

Synthesis and Characterization of Phthalocyanines Containing Four 11-Membered Triaza Macrocycles

Zehra Altuntaş Bayır, Esin Hamuryudan and Özer Bekaroğlu*

Technical University of Istanbul, Department of Chemistry, 80626, Maslak, Istanbul, Turkey

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New metallophthalocyanines (M = Cu, Zn, Ni or Co) substituted in peripheral positions with four 11-membered triaza macrocycles are prepared from 1,4,7-tris(*p*-tolylsulfonyl)-1,4,7-triazaheptane and 1,2-dibromo-4,5-bis(bromomethyl)benzene or the corresponding anhydrous metal salt [CuCN, Zn(O₂CMe)₂, NiCl₂ or CoCl₂].

In recent years, phthalocyanines have been studied extensively with respect to their potential importance for technological applications.¹ These materials are of specific interest for their special properties such as photoconductivity, electrochromism, catalytic and photovoltaic effects.^{2–5} The attractive and challenging characteristics

of phthalocyanines are their great variety, chemical stability, the relative ease with which they can be prepared and isolated, and the strong dependence of their properties upon substitution patterns. Incorporation of macrocyclic groups such as crown ethers, tetraaza or diazadioxo macrocycles onto the periphery of phthalocyanines has enhanced the solubility of these compounds and provided additional binding sites for different kinds of ions.^{9–12}

Here, we describe the synthesis of novel soluble metallophthalocyanines (M = Cu^{II} **3**, Zn^{II} **4**, Ni^{II} **5** and Co^{II} **6**) containing four 11-membered triaza macrocycles on the periphery.

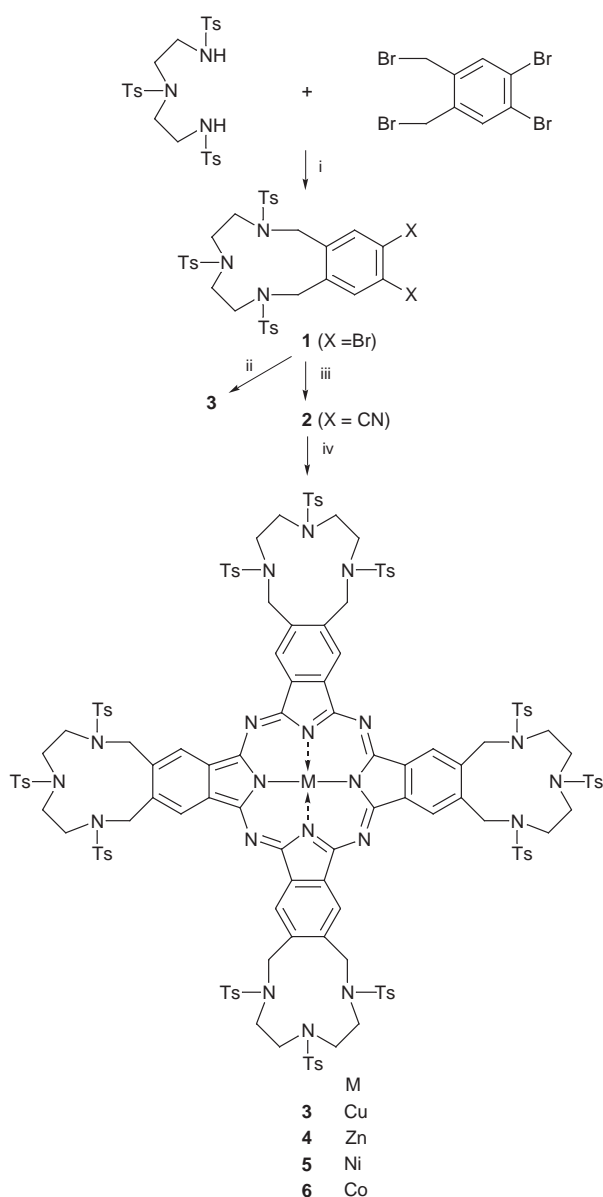
The first step in the synthetic procedure outlined in the Scheme is the formation of the 11,12-dibromo-2,5,8-tris(*p*-tolylsulfonyl)-2,3,4,5,6,7,8,9-octahydro-1*H*-2,5,8-benzotriazacycloundecine **1**. Triazamacrocycle **1** was obtained by the reaction of 1,2-dibromo-4,5-bis(bromomethyl)benzene with 1,4,7-tris(*p*-tolylsulfonyl)-1,4,7-triazaheptane in DMF in the presence of anhydrous potassium carbonate as the base.^{17,18}

The usual synthetic routes were applied to obtain the metallophthalocyanines. Dibromo derivative **1** was directly converted into the copper(II) phthalocyanine **3** by the reaction with CuCN in tetramethylurea (TMU). The dicyano derivative **2** was isolated under mild conditions according to the Rosenmund von Braun reaction. As a high-boiling aprotic solvent, quinoline was the solvent of choice for the preparation of phthalocyaninato-zinc(II) **4** and -nickel(II) **5**, whereas cyclotetramerization of **2** to the cobalt(II) derivative **6** was carried out in ethylene glycol. All phthalocyanines **3–6** were isolated by column chromatography on silica gel.

Spectral investigations of the newly synthesized compounds and phthalocyanines are consistent with the proposed structures. The obvious difference among the IR spectra of dibromo **1** and dicyano **2** derivatives is clear from the presence of C≡N vibration in **2** at 2220 cm⁻¹. The characteristic vibrations of tosyl groups in **1–2** appear at 1340–1160 and 1340–1170 cm⁻¹, respectively. ¹H NMR spectra of these compounds are closely similar to each other. In addition to aromatic protons in triaza macrocycles **1** and **2**, ArCH₂N and NCH₂ protons are observed at δ *ca.* 4.30, 3.47–3.41, respectively.

Cyclotetramerization of the dinitriles was confirmed by the disappearance of the sharp C≡N vibration at 2220 cm⁻¹ for compound **2**. ¹H NMR spectra of **4** and **5** are expected to show chemical shifts only slightly different from each other. The protons of ArCH₂N and NCH₂ appear at δ 5.05 and 3.51–3.28 for **4** and at δ 5.02 and 3.57–3.32 for **5**. Also it should be mentioned that all the peaks of both spectra are very broad, in contrast to the dibromo and dicyano derivatives.

The electronic spectra of **3–6** show the characteristic features of phthalocyanines with strong absorptions in the red (Q band) and near-UV (B band) regions. While the



Scheme Reagents: i, K₂CO₃, DMF; ii, CuCN, TMU; iii, CuCN, DMF; iv, metal salt, quinoline or ethylene glycol

*To receive any correspondence.

N-tosylated compounds **3–6** are soluble in halogenated hydrocarbons, their spectra in CHCl₃ show an intense Q band at the lowest energy side (670–690 nm) and a shoulder around 645 nm indicates aggregation.

Techniques used: ¹H NMR, IR, UV-VIS, mass spectrometry

References: 20

Scheme: 1

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