



2019

ANNUAL REPORT 2019

Prof. Nazario Martín León Universidad
Complutense de Madrid
Organic Chemistry Department
Chemistry Faculty
E- 28040 Madrid – Spain
Tel. +34 91.394.42.27
Web:
<http://www.nazariomartingroup.com/index.html>

1) J. M. Fernández-García, P. J. Evans, S. Filippone, M. A. Herranz, N. Martín, “Chiral Molecular Carbon Nanostructures”, *Acc. Chem. Res.* **2019**, *52*, 1565-1574 - DOI: [10.1021/acs.accounts.9b00144](https://doi.org/10.1021/acs.accounts.9b00144)



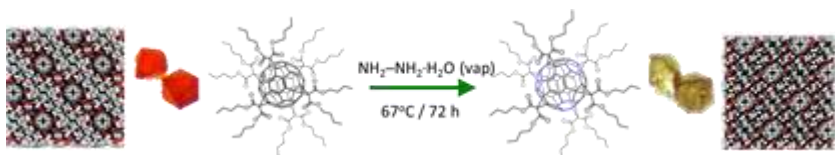
Conspectus

Chirality is a fascinating property present in naturally occurring and artificial molecules and materials, observable as chiroptical behavior. The emerging area of carbon nanostructures has undergone tremendous development, with a wide variety of carbon nanoforms reported over the last two decades. However, despite interest in merging chirality and nanocarbons, this has been successfully achieved only in empty fullerenes, whereas in other kinds of fullerenes or carbon nanostructures such as carbon nanotubes, graphene, and graphene quantum dots (GQDs), to name the most popular systems, it is almost unknown. Therefore, controlling chirality in carbon nanostructures currently represents a major challenge for the chemical community. In this Account, we show our progress in the synthesis of chiral molecular carbon nanostructures, namely, metallofullerenes, endohedral fullerenes, GQDs, and curved molecular nanographenes, by using asymmetric catalysis and both top-down and bottom-up chemical approaches. Furthermore, we bring in a new family of lesser-known molecular chiral bilayer nanographenes, where chirality is introduced from the starting helicene moiety and a single enantiomer of the nanographene is synthesized.

Some important landmarks in the development of chiral molecular carbon nanostructures shown in this Account are the application of synthesis-tailored, enantiomerically pure metallofullerenes as catalysts for hydrogen transfer reactions and the use of endohedral fullerenes to determine the effect of the incarcerated molecule in the carbon cage on the cis–trans stereoisomerization of optically active pendent moieties. Furthermore, the first top-down synthesis of chiral GQDs by functionalization with chiral alcohols is also presented. An emerging alternative to GQDs, when the desire for purity and atomistic control outweighs the cost of multistep synthesis, is the bottom-up approach, in which molecular nanographenes are formed in precise sizes and shapes and enantiomeric control is feasible. In this regard, a singular and amazing example is given by our synthesis of a single enantiomer of the first chiral bilayer nanographene, which formally represents a new family of molecular nanographenes with chirality controlled and maintained throughout their syntheses.

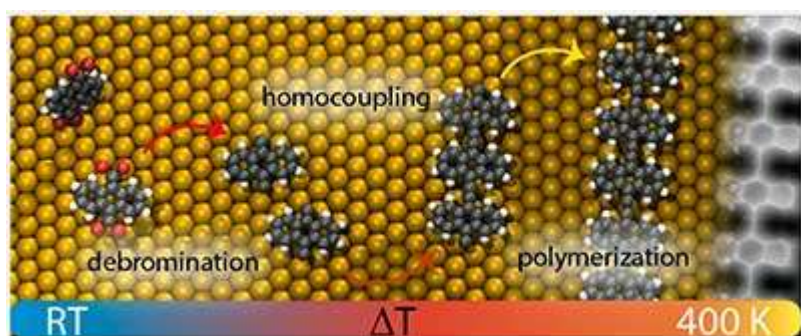
The aforementioned synthetic chiral nanostructures represent groundbreaking nanocarbon systems where chirality is a further dimension of structural control, paving the way to a new scenario for carbon nanoforms in which chirality selection determines the properties of these novel carbon-based materials. Fine-tuning of such properties is envisioned to impact biomedical and materials science applications.

2) E. Fernández-Bartolome, J. Santos, A. Gamonal, S. Khodabakhshi, L. J. McCormick, S. J. Teat, E. C. Sañudo, J. Sánchez Costa, N. Martín, “A Three-Dimensional Dynamic Supramolecular “Sticky Fingers” Organic Framework”, *Angew. Chem. Int. Ed.*, **2019**, *58*, 2310-2315 - DOI: [10.1002/anie.201812419](https://doi.org/10.1002/anie.201812419).



