A One-Pot Synthesis of New Macrocyclic Compounds with Tetraaminoethene Substructure☆

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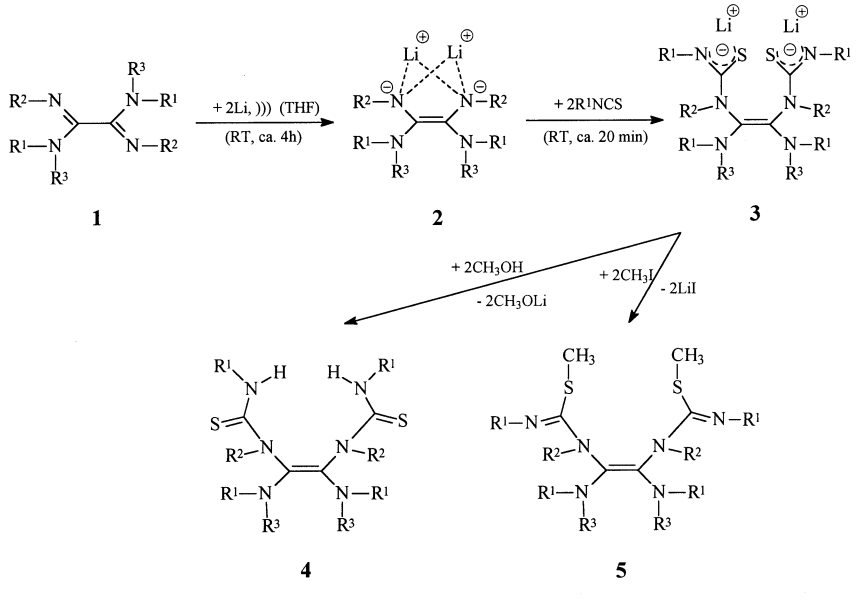
A convienent one-pot synthesis of macrocycles containing a tetraaminoethene substructure is described. Starting from oxalic amidines **1**, reduction with lithium and subsequent addition of phenyl isothiocyanate afforded the anionic bis(thiocarbamoyl) derivatives **3**. In the final step, a ring-closure reaction using a large number of α,ω-dielectrophilic building blocks yields the new macrocyclic compounds **6–14**.

Macrocyclic compounds present a very large variety of structures and properties ranging from the ligand to the complex and from the receptor to the supermolecule. A large number of macrocyclic ligands with different ring sizes and various heteroatom sequences have been synthesized[1][2][3]. The scientific and practical interest in such complexing species is undeniable. There are numerous applications of macrocyclic complexing agents in the fields of ion transport, analytical chemistry, bioorganic model systems, and phase-transfer catalysis.

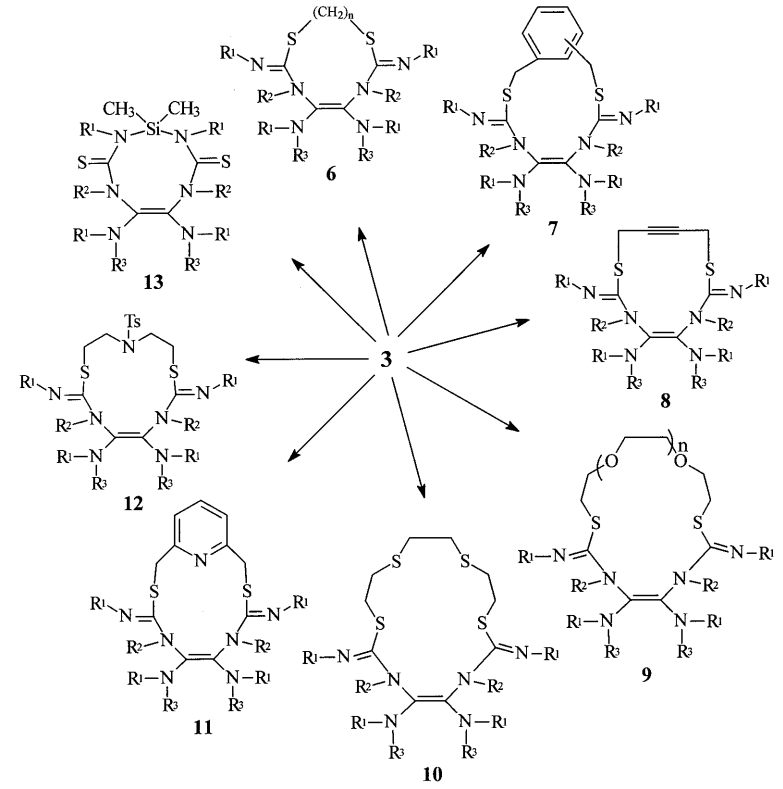
Recently, Märkl et al.[4] and Hoffman et al.[5] have described a general synthetic method for the incorporation of the dithiomaleonitrile unit into macrocycles containing various donor atoms. These crowns readily coordinate with heavy metal ions, forming endocyclic Ag^{I}[6][7] and Hg^{II}[8] complexes. The dithiomaleonitrile substructure bears an electron-deficient C=C double bond and therefore reduces the σ-donating ability of the sulfur atoms. Thus, the normally thiophilic metal ions preferentially coordinate to the macrocyclic oxygen atoms. In contrast, macrocycles with an electron-rich C=C double bond seem to be of interest because of their interaction with metal cations and in connection with possible electron-transfer processes. These circumstances encouraged us to synthesize macrocycles which contain an electron-rich C=C double bond.

Scheme 1



  1434–193X/98/0909–1803 $ 17.50+.50/0

Scheme 2



6	a	b	c	d	e	f	g	h	i
n	1	2	3	4	5	6	7	8	12

7	a	b
	1,2-	1,3-

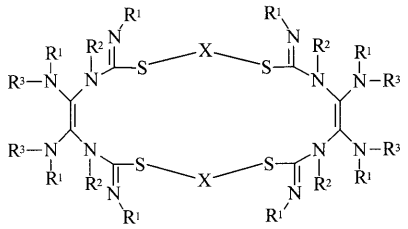
9	a	b	c
n	1	2	3

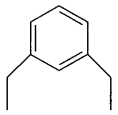
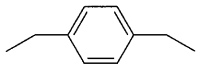
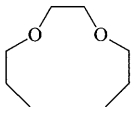
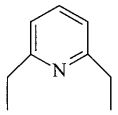
As previously published[9], we developed a new synthetic route to tetraaminoethene derivatives by a reduction/substitution sequence starting from oxalic amidines **1** (Scheme 1). Thus, the following alkylation, silylation, or acylation of the preformed dianion **2** constitutes a convenient route to highly substituted tetraaminoethenes[10]. The X-ray structural determination of **2** revealed a *cis*oid arrangement which might facilitate a cyclization by bielectrophilic building blocks. Based on these facts, an efficient one-pot synthesis of new macrocyclic compounds with tetraaminoethene substructure starting from **2** and phenyl isothiocyanate and a subsequent cyclization with α,ω-dielectrophiles was found.

Using THF as the solvent and lithium metal as the reducing agent, the persubstituted oxalic amidine **1** was converted quantitatively, in a short period of time, to the red dilithium salt **2**. To obtain new tetraaminoethenes, the quenching reaction of **2** was carried out with phenyl isothiocyanate. The Li diamide **2** reacted with two equivalents of the heterocumulene to the dilithium salt **3**, and subsequent treatment with methyl iodide gave, in a nearly quantitative yield, the isothiourea derivative **5**. The bifunctional thiourea **4** could be obtained in a similiar quenching reaction with methanol. The intermediary dilithium salts **2** and **3** formed were used without further purification. Unfortunately, all attempts to isolate single crystals of **3**, in order to obtain an X-ray crystal structural analysis, failed. Based on the reported structure of **2**[9] the bis-adduct **3** should contain the same (*Z*) arrangement. Surprisingly, only phenyl isothiocyanate reacts in this manner. For example, the reaction of **2** with methyl isothiocyanate as well as benzoyl isothiocyanate gave, after an aqueous workup, the starting amidine **1** as major product in both cases. This observation suggests an electron-transfer process between the dilithium salt **2** and the electron-poor heterocumulenes.

