



**HAL**  
open science

## Visible-light modulators and power limiters based on spin crossover material thin films

Stéphane Calvez, Lijun Zhang, Jesukpego Anorld Capo Chichi, Yuteng Zhang, Lionel Salmon, Gábor Molnár, Karl Ridier, Azzedine Bousseksou

► **To cite this version:**

Stéphane Calvez, Lijun Zhang, Jesukpego Anorld Capo Chichi, Yuteng Zhang, Lionel Salmon, et al.. Visible-light modulators and power limiters based on spin crossover material thin films. 2024 24th International Conference on Transparent Optical Networks (ICTON), Jul 2024, Bari (Italy), Italy. pp.1-4, 10.1109/ICTON62926.2024.10648037 . hal-04689918

**HAL Id: hal-04689918**

**<https://laas.hal.science/hal-04689918>**

Submitted on 11 Sep 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

# Visible-light modulators and power limiters based on spin crossover material thin films

Stéphane Calvez<sup>1</sup>, Lijun Zhang<sup>2</sup>, Jesukpego Anorld Capo Chichi<sup>1</sup>,  
Yuteng Zhang<sup>2</sup>, Lionel Salmon<sup>2</sup>, Gábor Molnár<sup>2</sup>, Karl Ridier<sup>2</sup>, and Azzedine Bousseksou<sup>2</sup>

<sup>1</sup> *Laboratoire d'Analyse et d'Architecture des Systèmes, CNRS UPR 8001, Université de Toulouse, 7 avenue du colonel Roche, F-31400 Toulouse, France*

<sup>2</sup> *Laboratoire de Chimie de Coordination, CNRS UPR 8241, Université de Toulouse  
205 route de Narbonne, F-31077 Toulouse, France*

Tel: +33 561 336 990, Fax: +33 561336 208, e-mail: [scalvez@laas.fr](mailto:scalvez@laas.fr)

## ABSTRACT

We review our recent studies on visible-light modulators exploiting a relatively uncommon yet attractive family of phase change materials, the spin crossover molecular complexes. In particular, we report different embodiments, based on thermally-activated thin films of the evaporable iron 1,2,4,-triazolyl borate compound, that have been successively designed and fabricated to obtain proof-of-principle demonstrators but also devices with enhanced modulation depth and spectral bandwidth. We show that the response of the components can be affected by self-heating, leading in turn to optical power limiting behaviour.

**Keywords:** phase change material, spin crossover complex, modulator, thermo-optic switch, optical limitation.

## 1. INTRODUCTION

Optical modulators are key devices in the implementation of reconfigurable photonic systems. In this context, over the last decade, an emerging research trend has been concerned with investigations of compact and efficient modulators embedding Phase Change Materials (PCMs) as the latter present large variations in their complex index of refraction upon externally imposed reversible switching between their various electronic or structural states [1], [2], [3].

In this contribution, we review recent investigations of visible-light modulators exploiting a relatively uncommon yet attractive family of PCMs, the spin crossover (SCO) molecular complexes. In particular, we report different embodiments, based on thermally-activated thin films of the evaporable iron 1,2,4,-triazolyl borate compound, that have been successively designed to obtain modulators operating in the visible range and presenting increasing modulation depth and spectral bandwidth. We also show that the response of the components combining the SCO material with metal layers is affected by self-heating and can lead to optical power limiting behaviour.

