

PhD Wiktor Lewandowski

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Laboratory of Organic Nanomaterials and Biomolecules

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ATTACHEMENT 3

Summary of scientific achievements in relation to habilitation procedure



Warsaw, Apr, 9th, 2019

1. NAME AND SURNAME

Wiktor Lewandowski

2. SCIENTIFIC DIPLOMA AND DEGREES

- 2013 **PhD in chemistry**, University of Warsaw, Faculty of Chemistry. Doctoral thesis "Synthesis and physicochemical properties of stilbene liquid crystalline ligands for nanoparticle surface modification", supervisor: Prof. Józef Mieczkowski
- 2008 **MSc in chemistry** within the frames of Inter-faculty Studies in Mathematics and Natural Sciences, University of Warsaw, Faculty of Chemistry, supervisor: Prof. Józef Mieczkowski
- 2008 **MSc in biotechnology** within the frames of Inter-faculty Studies in Mathematics and Natural Sciences, University of Warsaw, Faculty of Biology, supervisor: Prof. Aleksandra Skłodowska
- 2006 **BSc in biotechnology** within the frames of Inter-faculty Studies in Mathematics and Natural Sciences, University of Warsaw, Faculty of Biology, supervisor: Prof. Zdzisław Markiewicz

3. EMPLOYMENT

- 05.2016 - present Adjunct at the University of Warsaw, Faculty of Chemistry
- 10.2013 - 04.2016 Assistant at the University of Warsaw, Faculty of Chemistry

4. INDICATION OF THE ACHIEVEMENT RESULTING FROM ART. 16 SEC. 2 OF THE ACT OF 14 MARCH 2003 ON ACADEMIC DEGREES AND ACADEMIC TITLE, AND ON DEGREES AND TITLE IN THE FIELD OF FINE ARTS (JOURNAL OF LAWS OF 2017, ITEM 1789)

4.A TITLE OF THE SCIENTIFIC ACHIEVEMENT

Molecular architecture of organic, promesogenic ligands in the aspect of dynamic self-assembly of long-range ordered assemblies of nanoparticles.

4.B. THE LIST OF PUBLICATIONS CONSTITUTING THE SCIENTIFIC ACHIEVEMENT

Scientometric data according to the Web of Science database on 20/03/2019; IF according to the year of publication (IF₂₀₁₇ in the case of publications from 2017-2018); * corresponding author

- H1.** **W. Lewandowski***, M. Fruhnert, J. Mieczkowski, C. Rockstuhl, E. Górecka*, **2015**, Dynamically Self-Assembled Silver Nanoparticles as a Thermally Tunable Metamaterial **Nature Communications**, 6 (1), 6590, the number of citations: 52, IF = 11.329
Highlighted in: *Nature Materials*, **2015**, 14, 463.
My contribution to this work encompassed: development of the research concept, planning experiments, establishing and coordinating cooperation regarding modeling of optical properties of obtained materials, performing majority of the experimental work (synthesis and characterization of organic compounds, synthesis and physicochemical characterization of nanomaterials using TEM, NMR, DSC, XPS, SAXS, UV/Vis techniques), participation in ellipsometric measurements, collection and analysis of research results, main role in manuscript preparation for publication and participation in the publication process. I declare my percentage contribution to be equal to 70%.
- H2.** **W. Lewandowski***, T. Łojewska, P. Szustakiewicz, J. Mieczkowski, D. Pocięcha, **2016**, Reversible Switching of Structural and Plasmonic Properties of Liquid-Crystalline Gold Nanoparticle Assemblies **Nanoscale**, 8 (5), 2656–2663, the number of citations: 6, IF = 7.367
My contribution to this work encompassed: development of the research concept, planning experiments, performing majority of the experimental work (synthesis and characterization of L2 and L3 organic compounds, synthesis and physicochemical characterization of most of nanomaterials using NMR, TEM, SAXS, UV/Vis techniques, supervising the work of students - Tomiła Łojewska and Piotr Szustakiewicz), collecting and analyzing research results, the main role in manuscript preparation and publishing the article. I declare my percentage contribution to be equal to 75%.
- H3.** M. Bagiński, A. Szmurło, A. Andruszkiewicz, M. Wójcik, **W. Lewandowski***, **2016**, Dynamic Self-Assembly of Nanoparticles Using Thermotropic Liquid Crystals **Liquid Crystals**, 43 (13–15), 2391–2409, the number of citations: 10, IF = 2.661
My contribution to this work encompassed: development of a research concept, planning experiments, performing a part of experimental research (organic synthesis, supervising the work of students - Anna Szmurło, Aneta Andruszkiewicz, Maciej Bagiński), preparation of experimental results, planning the review part, the main role in manuscript preparation and publishing the article. I declare my percentage contribution to be equal to 75%.
- H4.** J. Grzelak, M. Żuk, M. Tupikowska, **W. Lewandowski***, **2018**, Modifying Thermal Switchability of Liquid Crystalline Nanoparticles by Alkyl Ligands Variation **Nanomaterials**, 8 (3), 147, the number of citations: 1, IF = 3.504
My contribution to this work encompassed: development of the research concept, planning experiments, performing part of the experimental work (organic synthesis, research using the TEM technique, SAXS measurements of partially oriented samples, supervising the work of students - Jan Grzelak, Maciej Żuk, Martyna Tupikowska), collecting and analyzing research

results, manuscript preparation and publishing the article. I declare my percentage contribution to be equal to 80%.

- H5.** M. Bagiński, E. Tomczyk, A. Vetter, R.N.S. Suryadharma, C. Rockstuhl, **W. Lewandowski***, **2018**, Achieving Highly Stable, Reversibly Reconfigurable Plasmonic Nanocrystal Superlattices through the Use of Semifluorinated Surface Ligands
Chemistry of Materials, 30 (22), 8201–8210, the number of citations: 0, IF = 9.890
My contribution to this work encompassed: development of the research concept, planning experiments, establishing and coordinating cooperation regarding modeling of optical properties of obtained materials, synthesis and characterization of L2 and L3 compounds, physicochemical characterization of nanomaterials based on L2 and L3 ligands using TEM, SAXS, UV/Vis techniques, the main role in manuscript preparation and publishing the article. I declare my percentage contribution to be equal to 60%.
- H6.** **W. Lewandowski**, M. Wójcik, E. Górecka*, **2014**, Metal Nanoparticles with Liquid-Crystalline Ligands: Controlling Nanoparticle Superlattice Structure and Properties
ChemPhysChem, 15 (7), 1283–1295, the number of citations: 27, IF = 3.419
My contribution to this work encompassed: participation in determination of the subject of the review, the leading role in writing chapters 4, 5 and 6 (collecting material, preparing figures and schemes). I declare my percentage contribution to be equal to 40%.
- H7.** **W. Lewandowski**, E. Górecka*, **2017**, Liquid crystals from mesogens containing gold nanoparticles,
in **Liquid Crystals with Nano and Microparticles**, World Scientific Publishing Co. Pte. Ltd., 571-602, the number of citations: 0
My contribution to this work encompassed: defining the subject of the review work, participation in literature review on the topic of interest and the main role in writing the manuscript (preparation of the tables, figures). I declare my percentage contribution to be equal to 80%.

Summary:

Total number of publications:	7
Total impact factor:	38.170
Total number of citations:	96

4.C. DESCRIPTION OF THE SCIENTIFIC GOAL AND THE RESULTS DESCRIBED IN THE PUBLICATIONS

CONSTITUTING SCIENTIFIC ACHIEVEMENT AS WELL AS DISCUSSION OF THEIR PRACTICAL IMPORTANCE

I. Scientific goal

The main goal of the outlined series of articles was employing organic chemistry tools towards achieving dynamic, plasmonic nanomaterials. The planned materials comprised two basic building blocks: (i) metallic core, that is a source of plasmonic properties and (ii) monolayers of promesogenic (and alkyl) organic ligands equipped with a thiol group responsible for controlled and dynamic self-assembly properties of the structure. The idea that stood behind development of molecular architecture of organic ligands was to achieve organic/inorganic nanomaterials that exhibit:

- long-range ordered, switchable structure in the solid state,
- dynamic changes of optical properties,
- quick structural response in response to external stimuli,
- high chemical stability and durability against multiple switching cycles.

Meeting the set synthetic goals would allow to obtain nanomaterials with properties suitable for new generations of photonic devices.

