Triazoleporphyrazines: A New Class of Intrinsically Unsymmetrical Azaporphyrins

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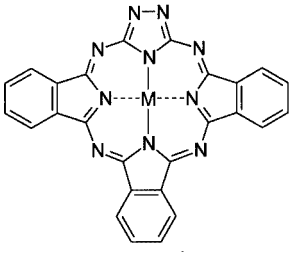
Triazoleporphyrazine **5** has been prepared by means of a "3+1" crossover condensation of the pyrroline derivative **6** with 3,5-diamino-1,2,4-triazole. Metallation of **5** under standard conditions afforded the metallotriazoleporphyrazines **7**. In contrast with the porphyrinic nature observed for its triazoleporphyrin counterpart **3**, the free base triazoleporphyrazine **5** possessed a cross-conjugated, hemiporphyrazine-like character. On the other hand, the metallated macrocycles **7** exhibited spectroscopic features that suggested a triazolephthalocyanine-porphyrazine hybrid structure for these compounds.

Introduction

Our research group has been involved for several years in the design of new core-modified azaporphyrins and phthalocyanines.[1−5] One of our main topics is the modification of the azaporphyrinic ring by replacement of one or more isoindole subunits of the phthalocyanine skeleton by other heterocycles such as 1,2,4-triazole and 1,3,4-thiadiazole. We have hence synthesized a variety of triazolehemiporphyrazines,[3] and have studied their optical and liquid crystalline properties.[3] Furthermore, we have prepared heterobinuclear and heterotrinuclear phthalocyanine-hemiporphyrazine hybrids with extended conjugation[6] and have reported the first examples of triazolehemiporphyrazine[7] and thiadiazolehemiporphyrazine,[8] expanded heteroannulenes with unusual coordination features, such as the ability to bind two or three metal ions, respectively, within their central cavities.

In addition, we have described the synthesis, characterization, and study of the properties of "*triazolephthalocyanines*" (**1**).[9] These intrinsically unsymmetrical compounds, reported for the first time by us in 1994,[10] are aromatic phthalocyanine analogues in which one isoindole moiety has formally been replaced by a 1,2,4-triazole subunit. The introduction of this heterocycle into the phthalocyanine framework gives rise to a lower degree of electronic delocalization, which results in a hypsochromic shift of its Q-band relative to the corresponding phthalocyanine absorption. Thus, while the UV/Vis spectrum of (tetra-*tert*-butylphthalocyaninato)nickel(II), for example, is dominated by an intense absorption centered at 670 nm, tri-*tert*-butyl-substituted (triazolephthalocyaninato)nickel(II) displays its Q-band at the shorter wavelength of 623 nm.



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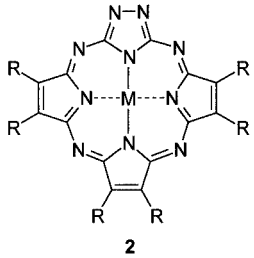

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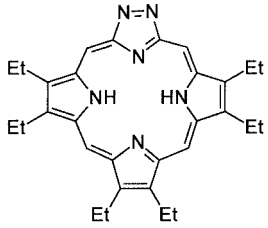

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The lack of any symmetry center in these derivatives makes them good targets for the development of materials with nonlinear optical applications.[11,12] Furthermore, macrocycles substituted with six lipophilic chains show liquid-crystal behavior, and their amphiphilic structure, characterized by a polar 1,2,4-triazole head and an aromatic macrocycle, is especially appropriate for Langmuir−Blodgett film formation.[9]

