Expanded Phthalocyanine Analogues: Synthesis and Characterization of New Triazole-Derived Annulenes Containing Six Heterocyclic Subunits

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Dedicated to Professor Fred Wudl on occasion of his 60th birthday

Abstract: A series of heteroannulenes **3a–f** containing four subunits of isoindole, two 1,2,4-triazole moieties, and six aza bridges have been synthesized by dimerization of the corresponding metallated, three-unit intermediates **5a–f**. All these 28 π-electron triazolephthalocyanine derivatives coordinate two metal ions within their central cavity and are the first examples of expanded heterophthalocyanines. Spectroscopic properties of these macrocycles show evidence for extended conjugation and antiaromaticity. The nature of the metal ions plays a definite role in the electronic properties of these derivatives.

Keywords: annulenes · expanded macrocycles · nickel · phthalocyanines · triazoles · zinc

Introduction

The unique electrical, optical, and liquid crystalline properties of some unsaturated metallomacrocycles like porphyrins[1] and phthalocyanines,[2] together with their high thermal, optical, and chemical stability, are some of the main reasons for their development over the last few decades.[3] Among them, phthalocyanines, which have commonly been used as pigments and dyes, are to be noted owing to their singular electronic and physicochemical features.[2–4] They show intense absorption bands in the visible region at 650–700 nm (Q-band) corresponding to HOMO–LUMO $\pi \rightarrow \pi^*$ transitions, and the position of this Q-band may be modulated by varying the nature of the central metal atom, its oxidation state, or by increasing π conjugation.[5]

The search for new molecular materials[6] has stimulated research towards new structurally modified polypyrrolic systems with potential applications in semiconductors technology and optoelectronics.[7] A very promising trend in the development of improved porphyrinic and azaporphyrinic systems is the variation of the number of pyrrole moieties that constitute the macrocycle. Thus, for example, subphthalocyanines[8] are aromatic macrocycles consisting of three subunits of isoindole with a boron atom within their central cavity. With respect to larger systems, a big effort has been devoted to the area of "expanded porphyrins",[9] and consequently a large diversity of substances such as sapphyrins,[10] tetraoxaporphyrins,[11a–c] hexaphyrins,[11d–g] and others[12] have been reported. In contrast, few examples of "expanded phthalocyanines" have appeared to date, and they have only been focused on the so-called superphthalocyanines,[13] which are structures made up of five isoindole subunits that are able to complex the bulky uranyl cation within their central binding core.

Expanded macrocycles possess not only a larger cavity than that of the corresponding phthalocyanine or porphyrin, but also an increased degree of conjugation; this results, in many cases, in a bathochromic shift in wavelength of their corresponding Q-band.[9] This fact is very advantageous since it allows the tuning of some physical properties of these compounds in order to obtain, for example, third-order nonlinear optical materials[14, 7b, 7c] and infrared-absorbing chromophores suitable to be used in areas such as digital data storage,[15] security marking, or optical limiting.[16] More recently, research on these systems has also been focussed on their biomedical applications, especially in photodynamic therapy (PDT), for which absorption of light at wavelengths greater than 630 nm are necessary,[17] and in soft tissue imaging with computer image enhancement.[18] From a different point of view, the study and characterization of different expanded macrocycles also renders a detailed understanding on questions of ring size, aromaticity, and factors controlling effective macrocyclic stability.[9]

Our interest in the design and synthesis of new phthalocyanine analogues has led us to develop several classes of

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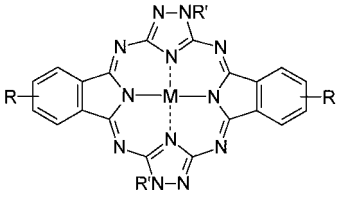
molecules by the introduction of other coordinating heterocycles to replace one or two isoindole moieties in the phthalocyanine structure. Thus, we have prepared a variety of the nonaromatic hemiporphyrazines[19, 20] (**1**) and studied their electric,[19, 21] optical,[22] and liquid crystal[23] properties.



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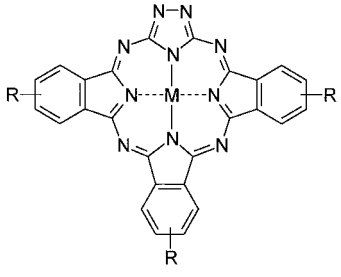
Furthermore, we have described binuclear phthalocyanines,[24] heterobinuclear phthalocyanine–hemiporphyrazine hybrids,[24, 25] and heterotrinuclear phthalocyanine–hemiporphyrazine–phthalocyanine hybrids[25], the Q-bands of which, are shifted to longer wavelengths into the red region, as a consequence of the increased conjugation.

In addition, we reported for the first time the formal replacement of an isoindole ring in the phthalocyanine skeleton, by a 1,2,4-triazole subunit, to afford a fully conjugated 18 π-electron macrocycle,[26] which has been called triazolephthalocyanine (**2**), and we have studied its supramolecular organization[27] as well as the electric and optical properties[28] of these derivatives.



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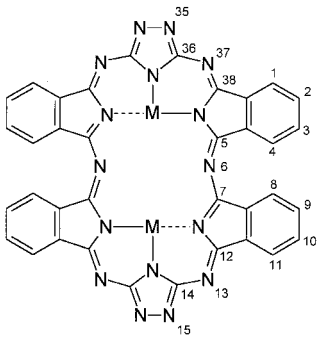

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Now, we report on the synthesis and characterization of a new type of phthalocyanine analogue **3** that consists of four subunits of isoindole and two triazole moieties and which is able to coordinate two metal ions within its central binding core. To the best of our knowledge this is the only reported example of an expanded heterophthalocyanine derivative.

