J. Org. Chem. **2001,** *66,* 89−93

Synthesis of Nickel(II) Triazolenaphthalocyanine and Related Macrocycles†

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Received July 10, 2000

The synthesis of novel monbenzotriazolephthalocyanines (**3**−**6**), low-symmetry phthalocyanine analogues, is described for the first time using a novel and simple stepwise strategy which involves the use of substituted naphthalodinitriles **8**−**11** and appropriately substituted three-unit compounds such as **7**. Belonging to the same family, compound **1**, which we have called triazolenaphthalocyanine, has been prepared by a statistical method from compound **2** and 3,5-diamino-1,2,4-triazole. Compound **1** shows a bathochromic shift of the Q-band in UV−vis spectrum due to the fusing of benzene rings to the triazolephthalocyanine core.

Introduction

Phthalocyanines (Pcs)[1,2] are considered promising targets as molecular materials in many application fields. One of the most interesting characteristics of these highly conjugated planar macrocycles is their chemical versatility. Many derivatives of these compounds can be prepared not only by changing the nature of the central metal atom as well as the nature, number and position of the substituents, but also by formally fusing additional aromatic rings to the central core; or by forming planar or linear hetero- or homooligomers. All these modifications open the way to modulate the physicochemical parameters of the macrocycles and, therefore, their properties and technological utility.

Much effort has been devoted to nonlinear optical applications of phthalocyanines where these compounds have emerged as important materials for second harmonic generation because of the noncentrosymmetric characteristics they can present.[3] In this regard, the formal replacement of one isoindole subunit of the Pc core by another (hetero)aromatic moiety affords a useful approach for the preparation of low-symmetry Pc-related systems,[4] a goal actively pursued in our research group.[5]

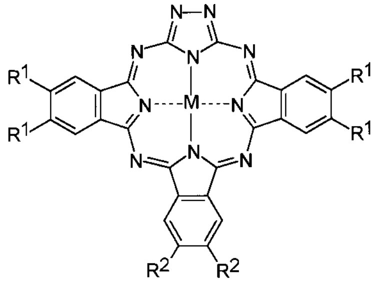

Figure 1. Triazolephthalocyanines.

In particular, triazolephthalocyanines (Tpcs)[6] (Figure 1), isoelectronic core-modified phthalocyanines in which one isoindole ring has been formally replaced by a 1,2,4-triazole subunit, are A_3B-type Pc analogues with high potential for constructing organic molecular materials. In fact, these molecules show not only second and third-order nonlinear optical responses[7] but also conducting properties,[8] a high thermal stability,[9] and the capability of being organized at a supramolecular level in Langmuir−Blodgett films[10,11] or liquid-crystal arrangements.[12]

The UV−vis spectrum of the nickel *tert*-butyltriazolephthalocyanine (Figure 1, $R^1 = H$, R^2, $R^2 = H$, *t*-Bu) is represented in Figure 2 together with the spectrum of the tetra-*tert*-butylphthalocyanine for comparative purposes. Triazolephthalocyanines show a Q-band that is less intense and quite blue shifted with relation to the

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† Dedicated to Professor José Barluenga on the occasion of his 60th birthday.

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10.1021/jo001039p CCC: $20.00 © 2001 American Chemical Society
Published on Web 12/14/2000

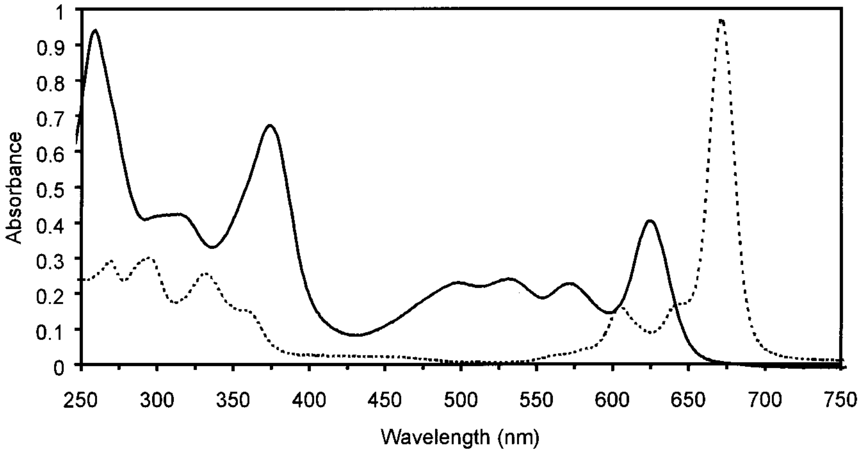
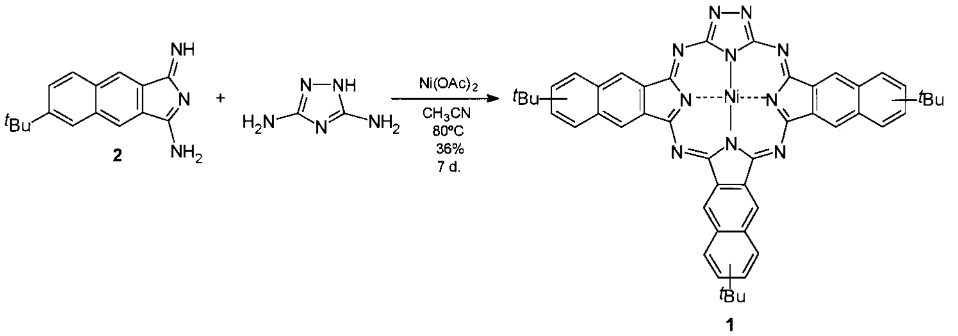


