DOI: 10.1002/ejoc.200800778

Multivalent 1-Oxa-3,5,7-triazahepta-1,3,5-trienes: Synthesis, Structural Properties and Metal Coordination^[‡]

Jan-Bernd Greving,^[a] Henrik Behrens,^[a] Roland Fröhlich,^[a] and Ernst-Ulrich Würthwein*^[a]

Keywords: Ligand design / Oligonitriles / N ligands / Pincer complexes / Ring-opening reaction

Nucleophilic ring opening of bis- and tris(1-oxa-3,5-diazinium) salts **1** with *n*-propylamine leads to the bis- and tris-(armed) oligonitrile derivatives **3** and **8** with secondary amino groups in the side chain. Alternatively, treatment of simple 1-oxa-3,5-diazinium salts **2** with primary and secondary diand triamines offers a convenient pathway for the synthesis of bis- and tris(armed) oligonitriles **4**, **5** and **7**. 2,6-Diaminopyridine furnishes the new pincer-type ligand **6** upon reaction with 1-oxa-3,5-diazinium salt **2a**. Multivalent oligonitriles **4**, **6**, **7** and **8** containing secondary amino groups are able to form intra- and intermolecular hydrogen bonds in the solid state as detected by X-ray crystallography. The oligonitriles **3a,b, 4b,d,h, 6** and **7a** form coordination complexes with various Zn^{II} , Cu^{II} , Co^{II} , Ni^{II} and Pd^{II} salts acting as bidentate ligands to give six-membered chelates of 1:1, 1:2 and 2:2 ligand/metal ion ratios. More complex structures are obtained from pincer ligand **6** with $PdCl_2$ [compound **6**·(**PdCl_2**)₂] and from the tridentate ligand **7a** in reactions with Ni(ClO₄)₂ (compound **9**). All new complexes were characterized by Xray crystallography.

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Introduction

In recent years, oligonitriles as heteroanalogues of polyacetylenes have found our synthetic and theoretical interest for various reasons. Due to the polyunsaturated chain of adjacent C=N units, special electronic and molecular structures as well as interesting redox and NLO properties are observed.^[1] These oligomers offer oxygen and nitrogen lone pairs as potential binding sites for metal complexation.^[1,2] In particular, branched pyridine-based pincer ligands (Scheme 1) have found applications as powerful ligands for the complexation of various transition metal ions.^[3] Such novel pincer-type ligands are thermally, moisture- as well as air-stable, and their palladium complexes display high catalytic activity, e.g. in Suzuki–Miyaura cross-coupling reactions.



Scheme 1.

[‡] Unsaturated Hetero Chains, XVI. Part XV: Ref.^[12]

 [a] Organisch-Chemisches Institut, Westfälische Wilhelms-Universität, Corrensstraße 40, 48149 Münster, Germany

Fax: +49-251-83-39772 E-mail: wurthwe@uni-muenster.de

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The shorter homologues of oligonitriles, e.g. 1,3,5-triazapentadienes^[4] and *N*-acylamidines^[5] as nitrogen analogues of the intensively investigated β -diketimines and β -imino ketones, respectively, have also found applications in coordination chemistry, as they are quite potent bidentate chelating ligands.^[6,7] In general, treatment of these ligands with transition metal ions leads to six-membered chelate complexes. These compounds also show activity as pre-catalysts in Heck, Suzuki–Miyaura and Sonogashira cross-coupling reactions.^[4,5]

In this paper we extend our studies on oligonitriles to such novel polyfunctional bis- and tris(armed) derivatives, which may find use in supramolecular chemistry. For their synthesis we are describing two different, yet alternative routes for examples with two or three binding sites of the 1-oxa-3,5,7-triazahepta-1,3,5-triene type. Using both complementary routes, we obtained the title compounds containing two or three nonplanar, three-dimensional C=N-C=N-C=O chains, which are interconnected by various flexible or stiff, aliphatic or aromatic linkers. As in the other known examples, each chain with its lone pairs at the nitrogen and oxygen atoms is expected to serve as potent multidentate ligand, thus building up a multivalent complexation environment. Furthermore, the numerous C=N bonds may give rise to π -complexation. Depending on one hand on the nature of the spacer between the chains and on the other hand on the transition metal ion, it was possible to synthesise both mononuclear and dinuclear metal complexes with individual or cooperative properties. The structures in the solid state of some of the new ligands and all of the new complexes were studied by X-ray diffraction.

Results and Discussion

Synthesis of the Di- and Trifunctional 1-Oxa-3,5,7-triazaheptatrienes

For a detailed study of the properties of di- and trifunctional oligonitriles with multiple 1-oxa-3,5,7-triazaheptatriene subunits we developed two alternative synthetic approaches based on the nucleophilic ring opening reaction of 1-oxa-3,5-diazinium salts, as first reported by Fuks, Strebelle and Wenders,^[8] and then further investigated in our group.^[9] Both these synthetic pathways are based on the modular use of amines and 1-oxa-3,5-diazinium salts. On one hand monoamines as nucleophiles were treated with bis- and tris(1-oxa-3,5-diazinium) salts 1 as the respective bis- and tris(electrophiles), leading to the corresponding polyfunctional 1-oxa-3.5-diazahexatriene derivatives 3 with peripheral amino groups at carbon atom C6, originating from the applied amine. On the other hand, we applied diand triamines as bis- or tris(nucleophiles) in ring opening reactions of simple 1-oxa-3,5-diazinium salts 2 for the synthesis of the respective 1-oxa-3,5,7-triazahepta-1,3,5-trienes 4 (Scheme 2), where the amino functions (N7) are part of the molecular backbone.

The bis(electrophilic) pathway starts with the synthesis of bis(1-oxa-3,5-diazinium) salts $1a-c^{[10]}$ from dicarbonyl

dichlorides like terephthalic dichloride, adipic dichloride or sebacic dichloride, disubstituted cyanamides and a Lewis acid (tin tetrachloride in dichloromethane as solvent or neat tin tetrachloride). The subsequent nucleophilic ring opening by treatment with *n*-propylamine leads to the bis(armed) compounds **3a–c** (Scheme 3) in 37 to 79% yield.

On the other hand, the use of monoacyl chlorides, cyanamides and Lewis acids in the first reaction step leads to simple 1-oxa-3,5-diazinium salts 2.^[8,9] Treatment of such heterocycles (**2a**) with suitable diamines (aliphatic diamines, *trans*-1,2- and *trans*-1,4-cyclohexanediamines and *m*- and *p*xylylenediamines) provides access to two-armed ligands **4a**– **h** (Scheme 4) in 34–65% yield.





Scheme 2.

 $4 \text{ R-C} \equiv N \xrightarrow{2 \text{ SnCl}_4}_{1 \text{ h, 150 °C}} \frac{1}{1 \text{ h, 150 °C}} \xrightarrow{N \text{ N}}_{1 \text{ a-c}} 2 \frac{\text{SnCl}_5}{1 \text{ a-c}} \xrightarrow{N \text{ N}}_{R} \xrightarrow{2 \text{ nPr-NH}_2}_{-2 \text{ HSnCl}_5} \xrightarrow{N \text{ HPr R}}_{L} \frac{1}{2 \text{ a-c}} \xrightarrow{N \text{ HPr R}}_{L} \frac$

Scheme 3.



Scheme 5.

In order to extend the scope of this bis(nucleophilic) route, 1-oxa-3,5-diazinium salts **2a** and **2b** were also treated with secondary amines like piperazine, N,N'-dimethylethylenediamine or N,N'-diethyl- and N,N'-diphenyl-*p*-xylylenediamine. In all cases, we obtained the respective divalent oligonitriles **5a–e** in yields of 9–79% (Scheme 5, Table 1). Sterically demanding nucleophiles gave the lowest yields.

Table 1. Substitution patterns for compounds 2 and 5 and (isolated) yields for compounds 5.

2	5	R ¹	R ²	-Z-	R ³	Yield
a	a	NEt ₂	Ph	-(CH ₂ CH ₂)-	-(CH ₂ CH ₂)-	77%
a	b	NEt ₂	Ph	-(CH ₂ CH ₂)-	Me	79%
a	c	NEt ₂	Ph	-(1,4-CH ₂ C ₆ H ₄ CH ₂)-	Et	50%
b	d	$4-BrC_6H_4$	$4-BrC_6H_4$	-(1,4-CH ₂ C ₆ H ₄ CH ₂)-	Et	10%
a	e	NEt ₂	Ph	-(1,4-CH ₂ C ₆ H ₄ CH ₂)-	Ph	9%
b	f	$4-BrC_6H_4$	$4\text{-}BrC_6H_4$	$-(1,4-CH_2C_6H_4CH_2)-$	Ph	12%

Interestingly, this approach is also applicable to the synthesis of pincer ligands. Treatment of 2a with 2,6-diaminopyridine affords compound 6, which for the first time offers seven adjacent C–N subunits with two terminal carbamoyl functions (Scheme 6). This type of compounds may well serve as a polyvalent ligand for metal coordination (see below).



Scheme 6.

For the synthesis of oligonitrile derivatives with three arms we also used the two approaches mentioned above. By treatment of 1,3,5-oxadiazinium salts 2 with a suitable triamine we were able to prepare a series of crystalline tris-(armed) 1-oxa-3,5-diazahexatrienes 7a-d with a different number and locations of amino groups and, consequently, differing electronic properties, in yields of 18-63% (Scheme 7).

In an analogous manner, tris(electrophiles) like $1d^{[11]}$ react with primary amines to give the corresponding tris-(armed) 1-oxa-3,5-diazahexatriene derivative 8 (Scheme 8)



Scheme 7.



Scheme 8.

in 37% yield. The crystal diffraction study of 1d, carried out in our laboratory, indicates a perfect planar molecular structure of the trication of 1d.

Structural Properties of the Di- and Trifunctional 1-Oxa-3,5,7-triazaheptatrienes

Recently,^[12] we reported on the formation of hydrogenbonded superstructures, which were observed in the case of monofunctional oligonitriles containing primary or secondary amino groups. In those structures intermolecular hydrogen bonds were formed by the amine hydrogen atom of one molecule and the carbonyl oxygen atom of the neighbouring molecules as hydrogen-bond acceptors. Analogously, oligonitriles containing secondary amino groups like **4**, **6**, **7** and **8** are expected to form intra- and intermolecular hydrogen bonds. Indeed, such hydrogen bonds are observed in the solid state by X-ray diffraction for **4d**,**g**,**h** and **7b** causing interesting aggregation phenomena in the solid state.

Due to the difunctional nature of the 1,4-diaminocyclohexane-based oligonitrile **4g** four intermolecular N–H···O hydrogen bonds to four different molecules are found re-



Figure 1. Molecular structure of **4g** in the solid state (top) and aggregation by hydrogen bonding (bottom).



sulting in a supramolecular grid (Figure 1). For 4g, in the $-N-H\cdots O=C$ subunit the N-O distance amounts to 3.058 Å.

In contrast, due to the close neighbourhood of the oligonitrile chains, **4h** prefers intramolecular N–H···O interactions (N–O distance 2.824, 2.995 Å) between the nonplanar, strongly twisted three-dimensional chains resulting in a doubly bridged pseudo-polyazamacrocyle (Figure 2) without intermolecular aggregation.



Figure 2. Molecular structure of 4h in the solid state.

Intramolecular interactions are also observed in solidstate structures for the examples of the two trimethylenebased oligonitriles **4b** and the corresponding tris(armed) compound **7b**. In **7b**, due to the flexibility of the spacers, the amine protons are in plane with the carbonyl oxygen atoms and contribute to three intramolecular hydrogen bonds resulting in three pseudo-polyazamacrocycles, which are interconnected by the central tris(2-aminoethylamine) unit (Figure 3). For **7b**, the N–O distances are found to be between 2.827 and 2.860 Å and for **4b** at 2.775 Å.



Figure 3. Molecular structure of 7b in the solid state.

Complexation Reactions

Various metal complexes of difunctional oligonitriles were easily obtained by co-dissolving the metal salts with the ligands 3–7 and subsequent crystallization, which was usually induced by adding less polar solvents to the reaction mixture.

Thus, **3a** and **3b** form a common type of a dinuclear chelate complex with Zn^{II}, Co^{II} und Cu^{II} halogenides, independent of the nature of the metal salt and the linker separating the two functional oligonitrile chains (Scheme 9).



Scheme 9.

According to Scheme 9 and Figures 4 and 5 the metal centres coordinate in all cases to the oxygen atom of the carbamoyl mojety and to the nitrogen atom N5 forming a six-membered non-planar chelate structure with a tetravalent metal centre. Interestingly, the metal-metal distances of **3a·ZnBr**₂ (Figure 4) and **3a·CoCl**₂ (Zn–Zn 11.561 Å; Co– Co 11.487 Å) are longer than in the complexes 3b·ZnBr₂ and **3b**·CuCl₂ (Zn–Zn 8.959 Å; Cu–Cu 7.686 Å). This observation might be explained by the stiffness of the phenylderived spacer in 3a. Consequently, the metal ions of 3b·ZnBr2 and 3b·CuCl2 are bonded more on the inside of the ligand, while 3a acts more as an exo-receptor. As expected, the Zn^{II} and Co^{II} ions show a tetrahedral environment, whereas in 3b·CuCl₂ a strongly distorted Cu^{II} ligand sphere is observed (Figure 5).



Figure 4. Molecular structures of 3a·ZnBr₂ in the solid state.

Due to the mobility of the amine protons the multiarmed oligonitriles 4 with secondary amines as part of the CN backbone offer an even larger structural variety. Depending on the nature of the spacer between the chains it is possible to synthesize 1:1 as well as 2:2 metal complexes (Scheme 10).

In the dinuclear 2:2 oligonitrile/metal complex $4b \cdot Ni(ClO_4)_2$ two of the bis(armed) oligonitriles 4b act as bis(bidentate) chelate ligands with the individual oligonitrile chains linked together by two octahedrally coordinated nickel(II) ions (Figure 6). Here, the metal-metal distance amounts to 7.75 Å.



Figure 5. Molecular structures of 3b·CuCl₂ in the solid state.





Figure 6. Molecular structure of 4b·Ni(ClO₄)₂ in the solid state.

If the alkyl spacer between the individual oligonitrile chains of the ligand is elongated to eight methylene groups (4d), cooperative effects between both oligonitrile chains are

observed. In this case the bis(armed) oligonitrile ligand acts as a tetradentate "pincer" ligand and forms a cyclic structure $[4d\cdot Ni(NO_3)_2]$ coordinating the metal centre. This complex is further stabilized by intramolecular N–H···O interactions, caused by the amine protons and the coordinated nitrate ions (Figure 7).



Figure 7. Molecular structure of 4d·Ni(NO₃)₂ in the solid state.

Furthermore, we were also able to isolate a chiral nickel(II) complex, 4h·Ni(NO₃)₂, (Figure 8) from the chiral *trans*-1,2-cyclohexanediamine-derived ligand 4h and nickel(II) nitrate in acetonitrile after precipitation with diethyl ether in 88% yield. The structure displays the mutual coordination abilities of both triazapentadienes and N-acylamidines. Hence, one chain coordinates using the oxygen atom of the carbamoyl mojety and the nitrogen atom N5 (as in 3a·ZnBr₂ and 3a·CoCl₂, Figure 4). The second binding site coordinates to the nickel ion involving two nitrogen atoms, thus forming a typical six-membered chelate ring as in 1,3,5-triazapentadiene complexes described in the literature.^[4] This coordination mode produces an additional seven-membered chelate ring incorporating the cyclohexyl moiety.