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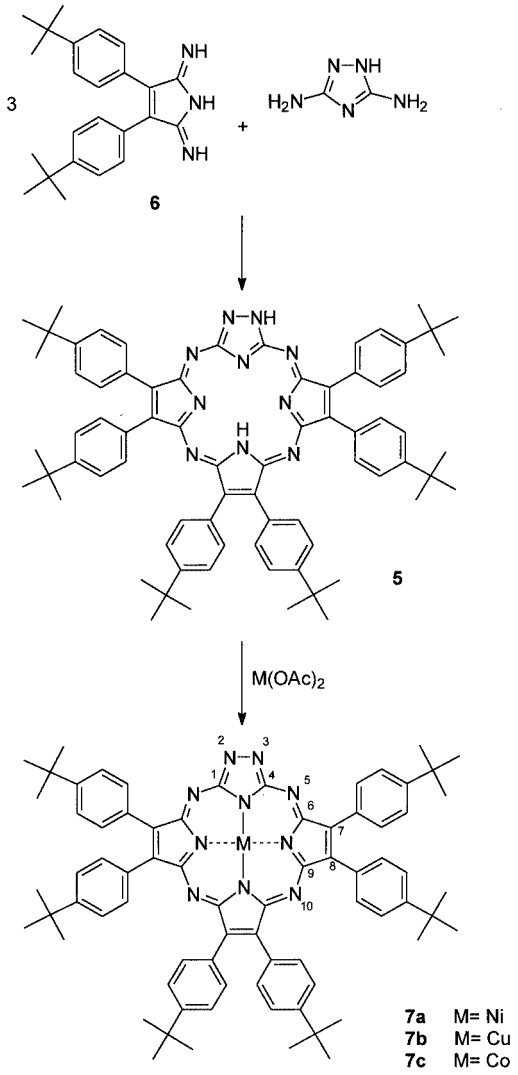
Despite all the characteristics described above, there are two main problems that reduce the potential of these metallomacrocycles. One of these, associated with their pseudophthalocyanine nature, is the limited solubility of many of these derivatives in organic solvents. This fact in itself constitutes a drawback to their practical usefulness, and together with their tendency to aggregate in solution, makes their purification and characterization more difficult. The second point concerns their synthetic availability. The synthesis of nickel- and copper-metallated triazolephthalocyanines can be carried out straightforwardly, either in one step, by crossover condensation of a diiminoisoindoline derivative with 3,5-diamino-1,2,4-triazole in the presence of a metal salt,[9] or stepwise, by template condensation of a three-unit intermediate and a diiminoisoindoline.[13] Conversely, the introduction of other inner metals remains a difficult task,[9] and only very recently have we succeeded in the preparation of some metal-free derivatives.[14] However, their purification is even more arduous than that of the metallated compounds, and in some cases impracticable due to their lability in silica gel.

As a possible approach to solving some of these problems, we wondered whether the corresponding triazoleporphyrazines **2** could be synthesized from substituted maleonitriles, by similar procedures. The development of such a methodology might provide a route to more soluble products with less tendency to aggregate in solution, and therefore easier to purify and characterize. In addition, the different chemical properties and stabilities of porphyrazines and phthalocyanines drove us to anticipate some differences for the new series − such as, for example, stronger coupling between the peripheral substituents and the macrocyclic core − that might be advantageous for some kinds of applications. Thus, as an extension of our work in this field, we report previous studies on the preparation and characterization of novel core-modified porphyrazines that we have named triazoleporphyrazines.

Results and Discussion

2,3-Bis(*tert*-butylphenyl)fumaronitrile **4**[15] was chosen as a precursor, since this kind of substitution should produce soluble compounds and be inert enough under the reaction conditions.

The preparation of porphyrazines is usually carried out by Linstead macrocyclization[16] of suitably functionalized maleonitrile derivatives. This method, which involves the magnesium-template tetramerization of a dinitrile or its pyrroline derivative, followed by demetallation by treatment with acids to afford the free-base porphyrazine and further metallation with a suitable metal salt, is not necessary for the synthesis of the triazole-derived analogues. Triazoleporphyrazine **5** was prepared by direct condensation of the pyrrolinediimine **6**[17] and 3,5-diamino-1,2,4-triazole (guanazole), in stoichiometric ratio, in anhydrous *n*-butyl alcohol at reflux temperature (Scheme 1). Column chromatography on silica gel, with a 4:1 mixture of hexane and dioxane as eluent, afforded macrocycle **5** in 42% yield.



Scheme 1

Comparison of the conditions described above with those required for the preparation of the metal-free triazolephthalocyanine counterparts, reveals triazoleporphyrazine **5** to be more stable than the latter. Thus, metal-free triazolephthalocyanines cannot be obtained in alcoholic solvents such as butanol or 2-ethoxyethanol, due to their tendency to be cleaved by nucleophilic attack on their iminic double bonds;[9,18] the use of other polar solvents such as butyronitrile is therefore necessary.[14] Furthermore, triazoleporphyrazine **5** can be synthesized directly from a pyrrolinediimine precursor in the absence of any metal-template or base, an unusual fact that contrasts with the standard synthetic procedure to obtain porphyrazines.[19]

The metal complexes **7a**−**c** were each prepared by treatment of the free base **5** with the appropriate metal acetate in DMF at 100 °C. Under these conditions, yields of 78−90% (33−38% overall yield with respect to guanazole) were achieved.

