

Development of robust chiroptical systems through spirobifluorenes

Julia Portela-Pino¹  | María Talavera²  | Stefano Chiussi³  |
Sandra Bolaño²  | Ángeles Peña-Gallego¹  | J. Lorenzo Alonso-Gómez⁴ 

¹University of Vigo, Physical Chemistry Department, Vigo, Spain

²University of Vigo, Inorganic Chemistry Department, Vigo, Spain

³CINTECX, University of Vigo, Applied Physic Department, Vigo, Spain

⁴CINTECX, University of Vigo, Organic Chemistry Department, Vigo, Spain

Correspondence

Ángeles Peña-Gallego, University of Vigo, Physical Chemistry Department, Vigo, Spain.

Email: mpena@uvigo.es

J. Lorenzo Alonso-Gómez, CINTECX, University of Vigo, Organic Chemistry Department, Vigo, Spain.

Email: lorenzo@uvigo.es

Funding information

Ministerio de Ciencia e Innovación,

Grant/Award Number:

TED2021-131760B-100; Xunta de Galicia,

Grant/Award Number: ED431C 2017/51;

Ministerio de Universidades; European

Union NextGenerationEU/PRT

Abstract

Chiroptical responses are valuable for the structural determination of dissymmetric molecules. However, the development of everyday applications based on chiroptical systems is yet to come. We have been earlier using axially chiral allenes for the construction of linear, cyclic, and cage-shaped molecules that present remarkable chiroptical responses. Additionally, we have developed chiral surfaces through upstanding chiral architectures. Since the goal is to obtain robust chiroptical materials, more recently we have been studying spirobifluorenes (SBFs), a well-established building block in optoelectronic applications. After theoretical and experimental demonstration, the suitability of chiral SBFs for the development of robust chiroptical systems was certified by the construction all-carbon double helices, flexible shape-persistent macrocycles, chiral frameworks for surface functionalization, and structures featuring helical or spiroconjugated molecular orbitals. Here, we give an overview of our contribution to these matters.

KEYWORDS

chiral axes, helical molecular orbitals, spirobifluorenes (SBFs), spiroconjugation, surface functionalization

1 | INTRODUCTION

Chirality is a property directly linked to the structural conformation of molecules in space. It is a characteristic of molecules that describe the inability to overlap with their mirror image. For optical activity to exist, typically molecules have a stereogenic center or asymmetric carbon.¹ However, other chiral elements, such as chiral axis, can also be used to introduce chirality.² Examples of axially chiral molecules can be found in systems such as allenes³ or spiranes,^{4,5} the latest being

bicyclic compounds with at least two rings connected via a single atom.

Recently, interest has arisen in developing chiral systems that present strong chiroptical responses.^{6,7} In this regard, we have developed axially chiral allenes⁸ presenting g-factors of approximately 0.01 however suffering from stability.⁹ With the aim to overcome the stability issues, we have moved our attention to chiral spirobifluorenes (SBFs).¹⁰ In order to get an understanding on the mechanisms originating the observed chiroptical responses, we combined our experimental studies with

This is an open access article under the terms of the [Creative Commons Attribution-NonCommercial License](https://creativecommons.org/licenses/by-nc/4.0/), which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

© 2023 The Authors. *Chirality* published by Wiley Periodicals LLC.

theoretical predictions using density functional theory (DFT).¹¹ While the use of different functional groups explores their compatibility with axially chiral SBFs, the development of D_n -symmetric cyclic systems exploits the advantage of alignment between transition electric and magnetic dipole moments to boost the chiroptical responses. Following this strategy, we have gained knowledge that can be applied for the design of *ad hoc* robust chiroptical systems.

2 | WHY CHIRAL AXES?

Building blocks such as allenes or SBFs may present axial chirality when appropriately functionalized. In such cases, a chiral axis is present when the two functional groups in each of the connected orthogonal planes are different from each other (R_1 and R_2 in Figure 1).

Axially chiral building blocks are attractive since they can be used for the development of molecular structures with very distinct geometries by carefully selecting the absolute configuration of the constituting chiral building blocks.^{12,13} For instance, the different combinations of absolute configuration of the constituting allenes in cyclic tetrameric alleno-acetylenic macrocycles leads to crown-, twist-, chair-, and boat-shaped structures (Figure 2).⁸ Remarkably, the homochiral crown-shaped stereoisomers presented among the highest chiroptical responses for purely organic compounds. Also, open oligomers bearing two, four, eight, or 16 chiral allenes showed remarkable

chiroptical amplification compared with the single chiral allene justified by a helical conformational preference.¹⁴