Figure 2. UV−vis spectra in $CHCl_3$ of the *tert*-butyltriazolephthalocyanine (solid line) and the tetra-*tert*-butylphthalocyanine (dotted line).

Scheme 1



phthalocyanine Q-band (ca. 626 nm). Furthermore, contrary to phthalocyanines, Tpcs present absorption bands within the range of 450−580 nm.

The fusion of one,[13] three,[14] or four benzene rings (naphthalocyanines)[15] to the Pc core has been used, besides the introduction of specific substituents, as a strategy for the modulation of the phthalocyanine electronic properties. Particularly, linear fusion induces a bathochromic shift of the Q-band as predicted by theoretical calculations.[16]

Following our interest in the preparation of Tpcs[7−12] with improved NLO properties, the synthesis of triazolephthalocyanines presenting additional fused benzene rings is considered an aim in order to dilucidate whether and in which extent such modification in the macrocyclic structure influences the electronic properties and can achieve new red-shifted triazolephthalocyanines.

Thus, we report here for the first time the synthesis and characterization of a triazolenaphthalocyanine (compound **1**) and several monobenzotriazole-phthalocyanines (compounds **3**−**6**). The former presents one benzene ring fused to each isoindole subunit, while the latter present one benzene ring fused to the isoindole subunit opposite to the triazole moiety.

Results and Discussion

The statistical condensation of a certain 1,3-diiminoisoindoline and 3,5-diamino-1,2,4-triazole in a 3:1 molar ratio in the presence of a metal salt yields triazolephthalocyanines in which all the isoindole subunits show the same substitution pattern.[17] In a similar manner, we have afforded **1** (Scheme 1) by reacting the 3-amino-6-*tert*-butyl-1-imino-1*H*-benzo[*f*]isoindole (**2**) with guanazole in the presence of nickel acetate. Compound **2** was obtained by bubbling NH_3 gas in a methanol solution of 5-*tert*-butyl-1,2-dicyanonaphthalene (**8**) in the presence of NaOMe.[18] Reaction temperatures higher than 80 °C in the synthesis of **1** give rise to a sensible quantity of the tetra-*tert*-butylnaphthalocyanine obtained as byproduct. This is easy to detect by means of UV−vis spectroscopy since it presents a Q-band centered at 765 nm. Compound **1**, purified by chromatographic methods, shows a UV−vis spectrum with the same pattern of the related triazolephthalocyanines except that the Q-band is bathochromically shifted to 685 nm.

Unsymmetrically substituted triazolephthalocyanines such as those represented in Figure 1 are obtained from a three-unit compound (like **7** in Scheme 2) by condensation with the corresponding diiminoisoindoline in the presence of a metal salt.[19] For applying the same strategy to the preparation of monobenzotriazolephthalocyanines such as **3**−**6**, it would be necessary to prepare substituted diiminobenzoisoindolines such as **2** (in Scheme 1) which would be reacted with **7** in appropriate conditions. However, it is well-known that the typical reaction conditions of transforming phthalonitriles into diiminoisoindolines (MeOH/NaOMe, reflux) cannot be applied to 1,4-