Metallotriazoleporphyrazines may alternatively be synthesized by the reported procedure for nickel(II) triazolephthalocyaninatos,[10] which consists of the crossover macrocyclization of the pyrrolinediimine **6** and guanazole in 2-ethoxyethanol at 135 °C, in the presence of a metal template. This method, however, was less efficient than the stepwise procedure. Thus, for example, **7a** with a nickel(II) ion within its central binding core was obtained in 14% yield after purification of the crude material by chromatography on silica gel with a 4:1 mixture of hexane and dioxane as eluent. Macrocycles **5** and **7a**−**c** were characterized by NMR, UV, MS, and IR.

The free base triazoleporphyrazine **5** possesses an 18π-electron, cross-conjugated, nonaromatic structure, similar to that of the phthalocyanine-derived series,[14] as evidenced by its spectroscopic features discussed below. The electronic alteration of macrocycle **5** with respect to its analogous triazoleporphyrin **3**[20] does not correlate with the changes produced by the formal replacement of the four *meso*-carbon bridges in the porphyrin ring by four *meso*-nitrogens, on going from porphyrins to porphyrazines. Tetraazaporphyrins (porphyrazines) may be regarded as porphyrin-phthalocyanine hybrids, although they are more similar to the latter, and they exhibit electronic properties that differ substantially from those displayed by porphyrins. Hence, whereas the UV/Vis spectra of the porphyrins are dominated by a band in the blue region at ca. 400−450 nm (Soret band), the electronic spectra of tetraazaporphyrins are characterized by a blue-shifted, less intense Soret band, accompanied by other equally intense absorptions, in the red region namely a Q-band, in the 550−700 nm range.[19]

The substitution of a pyrrole ring in the porphyrin framework by the 1,2,4-triazole moiety does not produce any substantial change in the porphyrin nature apart from the consequent loss of symmetry, from D_{4h} to C_{2v}. As a result, the aromatic 2,3-diazaporphyrin **3** exhibits a strong, split Soret band centered at 406 nm,[20] whereas the corresponding B-band of 2,3,7,8,12,13,17,18-octaethylporphyrin appears at 398 nm.[21] Consequently, on going from porphyrazines to triazoleporphyrazines we should expect typical broadened or split porphyrazinic bands in the UV/Vis, as a consequence of the symmetry reduction. In contrast, the different electronic properties of the triazoleporphyrazine **5** with respect to the similarly substituted octakis(*tert*-butylphenyl)porphyrazine were diagnostic of its altered character.

The UV/Vis spectrum of compound **5** (Figure 1), which did not fit the characteristic porphyrazine pattern, was made up of four sharp absorptions at 323, 417, 486, and 530 nm. This means that the lowest-energy band displayed by **5** was blue-shifted by 136 nm in comparison with the equivalent absorption of its counterpart porphyrazine.[15]

^{1}H NMR spectroscopy of compound **5** demonstrated that this phenomenon should not just be attributed to a lower degree of electronic delocalization in triazoleporphyrazines than in porphyrazines. Thus, the chemical shift of δ = 7.23 ppm observed for the phenyl protons of the free base **5**, high-field shifted by 0.5 and 0.3 ppm with respect

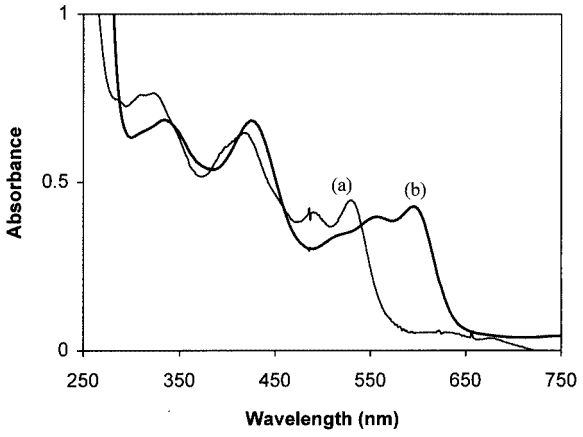


Figure 1. UV/Vis spectra of (a) **5** ($c = 2.10 \times 10^{-5}$) and (b) **5** + DBU ($c = 1.80 \times 10^{-5}$) in chloroform

