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Twisted pyrene-fused azaacenes†

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An approach for introducing twists in pyrene-fused azaacenes is reported. Depending on the volume and the rigidity of the silyl groups, different-sized twist angles, which oscillate between 4° and 24°, are induced along the longitudinal conjugated backbone.

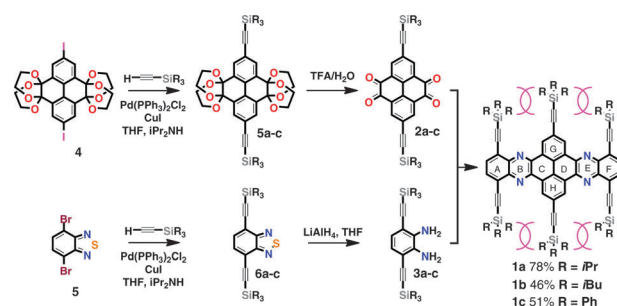
Significant advances in electronics¹ and plasmonics² are expected to arise from customised polycyclic aromatic hydrocarbons (PAHs). The planar structure of PAHs can be constrained into exotic twisted conformations by means of congested substitution patterns,³ which has provided exceptional optoelectronic properties,⁴ enhanced solubility,⁵ and unique intermolecular π -contacts.⁶ Among these, twisted pyrene-fused acenes^{4b,7} have emerged not only as challenging compounds from the synthetic point of view, but also as promising p-type materials for OLED applications.^{4b} Their parent pyrene-fused azaacenes are electronically complementary (n-type) and easier to synthesise by means of pyrazine-type cyclocondensations, which has allowed the preparation of higher pyrene-fused oligomers⁸ and polymers.⁹ However, no strategies to deliberately twist pyrene-fused azaacenes have been described.

In this communication, we report a synthetic approach for introducing twists in pyrene-fused azaacenes, which is based on the introduction of acetylene substituents with bulky silyl groups in confronting positions (Scheme 1). Depending on the volume and the rigidity of the silyl groups, different-sized twist

angles, which oscillate between 4° and 24°, are induced along the longitudinal conjugated backbone. Additionally, DFT calculations show that the LUMO and LUMO+1 are mostly degenerate and interchange for larger twists.

Pyrene-fused hexacene **1a**^{8c} with six confronting triisopropylsilyl (TIPS) substituents was obtained by cyclocondensation of **2a**^{8c} and **3a**¹⁰ in good yields (78%). Although **1a** is known,^{8c} no crystallographic structure has been reported. After many attempts, it was possible to obtain crystals suitable for X-ray crystallography by slow evaporation of CHCl₃/MeOH solutions of **1a** (Fig. 1). X-ray diffraction studies evidence an alternated twisted structure for hexacene **1a**, in which the two quinoxaline units are in the same plane and the pyrene is tilted. A quinoxaline–pyrene twist angle of 6° and an end-to-center twist angle of 5° were observed.^{11,12} Although the TIPS groups are very large, the offset between the quinoxaline and pyrene moieties limits the spatial overlap among TIPS groups.

The observed deviations encouraged us to further develop this approach to obtain pyrene-fused azaacenes with a higher twist. Much bulkier triisobutylsilyl (TIBS) substituents were introduced in order to overcome the offset of the central and lateral substituents. In this case, **2b** was synthesised from compound **4**^{8e} by Sonogashira coupling with (triisobutylsilyl)-acetylene¹³ followed by acid hydrolysis (Scheme 1). Diamine **3b** was prepared by Sonogashira cross-coupling between commercially available **5** and (triisobutylsilyl)acetylene¹³ followed by reduction with LiAlH₄ (Scheme 1). Pyrene-fused hexacene **1b**

Scheme 1 Synthesis of twisted pyrene-fused azaacenes **1a–c**.

