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## Metal complexes bearing photochromic ligands: photocontrol of functions and processes

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Metal complexes associated with photochromic molecules are attractive platforms to achieve smart light-switching materials with innovative and exciting properties due to specific optical, electronic, magnetic or catalytic features of metal complexes and by perturbing the excited-state properties of both components to generate new reactivity and photochemical properties. In this overview, we focus on selected achievements in key domains dealing with optical, redox, magnetic properties, as well as application in catalysis or supramolecular chemistry. We also try to point out scientific challenges that are still faced for future development and applications.

### Introduction

Stimuli-responsive systems are now serving as precursors for the next-generation of artificial interactive materials with, for instance, molecular switches and motors.<sup>1,2</sup> In addition to the targeted development of a variety of applications, those systems are fascinating research objects having relevance in very fundamental questions. The use of light to trigger the functions of various molecular tools is attractive based on its spatial or temporal resolution, non-invasive and traceless character, exact energy tuning and ease of handling.<sup>3</sup>

Organometallic and coordination compounds are known for their specific and outstanding optical, electronic, magnetic or catalytic features. Therefore, these classes of compound appear as attractive platforms to achieve smart light-switching materials with innovative and exciting properties. A versatile approach toward the development of such tools is the incorporation of photochromic units into such molecular complexes. Indeed, combining metal complexes with photochromic units opens the possibility of perturbing the excited-state properties of both components and the generation of new reactivity and photochemical properties.<sup>4</sup>

Reversible photoinduced isomerization of photochromic units usually leads to a reversible change of one or several properties of the system components.<sup>1-3, 5, 6</sup> Besides color changes, during the reversible photoisomerization of a photochromic unit, its physical/chemical properties, such as fluorescence, magnetism, refractive index, geometry, electrochemical properties, conductivity, as well as chemical reactivity can be modified which confers to these materials great industrial and academic interests for applications. Photochromic materials have been long used in daily life as sunglasses, textiles, cosmetics, and more recently have attracted great interest in future optic-

electronic devices, computing and data storage, imaging, photopharmacology and to control biological features. Depending on the target application, the use of bistable (P-type) or thermally reverting (T-type) photochromic units has to be considered. Until now, diarylethenes (DTE, P-type),<sup>5</sup> azobenzenes<sup>6</sup> and spiropyrans<sup>7</sup> (both T-type) are the most representative photochromic units that undergo a reversible photoreaction. DTE, in certain cases, can switch between states by oxidation or reduction (*vide infra*).

On the whole, we can consider two strategies to achieve light-switching of metal complexes. One of these focuses on how metal coordination affects isomerization of the photochromic moiety, by stabilizing a metastable state via metal-ligand interactions for instance. The other interest focuses on how structural conversion at the photochromic moiety affects the properties of the complex. Perhaps, one of the most basic well-known effect is that the presence of a heavy atom facilitates intersystem crossing (ISC) and access to the triplet excited states and consequently to specific photostationary states, lifetimes, emission efficiencies. A second important effect is the possibility of energy or electron transfer allowing photoswitching in the visible range by stimulation at the metal complex moiety (*vide infra*).<sup>8</sup> Manipulation of other metal-based properties in photochromic metal complexes via changes in ligand field strength or symmetry, electronic properties, excited states nature, volume or molecular geometry can also be very attractive to achieve controllable materials with photoregulation of various properties. Indeed, an important advantage of using metal centers in such applications is the facility to tune the properties with energy level adjustments by changing the metal used and by engineering the ligands. This may provide key features for photocontrollable molecular and supramolecular systems for *inter alia* memories, super resolution imaging, encryption, sensing, catalysis, machinery and biotechnology.

In this article, we will focus on noticeable achievements highlighting the different strategies that have been developed

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with molecular metal complexes of d and f transition metals in key domains dealing with optical, redox, magnetic properties, as well as application in catalysis or supramolecular chemistry. With this general overview, we will try to point out scientific challenges that are still faced in the field and attempt to draw perspectives for future developments/applications.

## Optical properties

Attaching metal containing fragments to organic photochromic molecular switches allows the perturbation of the excited-state properties of both components, sometimes leading to deactivation by the interaction between these two moieties. The reason for this deactivation is usually complicated, but roughly involves ground state interactions and excited-state interactions.<sup>4</sup> However, the challenge consisting in the switching of photochemical properties such as luminescence or Non Linear Optical (NLO) properties in addition to color is most often successful. Most of the photochromic molecular switches are known undergo isomerization via singlet excited states within several picoseconds and, as heavy atom facilitates ISC to triplet excited states, new characteristic features of the processes are observed in metal complexes. As a key feature, triplet MLCT photosensitization of the ring-closing reaction of DTE has been reported in many systems via singlet MLCT and ISC leading to the sensitization of the photochromic reactive triplet state in the visible range.<sup>8</sup> Thus, photochromism can be extended from the UV region in the free ligand to the less harmful visible and even NIR ranges owing to MLCTs. Note that this feature can be precluded if conjugation is interrupted between the photochromic unit and the complex.<sup>9</sup>

Concerning luminescence, which is involved in a wealth of discoveries applicable in real life, switches featuring a dynamic emission response also offer new possibilities with chemical sensors, smart materials like electrofluorochromic displays,<sup>10</sup> or high resolution cell imaging tools.<sup>11–13</sup> Emission intensity modulation was demonstrated in an early work by Lehn's group with a 4-py-DTE-tungsten pentacarbonyl complex weakly emissive in the open form and strongly emissive in the closed forms.<sup>14</sup> Also, Yam and coworkers observed in a Rhenium DTE complex a red shift of the emission band upon photocyclisation.<sup>15</sup> Since then, numerous, and extensively reviewed, systems have been developed with transition metals and with lanthanide ions with mono- or multimetallic complexes incorporating principally stilbene-, azo-, spirooxazine-, and DTE-containing ligands.<sup>8, 16, 17, 18</sup>

In the same spirit, switching NLO properties with metal complexes is also attracting interest for material applications because this property could be fine-tuned by the choice of the metal system and/or modification of the photochromic ligand.<sup>8, 19, 20</sup> In addition, multifunctionality of the assembly, thanks to the metal unit properties (redox, magnetic...), may provide features of great potential for materials. However, those systems remain less developed than their organic counterparts.<sup>21</sup> As an example, incorporation in devices with relevant metal complexes<sup>22</sup> and in particular in monolayers as

developed for organic ones,<sup>23</sup> remains to be more investigated for further applications.

