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Twisted Aromatics

Hexaazatrinaphthylenes with Different Twists

Sunil Choudhary,[c, d] Cristian Gozalvez,[a] Alexander Higelin,[e] Ingo Krossing,[c, e]
Manuel Melle-Franco,[f] and Aurelio Mateo-Alonso*[a, b]

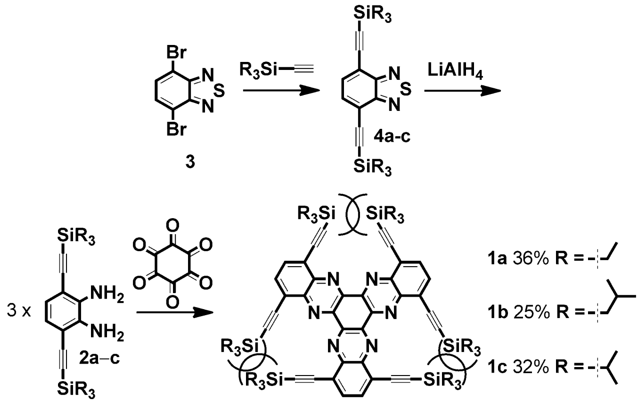
Dedicated to Prof. Maurizio Prato on the occasion of his 60th birthday

Abstract: A synthetic strategy that allows the induction of twist angles of different sizes in 5,6,11,12,17,18-hexaazatrinaphthylene (HATNA) chromophores is reported. The different twist angles are accompanied by measurable changes in the emission and electrochemical characteristics of HATNA.

Polycyclic aromatic hydrocarbons (PAHs) have received a great deal of attention because they are being developed into increasingly better performing semiconductors.[1] Both carbonaceous and nitrogenated PAHs with a C_3 symmetry, such as starphenes[2] and cloverphenes,[3] are particularly interesting because they have shown high stabilities, even for derivatives with a high degree of conjugation. Among these PAHs, 5,6,11,12,17,18-hexaazatrinaphthylene (HATNA) derivatives have arisen as promising n-type semiconductors with charge mobilities as high as 0.9 cm^{2}V^{-1}s^{-1}.[2b,d–f]

In some cases, C_3-symmetrical PAHs can adopt twisted conformations as the result of the steric strain induced by overcrowding or congestion of the aromatic core by substituents.[2c,3a–d,f,g] Significant effort has been dedicated to the synthesis and study of twisted PAHs,[4] because these compounds have enhanced stabilities and unique electronic and chiroptical properties, deriving from their distorted molecular structure and packing properties. Some of the effects of linear twists on the optoelectronic properties of PAHs have been suggested by Wudl et al.[4f] and confirmed theoretically by Houk et al.[5] However, to the best of our knowledge, no experimental correlation between twist size and optoelectronic properties has been reported. This is because the strategies used to longitudinally twist the aromatic core utilise substituents that have a direct electronic influence on the PAH core that makes the assignment of any effects derived from the twists difficult.[4b–l]

We describe herein a synthetic strategy that allows the induction of twist angles of different size in HATNA chromophores. Our twisting approach is based on the introduction of rigid acetylenes with large silyl substituents in positions that force the aromatic core to deviate from planarity, leading to twisted-HATNA **1** (Scheme 1). Increasing the size and rigidity of the terminal silyl groups (triethylsilyl < triisobutylsilyl < triisopropylsilyl) results in a substantial increase in the size of the twist angle of the HATNA core. Most importantly, the influence of these substituents on the optoelectronic properties is almost negligible because of their aliphatic nature and their distance to the aromatic core, as illustrated by parallel studies carried out on reference compounds. Therefore, any change observed on the properties is undoubtedly owed to the size of the twist angle and not related to the substituents. The different twist angles are accompanied by measurable changes in



Scheme 1. Synthesis of twisted-HATNA **1a**–**c**.

