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Synthesis and Spectroscopic Investigations of IV-A Group Phthalocyanines Containing Macrocycle Moieties

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ABSTRACT

Group IV-A (Si, Ge, Sn and Pb) phthalocyanines with eight-(12-aneN$_4$), moieties have been prepared from dicyano and diiminoisoindoline derivative or metal-free phthalocyanine and the corresponding metal salts. The axial groups attached to Si, Ge and Sn are two chlorides, hydroxides, phenolates or thiophenolates. The new compounds have been characterized by elemental analysis, IR, UV/VIS and NMR spectroscopy and thermogravimetric analysis. The thermal stability of group (IV-A) metal phthalocyanines is confirmed by the higher initial decomposition points (255–390°C) compared to those of the corresponding transition-metal phthalocyanines. © *1998 Elsevier Science Ltd*

Keywords: synthesis, spectroscopic investigation, group IV-A phthalocyanines, macrocycle.

INTRODUCTION

Phthalocyanine (Pc) compounds were discovered over 60 years ago and metallophthalocyanines subsequently became of wide interest, and found practical applications in the pigment industry and in photochemistry and catalysis [1]. Since the fundamental molecular properties of Pc compounds are strongly dependent on the π-electron system, much effort has been devoted to studies of extended Pc compounds which have additional aromatic rings on the skeleton of a Pc molecule [2]. The arrangement in segregated

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stacks can be achieved by connecting metallomacrocycles, e.g. phthalocyanines with strong covalent linkages perpendicular to the planes.

The group IV-A metal phthalocyanines are of interest because various groups can be attached to the axial positions. Furthermore, some of these compounds are capable of forming linear stacked polymers, which represents an effective approach to building metallo macrocyclic conductors [3,4].

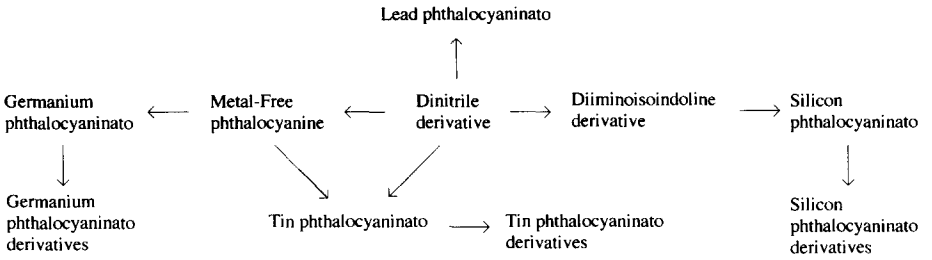
The syntheses of a variety of substituted phthalocyanines both metallo and nonmetallo have been reported [2]. The main purpose for such substitution has been to enhance Pc's very limited solubility. Peripheral substitution of these metallomacrocycles with long alkyl chains [5], sulfonyl [6], carboxyl [7], amino [8], crown ether [9–11], thio ether [12], thio-oxa ether [13] or aza moieties [14–16] significantly enhance their solubility. We have previously synthesised a series of phthalocyanines substituted with an aza-macrocycle moiety these were soluble in common organic solvents and are capable of binding transition metal cations. An additional advantage of using an aza macrocycle substituent was the solubility in water obtained by quaterization of the aza function. Preliminary findings on phthalocyanines, with a detailed study of 12-membered derivatives have been reported recently by us, and phthalocyanines substituted with 12-membered, tetraazamacrocycles provided donor sites for binding transition-metal ions, leading to nononuclear complexes [17,18]. This investigation of metal phthalocyanines and other members of the phthalocyanine system is a continuation of our research into the chemistry and properties of phthalocyanine complexes of the group IV metals.