Abstract in Spanish: *Se ha sintetizado una serie de heteroanulenos **3a–f** que contienen cuatro unidades de isoindol, dos agrupaciones 1,2,4-triazol y seis puentes aza, por reacción de dimerización de los correspondientes intermedios metalados de tres unidades **5a–f**. Todos estos derivados de triazoloftalocianina con 28 electrones π, coordinan dos iones metálicos en su cavidad central y son los primeros ejemplos de heteroftalocianinas expandidas. Las propiedades espectroscópicas de estos macrociclos evidencian su conjugación extendida y antiaromaticidad, mientras que la naturaleza de los iones metálicos juega un papel decisivo en las propiedades electrónicas de estos derivados.*

Results and Discussion

In a previous paper[20] we described the synthesis of 1,3-bis[(3′-imino-1′-isoindolinylidene)amino]-1,2,4-triazole (**4a**) and its nickel complex **5a**, obtained by metallation of the free base. Now, we have prepared the substituted three-unit intermediates **4b** and **c**, the nickel complex **5b**, and the novel three-unit zinc complexes **5d** and **e** by using a similar procedure to that reported for the nickel derivatives.[20] In contrast with their respective free bases **4**, which undergo thermal cleavage affording the corresponding hemiporphyrazines **1** as final products when heated at 135 °C in 2-ethoxyethanol,[20] the metallated compounds **5** do not split under heating. On the contrary, they self-condense through their "outer" iminic double bond. Therefore, expanded analogues **3a–f** were achieved by dimerization of the corresponding three-unit intermediates **5a–f** in 2-ethoxyethanol at reflux temperature (Scheme 1).

Compounds **5c** and **f** turned out to be quite reactive and could not be isolated, since mixtures of them and the corresponding macrocycles **3c** and **f** were obtained in the metallation step of **4c**. No explanation has been found for the higher reactivity of **5c** and **f** in comparison with that of **5a**, **b**, **d**, and **e**.

A common feature of macrocycles **3** is their instability in strong acid media denoting their Schiff base character, and whereas red is the color exhibited by the bisnickel compounds **3a–c**, zinc complexes **3d–f** were collected as orange crystalline solids.

Peripherally substituted derivatives **3b**, **c**, **e**, and **f** were obtained as mixtures of the theoretical seven structural isomers and their purification was carried out by chromatography on silica gel, previously deactivated with 1% triethylamine. Under these conditions yields of 28–59% were gained, and all spectroscopic data were taken from mixtures of isomers. Moreover, it was possible to isolate the major isomer of **3f** (inferred from the ^{13}C NMR spectrum of the mixture of structural isomers) by standard column chromatography. Unsubstituted compounds **3a** and **d**, which are scarcely soluble in organic solvents, were obtained in 81% and 69% yield, respectively, after purification by triturating in 2-ethoxyethanol and then hot methanol. Further recrystallization from α-chloronaphthalene afforded analytical samples.

The expanded analogues **3** may also be prepared by condensation of a suitable 1,3-diiminoisoindolenine with 3,5-diamino-1,2,4-triazole (guanazole) in stoichiometric ratio in the presence of the appropriate metal acetate in acetonitrile at 70 °C. However, this one-step method is not very convenient, since mixtures of **3** and triazolephthalocyanines of type **2** are obtained, thus making the isolation step more difficult. Indeed, in most of the cases yields are significantly lower than the overall yield of the stepwise procedure, due to the arduous purification process. Thus, for example, the one-step method affords 12% of macrocycle **3b**,whereas the yield for

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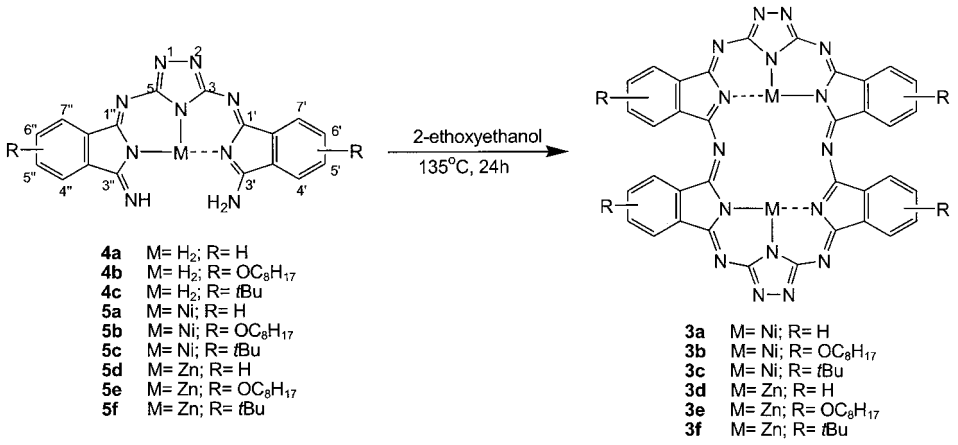

4a M= H_2; R= H
4b M= H_2; R= OC_8H_{17}
4c M= H_2; R= *t*Bu
5a M= Ni; R= H
5b M= Ni; R= OC_8H_{17}
5c M= Ni; R= *t*Bu
5d M= Zn; R= H
5e M= Zn; R= OC_8H_{17}
5f M= Zn; R= *t*Bu

3a M= Ni; R= H
3b M= Ni; R= OC_8H_{17}
3c M= Ni; R= *t*Bu
3d M= Zn; R= H
3e M= Zn; R= OC_8H_{17}
3f M= Zn; R= *t*Bu

Scheme 1. Synthesis of expanded phthalocyanine analogues **3**.

the same compound (with respect to the iminoisoindolenine precursor) obtained through the stepwise method is 20%.

