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From Byproducts to Efficient Fluorophores: A Route to the Synthesis of Fluorubines

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Abstract: The reaction of bis(imidoyl) chlorides of oxalic acid with monoalkyl hydrazines leads to substituted Δ^2-1,2-diazetines, which are versatile building blocks for ring-transformation reactions. One remarkable product originating from side reactions featured by a strong orange/red fluorescence was confirmed as a novel fluorubine derivative. In continuing our studies to substituted oligoazaacenes, we developed several synthetic entries to build up novel fluorubine derivatives, in which particularly aminobridged bis(quinoxaline)s are the key products for cationic hexaazapentacenes. We would like to discuss the possible formation pathways of these fluorubine derivatives, which exhibit interesting photophysical and chemical properties. The structures of all new derivatives were confirmed by common analytical methods (NMR spectroscopy, CV, UV/Vis, mass spectrometry, elemental analysis, and X-ray structural analysis) and will be discussed on selected examples in more detail.

Keywords: cyclization reactions · dyes/pigments · fluorescence · fluorubines · pentacenes

Introduction

The easily accessible bis(imidoyl) chlorides of oxalic acid **1** were developed as C2-building blocks by our group. Due to their well-tuned selectivity, they are versatile educts for cyclization reactions with different types of binucleophiles. One specific feature is their marked tendency to undergo cascade reactions. For example, their multistep one-pot reactions with amidinium salts form the basis for the synthetic entry to tetraazafulvalenes and vinylogous derivatives,[1] which themselves provide the preconditions for the construction of novel functional dyes.[2] In 2002 we reported on the synthesis of Δ^2-1,2-diazetines **2** by a simple cycloacylation reaction of monosubstituted hydrazines with **1** (Scheme 1).[3] Due to their ring strain, these four-ring systems proved to be valuable starting materials for transformation reactions to yield several, in a wide range of variable substitutable, five- and six-membered heterocycles.[4] Surprisingly, cationic derivatives of fluorubines (dihydro-5,6,7,12,13,14-hexaazapentacenes) **3** were identified as byproducts in some cases. These

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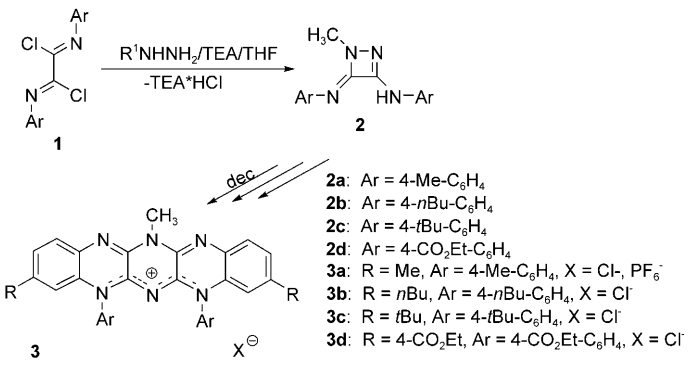


Scheme 1. From byproduct to novel highly functionalized fluorubines **3**.

derivatives and especially their solutions are characterized by strong orange/red fluorescence with high fluorescence quantum yields. Additionally, they exhibit a remarkable stability against oxidative damage. For example, a sample of **3a** in *ortho*-dichlorobenzene did not bleach when exposed to daylight for three years—only loss of the solvent was observed—which is really remarkable for organic dyes. Such well-defined highly functionalized fluorubines similar to **3** are not mentioned in the chemical literature up to date. Since the first recommendation of the "classical fluorubines" by Hinsberg in 1903, several papers that deal with syntheses and applications of the 6,13-dihydroform of fluorubines **4** can be found.[5]

On the other hand, during the past years the immense progress in the field of applied organic materials, for example, conjugated polymers, organic light-emitting diodes, and organic semiconductors (OFET's), shows the necessity to develop novel well-tuned materials. In comparison to the wide range of available p-type single molecules and polymeric-organic materials, such as pentacene and thiophene-based materials, there only exist few examples that deal with n-type devices.[6] One possibility to overcome this deficit can be achieved by the introduction of electron-accepting groups, such as fluorine or cyanosubstituents.[7] A second possibility to get an access to electron-deficient molecules is based on the successive replacement of CH moieties by nitrogen. In 2007, Winkler showed in a theoretical work that in this manner the HOMO/LUMO energies, which represent an important feature for organic devices, of linear fused azaacenes could be effectively influenced.[8] So there exist several molecular examples, such as the diphenylanthraazolines, 5*H*,7*H*- and 5*H*,12*H*-dihydroqinoxalino-[2,3*b*]phenazines, and dicyanopyrazinoquinoxalines, that are handled as potent n-type as well as p-type organic semiconductors.[9] Stimulated by the challenge to develop novel, stable electron-deficient materials, such as **3**, and by the lack of their synthesis, we have developed several independent syntheses for linear-fused hexaazapentacenes. In this paper, we are going to present one of our novel synthetic possibilities to achieve aza-based polynuclear acenes. In addition, we will discuss the structures, their photophysical and redox chemical characteristics, and their possible formation mechanisms in more detail.

