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Polyazaacenes – On the Way to Stable, Fluorescent and Redox-Active Derivatives

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Dedicated to Prof. Dr. Manfred Christl, Würzburg, on the occasion of his 65th birthday

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A new synthetic method for the preparation of polyazaacenes is described starting from two different nucleophilic building blocks. Disubstituted oxalic amidines **1** can be cyclized under mild conditions with 2,3-dichloro-5,6-dicyanopyrazine (**3**) to yield 5,6-dihydropyrazino[2,3-*b*]pyrazines **4a–c**. By employing higher temperatures and 2 equiv. of **3**, octaazanaphthacene **6** can be isolated. Similarly, pyrazino[2,3-*b*]pyrazines **2** and bielectrophile **3** yielded novel dodecaazahexacenes **8** in addition to semicyclized derivative **9**. When tetraazafulvalene **10d** was heated in the presence of an amine in xylene in the presence of oxygen, octaazahexacene **13** was isolated as the main product. Instead of pyrazino[2,3-*b*]pyrazines **2**, this highly fluorescent polyazaacene was formed from a cascade reaction which involves a dyotropic rearrangement, an intramolecular Diels–Alder reaction and a multistep redox reaction.

Introduction

Acenes are derived from the parent compound anthracene by linear annulation with further benzo rings. In contrast to anthracene itself, the homologues exhibit an increase in their reactivity and parallely, a crucial shift in the longest wavelength absorption. Whereas tetracene is still relatively stable, the deeply coloured pentacene, hexacene and heptacene are air- and light sensitive. This behaviour can easily be explained by a decrease in the aromaticity which is accompanied by an increase in the polyene character of the compound, which intensifies the colour. The stabilization of higher acenes is possible by substitution with aryl substructures (rubrene) or by angular ring fusion. Another approach used to stabilize these systems exists by the replacement of CH groups by an aza nitrogen. This substitution results in higher stabilities towards oxidation and in addition, introduces a new pattern of polarity into the system. As a synthetic consequence, acenes which possess aza nitrogen atoms should be accessible for modifications such as protonation, alkylation and formation of *N*-oxides. On the other hand, azaacenes are electronically "umpoled" systems bearing acceptor properties. Furthermore, the rigid system of such polyazaheterocycles often shows intense fluorescence, which makes them applicable as marker molecules.[1] Because they are representative derivatives, substituted quinoxalino[2,3-*b*]phenazines[2] and their regioisomers[3] are well-known; however, nitrogen-rich azaacenes are rather rare. Only a few literature reports exist that deal with the synthesis of systems possessing more than two linear condensed pyrazine rings including their hydro derivatives such as fluorubine,[4] 5,10-dihydropyrazino[2,3-*b*:2′,3′-*e*]-pyrazines,[5,6] decaazapentacenes[7] and octaazadihydrohexacenes.[8]

Disubstituted oxalic amidines **1**,[9] which were already used as building blocks for five-membered heterocyclic ring systems,[10,11] should also be applicable to six-membered rings. Moreover, we demonstrate that the dyotropic rearrangement of 1,4,5,8-tetraazafulvalenes allows easy access to tetrasubstituted pyrazino[2,3-*b*]pyrazines **2**.[12] Such previously unknown compounds should be tested for ring fusion reactions through all four nucleophilic amino functions (Scheme 1).

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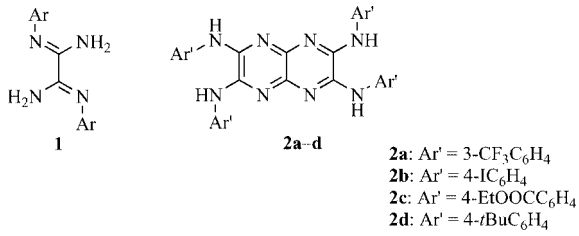
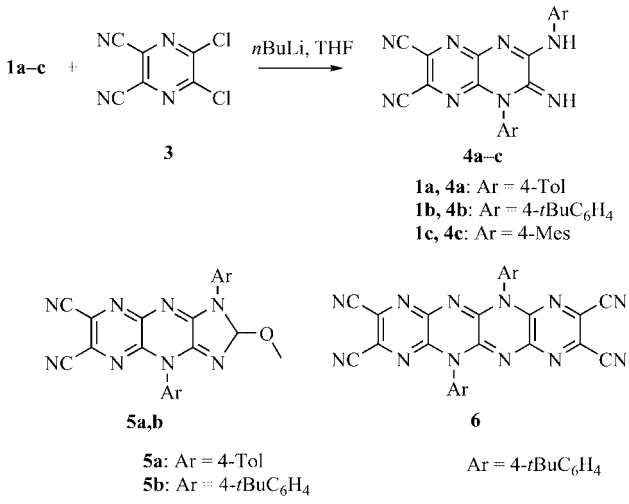


Scheme 1. Building blocks for polyazaacenes based on bis(amidine)s **1** and pyrazino[2,3-*b*]pyrazines **2**.

Results and Discussion

First, 2,3-dichloro-5,6-dicyanopyrazine (**3**) was employed as a bielectrophilic partner in order to synthesize polyazaacenes. This easily accessible pyrazine constitutes a valuable building block for a series of azaheterocycles.[13] Some derivatives obtained in this manner have strong electron-accepting properties and thus can be used for the construction of air-stable *n*-type transistors in organic FET devices.[14]

In the first step, amidines **1a**–**c** were deprotonated by means of *n*BuLi at –78 °C. Upon addition of cyclization partner **3**, 5,6-dihydropyrazino[2,3-*b*]pyrazines **4a**–**c** were formed in yields up to 70% in a smooth reaction. The structures of bicyclic products **4** were assigned by elemental analyses, mass spectra and NMR spectroscopy. In addition, X-ray crystal structure analysis was performed from a single crystal of derivative **4a**. The structure in Figure 1 clearly shows that the cyclization reaction occurred by attack at two different nitrogen atoms in amidine **1**. The bicyclic pyrazinopyrazine has an almost planar geometry, only the tolyl substituent at the ring nitrogen is twisted out of plane. In the solid state as well as in solution (NMR experiments), only one prototropic isomer could be detected in which the hydrogen is located at the exocyclic arylamino group (Scheme 2, Figure 1).