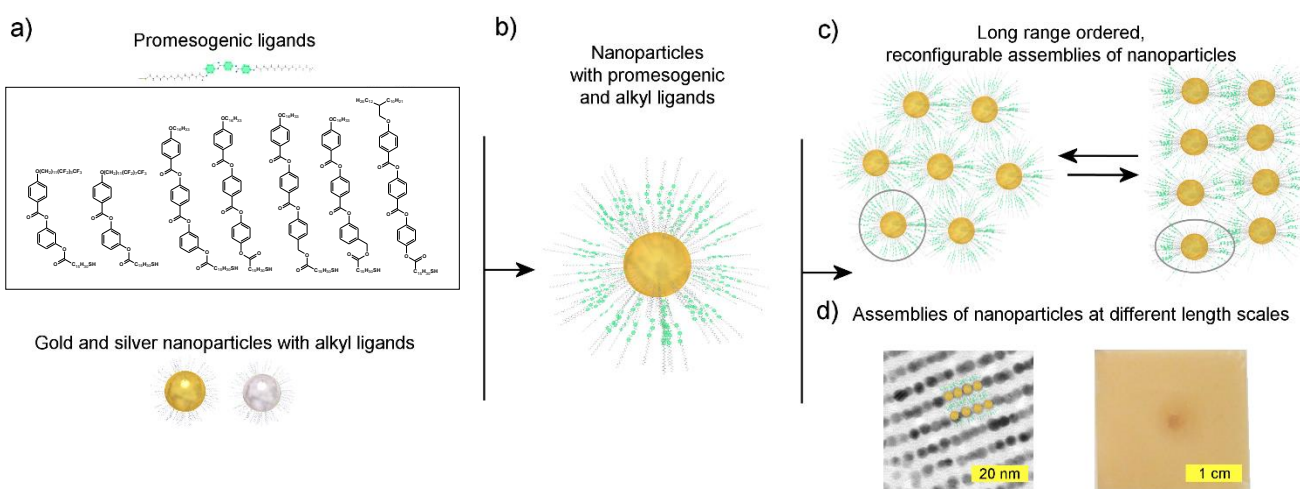


Figure 1. A schematic representation of the general idea of outlined works. (a) Structures of promesogenic ligands and schematic representation of metallic cores of nanoparticles. (b) Scheme representing a nanoparticle with a monolayer of promesogenic and alkyl coligands grafted to its surface, referred to as mesogenic nanoparticle. (c) Scheme representing process of dynamic self-assembly of mesogenic nanoparticles that is driven by the change of spatial distribution of promesogenic ligands around metallic cores of nanoparticles. (d) Nanoparticle aggregates: transmission electron microscopy image that shows a lamellar aggregate of nanoparticles (on the left) as well as a thin film of nanoparticles on a glass substrate that was prepared using spin-coating technique (on the right).

The outlined research encompassed planning of molecular architecture of promesogenic compounds, their synthesis, synthesis of plasmonic (metallic) nanoparticles as well as combining both components towards achieving final nanomaterials with unique optical characteristic. At each stage of the work it was necessary to perform full characterization of achieved structures. A schematic flowchart of the outlined series of articles is presented in Figure 1.

II. Introduction

II.A Chemical derivatization of nanomaterials

Nanotechnology is one of the fastest growing fields of science, which, among other factors, results from the development of synthetic and analytical techniques that allow for effective work with nanostructures. Development in this research area enabled discovery and examination of properties of various types of nanomaterials, e.g. carbon nanotubes, graphene, graphene oxide and metal nanoparticles.¹⁻³ Further development, especially in the context of practical applications of nanomaterials, translates often to the requirement of endowing them with compatibility with various solvents,⁴ enhancement of durability,⁵ precise control of the symmetry of materials made with them⁶ and effective formation of composites.⁷ These goals can be reached via chemical modification of nanomaterials, often with the use of organic chemistry methods, which translates to the growth of interest in using classical organic chemistry tools in nanotechnology.

In the case of metal nanoparticles a breakthrough discovery in chemical modification of their surface was reported 25 years ago.⁸ At that time group led by David Schiffrin published an easy, quick and efficient method for the synthesis of spherical, small (2-5 nm diameter), hydrophobic gold nanoparticles.⁹ These nanoparticles were stabilized with a monolayer of alkyl thiols attached to the metallic core. The presence of organic shell ensured stability of dispersion of nanoparticles in nonpolar solvents. Soon after, chemical methods for gold nanoparticles surface modification were developed that relied on the use of ligand exchange reaction or chemical transformation using terminal groups of functionalized ligands.¹⁰⁻¹⁴ The breakthrough novelty of this research was to prove that organic chemistry methods can be successfully used to modify the surface of nanoparticles and that properties of obtained nanomaterials are mainly determined by the type of surface ligands.

During my doctorate the issue of chemical modification of nanomaterials was at the center of my interests. I participated, among other projects, in the development of a new method for producing a carboxylic derivative of reduced graphene oxide,^{A2,P1} which, owing to this modification, formed stable suspensions in water. I also synthesized (pro)mesogenic ligands to modify the surface of very small nanoparticles to obtain static, long-range ordered aggregates of very small nanoparticles.^{A1,A7} Within the outlined series of works I focused primarily on working with plasmonic nanoparticles in dynamic assemblies.

II.B Plasmonic nanoparticles

Studies related to plasmonic nanoparticles (showing the effect of localized surface plasmon resonance) hold a special place in the field of nanotechnology.¹⁵ Owing to their unique optical properties, plasmonic nanoparticles can be the basis for construction of future generations of ultrasensitive biosensors,¹⁶ organic reaction catalysts,^{17,18} photovoltaic devices¹⁹ or metamaterials,²⁰⁻²² allowing to solve many technological/engineering. A wide range of applications and the ability to create metamaterials (structures with properties not found in nature, properties that depend on the spatial distribution of building blocks forming the materials) have resulted in increased interest in plasmonic nanoparticles, and also was one of the factors contributing to establishing research centers dedicated, among others topics, to the subject of plasmonic nanomaterials (e.g. Center of Plasmonics and Metamaterials, Imperial College London).

One of the important issues related to development of research on plasmonic nanoparticles was (and still is) optimization of their optical properties by the means of modification of their composition, size and the shape.^{23,24} However, relatively recently, it has been proven that also distance between

nanoparticles determines the properties of materials built with them.^{25,26} For this reason, the issue of precise control of the internal symmetry of nanoparticle aggregates has become extremely important. Currently, the aim is to obtain dynamic (reconfigurable, switchable) nanomaterials, i.e. those in which the distance between nanoparticles can be reversibly changed by applying an external stimuli (already after the formation of a long-range ordered structure).^{27,28} This issue is important not only from the point of view of basic research, but also from the point of view of the use of this type of materials in multi-channel data processing²⁹ or for obtaining switchable metamaterials.^{20,30} The aim of outlined series of works was the development of reconfigurable nanoparticle assemblies capitalizing on the process of dynamic self-assembly.

II.C Dynamic self-assembly of nanoparticles

Over the last decade, several methods for achieving dynamic self-assembly of plasmonic nanoparticles have been developed. They can be classified in various ways, for example depending on:

- nature of the external stimuli that is used to trigger the change:
 - chemical (solvents, pH, metal ions, gases, bio-macromolecules and redox signals),^{28,31}
 - physical (mechanical, temperature, magnetic field, light),^{28,31}
- type of material that is sensitive to external stimuli:
 - ligands attached to nanoparticle surface (DNA, low molecular weight organic molecules),^{32,33}
 - matrix (polymers, liquid crystals).^{33,34}

The main factors limiting the use of most of the above methods in future generations of photonic devices, in particular in the case of metamaterials, is often the low volume percentage of metal in the composite³⁵ and the fact that solvent is required to achieve switching.^{26,36} Development of dynamic self-assembly methods of plasmonic nanoparticles that combat these challenges is a big challenge. One of the few techniques that has the potential to overcome these limitations is based on the modification of the surface of nanoparticles with mesogenic or promesogenic ligands. I used this strategy throughout the course of the outlined series of works and reviewed this research area in articles [H6] and [H7].

III. Results

III.A Liquid-crystalline nanoparticles

Before I proceed to discuss the topic, I will introduce definitions that will be used throughout the text. Mesogenic compounds are substances that form liquid crystalline phases. Promesogenic compounds, despite molecular architecture similar to mesogenic compounds, do not form liquid crystalline phases, however, they may, for example after being grafted to the surface of nanoparticles, induce the mesogenic properties of the obtained hybrid materials. That is why, in the literature, nanoparticles coated with (pro)mesogenic compounds (either mesogenic or promesogenic), forming anisotropic systems and responding to external stimuli, are called liquid crystalline nanoparticles (LC NPs).^{37,38} Herein, LC NPs will also be referred to as hybrid nanomaterials, due to their organic / inorganic nature.

The introduction of (pro)mesogenic ligands to nanoparticle surface has been an intensively developed research area over the last fifteen years.³⁹⁻⁴⁷ A number of research groups have shown that using this strategy, one can obtain a wide range of anisotropic (symmetry other than the densest packing structures), long-range ordered aggregates of nanoparticles. Observed properties result from interactions between (pro)mesogenic ligands, which translate to anisotropic distribution of ligands around nanoparticles at low temperatures and ensure anisotropic, overall shape of hybrid nanoparticles. This shape can be further modified by changing the spatial distribution of ligands, e.g. as a result of raising the temperature of the system (Figure 1c).

At the beginning of research related to the presented series of publications, I took part in writing a review article on liquid-crystalline nanoparticles. The goal I set myself was to describe three important aspects of this field related to reconfigurability and functionality of this type of materials:

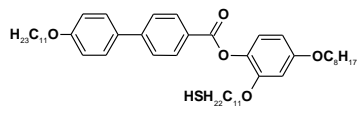
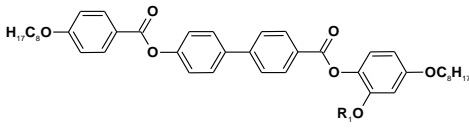
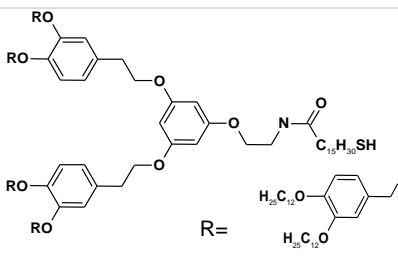
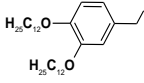
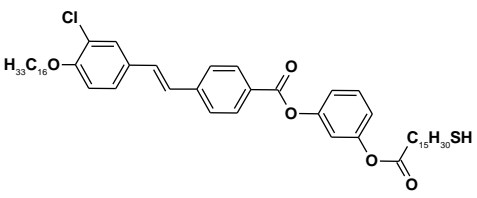
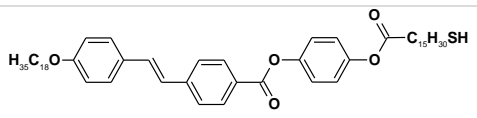
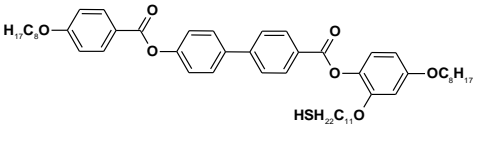
- dynamic control of symmetry of the long-range ordered aggregate of nanoparticles resulting from the variable spatial distribution of ligands around nanoparticle (Figure 1c),
- thermal stability of anisotropic, long-range ordered structures built with nanoparticles,
- obtaining functional systems - most of the works published until 2014 were based on the use of small gold nanoparticles that do not show plasmonic absorption, while systems based on larger, plasmonic nanoparticles were rarely described.