Results and Discussion

Due to its characteristic AA′XX′-pattern in proton resonance spectroscopy, the *p*-tolyl group (Scheme 1; Ar = 4-Me-C_6H_4) is one of our most used substructures for the synthesis of novel heterocycles based on **1**. Decomposition of a corresponding substituted Δ^2-1,2-diazetine (**2a**) furnished a potpourri of oligo- as well as polymeric derivatives originating from isonitriles. To our surprise, a substance showing a strong orange fluorescence on TLC was detected. This side reaction occurred in approximately 1% and was always present in daylight and by use of halogenated solvents, such as chloroform. The isolation and characterization of this photochemical-induced "byproduct" by means of NMR spectroscopy and MS led us to the assumption that a dimerization of **2** by *ortho*-annulation of the aromatic rings and formal loss of methylhydrazine has occurred. The crucial indication was the ^{1}H NMR spectrum of **3a** in which a singlet at $\delta = 6.49$ ppm in the region of the aromatic protons was clearly detectable. In addition to these experimental results, we have found that a quaternization of one nitrogen atom, which leads to the cationic charge of derivative **3a**, has occurred. We confirmed these findings by HRMS, which showed that the estimated mass of m/z: 509.2448 u for the cationic core ($[C_{33}H_{29}N_6]^+$) of **3a** is in agreement with the measured mass of m/z: 509.2461 u. After anion exchange into hexafluorophosphate, single-crystal X-ray analysis delivered the unambiguous structural assignment of the dihydro-5,6,7,12,13,14-hexaazapentacenium salt **3a** (Figure 1) in which the *ortho*-annulation of N1/N5 at positions C1/C14 took place. In addition, one molecule of dioxane was incorporated into the molecular unit cell.[10]

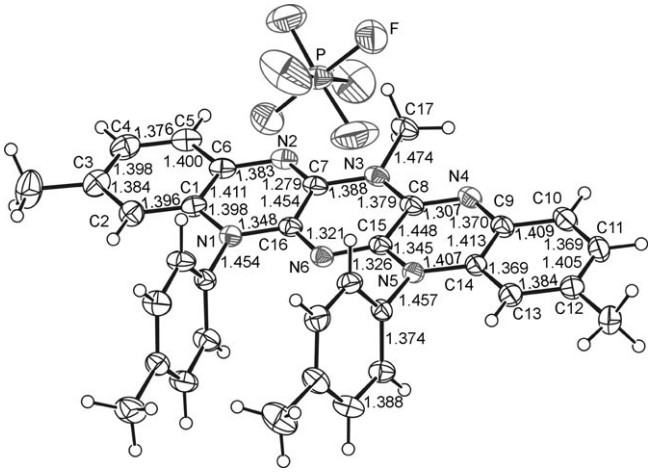


Figure 1. Solid-state structure and bond lengths of the cationic fluorubine derivative **3a** (Scheme 1; Ar = 4-Me-C_6H_4, R = Me, X = PF_6^-).[10]

As depicted in Figure 1, the nitrogen atoms N1, N3, and N5 at the positions 5, 7, and 13 of the fluorubine core are substituted with a remarkable selectivity. In view of the structure-determining bond lengths of **3a**, almost alternating distances between the neighboring atoms were measured. This result points out the efficient delocalization of the conjugated system. The cationically charged derivatives **3** represent the alkylation products (at position 13) of the mesoionic derivatives **5** (Figure 2), which themselves are not mentioned in the chemical literature and represents the diaza-homologues of 5*H*,7*H*-5,7-diphenyl-dihydroquinoxalino-[2,3*b*]phenazines. From this point of view, they can be regarded as zwitterionic "double-barreled" cyanine dyes, in which the negative strain is formally alkylated. The slightly shortened bond lengths between C7/N2 (1.279 Å) and C8/N4 (1.307 Å), which indicate a partial double-bond charac-