to the same protons in the pyrrolinediimine precursor **6**, suggested the absence of aromaticity in macrocycle **5**. We were unable to detect any signal that might be attributable to the triazolic proton.[22] Still, the nonaromatic nature of the free base derivative **5** was clearly manifested by a broad signal at δ = 15.2 ppm corresponding to the pyrrole NH, the low-field shift of which denoted not only the presence of intramolecular hydrogen bonds, but also, and more importantly, the lack of a diamagnetic ring current in this compound.[23]

On the other hand, metallotriazoleporphyrazines are far from being just the porphyrazinic version of metallated triazolephthalocyanines, but may be viewed rather as porphyrazine/triazolephthalocyanine hybrids. Hence, whereas their UV/Vis profiles resembled those of their triazolephthalocyanine counterparts, macrocycles **7a**−**c** exhibited B and Q-bands in the same wavelength ranges as metal(II) octakis(*tert*-butylphenyl)porphyrazinato,[15] with lowest-energy absorptions of 602−630 nm denoting their aromatic, porphyrazinic nature (Figure 2). The different character of free base and metallated triazoleporphyrazines was also evidenced by their NMR spectra. In its ^{1}H NMR, compound **7a** showed four well resolved doublets centered at δ = 8.08, 8.02, 7.61 and 7.52 ppm, attributable to the benzene rings that are deshielded by 0.1−0.3 ppm with respect to the two doublets displayed by the pyrroline derivative,[17] as a consequence of the porphyrazinic diatropicity.

The divergent results obtained by substitution of a pyrrole in a porphyrin and a porphyrazine, or an isoindole in a phthalocyanine, by a 1,2,4-triazole ring, must emanate from the different features of the *meso*-carbon and nitrogen bridges. The stabilization of the 1*H*- or 2*H*-tautomers relative to the 4*H*-tautomer in 1,2,4-triazoles is well established,[24] and has been associated with the formation of cyclic dimer-type hydrogen bonds involving the N-1 and N-2 atoms of the rings, with an exchange of the protons between two molecules.[25] Taking into account that these hydrogen bonds are strongly influenced by the nature of the substituents at the 3- and the 5-positions,[25] we can expect

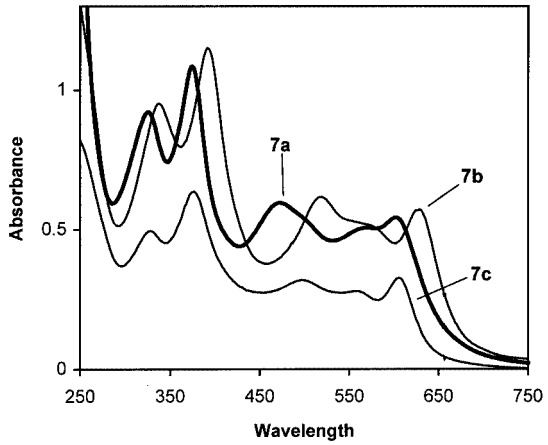


Figure 2. UV/Vis spectra of **7a** ($c = 1.71 \times 10^{-5}$), **7b** ($c = 2.05 \times 10^{-5}$), and **7c** ($c = 7.65 \times 10^{-6}$) in chloroform

different proclivities to tautomerize towards the 4*H*-isomer for triazoleporphyrins and triazoleazaporphyrins. Thus, the achievement of an energetically more favored macroaromatic structure could be the driving force for an unusual triazolic prototropic shift to the 4*H*-tautomer in the case of triazoleporphyrins. However, the stronger tendency towards hydrogen binding of their *meso*-nitrogen-bridged counterparts (namely the triazoleporphyrazines), and consequently their lesser ability to tautomerize, would prevent the fulfillment of the corresponding 18π-electron, aromatic tautomer. The introduction of a metal(II) into the heteroannulene central cavity with concomitant deprotonation of the macrocycle shifts the equilibrium towards a "4*H*-triazole arrangement", with a subsequent dramatic change in the character of the macrocycle. The last hypothesis was supported by the electronic changes observed on deprotonation of **5** with DBU. In this case the anion of triazoleporphyrazine **5** displayed a UV/Vis spectrum resembling those exhibited by the metal complexes **7a**–**c** (see Figures 1 and 2 above), with a lowest-energy absorption at 592 nm, similar to that of the (triazoleporphyrazinato)nickel(II) complex **7a**.