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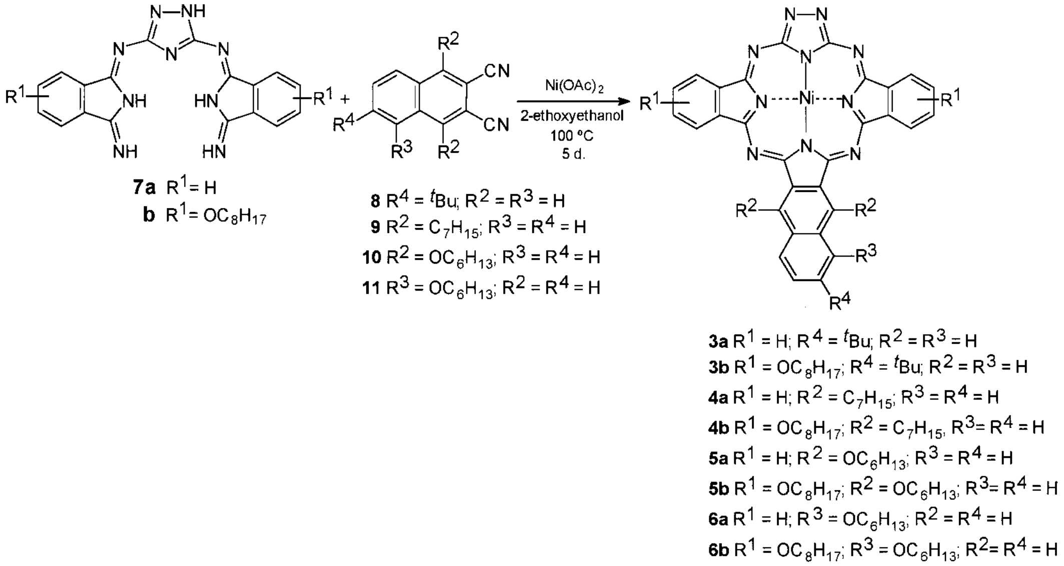
Scheme 2



dialkoxy-2,3-dicyanonaphthalenes such as **10**, since a trans-alkoxylation reaction (S_NAr) takes place with methanol.[20] This fact limits the applicability of the iminoisoindoline method to the naphtho series. To overcome this problem, we have successfully tested the direct condensation of a dicyanonaphthalene like **8**−**11** to a compound of type **7** for obtaining monobenzotriazolephthalocyanines **3**−**6**.

Thus, macrocycles **3**−**6** were prepared by reacting the three-unit compound **7a** or **7b** with a 2,3-dicyanonaphthalene (**8**−**11**, Scheme 2) in the presence of nickel acetate using either phenol or 2-ethoxyethanol as solvent at 100 °C. The three-unit compounds **7a**[21] and **7b**,[12] as well as the 2,3-dicyanonaphthalenes **8**,[22] **9**,[15] **10**, and **11**[23] were synthesized following methodologies reported in the literature.

While compounds **3a**,**b**, **4b**, **5b**, and **6b** are soluble in common apolar organic solvents, **4a**, **5a**, and **6a** are only slightly soluble in solvents such as chloroform or chloronaphthalene. The comparison of **4a**, **5a**, and **6a** with triazolephthalocyanines bearing no substituents at the isoindole subunits adjacent to the triazole[24] indicates that (except for **3a**) the fusion of a benzene ring induces a decrease of the solubility, as already observed for naphthalocyanines.[18,23] This effect is compensated by introducing octyloxy groups at the “lateral” isoindole subunits as it occurs for **4b**, **5b**, and **6b**. Chromatographic methods are appropriate to purify those compounds which are soluble enough. However, these compounds show a high affinity for the silica gel or alumina and quite polar eluents must be used (CH_2Cl_2/MeOH in a 4:1 relation). Concerning the less soluble derivatives, purification must be done by trituration in different solvents followed by extraction with hot chloronaphthalene.

An experiment was done in order to prepare **3a** starting from the 3-amine-6-*tert*-butyl-1-imine-1*H*-benzo[*f*]isoindole (**2**) instead of naphthalonitrile **8**. The desired macrocycle **3a** was obtained, as observed by FAB-MS, accompanied by the tetra-*tert*-butylnaphthalocyanine resulting from the autocondensation of **2**, which shows higher reactivity than **8**. In this reaction other minor compounds coming from transformations of **7a** were also detected by FAB-MS, thus lowering the yield of **3a**. The aggregation tendency of these compounds precludes their chromatographic separation and, therefore, their isolation and identification.

On the contrary, following the synthetic method depicted in Scheme 2, 2,3-dicyanonaphthalenes do not undergo autocondensation[25] and the related naphthalocyanines are not obtained as side-products.

All the compounds were characterized by mass spectroscopy, UV−vis, IR, ^1H NMR, and elemental analysis; the NMR spectra, especially ^{13}C NMR, seemed to be unhelpful, probably due to aggregation of the compounds at the concentrations used. On the other hand, compounds **3b**, **4b**, **5b**, and **6b** are mixtures of isomers, which makes the signal assignment more difficult.

The UV−vis spectra of the benzotriazolephthalocyanine derivatives described in this paper show the typical pattern of triazolephthalocyanine spectra (Figure 3).

