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Device-Compatible Chiroptical Surfaces through Self-Assembly of Enantiopure Allenes

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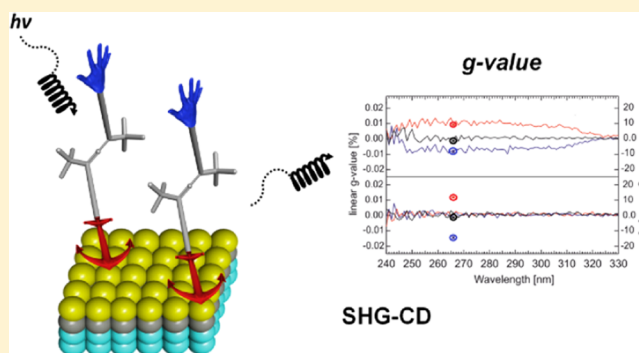
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Supporting Information

ABSTRACT: Chiroptical methods have been proven to be superior compared to their achiral counterparts for the structural elucidation of many compounds. To expand the use of chiroptical systems to everyday applications, the development of functional materials exhibiting intense chiroptical responses is essential. Particularly, tailored and robust interfaces compatible with standard device operation conditions are required. Herein, we present the design and synthesis of chiral allenes and their use for the functionalization of gold surfaces. The self-assembly results in a monolayer-thin room-temperature-stable upstanding chiral architecture as ascertained by ellipsometry, X-ray photoelectron spectroscopy, and near-edge X-ray absorption fine structure. Moreover, these nanostructures anchored to device-compatible substrates feature intense chiroptical second harmonic generation. Both straightforward preparation of the device-compatible interfaces along with their chiroptical nature provide major prospects for everyday applications.



forming a complex with a chiral host, a task far from trivial for nonchiral techniques.^{1,10} In this regard, there are several studies focused on the design and synthesis of systems presenting enhanced chiroptical responses in the search for applications in solution.^{11–15} On the other hand, the construction of chiroptical surfaces is required to develop lab-on-chip devices. However, the limited knowledge regarding the interfacial integration of chiroptical compounds has hampered to date the emergence of chiroptical sensors for everyday use. In that respect, Lakey and co-workers observed folding in a monolayer of a 22 kDa protein domain,¹⁶ and Wälti's group studied the influence of two-dimensional organization on the conformational state in a peptide monolayer using a circular dichroism (CD).¹⁷ Yada and co-workers used the same technique to study the influence of an electric field on oriented films of lipid bilayers.¹⁸ Additionally, Govorov and co-workers have been

■ INTRODUCTION

Non-superimposable systems with their mirror images are set to be chiral and may exist in two enantiomeric forms. The two opposite enantiomers of a molecule are indistinguishable when interacting with an achiral entity. However, as in the famous case of thalidomide, when interacting with another chiral entity, they may respond in a different way. Also, light can be chiral, like the case of circularly polarized light. Although a racemic mixture or rac, a 1:1 mixture of two enantiomeric counterparts, is not distinguishable spectroscopically from an achiral system, the opposite response of enantiopure chiral systems when interacting with lights of contrary chirality gives rise to chiroptical spectroscopies.^{1,2} These spectroscopies present remarkably high sensitivity to conformational changes and supramolecular interactions. As a consequence, they are routinely used not only for absolute configuration determination^{3–5} and conformational assignments^{6,7} but also for the characterization of molecular assemblies where at least one of the components is chiral.^{8,9} Moreover, a guest molecule may be identified by the characteristic chiroptical responses when

forming a complex with a chiral host, a task far from trivial for nonchiral techniques.^{1,10} In this regard, there are several studies focused on the design and synthesis of systems presenting enhanced chiroptical responses in the search for applications in solution.^{11–15} On the other hand, the construction of chiroptical surfaces is required to develop lab-on-chip devices. However, the limited knowledge regarding the interfacial integration of chiroptical compounds has hampered to date the emergence of chiroptical sensors for everyday use. In that respect, Lakey and co-workers observed folding in a monolayer of a 22 kDa protein domain,¹⁶ and Wälti's group studied the influence of two-dimensional organization on the conformational state in a peptide monolayer using a circular dichroism (CD).¹⁷ Yada and co-workers used the same technique to study the influence of an electric field on oriented films of lipid bilayers.¹⁸ Additionally, Govorov and co-workers have been

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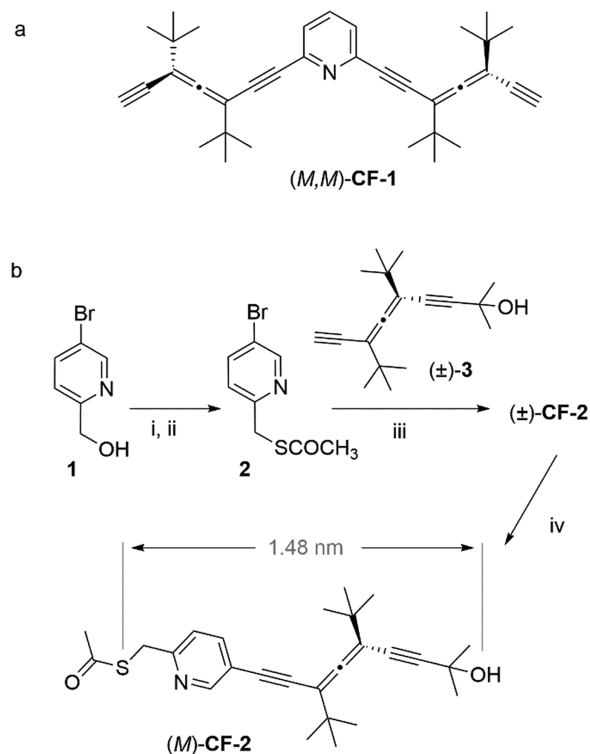
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exploring the chiroptical amplification of thick (~ 10 nm) layers of biomolecules by surface plasmon resonance.¹⁹ However, the complex conformational dynamics and multiple chemical interactions possible for such large molecular systems represent complications with respect to the development of everyday chiroptical applications.