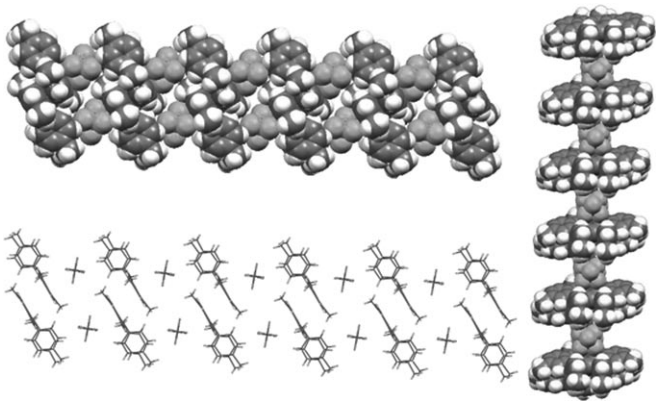


Figure 2. Packing effects of the crystal lattice of the fluorubine derivative **3a** (Scheme 1: Ar = 4-Me-C_6H_4, R = Me, X = PF_6^-).[10]

This result is in good agreement with the band gap of 2.08 eV, which we have determined by electrochemical measurements (E_g^{ec}). We found in initial cyclic voltammetry experiments and more clearly in differential pulse polarography measurements in CH_2Cl_2 one oxidation peak (1.65 V) and two reduction potentials (−0.43, −1.0 V). Taking the assumption that the oxidation peak of ferrocene/ferrrocenium in CH_2Cl_2 in our measurements is situated at $E_{1/2} = 0.71$ V and that the energy level of this system below vacuum is −4.80 eV, we estimate that the HOMO-edge (ionization potential) of **3a** is situated at −5.74 eV and the LUMO-edge (electron affinity) at −3.66 eV.

Stimulated by theses interesting features, we tried to improve this synthesis of azaacenes **3**. However, all further attempts to develop an efficient and practicable protocol, based on the polychromatic irradiation of **2a** were not sufficient. Thus, irradiation of Δ^2-1,2-diazetines **2b–e** in tetrachloromethane with daylight for approximately four weeks produced in traces the fluorubine derivatives **3b–d**. The decomposition of the naphthalene-substituted 1,2-diazetine **2e** was studied too and the formation of a double benzo-annulated derivative of fluorubine **3e** was observed (Scheme 2). In comparison to derivative **3a**, the absorption maximum of this hexaazapentacene has a bathochromic shift of about 40 nm ($CHCl_3$: $\lambda_{max} = 587$ nm).

Furthermore, we choose the Δ^2-1,2-diazetine **2a** as model compound and irradiated it with monochromatic light at its absorption maximum ($\lambda_{max} = 365$ nm) with different irradiation intervals and times and in several different solvents.

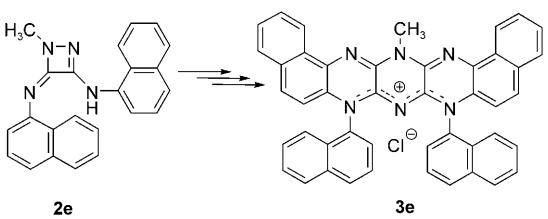
ter, as well as the slightly elongated bond lengths of C7/N3 (1.388 Å) and C8/N3 (1.379 Å) support this assumption. On the other hand, the positive valence band is predominantly located between the nitrogen atoms N1 and N5. The molecular plane of the fluorubine core is nearly planar and the methyl subsituent at N3 is slightly twisted out of it by approximately 10°. In addition, herein the *p*-tolyl substituents at positions N1 and N5 show an orthogonal arrangement. Due to π–π interactions between the fluorubine molecules, the formation of molecular-stacked dimers ($d \approx 3.41$ Å) was observed in the crystal lattice. These dimers themselves are connected by two hexafluorophosphate anions to build up "molecular wires", which, in principle, could have good preconditions for charge-transport processes. Additionally, packing elements of the herring bone conformation can be recognized in the crystal lattice of the "face-to-face" packed dimeres of **3a**.

Table 1. Optical data of selected compounds, the full data are attached in the Supporting Information.

No	R[1][a]	R[b]	Ar[b]	λ_{max}^{abs} [c] [nm]	λ_{max}^{em} [c] [nm]	Stokes shift [cm^{-1}]	ϕ_f[d] [%]	$E_{g,10\%}^{opt}$ [e] [eV]
3a	Me	Me	4-Me-C_6H_4	546	563	553	92	2.18
3b	Me	*n*Bu	4-*n*Bu-C_6H_4	546	569	740	90	2.16
3c	Me	*t*Bu	4-*t*Bu-C_6H_4	546	569	740	93	2.16
3d	Me	CO_2Et	4-CO_2Et-C_6H_4	531	546	517	94	2.25
3e	Me	–	naphthyl	587	615	775	67	1.99
3f	Me	H	C_6H_5	528	546	624	100	2.25
3g	*n*Pr	H	C_6H_5	530	552	752	98	2.24
3h	4-Me-C_6H_4	H	C_6H_5	529	551	755	97	2.24

[a] See Scheme 3. [b] See Scheme 1. [c] Measured in $CHCl_3$. [d] ϕ_f in $CHCl_3$ vs. rhodamine 6G in EtOH. [e] Optical band gap ($E_{g,10\%}^{opt}$) estimated by the 10% method.