Scheme 2. Synthesis of ring-fused pyrazines **4**–**6**.

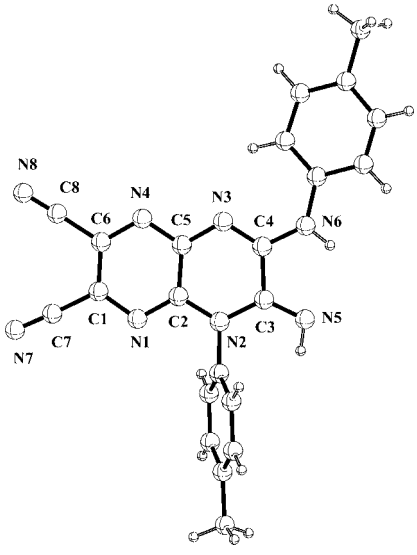


Figure 1. Solid state (X-ray) structure of compound **4a**, selected bond lengths [Å]: N2–C3 1.393, C4–N6 1.354, C3–N5 1.278, N3–C4 1.301, N2–C2 1.362, N3–C5 1.344, C2–C5 1.452, C3–C4 1.508.

Because of their vicinal amino substructure, compounds **4** can be further converted into azaheterocycles, as exemplified by hexaazacyclopentanaphthalenes **5a**,**b**. Thus, simple heating of derivatives **4a**,**b** in orthoformate yielded yellow fluorescent tricycles **5a**,**b**. No twofold cyclization reaction of derivatives **1** could be observed upon the employment of an excess of bielectrophile **3**. However, the desired twofold ring fusion products of type **6** could be synthesized by reacting molten **4b** with **3** at 200 °C under an atmosphere of argon. After purification by flash chromatography, new C_2-symmetrical octaazanaphthacene **6** was isolated in a yield of 50% as yellow crystals. Despite its rigidity, this derivative is relatively soluble in different solvents. In acetonitrile, it displays fluorescence with a maximum at λ = 487 nm (φ_{Fl} = 0.55) and a small Stokes shift of 5 nm.

Because of their chelating substructure, derivatives of type **4** are a good choice for the construction of metal complexes. For example, the complexation reaction of **4a** with $NiCl_2$ resulted in the formation of square planar Ni^{II} complex **7**. From a red single crystal, the crystal structure of **7** was obtained and the result is depicted in Figure 2 (Scheme 3).

However, similarly to the reaction of molten **1** with **3**, new polyazaacenes of type **8** could be prepared starting from pyrazino[2,3-*b*]pyrazines **2a**. Their NMR spectra suggest a high molecular symmetry by single signal sets. This novel dodecaazahexacene displays fluorescence at λ = 522 nm (excitation at λ = 517 nm) in solution with quantum yields of 35% and a small Stokes shift. As a byproduct, semicyclic derivative **9** was isolated. By means of 2D NMR experiments, the predominance of the prototropic isomer was confirmed in which the two NH-protons are located at exocyclic aryl–nitrogen and pyrazine ring nitrogen atoms. In contrast to fully cyclized derivative **8**, this azacycle shows no fluorescence (Scheme 4).

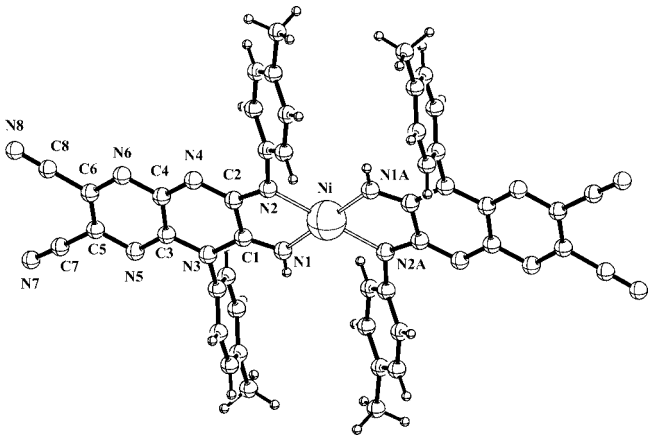
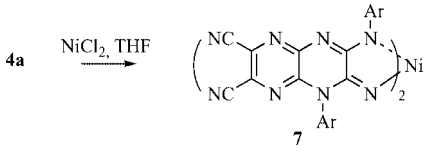
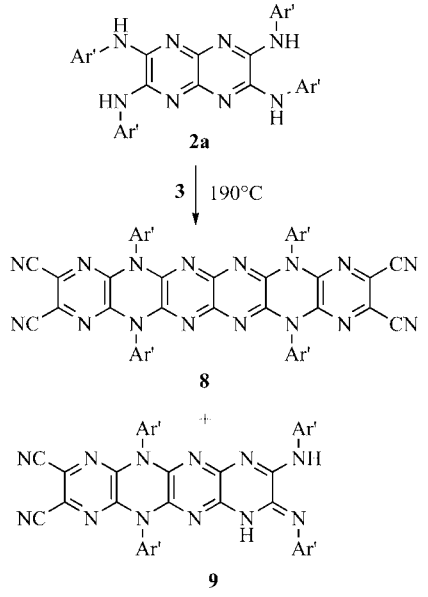


Figure 2. Solid state (X-ray) structure of compound **7**, selected bond lengths [Å]: Ni–N2 2.091, Ni–N1 2.021, N2–C2 1.312, N1–C1 1.276, C1–N3 1.387, C2–N4 1.352, C1–C2 1.492, N4–C4 1.332, N3–C3 1.386; selected bond angles [°]: N1–Ni–N1A 180.00, N1–Ni–N2 79.12, N1–Ni–N2A 100.88, N1A–Ni–N2 100.88, N1A–Ni–N2A 79.12, N2–Ni–N2A 180.00, N1–C1–C2 118.52, N1–C1–N3 124.12, N2–C2–N4 125.02, N2–C2–C1 112.79, N4–C2–C1 122.19.



Scheme 3. Complexation reaction of **4a** with $NiCl_2$.

