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Synthesis of the First Nonmetalated Triazolephthalocyanine Derivatives†

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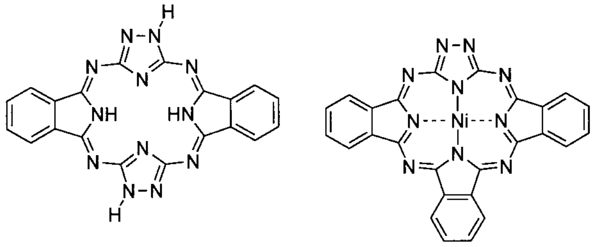
Abstract: The synthesis of nonmetalated triazolephtahlocyanines is described for the first time. These compounds have been prepared by both one-step and stepwise procedures. Their spectroscopic data reveal a nonaromatic cross-conjugated 18π-electron structure in contrast to their aromatic metalated derivatives.

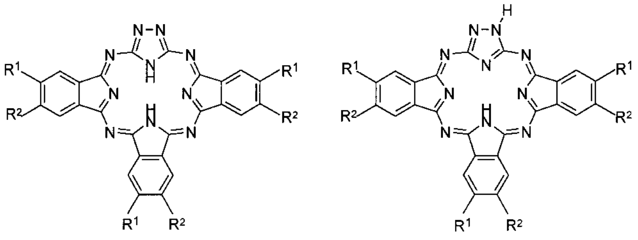
The formal substitution of one isoindole subunit in a metallophthalocyanine[1,2] by a 1,2,4-triazole moiety affords a novel class of intrinsically unsymmetric 18-π-electron fully conjugated metallomacrocycle, which we have called metallotriazolephthalocyanine[2b,3] (**MTpc**, Figure 1). In addition to their inherent theoretical interest as new aromatic macrocycles, MTpc's have shown to be promising building blocks for the development of gas sensors based on semiconducting Langmuir−Blodgett films.[4] Macromolecular arrangements such as liquid−crystalline mesophases can also be achieved with adequately substituted metallotriazolephthalocyanines.[5] On the other hand, they show interesting NLO properties.[6,7]

Two general synthetic methodologies had been applied for obtaining metallotriazolephthalocyanines,[3] mainly Cu and Ni derivatives, although prelimary studies of non-substituted MTpcs containing other central metals have also been reported.[8] However, despite many efforts, the parent nonmetalated macrocycles had not yet been prepared up to now.



H$_2$Thp **MTpc**

Figure 1. Hemiporphyrazine free base (**H$_2$Thp**) and metallotriazole− phthalocyanine (**MTpc**).



a **b**

H$_2$Tpc

Figure 2. Possible structures for triazolephthalocyanine free bases (**H$_2$Tpc**).

Contrary to metallotriazolephthalocyanines, the molecular structure of the free base analogues (**H$_2$Tpc** in Figure 2) appears to be controversial in a first approach. Tpc's can be considered as macrocycles that are structurally at the halfway between phthalocyanines and hemiporphyrazines (**H$_2$Thp** in Figure 1).[9] A first possible structure for Tpc free bases **H$_2$Tpc**, by analogy with their metalated derivatives **MTpc**, is represented in Figure 2, structure **a**, where both isoindolic and triazolic hydrogens remain inside the macrocyclic cavity.[10] Such a structure is reminiscent of phthalocyanine free bases[1] and presents an 18-π-electron fully conjugated system. However, another tautomeric molecular structure obtained by moving the triazolic hidrogen to an external position can also be envisaged as shown in structure **b** (Figure 2). Structure **b** resembles the hemiporphyrazine free bases structure[9] (**H$_2$Thp**) and is nonaromatic since it presents 18 π-electrons in a cross-conjugated structure. Although a tautomeric equilibrium between **a** and **b** is possible, the most probable is the preponderance of either the phthalocyanine-type structure **a** or the hemiporphyrazine-type structure **b**. We will demonstrate in this paper that **b** is the preferred tautomer for Tpc free bases (**H$_2$Tpc**).

Here, we describe for the first time the preparation of triazolephthalocyanine free bases (H$_2$Tpc) **1**−**6** (Schemes 1 and 2).

