

## Photostability

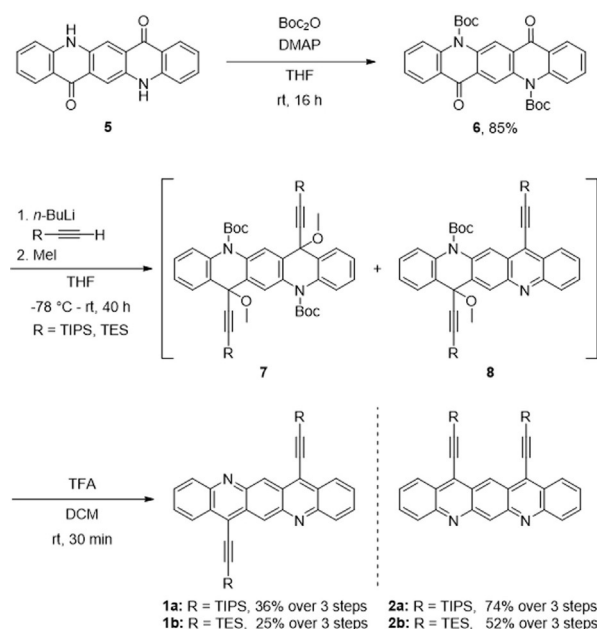
## Diazapentacenes from Quinacridones

Thomas Wiesner, Lukas Ahrens, Frank Rominger, Jan Freudenberg,\* and Uwe H. F. Bunz\*<sup>[a]</sup>

**Abstract:** Bis(silylethynylated) 5,7- and 5,12-diazapentacenes were synthesized from *cis*- and *trans*-quinacridone using protection, alkylation and deoxygenation. The solid-state packing of the targets is determined by choice and position of the silylethynyl substituents. The position of the substituents and nitrogen atoms influence the optical properties of the targets.

Herein, we disclose a strategy to transform industrially produced acridones into azaacenes. We convert *cis*- and *trans*-quinacridone,<sup>[1,2]</sup> into silylethynylated 5,7- (“*cis*”) and 5,12- (“*trans*”) diazapentacenes **1** and **2** and compare their properties with respect to solid-state packing and (photochemical) stability. (Aza-)acenes are structurally and fundamentally attractive; they find use in organic electronics.<sup>[3]</sup> Stabilization and solubilization<sup>[4]</sup> of larger azaacenes (e.g.  $\geq 5$  annulated rings) is achieved by triisopropylsilylethynyl substituents (e.g. in TIPS-Pen,<sup>[5]</sup> TIPS-TAP<sup>[6]</sup>) or building blocks that provide additional Clar sextets to the aromatic backbone.<sup>[7]</sup> Their solid-state packing (brickwall) allows charge carrier mobilities  $> 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , both *n*- and *p*-type,<sup>[8]</sup> but critically depends on the nature and position of the substituents.<sup>[9]</sup> Silylethynyl groups retard oxidation<sup>[10]</sup> and decrease rates of [4+4] cycloaddition to acene dimers.<sup>[11]</sup>  $D_{2h}$ -symmetric *peri*-substituted (aza)acenes are almost unknown.<sup>[12]</sup> Grimsdale et al. disclosed two only moderately stable 5,7-diazapentacenes (**1**; R = hexyl or phenyl<sup>[13]</sup>) obtained via a Cu<sup>I</sup>-catalyzed reaction of diphenyliodonium triflate with aminophenones—an approach to substituted (hetero)acenes; these are commonly synthesized via nucleophilic addition to quinone precursors followed by deoxygenation.<sup>[14]</sup> This established procedure allows facile introduction of different substituents.

We added lithiated silylacetylenes to linear *cis*-<sup>[1a]</sup> (**S6**) and *trans*-quinacridone (**5**) after protection of the amine functions with Boc anhydride (Scheme 1, see Scheme S1 in the Support-



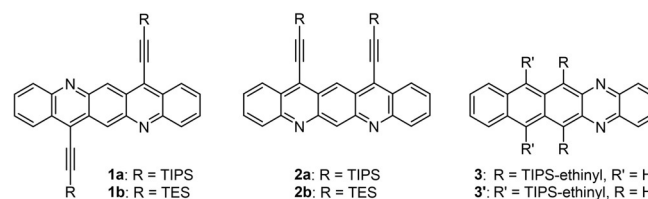
**Scheme 1.** Synthetic route towards diazapentacenes **1 a,b**. Synthesis of **2 a,b** is carried out accordingly (Scheme S1).