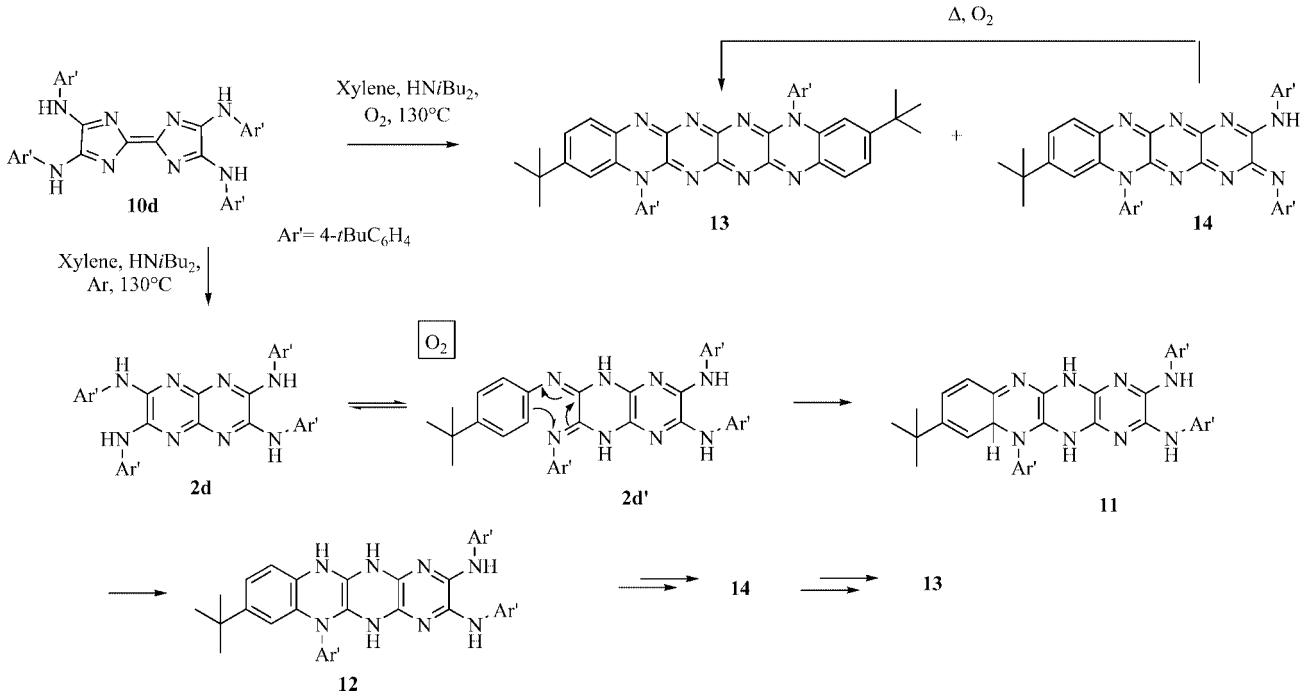


Scheme 4. Cyclization reaction of pyrazino[2,3-*b*]pyrazines **2** with 2,3-dichloro-5,6-dicyanopyrazine **3**.

The dyotropic rearrangement of 1,4,5,8-tetraazafulvalenes **10a**–**c** (Ar′ = 3-$CF_3C_6H_4$, 4-IC_6H_4, 4-$EtOOCC_6H_4$) [12] (which forms the basis for the synthesis of compounds **2**) could now be optimized. Here, an unexpected reaction was observed: whereas strong yellow fluorescent pyrazinopyrazines **2a**–**c** were easily formed, **2d** could be isolated only under strict exclusion of oxygen. However, when this rearrangement was carried out in the presence of oxygen, tetraazafulvalene **10d** was transformed into a new product which could be detected by TLC by way of its strong red fluorescence. The structure of this deep blue compound was assigned by HRMS, NMR and UV/Vis data as well as chemical transformations. Hence, it possesses the structure of an aryl-substituted derivative of octaazahexacene **13** (Scheme 5).

As a first step of the mechanism, we postulate the dyotropic rearrangement of tetraazafulvalene **10d** into pyrazinopyrazine **2d**. The latter compound should also exist as prototropic isomer **2d′** possessing an exocyclic *s*-cis 1,4-diazadiene unit which fulfills the requirements for a subsequent reaction cascade. DFT calculations predict a relative free energy of only +37 kJ/mol for tautomer **2d′** compared to **2d** (see Experimental Section, Computational Methods). As the key step of the reaction, an intramolecular [4+2] cycloaddition takes place followed by rearomatization to give tetrahydrotetraazanaphthalene **12**. In this reaction, the preformed 1,4-diazadiene acts as the (dihetero)diene and the benzene ring as the dienophile. Generally, thermally induced [4+2] cycloaddition reactions which yield a cyclohexa-1,3-diene originating from benzene are extremely rare. Only in one case has such a reaction been described with the use of a specially designed organic ring system which reacts in an unselective reaction at high temperatures.[15] In other cases, a fast rearrangement of the cyclohexa-1,3-diene intermediate resulted in the formation of an aromatic ring.[16] Very recently,[17] an example of an intramolecular metal-mediated case was described for the first time. Thus, a twofold cycloaddition–rearomatization cascade sequence may lead to the formation of a system consisting of four fused pyrazines with two peripheral benzo rings and two electron rich tetraaminoethene substructures **12**. Finally, a multistep oxidation by oxygen takes place forming the stable quinoid system of **13**. This is in agreement with experimental findings for other tetraaminoethenes derived from imidazoles[18] and 2,2′-biimidazoles.[19] Furthermore, these observations were proposed by earlier works of Armand and Badger[20,21] who reported structures and stabilities of ring-fused pyrazines and their 1,4-dehydroderivates connected with their redox behaviour.