The above mentioned review allowed me to notice that until I undertook the outlined research topic, there were no examples of dynamic aggregates built of mesogenic nanoparticles that would show switchable optoelectronic properties. Achieving this type of materials become the goal of my work.

In an updated literature review [H7], I more broadly described the synthesis and examination of nanoparticles coated with (pro)mesogenic ligands, principles of designing liquid-crystalline nanoparticles architecture and summarized possibilities this strategy offers in the context of achieving dynamic reconfiguration of nanoparticle aggregates (Table 1). One of the important aspects considered in this work was to emphasize the innovative character of dynamic control over symmetry of nanoparticle aggregates using light stimuli. Moreover, I introduced a metamaterial-relevant classification of dynamic materials built with nanoparticles based on switching between: (i) ordered and isotropic phases, (ii) different, long-range ordered phases.

Based on the knowledge acquired when preparing the review articles,^{H6,H7} as well as research conducted throughout my PhD thesis work^{A1,A7} and later^{A8}, I determined that to induce liquid-crystalline properties of nanoparticles one needs to decorate their surface with ligands comprising: an alkyl spacer unit equipped with a binding moiety (e.g. a thiol group for Au and Ag nanoparticles), a rigid core comprising aromatic rings (most commonly a biphenyl unit^{42,45,48}), as well as a flexible terminal chain (usually alkyl or alkoxy). Bearing in mind these concepts and using the rich literature on mesogenic compounds, I undertook the project of developing new, (pro)mesogenic ligands that would favor formation of reconfigurable aggregates of plasmonic nanoparticles.

Table 1. Summary of the structure and properties of chosen nanoparticles stabilized with (pro)mesogenic ligands. Symbols: g, N, Iso, Cr, HS, SC, BCO, Sm stand for glass-like, nematic, isotropic, crystal, 2D hexagonal, simple cubic, body centered orthogonal and smectic phases, respectively; dec stands for material decomposition.^{H6, H7}

Structure of (pro)mesogenic ligand	Structure of alkyl coligand	NPs type and size	Phase sequence	Structural parameters of phases	Literature reference
	C ₁₆ H ₃₃ SH	Au, 1.6±0.4 nm	g (3 °C) N (43.8 °C) Iso	not available	48
 R ₁ =C ₁₁ H ₂₂ Si(CH ₃) ₂ OSi(CH ₃) ₂ C ₁₀ H ₂₀ NH ₂	C ₁₂ H ₂₅ NH ₂	Au 9.98±2.2 nm	Cr (37.5 °C) N (94.5 °C) Iso	not available	42
 R = 	C ₁₂ H ₂₅ SH HOOC(CH ₂) ₁₅ SH	Au 6.8±0.7 nm	(0 °C) HS (130 °C) SC (220 °C) dec	HS: a~20.4 nm SC: a~12.5 nm	43
	C ₄ H ₉ SH	Au ~2.2 nm	BCO (130 °C) Iso	a~5.6 nm b~11.8 nm c~3.4 nm	A7
	C ₈ H ₁₇ SH	Au ~2.2 nm	BCO (110 °C) Iso	a~5.6 nm b~11.0 nm c~3.3 nm	A7
	C ₁₂ H ₂₅ SH	Au ~2.2 nm	BCO (93 °C) Iso	a~13.0 nm b~9.0 nm c~3.9 nm	A7
	C ₈ H ₁₇ SH	Ag, 4.4±0.3 nm	Sm (170 °C) dec	c~13.1 nm a~6.6 nm	A8
	C ₁₂ H ₂₅ SH	Au, 2.0±0.4 nm	R $\bar{3}$ m (126 °C) Iso	R $\bar{3}$ m: a~8 nm c~3.5 nm	45

III.B Developing a reversible, switchable metamaterial built with nanoparticles

In order to obtain a reversibly switchable assembly of nanoparticles that would exhibit switchable optoelectronic properties, I had to properly design structure of the hybrid nanomaterial. Firstly, I focused on designing (pro)mesogenic ligands. I decided to use a ligand with an elongated, rod-like core, as such LC ligands usually ensure lower phase transition temperatures compared to branched (dendrimeric) ligands. In contrast to most of the previous studies on rod-like ligands, I did not introduce a biphenyl unit into the structure and joined aromatic rings using ester moieties. In the literature it was noted that similar mesogenic compounds exhibited phase polymorphism,⁴⁹ which I considered a good prognosis in the context of achieving dynamic nanomaterial. It is also worth to

note, that similar structures were also the basis for obtaining various mesogens.^{50–54} In the end, I designed the structure of compound **lig_1** (Figure 2), which, despite anisotropic shape of molecules, did not form liquid crystalline phases. It is worth to note that the melting of **lig_1** crystals into the isotropic phase took place at a moderate temperature (~87 °C), as I confirmed with differential scanning calorimetry (DSC) measurements.

I obtained **lig_1** compound in a multistep organic synthesis (Figure 2). The proposed synthetic path has been improved in comparison to previously conducted syntheses of promesogenic ligands – thiol moiety was introduced in a single reaction of 16-mercaptohexadecanoic acid with the phenol derivative **5** (Figure 2), instead of a two-step process (reaction with 16-bromohexadecanoic acid and then substituting -Br with -SH). With this approach I facilitated the product purification process (the investigated types of bromides and thiols have similar retention factors), reducing the risk of contamination of the product with traces of bromides that could translate into variability of phase sequence of hybrid materials. I confirmed structure of the organic compounds using nuclear magnetic resonance (NMR) spectroscopy and elemental analysis (EA) methods.

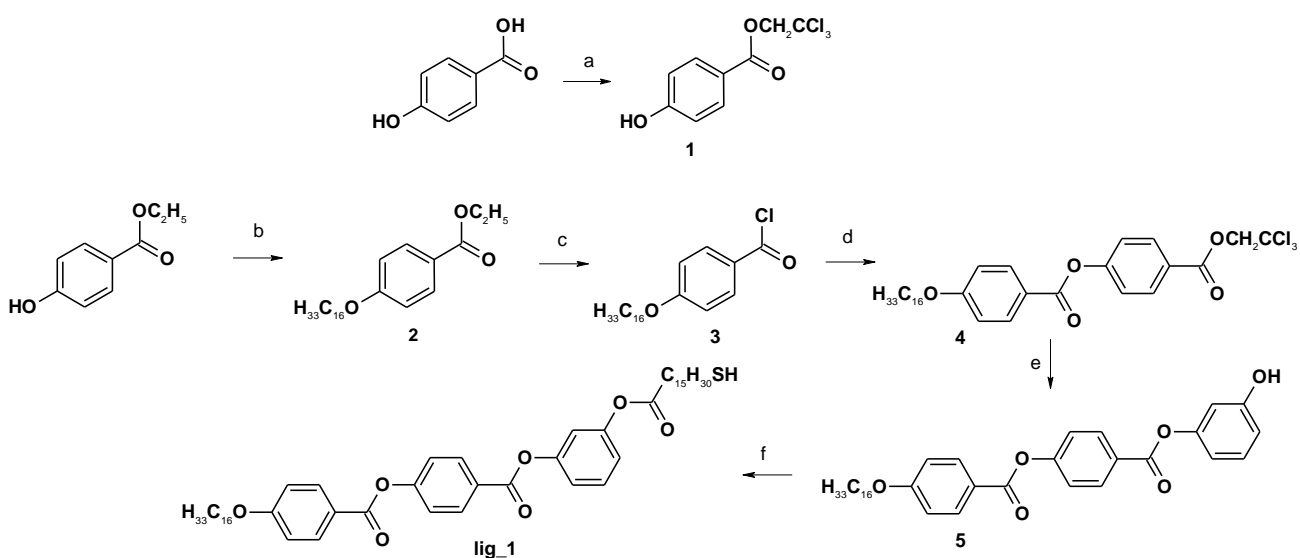


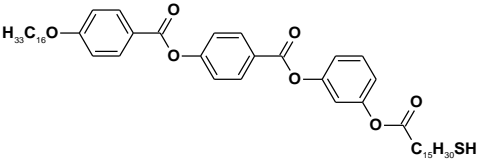
Figure 2. Synthetic path leading to **lig_1** molecule. (a) NaHCO_3 , 2,2,2-trichloroethanol. (b) 1-bromohexadecane, K_2CO_3 , KI, DMF. (c) 1. KOH, EtOH; 2. $(\text{COCl})_2$, toluene, rfx. (d) 1, TEA, DMAP, THF. (e) 1. Zn/ CH_3COOH ; 2. $(\text{COCl})_2$, toluene, rfx; 3. resorcinol, TEA, DMAP, THF. (f) 16-mercaptohexadecanoic acid, DCC, DMAP, THF.

