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Unprecedented induced axial chirality in a molecular BODIPY dye: strongly bisignated electronic circular dichroism in the visible region†

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Enantiomeric bis(BODIPYs) 1a and 1b exhibit strong bisignated ECD due to the formation of a stable helical conformation with induced axial chirality, which allows efficient exciton coupling of the BODIPY chromophores in the Vis region.

Axial chirality, which is observed in helical molecules, polymers and supramolecular polymers with non-superimposable left- and right-handed configurations or conformations, has been intensively studied during the last few years due to its significance in different fields such as asymmetric synthesis, optics (including nonlinear optics), electronics, sensors, liquid crystals, natural products or drug discovery.[1] Configurationally stable helical molecules having π-conjugated systems to allow efficient light absorption and emission (luminophores), such as helicenes or 1,1′-binaphthyls, are especially important due to their significant chiroptical properties, *i.e.*, optical rotation, circular dichroism (CD) or circularly polarized luminescence (CPL);[2] whereas configurationally labile π-conjugated helical molecules, such as bridged biphenyls or trityl propellers, have found a valuable application as chiroptical probes for the detection and quantification of enantiomers (chiral sensing).[3] On the other hand, some helical molecular and supramolecular systems based on 1,1′-binaphthyl and naphthalenediimide, respectively, have been reported as interesting CD sensors for valuable C_{60}.[4]

Boron dipyrromethene (BODIPY) dyes constitute one of the most important families of luminophores, due to their particular easily-tunable absorption and emission properties, as well as their processability properties due to high solubility and stability in many solvent systems.[5] The strong absorption and emission of the π-conjugated BODIPY system in the visible (Vis) region of the electromagnetic spectrum makes this system highly interesting for the development of valuable technological applications, such as chemosensors and probes, biological labels, dye lasers, photodynamic therapy agents, and a plethora of photonic devices, including solar-light harvesting antennae or solar cells.[6] Despite the important role that chirality can play in such technologies (due to its participation in key chiral-recognition phenomena or key chiral modulation of material morphologies and properties),[7] as well as in the development of new technologies based on chiroptical properties (*e.g.*, CPL-based sensing),[8] chiral BODIPYs are still scarce,[9] and the particularly interesting helical chiral BODIPYs are almost unexplored.

CD, mainly electronic CD (ECD), is the best way to investigate the formation of helices with induction of axial chirality.[2,10] Moreover, detection of a strongly bisignated ECD, *i.e.*, by showing a clear Cotton effect (CE), is interesting since it can be used as a response signal for the development of chiroptical sensors.[8,11] However, despite the strong absorption of the BODIPY chromophore in the Vis region, clearly bisignated ECDs have been only detected in the ultraviolet (UV) region for BODIPYs based on axially chiral 1,1′-binaphthyl units, where the CE is associated to the absorption of the inherently helical binaphthyls.[9b,h] On the other hand, the Vis CEs described so far for chiral BODIPYS are weak and strongly asymmetric (not clearly bisignated),[9b,d,f,h] suggesting poor helicity or inefficient exciton coupling of the BODIPY chromophore at best.

Herein we report the synthesis and chiroptics (optical rotation and ECD) of stereoisomeric bis(BODIPYs) **1** (Fig. 1), demonstrating the existence of a preferred helical conformation and configuration for **1a** and **1b**.

Bis(BODIPYs) **1a**, **1b** and **1c** (Fig. 1) were straightforwardly obtained from previously reported 3,5-dichloro-8-(4-methylphenyl)-*F*-BODIPY,[12a] by nucleophilic aromatic (BODIPY) substitution (Dehaen's methodology)[12] with (*R*,*R*)-, (*S*,*S*)- and *meso*-(*R*,*S*)-1,2-diphenyl-1,2-ethanodiamine (see Experimental section and Fig. S1 in ESI†). The corresponding mono(BODIPYs) **2a**, **2b** and (±)-**2c** (see Fig. S1 in ESI†), resulting from single mono *N*-arylation of the used diamines, were also obtained as side products. Diluted solutions ($\sim 10^{-6}$ M) of **1a** and **1b** exhibited giant optical rotations (see Fig. S2 in ESI†) and, more importantly, strong, clearly-bisignated and symmetric ECDs, with the CE cross point at a Vis wavelength (λ) value of 492 nm (Fig. 2).