Triazolephthalocyanines **1**−**3** present the same substitution pattern at all three isoindole subunits and were

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† This paper is dedicated to Prof. Dr. Dr. h.c. Michael Hanack on the occasion of his 70th birthday.

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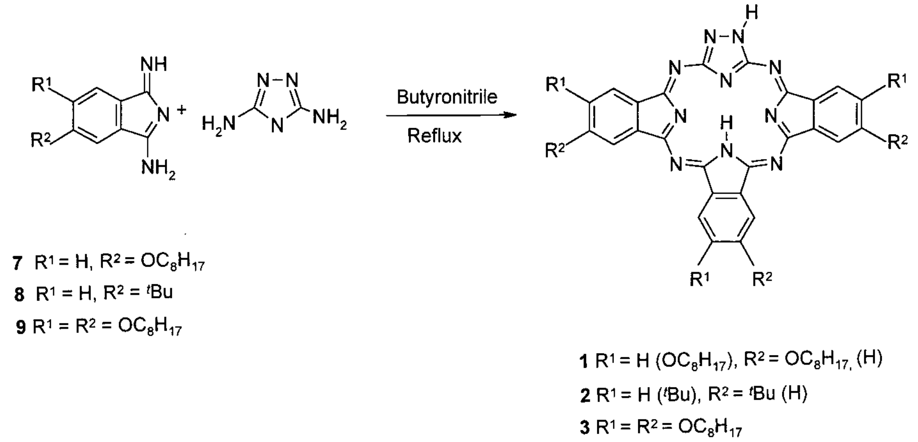
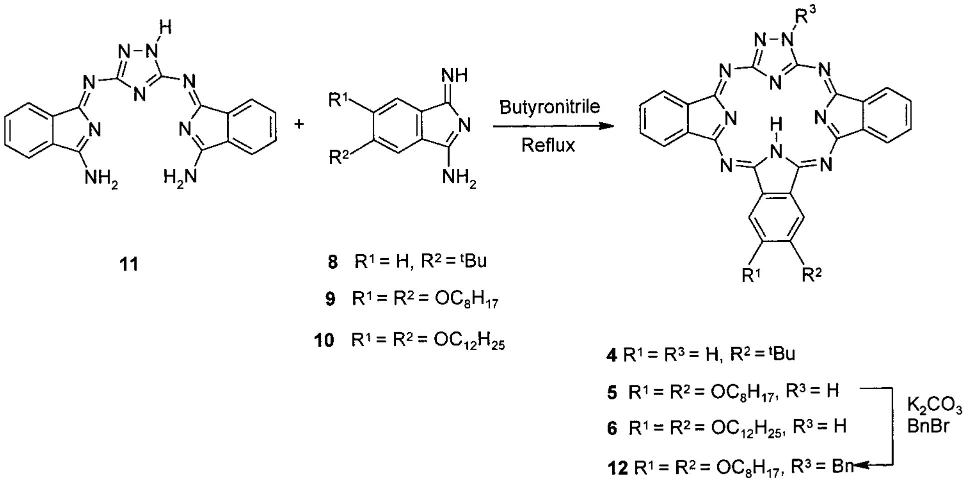
Scheme 1



7 $R^1 = H, R^2 = OC_8H_{17}$
8 $R^1 = H, R^2 = {}^tBu$
9 $R^1 = R^2 = OC_8H_{17}$

1 $R^1 = H\ (OC_8H_{17}), R^2 = OC_8H_{17}\ (H)$
2 $R^1 = H\ ({}^tBu), R^2 = {}^tBu\ (H)$
3 $R^1 = R^2 = OC_8H_{17}$

Scheme 2



11

8 $R^1 = H, R^2 = {}^tBu$
9 $R^1 = R^2 = OC_8H_{17}$
10 $R^1 = R^2 = OC_{12}H_{25}$

4 $R^1 = R^3 = H, R^2 = {}^tBu$
5 $R^1 = R^2 = OC_8H_{17}, R^3 = H$
6 $R^1 = R^2 = OC_{12}H_{25}, R^3 = H$
12 $R^1 = R^2 = OC_8H_{17}, R^3 = Bn$

therefore synthesized by the statistical condensation[3] of the corresponding 1,3-diiminoisoindoline **7**−**9** and 3,5-diamino-1,2,4-triazole in a 3:1 molar ratio (Scheme 1). Compounds **1** and **2** are mixtures of the corresponding regioisomers.