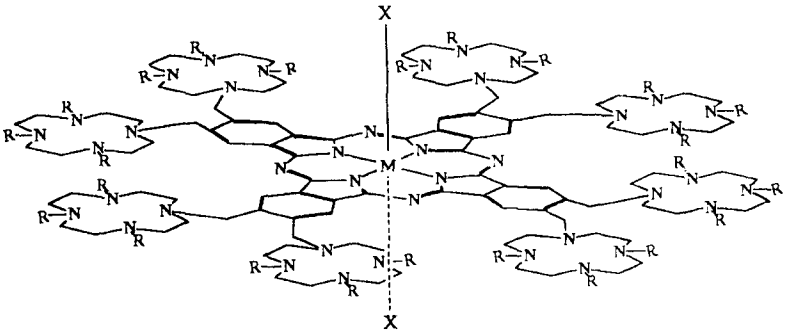
The present paper describes the synthesis of metal phthalocyanines (Si, Ge, Sn and Pb) containing eight 12-membered tetraazamacrocyclic units.

RESULTS AND DISCUSSION

The dicyano derivative was obtained from the dibromo derivate by refluxing with CuCN in dry DMF [19,20]. Si, Ge, Sn and Pb (Group-IV-A) metal phthalocyanines were synthesised either from the dicyano and diiminoisoindoline derivative or from the metal-free phthalocyanine (H_2Pc) and the corresponding metal salts (Scheme 1).

With respect to the routes previously found to be useful for the preparation of silicon phthalocyanines, the synthesis of dichlorosilicon phthalocyanine ($SiPcCl_2$) from $SiCl_4$ and the dicyano compound could not be accomplished. To obtain $SiPcCl_2$, the dicyano compound should be first converted into the diiminoisoindoline derivative, which then gives the desired phthalocyanine when reacted with $SiCl_4$ under an N_2 atmosphere [2,21], Since $SiCI_4$ can be hydrolyzed to the dihydroxy derivative $SiPc(OH)_2$ by treating with a suitable organic base (e.g. Et_3N) it appears that $SiPcCl_2$ is a suitable intermediate for the synthesis of silicon phthalocyanines.





R: P-Me$C_6H_9SO_2$

Complex	2	3	4	5	6	7	8	9	10	11	12	13	14
M	Si	Si	Si	Si	Ge	Ge	Ge	Ge	Sn	Sn	Sn	Sn	Pb
X	Cl	OH	Sph	Oph	Cl	OH	Sph	Oph	Cl	OH	Sph	Oph	--

Scheme 1

Ge and Sn are other group IV-A elements capable of forming an extensive series of phthalocyanines [10,21,22]. Dichlorophthalocyaninatogermanium ($GePcCl_2$) and dichlorophthalocyaniatotin ($SnPcCl_2$) were obtained only by reacting metal-free phthalocyanine (H_2Pc) directly with $GeCl_4$ and $SnCl_4$ in quinoline. Dichlorophthalocyaninatotin formation are derived from the metal salt, when the dichloro tin(IV) phthalocyanine derivative is obtained from the phthalonitrile derivative in 1-chloronaphthalene; the divalent tin derivative $SnCl_2$ has therefore been used [22]. Trans-chloro substituents can be hydrolyzed into the dihydroxy derivative [$GePc(OH_2)$] and [$SnPc(OH)_2$], analogous to the Si derivatives. Aqueous Et_3N has been shown to be the best medium for the hydrolysis [4].

Replacement of the OH groups with thiophenolates and phenolates was carried out by treating $Si(OH)_2$, $Ge(OH)_2$ and $Sn(OH)_2$ with an excess of thiophenol and phenol, respectively, at 140–150°C.

Leadphthalocyaninate (PbPc) was obtained by portionwise addition of PbO, as described by Linstead and coworkers [23], PbPc is soluble in variouos organic solvents (chloroform, dichloromethane, DMF and DMSO) as most of the other aza macrocycle group containing transition-metal (II) phthalocyaninate complexes [15,18].

Elemental analytical results of compounds 1–14 showed good agreement with the calculated values (Table 1).

Infrared data were consistent with this proposed structure. There is an extensive phthalocyanine vibrational spectra, and the $M(Pc)Cl_2$ and $M(Pc)(OH)_2$ compounds conform well to published criteria, differing only, for constant M, in transitions attributable to the axial ligands [2,24–27]. The IR absorption spectrum of these phthalocyanine derivatives (Si, Ge, Sn and Pb) showed characteristic $-SO_2$(2–14) and $-(OH)_2$(3,7,11) vibrational bands at 1160, 1330 and 3350–3450 cm^{-1}.

