



Organic Materials Hot Paper

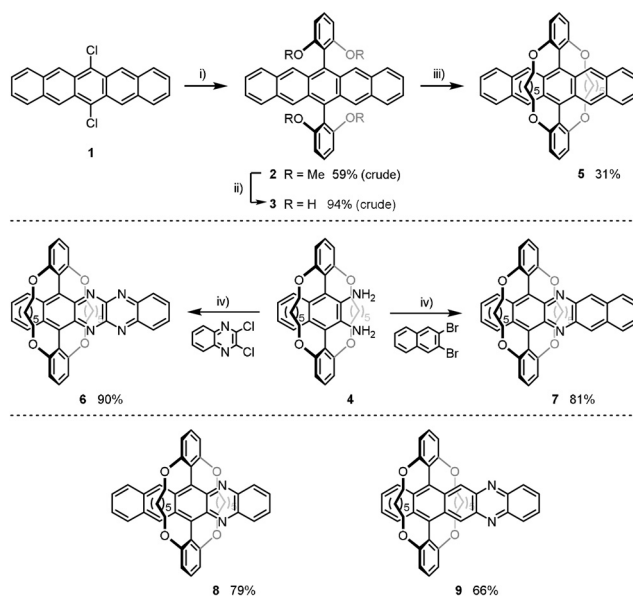
# (Aza)Pentacenes Clipped into a Ring: Stabilization of Large (Aza)Acenes

Lukas Ahrens, Olena Tverskoy, Svenja Weigold, Michael Ganschow, Frank Rominger, Jan Freudenberg,\* and Uwe H. F. Bunz\*

**Abstract:** A doubly alkylene bridged 6,13-diphenylpentacene and analogously bridged azapentacenes were prepared; they are persistent. The doubly bridged azapentacenes display superior photochemical, oxidative and thermal stabilities compared to azapentacenes protected by bis(TIPS-ethynyl)-substituents—clipping an azaacene into a large ring is a viable complement in stabilization.

Stabilization and solubilization of larger acenes and heteroacenes, that is,  $\geq 5$  rings, is challenging, yet important to fully unlock their properties.<sup>[1]</sup> Aryl substituents attached at strategic positions of a large acene fulfills this need to a degree. Yet, the use of bis(trialkylsilylethynyl)-groups in 2001 changed the situation.<sup>[2]</sup> The silylethynyl substituents enjoy a near monopoly in the stabilization of larger (hetero)acenes—heptacene can be stabilized and solubilized with just two of them.<sup>[3]</sup> Additional auxiliary arene substituents are necessary for nonacenes to survive.<sup>[4]</sup> However, there should be alternative stabilization modes of similar efficiency. Kobayashi et al. demonstrated doubly alkylene bridged anthracenes as photoemitters with improved photostability when compared to 5,9-diphenylanthracene.<sup>[5]</sup> Yet, these systems were not compared to their analogous 5,9-bis(triisopropylsilylethynyl)anthracenes to gauge relative stability. Double bridging was also employed to twist anthracene,<sup>[6]</sup> to ring perylenebisimides<sup>[7]</sup> and to shield polythiophene derivatives.<sup>[8]</sup>

Kobayashi's encapsulation should be applicable to larger acenes. Herein, we present stable and soluble, modularly synthesized doubly bridged (aza)pentacenes **5–9** (Scheme 1). Starting from **1**, double Suzuki coupling furnishes **2**. Removal of the methyl groups with BBr<sub>3</sub> is followed by transformation



**Scheme 1.** Synthesis of doubly alkylene bridged (aza)pentacenes **5–9**. Conditions: i) ArB(OH)<sub>2</sub>, K<sub>3</sub>PO<sub>4</sub>, Pd<sub>2</sub>(dba)<sub>3</sub>, XPhos, 1,4-dioxane, H<sub>2</sub>O, 100 °C, 7 d; ii) BBr<sub>3</sub>, DCM, –78 °C → r.t., 2 d → 7 d; iii) K<sub>2</sub>CO<sub>3</sub>, Br(CH<sub>2</sub>)<sub>7</sub>Br, DMF, 40 °C → 80 °C, 3 d; iv) 1.) Cs<sub>2</sub>CO<sub>3</sub>, RuPhos Pd G1 (10 mol%), toluene, 110 °C, 15 h; 2.) MnO<sub>2</sub>, DCM, r.t., 30 min.