The Q-band wavelengths of the benzotriazolephthalocyanines prepared in this paper are listed in Table 1, whereas the values corresponding to already reported triazolephthalocyanines are included in Table 2. Triazolephthalocyanines (Table 2) present a Q-band which falls into the range of 625−676 nm, the less energetic Q-bands being obtained for those hexasubstituted Tpcs bearing at least four long alkoxy chains (667−676 nm). Concerning compounds **3**−**6** (Table 1), the value range falls between 631 and 649 nm (Table 1).

The comparison between the series $R^1 = H$ of triazolephthalocyanines and monobenzotriazolephthalocyanines show that the fusion of one benzene ring induces a slight bathochromic shift of about 5−10 nm. Within the monobenzotriazolephthalocyanines those where $R^1 = OC_8H_{17}$ are also slightly red-shifted in relation to those where $R^1 = H$. Among the latter, the results suggest that

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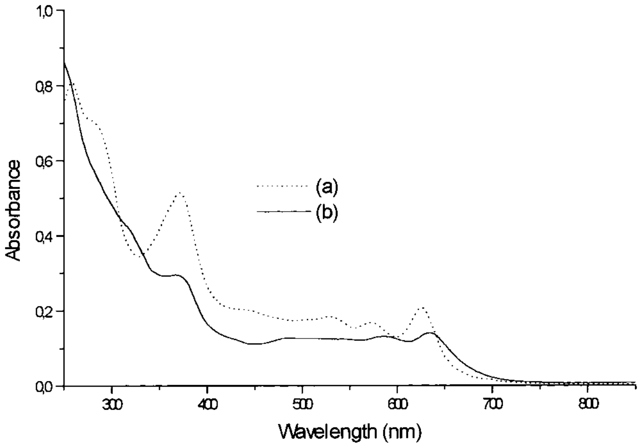
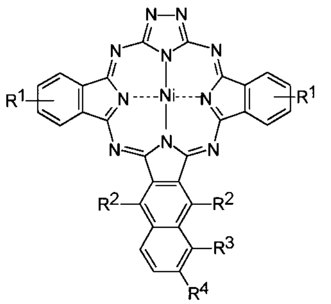


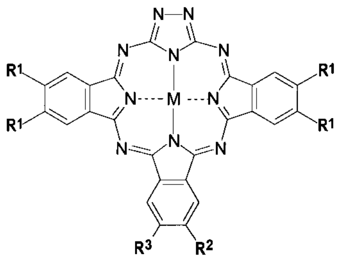
Figure 3. UV−vis spectra in $CHCl_3$ of the dioctyloxytriazolephthalocyanine (a, dotted line, 1.85×10^{-5} M) and the 9-hexyloxymonobenzotriazolephthalocyanine (b, solid line).

Table 1. Q-Band Wavelengths of Substituted Monobenzotriazolephthalocyanines



	$R^1 = H$	$R^1 = OC_8H_{17}$
$R^4 = {}^tBu$ ($R^2 = R^3 = H$)	631 (**3a**)	638 (**3b**)
$R^2 = C_7H_{15}$ ($R^3 = R^4 = H$)	636 (**4a**)	635 (**4b**)
$R^2 = OC_6H_{13}$ ($R^3 = R^4 = H$)	638 (**5a**)	649 (**5b**)
$R^3 = OC_6H_{13}$ ($R^2 = R^4 = H$)	642 (**6a**)	646 (**6b**)

Table 2. Q-Band Wavelengths of Some Substituted Triazolephthalocyanines



	M = Ni	M = Cu
$R^1 = R^3 = H$, $R^2 = {}^tBu$	625[19]	
$R^1 = R^3 = H$, $R^2 = OC_8H_{17}$	629[19]	633[7]
$R^1 = R^3 = H$, $R^2 = O(CH_2)_2Tiof$	632[8]	637[28]
$R^1 = H$, $R^2 = R^3 = OC_{12}H_{25}$	627[19]	
$R^1 = R^2 = R^3 = OC_8H_{17}$	671[10]	676[12]
$R^1 = R^2 = R^3 = OC_{12}H_{25}$	673[7]	676[12]
R^1=OC_8H_{17}, $R^2 = R^3 = OCH_2CON(C_8H_{17})_2$	667[12]	
R^1 =R^2 =R^3 =$OCH_2CON(C_8H_{17})_2$	633[12]	
$R^1 = OCH_3$, $R^2 = R^3 = OC_8H_{17}$	632[11]	

the position of the alkoxy groups can play an important role in determining the position of the Q-band, as it occurs in phthalocyanines and naphthalocyanines.[15,20,26,27] Particularly, the peripheral position occupied by R^3 seems to be associated to a bathochromic shift with respect to the other positions.