The optical absorption maximum of fluorubine **3a** in chloroform lies at 546 nm combined with a small Stokes shift of 553 cm^{-1} and a high fluorescence quantum yield (ϕ_f) of 92%. Additionally, we observed negative solvatochromic behavior from its UV/Vis spectra. Thus increasing the polarity of the solvent leads to hypsochromically shifted absorption maxima (CH_2Cl_2: $\lambda_{max} = 553$, $CHCl_3$: 546, THF: 540, methanol: 537 nm). We estimated the optical band gap (E_g^{opt}) of this molecule by two methods, namely the so-called 10% method ($E_{g,10\%}^{opt}$; of the absorption maxima at the lower-energy site), which was introduced by Hörhold and the commonly used tangential through the turning point method ($E_{g,T}^{opt}$).[11] Both methods delivered nearly similar results, but we would like to mention that the 10% method is still easier in its handling. However, as listed in Table 1 we found an optical band gap of approximated 2.19 eV for **3a**.



2e **3e**

Scheme 2. Formation of the naphthalene-substituted derivative **3e** (Ar = 1-naphthyl, X = Cl^-).

Unfortunately, in view of the selective formation of **3a**, these experiments have failed up to now. As mentioned above, **2a** is unstable towards irradiation in chloroform. In tetrachloromethane and less efficiently in chloroform, a transient with a broad absorption peak at 490 nm was observed, with the solute irreversibly decomposed. These findings point towards an electron transfer to the solvent as the primary process.

Without going into details here, we can safely conclude from this series of long-term irradiation experiments that more than one photon of different energy is required to generate the final product. In our belief, the mechanism of this cascade reaction proceeds in three steps. First, an *ortho*-annulation process forms the quinoxaline subunit. This cyclization sequence most likely represents the initial step and will be discussed here. Subsequently, the cleavage of the four-membered diazetine under formation of a reactive intermediate might take place. Finally, a dimerization involving the extrusion of a MeNN fragment yields the fluorubines. To understand these results, we used DFT calculations on the B3LYP/6-31g(d) level[12] to investigate the reaction coordinate of the ring annulation reaction of a hypothetical phenyl-substituted 1,2-diazetine **2f** (Scheme 1; R = H, Ar = C_6H_5), in which the reaction takes place between the arylamine nitrogen C–NHAr and the *ortho* carbon atom position of the imine-substituted aryl moiety C=NAr (π^6-electrocyclic reaction). The most stable form with respect to *syn*/*anti* isomerism and tautomerism (**2f-A**; Figure 3) was used. This

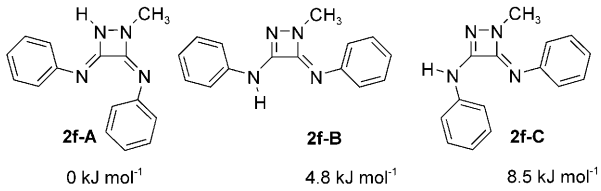


Figure 3. Investigated isomers and relative energies of the three energetically preferred prototropes of hypothetical 1,2-diazetine **2f** based on the theoretical level of B3LYP/6-31g(d).[12]

tautomeric form is 4.8 kJ mol^{-1} more stable than the most stable *syn*/*anti* isomer with the mobile proton residing on one of the exocyclic nitrogen atoms (**2f-B**). Rotating the phenylamino group leads to a further rotamer sterically suitable for an electrocyclization (**2f-C**), which is another 3.7 kJ mol^{-1} more unstable. Due to the low energetic barriers, the coexistence of such isomers was confirmed by NMR spectroscopic experiments. Obviously, these isomers rapidly interconvert on the time scale of NMR spectroscopy, thus we were unable to assign a particular isomer as predominating in solution. The essential conclusions derived from these calculations are: the cyclized product of the radical anion does not possess a minimum and, if photochemically generated as an intermediate, should undergo an extremely rapid ring cleavage. The cyclized product of the neutral molecule exhibits a shallow minimum of about 7.6 kJ mol^{-1} with respect to cleavage. Hydrogen-shift reactions that lead to much more stable isomers are predicted to show significantly higher barriers. (oxidation would produce a radical that should be stabilized by cleavage of the N–N bond.) The radical cation shows a minimum which allows further reactions to compete with ring cleavage with a calculated barrier of 18.0 kJ mol^{-1}.