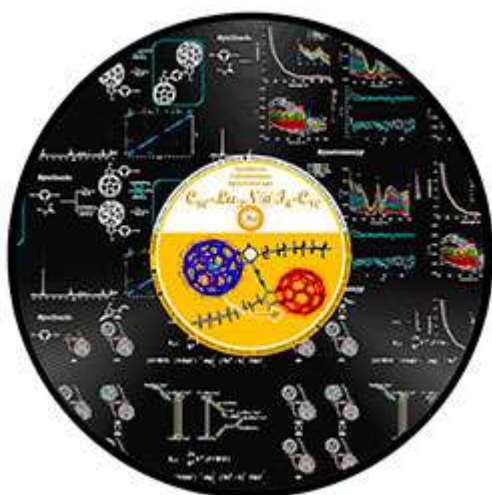
Engineering high-recognition host-guest materials is a burgeoning area in basic and applied research. The challenge of exploring novel porous materials with advanced functionalities prompted us to develop dynamic crystalline structures promoted by soft interactions. The first example of a pure molecular dynamic crystalline framework is demonstrated, which is held together by means of weak "sticky fingers" van der Waals interactions. The presented organic-fullerene-based material exhibits a non-porous dynamic crystalline structure capable of undergoing single-crystal-to-single-crystal reactions. Exposure to hydrazine vapors induces structural and chemical changes that manifest as toposelective hydrogenation of alternating rings on the surface of the [60]fullerene. Control experiments confirm that the same reaction does not occur when performed in solution. Easy-to-detect changes in the macroscopic properties of the sample suggest utility as molecular sensors or energy-storage materials.

3) A. Sánchez-Grande, B. de la Torre, J. Santos, B. Cirera, K. Lauwaet, T. Chutora, S. Edalatmanesh, P. Mutombo, J. Rosen, R. Zbořil, R. Miranda, J. Björk, P. Jelínek, N. Martín, D. Écija, "On-surface synthesis of ethynylene bridged anthracene polymers", *Angew. Chem. Int. Ed.*, **2019**, *58*, 6559-6563 - DOI: [10.1002/anie.201814154](https://doi.org/10.1002/anie.201814154).



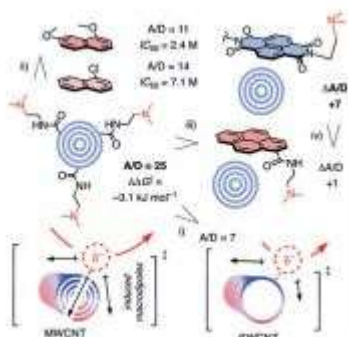
Engineering low-band-gap π -conjugated polymers is a growing area in basic and applied research. The main synthetic challenge lies in the solubility of the starting materials, which precludes advancements in the field. Here, we report an on-surface synthesis protocol to overcome such difficulties and produce poly(p-anthracene ethynylene) molecular wires on Au(111). To this aim, a quinoid anthracene precursor with =CBr₂ moieties is deposited and annealed to 400 K, resulting in anthracene-based polymers. High-resolution nc-AFM measurements confirm the nature of the ethynylene-bridge bond between the anthracene moieties. Theoretical simulations illustrate the mechanism of the chemical reaction, highlighting three major steps: dehalogenation, diffusion of surface-stabilized carbenes, and homocoupling, which enables the formation of an ethynylene bridge. Our results introduce a novel chemical protocol to design π -conjugated polymers based on oligoacene precursors and pave new avenues for advancing the emerging field of on-surface synthesis.

4) M. Izquierdo, B. Platzer, A. J. Stasyuk, O. A. Stasyuk, A. A. Voityuk, S. Cuesta, M. Solà, D. M. Guldi, N. Martín, "All-Fullerene Electron Donor–Acceptor Conjugates", *Angew. Chem. Int. Ed.* **2019**, *58*, 6932-6937 - DOI: [10.1002/anie.201901863](https://doi.org/10.1002/anie.201901863)



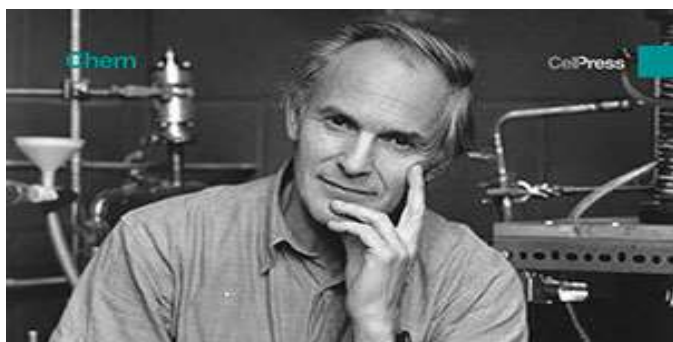
The synthesis and characterization of a covalent all-fullerene C60-Lu3N@Ih-C80 electron donor–acceptor conjugate has been realized by sequential 1,3-dipolar cycloaddition reactions of azomethine ylides on Lu3N@Ih-C80 and C60. To the best of our knowledge, this is the first time that two fullerenes behaving as both electron donor (Lu3N@Ih-C80) and acceptor (C60) are forming an electroactive dumbbell. DFT calculations reveal up to 16 diastereomeric pairs, that is, 8 with syn and 8 with anti orientation, with the anti-RSSS isomer being the most stable. Spectroelectrochemical absorption and femtosecond transient absorption experiments support the notion that a C60^{•-}-Lu3N@Ih-C80^{•+} charge-separated state is formed. Spin conversion from the charge-separated singlet state C60^{•-}-Lu3N@Ih-C80^{•+} into the corresponding triplet state is facilitated by the heavy-atom effect stemming from the Lu3N-cluster, which, in turn, slows down the charge recombination by one order of magnitude.

