

CHEMISTRY A European Journal



Accepted Article

Title: Azabora[5]helicene Charge-Transfer Dyes Show Efficient and Spectrally Variable Circularly Polarized Luminescence

Authors: Zoe Domínguez, Rocío López-Rodríguez, Eleuterio Álvarez, Sergio Abbate, Giovanna Longhi, Uwe Pischel, and Abel Ros

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Chem. Eur. J. 10.1002/chem.201801908

Link to VoR: http://dx.doi.org/10.1002/chem.201801908

Supported by ACES



WILEY-VCH

Azabora[5]helicene Charge-Transfer Dyes Show Efficient and Spectrally Variable Circularly Polarized Luminescence

Zoe Domínguez,^[a] Rocío López-Rodríguez,^[b,c] Eleuterio Álvarez,^[b] Sergio Abbate,^[d] Giovanna Longhi,^{*[d]} Uwe Pischel,^{*[a]} and Abel Ros^{*[b,c]}

Dedicated to Professor Rosario Fernández on the occasion of her 60th birthday

Abstract: Three helicenes based on a borylated arylisoquinoline skeleton have been prepared in their enantiopure forms and characterized with respect to their photophysical properties, including the use of chiroptical spectroscopies. The dyes show varying charge-transfer character and efficient emission (quantum yields between 0.13 and 0.30, in toluene), which is governed by the electron-donor substitution (p-MeO-phenyl, p-Me₂N-phenyl) at the helicene. Marked differences in the emission wavelength and Stokes shift are observed, with the dimethylamino-substituted derivative emitting most red-shifted (maximum at ca. 590 nm) and displaying the highest Stokes shift (ca. 6000 cm⁻¹) in toluene. The helicenes show electronic circular dichroism (ECD) and significant circularly polarized luminescence (CPL) with dissymmetry factors of up to 3.5 \times 10⁻³. The sign of the ECD band corresponding to the first transition and the CPL spectrum depend sensibly on the electron-donor substitution.

charge-transfer fluorophores with application potential in bioimaging.^[9, 10, 28] With the idea to further enrich the photophysics of this fascinating platform we have built on their biaryl structure, which provides a means to arrive at dyes with helical chirality and the corresponding observation of interesting chiroptical properties, including the detection of circularly polarized luminescence (CPL).[29-32] The phenomenon is well established for supramolecular assemblies or nanostructures.^{[29,} ^{33-40]} However, the observation of CPL from small organic molecules (SOMs), albeit generally showing smaller dissymmetry factors (g), has recently created considerable interest in the dye chemistry community.^[30] Potential applications are chiral sensing or the preparation of chiroptical systems with innovative photophysical design.^[29, 30, 41-46] Helicenes belong to the most frequently reported CPL-SOM architectures, among them carbo[n]helicenes,^[33, 47-51] helicenes that incorporate (azahelicenes,^[52-55] oxahelicenes,^{[34,} heteroatoms thiahelicenes^[56]), and metallahelicenes.^[57, 58]

Introduction

Four-coordinate organoboron chelates^[1-3] are attractive targets for the design of photostable fluorescent dyes for the most varied applications, including bioimaging,^[4-12] sensing,^[13-17] and organic light-emitting diodes.^[18] Much effort has been dedicated to the development of synthetically flexible platforms which enable the photophysical fine-tuning of the dyes.^[3, 9-11, 19-27] As part of our own research program we have developed borylated arylisoquinoline (BAI) dyes, which in their N,C-chelate variant are strongly emitting, solvatochromic, and two-photon-absorbing

[a]	Z. Domínguez, Dr. U. Pischel
	CIQSO - Centre for Research in Sustainable Chemistry and
	Department of Chemistry
	University of Huelva
	Campus de El Carmen s/n, E-21071 Huelva (Spain)
	E-mail: uwe.pischel@diq.uhu.es
[b]	Dr. R. López-Rodríguez, Dr. E. Álvarez, Dr. A. Ros
	Institute for Chemical Research (CSIC-US)
	C/Américo Vespucio 49, E-41092 Seville (Spain)
	E-mail: abel.ros@iiq.csic.es
[c]	Dr. R. López-Rodríguez, Dr. A. Ros
	Department of Organic Chemistry and Innovation Centre in
	Advanced Chemistry (ORFEO-CINQA)
	University of Seville
	C/Prof. García González 1, E-41012 Seville (Spain)
[d]	Prof. Dr. S. Abbate, Prof. Dr. G. Longhi
	Department of Molecular and Translational Medicine
	University of Brescia
	Viale Europa 11, 25123 Brescia (Italy)
	E-mail: giovanna.longhi@unibs.it

Supporting information for this article is given via a link at the end of the document.



Figure 1. Structures of the two enantiomers of the helicenes 10–12.

However, despite the fact that several Bodipy-based chiral architectures were found to show significant CPL effects, [39, 46, 59-^{64]} azabora[n]helicenes, that incorporate boron directly in the helical architecture, were reported only in a single work so far.^[65] These systems build on borylated arylpyridine N,C chelates. Their emission maximum can be fine-tuned by the helicene length, but even for n = 10 the maximum stays ca. 20 nm below 500 nm. Using an isoquinoline fragment instead of a pyridine, the charge-transfer properties of the dyes become more pronounced,^[9, 20, 24, 28] as we have shown for related BAI dyes. In order to explore the possibility to combine the charge-transfer features with the observation of spectrally-tunable CPL emission,^[54, 56] we have prepared new members of the BAI dye platform that contain a shielding phenyl ring at the 8-position of the naphthyl moiety (see Figure 1). This structural feature introduces steric hindrance which enables the separation of the helically chiral enantiomers of the dyes. Further, the additional phenyl ring can be used to integrate electron-donating

substituents such as -OMe or -NMe₂ at its *para* position. Intense CPL emission above 500 nm was observed especially for the dyes **11** and **12**. The stronger electron-donating -NMe₂ shifts the emission maximum even close to 600 nm. These new BAI dyes usefully complement a previously investigated series of racemic

Results and Discussion

Synthesis

The synthesis of the desired helicene products 10-12, containing different aryl fragments at the 8-position of the naphthyl moiety, started with the selective Pd-catalyzed Suzuki coupling reaction of 1,8-dibromonaphthalene with a series of boronic acids (Scheme 1). This provided the corresponding monoarylated products 1-3 in moderate to good yields of

BAI dyes with demonstrated applications in bioimaging.^[9, 10] Further, this work provides an attractive path for the design of spectrally fine-tuned emission of CPL-SOM architectures.^[30, 54, 56, 63]

65–75%. The lithiation/borylation at the remaining bromosubstituted position, followed by the one-pot Pd-catalyzed Suzuki coupling reaction with 1-chloroisoquinoline afforded the compounds **4–6** in yields of 71–82%. Although these products have axial chirality, the corresponding racemization barrier is assumed to be low, which allows the free rotation around the chiral axis at room temperature.