The next challenge was to choose metallic core of nanoparticles. In order to obtain nanomaterials endowed with strong plasmonic properties, it would be preferable to use silver nanoparticles with a large metal core size.^{55,56} However, in order to obtain effective shape changes of hybrid nanoparticles (Figure 1c), metal core size should be comparable to the (pro)mesogenic molecules length (so far most of the work on LC NPs was based on nanoparticles with diameter smaller than 4 nm^{39–41,44–47}). Taking the above into consideration, I decided to obtain 4-5 nm diameter, hydrophobic silver nanocrystals.

In order to obtain the target hybrid nanomaterial (Ag nanoparticles stabilized with a thiol monolayer comprising: **lig_1** and dodecanethiol molecules) I carried out a ligand exchange reaction which yielded **hyb_I** nanomaterial (Table 2). In comparison to the sole published work devoted to mesogenic silver nanoparticles,^{A8} I improved the ligand exchange process by modifying the mixture of solvents used. The proposed change allowed to conduct ligand exchange reaction at room

temperature, limiting the coalescence of nanoparticles (increasing efficiency of the reaction). Using transmission electron microscopy (TEM), I was able to confirm that after the ligand exchange reaction the size of metallic cores was 4.7 ± 0.6 nm. By analyzing X-ray photoelectron spectroscopy spectra (XPS), I determined the molar ratio of primary and secondary ligands in the organic monolayer stabilizing nanocrystals, $n_{C_{12}H_{25}SH}/n_{lig_1} \sim 1$. Further confirmation of composition of the organic shell I got from thermogravimetric analysis (TGA) and NMR studies.

Table 2. Summary of the structure and mesogenic as well as optical properties of hybrid material **hyb_I**. Symbols: Lm, Iso stand for lamellar and isotropic phases, respectively.^{H1}

Structure of promesogenic ligand	Structure of alkyl coligand	NPs type and size	Phase sequence	Structural and optical parameters of phases	Material /literature reference
 <p style="text-align: center;">lig_1</p>	$C_{12}H_{25}SH$	Ag, 4.7 ± 0.6 nm	Lm (85°C) Iso	Lm: c~8.4 nm d~6.1 nm Iso: d~7.2nm $\lambda_{max(30^\circ C_Lm)} \sim 466$ nm $\lambda_{max(120^\circ C_Iso)} \sim 446$ nm	hyb_I ^{H1}

After successful preparation of the hybrid nanomaterial, I went on to study the structural aggregates of nanoparticles in a condensed state (thin film formed after evaporation of the solvent). In order to confirm the reversible switchability of the proposed material I used small angle X-ray scattering (SAXS) technique. Results of the measurements at 30 and 120 °C (Figure 1a,b in [H1]), evidenced a thermally-driven, dynamic reorganization of nanoparticles arrangement within the material. I interpreted the diffractograms as corresponding to a lamellar phase (Lm) at low temperature and isotropic phase (Iso) at elevated temperature (Figure 3a, Table 2). I confirmed correctness of the phase **hyb_I** assignment by preparing and SAXS measurements of a partially-oriented sample (Figure 3e) as well as owing to TEM imaging of a heat-annealed sample (Figure 3b, c). Importantly, SAXS studies showed that the distance between the nearest neighbor nanoparticles in the Lm and Iso phases differs by 1.1 nm, which suggested that this material may exhibit switchable plasmonic properties.

UV/Vis measurements of **hyb_I** in the solid state, carried out at 30 and 120 °C (that is at temperatures corresponding to nanoparticle arrangement in Lm and Iso phases), allowed me to confirm that the **hyb_I** material exhibits switchable optical properties - position of the plasmonic band maxima shifted from 466 nm (30 °C) to 446 nm (120 °C, Figure 3d). It is worth noting that such UV/Vis measurements (for solids as a function of temperature) are rarely performed, thus required development of an appropriate methodology.

To obtain detailed information on structural and functional response of **hyb_I** material to temperature changes I planned and performed a series of measurements at temperatures between 30 and 120 °C (SAXS, DSC, UV/Vis). I have shown, that within the range of temperatures corresponding to phase transition (70 – 95 °C) there is an abrupt change of optical properties of the material. However, I also noted a shift of the position of plasmonic band maxima when heating the material from 30 to 70 °C, that is in temperature range of Lm phase existence. Based on correlation of SAXS and UV/Vis measurements results I have shown that the observed effect is most probably caused by growing inter-particle distance within layers. Thus, I obtained precise information, allowing to correlate

structure and optical properties of nanoparticle assemblies. Further, I confirmed that **hyb_I** assemblies can be reversibly reconfigured (4 cycles, Figure 3h in [H1]).

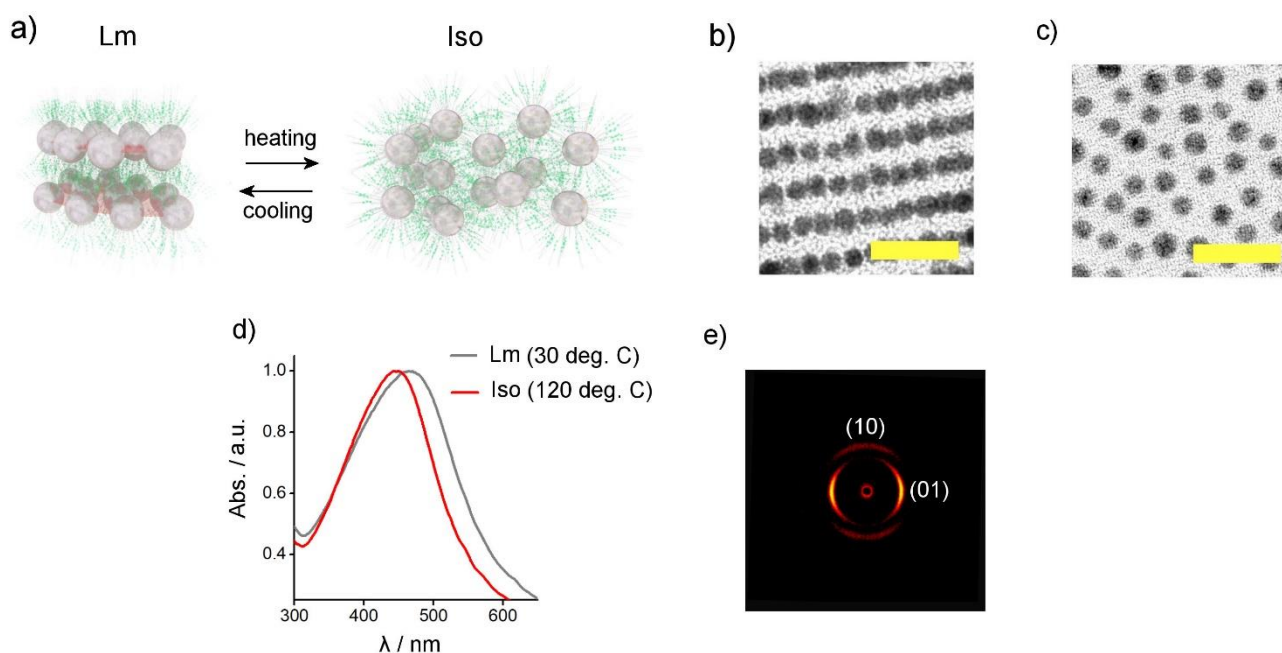


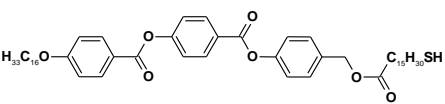
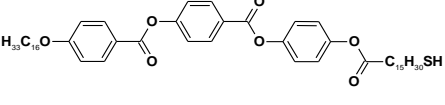
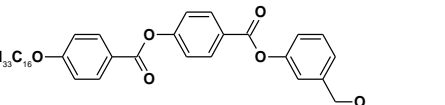
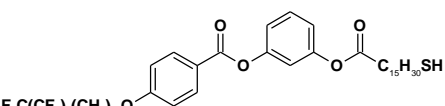
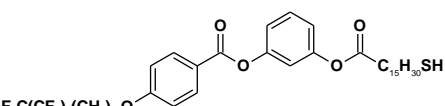
Figure 3. Structural characteristics of **hyb_I** material. (a) Schematic representation of the spatial distribution of nanoparticles and ligands in lamellar (Lm) and isotropic (Iso) phases. (b) TEM micrograph of the nanoparticle aggregate corresponding to Lm phase. (c) TEM micrograph of the nanoparticle aggregate corresponding to Iso phase. Scale bars in panels (b) and (c) correspond to 20 nm. (d) UV/Vis absorbance spectra of thin films of **hyb_I** material at different temperatures. (e) The diffractogram obtained for the semi-oriented sample of **hybrid_I**. Signal indexation is indicated.

At this point I decided to contact Prof. Carsten Rockstuhl, an expert in theoretical modelling of optical properties of plasmonic nanoparticles. Based on structural parameters of **hyb_I** phases that I provided, the team of Prof. Rockstuhl was able to recreate experimental results of UV/Vis measurements. Inspired by a paper which has shown that some assemblies made of silver nanoparticle can exhibit epsilon-near-zero (ENZ) properties,⁵⁷ I also asked to calculate real and imaginary parts of the effective permittivity of the analyzed hybrid material at Lm and Iso phases. Results of modelling indicated that **hyb_I** material fell into the ENZ class of metamaterials. It was the first example of a switchable ENZ metamaterial made with nanoparticles. We further confirmed ENZ properties of **hyb_I** using ellipsometry.

III.C Modifying molecular architecture of promesogenic ligands

The above-described research turned out to open the access to an interesting class of dynamic metamaterials, but the stability of **hyb_I** has been confirmed for a limited number of heating/cooling cycles. In addition, **hyb_I** exhibited a short-range ordered structure at high temperature and required slow cooling to achieve long-range order at low temperatures. These features are disadvantageous from the point of view of metamaterial applications. In subsequent studies described in [H2, H4, H5] I showed how, by modifying the molecular architecture of promesogenic ligands, one can overcome these limitations.