5. A.-B. Bornhof, M. Vázquez-Nakagawa, L. Rodríguez-Pérez, M. A. Herranz, N. Sakai, N. Martín, S. Matile, J. López-Andarias “Anion– π Catalysis on Carbon Nanotubes”, *Angew. Chem. Int. Ed.*, **2019**, *58*, 16097-16100 - DOI: [10.1002/anie.201909540](https://doi.org/10.1002/anie.201909540)



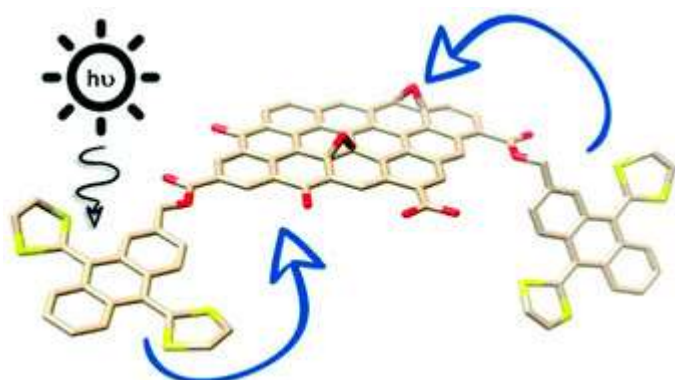
Induced π acidity from polarizability is emerging as the most effective way to stabilize anionic transition states on aromatic π surfaces, that is, anion– π catalysis. To access extreme polarizability, we propose a shift from homogeneous toward heterogeneous anion– π catalysis on higher carbon allotropes. According to benchmark enolate addition chemistry, multi-walled carbon nanotubes equipped with tertiary amine bases outperform single-walled carbon nanotubes. This is consistent with the polarizability of the former not only along but also between the tubes. Inactivation by π -basic aromatics and saturation with increasing catalyst concentration support that catalysis occurs on the π surface of the tubes. Increasing rate and selectivity of existing anion– π catalysts on the surface of unmodified nanotubes is consistent with transition-state stabilization by electron sharing into the tubes, i.e., induced anion– π interactions. On pristine tubes, anion– π catalysis is realized by non-covalent interfacing with π -basic pyrenes.

6) N. Martín, “The Legacy of Sir Harold W. Kroto: Fullerenes and Beyond”, *Chem*, **2019**, *5*, 733-738 - DOI: [10.1016/j.chempr.2019.03.015](https://doi.org/10.1016/j.chempr.2019.03.015)



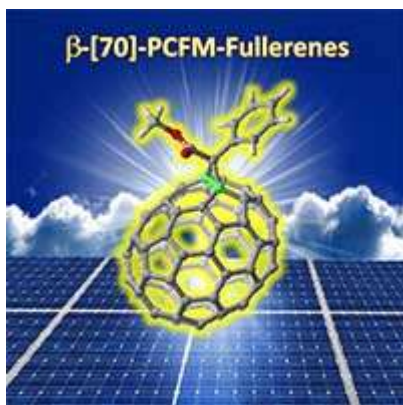
Induced π acidity from polarizability is emerging as the most effective way to stabilize anionic transition states on aromatic π surfaces, that is, anion- π catalysis. To access extreme polarizability, we propose a shift from homogeneous toward heterogeneous anion- π catalysis on higher carbon allotropes. According to benchmark enolate addition chemistry, multi-walled carbon nanotubes equipped with tertiary amine bases outperform single-walled carbon nanotubes. This is consistent with the polarizability of the former not only along but also between the tubes. Inactivation by π -basic aromatics and saturation with increasing catalyst concentration support that catalysis occurs on the π surface of the tubes. Increasing rate and selectivity of existing anion- π catalysts on the surface of unmodified nanotubes is consistent with transition-state stabilization by electron sharing into the tubes, i.e., induced anion- π interactions. On pristine tubes, anion- π catalysis is realized by non-covalent interfacing with π -basic pyrenes.

7) T. Scharl, A. Ferrer-Ruiz, A. Saura-Sanmartín, L. Rodríguez-Pérez, M. A. Herranz, N. Martín, D. M. Guldi, "Charge Transfer in Graphene Quantum Dots Coupled with Tetrathiafulvalenes", *Chem. Commun.*, **2019**, *55*, 3223-3226 - DOI: [10.1039/C8CC09990A](https://doi.org/10.1039/C8CC09990A)



Water-soluble fluorescent graphene quantum dots have been successfully prepared through a top-down approach, that is, starting with graphite, and covalently functionalizing it with π -extended tetrathiafulvalene. Charge transfer investigations reveal noticeably slower charge recombination when compared with exTTF nanoconjugates featuring carbon nanodots, for which a larger presence of trap states is observed.

8) S. Vidal, M. Izquierdo, S. Filippone, I. Fernández, S. Akin, J-Y. Seo, S. M. Zakeeruddin, M. Graetzel, N. Martín, "Site-selective Synthesis of β -[70]PCBM-like Fullerenes: Efficient Application in Perovskite Solar Cells", *Chem. Eur. J.*, **2019**, *25*, 3224-3228 - DOI: [10.1002/chem.201806053](https://doi.org/10.1002/chem.201806053).



