

Synthesis and Characterization of Novel Phthalocyanines Substituted with Four Tetraaza Macrocycles

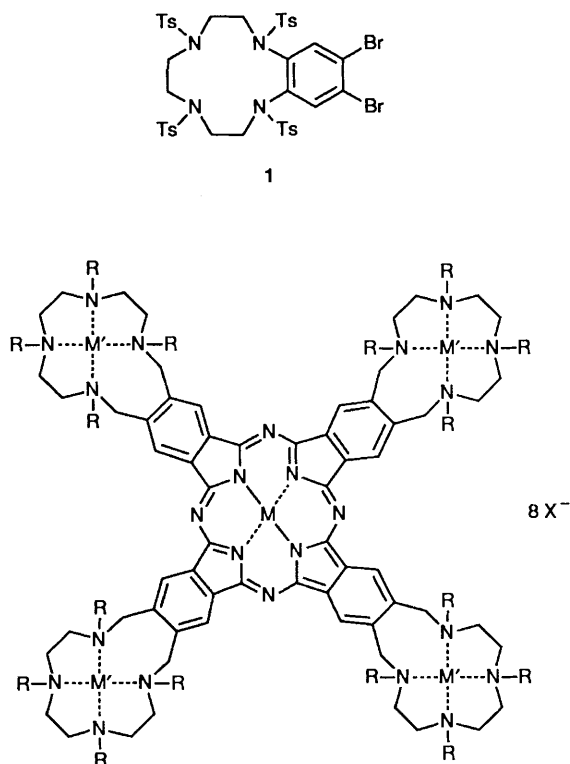
Makbule Koçak, Ali Cihan, Ali İ.Okur and Özer Bekaroğlu*

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

A novel copper phthalocyanine substituted with four 14-membered tetraaza macrocycles and its pentanuclear nickel(II) complex were synthesized and characterized by elemental analysis, and IR and UV spectroscopy.

Substitution of planar rigid phthalocyanine cores with flexible chains is known to lead to highly ordered systems.¹ In the case of crown ethers as substituents, the molecules possess the capability of forming ion channels allowing the migration of alkali and alkaline earth cations.²⁻⁴ Also, polyaza macrocycles have received considerable attention recently because of the transition metal-binding properties of the polyaza cavity.⁵

These studies suggest that a suitable combination of polyaza macrocycle and phthalocyanine may allow new functionalized materials to be prepared which are of importance for both biochemistry and materials science. In this context, water-soluble pentanuclear phthalocyanines are relevant as sensitizers in photodynamic cancer therapy⁶ or the symmetry properties can be considered in connection with optical



Ts = *p*-MeC₆H₄SO₃

	M	M'	R	X
2	Cu	—	Ts	—
3	Cu	—	H	—
4	Cu	Ni	H	Cl

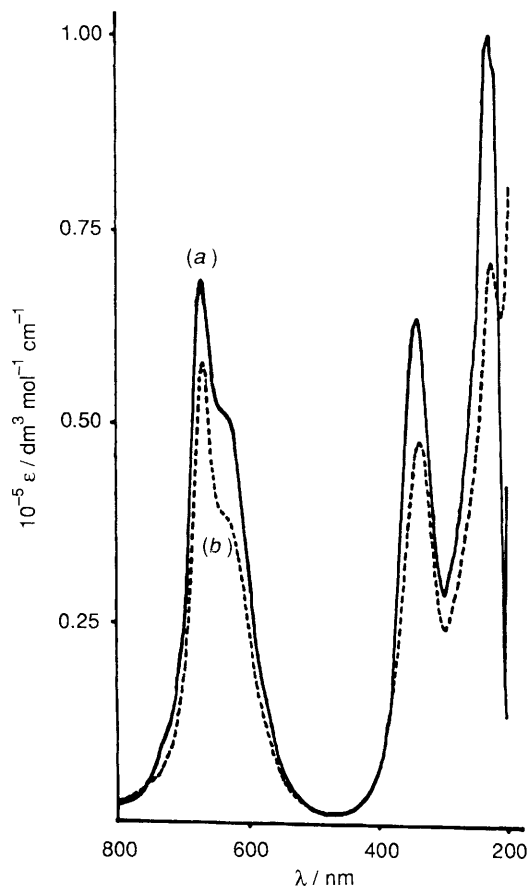


Fig. 1 UV-VIS spectra of (a) **3**, and (b) **4** in EtOH-H₂O (8:1)

properties.⁷ This communication describes for the first time the synthesis of compounds **2–4** linking phthalocyanines with tetraaza macrocycles.