The exploration of chiroptical responses on the surfaces functionalized with a single monolayer of small molecules (<500 Da) for an enhanced conformational control has remained challenging so far. Although the formation of stable interfaces was demonstrated with chiral porphyrins²⁰ or cyclodextrins,²¹ their chiroptical properties remain unexplored.

In contrast to most of the chiral molecules where the chirality comes from chiral centers with notation (*R*) or (*S*) following the Cahn–Ingold–Prelog rules,²² the chiral axes such as allenes^{7,11,15} or spiranes^{23,24} with (*P*) of (*M*) configuration have been proven to be useful chiral elements for the construction of systems with remarkable chiroptical responses in solution. With the aim of developing versatile chiroptical surfaces, we have previously investigated the self-assembly of enantiopure (*M,M*)-CF-1 comprising two diethynylallenes on a single crystal surface (Scheme 1a). Under such ideal conditions, we demonstrated the formation of upstanding chiral architectures (UCAs), in which the single chiral molecules are arranged perpendicular to the underlying substrate as two-dimensional nanostructures with the possibilities of postsynthetic modification.²⁵ However, the weak molecule–substrate interactions

Scheme 1. (a) Structure of (*M,M*)-CF-1 Previously Used for Surface Functionalization;²⁵ (b) Synthesis and Enantiomeric Resolution of (\pm)-CF-2^a



^aReagents and conditions: (i) mesyl chloride, Et₃N, CH₂Cl₂, 0–25 °C, 22 h; (ii) CH₃COSK, dimethylformamide, 0–25 °C, 4 h, 80%; (iii) Et₃N, [Pd(PPh₃)₄], tetrahydrofuran, 65 °C, 72 h, 46%; (iv) Chiralpak IA, 96:4 *n*-Hex/*i*-PrOH, 4.0 mL min⁻¹. The shown length of (*M*)-CF-2 was predicted at the AM1 level of theory.

hindered the exploration of the chiroptical responses of the formed chiral surfaces at room temperature (RT). Herein, we present the design and synthesis of enantiopure (*P*)-CF-2 and (*M*)-CF-2 (Scheme 1) and their use for surface functionalization. The high stability of the formed self-assemblies enabled the construction of monolayer-thin device-compatible interfaces presenting a strong chiroptical second harmonic generation (SHG).

RESULTS AND DISCUSSION

The synthesis of (\pm)-CF-2 started from alcohol **1**, which was treated with mesyl chloride at 0 °C, and a subsequent treatment with potassium thioacetate in *N,N*-dimethylformamide leads to thioacetate pyridine **2** in 80% yield (Scheme 1b). Sonogashira reaction of pyridine **2** with axially chiral diethynylallene (\pm)-**3** catalyzed by [Pd(PPh₃)₄] with Et₃N in tetrahydrofuran afforded the desired chiral compound (\pm)-CF-2. Enantiomeric resolution was carried out using the chiral stationary phase Chiralpak IA. Assignment of the absolute configuration was performed by comparison of the CD spectrum of (*P*)-CF-2 synthesized from enantiopure (*P*)-**3** with the two fractions of the enantiomeric resolution. Thermal and photostability of (*M*)-CF-2 in solution as determined by CD were considered sufficient to employ these chiral molecules for the construction of chiroptical surfaces (for more details, see the Supporting Information (SI)).

Monolayer preparation of enantiopure (*M*)-CF-2 and (*P*)-CF-2 and racemate (\pm)-CF-2 onto template-stripped Au substrates (AuTS) was performed by immersion in a toluene solution. Ellipsometry data analysis considering a two-layer model showed 1.49 ± 0.12 nm thickness for the monolayer, which is comparable with the predicted length of the molecule plus the Au–S bond (Scheme 1). This supports the fact that the CF-2 molecules are mostly standing straight up from the substrate at RT as previously proposed for CF-1 at lower temperatures.

Conductance plots of current–density, *J*, versus potential, *V* are typically used to obtain information regarding the nature and quality of molecular layers. In tunneling junctions, the dependence of *J* on the molecular length, *d*, can be approximated by the equation $J(V) = J_0 e^{-\beta d}$, where *J*₀ is the injection current and β is the decay coefficient. Because *J*₀ is defined by the two molecule/electrode interfaces and does not vary significantly between conjugated hydrocarbons, we compared the conductance plots of the self-assembly of (*M*)-CF-2 with the one of the known self-assembly of *S,S'*-(ethyne-1,2-diylbis(4,1-phenylene)) diethanethioate (OPE2).²⁶ Because OPE2 is a conjugated molecule of comparable length to (*M*)-CF-2, the observed overlap between the plots of the two systems is a strong evidence that (*M*)-CF-2 forms densely packed self-assemblies of upright molecules uniformly bound to the substrate. On the other hand, because allenes may present photoinstability under certain conditions,^{27,28} the same measurements were performed during and after light irradiation to evaluate this aspect, with no significant changes observed, suggesting a strong structural stability of the self-assembled (*M*)-CF-2 monolayers at room temperature (Figure 1, for more information see the SI).

