Novel Homo- and Heterodimetallic Heterobinuclear Phthalocyaninato-Triazolehemiporphyrazinate Complexes

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A family of unsymmetrical heterobinuclear phthalocyaninato−triazolehemiporphyrazinate (Pc-Thp) complexes **2a**−**e** has been synthesized for the first time by statistical mixed condensation of regioisomerically pure dicyanotriazolehemiporphyrazinates **5a**,**b** with differently substituted phthalonitrile derivatives **6** and **7**. This stepwise approach allows to prepare heterodimetallic complexes **2b** and **2d** incorporating Ni(II) or Zn(II) in the cavity of each macrocyclic unit as well as a "push−pull" homodimetallic Pc−Thp compound, **2e**, bearing acceptor $(SO_2C_8H_{17})$ and donor (OC_8H_{17}) substituents. The UV−vis spectra of compounds **2a**−**e** in $CHCl_3$ exhibit a broad and split Q-band indicative of intra- and intermolecular interactions. Moreover, a strong red-shifting (25−50 nm) relative to the octasubstituted mononuclear Pc compounds is observed, which is in agreement with the enlargement of the π-conjugated Pc system. Interestingly, the optical behavior of Pc-Thp compounds **2a**−**d** is driven by the central metal included into the Pc moiety. Compound **2e** exhibits a low degree of intermolecular interactions in solution taking into account its UV−vis and ${}^1H$ NMR spectra.

Introduction

The aggregation of phthalocyanines[1−3] (Pcs) has been extensively studied to elucidate how these molecules interact intermolecularly in solution. These studies have shown that the coupling between electronic states of two or several Pcs leads to important changes in the absorption spectra of these compounds, namely a decrease in the intensity of the Q-band which is at the same time blue-shifted. However, very few examples of intramolecular interactions between Pc units have been studied in homodimetallic binuclear phthalocyanine systems in which the Pc units have been connected through π-conjugated condensed systems such as benzene[4] or naphthalene[5] rings. Other relevant examples of Pc dimeric systems are the homodimetallic ethynyl- or butadiynyl-bridged bisphthalocyanines described by others[6] and us.[7] In all these cases, the Q-band undergoes a shift to the near-IR region, which has been attributed to the enlarge-

ment of the π-conjugated system, with concomitant splitting of the Q-band as a consequence of intramolecular electron coupling between the Pc units. The same strong red-shifting of the Q-band has been observed in mononuclear phthalocyanines in which the π-system has been extended by annelation with other benzene units[8] and to a lesser extent by introduction of π-conjugated substituents.[9]

Much less effort has been focused on the preparation of heterodimetallic[7] or heterobinuclear[10] Pc systems. These compounds are potentially useful in electron-transfer processes.[11] The difficulty in preparing unsymmetrical Pcs[10,12] bearing appropriate substituents, e.g. two *o*-cyano groups,[10,12a] that can be further reacted to form heterodimetallic binuclear Pc derivatives, may explain the absence of a variety of unsymmetrical bis-

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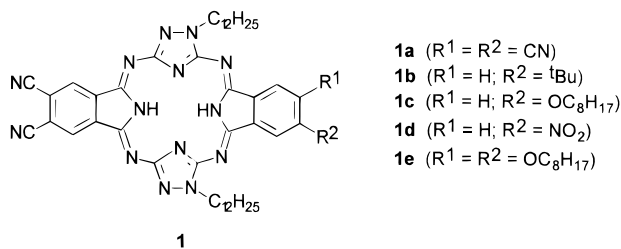(9) (a) de la Torre, G.; Torres, T. *J. Porphyrins Phthalocyanines* **1997**, *1*, 221. (b) Tian, M.; Wada, T.; Kimura-Suda, H.; Sasabe, H. *J. Mater. Chem.* **1997**, *7*, 861. (c) Tian, M.; Wada, T.; Sasabe, H. *J. Heterocyclic Chem.* **1997**, *34*, 171. (d) Tian, M.; Wada, T.; Kimura-Suda, H.; Sasabe, H. *Mol. Cryst. Liq. Cryst.* **1997**, *294*, 271.
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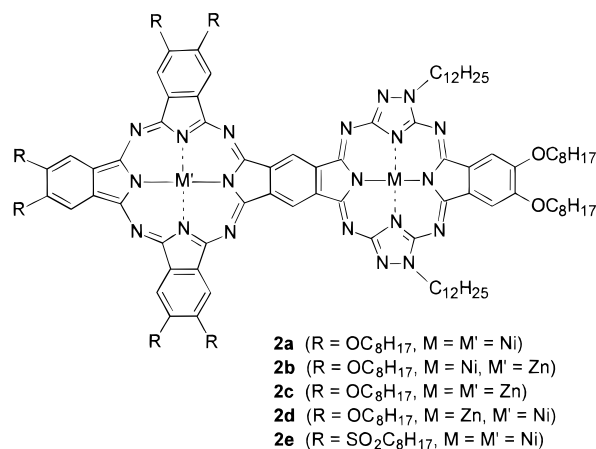
Chart 1