Finally, we have to remind that compound **1** (Scheme 1) shows a Q-band at 685 nm. Thus, on going from the *tert*-butyltriazolephthalocyanine ($R^1 = R^3 = H$; $R^2 = {}^tBu$ in Table 2), with the Q-band at 625 nm, to the tri-*tert*-butyltriazolenaphthalocyanine **1**, the fusion of three benzene rings induces a bathochromic shift of 60 nm in the Q-band. This shift is comparable to the one observed on going from phthalocyanines to naphthalocyanines for which the fusion of four benzene rings induces a bathochromic shift of 70−90 nm.[1]

Conclusions

In conclusion, the fusion of one benzene ring at the position opposite to the triazole subunit in triazolephthalocyanines induces electronic changes that are lower than those obtained by introducing adequate substituents (e.g. four long alkoxy chains). However, the formal fusion of three benzene rings has a quite stronger effect since it shifts the Q-band up to 685 nm. Until now, this is the most important bathochromic shift observed for a triazolephthalocyanine derivative.

In summary, we have developed a method for the preparation of triazolenaphthalocyanines using easily available dinitriles as precursors and have studied the optical spectra of these compounds for the first time in comparison with those of triazolephthalocyanines already known. These new systems are interesting targets for studying second-order nonlinear optical properties.

Experimental Section

Synthesis. Compounds **2**,[18] **7**,[21,28] **8**,[22] **9**,[23] **10**,[23] and **11**[15] 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.

3,12,21-Tri-*tert*-butyl-10,13:27,30-diimino-7,32:18,25-dinitrilotrinaphtho[2′,3′-*f*:2′,3′-*k*:2′,3′-*p*][1,2,4,9,14,19]hexaazacycloeicosinato(2−)-N^{33},N^{34},N^{35},N^{36}-nickel(II) (1). A mixture of 99 mg (0.39 mmol) of **2**, 14 mg (0.14 mmol) of guanazole, and 33 mg (0.13 mmol) of $Ni(OAc)_2 \cdot 4H_2O$ was refluxed in acetonitrile (6 mL) under argon atmosphere for 7 days. After removal of the solvent, the compound was purified by column chromatography on silica gel previously neutralized with THF/NEt_3 10:1. THF was first employed as eluent in order to separate the naphthalocyanine obtained as byproduct. Then, CH_2Cl_2/MeOH 10:2 was used to isolate **1**. After elimination of the eluent under reduced pressure the solid obtained was dissolved in chloroform and filtered in order to eliminate insoluble residues: yield 40 mg (36%); mp > 300 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.8−6.7 (m, 15H arom), 1.4 (broad s, 27H, *t*-Bu); IR (KBr) ν 3437, 2957, 2907, 2867, 1728 (w), 1632, 1616 (s), 1600, 1508, 1475 (vs), 1467 (vs), 1419, 1395, 1357 (s), 1317, 1273, 1259, 1165, 1147 (s), 1124, 1098, 1053, 907, 815, 763; UV−vis ($CHCl_3$) λ_{max} (log ϵ ($dm^3\ mol^{-1}\ cm^{-1}$)) 299 (4.51), 385 (4.13), 472 (3.96), 516 (3.91), 561 (3.75), 627 (3.64), 685 (3.68); FAB-MS (3-NOBA) m/z = 841 $[M + H]^+$. Anal. Calcd for $C_{50}H_{42}N_{10}Ni \cdot 2H_2O$: C, 68.42; H, 5.28; N, 15.96. Found: C, 67.98; H, 5.12; N, 15.45.

10-*tert*-Butyl-7,14:23,26-diimino-5,28:16,21-dinitrilodibenzo[*f*,*p*]naphtho[2′,3′-k][1,2,4,9,14,19]hexaazacycloeicosinato(2−)-N^{29},N^{30},N^{31},N^{32}-nickel(II) (3a). A solution of 100 mg (0.28 mmol) of the three-unit compound **7a**, 66 mg (0.28 mmol) of **8**, and 70 mg (0.28 mmol) of $Ni(OAc)_2 \cdot 4H_2O$ were heated in 10 mL of 2-ethoxyethanol at 100 °C for 10 days under argon atmosphere. After cooling, ethyl ether was added and the precipitate was separated by centrifugation and triturated in cold methanol for one night. The solid was

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then washed with THF and extracted with cold chloroform: yield 45 mg (26%); mp > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.8−6.5 (m, 13H arom), 1.4 (broad s, 9H, *t*-Bu); IR (KBr) ν 3448, 2954, 2864, 1732 (w), 1644, 1603, 1573, 1491 (vs), 1470 (vs), 1372, 1327, 1289, 1259, 1193, 1132, 1092, 1028, 949, 907, 816, 750, 724, 698, 646, 473 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ϵ ($dm^3\ mol^{-1}\ cm^{-1}$)) 241 (5.62), 259 (5.64), 292 (5.50), 317 (5.49), 366 (5.35), 459 (5.06), 488 (5.08), 530 (5.09), 576 (5.12), 631 (5.23); FAB-MS (3-NOBA) *m*/*z* 629 $[M + H]^+$. Anal. Calcd for $C_{34}H_{22}N_{10}Ni{\cdot}2H_2O$: C, 61.38; H, 3.94; N, 21.05. Found: C, 60.84; H, 3.92; N, 20.67.