In the IR spectra of the silicon phthalocyanines, the axial substituents can be clearly differentiated. For $SiPcCl_2$, the Si–Cl absorptions are observed at 510 cm^{-1} [28,29]. In the case of the dihydroxy silicon phthalocyanines $SiPc(OH)_2$, this band disappears, while the absorptions at 830 cm^{-1} are attributed to O–Si–O asymmetric stretching [2]. A weak band at the same frequency in the spectrum of $SiPcCl_2$ could be a consequence of partial hydrolysis.

The transitions in the $GePc(OH)_2$ infrared spectra showed at 760, 730 and 660 cm^{-1} and transitions at these wavelengths are also observed in $GePcCI_2$. The weak absorptions at 690 and 660 cm^{-1} are also commonly observed

TABLE 1
Analytical Data for the Starting Material and the Phthalocyanines

	Found (%)				*Calc. (%)*			
Compound	*C*	*H*	*N*	*S*	*C*	*H*	*N*	*S*
1	56.83	5.81	10.66	13.40	56.79	5.77	10.71	13.37
2	56.59	5.61	9.50	13.45	56.48	5.53	9.60	13.31
3	56.96	5.63	9.68	13.51	56.84	5.57	9.76	13.40
4	57.68	5.64	9.30	14.18	57.51	5.57	9.45	14.05
5	57.96	5.70	9.38	13.15	57.82	5.60	9.50	13.05
6	56.15	5.56	9.50	13.34	56.04	5.49	9.61	13.21
7	56.51	5.60	9.55	13.38	56.40	5.53	9.68	13.29
8	57.24	5.61	9.20	14.17	57.07	5.53	9.38	13.96
9	57.48	5.65	9.30	13.14	57.38	5.56	9.43	12.95
10	55.74	5.55	9.41	13.28	55.61	5.45	9.54	13.10
11	56.15	5.96	9.49	13.30	55.96	5.86	9.60	13.19
12	56.76	5.61	9.21	14.05	56.64	5.49	9.31	13.85
13	57.19	5.60	9.27	12.99	56.95	5.51	9.36	12.85
14	55.60	5.57	9.38	13.16	55.44	5.43	9.51	13.04

phthalocyanine absorptions. The O–Ge–O asymmetric stretch is assigned at 660 cm^{-1}, which is a typical value for germanols [24,30].

Sn–Cl absorptions observed at 440 cm^{-1} in the IR spectrum of $SnPcCl_2$ disappeared after hydrolysis 2. The Sn–O stretch and vibration bands of $SnPc(OH)_2$ can be assigned to peaks at 490–580 cm^{-1} [24].

Comparison of the IR spectral data clearly indicated the formation of complexes (3,7,11) by the disappearance of the HO–M–OH band at 3450–3350 cm^{-1} in the SPh and OPh derivatives.

^{1}H-NMR investigation of the silicon phthalocyanine 2 and of the lead phthalocyanine 14 showed broad absorptions, probably caused by the aggregation of planar phthalocyanines which is frequently encountered at the high concentrations generally used for NMR measurements [18].

For silicon phthalocyanines, only $SiPcCl_2$ is sufficiently soluble in suitable solvents (e.g. DMSO) to obtain a ^{1}H-NMR spectra. The signals of the aromatic protons appear at 7.90–6.75 ppm, while those of the aliphatic protons of N–CH_2–CH_2–N moieties and bridged methylene protons (Ar–CH_2–N) and methyl protons (Ar–CH_3) are observed between 4.10–2.95, and 4.40 and 2.33 ppm.

In the ^{1}H-NMR spectrum of PbPc in DMSO, the signals of the aromatic protons appear at 8.45–6.90 ppm; those of the aliphatic protons of N–CH_2–CH_2–N moieties and bridged methylene protons (Ar–CH_2–N) and methylene protons (Ar-CH_3) are observed between 4.20–3.05, and 4.53 and 2.51 ppm.