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† Electronic supplementary information (ESI) available: Experimental section, Fig. S1–S8 and Table S1, as well as ^{1}H and ^{13}C NMR spectra of new compounds. See DOI: 10.1039/c3cc47570k

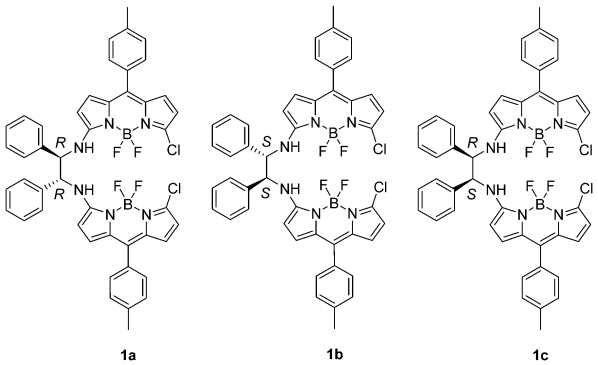

Fig. 1 Studied stereoisomeric bis(BODIPYs) **1**.

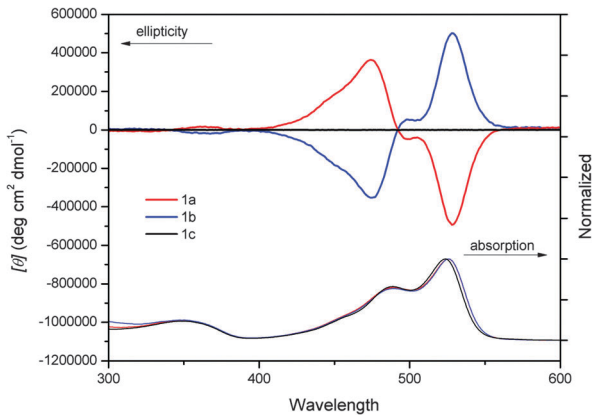

Fig. 2 ECD (above) and UV-Vis absorption (below) spectra of **1** (5.0×10^{-6} M in $CHCl_3$).

ECD was also observed at higher concentrations (up to $\sim 2 \times 10^{-5}$ M) without significant variation of shape and extrema λ (see Fig. S3 for **1a** in ESI†). The detected strong CE in the Vis region is undoubtedly associated to the absorption of the BODIPY chromophore (Fig. 2, and Table S1 in ESI†), as well as to a preferred helical conformation allowing efficient exciton coupling between the single BODIPY units located at the ends of the helix, as demonstrated below. In contrast, diastereomeric **1c** and mono(BODIPYs) **2** showed silent ECD (see Fig. 2 for **1c**).

Optical rotations of **1a** and **1b** were found to be strongly dependent on concentration (see Fig. S2 in ESI†), suggesting the existence of supramolecular aggregation. Hence, the observed bisignated ECDs for **1a** and **1b** could have originated due to the formation of a supramolecular polymeric helix with a preferred configuration for the chiral axis in each case, right-handed (*P*) or left-handed (*M*), induced by the own chirality (central chirality) of the involved monomers.[2d,h] In the case of *meso*-**1c**, the possible preferred supramolecular helix would be formed without any chiral amplification (deracemization),[13] giving rise to silent ECD, as it is actually observed. However, the hypothesis of supramolecular helices must be disregarded because highly-sensitive variable-concentration (VC) photoluminescence experiments (from 10^{-6} M to 10^{-3} M) carried out for **1b** did not show any relevant change (see Fig. S4 in ESI†). Moreover, variable temperature (VT) ECD experiments carried out for **1a** and **1c** (from 280 to 360 K, for diluted $\sim 4 \times 10^{-6}$ M solutions in 1,1,2,2-tetrachloroethane for a wider heating range) did not show either silent ECD for **1a** at a relatively high temperature (although molar ellipticity, [θ], decreases upon increasing the temperature, see Fig. S5 in ESI†), or ECD for **1c** at a relatively low temperature. All these experiments demonstrate that the studied chiral bis(BODIPYs) **1** act as single (non-interacting) molecules, at least at the diluted concentrations used for recording the ECDs. On the other hand, VC ^{1}H NMR experiments carried out for **1a** in a range of high concentrations (from 4.0×10^{-4} to 1.1×10^{-2} M in $CDCl_3$) showed very small variations in the chemical shift (up to 0.03 ppm), but always in the same direction: each mobile signal (amino and BODIPY-core protons) always shifted to a lower (or to a higher) field as the concentration changed (see Fig. S6 in ESI†). This result suggests weak supramolecular interactions at relatively high concentrations, and explains the observed dependence of the optical rotation on the concentration.

