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Bromination Improves Tetraazapentacene's Electron Mobilities

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Abstract: A cyclocondensation-based preparation of tetrabromotetraazapentacene (**BrTAP**) is described using TIPS-ethynyl-substituted diaminoarenes with *in-situ* obtained 4,5-dibromocyclohexa-3,5-diene-1,2-dione. **BrTAP** is easily reduced to its *air stable* radical anion; electron mobilities $> 0.56 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ are achieved in thin film transistors.

Azaacenes^[1,2,3] are electron-poor counterparts of acenes.^[4] Applications of azaacenes and azaarenes range from emitters in organic light-emitting diodes (OLEDs),^[5] to electron-transporters in solar cells (SC)^[6,7] and n-type semiconductors in field-effect transistors (FETs).^[8,9] Among azaarenes, 6,13-bis(triisopropylsilyl)ethynyl-5,7,12,14-tetraaza-pentacene (**TIPSTAP**)^[10] showed an electron mobility of over $11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in organic field-effect transistors (FETs).^[11] **TIPSTAP** is isostructural with 6,13-bis(triisopropylsilyl)ethynylpentacene (**TIPSPen**), featuring a brick-wall packing motif and nearly identical cell parameters.^[12] Introduction of nitrogen atoms into the π -system changes the electronic structure within the pentacene frame. Peripheral substitution of the aromatic system alters the electronic properties and the morphology further. Herein we describe an alternative access to **1** (**BrTAP**, Figure 1).^[13] The electronegative bromine atoms lead to a higher electron affinity and increase the electron mobility in FETs. Our synthetic concept exploits thiadiazolo[3,4-*b*]phenazine **2**.

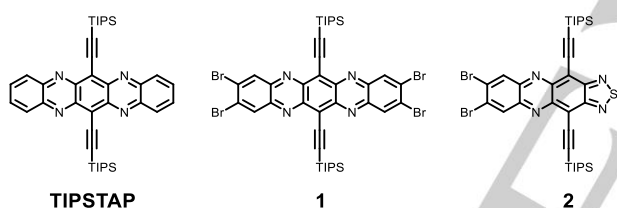
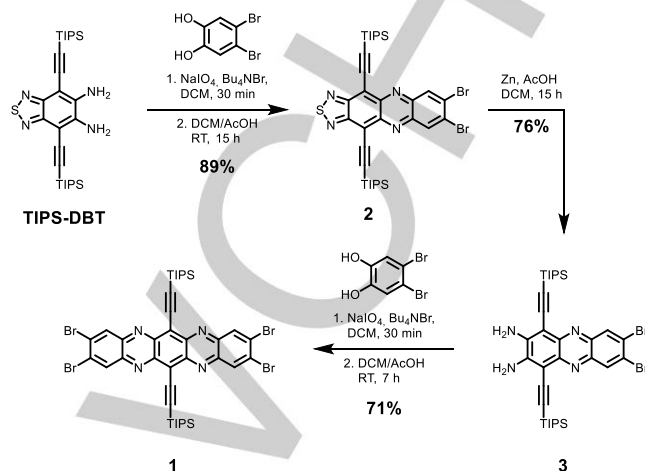


Figure 1. **TIPSTAP**, **BrTAP 1** and thiadiazolo[3,4-*b*]phenazine **2**.

Our previous synthesis of **1** gave the material in only 10 % yield and lacked reproducibility.^[13] Herein, **1** is synthesized from **TIPS-DBT** (Scheme 1). Cyclocondensation reaction with *in-situ* oxidized 4,5-dibromocatechol furnishes **2**. Subsequently, a reductive ring opening with Zn in acetic acid and a second condensation reaction with 4,5-dibromocatechol in the presence of periodate yielded **1** in 71 %, a significant improvement upon the previously reported route. The electron affinities were calculated at the level of DFT/CAM-B3LYP to be 4.03 eV for the parent **TIPSTAP** and 4.33 eV for **1**, making **1** attractive for n-channel semiconductors; the first reduction potential of **1** is remarkable (-0.7 V vs. ferrocene), suggesting that the radical anion might be air stable.^[13]



Scheme 1. Synthesis of brominated thiadiazolo[3,4-*b*]phenazine **2**. Reductive ring opening and subsequent condensation with 4,5-dibromo-benzene-1,2-diol leads to **TIPSTAP** derivative **1**.