10-*tert*-Butyl-2,18-dioctyloxy-7,14:23,26-diimino-5,28:16,21-dinitrilodibenzo[*f*,*k*]naphtho[2′,3′-*p*][1,2,4,9,14,19]hexaazacycloeicosinato(2−)-N^{29},N^{30},N^{31},N^{32}-nickel(II) (3b). A solution of 100 mg (0.16 mmol) of the three-unit compound **7b**, 37 mg (0.16 mmol) of **8**, and 41 mg (0.16 mmol) of $Ni(OAc)_2{\cdot}4H_2O$ were heated in 7 mL of 2-ethoxyethanol at 100 °C for 10 days under argon atmosphere. After cooling, the precipitate mixture was centrifuged and the solid was purified by column chromatography (silica gel) using CH_2Cl_2 and CH_2Cl_2/MeOH 40:1 as eluents: yield 20 mg (14%); mp > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.8−6.6 (m, 11H arom), 3.7 (m, 4H, OCH_2), 2.0−0.9 (m,30H, CH_2, CH_3), 1.4 (broad s, 9H, *t*-Bu); IR (KBr) ν 3065, 2925, 2854, 1734 (w), 1652 (w), 1603, 1576, 1506, 1485 (vs), 1465 (vs), 1372, 1334, 1282, 1241, 1128, 1067, 827 (w), 761; UV−vis ($CHCl_3$) λ_{max} (log ϵ ($dm^3\ mol^{-1}\ cm^{-1}$)) 273 (4.76), 320 (4.55), 360 (4.41), 475 (4.26), 517 (4.22), 577 (4.18), 638 (4.19); FAB-MS (3-NOBA) *m*/*z* 885 $[M + H]^+$, 773 $[M - C_8H_{17} + 2H]^+$, 661 $[M - 2C_8H_{17} + 3H]^+$, 645 $[M - C_8H_{17} - OC_8H_{17} + 3H]^+$. Anal. Calcd for $C_{50}H_{54}N_{10}NiO_2{\cdot}2H_2O$: C, 65.15; H, 6.34; N, 15.20. Found: C, 64.67; H, 6.29; N, 14.94.

8,13-Diheptyl-7,14:23,26-diimino-5,28:16,21-dinitrilodibenzo[*f*,*k*]naphtho[2′,3′-*p*][1,2,4,9,14,19]hexaazacycloeicosinato(2−)-N^{29},N^{30},N^{31},N^{32}-nickel(II) (4a). A solution of 100 mg (0.28 mmol) of **7a**, 105 mg (0.28 mmol) of **9**, and 70 mg (0.28 mmol) of $Ni(OAc)_2{\cdot}4H_2O$ in 6 mL of phenol was heated at 100 °C for 4 days under argon atmosphere. After cooling, ethyl ether was added, the suspension was centrifuged, and the solid was washed with ethyl ether and hot chloroform. The solid was then extracted by grinding in chloronaphthalene at 115 °C for 2 days. After removal of the solvent under vacuum, the product was finally washed with methanol: yield 15 mg (7%); mp > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7,8−6,7 (m, 12H arom.); 3,5 (m, 4H, CH_2); 1,9−0,9 (m,26H, CH_2, CH_3); IR (KBr) ν 3420, 2924, 2853, 1651, 1608, 1562, 1497 (vs), 1473, 1379, 1317, 1192, 1101, 925, 837, 760, 724, 700; UV−vis ($CHCl_3$) λ_{max} (log ϵ ($dm^3\ mol^{-1}\ cm^{-1}$)) = 274 (5.23), 354 (4.32), 513 (4.01), 579 (4.01), 636 (4.04); FAB-MS (3-NOBA) *m*/*z* = 769 $[M + H]^+$, 599 $[M - 2C_6H_{13} + H]^+$. Anal. Calcd for $C_{44}H_{40}N_{10}Ni{\cdot}2H_2O$: C, 65.76; H, 5.52; N, 17.43. Found: C, 65.45; H, 5.70; N, 17.62.