Scheme 1. Synthesis of arylisoquinolines 4-6.

With the arylisoquinolines at hand, we decided to synthesize the axially chiral bromide 7 (see Scheme 2) as a model substrate. Thus, following a previously developed C-H borylation/bromination methodology,^[9, 66] the bromide (\pm) -7 was obtained from 4 in 65% yield (Scheme 2). The enantiomers were separated by semipreparative chiral high-performance liquid chromatography (see conditions in the Supporting Information); a_R -7 (retention time $R_t = 7.11$ min) and a_S -7 ($R_t = 9.05$ min) enantiomers with an enantiomeric ratio (er) > 99:1 were obtained. The X-ray single-crystal study of enantiopure as-7 allowed the unambiguous assignment of the absolute configuration (see Scheme 2 and Supporting Information). Finally, a lithiationborylation sequence^[9] enabled the synthesis of the desired azabora[5]helicene 10. In short, submitting the enantiopure bromides a_{R} -7 and a_{S} -7 to a Br-Li exchange reaction at low temperature (-78 °C) in tetrahydrofuran, followed by the reaction of the lithiated intermediate with F-B(Mes)₂ (-78 °C \rightarrow 25 °C)

yielded **10** as enantiomeric *M* and *P* forms with moderate 38–42% yields and an er > 99:1. The assignment of the absolute configuration of the helicene was based on the crystal structure of a_s -7.

The helicenes **11** and **12** could be synthesized in principle in the same way as above described for **10**. However, in the course of the preparation of **10** we noted in an individual experiment that a small temperature rise to above -60 °C during the lithiation step of **7** caused already a partially racemized helicene product. Therefore we decided to reduce the racemization risk by synthesizing the compounds **11** and **12** first as racemic mixture and subsequently performing the chromatographic separation of the enantiomers.^[67] Using the same C–H borylation/bromination strategy as for the synthesis of (±)-**7** (see above), the axially chiral bromide (±)-**8** was obtained as racemate in a yield of 54% (Scheme 3).

WILEY-VCH



Scheme 3. Preparation of the enantiopure azabora[5]helicenes 11 and 12 in their M and P forms. The inset shows the ORTEP diagram of (±)-11. The thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N2–B2 1.666(3), C55–B2 1.612(3), N2–C45–C54–C55 21.0, C46–C45–C54–C63 30.0. Although only the P-11 enantiomer is displayed, the unit cell contains both enantiomers (see CIF file).

However, in the case of the preparation of the NMe₂derivative (\pm)-**9** a partial demethylation reaction was observed, and therefore, an optimization of the bromination conditions was required (Scheme 3). Thus, reducing the amount of CuBr₂ to 1 equiv. and limiting the reaction time (see Supporting Information), the desired bromide (\pm)-**9** was obtained in 46% yield together with the formation of the partially demethylated product (\pm)-**9'** in 24% yield. The undesired (\pm)-**9'** was selectively transformed into (±)-9 by a reductive amination using paraformaldehyde/NaBH₄ and 2,2,2-trifluoroethanol (TFE) as the solvent (Scheme 3).^[68] The subsequent lithiation-borylation sequence of the bromides (±)-8 and (±)-9 afforded the racemic helicenes (±)-11 and (±)-12, respectively, in moderate yields (49% and 54%, respectively). Crystals of (±)-11 of sufficient quality for single-crystal X-ray analysis were obtained. The crystal structure (inset Scheme 3)^[69] evidenced the helical chirality of the compound. A more

WILEY-VCH

distorted and bent structure (dihedral angles: N2-C45-C54-C55 21.0°, C46-C45-C54-C63 30.0°) than the previously crystallized N,C-chelate^[9] without substitution at the 8-position (dihedral angles: N1-C1-C10-C11 16.8°, C2-C1-C10-C19 27.7°) was notorious. The helicene racemates were resolved into the enantiopure forms by semipreparative CSP-HPLC separation, and the absolute configurations were first assigned by comparison of the optical rotation ($[\alpha]^{20}{}_{\rm D}$ –96.8° for *P*-**11** and +94.8° for *M*-**11**, *c* 0.05 in CHCl₃; $[\alpha]^{20}{}_{\rm D}$ –72.7° for *P*-**12** and +70.2° for *M*-**12**, c 0.1 in CHCl₃) with that of the previously assigned *P*-**10** ($[\alpha]^{20}{}_{\rm D}$ –106.4°; *c* 0.1 in CHCl₃). This assignment was further confirmed by the correspondence of experimental and calculated ECD spectra; see Supporting Information.

Table 1. Photophysical properties of the dyes 10–12 in aerated solutions.										
	λ _{abs,max} (nm) ^[a] [ε (M ⁻¹ cm ⁻¹)]	λ _{fluo,max} (nm) ^[b]	Δv (cm ⁻¹) ^[c]	$\Phi_{fluo}^{[d]}$	τ _{fluo} (ns) ^[e]	$10^7 \times k_r (s^{-1})^{[f]}$	$10^7 x k_{nr} (s^{-1})^{[g]}$			
Toluene										
10	414 [8200]	495	4000	0.29	4.8 (89%)	6.0	15			
11	420 [7400]	502	3900	0.30	7.7 (81%)	3.9	9.1			
12	433 [4000]	586	6000	0.13	19.9 (86%)	0.65	4.4			
Acetonitrile										
10	411 [7600]	499	4300	0.28	6.4 (85%)	4.4	11			
11	418 [7000]	510	4300	0.29	9.9 (92%)	2.9	7.2			
12	430 [3400]	~680 ^[h]	8500	<0.005	[1]					

[a] UV/vis absorption maximum of the long-wavelength band (>400 nm). In square brackets the corresponding molar absorption coefficients are provided. [b] Maximum of the fluorescence emission. [c] Stokes shift. [d] Fluorescence quantum vield, error 20%, Measured by the relative method against quinine sulfate as standard or using 4-amino-N-propyl-1,8naphthalimide as secondary reference (for 12); see Experimental Section. [e] Fluorescence lifetime, error 5%. Only the main decay component is given (weight in parenthesis). [f] Radiative decay rate constant; k_r = Φ_{fluo}/τ_{fluo} . [g] Non-radiative decay rate constant; $k_{nr} = (1-\Phi_{fluo})/\tau_{fluo}$. [h] The dye, that was purified with the greatest care, showed a small fluorescence signal (at 500 nm) of a very minor impurity (not detectable in CSP-HPLC; see Supporting Information). This signal was safely discarded based on its non-matching excitation spectrum. Excitation at the red edge of the absorption spectrum yields the undisturbed observation of a very broad emission at ca. 680 nm (see Supporting information), having an excitation spectrum that matches the absorption spectrum of 12. [i] Not determined due to very low fluorescence.

