Abstract: Bis(silylenylated) 5,7- and 5,12-diazapentacenes were synthesized from cis- and trans-quinacridone using protection, alkyynylation and deoxygenation. The solid-state packing of the targets is determined by choice and position of the silylenyl 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[1, 2] into silylenylated 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 trisopropylsilylenyl 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 cmV⁻¹s⁻¹, both n- and p-type,[8] but critically depends on the nature and position of the substituents.[9] Silylenyl groups retard oxidation[10] and decrease rates of [4+4] cycloaddition to acene dimers.[11] D₂₀-symmetric peri-substituted (aza)acenes are almost unknown.[12] Grimsdale et al. disclosed two only moderately stable 5,7-diazapentacenes (1; R = hexyl or phenyl[13]) obtained via a Cu⁺-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.[14] This established procedure allows facile introduction of different substituents.

We added lithiated silylacetylenes to linear cis-[1a] (S6) and trans-quinacridone (5) after protection of the amine functions with Boc anhydride (Scheme 1, see Scheme S1 in the Supporting Information 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 elimination to furnish trisopropylsilylenylated diazapentacenes 1a,b and 2a,b as intensely colored blueish-green solids (Figure 1). Note that concentrated solutions of TES-substituted 2b 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 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

Figure 1. Structures of diazaacenes (quinacridones) 1 and 2 and regioisomeric diazapentacenes 3 and 3’.
The optoelectronic properties of cis- and trans-diazapenta-
cenes 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 α-bands of weakly emissive 1a are distinctive with
λ_{max,abs} = 611 nm (λ_{max,em} = 630 nm, see Figure S5 for an emis-
sion spectrum). Spectral features of non-emissive 2a are
broader and slightly red-shifted to λ_{max,abs} = 631 nm. The ab-
sorbance 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 aggre-
gation in solution. 1 and 2 display blue-shifted absorption in
comparison to 3 and 3’. (Figure 2; 3: λ_{max,abs} = 697 nm, 3’:
λ_{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).

Compound 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, Tables S1, S2). 1a,b and 2a,b are stable in
dilute solution (Figures S1–S4, c = 10^{-4} M) under ambient
atmosphere in the dark. When exposed to light under ambient

amorphous solid at −20 °C. All of the other compounds are
stable at 5 °C for several months.

The opto-electronic properties of cis- and trans-diazapenta-
cenes are distinctive with

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![Figure 2](image1.png)

**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.

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![Figure 3](image2.png)

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

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| Compound | λ_{max,abs} [nm] | λ_{max,em} [nm] | Opt. gap [eV] | E^c [V] |
|----------|----------------|----------------|--------------|---------|
| 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[1b]    | 697            | 709            | 1.74         | −1.05   |
| 3’       | 661            | 681            | 1.82         | −1.16   |

[a] Absorption measurements were performed in n-hexane. λ_{max,abs} denotes the local absorption maximum at the longest wavelength. (b) Calculated from λ_{max,abs}.

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

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The authors currently work on the synthesis of tri- and tetraaza-derivatives of pentacenes. By using a central pyrazinic ring, a higher oxidative stability is expected. The presence of a nitrogen atom increases the electron density and the smaller TES groups are beneficial for solid-state packing, thus defining stability and decomposition pathways. cis-Diaza-pentacenes 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, 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 cycladdition activity. Such targets might be attractive n-types semiconductors.

Experimental Section

Crystallographic data

Deposition Number(s) 2040676 (1a), 2040677 (1b), 2040678 (2a), 2040679 (2b), 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.

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

In an oven-dried Schlenk tube under argon atmosphere, 2.5 m nBuLi (312 µL, 78.0 µmol, 4.00 equiv., in n-hexane) was slowly added to a solution of TIPS-acetylene (263 µL, 1.17 mmol, 6.00 equiv.) in anhydrous THF at −78 °C. After stirring for 1 h, Boc-protected quinacridone 6 (100 mg, 190 µmol, 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 µL, 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 µL, 7.80 mmol, 40.0 equiv.). 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 layer 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 µmol, 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 ppm (m, 36H). ¹³C NMR (101 MHz, CDCl₃) 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 ppm. IR (neat) ν = 2943, 2859, 1526, 1467, 1429, 1396, 1060, 990, 755, 735, 662, 607, 455, 436 cm⁻¹. HRMS (ESI⁺) m/z calcd (%) for C₆H₅N₂S₂: 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 • photostability • quinacridines • semiconductors • solid-state packing

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