Figure 8. Molecular structure of 4h·Ni(NO₃)₂ in the solid state.

Some of the polyvalent, structurally flexible ligands are able to interact with different metal ions, each in an individual manner. Thus, treatment of the pincer ligand **6** with bis(benzonitrile)palladium(II) dichloride yielded to the dinuclear coordination compound **6**·(PdCl₂)₂, whereas nickel(II) chloride produced the mononuclear complex **6**·Ni(NO₃)₂ (Scheme 11).



Scheme 11.

The Pd^{II} centres of $6 \cdot (PdCl_2)_2$ are coordinated by four different nitrogen donor atoms of the symmetrical, bifunctional ligand 6 (Figure 9). Each binding site forms a sixmembered chelate ring. Similar as in the other dinuclear complexes, the Pd–Pd distance of 3.338 Å excludes any stronger metal–metal interaction.



Figure 9. Molecular structure of 6 (PdCl₂)₂ in the solid state.

The solid-state structure of the octahedral complex $6 \cdot Ni(NO_3)_2$ shows many similarities with other pyridinebased pincer complexes reported recently from our laboratory:^[3] here, the ligand 6 acts in a pentadentate fashion, while one solvent molecule (methanol) occupies the sixth coordination site (Figure 10).



Figure 10. Molecular structure of the dication of $6 \cdot Ni(NO_3)_2$ in the solid state.

Similar to **4h**, the tris(armed) ligand **7a** forms a 1:1 tris-(chelate) complex, **7a**·Ni(ClO₄)₂, featuring a 1,3,5-triazapentadiene-derived chelate ring as well as a typical *N*-acylamidine coordination (Scheme 12, Figure 11). Interestingly, one of the three arms of the ligand is shortened during the complexation reaction: If **7a** is treated with nickel(II) perchlorate and triethylamine in methanol as solvent at 55 °C, one of the three diethylcarbamoyl groups is cleaved off by nucleophilic attack producing an *N*-benzoylbenzamidine subunit resulting in compound **9** in 37% yield. Another interesting feature of this complex is a free oligonitrile chain not used for coordination, which possibly can be used for further complexation reactions.



Scheme 12.



Figure 11. Molecular structure of 9 in the solid state.

Conclusions

We have developed two alternative synthetic pathways for the synthesis of branched bis- and tris(armed) oligonitrile compounds. They are both based on nucleophilic ring opening reactions of 1-oxa-3,5-diazinium salts. Thus, on one hand reactions of bis- and tris(1-oxa-3,5-diazinium) salts 1 with *n*-propylamine lead to the bis- and tris(armed) oligonitrile derivatives 3 and 8 with secondary amino groups in the side chain. On the other hand, treatment of simple 1-oxa-3,5-diazinium salts 2 with primary and secondary di- and triamines provides access to the bis- and tris(armed) oligonitriles 4, 5 and 7. 2,6-Diaminopyridine has been employed for a new pincer-type ligand **6** in the reaction with 1-oxa-3,5-diaziniuim salt **2a**. Aggregation properties of the multivalent oligonitriles **4**, **6**, **7** and **8** containing secondary amino groups have been recognized by X-ray crystallography. These compounds are able to form intra- and intermolecular hydrogen bonds in the solid state. The oligonitriles **3a,b**, **4d,h**, **6** and **7a** form coordination complexes with various Zn^{II}, Cu^{II}, Co^{II}, Ni^{II} and Pd^{II} salts acting as bidentate ligands to give six-membered chelates. More complex structures are obtained from pincer ligand **6** with PdCl₂ [compound **6**·(PdCl₂)₂] and from the tridentate ligand **7a** in reactions with Ni(ClO₄)₂ [compound **7a**·Ni(ClO₄)₂]. At present, we are interested in possible catalytic properties of the coordination compounds in organic synthesis.

Experimental Section

Materials and Methods: IR: Nicolet 5DXC. ¹H NMR: Bruker WM 300 (300.13 MHz), Bruker AMX 400 (400.13 MHz), Varian IN-OVA 500 (499.8 MHz) and Varian Unity 600 (599.86 MHz); internal reference tetramethylsilane. ¹³C NMR: Bruker WM 300 (75.47 MHz), Bruker AMX 400 (100.61 MHz), Varian INOVA 500 (125.7 MHz) and Varian Unity 600 (150.84 MHz); internal reference solvent. CHN elemental analysis: Elementar Vario El III. Melting points are uncorrected. All solvents were rigorously dried by standard methods. When necessary, the experiments were carried out with complete exclusion of moisture (argon, septum-syringe technique) in glassware that had been thoroughly dried by repeated heating under argon and subsequent evacuation.

2,2',2''-(1,3,5-Phenylene)tris[4,6-bis(diisopropylamino)-1-oxa-3,5-diazinium] Tripentachlorostannate (1d): According to the procedure described by Tashtoush and Al-Talib^[11] **2b** was prepared from trimesic trichloride (2.66 g, 10.0 mmol), diisopropylcyanamide (7.60 g, 60.0 mmol) and tin tetrachloride (2.4 mL, 30.0 mmol). Yield: 14.87 g (8.3 mmol, 83%, ref.^[11] 87%), orange solid, m.p. 184 °C (ref.^[11] 187–189 °C).

X-ray Crystal Structure Analysis of 1d:^[13] Formula $C_{51}H_{87}N_{12}O_3\cdot 3SnCl_5OH_2\cdot CH_3CN$, M = 1899.25, orange crystal $0.20 \times 0.20 \times 0.15$ mm, a = 49.978(1), b = 9.972(1), c = 17.696(1) Å, V = 8819.3(10) Å³, $\rho_{calcd.} = 1.430$ gcm⁻³, $\mu = 1.343$ mm⁻¹, empirical absorption correction ($0.775 \le T \le 0.824$), Z = 4, orthorhombic, space group *Pnma* (No. 62), $\lambda = 0.71073$ Å, T = 198(2) K, ω and ϕ scans, 60198 reflections collected ($\pm h, \pm k, \pm l$), [($\sin \theta / \lambda$] = 0.67 Å⁻¹, 10946 independent ($R_{int} = 0.044$) and 8289 observed reflections [$I \ge 2\sigma(I)$], 499 refined parameters, R = 0.059, $wR^2 = 0.211$, max./min. residual electron density 2.32/–1.08 eÅ⁻³, the remaining density (probably disordered acetonitrile) could not be described in a chemically meaningful way, hydrogen atoms calculated and refined as riding atoms.

2,4,6-Tris(4-bromophenyl)-1-oxa-3,5-diazinium Pentachlorostannate (2b): In analogy to the procedure described by Tashtoush and Al-Talib^[10] **2b** was prepared from 4-bromobenzoic chloride (32.10 g, 147 mmol), 4-bromobenzonitrile (53.30 g, 294 mmol) and tin tetra-chloride (17.2 mL, 147 mmol). Yield: 111.79 g (134.0 mmol, 91%), yellow solid, m.p. 195 °C. IR (KBr): $\tilde{v} = 3085$ (w, CH_{arom}), 1733 (m, C=O), 1647 (m, C=N), 1614 (m, C=N), 1585 (s, C=C), 1571 (s, C=C), 1544 (m), 1490 (m), 1465 (m), 1446 (m), 1419 (m), 1396 (m), 1375 (m), 1332 (m), 1299 (m), 1224 (m), 1174 (m), 1114 (w), 1066 (m), 1004 (m), 935 (w), 835 (w), 792 (m), 748 (w), 723 (w), 661

(w), 644 (w), 622 (w) cm⁻¹. $C_{21}H_{12}Br_3Cl_5N_2OSn$ (844.00): calcd. C 29.88, H 1.43, N 3.32; found C 30.14, H 1.68, N 3.21.

1-Oxa-3,5-diazahexatrienes 2–5. General Procedure: A suspension of the 1-oxa-3,5-diazinium salt^[1,10,12] in dry dichloromethane was treated with the respective amine at 0 °C. The reaction mixture was warmed slowly to room temperature and was then stirred overnight. The next day, the resulting solution was washed with sodium hydroxide solution, and the aqueous layer was extracted three times with dichloromethane. The combined organic layers were dried with potassium sulfate, and the solvent was removed in vacuo. The crude product was purified by column chromatography or recrystallisation.

1,4-Bis[3,5-bis(diisopropylamino)-1-propylamino-6-oxa-2,4-diaza-1,3,5-hexatrienyl]benzene (3a): From 2,2'-(1,4-phenylene)bis[4,6bis(diisopropylamino)-1-oxa-3,5-diazinium] dipentachlorostannate (1a)^[10] (4.52 g, 3.7 mmol) and *n*-propylamine (1.5 mL, 14.8 mmol). The crude product was purified by column chromatography with tert-butyl methyl ether as eluent. Yield: 2.21 g (2.9 mmol, 79%), colourless solid, m.p. 154 °C. $R_{\rm f} = 0.06$ (*tert*-butyl methyl ether). ¹H NMR (300.13 MHz, CDCl₃): δ = 1.05–1.10 (br., 18 H, NCH₂CH₂CH₃/NCHCH₃), 1.32-1.42 (br., 36 H, NCHCH₃) 1.73-1.80 (br., 4 H, NCH₂CH₂CH₃), 3.49–3.55 (br., 4 H, NCH₂CH₂CH₃), 3.74–4.17 (br., 8 H, NCHCH₃), 5.03 (br., 2 H, NH), 7.67 (s, 4 H, CH_{arom}) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 11.2, 20.9, 22.6, 44.1, 46.1 (br., CH_{aliph}), 127.3 (CH_{arom}), 136.8 $(i-C_{arom.})$, 156.8, 158.1 (CN), 161.9 (CO) ppm. IR (KBr): $\tilde{v} = 3298$ (m, NH), 3066 (s, CH_{arom}), 2964 (s, CH_{aliph}), 2927 (s, CH_{aliph}), 2873 (s, CH_{aliph}), 1623 (vs, C=O/C=N), 1569 (vs, C=C), 1519 (s), 1467 (s), 1438 (s), 1431 (s), 1369 (s), 1313 (s), 1220 (s), 1149 (m), 1130 (m), 1055 (sh), 1041 (m), 966 (w), 919 (w), 885 (w), 860 (w), 846 (w), 781 (w), 761 (w), 653 (w), 611 (w), 580 (w), 511 (w) cm⁻¹. MS (EI, 70 eV): m/z (%) = 753 (1) [M]⁺, 653 (2) [M – N*i*Pr₂]⁺, 551 (7) $[M - 2 NiPr_2]^+$, 507 (2), 400 (11), 340 (80), 296 (9), 171 (9), 128 (30) [*i*Pr₂NCO]⁺, 100 (20) [*i*Pr₂N]⁺, 86 (100), 58 (20) [NHPr]⁺. C42H76N10O2 (753.13): calcd. C 66.98, H 10.17, N 18.60; found C 67.21, H 10.02, N 18.48.

1,4-Bis[3,5-bis(dimethylamino)-1-propylamino-6-oxa-2,4-diaza-1,3,5-hexatrienyl]butane (3b): From 2,2'-(1,4-butylene)bis[4,6bis(dimethylamino)-1-oxa-3,5-diazinium] dihexachloroantimonate (**1b**)^[10] (4.41 g, 4.2 mmol) and *n*-propylamine (1.5 mL, 16.8 mmol). The crude product was purified by column chromatography with acetone with 3% triethylamine as eluent. Yield: 1.15 g (2.3 mmol, 50%), colourless solid, m.p. 173 °C. $R_{\rm f} = 0.14$ (acetone with 3%) triethylamine). ¹H NMR (300.13 MHz, CDCl₃): $\delta = 0.80-0.85$ (br., 6 H, NCH₂CH₂CH₃), 1.44–1.51 (m, 8 H, NCH₂CH₂CH₃/ CH₂CH₂CH₂CH₂), 2.19–2.24 (br., 4 H, CH₂CH₂CH₂CH₂), 2.85 (br., 24 H, NCH₃), 3.07-3.12 (br., 4 H, NCH₂CH₂CH₃), 5.73 (br., 2 H, NH) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 11.3, 22.2, 25.4, 29.1, 32.1, 37.0, 43.0 (br., CH_{aliph.}), 159.8, 160.1 (CN), 164.0 (CO) ppm. IR (KBr): $\tilde{v} = 3243$ (m, NH), 2927 (m, CH_{aliph}), 2886 (m, CH_{aliph.}), 2848 (w, CH_{aliph.}), 1619 (s, C=O), 1610 (s, C=N), 1552 (s), 1521 (s), 1475 (s), 1434 (s), 1386 (s), 1342 (s), 1270 (m), 1193 (m), 1176 (m), 1139 (m), 1079 (w), 1033 (m), 921 (w), 883 (w), 815 (w), 779 (w), 730 (w), 663 (w), 636 (w), 553 (w), 482 (w) cm⁻¹. MS (EI, 70 eV): m/z (%) = 508 (5) [M]⁺, 464 (4) [M - NMe₂]⁺, 419 (64) [M - 2 NMe₂]⁺, 360 (6), 306 (17), 264 (21), 223 (23), 210 (17), 193 (15), 139 (13), 114 (19), 72 (100). C₂₄H₄₈N₁₀O₂ (508.71): calcd. C 56.67, H 9.51, N 27.53; found C 56.61, H 9.38, N 27.47.

1,8-Bis[3,5-bis(dimethylamino)-1-propylamino-6-oxa-2,4-diaza-1,3,5-hexatrienyl]octane (3c): From 2,2'-(1,8-octylene)bis[4,6-bis(dimethylamino)-1-oxa-3,5-diazinium] dihexachloroantimonate (**1c)**^[10] and *n*-propylamine (9.8 mL, 120.0 mmol). The crude prod-



uct was purified by column chromatography with tert-butyl methyl ether as eluent. Yield: 6.21 g (11.0 mmol, 37%), colourless solid, m.p. 138 °C. $R_f = 0.15$ (*tert*-butyl methyl ether). ¹H NMR $(300.13 \text{ MHz}, \text{CDCl}_3): \delta = 0.89-0.94 \text{ (m, 6 H, NCH}_2\text{CH}_2\text{CH}_3),$ 1.25 (br., 8 H, CH₂), 1.48 (br., 4 H, CH₂), 1.50-1.63 (m, 4 H, NCH₂CH₂CH₃), 2.25–2.30 (br., 4 H, CH₂), 2.95 (br., 24 H, NCH₃), 3.20 (br., 4 H, NCH₂CH₂CH₃), 5.46 (br., 2 H, NH) ppm. ¹³C NMR $(75.47 \text{ MHz}, \text{ CDCl}_3): \delta = 11.3 (\text{NCH}_2\text{CH}_2\text{CH}_3), 22.2, 26.5, 28.9,$ 29.1, 33.1, 37.1, 43.1 (CH₂, NCH₃, NCH₂CH₂CH₃), 160.2, 161.3 (CN), 163.2 (CO) ppm. IR (KBr): $\tilde{v} = 3239$ (m, NH), 2936 (m, CH_{aliph.}), 2893 (m, CH_{aliph.}), 2852 (w, CH_{aliph.}), 1623 (s, C=O), 1606 (s, C=N), 1555 (s), 1523 (s), 1468 (s), 1441 (s), 1385 (s), 1312 (s), 1289 (m), 1182 (m), 1176 (m), 1140 (m), 1082 (w), 1027 (m), 929 (w), 874 (w), 817 (w), 780 (w), 746 (w), 667 (w), 656 (w), 548 (w), 482 (w) cm⁻¹. MS (EI, 70 eV): m/z (%) = 474 (8) [M – 2 NMe₂]⁺, 431 (5) [474 – Pr]⁺, 389 (1) [431 – Pr]⁺, 362 (2), 320 (11), 279 (63), 223 (16), 209 (100), 154 (42), 114 (11), 71 (31). C₂₈H₅₆N₁₀O₂ (564.81): calcd. C 59.54, H 9.99, N 24.80; found C 59.38, H 9.94, N 24.68.