The theoretical and experimental findings point against a second possible reaction mechanism, similar to those *ortho*-annulation reactions reported by Sakurai,[13] which we first assumed as a possible pathway for our reactions. In these photochemical-supported reactions, a base, such as triethylamine, formed an ion pair with the substrate. In contrast to them, a mechanism that involves the ring cleavage of a cationic intermediate seems to be more plausible and is currently one of our further research fields. Some very recent experimental findings have indicated that the key step seems to be the formation of aminyl radical cations that are capable of cyclizing intramolecularly. We will discuss the mechanism of these remarkable *ortho*-annulation reactions in more detail in a forthcoming paper.

Hence, at this point we focused our work on step-by-step synthesis of the novel fluorubine derivatives. The most common way to deliver the "classical fluorubines" **4** can be achieved by the Hinsberg protocol,[5a] in which 2,3-dichloro- and 2,3-diaminoquinoxalines are melted together. Several authors have described syntheses of similar 6,13-dihydro-5,6,7,12,13,14-hexaaza-pentacenes **4**, which are used up to date as functional dyes, especially for inkjet printers and synthetic fibres.[5b,k] In 2009, a paper that deals with the synthesis and self-assembly of 5,14-dihydro-5,6,7,12,13,14-hexaazapentacenes was been published by Hill and Ariga.[5l] To the best of our knowledge, structurally well-defined 5,7-dihydroderivatives, such as derivatives **3** and **5** (Figure 4) are unknown to date.

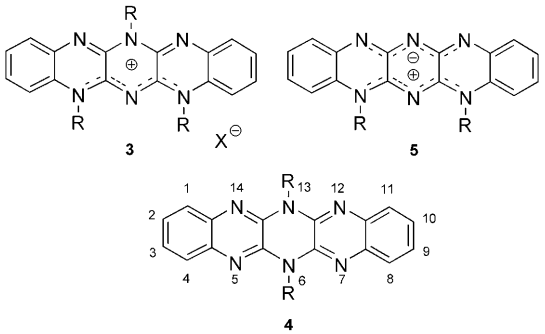
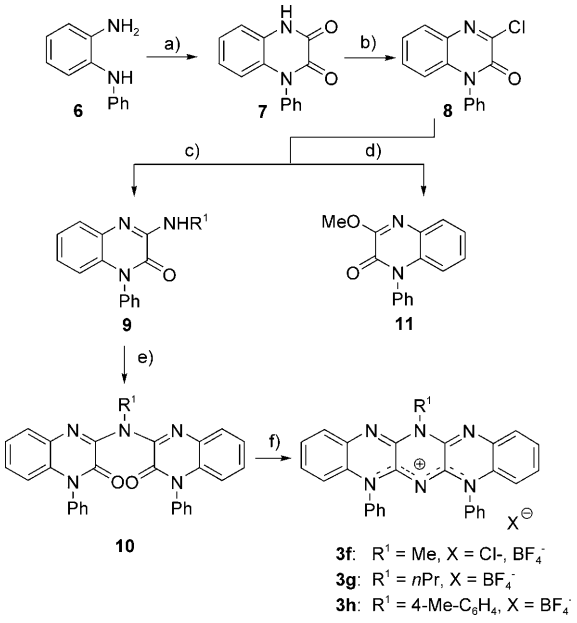


Figure 4. Selected isomeric fluorubines **3**–**5**.

For our synthetic purpose of building up the fluorubine derivatives **3**, we choose the cyclization reaction of commercially available *N*-phenyl-phenylenediamine (**6**) with oxalic acid diethylester to yield the *N*-phenyl substituted quinoxaline-2,3-dione (**7**). In a second step, it was converted by means of thionyl chloride into 3-chloro-quinoxaline-2-one

(**8**). The subsequent aminolysis reaction of **8** with selected amines yielded the crystalline 3-aminoderivatives **9a–e** in very good yields (80–100%, Scheme 3). 3-Aminoalkyl/aryl-



Scheme 3. General syntheses of amino-substituted quinoxalines **9a–e**, amino-bridged bis(quinoxaline)s **10a–e** (**9**/**10a**: R^1 = Me, **9**/**10b**: R^1 = *n*Pr, **9**/**10c**: R^1 = 4-Me-C_6H_4, **9**/**10d**: R^1 = 4-Me_2N-C_6H_4, **9**/**10e**: R^1 = 4-*t*Bu-Me_2SiO-C_6H_4), and fluorubines of type **3**. a) $(EtCO_2)_2$, 160°C; b) $SOCl_2$, toluene, 110°C; c) R^1NH_2, THF, RT to 65°C; d) NaOMe, THF, MeOH, RT; e) 1) KH, THF; 2) **8** (R^1 = Ar), BINAP/$[Pd(PPh_3)_4]$ (10 mol%); f) Pathway A: 1) PCl_5, CH_2Cl_2, RT; 2) NH_3, THF, RT; 3) NH_4Cl, DMF, 160°C; Pathway B: Tf_2O, CH_2Cl_2, RT; 2) NH_3, CH_2Cl_2, RT; 3) NH_4Cl, mesitylene, 160°C.