The integrity of the self-assembled CF-2 molecules after self-assembly was confirmed by the observed C 1s and N 1s X-ray photoelectron spectroscopy (XPS) spectra, each with a single distinguishable peak centered around 285 and 400 eV, respectively (Figure 2a,b). Therefore, no significant degradation

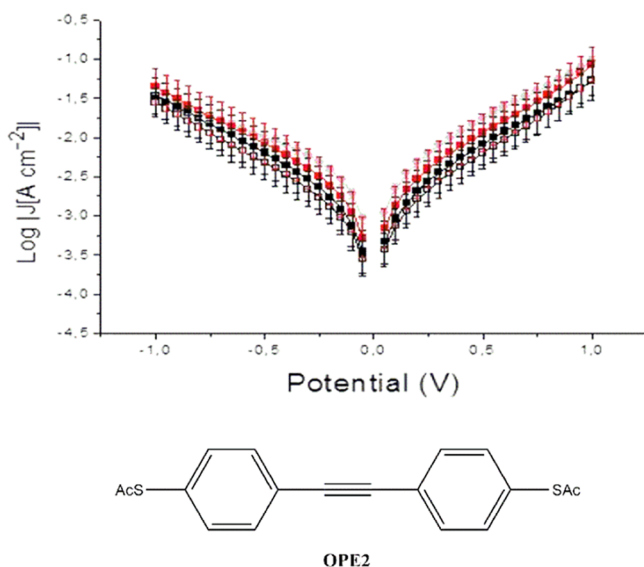


Figure 1. Semilog plot of J vs V for EGaIn/Ga₂O₃/(*M*)-CF-2 UCA/AuTS junctions in the dark (black), after illumination in the light (red), and in the dark after illumination step (hollow), and EGaIn/Ga₂O₃//OPE2/AuTS junctions (gray). Error bars are per-junction confidence intervals calculated using $\alpha = 0.95$. The samples were first measured in the dark using a red light source as dim as possible to position the tip on the substrate; they were then irradiated at 256 nm (60 W) for 30 min and measured again in a fully lit environment; finally, the samples were let to rest for 1 h in the dark before being measured again using the initial conditions. UCA stands for upstanding chiral architectures.

to organometallic alkylnylic^{29,30} or metal–organic pyridinic^{31,32} species occurred during preparation (cf. discussion in the SI). The S 2p signature reveals a dominating doublet (green, with S 2p_{3/2} component binding energy amounting to 162 eV, Figure 2c) matching nicely with the sulfur reference spectrum of an alkanethiol self-assembled monolayer (SAM) on the same substrate type (C14-S/Au, cf. Figure S11a) and previously reported values,^{33–36} thus indicating successful anchoring through thiolate chemisorbed to the Au substrate. The minority species (blue components) is attributed to the presence of an organothiol with a different chemical nature resulting, e.g., from anchoring at step edges or different adsorption configurations. In SAMs constructed from aryl-containing compounds on untreated commercial Au/Mica substrates such features are commonly observed.^{37–40} Potentially, the peak could originate from atomic sulfur from cracked molecules or contamination.^{41,42} However, this is not likely because the signature of a sample with atomic sulfur is different (see discussion related to Figure S11b in the SI). Noteworthy, the absence of further sulfur peaks, specifically at higher binding energy around 164 eV, indicates the absence of a multilayer formation through the utilized preparation process.⁴³ Additionally, the O 1s XPS spectrum (Figure 2d) is fitted with one component binding energy of 532 eV, which corresponds to a terminal dimethyl alcohol group.³⁰ The width of the peak (fwhm = 2.08 eV) is larger than the expected width for a single species (~1.5 eV). We attribute this broadening to the OH groups experiencing different noncovalent interactions with neighboring molecules,⁴⁴ consistent with the inhomogeneity of the film indicated by the previous XPS spectra. Overall, these data confirm not only the abstraction of the acetyl moiety and the efficient chemisorption via the thiolate group of (*M*)-CF-2 molecules

but also the RT stability of the formed UCAs and their persistence under ambient conditions over several days.

For a more structural elucidation, near-edge X-ray absorption fine structure (NEXAFS) N K-edge spectra were taken with three different incident angles $\theta = 25, 53,$ and 90° (Figure 2e). The π^* -region (below 404 eV) contains two discernible and differently broadened peaks, thus a richer structure than pure pyridine.⁴⁵ The more complex signature is explained by the interaction with the nearby ethynylene π -system and packing effects inducing splitting of resonances and intensity redistribution.^{46–48} The spectra exhibit no discernible angular dependence of the first two π^* resonances centered at 399 and 401 eV. A fitting of the leading edge of the experimental spectra with Voigt peaks (Figure S12a) and comparison of the peak intensities to theoretical curves⁴⁹ indicate an average adsorption angle α of the pyridine moiety between 50 and 60° (between the normal of the ring plane and the surface normal, Figure S12b), clearly ruling out a flat adsorption geometry as the dominant configuration. On the other hand, the consistent anchoring via the thiol groups rules out a random orientation of the pyridine rings.⁵⁰ Thus, even though the quality of the film is inferior to what has been achieved with simple alkene SAMs, the combined X-ray spectroscopic data evidence the formation of a monolayer-thin CF-2 upstanding chiral architecture and indicate a preferential average inclination of the molecular backbone of approximately 30° (Figure 2f, for more detail see the SI), in accordance with the ellipsometry experiments.