Compound **1** was prepared from 1,2-bis(bromomethyl)-4,5-dibromobenzene with *N,N',N'',N'''*-tetrakis(*p*-tolylsulphonyl)-triethylenetetramine in dimethylformamide (DMF) containing K₂CO₃ as the base.^{8,9} Cyclotetramerization of **1** in tetramethylurea in the presence of CuCN gave **2** which was purified by column chromatography [silica gel, chloroform-methanol, 20:1 (v/v)], yield 31%, for which C, H and N elemental analyses were satisfactory; λ_{\max}/nm (log ϵ) (CHCl₃): 682 (6.08), 650 (5.34), 640 (5.35) and 345 (5.70).

The tosyl groups in **2** were hydrolysed by heating in conc. sulphuric acid for 3 h at 100 °C.^{10,11} After neutralization with 1 mol dm⁻³ aqueous NaOH, complex **3**[†] was obtained as a dark blue product soluble in ethanol. Treatment of **3** with the stoichiometric amount of NiCl₂ in absolute ethanol lead to the precipitation of **4**.[†] The solubility of **4** in water and precipitation of AgCl on treatment with aqueous AgNO₃ indicate the ionic character of the product; consequently, the nickel moieties are square planar rather than octahedral.

The visible absorption spectra of the phthalocyanines **3** and **4** in ethanol–water 8:1, (v/v) are similar (Fig. 1). Since

nickel(II) complexes of tetraaza macrocycle do not have as intense absorptions as the B and Q bands of phthalocyanines, this result is in accord with expectations.¹² We can also conclude that in solution nickel(II) ions are coordinated with each macrocycle separately so no aggregation occurs as a result of interaction of the metal ions with two macrocyclic groups.

This work was supported by DPT of Turkey (Project No. 89 K 120600).

Received, 5th December 1990; Com. 0105483F

References

- 1 C. Piechocki and J. Simon, *Nouv. J. Chim.*, 1985, **9**, 159.
- 2 A. R. Koray, V. Ahsen and Ö. Bekaroglu, *J. Chem. Soc., Chem. Commun.*, 1986, 932.
- 3 V. Ahsen, E. Yilmazer, M. Ertas and Ö. Bekaroglu, *J. Chem. Soc., Dalton Trans.*, 1988, 401.
- 4 C. Sirlin, L. Bosio, J. Simon, V. Ahsen, E. Yilmazer and Ö. Bekaroglu, *Chem. Phys. Lett.*, 1987, **139**, 362.
- 5 E. Kimura, A. Sakonaka, T. Yatsunami and M. Kodama, *J. Am. Chem. Soc.*, 1981, **103**, 3041.
- 6 C. C. Leznoff, S. Vigh, P. I. Svirskaya, S. Greenberg, D. M. Drew, E. Ben-Hur and I. Rosenthal, *Photochem. Photobiol.*, 1989, **49**, 279.
- 7 J. Simon, P. Bassoul and S. Norvez, *New J. Chem.*, 1989, **13**, 13.
- 8 H. Koyama and T. Yoshino, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 481.
- 9 F. Chavez and A. D. Sherry, *J. Org. Chem.*, 1989, **54**, 2990.
- 10 E. Buhleier, W. Raschofer, W. Wehner, F. Luppertz and F. Vögtle, *Liebigs Ann. Chem.*, 1977, 1340.
- 11 W. Raschofer and F. Vögtle, *Liebigs Ann. Chem.*, 1977, 1340.
- 12 R. Smierciak, J. Passariello and E. L. Blinn, *Inorg. Chem.*, 1977, **16**, 2646.

[†] Complexes **3** and **4** were characterized by elemental analysis and IR and UV spectroscopy. Selected spectroscopic data: complex **3**, IR (KBr disc): ν/cm^{-1} 3280, 2920, 2840, 1615, 1450, 1155, 1100, 1020 and 745; and λ_{\max}/nm (log ϵ) (EtOH): 674 (4.75), 634 (4.49) and 342 (4.59). Complex **4**: ν/cm^{-1} (KBr disc): 3230, 2940, 2860, 1615, 1440, 1310, 1150, 1100, 1010 and 750; λ_{\max}/nm (log ϵ) (water): 670 (4.60), 644 (4.62) and 338 (4.61); Found: C, 43.75; H, 5.1; N, 18.5; Cu, 3.5; Ni, 13.0; Cl, 16.1; C₆₄H₈₈N₂₄CuNi₄Cl₈ requires C, 43.3; H, 5.0; N, 18.9; Cu, 3.4; Ni, 13.2; Cl 16.0%.