UV/vis-Absorption and Fluorescence Spectroscopy

The photophysical properties of the dyes were determined in toluene and in acetonitrile solution, using UV/Vis-absorption spectroscopy, fluorescence spectroscopy, and time-resolved single-photon counting. This yielded insights into the electronic structure of the investigated azaborahelicene dyes. The key data are summarized in Table 1 and spectra are shown in Figure 2. The dyes **10** and **11** show a typical long-wavelength absorption

band at λ > 400 nm, that has been already seen for the analogous dye that lacks the additional phenyl substitution at the 8-position of the naphthalene.^[9] However, in the case of dye **12** this band is just observed as a shoulder and with a smaller molar absorption coefficient. In both solvents a red-shift of this band is noted with increasing electron-donor strength of the phenyl substituent, *i.e.*, $\Delta\lambda$ = 19 nm for **12** versus **10**. Even more significant is the substituent effect on the fluorescence emission. While a small red-shift of the emission maximum is observed for the introduction of the OMe substituent, i.e., $\Delta\lambda = 7-11$ nm for **11** versus 10 in both solvents, the stronger electron-donating NMe₂ substituent in dye 12 has a dramatic effect. For the latter dye a further red-shifted (λ_{max} = 586 nm) and considerably broadened emission band was noted in toluene ($\Delta\lambda$ = 91 nm for 12 versus 10). In the more polar acetonitrile dye 12 is only very weakly fluorescent, showing a very broad band with a maximum at ca. 680 nm. The Stokes shifts are elevated (ca. 4000 cm⁻¹ for 10 and 11 and ca. 6000-8500 cm⁻¹ for 12), corroborating the involvement of charge-transfer phenomena in the photophysical properties of the helicenes.



Figure 2. UV/vis-absorption and fluorescence spectra of the helicenes 10 (top), 11 (middle), and 12 (bottom) in aerated toluene solution. The dye concentration was *ca.* $10-30 \ \mu$ M.

The fluorescence quantum yield is *ca.* 0.3 for the azabora[5]helicene dyes **10** and **11** in toluene and in acetonitrile. For dye **12** this value is somewhat lower in toluene ($\Phi_{fluo} = 0.13$), but still maintained at a significant level. However, such drop is not unexpected for charge-transfer fluorophores such as **12**, resulting from a more efficient non-radiative deactivation (*e.g.*, internal conversion, reverse charge transfer) of energetically lower lying emissive states. This observation is often referred to as energy-gap law.^[9-11] Directly related is the observation that in the polar acetonitrile the charge-transfer state seems energetically stabilized to such extent that only a very weak and further red-shifted emission is observed for **12**. For the dyes **10** and **11** the fluorescence lifetimes were determined as *ca.* 4.8–7.7 ns in toluene and *ca.* 6.4–9.9 ns in acetonitrile, being

longest for dye **11** in both solvents (see Table 1). However, for **12** a remarkably long lifetime of 19.9 ns as main component of the decay trace was found in toluene. For further insight the radiative (k_r) and non-radiative (k_{nr}) decay rate constants were calculated (Table 1). As expected for a fluorescence quantum yield much smaller than 1, the non-radiative decay has a substantial contribution. The ratio k_{nr}/k_r for **10** and **11** is comparable (*ca.* 2.3–2.5), but dye **12** stands out with a much more dominant non-radiative decay ($k_{nr}/k_r = 6.8$). The thermodynamically more favorable charge-transfer in **12** lowers the energy of the emissive state and the energy-gap law

promotes the excited-state decay via non-radiative channels.

15 20 30 15 10 20 10 10 5 Δε (M⁻¹cm⁻¹) 5 0 0 0 -5 -5 -10 -10 -20 -10 -15 -20 -15 400 500 500 400 500 300 300 400 300 λ (nm) λ (nm) λ (nm)

Figure 3. ECD spectra of 10 (left), 11 (middle), and 12 (right) in aerated toluene solution. The dye concentration was *ca.* $250-400 \mu$ M (see Experimental Section). The red spectra correspond to the *P*-isomer and the black spectra to the *M*-isomer.

Chiroptical Spectroscopy

The separated M- and P-enantiomers were submitted to electronic circular dichroism (ECD) spectroscopy in toluene. Both dyes show nearly perfect mirror-imaged Cotton effects for the two enantiomeric forms (see Figure 3). Hence, the ECD spectra will be discussed in the following only for one of the enantiomers (M-form). M-10 has positive bands at 298 nm ($\Delta \epsilon$ = 11 $M^{-1}cm^{-1}$) and at 430 nm ($\Delta \epsilon$ = 5 $M^{-1}cm^{-1}$) and a negative band at 317 nm ($\Delta \epsilon$ = -8 M⁻¹cm⁻¹). This translates to a dissymmetry factor of $|g_{abs}| = 7 \times 10^{-4}$ for the longest wavelength ECD band (430 nm). For helicene M-11 positive bands at 298 nm ($\Delta \epsilon$ = 18 M⁻¹cm⁻¹) and at 347 nm ($\Delta \epsilon$ = 8 M⁻¹cm⁻¹) and a negative band at 320 nm ($\Delta \varepsilon = -8 \text{ M}^{-1} \text{cm}^{-1}$) were observed. At 452 nm a very weak negative band was seen ($\Delta \varepsilon$ *ca*. 1 M⁻¹cm⁻¹). The $|g_{abs}|$ value for the ECD maximum at 347 nm is 1.1×10^{-3} , while for 452 nm the corresponding value is 5.6×10^{-4} . Finally, for *M*-12 positive bands at 303 nm ($\Delta \epsilon = 28 \text{ M}^{-1} \text{ cm}^{-1}$) and 392 nm ($\Delta \epsilon$ = 13 M⁻¹cm⁻¹) as well as a negative band at 458 nm ($\Delta \epsilon$ = $-6 \text{ M}^{-1}\text{cm}^{-1}$) were observed. The dissymmetry factor for the first transition is $|g_{abs}| = 2.0 \times 10^{-3}$ at 458 nm. The sign of the long-wavelength band, corresponding to the first transition, is inverted when comparing the ECD spectra of the corresponding enantiomers of **10** *versus* **11** or **12**. This switch of sign is confirmed by time-dependent density-functional theory (TD-DFT) calculations of the rotational strength, as will be discussed below.