To test this hypothesis, we prepared a solution of the dianion of **1** in THF by reduction with $[\text{K}(18\text{-crown-6})(\text{THF})_2]$ anthracenide. Remarkably, this dianion is stable under nitrogen; it does not lose bromide ions or form the organo potassium compound under these conditions. Upon bubbling air through the solution of the dianion, according to UV-vis spectroscopy, it is oxidized *not* to the neutral species but to the radical anion, which is stable under ambient conditions in air for weeks in diethyl ether solution, as the first electrochemical reduction potential of oxygen is around -0.7 V . This is supported by the computed relative stabilities of the neutral, anion and dianion of **1** in THF. While only about 3.36 eV are required to remove an electron from **1**²⁻ to arrive at **1**^{•-}, approximately 4.33 eV are needed to oxidize the anion back to the neutral **BrTAP**.

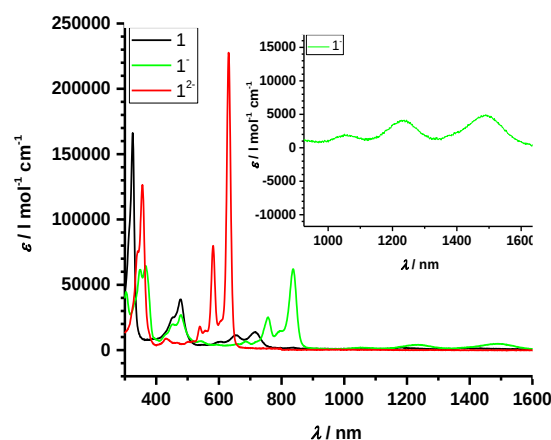


Figure 2. Absorption spectra of **1** in its neutral (black), mono- (green) and dianionic form (red) determined by spectroelectrochemistry in THF/TBA-PF₆.

Figure 2 shows the absorption spectra of the neutral compound, the radical anion and the dianion of **1**. As in the case of **TIPSTAP**, the spectrum of the radical anion is most red-shifted, followed by that of

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neutral **1**.^[14] The dianion has the most blue-shifted absorption spectrum and its solution in Et₂O is somewhat fluorescent (quantum yield 3.5%), despite the presence of the four bromine atoms, which would be expected to facilitate intersystem crossing due to the heavy-atom effect. The small Stokes shift reveals the π - π^* nature of the S₀-S₁ transition as well as the fluorescence nature of the emission, which is supported by the emissive lifetimes ($\tau_1 < 1$ ns (26%), $\tau_2 = 2.0$ ns (22%), $\tau_3 = 4.5$ ns (52%)). The lowest computed vertical electronic transitions of **1**, its monoanion and dianion at the level of TDDFT/CAM-B3LYP follow the trend of the experimental data (Table 1). The optical properties and excited electronic states are, in general, very similar to that of **TIPSTAP** and its reduced species.

Table 1. Computed relative energies (ΔE) and vertical excited states of **1**, its anion **1^{•-}** and dianion **1²⁻** at the DFT(TDDFT)/CAM-B3LYP/6-311++G** level using Q-Chem 5.0.

	1	1^{•-}	1²⁻
$\Delta E^{[a]}$	0	-4.33	-7.69
BS ₁ ^[b]	1.91 (0.27) [650 nm]	0.97 (0.10) [1280 nm]	2.39 (1.36) [519 nm]
BS ₂ ^[b]	3.09 (1.03) [401 nm]	1.87 (0.43) [662 nm]	

[a] Relative energies in eV. The energy of neutral **1** is set to zero. [b] Vertical excitation energies of bright states (BS) in eV, oscillator strengths in parentheses, absorption wavelengths in brackets.

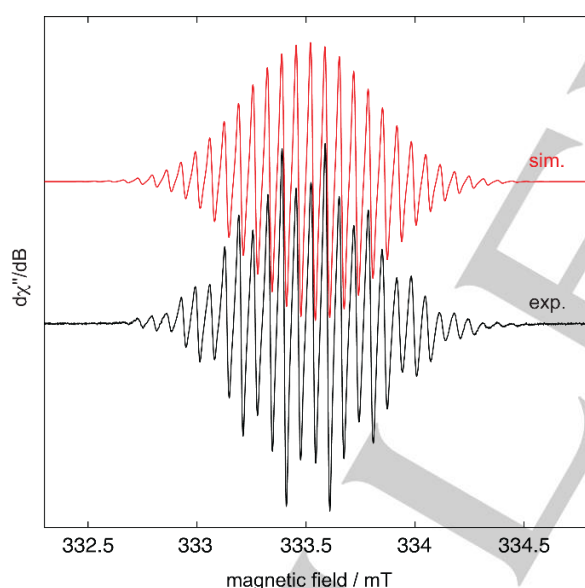


Figure 3. Simulated and experimental EPR spectrum of **1^{•-}**.