Particularly, a pyridine [14₂] allenophane showed the ability to encapsulate a diiodo-perfluorinated compound via halogen bonding (Figure 3).¹⁵

Additionally, the development of covalent organic helical cages bearing six chiral allenes¹⁶ showed the ability to entrap organometallic sandwich compounds and detect them via chiroptical spectroscopies.¹⁷ On the

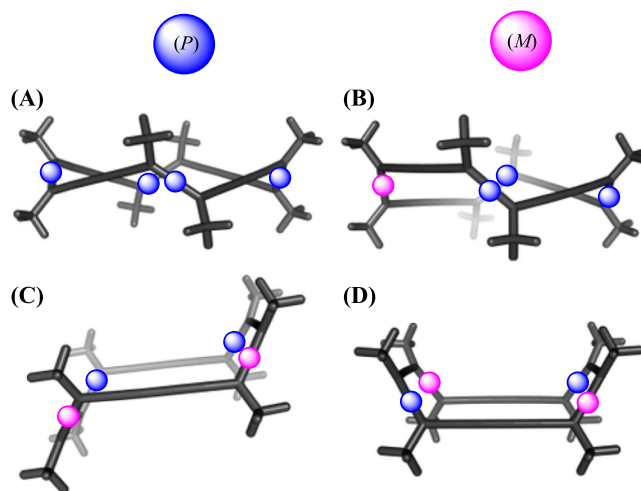


FIGURE 2 Representation of (A) (*P,P,P,P*) crown-shaped, (B) (*P,P,P,M*) twist-shaped, (C) (*P,P,M,M*) chair-shaped, and (D) (*P,M,P,M*) boat-shaped tetrameric alleno-acetylenic macrocycles.⁸ Blue/pink spheres stand to (*P*)/(*M*) absolute configuration of the allenic units.

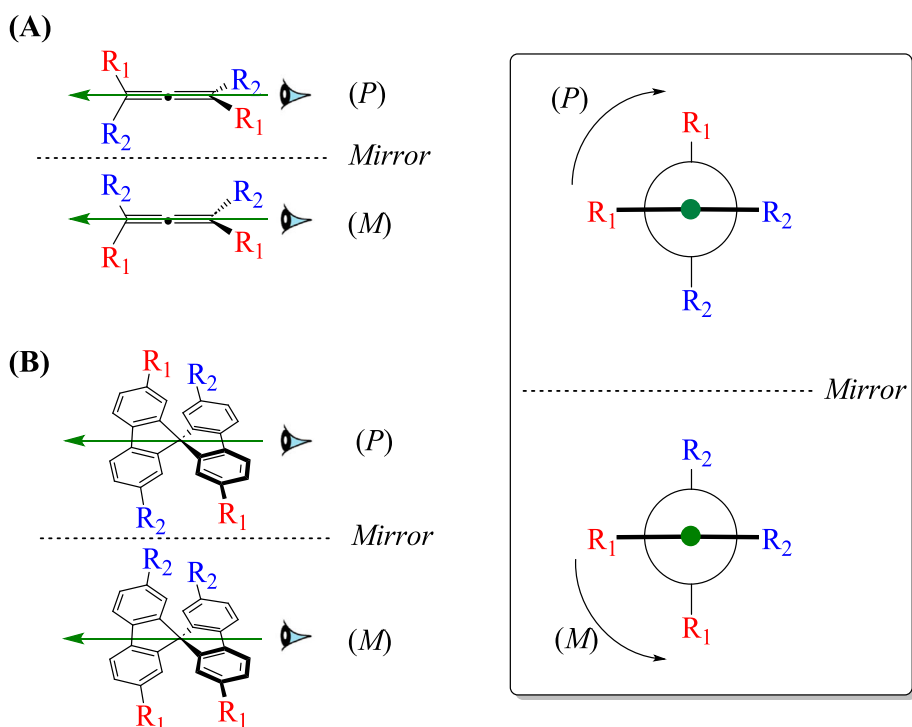


FIGURE 1 (left) Representation of both enantiomers of an allene (A) and an SBF (B) and (right) representation of the absolute configuration assignment of a chiral axis according to the Cahn–Ingold–Prelog rules.

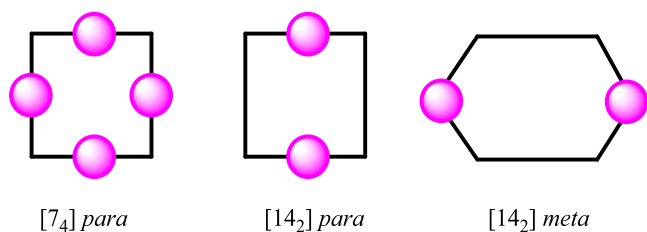


FIGURE 3 Simplified representation of *para* [7₄] and [14₂] as well as *meta* [14₂] allenophanes. Pink circles represent aromatic rings.