substituted quinoxaline-2-ones of type **9** were already described in the literature before.[14] Due to their physiological activity, for example, as inhibitors of glycogen-phosphorylase,[14c] different syntheses have been developed in the past decades and a wide range of patents have claimed their features.[14f–j] In a further step, the amino derivatives **9a–e** were acylated with **8** to yield the desired symmetrical amino-bridged bis(quinoxaline)s **10a–e**. Surprisingly, these bis(quinoxaline)s of type **10**, which can be regarded as tertiary aryl/heteroaryl amines, are also not mentioned in the literature to date. There only exists a few data dealing with the syntheses and properties of similar but unsubstituted 2-aminoderivatives and 3-alkyl- and 3-aminoalkyl substituted bis(quinoxaline)s.[15] The chemical nature of the base was one of the decisive factors in the transformation of **9** into **10**. All attempts to use Huenig's base or *n*BuLi in THF and also the reaction in DMF/K_2CO_3 at 150°C did not furnish the desired amino-bridged bis(quinoxaline)s **10**. However, sodium and potassium hydride proved to be suitable for such acylation processes. To achieve a homogenous reaction, we favored potassium hydride, which formed a more soluble amide deriving from **9**. Upon subsequent addition of the chloro-derivative **8** to the potassium salt of **9** the alkylamin-bridged bis(quinoxaline)s **10a**,**b** were obtained in yields of 90 and 60%. Within the use of a similar protocol to generate the aryl amine-bridged bis(quinoxaline)s **10c–e**, all attempts failed without the use of the Pd^0/2,2′bis(diphenylphosphino)-1,1′-binaphthyl (BINAP)-system under Hartwid–Buchwald conditions. Otherwise, the use of bases, such as alkali alkoxides, led to a straight reaction to the corresponding alkoxy derivatives[14g,h] exemplified by the conversion of **8a** with NaOMe in THF/MeOH to yield the methoxy-derivative **11a** (Scheme 3). Similarly, we employed a modified protocol, in which at first KH is used as a base, followed by cross-coupling delivering the best results for the aromatic-substituted derivatives of **10**. Elemental analysis and NMR spectroscopic/MS data confirmed the presence of 1:1 acylation products. We succeeded in obtaining single crystals of bis(quinoxaline)s **10a** (R^1 = Me) and of derivative **10d** (R^1 = 4-Me_2N-C_6H_4) and confirmed our postulated structures by X-ray structural analysis.[10]

The solid-state structure of derivative **10a** is depicted in Figure 5. Conspicuously, both quinoxaline moieties are twisted within a dihedral angle of approx. 35° and show a *cis* ar-

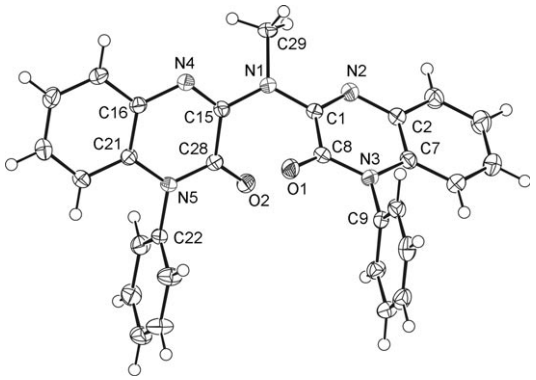
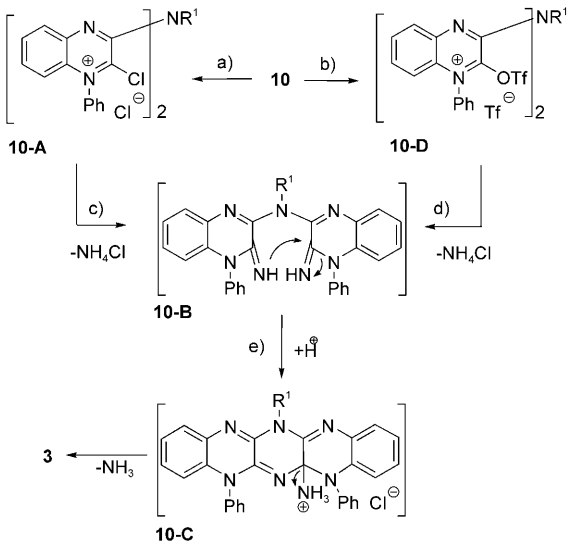


Figure 5. Solid-state structure of the aminomethyl-bridged bis(quinoxaline) **10a**.[10]

rangement in view to each other. Due to the formation of a partial amidinium resonance between N1–C1–N2 and between N1–C15–N4, the bond lengths of N1–C1 (1.389 Å) and N1–C15 (1.390 Å) are slightly shortened in comparison to typical C–N single bonds, such as N1–C29 (1.465 Å).