of the resorcinic intermediate with 1,7-dibromoheptane in DMF (K<sub>2</sub>CO<sub>3</sub> as base) to furnish jacketed pentacene **5**. The double cyclization was performed at concentrations of 5 mmol L<sup>–1</sup>. For the azaacenes **6** and **7**, the bridged diamino-naphthalene **4** was obtained from naphthothiadiazoloquinone. Addition of lithiated 1,3-dimethoxybenzene and reduction with sodium hypophosphite, followed by the opening of the thiadiazole ring by SmI<sub>2</sub> gives **4**. Diamino-naphthalene **4** couples under established Pd-catalyzed conditions<sup>[9,10,11a,b,12]</sup> with 2,3-dihaloarenes to give the azapentacenes **6** and **7**. If the doubly bridged diaminoanthracene is employed, **8** results, while **9** is obtained by coupling of *ortho*-phenylenediamine with the encapsulated 2,3-dibromoanthracene. **6–9** form as the *N,N'*-dihydro-compounds—these are oxidized by MnO<sub>2</sub> into the azaacenes.

The consanguine TIPS-ethynyl(aza)acenes are literature known and were prepared as reference substances.<sup>[2,11,12]</sup> Figure 1 displays a photograph of dilute solutions of **5–9** and of **5**<sub>TIPS</sub>–**9**<sub>TIPS</sub>. The visual colors are similar—their slight variations (cf. **5** and **5**<sub>TIPS</sub>) are due to the TIPS-ethynyl groups enlarging the conjugated  $\pi$ -system. The doubly alkylene bridged (aza)acenes display in general broader and blue-shifted features in the Uv-vis spectra (Figure 2). This is not

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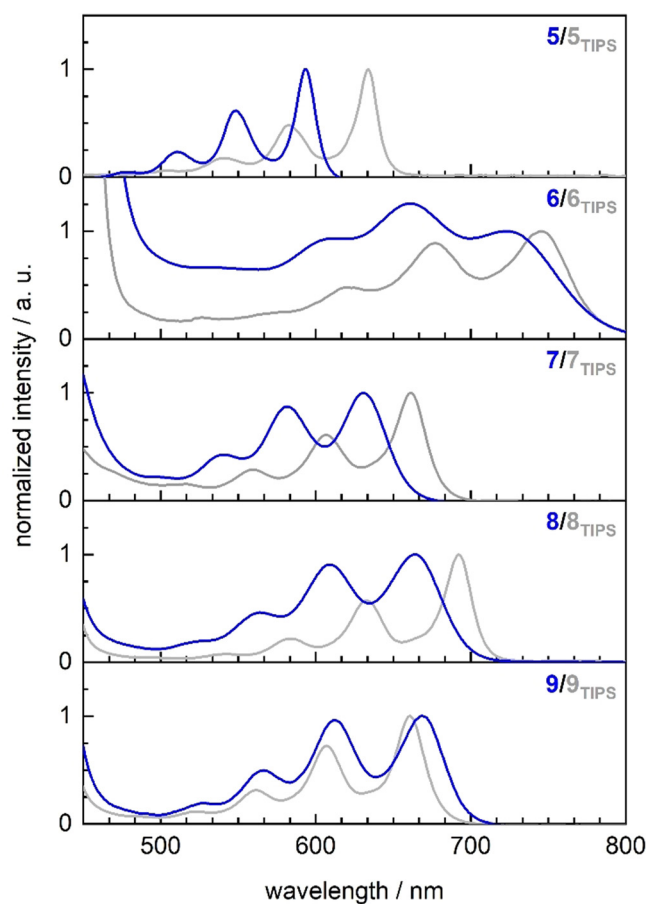
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<https://doi.org/10.1002/anie.202015348>.

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**Figure 1.** Photographs of doubly alkylene bridged (aza)pentacenes **5–9** (top, from left to right) and their respective TIPS-ethynyl-substituted analogues **5<sub>TIPS</sub>–9<sub>TIPS</sub>** (bottom, from left to right) under daylight in *n*-hexane.



**Figure 2.** Normalized absorption spectra of doubly alkylene bridged (aza)pentacenes **5–9** and their consanguine silylated counterparts **5<sub>TIPS</sub>–9<sub>TIPS</sub>** in dilute *n*-hexane solution. See SI for full spectra.

the case for **9**— $\lambda_{\text{max}}$  of **9<sub>TIPS</sub>** is blue shifted, possibly due to an increased donor-acceptor character of **9** in comparison to **9<sub>TIPS</sub>**. The doubly bridged azaacenes appear non-emissive, similar to their TIPS-congeners, only **5** fluoresces notably.