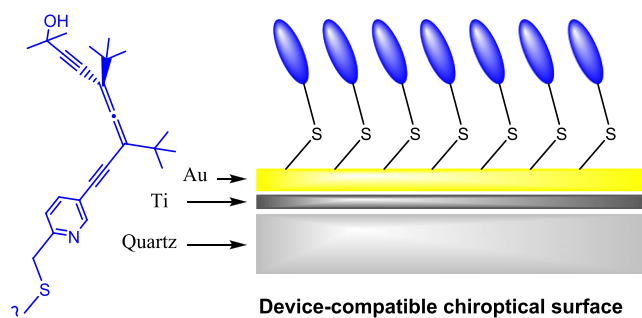


FIGURE 4 Simplified representation of the developed device-compatible chiroptical surface. The blue spheres represent the chiral allenes.¹⁹

search for chiroptical application, we have explored the behavior of chiral allenes on surfaces by scanning tunneling microscopy and demonstrated the transfer of chirality from the single molecule to the 2D network of molecules presenting and up-standing morphological self-assembly.¹⁸ However, these studies were performed at low temperatures, and even when they have served as a toll for a fundamental understanding, they cannot be directly used in real applications.

3 | DEVICE-COMPATIBLE CHIROPTICAL SURFACES

To enable day-to-day implementation of chiroptical applications, the development of device compatible chiroptical systems is essential. With this idea in mind, we have developed a semitransparent quartz substrate with an Ti/Au coating. While the Au layer allows for an efficient anchoring of the chiral molecules containing a thioacetate via S–Au bond formation, the Ti layer was necessary to prevent the Au layer to detach from the quartz plate (Figure 4).¹⁹ Attachment of chiral allenes was performed via sublimation. Characterization with X-ray photoelectron spectroscopy and N K-edge near-

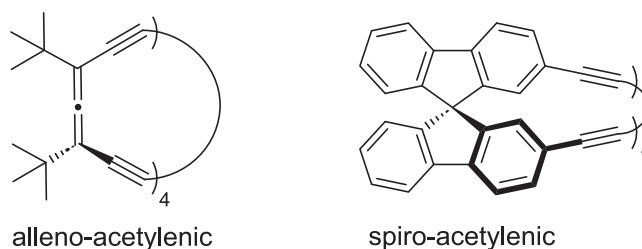


FIGURE 5 Simplified representation of tetrameric alleno-acetylenic and spiro-acetylenic macrocycles.⁴

edge X-ray absorption fine structure uncovered the structure of the formed monolayers as up-standing chiral architectures (UCAs). Additionally, second-harmonic generation circular dichroism showed the chiroptical activity of the monolayers at room temperature. Since access to UCAs with diverse chemical functionality is synthetically possible, these systems have enormous potential for the development of chiroptical applications.

The development of chiroptical applications needs to use robust chiroptical systems that are stable under the desired operating conditions. To overcome the stability limitations of diethynyl allenes, as these systems may undergo photo/thermal isomerization under certain conditions,⁹ we aimed for SBFs,⁵ a chemical family known for its robustness in state-of-the-art optoelectronic applications, as suitable fragment for the development of axially chiral robust systems.

4 | FROM ALLENES TO SPIROBIFLUORENES

Spirobifluorenes, as allenes, may also present axial chirality (Figure 1). In order to evaluate the potential of SBFs for the development of systems presenting strong chiroptical response, we have compared the theoretical chiroptical responses of alleno-acetylenic and spiro-acetylenic cyclic tetramers.⁴ The analysis indicated that the rigidity of the SBF skeleton yields cyclic oligomeric systems with high conformational stability. Additionally, the electronic properties combined with the geometry of SBF macrocycles render chiroptical intensities comparable with those of their allenic counterparts (Figure 5).