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[a] C. Gozalvez, Prof. A. Mateo-Alonso
POLYMAT, University of the Basque Country UPV/EHU
Avenida de Tolosa 72, 20018 Donostia-San Sebastian (Spain)
Fax: (+34) 943 50 6062
E-mail: amateo@polymat.eu

[b] Prof. A. Mateo-Alonso
Ikerbasque, Basque Foundation for Science
48011 Bilbao (Spain)

[c] S. Choudhary, Prof. I. Krossing
School of Soft Matter Research
Freiburg Institute for Advanced Studies (FRIAS)
Albert-Ludwigs-Universität Freiburg
Albertstrasse 19, 79104 Freiburg (Germany)

[d] S. Choudhary
Institut für Organische Chemie und Biochemie
Albert-Ludwigs-Universität Freiburg
Albertstrasse 21, 79104 Freiburg (Germany)

[e] A. Higelin, Prof. I. Krossing
Institut für Anorganische und Analytische Chemie
Albert-Ludwigs-Universität Freiburg
Albertstrasse 21, 79104 Freiburg (Germany)

[f] Prof. M. Melle-Franco
Centro de Ciências e Tecnologias de Computação, CCTC
Universidade do Minho, 4710-057 Braga (Portugal)

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the emission and electrochemical characteristics of twisted-HATNA, confirming that longitudinal twists provide an additional dimension to modulate the properties of organic semiconductors.

The synthesis of twisted-HATNA **1a**–**c** was carried out following the route depicted in Scheme 1. Diamines **2a** and **2c** were prepared following a route developed by Bunz and co-workers,[6] whereas **2b** was synthesised by a modification of this procedure. Commercially available **3** is functionalised by Sonogashira coupling with (triethylsilyl)acetylene, (triisobutylsilyl)-acetylene[7] or (triisopropylsilyl)acetylene to obtain **4a**–**c**, which after reduction with $LiAlH_4$ yield **2a**–**c**. Remarkably, the tricyclocondensation of diamines **2a**–**c**, independently, with the commercially available hexaketocyclohexane in acetic acid heated to reflux, proceeded smoothly; the size of the substituents had no apparent influence on the reaction, which yielded **1a**–**c** with moderate yields (25–36%).

The DFT-calculated structure of **1a**[8] reveals that the triethylsilyl substituents force the HATNA core to deviate substantially from planarity, to adopt an asymmetrical propeller-like structure (Figure 1). An average twist angle of 51° between blades (48, 49 and 55° for each blade) and an average end-to-end twist angle of 15° (12, 16 and 17° for each blade) are observed.[9] This model is built using the same level of calculations (LDA 6-31g*) that reproduce the X-ray crystallographic structures of **1b** and **1c** given below, which confirms its suitability to estimate the structural distortions of **1a**.

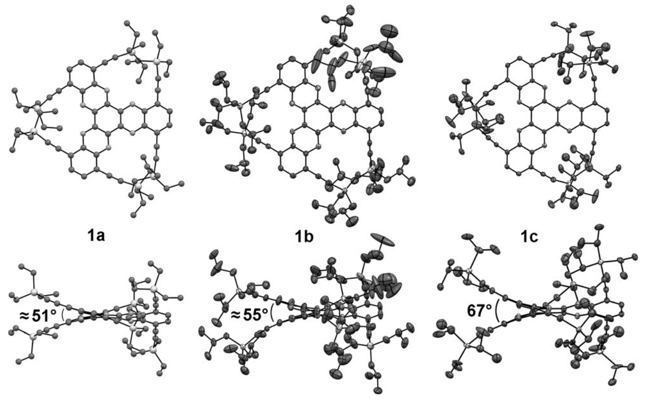

Figure 1. Top and side views of the DFT-optimised structure of compound **1a** and of the X-ray structures of compounds **1b** and **1c** (ellipsoids are shown at a 50% probability level, hydrogen atoms are omitted for clarity). Twist angles between blades are given.