Table 3. Summary of the structure and mesogenic as well as optical properties of hybrid materials obtained using **lig_2**, **lig_3**, **lig_4**, **lig_5** and **lig_6** ligands. Symbols: Lm, Iso, SRO, Lm_{mod}, BCT, BCC, FCC stand for lamellar, isotropic, short-range ordered, modulated lamellar, body centered tetragonal, body centered regular, phases respectively; dec stands for material decomposition.^{H2,H3}

Structure of promesogenic ligand	Structure of alkyl coligand	NPs type and size	Phase sequence	Structural and optical parameters of phases	Material /literature reference
 <p>lig_2</p>	C ₁₂ H ₂₅ SH	Au, ~2.2 nm	Lm (55°C) Iso	Lm: d~7.4 nm a~3.3 nm Iso: a~5.0 nm	hyb_II ^{H2}
	C ₁₂ H ₂₅ SH	Au, ~4.4 nm	SRO	a _{30°C} ~8.5 nm	hyb_III ^{H2}
	C ₁₂ H ₂₅ SH	Ag, ~4.8 nm	SRO	a _{30°C} ~9.0 nm a _{130°C} ~10.5 nm	hyb_IV ^{H2}
 <p>lig_3</p>	C ₁₂ H ₂₅ SH	Au, ~2.2 nm	2D, centered orthorhombic (130°C) Lm (150°C) dec	2D, centered orthorhombic: a~3.3 nm c~14.7 nm	hyb_V ^{H2}
	C ₁₂ H ₂₅ SH	Au, ~4.4 nm	Lm _{mod}	d~11.6 nm; a _{mod} ~24.2 nm	hyb_VI ^{H2}
	C ₁₂ H ₂₅ SH	Ag, ~4.8 nm	Lm (150°C) dec	Lm: d~8.4 nm a~6.3 nm	hyb_VII ^{H2}
 <p>lig_4</p>	C ₁₂ H ₂₅ SH	Au, ~2.2 nm	2D, centered orthorhombic (120°C) Iso	2D, centered orthorhombic: a _{30°C} ~3.2 nm c _{30°C} ~15.3 nm a _{120°C} ~3.3 nm c _{120°C} ~14.1 nm Iso: a~4.7 nm	hyb_VIII ^{H2}
	C ₁₂ H ₂₅ SH	Au, ~4.4 nm	BCT (95°C) BCC	Tet: a _{30°C} ~5.5 nm c _{30°C} ~16.2 nm a _{90°C} ~5.76 nm c _{90°C} ~14.9 nm BCC: a _{100°C} ~8.25 nm, a _{140°C} ~8.29 nm λ _{max(30°C_Tet)} ~523 nm λ _{max(140°C_BCC)} ~531 nm	hyb_IX ^{H2}
	C ₁₂ H ₂₅ SH	Ag, ~4.8 nm	Lm (90°C) Iso	Lm: d~8.6 nm a~6.2 nm Iso: d~7.5 nm	hyb_X ^{H2}
 <p>lig_5</p>	C ₁₂ H ₂₅ SH	Ag, 5.2±0.4 nm	Lm (90°C) BCC	Lm: d~10.9 nm a~6.9 nm λ _{max(30°C_Lm)} ~470 nm λ _{max(120°C_BCC)} ~451 nm	hyb_XI ^{H5}
 <p>lig_6</p>	C ₁₂ H ₂₅ SH	Ag, 5.2±0.4 nm	Lm (60°C) BCC (110°C) FCC	Lm: d~11.0 nm a~6.5 nm BCC: a~11.4 nm FCC: a~15.0 nm λ _{max(30°C_Lm)} ~479 nm λ _{max(70°C_BCC)} ~442 nm λ _{max(130°C_FCC)} ~438 nm	hyb_XII ^{H5}

First, I decided to optimize molecular architecture of promesogenic ligand towards achieving reversibly reconfigurable assemblies of NPs, that exhibit switchability between distinct, long-range ordered phases. Towards this aim, I designed three new promesogenic ligands in which I retained

the general architecture of **lig_1** molecule, however, I diversified the substituents of the aromatic ring that is the closest to the surface of a nanoparticle. The synthetic scheme is presented in Figure 4. I supervised **lig_2** ligand synthesis and synthesized ligands **lig_3** and **lig_4**.

For the first time in the case of liquid crystalline nanoparticles research, the obtained ligands were attached to more than one type of nanoparticles (different in both metallic core composition and size). This approach allowed me to broadly analyze the correlation between building blocks of hybrid materials (core, ligands) and their properties (**hyb_II** – **hyb_X**, Table 3). SAXS measurements of plasmonic nanomaterials obtained using **lig_2** and **lig_3** ligands did not evidence the expected results, i.e. the obtained assemblies were either short range ordered (**hyb_III**, **hyb_IV**) or these materials were static (**hyb_VI**, **hyb_VII**). Plasmonic, dynamic assemblies of nanoparticles were obtained using **lig_4** compound.

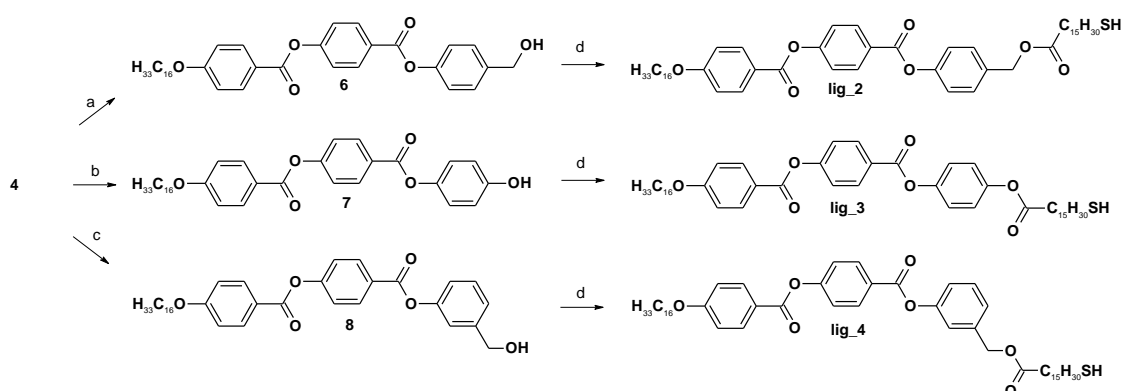


Figure 4. Synthetic path leading to **lig_2**, **lig_3** and **lig_4** molecules. Scheme of synthesis of compound **4** is given in Figure 1. (a) 1. Zn/CH₃COOH; 2. (COCl)₂, toluene, rfx; 3. 4-hydroxybenzyl alcohol, TEA, DMAP, THF. (b) 1. Zn/CH₃COOH; 2. (COCl)₂, toluene, rfx; 3. hydroquinone, TEA, DMAP, THF. (c) 1. Zn/CH₃COOH; 2. (COCl)₂, toluene, rfx; 3. 3-hydroxybenzyl alcohol, TEA, DMAP, THF. (d) 16-mercaptohexadecanoic acid, DCC, DMAP, THF.

The most important achievement of this study was preparation of the first aggregate of plasmonic, liquid crystalline nanoparticles (**hyb_IX**), which exhibited: (i) switchability between two phases with long-range, 3D order as well as (ii) dynamic optical properties. Namely, as I demonstrated using SAXS measurements, **hyb_IX** nanoparticles showed reconfigurability between body centered tetragonal (BCT) and body centered cubic systems (BCC, Figure 5, Table 3). It should be emphasized, that in this case (in contrast to **hyb_I**), slow cooling rate was not required to produce a long-range ordered aggregate at low temperature. The change of symmetry of the aggregate was accompanied by an 8 nm shift of plasmonic band maxima, as I demonstrated with UV/Vis measurements. In conclusion, the proposed molecular architecture of **lig_4** allowed for overcoming few challenges of reconfigurable, long-range ordered assemblies of nanoparticles for photonic applications. However, the relatively high temperature of phase transition limited the stability of nanomaterials. I assumed that this problem can be faced by further modification of the architecture of promesogenic ligands.

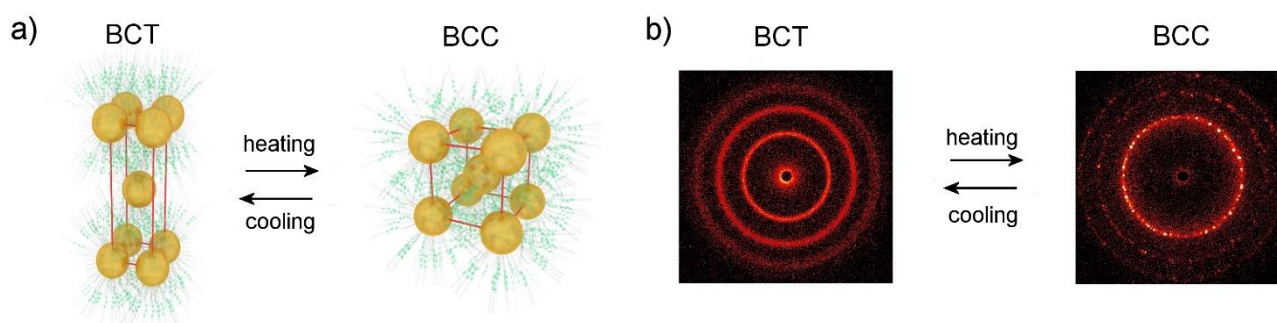


Figure 5. Structural characteristics of **hyb_IX** material. (a) Schematic representation of the spatial distribution of nanoparticles and ligands in body centered tetragonal (BCT) and body centered cubic (BCC) phases. (b) SAXS diffractograms of unaligned sample collected at 30 and 120 °C.