Drawing on the significant emission of the herein investigated helicenes the measurement of circularly polarized luminescence (CPL) was attempted; see Figure 4. Dye 10 showed nearly mirror-imaged CPL spectra for the two enantiomers, peaking at ca. 480 nm. Besides, a small band at ca. 540 nm was detected. While an artifact is safely excluded (see measurement conditions in Experimental Section), the origin of this band is not entirely clear. The dissymmetry factor was determined as $|g_{lum}| = 2.5 \times 10^{-4}$. The OMe-substituted **11** showed a stronger CPL spectrum with a maximum at 500 nm and a dissymmetry factor of $|g_{lum}| = 9.5 \times 10^{-4}$. In accordance with the conventional emission spectroscopic measurements, dye 12 showed strongly red-shifted CPL signals with a maximum at about 590 nm. The dissymmetry factor |g_{lum}| reaches a value of 3.5×10^{-3} . Recently, it was shown for distorted helical Bodipy architectures that an increase of charge-transfer character of the emitting state yields higher dissymmetry factors as a consequence of a reduced electric transition dipole moment. $^{\left[64\right] }$ We find this theoretically expected relation nicely confirmed in the herein investigated dye series, spanning |g_{lum}| values of about one order of magnitude when comparing 10 and 12.

Interesting is the comparison between the herein observed values of the dissymmetry factors with those of other helicenes and helicenoids.^[32] The g_{abs} factors are well in the range of those observed for small [*n*]helicenes (n = 4–6). The same can be affirmed for the g_{lum} factors of **10** and **11**, while the value for **12** is higher than usually observed for this class of CPL-SOM. Recently, the correlation of both g factors for the most common



ARTICLE

CPL-SOM architectures was investigated.^[32] The ratio g_{lum}/g_{abs} for **10** is 0.36. This is in accordance with the observation for other [4]- and [5]-helicenes. The same ratio for **11** and **12** is 1.70 and 1.75, respectively, being clearly outliers in the g_{abs} - g_{lum} plot (see Supporting Information). In the first case (dye **11**) the high ratio is due to the very weak ECD band for the lowest energy transition at 452 nm. For **12** a more accentuated change of electronic structure upon excitation, being in line with the comparably more pronounced charge-transfer character of the dye, is held responsible for the observation.

In accordance with the observations made for the first transition band in the ECD spectrum, the signs of the CPL emission band of the corresponding enantiomers are inverted for **10** *versus* **11** or **12**. Further, the sign of the long-wavelength ECD band coincides with the sign of the CPL signal. This would be expected for the case that the lowest-energy absorption transition and emission are corresponding^[70] and similar observations were made for other helicenes.^[48, 71] In the case of charge-transfer fluorophores this relation is not *ad hoc* expected, because the excited state that is populated by absorption and the emissive state are significantly different (as expressed by the rather large Stokes shift, see Table 1). However, for the herein investigated dyes the chiroptical properties seem conserved in going from the ground- to the excited-state, yielding correspondence of the first-transition ECD and CPL signs.

Table 2. TD-DFT calculated absorption and emission energies (ΔE), dipole strength (D), rotational strength (R), and angle formed by electric (E) and magnetic transition moments (M) of the principal conformers in their ground state and in their first excited singlet state.

Conformation [weight %] ^[a]	∆E _{calc} (eV)	∆E _{exp} (eV)	D (10 ⁻⁴⁰ esu ² cm ²)	R (10 ⁻⁴⁴ esu ² cm ²)	E-M angle (º)
Ground state					
10 a [97]	3.35 (S₁←S₀)	2.99	146045	18.24	84
11 a [58]	3.30 (S₁←S₀)	2.95	133666	-16.19	96
11 b [39]	3.31 (S₁←S₀)	2.95	135995	-2.15	91
12 a [97]	3.19 (S₁←S₀)	2.86	91810	-50.32	114
Excited state					
1 0 a	2.69 (S₁→S₀)	2.50	183491	13.89	87
11 a	2.63 (S ₁ →S ₀)	2.47	161906	-31.19	97
11 b	2.65 (S₁→S₀)	2.47	168502	-11.09	92
12 a	2.60 (S ₁ →S ₀)	2.12	66611	-75.97	129

[a] The weight of the main conformations in the ground state is given in parentheses. See structures of conformations in Figure 5 (for helicene **10**) and in the Supporting Information (for **11** and **12**). Similar conformations with respect to the mesitylene groups were observed for all dyes. In the case of **11**, two conformers are given, differing by the orientation of the OMe group. All calculations were done for the *M*-isomer.

Density-Functional Theory Calculations

Taking into account the rotational flexibility of the mesitylene rings and in order to shine more light on the chiroptically active conformations of the investigated azabora[5]helicene dyes, density-functional theory (DFT) and time-dependent densityfunctional theory (TD-DFT) calculations at the cam-B3LYP/def2SVP level of theory were performed. For dye 10 two different conformers were found, which differ in the relative orientation of the mesitylene groups (see Figure 5 for M-10). The energetically most stable conformation (10a, Figure 5) is the main contributor (97%). Dye 11 presents additional conformational freedom through the rotation of the OMe group. However, the resulting conformers show only minor energetic differentiation (0.2 kcal mol⁻¹). The main conformations of helicene 11 (see 11a and 11b in the Supporting Information), considering the relative orientation of the mesitylene groups. contribute with a total of 97%. Noteworthy, the mesitylene groups orient in a very similar way as for 10a. The same dominant conformation (97%) is also present for compound 12 (see structure **12**a in the Supporting Information). In consequence, the main conformers present nearly superimposable structures for the three compounds (see Supporting Information). However, it is noticeable that the ECD spectra are quite different. In all cases, the calculated ECD spectra, obtained by Boltzmann averaging the contributions of the individual conformers, reproduce very well the experimentally observed spectra of the three helicenes (see Supporting Information).