8,13-Diheptyl-2,18-dioctyloxy-7,14:23,26-diimino-5,28:16,21-dinitrilodibenzo[*f*,*k*]naphtho[2′,3′-*p*][1,2,4,9,14,19]hexaazacycloeicosinato(2−)-N^{29},N^{30},N^{31},N^{32}-nickel(II) (4b). A solution of 100 mg (0.16 mmol) of **7b**, 59 mg (0.16 mmol) of **9**, 40 mg (0.16 mmol) of $Ni(OAc)_2{\cdot}4H_2O$, and 6 mL of 2-ethoxyethanol was heated at 105 °C for 4 days under argon atmosphere. After removal of the solvent, the solid was purified by column chromatography (silica gel), by eluting first with CH_2Cl_2 and progressively increasing the polarity until reaching CH_2Cl_2/MeOH 10:2.5: yield 30 mg (18%); mp > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.8−6.7 (m, 10H arom), 3.7 (m, 8H, OCH_2, CH_2), 2.0−0.9 (m, 56H, CH_2, CH_3); IR (KBr) ν 2925, 2853, 1653 (w), 1607, 1568, 1484, 1465(vs), 1374, 1330, 1282, 1239, 1079, 829 (w), 761; UV−vis ($CHCl_3$) λ_{max} (log ϵ ($dm^3\ mol^{-1}\ cm^{-1}$)) = 270 (4.74), 366 (4.40), 400 (4.39), 537 (4.21), 590 (4.17), 635 (4.09); FAB-MS (3-NOBA) *m*/*z* = 1026 $[M + H]^+$. Anal. Calcd for $C_{60}H_{74}N_{10}NiO_2{\cdot}2H_2O$: C, 67.86; H, 7.40; N, 13.19. Found: C, 67.52; H, 7.22; N, 13.29.

8,13-Dihexyloxy-7,14:23,26-diimino-5,28:16,21-dinitrilodibenzo[*f*,*k*]naphtho[2′,3′-*p*][1,2,4,9,14,19]hexaazacycloeicosinato(2−)-N^{29},N^{30},N^{31},N^{32}-nickel(II) (5a). A solution of 100 mg (0.28 mmol) of **7a**, 115 mg (0.29 mmol) of **10**, and 70 mg (0.28 mmol) of $Ni(OAc)_2{\cdot}4H_2O$ in 10 mL of 2-ethoxyethanol was heated at 110 °C for 5 days under argon atmosphere. Compound **5a** was purified following the same procedure described for **4a**: yield 13 mg (6%); mp > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.8−6.7 (m, 12H arom), 3.5 (m, 4H, OCH_2), 2.0−0.9 (m, 22H, CH_2, CH_3); IR (KBr) ν 3295, 2925, 2857, 1637, 1603, 1559, 1541, 1486 (vs), 1469 (vs), 1397, 1375, 1326, 1290, 1192, 1087, 758, 723; UV−vis ($CHCl_3$) λ_{max} (log ϵ ($dm^3\ mol^{-1}\ cm^{-1}$)) 244 (4.67), 351 (4.40), 488 (4.18), 522 (4.15), 554 (4.11), 638 (3.99); FAB-MS (3-NOBA) *m*/*z* 687 $[M - C_6H_{13} + H]^+$; 603 $[M - 2C_6H_{13} + H]^+$. Anal. Calcd for $C_{42}H_{36}N_{10}NiO_2{\cdot}2H_2O$: C, 62.47; H, 4.99; N, 15.35. Found: C, 62.35; H, 5.03; N, 15.66.

8,13-Dihexyloxy-2,18-dioctyloxy-7,14:23,26-diimino-5,28:16,21-dinitrilodibenzo[*f*,*k*]naphtho[2′,3′-*p*][1,2,4,9,14,19]hexaazacycloeicosinato(2−)-N^{29},N^{30},N^{31},N^{32}-nickel(II) (5b). A solution of 100 mg (0.16 mmol) of **7b**, 62 mg (0.16 mmol) of **10**, and 40 mg (0.16 mmol) of $Ni(OAc)_2{\cdot}4H_2O$ was heated in 6 mL of 2-ethoxyethanol at 105 °C for 4 days under argon atmosphere. Compound **5b** was purified following the same procedure described for **4b**: yield 30 mg (18%); mp > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.9−6.6 (m, 10H arom), 3.7 (m, 8H, OCH_2), 2.0−0.9 (m, 52H, CH_2, CH_3); IR (KBr) ν 2925, 2854, 1733, 1650 (w), 1602, 1573, 1539, 1507, 1488 (vs), 1470 (vs), 1370, 1334, 1284, 1238, 1074, 835, 761; UV−vis ($CHCl_3$) λ_{max} (log ϵ ($dm^3\ mol^{-1}\ cm^{-1}$)) 260 (4.66), 365 (4.19), 399 (4.11), 473 (3.92), 590 (3.72), 649 (3.68); FAB-MS (3-NOBA) *m*/*z* 1029 $[M + H]^+$; 945 $[M - C_6H_{13} + 2H]^+$; 861 $[M - 2C_6H_{13} + 3H]^+$; 749 $[M - 2C_6H_{13} - C_8H_{17} + 4H]^+$; 636 $[M - 2C_6H_{13} - 2C_8H_{17} + 5H]^+$. Anal. Calcd for $C_{58}H_{70}N_{10}NiO_4{\cdot}2H_2O$: C, 65.35; H, 7.00; N, 15.51. Found: C, 65.00; H, 6.82; N, 15.19.