After preparing the open-chain derivatives **4** and **5**, we tried to synthesize macrocyclic compounds starting from **3** and bielectrophilic building blocks. Several types of macrocycles have been synthesized. First, the simple diazadithia

Scheme 3



14	X
a	-$(CH_2)_6$-
b	-$(CH_2)_8$-
c	
d	
e	
f	

$R^1 = C_6H_5$ $R^2 = 4\text{-}CH_3C_6H_4$ $R^3 = CH_3$

macrocycles of type **6** were prepared by cyclization of **3** with α,ω-dibromoalkanes $Br[CH_2]_nBr$, (n = 1−8, 12). The reaction of **3** with the dibromides with n = 1, 2, 3, 4 furnished in good yields (43−88%) the stable heterocyclic compounds **6a−d** without formation of larger rings. The structures of **6a−d** were assigned on the basis of ^{1}H-, ^{13}C-NMR and mass spectra. The surprisingly high yields of **6a−d** might reflect the *cis*oid arrangement to the dilithium salt of **3**. The cycloalkylation with the dibromides with n = 5 gave 1:1 (37−52% yield) and 2:2 macrocycles. As representative compounds with 2:2 stoichiometry the derivatives **14a** (n = 6, 27% yield) and **14b** (n = 8, 26% yield) were isolated and characterized by electro-spray mass spectrometry. ^{13}C-NMR spectra of compounds **6e**, **g** (n = 5, 7) show a single set of signals at room temperature, especially in the case of the CH_3 and CH_2 carbon atoms. In contrast, the spectra of macrocycles **6d**, **f**, **h**, **i** (n = 4, 6, 8, 12) display double sets of signals. In addition to which the ^{1}H- as well as the ^{13}C-NMR spectra show broad signals. By lowering the temperature, the line width of some signals decreases whereas other signal groups were broadened, indicating a multicomponent equilibrium of ring conformations. Starting from α,α′-dibromo-*o*-xylene the benzo derivative **7a** was obtained. In a similiar manner, the *meta*-bridged compound **7b** was prepared as mixture with the corresponding 2:2 product **14c**. As expected, α,α′-dibromo-*p*-xylene gave only the macrocycle **14d** in a yield of 59%. Moreover, it is noteworthy that 1,4-dichloro-2-butyne led only to the 1:1 product **8**.

We have employed the procedure shown in Scheme 2 to synthesize also the crown ether derivatives **9a−c** from the appropriate ethyleneglycol ditosylates. One exception was the triethyleneglycol building block which formed, in addition to **9a**, the 32-membered macrocycle **14e**.

The new starting material of type **3** allowed also the introduction of further sulfur- and nitrogen-containing substructures into the macrocycles. As shown in Scheme 2, the compounds **10**, **11**, and **12** (33−37%) could be prepared and isolated by simple flash-chromatography. The acyclic precursor of compound **10** was formed by chlorination of ethanedithiol with thionyl chloride and was used without further purification. The substitution reaction between **3** and this dichloride requires higher temperatures (60−70°C). Starting from the commercially available 2,6-bis(chloromethyl)pyridine the crown compound **11** was synthesized as a byproduct in addition to the large-ring heterocycle **14f**. Finally, a ring closure can be effected by silicon compounds like dichlorodimethylsilane leading to the 9-membered cyclic bis(thiourea) derivative **13** in good yield. In the ^{13}C-NMR spectrum of **13**, the ambidoselective ring formation was confirmed by the typical absorption of both thiocarbonyl C atoms at δ = 195.77.

The X-ray structural analyses, obtained from single crystals of **6a**, **7a**, and **10** are shown in Figure 1. Bond lengths correspond to previously reported tetraaminoethene structures[10]. Compound **6a** differs from **7a** in the positions of the sulfur atoms. The rigide *ortho*-xylene fragment of **7a** adopts a coplanar position to the tetraaminoethene unit. Therefore this unit forces the S atoms in an *exo-anti* position. The X-ray structural analysis of **10** shows the *exo*dentate positions of the S atoms, which is in accordance with the corresponding 1,4,7,10-tetrathiacyclododecane[11].

The electron-withdrawing effect of the isothiourea subunits reduce the electron density of the electron-rich C=C double bond. This, and the sterically overloaded C=C double bond, explain the unexpected stability of the described macrocycles in contrast to alkyl-substituted tetraaminoethenes[12].

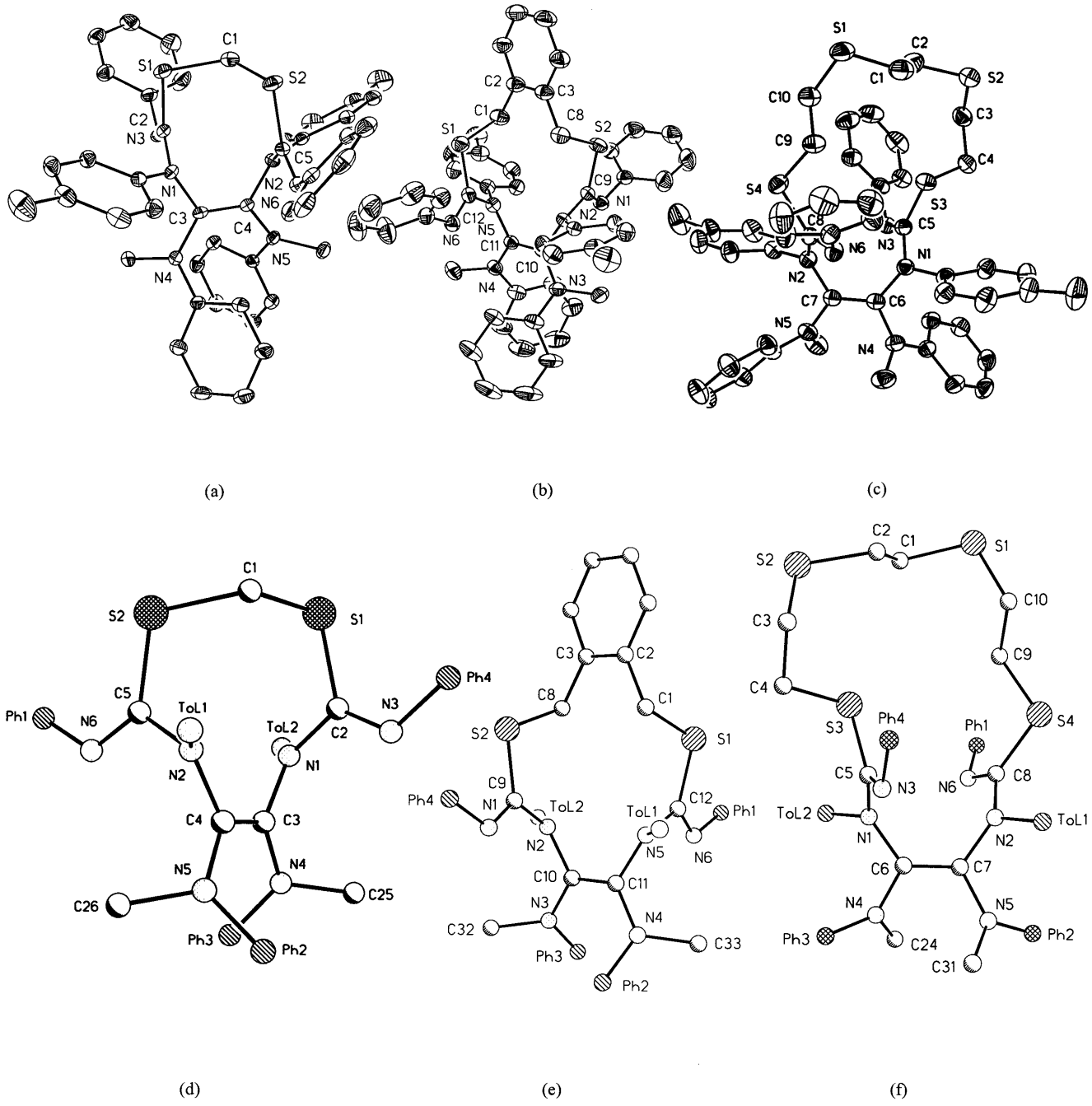
We have presented a general method, which does not require the use of high dilution techniques, to synthesize macrocyclic derivatives with tetraaminoethene substructure containing mixed oxygen, sulfur, and nitrogen heteroatoms. Future work will explore the coordination chemistry of this class of macrocycles.