The symmetry, as well as the extended conjugated 28 π-electron system and antiaromatic character of these expanded macrocycles are particularly evidenced by their spectroscopic properties. Hence, all compounds show intensive isotopic clusters in FAB or MALDI TOF MS at $[M+H]^+$ which corroborate their structures. Moreover, two groups of bands at 1650–1550 cm^{-1} and 1525–1454 cm^{-1} assignable to C=N and C=C stretching vibrations, respectively, dominate the infrared spectra.

Their ^1H NMR spectra show the expected characteristic signals for every type of proton, pointing out the paratropic antiaromatic character of the ring system. Interestingly, aromatic protons of the macrocycles **3b** ($\delta = 6.6–7.7$) appear at the same range ($\delta = 6.8–7.8$) as those of their related hemiporphyrazine analogue **1a** (M = Ni, R = OC_8H_{17} and R′ = $C_{12}H_{25}$),[29] and this is also observed for the aliphatic OCH_2 protons of **3b** ($\delta = 3.90$) and **1a** ($\delta = 3.96$). This fact reveals the low degree of π-electron delocalization for these expanded analogues, whose magnitude seems to be similar to that exhibited by hemiporphyrazines.[19] The small decrease of diatropicity with respect to the isoindolenine precursors (upfield shift of about 0.2–1.0 ppm) is understandable taking into account the electron-withdrawing character of the triazole moiety compensating the shielding effect of the paramagnetic ring current. Besides, a distortion of the macrocycles along with interference in overlap between atomic orbitals in the π system could be responsible for the low antiaromaticity observed.[30]

^{13}C NMR spectra of macrocycles **3** are in good agreement with the proposed structure. Assignments were performed on the basis of DEPT experiments and by comparison with related derivatives previously reported.[20, 31] Therefore, eight groups of signals corresponding to the macrocyclic skeleton are discernible for compound **3c**, while compounds **3b** and **f** exhibit the expected nine sets of signals, in accordance to their structural pattern, in addition to either seven sets of peaks due to the octyloxy substituents of **3b**, or two sets assignable to the *tert*-butyl moieties of **3c** and **f**.

Compound **3e** had a larger tendency to aggregate in solution and gave a badly resolved ^1H NMR spectrum, whereas only aliphatic signals could be observed in the ^{13}C NMR spectrum. In contrast, the *tert*-butyl substitution of compound **3f** permitted the isolation of the major isomer,[32] to which either structure **A** or **B** (Figure 1) has been assigned, on the basis of its spectroscopic features.[33]

Therefore, ^{13}C NMR spectrum of this single isomer revealed the presence of a system with a high degree of symmetry and which exhibited eight signals corresponding to the macrocyclic backbone. A detailed analysis of the ^{13}C NMR spectrum of the **3f** mixture of isomers, showed three signals at $\delta = 158.2$, 156.2, and 155.1 assignable to the triazole carbons, together with seven different signals at $\delta = 174.8$, 174.7, 169.6, 169.3, 163.7, 162.0, and 161.7 that correspond to the iminic carbons, as well as three

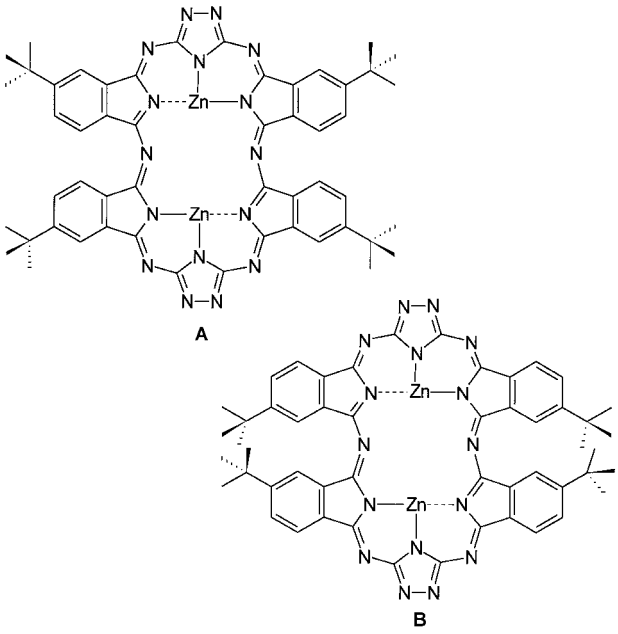

Figure 1. Proposed structures for the major isomer of **3f**.

different signals for the quaternary *tert*-butyl carbons at $\delta =$ 35.6, 35.5, 35.4. The single isomer **3f** exhibited only one signal for the triazole carbon at $\delta = 158.2$, in addition to one signal for the iminic carbon C-38 and another one corresponding to C-5 at $\delta = 169.6$ and 169.3, respectively, along with a solitary signal for the quaternary *tert*-butyl carbon at $\delta = 35.6$. Moreover, the ^1H NMR spectrum of this compound showed a unique kind of isoindole ring with two different doublets at $\delta = 7.74$ and 7.85 ($J = 7.6$ Hz), together with a broad singlet at $\delta = 7.78$, whereas the ^1H NMR spectrum corresponding to the mixture of isomers exhibited in the aromatic region a complex set of signals at $\delta = 8.1–7.7$.

The electronic spectra of the expanded derivatives **3** are dominated by an intense band in the 271–279 nm region (Figure 2), followed by a less intense (50–75% as intense as the highest energy transition) Soret-like band at 338–402 nm, and the lowest energy bands (HOMO–LUMO $\pi \rightarrow \pi^*$ transitions), which are significantly red-shifted relative to hemiporphyrazines **1**. This last feature is diagnostic of their 28 π-electron extended conjugation.