N,N'-Bis(3,5-dimorpholino-1-phenyl-2,4-diaza-6-oxa-1,3,5-hexatrienyl)ethylenediamine (4a): From a solution of 2-(diethylamino)-4,6diphenyl-1,3,5-oxadiazinium pentachlorostannate (2a)^[1] (6.07 g, 10.0 mmol) in 40 mL of dry dichloromethane and ethylenediamine (0.30 g, 5.0 mmol). Purification by medium-pressure chromatography (cyclohexane/ethyl acetate, 2:1 + 5% of triethylamine) and recrystallisation from acetone. Yield: 2.18 g (3.3 mmol, 65%), colourless solid, m.p. 208 °C. $R_{\rm f} = 0.36$ (cyclohexane/ethyl acetate, 2:1 + 5% of triethylamine). ¹H NMR (400.13 MHz, CDCl₃): δ = 0.85-0.92 (m, 12 H, CH₃), 1.86 (br., 1 H, NH), 2.83 [s (br.), 4 H, NCH₂CH₃], 2.96 (q, ³J = 7.2 Hz, 4 H, NHCH₂), 3.49 [s (br.), 4 H, NCH₂CH₃], 7.18–7.39 (m, 12 H, CH_{arom}), 7.55–7.57 (m, 4 H, o-CH_{arom.}), 8.03-8.05 (m, 4 H, o-CH_{arom.}) ppm. ¹³C NMR $(100.61 \text{ MHz}, \text{ CDCl}_3): \delta = 13.3, 13.5 (CH_3), 38.9 (NCH_2), 39.7,$ 41.5 (NCH₂CH₃), 127.6, 127.7, 128.1, 128.6, 130.1, 130.3, (CH_{arom.}), 134.3, 137.8 (*i*-C_{arom.}), 159.8 163.4 (CN), 163.8 (CO) ppm. IR (KBr): \tilde{v} = 3340 (m, NH), 3062 (w, CH_{arom}), 3026 (w, CH_{arom}), 2972 (m, CH_{aliph}), 2925 (m, CH_{aliph}), 2868 (w, CH_{aliph}), 1598 (vs, C=O), 1564 (vs, C=C), 1539 (vs, C=C), 1490 (m, C=C), 1463 (s), 1452 (s), 1429 (s), 1415 (s), 1375 (s), 1359 (s), 1313 (s), 1299 (m), 1272 (vs), 1224 (m), 1193 (w), 1159 (m), 1130 (m), 1099 (w), 1080 (w), 1070 (w), 1047 (w), 896 (m), 846 (w), 810 (w), 773 (m), 707 (m), 692 (s), 663 (m) cm⁻¹. MS (ESI): m/z = 671 [M + H]⁺, 379 [C₂₃H₃₀N₄OH]⁺. HR ESI MS [M + H]⁺: calcd. 671.3816; found 671.3817. $C_{40}H_{46}N_8O_2$ (670.37): calcd. C 71.62, H 6.91, N 16.70; found C 71.41, H 6.91, N 16.32.

N,N'-Bis[5-(diethylamino)-1,3-diphenyl-2,4-diaza-6-oxa-1,3,5-hexatrienyl]-1,3-propylenediamine (4b): From 2-(diethylamino)-4,6-diphenyl-1,3,5-oxadiazinium pentachlorostannate (2a)^[1] (6.07 g, 10.0 mmol) in dry dichloromethane (40 mL) and 1,3-diaminopropane (0.37 g, 5.0 mmol). The crude solid product was purified by recrystallisation from acetone. Yield: 1.71 g (2.5 mmol, 50%), colourless solid, m.p. 148 °C. ¹H NMR (400.13 MHz, CDCl₃): δ = 1.01 (t, ${}^{3}J$ = 6.6 Hz, 6 H, CH₃), 1.09 (t, ${}^{3}J$ = 7.8 Hz, 6 H, CH₃), 2.23 (br., 2 H, CH₂), 2.78 (q, ${}^{3}J$ = 7.1 Hz, 4 H, NCH₂CH₃), 3.06 $(q, {}^{3}J = 7.8 \text{ Hz}, 4 \text{ H}, \text{NCH}_{2}\text{CH}_{3}), 3.78 (br., 4 \text{ H}, \text{NCH}_{2}), 7.03-7.42$ (m, 12 H, CH_{arom}), 7.40–7.43 (m, 4 H, o-CH_{arom}), 7.93–7.96 (m, 4 H, *o*-CH_{arom}) ppm. ¹³C NMR (100.63 MHz, CDCl₃): δ = 13.8 (CH₃), 26.8 (CH₂), 39.9, 40.6, 41.5 (NCH₂), 127.8, 128.2, 128.6, 130.1, 130.3, (CH_{arom}), 135.0, 137.9 (*i*-C_{arom}), 158.3, 163.1 (CN), 164.0 (CO) ppm. IR (KBr): $\tilde{v} = 3264$ (br., NH), 3064 (w, CH_{arom}), 2969 (m, CH_{aliph}), 2930 (m, CH_{aliph}), 1596 (br., C=O), 1573 (br., C=N), 1534 (br., C=N), 1489 (w, C=C), 1460 (br), 1418 (m), 1376 (s), 1313 (m), 1276 (vs), 1226 (w), 1154 (w), 1092 (w), 1023 (w),

978 (w), 907 (w), 811 (w), 773 (m), 693 (s), 659 (w), 605 (w), 537 (w) cm⁻¹. MS (EI, 70 eV): m/z (%) = 684 (8) [M]⁺, 613 (15) [M – NEt₂]⁺, 539 (6) [M – 2(NEt₂)]⁺, 290 (32) [C₁₈H₁₆N₃O]⁺, 213 (5.8) [C₁₂H₁₁N₃O]⁺. C₄₁H₄₈N₈O₂ (684.88): calcd. C 71.90, H 7.06, N 16.36; found C 71.59, H 6.80, N 16.32.

X-ray Crystal Structure Analysis of 4b:^[13] Formula C₄₁H₄₈N₈O₂, M = 684.87, colourless crystal $0.30 \times 0.20 \times 0.20$ mm, a = 17.960(1), b = 13.800(1), c = 16.222(1) Å, $\beta = 107.80(1)^\circ$, V = 3828.1(4) Å³, $\rho_{\text{calcd.}} = 1.188 \text{ g cm}^{-3}$, $\mu = 0.597$ mm⁻¹, empirical absorption correction (0.841 $\leq T \leq 0.890$), Z = 4, monoclinic, space group *Cc* (No. 9), $\lambda = 1.54178$ Å, T = 223 K, $\omega/2\theta$ scans, 4036 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin $\theta)/\lambda$] = 0.62 Å⁻¹, 4036 independent and 3826 observed reflections [$I \geq 2 \sigma(I)$], 478 refined parameters, R = 0.036, $wR^2 = 0.119$, max./min. residual electron density 0.23/–0.20 eÅ⁻³, Flack parameter –0.3(3), hydrogen atoms at N from difference Fourier calculations, others calculated and all refined as riding atoms.

N,N'-Bis[5-(diethylamino)-1,3-diphenyl-2,4-diaza-6-oxa-1,3,5-hexatrienyl]-1,6-hexylenediamine (4c): From a solution of 2-(diethylamino)-4,6-diphenyl-1,3,5-oxadiazinium pentachlorostannate (2a)^[1] (6.07 g, 10.0 mmol) in dry dichloromethane and 1,6-hexanediamine (0.64 g, 5 mmol). The resultant precipitate was purified by recrystallisation from hot acetone. Yield: 1.23 g (1.7 mmol, 34%), colourless solid, m.p. 164 °C. ¹H NMR (400.13 MHz, CDCl₃): δ = 0.98 (t, ${}^{3}J$ = 7.6 Hz, 6 H, CH₃), 1.09 (t, ${}^{3}J$ = 6.8 Hz, 6 H, CH₃), 1.46 (br., 4 H, CH₂), 1.71 (br., 4 H, CH₂), 3.04 (q, ${}^{3}J$ = 7.1 Hz, 4 H, NCH₂CH₃), 3.29 (q, ${}^{3}J$ = 6.4 Hz, 4 H, NCH₂CH₃), 3.47 [q, ${}^{3}J$ = 6.9 Hz, 4 H, NCH_{2(hexane)}], 5.38 (br., NH), 7.20-7.29 (m, 12 H, CH_{arom.}), 7.51–7.53 (m, 4 H, *o*-CH_{arom.}), 7.79–7.81 (m, J = 7.6 Hz, 4 H, *o*-CH_{arom}) ppm. ¹³C NMR (100.63 MHz, CDCl₃): δ = 13.5, 13.9 (CH₃), 26.8, 27.9, 28.8 (CH₂), 40.0, 41.8, 42.4 (NCH₂), 127.5, 1 127.8, 128.4, 128.4, 130.2 (CH_{arom.}), 135.3, 137.5 (*i*-C_{arom.}), 158.3, 162.9 (CN), 164.1 (CO) ppm. IR (KBr): v = 3253 (br., NH), 3056 (w, CH_{arom.}), 2970 (s, CH_{aliph.}), 2931 (s, CH_{aliph.}), 2871 (w, CH_{aliph}), 1617 (br., C=O), 1560 (br., C=N), 1540 (br., C=N), 1490 (m, C=C), 1468 (s), 1425 (br), 1377 (s), 1351 (w), 1332 (w), 1311 (s) 1276 (vs), 1231 (w), 1185 (w), 1152 (s), 1118 (w), 1106 (m), 1079 (w), 1055 (m), 1022 (m), 978 (w), 959 (w), 923 (w), 899 (s), 849 (w), 809 (m), 793 (w), 780 (s), 725 (w), 695 (s), 661 (m), 618 (w), 607 (w), 570 (w) cm⁻¹. MS (ESI): $m/z = 765 [M + K]^+$, 749 [M + Na^{+} , 727 $[M + H]^{+}$, 693 $[(M + K) - NEt_2]^{+}$, 654 $[(M + H) - NEt_2]^{+}$ NEt_2 ⁺. MS (EI, 70 eV): m/z (%) = 580 (40), 318 (100), 274 (59), 234 (27), 159 (22), 103 (97), 56 (68). C₄₄H₅₄N₈O₂ (726.44): calcd. C 72.70, H 7.49, N 15.41; found C 72.55, H 7.39, N 15.40.

N,N'-Bis[5-(diethylamino)-1,3-diphenyl-2,4-diaza-6-oxa-1,3,5-hexatrienyl]-1,8-octylenediamine (4d): From 2-(diethylamino)-4,6-diphenyl-1,3,5-oxadiazinium pentachlorostannate (2a)^[1] (6.07 g, 10.0 mmol) in dry dichloromethane (40 mL) and 1,8-octanediamine (0.72 g, 5.0 mmol). The crude solid product was purified by recrystallisation from acetone. Yield: 2.30 g (3.0 mmol, 60%), colourless solid, m.p. 185 °C. ¹H NMR (300.13 MHz, CDCl₃): δ = 1.03 (t, ${}^{3}J$ = 8.4 Hz, 6 H, CH₃), 1.14 (t, ${}^{3}J$ = 7.1 Hz, 6 H, CH₃), 1.37 (br., 8 H, CH₂), 1.68 (br., 4 H, CH₂), 3.08 (q, ³*J* = 8.4 Hz, 4 H, NCH_2CH_3), 3.33 (q, ${}^{3}J = 9.2$ Hz, 4 H, NCH_2CH_3), 3.46 [br., 4 H, NCH_{2(octane)}], 5.19 (br., NH), 7.21-7.30 (m, 12 H, CH_{arom}), 7.52-7.54 (m, 4 H, o-CH_{arom}), 7.78–7.80 (m, 4 H, o-CH_{arom}) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 13.5, 13.9 (CH₃), 27.0, 29.0, 29.2 (CH₂), 40.7, 41.8, 42.6 (NCH₂), 127.5, 127.8, 128.4, 128.5, 130.2 (CH_{arom.}), 135.3, 137.4 (*i*-C_{arom.}), 158.3, 162.9 (CN), 164.2 (CO) ppm. IR (KBr): \tilde{v} = 3259 (br., NH), 3061 (m, CH_{arom}), 2971 (m, CHaliph.), 2930 (s, CHaliph.), 2856 (m, CHaliph.), 1595 (vs, C=O), 1572 (br., C=N), 1533 (br., C=N), 1490 (m, C=C), 1458 (s), 1418 (m), 1376 (m), 1315 (m) 1276 (vs), 1226 (w), 1156 (s), 1096 (m),

1027 (w), 953 (w), 908 (w), 858 (w), 775 (s), 711 (m), 695 (s), 658 (w), 604 (w), 539 (w) cm⁻¹. MS (ESI): $m/z = 794 [M + K]^+$, 777 $[M + Na]^+$, 755 $[M + H]^+$, 682 $[(M + H) - NEt_2]^+$, 609 $[(M + H) - 2 (NEt_2)]^+$, 377. MS (EI, 70 eV): m/z (%) = 608 (13), 403 (14), 360 (25), 346 (22), 249 (43), 159 (11), 103 (100). $C_{44}H_{54}N_8O_2$ (754.46): calcd. C 73.18, H 7.74, N 14.84; found C 72.64, H 7.47, N 14.73.