Figure 5. Conformations of helicene 10 (*M*-isomer). The conformer on the left is the main contributor (97%). Note that the two conformers only differ in the orientation of the two mesitylene units. Similar conformations with respect to the mesitylene groups were observed for the helicenes 11 and 12 (see Supporting Information).

The frontier orbitals for the most stable conformations of the dyes **10–12** (see above) were calculated in the ground state (see Figure 6 for the *M*-isomers). The HOMO orbital of the three dyes presents some significant differences. While this orbital is mainly localized on one of the mesitylene groups in the case of **10**, it is partially delocalized from the mesitylene towards the phenyl-OMe in **11** and dominantly located at the phenyl-NMe₂ moiety in **12**. Hence, the HOMO localization follows the electrondonor capacity of the phenyl residue, clearly supporting the charge-transfer character of the dyes, especially of **11** and **12**. However, the LUMO of all three dyes is always localized on the

helicene backbone. The calculated $S_1 {\leftarrow} S_0$ transition energy follows nicely the trend of the absorption maxima of the helicenes, see Table 2.

To gain additional insight into the origin of the changes of the chiroptical properties upon substitution, particularly considering the change in sign of the first ECD transition of dye 10 versus dye 11 or 12, the dipole (D) and rotational strengths (R) for the *M*-isomers of each dye were calculated (see Table 2). The first transition for dye M-10 involves a positive rotational strength, in agreement with the experimental observations made by ECD spectroscopy. On the contrary, for dye M-11 the rotational strength of the first transition adopts negative values, which is again in strict agreement with the experiment. As noted above, in case of dye M-11 the ECD band corresponding to the first transition is very weak and calculations show that the sign of the rotational strength is "non-robust", i.e., different functionals lead to a "toggling" of the sign. This is reflected also by the fact that electric dipole (E) and magnetic dipole transition moments (M) are nearly perpendicular one to another (see Table 2), a situation similar to that observed for other simple helicenes.^[48, 71]. Finally, dye M-12 presents a strong ECD band corresponding to the first transition, which matches the calculated quite intense negative rotational strength.



Figure 6. Contour plots of the frontier orbitals, HOMO (bottom) and LUMO (top), of the helicenes 10, 11, and 12. Note that the *M*-isomer is shown.

The three compounds have been optimized also in their first excited state at the same level of theory as adopted for ground state (cam-B3LYP/def2SVP). Structural information is reported in Supporting Information also showing graphically how the different structures superimpose. The excited-state geometry differs from the ground state structure for both compounds **10** and **11**, but it is on the contrary quite similar for compound **12**. The calculated rotational strengths reproduce the observed CPL results, especially the experimentally observed switch in sign for the corresponding enantiomers of **10** *versus* **11** or **12** (see Table 2). Regarding the frontier orbitals that are involved in the emissive $S_1 \rightarrow S_0$ transition (see contour plots in the Supporting Information), one can observe that the LUMO orbitals are very similar to the orbitals calculated for the ground state. Some

differences are observed concerning the HOMO orbitals: in particular for **10** and **11** the HOMO orbital calculated in the excited-state geometry is less delocalized on the mesitylene groups and involves only the helicene moiety and the phenyl or substituted phenyl group. Especially pronounced differences are observed for compound **11** for which the (negative) rotational strength is significantly enhanced in the excited state in comparison to ground state; this is reflected also by the observation that the angle between the electric and magnetic transition moment is further deviated from 90° (Table 2). At the bottom line this allows us to explain the intense CPL signal of **11**, despite the low rotational strength of the first transition, observed in ECD spectroscopy.

Conclusions

Conveniently modified four-coordinate organoboron N,Cchelates with an arylisoquinoline backbone can be separated into their enantiomeric azabora[5]helicenes. Some of these new dyes show intense CPL emission with significant dissymmetry g factors. The CPL can be spectrally fine tuned by drawing on the charge-transfer character of the emissive state. Hence, the variation of the electron-donating substituents enables the observation of efficient CPL above 500 nm or even provides a means to obtain CPL signals close to 600 nm in the case of helicene **12**. The different substituent effects on the sign of the ECD and CPL spectra can be rationalized by TD-DFT calculations. The fruitful combination of charge-transfer effects and chiroptical properties provide an approach for the tailored design of SOM-CPL architectures.

Experimental Section

Materials. The details of the synthetic procedures of the helicenes 10-12 (see Schemes 1–3) and their precursors as well as the analytical characterization data can be found in the Supporting Information.

Optical Spectroscopy. Conventional absorption and fluorescence measurements were done on aerated acetonitrile or toluene solutions of the compounds (10-20 $\mu\text{M},$ assuring that the absorbance at the excitation wavelength did not exceed 0.2) in guartz cuvettes of 1 cm optical pathlength. The UV/Vis-absorption spectra were registered with a UVPC-1603 spectrometer (Shimadzu), Steady-state fluorescence spectra were obtained with a standard fluorimeter (Varian Cary Eclipse) with a pulsed Xe lamp. The samples were excited by irradiating into the longest wavelength absorption band of the dyes. The fluorescence quantum yields of 10 and 11 are referenced against quinine sulfate in 0.05 M H₂SO₄ ($\Phi_{fluo} = 0.55$) as standard,^[72, 73] while dye **12** was measured against 4-amino-N-propyl-1,8-naphthalimide (Φ_{fluo} = 0.48 in acetonitrile).^[11] The emission lifetimes were measured by means of timecorrelated single-photon-counting with a FS920 fluorescence equipment from Edinburgh Instruments. A picosecond pulsed diode laser was used employed as excitation source (EPL-445: λ_{exc}= 442.2 nm, pulse width 78.3 ps) and the fitting of the kinetic decay traces was done by deconvolution from the instrument response function.

