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Azaanalogs of phthalocyanine: syntheses and properties

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Contents

Abstract

Structural data, nomenclature, synthetic routes and spectral properties of the majority of known azaanalogs of phthalocyanines are presented. Among the synthetic procedures, the preparation and purification of both lipophilic and water soluble azaphthalocyanines are described. The physico-chemical properties of these compounds are strongly influenced by the presence of exocyclic nitrogen atoms, which are more basic than the meso atoms of the porphyrazine macroring. This increased basicity of the azaanalogs, compared with the corresponding phthalocyanines, explains their tendency to form stable hydrates and their specific affinity for protons in acidic media. The hypsochromic shift of the Q-band in the electronic spectra of the azaanalogs of phthalocyanine, naphthalocyanine and anthracyanine, resulting from the aza substitution in the fused benzo rings, is shown to depend on

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the number and position of the heterocyclic N atoms in the macrocycle. The effect of aza substitution on the absorption spectra becomes more pronounced in the case of linearly annelated azaphthalocyanines. In contrast, sequential linear annelation alone induces a strong bathochromic displacement of the Q-band. The recent data concerning the angular annelation of octaazanaphthalocyanine suggest that each angularly condensed benzo ring contributes to a hypsochromic shift of the main absorption maximum of 10–15 nm. Such data are essential in the design of new phthalocyanine related compounds with 'tuned' absorption maxima and selected solubility, as substrates for new materials.

Keywords: Annelation; Azasubstitution; Phthalocyanine azaanalogue

1. Introduction

The azaanalogs of the phthalocyanines (azaPcs) are heterocyclic Pc analogs which have been extensively studied over the past decade. Potential applications which have been addressed include their use as textile bleaching agents, photoinactivators for controlling growth of microorganisms [1], catalysts for oxygen reduction [2,3], materials for electrochromic displays [4–6], media for optical data storage with large memory capacity [7–14], inhibitors of thermal degradation of polymers [15] and photosensitizers for photodynamic therapy of cancer [16,17].

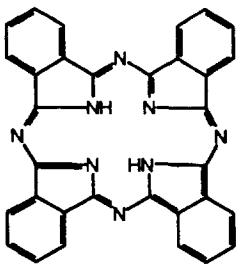
The synthesis of heterocyclic Pc analogs was initially reported in 1937 by Linstead and coworkers [18,19]. The benzo rings of these compounds were substituted by heterocycles, such as thiophene, thionaphthalene, pyridine and pyrazine. The preparation of azaPcs was described in the 1960s [20–23], and their photoelectrical [24], absorbance [25,26] and catalytic properties [27] were studied.

A significant contribution to the development of the chemistry of azaPcs was made by Galpern and Luk'yanets who described the synthesis and properties of a series of AzaPcs differing in the number and localization of N atoms in the macrocycle, as well as in the number of linearly condensed benzo rings. These authors also developed the methods for preparing *tert*-butyl-substituted analogs of Pc and naphthalocyanine (Nc). The high solubility of these compounds in common organic solvents allowed for studies of their spectral properties in solutions. The main changes in the UV–vis spectra of Pc and Nc resulting from azasubstitution and linear annelation of the macrocycles, were established experimentally and were shown to fit well with the results of quantum chemical calculations [28–31].

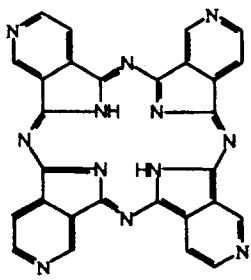
Subsequent reports detailed the synthesis of a series of azaPcs soluble in water [17,32] and in organic solvents [33–35] which permitted studies on the effect of the aryl substitution and angular annelation on the electronic spectra of octaazaanalog phthalocyanines (octaazaPcs), octaazaanalog naphthalocyanines (octaazaNcs) and tetraazaanalog naphthalocyanines (tetraazaNcs).

This paper reviews the synthetic routes leading to azaPcs and highlights the properties of the latter compounds compared with their carbocyclic analogs.

