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Stepwise Synthesis of Soluble Substituted Triazolephthalocyanines

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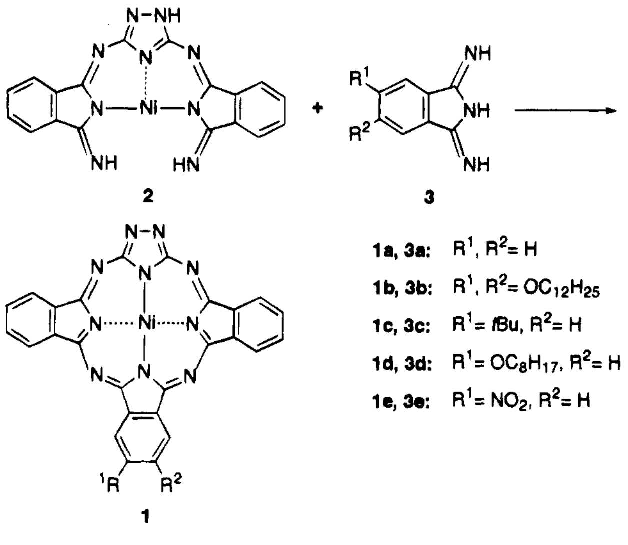
Introduction

The search for new structural modifications of porphyrins[1] and phthalocyanines[2] has been very active in the last years. These compounds, especially phthalocyanines, have not only theoretical interest as Hückel aromatic systems but also practical importance as potential building blocks for the construction of new molecular materials for semiconductor technology and optoelectronics.[2,3] Thus, the study of the nonlinear optical (NLO) properties of conjugated π-donor−acceptor organic molecules able to display particular physical properties, e.g., large second-order polarizabilities,[4] such as metallophthalocyanines[5] and porphyrins,[6] has intensified. In connection with our studies of electrical[7] and optical[8] properties of azaporphyrinic systems, our interest is mainly focused on the preparation of new unsymmetrical phthalocyanine analogues.[9]

Recently,[9a] we have reported for the first time the formal exchange of an isoindole ring of phthalocyanine with 1,2,4-triazole to afford an 18π-electron fully conjugated macrocycle **1a**, for which the trivial name triazolephthalocyanine has been suggested.[10] However, the one-step nickel(II) template-assisted synthetic method followed for the preparation of **1a** does not allow the synthesis of derivatives with different types and degrees of substitution on each of the three isoindole moieties.[11] This is a serious drawback to the development of unsymmetric systems related to **1a**, which might be substituted by both electron donor and acceptor groups, in order to promote strong intramolecular charge-transfer excitations, prerequisite for achieving large second-order nonlinear optical (NLO) responses.[4]

Scheme 1. Synthesis of Substituted Triazolephthalocyanines 1a-d

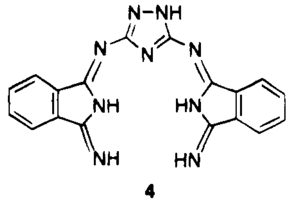


This paper reports a stepwise, widely applicable strategy for the preparation of unsymmetrically substituted triazolephthalocyanines, some of which are soluble in organic solvents.[12] Few examples of stepwise syntheses of phthalocyanines or phthalocyanine analogues have been reported.[2,10]

Results and Discussion

Recently, we described the preparation of the three-unit nickel complex **2**.[9b] Compound **2** was reacted with different substituted 1,3-diiminoisoindolines **3a-e** in equimolar amounts at relatively low temperature (55 °C) to yield the corresponding triazolephthalocyanines **1a-e** in 35−60% yield as dark violet powders (Scheme 1).

Compounds **1a-e** can be also obtained from 1,3-bis((3′-imino-1′-isoindolinylidene)amino)-1,2,4-triazole (**4**) in a two-step one-pot reaction by successive treatment with nickel(II) acetate at 80 °C and then with the corresponding 1,3-iminoisoindoline at lower temperature (55 °C).



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(10) There are few reports on noncentrosymmetric phthalocyanines or phthalocyanine analogues due to their preparative difficulties. See, for example, Kobayashi, N.; Kondo, R.; Nakajima, S.; Osa, T. *J. Am. Chem. Soc.* **1990**, *112*, 9640 and references therein. Jackson, A. H. In *The Porphyrins*; Dolphin D., Ed.; Academic Press: New York, 1979; Vol. 1, pp 380−381.