This work was supported by the *Deutsche Forschungsgemeinschaft* (SFB 436) and the *Fonds der Chemischen Industrie*.

Experimental Section

General: CHN Analyses: Leco CHN automat CHNS-932. − MS: Finnigan MAT SSQ 710. − Melting points (uncorrected): Cambridge Instruments micro hot stage Galen III according to Boetius. − Chemical yields are not optimized. − All reactions were monitored by TLC carried out on 0.25-mm Merck Al_2O_3 plates

Figure 1. ORTEP plots of compounds **6a** (a), **7a** (b), **10** (c), and their reduced views **6a** (d), **7a** (e), **10** (f)



using UV light. – Column chromatography: 0.040–0.063 mm Merck Al_2O_3. Solvents were dried and freshly distilled. – THF was distilled from Na/benzophenone. – ^1H and ^{13}C NMR: Bruker AC 250 and DRX 400. 5-mm multinuclear probe head. ^1H-NMR shifts: relative to ^1H signals of the solvent.

Preparation of Dilithium Complex **2**[3]: 0.5 g (1.1 mmol) of **1** was dissolved under argon in ca. 30 ml of THF in a 250-ml Schlenk vessel and 0.3 g (4.3 mmol) of lithium was added. The mixture was brought to reaction in an ultrasonic bath. After 3 h, a clear red solution was obtained from which excess lithium was removed by filtration.

Preparation of Dilithium Complex **3**: 0.3 g (2.2 mmol) of phenyl isothiocyanate was added to a solution of 0.5 g (1.1 mmol) of **2** under stirring at room temp. After completion of the addition, the mixture was stirred until the solution was pale yellow (20 min). The intermediary formed dilithium salts **2** and **3** were used without further purification.

General Procedure for the Synthesis of Compounds **4–14**: 2.2 mmol of monofunctional (**4**, **5**) or 1.1 mmol of bifunctional electrophiles (**6–14**) was added to a solution of 0.8 g (1.1 mmol) of **3** under stirring at room temp. After completion of the addition, the mixture was stirred for 24–48 h. The solvent was evaporated in vacuo, the residue taken up in toluene and the lithium salt filtered off. The products were purified by column chromatography on Al_2O_3 [toluene/heptane (8:2) as mobile phase] or by recrystallization from *n*-heptane (**4**, **5**).

Acyclic Thiourea Derivative **4**: Yield 95% (0.77 g), orange crystals, mp 178°C. – ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 2.19 (br. s, 3 H), 2.48 (br. s, 1 H), 2.52 (br. s, 3 H), 2.78 (br. s, 2 H), 3.26 (br. s, 2 H), 3.58 (br. s, 1 H), 5.23 (br. s, 1 H), 6.29 (m, 2 H), 6.72 (m, 5 H), 7.06 (d, 6 H), 7.46 (m, 15 H), 10.36 (br. s, 1 H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.95 (4-$CH_3C_6H_4$), 21.24 (4-$CH_3C_6H_4$), 33.61 (NCH_3), 35.90 (NCH_3), 37.06 (NCH_3), 40.79 (NCH_3), 114.89, 115.49, 118.76, 119.06, 119.47, 120.79, 121.06, 123.64, 125.21, 126.08, 126.81, 127.16, 128.26, 128.70, 129.14, 129.61, 130.49, 131.81, 138.24, 138.72, 139.99, 143.72, 146.93, 147.30, 182.63, 183.06, 184.36. – MS (CI with H_2O); *m/z* (%): 719 (1) [M^+ + 1], 342 (78), 243 (14), 136 (100), 108 (59). – $C_{44}H_{42}N_6S_2$ (719.0): calcd. C 73.54, H 5.85, N 11.70, S 8.91; found C 73.18, H 5.87, N 11.67, S 8.84.

Acyclic Isothiourea Derivative **5**: Yield 92% (0.75 g), yellow crystals, mp 165°C. – ^{1}H NMR (CD_2Cl_2, 250 MHz): δ = 1.85 (m, 6 H), 2.29 (s, 6 H), 2.87 (m, 6 H), 7.20 (m, 28 H). – ^{13}C NMR (CD_2Cl_2, 62 MHz): δ = 16.44, 21.10, 34.63, 41.32, 115.21, 116.51, 118.87, 122.12, 123.61, 126.54, 128.14, 129.20, 130.43, 132.17, 135.51, 140.77, 146.09, 147.73, 148.76, 154.00, 157.97. – MS (CI with H_2O); *m/z* (%): 747 (17) [M^+ + 1], 746 (10) [M^+], 447 (10), 391 (14), 269 (11), 221 (70), 165 (100), 108 (11), 57 (68). – $C_{46}H_{46}N_6S_2$ (747.1): calcd. C 73.96, H 6.21, N 11.25, S 8.58; found C 73.69, H, 6.39, N 11.34, S 8.34.

N6,N7-Dimethyl-5,8-bis(4-methylphenyl)-N6,N7-diphenyl-4,9-bis(phenylimino)-4,5,8,9-tetrahydro-1,3,5,8-dithiadiazonine-6,7-diamine (**6a**): Yield 87% (0.71 g), yellow crystals, mp 242°C. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.20 (s, 6 H, 4-$CH_3C_6H_4$), 2.83 (s, 6 H, NCH_3), 4.01 (s, 2 H, $-CH_2-$), 6.72 (m, 2 H, *p*-H, >NC_6H_5), 6.94 (d, 4 H, *o*-H, 4-$CH_3C_6H_4$), 7.02 (m, 8 H, *o*-, *m*-H, >NC_6H_5), 7.12 (d, 4 H, *m*-H, 4-$CH_3C_6H_4$), 7.17 (t, 2 H, *p*-H, =NC_6H_5), 7.22 (m, 4 H, *o*-H, =NC_6H_5), 7.41 (m, 4 H, *m*-H, =NC_6H_5). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.75 (4-$CH_3C_6H_4$), 32.61 (CH_2), 38.52 (NCH_3), 115.36, 118.57, 121.09, 122.06, 124.82, 127.82, 127.94, 128.82, 129.44, 133.06, 139.63, 146.60, 147.50, 156.11. – MS (CI with H_2O); *m/z* (%): 731 (100) [M^+ + 1], 549 (12), 477 (10), 447 (21), 223 (20), 176 (15), 136 (48). – $C_{45}H_{42}N_6S_2$ (731.0): calcd. C 73.97, H 5.75, N 11.51, S 8.77; found C 74.01, H 5.62, N 11.63, S 8.64.