1a (R^1 = R^2 = CN)
1b (R^1 = H; R^2 = ^{t}Bu)
1c (R^1 = H; R^2 = OC$_8$H$_{17}$)
1d (R^1 = H; R^2 = NO$_2$)
1e (R^1 = R^2 = OC$_8$H$_{17}$)

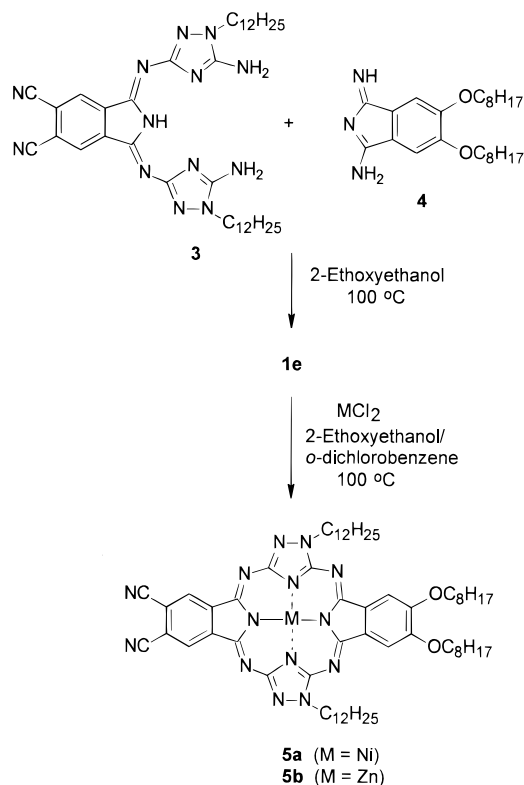phthalocyanine systems in comparison with the plethora of porphyrinic analogues.[13]

Triazolehemiporphyrazines[14] (Thps) are a family of Pc analogues in which two isoindole units have been formally replaced by two 1,2,4-triazole moieties. Their absorption spectra show several maxima in a completely different region in which the Q-band of Pcs is present.[14b] Recently, we have published a stepwise synthetic approach[15] that allows to prepare regioselectively unsymmetrically substituted dicyanotriazolehemiporphyrazines **1a**−**d** (Chart 1). The functionalization of one of the isoindole units of the molecule with two cyano groups in an ortho substitution pattern makes these macrocycles very attractive as noncentrosymmetric "push−pull" molecules for second harmonic generation[16] (SHG) as well as starting materials in the stepwise synthesis of Thp-based ladder oligomers.[17]

In this paper we describe the methodology to prepare homo- and heterodimetallic heterobinuclear phthalocyaninato-triazolehemiporphyrazinate (Pc-Thp) complexes **2** (Chart 2) and their characterization by UV−vis spectroscopy as well as by mass spectrometry (MALDI-TOF technique). This family of π-conjugated binuclear macrocycles is described for the first time in this manuscript. Some preliminary considerations about inter- and intramolecular interactions in this kind of molecules are also drafted. We expect these Pc-Thp complexes to exhibit remarkable electronic and optical properties since they should combine the unique Pcs[18] and Thp[14a] characteristics.

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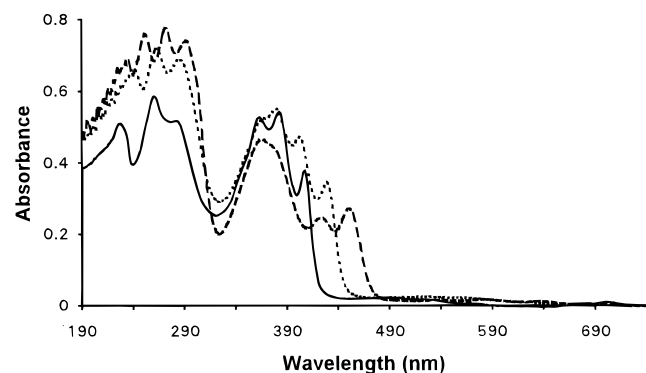
Chart 2

2a (R = OC$_8$H$_{17}$, M = M' = Ni)
2b (R = OC$_8$H$_{17}$, M = Ni, M' = Zn)
2c (R = OC$_8$H$_{17}$, M = M' = Zn)
2d (R = OC$_8$H$_{17}$, M = Zn, M' = Ni)
2e (R = SO$_2$C$_8$H$_{17}$, M = M' = Ni)

Scheme 1

2-Ethoxyethanol
100 °C

1e

MCl$_2$
2-Ethoxyethanol/
o-dichlorobenzene
100 °C

5a (M = Ni)
5b (M = Zn)

Results and Discussion

Synthesis and Spectroscopic Characterization of the Dicyanotriazolehemiporphyrazinates 5a,b. Triazolehemiporphyrazine **1e** was prepared by reacting the three-unit compound **3**[15] and diiminoisoindoline **4**[19] in 2-ethoxyethanol at 100 °C (Scheme 1). As in the previous examples described by us,[15] cleavage of the precursor **3** does not take place in the reaction conditions, allowing to obtain a single regioisomer in good yield (ca. 60%). The ^{1}H NMR spectrum of compound **1e** recorded in CDCl$_3$ showed two broad signals at 15.6 and 15.2 ppm for the internal NH protons of the macrocycle and two singlets at 8.03 and 6.93 ppm for the two differently substituted isoindole units. When using more concentrated NMR samples, all the resonances experience an upfield shift as a consequence of intermolecular π−π interactions between the aromatic rings.[14b]