On the contrary, triazolephthalocyanines **4**−**6** are substituted only at the isoindole subunit opposite to the triazole moiety, so that the stepwise route depicted in Scheme 2 had to be used. A three-unit compound **11** was then first prepared to be finally condensed with the corresponding diiminoisoindoline **8**−**10**. Compounds **7**,[11] **8**,[12] **9**[13,14] **10**,[14,15] and **11**[16] were obtained following methodologies already reported in the literature.

The key point in the preparation of compounds **1**−**6** is the use of a polar non-nucleophilic solvent like butyronitrile, to avoid the cleavage of the final compounds and even of the three-unit intermediates **I-T-I** (where **I** = isoindole, **T** = triazole), like **11**, in the presence of alcoholic solvents typically used in the preparation of metallotriazolephthalocyanines (i.e., 2-ethoxyethanol).[3] Such cleavage, produced by nucleophilicity attack to the iminic double bonds, had been described previously by us for related species.[17] The reaction dilution also has to be carefully controlled, to optimize the yield of the final triazolephthalocyanine by minimizing the formation, as side-product, of a five-unit heterooligomer **I-T-I-T-I** (**I** = isoindole, **T** = triazole), identified by FAB-mass spectrometry.

Macrocycles **1**−**3** are soluble in butyronitrile and their purification was done by column chromatography. The hexasubstituted compound **3** was unstable in silica gel, even after deactivation of the latter with NEt_3 in THF, and could not be satisfactorily purified for analysis although IR and FAB-mass spectra proved its nature.

Contrary to **1**−**3**, derivatives **4**−**6**, due to the different substitution degree, are insoluble in butyronitrile. Thus, they precipitate in the reaction media and their purification has to be achieved by grinding them in cold dried MeOH in order to eliminate the nonreacted three-unit compound **I-T-I** and the five-unit side-product **I-T-I-T-I**.

Compounds **1**−**6** have a lower chemical stability than their metalated analogues and decompose very easily in the presence of acid traces (silica gel, etc.). However, they are stable when trying to react them with diiminoisoin-

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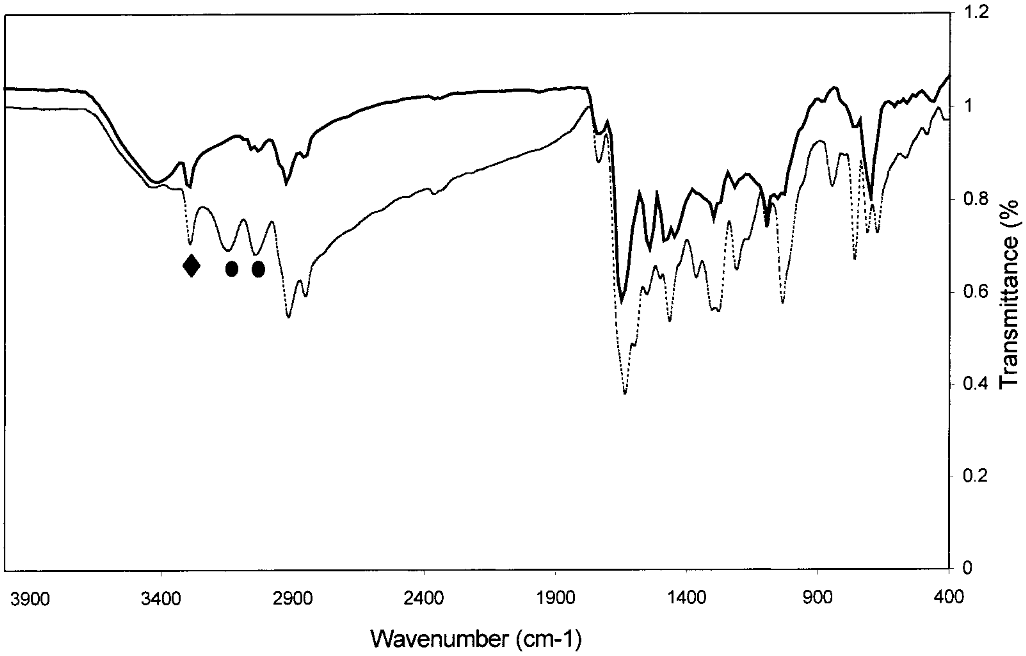


Figure 3. IR spectra of triazolephthalocyanines **5** (thin line) and **12** (solid line) in KBr.