## 2. Spin CrossOver Materials

Molecular spin-crossover (SCO) materials are metal-bearing complexes in which spin-state switching between the low-spin (LS) near-diamagnetic and the high-spin (HS) paramagnetic electronic configurations of the metal ion  $d^4$ - $d^7$  electrons can be induced by the application of an external stimuli such as temperature, pressure or light irradiation [4], [5]. Of particular relevance for their use in photonics is the fact that these compounds typically exhibit a spin-transition-related change of the refractive index in the range of 0.01–0.1 over a broad spectral range [6], [7], [9]. As an example, the evolution of the dielectric constant of a representative complex, the  $[\text{Fe}(\text{HB}(1,2,4\text{-triazol-1-yl})_3)_2]$ , as a function of temperature is presented in the left part of Figure 1. The most significant change is seen to take place in the ultraviolet part of the spectrum where the variation in the absorption (extinction coefficient) directly stems from the change in the material spin-state and orbital occupancy. However, there is also a notable absorption-free modification of the refractive index over the whole visible range, which can be attributed to the accompanying reduction in the metal-ligand bond length and variation of the ligand-metal-ligand angles (leading to a concomitant ~4.7% contraction in thickness of the thermally-evaporated thin films) upon heating. This feature, which is the prime property used in the hereafter-studied modulators, is illustrated on the right part of Figure 1. More specifically, a ~0.07 refractive index variation at a wavelength of 532 nm is shown to occur around the spin transition temperature of 65°C with a sharp (~12°C) sigmoidal-like dependence.

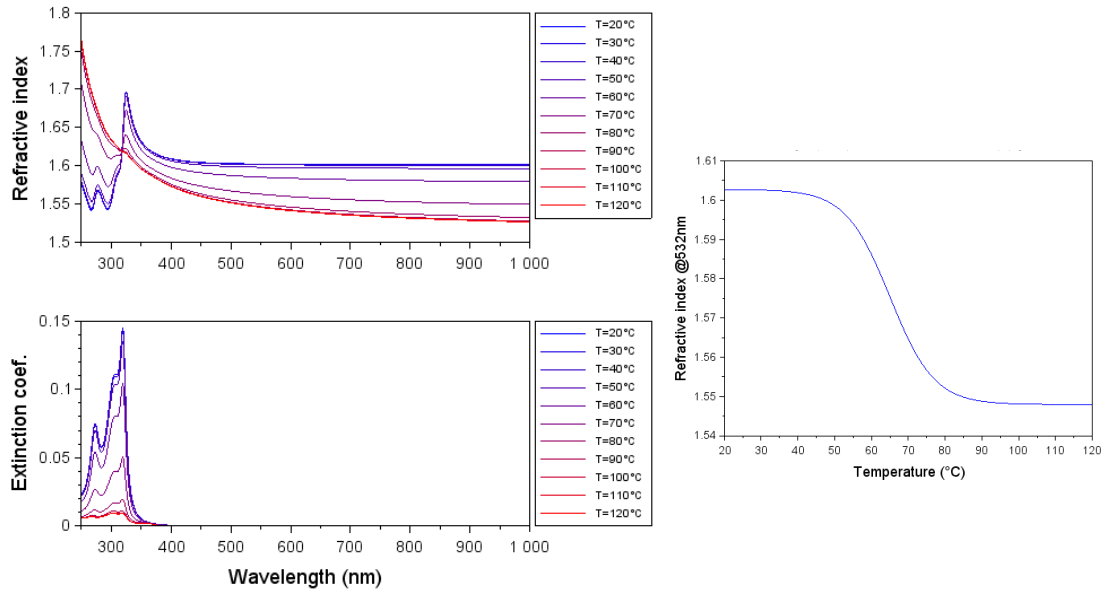


Figure 1. left: Dielectric constant evolution of the iron 1,2,4-triazolyl borate compound with temperature as determined by spectroscopic ellipsometry and absorption measurements [7], [8]. right: Temperature dependence of the refractive index at a wavelength of 532 nm.

### 3. SCO-based optical modulators

The primary objective of the first set of SCO-based visible optical modulators that we studied was to showcase that these materials could be more than thermochromic compounds [10] and serve as embedded activation materials in thermally-driven optical switches.