Identical solutions in toluene contained in guartz cuvettes of 2 mm optical pathlength were used first for ECD and then for CPL measurements. adopting concentrations of 0.25 mM, 0.3 mM, and 0.4 mM for 10, 11, and 12, respectively. Aggregation effects at these concentrations were excluded based on the fact that the ECD spectra matched those measured in diluted solutions (down to 10-20 μ M). A Jasco 815SE spectropolarimeter was employed for ECD measurements (time constant = 2 s, monochromator velocity 100 nm/min). For CPL we used a homemade instrument as described in previous works;[74, 75] the excitation radiation was brought to the cell from a Jasco FP8200 fluorimeter through an optical fiber containing water. An excitation wavelength of 440 nm was used for 10, 420 nm for 11, and 475 nm for 12. A 90°-scattering geometry was chosen, excitation with light polarized along the direction of collection of the emitted light was essential to avoid linearly polarized contributions;^[75] 8 scans were taken for compound 10 and 5 scans for compound 11 and 12.

Computational Methods. Density Functional Theory (DFT) calculations have been carried out with the Gaussian16 quantum chemistry code.^[76] Molecular structures have been optimized in their ground state and first excited state (by DFT and TD-DFT calculations) at the cam-B3LYP/def2SVP level of theory.^[77, 78] The transition energies, dipole strengths, and rotational strengths have been calculated by using TD-DFT (70 states have been considered for the calculations). A constant bandwidth of 0.2 eV was applied to each transition.

Acknowledgements

This work was financially supported by the Spanish Ministry of Economy, Industry, and Competitiveness (CTQ2014-54729-C2-1-P for U.P., CTQ2013-48164-C2-1-P, CTQ2013-48164-C2-2-P for A.R., Ramon y Cajal contract RYC-2013-12585 for A.R., PhD fellowship BES-2015-074458 for Z.D.), the ERDF, the Junta de Andalucía (2012/FQM-2140 for U.P. and 2012/FQM-1078 for A.R.), Fondazione Cariplo and Regione Lombardia (Big&Open Data Innovation Laboratory, BODal-Lab, University of Brescia). We further acknowledge the use of computer and software facilities at CINECA - Via Magnanelli 6/3 40033 - Casalecchio di Reno (Bologna), Italy. A.R. thanks Prof. J. M. Lassaletta (CSIC, Univ. Seville) and Prof. R. Fernández (Univ. Seville) for their continuous support and helpful discussions.

Keywords: boron • helicene • push-pull chromophores • circular dichroism • circularly polarized luminescence

- [1] A. Loudet, K. Burgess, Chem. Rev. 2007, 107, 4891-4932.
- [2] G. Ulrich, R. Ziessel, A. Harriman, Angew. Chem. Int. Ed. 2008, 47, 1184-1201.
- [3] D. Frath, J. Massue, G. Ulrich, R. Ziessel, Angew. Chem. Int. Ed. 2014, 53, 2290-2310.
- [4] Q. Zheng, G. Xu, P. N. Prasad, Chem. Eur. J. 2008, 14, 5812-5819.
- [5] S. Zhang, T. Wu, J. Fan, Z. Li, N. Jiang, J. Wang, B. Dou, S. Sun, F. Song,
- X. Peng, Org. Biomol. Chem. 2013, 11, 555-558. [6] X. Zhang, Y. Xiao, J. Qi, J. Qu, B. Kim, X. Yue, K. D. Belfield, J. Org. Chem. 2013, 78, 9153-9160.
- [7] S. Kolemen, M. Isık, G. M. Kim, D. Kim, H. Geng, M. Buyuktemiz, T. Karatas, X.-F. Zhang, Y. Dede, J. Yoon, E. U. Akkaya, Angew. Chem. Int. Ed. 2015, 54, 5340-5344.
- [8] T. Kowada, H. Maeda, K. Kikuchi, Chem. Soc. Rev. 2015, 44, 4953-4972.

[9] V. F. Pais, M. M. Alcaide, R. López-Rodríguez, D. Collado, F. Nájera, E. Pérez-Inestrosa, E. Álvarez, J. M. Lassaletta, R. Fernández, A. Ros, U. Pischel, Chem. Eur. J. 2015, 21, 15369-15376.

[10] V. F. Pais, P. Ramírez-López, A. Romero-Arenas, D. Collado, F. Nájera, E. Pérez-Inestrosa, R. Fernández, J. M. Lassaletta, A. Ros, U. Pischel, J. Org. Chem. 2016. 81. 9605-9611.

[11] F. M. F. Santos, J. N. Rosa, N. R. Candeias, C. Parente Carvalho, A. I. Matos, A. E. Ventura, H. F. Florindo, L. C. Silva, U. Pischel, P. M. P. Gois, Chem. Eur. J. 2016, 22, 1631-1637.

[12] D. Frath, P. Didier, Y. Mély, J. Massue, G. Ulrich, ChemPhotoChem 2017, 1. 109-112.

[13] A. Coskun, E. U. Akkaya, J. Am. Chem. Soc. 2006, 128, 14474-14475.

[14] S. O. McDonnell, D. F. O'Shea, Org. Lett. 2006, 8, 3493-3496.

[15] O. A. Bozdemir, R. Guliyev, O. Buyukcakir, S. Selcuk, S. Kolemen, G. Gulseren, T. Nalbantoglu, H. Boyaci, E. U. Akkaya, J. Am. Chem. Soc. 2010, 132, 8029-8036.

[16] L.-Y. Niu, Y.-S. Guan, Y.-Z. Chen, L.-Z. Wu, C.-H. Tung, Q.-Z. Yang, J. Am. Chem. Soc. 2012, 134, 18928-18931

[17] S. Erbas-Cakmak, O. A. Bozdemir, Y. Cakmak, E. U. Akkaya, Chem. Sci. 2013, 4, 858-862.

[18] Y.-L. Rao, S. Wang, Inorg. Chem. 2011, 50, 12263-12274.

[19] Y.-L. Rao, H. Amarne, S.-B. Zhao, T. M. McCormick, S. Martić, Y. Sun, R.-Y. Wang, S. Wang, J. Am. Chem. Soc. 2008, 130, 12898-12900.

[20] H. Amarne, C. Baik, S. K. Murphy, S. Wang, Chem. Eur. J. 2010, 16, 4750-4761.

[21] D. Frath, A. Poirel, G. Ulrich, A. De Nicola, R. Ziessel, Chem. Commun. 2013, 49, 4908-4910.