With the aim to validate experimentally the reliability of SBFs for the construction of structures presenting strong chiroptical responses, we developed synthetic methodologies to open access to dimeric, trimeric and tetrameric spiro-acetylenic macrocycles. These three oligomers have very distinct geometries: (i) the dimeric represents an all-carbon double helix stiff structure,²⁰

(ii) the trimeric, also very stiff, presents an adequate twist between the fluorene units connected via the butadiyne moieties to feature helical molecular orbitals,²¹ while molecular dynamic simulations predicted (iii) that the tetrameric is a flexible shape-persistent macrocycle.²¹ All of them present *g*-factors approximately 0.007, comparable to reported alleno-acetylenic macrocycles³ and, notably, thermal stabilities above 250°C.²¹

Once demonstrated the suitability of SBFs for the construction of chiroptical systems presenting both high chiroptical intensity responses and thermal stabilities, our effort was focused on the modulation of the electronic and chemical properties of chiral SBFs to enable their implementation in industrial applications. SBFs can present substituents in different positions of the molecule. However, substitution at position 2 is known to be more reactive and it shows a higher impact on the optical properties of the system since the substituents in this position present an extended π -conjugation with the fluorene moiety due to the *para*-substitution pattern and the minimization of steric interactions (Figure 6).²²

Therefore, we centered our attention on the development of 2,2'-disubstituted SBFs for the development of chiroptical SBFs.

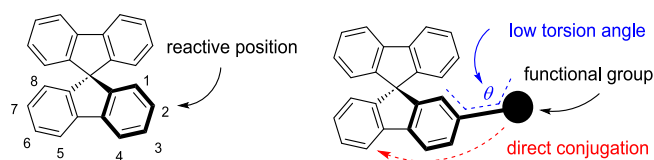


FIGURE 6 Numbering of positions in SBF and representation of functionalization over position 2.

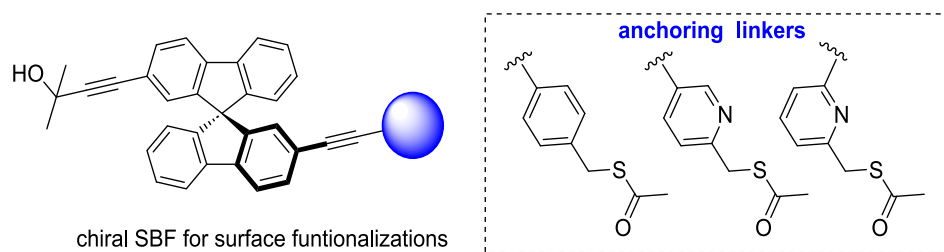


FIGURE 7 Representation of chiral SBFs developed for surface functionalization.²³

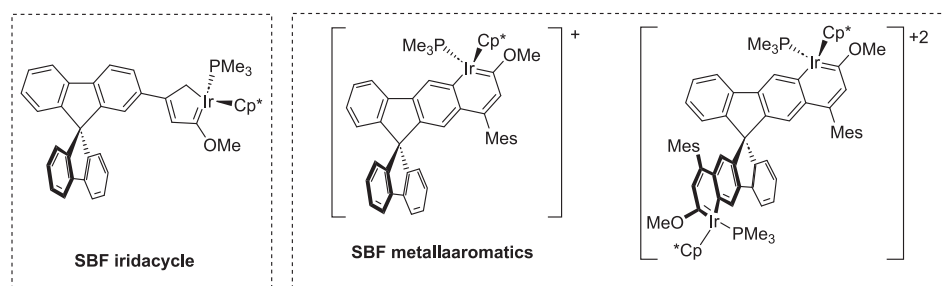


FIGURE 8 Schematic representation of SBF iridacycle²⁵ and SBF metallaaromatic systems^{26,27} Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl; Mes = mesityl.

5 | SPIROBIFLUORENES FOR SURFACE FUNTIONALIZATION

Following our methodology for the development of device compatible chiroptical surfaces, we proceeded with the synthesis of chiral SBFs presenting different aromatic rings for surface functionalization.²³ All derivatives showed thermal stabilities above 170°C under air. The enantiomeric resolution was performed successfully using the chiral stationary phase Chiralpak IA (Figure 7).

The UV/Vis and ECD spectra of these systems showed the lowest electronic transitions at around 350 nm. In order to modulate the spectral range of chiroptical systems, we have explored different approaches as indicated below.

6 | METALLAAROMATIC SPIROBIFLUORENES

Metallaaromatic compounds present a metal atom in the position of at least one of the ring carbon atoms. This chemical modification is known to greatly modulate the optical properties compared with purely organic counterparts. In order to open access to metallaaromatic SBFs, we followed Bolaño's synthetic methodology involving an orthometallation reaction.²⁴ When the propargyl precursor used presented an SBF and a methyl group, the reaction yielded an SBF iridacyclic compound (Figure 8).²⁵ In order to drive the reaction to metallaaromatic formation over the SBF unit, the methyl group of the propargyl precursor was replaced by a mesityl group.²⁶ The same methodology was applied to an SBF substituted with two

propargyl groups to render a dimetallaaromatic SBF.²⁷ Remarkably, both systems present thermal stabilities above 200°C and a remarkable red shift compared with bare SBF.