We thus designed, fabricated and tested Fabry-Perot interferometers constituted of a SCO thin film surrounded by silver mirrors. The design was based on thin film reflection/transmission simulations based on conventional transfer-matrix method [11] and the material dispersion relations presented in Figure 1 and in reference [12] for silver. For a symmetric device (as suitable for transmission experiments), best performance in terms of modulation depth was predicted for 50-nm-thick metal layers (see Figure 2 left), somewhat at the expense the spectral optical acceptance bandwidth (see Figure 2 centre). The SCO layer thickness was set to 115 nm to obtain resonance at  $\sim 450$  nm for a sample probed at  $60^\circ$  of incidence and at temperature of  $25^\circ\text{C}$  (LS state). The modulators were made by successive thermal evaporations of the metal and SCO layers on a fused silica substrate. Their experimental assessment showed that the highest spin-state-switching-induced resonance shift and thereby modulation depth were achieved under TE-polarized illumination at high angle of incidence, reaching  $\sim 30\%$  reflectivity variation over a  $\sim 8$ -nm spectral bandwidth [7].

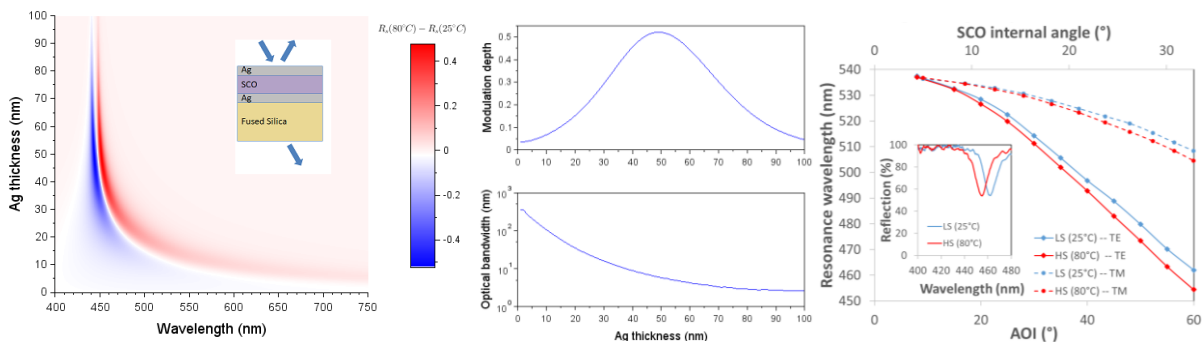


Figure 2. Ag-mirror Fabry-Perot interferometer embedding a 115nm-thick SCO layer under TE-polarized excitation at  $60^\circ$  of incidence: predicted modulation properties (left) as a function of the mirror thickness and (centre) resulting trade-off; experimental results of the obtained spectral shifts and angular tuning.

To improve performance, we chose to investigate prism-coupled Fabry-Perot interferometers (schematically represented in the inset of Figure 3 left) capitalizing on the associated increased angles of incidence and the total-internal reflection at the interface between the SCO layer and the surrounding air. Practical devices were made on purchased N-BK7 half-cube prisms by coating by thermal evaporation the surface opposite to the right-angle corner with Ag and SCO material. Angular reflectivity measurements were carried out under low-power laser excitation at 532 nm for several sample temperatures, demonstrating a large ( $\sim 5^\circ$ ) angular shift upon SCO spin-state switching (see Figure 3 centre). Both the modulation depth and spectral bandwidth of modulation were increased respectively to 60% and  $\sim 60$  nm [9]. Power-dependent measurements revealed an optical limiting behaviour (especially for AOI= $57^\circ$ , see Figure 3 right), resulting from the self-switching induced by the heat generated in the absorbing Ag layer.