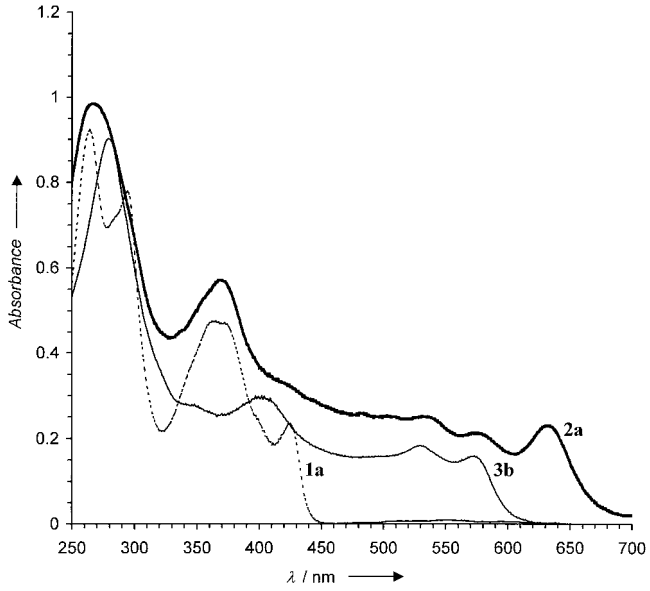

Figure 2. UV/Vis spectra of **1a** (6.98×10^{-6} M), **2a** (1.80×10^{-5} M) and **3b** (1.10×10^{-5} M) in chloroform.

The exact position of the Q-like bands is strongly influenced by the nature of the coordinating metal atoms. Hence, the UV-visible spectra of compounds **3d–f** with two zinc ions within the central cavity show bands at 470–489 nm, that is, 45–64 nm red-shifted with respect to the lowest energy band of hemiporphyrazine **1a** (M = Ni, R = OC_8H_{17}, R′ = $C_{12}H_{25}$).[29] This effect is especially pronounced in nickel-metallated analogues **3a–c** for which bathochromic shifts of 134–148 nm toward longer wavelengths (Figure 3) with respect to compound **1a** are observed. On the other hand Q-like bands of expanded analogues are blue-shifted when compared to the related 18 π-electron triazolephthalocyanine **2a** (M = Ni, R = OC_8H_{17}). This fact may be attributed to the lack of aromaticity of **3**.

The reason for the striking red shift of the bands in nickel complexes is not clear. Most porphyrin and phthalocyanine researchers interpret bathochromic shifts in the electronic spectra as a sign of macrocycle nonplanarity,[34] and some authors have determined the factors that control nonplanar distortions in porphyrins and porphyrazines.[35] In addition to the inherently different tendency to ruffle of every class of macrocycle, other factors like nature of the axial ligands,[35] core size and M–N distance,[36] peripheral substituents,[37] crystal packing,[38] or metal ion size[35] have been found responsible for the observed nonplanarity of several macrocycles. In our case, no substantial effect seems to arise from the peripheral substitution. Based on the studies mentioned above, it appears possible that the observed differences in the UV-visible spectra of nickel and zinc expanded analogues **3** are the result of a larger nonplanar distortion of the bisnickel derivatives with respect to the zinc complexes. Similar metal-ion effects have been found recently for Ni^{II} hydroporphyrins and Ni^{II} *meso*-tetrakis(perfluoroalkyl)porphyrins, these metallomacrocycles being more ruffled than analogous Zn^{II} hydroporphyrins and Zn^{II} *meso*-tetrakis(perfluoroalkyl)porphyrins, respectively.[34a, 36]

In conclusion, 28 π-electron triazolephthalocyanine analogues have been prepared. These Schiff base derived compounds constitute the highest order expanded heterophthalocyanines characterized to date. The general and stepwise character of the preparative method provides an entry to other expanded analogues including less symmetric systems.

Experimental Section

Melting points were determined with a Büchi 504392 S apparatus and are uncorrected. UV/Vis spectra were recorded with Perkin–Elmer Lambda 6 and Hewlett–Packard 8453 instruments. IR spectra were recorded with Philips PU 9716 and Bruker Vector 22 spectrophotometers. FAB–MS and HRMS spectra were determined on a VG AutoSpec instrument. MALDI-TOF MS were recorded with a Bruker Reflex III spectrometer. NMR spectra were recorded with Bruker WM 200 SY, AC 300, and DRX 500 instruments. Elemental analyses were performed with a Perkin–Elmer 2400 apparatus. Column chromatographies were carried out on silica gel Merck-60 (230–400 mesh, 60 Å), and TLC on aluminum sheets precoated with silica gel 60 F_{254} (Merck). Gel-permeation chromatography was carried out on Biobeads SX-3. Chemicals were purchased from Aldrich and used as received without further purification.

***N*³-[(1′*Z*)-5′(6′)-octyloxy-3′-amino-1*H*-isoindol-1′-ylidene]-*N*⁵-[(1″*Z*)-5″(6″)-octyloxy-3″-imino-2″,3″-dihydro-1*H*-isoindol-1″-ylidene]-4*H*-1,2,4-triazole-3,5-diamine (4b)**: A mixture of 5-octyloxy-1,3-diiminoisoindoline (5 g, 18.28 mmol) and 3,5-diamino-1,2,4-triazole (0.91 g, 9.14 mmol) in dry methanol (50 mL) was heated under reflux for 4 d. The precipitate was filtered and repeatedly triturated in hot methanol to afford the three-unit intermediate **4b** as an orange solid (4.80 g, 85%). M.p. 170 °C (decomp); ^{1}H NMR (200 MHz, [D]TFA): δ = 8.2–7.5 (3m, 6H; H-arom), 4.3 (m, 4H; OCH_2), 2.0 (m, 4H; OCH_2CH_2), 1.5 (s, 20H; CH_2), 0.9 (m, 6H; CH_3); ^{13}C NMR (50 MHz, [D]TFA): δ = 169.7, 167.7, 167.0, 166.2 (C-1′, C-3′, C-1″, C-3″), 157.6, 157.2, 156.9 (C-3, C-5), 138.0, 130.8, 129.3 125.0, 123.2, 118.5, 112.3 (C-3a′, C-4′, C-5′, C-6′, C-7′, C-7a′, C-3a″, C-4″, C-5″, C-6″, C-7″, C-7a″), 71.7 (OCH_2), 32.9, 30.3, 29.8, 26.8, 23.6 (CH_2), 14.0 (CH_3); IR (KBr): $\tilde{\nu}$ = 3400–3000 (N–H), 2920, 2860 (C–H), 1690, 1620 1540 (C=N), 1490, 1420, 1290, 1230, 1060, 750 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 611 (2) $[M]^+$, 355 (100) $[M-2C_8H_{16}O]^+$; elemental analysis calcd (%) for $C_{34}H_{45}N_9O_2$ (611.79): C 66.75, H 7.41, N 20.61; found C 66.40, H 7.12, N 20.73.

