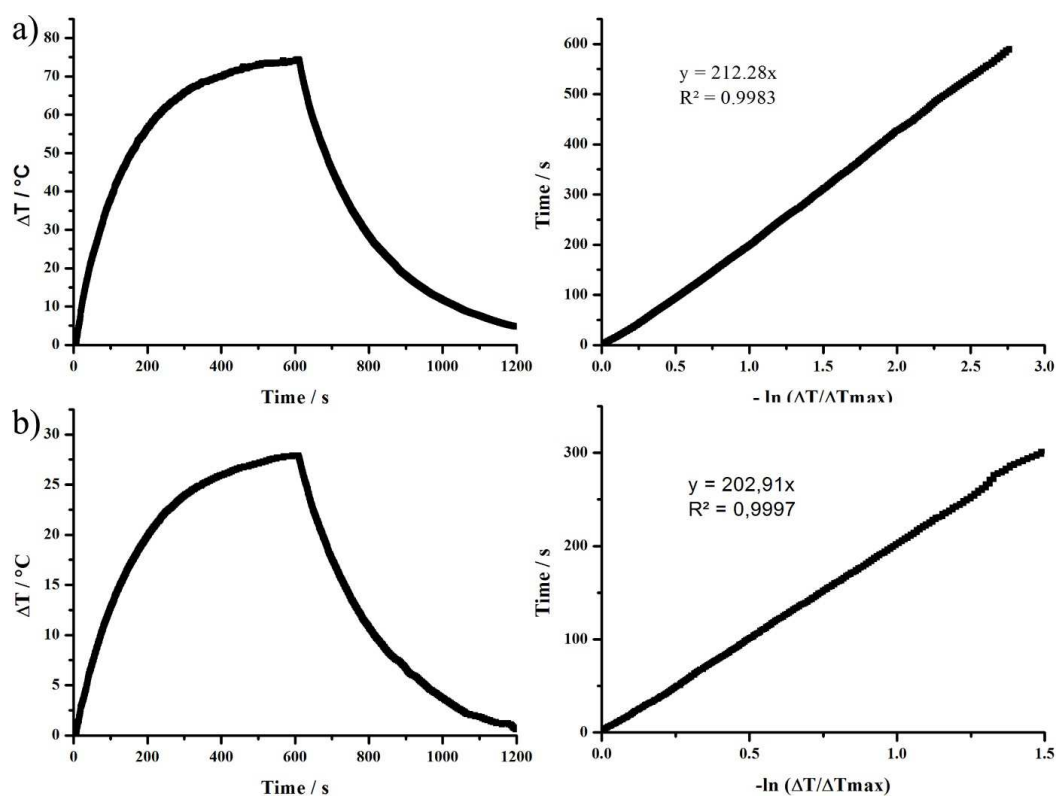


Figure S3. a) (Left) Temperature profile of the suspension of compound **1** in toluene ($C = 2.5 \times 10^{-5} \text{ mol.L}^{-1}$) when illuminated with a 940 nm laser (5 W.cm^{-2}) during 10 min and after turning off of the laser during 10 min; (Right) time constant for heat transfer is determined by applying the linear time from the cooling period (from 600 to 1200 s) versus negative natural logarithm of the driving force temperature. b) (Left) Temperature profile of the suspension of compound **2** in toluene ($C = 1.2 \times 10^{-5} \text{ mol.L}^{-1}$) when illuminated with a 940 nm laser (5 W.cm^{-2}) during 10 min and after turning off of the laser during 10 min; (Right) time constant for heat transfer is determined by applying the linear time from the cooling period (from 600 to 1200 s) versus negative natural logarithm of the driving force temperature.

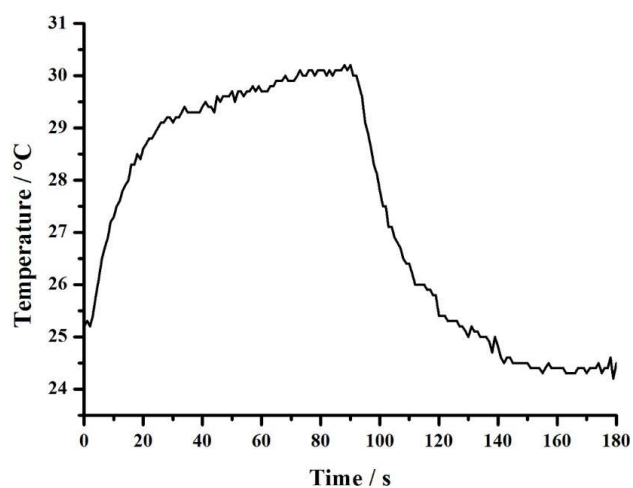


Figure S4. Temperature profile of the glass support without nickel-bis(dithiolene) complexes irradiated at 940 nm with a laser density of 2.5 W.cm^{-2} for 90 s.

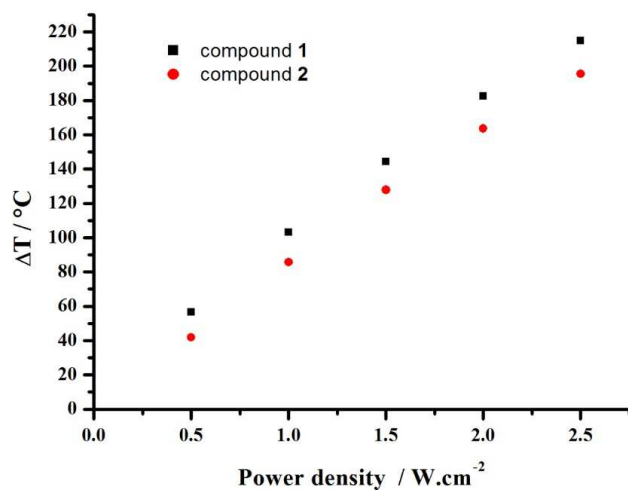


Figure S5. Evolution of the maximum temperature increase (ΔT) as a function of the power density (measurements performed on thin films).

¹ K. Ohta, Y. Inagaki-Oka, H. Hasebe and I. Yamamoto, *Polyhedron*, 2000, **19**, 267–274.

² S. Debnath, H. F. Srouf, B. Donnio, Marc Fourmigue and F. Camerel, *RSC Adv.*, 2012, **2**, 4453-4462.