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Isomerically Pure Star-Shaped Triphenylene-Perylene Hybrids Involving Highly Extended π Conjugation

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Abstract: The synthesis and characterization of a new type of a highly conjugated heterocyclic π -chromophore, consisting of a central triphenylene core fused with three perylene–monoimide units (star-shaped molecule) is described. By judicious bay-functionalization with tert-butylphenoxy substituents, aggregation was completely prevented in common organic solvents, allowing for a straightforward purification and, for the very first time, the complete separation of the constitutional isomers by HPLC. Both isomers can be easily distinguished by means of several conventional spectroscopic techniques. Furthermore, we have illustrated the absence of supramolecular aggregates and enhanced processability by noncovalent functionalization of graphene substrates, showing an outstanding homogeneity and observing a different doping behavior in both isomers, being possible to distinguished by Raman spectroscopy.

Introduction

Perylenetetracarboxylic diimide (PDI)-based materials have become increasingly attractive due to their good charge-carrier mobilities, excellent light absorption in the wavelength range of the visible light, as well as high thermal, chemical, and photostability.^[1-9] Beyond optoelectronics, PDIs have been extensively used in the dispersion and noncovalent functionalization of synthetic carbon allotropes such as carbon nanotubes or graphene and in novel 2D materials.^[10-13] Moreover, in the last years several efforts have been devoted to the design and synthesis of highly extended heterocyclic π systems with extraordinarily large seas of conjugated π electrons.^[14,15] A characteristic feature of this family is the continuous bathochromic shift of the absorption and fluorescence emission bands as a consequence of the extension of the conjugated π -system.^[1,16-21]

The arrangement of PDI-based molecules can be tailored by supramolecular design, inducing perylene core twisting enforced by bay substituents, by the attachment of trialkoxyphenyl wedges, or by a head-to-tail alignment through hydrogenbonding interactions.^[22,19,23,9] PDIs have been extensively

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studied as exciting building blocks for the supramolecular construction of aggregates, but when it comes to π -extended PDI-based macromolecules, like n-type disk-shaped molecular systems, the number of studies is very scarce. These molecules endowed with C_3 symmetry exhibit appealing spectroscopic effects of interest in highly anisotropic media like liquid crystals as well as in molecular electronics.^[1,3] Usually, disk-shaped molecules containing polycyclic aromatic cores have a strong tendency to aggregation into 1D columns, endowing them with anisotropic charge transport properties. Along this front, Liu and co-workers developed a PDI-based C₃-symmetric star-shaped molecular skeleton exhibiting good electron mobility with a remarkably charge transport anisotropy.^[24,25] However, these systems strongly aggregate and are almost insoluble in common organic solvents, severely limiting their characterization (e.g. by ¹H NMR) and processability. Moreover, as a consequence of the condensation reaction between hexaaminotriphenylene and the corresponding anhydrides, these trimeric molecules are obtained as a statistical mixture of cis- (symmetric) and trans-(asymmetric) isomers, which to the best of our knowledge, have never been successfully separated.

Herein, we designed and synthesized a highly extended conjugated star-shaped molecule (see Scheme 1) that contains a triphenylene core fused with three bay-functionalised twisted peryleneimide imidazole "arms". Although these architectures do not contain long and highly flexible side groups in their imide periphery they are highly soluble in organic solvents.^[26] Moreover, we successfully separated constitutional isomers by means of HPLC for the very first time, and differentiated them using several spectroscopic techniques including NMR and Raman spectroscopy. Further we have found that these isomerpure star-shaped molecules form densely packed molecular films on CVD graphene with exceptionally high homogeneity.

Results and Discussion

The targeted star-shaped PDI (Scheme 1) was assembled by the condensation of hexamino triphenylene and perylene monoimide building blocks requiring a multistep synthetic sequence. One of the most common features in highly extended π systems is their tendency to aggregate via π - π stacking leading to virtually insoluble materials that complicate their purification, characterization, and processing $^{\left[27-30\right] }$ To overcome this hurdles, a widespread approach to obtain soluble aromatic system derivatives is based on the incorporation of bulky solubilising groups or long alkyl chains in the periphery^[19,31] as well as by distortion of their planarity.^[28,32] Specifically, the methodology for the synthesis of soluble PDI derivatives is the introduction of branched or long alkyl tails at the imide positions^[19,30] and bulky groups like *p-tert*-butilphenoxy at the bay positions.^[20,33,19,23] As expected, the incorporation of four bulky aryloxy groups attached to the bay positions of each PDI

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derivative arm lead to a significant distortion of the planar geometry of the PDI moiety. This is attributed to the repulsive interactions between these sterically encumbered substituents and consequently the PDI twisted out position from the plane preventing the intermolecular π - π stacking.^[34-36] Hence, according to Scheme 1, the first part of the synthetic approach started from the 1,6,7,12-tetrachloroperylene-3,4:9,10-tetracarboxylic dianhydride **1**



Scheme 1. Synthetic sequence of **9**. Reagents and conditions: a) 3-Pentylamine, imidazole, 3 h, 100 °C, N₂; b) 4-*tert*-butylphenol, K₂CO₃, NMP, 16 h, 120 °C; c) KOH, isopropanol:H₂O mixture, 1.5 h, 100 °C; d) Br₂, Fe powder, nitrobenzene, 16 h, 205 °C; e) benzophenone imine, $Pd_2(dba)_3$, *rac*-BINAP, NaOC(CH₃)₃, toluene, 16 h, 110 °C, N₂; f) HCl 2M, THF, 30 min, rt; g) Zn(OAc)₂, dry quinoline, 18 h, 180 °C, N₂.