The nickel(II) and zinc(II) triazolehemiporphyrazinate complexes **5a,b** were obtained by heating the free-base

Figure 1. UV−vis absorption spectra in CHCl$_3$ of (a) metal-free triazolehemiporphyrazine **1e** (9.4×10^{-6} M, continuous line), (b) Ni(II) complex **5a** (1.2×10^{-5} M, dashed line), and (c) Zn(II) complex **5b** (1.2×10^{-5} M, dotted line).

1e in a mixture of 2-ethoxyethanol and *o*-dichlorobenzene at 100 °C in the presence of a slight excess of the corresponding metal(II) chloride. The use of acetate salts in the metalation reaction lowered the yields of the triazolehemiporphyrazinates **5a** and **5b**, probably as a consequence of the nucleophilic attack, catalyzed by traces of acid, of the anion on the imino groups and subsequent ring opening and partial decomposition of the macrocycle **1e**. The lack of stability of hemiporphyrazinic free bases in the presence of nucleophiles and acid media in comparison with their phthalocyanine counterparts is due to the nonaromatic nature of these macrocycles. These compounds are actually Schiff base analogues.

The introduction of a metal in the cavity of the macrocycle leads to interesting changes in the ^{1}H NMR spectra of the macrocycles. Thus, the two singlets assigned to the aromatic units of the nickel(II) complex **5a** are strongly upfield shifted (ca. 0.4 ppm) with respect to the free base **1e**, whereas in the case of the Zn(II) complex **5b** the same signals are slightly downfield shifted (ca. 0.1 ppm).

A dramatic metal-dependence effect has also been observed in the UV−vis spectra of the triazolehemiporphyrazinates recorded in CHCl$_3$ (Figure 1). In both Ni(II) and Zn(II) metal complexes, the absorption maxima undergo a strong batochromic shift, with the highest wavelength bands at ca. 407 nm in **1e** and at 451 and 429 nm in **5a** and **5b**, respectively. However, no concentration dependence (in the range $10^{-4}–10^{-6}$ M) of the absorption maxima wavelengths has been observed in the UV−vis spectra of these compounds.

Synthesis of the Phthalocyaninato−Triazolehemiporphyrazinate Complexes. The homo- and heterodimetallic phthalocyaninato−triazolehemiporphyrazinate complexes **2a** and **2b** were prepared by statistical condensation of nickel(II) dicyanohemiporphyrazinate **5a** and phthalonitrile **6**[19] in the presence of either nickel or zinc chloride as template (Scheme 2). A mixture of *N,N*-dimethylaminoethanol (DMAE) and *o*-dichlorobenzene was employed as solvent in order to solubilize the starting materials when heating at ca. 145 °C. The crude products were purified several times by column chromatography on silica gel and/or by gel-permeation chromatography, using a Bio-Beads SX-1 column, until pure samples of compounds **2a** and **2b** were obtained as dark

Scheme 2
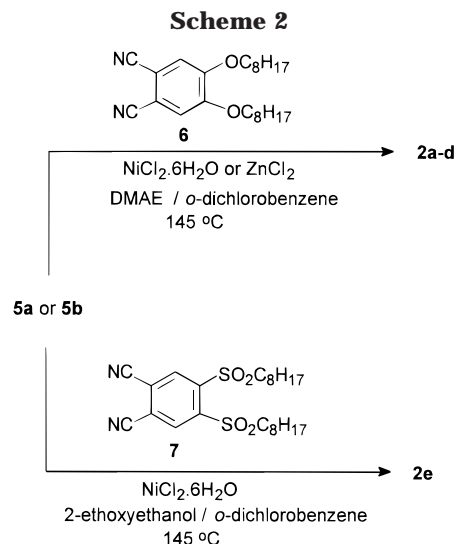
green powders in ca. 10% yield. The collected fractions gave single spots in TLC. Similarly, the binuclear systems **2c** and **2d** have been prepared employing the Zn(II) hemiporphyrazinate **5b** as starting material and purified by column chromatography on silica gel. In all the cases, the component of the first eluted fraction was identified as the corresponding octa(octyloxy)phthalocyanine complex, formed by self-condensation of phthalonitrile **6** in ca. 15−20% yield. However, self-condensation products of triazolehemiporphyrazine **5a** or **5b** were not detected in any of the cases.

