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HIGHLY FLUORESCENT HETEROCYCLES BASED ON PYRAZINO FUSED 1,4,5,8-TETRAAZAFULVALENES

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Abstract - Some new pyrazino-fused 1,4,5,8-tetraazafulvalenes of type (**3-5**) were synthesized and their structures were confirmed by IR, UV-VIS, ^{1}H NMR spectra and elemental analysis. The X-Ray crystal structure analysis of a single crystal of derivative (**3c**) revealed a nearly ideal planarized heterofulvalene subunit. The new prepared tricyclic tetraazafulvalenes of type (**3**) show strong red fluorescence at 605 nm.

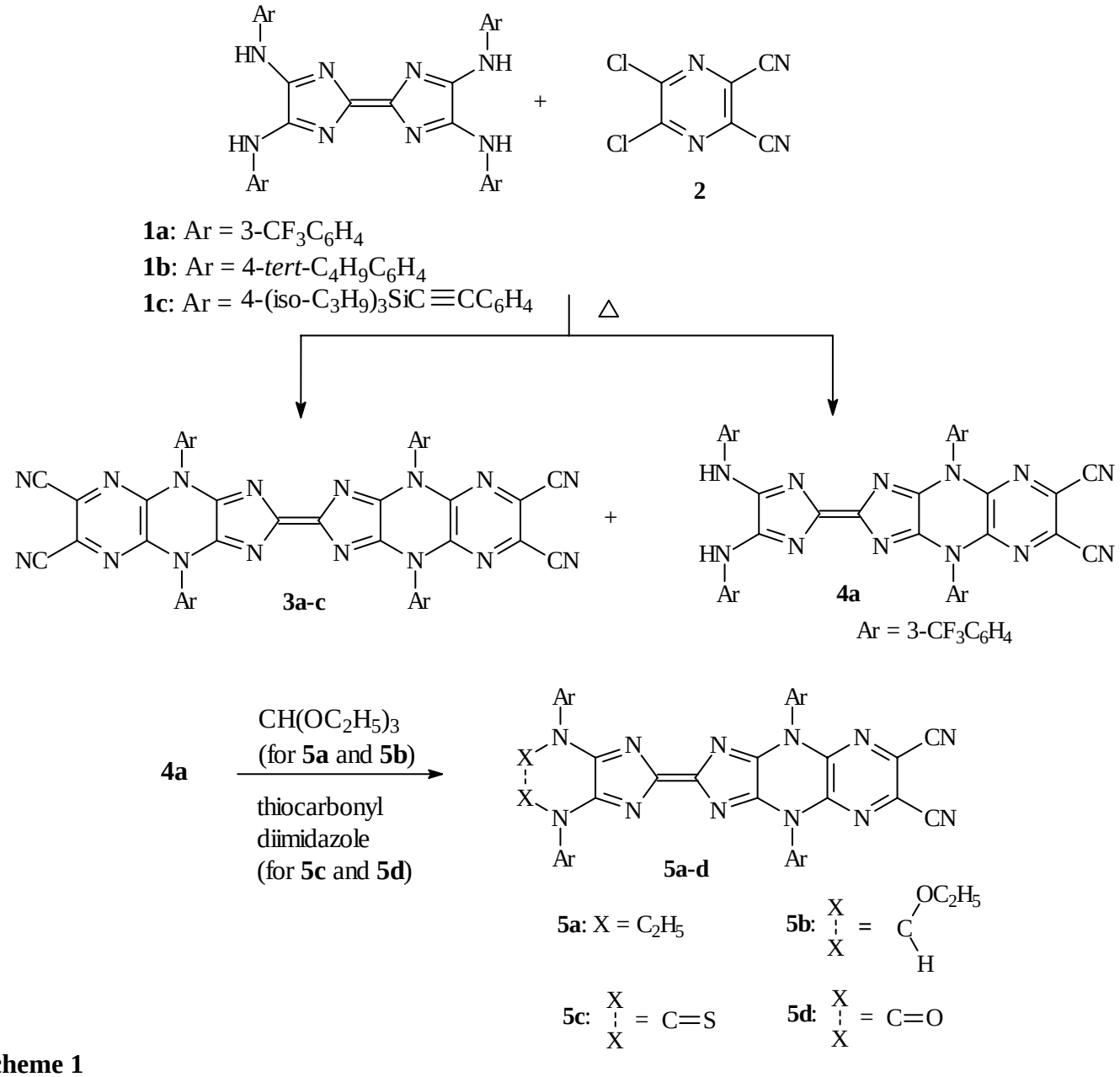
Substitution of the electron donating sulfur atoms in well-studied and for material science important tetrathiafulvalenes by aza nitrogen atoms leads to a new class of electronically inverted (electron acceptor) heterofulvalenes, namely the 1,4,5,8-tetraazafulvalenes (**1**). In contrast to the tetrathiafulvalenes there exists only a few data for corresponding aza derivatives. [1] In order to remedy this deficiency, we have developed numerous new syntheses for obtaining 1,4,5,8-tetraazafulvalenes (**1**) as well as their vinylogous derivatives. [2-5] All new obtained tetraazafulvalenes are redox active chromophoric systems and could possibly be quite interesting for the development of new functional dyes. In addition, various derivatizations such as alkylations, [2] acylations [3] and ring closure reactions [2,3,6] of the four secondary amino groups present in **1** have been studied. On the other hand, we have demonstrated that aromatic

halogen atoms can be replaced by different amines under the conditions of the Hartwig-Buchwald reaction. [7] Finally, we could extent the palette of functionalized tetraazafulvalenes by replacing the aromatic halogen atoms with carbon-carbon double bond systems (Heck reaction) as well as with numerous acetylenes under Sonogashira conditions. [8]