To reduce the phase transition temperatures of hybrid nanomaterials, I decided to use promesogenic ligands with stiff, anisotropic core comprising fewer aromatic rings. However, it should be remembered that in the case of LC NPs, this approach may result in a reduced tendency of ligands to spatially segregate. In order to overcome this limitation, I suggested that a semifluorinated terminal chain, which tends to separate from organic hydrocarbon compounds, should be introduced into the structure of promesogenic ligands.^{58–62}

In line with the above considerations, I designed, synthesized and confirmed the structure of **lig_5** and **lig_6** ligands (Figure 6). These are bicyclic compounds (in comparison to the tricyclic **lig_1**—**lig_4** molecules) that bear a semifluorinated alkyl terminal chain.

In order to maximize optical response of hybrid nanoparticles system, I decided to use silver nanoparticles with diameter larger than in previous studies (5.2 ± 0.4 nm).

I used **lig_5** and **lig_6** compounds as well as silver nanocrystals in ligand exchange reactions to obtain two hybrid nanomaterials **hyb_XI** and **hyb_XII** (Table 3). With SAXS measurements, I confirmed that **hyb_XI** material shows a long-range ordered, reversibly switchable structure (phase sequence: Lm 90 °C BCC). I have also shown that changes of the symmetry are accompanied by a 19 nm shift of the position of plasmon band maximum. Unfortunately, SAXS investigations indicated low stability of this material - after seven heating/cooling cycles I noticed that full width at half maximum of the main diffraction signal for the BCC structure significantly increased (Figure S6e in the supplementary material for publication [H5]), which indicated a decrease of positional correlation range of nanoparticles. For this reason, I decided to focus on **hyb_XII** nanomaterial based on **lig_6** ligand, which had a shorter fluorinated part of the terminal chain. I hoped that this relatively small change of architecture of ligand would translate to lowering the phase transition temperature of hybrid nanomaterial.

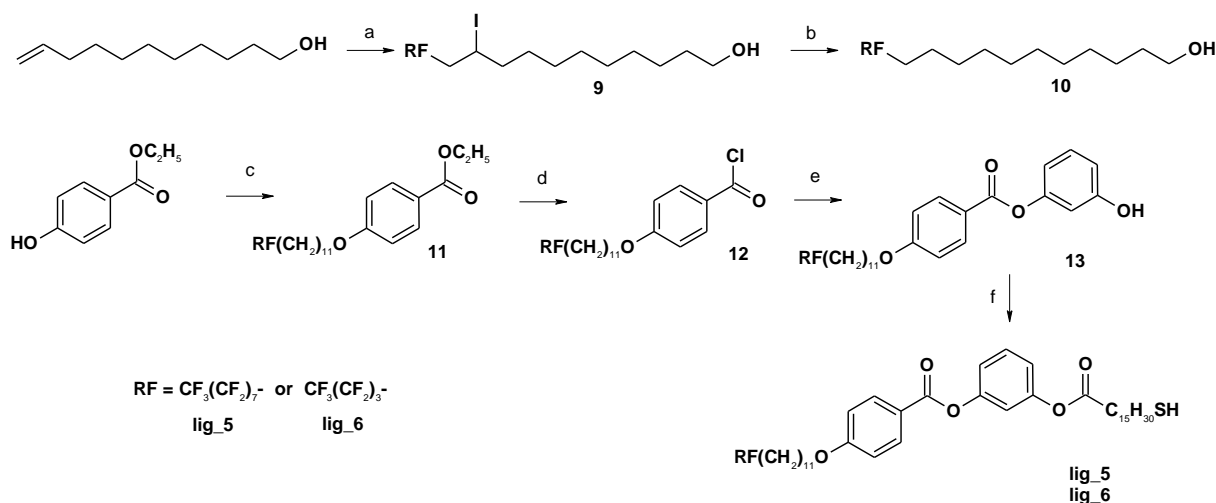


Figure 6. Synthetic path leading to **lig_5** and **lig_6** molecules. (a) $\text{C}_8\text{F}_{17}\text{I}$ or $\text{C}_4\text{F}_9\text{I}$, NaHCO_3 , $\text{Na}_2\text{S}_2\text{O}_4$, CH_3CN , H_2O . (b) Zn , HI , ethanol, rfx. (c) **10**, DIAD, Ph_3P , ultrasounds, THF. (d) 1. KOH/EtOH , rfx; 2. $(\text{COCl})_2$, toluene, rfx. (e) Resorcinol, TEA, DMAP, THF. (f) 16-mercaptohexadecanoic acid, DCC, DMAP, THF.

Based on SAXS measurements of **hyb_XII** material, I determined its phase sequence: Lm (60 °C) BCC (110 °C) FCC (Figure 7a,b, Table 3). The developed material was the first example of a silver nanoparticle aggregate that showed reconfigurability between three different long-range ordered phases. The observed structural changes were accompanied by switchability of optical properties, as I demonstrated by UV/Vis measurements. An important achievement was recording the highest ever shift of plasmon band maximum observed for long-range ordered aggregates of mesogenic nanoparticles in the solid state (as much as ~ 41 nm). Importantly, experimental results of UV/Vis measurements were in perfect agreement with theoretically modeled properties.

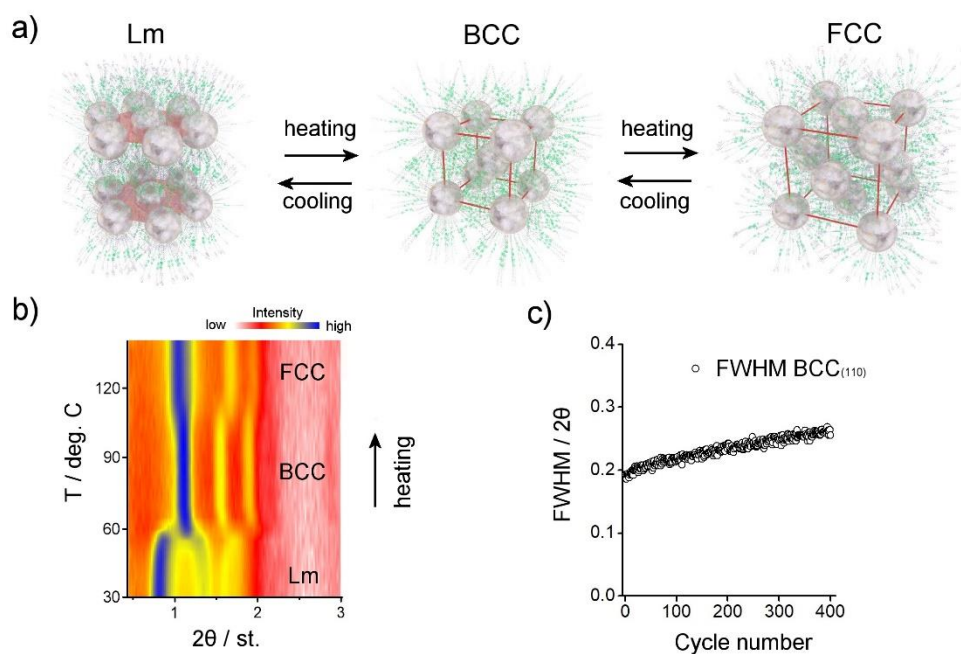


Figure 7. Structural characteristics of **hyb_XII** material. (a) Schematic representation of the spatial distribution of nanoparticles and ligands in lamellar (Lm), body centered cubic (BCC) and face centered cubic (FCC) phases. (b) A map showing evolution of diffractogram of the hybrid material during heating. (c) Dependence of full width at half maximum of the main BCC diffraction peak (110), depending on the number of sample heating/cooling cycles (30/70 °C).

From the point of view of stability of **hyb_XII** nanomaterial, a crucial observation was that the first phase transition (between the Lm and BCC structures) occurred at 60 °C, i.e. at a lower temperature than in the case of previously tested hybrid silver nanoparticles.^{H1,H2} For this reason, I decided to test the stability of **hyb_XII** material against many switching cycles between Lm and BCC phases. When analyzing the literature, I noticed that in the case of reconfigurable nanoparticle aggregates, switchability (stability) studies are limited to tens of cycles, which seems to be a small number in the context of future applications in photonic devices.⁶³⁻⁶⁵ Thus, I decided to perform stability tests using an order of magnitude more cycles. The experimental results allowed me to prove that **hyb_XII** material can be switched even 400 times, accompanied with full width at half maximum of the main BCC diffraction phase increase by about 35% (Figure 7c), i.e. less than in the **hyb_XI** material after just seven cycles. In my opinion, an important observation in the context of research on switchable structures was that changes in the diffraction pattern associated with slow degradation of the material were hardly visible during the first dozen or so cycles. This means that it is easy to overestimate the stability of dynamic nanomaterial based on short switching studies and emphasizes the need for longer testing of the reconfiguration of nanoparticle aggregates.

Summing up, owing to the proposed **lig_6** promesogenic ligand structure, it was possible to develop a dynamic, plasmonic nanomaterial that exhibits perspective properties in terms of the speed of reconfiguration, stability and optical response.