***N*³-[(1′*Z*)-5′(6′)-*tert*-butyl-3′-amino-1*H*-isoindol-1′-ylidene]-*N*⁵-[(1″*Z*)-5″(6″)-*tert*-butyl-3″-imino-2″,3″-dihydro-1*H*-isoindol-1″-ylidene]-4*H*-1,2,4-triazole-3,5-diamine (4c)**: A solution of 5-*tert*-butyl-1,3-diiminoisoindoline (200 mg), 1.0 mmol) and guanazole (40 mg, 0.4 mmol) in a mixture of acetonitrile (10 mL) and methanol (1 mL) was heated at 70 °C for 3 d. The precipitate was filtered and repeatedly triturated in diethyl ether to afford **4c** as an orange solid (150 mg, 80%). M.p. >250 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.5–7.5 (4m, 6H; H-arom), 1.30 (s, 9H; CCH_3), 1.20 (s, 9H; CCH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 163.9 (C-3′, C-3″), 156.6, 155.2 (C-1′, C-1″ C-3, C-5), 130.1, 129.7, 128.7, 123.4, 123.0, 122.6, 121.8, 120.1, 119.4, 119.1 (C-3a′, C-4′, C-5′, C-6′, C-7′, C-7a′, C-3a″, C-4″, C-5″, C-6″, C-7″, C-7a″), 35.8 ($C(CH_3)_3$), 31.7 ($C(CH_3)_3$); IR (KBr): $\tilde{\nu}$ = 3211 (N–H), 2963, 1638 (C=N), 1540, 1456, 1406, 1365, 1326, 1262, 1141, 1083, 880, 841, 767 cm^{-1}; MS (FAB, *m*-NBA): *m*/*z*: 468 $[M+H]^+$; elemental analysis calcd (%) for $C_{26}H_{29}N_9$ (467.57): C 66.79, H 6.25, N 26.96; found C 66.45, H 6.12, N 26.67.

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N^3-[(1′*Z*)-5′(6′)-octyloxy-3′-amino-1*H*-isoindol-1′-ylidene]-N^5-[(1″*Z*)-5″(6″)-octyloxy-3″-imino-2″,3″-dihydro-1*H*-isoindol-1″-ylidene]-3,5-diamino-4*H*-1,2,4-triazolatonickel(II) (5b): Compound **4b** (200 mg, 0.33 mmol) and $Ni(AcO)_2 \cdot 4H_2O$ (81 mg, 0.33 mmol) were stirred in 2-ethoxyethanol (20 mL) at room temperature for 24 h. After filtration, the solid was washed with methanol to yield **5b** as a dark reddish solid (220 mg, 65 %). M.p. >250 °C; IR (KBr): $\tilde{\nu}$ = 3144, 3065 (N–H), 2924, 2854 (C–H), 1637, 1616 (C=N), 1487, 1468, 1389, 1366, 1285, 1242, 1084, 831, 781 cm^{-1}; MS (FAB, 3-NOBA + TFA): *m*/*z*: 668, 670 $[M+H]^+$; HRMS (FAB) calcd for $C_{34}H_{44}N_9NiO_2$: 668.2971, found 668.3001.

N^3-[(1′*Z*)-3′-amino-1*H*-isoindol-1′-ylidene]-N^5-[(1″*Z*)-3″-imino-2″,3″-dihydro-1*H*-isoindol-1″-ylidene]-3,5-diamino-4*H*-1,2,4-triazolatozinc(II) (5d): A mixture of **4a**[20] (500 mg, 1.41 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (309 mg, 1.41 mmol) in 2-ethoxyethanol (40 mL) was stirred at room temperature for 24 h. After centrifugation and removal of the liquid phase, the solid was triturated in hot methanol, filtered and dried to give **5d** as a dark orange solid (512 mg, 87 %). M.p. >250 °C; IR (KBr): $\tilde{\nu}$ = 3296 (N–H), 2926 (C–H), 1610, 1559 (C=N), 1470, 1413, 1333, 1228, 1187, 1117, 766, 710 cm^{-1}; MS (FAB, *m*-NBA + TFA): *m*/*z*: 418–422 $[M+H]^+$; HRMS (FAB) calcd for $C_{18}H_{12}N_9Zn$: 418.0507, found 418.0495.