Thus, an imidization reaction of **1** with 3-pentylamine in imidazole at 100 °C under N₂ provides, after acidic work-up, the symmetrically *N*,*N*-substituted PDI (**2**) as a red solid with 83 % yield. The subsequent nucleophilic substitution of bay chlorine atoms by 4-*tert*-butylphenolate in deaerated NMP at 120°C yielded tetraphenoxyperylene dimide **3**, which was subsequently partially hydrolyzed to afford the perylene monoimide

monoanhydride 4 in 18 % yield as a red solid (see Figures S1-2).

Once **4** was obtained, the second part of the synthetic procedure consisted in the preparation of the triphenylene core (Scheme 1 center).^[37,38] Thus, reaction of triphenylene **5** with Br₂ in nitrobenzene at 205°C in the presence of Fe powder provides **6** with 85% yield. Then, cross coupling reaction of the brominated



Figure 1. ^1H NMR spectrum of compound 9 in 1,1,2,2-tetrachloroethane-d2 at 363 K.

triphenylene with benzophenone imine in toluene catalyzed by $Pd_2(dba)_3$ using *rac*-BINAP as ligand in the presence of NaOC(CH₃)₃ afforded **7** as a yellow solid in good yield. The last stage in building up the structure of the star-shaped target molecule consisted in linking the individual perylene monoimide monoanhydride **4** with **7**.

After deprotection of the amino groups, which was carried out with 2M HCI in THF to furnish 8 in 81 % yield. Finally, the target molecule was successfully obtained in one step from 4 by reaction with 8 in dry quinoline in the presence of Zn(OAc)₂ at 180 °C for 18 h. Under these conditions, final 9 was isolated as a dark blue solid in 53% yield (Scheme 1 bottom). As expected this large π-conjugated architecture exhibits a pronounced aggregation leading to difficulties in its processing and characterization.^[24] Indeed, despite the introduction of the bayfunctional tert-butoxy moieties - which remarkably improved the solubility of the molecule – the ¹H NMR spectrum of 9 recorded in chloroform-d1 at room temperature showed a significant signal broadening in the aromatic region caused by aggregation. One approach to circumvent this problem is to change the deuterated reference solvent. Along this front, different organic solvents like benzene-d6 or dichloromethane-d2 among others

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were explored and despite the good solubility of the molecule, the ¹H NMR spectra resulted to be very broad even at high temperatures (see Figure S3). This is due to the interactions with the solvent and the balance of $\pi-\pi$ interactions between the extended π systems. However, the strong π - π interactions could be overcome by using 1,1,2,2-tetrachloroethane-d2, resulting in sharper NMR signals, indicative of a reduced aggregation. Additionally, the behavior of 9 under temperaturedependent ¹H NMR spectra was investigated. Figure 1 shows the ¹H NMR spectrum of 9 in 1,1,2,2-tetrachloroethane-d2 measured at 363 K, in which the aromatic proton signals became sharpened and a much better resolution was observed (see Figures 1 and S4). Nonetheless, despite all the dilution conditions applied in the spectroscopic measurements, the full characterization based on the analysis of ¹³C NMR spectroscopy failed to reliably confirm the proposed structure. This may be attributed to the residual aggregation of the molecules in the selected deuterated solvent even at elevated temperatures. Further characterization by high-resolution mass spectrometry measurements was conducted to verify the composition of the final product (see Figure 2 inset).

As can be seen in the inset of Scheme 1, a mixture of all-*trans*- $(C_{3h}$ symmetry) and mono-*cis* (C_s symmetry) isomers resulting from the random orientation of the perylene monoimide during the condensation reaction on the central hexaminotriphenylene of compound **9** was formed. Analysis of the ¹H NMR spectrum of the final compound presented in Figure 1 revealed two sets of signals with different intensities in the aromatic region indicating that **9** was a statistical mixture of the C_{3h} and C_s isomer with yields of *ca.* 25 % and 75 %, respectively.

The separation of the isomers of **9** was expected to be very challenging. Indeed, only a few reports on the separation of 1,6and 1,7-regioisomers of dibromo, diphenoxy, and dipyrrolidinyl substituted perylene diimides derivatives have been reported so far. Typical separation routes consist of crystallization^[39] or differences in solubility.^[40] In the case of π -extended molecules the separation of individual isomers appears to be challenging, firstly because of relatively poor solubility, and secondly due to a very similar chromatographic mobilities.