N4,N5-Dimethyl-3,6-bis(4-methylphenyl)-N4,N5-diphenyl-2,7-bis(phenylimino)-2,3,6,7,9,10-hexahydro-1,8,3,6-dithiadiazecine-4,5-diamine (**6b**): Yield 81% (0.68 g), yellow crystals, mp 261°C. – ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 2.25 (s, 6 H), 2.75 (m, 2 H), 2.89 (s, 6 H), 3.12 (m, 2 H), 6.66 (t, 2 H), 6.98 (t, 6 H), 7.11 (m, 6 H), 7.24 (t, 4 H), 7.32 (d, 4 H), 7.50 (t, 4 H), 7.65 (m, 2 H). – ^{13}C NMR (CD_2Cl_2, 100 MHz): δ = 20.90 (4-$CH_3C_6H_4$), 33.37 (CH_2), 34.43 (NCH_3), 116.10, 118.91, 122.54, 124.91, 125.83, 128.00, 128.70, 129.05, 129.28, 135.02, 140.92, 147.46, 148.26, 159.13. – MS (CI with H_2O); *m/z* (%): 745 (50) [M^+ + 1], 477 (10), 447 (46), 342 (11), 269 (18), 223 (29), 209 (10), 136 (100), 93 (22). – $C_{46}H_{44}N_6S_2 \cdot (C_2H_5)_2O$ (745.0 + 74.1): calcd. C 73.32, H 6.64, N 10.26, S 7.83; found C 73.09, H 6.52, N 10.37, S 8.06.

N4,N5-Dimethyl-3,6-bis(4-methylphenyl)-N4,N5-diphenyl-2,7-bis(phenylimino)-1,8-dithia-3,6-diaza-4-cycloundecene-4,5-diamine (**6c**): Yield 88% (0.75 g), yellow crystalline solid, mp 258°C. – ^{1}H NMR (CD_2Cl_2, 250 MHz): δ = 1.64 (m, 2 H), 2.25 (s, 6 H), 2.40 (m, 2 H), 2.90 (s, 6 H), 3.45 (m, 2 H), 6.66 (t, 2 H), 6.96 (t, 6 H), 7.18 (m, 8 H), 7.31 (d, 4 H), 7.51 (m, 8 H). – ^{13}C NMR (CD_2Cl_2, 62 MHz): δ = 20.92 (4-$CH_3C_6H_4$), 29.57 (CH_2), 31.72 (CH_2), 33.51 (NCH_3), 116.34, 118.89, 122.47, 124.28, 125.25, 127.98, 129.31, 134.76, 141.00, 147.75, 148.74, 159.76. – MS (CI with H_2O); *m/z* (%): 759 (20) [M^+ + 1], 284 (15), 283 (100), 223 (14), 210 (25), 205 (15), 151 (23), 136 (36), 93 (91). – $C_{47}H_{46}N_6S_2$ (759.1): calcd. C 74.37, H 6.11, N 11.07, S 8.45; found C 74.23, H 6.20, N 10.63, S 8.93.

N4,N5-Dimethyl-3,6-bis(4-methylphenyl)-N4,N5-diphenyl-2,7-bis(phenylimino)-1,8-dithia-3,6-diaza-4-cyclododecene-4,5-diamine (**6d**): Yield 43% (0.37 g), pale yellow crystals, mp 148°C. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.96 (t, 1.5 H), 1.35 (m, 0.5 H), 1.75 (m, 2 H), 2.03 (m, 3 H), 2.20 (br. s, 2.5 H), 2.30 (s, 4 H), 2.67 (s, 4 H), 2.81 (s, 2 H), 3.44 (m, 0.5 H), 6.37 (dd, 1 H), 6.65 (m, 2 H), 6.91 (m, 7 H), 7.15 (m, 7 H), 7.28 (m, 5 H), 7.35 (m, 3 H), 7.47 (m, 2 H), 8.34 (dd, 1 H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.85 (4-$CH_3C_6H_4$), 21.25 (4-$CH_3C_6H_4$), 21.74 (CH_2), 24.37 (CH_2), 30.19 (CH_2), 32.36 (CH_2), 33.09 (NCH_3), 40.59 (NCH_3), 109.80, 115.04, 116.11, 118.39, 121.08, 122.00, 122.64, 123.74, 127.27, 127.49, 127.88, 128.65, 128.91, 128.97, 129.04, 132.90, 134.29, 139.08, 140.87, 145.56, 148.78, 149.45, 150.32, 160.44. – MS (CI with H_2O); *m/z* (%): 773 (76) [M^+ + 1], 447 (11), 223 (18), 209 (10), 137 (56), 135 (65), 93 (100). – $C_{48}H_{48}N_6S_2 \cdot 2\ CH_3COCH_3$ (773.1 + 116.2): calcd. C 72.94, H 6.55, N 9.45, S 7.21; found C 72.95, H 6.60, N 9.75, S 7.30.

N4,N5-Dimethyl-3,6-bis(4-methylphenyl)-N4,N5-diphenyl-2,7-bis(phenylimino)-1,8-dithia-3,6-diaza-4-cyclotridecene-4,5-diamine (**6e**): Yield 52% (0.46 g), pale yellow crystals, mp 184°C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.42 (m, 6 H), 2.29 (br. s, 8 H), 2.81 (br. s, 8 H), 6.64 (m, 2), 6.99 (m, 10 H), 7.23 (m, 10 H), 7.45 (m, 4 H), 7.70 (m, 2 H). – ^{13}C NMR (62 MHz, $CDCl_3$): δ = 21.00 (4-$CH_3C_6H_4$), 24.70 (CH_2), 27.09 (CH_2), 32.07 (CH_2), 33.49 (NCH_3), 116.69, 118.52, 121.74, 123.52, 127.64, 128.85, 129.13, 130.67, 135.43, 139.96, 148.25, 158.45. – MS (CI with H_2O); *m/z* (%): 787 (1) [M^+ + 1], 149 (16), 136 (100). – $C_{49}H_{50}N_6S_2$ (787.1): calcd. C 75.72, H 6.53, N 10.09, S 7.70; found C, 75.75; H 6.85, N 10.11, S 7.58.

N4,N5-Dimethyl-3,6-bis(4-methylphenyl)-N4,N5-diphenyl-2,7-bis(phenylimino)-1,8-dithia-3,6-diaza-4-cyclotetradecene-4,5-diamine (**6f**): Yield 41% (0.37 g), pale yellow crystalline solid, mp 239°C. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.31 (m, 8 H), 2.29 (br. s, 8 H), 2.76 (br. s, 8 H), 6.60 (m, 2 H), 7.01 (m, 18 H), 7.38 (t, 5 H), 7.69 (m, 3 H). – ^{13}C NMR ($CDCl_3$, 62 MHz): δ = 21.03 (4-$CH_3C_6H_4$), 25.17 (CH_2), 27.28 (CH_2), 28.67 (CH_2), 31.80 (CH_2), 32.49 (CH_2), 33.66 (CH_2), 115.82, 117.03, 118.56, 121.37, 122.95, 127.27, 127.61, 128.75, 128.92, 129.15, 129.53, 131.15, 135.72, 139.77, 148.20, 157.5. – MS (CI with H_2O); *m/z* (%): 801 (16) [M^+ + 1], 447 (23), 391 (18), 300 (21), 279 (37), 205 (60), 149 (48), 136 (100), 120 (49), 93 (28). – $C_{50}H_{52}N_6S_2$ (801.2): calcd. C 74.96, H 6.54, N 10.49, S 8.00; found C 74.52, H 6.69, N 10.37, S 8.32.