Currently, the design of photoswitchable NIR emitters could open new perspectives for super-resolution imaging and biosensing,<sup>24–30</sup> because of the high transparency of biological tissue in this spectral range. In the field of material science, it opens new possibilities with integration of NIR emission difficult or impossible to detect with the naked eye in anti-counterfeiting technologies or to increase the usable wavelength range for information coding.<sup>31, 32, 33</sup> In that direction, NIR emitting lanthanides, which feature narrow, sharp and intense emission lines, strongly contrasting with that of low band gap organic compounds displaying broad and featureless emission, attract peculiar attention. Thus, our group, among others, became very interested in the design of lanthanide complexes with controllable NIR emission expecting that these specificities of lanthanide-based emission would reinforce the advantages offered by a dynamic emission response in the fields of bio-imaging and smart materials.<sup>20</sup>

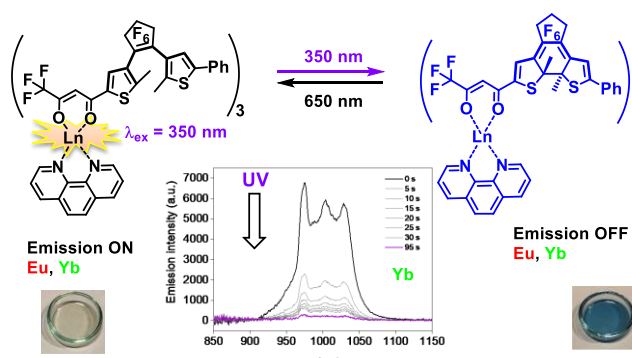


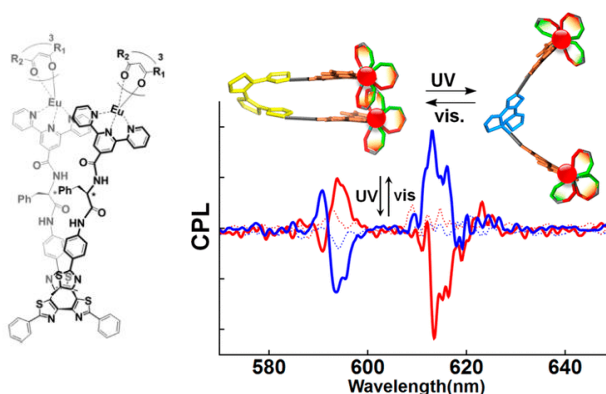
Figure 1: Photomodulation of Ln emission. Adapted from ref 34.

We recently described seminal studies of photo controllable lanthanide complexes built with a DTE unit and emitting in the NIR range. In particular, we accomplished the double photochemical and electrochemical control of Yb(III) luminescence.<sup>35</sup> The system takes benefit of the photo-stimulation of three DTE units coordinated to the Yb(III) center by a  $\beta$ -diketonate moiety, and of the redox active carbon-rich ruthenium antenna. Thanks to a MLCT transition ( $\lambda_{\max}=450$  nm) used to trigger ytterbium response in a non-destructive way at  $\lambda_{\max}=980$  nm, we showed the reversible vanishing of the luminescence signal after DTE closure/opening. A dynamic photoswitching response could also be demonstrated: when excitation is performed at the UV photocyclization wavelength using the DTE  $\beta$ -diketonate ligands or the bipyridine unit as sensitizers. In light of these results, we further developed a simpler and highly stable system by mixing the same DTE entities and the lanthanide(III) ion with one phenanthroline unit (Figure 1).<sup>34</sup> This new dynamic system shows two ways for encryption: (i) coloration and discoloration of the photochromic entities can be used to draw (350 nm) or erase (visible light) a colorful code, and (ii) gradual vanishing and restoration of the lanthanide ion emission is activated with the same set of stimuli down to 3% of the initial emission intensity. These features are perfectly maintained when the system was embedded in a

polydimethylsiloxane polymer and open actual opportunities for applications such as anti-counterfeiting. Importantly, while many closed DTEs have their visible absorption around 600 nm and then seem more adapted to switch-off Europium luminescence, we have demonstrated that their behavior is actually more versatile and can be used for quenching NIR emitters.

The next step towards applications will now consist in the optimization of the observed behaviors in terms of brightness in the ON state and of contrast between the ON and OFF states. This can rely on improving the sensitization in the ON state and blocking the deleterious non-radiative processes by optimizing the photochromic unit architecture and the positioning of the different excited states.<sup>36</sup>

The possibility to switch NIR emitters reversibly can provide security tags with more advanced encryption methods to reach multi-level security tags, and for the achievement of new PUF (Physically Unclonable Functions).<sup>37</sup> Also, despite the progress, developments of photochromic biomaterials is often limited to the use of short wavelength UV light and is desirable in the therapeutic window of 650–900 nm along with good water solubility. Therefore, the development of water-soluble photochromic biomaterials is still important for applications in biomedicine.<sup>38, 39</sup> Given the vast collection of possible metal-ligand combinations and engineering of functional ligand to improve switching features, we foresee many improvements and it seems very appealing to continue to explore NIR emission photoswitching.



**Figure 2:** dynamic on-off photoswitching of CPL in a binuclear europium complex system. Adapted from ref 40.

Modulation of Circularly Polarized Luminescence (CPL) activity also constitutes a particularly interesting challenge.<sup>41</sup> Indeed, CPL provides the differential emission intensity of right- and left circularly polarized light, and the CPL technique is expected to find potential applications in sensors, displays, and advanced information technologies. Unlike organic fluorophores, large dissymmetry values have been observed with Ln complexes with chiral coordination geometries. Recently, Kawai's group has demonstrated a high-contrast CPL switching using a chiral DTE-dinuclear Eu(III) complex with asymmetric  $\beta$ -diketonate ligands (Figure 2).<sup>40</sup> The chiral arrangement of inherently chiral coordination units is introduced by the helical photoresponsive framework, leading to the enriched population of a coordination geometry with a one-handed ligand orientation in

the Eu(III) sites. This hierarchical chirality could thus be reversibly switched. More recently, a chiral triple-stranded Eu(III) helicate with ligands composed of photochromic diarylethene moieties as spacers and two chiral 2,6-dipicolinic amides as coordination units was designed. The photochromic process caused variations in the electronic structure and ligand conformation, and led to on/off CPL switch.<sup>42</sup> This concept has not been yet extended to NIR emitters.