To face this challenge, high-performance liquid chromatography (HPLC) with a COSMOSIL-5PBB-R semi preparative column (10 × 250 mm) using CH₂Cl₂:toluene:MeOH - (25:35:40) mixture as selected mobile phase was employed. Figure 2 shows the HPLC profile of 9, whose peaks could be assigned to the C_{3h} and C_s isomer based on their relative intensities. The configurations of isolated isomers were unambiguously assigned on the basis of ¹H NMR analysis of signals of the perylene core and triphenylene core protons. The ¹H NMR spectra of the C_{3h} and C_s isomer of **9** as well as its statistical mixture in 1,1,2,2tetrachloroethane-d2 at 363 K are presented in Figures 3 and S5–6. The ¹H NMR of the C_s isomer (Figure 3 top) exhibits 6 singlets between 9.05-9.85 ppm (bay region in the triphenylenecore). As expected 12 protons of the perylene moiety appears in the region of 8.18-8.70 ppm (according integration), although only 11 singlets can be detected because of overlapping of two signals. Hence, the

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Figure 2. HPLC profile of **9** COSMOSIL-5PBB-R (10 × 250 mm; eluent CH₂Cl₂:toluene:MeOH 25:35:40; flow rate 5.0 mL/min; 50 °C; detection 630 nm). The collection regions are highlighted by blue (C_s isomer) and green (C_{3h} isomer). Insert: MALDI mass spectrum of **9** and calculated and experimentally observed isotopic distribution MS pattern.

assignment of the first elution phase at 6.1 min to the isomer with C_s symmetry based on the peaks intensity of the HPLC chromatogram was confirmed. For the minor isomer (second elution phase at 7.2 min) 2 and 4 singlets (triphenylene and perylene protons, respectively), were detected in agreement with the expected C_{3h} symmetry (Figure 3 center). The NMR spectroscopic data recorded for **9** (Figure 3 bottom) exhibited the combination of both isomer signals in the spectrum.

The successful isomers separation was further evidenced by attenuated total reflectance infrared spectroscopy (ATR-FTIR). The direct comparison of the spectra of the C_{3h} and C_s isomers revealed a rather similar behavior (see Figure 4 and S7). In both cases, characteristic stretching vibrations of perylene derivatives at 1694(1690) cm⁻¹ and 1654(1653) cm⁻¹ corresponding to the *N*-imides carbonyl groups were observed for the C_{3h} and C_s



Figure 4. AFT-IR spectra of the $C_{3\hbar}$ (red) and C_s (blue) isomer of ${\bf 9}$ in the region between 1600-1850 $cm^{-1}.$

isomers, respectively (Figure 4). It is worth noting that, in addition to these vibrations, the FT-IR spectrum displayed an additional signal at 1735 cm⁻¹, which is remarkable more intense for the C_s isomer. The lower molecular symmetry increases the molecular dipole moment, which typically enhance IR active vibrational modes. Thus, the band at 1735 cm⁻¹ is assigned to C=O vibration of the asymmetric N-imine carbonyl because of the C_3 symmetry breaking in the C_s isomer.^[41]

Steady-state absorption studies in 1,1,2,2-tetrachloroethane at 298 K of the target molecule as well as the different building blocks were carried out. The UV-Vis absorption spectrum of **4** and **9** is dominated by characteristic π – π * transitions showing a maximum absorption at 592 and 645 nm, respectively (Figure 5). It is noteworthy to mention that **9** exhibited a bathochromic shift of 53 nm in the absorption maximum, attributed to the extensive conjugation of its 156 π electrons in the star-shaped molecule, higher than those previously observed for benz-bimidazole-bridged perylenes^[15] or fused perylene–phthalocyanine hybrids.^[14]



Figure 3. Selected sections of the ¹H NMR spectra of C_{3h} and C_s isomer of 9 as well as its statistical isomers mixture in 1,1,2,2-tetrachloroethane-d2 at 363 K.

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Figure 5. (A) UV-Vis absorption spectra of **9** (black) and the isolated chromophores **4** (red) and **8** (green) in 1,1,2,2-tetrachloroethane at room temperature. The concentration of each sample was 8×10^{-5} M. (B) Steady-state emission spectra of the C_{3h} (red) and C_s (blue) isomers of **9** in 1,1,2,2-tetrachloroethane at room temperature.

This fact indicates an utterly new arrangement of the electron levels from which the optical excitation is facilitated. In the case of tetraryloxy-substitued PDI chromophores, the maximum absorption band indicates strongly allowed electronic $S_0 \rightarrow S_1$ transitions, generally found in the 400–600 nm range for these sort of molecules, and is characterized by three well resolved vibronic peaks.^[42–46] The ratio between the (0,0) and (0,1) transitions were remarkably larger than 1.6, indicative of monomeric units in solution for both molecules.^[47] The broad absorption behavior of **9** covers a larger part of the UV and visible region (250–750 nm), being of interest for those applications requiring larger absorption crossections in the visible region of the electromagnetic spectra (*e.g.*, photovoltaic devices).