ing Information for the reaction sequence involving *cis*-quinacridone). Workup with MeI gives a mixture of **7** and **8**. The same reactivity is also observed when starting from *cis*-quinacridone. Treatment of the mixture with TFA results in deprotection of the amine(s) with concomitant methanol elimination to furnish triisopropylsilyl- and triethylsilylethynylated diazapentacenes **1 a,b** and **2 a,b** as intensely colored blueish-green solids (Figure 1). Note that concentrated solutions of TES-substituted **2 b** decomposed during workup at ambient temperature even under protective atmosphere (vide infra, see Figure 3 for one of the decomposition Diels–Alder adducts); TIPS-substituted **2 a** is stable. Yet, performing workup, extraction, chromatography and solvent removal at temperatures below 0 °C allows isolation of pure **2 b** which is stable as an

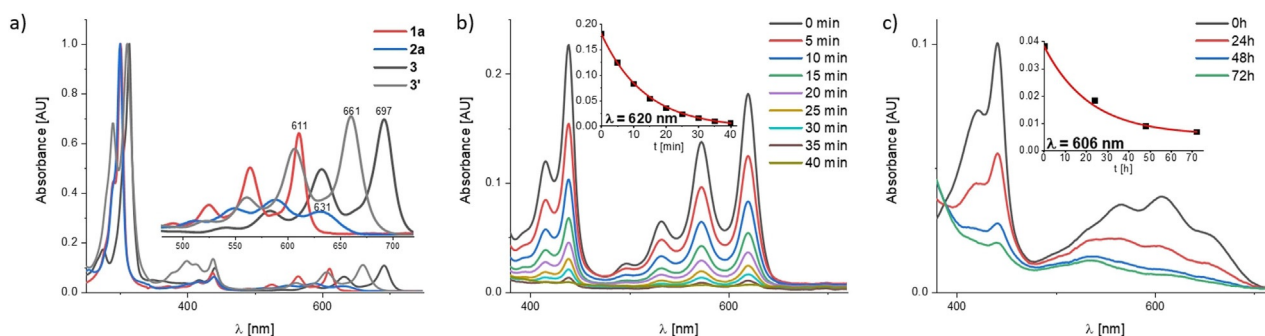
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**Figure 1.** Structures of diazaacenes (quinacridines) **1** and **2** and regioisomeric diazapentacenes **3** and **3'**.



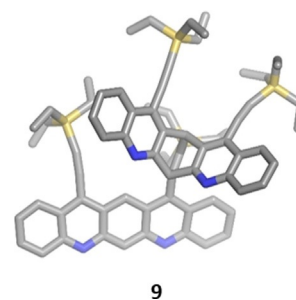
**Figure 2.** a) Normalized absorption spectra of **1a**, **2a** and **3** in *n*-hexane. b) Stability of **1b** in DCM under ambient light and atmosphere. c) Stability of **2b** in DCM under ambient light and atmosphere.

amorphous solid at  $-20^{\circ}\text{C}$ . All of the other compounds are stable at  $5^{\circ}\text{C}$  for several months.

The optoelectronic properties of *cis*- and *trans*- diazapentacenes **1** and **2** differ. The silyl group (TIPS vs. TES) has no effect. Figure 2 compares the absorption spectra of **1a** and **2a** (hexane, see Figures S2, S4 for spectra of **1b** and **2b**). The *p*- and  $\alpha$ -bands of weakly emissive **1a** are distinctive with  $\lambda_{\text{max,abs}}=611\text{ nm}$  ( $\lambda_{\text{max,em}}=630\text{ nm}$ , see Figure S5 for an emission spectrum). Spectral features of non-emissive **2a** are broader and slightly red-shifted to  $\lambda_{\text{max,abs}}=631\text{ nm}$ . The absorbance spectra (Figure S6) are concentration independent. DOSY studies (Figure S7) result in similar diffusion coefficients. Thus, UV-vis peak broadening of **2** is not attributable to aggregation in solution. **1** and **2** display blue-shifted absorption in comparison to **3** and **3'** (Figure 2; **3**:  $\lambda_{\text{max,abs}}=697\text{ nm}$ , **3'**:  $\lambda_{\text{max,abs}}=661\text{ nm}$ ), the extent of which depends on the position of the nitrogen and to a lesser extent on the position of the alkyne groups as suggested by our computational study (Table S2).