N,N'-Bis[5-(diethylamino)-1,3-diphenyl-2,4-diaza-6-oxa-1,3,5-hexatrienyl]-m-xylylenediamine (4e): From 2-(diethylamino)-4,6-diphenyl-1,3,5-oxadiazinium pentachlorostannate (2a)^[1] (3.6 g, 6.0 mmol) in dry dichloromethane (30 mL) and *m*-xylylenediamine (0.4 g, 3.0 mmol). The crude solid product was purified by recrystallisation from acetone. Yield: 0.8 g (1.1 mol, 37%), colourless solid, m.p. 74 °C. ¹H NMR (300.13 MHz, CDCl₃): δ = 1.01 (t, ${}^{3}J = 11.7$ Hz, 12 H, CH₃), 3.10 (q, ${}^{3}J = 11.7$ Hz, 8 H, CH₂), 4.71 (d, ${}^{3}J$ = 2.7 Hz, 4 H, CH₂), 6.10 (s, 2 H, NH), 7.10–7.81 (m, 24 H, CH_{arom.}) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 13.4, 13.9 (CH₃), 39.9, 41.7 (NCH₂), 46.1 (Aryl-CH₂), 126.7, 127.4, 127.5, 127.7, 128.4, 128.5, 128.6 (Carom.), 130.2, 131.8 (p-Carom.), 134.9, 137.4, 138.9 (i-Carom.), 158.1, 162.9 (CN), 164.1 (CO) ppm. IR (KBr): $\tilde{v} = 3275$ (m, NH), 3058 (m, CH_{arom}), 2970 (m, CH_{aliph}), 2927 (s, CH_{aliph}), 1612 (vs, C=O), 1573 (s, C=N), 1529 (s, C=N), 1490 (m, C=C), 1460 (s, C=C), 1454 (s, C=C), 1375 (s), 1311 (s), 1274 (s), 1153 (m), 1099 (m), 900 (w), 775 (m), 694 (s) cm⁻¹. MS (ESI): $m/z = 769 [M + Na]^+$, 747 [M + H], 674.3 [(M + H) -NEt₂]⁺. C₄₆H₅₀N₈O₂ (746.41). calcd. C 73.97 H 6.75 N 15.00; found C 73.56 H 6.61 N 14.98.

N,N'-Bis[5-(diethylamino)-1,3-diphenyl-2,4-diaza-6-oxa-1,3,5-hexatrienyl]-p-xylylenediamine (4f): From 2-(diethylamino)-4,6-diphenyl-1,3,5-oxadiazinium pentachlorostannate (2a)^[1] (6.07 g, 10.0 mmol) in dry dichloromethane (40 mL) and p-xylylenediamine (0.67 g, 5.0 mmol). The crude solid product was purified by recrystallisation from acetone. Yield: 1.66 g (2.3 mmol, 46%), colourless solid, m.p. 138 °C. ¹H NMR (300.13 MHz, CDCl₃): δ = 0.96 (t, ${}^{3}J$ = 7.6 Hz, 6 H, CH₃), 1.05 (t, ${}^{3}J$ = 6.8 Hz, 6 H, CH₃), 3.00 (q, ${}^{3}J$ = 7.6 Hz, 4 H, NCH₂CH₃), 3.26 (q, ${}^{3}J$ = 6.8 Hz, 4 H, NCH₂CH₃), 4.55 (d, ${}^{3}J$ = 7.12 Hz, 4 H, NCH₂), 7.12–7.30 (m, 12 H, CH_{arom.}), 7.46 (br., 8 H, o-CH_{arom.}), 7.58–7.61 (m, 4 H, CH_{arom.}) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 13.4, 13.9 (CH₃), 38.7, 38.9, 39.2, 39.5, 39.8, 40.1, 40.4, 40.9, 44.6 (NCH₂), 127.6, 127.9, 129.9, 130.1 (CH_{arom.}), 134.7, 136.81, 137.9 (*i*-C_{arom.}), 157.9, 161.8 (CN), 163.4 (CO) ppm. IR (KBr): $\tilde{v} = 3420$ (br., NH), 3059 (m, CH_{arom.}), 2972 (m, CH_{aliph.}), 2930 (m, CH_{aliph.}), 1613 (vs, C=O), 1571 (m, C=N), 1536 (br., C=N), 1490 (w, C=C), 1468 (s), 1422 (m), 1376 (m), 1338 (w) 1275 (vs), 1224 (w), 1155 (m), 1097 (m), 1019 (w), 928 (w), 896 (w), 776 (m), 728 (w), 696 (s), 661 (w), 603 (w) cm⁻¹. MS (ESI): $m/z = 785 [M + K]^+$, 769 [M + Na]⁺, 747 $[M + H]^+$, 674 $[(M + H) - NEt_2]^+$, 601 $[(M + H) - 2 NEt_2]^+$. MS (EI, 70 eV): m/z (%) = 329 (23), 262 (2), 250 (100), 183 (3), 147 (8), 104.1 (42), 80 (45). C₄₆H₅₀N₈O₂ (746.41): calcd. C 73.97, H 6.75, N 15.00; found C 73.72, H 6.55, N 15.06.

N,*N*'-**Bis**[5-(diethylamino)-1,3-diphenyl-2,4-diaza-6-oxa-1,3,5-hexatrienyl]-1,4-cyclohexanediamine (4g): From a solution of 2-(diethylamino)-4,6-diphenyl-1,3,5-oxadiazinium pentachlorostannate (2a)^[1] (6.07 g, 10.0 mmol) in 40 mL of dry dichloromethane and 1,4-*trans*-diaminocyclohexane (0.6 g, 5.0 mmol). The resultant precipitate was purified by recrystallisation from hot acetone. Yield: 2.30 g (2.3 mol, 64%), colourless solid, m.p. 211 °C. ¹H NMR (599.86 MHz, CDCl₃): δ = 1.04 (t, ³*J* = 7.1 Hz, 6 H, CH₃), 1.38 (t, ³*J* = 7.1 Hz, 6 H, CH₃), 1.38–1.41 (m, 4 H, CH₂), 2.35 (d, ³*J* = 5.9 Hz, 4 H, CH₂), 3.04 (q, ³*J* = 7.1 Hz, 4 H, NCH₂CH₃), 3.31 (q, ³*J* = 7.1 Hz, 4 H, NCH₂CH₃), 3.89 [br., 2 H, NCH_(cyclohexane)], 5.11 (br., NH), 7.17–7.29 (m, 12 H, CH_{arom}.), 7.52–7.54 (m, 4 H, *o*- CH_{arom.}), 7.65–7.78 (m, 4 H, *o*-CH_{arom.}) ppm. ¹³C NMR (150.84 MHz, CDCl₃): δ = 13.5 (CH₃), 13.9 (CH₃), 31.1 (CH₂), 39.9 (NCH₂CH₃), 41.7 (NCH₂CH₃), 50.5 [NCH_(cyclohexane)], 127.4, 127.7, 128.3, 128.3, 130.1, 130.1, (CH_{arom.}), 135.1, 137.1 (*i*-C_{arom.}), 157.4, 162.7 (CN), 164.2 (CO) ppm. IR (KBr): \tilde{v} = 3259 (br., NH), 3061 (m, CH_{arom.}), 2967 (m, CH_{aliph.}), 2931 (s, CH_{aliph.}), 2868 (w, CH_{aliph.}), 1619 (br., C=O), 1558 (br., C=N), 1538 (br., C=N), 1490 (m, C=C), 1447 (br), 1421 (s), 1376 (m), 1361 (m), 1315 (vs), 1274 (vs), 1237 (w), 1154 (vs), 1116 (s), 951 (m), 925 (m), 877 (m), 792 (w), 777 (vs), 695 (vs), 639 (w), 603 (w), 509 (w) cm⁻¹. MS (ESI): *m*/*z* = 764 [M + K]⁺, 747 [M + Na]⁺, 725 [M + H]⁺, 652 [(M + H) – NEt₂]⁺, 379, 249. MS (EI, 70 eV): *m*/*z* (%): 329 (23), 262 (2), 250 (100), 183 (3), 147 (8), 104 (42), 80 (45). C₄₄H₅₂N₈O₂ (724.94): calcd. C 72.90, H 7.23, N 15.46; found C 72.84, H 7.01, N 15.49.

X-ray Crystal Structure Analysis of 4g:^[13] Formula $C_{44}H_{52}N_8O_2$ · $3C_3H_6O$, M = 841.09, colourless crystal $0.35 \times 0.30 \times 0.10$ mm, a = 11.733(1), b = 12.413(1), c = 16.363(1) Å, $\beta = 98.43(1)^\circ$, V = 2357.4(4) Å³, $\rho_{calcd.} = 1.185$ gcm⁻³, $\mu = 0.605$ mm⁻¹, empirical absorption correction ($0.816 \le T \le 0.942$), Z = 2, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 1.54178$ Å, T = 223 K, $\omega/2\theta$ scans, 9715 reflections collected ($\pm h$, $\pm k$, $\pm l$), [($\sin\theta$)/ λ] = 0.62 Å⁻¹, 4808 independent ($R_{int} = 0.031$) and 3813 observed reflections [$I \ge 2\sigma(I)$], 288 refined parameters, R = 0.042, $wR^2 = 0.124$, max./min. residual electron density 0.26/–0.22 e Å⁻³, hydrogen atom at N7 from difference Fourier calculations, other calculated and all refined as riding atoms.

N,N'-Bis[5-(diethylamino)-1,3-diphenyl-2,4-diaza-6-oxa-1,3,5-hexatrienyl]-1,2-trans-cyclohexanediamine (4h): To a solution of 2-(diethylamino)-4,6-diphenyl-1,3,5-oxadiazinium pentachlorostannate $(2a)^{[1]}$ (3.61 g, 6.0 mmol) in dry dichloromethane *trans*-1,2-diaminocyclohexane (0.32 g, 3.0 mmol) was added. The resultant precipitate was purified by recrystallisation from hot aceton. Yield: 1.27 g (1.3 mmol, 46%), colourless solid, m.p. 175 °C. ¹H NMR $(300.13 \text{ MHz}, \text{CDCl}_3): \delta = 0.86 \text{ (t, } {}^{3}J = 7.1 \text{ Hz}, 6 \text{ H}, \text{NCH}_2\text{CH}_3),$ 0.99 (t, ${}^{3}J = 7.1$ Hz, 6 H, NCH₂CH₃), 0.99 (br., 2 H, CH₂), 1.25, 1.38, 1.52 (br., 6 H, CH₂), 3.05 (m, 8 H, NCH₂), 4.03 (s, 2 H, NCH) 7.22-7.42 (m, 12 H, CH_{arom.}), 7.73-7.86 (m, 4 H, CH_{arom.}), 7.98-8.00 (m, 4 H, o-CH_{arom}) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 13.5, 13.9 (CH₃), 24.7, 33.0 (CH₂), 39.7, 41.5 (NCH₂), 55.1 (NCH), 127.9, 128.2, 128.5, 130.3, 130.6 (Carom.), 135.4, 136.5 (i-C_{arom.}), 156.1, 162.3 (CN), 164.7 (CO) ppm. IR (KBr): $\tilde{v} = 3298$ (s, NH), 3060 (m, CH_{arom.}), 2976 (m, CH_{aliph.}), 2931 (s, CH_{aliph.}), 2858 (m, CH_{aliph}), 1654 (vs, C=O), 1604 (vs, C=N), 1548 (vs, C=N), 1502 (vs, C=C), 1490 (s, C=C), 1448 (s, C=C), 1417 (s), 1377 (s), 1326 (s), 1271 (vs), 1224 (m), 1190 (m), 1157 (s), 1101 (m), 1072 (m), 1026 (m), 927 (m), 900 (m), 877 (m), 755 (m), 694 (s) cm⁻¹. MS (ESI): m/z (%) = 747 [M + Na]⁺, 725 [M + H]⁺, 182. C44H52N8O2 (724.42): calcd. C 72.90, H 7.23, N 15.46; found C 73.82, H 7.13, N 15.49.

X-ray Crystal Structure Analysis of 4h:^[13] Formula C₄₄H₅₂N₈O₂, M = 724.94, light yellow crystal $0.25 \times 0.25 \times 0.15$ mm, a = 10.138(1), b = 16.362(1), c = 23.918(1) Å, V = 3967.5(5) Å³, $\rho_{calcd.} = 1.214$ g cm⁻³, $\mu = 0.077$ mm⁻¹, empirical absorption correction (0.981 $\leq T \leq 0.989$), Z = 4, orthorhombic, space group $P2_12_12_1$ (No. 19), $\lambda = 0.71073$ Å, T = 198 K, ω and ϕ scans, 16673 reflections collected ($\pm h, \pm k, \pm l$), [($\sin\theta$)/ λ] = 0.67 Å⁻¹, 9548 independent ($R_{int} = 0.037$) and 5926 observed reflections [$I \geq 2\sigma(I)$], 499 refined parameters, R = 0.060, $wR^2 = 0.118$, max./min. residual electron density 0.21/-0.17 e Å⁻³, Flack parameter -0.3(12), hydrogen atoms at N4 from difference Fourier calculations, others calculated and all refined as riding atoms.

N,*N*′-**Bis**[**5-(diethylamino)-1,3-phenyl-2,4-diaza-6-oxa-1,3,5-hexatrienyl]piperazine (5a):** From 2-(diethylamino)-4,6-diphenyl-1,3,5-oxadiazinium pentachlorostannate (2a)^[1] (3.61 g, 6.0 mmol), 0.6 mL (6.0 mmol) triethylamine and piperazine (0.26 g, 3.0 mmol) in 40 mL of dry dichloromethane. The crude solid product was purified by recrystallisation from acetone. Yield: 3.23 g (4.7 mmol, 77%), colourless solid, m.p. 231 °C. ¹H NMR (300.13 MHz, CDCl₃): $\delta = 0.98-1.02$ (t, ³J = 7.1 Hz, 6 H, NCH₃), 1.19-1.23 (t, ${}^{3}J = 7.1$ Hz, 6 H, NCH₃), 3.05–3.12 (q, ${}^{3}J = 7.1$ Hz, 4 H, NCH₃), 3.38-3.44 (q, ${}^{3}J$ = 7.1 Hz, 4 H, NCH₃), 3.57 (br., 8 H, CH₂), 7.17-7.39 (m, 16 H, CH_{arom}), 7.64–7.66 (d, ${}^{3}J$ = 6.9 Hz, 4 H, *o*-CH_{arom}) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 13.9, 14.4 (NCH₂CH₃), 40.7, 42.3 (NCH₂), 46.5–46.8 (br., CH₂), 128.1, 128.6, 130.1, 130.6, 133.5 (Carom.), 137.7 (i-Carom.), 160.6, 163.4 (CN), 164.3 (CO) ppm. IR (KBr): \tilde{v} = 3058 (m, CH_{arom.}), 3024 (m, CH_{arom.}), 2970 (m, CH_{aliph}), 2931 (m, CH_{aliph}), 2871 (m, CH_{aliph}), 1639 (vs, C=O), 1610 (vs, C=N), 1593 (vs, C=N), 1573 (vs, C=N), 1492 (m, C=C), 1438 (s), 1419 (vs), 1365 (s), 1313 (s), 1265 (vs), 1245 (vs), 1164 (m), 1153 (s), 1082 (s), 1008 (s), 974 (m), 943 (m), 779 (s), 732 (m), 698 (s) cm⁻¹. MS (ESI): m/z (%) = 719 [M + Na]⁺, 697 [M + H]⁺. C₄₂H₄₈N₈O₂ (696.39): calcd. C 72.39, H 6.94, N 16.08; found C 72.32, H 6.85, N 16.07.