As a byproduct, deep purple compound **14** could be isolated. Its structure has been solved by 2D NMR experiments and HRMS. Because of the fact that **14** yields **13** by neat conversion by heating in the presence of oxygen, it can be regarded as a semicyclized precursor of **13**. Further evidence for the structure of **13** results from its reduction with sodium dithionite in a THF/water mixture. Immediately, the intense red fluorescence turned yellow, which originated from the formation of reduced form **15**. Derivative **14** shows the same redox behaviour; hence, reduced aromatic structure **16** is describable. Exposure to air caused the regeneration of the fluorescence. This colour change is fully reversible and can be repeated several times. Cyclic voltammetric measurements revealed two reversible one-electron

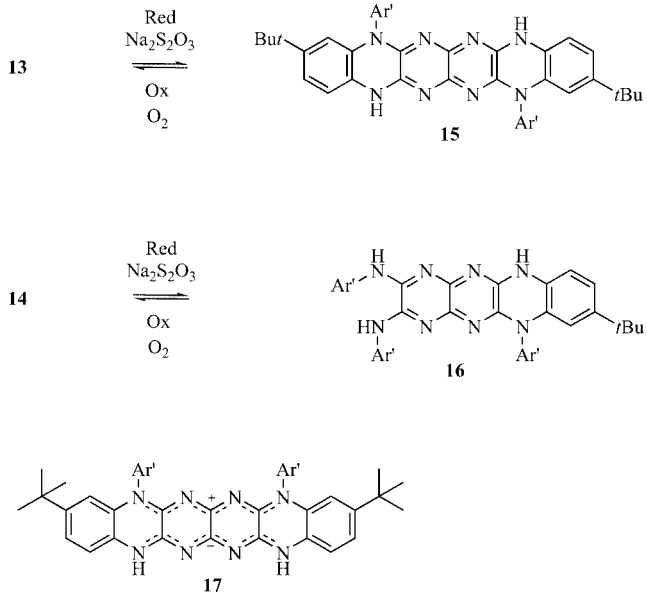


Scheme 5. Mechanism proposed for the formation of octaazahexacenes of type **13**.

reduction potentials at –0.5 V, –1.1 V for **13** and –0.3 V, –1.0 V for **14**.

A zwitterionic structure as in *syn*-derivate **17** can be excluded because of the fact that derivatives of type **13** show no solvatochromism.[22–24] The emission spectrum of derivative **13** is symmetrical to its absorption spectrum and shows only a small Stokes shift of about 4 nm.

Upon protonation with perchloric acid, a bathochromic shift of 50 nm was observed, which is reversible upon the addition of base. In 1890, Fischer and Hepp[3] reported similar spectral properties for fluorinidine, which possess an analogous quinone-like substructure (Scheme 6).



Scheme 6. Redox behaviour of systems **13** and **14**, zwitterionic structure for *syn*-derivative **17**.

Experimental Section

General Information: Reagents were purchased from Aldrich, Acros or Fluka and used without further purification. Solvents were purified by distillation with the appropriate drying agent. Reactions were performed under a dry atmosphere of argon by using standard Schlenk techniques. The solvents used (THF, xylene) were dried by distillation over sodium and benzophenone. Liquid chromatography was performed with columns of silica gel 60 Å, Merck, 0.040–0.063 mesh or alumina 90 Å, Merck, 0.063–0.200 mesh, activity I. TLC for reaction monitoring was performed with plates of thickness 0.2 mm, Roth, Polygram SIL G/UV254 or Polygram ALOX N/UV254. NMR experiments were performed with a Bruker AC 250 und Bruker AC 400. Chemical shifts are reported as δ values relative to TMS, defined as δ = 0.00 ppm (^{1}H NMR) or δ = 0.0 ppm (^{13}C NMR). Mass spectra were performed with a Quadrupol SSQ 710 Finnigan MAT or Finnigan MAT 900 XL TRAP instrument. Elemental analyses were measured with a LECO, CHNS-932 analysis instrument. Melting points were determined with a Galen III (Boetius System, Cambridge Instruments) and are uncorrected. Absorption spectra were recorded with a Perkin–Elmer Lambda 19 spectrophotometer. Fluorescence quantum yields were calculated according to the procedure outlined by Demas and Crosby[25] against quinine sulfate in 0.1 M sulfuric acid as standard with an LS 50 luminescence spectrometer (Perkin–Elmer). Cyclic voltammetry (CV) experiments were conducted at 298 K by using a Metrohm 663 VA 25-mL cell [10 mL solution of 3 mg of each compound dissolved in 0.3 g Bu_4NBF_4 (99%) in CH_2Cl_2 (99.9%)] equipped with a glassy carbon working electrode, a platinum counter electrode, and a silver wire, which worked as a pseu-

doreference electrode. All potentials reported in this work were measured against the ferrocenium/ferrocene (Fc^+/Fc) redox couple. All of the electrolyte solutions were deoxygenated by bubbling argon gas through the solution for at least 10 min.

Crystal Structure Determination: The intensity data for the compounds were collected with a Nonius Kappa CCD diffractometer by using graphite-monochromated Mo-K_α radiation. For compound **7**, measurements were carried out at beamline ID11 at the European Synchrotron Radiation Facility (ESRF). Data were collected with a Bruker "Smart" CCD-camera system at fixed 2θ, while the sample was rotated over 0.1° intervals during 2 s exposures with the use of monochromated radiation from λ = 0.42468 Å. Data were corrected for Lorentz and polarization effects, but not for absorption effects.[26–28] The structures were solved by direct methods (SHELXS[29]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[30]). All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically:[31] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for 4a:[31] $C_{22}H_{16}N_8{\cdot}C_2H_6OS$, FW = 548.68 g mol^{-1}, orange prism, size 0.03 × 0.03 × 0.02 mm^3, orthorhombic, space group $Pna2_1$, a = 18.2722(6), b = 5.7074(3), c = 26.1666(9) Å, V = 2728.8(2) Å^3, T = –90 °C, Z = 4, $\rho_{calcd.}$ = 1.336 g cm^{-3}, μ (Mo-K_α) = 2.35 cm^{-1}, F(000) = 1152, 11461 reflections in h(–20/23), k(–6/7), l(–33/33), measured in the range 2.23° ≤ Θ ≤ 27.46°, completeness Θ_{max} = 99.6%, 5557 independent reflections, R_{int} = 0.0689, 3711 reflections with $F_o > 4\sigma(F_o)$, 343 parameters, 1 restraints, R_{1obs} = 0.0927, wR_{2obs} = 0.2350, R_{1all} = 0.1375, wR_{2all} = 0.2715, GOOF = 1.043, Flack-parameter 0.24(19), largest difference peak and hole: 2.041/–0.529 e Å^{-3}.