The EPR of **1^{•-}** is shown in Figure 3. The simulated spectrum gives $g_{iso} = 2.005$, $a(^{14}\text{N}) = 3.7$ MHz, $a(^1\text{H}) = 3.7$ MHz, $a(^{79,81}\text{Br}) = 1.8$ MHz. The hyperfine coupling of nitrogen in **1^{•-}** is much smaller than that in the **TIPSTAP** radical anion ($a(^{14}\text{N}) = 5.32$ MHz), while the hyperfine coupling constants of the protons in **TIPSTAP^{•-}** are smaller than those in **1^{•-}**. This indicates that for **1^{•-}** the unpaired electron resides more on the outer rings than on the inner rings, which is the case for **TIPSTAP^{•-}**, which is an indication of the inductive effect of the bromine substituents. The computed natural charges at DFT/CAM-B3LYP support this finding (Supporting Information). The EPR spectrum of **1^{•-}** seems to be affected by anisotropic effects but changing the solvents or concentration did not significantly improve its symmetry.

Addition of the bromine atoms does indeed lead to a shift of negative charge towards the outer rings. This effect is more pronounced for the anionic and dianionic species than for the neutral **1**. This observation will be important for the discussion of the device results. Quantum chemical calculations confirmed that **1²⁻** is a singlet, as the triplet state lies 1.159 eV above that of the singlet.

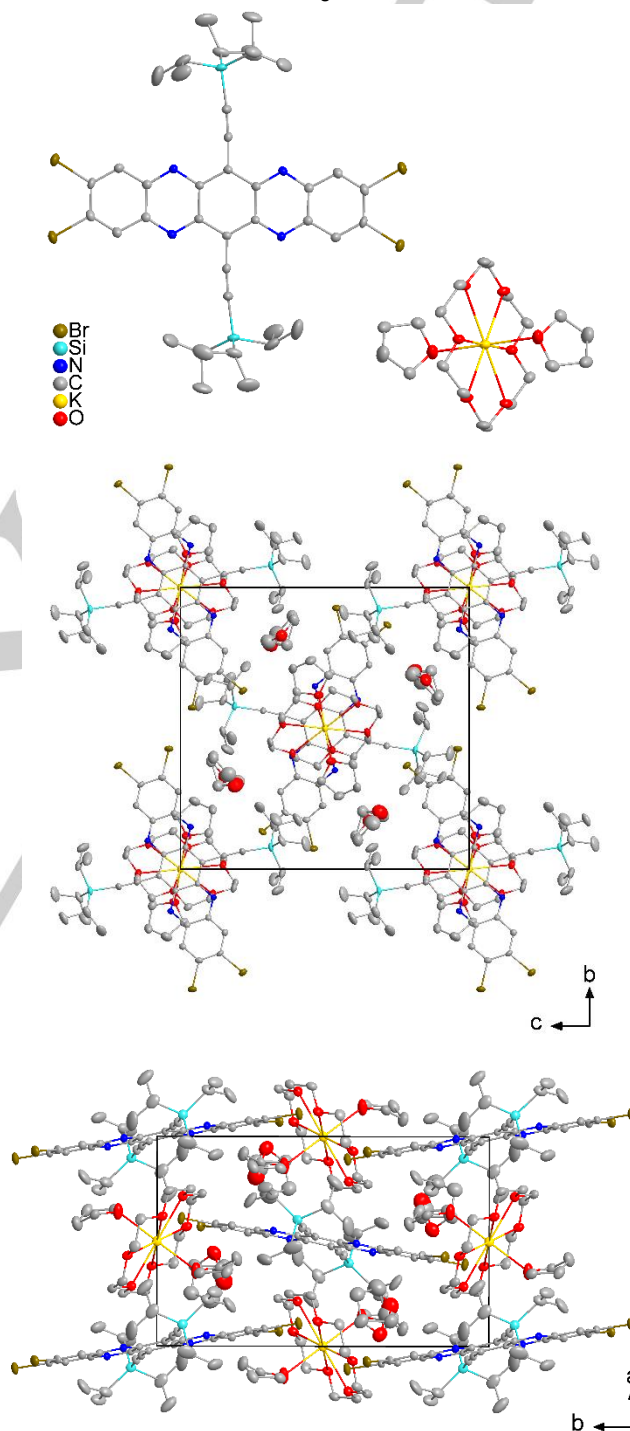


Figure 4. Crystal structure of **1K1**. Molecular structure (top) and two views of the packing of the molecules (middle, bottom).