N4,N5-Dimethyl-3,6-bis(4-methylphenyl)-N4,N5-diphenyl-2,7-bis(phenylimino)-1,8-dithia-3,6-diaza-4-cyclopentadecene-4,5-diamine (**6g**): Yield 37% (0.34 g), pale yellow crystals, mp 255°C. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.22 (m, 6 H), 1.49 (m, 4 H), 2.30 (br. s, 8 H), 2.73 (s, 6 H), 2.85 (m, 2 H), 6.58 (m, 2 H), 6.79 (m, 8 H), 6.89 (m, 4 H), 7.04 (m, 6 H), 7.28 (m, 4 H), 7.59 (m, 4 H). – ^{13}C NMR ($CDCl_3$, 62 MHz): δ = 21.03 (4-$CH_3C_6H_4$), 24.40 (CH_2), 24.98 (CH_2), 26.73 (CH_2), 31.35 (CH_2), 117.30, 118.69, 121.02, 122.51, 127.60, 128.64, 129.15, 135.74, 139.57, 147.97, 148.22, 157.54. – MS (CI with H_2O); *m/z* (%): 815 (2) [M^+ + 1], 107 (7), 89 (100). – $C_{51}H_{54}N_6S_2$ (815.2): calcd. C 75.14, H 6.68, N 10.31, S 7.87; found C 74.89, H 6.60, N 10.47, S 7.98.

N4,N5-Dimethyl-3,6-bis(4-methylphenyl)-N4,N5-diphenyl-2,7-bis(phenylimino)-1,8-dithia-3,6-diaza-4-cyclohexadecene-4,5-diamine (**6h**): Yield 41% (0.38 g), yellow amorphous solid. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.21 (m, 12 H), 1.99 (m, 2 H), 2.31 (m, 8 H), 2.69 (m, 6 H), 6.75 (m, 16 H); 7.25 (m, 10 H), 7.60 (m,

2 H). − ^{13}C NMR ($CDCl_3$, 62 MHz): δ = 20.97 (4-$CH_3C_6H_5$), 21.10 (4-$CH_3C_6H_5$), 23.76 (CH_2), 25.13 (CH_2), 25.59 (CH_2), 26.17 (CH_2), 26.45 (CH_2), 28.02 (CH_2), 31.90 (CH_2), 32.49 (CH_2), 40.55 (NCH_3), 114.54, 117.01, 117.88, 118.57, 121.18, 122.19, 122.83, 127.67, 128.20, 128.47, 128.62, 129.01, 130.88, 131.94, 135.29, 135.52, 139.76, 140.15, 145.76, 148.01, 149.43, 152.03. − MS (CI with H_2O); *m/z* (%): 830 (20) [M^+ + 2], 829 [M^+ + 1] (47), 491 (10), 328 (18), 326 (17), 192 (87), 191 (100), 136 (57), 111 (64). − $C_{52}H_{56}N_6S_2$ (829.2) calcd. C 75.32, H 6.81, N 10.13, S 7.73; found C 75.21, H 6.59, N 10.28, S 7.71.

N4,N5-Dimethyl-3,6-bis(4-methylphenyl)-N4,N5-diphenyl-2,7-bis(phenylimino)-1,8-dithia-3,6-diaza-4-cycloicosene-4,5-diamine (**6i**): Yield 49% (0.49 g), yellow amorphous solid. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.19 (m, 20 H), 2.30 (m, 11 H), 2.76 (m, 5 H), 6.86 (m, 28 H). − ^{13}C NMR ($CDCl_3$, 62 MHz): δ = 21.00 (4-$CH_3C_6H_5$), 21.46 (4-$CH_3C_6H_4$), 25.76 (CH_2), 26.52 (CH_2), 27.01 (CH_2), 28.13 (CH_2), 28.18 (CH_2), 28.76 (CH_2), 29.41 (CH_2), 29.48 (CH_2), 29.71 (CH_2), 32.04 (CH_2), 32.85 (CH_2), 33.05 (CH_2), 34.01 (CH_2), 40.72 (NCH_3), 114.79, 115.10, 116.81, 118.07, 118.42, 121.11, 122.06, 123.10, 125.31, 126.61, 127.58, 128.23, 128.47, 128.65, 129.04, 134.94, 135.32, 137.86, 140.07, 140.71, 145.79, 148.17, 149.36. − MS (CI with H_2O); *m/z* (%): 885 (18) [M^+ + 1], 447 (20), 249 (93), 247 (100), 209 (16), 182 (12), 136 (72), 93 (18). − $C_{56}H_{64}N_6S_2$ (885.3): calcd. C 75.97, H 7.29, N 9.50, S 7.24; found C 75.67, H 7.39, N 9.14, S 7.46.

N5,N6-Dimethyl-4,7-bis(4-methylphenyl)-N5,N6-diphenyl-3,8-bis(phenylimino)-1,3,4,7,8,10-hexahydro-2,9,4,7-benzodithiadiazacyclododecine-5,6-diamine (**7a**): Yield 87% (0.8 g), pale yellow crystals, mp 293°C. − ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 2.30 (s, 6 H, 4-$CH_3C_6H_4$), 2.96 (s, 6 H, NCH_3), 3.20 (d, 2 H, CH_2), 4.69 (d, 2 H, CH_2), 6.68 (t, 2 H, >NC_6H_5), 6.90 [dd, 2 H, 1,2-$(CH_2)_2C_6H_4$], 6.99 (m, 6 H, 4-$CH_3C_6H_4$/>NC_6H_5), 7.06 [dd, 2 H, 1,2-$(CH_2)_2C_6H_4$], 7.18 (m, 8 H, 4-$CH_3C_6H_4$/>NC_6H_5/=NC_6H_5), 7.34 (d, 4 H, =NC_6H_5), 7.43 (t, 4 H, =NC_6H_5), 7.56 (dd, 2 H, 4-$CH_3C_6H_4$), 7.76 (dd, 2 H, 4-$CH_3C_6H_4$). − ^{13}C NMR (CD_2Cl_2, 100 MHz): δ = 21.00 (4-$CH_3C_6H_5$), 33.53 (NCH_3), 34.98 (CH_2), 116.38, 118.95, 122.44, 124.42, 126.20, 127.99, 128.52, 129.36, 129.54, 129.63, 129.74, 130.91, 135.02, 135.73, 141.28, 147.73, 148.28, 159.86. − MS (CI with H_2O); *m/z* (%): 821 (44) [M^+ + 1], 342 (13), 223 (20), 136 (100), 93 (25). − $C_{52}H_{48}N_6S_2 \cdot CH_3COCH_3$ (821.1 + 58.1): calcd. C 75.14, H 6.19, N 9.52, S 7.29; found C 75.13, H 6.44, N 9.51, S 7.39.

N6,N7-Dimethyl-5,8-bis(4-methylphenyl)-N6,N7-diphenyl-4,9-bis(phenylimino)-3,10-dithia-5,8-diazabicyclo[10.3.1]hexadeca-1(16),6,12,14-tetracene-6,7-diamine (**7b**): Yield 55% (0.51 g), pale yellow crystalline solid, mp 196°C. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.31 (s, 3 H), 2.32 (s, 1 H), 2.41 (s, 2 H), 2.49 (s, 4 H), 2.78 (s, 2 H), 3.09 (d, 1 H), 3.34 (d, 1 H), 3.57 (d, 1 H), 3.75 (d, 1 H), 6.49 (d, 2 H), 7.51 (m, 30 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.05 (4-$CH_3C_6H_5$), 21.27 (4-$CH_3C_6H_5$), 32.92 (NCH_3), 35.91 (CH_2), 36.29 (CH_2), 40.35 (NCH_3), 114.61, 117.64, 117.96, 121.39, 121.65, 122.36, 123.02, 125.35, 126.28, 127.62, 128.28, 128.55, 128.86, 129.06, 129.08, 129.40, 133.99, 137.37, 138.83, 139.30, 146.05, 148.41. − EI MS; *m/z*: 821.7 [M + H]$^+$. − $C_{52}H_{48}N_6S_2$ (821.1): C 75.58, H 6.22, N 9.80, S 7.47; found C 75.25, H 6.42, N 9.74, S 7.59.

