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Easily processable spin filters: exploring the chiral induced spin selectivity of bowl-shaped chiral subphthalocyanines†

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High spin polarization (SP) in studies of chiral induced spin selectivity (CISS) is only observed when chiral molecules are properly organized. This is generally achieved by using anchoring groups or complex supramolecular polymers. A new class of spin filters based on bowl-shaped aromatics is reported, which form high-quality thin-films by simply spin-coating and displaying high spin filtering properties. In particular, we fabricate devices containing enantiopure tribromo-subphthalocyanines (SubPcs), and measure the CISS effect by means of magnetic conductive probe atomic force microscopy (mc-AFM). Circular dichroism and AFM experiments reveal that the resulting thin-film presents a well-ordered chiral structure. Remarkably, the resulting devices show SPs as high as ca. 50%, which are comparable to those obtained by using the current complex methodologies. These results boost the potential of bowl-shaped aromatics as easily processable spin filters, opening new frontiers toward realistic and efficient spintronic devices based on the CISS effect.

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Introduction

Spintronics, the combination of spin properties with electronics, is an attractive approach due to its potential in reducing noise and energy consumption in transferring and manipulating information.¹ In recent years, it has been widely demonstrated that certain chiral organic molecules are able to produce spin polarized currents when electrons flow through them. In other words, chiral molecules can serve as spin filters. This fascinating property is known as chirality-induced spin selectivity (CISS) and, in a matter of few years, has become a hot topic because of its ability to produce large spin polarizations (SPs) even at room temperature.^{2–4} The CISS effect has also found important applications in many other fields, such as catalysis,⁵ enantio-separation,⁶ long range electron transfer,⁷ and bio-recognition.⁸

The CISS effect has been studied by means of numerous experimental techniques,^{9–14} and has been explored in multiple systems, including biomolecules (e.g., DNA, peptides, and

proteins),^{15–17} helicenes^{18–20} or chiral polymers.²¹ Among the most employed techniques, magnetic conductive probe atomic force microscopy (mc-AFM) actually holds a privileged position by virtue of its numerous advantages. As discussed below, mc-AFM measurements involve the deposition of chiral molecules on a gold-coated nickel surface (Au/Ni). The way in which the molecules are organized on the Au/Ni surface strongly affects the spin filtering efficiency. For obtaining reproducible results and in order to find correlation between molecular properties and spin filtering, the molecules must be organized in a well-defined way on the surface. The control of molecular orientation, however, is far from trivial given the entropy factor that leads to the creation of disorder in the adsorbed layer. In order to ensure organization, researchers have followed two main strategies (Fig. 1a and b): (a) the preparation of self-assembled monolayers (SAMs) employing chiral molecules equipped with anchoring groups (e.g., –SH or –OH)^{9,18,21–23} and (b) the use of flat, π -conjugated molecules (e.g., porphyrins and polycyclic hydrocarbons) able to self-assemble into chiral, columnar stacks.^{24,25} In the first case, the spin selectivity is measured along the main molecular axis, which is perpendicular to the substrate plane. By contrast, in method (b) the polymers lay on the Au/Ni surface and the CISS effect is measured perpendicular to the main molecular axis. These methods, although efficient and elegant, present major drawbacks. On one hand, method (a) requires the post- or pre-synthetic functionalization of the chiral molecule, which introduces complexity to the synthesis. Moreover, the number of molecules compatible with this technique is limited. On the other hand, method (b) requires a careful design and extensive

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Fig. 2 (a) Molecular structures of *P*- and *M*-SubPcBr₃. (b) Circular dichroism spectra of enantiopure *M*-SubPcBr₃ (blue spectrum) and *P*-SubPcBr₃ (red spectrum) in toluene (concentration = 2×10^{-5} M). (c) UV-vis absorption spectra of enantiopure *M*-SubPcBr₃ (blue spectrum) and *P*-SubPcBr₃ (red spectrum) in toluene (concentration = 7×10^{-6} M). (d) AFM image of the substrate on which the *M*-SubPcBr₃ molecules were deposited via spin-coating. (e) Solid-state CD spectra measured on quartz substrates of spin-coated enantiopure *M*-SubPcBr₃ (blue spectrum), *P*-SubPcBr₃ (red spectrum) and *rac*-SubPcBr₃, and (f) the absorption spectrum of respective surfaces.