Crystal Data for 7:[31] $C_{48}H_{40}N_{16}NiO_2S_2$, FW = 995.79 g mol^{-1}, orange prism, size 0.02 × 0.02 × 0.01 mm^3, monoclinic, space group $P2_1/c$, a = 9.0737(9), b = 11.5249(10), c = 23.164(3) Å, β = 97.005(4)°, V = 2404.3(4) Å^3, T = 100 °C, Z = 2, $\rho_{calcd.}$ = 1.376 g cm^{-3}, μ (λ = 0.42468 Å) = 2.93 cm^{-1}, F(000) = 1032, 24079 reflections in h(–11/11), k(–14/14), l(–23/28), measured in the range 1.61° ≤ Θ ≤ 15.39°, completeness Θ_{max} = 84.9%, 4186 independent reflections, R_{int} = 0.0403, 3948 reflections with $F_o > 4\sigma(F_o)$, 313 parameters, 0 restraints, R_{1obs} = 0.0541, wR_{2obs} = 0.1471, R_{1all} = 0.0565, wR_{2all} = 0.1488, GOOF = 1.096, largest difference peak and hole: 0.696/-0.789 e Å^{-3}

Computational Methods: Tetraazanaphthalenes **2d** and **2d′** were calculated with Ar′ = phenyl. For all DFT Calculations (program Gaussian03[32]) the 6-311G(d,p) standard basis set[33] was used. Geometry optimisations with default values for grid and convergence parameters were made using the hybrid functional B3LYP.[34] The optimised structures were verified to be true minima by analytical determination of harmonic frequencies.

General Procedure for the Synthesis of Pyrazino[2,3-*b*]pyrazines of Type 4: *n*BuLi (5 mL, 0.01 mol, 2 M solution in *n*-hexane) was added dropwise to a solution of bis(amidine) **1** (0.005 mol) in freshly dried THF (30 mL) at –78 °C. After stirring the reaction mixture for 20 min, 2,3-dichloro-5,6-dicyanopyrazine **3** (1.0 g, 5 mmol) was added, and the mixture was stirred for one hour while slowly warming to room temperature to give an brown–orange solution. The solution was evaporated to dryness in vacuo. Then, chloroform was added and the resulting solution was washed several times with water. After drying the solution with Mg_2SO_4, it was evaporated and the residue was purified by column chromatography (silica, toluene/ethyl acetate, 19:1).

6-Imino-5-(4-tolyl)-7-(4-tolylamino)-5,6-dihydropyrazino[2,3-*b*]-pyrazine-2,3-dicarbonitrile (4a): Following the general procedure, the reaction with **1a** gave 1.2 g of a yellow solid, 60% yield. M.p. > 250 °C. ^{1}H NMR (250 MHz, [D$_8$]THF): δ = 9.88 (s, 1 H, NH), 7.89 (d, ^3J = 7.5 Hz, 2 H, tolyl), 7.68 (s, 1 H, NH), 7.37 (d, ^3J = 10 Hz, 2 H, tolyl), 7.02 (m, 4 H, tolyl), 2.42 (s, 3 H, CH_3); 2.24 (s, 3 H, CH_3) ppm. ^{13}C NMR (62 MHz, [D$_8$]THF): δ = 151.7, 145.2, 144.7, 141.4, 140.3, 135.1, 135.0, 131.2, 130.8, 129.3, 128.4, 126.0, 123.6, 121.4, 114.0, 20.4, 20.1 ppm. UV/Vis (CH_3CN): λ_{max} (log ε) = 226 (4.4), 278 (4.1), 392 (4.5) nm. DEI-MS: *m*/*z* (%) = 392 (55) [M]$^+$, 391 (100), 377 (100), 349 (5), 301 (10), 286 (5), 181 (15), 131 (10), 116 (10), 91 (80), 65 (55), 39 (30), 28 (55). $C_{22}H_{16}N_8$ (392.42): calcd. C 67.34, H 4.11, N 28.55; found C 67.68, H 4.59 N 28.39.

5-(4-*tert*-Butylphenyl)-7-(4-*tert*-butylphenylamino)-6-imino-5,6-dihydropyrazino[2,3-*b*]pyrazine-2,3-dicarbonitrile (4b): Following the general procedure, the reaction with **1b** gave 1.67 g of a yellow solid, 70% yield. M.p. > 250 °C. ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 10.56 (s, 1 H, NH), 7.89 (d, ^3J = 7.5 Hz, 2 H, phenyl), 7.82 (s, 1 H, NH), 7.71 (d, ^3J = 10 Hz, 2 H, phenyl), 7.47 (d, ^3J = 10 Hz, 2 H, phenyl), 7.34 (d, ^3J = 7.5 Hz, 2 H, phenyl), 1.38 (s, 9 H, $C(CH_3)_3$), 1.31 (s, 9 H, $C(CH_3)_3$) ppm. ^{13}C NMR (62 MHz, [D$_8$]-THF): δ = 152.4, 149.2, 148.0, 146.1, 145.0, 144.8, 128.3, 127.4, 125.8, 125.2, 124.7, 122.8, 122.5, 121.1, 114.8, 114.5, 34.6, 34.2, 31.3, 31.1 ppm. UV/Vis (CH_3CN): λ_{max} (log ε) = 393 (4.3), 280 (4.1), 225(4.3) nm. DEI-MS: *m*/*z* (%) = 476 (20) [M]$^+$, 419 (100), 195 (10), 115 (20), 57(20). $C_{28}H_{28}N_8$ (476.58): calcd. C 70.57, H 5.92, N 23,51; found C 71.98, H 6.88, N 22.15.