We report on the site-selective synthesis of PCBM-like [70]fullerene site-isomers, where the elusive β -site-isomers are, for the first time, the major product in a (cyclo)addition chemical reaction involving [70]fullerene. The reaction involves a straightforward cyclopropanation of [70]fullerene from sulfonium salts, affording a mixture of α and β site-isomers in good yields. Amazingly, the preference for the α - or β -site-isomer can be efficiently controlled by means of the solvent polarity! DFT theoretical calculations (DMF and toluene) nicely predict that, although the formation of the α -adduct is, as expected, thermodynamically favored, the selectivity of the process is determined by the energy difference of the respective transition states. Furthermore, the employ of α or/and β site-isomers, as pure materials or as a mixture of them, used as templating agent, has been evaluated in perovskite solar cells. The positive influence of the [70]fullerenes by passivating the voids/pin-holes and/or deep slits, is reflected in highly efficient and stable bulk heterojunction perovskite solar cells, whose performance (around 20 %) is slightly but consistently depending on the isomeric fullerene composition. These experimental findings pave the way to investigate a new reactivity on C70 and to explore the properties of the less-known β -derivatives.

9) J. Urieta-Mora, I. Zimmermann, J. Aragón, A. Molina-Ontoria, E. Ortí, N. Martín, M. K. Nazeeruddin, "Dibenzoquinquethiophene- and Dibenzosexithiophene-Based Hole-Transporting Materials for Perovskite Solar Cells", *Chem. Mater.* **2019**, *31*, 6435–6442 - DOI: [10.1021/acs.chemmater.8b04003](https://doi.org/10.1021/acs.chemmater.8b04003)



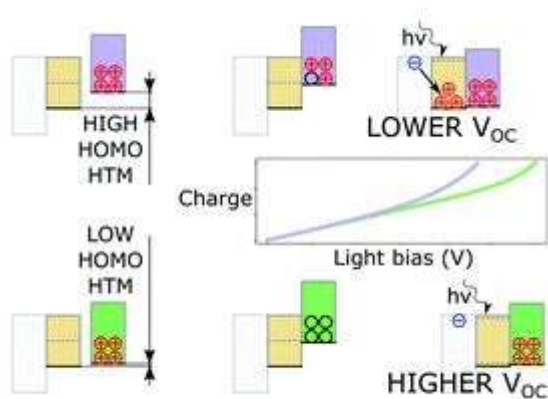
Fused oligothiophene-based π -conjugated organic derivatives have been widely used in electronic devices. In particular, two-dimensional (2D) heteroarenes offer the possibility of broadening the scope by extending the π -conjugated framework, which endows enhanced charge transport properties due to the potential intermolecular π - π stacking. Here, the synthesis and characterization of two new small-molecule hole-transporting materials (HTMs) for perovskite solar cells (PSCs) are reported. The newly custom-made compounds are based on dibenzoquinquethiophene (DBQT) and dibenzosexithiophene (DBST) cores, which are covalently linked to triphenylamine moieties to successfully afford the four-armed tetrakis(triphenylamine) (TTPA) derivatives TTPA-DBQT and TTPA-DBST. The combination of these novel central scaffolds with the electron-donor TTPA units bestow the resulting HTMs with the appropriate energy levels and, therefore, good electronic contact with the perovskite for extracting the hole efficiently. TTPA-DBQT surpasses TTPA-DBST not only in terms of conductivity but also in light-to-energy conversion efficiency using conventional mesoscopic n-i-p perovskite devices, 18.1% and 14.3%, respectively. These results were systematically compared with the benchmark HTM, 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD). Additionally, scanning electron microscopy (SEM) hints that TTPA-DBQT forms high quality and fully homogeneous films, whereas TTPA-DBST leads to the formation of thinner films with pinholes, which explains its lower fill factor despite its better hole-extraction properties owing to its more planar π -extended scaffold.

10) J. Mateos-Gil, J. Calbo, L. Rodríguez-Pérez, M. A. Herranz, E. Ortí, N. Martín, "Carbon Nanotubes Conjugated with Triazole-Based Tetrathiafulvalene-Type Receptors for C60 Recognition", *ChemPlusChem*, **2019**, *84*, 730-739 - DOI: [10.1002/cplu.201900078](https://doi.org/10.1002/cplu.201900078)



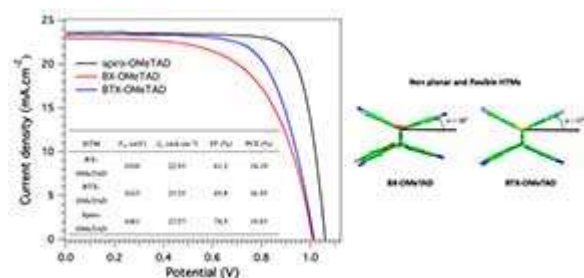
Fullerene receptors prepared by a twofold CuI-catalyzed azide-alkyne cycloaddition reaction with π -extended tetrathiafulvalene (exTTF) have been covalently linked to single-walled carbon nanotubes and multi-walled carbon nanotubes. The nanoconjugates obtained were characterized by several analytical, spectroscopic and microscopic techniques (TEM, FTIR, Raman, TGA and XPS), and evaluated as C60 receptors by using UV-Vis spectroscopy. The complexation between the exTTF-triazole receptor in the free state and C60 was also studied by UV-Vis and ^1H NMR titrations, and compared with analogous triazole-based tweezer-type receptors containing the electron-acceptor 11,11,12,12-tetracyano-9,10-anthraquinodimethane and benzene rings instead of exTTF motifs, providing in all cases very similar values for the association constant ($\log K_a \approx 3.0-3.1$). Theoretical density functional theory calculations demonstrated that the enhanced interaction between the host and the guest upon increasing the size of the π -conjugated arms of the tweezer is compensated by an increase in the energy penalty needed to distort the geometry of the host to wrap C60.