A "push−pull" homodimetallic Pc-Thp system **2e** bearing acceptor (SO$_2$C$_8$H$_{17}$) substituents on the Pc subunit and donor (OC$_8$H$_{17}$) substituents on the Thp moiety has been also prepared using the methodology mentioned above. Thus, condensation reaction of Ni^{II}Thp **5a** and phthalonitrile **7**[20] in a mixture of 2-ethoxyethanol/*o*-dichlorobenzene was carried out in the presence of NiCl$_2$·6H$_2$O at 145 °C (Scheme 2). Purification of the crude product by column chromatography on silica gel afforded compound **2e** in low yield (10%), which was eluted before the symmetric nickel(II) octa(octylsulfonyl)phthalocyanine. In this case DMAE was not used to prevent lateral reactions on the SO$_2$C$_8$H$_{17}$ groups.

The characterization of the compounds **2a**−**e** by FAB mass spectrometry was unsuccessful. However, peaks for the corresponding molecular ions of **2a**−**e** were observed when the matrix-assisted laser desorption ionization−time-of-flight (MALDI-TOF) technique was used. A representative example of the spectra obtained for these binuclear derivatives is shown in Figure 2. The low-resolution of the instrument employed to obtain these mass spectra prevents the observation of the complex isotopic distributions expected for the molecular ions. Additionally, peaks corresponding to double the molecular mass were observed. The intensity of these varied both with the type of matrix used and the level of laser power employed. The best spectra were obtained from a dithranol matrix.

Elemental analyses were achieved for compounds **2c**, **2d**, and **2e**, in which several water molecules were included. The presence of water was confirmed by ^{1}H NMR spectroscopy.

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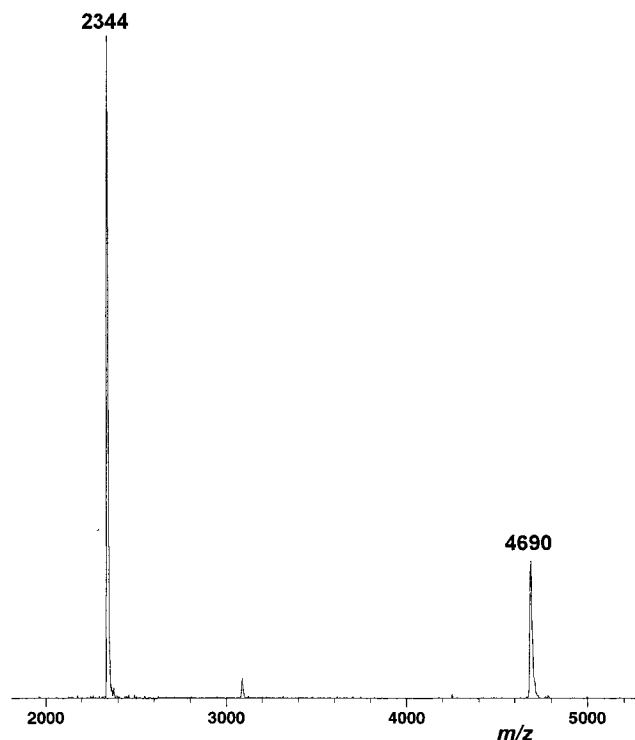
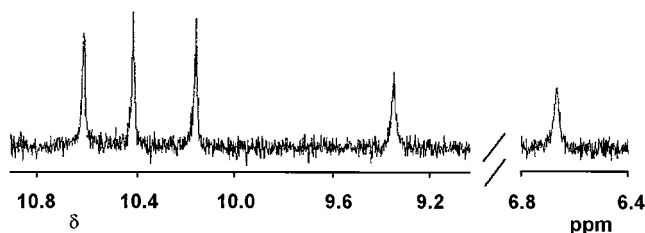**Figure 2.** MALDI-TOF spectrum of **2c** obtained from a dithranol matrix.

Figure 3. Partial ^{1}H NMR spectrum (2×10^{-3} M, CDCl$_3$, 300 MHz, room temperature) of compound **2e**.

^{1}H NMR spectra of compounds **2a**–**e** were recorded in both CDCl$_3$ and TFA-d_1. In most of the cases (**2a**–**d**) only broad signals were observed due to the intermolecular aggregation of the macrocycles in those concentrated samples. Particularly, aromatic signals are not even observed in the spectrum of **2a**, in consonance with the UV–vis spectrum of this compound (vide infra) in which very broad Q-bands are dominant in the visible region. ^{1}H NMR spectra of compound **2b** were additionally recorded in C$_2$D$_2$Cl$_4$ at different temperatures to obtain well-resolved signals. However, the spectra did not show any significant change over the temperature range from 25 to 120 °C. Surprisingly, the ^{1}H NMR spectrum of the bis(macrocycle) **2e** (Figure 3) showed well-resolved easily assignable signals in accordance with the proposed structure. Thus, five singlets at 10.59, 10.38, 10.11, 9.26, and 6.69 ppm corresponding to the aromatic protons were observed. The high resolution in the spectrum of **2e** is indicative of a low degree of molecular interactions in solution, which can be due to the polarity of the sulfonyl groups surrounding the Pc core.