We have carried out a computational study of bis(BODIPYs) **1** (see Computational methods and Fig. S7 in ESI†) in order to support the formation of molecular helices with induced axial chirality for **1a** and **1b**, as well as the existence of exciton coupling between the BODIPY units located in such helices. The conducted calculations showed that **1a** and **1b** adopt a stable helical conformation (***h*1a** and ***h*1b**) with a preferred axial configuration avoiding sterical constraints: (*P*) for ***h*1a** and (*M*) for ***h*1b** (see Fig. 3 for **1a** and Fig. S7 in ESI†). Moreover, when the (*M*) configuration is tried to be optimized for ***h*1a**, or (*P*) for ***h*1b**, the helix becomes unstable and curls up, giving rise to a pleated new conformation (***p*1a** or ***p*1b**), where the exciton coupling of the BODIPY units must be deactivated by loss of axial chirality (silent-ECD conformations).‡ On the other hand, no helical conformation was computationally found for **1c**, and only the pleated conformation ***p*1c**, similar to ***p*1a** or ***p*1b**, was computed as stable (see Fig. S7 in ESI†).

The observed decrease of [θ] for **1a** upon heating (see Fig. S5 in ESI†) can be now explained by a loss of exciton-coupling efficiency due to an increase in the conformational mobility of ECD-active ***h*1a** (*i.e.*, loss of helicity). On the other hand, the computed preferred axial configurations for the helical conformations agree with the observed CE signs. Thus, according to the exciton chirality method,[10] a negative CE is predicted for **1a** due to preferred (*R*,*R*,*P*)-***h*1a**, while a positive CE is predicted for **1b** due to preferred (*S*,*S*,*M*)-***h*1b** (*cf.*, Fig. 2 and 3 for **1a**).

The performed computations also support the possibility of exciton coupling between the identical BODIPY chromophores

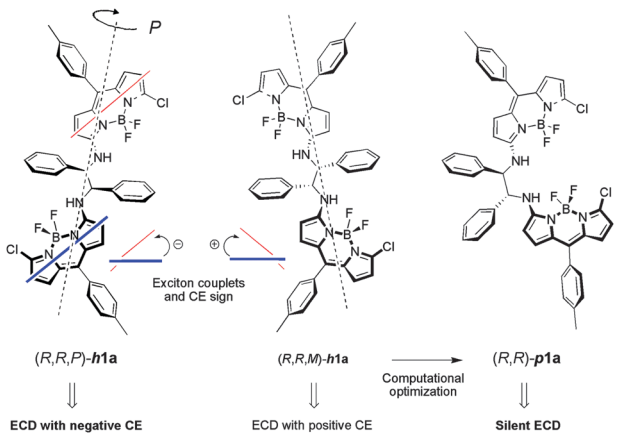

Fig. 3 Helical and pleated conformations of **1a**.