Lastly, we can mention that innovative multiple state materials in the solid state are highly desirable for potential applications in memory storage. Recently, the Yam's group reported the first series of photochromic benzo[b]phosphole alkynylgold(I) complexes that displays a DTE structure with phosphole rings. Gold(I) complexes are known for their mechanochromic properties associated with aurophilic interactions upon mechanic stimulation, and these complexes display independent photochromic and mechanochromic properties allowing them to serve as novel multi stimuli-responsive materials with reversible multistates with the help of light and mechanical forces.<sup>43</sup> This work encourages more investigations of photochromic metal complexes with interesting photocontrollable functions.

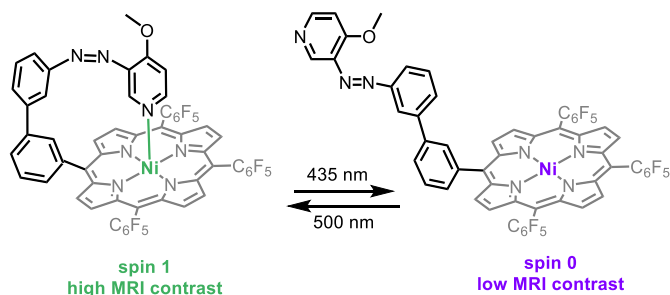
## Magnetism

The search for photomagnetic effects in molecular materials is linked with the discovery of various phenomena that allow to manipulate a system magnetization with photons. These phenomena include photo-induced change by valence tautomerism,<sup>44, 45</sup> Spin Cross Over (SCO)<sup>46, 47</sup> or electron transfer.<sup>48</sup> Herein, we only focus on light induced changes due to organic photochromism and focus on its impressive effect on bistable magnetic systems such as complexes with spin state switching<sup>49</sup> or Single Molecule Magnets (SMM).<sup>50, 51</sup>

Spin-crossover metal complexes are among the most successful materials for molecule-based devices as they can be switched between a diamagnetic low-spin state and a paramagnetic high-spin state thermally and sometimes optically through the Light-Induced Excited Spin State Trapping (LIESST) effect at low temperature. Only a few examples of SCO materials with strong intramolecular interactions exhibit bistability at room temperature and in such cases light irradiation can induced the desired phase and magnetic properties change. Organic photochromism, especially of P type, can provide complementary features to SCO complexes such as room temperature switchability through ligand-driven light induced spin change. A representative example of this strategy, which has been recently reviewed,<sup>52</sup> is given with the introduction of a phenanthroline fused DTE ligand into a spin-crossover iron(II) complex. The change in ligand field strength upon isomerization of this unit is enough to drive a reversible (but incomplete) spin conversion in the solid state and at room temperature.<sup>53</sup> The light responsiveness can be transferred to thin films on Au (111)<sup>54</sup> but not to a sub monolayer on HOPG where a non-photochromic parallel conformer of the complex is preferentially adsorbed.<sup>55</sup> Triple-stranded helical dinuclear iron

complexes with SCO behaviour were also assembled with DTE ligands.<sup>56</sup>

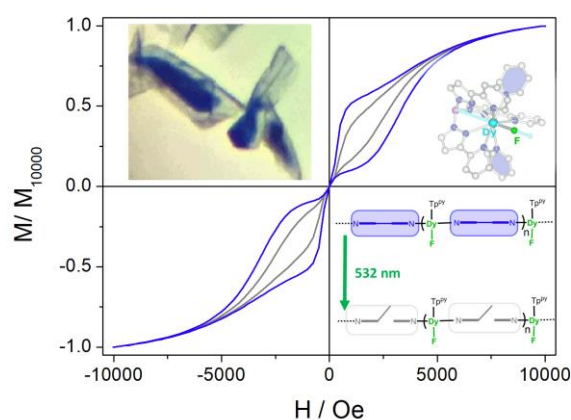
Organic photochromism can actually drive a more drastic change in the coordination sphere of metal complexes as shown by the elegant “record player design” reported by Herges.<sup>57</sup> A square planar nickel complex Ni-tetrakis(pentafluorophenyl)porphyrin irradiated with blue-green light undergoes additional coordination of a tethered pyridine ligand, brought in the vicinity of the nickel center by the isomerization of an azobenzene to its *cis* configuration (Figure 3). The change in coordination number between  $n = 4$  and 5 is accompanied by an electronic rearrangement from a diamagnetic to a paramagnetic state. The process, called light-driven coordination-induced spin-state switching (LD-CISSS) achieves magnetic bistability at room temperature, which unlike SCO, is obtained without cooperative effects, on non-interacting molecules in solution. The paramagnetic *cis* isomer of such complexes is active as contrast agent for magnetic resonance imaging. As a result, the contrast could be switched on upon irradiation with 500 nm light, and off with 435 nm light. Interesting recent developments of this work include improved long term switching stability<sup>58</sup>, transfer to aqueous solutions and human serum,<sup>59</sup> and to surfaces,<sup>60</sup> and finally optimization of the photoinduced state lifetime to allow T monitoring.<sup>61</sup>



**Figure 3:** Record player design for Light-Driven Coordination Induced Spin State Switching. Adapted from ref 58.

Last decade's discoveries of extremely promising SMMs, such as dysprosium sandwich complexes with 80 K magnetic hysteresis<sup>62, 63</sup> has given substance to the idea of using molecules as magnetic memories in the future. Lanthanide based SMM are considered as excellent candidates to construct molecular switches because they are very sensitive to the subtle changes of structure (geometry, bond distance...), and they are increasingly used for light-, solvato-, proton- and redox-switching of SMM properties as recently reviewed.<sup>64,65</sup> The research of stimuli-responsive SMMs is, however, still in its early stages. A major problem is that with DTE, the light-driven structural changes hardly alter the first coordination sphere of the metal complexes. Nevertheless, such structural changes can lead to some extent to modulation of electronic properties, molecular geometry and intermolecular interactions providing other means to externally manipulate the magnetic response. Examples include photochemical control of [Mn<sub>4</sub>] clusters assembled in one-dimensional (1D) structure with DTE linkers through the change in magnetic interactions,<sup>66</sup> and the first explorations of a lanthanide based systems, namely a Dy(III)-