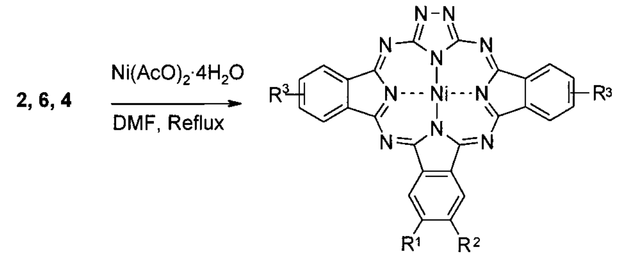
dolines in order to test a possible isoindole-subunit scrambling, being the macrocycle recovered unaltered. Thermal stability has also been proved by refluxing the macrocycles in butyronitrile.

IR spectra (Figure 3) are particularly interesting since they enlighten the problem of elucidating the molecular structure of the nonmetalated triazolephthalocyanines, especially regarding the position of the two aminic hydrogens. All Tpc free bases show three bands at the 3000 cm^{-1} region: two bands of medium intensity at 3040–3080 and 3130–3170 (● in Figure 3) cm^{-1} and a third band, of variable intensity, at 3280–3300 cm^{-1} (◆ in Figure 3). After comparison with phthalocyanine and hemiporphyrazine free bases and other triazole-containing macrocycles,[9,18] the former two bands (●) must be assigned to a triazolic hydrogen located at the periphery of the macrocycle. The third band at 3280–3300 cm^{-1} corresponds to an inner isoindolic hydrogen (◆). Such assignation gives us for Tpc free bases a structure of type **b** (Figure 2). To confirm this, we have prepared the Tpc free base **12** (Scheme 2) substituted in the triazole by alkylation of compound **5** with benzyl bromide.

The disappearance of the triazolic external hydrogen in compound **12** is accompanied, as expected, by the disappearance in its IR spectrum of both bands (●) centered at 3045 and 3149 cm^{-1} in the particular case of **5** (Figure 3).

Furthermore, the assumption that nonmetalated Tpc's present a hemiporphyrin-like structure (structure **b** in Figure 2) is consistent with the behavior of the UV–vis spectra. While metalated triazolephthalocyanines show a Q-band centered at about 630 nm, Tpc free bases show at the visible region a band that appears to be centered at a much lower wavelength (about 500 nm). This strong ipsochromic shift of 100 nm suggests a decrease of the conjugation degree of the nonmetalated macrocycles compared to the metalated ones, a decrease that can be actually justified by the adoption of a cross-linked conjugated hemiporphyrazine-like structure.

Scheme 3



13 $R^1 = R^3 = {}^tBu$, $R^2 = H$

14 $R^1 = R^2 = OC_{12}H_{25}$, $R^3 = H$

15 $R^1 = {}^tBu$, $R^2 = R^3 = H$

The ^1H NMR of Tpcs free bases show a peak for the triazole hydrogen at 10.3 ppm, which disappears in the presence of deuterated water. As is expected, the peak is missing in MTpcs **12**.

Compounds **13**, **14**,[4b] and **15**[4b] (Scheme 3) were obtained by direct metalation of compounds **2**, **6**, and **4**, respectively. The metalation was carried out by refluxing the starting materials for 24 h under inert atmosphere in the presence of nickel acetate in dry DMF. On going from **2**, **6**, and **4** to **13**, **14**, and **15**, the phthalocyanine-type structure is recovered and thus a higher conjugation degree which is reflected in the appearance of a Q-band at 627 nm in the UV–Visible spectra of these last compounds. Obviously, concerning IR data, the hydrogen bands in the region of 3000 cm^{-1} disappear for the metalated compounds.