Compound **1a** ( $-1.24\text{ V}$  vs.  $\text{Fc}/\text{Fc}^+$ , CV) and **2a** ( $-1.39\text{ V}$  vs.  $\text{Fc}/\text{Fc}^+$ , CV) are less easily reduced than **3** ( $-1.05\text{ V}$  vs.  $\text{Fc}/\text{Fc}^+$ , CV). The *trans*-isomers are more electron-deficient than the *syn*-quinacridines (order of reduction potentials:  $3 > 3' > 1a,b > 2a,b$ ). The electron affinity is independent of the silyl substituent (Table 1, Tables S1, S2). **1a,b** and **2a,b** are stable in dilute solution (Figures S1–S4,  $c=10^{-6}\text{ M}$ ) under ambient atmosphere in the dark. When exposed to light under ambient

atmosphere, solutions of **1a,b** react within the hour (Figure 2b) forming colorless products. Single crystals of these products were unstable under X-ray conditions. HRMS indicates peroxide formation (Figure S12) and/or follow-up degradation products.<sup>[15]</sup> *cis*-Quinacridines are more stable: **2a,b**, are stable for up to 3 days. Similarly, Grimsdale et al. reported discoloration of their phenyl substituted derivative during “several days”. **2b** is persistent in the dark under ambient conditions for 4 d at concentrations of up to  $5 \times 10^{-4}\text{ M}$  ( $0.28\text{ mg mL}^{-1}$ , Figure S4). Concentrating **2b** at room temperature results in the dimer **9** (Figure 3). *Trans*-quinacridines **1a,b** pack in a one-di-



**Figure 3.** At high concentrations **2b** reacts via thermally allowed [4+2] cycloaddition forming the dimer **9**.

mensional staircase barely influenced by the size of the silyl group (Figure 4). The  $\pi$ - $\pi$ -stacking distances ( $3.47\text{ \AA}$  for **1a**,  $3.48\text{ \AA}$  for **1b**) are tight. **2a** packs in one-dimensional dimeric staircase without  $\pi$ - $\pi$ -overlap between the dimers. In contrast to **1a,b** the TIPS-groups are an integral part of the one-dimensional stacks and do not separate adjacent layers from one another. **2b** crystallizes in a dimeric herringbone arrangement with  $\pi$ - $\pi$ -distances amounting to  $3.52\text{ \AA}$  between the dimer pairs and  $3.33\text{ \AA}$  within the dimers—the  $\pi$ - $\pi$ -overlap is higher than for **1a,b** or **2a** and might be an attractive organic semiconductor. The IP and EA of **2b** do not match with standard electrode materials (Au or Ag), their application is being evaluated at the moment.

In conclusion, four silylethynylated 5,7- and 5,12-diazapentacenes (**1a,b** and **2a,b**) were obtained from *cis*- and *trans*-quinacridones. Regioisomerism and steric demand of the substitu-

Table 1. Optical, electrochemical and quantum-chemical data.				
Compound	$\lambda_{\text{max,abs}}$ [nm] <sup>[a]</sup>	$\lambda_{\text{onset,abs}}$ [nm] <sup>[a]</sup>	Opt. gap [eV] <sup>[b]</sup>	$E^{(0/-)}$ [V] <sup>[c]</sup>
<b>1a</b>	611	622	1.99	-1.24
<b>1b</b>	610	623	1.99	-1.18
<b>2a</b>	631	659	1.88	-1.39
<b>2b</b>	637	662	1.87	-1.30
<b>3</b> <sup>[16]</sup>	697	709	1.74	-1.05
<b>3'</b>	661	681	1.82	-1.16

[a] Absorption measurements were performed in *n*-hexane.  $\lambda_{\text{max,abs}}$  denotes the local absorption maximum at the longest wavelength. [b] Calculated from  $\lambda_{\text{onset,abs}}$ . [c] First reduction potentials measured by cyclic voltammetry (CV) in dichloromethane with  $\text{Bu}_4\text{NPF}_6$  as the electrolyte against  $\text{Fc}/\text{Fc}^+$  as an internal standard ( $-5.10\text{ eV}$ )<sup>[17]</sup> at  $0.2\text{ mV s}^{-1}$ .