Ho(III) dinuclear complex,<sup>67</sup> but the effects remain weak. Recently, we reported a photochromic chain based on the assembly of a magnetically anisotropic compound [Dy(Tppy)(pyridine)<sub>2</sub>]PF<sub>6</sub> (Tppy = tris(3-(2-pyridyl)pyrazolyl)hydroborate), including a classical DTE linker.<sup>68</sup> Photocrystallography investigations showed that continuous irradiation of a single crystal of the closed form resulted in variations of the unit cell parameters until full conversion was reached. Unlike previously investigated systems, the compound shows a magnetic hysteresis, therefore allowing to explore how the remote change in the DTE structure impact the magnetic bistability (Figure 4). Note that Zheng also reported a Dy(III)-compound exhibiting a reversible transformation in an anthracene-based lanthanide complexes with a [4 + 4] cycloaddition reaction of neighboring anthracene units showing modulation of magnetic properties and emission.<sup>69</sup>



**Figure 4:** Modulation of magnetic hysteresis in DTE-Dy-F assemblies. Adapted from ref 68.

Photochromic spirooxazines and spiropyrans are also efficient optical switches that exhibit rapid switching times (picoseconds) to their photomerocyanine isomers, and back conversion can occur either with visible light excitation or thermally. Within spirooxazine cobalt-dioxolene complex, the photochromic ligand undergoes massive structural and electronic reorganization associated with a change in ligand field that triggers a reversible intramolecular charge-transfer coupled spin-transition process at the cobalt center.<sup>45</sup> The profound reorganization upon isomerization, occurring at the solid state, is highly desirable for SMM switching and could lead to a lanthanide complex with switchable coordination number since only the merocyanine is coordinating. Recently, we proved that such merocyanine ligand can create axial anisotropy within dysprosium complexes thanks to the strong phenolate-dysprosium bond and investigated how the isomerization processes to the spiropyran are actually hampered by coordination.<sup>70</sup> At best, only the *trans*-*cis* isomerization of the merocyanine ligand could be induced under irradiation, associated with slight magnetic modulation in frozen solution.<sup>71</sup>

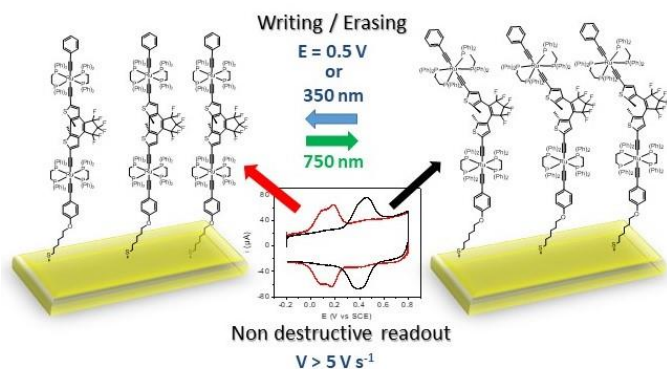
Overall, it is worth to note that until now, On-Off switching of SMM has not been realized using organic photochromism, while

it was recently observed with photoinduced electron transfer (PET) from inorganic Dy(III) clusters with oxo ligands to pyridinium cations.<sup>72</sup> However, as any slight change of the first coordination environment of lanthanide ions usually has remarkable impact on the magnetic relaxation, such objective is possible. It will rely on the researcher imagination to achieve the accurate change in a lanthanide ion environment in order to obtain strong magnetic anisotropy in one state and an efficient photoswitching event.

At the end of this section, we would like to point out the innovative approach of Aromi *et al.* to provide DTE-light switchable qubits systems where the magnetic interaction between weakly coupled spins with long quantum coherence can be switched on and off with light.<sup>73, 74</sup> These systems are of interest for quantum computing realizations.

## Redox processes and charge transport

Metal complexes often display reversible oxidation or reduction processes useful for various purposes. Association of photoswitches to metal complexes in one or several ligands allows the light-controlled shift of frontier orbital energies of these ligands, possibly affecting the overall metal complex orbitals and their redox potentials. This topic has been widely explored since the early work by Coudret with DTE<sup>75</sup> and Nishihara with azoferrocene,<sup>76</sup> and this phenomena has been now reported with several types of photochromic ligands, including diazobenzene,<sup>77</sup> dimethyldihydropyrene (DHP),<sup>78, 79</sup> DTE,<sup>80–88</sup> additionally showing that regulation of charge delocalization between remote metal centers or, more interestingly, that redox assisted ring closing of the photochromic by the redox active metal centers are possible.<sup>80</sup>

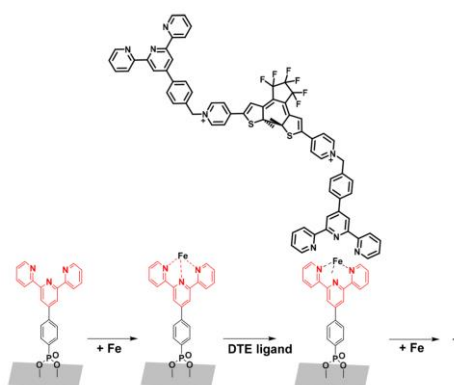


**Figure 5:** SAM of a DTE-ruthenium bimetallic complex for electro-optical memories. Adapted from ref 89.

This last feature more recently led to versatile photochromism /electrochromism at low voltage (0.4–0.5 V versus SCE) by immobilization of a DTE complex in SAMs at gold surfaces with retention of the properties to be fully exploited in applications. As expected, the association of two ruthenium-arylacetylide complexes with one DTE unit shows a shift of the electrochemical oxidation of the metal complex signal towards more negative potentials upon photochemical closure due to a larger conjugation along with an efficient electrochemical ring closure at low potential (0.5 V vs. SCE) (Figure 5).<sup>90</sup> More

interestingly, the electrochemical switching does not occur if the potential cycling is performed at high scan rates ( $>5 \text{ V s}^{-1}$ ) as the electrochemically-triggered isomerization process is a slow process. This behavior opens the possibility of a “non-destructive” readout for data storage with high versatility since the information could be written either electrochemically or photochemically. Further association of such systems with functional unit(s) displaying optical, magnetic or other properties can potentially lead to even more complex multifunctional systems on surfaces with photo-responsive *and* redox triggered molecular junctions for the development and miniaturization of logic components, as we previously demonstrated with closely related systems.<sup>91</sup>