The metalation of Tpc free bases opens the way to a convergent new synthetic methodology for obtaining metallotriazolephthalocyanines. This fact is far from being unimportant since the preparation of metalated Tpcs containing metals other than Cu or Ni has shown

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to be difficult by the usual methods.[3] Moreover, in many cases the isolation of Cu and Ni complexes from template macrocyclations becomes difficult.

In summary, we have prepared for the first time a series of triazolephthalocyanine free bases and elucidated the molecular structure of such macrocycles. While the metalated analogues MTpcs present a phthalocyanine-type aromatic structure, non- metalated H_2Tpcs appear to be hemiporphyrazine-like cross-conjugated systems thus affecting IR and UV spectral behavior. We have also proved the capability of H_2Tpcs of being metallized, thus opening the way for the preparation, in a convergent pathway, of different metal containing triazolephthalocyanines. This point is interesting for some applications for which the nature of the central metal is determinative. For example, self-assembled monolayers (SAM) analyzed by fluorescence methods cannot bear fluorescence quenching metals such as Cu and Ni.

Experimental Section

Compounds **7**−**10** have been previously described. Starting materials were purchased from Aldrich Chemical Co. and used as received without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature.

General Statistical Method for the Preparation of 1−**3.** A mixture of 0.52 mmol (52 mg) of 3,5-diamino-1,2,4-triazole and 1.56 mmol of the corresponding 1,3-diiminoisoindolines **7**−**9** was heated in 20 mL of refluxing butyronitrile under argon atmosphere for 3 days. After cooling and filtration to eliminate any insoluble residue, the solvent was evaporated. The solid obtained was washed with diethyl ether and purified by column chromatography over silica gel previously neutralized with THF/Et_3N 10:1, employing first THF as eluent, to eliminate traces of phthalocyanine formed as side product in the reaction, followed by Cl_2CH_2/MeOH 10:2. The compound was finally washed with hexane in a Soxhlet extractor.

2(3),9(10),16(17)-Trioctyloxy-7,12:21,24-diimino-5,26:14,19-dinitrilotribenzo[*f*,*k*,*p*][1,2,4,9,14,19]hexaazacycloeicosine (1). Yield: 27%. Mp > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.1−7.3 (m, 9H); 4.1−3.0 (m, 6H); 2.0−1.0 (m, 45H). IR (KBr): ν 3295, 3160, 3080, 2925, 2855, 1616, 1490, 1467, 1365, 1319, 1284, 1241, 1043, 833, 763, 729 cm^{-1}. UV−vis ($CHCl_3$): λ_{max} (log ϵ (dm^3 mol^{-1} cm^{-1})) 272 (5.23), 348 (4.54), 452 (4.07), 510 (3.80). FAB-MS (*m*-NBA): *m/z* 851 [M + H]$^+$. Anal. Calcd for $C_{50}H_{62}N_{10}O_3 \cdot 2H_2O$: C, 67.70; H, 7.50; N, 15.79. Found: C, 66.82; H, 7.24; N, 15.45.

2(3),9(10),16(17)-Tri-*tert*-butyl-7,12:21,24-diimino-5,26:14,19-dinitrilotribenzo[*f*,*k*,*p*][1,2,4,9,14,19]hexaazacycloeicosine (2). Yield: 35%. Mp > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.4 (s, H); 8.1−7.7 (m, 9H); 1.4−1.2 (m, 27H). IR (KBr): ν 3301, 3170, 3061, 2960, 2868, 1621, 1538, 1485, 1363, 1313, 1257, 1200, 1040, 839, 763, 674 cm^{-1}; UV−vis ($CHCl_3$): λ_{max} (log ϵ (dm^3 mol^{-1} cm^{-1})) 267 (sh) (3.28), 334, (3.16), 347 (3.15), 503 (2.52). FAB-MS (*m*-NBA): *m/z* 635 [M + H]$^+$. Anal. Calcd for $C_{38}H_{38}N_{10}$: C, 71.90; H, 6.03; N, 22.07. Found: C, 71.85; H, 5.81; N, 22.21.