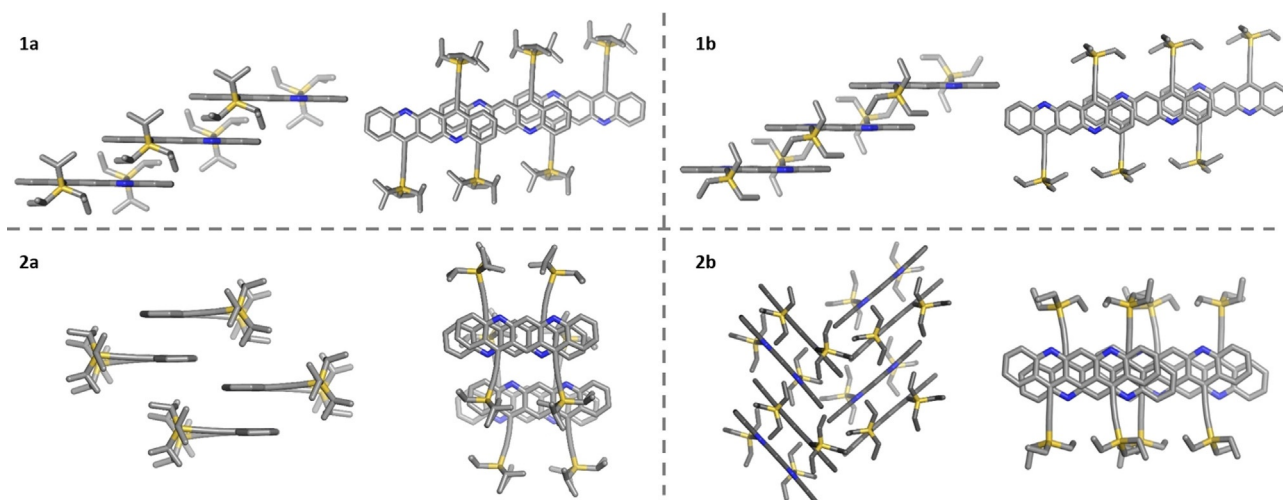


Figure 4. Solid state packing of **1 a,b** and **2 a,b**.

ents defines stability and decomposition pathways. *cis*-Diazapentacenes are more stable with respect to oxidation. While the smaller TES groups are beneficial for solid-state packing, they render **2 b** susceptible to dimerization via Diels–Alder reactions, although **2 b** can be handled at concentrations relevant for device fabrication. To increase stability and lower the frontier orbital energies, that is, the electron affinities, we currently work on the synthesis of tri- and tetraaza-derivatives of **1** and **2**. A central pyrazinic ring should increase oxidative stability and suppress cycloaddition activity. Such targets might be attractive n-type semiconductors.

## Experimental Section

### Crystallographic data

Deposition Number(s) 2040676 (**1 a**), 2040677 (**1 b**), 2040678 (**2 a**), 2040679 (**2 b**), and 2040679 (**9**) contain(s) 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).

### Representative procedure towards 5,12-diaza-7,14-(triisopropylethynyl)pentacene (**1 a**)

In an oven-dried Schlenk tube under argon atmosphere, 2.5 M *n*BuLi (312  $\mu$ L, 78.0  $\mu$ mol, 4.00 equiv., in *n*-hexane) was slowly added to a solution of TIPS-acetylene (263  $\mu$ L, 1.17 mmol, 6.00 equiv.) in anhydrous THF at  $-78^\circ\text{C}$ . After stirring for 1 h, Boc-protected quinacridone **6** (100 mg, 190  $\mu$ mol, 1.00 equiv.) was added to the solution and the reaction was allowed to stir overnight while allowing the reaction to warm to room temperature. The reaction was subsequently quenched by addition of methyl iodide (120  $\mu$ L, 1.90 mmol, 10.0 equiv.) and stirred for 8 h. A small amount of saturate aqueous ammonium chloride solution was added and the phases were separated. After concentrating of the organic layer in vacuo, the crude product was redissolved in DCM, washed with water, dried over magnesium sulfate and evaporated under reduced pressure. It is then dissolved in DCM (5 mL) and TFA (500  $\mu$ L, 7.80 mmol, 40.0 equiv.) is added to the mixture. After

stirring at  $0^\circ\text{C}$  for 30 min an excess of sat. aqueous sodium bicarbonate solution is added and stirred until the bright green solution turned dark. The organic layer was separated, dried over  $\text{Na}_2\text{SO}_4$  and evaporated under reduced pressure. As an eluent for purification via column chromatography a mixture of petrol ether and ethyl acetate (97:3) was chosen. The product was obtained as a dark solid and was recrystallized by overlaying a saturated dichloromethane solution with methanol to yield black crystalline needles with a metallic lustre (48.5 mg, 72.1  $\mu$ mol, 36% overall yield). NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.67 (s, 2H), 8.52 (d,  $J$  = 8.8 Hz, 2H), 8.21 (d,  $J$  = 8.9 Hz, 2H), 7.75 (m, 2H), 7.59–7.44 (m, 2H), 1.47–1.36 (m, 6H) 1.34 ppm (m, 36H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 151.3, 144.7, 131.1, 130.8, 128.4, 128.2, 127.9, 127.8, 127.2, 127.1, 111.6, 101.5, 77.4, 19.1, 11.7 ppm. IR (neat)  $\tilde{\nu}$  = 2943, 2859, 1526, 1456, 1429, 1396, 1060, 990, 879, 755, 662, 607, 455, 436  $\text{cm}^{-1}$ . HRMS (ESI+):  $m/z$  calcd (%) for  $\text{C}_{42}\text{H}_{52}\text{N}_2\text{Si}_2$ : 640.3669; found 641.3750 ( $M+H^+$ ). M.p.: 220–230  $^\circ\text{C}$  (dec.).

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## Conflict of Interests

The authors declare no conflict of interests.

**Keywords:** azaacenes · photostability · quinacridines · semiconductors · solid-state packing

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