Nevertheless, the use of metal complexes/photochromic association for their peculiar properties has been scarcely reported in junctions, and it is important to note that most of the systems display charge transport mechanism via direct tunneling with ON/OFF conductance ratios below two orders of magnitude. Replacing monolayers by multilayers with photoactive molecules has been envisioned as a new strategy involving charge hopping transport mechanism along the nanowire. A first switchable coordination polymer based on a DHP terpyridine derivative and zinc metal ions was described with a modest ON/OFF conductance ratio of 4.<sup>92</sup> In order to build a better system combining photomodulation of charge transport and rectification properties, the same authors designed an iron metallopolymer based on a DTE core with a ditopic ligand formed by two chelating terpyridine units linked to a DTE core to ensure the formation of supramolecular metallopolymer (Figure 6).<sup>93</sup> The introduction of pyridinium units in the organic spacers affords a system with additive redox properties, flexibility to the wires on the surface and giving rise to a hopping mechanism. The molecular junctions present a reversible and rapid photoconversion, along with asymmetric J/V curves with a rectification ratio around 200 in both photostationary states and an ON/OFF ratio up to 120 (4 layers).



**Figure 6:** Sequential Assembly of an ITO/(Fe-tpy-DTEc-tpy)<sub>n</sub> Film. Adapted from ref 93.

For additional improvements of light-switchable molecular junctions, further deep and systematic research studies with metal complexes including photochromic units improving their response in solid-state devices are required, from both fundamental understanding and practical application

viewpoints. In addition to the fact that the metal center can play a central role in manipulating the conductance of a molecular junction featuring a conjugated molecule, it was also suggested that organometallic and coordination complexes in single-molecule conductance device can afford efficient thermoelectric features.<sup>94-96</sup> Theoretical studies even suggest that mastering the thermocurrent can lead to thermoelectric energy harvesters with unprecedentedly high efficiencies: this can be achieved by engineering molecule length, optimizing the tunnel coupling strength of molecules via chemical anchor groups, or by creating localized states in the backbone with quantum interference features. Metal acetylides such as ruthenium complexes,<sup>94, 95</sup> or coordination compounds including gadolinium affording a high-spin magnetic centre<sup>96</sup> were proposed as remarkable candidates. Besides solving these energy control problems, the development of such systems could provide thermal nano-detectors, nano-coolers or more generally nano-regulators. Moreover, for applications, the ON and OFF switching functionality of the devices is required, and this essential on-demand processing has not been addressed yet. Thus, the remote control of the thermoelectric properties by altering the charge conductance should be addressable with metal complexes bearing photochromic unit and the systems will concomitantly handle further properties proper to the metal center (photophysical, redox, magnetic...).

## Catalysis

In the field of catalysis, switchable catalysis offers a mean to toggle catalysts between different distinct states that display different activities in terms of efficiency, chemo or stereoselectivity, or other characteristics that control a chemical reaction to achieve transformations in a temporally/spatially resolved fashion, thanks to specific changes in structure or electronic property. With a reversible photochromic system, removal of irradiation or a different irradiation causes the catalyst to revert to its initial form. Therefore, reactions can be adjusted between active and inactive states. This topic was recently reviewed with metal complexes.<sup>97-100</sup>

As far as the DTE unit is concerned, since the seminal work by Branda in 2005 on stereoselectivity of Cu(I)-catalyzed cyclopropanation of styrene,<sup>101</sup> ratio of activity (kinetic ratio between "fast" and "slow" states) stands from 1.1 to about 3 excepted in a key work reported in 2013 by Bielawski and coworkers.<sup>102</sup> In this work, the authors reported a photochromic dithienylethene-annulated N-heterocyclic carbene (NHC)-Rh(I) complex, and it was reasoned that the DTE unit in to the backbone of an NHC scaffold will provide a mean to modulate the electron donating ability of the carbene atom through light irradiation and then its intrinsic reactivity as a hydroboration catalyst. In particular, styrene hydroboration with pinacolborane led to a ratio close to one order of magnitude (9.2), and the rate of the reaction was efficiently switched over time through alternate exposure to UV and visible light. This effect is due to inhibition of the rate-determining reductive elimination step arising from a decrease

in electron-donating ability of the photocyclized NHC ligated to the metal center. The resulting rate switching was a significant breakthrough, but it has not been improved so far with any reaction. Also, note that with the exception of a first report by Branda dealing with photoswitchable Cu(II) complexes bearing DTE-photochromic diphosphine ligands for the hydroboration of 4-fluorostyrene with pinacolborane, there has been no real attempt to control the stereochemical outcome.<sup>103</sup>

Photoswitchable catalysis based on isomerization of double bonds was also reported<sup>104</sup> with diazo and stilbene derivatives through the incorporation of photoisomerisable double bonds into the structure of the catalysts to exploit the conformational flexibility as enzymes do. Increase in catalytic activity can be achieved through the promotion of metal cooperativity such as in chiral salen Ti<sup>IV</sup> complexes with flexible alkyl-terminated azobenzene linkers for asymmetric sulfoxidation<sup>105</sup> (Figure 7), or in bimetallic gold(I) complex for intramolecular hydroamination (30% increase in yield).<sup>106</sup> Azobenzenes have also been incorporated in phosphine ligands to control the catalytic activity of the corresponding metal complexes. A Rh(bis)diphosphine CO<sub>2</sub> hydrogenation activity was modulated (40% faster), thanks to a subtle change in the bite angle arising from steric strain due to the azobenzene-containing ligand.<sup>107</sup> A ruthenium-catalyzed hydrolysis of ammonia-borane for photocontrolled hydrogen generation for chemical hydrogen storage materials was achieved.<sup>108</sup> Such an isomerization also led to a variation of the types of aggregates in the catalytic medium for palladium-catalyzed cleavage of allylundecyl-carbonate in a heptane/water biphasic reaction medium.<sup>109</sup> Some example of phosphine modification with stilbene or stiff-stilbene for Pd catalyzed reactions, such as the Z-E photoisomerization of the stilbene unit changing the dihedral angle of the chelating diphosphine or changing the helical chirality of the coordinating *cis*-diphosphine were also reported to photocontrol the stereochemical result which is particularly desirable for the pharmaceutical industry.<sup>104</sup>

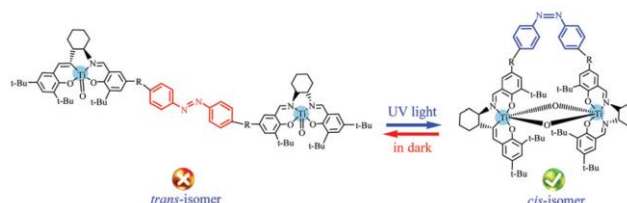


Figure 7: Design of a photo-controlled cooperative Ti(salen) catalyst. Adapted from ref 105.