The UV/VIS absorption spectra of these complexes exhibit Q and B bands, which are the characteristic bands for phthalocyanine complexes (Table 2) [31]. The spectral properties of transition metal complexes of eight azamacrocycles group have been investigated. The spectra of Si, Ge, Sn and Pb complexes are essentially the same as for transition metals, with the exception

TABLE 2
Electronic Spectral Data for the Phthalocyanine Complexes

Compound	λ *max* nm^{-1} (ε/dm^3 mol^{-1} cm^{-1})											
2	226	(6584)	295	(9607)	355	(10023)	451	(11815)	670	(3464)	—	—
3	230	(5350)	285	(8910)	370	(10500)	445	(10890)	680	(2600)	—	—
4	250	(6200)	290	(8600)	365	(10980)	450	(11310)	665	(3110)	—	—
5	252	(5800)	288	(8850)	360	(10970)	452	(11420)	665	(3200)	—	—
6	215	(180)	302	(440)	374	(5500)	452	(4240)	620	(424)	703	(2400)
7	300	(150)	384	(547)	400	(527)	449	(175)	602	(292)	689	(1219)
8	210	(360)	391	(518)	410	(479)	450	(248)	602	(300)	687	(1131)
9	278	(290)	384	(1187)	442	(419)	613	(238)	689	(1029)	—	—
10	253	(20264)	293	(2150)	332	(3151)	460	(849)	625	(566)	736	(340)
11	250	(22200)	291	(3510)	350	(3200)	452	(865)	610	(613)	730	(353)
12	265	(19210)	287	(3465)	362	(3185)	450	(863)	615	(600)	732	(328)
13	264	(20150)	285	(3450)	365	(3080)	450	(855)	610	(592)	730	(325)
14	240	(25300)	302	(4710)	380	(3615)	460	(1225)	640	(860)	743	(840)

TABLE 3
Thermal Properties of the Phthalocyanine Complexes

Compound	*Initial decomp. temp. (°C)*	*Main decomp. temp. (°C)*
2	290	405
3	310	495
4	260	420
5	255	425
6	290	450
7	300	470
8	270	450
9	265	460
10	350	465
11	370	490
12	320	465
13	315	460
14	390	510

of new bands being found around the 450 nm region. The Q band in the MPc complexes red shifts, viz SiPc (max. 670 nm), GePc (max. 703 nm), SnPc (max. 736 nm) and PbPc (max. 743 nm).

The thermal properties of the new phthalocyanine complexes 2–14 were investigated by thermogravimetric analysis (TGA) (Table 3). Initial decomposition occurs at *ca* 255–390°C and then extensive decomposition occurs at temperatures between 405 and 510°C. The extensive decomposition temperatures are higher than those found for aza macrocycle-substituted [16,18,32] and crown ether-substituted [33] phthalocyanine and its transition-metal complexes. Thus, it is apparent that decomposition temperatures of the phthalocyanine complexes are increased by the catalytic effect of Group-IV-A metals.

EXPERIMENTAL

IR spectra were recorded on a Mattson 1000 FT IR Spectrometer (KBr). Electronic spectra were recorded on a Unicam UV/VIS Spectrometer. ^{1}H-NMR and ^{13}C-NMR studies were made on a Bruker AC-200 FT-NMR Spectrometer. Thermogravimetric analyses were obtained on a Rigaku TG 8110 simultaneous thermal analyser combined with a TAS 100 at 10°C min^{-1} in a nitrogen flow. Elemental analyses were performed by the Instrumental Analysis Laboratory of Tübitak Gebze Research Center. The phthalonitrile derivative and metal-free phthalocyanine (H_2Pc) were synthesized according to the reported procedure [18].