Electronic Absorption Spectra. The UV–vis spectra in CHCl$_3$ of the heterobinuclear compounds **2a**–**e** (some of them are represented in Figure 4) show a broad and split Q-band from the Pc subunit at λ 600–800 nm
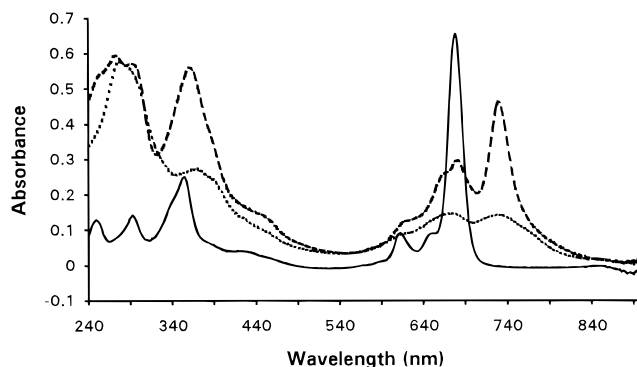

Figure 4. UV–vis absorption spectra in CHCl$_3$ of (a) octa-(octyloxy)PcZn (9.2×10^{-6} M, continuous line), (b) compound **2a** (1.5×10^{-5} M, dotted line), and (c) compound **2b** (8.6×10^{-6} M, dashed line).

with smaller absorption coefficient and at longer wavelength than the corresponding mononuclear Ni(II) or Zn(II) octa(octyloxy)phthalocyanines. In addition, strong absorptions around 250–450 nm corresponding to the Thp unit are observed in a similar spectral region to that present in the UV–vis spectra of the mononuclear Ni(II) or Zn(II) hemiporphyrazines **5a** or **5b** (Figure 1). This absorption also includes the Soret band belonging to the Pc moiety of **2a**–**e**. These spectra indicate that the particular Pc and the Thp electronic characteristics are basically kept in the hybrid Pc-Thp compounds, being the most remarkable electronic change the red-shifting (more than 50 nm with regard to the octa(octyloxy)Pc's) of the Q-band of the Pc subunit, as a consequence of the enlargement of the π-conjugated system.[8] The broadening and splitting of the Q-band observed in the UV–vis spectra of the Pc-Thp systems **2a**–**e** can be attributed, according to similar examples reported in the literature,[4] to intramolecular electron coupling between the two halves of the molecules. However, these compounds should be considered as unsymmetrically substituted phthalocyanines, for which Q-band splitting has been usually reported.[9,12,21] For this reason, symmetry factors could additionally contribute to the splitting observed in the UV–visible spectra of Pc-Thp derivatives. On the other hand, intermolecular interactions (aggregation) should also play an important role since these binuclear derivatives are π-extended Pc systems, which are expected to undergo aggregation easier than the mononuclear Pc derivatives.[4b]

The UV–vis spectra in CHCl$_3$ of the heterobinuclear compounds **2a** and **2d**, both having a nickel atom in the Pc subunit, are very similar. The Q-band is very broad, showing two absorption maxima at 732 and 672 nm in **2a** (Figure 4), and at 721 and 666 nm in **2d**. On the other hand, compounds **2b** and **2c**, which are both ZnPc derivatives, show fairly similar UV–vis spectra, exhibiting a narrower Q-band at 730 nm (Figure 4) with larger extinction coefficient than in the case of **2a** and **2d**. In the case of **2b** and **2c** additional less intense bands at ca. 660–680 nm are also present. According to these observations, the optical behavior of Pc-Thp compounds **2a**–**d** seems to be driven by the central metal included into the Pc moiety. Since **2a**–**d** are structurally similar compounds and, therefore, they should exhibit similar

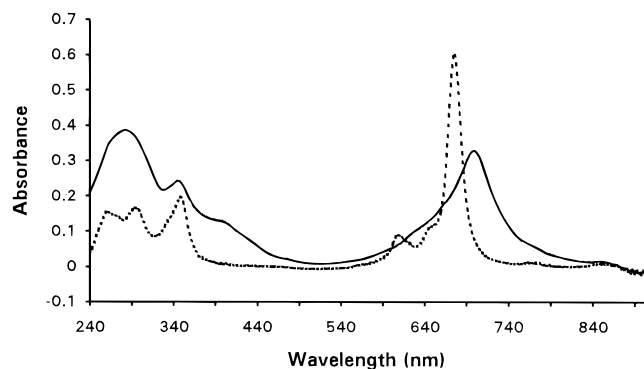(21) de la Torre, G.; Martínez-Díaz, M. V.; Torres, T.; *J. Porphyrins Phthalocyanines*, in press.

Figure 5. UV−vis absorption spectra in CHCl₃ of (a) octa-(octylsulfonyl)PcNi (8.4 × 10⁻⁶ M, dotted line) and (b) compound **2e** (5.1 × 10⁻⁶ M, continuous line).

electronic absorption spectra, a reasonable explanation for the remarkable broadening of the Q-band in the NiPc series could be a higher degree of aggregation in solution for **2a** and **2d** than for their ZnPc counterparts **2b** and **2c**.