The exploration of chiroptical properties of interfaces is greatly hindered by the small amount of molecules as compared to solution-based setups, rendering the analysis challenging due to the minute amount of the response signal. To improve chiroptical sensitivity, extensive efforts have been made in the development of more sophisticated techniques.⁵¹ In this regard, nonlinear chiral effects have been shown to be up to 3 orders of magnitude larger than the corresponding linear ones.^{52–55} To evaluate the chiroptical properties of the CF-2 self-assemblies, we measure the second harmonic generation circular dichroism (SHG-CD).^{52–54,56–58} The corresponding g -values were then calculated according to the following equation (LCP and RCP stand for left and right circularly polarized light, respectively)

$$g_{\text{SHG}} = \frac{\text{SHG}_{\text{LCP}} - \text{SHG}_{\text{RCP}}}{\left(\frac{\text{SHG}_{\text{LCP}} + \text{SHG}_{\text{RCP}}}{2}\right)}$$

We observed a 1000-fold magnification of the SHG-CD g -values for monolayer-thin films of (*P*)-CF-2 and (*M*)-CF-2 molecules compared to the linear CD g -values of CF-2 in a multilayer or solution. These results enabled the clear observation of the chiroptical response for the developed device-compatible surfaces (Figure 3, see also Figure S2 in the SI).

CONCLUSIONS

In conclusion, we have designed and synthesized enantiopure (*P*)-CF-2 and (*M*)-CF-2 and successfully anchored them to Au surfaces to construct stable upstanding chiral architectures. The self-assembly was verified by means of ellipsometry, XPS, and NEXAFS. More importantly, SHG-CD measurements proved that the afforded molecule-thin sheets possess chiroptical activity. These interfaces were successfully integrated in electronic circuitry, thus demonstrating suitability for optoelectronic devices. The higher accuracy and reliability offered by chiroptical sensing techniques along with the more character-