2,3,9,10,16,17-Hexaoctyloxy-7,12:21,24-diimino-5,26:14,19dinitrilotribenzo[*f*,*k*,*p*][1,2,4,9,14,19]hexaazacycloeicosine (3). Yield: 67%. Mp > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.0−7.2 (m, 6H); 4.3−3.0 (m, 12H); 2.0−0.5 (m, 90H). IR (KBr): ν 3298, 3169, 3080, 2924, 2853, 1631, 1602, 1562, 1503, 1464, 1340, 1284, 1215, 1035, 879, 773, 762 cm^{-1}. MS (MALDI): *m/z* 1235 [M + H]$^+$. UV−vis ($CHCl_3$) broad bands from 250 to 500 nm difficult to assign.

General Stepwise Method for the Preparation of 4−**6.** A mixture of 0.50 mmol (180 mg) of **11** and 0.50 mmol of the corresponding diiminoisoindolines **8**−**10** was refluxed in butyronitrile (40 mL) under argon atmosphere for 4 days. After filtration, the solid was washed first with diethyl ether and then ground in cold dried MeOH and filtered again to yield **4**−**6**.

9-*tert*-Butyl-7,12:21,24-diimino-5,26:14,19-dinitrilotribenzo[*f*,*k*,*p*][1,2,4,9,14,19]hexaazacycloeicosine (4). Yield: 38%. Mp > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.0−7.4 (m, 11H); 1.5 (s broad 9H). IR (KBr): ν 3294, 3147, 3042, 2963, 2899, 1638, 1555, 1475, 1363, 1311, 1201, 1165, 1041, 840, 761, 683 cm^{-1}. UV−vis ($CHCl_3$): λ_{max} (log ϵ (dm^3 mol^{-1} cm^{-1})) 280 (sh) (2.28), 348 (2.32), 499 (1.72). MS (MALDI): *m/z* = 524 [M + H]$^+$. Anal. Calcd for $C_{30}H_{22}N_{10}$: C, 68.95; H, 4.24; N, 26.80. Found: C, 68.59; H, 4.20; N, 26.45.

9,10-Dioctyloxy-7,12:21,24-diimino-5,26:14,19-dinitrilotribenzo[*f*,*k*,*p*][1,2,4,9,14,19]hexaazacycloeicosine (5). Yield: 15%. Mp > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.0−7.5 (m, 10H); 4.0−3.0 (m, 4H); 2.0−1.0 (m, 30H). IR (KBr): ν 3292, 3149, 3045, 2919, 2853, 1600, 1554, 1502, 1466, 1364, 1304, 1280, 1212, 1036, 762, 714 cm^{-1}. UV−vis ($CHCl_3$): λ_{max} (log ϵ (dm^3 mol^{-1} cm^{-1})) 251 (4.07), 283 (sh) (3.96), 348 (3.89), 500 (3.30). MS (MALDI): *m/z* 723 [M + H]$^+$. Anal. Calcd for $C_{42}H_{46}N_{10}O_2$: C, 69.78; H, 6.41; N, 19.38. Found: C, 69.53; H, 6.35; N, 19.26.

9,10-Didodecyloxy-7,12:21,24-diimino-5,26:14,19-dinitrilotribenzo[*f*,*k*,*p*][1,2,4,9,14,19]hexaazacycloeicosine (6). Yield: 25%. Mp > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.0−7.5 (m, 10H); 4.0−3.0 (m, 4H); 2.0−1.0 (m, 46H). IR (KBr): ν 3282, 3137, 3049, 2920, 2850, 1597, 1543, 1503, 1464, 1365, 1330, 1280, 1227, 1041, 760, 725 cm^{-1}. UV−vis ($CHCl_3$): λ_{max} (log ϵ (dm^3 mol^{-1} cm^{-1})) 280 (4.39), 348 (4.31), 499 (3.79). MS (MALDI) *m/z* = 835 [M + H]$^+$. Anal. Calcd for $C_{50}H_{62}N_{10}O_2$: C, 71.91; H, 7.48; N, 16.77. Found: C, 71.85; H, 7.52; N, 16.82.