To study the influence of aggregation on the optical behavior of these binuclear systems, UV−vis spectra of compounds **2a**−**d** were recorded at different concentrations. Surprisingly, the spectra of derivatives **2a**−**d** were essentially unchanged in the concentration range studied (ca. 10⁻⁴ to 8 × 10⁻⁷ M in CHCl₃). A tentative explanation to this observation could be that compounds **2a**−**d** form aggregates in all the range of concentrations studied, at a different extent depending on the nature of the metallic atoms included in the macroring cavities. The hypothesis of the occurrence of agregation phenomena in solution of compounds **2a**−**d** is in good agreement with the low resolution found in the ¹H NMR spectra of **2a**−**d** (vide supra) at higher concentrations.

In addition, solvent-dependence experiments have been carried out with a representative of this series, compound **2b**. The UV−vis spectrum of this derivative changes dramatically in other solvent systems, such as toluene, pyridine, THF, 1-chloronaphthalene, or mixtures of CHCl₃ and MeOH. A broadening of the maximum centered at 730 nm in CHCl₃ is observed in all the cases, being this effect more relevant when using 1-chloronaphthalene or toluene as solvents. These changes could point out a different degree of intermolecular interactions when varying the nature of the solvent.

On the other hand, the optical behavior of the donor−acceptor substituted Pc-Thp system **2e** is remarkably different (Figure 5). In this case, a single broad Q-band is dominant in the visible region and appears at longer wavelength (23 nm) in comparison with the symmetrically substituted nickel octa(octylsulfonyl)Pc. The intensity of this band is not concentration dependent in the range studied (ca. 10⁻⁴−10⁻⁶ M in CHCl₃). Moreover, the electronic absorption spectra of **2e** are also not solvent dependent, as it was pointed out by recording UV−vis spectra of **2e** in different solvents (toluene, pyridine, THF), since no significant changes in the intensity or wavelength of the bands were observed. In this case, intermolecular aggregation could be excluded, taking into account the well-resolved signals that the ¹H NMR spectrum in CHCl₃ exhibit at higher concentrations (vide supra).

In summary, the synthesis and electronic absorption properties of a series of homo- and heterodimetallic

heterobinuclear phthalocyaninato−triazolehemiporphyrazinate complexes have been described. This family of novel compounds may be of interest for the study of photoinduced electron transfer since a selective light-induced excitation either in the hemiporphyrazine or the phthalocyanine nuclei could be possible. In addition, the intrinsic unsymmetrical nature of these compounds, especially those having different central metal in each of the two macrorings and the ones bearing a donor−acceptor substitution pattern, makes them promising candidates for nonlinear optical applications.

Experimental Section

General. Phthalonitrile **6**[19] and **7**[20] were prepared according to previously described procedures. 2-Ethoxyethanol and *N,N*-dimethylaminoethanol were freshly distilled and collected in the presence of 4 Å molecular sieves before use. Merck Silica Gel 60 (particle size 0.040−0.063 mm) was used for chromatography. Bio-Beads S−X1 200−400 mesh (Bio-Rad Laboratories) were employed for gel permeation chromatography. Mass spectra were obtained from a Kratos Maldi 3 mass spectrometer utilizing a nitrogen laser operating at 337 nm. Samples were prepared for analysis by dissolving in chloroform (∼1 mg/mL) and mixing with an equal volume of matrix (dithranol, ∼10 mg/mL) before loading onto the sample target. After drying in air the samples were loaded into the instrument and spectra obtained by averaging 50 laser shots across the sample/matrix spot.

Dicyanotriazolehemiporphyrazine 1e. A mixture of **3** (0.8 g, 1.15 mmol) and the diiminoisoindoline **4** (0.51 g, 1.27 mmol) in 2-ethoxyethanol (27 mL) was heated at 100 °C for 24 h. The reaction mixture was cooled, and MeOH was added. A brown-reddish solid was precipitated and after centrifugation, the isolated solid was triturated with hot MeOH and filtered. Further purification was achieved by column chromatography on silica gel (MePh/MeOH 50:1). Yield 0.62 g (51%); mp >250 °C; ¹H NMR (200 MHz, CDCl₃) δ 15.6 (br s, 1H), 15.2 (br s, 1H), 8.03 (s, 2H), 6.93 (s, 2H), 4.0 (m, 8H), 1.9 (m, 8H), 1.5−1.1 (m, 56H), 0.9 ppm (m, 12H); ¹³C NMR (50 MHz, CDCl₃) δ 162.4, 155.7, 154.9, 153.3, 150.1, 137.9, 127.1, 127.0, 117.6, 114.5, 105.5, 69.7, 47.0, 31.9, 29.7, 29.6, 29.4, 29.3, 29.2, 29.0, 26.5, 26.0, 22.7, 14.1 ppm; IR (KBr) ν 3300 (NH), 2233 (C≡N), 1655 (C=N), 1281 (C−O−C) cm⁻¹; UV/vis (CHCl₃), λ_max (log ε/L mol⁻¹ cm⁻¹) 228 (4.73), 261 (4.79), 282 (4.74), 363 (4.75), 383 (4.76), 407 (4.60) nm; FAB-MS (3-NOBA), *m/z* 1063 (M + H)⁺. Anal. Calcd for C₆₂H₉₀N₁₄O₂·2H₂O (1099.52): C, 67.73; H, 8.62; N, 17.83. Found: C, 67.71; H, 8.19; N, 17.97.