(11) Thus, for example, the reaction of 5-(octyloxy)-1,3-diiminoisoindoline with 3,5-diamino-1,2,4-triazole in the presence of nickel(II) acetate furnished a mixture of the four possible trisubstituted regioisomers having one alkoxy group on each isoindole subunit. See ref 12.

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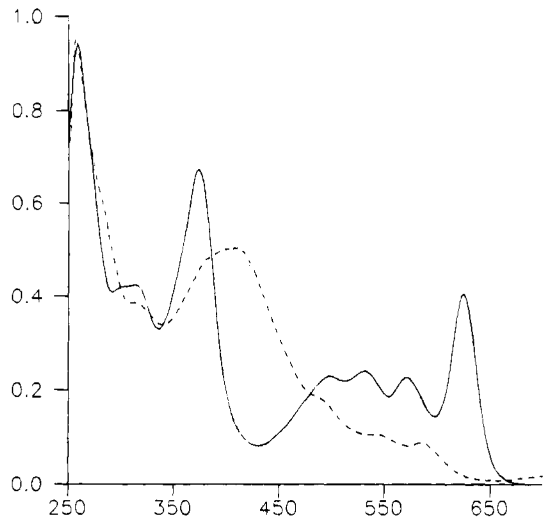

Figure 1. Electronic spectra (absorbance vs wavelength (nm)) of **1c** in chloroform (continuous line) and TFA (dashed line) at 2.1 × 10^{-5} mol L^{-1}.

The yields are comparable to those obtained by the previous method.

The IR spectra of triazolephthalocyaninatonickel(II) **1a-e** show a characteristic absorption band at 1600 cm^{-1} (middle intensity) and three more between 1450 and 1500 cm^{-1} (strong) attributed to C=N stretching vibrations. Similar type of bands, although weaker, appear at 1610, 1530, and 1470 cm^{-1} in phthalocyaninatonickel (NiPc). A characteristic absorption at 750 cm^{-1} (weak-medium) is assigned to out of plane C−H bonding vibrations in **1a-e**. The UV/vis spectrum of the *tert*-butyl derivative **1c** in chloroform (Figure 1, continuous line) is typical of triazolephthalocyanines **1b-d**. The spectrum is characterized by a Q-band at 623 nm and three weaker absorptions at shorter wavelength in the 500−580 nm region. The Soret or B band appears at 374 nm. This pattern is quite similar to that typical of a phthalocyanine.[13] The fine tuning of the positions of the absorption bands of phthalocyanines by peripheral substitution or formal replacement of isoindole moieties has become an important goal.[10] The relatively fine structure of all the bands in the spectrum of **1c** in chloroform disappears when it is determined in acidic media (trifluoroacetic acid, TFA) (Figure 1, dashed line).[14] The Q band is displaced toward shorter wavelengths and decreases in intensity while the B bands broaden and undergo a bathochromic shift. Similar spectral data were obtained for compounds **1a** and **1e** in TFA. These compounds are insoluble in chloroform.

Perhaps the most notable feature of the ^1H NMR spectra of alkoxytriazolephthalocyanines **1b** and **1d** in deuterated chloroform is the low chemical shifts of the aromatic protons. Thus, compound **1d** shows four broad multiplets between 6.4 and 7.6 ppm corresponding to the protons of both substituted and unsubstituted isoindole moieties. As expected, a stronger shielding is experienced by the protons in the ortho-position to the alkoxy substituent(s). These values are in total agreement with the chemical shifts observed for a tetraalkoxyphthalocyaninatonickel(II) in chloroform.[15] Finally, the FAB-MS spectra of all compounds show intensive isotopic clusters at $(M + H)^+$ which corroborate the structures of the compounds.

When the condensation reactions described above were carried out at higher temperatures (>100 °C) or with an excess of nickel(II) compound **2**, a mixture of compounds was obtained.