Synthesis of diiminoisoindoline derivative (1):

The phthalonitrile derivative 1, (1.06 g, 0.75 mmol) was added to dry methanol (20 ml) under a nitrogen atmosphere and sodium methoxide

(0.04 g, 0.75 mmol) in dry methanol (20 ml) was then added. Anhydrous ammonia gas was bubbled through and the solution was stirred at room temperature for 1 h. The solution was then heated to reflux for 6 h with continued addition of ammonia gas. The reaction mixture gradually turned greenish, during which time a greenish precipitate was observed. The reaction was cooled to room temperature and the addition of ammonia gas was discontinued; the mixture was then filtered and the diiminoisoindoline derivative obtained as pale yellowish-green crystals (from MeOH-Et_2O, 1:8). The product was soluble dichloromethane, chloroform, DMSO and DMF. Yield: 0.86 g (80%). vmax/cm^{-1}: 3270, 3090–2875, 1630, 1590, 1530, 1485, 1440, 1390, 1350, 1335, 1300, 1205, 1155 1110, 1085, 1040, 1010, 905, 930, 900, 805, 750, 720, 690, 650, 600, 480, 400. ^{1}H-NMR (DMSO-d_6): 8.60 (br, 3NH), 7.75–7.20 (m, 26H, arom.), 4.28 (s, 4H, Ar-CH_2), 3.68–2.83 (m, 32H, N-CH_2-CH_2-N), 2.36 (s, 18H, Ar-CH_3). ^{13}C-NMR (DMSO-d_6): 138.73, 138.60, 130.23, 130.15, 129.85, 127.73, 126.10, 126.01, 125.83, 125.03, 125.01, 123.75, 123.50, 123.05, 108.90, 48.50, 47.90, 46.55, 41.95, 41.50, 21.10, 20.95.

Synthesis of dichloro(eight(12-aneN_4)phthalocyaninato)silicon (2):

$SiCl_4$ (0.25 ml, 2.18 mmol) was added to 10 ml of anhydrous quinoline under nitrogen and heated to reflux temperature. At this temperature, a mixture of the diiminoisoindoline derivative (1.43 g, 1.0 mmol) in 10 ml of anhydrous quinoline was added to the solution. The mixture was refluxed for 1 h cooled to room temperature, filtered, and the residue washed first with $CHCl_3$ and then with EtOH and ethyl acetate and acetone. The finely ground green product was stirred in 50 ml of conc. H_2SO_4 at room temperature, overnight filtered, the filtrate poured into ice-water, and the resulting precipitate filtered. The product was then treated with conc. HCl (20 ml), filtered and washed with water until the filtrate was neutral, and then washed with ethanol and diethyl ether and dried *in vacuo* at 110°C. The product was soluble in hot DMSO. Yield: 0.65 g (45%). vmax/cm^{-1}: 3080–2870, 1635, 1595, 1560, 1490, 1460, 1390, 1360, 1340, 1310, 1230, 1160, 1120–1095, 1035, 890, 755, 730, 690, 660, 600, 510, 490–470, 415, 375. ^{1}H-NMR (DMSO-d_6): 7.90–6.75 (m, 104 H, arom.), 4.40 (s, 16 H, Ar-CH_2-N), 4.10–2.95 (m, 128 H, N-CH_2-CH_2-N), 2.33 (s, 72 H, Ar-CH_3).

Hydrolysis of (2) to the hydroxophthalocyaninatosilicon (3):

Compound 2 (1.0 g, 0.17 mmol) was hydrolysed in triethylamine-water (1:1 v/v) (10 ml) at room temperature by stirring for 3 days and then the mixture was evaporated to dryness. The dark green product was treated with water, ethanol and diethylether and dried *in vacuo* at 100°C. The product was soluble in hot DMSO. Yield: 0.89 g (90%). vmax/cm^{-1}: 3450–3350, 3080–2860, 1630,1590, 1560, 1495, 1460, 1390, 1365, 1340, 1300, 1220, 1160, 1120–1090, 1025, 900, 830, 750, 740, 695, 660, 490–475.

Synthesis of the bis(thiophenolato)phthalocyaninatosilicon (4):

A mixture of 3 (0.5 g, 0.086 mmol) and excess thiophenol was heated to 150°C under N_2 for 3 h. After cooling to room temperature, the precipicate was filtered off, washed several times with hot ethanol and diethylether and dried *in vacuo* at 100°C. The product was slightly soluble in DMSO. Yield: 0.34 g (66%). vmax/cm^{-1}: 3080–2830, 1610, 1500, 1440, 1380, 1340–1330, 1210, 1150, 1080, 1010, 900, 810, 780, 730, 710, 690, 650, 610, 540, 420.