N^3-[(1′*Z*)-5′(6′)-octyloxy-3′-amino-1*H*-isoindol-1′-ylidene]-N^5-[(1″*Z*)-5″(6″)-octyloxy-3″-imino-2″,3″-dihydro-1*H*-isoindol-1″-ylidene]-3,5-diamino-4*H*-1,2,4-triazolatozinc(II) (5e): A mixture of **4b** (200 mg, 0.33 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (72 mg, 0.33 mmol) in 2-ethoxyethanol (15 mL) was stirred at room temperature for 24 h. The precipitate was filtered, washed with methanol, and dried to give **5e** as a dark orange solid (105 mg, 48 %). M.p. >250 °C; IR (KBr): $\tilde{\nu}$ = 3294, 3165, 3067 (N–H), 2925, 2855 (C–H), 1670, 1616, 1603, 1551 (C=N), 1489, 1466, 1414, 1328, 1287, 1243, 1121, 1086, 1060, 1017, 769 cm^{-1}; MS (FAB, *m*-NBA + TFA): *m*/*z*: 674–679 $[M+H]^+$. HRMS (FAB) calcd for $C_{34}H_{44}N_9O_2Zn$: 674.2909; found 674.2906.

5,38:14,17:19,24:33,36-Tetraimino-[7,12:26,31]-dinitrilotetrabenzo[f,k,t,y]-[1,2,4,9,14,16,17,19,24,29]decaazacyclotriacontanato(4-)-N^{39},N^{40},N^{41},N^{42},N^{43},N^{44}-dinickel(II) (3a): A suspension of **5a** (250 mg, 0.62 mmol) in 2-ethoxyethanol (30 mL) was heated under reflux for 48 h. The precipitate was filtered, washed with hot 2-ethoxyethanol, and repeatedly triturated in boiling methanol to yield **3a** as a dark red solid (221 mg, 81 %). An analytical sample was recrystallized from α-chloronaphthalene. M.p. >250 °C; IR (KBr): $\tilde{\nu}$ = 3057, 2924 (C–H), 1620, 1600, 1550 (C=N), 1526, 1497, 1470, 1394, 1325, 1290, 1088, 752, 721 cm^{-1}; MS (FAB, 3-NOBA + TFA): *m*/*z*: 789–793 $[M+H]^+$; HRMS (FAB) calcd for $C_{36}H_{17}N_{16}Ni_2$: 789.053; found 789.054; UV/Vis (α-chloronaphthalene): λ_{max} (log ε) = 349 (5.15), 485 (4.77), 523 (4.84), 564 nm (4.78); elemental analysis calcd (%) for $C_{36}H_{16}N_{16}Ni_2 \cdot 5H_2O$: (880.08): C 49.13, H 2.98, N 25.46; found C 49.68, H 2.72, N 25.13.

2(3),9(10),21(22),28(29)-Tetraoctyloxy-[5,38:14,17:19,24:33,36]-tetraimino-[7,12:26,31]-dinitrilotetrabenzo[f,k,t,y][1,2,4,9,14,16, 17,19,24,29]decaazacyclotriacontanato (4-)-N^{39},N^{40},N^{41},N^{42},N^{43},N^{44}-dinickel(II) (3b): A suspension of **5b** (220 mg, 0.33 mmol) in 2-ethoxyethanol (11 mL) was heated under reflux for 36 h. The solid was filtered and triturated in boiling methanol. Column chromatography on silica gel (eluent: CH_2Cl_2/MeOH/Et_3N 15:1:0.2) and further recrystallization from CH_2Cl_2/MeOH afforded **3b** as a red solid (85 mg, 37 %). M.p.: 241 °C; ^1H NMR (200 MHz,$CDCl_3$): δ = 7.7, 7.4, 7.3 (3 m, 4 H; H-arom), 7.2, 7.0, 6.9 (3 br s, 4 H; H-arom), 6.6 (m, 4 H; H-arom), 3.9 (m, 8 H; OCH_2), 1.8 (m, 8 H; OCH_2CH_2), 1.3 (s, 40 H; CH_2), 0.9 (m, 12 H; CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.9, 163.3, 163.1 (C-5, C-7, C-12, C-19, C-24, C-26, C-31, C-38), 156.1, 155.9, 155.7 (C-14, C-17, C-33, C-36), 139.7, 139.3, 138.8, 136.5, 135.9, 135.8, 129.2, 129.1, 129.0, 125.3, 124.8, 123.8, 119.3, 110.0, 107.8, 107.2 (C-1, C-2, C-3, C-4, C-4a, C-7a, C-8, C-9, C-10, C-11, C-11a, C-19a, C-20, C-21, C-22, C-23, C-23a, C-26a, C-27, C-28, C-29, C-30, C-30a, C-38a), 69.2, 69.0, 68.9 (OCH_2), 32.3 (OCH_2CH_2), 30.1, 30.0, 30.0, 29.75, 29.72, 26.5, 23.1 (CH_2), 14.5 (CH_3); IR (KBr): $\tilde{\nu}$ = 2920, 2850, (C–H) 1650, 1600 (C=N), 1500, 1480, 1460, 1380, 1360, 1330, 1290, 1240, 1090, 830, 760 cm^{-1}; MS (FAB, 3-NOBA + TFA): *m*/*z*: 1302–1306 $[M+H]^+$, 1188–1192 $[M-C_8H_{17}]^+$, 1076–1080 $[M-2C_8H_{17}+H]^+$; MS (FD, CH_2Cl_2): *m*/*z*: 1302–1306 $[M+H]^+$; UV/Vis ($CHCl_3$): λ_{max} (log ε) = 279 (4.94), 350 (sh), 402 (4.47), 530 (4.26), 573 nm (4.19); elemental analysis calcd (%) for $C_{68}H_{80}N_{16}O_4Ni_2 \cdot 5H_2O$ (1392.94): C 58.63, H 6.51, N 16.09; found C 58.79, H 6.04, N 15.62.