In conclusion, we have achieved a new and versatile stepwise method for the preparation of unsymmetrically substituted triazolephthalocyanines **1** as an entry into the development of improved molecular materials for NLO applications.[5] The solubility of these triazolephthalocyanines has made possible the characterization of the family by means of UV/vis and ^1H NMR spectroscopy for the first time. Although the synthetic experiments were confined to the unsubstituted three-unit compound **2** and to nickel(II) as central metal for simplicity reasons, we are confident that our finding is of a general nature and may be used with synthetic purposes for the preparation of a variety of triazolephthalocyanines, substituted also in the isoindole moieties near the triazole ring and having different central transition metals (copper, cobalt, etc.).[12]

Experimental Procedures

General Procedure for the Preparation of [7,10:19,24-Diimino-5,26:12,17-dinitrilotribenzo[*f,g,p*][1,2,4,9,14,19]hexaazaeicosinato(2−)-N^{27},N^{28},N^{29},N^{30}]nickel(II) 1a-e. A mixture of **2**[9b] (0.47 g, 1.13 mmol) and **3a-e** (1.13 mmol) in 2-ethoxyethanol (50 mL) was stirred at 50 °C for 2 d. After filtration, the raw material was triturated successively with methanol and 2-ethoxyethanol at reflux temperature, and then the residue was repeatedly extracted with dichloromethane in the case of compounds **1b-d** or with 1-chloronaphthalene in the case of **1a** and **1e**. Finally, after vacuum evaporation of the solvent, the residue was washed with methanol and filtered. Compound **1b** can also be purified by column chromatography on silica gel (dichloromethane−methanol 10:1).

Alternatively, a mixture of **4** (0.4 g, 1.13 mmol) and $Ni(OAc)_2$ (0.28 g, 1.13 mmol) in 2-ethoxyethanol (40 mL) was heated at 80 °C for 2 h. After the mixture was cooled at 55 °C, **3a-e** (1.13 mmol) in 2-ethoxyethanol (10 mL) was added and the mixture was stirred for 48 h at this temperature. The solid was isolated by filtration, and it was treated as described above affording the corresponding triazolephthalocyaninatonickel(II) **1a-e**.

Data for **1a**: yield 60%; mp > 250 °C; ^1H NMR (200 MHz, *d*-TFA) δ 8.3 (m, 6H), 8.0 (m, 6H) ppm; ^{13}C NMR (200 MHz, *d*-TFA) δ 165.4, 134.1, 130.7, 130.0 ppm; FAB-MS (3-NOBA) *m/z* 523, 525 [$(M + H)^+$, 100]; UV/vis (TFA) λ_{max} (log $\epsilon/dm^3\ mol^{-1}\ cm^{-1}$) 258 (4.56), 293 sh, 310 sh, 397 (4.38), 487 (3.86), 582 (3.54) nm; IR (KBr) ν 3600−3200 (OH),1605, 1490, 1470, 1450 (C=N), 1235, 1080, 750, 735 (CH) cm^{-1}. Anal. Calcd for $C_{26}H_{12}NiN_{10}{\cdot}2H_2O$: C, 55.85; H, 2.88; N, 25.05. Found: C, 55.93; H, 2.68; N, 24.80.

Data for **1b**: yield 42%; mp > 250 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 7.6−6.6 (broad m, 10H), 4.2−3.4 (broad m, 4H), 2.0−1.1 (m, 40H), 0.96 (m, 6H) ppm; FAB-MS (3-NOBA) *m/z* 891, 893 [$(M + H)^+$, 100], 555, 557 [$([M - 2 \times C_{12}H_{24}] + H)^+$, 64];

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[13] Ortí, E.; Brédas, J. L.; Clarisse, C. *J. Phys. Chem.* **1990**, *92*, 1228 and references therein.

[14] Drastical changes in the electronic spectra of phthalocyanines and phthalocyanine analogues have been described as a function of the nature of the solvent as consequence of molecular agreggation. Sielcken, O. E.; van Tilborg, M. M.; Roks, M. F. M.; Hendriks, R.; Drenth,W.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1987**, *109*, 4261 and references therein. Duro, J. A.; Torres, T. *Chem. Ber.* **1993**, *126*, 269.

