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Diazapentacenes from Quinacridones

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Bis(silylethynylated) 5,7- and 5,12-diazapentacenes were synthesized from *cis*- and *trans*-quinacridone using protection, alkynylation 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.

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



We added lithiated silylacetylenes to linear *cis*^[15] (**S6**) and *trans*quinacridone (**5**) after protection of the amine functions with Boc anhydride (Scheme 1, see SI Scheme S1 for the reaction sequence involving *cis*-quinacridone). Workup with Mel 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

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elimination to furnish triisopropylsilyl- and triethylsilylethynylated diazapentacenes **1a,b** and **2a,b** as intensely colored blueishgreen solids. Note that concentrated solutions of TES-substituted **2b** decomposed during workup at ambient temperature even under protective atmosphere (*vide infra*, see Figure 4 for one of the decomposition Diels-Alder adducts); TIPS-substituted **2a** is stable. Yet, performing workup, extraction, chromatography and solvent removal at temperatures below 0 °C allows isolation of pure **2b** which is stable as an amorphous solid at -20 °C. All of the other compounds are stable at 5 °C for several months.



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

The optoelectronic properties of cis- and trans- diazapentacenes 1 and 2 differ. The silvl group (TIPS vs TES) has no effect. Figure 2 compares the absorption spectra of 1a and 2a (hexane, see SI Figure S2, S4 for spectra of **1b** and **2b**). The p- and α bands of weakly emissive 1a are distinctive with $\lambda_{max,abs}$ = 611 nm $(\lambda_{max,em} = 630 \text{ nm}, \text{ see SI Figure S5 for an emission spectrum}).$ Spectral features of non-emissive 2a are broader and slightly redshifted to $\lambda_{max,abs}$ = 631 nm. The absorbance spectra (Figure S6, SI) are concentration independent. DOSY studies (Figure S7, SI) 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: $\lambda_{max,abs}$ = 697 nm, 3': $\lambda_{max,abs}$ = 661 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, SI).

1a (-1.24 V vs Fc/Fc⁺, CV) and **2a** (-1.39 V vs Fc/Fc⁺, CV) are less easily reduced than **3** (-1.05 V vs Fc/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, Table S1, S2, SI). **1a,b** and **2a,b** are stable in dilute solution (Figure S1-S4, $c = 10^{-6}$ M) under ambient atmosphere in the dark. When exposed

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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, SI) and/or follow-up degradation products.^[16] *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•10⁻⁴ M (0.28 mgmL⁻¹, Figure S4, SI). Concentrating **2b** at room temperature results in the dimer **9** (Figure 4). *Trans*-quinacridines **1a,b** pack in a one-dimensional staircase barely influenced by the size of the silyl group (Figure 3). The π - π -stacking distances (3.47 Å for **1a**, 3.48 Å for **1b**) are tight. **2a** packs in one-dimensional dimeric staircase without π - π -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 π - π -distances amounting to 3.52 Å between the dimer pairs and 3.33 Å within the dimers – the π - π -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.



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.



Figure 3. Solid state packing of 1a,b and 2a,b.

Table 1. Optical, electrochemical and quantum-chemical data.

Compound	λ _{max,abs} [nm] ^[a]	λ _{onset, abs} [nm] ^[a]	Opt. gap [eV] ^[b]	E ^(0/-) [V] ^[c]
1a	611	622	1.99	-1.24
1b	610	623	1.99	-1.18
2a	631	659	1.88	-1.39
2b	637	662	1.87	-1.30
3 ^[17]	697	709	1.74	-1.05
3'	661	681	1.82	-1.16

^[a]Absorption measurements were performed in *n*-hexane. $\lambda_{max,abs}$ denotes the local absorption maximum at the longest wavelength. ^[b]Calculated from $\lambda_{onset,abs}$. ^[c]First reduction potentials measured by cyclic voltammetry (CV) in dichloromethane with Bu₄NPF₆ as the electrolyte against Fc/Fc⁺ as an internal standard (-5.10 eV) ^[18] at 0.2 mV s⁻¹.

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

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silylethynylated 5.7-In conclusion. four and 5.12diazapentacenes (1a,b and 2a,b) were obtained from cis- and trans-quinacridones. Regioisomerism and steric demand of the substituents defines stability and decomposition pathways. Cisdiazapentacenes are more stable with respect to oxidation. While the smaller TES groups are beneficial for solid-state packing, they render 2b susceptible to dimerization via Diels-Alder reactions, although 2b can be handled at concentrations relevant for device fabrication. To increase stability and lower the frontier orbital energies i.e. 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

CCDC 2040676 (1a), 2040677 (1b), 2040678 (2a), 2040679 (2b) and 2040679 (9) contain the supplementary crystallographic data for this paper. These are provided free of charge by The Cambridge Crystallographic Data Centre.

Representative procedure towards 5,12-diaza-7,14-(tri-*iso*-propylethynyl)-pentacene **1a**:

In an oven-dried Schlenk tube under argon atmosphere, 2.5 M n-BuLi (312 µL, 78.0 µmol, 4.0 eq., in n-hexane) was slowly added to a solution of TIPS-acetylene (263 µL, 1.17 mmol, 6.0 eq.) in anhydrous THF at -78 °C. After stirring for 1 h, Boc-protected quinacridone 6 (100 mg, 190 µmol, 1.00 eq.) 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 µL, 1.90 mmol, 10.0 eq.) 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 µL, 7.80 mmol, 40 eq.). is added to the mixture. After stirring at 0 °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 laver was separated, dried over Na₂SO₄ 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 μ mol, 36% overall yield). NMR (400 MHz, CDCl₃) δ = 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 (m, 36H). ^{13}C NMR (101 MHz, CDCl_3) δ = 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. IR (neat) v = 2943, 2859, 1526, 1456, 1429, 1396, 1060, 990, 879, 755, 662, 607, 455, 436 cm⁻¹. HRMS (ESI+): m/z calcd for C42H52N2Si2: 640.3669; found 641.3750 (M+H+). M.p.: 220-230°C (dec.).



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Conflict of Interests

The authors declare no conflict of interests.

Keywords: azaacenes • quinacridines • solid-state packing • photostability • semiconductors

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Piecing together a diazaacene: Starting from linear *cis*- and *trans*-quinacridones, the synthesis, characteristics and stability of four diazapentacenes are reported leading to a design rule for 12,14-alkynylated heteroacenes for organic electronics.

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