Table 1 displays the electronic properties of the targets and their first reduction potentials. As expected, tetraaza-derivative **6** is most easily reduced, while the other azaacenes display fairly similar reduction potentials ( $-1.4$  to  $-1.5$  V, vs.  $\text{Fc}/\text{Fc}^+$ ) and electron affinities. This trend is echoed in the silylethynylated (aza)acenes, which are more readily reduced due to the electronegative ethynyl substituents with reduction potentials ranging between  $-1.0$  to  $-1.2$  V for the diaza-derivatives.

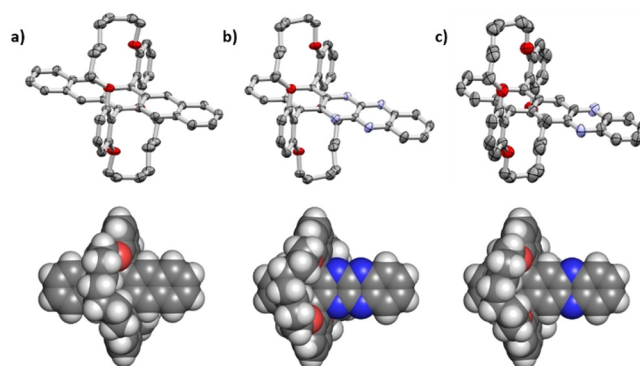
**Table 1:** Experimental and calculated (gas phase) properties of doubly alkylene bridged pentacenes **5–9** in solution (UV-vis: *n*-hexane; CV: DCM). For electrochemical and optical data of their consanguine TIPS-counterparts **5<sub>TIPS</sub>–9<sub>TIPS</sub>** see SI.

Compd	$\lambda_{\text{max, abs}}$ [nm]	$\lambda_{\text{max, em}}$ [nm]	$E^{(0/-)}$ [V] <sup>[a]</sup>	Ionization Potential/ HOMO [eV] <sup>[c]</sup> meas./ <sup>[d]</sup> calcd	Electron Affinity/ LUMO [eV] <sup>[b]</sup> meas./ <sup>[d]</sup> calcd
<b>5</b>	593	599	$-1.83$	$-5.30/-4.74$	$-3.27/-2.63$
<b>6</b>	721	–	$-0.91$	$-5.79/-5.53$	$-4.19/-3.48$
<b>7</b>	631	652	$-1.40$	$-5.57/-5.28$	$-3.70/-3.17$
<b>8</b>	663	687	$-1.51$	$-5.33/-4.94$	$-3.59/-2.89$
<b>9</b>	668	685	$-1.43$	$-5.44/-5.02$	$-3.67/-2.97$

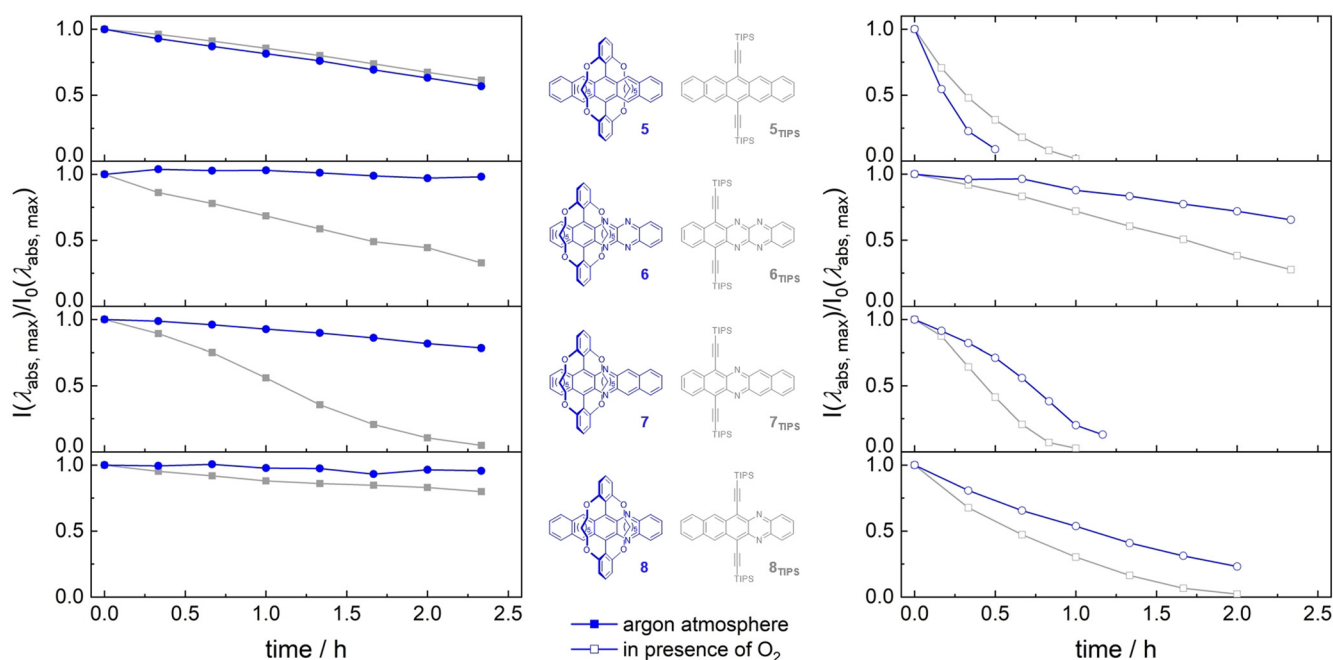
[a] First reduction potentials from cyclic voltammetry (CV) in DCM at room temperature with  $\text{Bu}_4\text{NPF}_6$  as the electrolyte against  $\text{Fc}/\text{Fc}^+$  as an internal standard ( $-5.10$  eV) at  $0.2$   $\text{Vs}^{-1}$ ; [b] electron affinity<sub>meas.</sub> =  $-e \times (5.1 \text{ V} + E^{(0/-)})$ ; [c] ionization potential<sub>meas.</sub> = electron affinity<sub>meas.</sub> – gap<sub>meas.</sub>; [d] obtained from DFT calculations (Gaussian16 B3LYP/def2-SVP// Gaussian16 B3LYP/def2-TZVP; TMS groups were used instead of TIPS).<sup>[14]</sup>