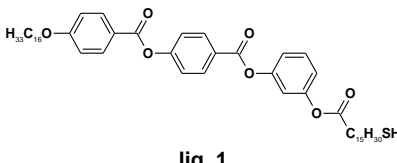
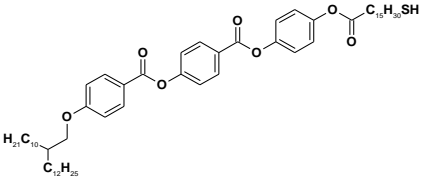
III.D Other methods to modify properties of reconfigurable assemblies of nanoparticles

Based on the analysis of hybrid materials described in reviews [H6] and [H7], I noticed that monolayer stabilizing liquid crystalline nanoparticles comprised: (i) solely (pro)mesogenic ligands or (ii) (pro)mesogenic ligands with alkyl coligands. In the latter case, it was shown that the length of the alkyl coligand may influence symmetry and reconfigurability of obtained structures, but analogous studies on the effect of functional groups presence in alkyl coligands were not reported. Therefore, I decided to investigate whether the use of different functionalised coligands, while keeping the same promesogenic ligand, would allow to observe changes in the structural properties of the obtained reconfigurable nanomaterials. This strategy seems reasonable, taking into account the time and resources required to synthesis (pro)mesogenic compound.

Based on the above assumptions, I designed five nanomaterials based on the **lig_1** ligand (Table 4):

- hybrid materials **hyb_XIII**, **hyb_XIV** and **hyb_XV**, based on gold nanocrystals, using dodecanethiol, hexadecanethiol or 1H,1H,2H,2H-perfluorodecanthiol coligands
- hybrid materials **hyb_XVI** and **hyb_XVII**, based on silver nanocrystals, using dodecanethiol or 11-mercapto-1-undecanol coligands.

Table 4. Summary of the structure and mesogenic properties of hybrid materials obtained using **lig_1** (except for one example shown in Table 2) and **lig_7** ligands. Symbols: BCT, Iso, BCO, SRO, Lm, FCC stand for body centered tetragonal, isotropic, body centered orthorhombic, short-range ordered, lamellar and face centered cubic phases, respectively.^{H3,H4}

Structure of promesogenic ligand	Structure of alkyl coligand	NPs type and size	Phase sequence	Structural and optical parameters of phases	Material /literature reference
 <p style="text-align: center;">lig_1</p>	C ₁₂ H ₂₅ SH	Au, 3.6±0.4 nm	BCT (100°C) Iso	Lm: d _{30°C} ~15.8 nm, a _{30°C} ~5.1 nm, d _{95°C} ~14.6 nm, a _{95°C} ~5.6 nm Iso: a~7.5 nm	hyb_XIII ^{H4}
	C ₁₆ H ₃₃ SH	Au, 3.6±0.4 nm	BCO (85°C) FCC	BCO: a _{90°C} ~6.7 nm c _{90°C} ~14.5 nm b _{90°C} ~4.6 nm FCC: a~12.8 nm	hyb_XIV ^{H4}
	CF ₃ (CF ₂) ₇ (CH ₂) ₂ SH	Au, 3.6±0.4 nm	SRO (80°C) BCO (110°C) FCC	BCO: a _{80°C} ~6.9 nm c _{80°C} ~13.8 nm b _{80°C} ~4.8 nm FCC: a~11.9 nm	hyb_XV ^{H4}
	C ₁₂ H ₂₅ SH	Ag, 5.1±0.3 nm	Lm (95°C) FCC	Lm: d _{30°C} ~9.1 nm a _{30°C} ~6.9 nm d _{90°C} ~8.2 nm a _{90°C} ~7.4 nm FCC: a~13.3 nm	hyb_XVI ^{H4}
	HO(CH ₂) ₁₁ SH	Ag, 5.2±0.4 nm	Lm (140°C) FCC	Lm: d _{30°C} ~10.4 nm a _{30°C} ~6.2 nm FCC: a~13.5 nm	hyb_XVII ^{H4}
 <p style="text-align: center;">lig_7</p>	C ₁₂ H ₂₅ SH	Ag, FCC ₁ : ~4.4 nm FCC ₂ : ~8.3 nm	FCC ₁ (180°C, 25 min) FCC ₂	FCC ₁ : a _{FCC1_180°C} ~15.2 nm FCC ₂ : a _{FCC2_180°C} ~20.8 nm	hyb_XVIII ^{H3}

An important observation made within the framework of this work was that lowering size distribution of mesogenic nanoparticles promotes formation of long-range ordered phases. This conclusion was based on the analysis of **hyb_XVI** material, which had composition similar to **hyb_I** material, but at elevated temperatures it formed FCC instead of an isotropic phase. However, the most important achievement of this part of the series of presented works, was confirmation that by using alkyl coligands, that have different functional groups, one can:

- modulate symmetry of obtained aggregates, e.g. different phases formed by **hyb_XIII** and **hyb_XV** materials (Table 4),
- affect the thermal stability of the low temperature phase, e.g. different phase transition temperatures **hyb_XVI** vs. **hyb_XVII** (Table 4).

It is also worth noting that the use of alkyl coligand with a terminal hydroxyl group (**hyb_XVII**), in comparison to the material with non-functionalized alkyl coligand (**hyb_XVI**), increases shape anisotropy of organic monolayer stabilizing nanoparticles, as concluded on the basis of diffraction peaks positions (Figure 8a).

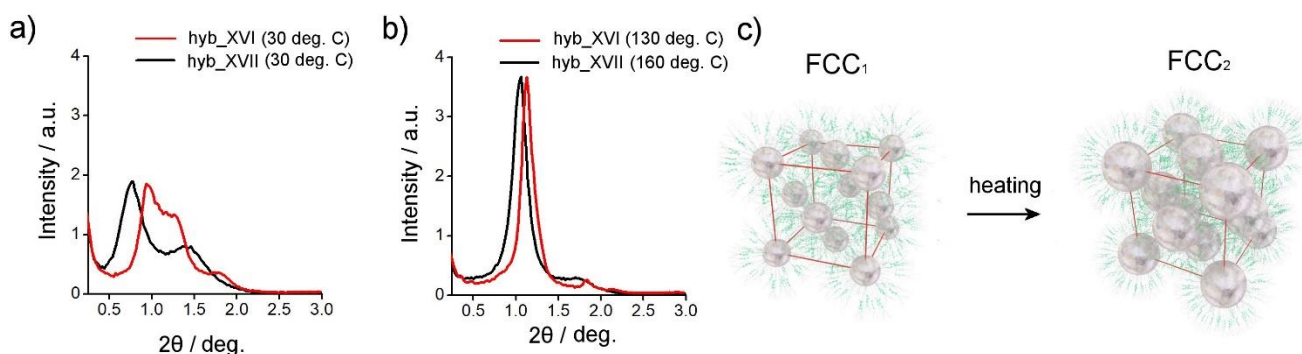


Figure 8. (a) Diffraction patterns of **hyb_XVI** and **hyb_XVII** materials at 30 °C (lamellar phases). (b) Diffraction patterns of **hyb_XVI** material at 130 °C and **hyb_XVII** material at 160 °C (face centered cubic phases). (c) Schematic representation of the spatial distribution of nanoparticles and ligands in FCC phases of **hyb_XVIII** material.

In the case of all of the above-described hybrid materials, dynamic self-assembly resulted from a change in the shape of the organic shell stabilizing metallic nanocrystals, which, as I explained in subsection III.B, limits the size of nanoparticles that we can use in this approach. One of the ways to overcome this limitation may be application of Ostwald ripening process to achieve a controlled increase of size of the metallic core of nanoparticles, already after preparing long-range ordered systems.³⁸ Motivated by a few works devoted to dynamic nanomaterials obtained this way,⁶⁶ I decided to investigate whether this approach can be used for nanoparticles stabilized with promesogenic ligands.

Bearing in mind that the mentioned process requires heating of the sample to high temperatures, I designed a promesogenic ligand (**lig_7**) which, I thought, due to bulky terminal group (branched alkyl chain), would support formation of long-range ordered phases at high temperatures by nanoparticles covered with it. Using the aforementioned ligand, I prepared hybrid materials with different molar ratio of **lig_7** to alkyl coligands. Importantly, SAXS measurements of nanoparticles dispersion indicated that the thermal stability of nanoparticles increased with growing content of **lig_7** in the monolayer stabilizing nanocrystals.

In further analysis we showed that hybrid material **hyb_XVIII**, with organic shell in 70% composed of promesogenic ligands, at 180 °C forms FCC structure with unit cell size ~15.2 nm. Based on the TEM and SAXS measurements, it can be assumed that under these conditions (immediately after heating) the metallic cores of the nanoparticles are of the same size as directly after the synthesis of the hybrid material. Importantly, further heating resulted in the formation of an FCC structure with a much larger unit cell size (~20.8 nm) suggesting an increase in the size of the metallic cores (Figure 8c). TEM imaging confirmed correctness of those hypothesis.

In conclusion, the above-discussed studies have shown that thermal stability of mesogenic nanoparticles can be controlled by incorporating appropriate coligands to their surface, and that Ostwald ripening process can be used for nanoparticles stabilized with promesogenic ligands to achieve switchable (though not reversible) self-assembly.

IV. Summary and future research goals

As my main achievements within the presented series of works I recognize:

- Development, synthesis and characterization of structure of **lig_1** ligand, which allowed to obtain reconfigurable, long-range ordered aggregates of nanoparticles. Importantly, the

strategy of obtaining dynamic nanomaterials did not require the presence of a solvent, which is important from the point of view of the use of nanomaterials in photonic devices.