Since the Ir metal atoms of these metallaaromatic systems feature chiral centers, the metallaaromatic SBF bearing one Ir atom is formed as a racemate while the SBF bearing two Ir chiral centers is formed as a mixture of three diastereoisomers due to the presence of a chiral axis.

7 | TETRACYANOETHYLENE (TCBD) SPIROBIFLUORENES

TCBDs are strong electron-acceptors that typically present interesting optical and nonlinear optical (NLO) properties.²⁸ Their synthesis through the reaction between tetracyanoethylene (TCNE) and electron rich acetylenes is considered among the click chemistry family because of the atomic economy and high yields. The optical properties of TCBD derivatives are dramatically changed compared with the acetylenic precursors. Therefore, in order to modulate the optical and chiroptical properties of SBFs, we have developed the synthesis of TCBD-SBFs stable up to 200°C and predicted high NLO properties (Figure 9).²⁹

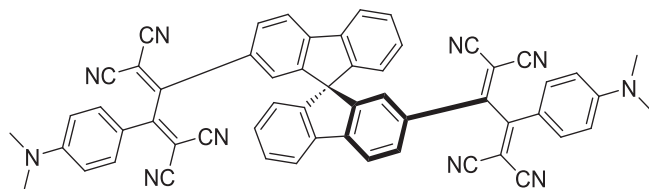


FIGURE 9 Representation of a TCBD-SBF.²⁹

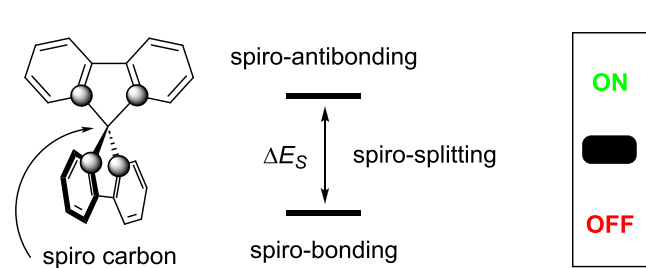


FIGURE 10 Representation of SBF and energy levels of spiro-bonding and spiro-antibonding generated by spiroconjugation. The ON/OFF switch stands for the presence or absence of spiroconjugation depending on the functionalization over the SBF unit.³¹

While the UV/Vis and ECD spectra of the acetylene bearing precursor is restricted to the UV region of the spectrum, the TCBD derivative absorption reaches the near infrared region.

8 | SPIROCONJUGATION EFFECTS IN SPIROBIFLUORENES

Spiroconjugation is a phenomenon that occurs when *p* orbitals of two π systems bonded from a common tetrahedral atom, called spiro carbon, interact. Because of this, spiro-bonding and spiro-antibonding molecular orbitals are formed. The energy difference that is established between the anti-bonding and bonding orbitals is called spiro-splitting (ΔE_S).³⁰ In the case of spirobifluorene compounds, as the fluorenes are perpendicular to each other, the *p* orbitals of the carbon atoms that are contiguous to the spiro carbon interact (Figure 10).

We evaluated the impact of spiroconjugation on the optical properties and chemical reactivity of spirobifluorene compounds via functionalization. For this purpose, functional groups with different electronic features were employed.³¹ Their reactivity along with DFT calculations showed that spiroconjugation is ON when SBFs present an electron-donating group such as aniline. On the other hand, comparison of experimental and predicted ECD responses of the disubstituted analogs unveiled that spiroconjugated molecular orbitals are strongly involved in the electronic transitions that give rise to the main features in the ECD and UV/Vis spectra of systems incorporating phenyl and nitrophenyl groups (Figure 11). As this study clearly showed that spiroconjugation can be modulated via functionalization in SBFs, we suggest the spiroconjugation should be taken into account when developing new chiroptical SBFs.

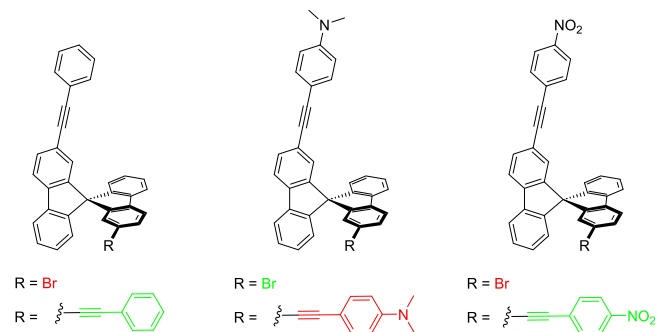


FIGURE 11 Representation of SBFs functionalized with functional groups of different electronic nature. Green and red stand for ON and OFF spiroconjugation, respectively.³¹