^a POLYMAT, University of the Basque Country UPV/EHU, Avenida de Tolosa 72, E-20018 Donostia-San Sebastian, Spain. E-mail: amateo@polymat.eu

^b School of Soft Matter Research, Freiburg Institute for Advanced Studies (FRIAS), Albert-Ludwigs-Universität Freiburg, Albertstraße 19, 79104 Freiburg, Germany

^c Institut für Organische Chemie und Biochemie, Albert-Ludwigs-Universität Freiburg, Albertstraße 21, 79104 Freiburg, Germany

^d Institut für Anorganische und Analytische Chemie, Albert-Ludwigs-Universität Freiburg, Albertstraße 21, 79104 Freiburg, Germany

^e Centro de Ciências e Tecnologias de Computação, CCTC Universidade do Minho, 4710-057 Braga, Portugal

^f Ikerbasque, Basque Foundation for Science, Bilbao, Spain

† Electronic supplementary information (ESI) available: Experimental details for the synthesis, characterisation and DFT calculations. CCDC 972121–972123. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc48742c

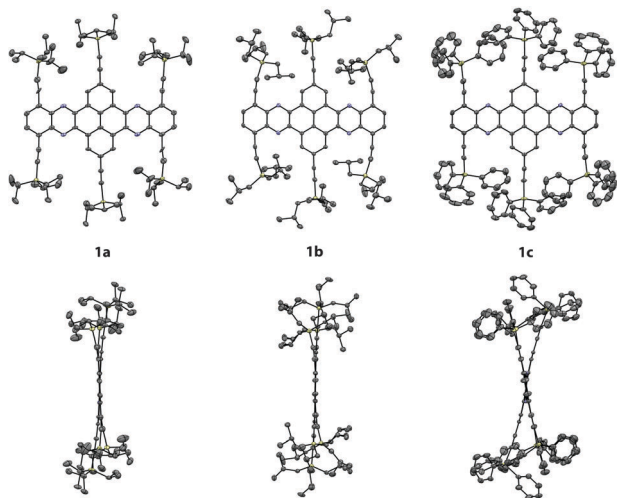


Fig. 1 Front and side views of the X-ray structure (ellipsoids at a 50% probability level) of compounds **1a**, **1b** and **1c**.

was obtained by cyclocondensation of **2b** and **3b** in 46% yields. Crystals suitable for X-ray crystallography were obtained by slow evaporation of CH_2Cl_2 –MeOH solutions of **1b** (Fig. 1). To our surprise the crystal structure of **1b** displayed a shorter quinoxaline–pyrene (4°) and end-to-center twist angles (0.5°). Even if this result is contradictory, since TIBS groups are more voluminous than TIPS, this can be easily rationalised in terms of rigidity. The additional methylene group increases the volume of TIBS; however, it also provides an additional degree of conformational freedom. Therefore, the enhanced flexibility allows the accommodation of all the substituents in the same plane to a greater extent, which results in smaller twist angles.

In order to overcome the offset between pyrene and quinoxaline substituents, we decided to introduce triphenylsilyl (TPS) groups, since they combine the bulkiness and rigidity of three phenyl rings. Pyrene-fused hexacene **3c** was obtained by cyclocondensation of tetraketone **1c** and diamine **2c**, which were synthesised following the same route set out in Scheme 1 but with (triphenylsilyl)acetylene. Slow evaporation of a CH_2Cl_2 solution of **3c** provided crystals suitable for X-ray diffraction. The crystal structure showed a clear alternate twist of the aromatic core out of the plane (Fig. 1). The angle between the quinoxaline and the pyrene moieties was found to be 24° with end-to-center angles of 21° , which largely surpassed the angles observed for **1a** and **1b**.

The absorption spectra of **1a–c** displayed well-resolved vibronic bands along the UV and the visible region consistent with the

molecular structure (Fig. 2) and with previous observations.^{8e} Almost identical absorption features were observed on **1a–c** ($\lambda_{\text{max}} = 435, 432$, and 436 nm , respectively) while some differences were discernible in the UV region for **1b**. Emission bands centred at $489, 487$ and 485 nm were observed respectively for **1a–c** ($\lambda_{\text{ex}} = 350 \text{ nm}$). The electron-deficient nature of the pyrene-fused azaacene core is reflected by cyclic voltammetry. Three electrochemical reduction waves were observed, the first two reversible and the third one irreversible. Shifts towards more cathodic potentials are observed when comparing the reduction waves of **1b** with **1a**. In contrast, the reduction waves of **1c** are anodically shifted, which is consistent with the more electron-withdrawing nature of TPS groups.