When comparing the absorption spectra of the separated C_{3h} and C_s isomers, we observed a shift of *ca*. 4 nm in the (0,0) peak, as well as an increased absorption (*ca*. twice) in the case of the asymmetric isomer in the whole spectra. The fluorescence emission spectra with a peak maximum at 669(680) nm for the C_{3h} and C_s isomers, respectively, revealed

a mirror-like image of the absorption spectra with a Stokes shift of 26(22) nm with respect to **4**. Remarkably, a shift of *ca*. 11 nm between both isomers was detected. The calculated quantum

yields were 0.09 ±0.01 and 0.03 ±0.01 for the C_{3h} and C_s isomers, respectively. Such a pronounced quenching of the emission has been previously observed for related PDIs endowed with 3,4,5-tridodecyloxyphenyl substituents on theimide N-atoms and having four *tert*-butilphenoxy substituents in the bay position.^[44]

To further confirm the solubility of **9** and its respective isolated isomers in 1,1,2,2-tetrachloroethane, concentration-dependent UV-Vis experiments were carried out.

Figure SI8 shows the spectra collected in a range of concentration comprising $5 \cdot 10^{-5} - 2 \cdot 10^{-4}$ M for both isomers, highlighting the increased processability of these extended aromatic macrocycles. Furthermore, temperature-dependent analysis in the 298–353 K range only revealed slight changes in the absorbance, in excellent agreement with the NMR studies (see Figure S9).

At this point, we decided to explore the processability of these pure isomers on surfaces in order to discover whether these molecules presented supramolecular aggregates or not. Firstly, both isomers were spin-coated at 2,000 rpm on SiO₂/Si substrates and thoroughly analysed by means of optical microscopy, scanning Raman microscopy (SRM), and atomic force microscopy (AFM) showing an inhomogeneous covering of the surface, with no signatures of specific supramolecular aggregation motifs and the presence of fluorescence in the Raman spectra (see Figures SI10-11). Moreover, when CVD graphene substrates are used – in which π -aromatic molecules tend to lie with the aromatic cores parallel to the surface, stabilised by van der Waals interactions^[48-53] - a very homogeneous fluorescence quenching was detected by Raman spectroscopy in the range of millimetres (Figure 6). It is worth to remark that normally it is not possible to measure Raman spectra of fluorescent molecules, however by non covalently binding to graphene or related 2D materials, a fluorescence quenching of the dye can be obtained as a consequence of an electron/energy transfer.[49,54,55] The homogeneity of the films was characterized by means of SRM in areas of $30 \times 30 \ \mu m^2$,

measuring with 1 µm steps (> 900 single point spectra) and using a grating of 1800 grooves mm⁻¹ (Figure 6a and Figures S12-13). The isolated isomers of the star-shaped molecules exhibited the characteristic Raman peaks associated to the tetraryloxy-substitued PDI chromophores when resonantly excited at 532 nm in backscattering geometry.^[49] As recently reported by Duesberg and co-workers, the ratio between the n_{Ag} (ca. 1351 cm⁻¹) and the G peak of the graphene substrate can be efficiently used as an estimation of the packing density.^[56,57] Indeed, both isomers exhibited very homogeneous mean PDIn_{Ag}/G ratios of 1.03 and 0.93 (FWHM 0.10 and 0.11) for the C_{3h} and C_s isomers, respectively, indicative of a high packing density (Figure 6b). Interestingly, thanks to the profound quenching of the fluorescence, it was possible to distinguish both isomers when analysing the PDI-related bands centered at ca. 1351, 1403, 1447 and 1548 cm⁻¹, showing a measurable shift to lower frequencies (mode softening) of all the Raman modes for the C_s with respect to the C_{3h} isomer in the 1.5–6.7 cm⁻¹ range (Figure 6c). To the best of our knowledge, this is the first time that constitutional isomers of polycyclic aromatic



Figure 7. (A) PDIv_{Ag}/G ratios Raman intensity mappings (measured over a $30 \times 30 \ \mu\text{m}^2$ area) of the C_{3h} and C_s isomers deposited on CVD graphene substrates, exhibiting a very high uniformity and homogeneous covering. The color code indicates the PDIv_{Ag} (*ca.* 1351 cm⁻¹) and graphene G band intensity ratios. (B) The corresponding PDIv_{Ag}/G histograms extracted from the statistical analysis of the Raman mappings showing narrow distributions centered at around *ca.* 1, indicative of a high packing density. (C) *Top:* Mean Raman modes of the C_{3h} and C_s isomers highlighting the softening of the Raman modes of the C_{3h} isomer, allowing its clear differentiation. *Bottom:* The characteristic G and 2D graphene Raman modes are shifted as a consequence of the charge transfer (molecular doping). The inset shows the 2D band mode stiffening, which is more intense in the case of

 C_{3h} isomer. (D) Topography AFM images of the C_{3h} and C_s isomers (RMS values are 1.6±0.7 and 0.9±0.2, respectively) exhibiting the characteristic corrugations and wrinkles of CVD graphene substrates.