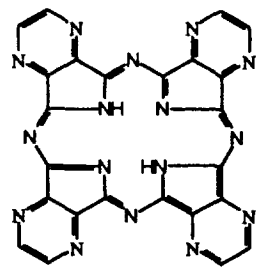
2. Nomenclature



Phthalocyanine = tetrabenzoporphyrazine



Tetra-3,4-pyridino-porphyrazine



Tetra-2,3-pyrazino-porphyrazine

The names of the azaPcs according to the IUPAC nomenclature are too unwieldy. This has created the need for a more convenient systematic nomenclature [18]. It was proposed to use the term porphyrazine for the central ring system of the Pc molecule. Individual compounds are named by attaching an appropriate prefix. Thus the systematic name for Pc itself on this basis is 29*H*,31*H*-tetrabenzo[*b,g,l,q*]porphyrazine (tetrabenzoporphyrazine). The corresponding compound with four 3,4-pyridine rings in lieu of four benzenes becomes 29*H*,31*H*-tetrapyridino[3,4-*b*:3′,4′-*g*:3″,4″-*l*:3‴,4‴-*q*]porphyrazine (tetra-3,4-pyridinoporphyrazine), the pyrazine-substituted analog is 29*H*,31*H*-tetrapyrazino[2,3-*b*:2′,3′-*g*:2″,3″-*l*:2‴,3‴-*q*]porphyrazine (tetra-2,3-pyrazinoporphyrazine).

3. Syntheses, purification and physico-chemical properties of the azaPcs

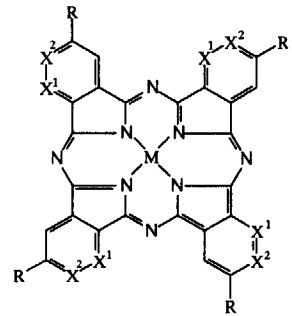
The essential information about structure, synthesis and spectral properties of a majority of known azaPcs is presented in Tables 1–6 and Schemes 1–7.

3.1. Lipophilic azaPcs

In the same manner that substituted phthalonitriles are the most useful intermediates in the synthesis of Pcs, the dinitriles of heterocyclic *o*-dicarboxylic acids are the best precursors for the synthesis of azaPcs. In contrast to most other derivatives of *o*-dicarboxylic acids, *o*-dinitriles afford pure azaPcs in high yields. Heterocyclic *o*-dinitriles are the only suitable precursors in the preparative synthesis of metal-free azaPcs (Scheme 1).

The most common way to obtain metal-free azaPcs includes demetallation of the magnesium or lithium complexes in conc. hydrochloric or sulfuric acid (Scheme 1, Methods 1A, 1B) [18,28,30,36,37]. Metal-free tetrapyridinoporphyrazine **1** (Table 1) was synthesized by treatment of the dicyanopyrazine, dissolved in *N,N*-dimethylaminoethanol, with ammonia (Scheme 1, Method 1C) [36]. Metal-free azaPcs were also

Table 1
Tetrapyridinoporphyrazines

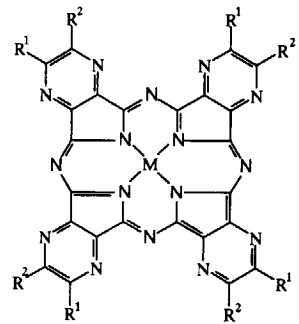


No.	X^1	X^2	R	M	Method of synthesis	λ_{max}(nm)(log ε)/relative intensity/[solvent][a]	Reference
1	N	CH	H	HH	1B, 1C	643 (4.82), 613 (4.18), 584 (4.06), 380 (4.34), 329 (4.45)/[DMF]	[18,36]
						672 (3.67), 652 (3.42), 618 (3.50), 681 (3.42), 574 (sh.), 339 (4.06), 256 (3.87)/[82% H_2SO_4]	[44]
2	N	CH	H	Cu	2A, 3A, 3B	651, 585/4.9 : 1/[quinoline]	[28,39]
						665 (4.87), 637 (4.63), 626 (4.57), 574 (4.15), 338 (4.61), 256 (4.50), 229 (4.56)/[94% H_2SO_4]	[44]
3	N	CH	H	VO	2B	663, 602/5.1 : 1/[quinoline]	[28]
4	N	CH	H	Cd	2C	648 (4.92), 618 (4.11), 586 (4.06), 380 (4.29), 328 (4.42)/[DMF]	[36]
5	N	CH	H	Zn	2B, 2C	642 (4.77), 613 (3.87), 382 (3.90), 390 (4.11), 329 (4.30)/[DMF]	[28,36]
6	N	CH	H	Mg	2D	643 (4.93), 616 (4.07), 582 (4.06), 366 (4.36), 329 (4.45)/[DMF]	[28,36]
7	N	CH	H	AlOH	2D	642, 616, 580, 436, 427/[DMF]	[36]
8	N	CH	H	$Si(OH)_2$	2B	639, 613, 579, 333/[DMF]	[57,58]
9	N	CH	H	$Ti(OH)_2$	2B	645/[70% H_2SO_4]	[57]