Single crystalline specimen of **5**, **6** and **9** were obtained by slow diffusion of methanol into a chloroform solution of the (aza)acene (Figure 3). Bond lengths and angles of the aromatic cores are in agreement with calculated values. Both **6** and **9** contain chloroform in the crystal lattice. The packing is dominated by van der Waals contacts of the bridging rings with each other.  $\pi$ - $\pi$ -contacts are not observed for the (aza)pentacenes (packing diagram see SI), as the double bridges dominate the supramolecular structure.

Important is the relative stability **5–9** under irradiation (Figure 4), performed under air and under argon ( $10^{-5}$   $\text{molL}^{-1}$ , DCM, ambient temperature).



**Figure 3.** Solid state structures of (aza)pentacenes **5** (a), **6** (b) and **9** (c). Top: Thermal ellipsoids set to 50% probability level. Bottom: Top-view of space-filling models.



**Figure 4.** Time-dependent evolution of UV/vis absorption intensities at  $\lambda_{\text{abs, max}}$  for **5–8** and **5-TIPS–8-TIPS** ( $10^{-5}$  mol L<sup>-1</sup>) after irradiation with a handheld UV lamp ( $\lambda_1 = 365$  nm and  $\lambda_2 = 254$  nm) in *n*-hexane at room temperature under argon atmosphere (left) and under ambient conditions (right). Distance to lamp was 5 cm for measurements under argon atmosphere and 20 cm under ambient conditions. **8** and **8-TIPS** show almost identical decomposition rates compared to **9** and **9-TIPS** (see SI, Figure S54), hence position of the sterically demanding group has less impact on stability compared to the position of nitrogen substitution.

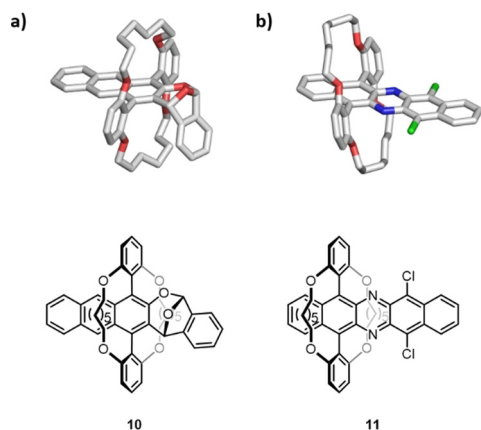
Under argon, **5** is of comparable stability to **5-TIPS**, but in air, **5** is more easily oxidized than **5-TIPS** (Figure 4). We isolated **10**, a rearrangement product of the *endo*-peroxide of **5**, identified under mass spectrometric conditions and by its single crystal structure (Figure 5 a). This rearrangement was previously described by Rigaudy et al. in the photolytic decomposition of anthracene.<sup>[15]</sup> We propose predominant formation of an 5,14-*endo*-peroxide for **5** due to steric shielding, whereas for **5-TIPS** the main product is the 6,13-*endo*-peroxide (98:2; 6,13- vs. 5,14-*endo*-peroxide).<sup>[16]</sup>