The results obtained from the mc-AFM experiments are presented in Fig. 3b–e. As shown in the current–voltage curves (*I*–*V*; Fig. 3b–d), the current displayed by both *M*- and *P*-SubPcBr₃ strongly depends on the direction of the magnetization of the substrate. Specifically, the *M*-SubPcBr₃ enantiomer exhibits higher currents when the substrate is magnetized with the magnetic field up. In contrast, in the case of *P*-SubPcBr₃ the current is lower with the same magnetization. Each curve is the

average of over 50 individual measurements. The semi log plots presented in the insets show a nonlinear dependence of the current on the applied potential and a difference in the threshold for the currents of the electrons with the two-spin polarization, which is characteristic of chiral systems and indicates no spin flipping during electron transmissions.⁴¹ The racemic compound does not show any spin preferred current, as shown in Fig. 3c. Therefore, we can conclude that



Fig. 3 Spin-dependent transport properties measured with mc-AFM. (a) mc-AFM setup in which SubPcBr₃ is deposited on the ferromagnetic substrate by spin-coating. (b), (c), and (d) present the averaged current versus voltage (*I*–*V*) curves recorded for *M*-, *rac*- and *P*-SubPcBr₃, respectively. The blue line represents the current for the SubPc layer when the magnet north pole is pointing up and red line for the magnet north pole pointing down with respect to the substrate. (e) Spin polarization percentage (SP%) as a function of applied bias for *M*-SubPcBr₃ (blue) and *P*-SubPcBr₃ (red).



enantiopure **SubPcBr₃** displays spin-selective charge transport. Subsequently, we quantified these spin-filtering properties by calculating the SP percentage. The dependence of SPs on the applied voltage is shown in Fig. 3e. Remarkably, average SPs as high as $+48 \pm 5\%$ and $45 \pm 5\%$ were obtained for **M-** and **P-SubPcBr₃**, respectively. These values are very high considering that there are no anchoring groups or supramolecular polymerization, which highlights the excellent capability of SubPcs to self-organize in thin-films. It is important to appreciate that this value is comparable to those obtained from previously reported – and more complex – methods. For instance, method (a) (*i.e.*, self-assembled monolayers) leads to SPs in the range of 40–60%. Notably, in the case of helicenes the spin-coating deposition of derivatives non-functionalized with anchoring groups produces SPs below 5%. This value, however, rose up to 50% upon functionalization with thiols and preparation of SAMs. On the other hand, method (b) (*i.e.*, prior formation of supramolecular polymers) produces SPs between 40% and 85%, depending on the strategy to achieve the chiral assembly (*e.g.*, the use of chiral side chains, chiral solvents, *etc.*).

Conclusions

In conclusion, we revealed the CISS effect of chiral SubPcs and its potential for spintronic devices. Although rationally controlling the organization of chiral molecules is still challenging, our result indicates that bowl-shaped π -conjugated molecules can form well-ordered, chiral thin-films with enough quality to serve as efficient spin filters, without the need of anchoring groups of complex supramolecular polymerization. We believe that this result will promote the study of the CISS effect of bowl-shaped aromatics and paves the way for realistic and efficient spintronic devices based on the CISS effect.

Author contributions

R. N. and T. T. designed the research. J. L. performed the synthesis and studied the thin-film formation of chiral SubPcs. D. K. B. and A. K. performed the device preparation, characterization and mc-AFM experiments. All authors contributed to the writing and editing of the paper. Overall, J. L., D. K. B. and A. K. contributed equally to this publication.

Conflicts of interest

The authors declare no competing financial interest.

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