Synthesis of the bis(phenolato)phthalocyaninatosilicon (5):

A mixture of 3 (0.5 g, 0.086 mmol) and excess phenol was heated to 150°C under N_2 for 3 h. After cooling to room temperature, the precipicate was filtered off, washed several times with hot ethanol and diethylether and dried *in vacuo* at 100°C. The product was slightly soluble in DMSO. Yield: 0.31 g (60%). vmax/cm^{-1}: 3080–2830, 1610, 1500, 1440, 1380, 1340–1330, 1210, 1150, 1080, 1010, 900, 810, 780, 730, 710, 690, 650, 610, 540, 420.

Synthesis of dichloro(eight(12-aneN_4)phthalocyaninato)germanium (6):

A mixture of H_2Pc (2.00 g, 0.35 mmol) and $GeCl_4$ (0.5 ml, 4.40 mmol) in anhydrous quinoline (2 ml) was heated at 220–230°C for 4 h under N_2. After cooling to room temperature, the crude product was treated with chloroform and filtered. It was refluxed with chloroform for 1 h, filtered to remove unreacted organic material and after washing with hot chloroform, the residue was then stirred in conc. H_2SO_4 (25 ml) for 5 h at room temperature and the mixture filtered. When the filtrate was poured into ice-water, the product separated as a dark green precipitate, which was then treated with conc. HCl and washed with water until the filtrate was free from any trace of HCl. The dark green product was then washed with ethanol and diethyl ether and dried *in vacuo* at 100°C. Yield: 1.15 g (56%). The product was soluble in hot DMSO. vmax/cm^{-1}: 3080–2860, 1620, 1600, 1500, 1430, 1390, 1340, 1310, 1160, 1120, 1080, 1010, 950, 890, 810, 760, 730, 690, 665, 620, 560, 510, 450, 430.

Hydrolysis of (6) to the hydroxophthalocyaninatogermanium (7):

Hydrolysis of $GePcCl_2$ to $GePc(OH)_2$: Prepared as described for $SiPc(OH)_2$, starting from $GePcCl_2$ (1.0 g, 0.17 mmol) and triethylamine-water (1/1 v/v) 10 ml. This product was soluble in hot DMSO. Yield: 0.65 g (65.6%). vmax/cm^{-1}: 3420–3350, 3080–2860, 1620, 1590, 1550, 1500, 1440, 1390, 1360, 1330, 1290, 1200, 1150, 1120–1080, 1010, 900, 810, 760, 730, 690, 660, 580, 510, 490–450, 430.

Synthesis of the bis(thiophenolato)phthalocyaninatogermanium (8):

Prepared as described for $SiPc(SPh)_2$, starting from $GePc(OH)_2$ (0.50 g, 0.086 mmol) and excess thiophenol. This product was slight soluble in DMSO. Yield: 0.4 g (77.5%). vmax/cm^{-1}: 3080–2830, 1610, 1500, 1440, 1380, 1340–1330, 1210, 1150, 1080, 1010, 900, 810, 780, 730, 710, 690, 650, 610, 540, 420.

Synthesis of the bis(phenolato)phthalocyaninatogermanium (9):

Prepared as described for $SiPc(OPh)_2$, starting from $GePc(OH)_2$ (0.50 g, 0.086 mmol) and excess phenol. This product was slightly soluble in DMSO. Yield: 0.35 g (68.2%). vmax/cm^{-1}: 3080–2860, 1630, 1590, 1500, 1460, 1390, 1350, 1330, 1310, 1200, 1150, 1080, 1010, 900, 820, 770, 730, 690, 660, 610, 550, 490–450, 420.

Synthesis of dichloro(eight(12-aneN_4)phthalocynaninato)tin (10):

Method A: A mixture of the dinitrile derivative (4.26 g, 3.0 mmol), anhydrous. $SnCl_2$ (0.284 g, 1.50 mmol) and 1-chloronaphthalene (25 ml) was heated and stirred at reflux temperature for 3 h under nitrogen. After cooling to room temperature the mixture was filtered and the resulting residue was then refluxed with chloroform and the liquor filtered. The resultant dark green powder was washed with hot ethanol and diethyl ether and dried *in vacuo* at 110°C. Yield: 1.94 g (44%).