By starting from **10** we developed two practicable procedures to yield the target molecules **3**. On the one hand, we used a three-step protocol in which at first a solution of **10** in dichloromethane was treated with phosphorous pentachloride. Therefore, the formation of the bis(iminium) salts **10-A** can be assumed (Scheme 4). By using toluene as a solvent in this reaction step, the formation of a yellow precipitate was detected, thus supporting our assumption. After removing and changing the solvent into THF, dried ammonia was passed through the reaction flask and the formation of a sluggish mixture was observed containing NH_4Cl and the possible bis(imino)-derivatives **10-B**. Due to the scrupulous sensitivity of these intermediates against moisture, whereby



Scheme 4. Postulated mechanism for the activation and cyclization sequence of bis(quinoxaline)s **10** by formation of fluorubines of type **3**. a) PCl_5, CH_2Cl_2, RT, 12 h; b) Tf_2O, CH_2Cl_2, RT, 12 h; c) NH_3, THF, RT, 1 h; d) NH_3, CH_2Cl_2, RT, 1 h; e) NH_4Cl, DMF, 160 °C, 24 h.

droxyphenoles into the well-known rhodamines occurs in yields between 5 and 35 % respectively.[17]

After anion exchange (Tf^-/Cl^- into BF_4^-) of derivative **3f**, we were able to achieve single crystals. The result of the single-crystal X-ray analysis and some bond parameters are depicted in Figure 6. In general, the bond lengths and structural parameters are very similar to that of **3a** (see above), only the molecular plane of the fluorubine core is more twisted than it. Additionally, we observed remarkable packing effects in the crystal lattice of **3f**. Due to π–π-interactions between the fluorubine cations of **3f**, there also exists molecular stacked dimers ($d \approx 3.37$ Å), which themselves are connected by two molecules of tetrafluoroborate. As consequence of this charge interaction between the fluorubine core on the one hand and the corresponding anion on the other hand, regular molecular architectures are built up (see the Supporting Information).

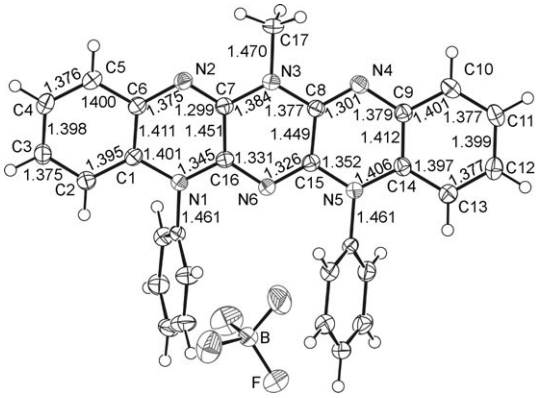


Figure 6. Solid-state structure of the cationic fluorubine derivative **3f** (Scheme 2; $R^1 = Me$, $X = BF_4^-$).[10]

hydrolysis to the starting materials **10** takes place immediately, no attempts for their isolation were made. In a final step, the solvent was changed once again into DMF, NH_4Cl was added, and the mixture was heated in a sealed tube at 160 °C for 24 h. Under these conditions, most likely the intramolecular formation of a cyclic aminal **10-B** takes place, which finally, upon protonation and elimination of ammonia, formed the cationic fluorubine derivatives **3**. In a second protocol, we activated the cyclic amide substructure with trifluoromethanesulfonic anhydride (Tf_2O) in dichloromethane,[16] which also leads to bis(iminium) salts **10-D** originating from oxygen sulfonation by formation of esters of trifluoromethanesulfonic acid (Scheme 4). These esters were converted directly into their imino homologues without changing the solvent. After removing the solvent, addition of NH_4Cl, and heating in mesitylene, the desired fluorubines **3** were furnished in comparable yields. We would like to note that this way is a bit more practicable, because it is not recommended to change the solvents before the final cyclization step. Furthermore, experiments with several high-boiling solvents in the final step showed that mesitylene leads to the formation of fewer byproducts, thus simplifying the workup.