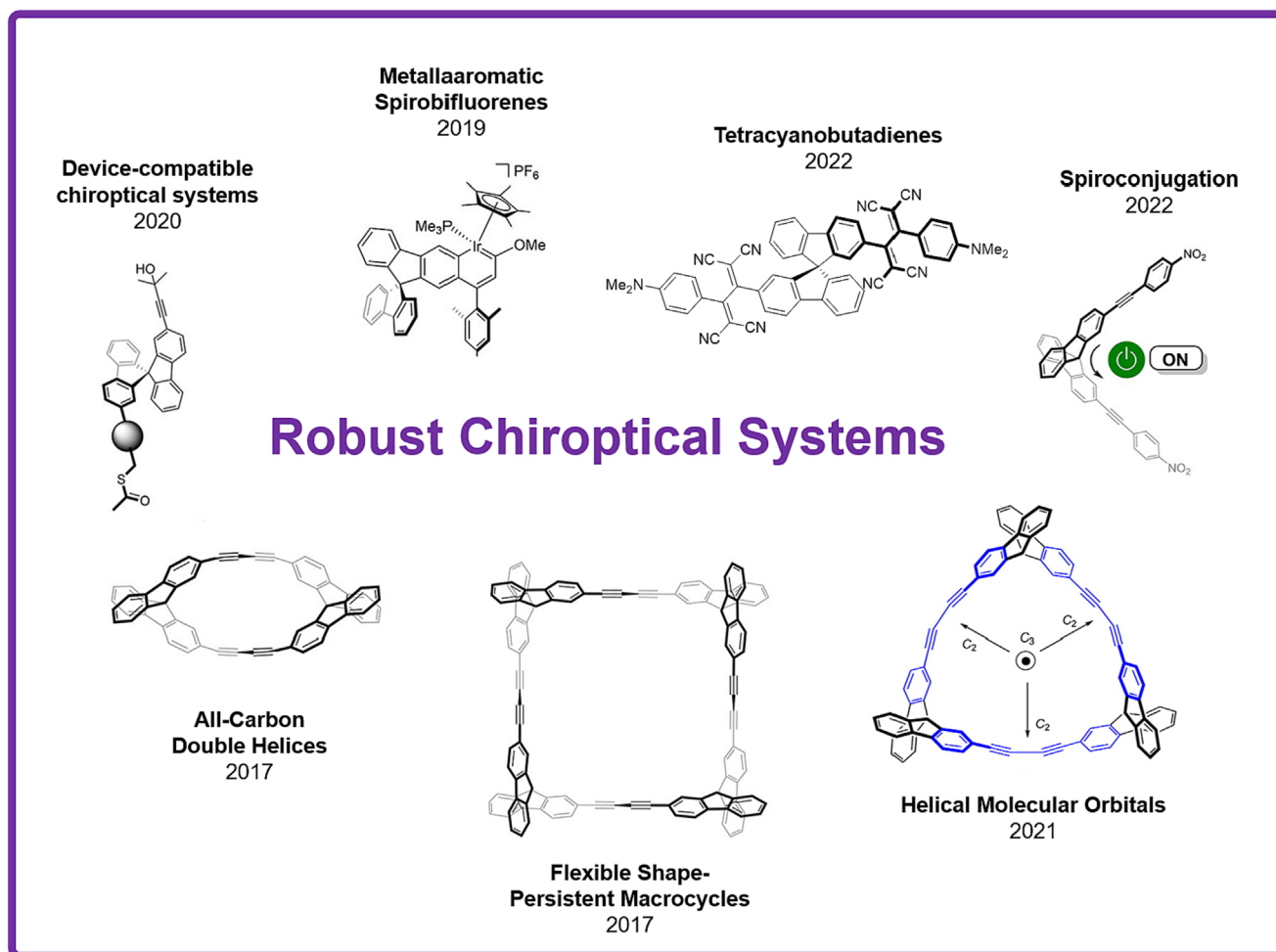


FIGURE 12 Overview of developed robust chiroptical systems: all-carbon double helices,²⁰ flexible shape-persistent macrocycles,²⁰ metallaaromatic SBFs,²⁶ device compatible chiroptical systems,¹⁹ helical molecular orbitals,²¹ spiroconjugation,³¹ and tetracyanobutadienes.²⁹

9 | CONCLUSIONS

Overall, in the last few years, we have demonstrated the suitability of SBFs as chiral building blocks for the development of robust chiroptical systems with thermal stabilities that are suitable for industrial applications. Their *g*-factors are reaching competitive values among purely organic compounds with the emergence of new chemical families: device-compatible chiroptical systems, metallaaromatic SBFs, tetracyanobutadiene SBFs, SBFs presenting spiroconjugation, all-carbon double helices, flexible shape-persistent macrocycles, and macrocycles featuring helical molecular orbitals (Figure 12).