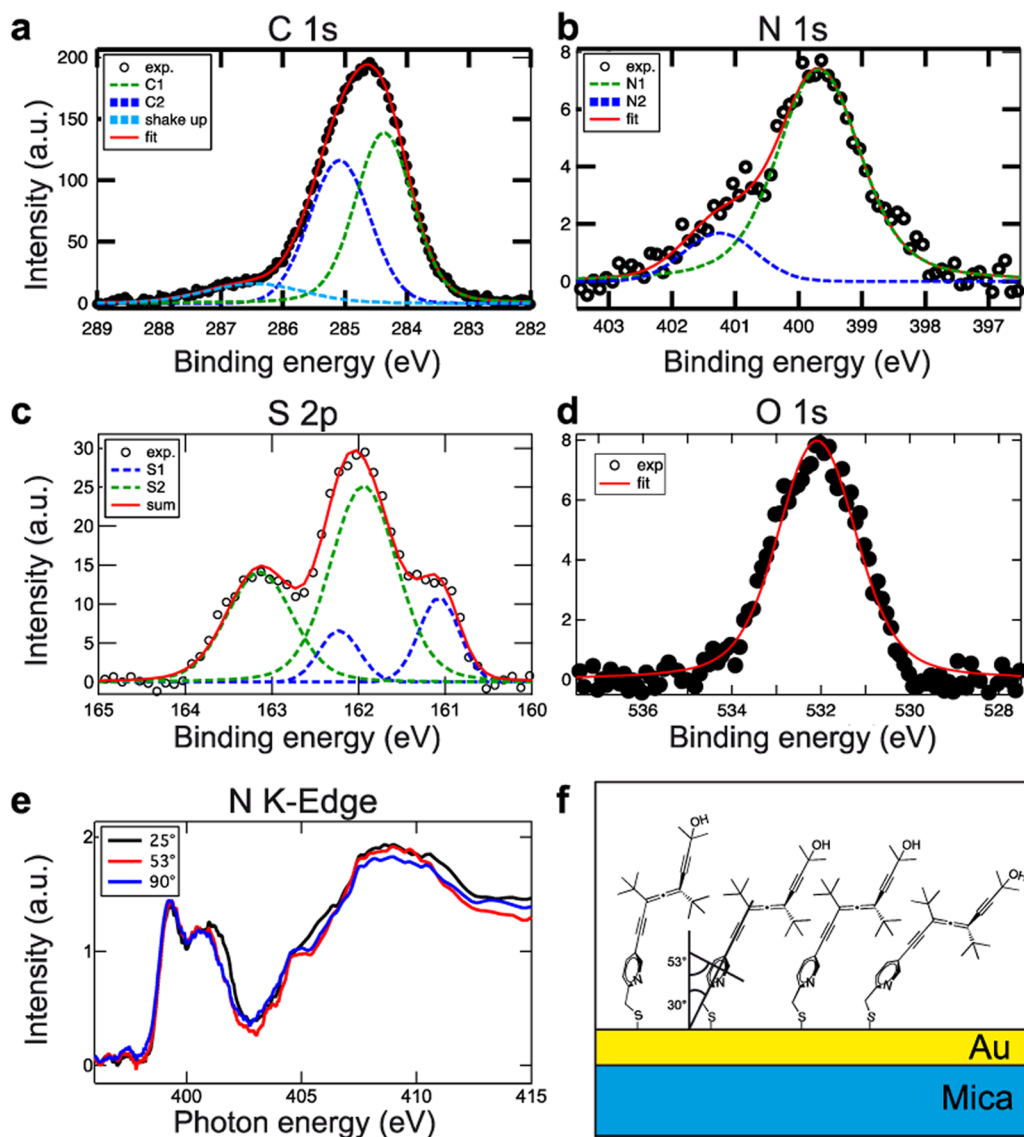


Figure 2. (a–d) XPS spectra of (*M*)-CF-2 framework on Au/Mica substrate the C 1s, N 1d, S 2p, and O 1s regions are depicted in (a), (b), (c), and (d), respectively. (e) The N K-edge near-edge X-ray absorption fine structure (NEXAFS) signatures recorded with three different incidence angles (25, 53, and 90°). (f) Scheme showing the proposed, approximate orientation of (*M*)-CF-2 molecules in the upstanding monolayer architecture.

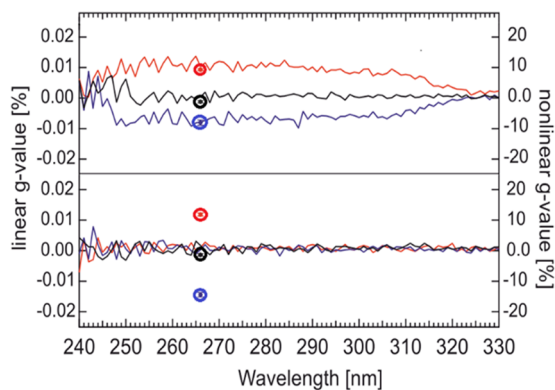


Figure 3. Multilayer (top), as obtained from sublimation of CF-2 by heating up to 230 °C at 10^{-8} kPa, and monolayer (bottom) circular dichroism (lines, left scales) and second harmonic generation (dots, right scales) measurements of (*M*)-CF-2 (red) and (*P*)-CF-2 (blue) upstanding architectures on custom-made transparent substrates (black).

istic signatures related to varying target compounds render upstanding chiral architectures as a promising novel class of robust chiroptical materials. We are currently pursuing nanoparticle stabilization and electric isolation of metal surfaces to develop chiroptical sensing with plasmonic nanoparticles, as well as to control and inhibit corrosion on artworks.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.langmuir.8b00305](https://doi.org/10.1021/acs.langmuir.8b00305).

Experimental procedures, spectral data, and computational study results (PDF)

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#A.O., R.P.-C, A.v.W, and M.P. contributed equally.

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Pescitelli, G.; Di Bari, L.; Berova, N. Application of Electronic Circular Dichroism in the Study of Supramolecular Systems. *Chem. Soc. Rev.* **2014**, *43*, 5211–5233.
- (2) Petrovic, A. G.; Navarro-Vázquez, A.; Alonso-Gómez, J. L. From Relative to Absolute Configuration of Complex Natural Products: Interplay Between NMR, ECD, VCD, and ORD Assisted by Ab Initio Calculations. *Curr. Org. Chem.* **2010**, *16*, 1612–1628.
- (3) Giorgio, E.; Roje, M.; Tanaka, K.; Hamersak, Z.; Sunjic, V.; Nakanishi, K.; Rosini, C.; Berova, N. Determination of the Absolute Configuration of Flexible Molecules by Ab Initio ORD Calculations: A Case Study with Cytosaxones and Isocytosaxones. *J. Org. Chem.* **2005**, *70*, 6557–6563.
- (4) Nakanishi, K.; Berova, N.; Polavarapu, P. L.; Woody, R. W. *Comprehensive Chiroptical Spectroscopy; Instrumentation, Methodologies, and Theoretical Simulations*; Wiley-VCH Verlag, 2013; Vol. 1.
- (5) Petrovic, A. G.; Berova, N.; Alonso-Gómez, J. L. *Structure Elucidation in Organic Chemistry*; Cid, M.-M., Bravo, J., Eds.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2015.
- (6) Alonso-Gómez, J. L.; Petrovic, A. G.; Harada, N.; Rivera-Fuentes, P.; Berova, N.; Diederich, F. Chiral Induction from Allenes into Twisted 1,1,4,4-Tetracyanobuta-1,3-Dienes (TCBDs): Conformational Assignment by Circular Dichroism Spectroscopy. *Chem. - Eur. J.* **2009**, *15*, 8396–8400.
- (7) Rivera-Fuentes, P.; Alonso-Gómez, J. L.; Petrovic, A. G.; Santoro, F.; Harada, N.; Berova, N.; Diederich, F. Amplification of Chirality in Monodisperse, Enantiopure Alleno-Acetylenic Oligomers. *Angew. Chem., Int. Ed.* **2010**, *49*, 2247–2250.
- (8) Gropp, C.; Trapp, N.; Diederich, F. Alleno-Acetylenic Cage (AAC) Receptors: Chiroptical Switching and Enantioselective

Complexation of Trans-1,2-Dimethylcyclohexane in a Diaxial Conformation. *Angew. Chem., Int. Ed.* **2016**, *55*, 14444–14449.

(9) Gidron, O.; Ebert, M.-O. O.; Trapp, N.; Diederich, F. Chiroptical Detection of Nonchromophoric, Achiral Guests by Enantiopure Alleno-Acetylenic Helicages. *Angew. Chem., Int. Ed.* **2014**, *53*, 13614–13618.