2(3),9(10),21(22),28(29)-Tetra-*tert*-butyl-[5,38:14,17:19,24:33,36]-tetraimino-[7,12:26,31]-dinitrilotetrabenzo[f,k,t,y][1,2,4,9,14,16,17,19,24,29]decaazacyclotriacontanato (4-)-N^{39},N^{40},N^{41},N^{42},N^{43},N^{44}-dinickel(II) (3c): A mixture of **4c** (114 mg, 0.24 mmol) and $Ni(OAc)_2 \cdot 4H_2O$ (57 mg, 0.24 mmol) in MeOH (20 mL) was heated under reflux for 4 d. After evaporation of the methanol, the solid was resuspended in water, filtered, and washed with the same solvent. Column chromatography on silica gel (eluent: CH_2Cl_2/MeOH/Et_3N 15:1:0.2) afforded **3c** as a red solid (37 mg, 28 %). M.p.: >250 °C; ^1H NMR (300 MHz,$CDCl_3$): δ = 8.1, 8.0, 7.9, 7.7, 7.5 (5 m, 12 H; H-arom), 1.47 (br s, 36 H; $C(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.3, 163.0, 162.9 (C-5, C-7, C-12, C-19, C-24, C-26, C-31, C-38), 156.5, 156.1, 155.4 (C-14, C-17, C-33, C-36), 136.7, 134.2, 134.1, 134.0 (C-2, C-4a, C-7a, C-10, C-11a, C-19a, C-21, C-23a, C-26a, C-29, C-30a, C-38a), 129.3, 128.4, 122.8, 122.6, 122.0, 121.9, 120.2, 119.1, 119.0 (C-1, C-3, C-4, C-8, C-9, C-11, C-20, C-22, C-23, C-27, C-28, C-30), 35.3, 35.1 ($C(CH_3)_3$), 31.0, 30.9 ($C(CH_3)_3$); IR (KBr): $\tilde{\nu}$ = 2962, 2870 (C–H), 1687 (C=N), 1569, 1481, 1462, 1418, 1365, 1318, 1286, 1196, 1126, 1097, 767, 679 cm^{-1}; MS (MALDI-TOF, dithranol): *m*/*z*: 1013–1017 $[M+H]^+$; HRMS (FAB) calcd for $C_{52}H_{49}N_{16}Ni_2$: 1013.3033; found 1013.3012; UV/Vis ($CHCl_3$): λ_{max} (log ε) = 271 (4.17), 360 (3.89), 519 (3.53), 559 nm (3.46); elemental analysis calcd (%) for $C_{52}H_{48}N_{16}Ni_2 \cdot 5H_2O$ (1104.51): C 56.55, H 5.29, N 20.29; found C 56.42, H 5.48, N 20.13.

5,38:14,17:19,24:33,36]-Tetraimino-[7,12:26,31]-dinitrilotetrabenzo[f,k,t,y]-[1,2,4,9,14,16,17,19,24,29]decaazacyclotriacontanato(4-)-N^{39},N^{40},N^{41},N^{42},N^{43},N^{44}-dizinc(II) (3d): The three-unit intermediate **5d** (100 mg, 0.24 mmol) was heated under reflux in 2-ethoxyethanol (12 mL) for 2 d. The suspension was centrifuged, and after removal of the liquid phase the solid was resuspended in methanol, filtered, and repeatedly triturated in boiling methanol to yield **3d** as a dark orange solid (76 mg, 69 %). M.p. >250 °C; IR (KBr): $\tilde{\nu}$ = 1639, 1620 (C=N), 1580, 1471, 1372, 1311, 1288, 1187, 1120, 1110, 1073, 770, 721 cm^{-1}; MS (FAB, *m*-NBA + TFA): *m*/*z*: 801–808 $[M+H]^+$; UV/Vis (α-chloronaphthalene): λ_{max} (log ε) = 361 (5.32), 377 (5.32), 441 (5.04), 472 nm (4.89); elemental analysis calcd (%) for $C_{36}H_{16}N_{16}Zn_2 \cdot 6H_2O$: (911.48): C 47.44, H 3.10, N 24.59; found C 47.83, H 3.08, N 24.20.

2(3),9(10),21(22),28(29)-Tetraoctyloxy-[5,38:14,17:19,24:33,36]-tetraimino-[7,12:26,31]-dinitrilotetrabenzo[f,k,t,y][1,2,4,9,14,16,17,19,24,29]decaazacyclotriacontanato (4-)-N^{39},N^{40},N^{41},N^{42},N^{43},N^{44}-dizinc(II) (3e): A suspension of **5e** (126 mg, 0.186 mmol) in 2-ethoxyethanol (8 mL) was heated under reflux for 36 h. The solid was filtered and triturated in boiling methanol and then in THF. Recrystallization from pyridine afforded **3e** as a reddish orange solid (72 mg, 54 %). M.p.: >250 °C; ^1H NMR (300 Mhz, 368 K, [D_5]pyridine): δ = 8.15, 8,10, 7.84 (3 m, 12 H; H-arom), 4.17 (m, 8 H; OCH_2), 1.8 (m, 8 H; OCH_2CH_2), 1.5–1.3 (m, 40 H; CH_2), 1.1–0.9 (m, 12 H; CH_3); ^{13}C NMR (75 MHz, [D_5]pyridine): δ = 68.7 (OCH_2), 32.3, 32.1, 31.9 (OCH_2CH_2), 30.1, 30.0, 29.8, 29.6, 29.5, 29.4, 26.3, 23.1, 22.9, 22.8, 22.7 (CH_2), 14.3, 14.2 (CH_3); IR (KBr): $\tilde{\nu}$ = 2924, 2854 (C–H), 1620, 1615, 1605 (C=N), 1503, 1454, 1383, 1322, 1279, 1239, 1227, 1187, 1057, 833, 770 cm^{-1}; MS (FAB, *m*-NBA + TFA): *m*/*z*: 1313–1321 $[M+H]^+$, 1201–1208 $[M-C_8H_{17}+H]^+$; UV/Vis ($CHCl_3$): λ_{max} (log ε) = 276 (5.66), 344 (5.52), 439 (5.38), 489 nm (5.26); elemental analysis calcd (%) for $C_{68}H_{80}N_{16}O_4Zn_2 \cdot 6H_2O$ (1424.33): C 57.34, H 6.51, N 15.73; found C 57.22, H 6.61, N 15.62.