The combination of theory and experiments in our studies has enabled the development of these systems, and we believe that they will significantly contribute to the emergence of everyday chiroptical applications, soon.

ACKNOWLEDGMENTS

This work was funded by Ministerio de Ciencia e Innovación (TED2021-131760B-100) and Xunta de Galicia (ED431C 2017/51), and Funding for open access charge: University of Vigo/CISUG. M. T. thanks Ministerio de Universidades and European Union NextGenerationEU/PRT for a Maria Zambrano contract.

ORCID

Julia Portela-Pino  <https://orcid.org/0000-0001-7499-9660>

Maria Talavera  <https://orcid.org/0000-0003-2635-4133>

Stefano Chiussi  <https://orcid.org/0000-0002-3933-8725>

Sandra Bolaño  <https://orcid.org/0000-0002-5013-9831>

Ángeles Peña-Gallego  <https://orcid.org/0000-0002-6898-8305>

J. Lorenzo Alonso-Gómez  <https://orcid.org/0000-0002-6107-0120>

REFERENCES

- Berova N, Nakanishi K, Woody RW. *Circular Dichroism: Principles and Applications*. Wiley; 2000.
- Berova N, Polavarapu PL, Nakanishi K, Woody RW. *Comprehensive Chiroptical Spectroscopy*. Wiley; 2012.
- Rivera-Fuentes P, Diederich F. Allenes in molecular materials. *Angew Chem Int Ed*. 2012;51(12):2818-2828. doi:10.1002/anie.201108001
- Castro-Fernández S, Cid MM, Silva López C, Alonso-Gómez JL. Opening access to new chiral macrocycles: from allenes to spiranes. *J Phys Chem A*. 2014;119(9):1747-1753. doi:10.1021/jp508414r
- Thiemann F, Piehler T, Haase D, Saak W, Lützen A. Synthesis of enantiomerically pure dissymmetric 2,2'-disubstituted 9,9'-spirobifluorenes. *European J Org Chem*. 2005;2005(10):1991-2001. doi:10.1002/ejoc.200400796
- Sato S, Yoshii A, Takahashi S, Furumi S, Takeuchi M, Isobe H. Chiral intertwined spirals and magnetic transition dipole moments dictated by cylinder helicity. *Proc Natl Acad Sci U S A*. 2017;114(50):13097-13101. doi:10.1073/pnas.1717524114
- Liu S, Xia D, Baumgarten M. Rigidly fused spiro-conjugated π -systems. *ChemPlusChem*. 2021;86(1):36-48. doi:10.1002/cplu.202000467
- Alonso-Gómez JL, Rivera-Fuentes P, Harada N, Berova N, Diederich F. An enantiomerically pure alleno-acetylenic macrocycle: synthesis and rationalization of its outstanding chiroptical response. *Angew Chem Int Ed*. 2009;48(30):5545-5548. doi:10.1002/anie.200901240
- Odermatt S, Alonso-Gómez JL, Seiler P, Cid MM, Diederich F. Shape-persistent chiral alleno-acetylenic macrocycles and cyclophanes by acetylenic scaffolding with 1,3-diethynylallenes. *Angew Chem Int Ed*. 2005;44(32):5074-5078. doi:10.1002/anie.200501621
- Ozcelik A, Pereira-Cameselle R, Alonso-Gómez JL. From allenes to spirobifluorenes: on the way to device-compatible chiroptical systems. *Curr Org Chem*. 2020;24(23):2737-2754. doi:10.2174/1385272824999201013164534
- Pescitelli G, Di Bari L, Berova N. Application of electronic circular dichroism in the study of supramolecular systems. *Chem Soc Rev*. 2014;43(15):5211-5233. doi:10.1039/C4CS00104D
- Neff RK, Frantz DE. Recent applications of chiral allenes in axial-to-central chirality transfer reactions. *Tetrahedron*. 2015; 71:7-18. doi:10.1016/j.tet.2014.08.030
- Wang C, Matile S. Anion- π catalysts with axial chirality. *Chem A Eur J*. 2017;23(49):11955-11960. doi:10.1002/chem.201702672
- Rivera-Fuentes P, Alonso-Gómez JL, Petrovic AG, et al. Amplification of chirality in monodisperse, enantiopure alleno-acetylenic oligomers. *Angew Chem Int Ed*. 2010;49(12):2247-2250. doi:10.1002/anie.200906191