The HOMO–LUMO gaps were estimated from the absorption onsets and are in the range of 2.7 eV (see Table 1). The LUMO levels were estimated from the potential onsets of the first reduction waves, which reflects the small influence of the alkyl nature of the TIPS and TIBS substituents at the acetylene ends for **1a** and **1b** while the E_{LUMO} for **1c** is substantially lowered as a consequence of the more electron-withdrawing nature of the TPS groups as described above.

A theoretical estimation of the HOMO and LUMO levels *in vacuo* (B3LYP/6-31G*) follows the same trends of the measured optical HOMO–LUMO gaps and electrochemical LUMO levels (Table 1), with a good agreement between measured and calculated HOMO–LUMO gaps. The overestimation of the energy levels is reasonable due to the lack of solvent in the simulations. As expected, both the HOMO and the LUMO orbitals span along the pyrene-fused hexacene core (Fig. 3). The geometrical shapes of the HOMO (B_{2g} symmetrical) remain invariable with respect to the size of the twist angle. Higher orbital coefficients are observed in the HOMO levels of **1a–c** on most of the peripheral rings (A and B) of the hexacene core and also on the external rings (G and H) of the pyrene moiety (the assignments of the rings corresponds to the lettering shown on Scheme 1). This is consistent with Clar rules¹⁴ that predict four sextets on the same rings. In the case of the LUMO, the shape of the orbitals (B_{1g} symmetrical) remains virtually unchanged for the less twisted pyrene-fused hexacenes **1a** and **1b**, which appeared to be more equally spread over the longitudinal axis of the pyrene-fused tetraazahexacene core in comparison to the HOMO. Nevertheless, the LUMO coefficients for **1a** and **1b** are larger on rings A, B, E and F and there is an almost negligible contribution from rings C and D. Notably, the shape of the LUMO orbitals in the more twisted **1c** (B_{3u} symmetrical) differs substantially from that observed in **1a** and **1b**. As a matter of fact, in **1c**, a new and larger contribution to the LUMO emerges from rings C and D with large orbital

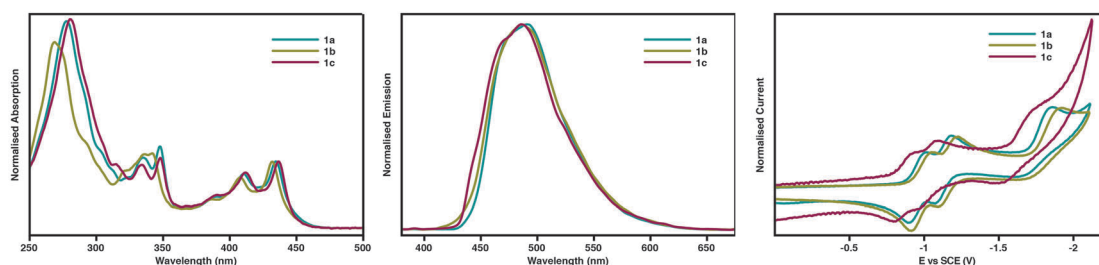
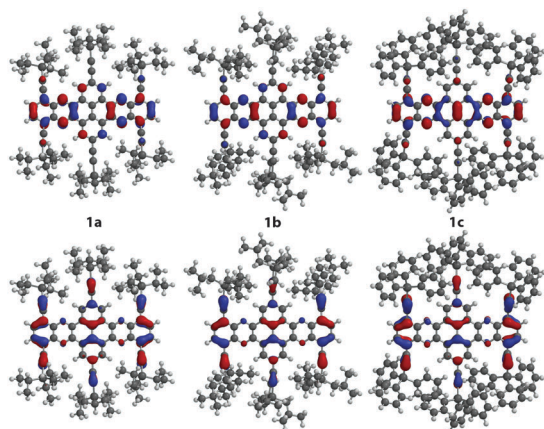


Fig. 2 Left: absorption of **1a–c**. Center: emission ($\lambda_{\text{ex}} = 350 \text{ nm}$) of **1a–c** in THF. Right: cyclic voltammograms of **1a–c** in THF (0.1 M $n\text{Bu}_4\text{PF}_6$).