- Optimization of the conditions of ligand exchange reaction on nanoparticles, which translated into a reduction of losses associated with coalescence of nanoparticles during this process.^{H1}
- Obtaining, for the first time, a reversibly switchable metamaterial with epsilon near zero properties built with nanoparticles.^{H1}
- Presenting evidence that the above-mentioned strategy of dynamic self-assembly allows for a continuous change of structural parameters of phases built with nanoparticles, which results from gradual, spatial reorganization of organic ligands around nanocrystals under heating/cooling. These results stand in opposition to the previously described reconfigurable, long-range ordered aggregates of nanoparticles, which can only be switched in an abrupt manner. The basis of uniqueness of the presented strategy is appropriate planning and synthesis of promesogenic ligands.^{H1,H2,H4,H5}
- Presenting evidence that this continuous change in the structural parameters of the phases translates into the possibility of observing gradual changes of optical properties of nanomaterials.^{H1}
- Development of **lig_4** ligand, which allowed to achieve much shorter switching times than the ones previously reported for reconfigurable, long-range ordered assemblies of nanoparticles.^{H2}
- Preparation of the first example of mesogenic nanoparticles (**hyb_IX**), which exhibited switchability between two long-range ordered, 3D structures. The change in the symmetry of the arrangement of nanoparticles was related to the modification of the optical properties of organic/inorganic nanomaterials and was enabled by the use of **lig_4** ligands. These properties are important in the context of metamaterial applications of nanostructures.^{H2}
- Development of promesogenic ligands containing a semifluorinated terminal alkyl chain that allowed to combine a number of important features of reconfigurable nanoparticle aggregates: the ability to reconfigure between 3D, long-range ordered phases, high structural anisotropy of low-temperature phase (which translates into a large optical response after switching to structure of the densest packing) as well as high stability.^{H5}
- Planning and performing X-ray measurements that allowed to test the durability of reconfigurable nanoparticle aggregates in an order of magnitude greater number of cycles than described so far in the literature. These measurements also revealed important information on the need for such tests, because the first dozen or so switching cycles may not indicate the degradation process in the long term.^{H5}
- Development of a simplified method of modifying the structural properties of reconfigurable nanoparticle aggregates through controlling composition of the organic coating of nanoparticles, specifically through the use of functionalized alkyl coligands together with promesogenic ligands. This strategy allowed for inducing changes in the symmetry of phases made with nanoparticles as well as allowed for modifying thermal stability of anisotropic assemblies. The latter may be of particular importance for photonic devices that require the use of anisotropic nanoparticle aggregates with high stability.^{H4}
- Design of mesogenic nanoparticles for which Ostwald ripening process could be used to modify the size of metallic nanocrystals after producing a long-range ordered aggregate.^{H5}
- Emphasizing the possibility of using liquid crystalline nanoparticles to prepare dynamic nanomaterials with switchable properties.^{H6, H7}

Promesogenic ligands developed within the frames of the outlined series of works are currently used to obtain dynamic self-assembly of semiconductor nanocrystals, reconfigurable binary systems as well as helical nanostructures (using a mesogenic matrix).

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5. OTHER SCIENTIFIC PUBLICATIONS AND ACHIEVEMENTS

5.A BIBLIOGRAPHIC SUMMARY OF SCIENTIFIC ACHIEVEMENTS

Total number of publications	18
Total number of book chapters	1
Total number of submitted/received patents	3
Total number of publications after receiving PhD degree	7
Total impact factor (according to the year published)	109.542
Total impact factor after receiving PhD degree	64.771
Citation report based on Web of Science at 20.03.2019	
Total number of citations	381
Number of citations without self-citations	338
Hirsch index	12

5.B THE LIST OF PUBLICATIONS ISSUED PRIOR TO RECEIVING PHD DEGREE (EXCEPT PUBLICATIONS LISTED IN CHAPTER 4)

- A1.** M. Wójcik, **W. Lewandowski**, J. Matraszek, J. Mieczkowski, J. Borysiuk, D. Pocięcha, E. Górecka,
Liquid-Crystalline Phases Made of Gold Nanoparticles.
Angew. Chem. Int. Ed. 2009, 48 (28), 5167–5169. IF = 11,829
- A2.** W.R. Collins, **W. Lewandowski**, E. Schmois, J. Walsh, T.M. Swager,
Claisen Rearrangement of Graphite Oxide: A Route to Covalently Functionalized Graphenes.
Angew. Chem. Int. Ed. 2011, 50 (38), 8848–8852. IF = 13,455
- A3.** E. Jaworska, **W. Lewandowski**, J. Mieczkowski, K. Maksymiuk, A. Michalska,
Critical Assessment of Graphene as Ion-to-Electron Transducer for All-Solid-State Potentiometric Sensors.
Talanta 2012, 97, 414–419. IF = 3,498
- A4.** E. Jaworska, **W. Lewandowski**, J. Mieczkowski, K. Maksymiuk, A. Michalska,
Non-Covalently Functionalized Graphene for the Potentiometric Sensing of Zinc Ions.
Analyst 2012, 137 (8), 1895–1898. IF = 3,969
- A5.** L. Drewniak, N. Maryan, **W. Lewandowski**, S. Kaczanowski, A. Skłodowska,
The Contribution of Microbial Mats to the Arsenic Geochemistry of an Ancient Gold Mine.
Environ. Pollut. 2012, 162, 190–201. IF = 3,730
- A6.** E. Jaworska, **W. Lewandowski**, J. Mieczkowski, K. Maksymiuk, A. Michalska,
Simple and Disposable Potentiometric Sensors Based on Graphene or Multi-Walled Carbon Nanotubes--Carbon-Plastic Potentiometric Sensors.
Analyst 2013, 138 (8), 2363–2371. IF = 3,906
- A7.** **W. Lewandowski**, K. Jatzczak, D. Pocięcha, J. Mieczkowski,
Control of Gold Nanoparticle Superlattice Properties via Mesogenic Ligand Architecture.
Langmuir 2013, 29 (10), 3404–3410. IF = 4,384

5.C THE LIST OF PUBLICATIONS AFTER RECEIVING OF THE PHD DEGREE PUBLISHED IN JOURNALS LISTED IN THE JOURNAL CITATION REPORTS (EXCEPT PUBLICATIONS LISTED IN CHAPTER 4)

- A8.** **W. Lewandowski**, D. Constantin, K. Walicka, D. Pocięcha, J. Mieczkowski, E. Górecka,
Smectic Mesophases of Functionalized Silver and Gold Nanoparticles with Anisotropic Plasmonic Properties.
Chem. Commun. 2013, 49 (71), 7845–7847. IF = 6,718
- A9.** A. Zep, M. Wójcik, **W. Lewandowski**, K. Sitkowska, A. Promiński, J. Mieczkowski, D. Pocięcha, E. Górecka,
Phototunable Liquid-Crystalline Phases Made of Nanoparticles.
Angew. Chemie Int. Ed. 2014, 53 (50), 13725–13728. IF = 11,261

- A10.** M. Wójcik, **W. Lewandowski**, M. Król, K. Pawłowski, J. Mieczkowski R. Lechowski, K. Zabielska,
Enhancing Anti-Tumor Efficacy of Doxorubicin by Non-Covalent Conjugation to Gold Nanoparticles - in Vitro Studies on Feline Fibrosarcoma Cell Lines.
PLoS One 2015, 10 (4), e0124955. IF = 3,057
- A11.** K. Zabielska-Koczywās, I. Dołka, M. Król, A. Zbikowski, **W. Lewandowski**, J. Mieczkowski, M. Wójcik, R. Lechowski,
Doxorubicin Conjugated to Glutathione Stabilized Gold Nanoparticles (Au-GSH-Dox) as an Effective Therapeutic Agent for Feline Injection-Site Sarcomas - Chick Embryo Chorioallantoic Membrane Study.
Molecules 2017, 22 (2). IF = 3,098
- A12.** K. Sułowska, K. Wiwatowski, P. Szustakiewicz, J. Grzelak, **W. Lewandowski**, S. Maćkowski,
Energy Transfer from Photosystem I to Thermally Reduced Graphene Oxide.
Materials, 2018, 11 (9), 1–11. IF = 2,467

5.D INVENTIONS AND DESIGNS FOR PRODUCTION AND MANUFACTURING THAT WERE PROTECTED AND WERE BEING DISPLAYED AT INTERNATIONAL OR NATIONAL EXHIBITION OR TRADE FAIRS

- P1.** T. M. Swager, W. R. Collins, **W. Lewandowski**, E. Schmois, S. Sydlík, J. Walish, J. B. Goods
Compositions comprising functionalized carbon-based nanostructures and related methods
International patent number: US9770709B2
Filing date: 03.11.2010
Application granted: 26.09.2017
- P2.** Z. Jańczuk, **W. Lewandowski**, A. Promiński, M. Wójcik
Method of recycling precious metals from waste materials and use of precious metal nanoparticles obtained by this method
The number of the Polish patent application: PL413456A1
Filing date: 07.08.2015
The number of international patent application: PCT/IB2016/054420, WO2017025834A1
Filing date: 25.07.2016
Dates of presentations: (1) 12.2017, Seoul International Invention Fair, South Korea, awarded with a silver medal, special prize awarded by King Abdulaziz University; (2) 10.2017, Materials Science & Technology, Pittsburgh, USA (3) 04.2018, 46th International Exhibition of Inventions, Geneva, Switzerland, awarded with a gold medal
- P3.** **W. Lewandowski**, M. Wójcik, A. Jędrych
Method of preparing biocompatible nanoparticles of platinum group metals, nanoparticles obtained in this way and their application
Application number: P.428014
Filing date: 04.12.2018
Dates of presentations: (1) 12.2018, 5th Kaohsiung International Invention and Design EXPO (KIDE), Kaohsiung, Taiwan, awarded with a gold medal, (2) 02.2019, Bangkok International Intellectual Property, Invention, Innovation and Technology Exposition (IPITEx), Bangkok, Thailand, awarded with a gold medal

Lewandowski