[15] The ^1H NMR in chloroform of a mixture of the four possible structural isomers of tetrakis(pentyloxy)phthalocyaninatonickel(II) obtained from 5-(pentyloxy)-1,3-diiminoisoindoline shows a multiplet centered at 7.3 ppm (aromatic protons in the *meta*-position to the alkoxy substituent; the signal lies partly under the chloroform signal) and several broad multiplets between 6.8 and 6.2 ppm (aromatic protons in the *ortho*-position). Hanack, M.; Sommerauer, M. Personal communication. Chemical shifts of aromatic protons in alkoxyphthalocyaninatonickel(II) complexes are strongly dependent on the substituent position and the type of the alkoxy substituent. Hanack, M.; Schmid, G.; Sommerauer , M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1422.

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) nm; IR (KBr) ν 3600−3300 (OH),1600, 1500, 1470, 1440 (C=N), 1290, 750 (CH) cm^{-1}. Anal. Calcd for $C_{50}H_{60}NiN_{10}O_2 \cdot 2H_2O$: C, 64.73; H, 6.95; N, 15.10. Found: C, 65.08; H, 7.08; N, 15.22.

Data for **1c**: yield 46%; mp > 250 °C; ^{1}H NMR (200 MHz, $CDCl_3$ + TFA (1 drop)) δ 8.6−7.5 (broad m, 11H), 1.59 (s, 9H) ppm; ^{1}H NMR (200 MHz, *d*-TFA) δ 8.4, 8.0 (2 × m, 11H), 1.67 (s, 9H) ppm; ^{13}C NMR (200 MHz, *d*-TFA) δ 166.8, 134.8, 132.1, 131.5, 33.8 ppm; FAB-MS (3-NOBA) *m/z* 579, 581 [(M + H)$^+$, 100]; 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) nm; UV/vis (*d*-TFA) λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}) 258 (4.78), 291 sh, 318 sh, 400 (4.58), 490 sh, 544 (3.90), 580 (3.84) nm; IR (KBr) ν 3600−3200 (OH),1600, 1490, 1470, 1450 (C=N), 1370, 1330, 750 (CH) cm^{-1}. Anal. Calcd for $C_{30}H_{20}NiN_{10} \cdot 2H_2O$: C, 58.56; H, 3.93; N, 22.76. Found: C, 58.76; H, 3.54; N, 22.60.

Data for **1d**: yield 35%; mp > 250 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.45 (m, 4H), 7.15, 7.0 (2 × m, 5H), 6.6 (m, 2H), 4.2−3.5 (m, 2H), 2.0−1.1 (m, 12H), 0.95 (m, 3H) ppm; FAB-MS (3-NOBA) *m/z* 651, 653 [(M + H)$^+$, 100], 539, 541 [([M − C_8H_{16}] + H)$^+$, 51]; UV/vis ($CHCl_3$) λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}) 260 (4.49), 369 (4.26), 497 (3.87), 531 (3.90), 572 (3.84), 629 (3.97) nm; IR (KBr) ν 3600−3300 (OH), 1600, 1490, 1470, 1450 (C=N), 1330, 750 (CH) cm^{-1}. Anal. Calcd for $C_{34}H_{28}NiN_{10}O \cdot 2H_2O$: C, 59.41; H, 4.69; N, 20.38. Found: C, 59.41; H, 4.69; N, 20.38.

Data for **1e**: yield 58%; mp > 250 °C; ^{1}H NMR (200 MHz, *d*-TFA) δ 9.5, 8.9, 8.7 (3 × m, 3H), 8.6 (m, 4H), 8.1 (m, 4H) ppm; FAB-MS (3-NOBA) *m/z* 568, 570 [(M + H)$^+$, 50], 523, 525 [([M − NO_2] + 2H)$^+$, 100]; UV/vis (TFA) λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}) 258 (4.58), 291 (4.46), 390 (4.43), 448 sh, 538 (3.75), 580 (3.50) nm; IR (KBr) ν 3600−3300 (OH), 1600 (C=N), 1500 (broad, NO_2 st as, C=N), 1470 (C=N), 1340 (NO_2 st si), 750, 730 (CH) cm^{-1}. Anal. Calcd for $C_{26}H_{11}NiN_{11}O_2 \cdot 2H_2O$: C, 51.69; H, 2.50; N, 25.50. Found: C, 51.83; H, 2.27; N, 25.36.

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