10	N	CH	H	$Ge(OH_2)$	2B	643, 616, 582, 341/[DMF] 646, 638, 615, 579, 342/[98% H_2SO_4]	[57,58]
11	N	CH	H	$ZrCl_2 \cdot 2ZrCl_4$	2B	651, 591/3.5:1/[DMF]	[59]
12	N	CH	H	$Zr(OH)_2$	2B	676/[60% oleum]	[50,59]
13	N	CH	H	$HfCl_2$	2B	649, 585/[DMF]	[47]
14	N	CH	H	ZrPc	—[b]		[40]
15	N	CH	H	HfPc	—[b]		[40]
16	N	CH	H	Co	2B	635, 590 sh./2.85:1/[quinoline]	[28,44]
					3A		[39]
17	N	CH	H	Ni	3A	668 (4.15), 631 (4.10), 592 (3.76), 300 (4.31), 229 (4.26)/[95% H_2SO_4]	[39,44]
18	$N^+CH_3(CH_3SO_4)^-$	CH	H	HH	6	642 (4.99), 583 (4.34), 396 (4.63), 318 (4.58), 300 (4.63)/[H_2O]	[36]
19	$N^+CH_3(CH_3SO_4)^-$	CH	H	AlOH	6	636 (4.47), 627 (4.46), 570 (3.83), 425 (4.06), 390 (4.27), 366 (4.27), 324 (4.30)/[H_2O]	[36]
20	$N^+CH_3(CH_3SO_4)^-$	CH	H	Zn	6	637 (4.93), 629 (4.93), 572 (4.20), 366 (4.55), 321 (4.47)/[H_2O]	[36]
21	$N^+CH_3(CH_3SO_4)^-$	CH	H	Co	6	616, 575 sh./2.80:1/[H_2O]	[39]
22	$N^+CH_3(CH_3SO_4)^-$	CH	H	Cu	6	626 (4.93), 568 (4.21), 358 (4.53), 323 (4.53)/[H_2O]	[36]
23	$N^+CH_3(CH_3SO_4)^-$	CH	H	Ni	6		[39]
24	CH	N	H	Cu	3A	705 (4.9), 680 (4.78), 375 (4.36)/[conc. H_2SO_4]	[54]
25	CH	$N^+(C_{18}H_{37})Br^-$	H	Cu	7	687, 339/0.8:1/[chloroform]	[54]
26	CH	N	^{t}Bu	VO	3A	700 (5.61), 630 (4.98), 342 (5.18)/[benzene] 680, 615, 345/3.8:1:2.0/[DMSO]	[29]
27	CH	N	^{t}Bu	Co	3A	672, 605, 325, 290 sh./3.15:1:1.80:1.40/[chloroform]	[29]

[a] DMF: *N*,*N*-dimethylformamide. [b] Condensation of Zr (Hf) tetrapyridinoporphyrazine with Pc.