Recently, we published a short and efficient synthesis of pyrazino-fused tetraazafulvalenes. [6] Their UV/VIS spectra revealed a longest wavelength absorption at 658 nm (log ε = 4.9) which means a bathochromic shift of about 140 nm as compared to the starting material. Despite of the high degree of planarization in that fused pyrazines fluorescence could not be detected.

Ring-fused pyrazines might be of interest as marker molecules in biochemistry and medicine, are able to form donor-acceptor complexes which show semi-conducting properties or may serve as light harvesting systems. In addition, they have found applications as building blocks for phthalocyanine-like macrocycles [9] and for nonlinear optical materials. [10]

In this paper, different pyrazino-fused 1,4,5,8-tetraazafulvalenes (**3-5,7**) were synthesized by condensation reaction of 2,3,6,7-tetrakis(arylamino) derivatives of type **1** with 2,3-dichloro-5,6-dicyanopyrazine (**2**). The best yields were obtained by simple heating (200^{o} C) of a mixture containing **1** and **2** without any solvent or base. As examplified by derivative (**3c**) the triisopropylsilyl (TIPS)-moiety is an efficient protecting group for terminal acetylenes under the conditions employed. In addition, the low solubility of tetraazafulvalenes can be enhanced by introducing such bulky silyl groups at the peripheral positions. The new derivatives of type (**3**) were obtained as blue solids upon purification by column chromatographie. In the well structured UV/VIS spectra of **3a-c** the longest wavelength absorptions are located between 580-590 nm (log ε: 4.9-5.2). In addition, they show especially in nonpolar solution a strong red fluorescence (**3c**: λ_{Em} = 604 nm, ϕ_F = 0.73 in toluene) with a small stokes-shift of 18 nm (Figure 1). The X-Ray analysis of the deeply blue crystals of **3c** succeeded and the result is shown in Figure 2. The crystal structure clearly verifies the successful ring-fusion reaction and in addition, a nearly ideal planarization of the tricyclic heterofulvalene.