Method B: Anhydrous $SnCl_4$ (0.10 ml, 0.85 mmol), anhydrous quinoline (20 ml) and metal-free phthalocyanine (H_2Pc) (1.0 g, 0.176 mmol) were mixed under nitrogen and stirred; the reaction mixture was then held at 220°C for 3 h, cooled to room temperature, diluted with quinoline/ethaol (1:2) (100 ml) and filtered. The residue was treated with conc. HCl (20 ml), the liquor filtered, washed neutral with water, and then washed with chloroform and diethyl ether and dried *in vacuo* at 110°C. The product was slightly soluble in DMSO. Yield: 0.41 g (40%) vmax/cm^{-1}: 3090–2860, 1610, 1600, 1440, 1410, 1330, 1310, 1290, 1160, 1110–1090, 1050, 990, 970, 870, 805, 780, 740, 715, 660, 640, 570, 490, 440, 350.

Hydrolysis of (10) to the hydroxophthalocyaninatotin (11):

Prepared as described for $SiPc(OH)_2$, starting from $SnPcCl_2$ (1.0 g, 0.17 mmol) and triethylamine-water (1:1 v/v) 10 ml. This product was soluble in hot DMSO. Yield: 0.79 g (80%). vmax/cm^{-1}: 3450–3350, 3080–2860, 1615, 1595, 1550, 1505, 1440, 1395, 1370, 1330, 1290, 1210, 1160, 1120–1090, 1000, 970, 860, 810, 795, 740, 710, 680, 650, 580, 500, 490.

Synthesis of the bis(thiophenolato)phthalocyaninatotin (12):

Prepared as described for $SiPc(SPh)_2$, starting from $SnPc(OH)_2$ (0.5 g, 0.085 mmol) and excess thiophenol. This product was soluble in hot DMSO. Yield: 0.34 g (66%). vmax/cm^{-1}: 3080–2870, 1620, 1600, 1550, 1500, 1435, 1390, 1360, 1335, 1290, 1210, 1155, 1115–1090, 1000, 970, 850, 800, 740, 705, 690, 650, 500, 490, 455, 430.

Synthesis of the bis(phenolato)phthalocyaninatotin (13):

Prepared as described for $SiPc(OPh)_2$, starting from $SnPc(OH)_2$ (0.5 g, 0.085 mmol) and excess phenol. This product was soluble in hot DMSO. Yield 0.36 g (70%). vmax/cm^{-1}: 3080–2870, 1620, 1595, 1550, 1505, 1435, 1395, 1360, 1340, 1290, 1210, 1150, 1115–1090, 1000, 970, 855, 800, 740, 705, 685, 660, 585, 510, 490, 450, 425.

Synthesis of phthalocyaninatolead (14):

The dinitrile derivative (1.06 g, 0.75 mmol) was heated to 200°C over 10 min and PbO (0.13 g, 0.56 mmol) was then added in four portions. The reaction was continued at 200°C for 4 h. After cooling to room temperature, liquor was filtered and the residue was stirred in CH_2Cl_2/CH_3OH 4:1 (50 ml) and then filtered. The filtrate was evaporated to dryness, and the resultant green product was separated by column chromotography (CH_2Cl_2/CH_3OH 10:1). The product was soluble in chloroform, dichloromethane, DMF and DMSO. Yield: 0.28 g (25%). vmax/cm^{-1}: 3090–2860, 1610, 1600, 1510, 1435, 1390, 1345, 1310, 1160, 1130, 1080, 1000, 950, 890, 810, 750, 735, 685, 620, 560, 510, 450, 440. ^{1}H-NMR(DMSO-d_6): 8.45–6.90 (m, 104 H, arom.), 4.53 (s, 16 H, Ar-CH_2-N), 4.20–3.05 (m, 128 H, N-CH_2-CH_2-N), 2.51(s, 72 H, Ar-CH_3).

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