Conclusions

New core-modified porphyrazine analogues, arising from the formal replacement of a pyrrole ring in the porphyrazinic skeleton by a 1,2,4-triazole moiety, have been synthesized. This new family shares some of the peculiarities of its phthalocyanine-related macrocycles, such as the nonaromatic nature of its free-base form and the aromaticity of the metallated derivatives. However, metallotriazoleporphyrazines may be considered as triazolephthalocyanine/porphyrazine hybrids, exhibiting absorptions in UV/Vis in the same energy ranges as their similarly substituted porphyrazines, this fact suggesting a similar degree of electronic delocalization in the two systems. The simplicity of the characterization of these compounds by standard spectroscopic techniques is the result of their lower degree of aggregation in solution, as would be expected from their porphyrazinic nature. On the other hand, the synthetic availability of different metallo complexes by straightforward metallation of the stable metal-free derivative has been proven, and opens a wide range of possibilities for these intrinsically unsymmetrical compounds. The synthesis of other metallotriazoleporphyrazines bearing substituents of different character, such as donor or acceptor, and their application for second harmonic generation are under investigation.

Experimental Section

General Remarks: UV/Vis spectra were recorded with a Hewlett–Packard 8453 instrument. IR spectra were recorded on a Bruker Vector 22 spectrophotometer. FAB-MS and HRMS spectra were determined on a VG AutoSpec instrument. MALDI-TOF MS was performed with a Bruker Reflex III spectrometer. NMR spectra were recorded with BRUKER WM 200 SY, BRUKER AC 300, and BRUKER DRX 500 instruments. Elemental analyses were performed with a Perkin–Elmer 2400 apparatus. Column chromatography was carried out on Merck 60 silica gel (230–400 mesh, 60 Å), and TLC on aluminum sheets precoated with 60 F_{254} silica gel (E. Merck). Chemicals were purchased from Aldrich Chemical Co. and used as received without further purification.

Triazoleporphyrazine (5): A mixture of the pyrroline derivative **6** (320 mg, 0.90 mmol) and 3,5-diamino-1,2,4-triazole (30 mg, 0.30 mmol) in anhydrous *n*-butyl alcohol (30 mL) was heated under reflux for 30 hours. The dark brown mixture was allowed to cool to room temperature and, after addition of MeOH (50 mL), the resulting precipitate was filtered, triturated with MeOH (2 × 50 mL), and dried. Column chromatography on silica gel, with a 4:1 mixture of hexane and dioxane, and further trituration with hexanes afforded **5** as a dark red solid. Yield 140 mg (42%). ^{1}H NMR ($C_2D_2Cl_4$, 300 MHz): δ = 15.24 (broad s, 1 H, NH), 7.26–7.21 (broad s, 24 H, arom), 1.24, 1.17, 1.16 (3 × s, 54 H, *t*Bu) ppm. IR (KBr): $\tilde{\nu}$ = 3460, 3380 (N–H), 3299 (N–H, pyrrole), 2962, 2904, 2868 (C–H), 1608, 1586 (C=N), 1494, 1475, 1461, 1392, 1363, 1269, 1109, 1088, 1021, 971, 835 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 242 (4.81), 323 (4.55), 417 (4.48), 486 (4.29), 530 nm (4.32). MS (LSIMS, *m*-NBA): *m*/*z* = 1109 [M^+], 1110 [M + H]$^+$, 1111 [M + 2 H$^+$], 1112 [M + 3 H$^+$], 1113 [M + 4 H$^+$], 2218 [2 M$^+$], 2219 [2 M + H$^+$], 2220 [2 M + 2 H$^+$], 2221 [2 M + 3 H$^+$], 2222 [2 M + 4 H$^+$]. $C_{74}H_{80}N_{10}$: calcd. C 80.1, H 7.3, N 12.6; found C 80.3, H 7.5, N 12.6.