11) I. Gelmetti, N. F. Montcada, A. Pérez-Rodríguez, E. Barrena, C. Ocal, I. García-Benito, A. Molina-Ontoria, N. Martín, A. Vidal-Ferran, E. Palomares, "Energy Alignment and Recombination in Perovskite Solar Cells: Weighted Influence on the Open Circuit Voltage", *Energy Environ. Sci.*, **2019**, *12*, 1309-1316 - DOI: [10.1039/C9EE00528E](https://doi.org/10.1039/C9EE00528E).



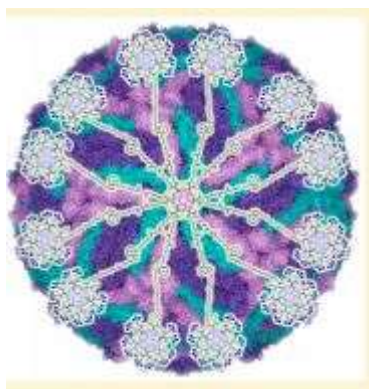
In this work, we assess the possible reasons for the differences observed in open circuit voltage (VOC) in mixed cation perovskite solar cells when comparing four different hole transport materials (HTMs), namely TAE-1, TAE-3, TAE-4 and spiro-OMeTAD. All these HTMs present close chemical and physical properties, however, once they are finally deposited onto the perovskite layer, the HTMs provide different performance characteristics. Additional to the evaluation of the HTM influence on recombination, we find that, upon deposition of the organic HTM on top of the perovskite, there is an important change in the energy level position, and the impact on the device VOC is discussed. We consider that this experimental observation could be general for other organic HTMs and would justify the difficulties in finding molecules and materials that could improve the efficiency of perovskite solar cells overcoming the solar-to-energy conversion efficiency of solar cells made using spiro-OMeTAD as a hole selective contact.

12) J. Urieta-Mora, I. García-Benito, I. Zimmermann, J. Aragón, P. D. García-Fernández, G. Grancini, A. Molina-Ontoria, E. Ortí, N. Martín, M. K. Nazeeruddin, "Non-Planar and Flexible Hole Transporting Materials from BisXanthene and Bis-Thioxanthene units for Perovskite Solar Cells", *Helv. Chim. Acta*, **2019**, *102*, e1900056 - DOI: [10.1002/hlca.201900056](https://doi.org/10.1002/hlca.201900056).

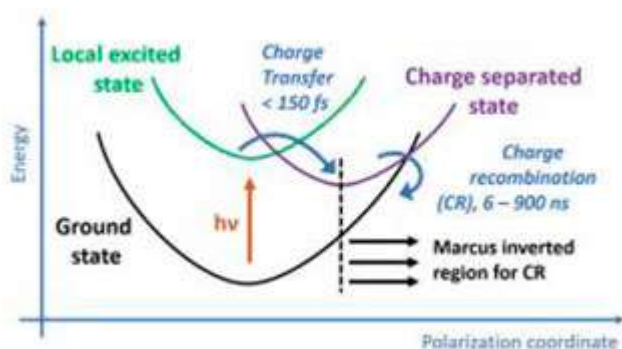


Two new hole-transporting materials (HTMs), BX-OMeTAD and BTX-OMeTAD, based on xanthene and thioxanthene units, respectively, and bearing p-methoxydiphenylamine peripheral groups, are presented for their use in perovskite solar cells (PSCs). The novelty of the newly designed molecules relies on the use of a single carbon-carbon bond 'C-C' as a linker between the two functionalized heterocycles, which increases the flexibility of the molecule compared with the more rigid structure of the widely used HTM spiro-OMeTAD. The new HTMs display a limited absorbance in the visible region, due to the lack of conjugation between the two molecular halves, and the chemical design used has a remarkably impact on the thermal properties when compared to spiro-OMeTAD. BX-OMeTAD and BTX-OMeTAD have been tested in $[(\text{FAPbI}_3)_{0.87}(\text{MAPbBr}_3)_{0.13}]_{0.92}[\text{CsPbI}_3]_{0.08}$ -based PSC devices exhibiting power conversion efficiencies of 14.19 and 16.55 %, respectively. The efficiencies reached, although lower than those measured for spiro-OMeTAD (19.63 %), are good enough to consider the chemical strategy used as an interesting via to design HTMs for PSCs.