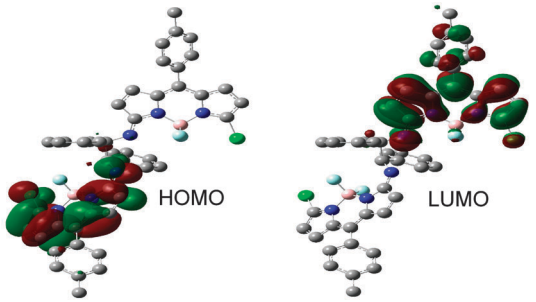

Fig. 4 Frontier molecular orbitals of (*R*,*R*,*P*)-***h*1a**.

of **1**, predicting that the observed Vis absorption of **1** is due to electron transfer from the HOMO to the LUMO, which are additionally located in different BODIPY units (see Fig. 4 for **1a**); *i.e.*, each BODIPY chromophore is at the same time active and passive toward the other (the perturber and the perturbed one).[10] This computational evidence agrees with the bathochromic shift of the absorption spectral bands of **1** with respect to **2** (see Fig. S8 and Table S1 in ESI†). The structure typology (bis(BODIPY) **1** instead of mono(BODIPY) **2**) was also found to influence the deactivation behaviour upon excitation, leading to a biexponential decay curve in the former compounds (see Table S1 in ESI†).§

In summary, we report and explain the ability of certain chiral, sterically hindered, and longitudinally spaced bis(BODIPYs) to adopt stable helical conformations with induction of axial chirality (centre-to-axial chirality transmission), thereby allowing efficient exciton coupling between identical BODIPY units by absorption of light in the Vis region. Further studies are now in progress to exploit the design of new helical chiral BODIPYs, as well as their possible applications in chiroptical technologies.

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Notes and references

‡ The mutual chiral orientation of the identical BODIPY chromophores imposed by the helical conformation is responsible for their efficient exciton coupling; *i.e.*, the axial chiral perturbation of the interacting chromophores, allowing large rotational strengths when the transition chromophore dipoles are interacting, must be higher than that exerted by its own chirality due to the existence of chiral centres (see ref. 10).
§ Asymmetrically-substituted BODIPY chromophore, BODIPY-amino phonon coupling broadening the spectral bands (ref. 12*b*) and free motion of the tolyl group enhancing non-radiative pathways (ref. 5*b*) determine the ground photophysical signatures of the studied luminophores.