(Triazoleporphyrazinato)nickel(II) (7a): A mixture of **5** (44 mg, 0.04 mmol) and $Ni(OAc)_2 \cdot 4H_2O$ (32 mg, 0.12 mmol) in DMF (15 mL) was stirred at 100 °C for 6 h. The reaction mixture was allowed to cool to room temperature and was then poured into water (100 mL). The resulting precipitate was filtered, and washed thoroughly with 1% ammonia solution, then with water, and finally with MeOH to give 44 mg, (90%) of a dark red solid. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 8.08, 8.02 (2 × d, *J* = 7.5 Hz, 12 H, arom), 7.61 (d, *J* = 7.5 Hz, 4 H, arom), 7.52 (d, *J* = 7.5 Hz, 8 H, arom), 1.48 (broad s, 54 H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 159.0 (C^1, C^4), 152.6, 151.8 (C^6, C^9, C^{11}, C^{14}, C^{16}, C^{19}), 147.0–145.0 ($C^{4'}$), 143.0–142.0 ($C^{1'}$), 133.0–132.0 ($C^{3'}$), 129.5–128.5 (C^7, C^8, C^{12}, C^{13}, C^{17}, C^{18}), 126.5–125.0 ($C^{2'}$), 35.2 (CCH_3), 31.9 (CCH_3) ppm. IR (KBr): $\tilde{\nu}$ = 2960, 2903, 2867 (C–H), 1609, 1501, 1462, 1445, 1362, 1342, 1269, 1137, 1109, 999,

956, 852, 838, 776, 767, 562 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 250 (5.03), 325 (4.73), 374 (4.80), 472 (4.54), 579 (4.47), 602 nm (4.50). MS (LSIMS, *m*-NBA): *m*/*z* = 1165−1168 [M^+], [M + H]$^+$. $C_{74}H_{78}N_{10}Ni$: calcd. C 76.2, H 6.7, N 12.0; found C 76.4, H 6.3, N 12.1.

(Triazoleporphyrazinato)copper(II) (7b): A mixture of **5** (44 mg, 0.04 mmol) and anhydrous $Cu(OAc)_2$ (18 mg, 0.10 mmol) in DMF (15 mL) was stirred at 100 °C for 6 h. After cooling to room temperature, the reaction mixture was poured into water (100 mL) and the resulting suspension was centrifuged. The precipitate was washed with 1% ammonia solution, then with water, and finally with MeOH. Column chromatography on silica gel with a 4:1 mixture of hexane and dioxane afforded, after washing with hexanes, 37 mg (78%) of **7b** as a dark red solid. IR (KBr): $\tilde{\nu}$ = 2966, 2956, 2904, (C−H), 1609, 1461, 1364, 1330, 1269, 1109, 929, 846, 838, 564 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 245 (4.83), 339 (4.66), 395 (4.74), 520 (4.48), 578 (4.40), 630 nm (4.44). MS (LSIMS, *m*-NBA): *m*/*z* = 1170−1173 [M^+], [M + H]$^+$. $C_{74}H_{78}N_{10}Cu$: calcd. C 75.9, H 6.7, N 12.0; found C 76.3, H 6.4, N 12.2.

(Triazoleporphyrazinato)cobalt(II) (7c): A mixture of **5** (44 mg, 0.04 mmol) and $Co(OAc)_2{\cdot}4H_2O$ (25 mg, 0.10 mmol) was heated at 100 °C in DMF (15 mL) for 6 h. The reaction mixture was allowed to cool to room temperature and poured into water (100 mL). The resulting suspension was centrifuged, and the precipitate was washed with 1% ammonia solution, water, and MeOH to give 39 g (82%) of a dark red solid. IR (KBr): $\tilde{\nu}$ = 2965, 2924, 2853, (C−H), 1634, 1461, 1364, 1262, 1109, 1017, 997, 855, 838, 805 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 247 (5.04), 331 (4.81), 378 (4.91), 500 (4.62), 564 (4.56), 609 nm (4.61). MS (LSIMS, *m*-NBA): *m*/*z* = 1166 [M^+], 1167 [M + H]$^+$, 1168 [M + 2 H]$^+$.$C_{74}H_{78}N_{10}Cu$: calcd. C 76.2, H 6.7, N 12.0; found C 76.4, H 6.6, N 11.7.

Acknowledgments

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