13) J. Ramos-Soriano, J. J. Reina, B. M. Illescas, N. de la Cruz, L. Rodríguez-Pérez, F. Lasala, J. Rojo, R. Delgado, N. Martín, "Synthesis of Highly Efficient Multivalent Disaccharide/[60]Fullerene Nanoballs for Emergent Viruses", *J. Am. Chem. Soc.*, **2019**, *141*, 15403–15412 - DOI: [10.1021/jacs.9b08003](https://doi.org/10.1021/jacs.9b08003)

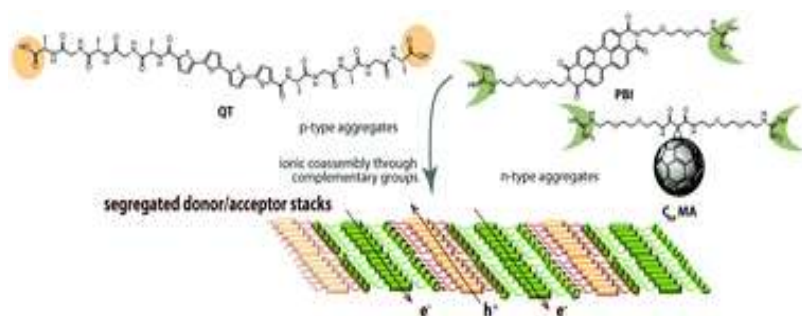


14) R. Sandoval-Torrientes, A. Gavrik, A. Isakova, A. Abudulimu, J. Calbo, J. Aragón, J. Santos, E. Ortí, N. Martín, V. Dyakonov, L. Lüer, "Minimizing geminate recombination losses in small-molecule-based organic solar cells", *J. Mater. Chem. C*, **2019**, *7*, 6641–6648 - DOI: [10.1039/c9tc00862d](https://doi.org/10.1039/c9tc00862d)



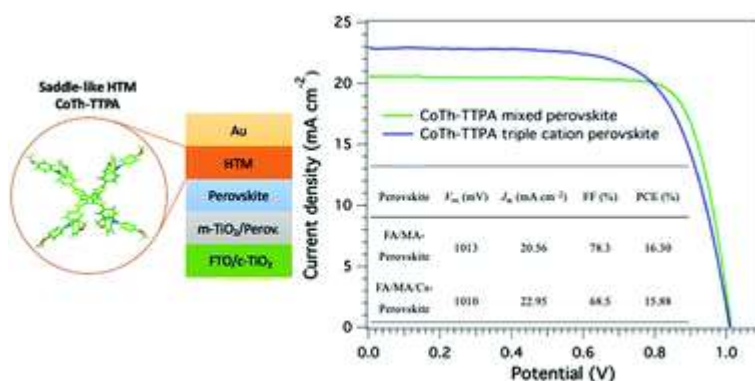
Small-molecule-based organic solar cells (OSCs) are a recurrent alternative to polymer-based OSCs. Due to the higher purity and definition of small molecules compared to polymers, the morphological requirements can be more relaxed. Here, we present a series of novel rhodanine-based small-molecule electron donors and blend them with the standard acceptor PC70BM. By performing a target analysis on femtosecond spectroscopy data, we quantify the rates of geminate charge recombination. We are able to reproduce these rates by applying the Marcus–Levich–Jortner equation, using results from quantum chemical calculations. This shows that in a series of differently substituted compounds, one can correctly predict trends in geminate recombination rates by relying only on quantities that are easy to measure (cyclic voltammetry, optical spectra) or that can be calculated by relatively inexpensive methods such as (TD)DFT. Our method should thus accelerate the search for high-performance small-molecule photovoltaic blends.

15) A. López-Andarias, C. Atienza, J. López-Andarias, W. Matsuda, T. Sakurai, S. Seki and N. Martín. "Assembly effect on the charge carrier mobility in quaterthiophene-based n/p-materials", *J. Mater. Chem. C*, **2019**, *7*, 6649-6655 - DOI:10.1039/c9tc00165d



Precise control of supramolecular polymerization by tuning the pH value of a peptide-based quaterthiophene donor moiety allows obtaining three different aggregates. Charge screening of the assemblies with different electron acceptor units steers the formation of n/p-co-assembled materials with appealing optoelectronic properties. We have demonstrated that control on the organization of the main building blocks drastically affects the conductivity properties of the mixed n/p-co-assemblies.

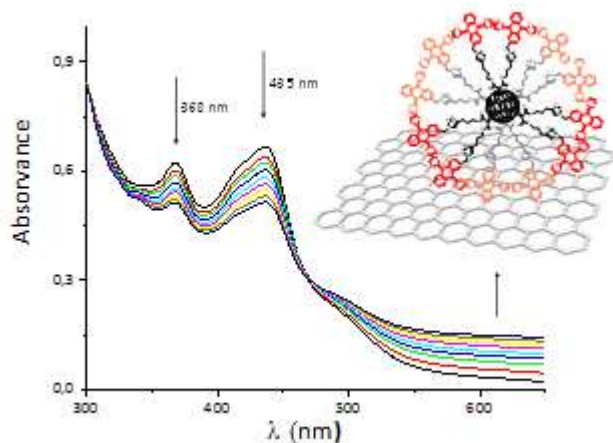
16) J. Urieta-Mora, I. García-Benito, I. Zimmermann, J. Aragón, J. Calbo, G. Grancini, A. Molina-Ontoria, E. Ortí, N. Martín, M. K. Nazeeruddin, "Saddle-like, p-conjugated, cyclooctatetrathiophenebased, hole-transporting material for perovskite solar cells", *J. Mater. Chem. C*, **2019**, *7*, 6656-6663 - DOI: 10.1039/c9tc00437h.