Among the reported works, there is a specific situation in which a photoswitchable catalyst is able to display on/off activity and a further control of substrate discrimination. Salicylaldimine Zn(II) complexes bearing azobenzene moieties unit were studied as catalysts for the Ring Opening Polymerization (ROP) of cyclic esters (Figure 8).<sup>110</sup> A 6-fold reactivity difference was realized for the ring-opening polymerization of  $\epsilon$ -caprolactone upon light irradiation, along with a high reactivity discrimination by comparison to other monomers in copolymerization reactions. This permitted the authors to carry out copolymerization experiments showing, for the first time, that

it was possible to control the composition of the formed copolymer by means of irradiation.

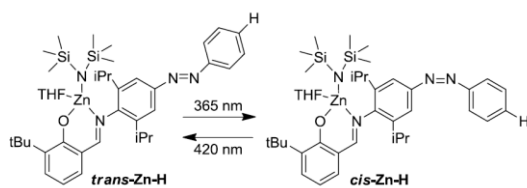


Figure 8: Catalyst for Light-Controlled ROP. Adapted from ref 110.

All these results show that a photochromic function on the ligand backbone can be a powerful strategy for catalysis control including to amplify/diminish the intrinsic ligand chirality and there is plenty of room for improvement in terms of ligand design. Nonetheless, there are still several unresolved challenges that need to be addressed to achieve applied synthetic tool and for multitasking catalysts or reactions in flow. Other reactions of interest such as deprotections and click-chemistry reactions have not been reported, and concerning stereochemical issues further investigations will be required in order to demonstrate their generality. Note that true ON/OFF switching of a DTE catalyst has not yet been demonstrated, but a true ON/OFF system might be difficult to achieve. More complex polydentate ligands are probably needed to impart more important electronic changes at the metal center to significantly enhance catalytic activities or selectivity.

Also, it would be highly necessary to increase the scope of monomers and polymerization reactions. Adjusting the length, composition, tacticity of a polymer during the process of its formation would allow achieving tailored properties, thereby enabling the design of the polymer produced. These polymerizations can potentially be regulated with high temporal and spatial precision, in strong contrast to traditional catalysis. However, such processes require several minutes of light irradiation and light is damaging. Though, the field of photoswitchable polymerization catalysis is highly promising and exciting due to its enormous potential: the translation of the information delivered by a photon into a chemical structure. Now, with this in hand, we can also expect from catalytic molecular machines to perform multiple stimuli-controlled catalytic tasks (sequential or parallel reactions), mimicking the mode of action observed in many enzymes from a reservoir of mixed substrates, in a controlled manner in a single vessel. To that regard, molecular machines and supramolecular chemistry combined with the progress achieved in metal catalysis hold great promises.

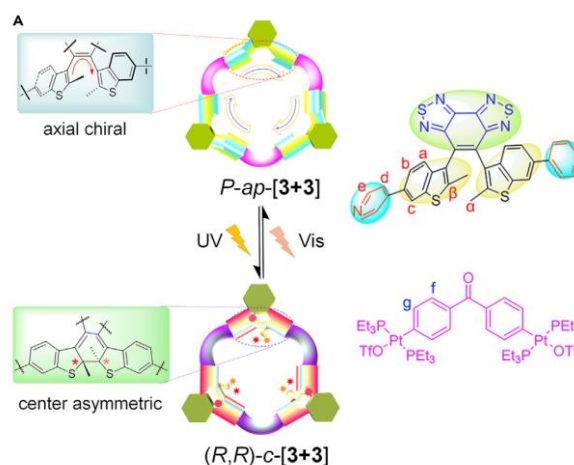
## Supramolecular chemistry

In the field of supramolecular chemistry, metal-mediated self-assembly are well known to lead to structural motifs such as helicates, grids, links, knots, spheres, polymers and more recently to cages. Since the early works by Yam, Brenda, Nishihara or Aida for instance,<sup>4</sup> the cross-field of metallo-supramolecular assemblies with photochromic complexes is still attracting attention with more complex structures and

functions. Here again, the aim of this approach is that the photochromic cores combined with metal center will achieve synergetic or new functions. Several 1D to 3D photo-switchable assemblies have been designed, and the field has been recently reviewed.<sup>111, 112</sup>

We can first mention that linear supramolecular polymers were designed based on Zn<sup>II</sup>/Co<sup>II</sup> terpyridine coordination nodes with photo isomerizable diazobenzene units.<sup>113, 114</sup> They can act as powerful gelating agents or self-assemble into 2D crystalline patterns. The resulting materials display light-triggered mechanical actuation, luminescent properties or self-healing abilities.

In the spirit of the planar assemblies developed by Stang, the first multi-DTE metallo-supramolecular hexagons, which undergo several cycles of color changes and fluorescence on/off, was designed by Zhu.<sup>115</sup> Then, a pyridyl appended stiff-stilbene monomer was used by Stang and co-workers.<sup>116</sup> In this assembly, the Z isomer favored the formation of Pt metallacycles, whereas irradiation of these metallacycles led to almost quantitative conversion to the E isomer into a linear metallosupramolecular polymer. Lately, in the same spirit of the planar assemblies, chiral and conformer dependent structures were reported for light-driven control in circular dichroism,<sup>111</sup> as well as photoswitchable luminescence in a heterometallic Ir-Pt macrocycle,<sup>117</sup> or controllable generation of singlet oxygen for biological applications by mixing porphyrin-functionalized and DTE-containing ligands.<sup>118</sup> Worth of note is a chiral metallacycle based on DTE with sterically hindered bisbenzo(thiadiazole) ethene bridge system (Figure 9). This trimer feature reversible phototriggered chirality transformation arising from axial helicity and central asymmetry switching and enabling bistable chiroptical switching useful for non-destructive information encoding.<sup>119</sup> Finally, very recently, a hexagon was modified with Feringa's molecular motor. Light driven rotation of the motors leads to reversible morphology transformations between cross-linked networks and primary supramolecular architectures of aggregates with heparin, offering perspectives to construct biomimetic hierarchical self-assembled systems and to fulfill functions reminiscent of dynamic polypeptide and protein