General Procedure for the Preparation of the Triazolehemiporphyrazinate Metal Complexes 5a,b. A mixture of hemiporphyrazine **1e** (0.10 g, 0.09 mmol) and the corresponding metal as chloride salt (0.11 mmol) in a 1:1 mixture of 2-ethoxyethanol/*o*-dichlorobenzene (4 mL) in a 1:1:2 molar ratio was heated at 100 °C for 36 h. The reaction was allowed to cool and MeOH was added. The precipitate was filtered off and washed with hot MeOH.

Data for **5a**: yield 95%; green powder; mp >250 °C; ¹H NMR (200 MHz, CDCl₃) δ 7.49 (s, 2H), 6.48 (s, 2H), 3.9 (m, 8H), 1.9 (m, 8H), 1.6−1.2 (m, 56H), 0.9 ppm (m, 12H); ¹³C NMR (50 MHz, CDCl₃) δ 162.4, 157.6, 154.0, 152.6, 149.7, 139.3, 128.7, 125.4, 115.9, 114.5, 104.2, 69.5, 46.9, 31.9, 29.7, 29.6, 29.4, 29.3, 29.0, 28.4, 26.5, 26.0, 22.7, 14.1 ppm; IR (KBr) ν 2233 (C≡N), 1624, 1601 (C=N), 1284 (C−O−C) cm⁻¹; UV/vis (CHCl₃) λ_max (log ε) 252 (4.78), 271 (4.79), 291 (4.77), 365 (4.57), 423 (4.29), 451 (4.34) nm; FAB-MS (3-NOBA), *m/z* 1122, 1121, 1120, 1119 (M + H)⁺. Anal. Calcd for C₆₂H₈₈N₁₄NiO₂ (1120.16): C, 66.48; H, 7.92; N, 17.51. Found: C, 66.57; H, 8.08; N, 17.64.

Data for **5b**: yield 94%; brown powder; mp >250 °C; ¹H NMR (200 MHz, CDCl₃), δ 8.2 (br s, 2H), 7.14 (s, 2H), 4.1 (m, 8H), 1.9 (m, 8H), 1.5−1.2 (m, 56H), 0.9 ppm (m, 12H); ¹³C NMR (50 MHz, CDCl₃) δ 169.7, 164.7, 160.0, 155.5, 152.6, 141.7, 131.1, 126.9, 117.1, 114.4, 106.4, 69.5, 46.4, 31.9, 29.6, 29.5, 29.3, 29.2, 29.1, 26.4, 26.1, 26.0, 22.7, 14.1 ppm; IR (KBr) ν

2232 (C≡N), 1649, 1601 (C=N), 1282 (C−O−C) cm^{-1}; UV/vis (CHCl$_3$), λ_{max} (log ϵ) 242 (4.73), 263 (4.76), 285 (4.74), 367 sh, 380 (4.65), 402 (4.58), 429 (4.44) nm; FAB-MS (3-NOBA), m/z 1129, 1128, 1127, 1126, 1125 (M + H)$^+$. Anal. Calcd for C$_{62}$H$_{88}$N$_{14}$O$_2$Zn·H$_2$O (1144.87): C, 65.05; H, 7.92; N, 17.13. Found: C, 64.86; H, 7.66; N, 17.31.

Synthesis of the Phthalocyaninato−Triazolehemiporphyrazinate Complexes 2a−d. A mixture of the triazolehemiporphyrazinate **5a** or **5b**, phthalonitrile **6**, and the corresponding metal(II) chloride in a 1:3:1.5 molar ratio was heated at 145 °C under an inert atmosphere in a 1:1 mixture of DMAE and *o*-dichlorobenzene for 36 h. The reaction mixture was cooled, and MeOH was added. The precipitate was filtered off and washed with MeOH. The crude product was purified as described below.

Data for **2a**: The crude product was first purified by column chromatography on silica gel (CH$_2$Cl$_2$/2-propanol 100:1) to elute the symmetric Ni(II) octa(octyloxy)phthalocyanine. Afterward, dimer **2a** was eluted with a mixture of CH$_2$Cl$_2$/2-propanol (50:1). Further purification was achieved by column chromatography on silica (MePh/Me$_2$CO 50:1). Yield 8%; dark green powder; mp >250 °C; ^{1}H NMR (200 MHz, TFA-d_1), δ 1.7−0.8 ppm (br m); IR (KBr) ν 1590 (C=N), 1521, 1279−1262 (C−O−C) cm^{-1}; UV−vis (CHCl$_3$), λ_{max} (log ϵ): 277 (4.57), 370 (4.25), 617 sh, 672 (3.98), 732 (3.97) nm; MALDI-TOF (dithranol), m/z 2330 (M + H$^+$).