Table 2
Tetra-2,3-pyrazinoporphyrazines

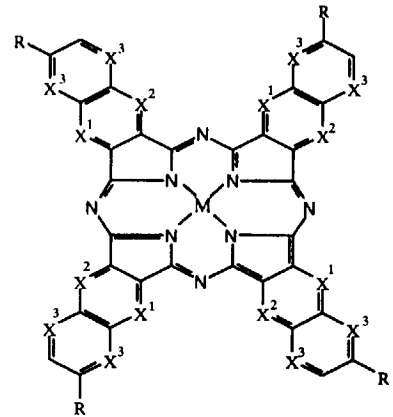


No.	R^1	R^2	M	Method of synthesis	λ_{max}(nm)(log ε)/relative intensity/[solvent]	Reference
28	H	H	HH	1A, 1B	642, 585/2.65 : 1/[quinoline]	[18,28]
29	H	H	Cu	2A		[18]
30	H	H	VO	2A	645, 588/4.7 : 1/[quinoline]	[28]
31	H	H	Co	2A	615, 560/2.5 : 1/[DMSO]	[28]
32	H	H	Zn	2A	635, 580/5.4 : 1/[DMSO]	[28]
33	H	H	$HfCl_2$	2A	639, 580/[DMF]	[40]
34	H	H	$ZrCl_2$	2A	647, 592/[DMF]	[40]
35	H	H	$SiCl_2$	2B	638, 575, 378/[quinoline]	[35]
36	H	H	$Si(OH)_2$	—[a]	634.5, 376/[quinoline]	[35]
37	H	H	SiX_2[b]	—[c]	624 (5.44), 597 (4.35), 566 (4.44), 337 (4.88)	[35]
38	^{t}-Bu	H	HH	1A	653 (5.08), 617 (4.95), 570 (4.34), 340 (5.02)/[chloroform]	[30,33]
39	^{t}-Bu	H	VO	3A	645 (5.14), 586 (4.42), 343 (4.9), 292 (4.71)/[chloroform]	[30]
40	^{t}-Bu	H	Cu	3A	631 (5.22), 572 (4.51), 340 (5.01), 294 (4.70)/[chloroform]	[30]
41	^{t}-Bu	H	Co	—[d]	616 (4.82), 560 (4.13), 422 (3.89), 334 (4.6)/[DMSO]	[33]
42	n-$C_{12}H_{25}$	n-$C_{12}H_{25}$	HH	1C	654 (5.18), 618 (5.06), 605 (4.72), 571 (4.38), 564 (4.38), 340 (5.06)/[chloroform]	[37]

43	n-$C_{12}H_{25}$	n-$C_{12}H_{25}$	Cu	2C	634 (5.25), 574 (4.50), 340 (4.99), 300 (4.71)/[chloroform]	[37]
44	Et	Et	HH	1C		[60,61]
45	n-Pr	n-Pr	HH	1C		[60,61]
46	n-C_5H_{11}	n-C_5H_{11}	HH	1C		[60,61]
47	n-C_7H_{15}	n-C_7H_{15}	HH	1C		[60,61]
48	n-C_9H_{19}	n-C_9H_{19}	HH	1C		[60,61]
49	n-$C_{11}H_{23}$	n-$C_{11}H_{23}$	HH	1C		[60,61]
50	Ph	Ph	HH	1A,1B	656 (4.95), 604 sh. (4.00), 596 (4.03), 372 (4.68)/[DMF] 678, 654, 614 sh., 590 sh., 366/3.88 : 3.68 : 1.48 : 1 : 3.05/[1-chloronaphthalene]	[33]
51	Ph	Ph	VO	2A	656 (5.19), 595 (4.42), 367 (4.94)/[DMSO]	[33]
52	Ph	Ph	$SiCl_2$	2B	664, 370/[quinoline]	[35]
53	Ph	Ph	$Si(OH)_2$	—[e]	658, 372/[quinoline]	[35]
54	Ph	Ph	SiX_2[f]	—[g]	645 (5.42), 617 (4.42), 584 (4.43), 369 (4.95)/[chloroform]	[35]
55	CO_2Et	CO_2Et	VO	2B	654 (5.38), 590 (4.68), 348 (5.02)/[chloroform]	[17,32]
56	CO_2Et	CO_2Et	Co	2B	640 (5.35), 580 (4.62), 338 (4.92)/[chloroform]	[17,32]
57	CO_2Et	CO_2Et	Cu	2B	647 (5.47), 584 (4.70), 348 (5.18)/[chloroform]	[17,32]
58	CO_2Et	CO_2Et	Zn	2B	658 (5.31), 599 (4.53), 388 (4.81), 335 (4.92), 302 (4.94)/[chloroform]	[17,32]
59	CO_2H	CO_2H	Cu	—[h]	637.5 (5.38), 579 (4.55), 351 (5.05)/[H_2O]	[17,32]
60	CO_2H	CO_2H	Zn	—[h]	640 (5.32), 581 (4.48), 353 (5.09)/[H_2O]	[17,32]
61	H	H	Yb[i]	2A	680/[DMF]	[6]

[a] Hydrolysis of compound **35** with H_2SO_4. [b] Where X is tri(n-hexyl)siloxy. [c] Reaction of compound **36** with chloro-tri(n-hexyl)silane in 3-picoline. [d] Metallation of compound **38** with $CoCl_2$ in chloroform–ethanol. [e] Hydrolysis of compound **52** with H_2SO_4. [f] Where X is tri(n-hexyl)siloxy. [g] Reaction of compound **53** with chloro-tri(n-hexyl)silane in 3-picoline. [h] Hydrolysis of the appropriate octa(ethoxycarbonyl) derivative. [i] Bis(tetra-2,3-pyrazinoporphyrazinato)ytterbium (III).