2(3),9(10),21(22),28(29)-Tetra-*tert*-butyl-[5,38:14,17:19,24:33,36]-tetraimino-[7,12:26,31]-dinitrilotetrabenzo[f,k,t,y][1,2,4,9,14,16,17,19,24,29]decaazacyclotriacontanato (4-)-N^{39},N^{40},N^{41},N^{42},N^{43},N^{44}-dizinc(II) (3f), mixture of isomers: A suspension of **4c** (100 mg, 0.20 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (40 mg, 0.20 mmol) was stirred in 2-ethoxyethanol at room temperature for 24 h and then refluxed in the same solvent for 48 h. Afterwards the solvent was evaporated at reduced pressure, and the crude product was resuspended in water, filtered, and washed with the same solvent. Column chromatography on silica gel (eluent: CH_2Cl_2/MeOH/Et_3N 15:1:0.2) and further gel-permeation chromatography on Biobeads SX-3 (eluent: chloroform) afforded **3f** as a dark orange solid (67 mg, 59 %). M.p.: >250 °C; ^1H NMR (300 MHz, [D_6]dmso): δ = 8.1, 8.0, 7.8–7.7 (3 m, 12 H; H-arom), 1.44, 1.33, 1.22 (3 s, 36 H; $C(CH_3)_3$); ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 174.8, 174.7, 169.6, 169.3, 163.7, 162.0, 161.7 (C-5, C-7, C-12, C-19, C-24, C-26, C-31, C-38), 158.2, 156.2, 155.1 (C-14, C-17, C-33, C-36), 139.1, 139.0, 138.7, 136.5, 136.1, 133.1, 131.8, 130.3 (C-2, C-4a, C-7a, C-10, C-11a, C-19a, C-21, C-23a, C-26a, C-29, C-30a, C-38a), 131.4, 130.0, 128.9, 123.0, 122.3, 119.8, 118.9 (C-1, C-3, C-4, C-8, C-9, C-11, C-20, C-22, C-23, C-27, C-28, C-30), 35.6, 35.5, 35.4 ($C(CH_3)_3$), 31.3, 31.0 ($C(CH_3)_3$); IR (KBr): $\tilde{\nu}$ = 2960, 2929, 2866, (C–H) 1719, 1647, 1623, 1584 (C=N), 1482, 1363, 1312, 1193, 1119, 1091 cm^{-1}; MS (FAB, *m*-NBA): *m*/*z*: 1025–1033 $[M+H]^+$; HRMS

(FAB) calcd for $C_{52}H_{49}N_{16}Zn_2$: 1025.2909; found 1025.2866; UV/Vis ($CHCl_3$): λ_{max} (log ε) = 275 (4.58), 346 (4.46), 441 (4.34), 469 nm (4.24); elemental analysis calcd (%) for $C_{52}H_{48}N_{16}Zn_2 \cdot 6H_2O$ (1135.91): C 54.98, H 5.32, N 19.73; found: C 54.54, H 5.49, N 19.93.

2(3),9(10),21(22),28(29)-Tetra-*tert*-butyl-[5,38:14,17:19,24:33,36]-tetraimino-[7,12:26,31]-dinitrilotetrabenzo[f,k,t,y][1,2,4,9,14,16, 17,19,24,29]decaazacyclotriacontanato (4-)-N^{39},N^{40},N^{41},N^{42},N^{43},N^{44}-dizinc (II) (3 f), single isomer: A single isomer of **3 f** was isolated by column chromatography of the crude mixture of isomers on silica gel with CH_2Cl_2/MeOH 7:1, and then on Biobeads SX-3 (eluent: chloroform). M.p.: > 250 °C; ^{1}H NMR (300 MHz,[D$_6$]dmso): δ = 7.85 (dd, J = 7.6 Hz, 4H; H-arom), 7.78 (br s, 4H; H-1, H-11, H-20, H-30 of **A** or H-4, H-8, H-23, H-27 of **B**), 7.74 (dd, J = 7.6 Hz, 4H; H-arom), 1.33 (s, 36H; C(CH$_3$)$_3$); ^{13}C NMR (75 MHz, [D$_6$]dmso): δ = 169.6, 169.3 (C-5, C-7, C-12, C-19, C-24, C-26, C-31, C-38), 158.2 (C-14, C-17, C-33, C-36), 133.1, 130.3 (C-2, C-4a, C-7a, C-10, C-11a, C-19a, C-21, C-23a, C-26a, C-29, C-30a, C-38a), 131.5, 123.0, 119.8 (C-1, C-3, C-4, C-8, C-9, C-11, C-20, C-22, C-23, C-27, C-28, C-30), 35.6 (*C*(CH$_3$)$_3$), 31.0, (C(*C*H$_3$)$_3$); IR (KBr): $\tilde{\nu}$ = 2964, 2919, 2860 (C–H) 1558 (C=N), 1483, 1417, 1129, 842, 770, 684 cm^{-1}; MS (FAB, *m*-NBA): *m*/*z*: 1025 – 1033 [*M*+H]$^+$; HRMS (FAB) calcd for $C_{52}H_{49}N_{16}Zn_2$: 1025.2909; found 1025.2907; UV/Vis ($CHCl_3$): λ_{max} (log ε) = 268 (4.37), 285 sh (4.29), 338 (4.13), 440 (4.07), 470 nm (3.94).

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