Scheme 1

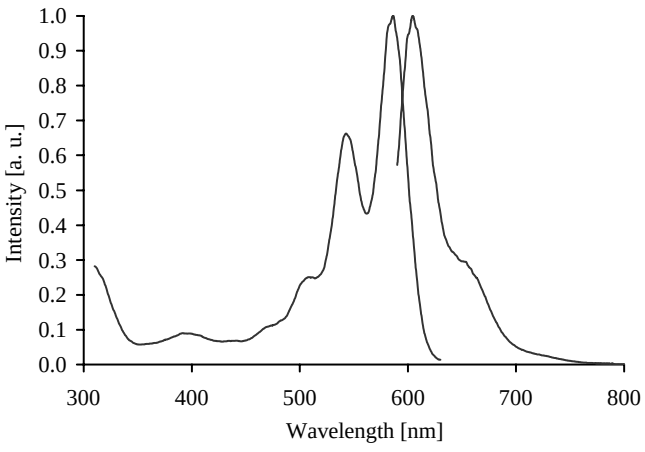


Figure 1: Normalised absorption and fluorescence spectra of **3c** in toluene

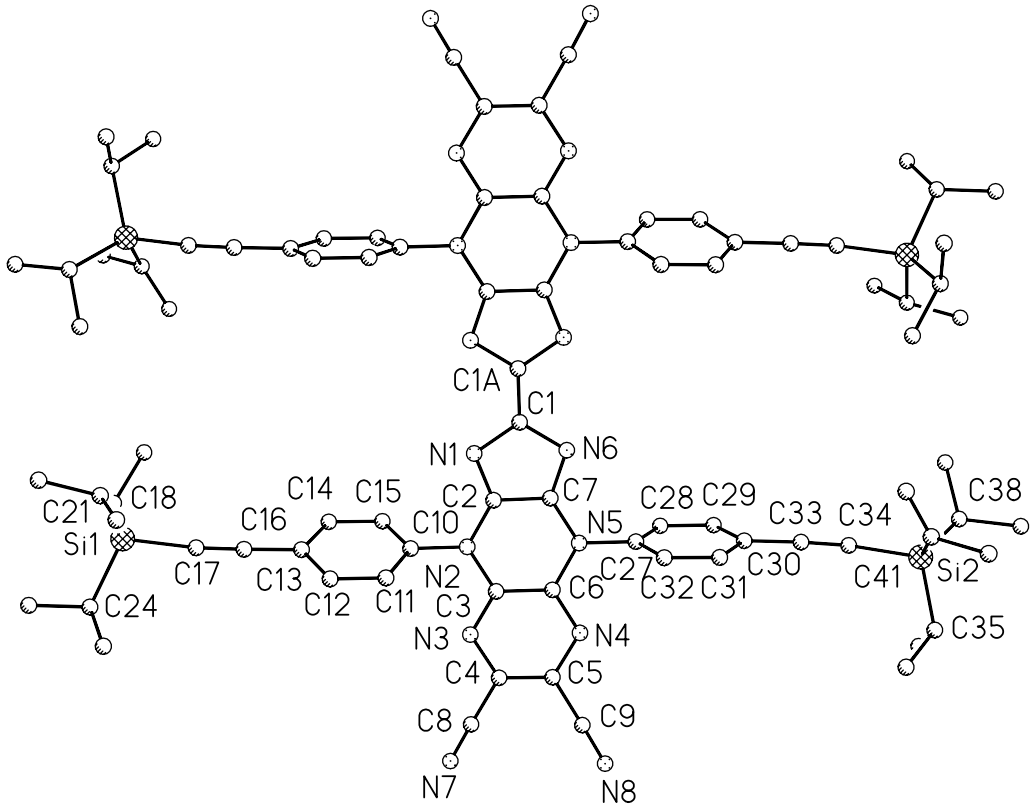
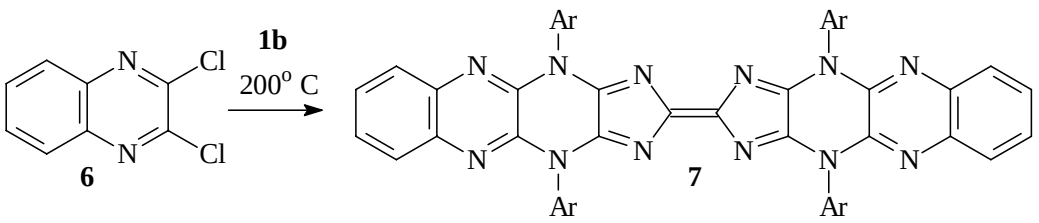


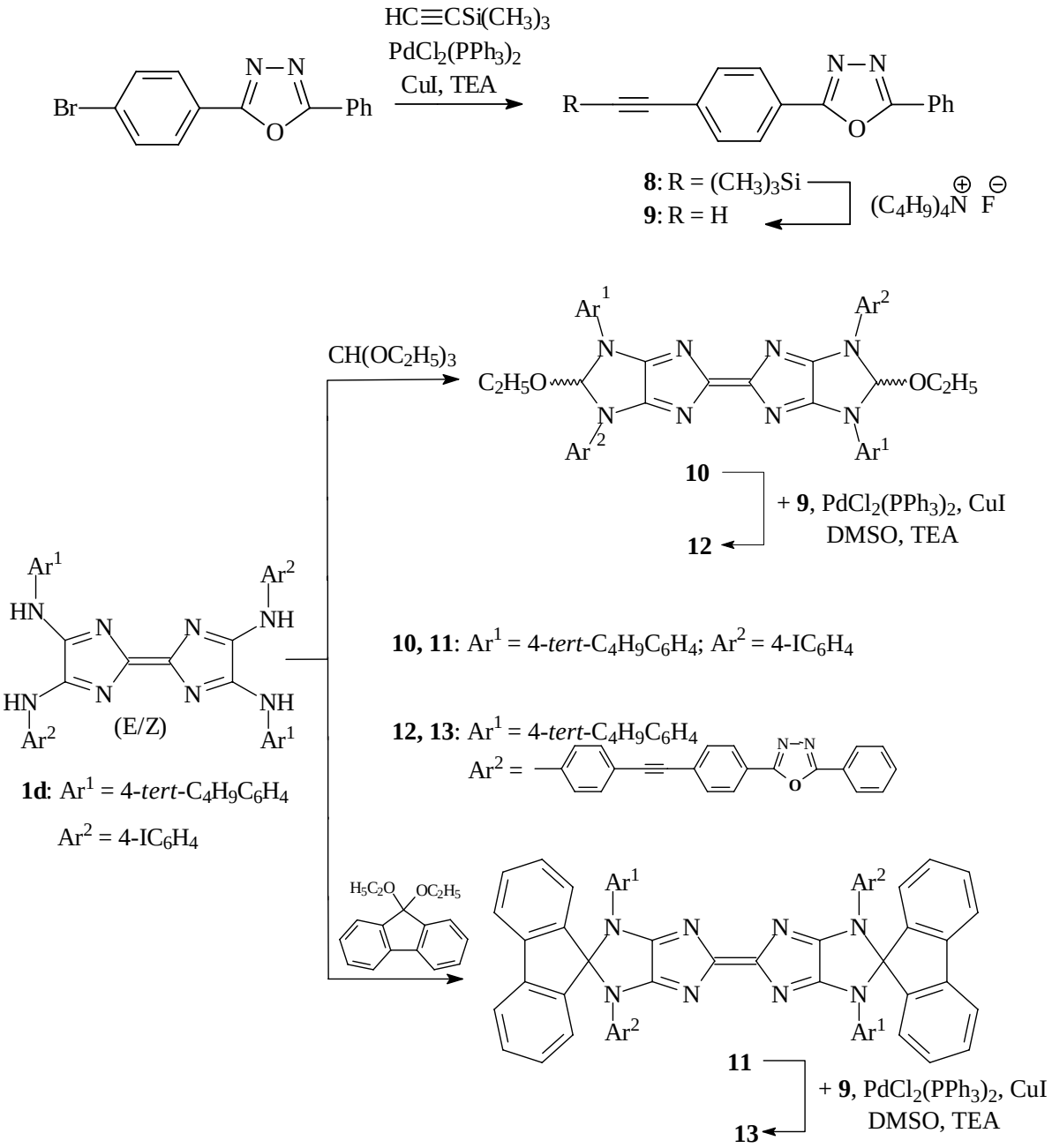
Figure 2: Molecular structure and atomic numbering for derivative (**3c**). Selected distances [Å] and angles [°]: C1-C1A 1.375(4), C7-C2 1.452(3), N1-C1 1.401(2), N1-C2 1.304(2), N2-C2 1.368(2), N2-C3 1.382(2), N3-C3 1.312(2), N3-C4 1.350 (3), C1A-C1-N1 122.3(2), C1-N1-C2 101.99(15).