6-Imino-5-(2,4,6-trimethylphenyl)-7-(2,4,6-trimethylphenylamino)-5,6-dihydropyrazino[2,3-*b*]pyrazine-2,3-dicarbonitrile (4c): Following the general procedure, the reaction with **1c** gave 1.57 g of a yellow solid, 70% yield. M.p. > 250 °C. ^{1}H NMR (250 MHz, [D$_6$]-DMSO): δ = 9.03 (s, 1 H, NH), 7.58 (s, 1 H, NH), 7.20 (s, 2 H, phenyl), 7.05 (s, 2 H, phenyl), 2.44 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 2.25 (s, 6 H, CH_3), 1.97 (s, 6 H, CH_3) ppm. ^{13}C NMR (62 MHz, [D$_8$]THF): δ = 152.7, 147.8, 147.4, 146.8, 139.5, 136.9, 134.6, 133.1, 129.2, 128.7, 128.1, 127.6, 127.1, 126.0, 116.8, 115.5, 113.2, 20.6, 20.4, 18.0, 17.4 ppm. UV/Vis (acetone): λ_{max} (log ε) = 386 (4.4) nm. DEI-MS: *m*/*z* (%) = 450 (10) [M+H]$^+$, 434(100), 421(20), 412(18). $C_{26}H_{24}N_8$ (448.53): calcd. C 69.62, H 5.39, N 24.98; found C 70.03, H 5.65, N 24.47.

General Procedure for the Synthesis of Derivatives of Type 5: A mixture of 5,6-dihydropyrazino[2,3-*b*]pyrazine **4** (25 mmol) and trimethylorthoformate (20 mL) in the presence of a small amount of *p*-TsOH was heated under reflux for 50 h under an atmosphere of argon. The reaction was monitored by TLC (silica, toluene/ethyl acetate, 10:1). After completeness of the reaction, the mixture was evaporated to dryness in vacuo, and the crude product was purified by column chromatography (silica, toluene/ethyl acetate, 19:1).

2-Methoxy-1,4-bis(4-tolyl)-2,4-dihydro-1*H*-1,3,4,5,8,9-hexaazacyclopenta[*b*]naphthalene-6,7-dicarbonitrile (5a): Following the general procedure, the reaction with **4a** gave 0.76 g of a yellow solid, 70% yield. M.p. 237 °C (dec.). ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 7.87 (d, ^3J = 8.5 Hz, 2 H, tolyl), 7.45 (m, 6 H, tolyl), 3.16 (s, 3 H, OCH_3), 2.47 (s, 3 H, CH_3-tolyl), 2.42 (s, 3 H, CH_3-tolyl) ppm. ^{13}C NMR (62 MHz, [D$_6$]DMSO): δ = 153.4, 151.6, 147.0, 142.3, 139.1, 136.3, 132.7, 131.3, 130.1, 129.7, 128.8, 128.1, 127.8, 125.2, 123.2, 121.3, 114.5, 114.3, 105.2, 49.9, 20.8, 20.6 ppm. UV/Vis (CH_3CN): λ_{max} (log ε) = 384 (4.5), 275 (4.2), 225 (4.4) nm. Fluorescence (CH_3CN): λ_{max} = 486, 508, 514 nm. DEI-MS: *m*/*z* (%) = 434 (40) [M]$^+$, 419 (60), 387 (10), 313 (5), 284 (5), 201 (10), 131 (10), 116(10), 91 (100), 65 (60). $C_{24}H_{18}N_8O$ (434.46): calcd. C 66.35, H 4.18, N 25.79; found C 65.75, H 4.18, N 24.98.

1,4-Bis(4-*tert*-butylphenyl)-2-methoxy-2,4-dihydro-1*H*-1,3,4,5,8,9-hexaazacyclopenta-[*b*]naphthalene-6,7-dicarbonitrile (5b): Following the general procedure, the reaction with **4b** gave 0.65 g of a yellow solid, 50% yield. M.p. > 250 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 65 °C): δ = 7.82 (d, ^3J = 8.8 Hz, 2 H, aryl), 7.64 (d, ^3J = 8.4 Hz, 2 H, aryl), 7.58 (d, ^3J = 8.8 Hz, 2 H, aryl), 7.43 (d, ^3J = 8.8 Hz, 2 H, aryl), 7.33 (s, 1 H, CH), 3.15 (s, 3 H, OCH$_3$), 1.38 (s, 9 H, C(CH$_3$)$_3$), 1.34 (s, 9 H, C(CH$_3$)$_3$) ppm. ^{13}C NMR (100 MHz, [D$_6$]-DMSO): δ = 154.2, 152.5, 152.1, 150.1, 147.6, 142.7, 133.2, 131.8, 128.1, 126.9, 126.5, 125.9, 125.7, 123.8, 121.9, 115.0, 114.8, 106.0, 50.5, 35.1, 34.9 31.6 ppm. UV/Vis (CH$_3$CN): λ_{max} (log ε) = 385 (4.5), 277 (4.2), 225 (4.4) nm. Fluorescence (CH$_3$CN): λ_{max} = 491 nm. Φ_{em} = 0.18. DEI-MS: *m*/*z* (%) = 518 (15) [M]$^+$, 487 (25), 461 (100), 429 (7), 244 (25), 118.2 (30), 115 (30), 91 (40), 57 (20). C$_{30}$H$_{30}$N$_8$O (518.62): calcd. C 69.48, H 5.83, N 21.61; found C 69.10, H 5.87, N 20.98.

5,11-Bis(4-*tert*-butylphenyl)-5,11-dihydro-1,4,5,6,7,10,11,12-octaazatetracene-2,3,8,9-tetracarbonitrile 6b: 5,6-Dihydropyrazino-[2,3-*b*]pyrazine **4b** (1 mmol) and 2,3-Dichloro-5,6-dicyanopyrazine-(**3**, 1.0 g, 5 mmol) were heated for 15 min at 200 °C under an atmosphere of argon. After cooling to room temperature, the crude product was purified by column chromatography (alumina, **3** was eluted by toluene and product **6b** by toluene/ethyl acetate, 15:1). Derivative **6b** was obtained as a yellow solid, 0.18 g (30% yield). M.p. > 250 °C. ^{1}H NMR (250 MHz, [D$_8$]THF): δ = 7.68 (d, ^3J = 8.7 Hz, 4 H, aryl), 7.65 (d, ^3J = 8.7 Hz, 4 H, aryl), 1.41 (s, 18 H, C(CH$_3$)$_3$) ppm. UV/Vis (CH$_3$CN): λ_{max} (log ε) = 482 (4.9), 452 (4.8), 425 (4.9), 403 (3.9), 330 (3.9), 258 (4.7), 232 (4.4) nm. Fluorescence (CH$_3$CN): λ_{max} = 487, 520 nm. Φ_{em} = 0.55. DEI-MS: *m*/*z* (%): 602 (15) [M]$^+$, 587 (30), 275 (15), 219 (100), 91 (90). ESI-HRMS: calcd. for C$_{34}$H$_{27}$N$_{12}$ 603.2481; found 603.2501.