Table 1 Selected photophysical and electrochemical data and experimental energy levels of **1a–c**

Compound	λ_{max}^a	λ_{onset}^a	λ_{em}^a	$E_{1/2}^I{}^b$	$E_{1/2}^{II}{}^b$	$E_{\text{pc}}^{III}{}^b$	E_{onset}^b	$E_{\text{gap(opt)}}^c$	$E_{\text{LUMO(CV)}}^d$	$E_{\text{gap(cal)}}^e$	$E_{\text{LUMO(cal)}}^e$
1a	435	460	489	−0.95	−1.12	−1.85	−0.82	2.69	−3.49	3.0	−2.7
1b	432	460	487	−0.98	−1.15	−1.92	−0.84	2.69	−3.46	3.1	−2.7
1c	436	455	485	−0.87	−1.05	−1.71	−0.70	2.72	−3.54	3.1	−2.8

^a Measured in THF (nm). ^b Measured from 0.1 M THF/*n*Bu₄PF₆ vs. SCE (V) using ferrocene (Fc) as internal reference ($E_{1/2\text{Fc}}^{\text{SCE}} = +0.48$ V). ^c Estimated from the absorption onset (eV). ^d Estimated from CV E_{ONSET} according to $E_{\text{LUMO}} = -4.8 - e(E_{\text{ONSET}} - E_{1/2\text{Fc}})$ where $E_{1/2\text{Fc}}$ was measured *in situ* (eV). ^e Calculated B3LYP/6-31G* using Spartan 10 (eV).

**Fig. 3** Shapes of LUMO (top) and HOMO (bottom) levels of **1a–c**.

coefficients that extend substantially the conjugation along the longitudinal backbone. A closer look at the simulations explains this trend. The LUMO and the LUMO+1 of pyrene-fused twistacenes **1** are practically degenerate. In the case of **1a** and **1b**, the B_{1g} symmetrical orbital corresponds to the LUMO while the B_{3u} symmetrical orbital corresponds to the LUMO+1. In the case of **1c** the LUMO and the LUMO+1 interexchange, thus the B_{3u} symmetrical orbital becomes the LUMO and the B_{1g} symmetrical becomes the LUMO+1. The silyl substituents do not contribute at all to the LUMO and the LUMO+1 of **1** as evidenced from the simulations, which implies that the LUMO/LUMO+1 exchange is the result of the twisted pyrene-fused hexacene core. This is confirmed by calculations carried out at the same level by increasing the twist angles on a model planar pyrene-fused hexacene with no substituents on the acetylenes (see Fig. S10 and Table S2, ESI†). The calculations indeed evidence that the LUMO/LUMO+1 energy difference decreases progressively with an increase of the size of the twist angle up to 24° after which the LUMO and LUMO+1 interchange.

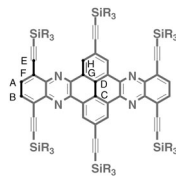
Overall we have reported a synthetic strategy that allows introduction of deliberately different-sized twist angles on pyrene-fused azaacenes. The larger twists are obtained as a compromise between volume and rigidity, as evidenced by X-ray crystallography. The structural characterisation is complemented by a detailed description of the optoelectronic and electrochemical properties that are used to estimate the energy of HOMO and LUMO levels. DFT calculations illustrate that for large twist angles an interchange of the LUMO and LUMO+1 levels of pyrene-fused azaacenes takes place, which results in LUMOs that differ substantially in terms of symmetry and conjugation. We believe that this trend provides new perspectives for pyrene-

fused azaacenes in fields in which electron-deficient organic materials are currently used, such as electronics and plasmonics.

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- The term quinoxaline–pyrene twist angle refers to the torsion angle between atoms A, B, C and D. The term end-to-end twist angle refers to the torsion angles between atoms E, F, G and H.



- 12 End-to-center twist angles are given instead of the standard end-to-end twist angles because of the alternate twists observed, otherwise the sum of two equal alternate end-to-center angles with opposite signs would be 0° .
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