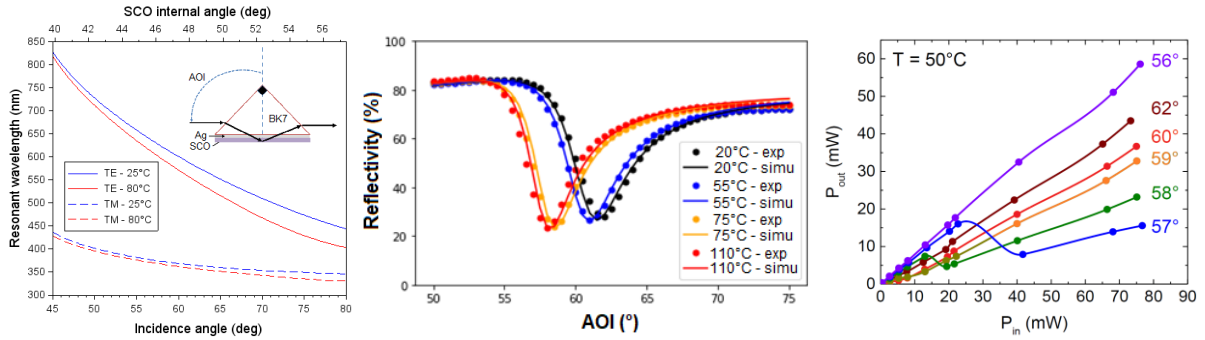


Figure 3. Prism-coupled Fabry-Pérot interferometer made of N-BK7 glass coated with a 35nm-thick Ag layer and a  $\sim 162$ -nm-thick SCO: Predicted angular dependence of the resonances (left); experimental results of temperature-dependent reflectivity and optical-limiting response.

In parallel, we have also numerically studied an alternative option to make broadband and high contrast SCO-based modulators whose working principle relies on the (frustrated) total internal reflections (TIR) occurring at the interfaces between a SCO layer and its surrounding high-refractive-index prisms (see schematic of Figure 4) [13]. Upon appropriate choice of the prism material and apex ( $112.6^\circ$ ) and for  $\sim 1\mu\text{m}$ -thick SCO layer, a modulation depth greater than 99% is expected with a  $>250$ -nm-large optical spectral bandwidth.

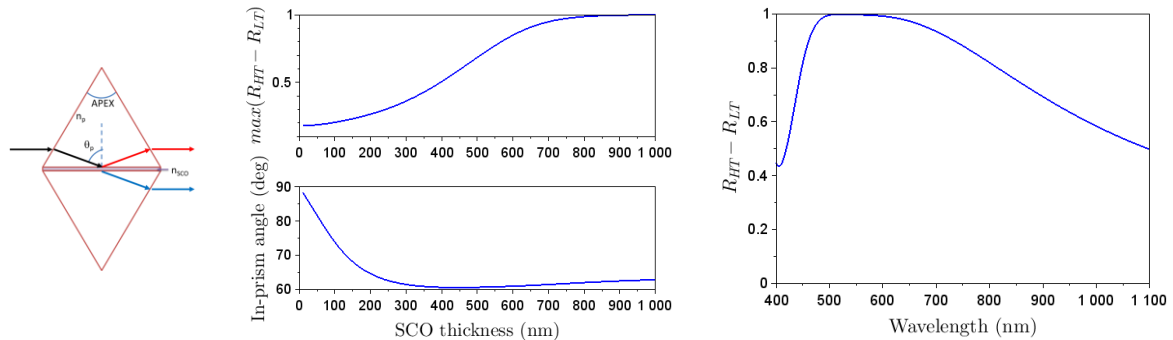


Figure 4. frustrated-total-internal-reflection SCO modulator: schematic (left); simulation of performance for configuration with SF11 prisms – SCO thickness dependence (centre) and spectral dependence (right).

#### 4. CONCLUSIONS

We have summarized our recent progress on optical modulators based spin crossover materials and more specifically the evaporable  $[\text{Fe}(\text{HB}(1,2,4\text{-triazol-1-yl})_3)_2]$  compound. To-date experimental demonstrations exploiting SCO-induced resonance shift of metal-mirror Fabry-Perot interferometers with air or BK7-prism-coupling have led to modulation with 30% (resp. 60%) modulation depth over 8 (resp. 60 nm) optical bandwidth. Numerical simulations on a frustrated-total-internal-reflection SCO modulator suggest that further performance improvements can be obtained when using this configuration. Finally, self-heating induced optical limiting behaviour was also observed in devices comprising metal layers.