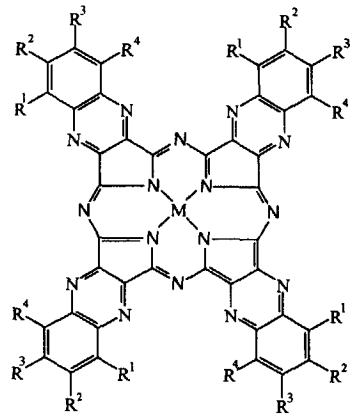
Table 3
2,3-AzaNcs



No.	X^1	X^2	X^3	R	M	Method of synthesis	λ_{max}(nm)(log ε)/relative intensity/[solvent]	Reference
62	N	CH	CH	H	HH	1B	714, 637/1.5:1.0/[DMSO]	[41]
63	N	CH	CH	H	Mg	2A	714, 680, 645, 444, 385, 334/6.3:2.0:2.0:1.0:3.6:5.5/[DMSO]	[41]
64	N	CH	CH	H	Zn	2A	714, 670, 465, 333/3.9:2.9:1.0:6.6/[DMSO]	[41]
65	N	CH	CH	H	Fe	2A	706, 637, 444, 357/1.5:1.0:1.8:6.1/[DMSO]	[41]
66	N	CH	CH	H	Cu	2A	695, 662, 465, 333/1.5:1.4:1.0:4.7/[DMSO]	[41]
67	N	CH	CH	H	Co	2A	704, 637, 444, 333/3.8:1.0:2.2:5.1/[DMSO]	[41]
68	N	CH	CH	H	Ni	2A	693, 654, 333/1.0:2.1:22.0/[DMSO]	[41]
69	N	CPh	CH	H	VO	3A	780 (5.29)/[chloroform]	[33]
70	N	N	CH	H	HH	1A	720, 680, 642/3.70:1.03:1/[quinoline]	[28]
71	N	N	CH	H	VO	2B	725, 660 sh./5:1/[quinoline]	[28]
72	N	N	CH	H	Co	2B	703, 650/3.40:1/[quinoline]	[28]
73	N	N	CH	H	Cu	2B, 4	712, 645/2.70:1/[quinoline]	[28]
74	N	N	CH	H	Zn	2B	718, 685, 655/7.15:1.10:1/[quinoline]	[28]
75	N	N	CH	H	$SiCl_2$	2B	715.5, 680, 379/[quinoline]	[35]
76	N	N	CH	H	$Si(OH)_2$	—[a]	702, 378/[quinoline]	[35]
77	N	N	CH	H	SiX_2[b]	—[c]	704 (5.60), 671 (4.53), 646 (4.52), 361 (5.20)/[chloroform]	[35]
78	N	N	CH	^{t}Bu	VO	2B	726 (4.99), 634 (4.64), 346 (4.70)/[DMF]	[62]
79	CH	CH	N	^{t}Bu	Cu	4	755, 675/5.10:1/[quinoline]	[46]

[a] Hydrolysis of appropriate dichlorosilicon complex. [b] Where X is tri(*n*-hexyl)siloxy. [c] Reaction of appropriate dihydroxysilicon complex with chloro-tri(*n*-hexyl)silane in 3-picoline.