Single crystals of **1b** were obtained by slow evaporation from $CHCl_3$/MeOH solutions. The crystal structure for **1b**[10] reveals a complex structure, in which two unsymmetrical and enantiomeric propeller-shaped structures are observed in the unit cell with an average twist angle of 55° between blades and an average end-to-end twist angle of 16°. One of the structures of **1b** is less distorted and shows 48, 52 and 57° torsion angles between blades and 9, 13 and 24° end-to-end twist angles for each blade. On the other hand, the second structure is more distorted, displaying 54, 57 and 62° torsion angles between blades and 16, 17 and 18° end-to-end twist angles for each blade (Figure 1). The DFT-calculated structure of **1b** predicts an average twist angle of 54°, which is in agreement with the X-ray diffraction data.

Similarly, slow evaporation of $CHCl_3$/MeOH solutions of **1c** yielded single crystals suitable for X-ray diffraction. The crystal structure of **1c**[11] shows a much more significant distortion of the HATNA core, consistent with the higher rigidity of triisopropyl substituents. For **1c** a 67° torsion angle between blades and a 20° end-to-end twist angle for each blade was observed. The DFT model is consistent with the crystallographic structure and a twist angle of 63° between blades was predicted. The underestimation of the twist angle is reasonable, because the simulations are carried out in vacuo.

The absorption features of **1a**–**c** are similar to those observed for HATNA derivatives, but appear bathochromically shifted (ca. 45 nm) because of extended conjugation with six acetylenes. When comparing the absorption spectra of **1a**–**c**, almost invariable absorption features were observed. Increasing bathochromic shifts, of approximately 1 nm, with increasing twist angles were discernible in the transitions between 300 and 500 nm (Figure 2 and Table 1). However, the same variations were observed in the absorption spectra of acenothiadiazoles **4a**–**c** (Table 1 and Figure S7 in the Supporting Information), which were used as a reference, illustrating that the twist angles have no effect on the absorption properties.

On the contrary, the different twist angles do have an influence on the emission characteristics of twisted-HATNA. On

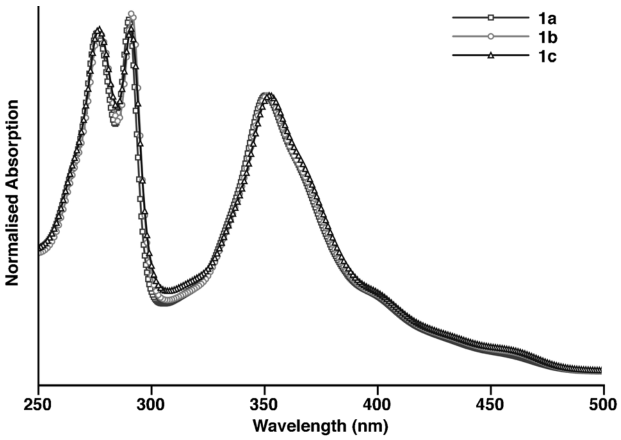

Figure 2. Normalised absorption spectra of **1a**–**c** in $CHCl_3$.

Table 1. Selected photophysical and electrochemical data for **1a**–**c** and **4a**–**c**.

	1a	1b	1c	4a	4b	4c
λ_{max}[a]	350	351	352	387	388	388
λ_{em}[a]	523	514	504	458	458	457
$E_{1/2}^{I}$[b]	−0.84	−0.95	−0.93	−1.20	−1.22	−1.21
$E_{1/2}^{II}$[b]	−1.12	−1.19	−1.15	–	–	–

[a] $CHCl_3$ [nm]. [b] *E* versus SCE [V] using ferrocene (Fc) as internal reference ($E_{1/2}^{Fc(SCE)} = +0.48$ V).