(10) Mineo, P.; Micali, N.; Villari, V.; Donato, M. G.; Scamporrino, E. Reading of Protein Surfaces in the Native State at Micromolar Concentrations by a Chirogenetic Porphyrin Probe. *Chem. - Eur. J.* **2012**, *18*, 12452–12457.

(11) Alonso-Gómez, J. L.; Rivera-Fuentes, P.; Harada, N.; Berova, N.; Diederich, F. An Enantiomerically Pure Alleno-Acetylenic Macrocyclic Synthesis and Rationalization of Its Outstanding Chiroptical Response. *Angew. Chem., Int. Ed.* **2009**, *48*, 5545–5548.

(12) Míguez-Lago, S.; Cid, M. M.; Alonso-Gómez, J. L. Covalent Organic Helical Cages as Sandwich Compound Containers. *Eur. J. Org. Chem.* **2016**, *2016*, 5716–5721.

(13) Walters, R. S.; Kraml, C. M.; Byrne, N.; Ho, D. M.; Qin, Q.; Coughlin, F. J.; Bernhard, S.; Pascal, R. A. Configurationally Stable Longitudinally Twisted Polycyclic Aromatic Compounds. *J. Am. Chem. Soc.* **2008**, *130*, 16435–16441.

(14) Dougherty, K. J.; Kraml, C. M.; Byrne, N.; Porras, J. A.; Bernhard, S.; Mague, J. T.; Pascal, R. A. Helical Mesobenzanthrones: A Class of Highly Luminescent Helicenes. *Tetrahedron* **2015**, *71*, 1694–1699.

(15) Míguez-Lago, S.; Llamas-Saiz, A. L.; Magdalena Cid, M.; Alonso-Gómez, J. L. A Covalent Organic Helical Cage with Remarkable Chiroptical Amplification. *Chem. - Eur. J.* **2015**, *21*, 18085–18088.

(16) Keegan, N.; Wright, N. G.; Lakey, J. H. Circular Dichroism Spectroscopy of Folding in a Protein Monolayer. *Angew. Chem., Int. Ed.* **2005**, *44*, 4801–4804.

(17) White, S. J.; Johnson, S. D.; Sellick, M. A.; Bronowska, A.; Stockley, P. G.; Wälti, C. The Influence of Two-Dimensional Organization on Peptide Conformation. *Angew. Chem., Int. Ed.* **2015**, *54*, 974–978.

(18) Fiche, J. B.; Laredo, T.; Tanchak, O.; Lipkowski, J.; Dutcher, J. R.; Yada, R. Y. Influence of an Electric Field on Oriented Films of DMPC/gramicidin Bilayers: A Circular Dichroism Study. *Langmuir* **2010**, *26*, 1057–1066.

(19) Maoz, B. M.; Chaikin, Y.; Tesler, A. B.; Elli, O. B.; Fan, Z.; Govorov, A. O.; Markovich, G. Amplification of Chiroptical Activity of Chiral Biomolecules by Surface Plasmons. *Nano Lett.* **2013**, *13*, 1203–1209.

(20) Paolesse, R.; Monti, D.; La Monica, L.; Venanzi, M.; Froiio, A.; Nardis, S.; Di Natale, C.; Martinelli, E.; D'Amico, A. Preparation and Self-Assembly of Chiral Porphyrin Diads on the Gold Electrodes of Quartz Crystal Microbalances: A Novel Potential Approach to the Development of Enantioselective Chemical Sensors. *Chem. - Eur. J.* **2002**, *8*, 2476–2483.

(21) Luo, M. L.; Zhang, W. G.; Zhang, S.; Fan, J.; Su, W. C.; Yin, X. Self-Assembly and Chiral Recognition of Quartz Crystal Microbalance Chiral Sensor. *Chirality* **2010**, *22*, 411–415.

(22) Cahn, R. S.; Ingold, C.; Prelog, V. Specification of Molecular Chirality. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385–415.

(23) Castro-Fernández, S.; Cid, M. M.; Alonso-Gómez, J. L.; Silva López, C.; et al. Opening Access to New Chiral Macrocycles: From Allenes to Spiranes. *J. Phys. Chem. A* **2015**, *119*, 1747–1753.

(24) Castro-Fernández, S.; Yang, R.; García, A. P.; Garzón, I. L.; Xu, H.; Petrovic, A. G.; Alonso-Gómez, J. L. Diverse Chiral Scaffolds from Diethynylspiranes: All-Carbon Double Helices and Flexible Shape-Persistent Macrocycles. *Chem. - Eur. J.* **2017**, *23*, 11747–11751.

(25) Zhang, Y.-Q.; Oner, M. A.; Cirera, B.; Palma, C.-A.; Castro-Fernández, S.; Míguez-Lago, S.; Cid, M. M.; Barth, J. V.; Alonso-Gómez, J. L.; Klappenberger, F.; et al. Morphological Self-Assembly of Enantiopure Allenes for Upstanding Chiral Architectures at Interfaces. *Chem. Commun.* **2014**, *50*, 15022–15025.

(26) Valkenier, H.; Huisman, E. H.; van Hal, P. A.; de Leeuw, D. M.; Chiechi, R. C.; Hummelen, J. C. Formation of High-Quality Self-

Assembled Monolayers of Conjugated Dithiols on Gold: Base Matters. *J. Am. Chem. Soc.* **2011**, *133*, 4930–4939.