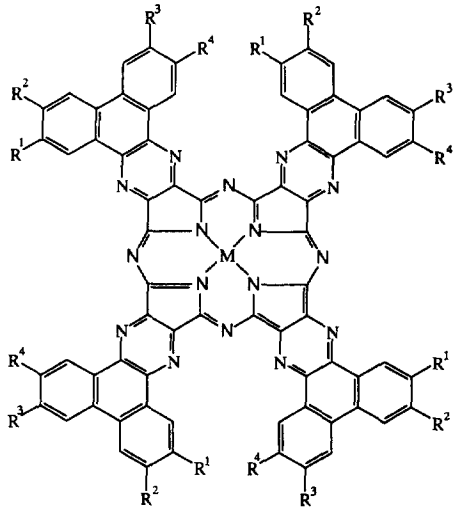
Table 4
Angularly annelated tetra-2,3-quinoxalinoporphyrazines



No.	R^1 R^2	R^3 R^4	M	Method of synthesis	λ_{max}(nm)(log ε)/relative intensity/[solvent]	Reference
80	benzo	H H	VO	2B	700, 360/1 : 1.2/[quinoline]	[34]
81	benzo	H H	Cu	2B	689, 360/1 : 1.25/[quinoline]	[34]
82	benzo	H H	$SiCl_2$	2B	699, 667.5, 378/[quinoline]	[35]
83	benzo	H H	$Si(OH)_2$	—[a]	698, 378/[quinoline]	[35]
84	benzo	H H	SiX_2[b]	—[c]	688 (5.80), 656 (4.74), 618 (4.76), 371 (5.25)/[chloroform]	[35]
85	benzo	benzo	HH	1A	Insoluble in organic solvents	[34]
86	benzo	benzo	VO	2A	706, 440/1.2 : 1/[quinoline]	[34]
87	benzo	benzo	GaOH	2B	694, 440/1.34 : 1/[quinoline]	[34]
88	benzo	benzo	AlOH	2B	692, 438/1.3 : 1/[quinoline]	[34]
89	benzo	benzo	Cu	2B	684, 460/1.4 : 1/[quinoline]	[34]
90	benzo	benzo	Co	2B	680, 452/1.2 : 1/[quinoline]	[34]
91	benzo	benzo	$SiCl_2$	2B	690, 376/[DMF]	[35]
92	benzo	benzo	$Si(OH)_2$	—[a]	680, 376/[DMF]	[35]
93	benzo	benzo	SiX_2[b]	—[c]	679, (5.56), 648 (4.80), 624 (4.77), 375 (5.09)/[chloroform]	[35]

[a] Hydrolysis of appropriate dichlorosilicon complex. [b] Where X is tri(*n*-hexyl)siloxy. [c] Reaction of appropriate dihydroxysilicon complex with chloro-tri(*n*-hexyl)silane in 3-picoline.

Table 5
Isomeric tetra-5,6-[(di-*tert*-butyl-9,10-phenanthro)-pyrazinoporphyrazines

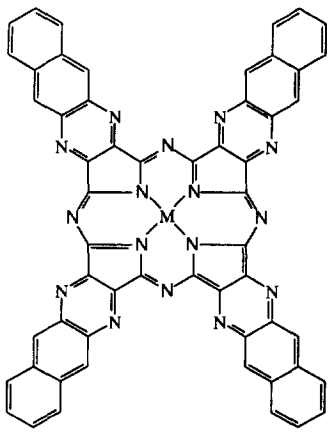


No.	R^1	R^2	R^3	R^4	M	Method of synthesis	λ_{max}(nm)(log ε) [chloroform]	Reference
94	^{t}Bu	H	^{t}Bu	H	Cu	2C	680 (4.88), 628 (4.4), 380 (4.58)	[34]
95	^{t}Bu	H	H	^{t}Bu	Cu	2C	680 (4.9), 628 (4.34), 378 (4.64)	[34]
96	H	^{t}Bu	^{t}Bu	H	Cu	2C	680 (4.91), 628 (4.3), 380 (4.6)	[34]
97	^{t}Bu	H	^{t}Bu	H	AlCl	2C	690 (4.95), 630 (4.4), 389 (4.7)	[34]
98	^{t}Bu	H	^{t}Bu	H	Zn	2C	692 (5.01), 630 (4.44), 387 (4.6)	[34]
99	^{t}Bu	H	^{t}Bu	H	VO	2C	704 (5.15), 642 (4.42), 354 (4.5)	[34]