The semi-cyclized products (**4**) could be isolated as byproducts in which both secondary amines allow a further functionalization. Thus, starting from **4a** the reaction with orthoformate is leading to alkylated **5a** as well as cyclized **5b** products. Furthermore, **4a** can be transformed with thiocarbonyl diimidazole resulting in new unsymmetric heterofulvalenes (**5c**) and (**5d**). Exceptionally **5b**, all unsymmetric derivatives did not show any fluorescence in different solvents.



Scheme 2

Encouraged by the stability and the absorption/emission properties of derivatives (**3**), other heterocycles which possess vicinal chlorine atoms were involved. In an analogous fashion, starting from **1a** the new ring-fused derivative (**7**) is now available with 2,3-dichloroquinoxaline (**6**) as cyclization partner. In the UV-VIS spectrum of the tetracyclic heterofulvalene (**7**) an increasing of absorption intensity was observed but in contrast to derivatives (**3**) no fluorescence could be detected.



Scheme 3

Based on these results a further goal was the construction of bichromophores which contain a tetraazafulvalene core. Therefore, the tetraazafulvalene (**1d**) (mixture of *E/Z*-isomers) which possess two different aryl residues has been prepared. Cyclization with orthoformate gave the imidazo-fused derivative (**10**), which was isolated as an unseparable mixture of *E/Z* and syn/anti-isomers. Analogously, simple heating of **1d** with fluorenone dimethylacetal gaves the bis-spiro compound (**11**) showing an orange-red fluorescence. Finally, the imidazo derivatives (**10**) and (**11**) have been then cross-coupled under the conditions of the sonogashira reaction leading to derivatives (**12**) and (**13**). Both compounds represent orange-red solids which show a strong greenish fluorescence.

EXPERIMENTAL

Materials and methods: The tetraazafulvalenes (**1a**), [2] (**1b**) [2] and (**1c**) [8] have been prepared according to the methods described in the literature. 2,3-Dichloro-5,6-dicyanopyrazine (**2**) was synthesized according to literature. [11] Other reagents were commercially available and were used without further purification. All solvents were of reagent grade and were dried and destilled before use.

All reactions were monitored by TLC, carried out on 0.25 mm Merck silicia gel plates ($60F_{254}$) using UV light. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DRX 400 or Bruker AC 250 spectrometer. Melting points are measured with a galen TM 3 apparatus and are uncorrected. UV-VIS spectra were recorded on a Perkin-Elmer Lambda 19 spectrophotometer. Fluorescence spectra were measured with an LS50B luminescence spectrometer (Perkin-Elmer). Fluorescence quantum yields were calculated relative to quinine sulfate in 0.1N H_2SO_4 used as a standard (ϕ_f = 0.55). MS spectra were taken from measurements on a Finnigan MAT SAQ 710 mass spectrometer. Elemental analyses were carried out in-house with an automatic analyzer LECO CHNS 932.

Crystal Structure Determination:

Data collection: The intensity data for the compound (**3c**) were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects, but not for absorption. [12,13]