General Procedure for the Rearrangement of 10 to Pyrazino[2,3-*b*]pyrazines of Type 2: The appropriate tetraazafulvalene **10a**–**c** (0.01 mol) was heated in xylene (100 mL) at 130 °C in the presence of diisobutylamine (1 mL) for 5–24 h. The completeness of the reaction was monitored by TLC (alumina, toluene/acetone/methanol, 20:20:1). The mixture was evaporated to dryness in vacuo and the crude product was purified by column chromatography (alumina, toluene/acetone). The rearrangement of **10d** was performed under an atmosphere of argon.

***N*,*N*′,*N*′′,*N*′′′-Tetrakis(3-trifluoromethylphenyl)pyrazino[2,3-*b*]-pyrazine-2,3,6,7-tetraamine (2a):** Following the general procedure, the reaction of **10a** gave 1.54 g of a orange solid, 20% yield. M.p. 170 °C (dec.). ^{1}H NMR (250 MHz, [D$_8$]THF): δ = 8.59 (s, 4 H, NH), 8.29 (m, 8 H), 7.55 (m, 4 H), 7.32 (d, $^3J_{H,H}$ = 7.8 Hz, 4 H) ppm. ^{13}C NMR (62 MHz, [D$_8$]THF): δ = 142.0, 140.6, 134.8, 131.3, 131.3, 130.2, 127.0, 122.7, 118.4, 116.1 ppm. UV/Vis (THF): λ_{max} (log ε) = 256 (4.3), 329 (4.4), 440 (4.3), 467 (4.3) nm. Fluorescence (CH$_3$CN): λ_{max} = 486 nm. Φ_{em} = 0.80. MS (FAB): *m*/*z* = 768 [M]$^+$, 426, 400, 210. ESI-HRMS: calcd. for C$_{34}$H$_{20}$F$_{12}$N$_8$ 768.1619; found 768.1563.

***N*,*N*′,*N*′′,*N*′′′-Tetrakis(4-iodophenyl)pyrazino[2,3-*b*]pyrazine-2,3,6,7-tetraamine (2b):** Following the general procedure, the reaction of **10b** gave 1.0 g of a orange solid, 10% yield. M.p. > 250 °C. ^{1}H NMR (250 MHz, [D$_8$]THF): δ = 8.24 (s, 4 H, NH), 7.64 (m, 16 H) ppm. ^{13}C NMR (63 MHz, [D$_8$]DMSO): δ = 142.6, 142.1, 139.5, 139.2, 136.4, 123.34 ppm. UV/Vis (CH$_3$CN): λ_{max} (log ε) = 270 (4.1), 334 (4.3), 450 (4.2), 475 (4.2) nm. Fluorescence (CH$_3$CN): λ_{max} = 501 nm. Φ_{em} = 0.50. DEI-MS: *m*/*z* = 999 [M−1]$^+$, 873 [M−I]$^+$.

***N*,*N*′,*N*′′,*N*′′′-Tetrakis(4-carboxyethylphenyl)pyrazino[2,3-*b*]-pyrazine-2,3,6,7-tetraamine (2c):** Following the general procedure, the reaction of **10c** gave 1.57 g of a orange solid, 20% yield. M.p. 240 °C (dec.). ^{1}H NMR (250 MHz, [D$_8$]THF): δ = 10.33 (s, 4 H, NH), 7.93–7.82 (m, 16 H), 4.25 [q, J = 7.0 Hz, 8 H, CH$_2$], 1.28 (t, J = 7.5 Hz, 12 H, CH$_3$) ppm. ^{13}C NMR (63 MHz, [D$_6$]DMSO): δ = 165.2, 158.7, 141.8, 130.0, 125.6, 120.0, 60.5, 14.1 ppm. UV/Vis (CH$_3$CN): λ_{max} (log ε) = 249 (3.8), 355 (3.9), 458 (3.6), 485 (3.7) nm. Fluorescence (CH$_3$CN): λ_{max} = 500 nm. Φ_{em} = 0.69. DEI-MS: *m*/*z* = 784 [M]$^+$, 755[M−C$_2$H$_5$]$^+$, 165 [NHC$_6$H$_4$COOCH$_2$CH$_3$]$^+$. ESI-HRMS: calcd. for C$_{42}$H$_{40}$N$_8$O$_8$ 784.2969; found 784.2941.

***N*,*N*′,*N*′′,*N*′′′-Tetrakis(4-*tert*-butylphenyl)pyrazino[2,3-*b*]pyrazine-2,3,6,7-tetraamine (2d):** Following the general procedure under an atmosphere of argon, the reaction of **10d** gave 1.8 g of a orange solid, 25% yield. M.p. 190 °C (dec.). ^{1}H NMR (250 MHz, [D$_8$]-THF): δ = 8.09 (s, 4 H, NH), 7.68 (d, ^3J = 7.1 Hz, 8 H), 7.27 (d, ^3J = 8.7 Hz, 8 H), 1.27 (s, 36 H, C(CH$_3$)$_3$) ppm. ^{13}C NMR (63 MHz, [D$_6$]DMSO): δ = 145.0, 141.6, 139.5, 135.7, 126.0, 120.1, 34.8, 31.9 ppm. UV/Vis (acetone): λ_{max} (log ε) = 449 (4.4), 473 (4.4) nm. DEI-MS: *m*/*z* = 721 [M]$^+$, 706, 689. ESI-HRMS: calcd. for C$_{46}$H$_{57}$N$_8$ 721.4706; found 721.471.