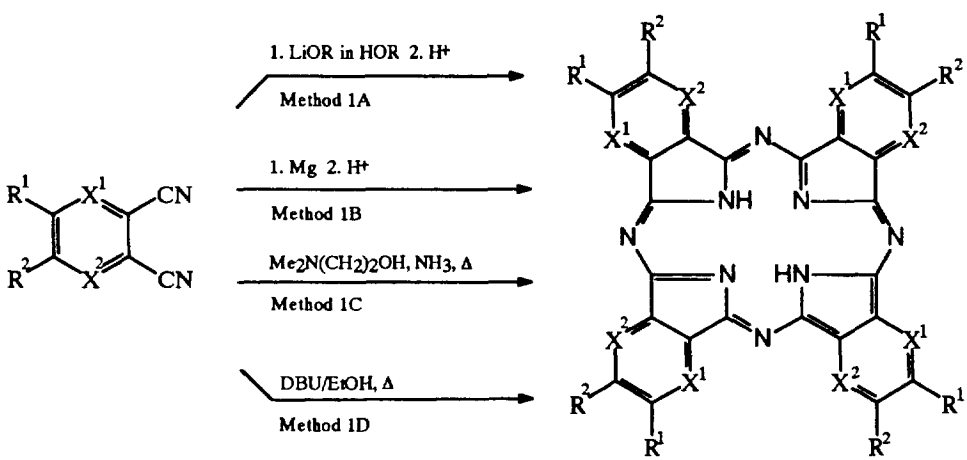
prepared from *o*-dinitriles using traditional catalysts of the template synthesis of Pc, such as organic bases (Scheme 1, Method 1D). Thus, compound **42** (Table 2) was obtained by heating the ethanolic solution of the corresponding *o*-dinitrile, containing 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) [37].

There are numerous methods for preparing metal complexes of azaPcs, since their synthesis is not restricted to the use of *o*-dinitrile as intermediates. However, compared with the carbocyclic analogs [38], many more examples of azaPc metal complex (azaPcM) syntheses involve *o*-dinitriles compared with other possible derivatives of heterocyclic *o*-dicarboxylic acids (Scheme 2). 2,3-Dicyanopyridine, 2,3-dicyanopyrazine and 2,3-dicyanoquinoline react with metal salts (anhydrous chlorides or acetates) in the absence of solvent upon heating to 190–200 °C (Scheme 2, Method 2A) [18,28,39–41], whereas substituted and condensed heterocyclic *o*-dinitriles require the presence of a solvent such as trichlorobenzene, quinoline or pyridine (Scheme 2, Method 2B). The azaPcs **5** (Table 1), **43** (Table 2), **100–103** (Table 6)

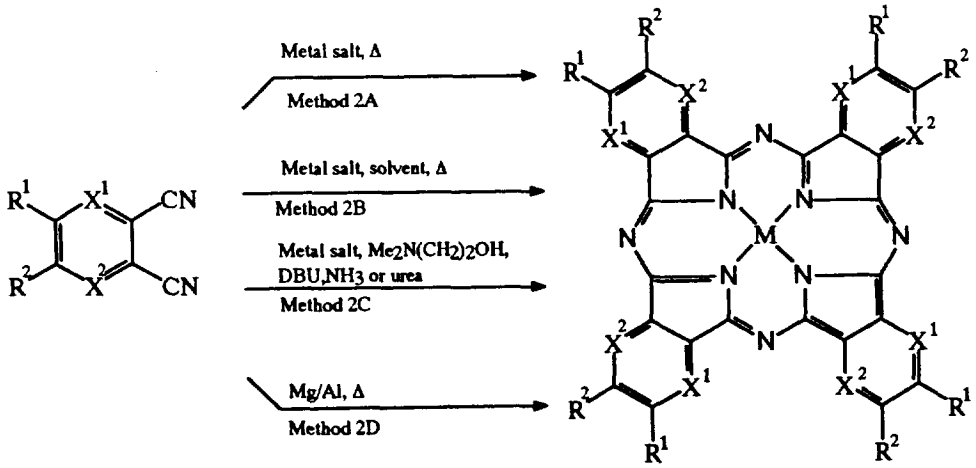
Table 6
Tetra-2,3-benzo[*g*]quinoxalinoporphyrazines



No.	M	Method of synthesis	λ_{max}(nm)/relative intensity/[quinoline]	Reference
100	VO	2C	830, 750/5:1	[42,63]
101	Co	2C	785, 730 sh.	[42]
102	Cu	2C	810, 765 sh.	[42]
103	Zn	2C	810, 760	[42]