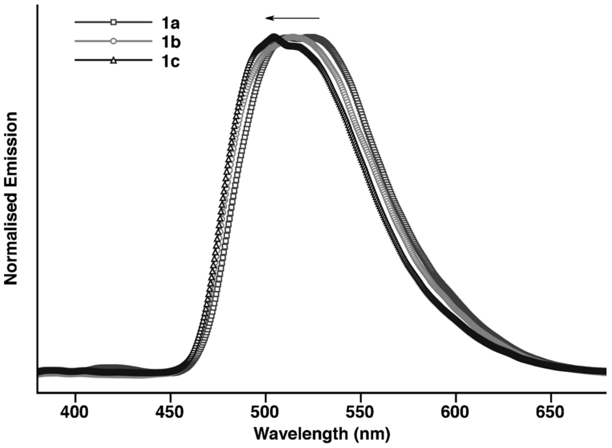

Figure 3. Normalised emission spectra ($\lambda_{ex} = 350$ nm) of **1a**–**c** in $CHCl_3$.

comparison of the emission spectra of **1a**–**c** (Figure 3 and Table 1), increasing hypsochromic shifts, as large as 19 nm, are clearly observed as the twist angles increase. In principle, it could be argued that such differences are an effect of the different substituents and not of the twist angles. However, parallel emission studies carried out on **4a**–**c** show an almost negligible effect of the substituents on the emission spectra (Table 1 and Figure S7 in the Supporting Information). Therefore, the changes observed in the emission properties of **1a**–**c** are undoubtedly due to the size of the twist angle and are not related to the substituents.

Similarly, the size of the twist angle also has an influence on the redox chemistry of the HATNA core. Cyclic voltammetry reveals a set of two reversible reductions for **1a**–**c** (Figure 4 and Table 1). Half-wave potential shifts ($\Delta E_{1/2}$) to more negative potentials are observed on comparison of the first reduction potentials of **1b** ($\Delta E_{1/2} = -110$ mV) and **1c** ($\Delta E_{1/2} = -90$ mV) with the less twisted **1a**. The same trend is observed in the second reduction wave on the comparison of **1b** and **1c** with the less twisted **1a** ($\Delta E_{1/2} = -90$ and -50 mV, respectively). The opposite trend is observed on the comparison of the $E_{1/2}$ value of the two reduction processes of **1b** with those of **1c**, which are more cathodic. Again, studies carried out on compounds **4a**–**c** (Table 1 and Figure S7 in the Supporting Information), as reference compounds, show an almost negligible effect of the substituents on the reduction potentials, corroborating that the changes observed in the reduction potentials of **1a**–**c** are indeed an effect of the size of the twist angle.

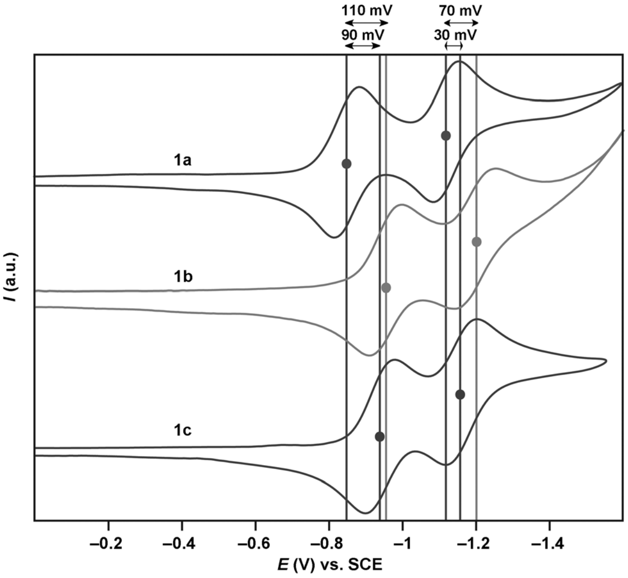

Figure 4. Cyclic voltammograms of **1a**–**c** at 100 mV s^{-1} in 0.1 M nBu_4NPF_6 in CH_2Cl_2 at room temperature. Dots and vertical lines indicate half-wave potentials. SCE = saturated calomel electrode.