Data for **2b**: The crude product was purified by column chromatography on silica gel (CH$_2$Cl$_2$/2-propanol, 20:1). Further purification was achieved by gel-permeation chromatography on a Bio-Beads SX-1 column using THF as eluent. A subsequent column chromatography on silica gel (CH$_2$Cl$_2$/2-propanol, 20:1) yielded **2b** as a dark green solid. Yield 10%; mp >250 °C; ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.3−7.1 (br m), 6.7−6.3 (br m), 2.2−2.0 (br m), 1.6−1.2 (br m), 1.1−0.8 ppm (br m); (200 MHz, TFA-d_1) δ 7.62 (s), 7.49 (s), 4.3 (m), 2.0, 1.8−1.2, 0.9 ppm (3 × br m); IR (KBr) ν 1589 (C=N), 1521, 1279 (C−O−C), 1105−1045 cm^{-1}; UV−vis (CHCl$_3$), λ_{max} (log ϵ): 273 (4.84), 290 (4.82), 362 (4.82), 450 sh, 615 sh, 680 (4.54), 730 (4.73) nm; MALDI-TOF (dithranol), m/z 2336 (M + H$^+$).

Data for **2c**: The crude product was purified by column chromatography on silica gel (CH$_2$Cl$_2$/MeOH 100:1 and then the polarity was gradually increased until 25:1). Further purification by a subsequent column chromatography on silica gel (CHCl$_3$/2-propanol 20:1) was necessary to obtain a pure product. Yield 11%; dark green solid; mp >250 °C; ^{1}H NMR

(300 MHz, TFA-d_1) δ 8.9 (br s), 7.9−7.6 (br s), 5.0−4.3 (br m), 3.2 (m), 2.5−0.8 ppm (3 × br m); IR (KBr), ν 1600 (C=N), 1538, 1279 (C−O−C), 1105−1045 cm^{-1}; UV−vis (CHCl$_3$), λ_{max} (log ϵ): 265 (4.98), 282 sh, 362 (5.00), 660 sh, 685 (4.72), 730 (4.79) nm; MALDI-TOF (dithranol) m/z 2344 [M$^+$, 100], 4690 [2M$^+$, 30]. Anal. Calcd for C$_{134}$H$_{196}$N$_{20}$O$_8$Zn$_2$·8H$_2$O (2490.0): C, 64.64; H, 8.58; N, 11.25. Found: C, 63.94; H, 8.73; N, 11.20.

Data for **2d**: The crude product was purified by column chromatography on silica gel (first CH$_2$Cl$_2$ was used as eluent and then polarity was gradually increased by addition of 2-propanol until a 50:1 ratio was employed). Yield 9%; mp >250 °C; ^{1}H NMR (300 MHz, TFA-d_1) δ 4.4 (br m), 2.2−0.9 ppm (3 × br m); IR (KBr) ν 1588 (C=N), 1537, 1280 (C−O−C), 1111−1061 cm^{-1}; UV−vis (CHCl$_3$) λ_{max} (log ϵ): 278 (5.13), 285 (5.13), 367 (4.89), 670 sh, 666 (4.63), 721 (4.56) nm; MALDI-TOF (dithranol) m/z 2336 (M + H$^+$). Anal. Calcd for C$_{134}$H$_{196}$N$_{20}$O$_8$NiZn·8H$_2$O (2483.3): C, 64.81; H, 8.60; N, 11.28. Found: C, 64.56; H, 8.85; N, 11.28.

Synthesis of the Phthalocyaninato−Triazolehemiporphyrazinate Complex 2e. A mixture of the triazolehemiporphyrazinate **5a** (60 mg, 0.054 mmol), phthalonitrile **7** (77 mg, 0.16 mmol), and NiCl$_2$·6H$_2$O (15 mg, 0.065 mmol) in a 1:2 mixture of 2-ethoxyethanol and *o*-dichlorobenzene (3 mL) was heated at 145 °C for 36 h under an inert atmosphere. The reaction mixture was cooled, and MeOH was added. The precipitate was filtered off and washed with MeOH. The crude product was purified by column chromatography on silica gel (CHCl$_3$). The first eluted product was identified as the dimer **2e**. Trituration with MeOH afforded the pure product. Yield 10%; mp >250 °C; ^{1}H NMR (300 MHz, CDCl$_3$), δ 10.59, 10.38, 10.11, 9.26, 6.69 (5 × s, 10H), 4.3, 4.1, 3.9, 3.7, 3.15 (5 × m, 20H), 2.25, 1.95, 1.8, 1.6, 1.5−1.0 (5 × m, 136H), 0.85 ppm (m, 30H); IR (KBr) ν 1590 (C=N), 1145 (S=O), 1120−1020 cm^{-1}; UV−vis (CHCl$_3$), λ_{max} (log ϵ): 284 (4.99), 345 (4.82), 398 sh, 698 (4.96) nm; MALDI-TOF (dithranol) m/z 2617 (M + H$^+$). Anal. Calcd for C$_{134}$H$_{196}$N$_{20}$Ni$_2$O$_{14}$S$_6$·6H$_2$O (2729.0): C, 58.98; H, 7.68; N, 10.27; S, 7.05. Found: C, 58.31; H, 7.97; N, 10.40; S, 6.72.