A flexible, saddle-like, π -conjugated skeleton composed of four fused thiophene rings forming a cyclooctatetrathiophene (CoTh) with four triphenylamines (CoTh-TTPA) is presented as a hole-transporting material (HTM) for perovskite solar cells. The new HTM shows a bright red color stemming from a direct conjugation between the TPA groups and the central CoTh scaffold. This results in a charge transfer band due to the combination of the weak acceptor moiety, the CoTh unit, and the electron-donating p-methoxytriphenylamine groups. CoTh-TTPA exhibits a suitable highest-occupied molecular orbital (HOMO) level in relation to the valence band edge of the perovskite, which ensures efficient hole extraction at the perovskite/HTM interface. It has been applied as the HTM in combination with a mixed perovskite ([FAPbI₃]0.85[MAPbBr₃]0.15) and a state-of-the-art triple cation perovskite ([FAPbI₃]0.87(MAPbBr₃)0.13]0.92[CsPbI₃]0.08) reaching noticeable light-to-energy conversion efficiencies of 16.3 and 15.9%, respectively. These values are slightly lower than those measured for the benchmark spiro-OMeTAD HTM.

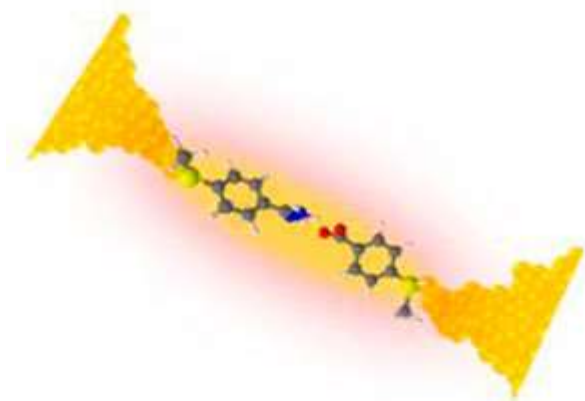
The HTM properties have been analyzed by means of photoluminescence and conductivity experiments, which demonstrated a better hole extraction and conductivity for spiro-OMeTAD.

17) A. Muñoz, L. Rodríguez-Pérez, S. Casado, B. M. Illescas, N. Martín, “Multivalent Fullerene/ π -Extended TTF Electroactive Molecules – Non-Covalent Interaction with Graphene and Charge Transfer Implications”, *J. Mater. Chem. C*, **2019**, *7*, 8962-8968 - DOI: [10.1039/C9TC02277E](https://doi.org/10.1039/C9TC02277E)



New multivalent and electroactive molecules based on 9,10-di(1,3-dithiole-2-ylidene)-9,10-dihydroanthracene (π -exTTF) and [60]fullerene were prepared via copper-catalyzed azide-alkyne cycloaddition click reaction in an efficient manner. Their non-covalent anchoring on the graphene surface was confirmed by TGA, FTIR spectroscopy, UV-vis spectroscopy, AFM, SEM and TEM characterization. Raman spectroscopy reveals the electronic nature of the supramolecular interactions.

18) V. Sacchetti, J. Ramos-Soriano, B. M. Illescas, M. T. González, D. Li, L. Palomino-Ruiz, I. R. Márquez, E. Leary, G. Rubio-Bollinger, F. Pauly, N. Agraït, N. Martín “Effect of Charge-Assisted Hydrogen Bonds on Single-Molecule Electron Transport” *J. Phys. Chem. C*, **2019**, *123*, 48, 29386-29393 - DOI: [10.1021/acs.jpcc.9b0685](https://doi.org/10.1021/acs.jpcc.9b0685)



The effect of the in-backbone presence of charge-assisted hydrogen bonds (CAHBs) in the conductance of single-molecule junctions has been studied by the scanning tunneling microscope break junction technique. In particular, two amidinium-carboxylate supramolecular complexes of different lengths have been tested. We observed that the ionic character that gives extra stability to the CAHB is a hindrance toward the electron transport through the complexes. Theoretical calculations using the DFT + Σ method indicate that both the highest occupied molecular orbital and lowest

unoccupied molecular orbital of the complexes are fully localized in only one of the moieties of the complex explaining the low single-molecular conductance of the compounds.

19) J. Calbo, A. de Juan, J. Aragó, J. Villalva, N. Martín, E. M. Pérez, E. Ortí, "Understanding the affinity of bis-exTTF macrocyclic receptors towards fullerene recognition", *Phys. Chem. Chem. Phys.*, **2019**, *21*, 11670-11675 - DOI: [10.1039/C9CP01735F](https://doi.org/10.1039/C9CP01735F).



A new series of fullerene receptors based on exTTF macrocycles with alkyl ether chains of increasing length is reported. The novel macrocyclic receptors are able to favourably interact with fullerene C60 through a synergistic combination of π - π , CH \cdots π and n \cdots π noncovalent interactions. We identify that the highest affinity towards C60 recognition is achieved for the host with the tightest fit; that is, the smallest receptor with a cavity large enough to host the buckyball inside (log K_a = 5.2 in chlorobenzene at 298 K). However, besides this expected observation, theoretical calculations evidence that the most stable self-assembling configuration corresponds for all the receptors to an outside-ring binding mode, in which the C60 guest is out of the cavity of the receptor. The higher stability of this configuration results from the smaller deformation energy it implies for the receptor, and allows to explain the experimental trends in the association constants.