assemblies.<sup>120</sup>

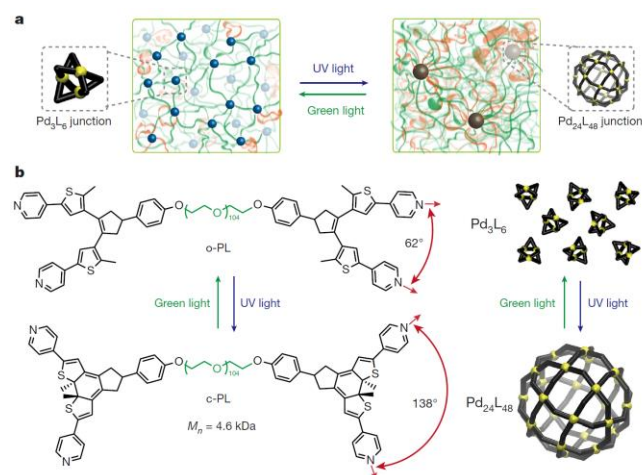
**Figure 9:** Light-triggered chiral transformation in enantiospecific photoreaction. Adapted from ref 119.

Nano cages, with inspiration from natural enzymes, also attract growing attention owing to their nano-scale cavities providing opportunities to achieve, *inter alia*, specific receptors or confined reaction pockets. In such assemblies, metal centers, mostly from the transition elements, are acting as nodes and organic ligands are serving as bridges to link the metals. They may contain different functionalities such as catalytic or recognition sites and conformational switches. A review has been recently dedicated to implementation of functions into self-assembled cages where a stimulus cause a response such as structural rearrangement, charge transfer between two components, change in guest-binding ability or the promotion of a chemical reaction.<sup>121</sup>

Organic photoswitches allow the control of such functionality by varying the cavity volume reversibly between two isomers. Clever has prepared ligands with DTE and achieved self-assemblies with Pd cations.<sup>122-124</sup> The studies show light-driven structural rearrangement of a small self-assembled triangular  $\text{Pd}_3(o\text{-L})$  and tetrahedral  $\text{Pd}_4(o\text{-L})_8$  structures based on DTE open isomer ligands (L) into a rhombicuboctahedral  $\text{Pd}_{24}(c\text{-L})_{48}$  sphere measuring about 6.4 nm across with the rigid closed isomer. This interconversion can be fully reversed. Also, a  $[\text{Pd}_2\text{L}_4]$  cage containing the DTE unit backbone and pyridine donors was shown to bind model guest compound  $[\text{B}_{12}\text{F}_{12}]_2$  in its open form while closure of all DTE switches resulted in significant reduction of guest binding affinity.<sup>124</sup> In a follow-up study, the DTE ligand was modified with two 7-iso-quinoline moieties as donors to form similar cages.<sup>122</sup> The open one can bind a chiral guest molecule, such as R- or S-camphor sulfonate (CSA). In contrast, the cage composed of C2-symmetric but quickly epimerizing DTE backbones does not show any chiroptical effects. The host-guest complex with enantiopure CSA shows a strong guest-induced circular dichroism effect in the absorption region of DTE units, pointing out a chirality transfer from the guest to the host. Guest ejection is also observed upon UV irradiation, which results in formation of the cage with all four photoswitches closed and locking the induced chirality with an enantiomeric excess close to 25%.

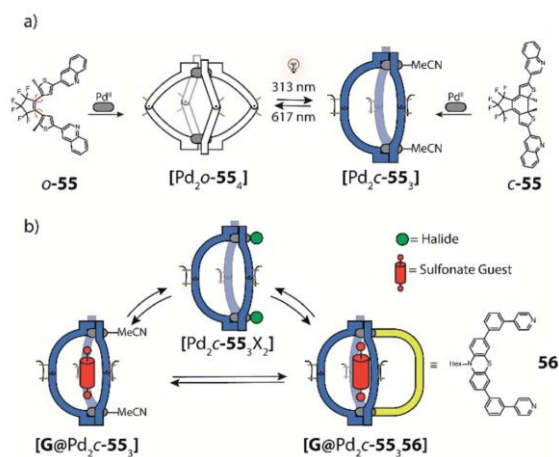
Light-controlled topology transformation of polymer networks with Pd-DTE metallacages as crosslinks, thanks to the two terminals of the PEG chains functionalized with DTE-dipyridinyl ligand, was also achieved (Figure 10).<sup>125</sup> The discrete DTE metallacages actually constitute the crosslinks of a polymer gel that shows structural conversion between small  $[\text{Pd}_3\text{L}_6]$  triangles and large  $[\text{Pd}_{24}\text{L}_{48}]$  cages, leading to a substantial change of the resulting polymer gel topology and *in fine* changing self-healing properties due to more topological defects in the closed form. Finally, we can mention a photoswitchable supramolecular gel, thanks to a metallacage in which metal-ligand coordination also plays a key role. Specifically, a metal-organic cage based on 3-pyridyl DTE and Pd(II) ions was reported to show solution-to-gel transformation by modification of the noncovalent interactions between the

metallacage, also providing a new approach to create cavities in supramolecular gels.<sup>126</sup>



**Figure 10:** (a) Schematic illustration of photo-regulated interconversion between two different network topologies. (b) Chemical structure of the photoresponsive polymer ligand and a schematic of cage interconversion. Adapted from ref 125.

A more intricate system that accepts the action of three different inputs to control the guest binding ability of a series of hosts was recently reported by the Clever group. DTE based backbones were employed with sterically demanding quinoline donors. Photoisomerization is able to tip the balance between formation of a cage with four open DTEs and a closed bowl containing only three DTE bridges (as closed form) for steric reasons in the square-planar Pd(II) coordination spheres. Whereas guest uptake differs between the cage and the bowl, the latter one could be modulated in its host properties by applying two further stimuli. First, replacement of the coordinated solvents by halide anions changes charge from  $4^+$  to  $2^+$ , decreasing affinity for anionic guest uptake. Secondly, a fourth ligand carrying less bulky pyridine donors could be included to obtain the first heteroleptic  $[\text{Pd}_2\text{c-L}_3\text{L}']$  motif containing two different ligands in a 3 : 1 ratio (Figure 11).<sup>127</sup> These results are expected to expand applications of photochromic materials in catalysis by regulating the catalyst environment. If this has not been achieved yet with molecular complexes, Au nanoparticles encapsulated in related organic



cage with open and closed states showed different catalytic activities for the reduction of 4-nitrophenol by a factor 2.<sup>128</sup>

**Figure 11:** (a) Photoswitching a quinolin-substituted ligand with DTE backbone allows cycling between a [Pd<sub>2</sub>L<sub>4</sub>] cage and [Pd<sub>2</sub>L<sub>3</sub>Solv<sub>2</sub>] bowl-shaped structure; (b) guest binding can be modulated by changing the host's charge from 4+ to 2+ by adding halide anions as trigger or by changing the cavity size via a fourth ligand (yellow). Adapted from ref 121.