molecules can be distinguished by Raman spectroscopy. Interestingly, a detailed inspection of the main graphene Raman modes revealed a shift in the position of the graphene bands as a consequence of the interaction with the star-shaped isomers, which is more remarkable in the case of the 2D band. The increase in the Raman modes is indicative of a charge transfer (molecular doping) and is in excellent agreement with previous reports on electron acceptor molecules interactions with graphene.^[58,59] This shift to higher frequencies (stiffening) of the G and 2D bands is related with changes in the electronic structure of electron–phonon interactions and suggest a different doping behavior for both isomers, being more intense for the C_{3h} one.^[58]

Furthermore, we inspected the samples by AFM, revealing the presence of the characteristic smooth graphene surfaces with the presence of wrinkles, in which thin layers of 9 isomers of ca. 3 nm thick were clearly observed, in excellent agreement with related water-soluble PDIs thicknesses determined bv spectroscopic ellipsometry.^[57] The rough mean square values (RMS) of the functionalized surfaces were 1.6±0.7 and 0.9±0.2 for the C_{3h} and C_s isomers, respectively, indicative of a very homogeneous and smooth surface (Figure 6d). Additionally, we have performed Raman mappings with an increased resolution of 200 nm demonstrating that the covering is completely homogeneous and is not depending on the corrugations and wrinkles of the graphene substrate (see Figures SI14-15). Interestingly, the molecules deposited on the graphene substrates where more resilient to washing steps than the ones deposited on SiO₂/Si.

To shine light on the stability of the star-shaped isomers of molecule **9** adsorbed to the graphene surface, we performed temperature-dependent statistical Raman spectroscopy (T-SRS). Figure 7 shows the evolution of the Raman peaks with temperature, surprisingly, the molecules start to be desorbed from the graphene surface at *ca.* 475 °C, showing a very high thermal stability. Finally, the pristine monolayer graphene surface was recovered after heating to 500 °C.

These results demonstrate that the star-shaped PDIs **9** can be used to produce homogeneous large areas of non-covalently functionalised graphene, and can be distinguished not only by means of NMR, UV-Vis, fluorescence or FT-IR, but also using Raman spectroscopy. The more abundant asymmetric isomer (C_s) exhibited the highest absorbance, the more pronounced bathochromic shift in both UV-Vis and fluorescence, as well as a characteristic amide peak in the FT-IR spectrum. Moreover, both isomers exhibited homogeneous packing on graphene surfaces exerting measurable G-band mode stiffening. Last but not least we have been able to differentiate both isomers by Raman spectroscopy showing a softening of all the Raman modes for the C_s isomer with respect to C_{3h} one.



Figure 8. Temperature-dependent statistical Raman spectroscopy (T-SRS) of **9** in the temperature region between 25 and 500 °C. Remarkably the pristine CVD graphene spectrum can be completely recovered after heating to 500 °C and cool down to room temperature.

Conclusions

In summary, we have designed and synthesized a highly soluble and very π -extended molecule consisting of a triphenylene core fused with three perylene derivatives yielding a macrocycle endowed with an extended conjugation of 156 $\pi\text{-electrons}.$ For the very first time, the respective C_{3h} and C_s isomers have been completely separated by means of HPLC. Both isomers exhibited a very high solubility in 1,1,2,2-tetrachloroethane and have been unambiguously characterized and distinguished by means of five spectroscopic techniques, namely ¹H NMR, ATR-FTIR, UV-Vis, fluorescence, and Raman spectroscopy. Finally, we explored the self-assembly of these molecules on graphene substrates by optical microscopy, scanning Raman microscopy, and AFM, showing a favorable processability of this star-shaped molecules. This work represents the first example of separation of constitutional isomers of disk-shaped polycyclic aromatic molecules, which can be clearly distinguished by means of several spectroscopic techniques thanks to its enhanced processability, and could be efficiently used for noncovalently functionalize graphene and related 2D materials. [54],48

Experimental Section

General. Tetrachloroperylene tetracarboxylic acid dianhydride (Cl₄-PTCDA) was purchased from abcr. 3-Pentylamine and bromine were provided from Acros Organics. Imidazole, *t*-butylphenol, *N*-methyl-2pyrrolidone (NMP), triphenylene, *rac*-BINAP, benzophenone imine, sodium *tert*-butoxide (NaOC(CH₃)₃), zinc acetate (Zn(OAc)₂), quinolone, tris(dibenzylideneacetone)dipalladium(0), toluene, tetrahydrofuran (THF), 1,1,2,2-tetrachloroethane, nitrobenzene, and triethylamine (Et₃N) were obtained from Sigma-Aldrich. Potassium carbonate (K₂CO₃) was ordered from SAFC. Acetic acid (HAc), hydrochloric acid (HCl), isopropanol, and potassium hydroxide (KOH) were bought from Grüssing. Biobeads-SX3 was purchased from BIO-RAD. Monolayer CVD graphene films deposited on 300 nm SiO₂/Si substrates were purchased from

NMR spectra were recorded on a Bruker Avance 400 (400 MHz) and a Jeol EX 400 (400 MHz) spectrometer. Chemical shifts are given in ppm and referenced to solvent signals. NMR solvents were purchased from VWR or DEUTERO. HRMS were recorded with Bruker microTOF II focus and maXis 4G instruments.