9-Hexyloxy-7,14:23,26-diimino-5,28:16,21-dinitrilodibenzo[*f*,*k*]naphtho[2′,3′-*p*][1,2,4,9,14,19]hexaazacycloeicosinato(2−)-N^{29},N^{30},N^{31},N^{32}-nickel(II) (6a). A solution of 100 mg (0.28 mmol) of **7a**, 78 mg (0.28 mmol) of **11**, and 70 mg (0.28 mmol) of $Ni(OAc)_2{\cdot}4H_2O$ was heated in 6 mL of phenol at 105 °C for 4 days under argon atmosphere. See **4a** for purification procedure: yield 30 mg (16%); mp > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7,8−6,7 (m, 11H arom), 3,6 (m, 6H, OCH_2), 2,0−0,9 (m, 41H, CH_2, CH_3); IR (KBr) ν 3450, 2927, 2857, 1605, 1575, 1492 (vs), 1472 (vs), 1346, 1321, 1270, 1194, 1134, 1099, 835, 755, 700; UV−vis ($CHCl_3$) λ_{max} (log ϵ ($dm^3\ mol^{-1}\ cm^{-1}$)) 258 (4.75), 298 (4.60), 314 (4.60), 374 (4.52), 521 (4.22), 554 (4.25), 589 (4.33), 643 (4.52); FAB-MS (3-NOBA) *m*/*z* = 673 $[M + H]^+$, 589 $[M + H - C_6H_{13} + H]^+$. Anal. Calcd for $C_{36}H_{26}N_{10}NiO{\cdot}2H_2O$: C, 60.95; H, 4.26; N, 19.74. Found: C, 60.52; H, 4.00; N, 19.45.

9-Hexyloxy-2,18-dioctyloxy-7,14:23,26-diimino-5,28:16,21-dinitrilodibenzo[*f*,*k*]naphtho[2′,3′-*p*][1,2,4,9,14,19]hexaazacycloeicosinato(2−)-N^{29},N^{30},N^{31},N^{32}-nickel(II) (6b). A solution of 100 mg (0.16 mmol) of **7b**, 44 mg (0.17 mmol) of **11**, and 43 mg (0.17 mmol) of $Ni(OAc)_2{\cdot}4H_2O$ was heated in 6 mL of phenol at 100 °C for 3 days under argon atmosphere. See **4b** for purification procedure: yield 30 mg (19%); mp > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.8−6.7 (m, 13H arom), 3.5 (m, 2H, OCH_2), 2.0−0.9 (m, 11H, CH_2, CH_3); IR (KBr) ν 2924, 2853, 1604, 1575, 1485 (vs), 1465 (vs), 1372, 1336, 1281, 1240, 1162, 1131, 1064, 832, 760; UV−vis ($CHCl_3$) λ_{max} (log ϵ ($dm^3\ mol^{-1}\ cm^{-1}$)) 268 (4.79), 364 (4.38), 502 (4.17), 549 (4.12), 589 (4.09), 646 (4.21); FAB-MS (3-NOBA) *m*/*z* 929 $[M + H]^+$, 817 $[M - C_8H_{17} + 2H]^+$, 733 $[M - C_8H_{17} - C_6H_{13} + 3H]^+$, 621 $[M - 2C_8H_{17} - C_6H_{13} + 4H]^+$. Anal. Calcd for $C_{52}H_{58}N_{10}NiO_3{\cdot}2H_2O$: C, 64.67; H, 6.47; N, 14.50. Found: C, 64.27; H, 6.21; N, 14.09.

Acknowledgment. This work was supported by CICYT and Comunidad de Madrid (Spain) through grants MAT-99-0180 and 07N/0020/98, respectively. A Graduated Research Fellowship of the Ministerio de Educación y Cultura to Mónica Nicolau is gratefully acknowledged.

JO001039P