- Castro-Fernández S, Lahoz IR, Llamas-Saiz AL, Alonso-Gómez JL, Cid M-M, Navarro-Vázquez A. Preparation and characterization of a halogen-bonded shape-persistent chiral alleno-acetylenic inclusion complex. *Org Lett*. 2014;16(4):1136-1139. doi:10.1021/ol403778f
- Míguez-Lago S, Llamas-Saiz AL, Magdalena Cid M, Alonso-Gómez JL. A covalent organic helical cage with remarkable chiroptical amplification. *Chem A Eur J*. 2015;21(50):18085-18088. doi:10.1002/chem.201503994
- Míguez-Lago S, Cid MM, Alonso-Gómez JL. Covalent organic helical cages as sandwich compound containers. *European J Org Chem*. 2016;2016(34):5716-5721. doi:10.1002/ejoc.201600997
- Zhang Y-Q, Öner MA, Lahoz IR, et al. Morphological self-assembly of enantiopure allenes for upstanding chiral architectures at interfaces. *Chem Commun*. 2014;50(95):15022-15025. doi:10.1039/C4CC06398H
- Ozcelik A, Pereira-Cameselle R, von Weber A, et al. Device-compatible chiroptical surfaces through self-assembly of enantiopure allenes. *Langmuir*. 2018;34(15):4548-4553. doi:10.1021/acs.langmuir.8b00305
- Castro-Fernández S, Yang R, García AP, et al. Diverse chiral scaffolds from diethynylspiranes: all-carbon double helices and flexible shape-persistent macrocycles. *Chem a Eur J*. 2017; 23(49):11747-11751. doi:10.1002/chem.201702986
- Ozcelik A, Aranda D, Gil-Guerrero S, et al. Distinct helical molecular orbitals through conformational lock**. *Chem a Eur J*. 2020;26(72):17342-17349. doi:10.1002/chem.202002561
- Sicard L, Quinton C, Peltier J-D, et al. Spirobifluorene regioisomerism: a structure-property relationship study. *Chem a Eur J*. 2017;23(32):7719-7727. doi:10.1002/chem.201700570
- Ozcelik A, Peña-Gallego MD, Pereira-Cameselle R, Alonso-Gómez JL. Design and synthesis of chiral spirobifluorenes. *Chirality*. 2020;32:464-473.
- Talavera M, Peña-Gallego Á, Alonso-Gómez JL, Bolaño S. Metallaaromatic biaryl atropisomers. *Chem Commun*. 2018; 54(78):10974-10976. doi:10.1039/C8CC06443A
- Pereira-Cameselle R, Peña-Gallego Á, Cid-Seara KM, Alonso-Gómez JL, Talavera M, Bolaño S. Chemoselectivity on the synthesis of iridacycles: a theoretical and experimental study. *Inorg Chim Acta*. 2021;517:120189. doi:10.1016/j.ica.2020.120189
- Arias-Coronado VC, Pereira-Cameselle R, Ozcelik A, et al. Spirobifluorene metallaaromatics. *Chem A Eur J*. 2019;25(59): 13496-13499. doi:10.1002/chem.201903213
- Talavera M, Pereira-Cameselle R, Peña-Gallego Á, et al. Optical and electrochemical properties of spirobifluorene iridanaphthalene complexes. *Dalton Trans*. 2022;52(2):487-493. doi:10.1039/D2DT03465D
- Ripoche N, Betou M, Philippe C, et al. Two-photon absorption properties of multipolar triaryl amino/tosylamido 1,1,4,4-tetracyanobutadienes. *Phys Chem Chem Phys*. 2021;23(39): 22283-22297. doi:10.1039/D1CP03346H
- Ozcelik A, Pereira-Cameselle R, Peña-Gallego Á, Alonso-Gómez JL. A tetracyanobutadiene spirobifluorene: synthesis, enantiomeric resolution and chiroptical properties. *European J Org Chem*. 2022;2022(16):e202101333. doi:10.1002/ejoc.202101333
- Schweig A, Weidner U, Hellwinkel D, Krapp W. Spiroconjugation. *Angew Chem Int Ed*. 1973;12(4):310-311. doi:10.1002/anie.197303101
- Ozcelik A, Aranda D, Pereira-Cameselle R, et al. ON/OFF spiroconjugation through peripheral functionalization: impact on the reactivity and chiroptical properties of spirobifluorenes. *Chem-PlusChem*. 2022;87(6):e202100554. doi:10.1002/cplu.202100554

How to cite this article: Portela-Pino J, Talavera M, Chiussi S, Bolaño S, Peña-Gallego Á, Alonso-Gómez JL. Development of robust chiroptical systems through spirobifluorenes. *Chirality*. 2023;1-7. doi:10.1002/chir.23624