[22] H. Lu, J. Mack, Y. Yang, Z. Shen, Chem. Soc. Rev. 2014, 43, 4778-4823. [23] S. P. J. T. Bachollet, D. Volz, B. Fiser, S. Münch, F. Rönicke, J. Carrillo, H. Adams, U. Schepers, E. Gómez-Bengoa, S. Bräse, J. P. A. Harrity, Chem. Eur. J. 2016, 22, 12430-12438.

[24] S. K. Mellerup, K. Yuan, C. Nguyen, Z.-H. Lu, S. Wang, Chem. Eur. J. 2016, 22, 12464-12472.

[25] M. M. Alcaide, F. M. F. Santos, V. F. Pais, J. I. Carvalho, D. Collado, E. Pérez-Inestrosa, J. F. Arteaga, F. Boscá, P. M. P. Gois, U. Pischel, J. Org. Chem. 2017, 82, 7151-7158.

[26] J. H. Golden, J. W. Facendola, D. Sylvinson M. R., C. Quintana Baez, P. I. Djurovich, M. E. Thompson, J. Org. Chem. 2017, 82, 7215-7222.

[27] M. Urban, K. Durka, P. Jankowski, J. Serwatowski, S. Luliński, J. Org. Chem. 2017, 82, 8234-8241.

[28] F. Boscá, M. C. Cuquerella, V. F. Pais, A. Ros, U. Pischel, ChemPhotoChem 2018, 2, 34-41.

[29] J. Kumar, T. Nakashima, T. Kawai, J. Phys. Chem. Lett. 2015, 6, 3445-3452.

[30] E. M. Sánchez-Carnerero, A. R. Agarrabeitia, F. Moreno, B. L. Maroto, G.

Muller, M. J. Ortiz, S. de la Moya, Chem. Eur. J. 2015, 21, 13488-13500. [31] G. Longhi, E. Castiglioni, J. Koshoubu, G. Mazzeo, S. Abbate, Chirality 2016, 28, 696-707.

[32] H. Tanaka, Y. Inoue, T. Mori, ChemPhotoChem 2018, 2, 386-402. [33] K. E. S. Phillips, T. J. Katz, S. Jockusch, A. J. Lovinger, N. J. Turro, J. Am. Chem. Soc. 2001, 123, 11899-11907.

[34] T. Kaseyama, S. Furumi, X. Zhang, K. Tanaka, M. Takeuchi, Angew. Chem. Int. Ed. 2011, 50, 3684-3687.

[35] T. Ikeda, T. Masuda, T. Hirao, J. Yuasa, H. Tsumatori, T. Kawai, T. Haino, Chem. Commun. 2012, 48, 6025-6027.

[36] F. Li, Y. Li, G. Wei, Y. Wang, S. Li, Y. Cheng, Chem. Eur. J. 2016, 22, 12910-12915.

[37] S. P. Morcillo, D. Miguel, L. Álvarez de Cienfuegos, J. Justicia, S. Abbate, E. Castiglioni, C. Bour, M. Ribagorda, D. J. Cárdenas, J. M. Paredes, L. Crovetto, D. Choquesillo-Lazarte, A. J. Mota, M. C. Carreño, G. Longhi, J. M. Cuerva, Chem. Sci. 2016, 7, 5663-5670.

[38] R. Aoki, R. Toyoda, J. F. Kögel, R. Sakamoto, J. Kumar, Y. Kitagawa, K. Harano, T. Kawai, H. Nishihara, J. Am. Chem. Soc. 2017, 139, 16024-16027. [39] M. Toyoda, Y. Imai, T. Mori, J. Phys. Chem. Lett. 2017, 8, 42-48.

[40] C. M. Cruz, I. R. Márquez, I. F. A. Mariz, V. Blanco, C. Sánchez-Sánchez, J. M. Sobrado, J. A. Martín-Gago, J. M. Cuerva, E. Maçôas, A. G. Campaña, Chem. Sci. 2018, 9, 3917-3924.

[41] H. Maeda, Y. Bando, K. Shimomura, I. Yamada, M. Naito, K. Nobusawa, H. Tsumatori, T. Kawai, J. Am. Chem. Soc. 2011, 133, 9266-9269.

[42] H. Maeda, T. Shirai, Y. Bando, K. Takaishi, M. Uchiyama, A. Muranaka, T. Kawai, M. Naito, Org. Lett. 2013, 15, 6006-6009.

[43] N. Saleh, B. Moore II, M. Srebro, N. Vanthuyne, L. Toupet, J. A. G. Williams, C. Roussel, K. K. Deol, G. Muller, J. Autschbach, J. Crassous, *Chem. Eur. J.* 2015, *21*, 1673-1681.

[44] M. Nakamura, J. Suzuki, F. Ota, T. Takada, K. Akagi, K. Yamana, Chem. Eur. J. 2016, 22, 9121-9124.

[45] J. Han, P. Duan, X. Li, M. Liu, J. Am. Chem. Soc. 2017, 139, 9783-9786.

[46] J. Jiménez, L. Cerdán, F. Moreno, B. L. Maroto, I. García-Moreno, J. L. Lunkley, G. Muller, S. de la Moya, *J. Phys. Chem. C* **2017**, *121*, 5287-5292.

[47] Y. Sawada, S. Furumi, A. Takai, M. Takeuchi, K. Noguchi, K. Tanaka, J. Am. Chem. Soc. 2012, 134, 4080-4083.

[48] S. Abbate, G. Longhi, F. Lebon, E. Castiglioni, S. Superchi, L. Pisani, F. Fontana, F. Torricelli, T. Caronna, C. Villani, R. Sabia, M. Tommasini, A. Lucotti, D. Mendola, A. Mele, D. A. Lightner, *J. Phys. Chem. C* **2014**, *118*, 1682-1695.

[49] H. Sakai, S. Shinto, J. Kumar, Y. Araki, T. Sakanoue, T. Takenobu, T. Wada, T. Kawai, T. Hasobe, *J. Phys. Chem. C* **2015**, *119*, 13937-13947.

[50] H. Oyama, M. Akiyama, K. Nakano, M. Naito, K. Nobusawa, K. Nozaki, Org. Lett. 2016, 18, 3654-3657.

[51] H. Sakai, T. Kubota, J. Yuasa, Y. Araki, T. Sakanoue, T. Takenobu, T. Wada, T. Kawai, T. Hasobe, *J. Phys. Chem. C* **2016**, *120*, 7860-7869.

[52] J. E. Field, G. Muller, J. P. Riehl, D. Venkataraman, J. Am. Chem. Soc. 2003, 125, 11808-11809.