Structure Solution and Refinement: The structures were solved by direct methods (SHELXS) [14] and refined by full-matrix least squares techniques against Fo^2 (SHELXL-97). [15] The hydrogen atoms were included at calculated positions with fixed thermal parameters. The molecule of **3c** which crystallizes with the solvent methylene chloride is disordered. The disorder could be solved for the structures. All non-hydrogen atoms were refined anisotropically. [15] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for **3c** [16]: $C_{86}H_{100}N_{16}Si_4$ * 2 C_3H_7NO * 2 CH_2Cl_2, Mr = 1786.22 $gmol^{-1}$, red-brown prism, size 0.08 x 0.06 x 0.01 mm^3, triclinic, space group P-1, a = 8.2071(2), b = 13.9726(3), c = 21.8503(5) Å, α = 89.202(1), β = 83.003(1), γ = 88.404(1)°, V = 2485.9(1) $Å^3$, T= -90 °C, Z = 1, $\rho_{calcd.}$ = 1.193 gcm^{-3}, μ (Mo-K_α) = 2.22 cm^{-1}, F(000) = 948, 17222 reflections in h(-10/9), k(-18/14), l(-28/26), measured in the range 1.73° ≤ Θ ≤ 27.48°, completeness Θ_{max} = 97.7 %, 11149 independent reflections, R_{int} = 0.022, 8502 reflections with $F_o > 4\sigma(F_o)$, 559 parameters, 0 restraints, $R1_{obs}$ = 0.062, wR^2_{obs} = 0.151, $R1_{all}$ = 0.085, wR^2_{all} = 0.170, GOOF = 1.015, largest difference peak and hole: 0.702 / -0.451 e $Å^{-3}$.

N^4,$N^{5'}$-Bis-(4-tert-butylphenyl)-N^5,$N^{4'}$-bis-(4-iodophenyl)[2,2']biimidazolylidene-4,5,4',5'-tetraamine ***(1d)***: Formamidinium acetate (9.78 g, 0.093 mol) and triethylamine (38.8 mL, 0.29 mol) were added to a solution of *N*-(4-iodophenyl)-*N*-(4-*tert*-butylphenyl)oxalodiimidoyl dichloride (49.3 g, 0.093 mol) in 200 mL acetonitrile and the resulting solution was heated under reflux for 3 h. After cooling to rt, the solvent was evaporated under reduced pressure to dryness. Methanol was added under vigorous stirring, the resulting solid was removed by filtration and then air-dried to provide brown-reddish crystals of compound (**1d**). Yield 24 g (26 %), mp 235-240°C (DMF), mixture of *E/Z* isomers. - ^{1}H NMR (250 MHz, DMSO-d_6): δ = 1.24 (s, 18H), 1.34 (s, 18H), 7.38-7.78 (m, 32H). MS (CI) *m/z* (%): 125(100), 157(97),

861(42)[M^+]. Anal. Calcd for $C_{38}H_{38}N_8I_2$: C, 53.04; H, 4.45; N, 13.02. Found: C, 53.14; H, 4.52; N, 12.94.

*General procedure for the synthesis of Tetraazafulvalenes (**3a-c**) and the semicyclized product (**4a**)*: Tetraazafulvalenes (**1a-c**) (0.13 mmol) and 2,3-dichloro-5,6-dicyanopyrazine (**2**) (300 mg, 1.51 mmol) were heated at 200^o C under argon for 15 min. After cooling to rt the crude product was purified by column chromatography (Al_2O_3, toluene/acetone). Recrystallization from DMF gave derivatives (**3a-c**) and (**4a**).

*4,9,4',9'-Tetrakis-(3-trifluoromethyl-phenyl)-4,9,4',9'-tetrahydro[2,2']bi[1,3,4,5,8,9-hexaaza-cyclopenta[b]naphthalenylidene]-6,7,6',7'-tetracarbonitrile (**3a**)*: Yield 68 mg (49 %), mp > 250°C (DMF). - ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.84 (m, 8H), 7.89 (m, 4H), 7.94 (d, *J* = 8.0 Hz, 4H). - UV-VIS (DMSO): λ_{max}/nm (log[ε/dm^3 mol^{-1} cm^{-1}]) 498 (4.2), 529 (4.6), 570 (4.8). F_{max}: 591 nm, ϕ_F = 0.69. - IR : ν_{max}/cm^{-1} 2213 (CN). MS (DCI, water) *m/z* (%): 162 (20), 306 (18), 1021 $(M+1)^+$. Anal. Calcd. for $C_{46}H_{16}N_{16}F_{12}$: C, 54.13; H, 1.58; N, 21.96. Found C, 54.25; H, 1.62; N, 21.86.

*4,9,4',9'-Tetrakis-(4-tert-butylphenyl)-4,9,4',9'-tetrahydro[2,2']bi[1,3,4,5,8,9-hexaaza-cyclopenta[b]naphthalenylidene]-6,7,6',7'-tetracarbonitrile (**3b**)*: Yield 65 mg (48%), mp >250°C (DMF). - ^{1}H NMR (THF-d_8) : δ = 1.32 (s, 36 H), 7.36 (d, *J* = 8.0 Hz, 8H), 7.52 (d, *J* = 8.0 Hz, 8H). - UV-VIS (toluene): 509 (4.5), 545 (4.9), 588 (5.1). F_{max}: 606 nm, ϕ_F = 0.72. IR : 2233 (CN). - MS (DCI, water) *m/z* (%): 972 (100) $(M)^+$. Anal. Calcd for $C_{58}H_{52}N_{16}$: C, 71.59; H, 5.39; N, 23.03. Found: C, 71.68; H, 5.46; N, 22.95.