MALDI-TOF HRMS were recorded with an UltrafleXtreme TOF/TOF (Bruker Daltonics). Analytical and preparative HPLC was carried out on a SHIMADZU Prominence system with CBM-20A system controller, LC-20A solvent delivery unit, SIL-20A auto-sampler, CTO-20A column oven, SPD-M20A photodiode array detector, and a DGU-20A on-line degassing unit.

The ATR-FTIR spectra were recorded on a BrukerTensor 27 (ATR or ZnSe plate) spectrometer.

Optical extinction and absorbance was measured on a Perkin Elmer Lambda 1050 spectrometer in extinction, in quartz cuvettes with a path length of 0.2 cm.

Fluorescence was acquired on a Horiba Scientific Fluorolog-3 system equipped with a 450 W Xe halogen lamp, double monochromator in excitation (grating 600 lines/mm blazed at 500 nm) and emission (grating 1.200 lines/mm blazed at 500 nm) and a PMT detector using quartz cuvettes with a path length of 0.2 cm.

Raman spectra were acquired on a LabRam HR Evolution confocal Raman microscope (Horiba) equipped with an automated XYZ table using 0.80 NA objectives. All measurements were conducted using an excitation wavelength of 532 nm, with acquisition times of 0.5–2.0 s and a grating of 1.800 grooves/mm. Maps of 30x30 μ m were recorded with a step size of 1 μ m, giving > 1.000 single-point spectra.

Temperature-dependent Raman measurements were performed in a Linkam stage THMS 600, equipped with a liquid nitrogen pump TMS94 for temperature stabilization under a constant flow of nitrogen. The measurements were carried out with a heating rate of 10 K.min⁻¹.

Atomic force microscopy (AFM) was carried out using a Bruker Dimension Icon microscope in tapping-mode. The samples were prepared by spin coating a solution of the separated isomers of molecule **9** at 5.000 rpm.

Synthesis of 2. A mixture of Cl₄-PTCDA (3.00 g, 5.63 mmol, 1 equiv.), imidazole (9.38 g) and 3-pentylamine (1.76 mL, 14.87 mmol, 2.6 equiv.) was refluxed at 100 °C under nitrogen atmosphere for 3 hours. After cooling the crude product to room temperature, a solution of HCl in EtOH (5 M, 225 mL) was added which resulted in the formation of a precipitate. Stirring was continued for a further 12 h. The precipitate was filtrated, washed with water until reaching neutrality, and dried in the oven at 100 °C overnight yielding **2** (3.11 g, 83%) as a red solid. The desired perylene diimide was used in the next step without further purification. Due to its low solubility in common organic solvents ¹H NMR and ¹³C NMR spectra were found to be coincident with those previously reported.^[60] HRMS: calculated. for $C_{34}H_{26}Cl_4N_2O_4$ 666.0647 [M]⁺; found 666.0642.

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Synthesis of 3. Compound 2 (3.11 g, 4.64 mmol, 1 equiv.), t-butylphenol (7.66 g, 51.02 mmol, 11 equiv.) and K₂CO₃ (8.33 g, 60.29 mmol, 13 equiv.) were dissolved in degassed anhydrous NMP (250 mL) and stirred at 120 °C for 16 hours under nitrogen atmosphere. After cooling the mixture to room temperature an aqueous solution of HCI (2 M, 120 mL) was carefully added. The mixture was stirred for another 4 hours. The precipitate formed was filtered, washed with water until reaching neutrality, and dried in the oven at 100 °C overnight vielding 3 (5.00 g. 96%) as a red solid, which was used for the next step without further purification. ¹H NMR (400 MHz, CDCl₃, 25°C): δ = 0.84 (t, J = 7.5 Hz, 12H, CH₃), 1.27 (s, 36H, CH₃), 1.76-1.88 (m, 4H, CH₂), 2.09-2.20 (m, 4H, CH₂), 4.90-4.98 (m, 2H, CH), 6.82 (d, J = 8.8 Hz, 8H, CH), 7.21 (d, J = 8.8 Hz, 8 H, CH), 8.19 (s, 4H, CH) ppm. ¹³C NMR (100 MHz, $CDCI_3$): δ = 11.3, 25.1, 31.5, 34.4, 57.6, 119.4, 119.7, 120.3, 126.6, 132.9, 147.2, 152.8, 156.0 ppm. HRMS: m/z: calculated for C74H78N2O8: 1122.4190 [M]; found: 1122.4192.