N,N'-Bis[5-(diethylamino)-1,3-phenyl-2,4-diaza-6-oxa-1,3,5-hexatrienyl]-N,N'-dimethylethylenediamine (5b): From 2-(diethylamino)-4,6-diphenyl-1,3,5-oxadiazinium pentachlorostannate (2a)^[1] (3.61 g, 6.0 mmol) in dry dichloromethane (30 mL), 0.6 mL (6.0 mmol) triethylamine and N, N'-dimethylethylenediamine (0.26 g, 3 mmol). The crude solid product was purified by column chromatography (ethyl acetate/cyclohexane, 1:2 + 5% triethylamine) following recrystallisation from acetone. Yield: 1.67 g (2.4 mmol, 79%), colourless solid. m.p. 107 °C. $R_{\rm f} = 0.08$ (cyclohexane/ethyl acetate, 2:1 with 5% triethylamine). ¹H NMR $(300.13 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 0.98-1.02$ (t, ${}^{3}J = 7.1 \text{ Hz}, 6 \text{ H}, \text{ CH}_3)$, 1.19–1.23 (t, ${}^{3}J$ = 7.1 Hz, 6 H, CH₃), 3.05–3.12 (q, ${}^{3}J$ = 7.1 Hz, 4 H, NCH₂), 3.38–3.44 (q, ³*J* = 7.1 Hz, 4 H, NCH₂), 3.57 [br., 8 H, NCH_{2(pip.)}], 7.17–7.39 (m, 16 H, CH_{arom.}), 7.64–7.66 (d, ³J = 6.9 Hz 4 H, *p*-CH_{arom}) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 13.3, 13.5 (CH₃), 38.9 (NCH₃), 39.7, 41.5 (NCH₂CH₃), 45.7 (NCH₂), 127.6, 128.1, 128.6, 130.1, 130.3 (Carom.), 134.3, 137.84 (i-Carom.), 159.8, 163.4 (CN), 163.8 (CO) ppm. IR (KBr): v = 3062 (m, CH_{arom.}), 3028 (w, CH_{arom.}), 2972 (s, CH_{aliph.}), 2925 (s, CH_{aliph.}), 2868 (m, CH_{aliph}), 1600 (vs, C=O), 1566 (vs, C=C), 1565 (vs, C=C), 1539 (vs, C=C), 1490 (s, C=C), 1463 (vs), 1452 (vs), 1429 (vs), 1415 (vs, C=C), 1377 (vs), 1313 (vs), 1299 (s), 1272 (vs), 1224 (m), 1193 (m), 1154 (m), 1130 (s), 1099 (m), 1080 (m), 1047 (s) 1026 (m), 1016 (m), 952 (w), 927 (w), 896 (s), 846 (m), 810 (m), 773 (s), 742 (w), 707 (vs), 692 (vs), 663 (s) cm⁻¹. MS (ESI): $m/z = 721 [M + Na]^+$, 699 [M + H]⁺. C₄₂H₅₀N₈O₂ (698.41): calcd. C 72.18, H 7.21, N 16.03; found C 72.20, H 6.78, N 16.18.

N,N'-Diethyl-N,N'-bis[5-(diethylamino)-1,3-phenyl-2,4-diaza-6-oxa-1,3,5-hexatrienyl]-p-xylylenediamine (5c): From a solution of 2-(diethylamino)-4,6-diphenyl-1,3,5-oxadiazinium pentachlorostannate $(2a)^{[1]}$ (3.61 g, 6.0 mmol) in dry dichloromethane, 0.6 mL (6.0 mmol) triethylamine and N, N'-diethyl-p-xylylenediamine (0.58 g, 3.0 mmol). The crude product was purified by column chromatography (cyclohexane/ethyl acetate, 5:1 with 5% triethylamine), and the resultant precipitate was purified by recrystallisation from hot acetone. Yield: 1.23 g (1.5 mmol, 50%), colourless solid, m.p. 138 °C. $R_{\rm f}$ = 0.03 (cyclohexane/ethyl acetate, 5:1 with 5% of triethylamine). ¹H NMR (300.13 MHz, CHCl₃): δ = 1.02– 1.24 (m, 18 H, NCH₂CH₃), 3.16 (q, ${}^{3}J$ = 6.9 Hz, 6 H, NCH₂), 3.44 $(q, {}^{3}J = 6.9 \text{ Hz}, 6 \text{ H}, \text{ NCH}_{2}), 4.56-4.84 (br., 4 \text{ H}, \text{ PhCH}_{2}) 7.14-$ 7.42 (br., 24 H, CH_{arom}) ppm. $^{13}\mathrm{C}$ NMR (75.47 MHz, CHCl₃): δ = 13.5, 13.9 (CH₃), 40.2, 42.0 (NCH₂), 127.5, 127.9, 128.0, 128.1, 129.2, 129.8 (Carom.), 133.9, 137.0, 137.9 (i-C), 163.5, 164.5 (NCO) ppm. IR (KBr): $\tilde{v} = 3058$ (m, CH_{arom}), 3028 (m, CH_{arom}), 2974 (m, CH_{aliph}), 2929 (m, CH_{aliph}), 2869 (m, CH_{aliph}), 1633 (vs, C=O), 1606 (vs, C=N), 1591 (vs, C=N), 1571 (vs, C=N), 1498 (m, C=C), 1469 (s), 1417 (s), 1375 (s), 1321 (s), 1271 (s), 1255 (s), 1224 (m), 1155 (m), 1064 (s), 1020 (m), 993 (m), 943 (m), 927 (w), 893 (m), 856 (w), 808 (m), 792 (m), 775 (m), 732 (m), 696 (m) cm⁻¹. MS (ESI): *m/z* (%) = 825 [M + Na]⁺, 803 [M + H]⁺. C₅₀H₅₈N₈O₂ (803.47): calcd. C 74.78, H 7.28, N 13.95; found C 74.54, H 7.20, N 13.95.

N,N'-Diethyl-N,N'-bis[1,3,5-tris(4-bromophenyl)-6-oxa-2,4-diaza-1,3,5-hexatrienyl]-p-xylylenediamine (5d): From 2b (0.98 g, 5.0 mmol), triethylamine (1.4 mL, 10.0 mmol) and N,N'-diethyl-pxylylenediamine (5.26 g, 10.0 mmol). The crude product was purified by column chromatography with petroleum ether/tert-butyl methyl ether (1:1) as eluent. Yield: 0.67 g (0.5 mmol, 10%), yellow solid, m.p. 178 °C. $R_f = 0.13$ (petroleum ether ether/tert-butyl methyl ether, 1:1). ¹H NMR (300.13 MHz, CDCl₃): $\delta = 1.05-1.29$ (br., 6 H, NCH₂CH₃), 3.13–3.59 (br., 4 H, CH₂), 4.37–4.79 (br., 4 H, CH₂), 6.97-7.17 (m, 8 H, CH_{arom.}), 7.43-7.70 (m, 18 H, CH_{arom.}), 7.93 (m, 2 H, CH_{arom.}) ppm. ¹³C NMR (75.47 MHz, $CDCl_3$): $\delta = 13.8$ (br., CH_3), 43.5, 51.2 (CH_2), 124.8, 126.02, 126.8 (*i*-C_{arom.}), 128.7, 129.3, 130.3, 130.5, 131.1, 131.3, 131.7 (CH_{arom.}), 136.0 (i-Carom.), 160.9, 162.0 (CN), 178.0 (CO) ppm. IR (KBr): v = 3083 (w, CH_{arom.}), 3060 (w, CH_{arom.}), 3031 (w, CH_{arom.}), 2962 (w, $CH_{aliph.}$), 2931 (w, $CH_{aliph.}$), 2871 (w), 1662 (s, C=O), 1635 (s, C=N), 1558 (s, C=C), 1496 (m), 1461 (m), 1394 (m), 1280 (m), 1166 (m), 1087 (m), 1068 (m), 1031 (m), 906 (m), 825 (m), 730 (m) cm⁻¹. MS (ESI): $m/z = 1286 [M + H]^+$. $C_{54}H_{48}Br_6N_6O_2$ (1292.43): calcd. C 50.18, H 3.74, N 6.50; found C 50.61, H 3.24, N 6.32.

X-ray Crystal Structure Analysis of 5d:^[13] Formula $C_{54}H_{42}Br_6N_6O_2$, M = 1286.40, colourless crystal $0.15 \times 0.10 \times 0.05$ mm, a = 16.551(1), b = 7.818(1), c = 20.084(1) Å, $\beta = 105.87(1)^\circ$, V = 2499.7(4) Å³, $\rho_{calcd.} = 1.709$ gcm⁻³, $\mu = 4.867$ mm⁻¹, empirical absorption correction ($0.529 \le T \le 0.793$), Z = 2, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.71073$ Å, T = 198 K, ω and ϕ scans, 20494 reflections collected ($\pm h, \pm k, \pm l$), [($\sin \theta$)/ λ] = 0.66 Å⁻¹, 5928 independent ($R_{int} = 0.062$) and 3790 observed reflections [$I^3 2 \sigma(I)$], 308 refined parameters, R = 0.048, $wR^2 = 0.109$, max./min. residual electron density 0.87/-0.73 eÅ⁻³, hydrogen atoms calculated and refined as riding atoms.

N,N'-Bis[5-(diethylamino)-1,3-phenyl-2,4-diaza-6-oxa-1,3,5-hexatrienyl]-N,N'-diphenyl-p-xylylenediamine (5e): From a solution of 2-(diethylamino)-4,6-diphenyl-1,3,5-oxadiazinium pentachlorostannate (2a)^[1] (3.61 g, 6.0 mmol) in dry dichloromethane, 0.6 mL (6.0 mmol) triethylamine and N,N'-diphenyl-p-xylylenediamine (0.95 g, 3.0 mmol). The crude product was purified by column chromatography (cyclohexane/ethyl acetate, 5:1 + 5% of triethylamine), and the resultant precipitate was purified by recrystallisation from hot acetone. Yield: 0.27 g (0.3 mmol, 9%), colourless solid, m.p. 198 °C. $R_{\rm f} = 0.053$ (cyclohexane/ethyl acetate, 5:1 + 5% of triethylamine).¹H NMR (400.13 MHz, CDCl₃): $\delta = 1.04$ (t, ³J = 9.2 Hz, 6 H, CH₃), 1.22 (t, ${}^{3}J$ = 9.2 Hz, 6 H, CH₃), 3.17 (q, ${}^{3}J$ = 9.2 Hz, 4 H, NCH₂), 3.46 (q, ${}^{3}J$ = 9.2 Hz, 4 H, NCH₂), 4.32 (s, 4 H, Aryl-CH₂), 4.77 (s, 4 H, Aryl-CH₂), 7.15–7.38 (m, 34 H, CH_{arom}) ppm. ¹³C NMR (100.61 MHz, CDCl₃): δ = 13.9, 14.4 (CH₃) 40.6, 42.3 (NCH₂), 52.9 (Aryl-CH₂), 127.9, 128.5, 129.1, 129.8, 130.3 (C_{arom.}), 133.9, 137.9 (*i*-C_{arom.}), 161.3, 163.6 (CN), 164.7 (CO) ppm. MS (ESI): $m/z = 949 [M + Na]^+$, 927 $[M + H]^+$, 622, 475 [M + 2 Na]⁺. C₆₀H₆₂N₈O₂ (927.20): calcd. C 77.72, H 6.74, N 12.09; found C 77.93, H 6.38, N 12.08.

N,N'-Dibenzyl-*N,N*'-bis[1,3,5-tris(4-bromophenyl)-6-oxa-2,4-diaza-1,3,5-hexatrienyl]-*p*-xylylenediamine (5f): From 2b (0.81 g, 5 mmol), triethylamine (1.4 mL, 10 mmol) and N,N'-diphenyl-p-xylylenediamine (5.26 g, 10 mmol). The crude product was purified by column chromatography with petroleum ether/tert-butyl methyl ether (3:1) as eluent. Yield: 0.83 g (0.6 mmol, 12%), yellow solid, m.p. 199 °C. $R_{\rm f} = 0.12$ (petroleum ether/*tert*-butyl methyl ether, 3:1). ¹H NMR $(300.13 \text{ MHz}, \text{CDCl}_3): \delta = 4.31-4.77 \text{ (br., 8 H, CH}_2), 7.02-7.12 \text{ (m,}$ 12 H, CH_{arom}), 7.35–7.48 (m, 18 H, CH_{arom}), 7.69–7.78 (m, 8 H, CH_{arom}) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 50.2, 50.6, 52.1 (CH₂), 125.1, 126.2, 126.9 (*i*-C_{arom.}), 127.0, 129.0, 129.4, 130.3, 130.5, 131.2, 131.4 (CH_{arom}), 134.2, 136.0, 136.2 (*i*-C_{arom}), 160.9, 162.0 (CN), 174.1 (CO) ppm. IR (KBr): \tilde{v} = 3085 (w, CH_{arom}), 3062 (w, CH_{arom}), 3031 (w, CH_{arom}), 2923 (w, CH_{aliph}), 2854 (w, CH_{aliph}), 1662 (s, C=O), 1635 (s, C=N), 1558 (s, C=C), 1494 (m), 1452 (m), 1251 (m), 1163 (m), 1068 (m), 1008 (m), 906 (m), 831 (m), 730 (w) cm⁻¹. MS (ESI): $m/z = 1411 [M + H]^+$. C₆₄H₅₂Br₆N₆O₂ (1416.57): calcd. C 54.26, H 3.70, N 5.93; found C 54.48, H 3.18, N 5.76.

X-ray Crystal Structure Analysis of 5f:^[13] Formula $C_{64}H_{46}Br_6N_6O_2$, M = 1410.53, colourless crystal $0.15 \times 0.07 \times 0.03$ mm, a = 18.402(1), b = 9.055(1), c = 18.417(1) Å, $\beta = 102.07(1)^{\circ}$, V = 3001.0(4) Å³, $\rho_{calcd.} = 1.561$ gcm⁻³, $\mu = 4.062$ mm⁻¹, empirical absorption correction ($0.581 \le T \le 0.888$), Z = 2, monoclinic, space group P2/c (No. 13), $\lambda = 0.71073$ Å, T = 198 K, ω and ϕ scans, 7497 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\theta)/\lambda] = 0.59$ Å⁻¹, 4792 independent ($R_{int} = 0.058$) and 2317 observed reflections [$I \ge 2\sigma(I)$], 352 refined parameters, R = 0.073, $wR^2 = 0.212$, max./ min. residual electron density 0.75/-0.67 eÅ⁻³, weakly diffracting crystal leading to reduced quality of the analysis, hydrogen atoms calculated and refined as riding atoms.