## ACKNOWLEDGEMENTS

The authors would like to acknowledge support from the Agence Nationale de la Recherche (project SCOPOL, ANR-22-CE09-0019), the University of Toulouse III (project AO Tremplin “MaCaPeSuMO”), and the Centre National de la Recherche Scientifique (project MITI “CMTS-SLM”). Part of the work was conducted at the LAAS-CNRS micro and nanotechnologies platform, which is a member of the French RENATECH network of cleanroom facilities. Lijun Zhang and Yuteng Zhang thank the China Scholarship Council for their respective PhD grant.

## REFERENCES

- [1] Z. Yang, C. Ko, et S. Ramanathan, « Oxide Electronics Utilizing Ultrafast Metal-Insulator Transitions », *Annu. Rev. Mater. Res.*, vol. 41, n° 1, p. 337- 367, août 2011, doi: 10.1146/annurev-matsci-062910-100347.
- [2] M. Wuttig, H. Bhaskaran, et T. Taubner, « Phase-change materials for non-volatile photonic applications », *Nat. Photonics*, vol. 11, n° 8, p. 465- 476, août 2017, doi: 10.1038/nphoton.2017.126.
- [3] Z. Gong *et al.*, « Phase change materials in photonic devices », *J. Appl. Phys.*, vol. 129, n° 3, p. 030902, janv. 2021, doi: 10.1063/5.0027868.
- [4] P. Gütllich et J. Jung, « Thermal and optical switching of iron(II) compounds », *J. Mol. Struct.*, vol. 347, p. 21- 38, mars 1995, doi: 10.1016/0022-2860(95)08534-3.
- [5] A. Bousseksou, G. Molnár, L. Salmon, et W. Nicolazzi, « Molecular spin crossover phenomenon: recent achievements and prospects », *Chem. Soc. Rev.*, vol. 40, n° 6, p. 3313, 2011, doi: 10.1039/c1cs15042a.
- [6] E. D. Loutete-Dangui *et al.*, « Thermal spin transition in  $[\text{Fe}(\text{NH}_2\text{-trz})_3]\text{Br}_2$  investigated by spectroscopic ellipsometry », *Phys. Rev. B*, vol. 75, n° 18, p. 184425, mai 2007, doi: 10.1103/PhysRevB.75.184425.
- [7] Y. Zhang *et al.*, « A molecular spin-crossover film allows for wavelength tuning of the resonance of a Fabry–Perot cavity », *J. Mater. Chem. C*, vol. 8, n° 24, p. 8007- 8011, 2020, doi: 10.1039/D0TC02094J.
- [8] L. Zhang *et al.*, « Thermo-Optical Switches Based on Spin-Crossover Molecules with Wideband Transparency », *Adv. Opt. Mater.*, vol. submitted, 2024.
- [9] L. Zhang *et al.*, « Thermo-Optical Switches Based on Spin-Crossover Molecules with Wideband Transparency », *Adv. Opt. Mater.*, p. 2303252, 2024, doi: 10.1002/adom.202303252.
- [10] O. Kahn et C. J. Martinez, « Spin-Transition Polymers: From Molecular Materials Toward Memory Devices », *Science*, vol. 279, n° 5347, p. 44- 48, janv. 1998, doi: 10.1126/science.279.5347.44.
- [11] C. C. Katsidis et D. I. Siapkas, « General transfer-matrix method for optical multilayer systems with coherent, partially coherent, and incoherent interference », *Appl. Opt.*, vol. 41, n° 19, p. 3978, juill. 2002, doi: 10.1364/AO.41.003978.
- [12] P. B. Johnson et R. W. Christy, « Optical Constants of the Noble Metals », *Phys. Rev. B*, vol. 6, n° 12, p. 4370- 4379, 1972.
- [13] S. Calvez, H. Camon, K. Ridier, G. Molnár, et O. Gauthier-Lafaye, « Broadband high-contrast visible optical switches based on a spin-crossover material », *Appl. Opt.*, vol. 61, n° 32, p. 9562, nov. 2022, doi: 10.1364/ao.473176.