[53] K. Nakamura, S. Furumi, M. Takeuchi, T. Shibuya, K. Tanaka, J. Am. Chem. Soc. 2014, 136, 5555-5558.

[54] J. Bosson, G. M. Labrador, S. Pascal, F.-A. Miannay, O. Yushchenko, H. Li, L. Bouffier, N. Sojic, R. C. Tovar, G. Muller, D. Jacquemin, A. D. Laurent, B. L. Guennic, E. Vauthey, J. Lacour, *Chem. Eur. J.* **2016**, *22*, 18394-18403.

 Guernino, E. Vadiney, J. Lacour, *Chem. Eur. J.* **2016**, *22*, 18394-18403.
[55] T. Otani, A. Tsuyuki, T. Iwachi, S. Someya, K. Tateno, H. Kawai, T. Saito, K. S. Kanyiva, T. Shibata, *Angew. Chem. Int. Ed.* **2017**, *56*, 3906-3910.

[56] Y. Yamamoto, H. Sakai, J. Yuasa, Y. Araki, T. Wada, T. Sakanoue, T. Takenobu, T. Kawai, T. Hasobe, *Chem. Eur. J.* 2016, *22*, 4263-4273.

[57] C. Shen, E. Anger, M. Srebro, N. Vanthuyne, K. K. Deol, T. D. Jefferson Jr., G. Muller, J. A. G. Williams, L. Toupet, C. Roussel, J. Autschbach, R. Réau, J. Crassous, *Chem. Sci.* **2014**, *5*, 1915-1927.

[58] J. R. Brandt, X. Wang, Y. Yang, A. J. Campbell, M. J. Fuchter, *J. Am. Chem. Soc.* **2016**, *138*, 9743-9746.

[59] E. M. Sánchez-Carnerero, F. Moreno, B. L. Maroto, A. R. Agarrabeitia, M. J. Ortiz, B. G. Vo, G. Muller, S. de la Moya, *J. Am. Chem. Soc.* **2014**, *136*, 3346-3349.

[60] R. B. Alnoman, S. Rihn, D. C. O'Connor, F. A. Black, B. Costello, P. G. Waddell, W. Clegg, R. D. Peacock, W. Herrebout, J. G. Knight, M. J. Hall, *Chem. Eur. J.* **2016**, *22*, 93-96.

[61] M. Saikawa, T. Nakamura, J. Uchida, M. Yamamura, T. Nabeshima, *Chem. Commun.* **2016**, *52*, 10727-10730.

[62] F. Zinna, T. Bruhn, C. A. Guido, J. Ahrens, M. Bröring, L. Di Bari, G. Pescitelli, *Chem. Eur. J.* **2016**, *22*, 16089-16098.

[63] C. Ray, E. M. Sánchez-Carnerero, F. Moreno, B. L. Maroto, A. R. Agarrabeitia, M. J. Ortiz, I. López-Arbeloa, J. Bañuelos, K. D. Cohovi, J. L. Lunkley, G. Muller, S. de la Moya, *Chem. Eur. J.* **2016**, *22*, 8805-8808.

[64] R. Clarke, K. L. Ho, A. A. Alsimaree, O. J. Woodford, P. G. Waddell, J. Bogaerts, W. Herrebout, J. G. Knight, R. Pal, T. J. Penfold, M. J. Hall, *ChemPhotoChem* **2017**, *1*, 513-517.

[65] C. Shen, M. Srebro-Hooper, M. Jean, N. Vanthuyne, L. Toupet, J. A. G. Williams, A. R. Torres, A. J. Riives, G. Muller, J. Autschbach, J. Crassous, *Chem. Eur. J.* **2017**, *23*, 407-418.

[66] A. Ros, B. Estepa, R. López-Rodríguez, E. Álvarez, R. Fernández, J. M. Lassaletta, *Angew. Chem. Int. Ed.* **2011**, *50*, 11724-11728.

[67] The stability of the enantiomers was tested for dye **12**. No racemization of an enantiopure sample in acetonitrile was observed by CSP-HPLC after standing for 18 hours at 25 °C in the dark.

[68] M. Tajbakhsh, R. Hosseinzadeh, H. Alinezhad, S. Ghahari, A. Heydari, S. Khaksar, Synthesis 2011, 490-496.

[69] Although the X-ray crystal structure in Scheme 3 only displays the *P*-11 enantiomer, the unit cell contains both enantiomers (see CIF files), since compound 11 was crystallized from a solution of the racemic mixture.

[70] H. P. J. M. Dekkers in Vol. Circular Dichroism: Principles and Applications Eds.: N. Berova, K. Nakanishi and R. W. Woody), John Wiley & Sons, New York, 2000, pp. 185-215.

[71] Y. Nakai, T. Mori, Y. Inoue, J. Phys. Chem. A 2013, 117, 83-93.

[72] W. H. Melhuish, J. Phys. Chem. 1960, 64, 762-764.

[73] W. H. Melhuish, J. Phys. Chem. 1961, 65, 229-235.

[74] E. Castiglioni, S. Abbate, G. Longhi, *Appl. Spectrosc.* **2010**, *64*, 1416-1419.

[75] E. Castiglioni, S. Abbate, F. Lebon, G. Longhi, *Methods Appl. Fluoresc.* 2014, 2, 024006.

[76] Gaussian 16, Revision A.03, M. J. Frisch et al., Gaussian, Inc., Wallingford CT, 2016.

[77] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* 2005, *7*, 3297-3305.
[78] T. Yanai, D. P. Tew, N. C. Handy, *Chem. Phys. Lett.* 2004, *393*, 51-57.

WILEY-VCH

Entry for the Table of Contents

ARTICLE

ARTICLE



A new twist! The dye family of borylated arylisoquinolines (BAI dyes) has new members. Enantiopure azabora[5]helicenes with varying charge-transfer character were prepared and their photophysical properties were determined. Spectrally variable and intense circularly polarized luminescence with high dissymmetry factors was observed. Further, the charge-transfer character of the dye determines the sign pattern of the chiroptical spectra.

Zoe Domínguez, Rocío López-Rodríguez, Eleuterio Álvarez, Sergio Abbate, Giovanna Longhi, * Uwe Pischel, * and Abel Ros*



Azabora[5]helicene Charge-Transfer Dyes Show Efficient and Spectrally Variable Circularly Polarized Luminescence