***N*^{23}-Benzyl-9,10-dioctyloxy-7,12:21,24-diimino-5,26:14,19-dinitrilotribenzo[*f*,*k*,*p*][1,2,4,9,14,19]hexaazacycloeicosine (12).** A mixture of **5** (50 mg, 0.1 mmol), K_2CO_3 (20 mg 0.1 mmol), and 18-crown-6 (0.1 mmol, 30 mg) in acetonitrile (20 mL) was heated under argon at 60 °C. After 15 min, benzyl bromide (17.1 mg, 0.1 mmol) was added. The reaction mixture was stirred for 48 h. The solvent was evaporated, water (20 mL) and $CHCl_3$ (20 mL) were added, extracted with $CHCl_3$ (3 × 20 mL), and the combined organic layers was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was precipitated with ether and filtrated to give a brown solid. Yield: 68%. Mp > 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.1−6.8 (broad m, 15H); 5.3−5.1 (m, 2H); 4.0−3.5 (m, 4H); 2.1−1.0 (m, 30H). IR (KBr): ν 3299, 2938, 2924, 2901, 1650, 1540, 1479, 1454, 1300, 1257, 1219, 1052, 765, 696, 680 cm^{-1}. UV−vis ($CHCl_3$): λ_{max} (log ϵ (dm^3 mol^{-1} cm^{-1})) 349 (4.63), 361 (4.67), 381 (4.61), 473 (sh) (3.76), 509 (3.96). MS (MALDI): *m/z* 813 [M + H]$^+$. Anal. Calcd for $C_{49}H_{52}N_{10}O_2$: C, 72.39; H, 6.45; N, 17.23. Found: C, 72.50; H, 6.56; N, 19.65.

General Method for Metalation. A mixture of 0.16 mmol of **2**, **6**, or **4** and 0.24 mmol (52 mg) of $Ni(AcO)_2 \cdot 4H_2O$ was refluxed in DMF (30 mL) under argon atmosphere for 24 h. After evaporation, the solid was washed with cold dried MeOH. The residue was then chromatographed on silica gel using CH_2Cl_2/MeOH 10:1 as solvent to yield the corresponding metalated compounds **13**, **14**, and **15**.

[2(3),9(10),16(17)-Tri-*tert*-butyl-7,12:21,24-diimino-5,26:14,19-dinitrilotribenzo[*f*,*k*,*p*][1,2,4,9,14,19]hexaazaeicosinato(2−)-*N*^{27},*N*^{28},*N*^{29},*N*^{30}]nickel(II) (13). Yield: 45%. Mp > 250 °C. H^1 NMR (300 MHz, *d*-TFA): δ 7.5−6.6 (broad m, 9H); 2.0−0.9 (m, 27H). IR (KBr): ν 2961, 2855, 1582, 1496, 1376, 1313, 1260, 1200, 766 cm^{-1}. UV−vis ($CHCl_3$): λ_{max} (log ϵ (dm^3 mol^{-1} cm^{-1})) 369 (3.46), 411 (3.44), 438 (3.41), 627 (3.11). EM-MALDI: *m/z* = 690 [M]$^+$. Anal. Calcd for $C_{38}H_{36}N_{10}Ni \cdot 2H_2O$: C, 62.74; H, 5.54; N, 19.25. Found: C, 62.58; H, 5.56; N, 19.83.

[9,10-Didodecyloxy-7,12:21,24-diimino-5,26:14,19-dinitrilotribenzo[*f*,*k*,*p*][1,2,4,9,14,19]hexaazaeicosinato-(2−)-*N*^{27},*N*^{28},*N*^{29},*N*^{30}]nickel(II) (14).[4b] Yield: 56%. Mp > 250 °C. UV−vis ($CHCl_3$): λ_{max} (log ϵ (dm^3 mol^{-1} cm^{-1})) 259 (4.83), 288 sh, 371 (4.68), 497 (4.24), 533 (4.22), 574(4.21), 627 (4.32).

9-*tert*-Butyl-7,12:21,24-diimino-5,26:14,19dinitrilotribenzo-[*f*,*k*,*p*][1,2,4,9,14,19]hexaazaeicosinato(2−)-*N*^{27},*N*^{28},*N*^{29},*N*^{30}]-nickel(II) (15).[4b] Yield: 35%. Mp > 250 °C. UV−vis ($CHCl_3$): λ_{max} (log ϵ (dm^3 mol^{-1} cm^{-1})) 259 (4.66), 313 (4.31), 374 (4.51), 497 (4.05), 531 (4.06), 572 (4.04), 625 (4.29).

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