(27) Odermatt, S.; Alonso-Gómez, J. L.; Seiler, P.; Cid, M. M.; Diederich, F. Shape-Persistent Chiral Allenyl-Acetylenic Macrocycles and Cyclophanes by Acetylenic Scaffolding with 1,3-Diethynylallenes. *Angew. Chem. Int. Ed.* **2005**, *44*, 5074–5078.

(28) Alonso-Gómez, J. L.; Schanen, P.; Rivera-Fuentes, P.; Seiler, P.; Diederich, F. 1,3-Diethynylallenes (DEAs): Enantioselective Synthesis, Absolute Configuration, and Chiral Induction in 1,1,4,4-Tetracyano-but-1,3-Dienes (TCBDs). *Chem. - Eur. J.* **2008**, *14*, 10564–10568.

(29) Zhang, Y.-Q.; Kepčija, N.; Kleinschrodt, M.; Diller, K.; Fischer, S.; Papageorgiou, A. C.; Allegretti, F.; Björk, J.; Klyatskaya, S.; Klappenberger, F.; Ruben, M.; Barth, J. V. Homo-Coupling of Terminal Alkynes on a Noble Metal Surface. *Nat. Commun.* **2012**, *3*, No. 1286.

(30) Gleason, N.; Guevremont, J.; Zaera, F. Thermal Chemistry of 2-Propanol and 2-Propyl Iodide on Clean and Oxygen-Pretreated Ni(100) Single-Crystal Surfaces. *J. Phys. Chem. B* **2003**, *107*, 11133–11141.

(31) Klappenberger, F.; Weber-Bargioni, A.; Auwärter, W.; Marschall, M.; Schiffrin, A.; Barth, J. V. Temperature Dependence of Conformation, Chemical State, and Metal-Directed Assembly of Tetrapyrrolyl-Porphyrin on Cu(111). *J. Chem. Phys.* **2008**, *129*, No. 214702.

(32) Li, Y.; Xiao, J.; Shubina, T. E.; Chen, M.; Shi, Z.; Schmid, M.; Steinrück, H.-P.; Gottfried, J. M.; Lin, N. Coordination and Metalation Bifunctionality of Cu with 5,10,15,20-Tetra(4-pyridyl)porphyrin: Toward a Mixed-Valence Two-Dimensional Coordination Network. *J. Am. Chem. Soc.* **2012**, *134*, 6401–6408.

(33) Cavalleri, O.; Gonella, G.; Terreni, S.; Vignolo, M.; Floreano, L.; Morgante, A.; Canepa, M.; Rolandi, R. High Resolution X-Ray Photoelectron Spectroscopy of L-Cysteine Self-Assembled Films. *Phys. Chem. Chem. Phys.* **2004**, *6*, 4042–4046.

(34) Fischer, S.; Papageorgiou, A. C.; Marschall, M.; Reichert, J.; Diller, K.; Klappenberger, F.; Allegretti, F.; Nefedov, A.; Wöll, C.; Barth, J. V. L-Cysteine on Ag(111): A Combined STM and X-Ray Spectroscopy Study of Anchorage and Deprotonation. *J. Phys. Chem. C* **2012**, *116*, 20356–20362.

(35) Zharnikov, M.; Grunze, M. Spectroscopic Characterization of Thiol-Derived Self-Assembling Monolayers. *J. Phys.: Condens. Matter* **2001**, *13*, 11333–11365.

(36) Cyganik, P.; Buck, M.; Strunskus, T.; Shaporenko, A.; Wilton-Ely, J. D. E. T.; Zharnikov, M.; Wöll, C. Competition as a Design Concept: Polymorphism in Self-Assembled Monolayers of Biphenyl-Based Thiols. *J. Am. Chem. Soc.* **2006**, *128*, 13868–13878.

(37) Luo, Y.; Bernien, M.; Krüger, A.; Hermanns, C. F.; Miguel, J.; Chang, Y.-M.; Jaekel, S.; Kuch, W.; Haag, R. In Situ Hydrolysis of Imine Derivatives on Au(111) for the Formation of Aromatic Mixed Self-Assembled Monolayers: Multitechnique Analysis of This Tunable Surface Modification. *Langmuir* **2012**, *28*, 358–366.

(38) Shaporenko, A.; Terfort, A.; Grunze, M.; Zharnikov, M. A Detailed Analysis of the Photoemission Spectra of Basic Thioaromatic Monolayers on Noble Metal Substrates. *J. Electron Spectrosc. Relat. Phenom.* **2006**, *151*, 45–51.

(39) Weidner, T.; Krämer, A.; Bruhn, C.; Zharnikov, M.; Shaporenko, A.; Siemeling, U.; Träger, F. Novel Tripod Ligands for Prickly Self-Assembled Monolayers. *Dalton Trans.* **2006**, 2767–2777.

(40) Chesneau, F.; Zhao, J.; Shen, C.; Buck, M.; Zharnikov, M. Adsorption of Long-Chain Alkanethiols on Au(111): A Look from the Substrate by High Resolution X-Ray Photoelectron Spectroscopy. *J. Phys. Chem. C* **2010**, *114*, 7112–7119.

(41) Buckley, A. N.; Hamilton, I. C.; Woods, R. An Investigation of the sulphur(-II)/sulphur(0) System on Bold Electrodes. *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, *216*, 213–227.

(42) Yang, Y. W.; Fan, L. J. High-Resolution XPS Study of Decanethiol on Au(111): Single Sulfur-Gold Bonding Interaction. *Langmuir* **2002**, *18*, 1157–1164.

