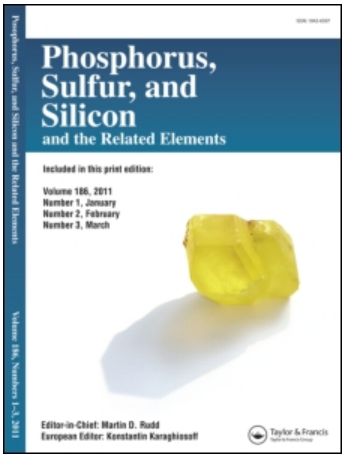

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Synthesis of Octasubstituted Metal Naphthalocyanines

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SYNTHESIS OF OCTASUBSTITUTED METAL NAPHTHALOCYANINES

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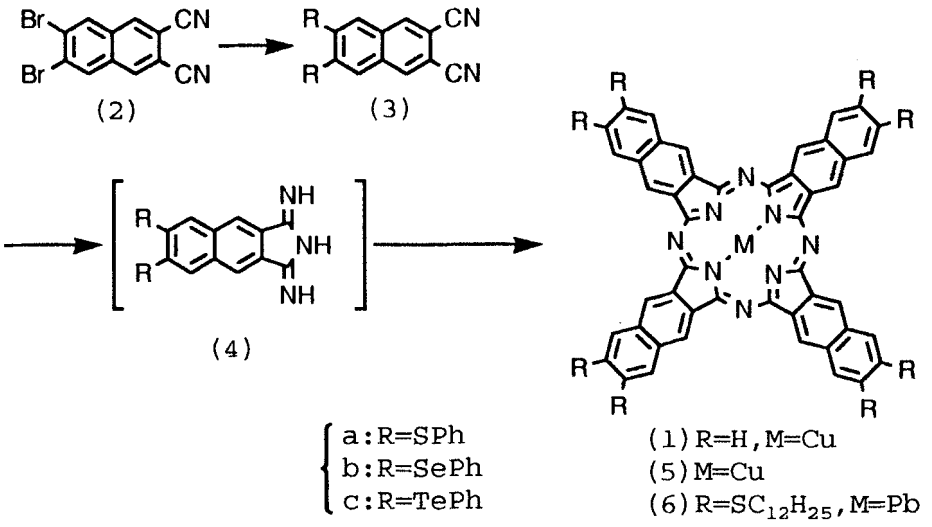
Abstract Naphthalocyanine metal complexes attached to chalcogen atoms between the naphthalocyanine ring and phenyl or alkyl groups were synthesized.

INTRODUCTION

We have investigated the synthesis and properties of phthalocyanines (Pcs)[1,2] and naphthalocyanines.[3] Some Pcs were applied to Langmuir-Blodgett films.[4] 2,3-Naphthalocyanines (Ncs), which have larger aromatic π-system than Pc, are much attention as near infrared dyes, semiconductor, agent for photodynamic therapy and so on. Especially, their electrical property has been interested because of the formation of one dimentional structure in stacked arrangement. On the other hand, tetrathiafulvalenes (TTF) are well known as an electron donor in the field of synthetic metals. Introduction of chalcogen atoms to the outer side chains of TTF brought about intermolecular interaction between these atoms.[5] In this paper, we report the synthesis of Ncs attached to chalcogen atoms (S, Se or Te) between the Nc ring and phenyl or alkyl groups.

RESULTS AND DISCUSSION

Octasubstituted metal Ncs (5) were synthesized according to Scheme. Intermediate, 6,7-dibromonaphthalene-2,3-dicarbonitrile (2), was prepared from o-xylene in three steps.[6] Reaction of 2 with chalcogelate ion gave the precursor (3). 5 was obtained via benzo[f]isoindoline derivative (4) from 3 in the presence of copper(I) chloride. Synthetic results of 5 listed in Table I. Since compound 5 was sparingly soluble in organic solvents and not sublimed under reduced



Scheme

pressure, 5 was washed with several organic solvents. Absorption spectrum of 5b was shown in Figure 1. 5a,b reveal strong single Q-band in the near infrared region and have bathochromic shift of Q-band about 20nm compared with unsubstituted Nc (1). Tellurium derivative 5c was obtained as brown powder and exhibited broad absorption pattern. Furthermore, soluble octadodecylthio-Nc lead(II) complex (6) expected large bathochromic shift was prepared from didodecylthio derivative of 3 (Table I). Compound 6 was soluble in haloalkanes, aryl halides and

TABLE I Synthetic results of naphthalocyanines 5 and 6.

Compd No.	Substituent at R	Yield (%)	Decompd point[a] (°C)	Q-band[b] (nm)
5a	PhS	16	387	802
5b	PhSe	51	350	803
5c	PhTe	35	336	848
6	$C_{12}H_{25}S$	68	234	851

a) Measured by TG-DTA under atmosphere.

b) In 1-chloronaphthalene.