Synthesis of 4. To a solution of 3 (4.99 g, 4.44 mmol, 1 equiv.) in a mixture of isopropanol (197 mL), and H₂O (11 mL), KOH (0.88 g, 15.61 mmol, 3.5 equiv.) was added dropwise. The resulting solution was refluxed at 100 °C with stirring for 1.5 hours. After cooling down the solution, an aqueous solution of HCI (6 M, 230 mL) and AcOH (74 mL) were added. The precipitate was filtered off, washed with water until reaching neutrality, and dried in the oven at 100 °C overnight. After double purification by plug of silica (CH₂Cl₂:n-hexane 34:66), 4 (0.84 g, 18%) was obtained as a pink solid. ¹H NMR (400 MHz, CDCl₃, 25°C): δ = 0.86 (t, J = 7.4 Hz, 6H, CH₃), 1.30 (s, 36H, CH₃), 1.77-1.91 (m, 2H, CH₂), 2.10-2.22 (m, 2H, CH₂), 4.90-5.00 (m, 1H, CH), 6.83 (d, J = 8.8 Hz, 8H, CH), 7.25 (d, J = 8.8 Hz, 8H, CH), 8.21 (s, 4H, CH) ppm. ¹³C NMR (100 MHz, CDCl₃): *δ* = 11.4, 25.2, 31.6, 34.6, 57.9, 118.1, 119.6, 119.7, 121.9, 122.0, 122.6, 127.0, 127.1 133.4, 133.4, 147.9, 148.0, 152.8, 152.9, 156.0, 157.0, 160.4 ppm. HRMS: m/z: calculated for C₆₉H₆₇NO₉: 1055,2710 [M]⁺; found: 1055,2711.

Synthesis of 9. Et₃N (0.07 mL, 0.52 mmol, 9 equiv.) was added dropwise to a suspension of 8 (30.88 mg, 0.06 mmol, 1 equiv.) in dry quinoline (6.20 mL) at room temperature under N2. The resulting mixture was stirred for 30 min and the excess Et₃N was removed under vacuum. Then, 4 (0.20 g, 0.19 mmol, 3.3 equiv.) and dry Zn(OAc)₂ (47.46 mg, 0.26 mmol, 4.5 equiv.) were added and the reaction was heated to 180 °C with stirring overnight. Afterwards, the mixture was allowed to cool down to room temperature and an aqueous solution of HCI (2 M, 10 mL) was added dropwise to quench the reaction. After stirring for 30 min at 40 °C. CH₂Cl₂ was added to the suspension and the lavers were separated. The combined organic layers were washed with an aqueous solution of HCI (2 M), brine, dried over anhydrous magnesium sulfate, and concentrated. The residue was dissolved in CH2Cl2 and passed through a pad of silica gel. The crude mixture was further purified by sizeexclusion chromatography on Biobeads-SX3 using CH₂Cl₂ as eluent yielding 9 as a dark blue solid (103.20 mg, 53.22 %). The individual isomers of 9 were separated on a COSMOSIL- 5PBB-R column (10 \times 250 mm; eluent CH₂Cl₂:toluene:MeOH 25:35:40; flow rate 5.0 mL/min; 50 °C; detection 630 nm) yielding the C_s isomer (75.64 mg, 73.31 %) and the C_{3h} isomer (27.55 mg, 26.80 %) as a dark blue solid.

9: ¹H-NMR (400 MHz, $C_2D_2CI_4$, 90 °C): δ = 0.88 (dd, *J* = 7.6 Hz and *J* = 7.6 Hz, 18H, CH₃), 1.28 (s, 40 H, 12 CH₃ of *C*_s isomer and 18 CH₃ of *C*_{3h} isomer), 1.30 (s, 13.5 H, 6 CH₃, *C*_s isomer), 1.31 (s, 13.5 H, 6 CH₃, *C*_s isomer), 1.22 (br. s, 40 H, 12 CH₃ of *C*_s isomer and 18 CH₃ of *C*_{3h} isomer), 1.22 (br. s, 40 H, 12 CH₃ of *C*_s isomer and 18 CH₃ of *C*_{3h} isomer), 1.81-1.95 (m, 6H, CH₂), 2.05-2.18 (m, 6H, CH₂), 4.85-4.96 (m, 3H, CH), 6.81-7.03 (m, 24H, CH), 7.20-7.32 (m, 24H, CH), 8.18 (s, 0.75 H, 1 CH, *C*_s isomer), 8.19 (s, 0.75 H, 3 CH, *C*_{3h} isomer), 8.21 (s, 0.75 H, 3 CH, *C*_{3h} isomer), 8.22 (s, 0.75 H, 1 CH, *C*_s isomer), 8.24 (s, 0.75 H, 1 CH, *C*_s isomer), 8.25 (s, 0.75 H, 1 CH, *C*_s isomer), 8.24 (s, 0.75 H, 1 CH, *C*_s isomer), 8.25 (s, 0.75 H, 1 CH, *C*_s isomer), 8.26 (s, 0.75 H, 1 CH, *C*_s isomer), 8.27 (s, 0.75 H, 1 CH, *C*_s isomer), 8.26 (s, 0.75 H, 1 CH, *C*_s isomer), 8.27 (s, 0.75 H, 1 CH, *C*_s isomer), 8.28 (s, 0.75 H, 1 CH, *C*_s isomer), 8.29 (s, 0.75 H, 1 CH, *C*_s isomer), 8.29 (s, 0.75 H, 1 CH, *C*_s isomer), 8.29 (s, 0.75 H, 1 CH, *C*_s isomer), 8.20 (s, 0.75 H, 1 CH, *C*_s isomer), 8.21 (s, 0.75 H, 1 CH, *C*_s isomer), 8.22 (s, 0.75 H, 1