*4,9,4',9'-Tetrakis-{4-[(triisopropylsilanyl)ethynyl]phenyl}-4,9,4',9'-tetrahydro[2,2']bi[1,3,4,5,8,9-hexaazacyclopenta[b]naphthalenylidene]-6,7,6',7'-tetracarbonitrile (**3c**)*: Yield 60 mg (50 %), mp >250°C (DMF). - ^{1}H NMR (CD_2Cl_2): δ = 1.09 (s, 72 H), 1.19 (s, 12 H), 7.29(d, *J* = 8.5 Hz), 7.62 (d, *J* = 8.5 Hz, 8 H). - UV-VIS (toluene): 508 nm (4.5), 543 (4.9), 586 (5.2). F_{max}: 604 nm, ϕ_F = 0.73. - IR (film): ν_{max}/cm^{-1} 2155 (C≡C), 2235 (CN). - MS (ESI) *m/z* (%): 1215.9 (30), 1469.8 (100)$(M+1)^+$, 1491.8 $(M+Na)^+$. Anal. Calcd for $C_{86}H_{100}N_{16}Si_4$: C, 70.26; H, 6.86; N, 15.24. Found: C, 70.06; H, 6.95; N, 15.43.

2-[4,5-Bis-(3-trifluoromethylphenylamino)imidazol-2-ylidene]-4,9-bis-(3-trifluoromethylphenyl)-4,9-

*dihydro-2H-1,3,4,5,8,9-hexaazacyclopenta[b]naphthalene-6,7-dicarbonitrile (**4a**)*: Yield 10 mg (10 %), mp> 250°C (DMF). - ^{1}H-NMR (250 MHz, CD_2Cl_2) : δ = 7.35 (m, 4H), 7.48 (d, *J* = 8.7 Hz, 1H), 7.63 (m, 4 H), 7.80 (m, 4H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.98 (s, 1H), 8.15 (d, *J* = 8.4 Hz, 1H). - UV-VIS (DMSO): λ_{max}/nm (log[ε/dm^3 mol^{-1} cm^{-1}]) 533 (4.7), 558 (4.8). – IR (film) : ν_{max}/cm^{-1} 2236 (CN). - MS (DCI, water) *m/z* (%): 149 (100), 537 (20), 894 (40)(M^+). Anal. Calcd for $C_{50}H_{18}N_{16}F_{12}$: C, 53.70; H, 2.03; N, 18.79. Found: C, 53.86; H, 2.09; N, 18.72.

*Syntheses of Unsymmetric Tetraazafulvalenes (**5a** – **5d**):* Compound (**4a**) (100 mg, 0.11 mmol) was heated in triethylorthoformate (5 mL) under reflux under a stream of argon for 12 h. The orthoformate was evaporated and the residue was purified by column chromatography with Al_2O_3 and toluene to give at first compound (**5a**) and then (**5b**).

*Compound (**5a**)*: Yield 30 mg (29 %), mp 206 °C (acetone). - ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 1.05 (t, *J* = 6.86 Hz, 6 H), 4.27 (q, *J* = 6.81 Hz, 4 H), 6.58 (dd, *J* = 6.72 and 7.81 Hz, 2 H), 6.68 (s, 2H), 7.03 (m, 4H), 7.75 (m, 4 H), 7.79 (dd, *J* = 7.80 and 8.03 Hz, 2 H), 7.86 (s, 2H). - UV-VIS (toluene): λ_{max}/nm (log[ε/dm^3 mol^{-1} cm^{-1}]) 566 (4.7). IR : ν_{max}/cm^{-1} 2230 (CN). - MS (DCI, water) *m/z* (%): 416 (90), 931 (20), 951 (60)$(M+1)^+$. Anal. Calcd for $C_{44}H_{26}N_{12}F_{12}$: C, 55.59; H, 2.76; N, 17.68. Found: C, 55.80; H, 2.81; N, 17.57.

*Compound (**5b**)*: Yield 50 mg (48 %), green crystals, mp 160°C (decomp). - ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 1.01 (t, *J* = 7.01 Hz, 3 H), 3.40 (q, *J* = 6.45 Hz, 2 H), 7.52 (d, *J* = 7.68, 2 H), 7.61 (dd, *J* = 7.84 and 8.07 Hz, 2H), 7.71 (m, 4 H), 7.90 (d, *J* = 7.68 Hz, 2H), 8.05 (s, 1H), 8.13 (m, 4 H), 8.24 (dd, *J* = 7.72 and 8.12 Hz, 2H). - UV/VIS (DMSO): 451 nm (4.5), 477 (4.7), 510 (4.8). - UV-VIS (toluene): λ_{max}/nm (log[ε/dm^3 mol^{-1} cm^{-1}]) 502 (4.8). F_{max}: 569 nm. MS (DCI, water) *m/z* (%): 526 (100), 931 (25), 951(50)$(M+1)^+$. Anal. Calcd for $C_{43}H_{22}N_{12}OF_{12}$: C, 54.33; H, 2.33; N, 17.68. Found: C, 54.44; H, 2.39; N, 17.60. Tetraazafulvalene (**4a**) (100 mg, 0.11 mmol) was heated with thiocarbonyldiimidazole (44 mg, 0.25 mmol) at 200°C for 15 min. The resulting mixture was purified by column chromatography (Al_2O_3,

toluene) to give derivatives (**5c**) and (**5d**). *Compound (**5c**)*: Yield: 42 mg (43 %), green crystals, mp >250°C (decomp). - UV-VIS (THF): λ_{max}/nm (log[ε/dm^3 mol^{-1} cm^{-1}]) = 528 (4.6), 550 (4.6). IR: ν_{max}/cm^{-1} 2238 (CN), 1729 (C=S). - MS (DCI, water) *m/z* (%): 391 (90), 847 (40), 889 (20)$(M+1)^+$. Anal. Calcd for $C_{53}H_{52}N_{12}S$: C, 71.60; H, 5.89; N, 18.90. Found: C, 71,89; H, 5.96; N, 18.78.