1 (*a*) K. Watanabe, K. Suda and A. Kazuo, *J. Mater. Chem. C*, 2013, **1**, 2797–2805; (*b*) Y.-Y. Yin, Y.-L. Zhao, J.-G. Ma, X.-C. Cao and P. Cheng, *Inorg. Chem.*, 2013, **52**, 3738–3743; (*c*) Y. Si and G. Yang, *RSC Adv.*, 2013, **3**, 2241–2247; (*d*) L. Pu, *Acc. Chem. Res.*, 2012, **45**, 150–163; (*e*) S. R. LaPlante, L. D. Fader, K. R. Fandrick, D. R. Fandrick, O. Hucke, R. Kemper, S. P. F. Miller and P. J. Edwards, *J. Med. Chem.*, 2011, **54**, 7005–7022; **45**, 150–163; (*f*) S. Schenker, A. Zamfir, M. Freund and S. B. Tsogoeva, *Eur. J. Org. Chem.*, 2011, 2209–2222; (*g*) G. Bringmann, T. Gulder, T. A. M. Gulder and M. Breuning, *Chem. Rev.*, 2011, **111**, 563–639; (*h*) J. Wang and B. L. Feringa, *Science*, 2011, **101**, 1429–1432; (*i*) J. Chen and N. Takenata, *Chem.–Eur. J.*, 2009, **15**, 7268–7276; (*j*) N. Avarvari and J. D. Wallis, *J. Mater. Chem.*, 2009, **19**, 4061–4076.
2 (*a*) C. Eerdun, S. Hisanaga and J.-I. Setsune, *Angew. Chem., Int. Ed.*, 2013, **52**, 929–932; (*b*) H. Oyama, K. Nakano, T. Harada, R. Kuroda, M. Naito, K. Nobusawa and K. Nozaki, *Org. Lett.*, 2013, **15**, 2104–2107; (*c*) T. Suzuki, Y. Sakano, T. Iwai, S. Iwashita, Y. Miura, R. Katoono, H. Kawai, K. Fujiwara, Y. Tsuji and T. Fukushima, *Chem.–Eur. J.*, 2013, **19**, 117–123; (*d*) F. Aparicio, F. García and L. Sánchez, *Chem.–Eur. J.*, 2013, **19**, 3239–3248; (*e*) N. Fuentes, A. Martin-Lasanta, L. Alvarez de Cienfuegos, R. Robles, D. Choquesillo-Lazarte, J. M. García-Ruiz, L. Martínez-Fernández, I. Corral, M. Ribagorda, A. J. Mota, D. J. Cárdenas, M. C. Carreño and J. M. Cuerva, *Angew. Chem., Int. Ed.*, 2013, **51**, 13036–13040; (*f*) T. Suzuki, H. Tamaoki, K. Wada, R. Katoono, T. Nehira, H. Kawai and K. Fujiwara, *Chem. Commun.*, 2012, **48**, 2812–2814; (*g*) Y. Haketa, Y. Bando, K. Takaishi, M. Uchiyama, A. Muranaka, M. Naito, H. Shibaguchi, T. Kawai and H. Maeda, *Angew. Chem., Int. Ed.*, 2012, **51**, 7967–7971; (*h*) T. Ikeda, T. Masuda, T. Hirao, J. Yuasa, H. Tsumatori, T. Kawai and T. Haino, *Chem. Commun.*, 2012, **48**, 6025–6027; (*i*) J.-M. Suk, V. R. Naidu, X. Liu, M. S. Lah and K.-S. Jeong, *J. Am. Chem. Soc.*, 2011, **133**, 13938–13941; (*j*) K. Takaishi, M. Kawamoto, K. Tsubaki, T. Furuyama, A. Muranaka and M. Uchiyama, *Chem.–Eur. J.*, 2011, **17**, 1778–1782.
3 C. Wolf and K. W. Bentley, *Chem. Soc. Rev.*, 2013, **42**, 5408–5424.
4 (*a*) E. Tamanini, G. Dan Pantos and J. K. M. Sanders, *Chem.–Eur. J*, 2010, **16**, 81–84; (*b*) M. Caricato, C. Coluccini, D. Dondi, D. A. Varder Griend and D. Pasini, *Org. Biomol. Chem.*, 2010, **8**, 3272–3280.
5 (*a*) G. Ulrich, R. Ziessel and A. Harriman, *Angew. Chem., Int. Ed.*, 2008, **47**, 1184–1201; (*b*) F. L. Arbeloa, J. Bañuelos, V. Martínez, T. Arbeloa and I. Lopez Arbeloa, *Trends Phys. Chem.*, 2008, **13**, 101–122; (*c*) A. Loudet and K. Burgess, *Chem. Rev.*, 2007, **107**, 4891–4932; (*d*) R. Ziessel, *C. R. Chim.*, 2007, **10**, 622–629.