N4,N5-Dimethyl-3,6-bis(4-methylphenyl)-N4,N5-diphenyl-2,7-bis(phenylimino)-1,8-dithia-3,6-diaza-4-cyclododecene-10-yne-4,5-diamine (**8**): Yield 65% (0.56 g), yellow crystalline solid, mp 226°C. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.31 (s, 6 H), 2.44 (s, 1 H), 2.48 (s, 2 H), 2.53 (s, 6 H), 2.58 (s, 1 H), 6.37 (dd, 2 H), 6.73 (d, 2 H), 6.79 (br. s, 2 H), 6.86 (t, 4 H), 7.10 (t, 4 H), 7.32 (m, 12 H), 8.12 (dd, 2 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.28 (4-$CH_3C_6H_5$), 22.91 (CH_2), 41.10 (NCH_3), 80.12, 115.23, 118.91, 122.40, 123.56, 128.34, 129.18, 129.80, 129.83, 130.22, 133.99, 138.39, 139.87, 146.83, 147.15, 149.62. − MS (CI with H_2O); *m/z* (%): 769 (0.4) [M^+ + 1], 243 (63), 136 (100), 108 (73). − $C_{48}H_{44}N_6S_2$ (769.1): calcd. C 74.96, H 5.77, N 10.93, S 8.34; found C 74.64, H 5.66, N 10.93, S 8.11.

N7,N8-Dimethyl-6,9-bis(4-methylphenyl)-N7,N8-diphenyl-5,10-bis(phenylimino)-1,14-dioxa-4,11-dithia-6,9-diaza-7-cyclohexadecene-7,8-diamine (**9a**): Yield 67% (0.63 g), yellow crystals; mp 207°C. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.22 (m, 7 H), 2.68 (m, 7 H), 3.14 (m, 3 H), 3.50 (m, 7 H), 6.77 (m, 18 H), 7.7.21 (m, 3 H), 7.31 (m, 4 H), 7.57 (m, 3 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.00 (4-$CH_3C_6H_5$), 32.58 (CH_2), 33.27 (CH_2), 40.88 (NCH_3), 68.17 (CH_2), 69.05 (CH_2), 69.83 (CH_2), 70.62 (CH_2), 115.04, 116.96, 118.28, 118.64, 121.28, 122.15, 122.72, 122.98, 127.24, 127.73, 128.49, 128.72, 128.84, 129.04, 130.60, 131.96, 135.23, 135.32, 139.79, 140.00, 145.55, 147.99, 149.10, 152.91, 156.50. − MS (CI with H_2O); *m/z* (%): 833 (3) [M^+ + 1], 550 (11), 447 (24), 343 (28), 342 (100), 223 (16), 209 (51), 195 (14), 181 (10), 136 (56), 108 (38). − $C_{50}H_{52}N_6O_2S_2$ (833.1): calcd. C 72.12, H 6.25, N 10.10, S 7.69; found C 71.70, H 6.31, N 9.66, S 7.66.

N7,N8-Dimethyl-6,9-bis(4-methylphenyl)-N7,N8-diphenyl-5,10-bis(phenylimino)-1,14,17-trioxa-4,11-dithia-6,9-diaza-7-cyclohenicosene-7,8-diamine (**9b**): Yield 47% (0.46 g), yellow amorphous solid. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 2 H), 2.28 (s, 3 H), 2.32 (s, 1 H), 2.93 (m, 10 H), 3.54 (12 H), 6.96 (m, 28 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.91 (4-$CH_3C_6H_4$), 20.99 (4-$CH_3C_6H_4$), 21.10 (4-$CH_3C_6H_4$), 32.66 (CH_2), 33.86 (CH_2), 40.84 (NCH_3), 68.79 (CH_2), 69.23 (CH_2), 69.96 (CH_2), 70.51 (CH_2), 70.93 (CH_2), 114.95, 116.78, 118.26, 118.56, 121.69, 121.93, 122.26, 122.74, 123.24, 126.77, 127.34, 127.67, 128.26, 128.83, 131.93, 135.15, 135.40, 139.91, 140.25, 145.62, 147.96, 149.17, 153.19, 157.25. − MS (CI with H_2O); *m/z* (%): 877 (7) [M^+ + 1], 447 (100), 223 (50), 182 (15), 93 (25). − $C_{52}H_{56}N_6O_3S_2$ (877.2): calcd. C 71.20, H 6.43, N 9.58, S 7.31; found C 71.67, H 6.58, N 9.78, S 6.96.

N7,N8-Dimethyl-6,9-bis(4-methylphenyl)-N7,N8-diphenyl-5,10-bis(phenylimino)-1,14,17,20-tetraoxa-4,11-dithia-6,9-diaza-7-cyclohexadecene-7,8-diamine (**9c**): Yield 31% (0.32 g), yellow amorphous solid. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.29 (m, 7 H), 2.87 (m, 10 H), 3.35 (m, 15 H), 7.08 (m, 28 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.99 (4-$CH_3C_6H_5$), 32.82 (CH_2), 33.70 (CH_2), 40.85 (NCH_3), 69.14 (CH_2), 69.32 (CH_2), 70.06 (CH_2), 70.33 (CH_2), 70.71 (CH_2), 70.81 (CH_2), 71.09 (CH_2), 114.99, 115.22, 116.75, 118.53, 121.63, 121.76, 122.16, 122.71, 123.22, 126.73, 127.64, 128.44, 128.80, 129.03, 129.49, 140.28, 147.96. − MS (CI with H_2O); *m/z* (%): 920 (8) [M^+], 446 (18), 390 (100), 343 (23), 277 (73). − $C_{54}H_{60}N_6O_4S_2$ (921.3): calcd. C 70.40, H 6.56, N 9.13, S 6.96; found C 70.08, H 6.64, N 9.01, S 7.00.

N4,N5-Dimethyl-3,6-bis(4-methylphenyl)-N4,N5-diphenyl-2,7-bis(phenylimino)-1,8,11,14-tetrathia-3,6-diaza-4-cyclohexadecene-4,5-diamine (**10**): Yield 37% (0.36 g), yellow amorphous solid. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.22 (s, 5 H), 2.36 (m, 9 H), 2.64 (s, 5 H) 2.64 (br. s, 1 H), 2.81 (m, 4 H), 6.26 (d, 2 H), 6.64 (d, 2 H), 6.80 (t, 2 H), 6.91 (m, 7 H), 7.06 (t, 2 H), 7.20 (m, 7 H), 7.31 (t, 2 H), 7.60 (d, 2 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.13 (4-$CH_3C_6H_4$), 29.83 (CH_2), 31.29 (CH_2), 36.49 (CH_2), 40.42 (NCH_3), 114.51, 116.73, 118.13, 122.49, 122.86, 127.26, 127.49, 127.72, 128.10, 128.23, 128.61, 128.81, 128.94, 129.04, 129.15, 131.98, 136.04, 139.59, 145.71, 149.38, 151.60. − MS (CI with H_2O); *m/z* (%): 865 (24) [M^+ + 1], 446 (18), 316 (22), 257 (20), 209 (31), 181 (37), 154 (47), 136 (100), 93 (60). − $C_{54}H_{60}N_6S_2O_2$

(865.2): calcd. C 69.70, H 6.37, N 9.57, S 15.29; found C 69.02, H 6.37, N 9.23, S 15.29.

N6,N7-Dimethyl-5,8-bis(4-methylphenyl)-N6,N7-diphenyl-4,9-bis(phenylimino)-3,6-dithia-5,8,16-triazabicyclo[10.3.1]hexadeca-1(16),6,12,14-tetraene-6,7-diamine (**11**): Yield 35% (0.32 g), pale yellow crystals, mp 145°C. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.21 (s, 6 H), 2.54 (s, 3 H), 2.71 (s, 3 H), 3.31 (d, 1 H), 3.52 (d, 1 H), 3.66 (m, 2 H), 6.98 (m, 31 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.96 (4-$CH_3C_6H_4$), 21.13 (4-$CH_3C_6H_4$), 32.85 (NCH_3), 37.17 (CH_2), 37.67 (CH_2), 40.90 (NCH_3), 114.89, 117.18, 117.79, 118.45, 120.03, 121.21, 121.64, 121.85, 122.01, 122.73, 125.74, 127.56, 128.34, 128.63, 129.60, 130.99, 133.36, 135.50, 136.07, 136.57, 137.32, 139.09, 146.12, 148.20, 148.40, 149.18, 149.37, 157.94, 158.89. − MS (CI with H_2O); *m/z* (%): 822 (12) [M^+ + 1], 447 (12), 223 (11), 136 (100). − $C_{51}H_{47}N_7S_2 \cdot 1.5\ CH_3COCH_3$ (822.7 + 87.1): calcd. C 73.26, H 6.20, N 10.78, S 7.05; found C 73.09, H 6.38, N 10.84, S 7.05.