We grew single crystals of **1^{•-}** suitable for X-ray-structure analysis (Figures 4 and 5). As in former reported radical anions of azaacenes,^[14] the potassium cation does not show any interaction

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with the negatively charged azaacene. As the charge is distributed over the large π -system, the radical anion lacks hard Lewis-basic properties, needed to coordinate to the potassium cation in the presence of THF. The packing of $1^{\bullet-} K^+$ is shown in the middle and bottom parts of Figure 4. The (18-crown-6)(THF)₂-coordinated potassium ions are located between the large π -systems, and the cations and anions do not interact strongly. Figure 5 shows the minute changes in bond lengths when going from **1** to its radical anion, which are mostly less than 0.02 Å. In the eastern and western rings of $1^{\bullet-}$ the bond length alternation, distinct in the structure of **1**, is diminished upon reduction.

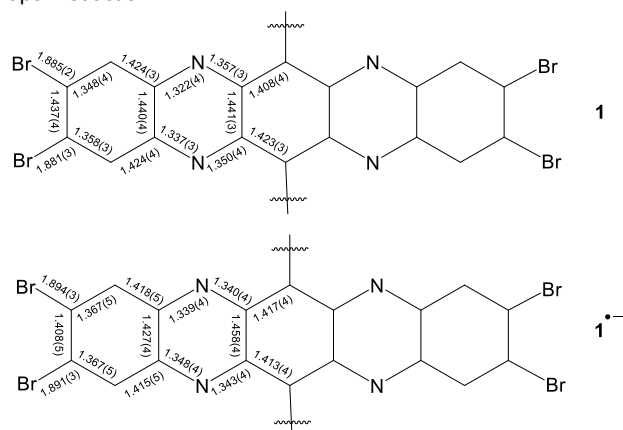


Figure 5. Bond length changes between **1** (top) and its radical anion (bottom).

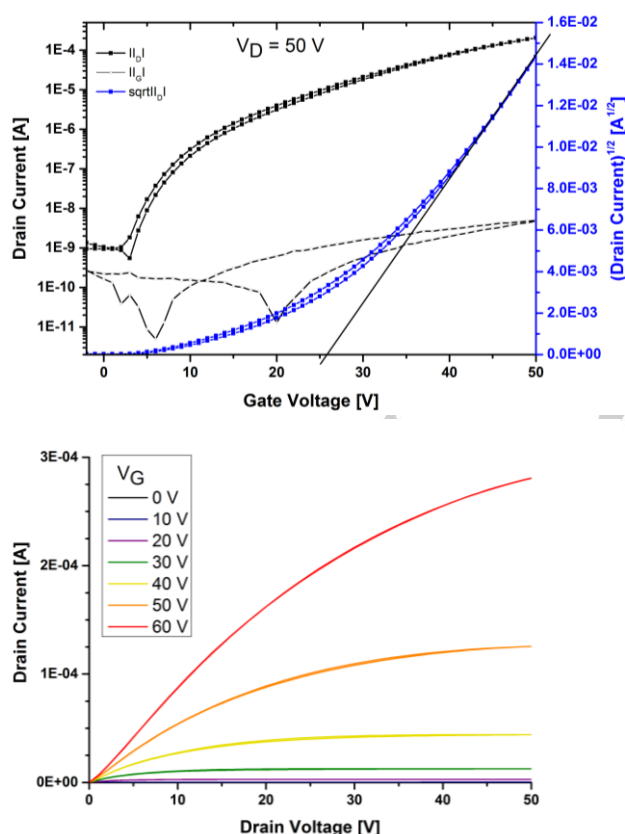


Figure 6. Transfer (top) and output characteristic (bottom) for **1**; device dimensions: $W = 8$ mm, $L = 38.62$ μ m.

To assess charge carrier mobilities of **BrTAP 1**, we fabricated bottom-gate/top-contact field effect transistors (FET). Structured silver

electrodes were thermally evaporated on to glass substrates and chemical vapor deposited parylene C was used as the dielectric. Compound **1** was dip coated from DCM (5 mg/mL – 5 mm/min) by dewetting via spinning. The devices were finished with thermally evaporated gold electrodes and measured under nitrogen. Both **BrTAP** and **TIPSTAP** showed n-channel FET behavior (Figure S5). Figure 6 displays the transfer (top) and output characteristics (bottom) of **1**. The on/off ratio is 10^5 and the average electron mobility is 0.26 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ with top mobilities of 0.56 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ for **1**.