6 (*a*) A. Kamkaew, S. H. Lim, H. B. Lee, L. V. Kiew, L. Y. Chung and K. Burgess, *Chem. Soc. Rev.*, 2013, **42**, 77–88; (*b*) L. Yuan, W. Lin, K. Zheng, L. He and W. Huang, *Chem. Soc. Rev.*, 2013, **42**, 622–661; (*c*) M. J. Culzoni, A. Muñoz de la Peña, A. Machuca, H. C. Goicochea and R. Babiano, *Anal. Methods*, 2013, **5**, 30–49; (*d*) S. Xiao, Q. Cao and D. Feijun, *Curr. Org. Chem.*, 2012, **16**, 2970–2981; (*e*) N. Boens, V. Leen and W. Dehaen, *Chem. Soc. Rev.*, 2012, **41**, 1130–1172; (*f*) M. Benstead, G. H. Mehl and R. W. Boyle, *Tetrahedron*, 2011, **19**, 90–92; (*g*) S. Kolemen, O. A. Bozdemir, Y. Cakmak, G. Barin, S. Erten-Ela, M. Marszalek, J.-H. Yum, S. M. Zakeeruddin, M. K. Nazeeruddin, M. Grätzel and E. U. Akkaya, *Chem. Sci.*, 2011, **2**, 949–954; (*h*) A. C. Benniston and C. Copley, *Phys. Chem. Chem. Phys.*, 2009, **11**, 4124–4131; (*i*) T. Rousseau, A. Cravino, T. Bura, G. Ulrich, R. Ziessel and J. Roncali, *Chem. Commun.*, 2009, 1673–1675; (*j*) A. Costela, I. García-Moreno and R. Sastre, *Phys. Chem. Chem. Phys.*, 2003, **5**, 4745–4763.
7 Y. Wang, J. Xu, Y. Wang and H. Chen, *Chem. Soc. Rev.*, 2013, **42**, 2930–2962.
8 (*a*) F. Song, G. Wei, X. Jinag, F. Li, C. Zhu and Y. Cheng, *Chem. Commun.*, 2013, **49**, 5772–5774; (*b*) J. Liu, H. Su, L. Meng, Y. Zhao, C. Deng, J. C. Y. Ng, P. Lu, M. Faisal, J. W. Y. Lam, X. Huang, H. Wu, K. Sing, K. S. Wong and B. Z. Tang, *Chem. Sci.*, 2012, **3**, 2737–2747; (*c*) H. Maeda, Y. Bando, K. Shimonura, I. Yamada, M. Naito, K. Nobusawa, H. Tsumatori and T. Kawai, *J. Am. Chem. Soc.*, 2011, **133**, 9266–9269.
9 (*a*) P. Bonaccorsi, M. C. Aversa, A. Baratucci, T. Papalia, F. Puntoiero and S. Campagna, *Chem. Commun.*, 2012, **48**, 10550–10552; (*b*) Y. Wu, X. Mao, X. Ma, X. Huang, Y. Cheng and C. Zhu, *Macromol. Chem. Phys.*, 2012, **213**, 2238–2245; (*c*) A. Nagai, K. Kokado, J. Miyake and Y. Chujo, *Polym. J.*, 2010, **42**, 37–42; (*d*) A. Haefele, C. Zedde, P. Retailleau, G. Ulrich and R. Ziessel, *Org. Lett.*, 2010, **12**, 1672–1675; (*e*) I. Móczár, P. Huszthy, Z. Maidics, M. Kádár and K. Tóth, *Tetrahedron*, 2009, **65**, 8250–8258; (*f*) A. Gossauer, F. Nydegger, T. Kiss, R. Sieziak and H. Stoeckii-Evans, *J. Am. Chem. Soc.*, 2004, **126**, 1772–1780; (*g*) G. Beer, K. Rurack and J. Daub, *Chem. Commun.*, 2001, 1138–1139; (*h*) G. Beer, C. Niederalt, S. Grimme and J. Daub, *Angew. Chem., Int. Ed.*, 2000, **39**, 3252–3255.
10 N. Berova, L. Di Bari and G. Pescitelli, *Chem. Soc. Rev.*, 2007, **36**, 914–931.
11 J. W. Canary, Z. Dai and S. Mortezaei, Spectroscopic Analysis: Chiroptical Sensors, in *Comprehensive Chirality*, ed. E. M. Carreira and H. Yamamoto, Elsevier, Amsterdam, 2012, vol. 8, pp. 600–624.
12 (*a*) T. Rohand, M. Baruah, W. Qin, N. Boens and W. Dehaen, *Chem. Commun.*, 2006, 266–268; (*b*) Y. A. Volkova, B. Brizet, P. D. Harvey, A. D. Averin, C. Goze and F. Denat, *Eur. J. Org. Chem.*, 2013, 4270–4279.
13 S. Azeroual, J. Surprenant, T. D. Lazzara, M. Kocun, Y. Tao, L. A. Cuccia and J.-M. Lehn, *Chem. Commun.*, 2012, **48**, 2292–2294.