*Compound (**5d**)*: Yield 15 mg (15 %). red crystals, mp >250°C (decomp). - UV/VIS (THF): λ_{max}/nm (log[ε/dm^3 mol^{-1} cm^{-1}]) 512 (4.5). - IR: ν_{max}/cm^{-1} 2237 (CN), 1724 (C=O). - MS (DCI, water) *m/z* (%): 391 (40), 647 (5), 873 (20)$(M+1)^+$. Anal. Calcd for $C_{53}H_{52}N_{12}O$: C, 72.91; H, 6.00; N, 19.25. Found: C, 73.02; H, 6.09; N, 19.16.

*Synthesis of tetraazafulvalene (**7**):* Tetraazafulvalene (**1b**) (100 mg, 0.13 mmol) and 2,3-dichloroquinoxaline (200 mg) were heated under argon for 8 h. After cooling to rt the crude product was purified by recrystallisation from DMF to give the tetracyclic derivative (**7**).

*Compound (**7**)*: Yield 42 mg, (33 %), green crystals, mp > 300 °C (DMF) - ^{1}H NMR (400 MHz, THF-d_8): δ = 1.29 (s, 36 H), 7.29 (d, *J* = 8.0 Hz, 8H), 7.34 (m, 16 H), 7.69 (m, 8 H). - UV-VIS (THF): λ_{max}/nm (log[ε/dm^3 mol^{-1} cm^{-1}]) 545 (5.1). - MS (DCI, water) *m/z* (%): 205 (100), 485 (40), 973 (60)$(M+1)^+$. Anal. Calcd for $C_{62}H_{60}N_{12}$: C, 76.52; H, 6.21; N, 17.27. Found C, 76.47; H, 6.25; N, 17.23.

*Synthesis of the acetylene (**9**):* To a solution of 2-(4-bromophenyl)-5-phenyl-1,3,4-oxadiazole (0.5 g, 1.6 mmol) in triethylamine (5 mL), $PdCl_2(PPh_3)_2$ (0.07 g, 0.1 mmol) and CuI (0.038 g, 0.2 mmol) were added and the mixture was then stirred under an argon atmosphere. After 10 min, trimethylsilylacetylene (0.7 mL, 6.4 mmol) was added by the syringe. The resulting mixture was heated at 100 °C under argon for 3 h. After cooling to rt, the solution was filtred off, washed with triethylamine (1x20 mL) and methylene chloride (1x10 mL). The solvents were evaporated under reduced pressure to give the crude product, which was subjected to column chromatography (Al_2O_3, toluene) to obtain the acetylene (**8**).

*2-(4-(Trimethylsilylethinyl)phenyl)-5-phenyl-1,3,4-oxadiazole (**8**)*: Yield 0.5 g (96 %), brown crystals, mp 154-156°C (heptane). - ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.21 (s, 9H), 7.46-7.56 (m, 5H), 8.00-8.09 (m, 4H). - MS (DEI) *m/z* (%): 183(40), 262(60), 277(23), 303(100), 318(91)[M^+]. Anal. Calcd for $C_{19}H_{18}N_2OSi$: C, 71.66; H, 5.70; N, 8.80. Found: C, 71.53; H, 5.73; N, 8.85.

Compound (**8**) was dissolved in THF (15 mL), Bu_4NF (1 M in THF, 0.4 mL) was added until TLC analysis showed complete conversion. The solution was evaporated to dryness under reduced pressure and the crude product was chromathographed with petrol ether/acetone (4:1) to give the acetylene (**9**).

*2-(4-Ethinylphenyl)-5-phenyl-1,3,4-oxadiazole (**9**)*: Yield 0.32 g (83 %), beige crystals, mp 114-117°C (toluene). - ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.28 (s, 1H), 7.56 - 7.61 (m, 5H), 8.12-8.19 (m, 4H). - UV-VIS (CH_2Cl_2) : λ_{max}/nm (log[ε/dm^3 mol^{-1} cm^{-1}]): 298 (4.9). F_{max}: 384, 364 nm. - MS (EI) *m/z* (%) = 189 (71), 246 (100)[M^+]. Anal. Calcd for C_{16} $H_{10}N_2O$: C, 78.04; H, 4.09; N, 11.38. Found: C, 78. 14; H, 4.03; N, 11.30.