We used the bis(quinoxaline)s **10a–e**, mentioned in Scheme 3, as starting materials for the cyclization sequence. In the case of the aliphatic bridged derivatives **10a**,**b** and the aryl derivative **10c**, we produced the highly functionalized 5,7-dihydro-5,6,7,12,13,14-hexaazapentacenium salts **3f–h** in a one-pot synthesis in yields of approximately 20–40 %. These currently achieved overall yields by conversion of **10** into **3** are not sufficient, but can be compared to those of similar systems. For instance, the thermal cyclization reaction of 4-bromo-benzaldehyde with substituted 2-amino-hy-

Unfortunately, our selected arylamine derivatives **10d–e** decomposed during the ring-closure procedure. Mainly, we reasoned these findings as due to their functional groups (**10d**: $R^1 = 4\text{-}Me_2N\text{–}C_6H_4$, **10e**: $R^1 = 4\text{-}t\text{BuMe}_2\text{SiO–}C_6H_4$), which are not stable enough under the investigated reaction conditions giving us undefined mixtures. From this point of view, there is currently a lack in the tolerance of certain functional groups (silylether, amino groups), which show themselves a high affinity to the Lewis acids Tf_2O or PCl_5. However, in general, it should be possible to introduce functionalized aryl moieties at position 13 (Figure 4), which is still one of our further research topics.

According to the extension of the conjugated π-system in the order **9**–**10**–**3**, a subsequent redshift in the absorption and emission spectra was observed. Exemplified by the methylamine derivative **9a** (Figure 7), the absorption maximum lies at 331 nm showing a Stoke's shift of approximatley 2800 cm^{-1}. In comparison, herein a significant Stoke's shift of 5086 cm^{-1} of bis(quinoxaline) derivative **10a** ($\lambda_{max} =$ 385 nm, $\phi_f \approx 0.1$) indicates a remarkable change of geometries in its ground and exited state. The final cyclization reaction of **10a** to **3f** is attended with a bathochromic shift of

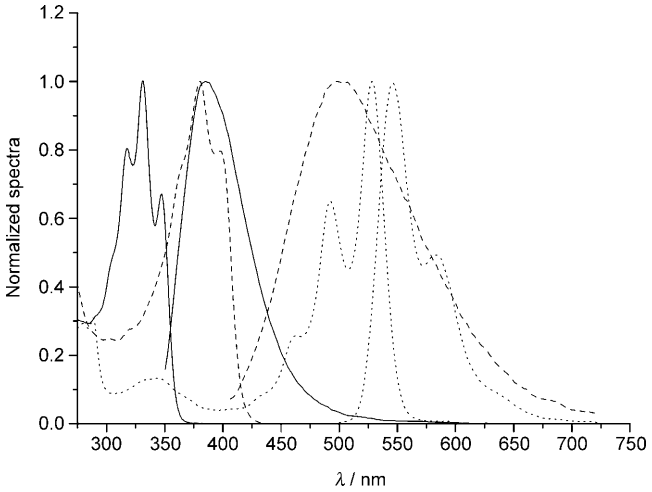


Figure 7. Normalized absorption and emission spectra of **3f**, **9a**, and **10a** measured in chloroform. ——: Absorption/emission spectra of **9a**; -----: absorption/emission spectra of **10a**; •••••: absorption/emission spectra of **3f**.

140 nm in its UV/Vis spectrum (**3f**: $\lambda_{max}=528$ nm) and additionally with a short Stoke's shift (624 cm^{-1}) and a high fluorescence quantum yield of 95%. Hand-in-hand to the red-shift in their absorption spectra, a shortening of the values of the optical band gaps energies can be recognized. Thus, the gap energy ($E_{g,10\%}^{opt}$) decreases from approximately 3.45 of derivative **9a** to 2.25 eV in derivative **3a**.

Conclusion

Based on the structure of a highly fluorescent decomposition product of Δ^2-1,2-diazetine **2a**, a novel route for the synthesis of functionalized fluorophores was developed. In this paper, the syntheses and the spectroscopic features of novel amino-bridged bis(quinoxaline)s **10** and their ring-closure products "fluorubines" **3** were described. The commercially available phenylenediamine **7** proved to be a suitable starting material. The new synthesized derivatives of hexaazapentacenes **3**, which are stable crystalline compounds, are featured by a strong fluorescence between 500–600 nm and high fluorescence quantum yields. It is noteworthy that the cationic fluorubines represent redox systems, which could make them powerful candidates for organic n-type devices. In a forthcoming paper, we will report on their use as starting materials for the construction of other functional dyes, which can be used as molecular sensors. Additionally, we will discuss in more detail the remarkable formation reaction pathway of **3** and the construction of further novel hexaazapentacene derivatives, such as **5**.

Experimental Section

Further details of the synthetic procedures, quantum chemical calculations and measurements can be found in the Supporting Information.

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