2,6-Bis{[5-(diethylamino)-1,3-diphenyl-2,4-diaza-6-oxa-1,3,5hexatrienyllamino {pyridine (6): From a solution of 2-(diethylamino)-4,6-diphenyl-1,3,5-oxadiazinium pentachlorostannate $(2a)^{[1]}$ (3.61 g, 6.0 mmol) in dry dichloromethane (40 mL) and 2,6diaminopyridine (0.65 g, 3.0 mmol). The resultant precipitate was purified by recrystallisation from hot acetone. Yield: 1.51 g (2.1 mmol, 70%), light yellow solid, m.p. 165 °C. ¹H NMR $(300.13 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 0.74$ (t, ${}^{3}J = 7.1 \text{ Hz}, 3 \text{ H}, \text{ CH}_2\text{CH}_3)$, 1.06 (m, 6 H, CH₂CH₃), 1.25 (t, ${}^{3}J$ = 7.1 Hz, 3 H, CH₂CH₃), 2.98 (m, 4 H, NCH₂), 3.47 (q, ${}^{3}J$ = 7.0 Hz, 2 H, NCH₂), 3.47 (q, ${}^{3}J$ = 7.0 Hz, 2 H, NCH₂), 3.58 (q, ${}^{3}J$ = 7.1 Hz, 2 H, NCH₂), 7.02–7.15 (m, 6 H, CH_{arom}), 7.25–7.35 (m, 9 H, CH_{arom}), 7.44–7.46 (m, 2 H, CH_{arom.}), 7.76–7.89 (m, 5 H, CH_{arom.}), 8.32–8.35 (m, 1 H, CH_{arom.}) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 13.0, 13.4, 13.8, 14.6 (CH₃), 39.9, 40.3, 41.7, 42.1 (br., CH₂), 110.8 (CN), 117.5, 127.5, 127.7, 127.8, 128.0, 128.2, 128.3, 128.7, 128.8, 129.8, 130.4, 130.4 (Carom.), 134.8, 136.4 139.9 (i-Carom.), 149.9, 154.8, 157.6, 161.8 (CN), 163.5 (CO) ppm. IR (KBr): $\tilde{v} = 3298$ (s, NH), 3060 (m, CH_{arom}), 2976 (m, CH_{aliph}), 2931 (m, CH_{aliph}), 2858 (m, CH_{aliph}), 1654 (vs, C=O), 1604 (vs, C=N), 1548 (vs, C=N), 1502 (m, C=C), 1490 (s, C=C), 1448 (s), 1417 (s), 1377 (s), 1326 (s), 1271 (vs), 1224 (m), 1190 (m), 1157 (s), 1101 (m), 1072 (m), 1026 (m), 927 (m), 900 (m), 877 (m), 755 (m), 695 (m) cm⁻¹. MS (ESI): m/z = 782, 742 [M + Na]⁺, 720 [M + H]⁺, 391. $C_{43}H_{45}N_9O_2$ (719.37): calcd. C 71.74, H 6.30, N 17.51; found C 71.60, H 6.20, N 17.45.

Tris(2-{[5-(diethylamino)-1,3-diphenyl-2,4-diaza-6-oxa-1,3,5-hexatrienyl]amino}ethyl)amine (7a): From 2-(diethylamino)-4,6-diphenyl-1,3,5-oxadiazinium pentachlorostannate (**2a**)^[1] (7.22 g, 12.0 mmol) in dry dichloromethane (30 mL) and tris(2-aminoethyl) amine (0.58 g, 4.0 mmol). The crude solid product was purified by recrystallisation from acetone. Yield: 2.68 g (2.5 mmol, 63%), colourless solid, m.p. 176 °C. ¹H NMR (300.13 MHz, CDCl₃): δ = 0.74 (t, ³J = 6.9 Hz, 9 H, CH₃), 0.84 (t, ³J = 6.9 Hz, 9 H, CH₃),



2.80–2.90 (br., 18 H, NCH₂), 3.53 [s, 6 H, NCH₂(tren)] 7.01–7.44 (m, 24 H, CH_{arom}), 7.81–7.83 (d, ${}^{3}J$ = 6.7 Hz, 6 H, *p*-CH_{arom}) ppm. 13 C NMR (75.47 MHz, CDCl₃): δ = 12.3, 12.9 (CH₃), 38.8, 39.6, 40.8 (NCH₂), 52.09 [NCH₂(tren)], 126.8, 127.2, 127.4 (C_{arom}), 129.0, 129.3 (*p*-C_{arom}), 134.3, 136.9 (*i*-C_{arom}), 157.6, 162.0 (CN), 162.9 (CO) ppm. IR (KBr): \tilde{v} = 3286 (s, NH), 3078 (m, CH_{arom}), 3060 (m, CH_{arom}), 3028 (m, CH_{arom}), 2974 (m, CH_{aliph}), 2931 (m, CH_{aliph}), 2871 (m, CH_{aliph}), 2792 (m, CH_{aliph}), 1608 (vs, C=O), 1570 (s, C=N), 1537 (vs, C=C), 1488 (m, C=C), 1463 (s), 1446 (s), 1417 (s), 1373 (s), 1315 (m), 1274 (s), 1155 (m), 1116 (m), 1064 (m), 1026 (w), 954 (vw), 929 (w), 900 (w), 877 (w), 808 (w), 773 (m), 711 (m), 694 (m), 659 (m) cm⁻¹. MS (ESI): *m*/*z* = 1084.6 [M + Na]⁺, 1062 [M + H]⁺, 542 [M + H + Na]²⁺, 531 [M + 2 H]²⁺, 495, 220. C_{63H75}N₁₃O₃ (1061.61): calcd. C 71.23, H 7.12, N 17.14; found C 70.84, H 6.92, N 17.11.

Tris(2-{[3,5-bis(diethylamino)-1-phenyl-2,4-diaza-6-oxa-1,3,5hexatrienyl]amino}ethyl)amine (7b): From 2,4-bis(diethylamino)-6phenyl-1-oxa-3,5-diazinium pentachlorostannate (2c)^[14] (7.15 g, 12.0 mmol) in dry dichloromethane (30 mL) and tris(2-aminoethyl)amine (0.58 g, 4.0 mmol). The crude product was purified by column chromatography with *n*-pentane/acetone (5:1) with 10% triethylamine as eluent. Yield: 0.81 g (0.7 mmol, 18%), colourless solid, m.p. 182 °C. $R_f = 0.55$ (*n*-pentane/acetone, 5:1 with 10% triethylamine). ¹H NMR (300.13 MHz, CDCl₃): $\delta = 0.51$ (s, 18 H, CH₃), 1.12 (s, 18 H, CH₃), 2.17–2.59 (br., 18 H, NCH₂), 3.44 (s, 12 H, NCH₂), 3.73 [s, 6 H, NCH_{2(tren)}], 7.26–7.40 (br., 12 H, CH_{arom}), 7.58-7.60 (br., 3 H, p-CH_{arom.}) ppm. ¹³C NMR (75.47 MHz, $CDCl_3$): $\delta = 13.9 (CH_3), 27.8, 39.6 (NCH_2), 41.9 (NCH_2), 52.8$ [NCH_{2(tren)}], 127.6, 127.7 (Carom.), 129.0 (p-Carom.) 136.7 (i-Carom.), 160.3, 160.5 (CN), 161.8 (CO) ppm. IR (KBr): $\tilde{v} = 3263$ (s, NH), 3082 (m, CH_{arom}), 3026 (m, CH_{arom}), 2974 (s, CH_{aliph}), 2927 (s, CH_{aliph.}), 2868 (m, CH_{aliph.}), 2777 (m, CH_{aliph.}), 2723 (m, CH_{aliph.}), 1604 (vs, C=O), 1583 (s, C=N), 1523 (vs, C=C), 1467 (vs, C=C), 1406 (vs), 1363 (s), 1357 (s), 1344 (s), 1319 (s), 1282 (vs), 1234 (s), 1166 (s), 1141 (m), 1089 (s), 1060 (s), 947 (w), 920 (w), 896 (w), 833 (vw), 812 (m), 769 (m), 754 (m), 692 (m) cm⁻¹. MS (ESI): m/z= 1047 $[M + H]^+$, 659. $C_{57}H_{90}N_{16}O_3$ (1046.73): calcd. C 65.36, H 8.66, N 21.40; found C 65.39, H 8.59, N 20.95.

X-ray Crystal Structure Analysis of 7b:^[13] Formula $C_{57}H_{90}N_{16}O_3$, M = 1047.45, colourless crystal $0.50 \times 0.320 \times 0.15$ mm, a = 11.978(1), b = 26.591(1), c = 19.989(1) Å, $\beta = 107.15(1)^{\circ}$, V = 6083.5(6) Å³, $\rho_{calcd.} = 1.144$ gcm⁻³, $\mu = 0.583$ mm⁻¹, empirical absorption correction ($0.759 \le T \le 0.918$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 1.54178$ Å, T = 223 K, ω and ϕ scans, 38310 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/ λ] = 0.59 Å⁻¹, 10071 independent ($R_{int} = 0.047$) and 6681 observed reflections [$I \ge 2\sigma(I)$], 706 refined parameters, R = 0.045, $wR^2 = 0.126$, max./ min. residual electron density 0.26/-0.20 e Å⁻³, hydrogen atoms at N4 from difference Fourier calculations, others calculated and all refined as riding atoms.

Tris{2-[(3,5-dimorpholino-1-phenyl-2,4-diaza-6-oxa-1,3,5-hexatrienyl)amino]ethyl}amine (7c): From 2,4-dimorpholino-6-diphenyl-1-oxa-3,5-diazinium pentachlorostannate (2d)^[14] (7.49 g, 12.0 mmol) and tris(2-aminoethyl)amine (0.58 g, 4.0 mmol). The crude product was purified by recrystallisation from acetone. Yield: 1.93 g (1.7 mmol, 43 %), colourless solid, m.p. 165 °C. ¹H NMR (300.13 MHz, CDCl₃): δ = 1.95 (br., 11 H, NCH₂), 3.00 (br., 15 H NCH₂), 3.69 (br., 34 H, NCH₂, OCH₂), 7.37–7.46 (m, 15 H, CH_{arom.}), 8.26 (s, 3 H, NH) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 38.6, 44.6 [NCH_{2(mor.)}], 52.4 [NCH_{2(tren)}], 66.3, 66.8 [OCH_{2(mor.)}], 127.6, 129.7 (C_{arom.}), 136.7 (*i*-C_{arom.}), 161.5, 161.6 (CN), 161.8 (CO) ppm. IR (KBr): \tilde{v} = 3286 (m, NH), 3101 (w, CH_{arom.}), 3060

(w, CH_{arom.}), 3026 (w, CH_{arom.}), 2958 (m, CH_{aliph.}), 2918 (m, CH_{aliph.}), 2895 (m, CH_{aliph.}), 2852 (s, CH_{aliph.}), 1612 (vs, C=O), 1598 (vs, C=N), 1573 (vs, C=N), 1523 (vs, C=C), 1454 (vs), 1431 (vs), 1404 (vs), 1359 (s), 1299 (s), 1284 (s), 1245 (vs), 1170 (s), 1112 (vs), 1068 (m), 1020 (m), 999 (s), 966 (m), 927 (w), 893 (w), 848 (m), 802 (m), 773 (m), 756 (m), 696 (m) cm⁻¹. MS (ESI): $m/z = 1153 [M + Na]^+$, 1031 [M + H]⁺, 102 [NEt₃ + H]⁺, 76 [Ph]⁺. C₅₇H₇₈N₁₆O₉ (1130.61): calcd. C 60.51, H 6.95, N 19.81; found C 60.01, H 7.03, N 19.63.

1,3,5-Tris[3,5-bis(diisopropylamino)-1-(propylamino)-6-oxa-2,4-diaza-1,3,5-hexatrienyl]benzene (8): From 2,2',2''-(1,3,5-phenylene)tris[4,6-bis(diisopropylamino)-1-oxa-3,5-diazinium] tris(pentachlorostannate) (1d)^[11] (14.87 g, 8.3 mmol) and *n*-propylamine (4.0 mL, 50.0 mmol). The crude product was purified by column chromatography with pentane/tert-butyl methyl ether (3:1) with 1% triethylamine as eluent. Yield: 4.00 g (3.1 mmol, 37%), light yellow solid, m.p. 92 °C. $R_f = 0.18$ (pentane/*tert*-butyl methyl ether, 3:1 with 1% triethylamine). ¹H NMR (300.13 MHz, CDCl₃): $\delta = 0.92-0.97$ (m, 9 H, NCH₂CH₂CH₃), 1.02–1.27 (br., 72 H, NCHCH₃), 1.58–1.70 (m, 6 H, NCH₂CH₂CH₃), 3.15–3.45 (br., 12 H, NCH), 3.72 (br., 6 H, NCH₂CH₂CH₃), 4.31 (br., 3 H, NH), 6.69-8.64 (br., 3 H, CH_{arom.}) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 11.6, 21.0, 21.3, 22.2 (CH₃), 44.1, 46.8, 50.9 (NCH, CH₂), 129.5, 133.7 (CH_{arom}), 155.2, 156.4 (CN), 162.8 (CO) ppm. IR (KBr): v = 3301 (w, NH), 3064 (w, $CH_{arom.}$), 2966 (s, $CH_{aliph.}$), 2931 (s, $CH_{aliph.}$), 2873 (m, CH_{aliph}), 1631 (s, C=O), 1579 (s, C=N), 1552 (s, C=C), 1442 (s), 1423 (s), 1365 (s), 1328 (s), 1220 (m), 1151 (m), 1132 (m), 1066 (w), 1041 (w) cm⁻¹. MS (ESI): $m/z = 1091 [M + H]^+$, 545 [(M + 2 H)/ 2^{+} , daughters of 1091: 1032 [(M + H) - NHPr]⁺, 990 [(M + H) - $NiPr_{2}^{+}$, 931 [(M + H) – 2 NHPr]⁺, 889 [(M + H) – NHPr – $NiPr_2$]⁺, 787 [(M + H) – 3 NHPr]⁺. C₆₀H₁₁₁N₁₅O₃ (1090.64): calcd. C 66.08, H 10.26, N 19.26; found C 65.69, H 10.37, N 19.08.

Metal Complexes of the Ligands 3–7. General Procedure: The ligand (0.05 mmol) and the metal salt (0.10 mmol) were co-dissolved in DMF or ethanol (2 mL). After centrifugation, diethyl ether was allowed to diffuse into the solution. Overnight coloured crystals were formed. After one week, these were collected, washed with diethyl ether, and dried under reduced pressure.

{1,4-Bis[3,5-bis(diisopropylamino)-1-(propylamino)-6-oxa-2,4-diaza-1,3,5-hexatrienyl]benzene}bis[zinc(II) dibromide] (3a·ZnBr₂): From 3a (38 mg, 0.05 mmol) and zinc(II) bromide (22 mg, 0.10 mmol) in DMF (2 mL). Yield: 32 mg (0.03 mmol, 53%), colourless crystals, m.p. 217 °C. IR (KBr): $\tilde{v} = 3251$ (m, NH), 3051 (s, CH_{arom.}), 2969 (s, CH_{aliph.}), 2941 (s, CH_{aliph.}), 2873 (s, CH_{aliph.}), 1616 (vs, C=O/C=N), 1566 (vs, C=C), 1521 (vs), 1459 (s), 1431 (s), 1366 (s), 1331 (s), 1215 (m), 1166 (m), 1118 (m), 1069 (m), 969 (w), 894 (w), 863 (w), 844 (w), 792 (w), 758 (m), 723 (w), 633 (w), 573 (w), 555 (w) cm⁻¹. MS (MALDI, matrix DCTB): m/z (%) = 978 (25) [M – ZnBr₂]⁺, 896 (20) [M – ZnBr₃]⁺, 753 (35) [M – 2 ZnBr₂]⁺, 652 (100) [M – 2 ZnBr₂ – N*i*Pr₂]⁺. UV/Vis (acetonitrile): λ_{max} (\tilde{v} , ε) = 249 (40160, 40933) 202 (49504 cm⁻¹, 61000 M⁻¹ cm⁻¹) n m. C₄₂H₇₆Br₄N₁₀O₂Zn₂ (1203.50): calcd. C 41.92, H 6.37, N 11.64; found C 41.22, H 6.19, N 11.34.