isomer), 8.23 (s, 0.75 H, 1 CH, C_s isomer), 8.49 (s, 0.75 H, 1 CH, C_s isomer), 8.50 (s, 0.75 H, 3 CH, C_{3h} isomer), 8.57 (s, 0.75 H, 1 CH, C_s isomer), 8. 58 (s, 0.75 H, 1 CH, C_s isomer), 8. 58 (s, 0.75 H, 1 CH, C_s isomer), 8. 58 (s, 0.75 H, 1 CH, C_s isomer), 8. 64 (s, 0.75 H, 3 CH, C_{3h} isomer), 8. 65 (s, 0.75 H, 1 CH, C_s isomer), 9.07 (s, 0.75 H, 1 CH, C_s isomer), 9.08 (s, 0.75 H, 1 CH, C_s isomer), 9.15 (s, 1.50 H, 1 CH of C_s isomer and 3 CH of C_{3h} isomer), 9.77 (s, 0.75 H, 1 CH, C_s isomer and 3 CH of C_{3h} isomer), 9.79 (s, 1.50 H, 1 CH of C_s isomer and 3 CH of C_{3h} isomer), 9.79 (s, 1.50 H, 1 CH of C_s isomer and 3 CH of C_{3h} isomer), 9.79 (s, 1.50 H, 1 CH of C₂₂₅H₂₀₇N₉O₂₁ 3370.5407 [M]⁺; found: 3370.5401.

9 (*C*_s): ¹H NMR (400 MHz, C₂D₂Cl₄, 90 °C): δ = 0.88 (dd, *J* = 7.6 Hz and *J* = 7.6 Hz, 6H, CH₃), 0.88 (dd, *J* = 7.6 Hz and *J* = 7.6 Hz, 6H, CH₃), 0.88 (dd, *J* = 7.6 Hz and *J* = 7.6 Hz, 6H, CH₃), 0.88 (dd, *J* = 7.6 Hz and *J* = 7.6 Hz, 6H, CH₃), 1.31 (s, 18H, CH₃), 1.33 (s, 18H, CH₃), 1.35 (s, 27 H, CH₃), 1.35 (s, 9H, CH₃), 1.81-1.95 (m, 6H, CH₂), 2.04-2.19 (m, 6H, CH₂), 4.85-4.96 (m, 3H, CH), 6.81-7.02 (m, 24H, CH), 7.20-7.32 (m, 24H, CH), 8.18 (s, 1H, CH), 8.19 (s, 1H, CH), 8.19 (s, 1H, CH), 8.22 (s, 1H, CH), 8.22 (s, 1H, CH), 8.23 (s, 1H, CH), 8.49 (s, 1H, CH), 8.57 (s, 1H, CH), 8.58 (s, 1H, CH), 9.15 (s, 1H, CH), 9.77 (s, 1H, CH), 9.78 (s, 1H, CH), 9.79 (s, 1H, CH) ppm. HRMS: *m/z*: calculated for C₂₂₅H₂₀₇N₉O₂₁ 3370.5407 [M]⁺; found: 3370.5401.

9 (C_{3h}): ¹H-NMR (400 MHz, C₂D₂Cl₄, 90 °C): δ = 0.88 (dd, *J* = 7.6 Hz and *J* = 7.6 Hz, 18H, CH₃), 1.30 (s, 54 H, CH₃), 1.34 (s, 27H, CH₃), 1.35 (s, 27H, CH₃), 1.81-1.94 (m, 6H, CH₂), 2.04-2.18 (m, 6H, CH₂), 4.91 (tt, *J* = 13.1 Hz and *J* = 6.3 Hz, 3H, CH), 6.81-7.02 (m, 24H, CH), 7.20-7.31 (m, 24H, CH), 8.18 (s, 3H, CH), 8.21 (s, 3H, CH), 8.50 (s, 3H, CH), 8.64 (s, 3H, CH), 9.10 (s, 3H, CH), 9.79 (s, 3H, CH) ppm. HRMS: *m/z*: calculated for C₂₂₅H₂₀₇N₉O₂₁ 3370.5407 [M]⁺; found: 3370.5401.

Acknowledgements

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Layout 1:

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We present a highly conjugated heterocyclic π-chromophore, consisting of a central triphenylene core fused with three perylene– monoimide arms. An unprecedented separation of the constitutional isomers was achieved by HPLC, being distinguished by ¹H NMR, ATR-FTIR, UV-Vis, fluorescence, and Raman spectroscopy. Its outstanding processability was demonstrated by noncovalent functionalization of graphene.



Edurne Nuin, Vicent Lloret, Konstantin Amsharov, Frank Hauke, Gonzalo Abellán and Andreas Hirsch*

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Isomerically Pure Star-Shaped Triphenylene-Perylene Hybrids Involving Highly Extended π Conjugation