In conclusion, we have reported a synthetic strategy that provides access to a new family of HATNA derivatives with different twist angles by introducing silyl groups with different size and rigidity. This has been evidenced by a combination of theoretical calculations and X-ray crystallography. In addition, this work provides direct experimental correlation between twist size and properties, since the influence of the carefully selected substituents with the electronic properties of the aromatic core is almost negligible. Therefore, the changes observed on the properties of twisted-HATNA are a direct effect of the size of the different twist angles and not of the substituents that can be considered electronically equivalent. In particular, increasing the size of the twist angles results in increasing hypsochromic shifts, in the emission characteristics of twisted-HATNA. Also, angle-dependent changes on the redox potentials of twisted-HATNA have been observed with $\Delta E_{1/2}$ as large as -110 mV. Further studies that combine synthesis and calculations will attempt to correlate solid-state and solution molecular conformations. These will provide a more detailed picture of the influence of the twist angles on the properties, in which symmetry might play a crucial role, and will allow the exploitation of the effects of non-planarity in the design of new organic semiconductors for specific applications.

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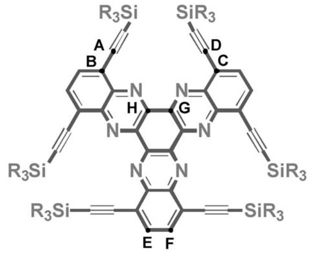
[8] Several attempts to obtain the crystal structure from crystals of **1a** were unsuccessful (R-factor = 20).

[9] In this paper the term "twist angle between blades" 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.



[10] CCDC-953876 contains the supplementary crystallographic data for **1b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif: $C_{216}H_{336}N_{12}Si_{12}$, $M_w = 3438.72$, triclinic, space group $P\bar{1}$, $a = 18.6464(3)$, $b = 21.2919(3)$, $c = 29.5274(4)$ Å; $\alpha = 80.5574(8)$, $\beta = 83.6978(8)$, $\gamma = 73.0153(8)^\circ$; $V = 11035.9(3)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.035\ \mathrm{Mg\,m^{-3}}$; $F(000) = 3796$; $\lambda = 0.71073$ Å; $T = 100(2)$ K; absorption coefficient = $0.120\ \mathrm{mm^{-1}}$; absorption correction: multiscan, $T_{min} = 0.6900$, $T_{max} = 0.7461$, $2\theta_{max} = 47.06^\circ$; number of (independent) reflections collected = 137731 (32717); largest peak/hole [eÅ^{-3}] = 1.69/−0.66; GooF = 1.040; $R1 = 7.47$ and $wR2 = 20.72$ for reflections $I > 2\sigma(I)$, $R1 = 10.52$ and $wR2 = 23.98$ for all reflections.

[11] CCDC-953875 contains the supplementary crystallographic data for **1c**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif: $C_{90}H_{132}N_6OSi_6$, $M_w = 1482.82$, trigonal, space group $R\bar{3}$, $a = 31.1383(3)$, $b = 31.1383(3)$, $c = 16.9549(3)$ Å; $\alpha = 90$, $\beta = 90$, $\gamma = 120^\circ$; $V = 14236.9(3)$ Å^3; $Z = 6$; $\rho_{calcd} = 1.038\ \mathrm{Mg\,m^{-3}}$; $F(000) = 4836$; $\lambda = 0.71073$ Å; $T = 100(2)$ K; absorption coefficient = $0.132\ \mathrm{mm^{-1}}$; absorption correction: multiscan, $T_{min} = 0.6761$, $T_{max} = 0.7461$, $2\theta_{max} = 57.61^\circ$, number of (independent) reflections collected = 73589 (7272); largest peak/hole [eÅ^{-3}] = 1.32/−0.35; GooF = 1.073; $R1 = 4.78$ and $wR2 = 13.61$ for reflections $I > 2\sigma(I)$, $R1 = 5.24$ and $wR2 = 14.01$ for all reflections.

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