As far as azobenzene is concerned, the seminal work by Fujita described Pd<sub>12</sub>(L)<sub>24</sub> cages with bis-pyridyl bent bridging ligands functionalized with azobenzene oriented toward the interior of the cage. The trans-to-cis isomerization causes an increase in dipole moment and reduces the hydrophobicity of the complex's interior. This feature was exploited for guest binding and release.<sup>129</sup> In a more recent example, a self-assembled structure was decorated on the exterior. An isophthalic acid linker combined with Cu(II) to achieve a (Cu<sub>2</sub>)<sub>12</sub>(L)<sub>24</sub> spherical complex. Ligand cis-to-trans isomerization led to its precipitation in CHCl<sub>3</sub> and the complex could be dissolved by back isomerization. Possibly, π-π interactions between complexes are weakened upon isomerization and the larger dipole moment of the cis-form enhances solubility in polar solvent.<sup>130</sup> The difference in solubility was used for the entrapment and release of a methylene blue guest or enhanced adsorption of propene by incorporating the 24 complex into mesoporous silica.<sup>131</sup> Note that few cages integrating azobenzene, as well as stiff stilbene, in their framework were also recently reported.<sup>112, 132</sup>

Overall, the controlled implementation of multiple functionalities into self-assembled objects featuring 3D nanoconfinements is a research field in its early stage. So far, only few examples where two or more functions have been combined in a single assembly were reported. Future work will lead to the rational growth of new behavior with the interaction of different functions within multicomponent complex systems. We can foresee that this control over structural rearrangements will lead to the development of novel tools for applications in sustainable synthesis, supramolecular catalysis, drug delivery, molecular electronics, and smart materials such as molecular machinery.

## Conclusions

During the recent two decades, metal complexes associated with photochromic molecules found various academic interests in materials and catalysis. Metal complexes provide an extensive efficiency in modulating optical and electronic properties of multicomponent functional systems with properties such as energy/electron transfer, conductivity, chirality, catalysis. As we presented in this article, a variety of photocontrollable molecular and supramolecular systems have been reported, introducing new perspectives in (NIR/chiral) light-absorbing or emitting centers, NLO, super resolution imaging, sensing, magnetism, molecular conductance, redox behavior, catalysis for functional devices, machinery and biotechnology or pharmacological properties. Though promising as anticipated, further improvements and optimization are still demanded to reach their full potential.

One of the most important issue for metal complexes and photochromic unit is photo fatigue-resistance. Triplet-sensitizing strategy using MLCT with transition metal complexes has been raised to circumvent this issue for visible/near infrared excitation of photochromic reactions. Compared with traditional ultraviolet light irradiation, visible/near-infrared light enjoys characteristics of low phototoxicity, high penetration, as well as low background that are highly desired in biotechnology and solid-state material applications. Nevertheless, more efficient triplet sensitizers and synergy between the components are further required together with shifting of the photoresponsive molecule excitation wavelength to the red/NIR range, improving photostationary state distributions, or engineering the half-life of the metastable state. Photochromic quantum yield is another significant issue as it directly reflects the efficiency of the material.

Also note that ligands that are capable of adopting more than two states may also offer new levels of enhanced functionality control of the interactive material with a significant increase in complexity. One may also envision merging light-switchable systems with other functional groups that respond to different stimuli. Researchers have attempted for decades to develop complex systems able to interact in an autonomous and self-regulatory manner, by analogy to those found in nature. For example, enzymes bring substrates into precise conformations and positions to lower activation barriers.<sup>133</sup> Thus, to achieve self-regulating properties with independent switching between states, systems with a high level of complexity and functionality are required. Different states should be able to "sense" one and other and to communicate and influence the accurate output. We also predict that the fast development of theoretical and computing chemistry will develop the design of metal complexes specifically adapted to a given property to reach very high degrees of conversion in a short period of time in both directions. This will boost the world of photoswitchable materials by enveloping new types of photochromic molecules with novel designs and performances.

Overall, metal complexes associated with photochromic units will play a role in the future since there are still plenty of challenges that remain to be addressed to control various material properties<sup>134</sup> or to achieve molecular machines performing synthesis.<sup>135, 136</sup>

## Conflicts of interest

There are no conflicts to declare.

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## Author biographies

Olivier Galangau obtained his PhD in chemistry in 2011 from École Normale Supérieure de Cachan, under the supervision of

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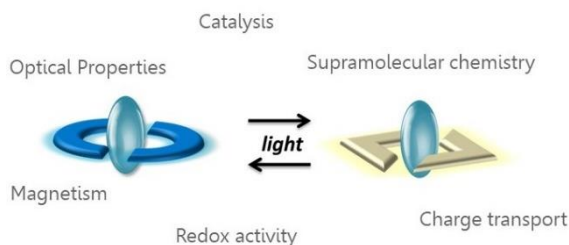
Lucie Norel received her Ph.D. from the University Pierre et Marie Curie in 2008, under the supervision of Prof. Cyrille Train and Dr. Yves Journaux. Following her postdoctoral training with Dr. Jeanne Crassous at University of Rennes 1 (UR1), she joined UR1 in 2009 as Assistant Professor. Her research interests are focused on molecular materials based on lanthanide coordination complexes for luminescence and magnetism.

Stéphane Rigaut received his Ph.D. from the University Bordeaux 1 in 1997, under the supervision of Prof. Didier Astruc and Dr. Marie Hélène Delville. Following a postdoctoral training with Larry Miller at the University of Minnesota, he joined the University of Rennes 1 in 1998 as an Assistant Professor and was promoted Full Professor in 2008. His research interests are focused toward metal complexes for functional molecular materials, including molecular electronics.



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