**6–9** are consistently more stable than their TIPS-ethynyl-congeners, both under argon but also under air. We note that

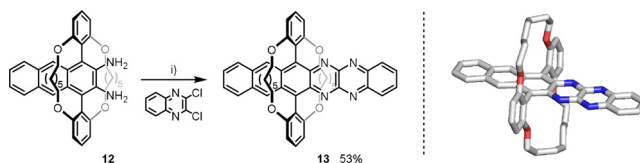
the position of the pyrazine unit and to a lesser effect the position of the substituents influence the reactivity for the TIPS-ethynyl substituted azaacenes. The bridged azaacenes **6**, **8** and **9** were still intact after 18 h irradiation under argon atmosphere. Irradiation in DCM under ambient conditions chlorinates the azaacenes, as verified by mass spectrometry. **7** furnishes **11** as one of the photoproducts (Figure 5 b) we could isolate. Generally, the mixtures formed during the photolysis of the azaacenes are difficult to separate and to characterize.

To expand the clipping-and-jacketing concept, we reacted **12** (Pd-catalyzed) with 2,3-dichloroquinoxaline, treated the coupling-product with PbO<sub>2</sub> and obtained the tetraazahexacene **13** in 53% yield (Scheme 2,  $\lambda_{\text{max abs}} = 946$  nm).<sup>[12]</sup> An X-ray analysis proves the topology; **13** crystallizes without solvent and displays  $\pi$ - $\pi$ -overlap involving the electron rich and electron poor parts of the hexacene, respectively (Figure 6).<sup>[18]</sup> **13** is stable and can be handled without any problem, demonstrating the use of jacketing.

In large azaacenes, Kobayashi's double alkylene bridging, termed "clipping-and-jacketing", is superior to TIPS-alkyne substituents with respect to stabilization. Tetraazahexacene



**Figure 5.** Identified products of photolytic decomposition reactions: Solid state structures of a) **10** produced in photolysis of **5** under air and b) decomposition product **11** formed from **7**.



**Scheme 2.** Synthesis of doubly alkylene bridged azahexacene **13**. Conditions: i) 1.) Cs<sub>2</sub>CO<sub>3</sub>, RuPhos Pd G1 (10 mol%), toluene, 110°C, 15 h; 2.) PbO<sub>2</sub>, DCM, 0°C, 30 min.

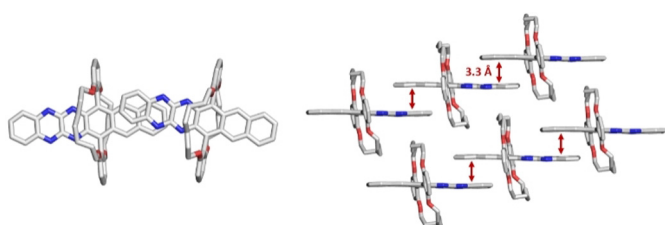


Figure 6. Packing of molecules of **13** in the single crystal.<sup>[18]</sup>

**13** packs in the single crystalline state with  $\pi$ - $\pi$ -stacking; it has not escaped our attention that molecules like **13** might be useful as n-channel semiconductors in thin-film transistors. Jacketing could emerge as powerful alternative to trialkylsilylalkynylation, particularly as nature and steric demand of the alkylene bridges—the jackets—are easily varied.

### Acknowledgements

Lukas Ahrens thanks the “Studienstiftung des deutschen Volkes” for a scholarship. We thank the DFG (SFB 1249) for generous support. Open access funding enabled and organized by Projekt DEAL.

### Conflict of interest

The authors declare no conflict of interest.

**Keywords:** acenes · organic materials · semiconductors · stabilization · X-ray diffraction

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- [18] Deposition Numbers 2044179 (for **5**), 2044180 (for **6**), 2044181 (for **9**), 2044182 (for **10**), 2044183 (for **11**), 2044184 (for **13**), 2044185 (for **S3**), 2044186 (for **S4**), 2044187 (for **S7**), 2044188 (for **S8**), 2044189 (for **S10**) and 2044190 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures)

Manuscript received: November 17, 2020

Accepted manuscript online: December 1, 2020

Version of record online: February 3, 2021