THESIS

TÍTULO: "Self-assembly of electroactive supramolecular architectures: a bio-inspired approach"

DOCTORANDO: Alicia López Andarias

UNIVERSIDAD: Complutense (Madrid)

AÑO LECTURA: 25 de octubre, 2019

FACULTAD/ESCUELA: Química

CALIFICACIÓN: Sobresaliente "cum laude" por unanimidad

TÍTULO: "Tuning the optoelectronic properties of graphene and carbon nanodots-based materials"

DOCTORANDO: Andrés Ferrer Ruiz

UNIVERSIDAD: Complutense (Madrid)

AÑO LECTURA: 7 de junio, 2019

FACULTAD/ESCUELA: Química

CALIFICACIÓN: Sobresaliente "cum laude" por unanimidad

TÍTULO: "Stereoselective synthesis of fullerenes: properties and photoelectrochemical applications"

DOCTORANDO: Rosa Girón Rubio

UNIVERSIDAD: Complutense (Madrid)

AÑO LECTURA: 11 de abril, 2019

FACULTAD/ESCUELA: Química

CALIFICACIÓN: Sobresaliente "cum laude" por unanimidad

TÍTULO: "Photosensitization of singlet oxygen: applications to the study of photooxidation of thioketones and photoeradication of H. pylori"

DOCTORANDO: Antonio José Sánchez Arroyo

UNIVERSIDAD: Complutense (Madrid)

FACULTAD/ESCUELA: Química

AÑO LECTURA: 1 de marzo, 2019

CALIFICACIÓN: Sobresaliente "cum laude" por unanimidad



Thesis Alicia López Andarías



Thesis Andrés Ferrer Ruiz



Thesis Rosa María Girón Rubio



Thesis Antonio José Sánchez

LECTURES

Fifth Erlangen Symposium “Synthetic Carbon Allotropes” “Chiral Synthetic Molecular Nanographenes”, Erlangen University, Erlangen (Germany), September 29th- October 2nd, 2019 (*Invited lecture*)

“ACS On Campus”, “Remarks on the Scientific Method”, Complutense University. Faculty of Chemistry, September 25th, 2019 (*Invited lecture*)

XXXVII Reunión Bienal de Química, RSEQ, “Synthetic Molecular Nanographenes by Design”, Auditorio Kursaal, San Sebastián (Donostia), Spain, May 26th- 30th, 2019 (*Invited lecture*)

Talents CNRS. MiniSymposium on Carbon Nanomaterials, “The Revival of Fullerenes”, Université de Strasbourg, Strasbourg (France), November 25th, 2019 (*Plenary lecture*)

Functional molecular materials, “Chirality in Nanographenes: A paradigmatic Case”, Centro de Congresos do Instituto Superior Tecnico, Lisbon (Portugal), October 14th, 2019 (*Invited lecture*)

XIX Jornada Científica del ICMol, "Multivalent Glycofullerenes for Emergent Viruses" ICMol (Valencia), December 13th, 2019 (*Plenary lecture*)

15th International Conference on Organic Electronics (ICOE-2019), “Synthetic Chiral Carbon Nanoforms” Hasselt University. Faculty of Chemistry, Hasselt, (Belgium), June 21-24, 2019 (*Invited lecture*)

International Symposium on Novel Aromatics (ISNA-18), “Synthetic Chiral Nanographenes”, Hokkaido University, Sapporo (Japan), July 21-26, 2019 (*Plenary lecture*)

75th Birthday of Jean-Pierre Sauvage, “Bottom-up Synthesis of (Chiral) π -Conjugated”, Strasbourg, (France), October 17-19, 2019 (*Plenary lecture*)

2D-Chem Valencia-Erlangen Symposium, "Chiral Synthetic Molecular Nanographenes", ICMol, Valencia (Spain), November 12-14, 2019 (*Plenary lecture*)

Master Universitario en Química Orgánica. Conferencia invitada. “Bottom-up Synthesis of (Chiral) Nanographenes”, Facultad de Química, Universidad Complutense (Madrid) Octubre 29, 2019 (*Invited conference*)

Entrega de premios de Tesis Doctorales. Sección territorial de Andalucía Occidental, RSEQ, “Nanociencia: la importancia de lo pequeño”, Sevilla. Facultad de Química, Universidad de Sevilla, Noviembre 29, 2019 (*Invited conference*)

Año internacional Tabla Periódica, "La Tabla Periódica de Mendeleiev: algunas curiosidades y mi elemento favorito", Huelva. Facultad de Química, Universidad de Huelva, Abril 9, 2019 (*Invited conference*)

In honour of Prof. Eugenio Coronado on his 60th birthday, “Symposium EC60”. Auditorium Marie Curie. Parc Científic de la Universitat de València, February 7th and 8th, 2019 (*Invited conference*)

Año internacional Tabla Periódica, “Nanociencia: la importancia de lo pequeño”, Ciudad Real. Facultad de Química, UCLM, Mayo 6, 2019 (*Invited conference*)

Ciclo de conferencias Ciencia para todos. “Una historia de la química actual: las nanoformas de carbono y Sir Harry W. Kroto”, Actividades de la Asociación Amigos del Museo de Ciudad Real-Convento de La Merced, Marzo 28, 2019 (*Invited conference*)