In comparison to similar devices fabricated from **TIPSTAP** (dip coated; average 3.9×10^{-3} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ and top 1.3×10^{-2} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$), compound **1** thus showed 43 times higher electron mobilities (calculated from top mobilities; 66 times higher calculated from average mobilities), see Table 2.

In summary, an improved, high-yielding synthesis of **1** was developed and its electronic and device properties were carefully investigated. Several important trends emerge. 1) Addition of four bromine substituents increases the electron affinity as it drastically stabilizes the anionic and dianionic species. As a consequence, the radical anion of **1** is now air-stable for at least 14 days. 2) The bromine substituents influence the distribution of the negative charges in the radical anion such that it has a higher probability of residing on the outer rings. This seems to lead to an increased transfer integral in the solid state of **1** in the presence of negative charges. 3) Electron mobilities of **1** of up to 0.56 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ were measured; this is over 50 times higher than that of **TIPSTAP** under identical processing conditions. Over all, bromination is a superb approach by which to improve the semiconducting properties of **TIPSTAP**.

Table 2. Summarized results from the optoelectronic characterization of the compounds.

	$\lambda_{\text{max,abs}}$ [nm] ^a	$E_{\text{affinity,CV}}$ [eV] ^b	$\mu_{\text{e,top}}$ [$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$] ^c	$\mu_{\text{e,average}}$ [$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$] ^c	$I_{\text{on}} / I_{\text{off}}$
TIPSTAP	680	3.99	1.3×10^{-2}	3.9×10^{-3}	10^4
1	718	4.19	5.6×10^{-1}	2.64×10^{-1}	10^5

^a Red-shifted maxima from the UV-vis spectra in hexane. ^b Extracted from the cyclic voltammetry measurements. [$E_{\text{affinity,CV}} = -4.80$ eV – $E_{(0/-1)}$] measured in CH_2Cl_2 with Bu_4NPF_6 as the electrolyte against Fc/Fc^+ as an internal standard at 0.2 mV/s. ^c Bottom-gate/top-contact FETs. Structured silver electrodes were thermally evaporated on to glass substrates and chemical vapor deposited parylene C was used as the dielectric. Semiconductors were dip coated from DCM (5 mg/mL – 5 mm/min). The devices were finished with thermally evaporated gold electrodes and measured in a nitrogen atmosphere.

EXPERIMENTAL SECTION

[K·18-crown-6·(THF)₂]⁺**1**^{•-} (**1K1**): In an argon-filled glove box, **1** (9.5 mg, 10 μ mol) and [K·18-crown-6·(THF)₂] anthracenide (6.9 mg, 11 μ mol) were dissolved in 2 mL of dry THF in a 20 mL vial and stirred for 10 min to generate a yellow solution. Orange crystals formed by slow diffusion of dry pentane into the reaction mixture at room temperature.

[K·18-crown-6·THF]₂²⁻**1K2**: In an argon-filled glovebox, **1** (6.2 mg, 6.5 μ mol) and [K·18-crown-6·(THF)₂] anthracenide (9.9 mg, 15 μ mol) were dissolved in 2 mL of dry THF in a 20 mL vial and stirred for 10 min to generate a red solution. Dark red crystalline solids formed by slow diffusion of dry pentane into the reaction mixture.

Keywords: n-channel semiconductor; azaacene; bromination; thin film transistor; radical anion

ASSOCIATED CONTENT

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Supporting Information: Synthetic protocols, analytical data, NMR spectra, optical spectra, electrochemical data as well as computational studies and crystal structures can be found in the supporting information.

Notes

The authors declare no competing financial interest.

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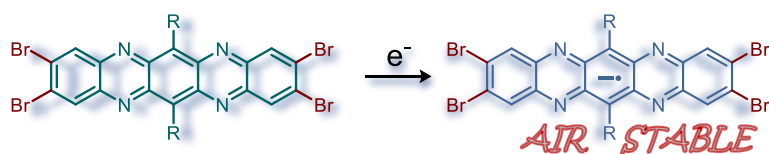
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A fully air stable radical anion results for a bis-TIPS-ethynyl-substituted tetraazapentacene if four bromine substituents are attached in the 2,3 and 9,10-positions. This material is – due to its deep LUMO (i.e. high electron affinity) a promising n-channel semiconductor, as the bromine substituents not only stabilize charge but also lead to a charge distribution that favors the outer rings and therefore allows better charge transport in the solid, crystalline state.

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