N4,N5-Dimethyl-3,6-bis(4-methylphenyl)-N4,N5-diphenyl-2,7-bis(phenylimino)-11-[(4-methylphenyl)sulfanyl]-1,8-dithia-3,6,11-triaza-4-cyclotridecene-4,5-diamine (**12**): Yield 33% (0.35 g), yellow crystalline solid, mp 267°C. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.28 (s, 6 H), 2.32 (s, 5 H), 2.75 (s, 8 H), 3.32 (m, 4 H), 6.62 (m, 2 H), 6.96 (m, 14 H), 7.20 (m, 8 H), 7.43 (m, 6 H), 7.63 (m, 2 H). − ^{13}C NMR ($CDCl_3$, 62 MHz): δ = 21.02 (4-$CH_3C_6H_4$), 21.39 (4-$CH_3C_6H_4$), 31.34 (CH_2), 46.68 (CH_2), 116.95, 118.92, 121.18, 123.67, 126.77, 127.72, 129.22, 129.55, 136.23, 136.94, 139.63, 143.17, 147.76. − MS (CI with H_2O); *m/z* (%): 942 (4) [M^+ + 1], 447 (16), 296 (100), 258 (20), 223 (30) 209 (32), 149 (15), 133 (39), 108 (27). − $C_{55}H_{55}N_7O_2S_3$ (942.3): calcd. C 70.10, H 5.88, N 10.41, S 10.21; found C 70.09, H 5.95, N 10.39, S 10.76.

2,2-Dimethyl-6,7-bis(methylanilino)-5,8-bis(4-methylphenyl)-1,3-diphenyl-2,3,4,5,8,9-hexahydro-1H-1,3,5,8,2-tetraazasilonine-4,9-dithione (**13**): Yield 82% (0.71 g), orange crystalline solid, mp 237°C. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.58 (s, 6 H), 2.37 (s, 6 H), 2.96 (s, 6 H), 6.74 (t, 2 H), 6.96 (t, 6 H), 7.10 (d, 6 H), 7.26 (d, 6 H), 7.36 (m, 6 H), 7,58 (br. s, 2 H). − ^{13}C NMR (CD_2Cl_2, 100 MHz): δ = 0.76 [$(CH_3)_2Si$], 20.92 (4-$CH_3C_6H_4$), 35.43 (NCH_3), 117.26, 119.50, 120.04, 120.71, 127.3, 127.72, 128.00, 128.41, 129.74, 130.24, 133.48, 141.45, 143.79, 146.65, 195.77. − MS (CI with H_2O); *m/z* (%): 775 (2) [M^+ + 1], 685 (6), 505 (7), 447 (35), 342 (7), 165 (19), 136 (100), 93 (21). − $C_{46}H_{46}N_6S_2Si$ (775.1): calcd. C 71.32, H 5.94, N 10.85, S 8.27; found C 70.87, H 6.12, N 10.53, S 8.21.

N4,N5,N18,N19-Tetramethyl-3,6,17,20-tetrakis(4-methylphenyl)-N4,N5,N18,N19-tetraphenyl-2,7,16,21-tetrakis(phenylimino)-1,8,15,22-tetrathia-3,6,17,20-tetraaza-4,18-cyclooctacosadiene-4,5,18,19-tetramine (**14a**): Yield 27% (0.24 g), yellow amorphous solid. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.93 (m, 20 H), 2.22 (m, 20 H), 2.74 (br. s, 12 H), 6.99 (m, 56 H). − ^{13}C NMR (CD_2Cl_2, 100 MHz): δ = 20.89 (4-$CH_3C_6H_4$), 21.04 (4-$CH_3C_6H_4$), 28.25 (CH_2), 28.48 (CH_2), 32.50 (CH_2), 33.42 (CH_2), 33.61 (CH_2), 40.79 (NCH_3), 114.88, 116.55, 118.12, 118.36, 121.50, 121.59, 121.92, 122.58, 123.12, 126.56, 127.12, 127.56, 128.21, 128.38, 128.61, 128.84, 130.02, 131.78, 134.90, 135.20, 139.81, 140.29, 145.55, 148.04, 149.20, 149.91, 152.79, 153.08, 153.36, 157.33. − EI MS; *m/z*: 1601.7 [M + H]$^+$. − $C_{100}H_{104}N_{12}S_4$ (1602.3): C 74.96, H 6.54, N 10.49, S 8.00; found C 74.57, H 6.74, N 10.30, S 8.27.

N4,N5,N20,N21-Tetramethyl-3,6,19,22-tetrakis(4-methylphenyl)-N4,N5,N20,N21-tetraphenyl-2,7,18,23-tetrakis(phenylimino)-1,8,17,24-tetrathia-3,6,19,22-tetraaza-4,20-cyclodotriacontadiene-4,5,20,21-tetramine (**14b**): Yield 26% (0.24 g), yellow amorphous solid. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.83 (m, 24 H), 2.20 (br. s, 20 H), 2.72 (br. s, 12 H), 6.97 (m, 56 H). − ^{13}C NMR (CD_2Cl_2, 62 MHz): δ = 20.98 (4-$CH_3C_6H_4$), 28.04 (CH_2), 28.68 (CH_2), 29.70 (CH_2), 32.74 (CH_2), 33.59 (CH_2), 33.88 (CH_2), 40.84 (NCH_3), 114.95, 116.66, 118.18, 121.65, 122.01, 122.56, 123.11, 125.74, 126.71, 127.60, 128.41, 128.64, 128.65, 129.55, 131.88, 135.22, 139.92, 140.37, 145.66, 148.12, 149.30, 153.10. − EI MS; *m/z*: 1657.1 [M + H]$^+$. − $C_{104}H_{112}N_{12}S_4$ (1658.4): calcd. C 75.36, H 6.76, N 10.14, S 7.73; found C 75.29, H 7.05, N 10.27, S 7.90.

N6,N7,N21,N22-Tetramethyl-5,8,20,23-tetrakis(4-methylphenyl)-N6,N7,N21,N22-tetraphenyl-4,9,19,24-tetrakis(phenylimino)-3,10,18,25-tetrathia-5,8,20,23-tetraazatricyclo[25.3.1.1^{12,16}]dotriaconta-1(31),6,12(32),13,15,21,29-octaene-6,7,21,22-tetramine (**14c**): Yield 32% (0.29 g), yellow crystalline solid, mp 251°C. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.63 (m, 14 H), 2.67 (m, 10 H), 3.16 (d, 4 H), 3.42 (d, 4 H), 6.92 (m, 64 H). − ^{13}C NMR (CD_2Cl_2, 62 MHz): δ = 20.98 (4-$CH_3C_6H_4$), 38.49 (CH_2), 40.68 (NCH_3), 114.77, 118.17, 122.17, 123.02, 127.02, 128.22, 128.51, 128.77, 129.65, 131.76, 135.57, 136.33, 139.34, 145.64, 148.82, 151.83. − HR EI MS; *m/z*: 1640.67667 [M]$^+$; calcd. for $C_{104}H_{96}N_{12}S_4$ 1640.67638.