3,11-Di-*tert*-butyl-5,13-bis(4-*tert*-butylphenyl)-5,13-dihydro-5,6,7,8,13,14,15,16-octaazahexacene (13): Tetraazafulvalene **10d** (7.68 g, 0.01 mol) was heated in the presence of oxygen at the same conditions as described for the synthesis of **2**. After 20 h, the reaction was stopped. Product **13**, which displays an intense red fluorescence, and precursor derivative **14** (deep purple, no fluorescent) were obtained by purification by column chromatography (alumina, toluene/acetone). Derivative **13** was obtained as a blue, green metallic shining solid, 3.56 g (50% yield). M.p. > 250 °C. ^{1}H NMR (400 MHz, [D$_8$]THF): δ = 7.75 (d, ^3J = 8.0 Hz, 4 H), 7.67 (d, ^3J = 8.0 Hz, 2 H), 7.46, 7.44 (dd, ^4J = 4.0 Hz, ^3J = 8.0 Hz, 2 H), 7.38 (d, ^3J = 8.0 Hz, 4 H), 6.70 (d, ^4J = 4.0 Hz, 2 H), 1.31 (s, 36 H, C(CH$_3$)$_3$) ppm. UV/Vis (CH$_3$CN): λ_{max} (log ε) = 271 (4.3), 482 (3.4), 482 (3.9), 515 (3.9), 554 (4.4), 599 (4.7) nm. Fluorescence (CH$_3$CN): λ_{max} = 603 nm. Φ_{em} = 0.88. DEI-MS: *m*/*z* = 716 [M+1]$^+$. ESI-HRMS: calcd. for C$_{46}$H$_{50}$N$_8$ 715.422; found 715.424.

8-*tert*-Butyl-6-(4-*tert*-butylphenyl)-3-(4-*tert*-butylphenylimino)-3,6-dihydro-1,4,5,6,11,12-hexaazanaphthacen-2-yl]-(4-*tert*-butylphenyl)-amine (14): The semicyclized product was obtained as a purple solid. M.p. > 250 °C. ^{1}H NMR (250 MHz, [D$_8$]THF): δ = 9.82 (s, 1 H), 7.99 (d, ^3J = 8.7 Hz, 2 H), 7.90 (d, ^3J = 8.7 Hz, 1 H), 7.64 (d, ^3J = 8.6 Hz, 2 H), 7.57 (dd, ^4J = 1.9 Hz, ^3J = 8.7 Hz, 1 H), 7.45 (d, ^3J = 8.6 Hz, 2 H), 7.35 (dd, ^4J = 1.6 Hz, ^3J = 8.6 Hz, 2 H), 7.18 (d, ^3J = 8.6 Hz, 2 H), 6.73 (s, 1 H), 1.82 (s, 9 H, C(CH$_3$)$_3$), 1.61 (s, 9 H, C(CH$_3$)$_3$), 1.36 (s, 9 H, C(CH$_3$)$_3$), 1.08 (s, 9 H, C(CH$_3$)$_3$) ppm. ^{13}C NMR (63 MHz, [D$_6$]DMSO): δ = 169.1, 155.1, 154.2, 153,4, 152.9, 152.2, 148.3, 147.8, 146.7, 145.9, 144.6, 144.0, 136.74, 135.5, 133.9, 131.5, 130,2, 127.5, 127.4, 126.3, 124.9, 124.6, 124.3, 124.1, 120.6, 112.2 ppm. UV/Vis (THF): λ_{max} (log ε) = 278 (3.9), 538 (3.9), 601 (3.6) nm. DCI-MS: *m*/*z* = 717 [M]$^+$. ESI-HRMS: calcd. for C$_{46}$H$_{53}$N$_8$ 718.4401; found 717.4407.

5,8,13,16-Tetrakis(3-trifluoromethylphenyl)-5,8,13,16-tetrahydro-1,4,5,6,7,8,9,12,13,14,15,16-dodecaazahexacene-2,3,10,11-tetracarbonitrile (8): 2a (0.004 g, 0.52 mmol) and 2,3-dichloro-5,6-dicyanopyrazine (**3**, 0.02 g, 0.1 mmol) were heated for 30 minutes at 200 °C under am atmosphere of argon. After cooling to room temperature, the crude product was purified. Starting material **3** was eluted by toluene by column chromatography (silica). The products were then eluted by TLC (silica, toluene/ethyl acetate, 2:1). Derivative **8** was obtained as an orange solid, 0.001 g (20% yield). M.p. > 250 °C. ^{1}H NMR (400 MHz, [D$_8$]THF): δ = 7.8 (d, ^3J = 8.0 Hz,

4 H), 7.70 (m, 4 H), 7.59 (s, 4 H), 7.55 (d, ^3J = 8.0 Hz, 4 H) ppm. UV/Vis (CH_3CN): λ_{max} = 264, 451, 482, 502, 517 nm. Fluorescence (CH_3CN): λ_{max} = 522 nm. Φ_{em} = 0.35. DEI-MS: *m*/*z* = 1020 $[M]^+$.

5,12-Bis(3-trifluoromethylphenyl)-9-(3-trifluoromethylphenylamino)-8-(3-trifluoromethylphenylimino)-5,7,8,12-tetrahydro-1,4,5,6,7,10,11,12-octaazanaphthacene-2,3-dicarbonitrile (9): This derivative was isolated as an orange solid, 0.0014 g (30% yield). M.p. > 280 °C. ^{1}H NMR (400 MHz, [D$_8$]THF): δ = 8.75 (s, 1 H, ring-NH), 8.15 (s, 1 H, exocyclic NH), 7.97 (d, ^3J = 8.4 Hz, 2 H), 7.87 (d, ^3J = 8.0 Hz, 2 H), 7.77 (m, 8 H), 7.43 (t, 2 H), 7.33 (d, ^3J = 7.6 Hz, 2 H) ppm. UV/Vis (THF): λ_{max} (logε) = 293 (4.3), 470 (4.3), 499 (4.4) nm. DCI-MS: *m*/*z* = 895 $[M]^+$. ESI-HRMS: calcd. for $C_{40}H_{18}F_{12}N_{12}$ 895.168; found 895.166.

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