*Synthesis of cyclic aminals (**10**) and (**11**):*

Compound (**10**) was prepared by condensation of **1d** (2.00 g, 2.32 mmol) with triethyl orthoformate (20 mL, 0.12 mol) by heating under reflux in an argon stream for 7 h. The cooled solution was evaporated to dryness under reduced pressure. Purification by column chromatography (Al_2O_3, petrol ether/toluene, 2:1) afforded **10** as green crystals 0.79 g (35%). mp 150-155°C (DMF), mixture of 4 isomers. - ^{1}H NMR (250 MHz, DMSO - d_6): δ = 0.95 (t, *J* = 7.0 Hz, 24 H), 1.24 (s, 72 H), 3.31 (q, *J* = 7.0 Hz, 16 H), 7.58-7.97 (m, 72 H). - UV-VIS (toluene) : λ_{max}/nm (log[ε/dm^3 mol^{-1} cm^{-1}]) 464 (4.9), 497 (5.0). F_{max}: 504, 543 nm, ϕ_F = 0.78 (toluene). - MS (CI) *m/z* (%) = 973(100)[M^+]. Anal. Calcd for C_{44} $H_{46}N_8O_2I_2$: C, 54.33; H, 4.77; N, 11.52. Found: C, 54.48; H, 4.84; N, 11.42.

Compound (**11**) was prepared by heating of **1d** (0.32 g, 0.37 mmol) with fluoren-9-one diethyl acetal (2.15 g, 8.46 mmol) in xylene (10 mL) under reflux in an argon stream for 7 h. The cooled solution was evaporated to dryness under reduced pressure and further purified by column chromatography (Al_2O_3, toluene and then toluene/acetone, 2:1). Spiro aminal (**11**) was obtained as brown crystals, 0.24 g (54 %). mp 100-105°C (acetone), mixture of *E/Z* isomers. - ^{1}H NMR (DMSO-d_6): δ = 1.26 (s, 36 H), 7.29-7.75 (m, 64H). - UV-VIS (toluene) : λ_{max}/nm (log[ε/dm^3 mol^{-1} cm^{-1}]) 476 (4.6), 506 (4.7). - MS (DCI, water) *m/z* (%): 218(42), 845(95), 1023(100), 1185(40)[M$^+$]. Anal. Calcd for C_{64} $H_{50}N_8I_2$: C, 64.87; H, 4.25; N, 9.46. Found: C, 64.99; H, 4.30; N, 9.34.

*Synthesis of cross-coupling products (**12**) and (**13**):* In a Schlenk tube a mixture of DMSO (9 mL) and TEA (9 mL) were added to $PdCl_2(PPh)_3$ (29 mg, 0.04 mmol) and CuI (0.018 g, 0.08 mmol. Upon addition of derivative (**10**) (in the case of **12**) (0.19 g, 0.20 mmol) or **11** (in the case of **13**) (0.24 g, 0.20 mmol) the mixture was stirred under argon atmosphere for 15 min. Acetylene (**9**) (0.101 g, 0.4 mmol) was then added and the resulting reaction mixture was stirred under argon, maintaining the temperature between 35-40°C for about 3 h until the reaction was completed by TLC. After cooling to rt, the triethylamine was removed under *vacuo*, and water was added affording a dark brown precipitate. The crude product was filtred off, washed with water (3x20 mL), and thoroughly dried. Purification was realized by chromatography on a short column (Al_2O_3, toluene, toluene/acetone). Recrystallization from acetone afforded the pure product (**12**) or (**13**).

*Compound (**12**)*: Yield 70 mg (30 %), red powder, mp 228-230°C (DMF), mixture of 4 isomers. - ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 1.01 (m, 24 H), 1.31 (s, 36 H), 1.46 (s, 36 H), 3.32 (m, 16 H), 7.42-8.10 (m, 144 H). - UV-VIS (toluene): λ_{max}/nm (log[ε/dm^3 mol^{-1} cm^{-1}]) 320 (4.8), 446 (4.7), 476 (4.9), 512 (5.1). F_{max} (toluene): 518 nm, 560. - IR: ν_{max}/cm^{-1} 2208 (C≡C). - MS (ESI, toluene/methanol) *m/z* (%): 635(100), 1184.5(30), 1209.5(40)[M$^+$]. Anal. Calcd for $C_{76}H_{64}N_{12}O_4$: C, 75.48; H, 5.33; N, 13.90. Found:

C, 75.61; H, 5.43; N, 13.78.

*Compound (**13**)*: Yield 76 mg (26 %), red powder, mp 190-192°C (DMF), mixture of *E*/*Z*-isomers. - ^{1}H NMR (250 MHz, $CDCl_3$): δ =1.18 (s, 18H), 1.26 (s, 18 H), 6.98-8.05 (m, 100 H). - UV-VIS (DMSO): λ_{max}/nm (log[ε/dm^3 mol^{-1} cm^{-1}]) 330 (4.8), 489 (4.6), 515 (4.8). - IR: ν_{max}/cm^{-1} 2210 (C≡C). - MS (ESI) *m/z* (%): 1420.5 (M^+)(100). Anal. Calcd for C_{96} $H_{68}N_{12}O_2$: C, 81.11; N, 4.82; N, 11.82. Found: C, 81.25; H, 4.90; N, 11.72.

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