N6,N7,N20,N21-Tetramethyl-5,8,19,20-tetrakis(4-methylphenyl)-N6,N7,N20,N21-tetraphenyl-4,9,18,23-tetrakis(phenylimino)-3,10,17,24-tetrathia-5,8,19,22-tetraazatricyclo[24.2.2.2^{12,15}]dotriaconta-1(28),6,12,14,20,26,29,31-octaene-6,7,20,21-tetramine (**14d**): Yield 59% (0.52 g), yellow crystalline solid, mp 243°C. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.21 (s, 6 H), 2.75 (s, 4 H), 2.83 (br. s, 2 H), 3.03 (d, 2 H), 3.68 (d, 2 H), 6.37 (d, 2 H), 6.47 (s, 4 H), 6.62 (d, 2 H), 6.83 (m, 6 H), 7.02 (m, 6 H), 7.25 (m, 10 H), 7.54 (d, 2 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.04 (4-$CH_3C_6H_4$), 38.00 (CH_2), 40.64 (NCH_3), 114.78, 118.23, 121.72, 122.28, 122.54, 126.98, 127.19, 127.79, 128.30, 128.48, 128.96, 129.21, 129.53, 131.82, 134.56, 135.52, 139.36, 145.50, 149.02, 151.32. − EI MS; *m/z*: 1641.2 [M + H]$^+$. − $C_{104}H_{96}N_{12}S_4$ (1642.30): calcd. C 76.06, H, 5.89, N 10.24, S 7.81; found C 75.81, H 6.22, N 10.13, S 7.80.

N7,N8,N23,N24-Tetramethyl-6,9,22,25-tetrakis(4-methylphenyl)-N7,N8,N23,N24-tetraphenyl-5,10,21,26-tetrakis(phenylimino)-1,14,17,30-tetraoxa-4,11,20,27-tetrathia-6,9,22,25-tetraaza-7,23-cyclodotriacontadiene-7,8,23,24-tetramine (**14e**): Yield 12% (0.11 g), yellow amorphous solid. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.20 (s, 10 H), 2.29 (s, 2 H), 2.47 (br. s, 4 H), 2.72 (br. s, 16 H), 3.08 (m, 16 H), 7.01 (m, 56 H). − ^{13}C NMR (CD_2Cl_2, 100 MHz): δ = 19.43 (4-$CH_3C_6H_4$), 30.75 (CH_2), 31.66 (CH_2), 39.30 (NCH_3), 67.61 (CH_2), 68.01 (CH_2), 68.25 (CH_2), 113.46, 115.21, 116.77, 117.07, 120.09, 120.50, 121.28, 121.76, 125.22, 125.82, 126.17, 126.95, 127.25, 127.53, 127.94, 130.36, 133.68, 133.91, 138.29, 138.57, 144.06, 146.32, 147.44, 151.10, 155.26. − EI MS; *m/z*: 1667.3 [M + H]$^+$. − $C_{100}H_{104}N_{12}O_4S_4$ (1666.3): calcd. C 72.12, H 6.25, N 10.10, S 7.69; found C 71.97, H 6.21, N 10.19, S 7.58.

N6,N7,N21,N22-Tetramethyl-5,8,20,23-tetrakis(4-methylphenyl)-N6,N7,N21,N22-tetraphenyl-4,9,19,24-tetrakis(phenylimino)-3,10,18,25-tetrathia-5,8,20,23,31,32-hexaazatricyclo[25.3.1.1$^{[12][16]}$]dotriaconta-1(31),6,12(32),13,15,21,27,29-octaene-6,7,21,22-tetramine (**14f**). Yield 19% (0.18 g), yellow crystalline solid, mp 177°C. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.22 (m, 14 H), 2.85 (m, 10 H), 3.71 (m, 8 H), 7.11, m, 62 H). − ^{13}C NMR (62 MHz, $CDCl_3$): δ = 21.06 (4-$CH_3C_6H_4$), 21.56 (4-$CH_3C_6H_4$), 33.63 (CH_2), 39.14 (CH_2), 39.73 (CH_2), 41.27 (NCH_3), 115.12, 116.79, 118.94, 122.07, 123.55, 125.65, 127.30, 128.11, 128.57, 129.37, 135.79, 136.97, 137.27, 138.36, 140.50, 146.03, 148.22, 156.34. − HR EI MS; *m/z*: 1642.66694 [M]$^+$; calcd. for $C_{102}H_{94}N_{14}S_4$ 1642.66688.

X-ray Crystallographic Study[13]. – *Crystal Data for* **6a**: $C_{45}H_{42}N_6S_2 \cdot H_2O$, M_r = 749.04 gmol^{-1}, orange prism, size 0.40 × 0.38 × 0.36 mm, triclinic, space group $P\bar{1}$ (No. 2), a = 12.522(1), b = 13.726(1), c = 15.347(1) Å, α = 96.48(1), β = 113.21(1), γ = 112.25(1)°, V = 2134.5(3) Å^3, Z = 2, $\rho_{calcd.}$ = 1.249 gcm^{-3}, μ(Mo-K_α) = 1.69 cm^{-1}, F(000) = 852, 7503 reflections in ±h, −k, ±l, measured in the range 2.59° ≤ Θ ≤ 24.64°, 7170 independent reflections, R_{int} = 0.014, 6216 reflections with $F_o > 4\,\sigma(F_o)$, 498 parameters, 2 restrains, R_{obs} = 0.075, wR_{obs}^2 = 0.209, *GOOF* = 1.043, largest difference peak and hole: 1.312 eÅ^{-3}, −0.87 eÅ^{-3}. – *Crystal Data for* **7a**: $C_{52}H_{48}N_6S_2$, M_r = 816.09 gmol^{-1}, yellow prism, size 0.40 × 0.36 × 0.34 mm, monoclinic, space group $P2_1/n$ (No. 14), a = 12.678(2), b = 23.423(1), c = 16.065(3) Å, β = 91.79(1)°, V = 4768(1) Å^3, Z = 4, $\rho_{calcd.}$ = 1.144 gcm^{-3}, μ(Mo-K_α) = 1.50 cm^{-1}, F(000) = 1736, 10015 reflections in ±h, −k, +l, measured in the range 2.20° ≤ Θ ≤ 26.31°, 9668 independent reflections, R_{int} = 0.021, 7535 reflections with $F_o > 4\,\sigma(F_o)$, 568 parameters, R_{obs} = 0.055, wR_{obs}^2 = 0.153, *GOOF* = 1.099, largest difference peak and hole: 0.39 eÅ^{-3}, −0.24 eÅ^{-3}. – *Crystal Data for* **10**: $C_{50}H_{52}N_6S_4$, M_r = 865.22 gmol^{-1}, orange prism, size 0.20 × 0.15 × 0.10 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 12.492(3), b = 14.528(3), c = 27.472(6) Å, β = 95.55(3)°, V = 4962(2) Å^3, Z = 4, $\rho_{calcd.}$ = 1.158 gcm^{-3}, μ(Mo-K_α) = 2.30 cm^{-1}, F(000) = 1832, 17036 reflections in +h, ±k, ±l, measured in the range 3.25° ≤ Θ ≤ 26.40°, 9866 independent reflections, R_{int} = 0.044, 6291 reflections with $F_o > 4\,\sigma(F_o)$, 541 parameters, R_{obs} = 0.080, wR_{obs}^2 = 0.249, *GOOF* = 1.205, largest difference peak and hole: 1.95 eÅ^{-3}, −0.45 eÅ^{-3}.

☆ Dedicated to Prof. *K. Burger* on the occasion of his 60th birthday.

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[13] Further details of the crystal structure investigations are available on requests from CCDC, 12 Union Road, GB-Cambridge CB2 1EZ, on quoting the depository numbers CCDC-101960 (**6a**), -101961 (**7a**), and -101962 (**10**), the names of the authors, and the journal citation.

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