X-ray Crystal Structure Analysis of 3a·**ZnBr**₂:^[13] Formula $C_{42}H_{76}Br_4N_{10}O_2Zn_2$, M = 1203.51, light yellow crystal $0.10 \times 0.05 \times 0.03$ mm, a = 10.073(1), b = 10.748(1), c = 13.410(1) Å, a = 75.43(1), $\beta = 73.18(1)$, $\gamma = 78.93(1)^\circ$, V = 1333.8(2) Å³, $\rho_{calcd.} = 1.498$ g cm⁻³, $\mu = 3.937$ mm⁻¹, empirical absorption correction ($0.694 \le T \le 0.891$), Z = 1, triclinic, space group $P\overline{1}$ (No. 2), $\lambda = 0.71073$ Å, T = 198 K, ω and ϕ scans, 14284 reflections collected ($\pm h, \pm k, \pm l$), [($\sin \theta$)/ λ] = 0.66 Å⁻¹, 6298 independent ($R_{int} = 0.045$) and 4335 observed reflections [$I \ge 2\sigma(I)$], 284 refined parameters,

R = 0.044, $wR^2 = 0.087$, max./min. residual electron density 0.60/-0.63 eÅ⁻³, hydrogen atom at N61 from difference Fourier calculations, others calculated and all refined as riding atoms.

{1,4-Bis[3,5-bis(diisopropylamino)-1-(propylamino)-6-oxa-2,4-diaza-1,3,5-hexatrienyl|benzene}bis[cobalt(II) dichloride] (3a·CoCl₂): From 3a (38 mg, 0.05 mmol) and cobalt(II) chloride hexahydrate (23 mg, 0.10 mmol) in DMF (2 mL). Yield: 30 mg (0.03 mmol, 60%), dark blue crystals, m.p. 251 °C. IR (KBr): v = 3255 (m, NH), 3058 (s, CH_{arom.}), 2970 (s, CH_{aliph.}), 2935 (s, CH_{aliph.}), 2875 (s, CH_{aliph}), 1608 (vs, C=O/C=N), 1558 (vs, C=C), 1523 (vs), 1456 (s), 1423 (s), 1367 (s), 1336 (s), 1215 (m), 1149 (m), 1136 (m), 1068 (m), 1041 (m), 964 (w), 889 (w), 867 (w), 840 (w), 796 (w), 754 (m), 711 (w), 624 (w), 578 (w), 547 (w) cm⁻¹. MS (MALDI, matrix DCTB): m/z (%) = 974 (10) [M - Cl]⁺, 939 (5) [M - 2 Cl]⁺, 881 (40) $[M - CoCl_2]^+$, 846 (100) $[M - CoCl_3]^+$, 810 (10) $[M - CoCl_3]^+$ CoCl₄]⁺, 753 (65) [M - 2 CoCl₂]⁺, 652 (100) [M - 2 CoCl₂ - $NiPr_2$]⁺. UV/Vis (acetonitrile): λ_{max} (\tilde{v} , ε) = 685 (14598, 231), 587 $(17035, 180), 233 (42918 \text{ cm}^{-1}, 17828 \text{ M}^{-1} \text{ cm}^{-1}) \text{ nm. } C_{42}H_{76}Cl_{4}$ -Co₂N₁₀O₂ (1012.80): calcd. C 49.81, H 7.56, N 13.83; found C 48.76, H 7.47, N 13.52.

X-ray Crystal Structure Analysis of 3a·CoCl₂:^[13] Formula $C_{42}H_{76}Cl_4Co_2 N_{10}O_2$, M = 1012.79, blue crystal $0.40 \times 0.25 \times 0.10 \text{ mm}$, a = 9.972(1), b = 10.746(1), c = 13.226(1) Å, a = 75.09(1), $\beta = 73.20(1)$, $\gamma = 78.82(1)^\circ$, V = 1300.1(2) Å³, $\rho_{calcd.} = 1.294 \text{ gcm}^{-3}$, $\mu = 0.886 \text{ mm}^{-1}$, empirical absorption correction ($0.718 \le T \le 0.917$), Z = 1, triclinic, space group $P\overline{1}$ (No. 2), $\lambda = 0.71073$ Å, T = 198 K, ω and ϕ scans, 12324 reflections collected ($\pm h$, $\pm k$, $\pm l$), [($\sin\theta$)/ λ] = 0.66 Å⁻¹, 6162 independent ($R_{int} = 0.035$) and 5154 observed reflections [$I \ge 2\sigma(I)$], 283 refined parameters, R = 0.035, $wR^2 = 0.085$, max./min. residual electron density 0.39/–0.39 e Å⁻³, hydrogen atom at N61 from difference Fourier calculations, others calculated and all refined as riding atoms.

{1,4-Bis[3,5-bis(dimethylamino)-1-(propylamino)-6-oxa-2,4-diaza-1,3,5-hexatrienyl]butane}bis[zinc(II) dibromide] (3b·ZnBr₂): From 3b (26 mg, 0.05 mmol) and zinc(II) bromide (22 mg, 0.10 mmol) in DMF (2 mL). Yield: 28 mg (0.03 mmol, 58%), colourless crystals, m.p. 190 °C. IR (KBr): $\tilde{v} = 3303$ (s, NH), 2966 (s, CH_{aliph}.), 2935 (s, CH_{aliph}.), 2875 (s, CH_{aliph}.), 1610 (vs, C=O/C=N), 1558 (vs, C=C), 1490 (s), 1411 (s), 1384 (s), 1286 (m), 1205 (m), 1141 (m), 1091 (w), 1043 (w), 972 (w), 896 (w), 846 (w), 827 (w), 756 (w), 707 (w), 676 (w) cm⁻¹. MS (MALDI, matrix DCTB): *m/z* (%) = 814 (10) [M – ZnBr]⁺, 734 (25) [M – ZnBr₂]⁺, 653 (30) [M – ZnBr₃]⁺, 509 (50) [M – 2 ZnBr₂ – 2 NMe₂]⁺. UV/Vis (acetonitrile): λ_{max} (\tilde{v} , ε) = 255 (39215, 26930), 217 (46082 cm⁻¹, sh, 24872 M⁻¹ cm⁻¹) nm. C₂₄H₄₈Br₄N₁₀O₂Zn₂ (959.08): calcd. C 30.06, H 5.04, N 14.60; found C 30.55, H 4.82, N 14.65.

X-ray Crystal Structure Analysis of 3b·ZnBr₂:^[13] Formula $C_{24}H_{48}Br_4N_{10}O_2Zn_2$, M = 959.10, colourless crystal $0.25 \times 0.15 \times 0.05 \text{ mm}$, a = 12.514(1), b = 10.913(1), c = 13.939(1) Å, $\beta = 102.67(1)^\circ$, V = 1857.2(3) Å³, $\rho_{calcd.} = 1.715 \text{ g cm}^{-3}$, $\mu = 5.631 \text{ mm}^{-1}$, empirical absorption correction ($0.333 \le T \le 0.766$), Z = 2, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.71073$ Å, T = 198 K, ω and ϕ scans, 12892 reflections collected ($\pm h$, $\pm k$, $\pm l$), [($\sin\theta/\lambda$] = 0.62 Å⁻¹, 3770 independent ($R_{int} = 0.056$) and 2488 observed reflections [$I \ge 2\sigma(I)$], 198 refined parameters, R = 0.047, $wR^2 = 0.103$, max./min. residual electron density 0.82/-0.59 e Å⁻³, hydrogen atom at N61 from difference Fourier calculations, others calculated and all refined as riding atoms.

{1,4-Bis[3,5-bis(dimethylamino)-1-(propylamino)-6-oxa-2,4-diaza-1,3,5-hexatrienyl]butane}bis[copper(II) dichloride] (3b·CuCl₂): From 3b (26 mg, 0.05 mmol) and copper(II) chloride (17 mg, 0.10 mmol) in DMF (2.0 mL). Yield: 34 mg (0.04 mmol, 87%), green crystals, m.p. 161 °C. IR (KBr): $\tilde{v} = 3273$ (m, NH), 3197 (m, NH), 2954 (s, CH_{aliph.}), 2933 (s, CH_{aliph.}), 2873 (s, CH_{aliph.}), 1604 (vs, C=O/C=N), 1564 (vs, C=C), 1467 (s), 1407 (s), 1390 (s), 1292 (m), 1278 (m), 1263 (m), 1199 (m), 1157 (w), 1143 (w), 1093 (w), 1047 (w), 983 (w), 875 (w), 854 (w), 756 (w), 715 (w), 682 (w), 592 (w) cm⁻¹. MS (MALDI, matrix DCTB): m/z (%) = 645 (20) [M – CuCl₂]⁺, 607 (15) [M – CuCl₃]⁺, 571 (55) [M – CuCl₄]⁺, 509 (50) [M – 2 CuCl₂ – 2 NMe₂]⁺. UV/Vis (acetonitrile): λ_{max} (\tilde{v} , ε) = 465 (21505, 101), 252 (39682, 7617), 216 (46296, 7904), 202 (49504 cm⁻¹, 8489 M⁻¹ cm⁻¹) nm. C₂₄H₄₈Cl₄Cu₂N₁₀O₂ (777.61): calcd. C 37.07, H 6.22, N 18.01; found C 36.90, H 6.08, N 17.62.

X-ray Crystal Structure Analysis of 3b·CuCl₂:^[13] Formula $C_{24}H_{48}Cl_4Cu_2N_{10}O_2 \cdot 2C_3H_7NO$, M = 923.80, green crystal $0.10 \times 0.05 \times 0.03$ mm, a = 7.591(1), b = 10.987(1), c = 13.858(1) Å, a = 108.91(1), $\beta = 96.37(1)$, $\gamma = 90.12(1)^\circ$, V = 1085.8(2) Å³, $\rho_{calcd.} = 1.413$ gcm⁻³, $\mu = 1.273$ mm⁻¹, empirical absorption correction $(0.883 \le T \le 0.963)$, Z = 1, triclinic, space group $P\overline{1}$ (No. 2), $\lambda = 0.71073$ Å, T = 198 K, ω and ϕ scans, 6094 reflections collected $(\pm h, \pm k, \pm l)$, $[(\sin\theta)/\lambda] = 0.59$ Å⁻¹, 3786 independent ($R_{int} = 0.057$) and 2534 observed reflections [$I \ge 2\sigma(I)$], 245 refined parameters, R = 0.066, $wR^2 = 0.164$, max./min. residual electron density 1.41/– 0.62 e Å⁻³, hydrogen atom at N61 from difference Fourier calculations, others calculated and all refined as riding atoms.

Bis(acetonitrile)bis{N,N'-bis[5-(diethylamino)-1,3-diphenyl-2,4-diaza-6-oxa-1,3,5-hexatrienyl]-1,3-propylenediamine}dinickel(II) Bis(perchlorate) [4b·Ni(ClO₄)₂]: A solution of 4b (68 mg, 0.1 mmol) in acetonitrile (1.9 mL) was treated with nickel(II) perchlorate (36 mg, 0.1 mmol). After removal of undissolved starting material by filtration, diethyl ether (10 mL) was carefully added to the filtrate to form an upper layer. After 3 d, blue crystals were formed. Yield: 50 mg (0.04 mol, 80%), blue crystals, m.p. 195 °C. ¹H NMR $(300.13 \text{ MHz}, \text{CDCl}_3)$: $\delta = 0.85 (\text{br.}), 0.99 (\text{br.}), 2.07 (\text{br.}), 2.73 (\text{br.})$ 3.14 (br.), 3.55 (br.), 7.32 (br.), 7.81 (br.), 8.03 (br.) ppm. ¹³C NMR $(75.47 \text{ MHz}, \text{ CDCl}_3): \delta = 12.4, 12.6 (CH_3), 25.5 (CH_2), 38.7 (br., 12.6)$ NCH₂), 126.4, 126.7, 126.8, 128.9, 129.1 (CH_{arom.}), 133.5, 136.2 (*i*-CH_{arom.}), 157.5, 160.7 (CN), 161.8 (CO) ppm. IR (KBr): $\tilde{v} = 3384$ (br., NH), 3075 (w, CH_{arom}), 2932 (w, CH_{aliph}), 1653 (m, C=O), 1623 (s, C=N), 1583 (s, C=N), 1473 (m, C=C), 1457 (m), 1436 (m), 1419 (m), 1298 (m), 1145 (vs), 1116 (vs), 1090 (vs), 700 (m), 637 (s), 629 (s) cm⁻¹. MS (ESI): m/z = 1630, 1528, 1185, 1134, 1013, 841, 685.5 [C₄₁H₄₈N₈O₂], 371. UV/Vis (acetonitrile): λ (\tilde{v} , ε) = 306 (sh, 32679, 5472), 243 (41152 cm⁻¹, 15935 M^{-1} cm⁻¹) nm. C86H108Cl4N18Ni2O22·2CH3CN (2080.57): calcd. C 51.84, H 5.41, N 13.43; found C 51.85, H 5.53, N 13.44.

X-ray Crystal Structure Analysis of 4b·Ni(ClO₄)₂:^[13] Formula $C_{41}H_{46}NiN_{18}O_2 \cdot 2CH_3CN \cdot H_2O \cdot 2ClO_4 \cdot 2C_4H_{10}O$, M = 1188.83, blue crystal $0.30 \times 0.30 \times 0.20$ mm, a = 12.620(1), b = 14.737(1), c = 17.209(1) Å, a = 95.72(1), $\beta = 101.72(1)$, $\gamma = 91.89(1)^\circ$, V = 3113.6(4) Å³, $\rho_{calcd.} = 1.268$ gcm⁻³, $\mu = 0.463$ mm⁻¹, empirical absorption correction ($0.874 \le T \le 0.913$), Z = 2, triclinic, space group $P\overline{1}$ (No. 2), $\lambda = 0.71073$ Å, T = 198 K, ω and ϕ scans, 34657 reflections collected ($\pm h, \pm k, \pm l$), [($\sin \theta$)/ λ] = 0.66 Å⁻¹, 14757 independent ($R_{int} = 0.063$) and 9480 observed reflections [$I \ge 2 \sigma(I)$], 667 refined parameters, R = 0.082, $wR^2 = 0.259$, max./min. residual electron density 1.71/-0.72 e Å⁻³, ether and acetonitrile molecules heavily disordered and refined with geometrical and thermal restraints, hydrogen atoms at O41 from difference Fourier calculations, others calculated and all refined as riding atoms.