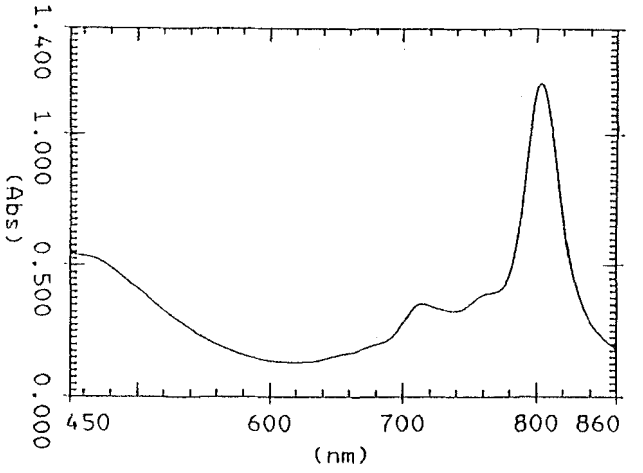


FIGURE 1 Absorption spectrum of 5b in 1-chloronaphthalene.

aromatic hydrocarbons. In the thermal analysis, a phase transition point was observed at 78°C.

EXPERIMENTAL

6,7-Diphenylselenonaphthalene-6,7-dicarbonitrile 3b.

The benzeneselenolate ion was generated from diphenyl diselenide (2m mol) with sodium borohydride (2.3mmol) in dry DMF (2ml) under a nitrogen atmosphere. After the solution was heated 70°, 2 (1.9mmol) in dry DMF (10ml) was added. The mixture was heated 100° for 6 hours. The product was extracted with methylene chloride, the organic layer was washed with water, dried over magnesium sulfate and concentrated in vacuo. The residue was chromatographed on silica gel using methylene chloride. The fraction was recrystallized from carbon tetrachloride to give pale yellow needles (yield 68%), mp 225-226°C. ^{1}H-nmr(acetone-d_6);7.27-7.76(m,arom,10H),7.79(s,5,8-arom,2H),8.37(s,1,4-arom,2H), MS (m/z);490(M^+), UV(CH_3Cl)λmax(log ε);316(4.76),288(4.46),242(4.72).
Anal. Calcd. for $C_{24}H_{14}N_2Se_2$:C,59.03;H,2.99;N,5.74.
Found:C,58.95;H,2.99;N,5.78.

6,7-Diphenylthionaphthalene-2,3-dicarbonitrile 3a.

Recrystallized from carbon tetrachloride to give white needles. Yield 20%, mp 256-257°C. ^{1}H-nmr(acetone-d_6);7.31-7.67(m,arom,10H),7.71(s,5,8-arom,2H),8.44(s,1,4-arom,2H), MS(m/z);394(M^+), UV(CH_3Cl)λmax(log ε);306(4.62),284(4.43),241(4.45),231(4.31).

Anal.Calcd. for $C_{24}H_{14}N_2S_2$:C,73.06;H,3.58;N,7.10.
Found:C,72.96;H,3.55;N,7.03.

6,7-Diphenyltelluronaphthalene-2,3-dicarbonitrle 3c.

Recrystallized from methanol to give yellow needles. Yield 59%, mp 203-205°C. ^{1}H-nmr($CDCl_3$):7.1-8.0(m,arom,14H), MS(m/z):590(M^+), UV (CH_3Cl)λmax(log ε):349(4.29),251(4.89).
Anal.Calcd. for $C_{24}H_{14}N_2Te_2$:C,49.23;H,2.41;N,4.78.
Found:C,49.12;H,2.55;N,4.58.

Octasubstituted-2,3-naphthalocyaninato copper(II) 5.

Anhydrous ammonia gas was bubbled through a stirring mixture of 3 (0.43mmol), sodium methoxide (0.22mmol) and methylcellosolve (5ml) for 30 min. With continued ammonia introduction, the mixture was heated 65° for 3 hours. The solution was evaporated in vacuo. Copper(I) chloride (0.22mmol) and quinoline (5ml) were added to the residue and refluxed for 2 hours. Methanol was added and the precipitate was filtered off, washed with acetone, methylene chloride and toluene.

Octadodecylthio-2,3-naphthalocyaninato lead(II) 6.

Prepared from 3(R=$SC_{12}H_{25}$), lead(II) chloride and 1,8-diazabicyclo[5.4.0]undec-7-ene in methylcellosolve according to the previous procedure.[3] Recrystallized from chloroform and acetone (1:1) to give deep green powder.
Anal.Calcd. for $C_{144}H_{216}N_8S_8Pb$:C,68.55;H,8.63;N,4.44.
Found:C,68.52;H,8.61;N,4.45.

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