(43) Weckenmann, U.; Mittler, S.; Naumann, K.; Fischer, R. A. Ordered Self-Assembled Monolayers of 4,4'-Biphenyldithiol on

Polycrystalline Silver: Suppression of Multilayer Formation by Addition of Tri-N-Butylphosphine. *Langmuir* **2002**, *18*, 5479–5486.

(44) Cossaro, A.; Puppini, M.; Cvetko, D.; Kladnik, G.; Verdini, A.; Coreno, M.; de Simone, M.; Floreano, L.; Morgante, A. Tailoring SAM-on-SAM Formation. *J. Phys. Chem. Lett.* **2011**, *2*, 3124–3129.

(45) Kolczewski, C.; Püttner, R.; Plashkevych, O.; Ågren, H.; Staemmler, V.; Martins, M.; Snell, G.; Schlachter, A. S.; Sant'Anna, M.; Kaindl, G.; Pettersson, L. G. M. Detailed Study of Pyridine at the C1 S and N1 S Ionization Thresholds: The Influence of the Vibrational Fine Structure. *J. Chem. Phys.* **2001**, *115*, 6426–6437.

(46) Carniato, S.; Ilakovac, V.; Gallet, J.-J.; Kukkk, E.; Luo, Y. Hybrid Density-Functional Theory Calculations of near-Edge X-Ray Absorption Fine-Structure Spectra: Applications on Benzonitrile in Gas Phase. *Phys. Rev. A* **2005**, *71*, No. 22511.

(47) Liu, J.; Schüpbach, B.; Bashir, A.; Shekhah, O.; Nefedov, A.; Kind, M.; Terfort, A.; Wöll, C. Structural Characterization of Self-Assembled Monolayers of Pyridine-Terminated Thiols on Gold. *Phys. Chem. Chem. Phys.* **2010**, *12*, 4459.

(48) Zhang, Y.-Q.; Björk, J.; Weber, P.; Hellwig, R.; Diller, K.; Papageorgiou, A. C.; Oh, S. C.; Fischer, S.; Allegretti, F.; Klyatskaya, S.; Ruben, M.; Barth, J. V.; Klappenberger, F. Unusual Deprotonated Alkynyl Hydrogen Bonding in Metal-Supported Hydrocarbon Assembly. *J. Phys. Chem. C* **2015**, *119*, 9669–9679.

(49) Stöhr, J.; Outka, D. A. Determination of Molecular Orientations on Surfaces from the Angular Dependence of near-Edge X-Ray-Absorption Fine-Structure Spectra. *Phys. Rev. B* **1987**, *36*, 7891–7905.

(50) Klappenberger, F.; Kühne, D.; Marschall, M.; Neppel, S.; Krenner, W.; Nefedov, A.; Strunskus, T.; Fink, K.; Wöll, C.; Klyatskaya, S.; Fuhr, O.; Ruben, M.; Barth, J. V. Uniform π -System Alignment in Thin Films of Template-Grown Dicarboxylic-Oligophenyls. *Adv. Funct. Mater.* **2011**, *21*, 1631–1642.

(51) Sofikitis, D.; Bougas, L.; Katsoprinakis, G. E.; Spiliotis, A. K.; Loppinet, B.; Rakitzis, T. P. Evanescent-Wave and Ambient Chiral Sensing by Signal-Reversing Cavity Ringdown Polarimetry. *Nature* **2014**, *514*, 76–79.

(52) Heister, P.; Lünskens, T.; Thämer, M.; Kartouzian, A.; Gerlach, S.; Verbiest, T.; Heiz, U. Orientational Changes of Supported Chiral 2,2'-Dihydroxy-1,1'-binaphthyl Molecules. *Phys. Chem. Chem. Phys.* **2014**, *16*, 7299–7306.

(53) Thämer, M.; Kartouzian, A.; Heister, P.; Gerlach, S.; Tschurl, M.; Boesl, U.; Heiz, U. Linear and Nonlinear Laser Spectroscopy of Surface Adsorbates with Sub-Monolayer Sensitivity. *J. Phys. Chem. C* **2012**, *116*, 8642–8648.

(54) Kartouzian, A.; Heister, P.; Thämer, M.; Gerlach, S.; Heiz, U. In-Line Reference Measurement for Surface Second Harmonic Generation Spectroscopy. *J. Opt. Soc. Am. B* **2013**, *30*, 541–548.

(55) Byers, J. D.; Yee, H. I.; Petralli-Mallow, T.; Hicks, J. M. Second-Harmonic Generation Circular-Dichroism Spectroscopy from Chiral Monolayers. *Phys. Rev. B* **1994**, *49*, 14643–14647.

(56) Thämer, M.; Kartouzian, A.; Heister, P.; Lünskens, T.; Gerlach, S.; Heiz, U. Small Supported Plasmonic Silver Clusters. *Small* **2014**, *10*, 2340–2344.

(57) Lünskens, T.; Heister, P.; Thämer, M.; Walenta, C. A.; Kartouzian, A.; Heiz, U. Plasmons in Supported Size-Selected Silver Nanoclusters. *Phys. Chem. Chem. Phys.* **2015**, *17*, 17541–17544.

(58) Lünskens, T.; Walenta, C. A.; Heister, P.; Kartouzian, A.; Heiz, U. Surface Oxidation of Supported, Size-Selected Silver Clusters. *J. Cluster Sci.* **2017**, 3185–3192.