 $\{N,N'-Bis[5-(diethylamino)-1,3-diphenyl-2,4-diaza-6-oxa-1,3,5-hexa-trienyl]-1,8-octylenediamine<math>$ nickel(II) Dinitrate $[4d\cdot Ni(NO_3)_2]$: A

solution of 4d (34 mg, 0.05 mmol) in chloroform (1.9 mL) was treated with nickel(II) nitrate (29 mg, 0.1 mmol). After removal of undissolved starting material by filtration, diethyl ether (10 mL) was carefully added to the filtrate to form an upper layer. After 3 d, green crystals were formed. Yield: 23 mg (0.03 mmol, 49%), green crystals, m.p. 180–181 °C. IR (KBr): $\tilde{v} = 3425$ (br., H₂O), 3226 (br., NH), 3060 (m, CH_{arom.}), 2972 (s, CH_{aliph.}), 2935 (s, CH_{aliph}), 2869 (w, CH_{aliph}), 1681 (s, C=O), 1624 (vs, C=O), 1612 (s, C=N) 1585 (vs, C=N), 1546 (vs, C=C), 1500 (vs, C=C), 1448 (vs), 1431 (vs), 1382 (vs), 1301 (vs), 1276 (vs), 1217 (m), 1176 (w), 1139 (m), 1101 (m), 1076 (w), 1024 (m), 966 (vw), 833 (vw), 827 (vw), 817 (vw), 806 (w), 777 (w), 752 (vw), 725 (m), 698 (s), 669 (w), 624 (vw) cm⁻¹. MS (ESI): 874 $[C_{46}H_{58}N_8NiO_2 \cdot NO_3]^+$, 811 $[C_{46}H_{57}N_8Ni]^+$, 777 $[C_{46}H_{58}N_8 + Na]^+$, 755 $[C_{46}H_{58}N_8 + H]^+$, 442 $[C_{46}H_{58}N_8Ni \cdot 2H_2O]^{2+}$, 406 $[C_{46}H_{58}N_8Ni]^{2+}$, 378 $[C_{46}H_{58}N_8 +$ 2H]²⁺. UV/Vis (acetonitrile): $\lambda_{max.}$ (\tilde{v} , ε) = 241 (41493 cm⁻¹, 85100 $\mbox{m}^{-1}\mbox{cm}^{-1})$ nm. $C_{46}H_{58}N_{10}NiO_8$ (936.37): calcd. C 58.92, H 6.23, N 14.94; found C 58.92, H 6.12, N 14.91.

X-ray Crystal Structure Analysis of 4d·Ni(NO₃)₂:^[13] Formula $C_{46}H_{58}N_{10}NiO_8\cdot 2CHCl_3$, M = 1176.47, green crystal $0.35 \times 0.30 \times 0.30 \text{ mm}$, a = 11.915(1), b = 19.990(1), c = 23.904(1) Å, $\beta = 100.57(1)^\circ$, V = 5596.9(6) Å³, $\rho_{calcd.} = 1.396$ g cm⁻³, $\mu = 0.692$ mm⁻¹, empirical absorption correction ($0.794 \le T \le 0.819$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.71073$ Å, T = 198 K, ω and ϕ scans, 47247 reflections collected ($\pm h, \pm k, \pm l$), [($\sin\theta$)/ λ] = 0.66 Å⁻¹, 13259 independent ($R_{int} = 0.055$) and 9464 observed reflections [$I \ge 2\sigma(I)$], 670 refined parameters, R = 0.053, $wR^2 = 0.148$, max./min. residual electron density 1.16/-0.57 e Å⁻³, hydrogen atoms at N from difference Fourier calculations, others calculated and all refined as riding atoms.

{*N*,*N*'-Bis[5-(diethylamino)-1,3-diphenyl-2,4-diaza-6-oxa-1,3,5-hexatrienyl]-1,2-trans-cyclohexanediamine}nickel(II) Dinitrate [4h·Ni(NO₃)₂]: Ligand 4h (36 mg, 0.05 mmol) and nickel(II) nitrate (29 mg, 0.1 mmol) were dissolved in acetonitrile (2 mL). After centrifugation to remove undissolved residues, diethyl ether was allowed to diffuse into the solution. Green crystals were formed overnight. After 5 d, they were collected, washed with diethyl ether and dried under reduced pressure. Yield: 37 mg (0.04 mmol, 88%), green crystals, m.p. 205 °C. IR (KBr): $\tilde{v} = 3255$ (m, NH), 3091 (w, CH_{arom.}), 3060 (w, CH_{arom.}), 3033 (w, CH_{arom.}), 2974 (m, CH_{aliph.}), 2931 (m, CH_{aliph.}), 2858 (s, CH_{aliph.}), 1652 (s, C=O), 1625 (s, C=O), 1604 (s, C=N), 1579 (s, C=N), 1560 (s, C=N), 1496 (s, C=N), 1458 (s, C=C), 1384 (vs, C=C), 1299 (s), 1278 (s), 1218 (w), 1139 (w), 1097 (w), 1078 (w), 1024 (w), 773 (w), 730 (w), 700 (m) cm⁻¹. MS (ESI): m/z (%) = 844 [C₄₄H₅₂N₉NiO₅]⁺, 781 [C₄₄H₅₁N₈NiO₂]⁺, 748 [C44H52N8O2 + Na]+, 726 [C44H52N8O2 + H]+. UV/Vis (acetonitrile): $\lambda_{\text{max.}}$ (\tilde{v} , ε) = 237 (42194 cm⁻¹, 41000 m⁻¹ cm⁻¹) nm. C46H56N8NiO4 (842.37): calcd. C 58.48, H 6.08, N 14.83; found C 58.86, H 6.00, N 14.92.

X-ray Crystal Structure Analysis of 4h·Ni(NO₃)₂:^[13] Formula $C_{44}H_{52}N_8NiO_2\cdot 2NO_3$, M = 907.67, green crystal $0.40 \times 0.35 \times 0.20$ mm, a = 22.106(1), b = 12.231(1), c = 18.015(1) Å, $\beta = 97.14(1)^\circ$, V = 4833.1(5) Å³, $\rho_{calcd.} = 1.247$ gcm⁻³, $\mu = 0.461$ mm⁻¹, empirical absorption correction ($0.837 \le T \le 0.914$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.71073$ Å, T = 198 K, ω and ϕ scans, 32485 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin $\theta)/\lambda$] = 0.67 Å⁻¹, 11935 independent ($R_{int} = 0.047$) and 8256 observed reflections [$I \ge 2\sigma(I)$], 600 refined parameters, R = 0.068, $wR^2 = 0.237$, max./min. residual electron density 1.43/–0.62 eÅ⁻³, hydrogen atoms at N from difference Fourier calculations, others calculated and all refined as riding atoms.



(2,6-Bis{[5-(diethylamino)-1,3-diphenyl-2,4-diaza-6-oxa-1,3,5-hexatrienyl]amino}pyridine)(methanol)nickel(II) Dinitrate [6·Ni(NO₃)₂]: 6 (36 mg, 0.05 mmol) and nickel(II) nitrate (29 mg, 0.1 mmol) were dissolved in methanol (1.9 mL). After centrifugation to remove any precipitate, diethyl ether was allowed to diffuse into the solution. After 3 d, light pink crystals precipitated. Yield: 38 mg (0.04 mmol, 82%), m.p. 211 °C. IR (KBr): $\tilde{v} = 3486$ (m, NH), 3062 (w, CH_{arom}), 2968 (m, CH_{aliph}), 2927 (m, CH_{aliph}), 2871 (w, CH_{aliph}), 2856 (w, CH_{aliph}), 2360 (w), 2343 (w), 1577 (s, C=O), 1566 (vs, C=N), 1467 (s, C=C), 1438 (m), 1417 (s), 1342 (m), 1282 (s), 1159 (w), 1099 (vs), 1078 (w), 1022 (w), 960 (vw), 914 (vw), 883 (vw), 777 (m), 698 (m) cm⁻¹. MS (ESI): m/z = 776 [C₄₃H₄₄N₉NiO₂]⁺. UV/Vis (acetonitrile): λ_{max} . (\tilde{v} , ε) = 248 (40322 cm⁻¹, 19100 m⁻¹cm⁻¹) nm. C₄₄H₄₉N₁₁NiO₉ (934.65): calcd. C 57.22, H 5.03, N 17.07; found C 57.06, H 4.87, N 17.09.

X-ray Crystal Structure Analysis of [6·Ni(NO₃)₂]:^[13] Formula $C_{43}H_{45}N_9NiO_2$ ·CH₃OH·2NO₃, M = 934.65, colourless crystal $0.45 \times 0.20 \times 0.20$ mm, a = 11.894(1), b = 13.522(1), c = 14.701(1) Å, a = 88.29(1), $\beta = 80.43(1)$, $\gamma = 80.34(1)^{\circ}$, V = 2298.4(3) Å³, $\rho_{calcd.} = 1.351$ gcm⁻³, $\mu = 0.489$ mm⁻¹, empirical absorption correction ($0.810 \le T \le 0.909$), Z = 2, triclinic, space group $P\overline{1}$ (No. 2), $\lambda = 0.71073$ Å, T = 198 K, ω and ϕ scans, 25540 reflections collected ($\pm h, \pm k, \pm l$), [($\sin \theta$)/ λ] = 0.66 Å⁻¹, 10912 independent ($R_{int} = 0.054$) and 8787 observed reflections [$I \ge 2\sigma(I)$], 603 refined parameters, R = 0.045, $wR^2 = 0.116$, max./min. residual electron density 0.42/-0.46 e Å⁻³, hydrogen atoms at N4 from difference Fourier calculations, others calculated and all refined as riding atoms.

(2,6-Bis{[5-(diethylamino)-1,3-diphenyl-2,4-diaza-6-oxa-1,3,5hexatrienyl]amino}pyridine)dipalladium(II) Tetrachloride (6·2PdCl₂): 6 (36 mg, 0.05 mmol) and bis(benzonitrile)palladium(II) dichloride (39 mg, 0.1 mmol) were dissolved in acetonitrile (1.9 mL). After centrifugation to remove any precipitate, diethyl ether was allowed to diffuse into the solution. After 1 week, orange crystals were formed. Yield: 34 mg (0.03 mol, 63%), m.p. 218 °C. IR (KBr): $\tilde{v} = 3486$ (m, NH), 3060 (m, CH_{arom}), 3037 (m, CH_{arom.}), 2968 (m, CH_{aliph.}), 2927 (s, CH_{aliph.}), 2862 (m, CH_{aliph.}), 2854 (m, CH_{aliph}), 2360 (m), 2341 (m), 1703 (vs, C=O), 1625 (s,C=O), 1598 (s, C=N), 1564 (s, C=N), 1546 (vs, C=N), 1512 (s, C=N), 1492 (s, C=C), 1466 (vs, C=C), 1382 (m), 1344 (m), 1299 (m), 1261 (s), 1240 (s), 1218 (m), 1178 (w), 1136 (m), 1093 (m), 1026 (m), 981 (w), 889 (w), 823 (w), 765 (m), 700 (m) cm^{-1}. MS (ESI): $m/z = 1034 [C_{43}H_{45}Cl_3N_9O_2Pd_2]^+$, 1000 $[C_{43}H_{44}N_9O_2^-$ PdCl₂]⁺, 824 [C₄₃H₄₄N₉O₂Pd]⁺. C₄₃H₄₅Cl₄N₉O₂Pd₂ (1071.05): calcd. C 48.06, H 4.22, N 11.73; found C 48.21, H 4.48, N 11.24.

X-ray Crystal Structure Analysis of (6·2PdCl₂):^[13] Formula $C_{43}H_{45}Cl_4N_9O_2Pd_2\cdot 2C_4H_{10}O\cdot CH_3CN$, M = 1263.77, orange crystal $0.35 \times 0.20 \times 0.10$ mm, a = 13.202(1), b = 15.628(1), c = 28.043(1) Å, $\beta = 98.16(1)^\circ$, V = 5727.3(6) Å³, $\rho_{calcd.} = 1.466$ g cm⁻³, $\mu = 0.867$ mm⁻¹, empirical absorption correction (0.751 $\leq T \leq 0.918$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.71073$ Å, T = 198 K, ω and ϕ scans, 28887 reflections collected ($\pm h, \pm k, \pm l$), [(sin θ)/ λ] = 0.62 Å⁻¹, 11369 independent ($R_{int} = 0.072$) and 7879 observed reflections [$I \geq 2 \sigma(I)$], 623 refined parameters, R = 0.063, $wR^2 = 0.183$, max./min. residual electron density 1.56/–0.81 eÅ⁻³, hydrogen atoms at N from difference Fourier calculations, others calculated and all refined as riding atoms.

(Aqua)[bis(2-{[5-(diethylamino)-1,3-diphenyl-2,4-diaza-6-oxa-1,3,5-hexatrienyl]amino}ethyl)(2-{[1,3-diphenyl-2-aza-4-oxa-1,3-butadienyl]amino}ethyl)amine]nickel(II) Bis(perchlorate) (9): To a solution of 7a (53 mg, 0.05 mmol) and nickel(II) perchlorate (36 mg, 0.1 mmol) in methanol (1.9 mL) triethylamine (50 µL) was

added at 55 °C. After 2 h at 55 °C, the reaction mixture was cooled slowly to room temperature, and diethyl ether was added to the resulting solution to form an upper layer. After 2 d, colourless crystals of **9** were collected. Yield: 23 mg (0.02 mmol, 37%), colourless crystals, m.p. 172 °C. IR (KBr): $\tilde{v} = 3286$ (m, NH), 3062 (m, CH_{arom}), 2976 (m, CH_{arom}), 2933 (m, CH_{aliph}), 2875 (m, CH_{aliph}), 1676 (s, C=O), 1618 (vs, C=O), 1600 (s, C=N), 1577 (s, C=N), 1510 (s, C=C), 1488 (vs, C=C), 1446 (vs), 1427 (vs), 1379 (s), 1271 (s), 1107 (vs), 1093 (vs), 916 (vw), 775 (w), 711 (w), 698 (m) cm⁻¹. MS (MALDI): m/z (%) = 1123 [C₅₈H₆₄N₁₁NiO₃]⁺, 510.9 [C₅₈H₆₅N₁₁NiO₃]²⁺. C₅₈H₆₇Cl₂N₁₁NiO₁₂·2ClO₄·2C₄H₁₀O·MeOH (1420.12): calcd. C 56.67, H 6.46, N 10.85; found C 56.39, H 6.13, N 11.09.

Analysis of 9:^[13] Crystal Structure Formula X-rav $[N(C_{21}H_{25}N_4O_2)_2(C_{16}H_{15}N_2O)]Ni \cdot H_2O \cdot 2ClO_4 \cdot 2C_4H_{10}O \cdot CH_3OH,$ M = 1420.12, colourless crystal $0.30 \times 0.30 \times 0.20$ mm, a =14.410(1), b = 14.851(1), c = 18.958(1) Å, a = 80.35(1), $\beta =$ 74.70(1), $\gamma = 68.85(1)^{\circ}$, $V = 3637.8(4) \text{ Å}^3$, $\rho_{\text{calcd.}} = 1.296 \text{ g cm}^{-3}$, μ = 0.410 mm⁻¹, empirical absorption correction ($0.887 \le T \le 0.923$), Z = 2, triclinic, space group $P\overline{1}$ (No. 2), $\lambda = 0.71073$ Å, T = 198 K, ω and ϕ scans, 40555 reflections collected $(\pm h, \pm k, \pm l)$, $[(\sin\theta)/\lambda]$ = 0.60 Å⁻¹, 12810 independent (R_{int} = 0.056) and 8751 observed reflections $[I \ge 2\sigma(I)]$, 893 refined parameters, R = 0.063, $wR^2 =$ 0.191, max./min. residual electron density 1.74/-0.55 e Å-3, hydrogen atoms at N and water from difference Fourier calculations, others calculated and all refined as riding atoms.

Acknowledgments

The authors thank the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 424 and European Graduate College "Template Directed Chemical Synthesis") and the Fonds der Chemischen Industrie (Frankfurt) for financial support.

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Published Online: October 27, 2008