Scheme 1



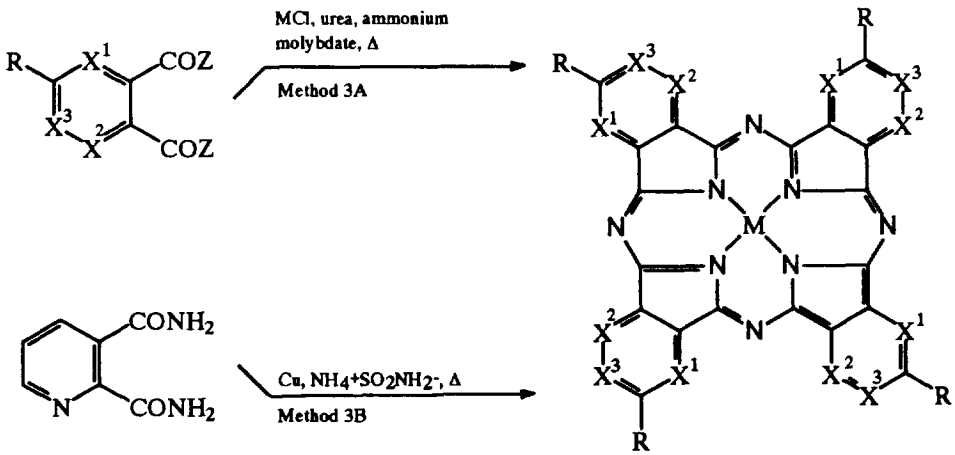
Scheme 2

were prepared by complexation of the corresponding dinitriles with metal salts in the presence of strong organic bases and/or ammonia (Scheme 2, Method 2C) [36,37,42]. The Mg and AlX complexes of tetra-2,3-pyridinoporphyrazine **6** and **7** (Table 1) were synthesized by heating of 2,3-dicyanopyridine with metal powder (Scheme 2, Method 2D) [28,36].

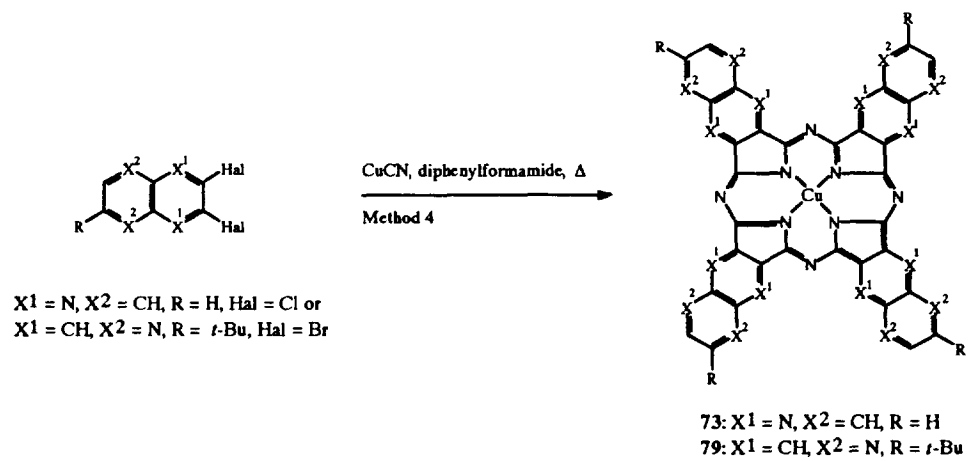
The use of heterocyclic *o*-dicarboxylic acids and *o*-diamides for the synthesis of azaPcM requires the presence of ammonia donors, such as urea or ammonium salts, in the reaction mixture. Thus, metal complexes of tetrapyridino- and tetrapyrazinoporphyrazine such as **2**, **16**, **24**, **39**, etc. (Tables 1 and 2) were obtained [43] from the appropriate *o*-dicarboxylic acids and metal salts in the urea melt in the presence of ammonium molybdate (Scheme 3, Method 3A) [18,29,30,39,43–45].

Method 3A is particularly convenient for the synthesis of soluble tetraazaPcs and octaazaPcs, such as tetra-2,3-(5-*tert*-butylpyrazino)porphyrazines **39** and **40** (Table 2), tetra-3,4-(6-*tert*-butylpyridino)porphyrazines **26** and **27** (Table 1) and vanadyl tetra-2,3-(4-phenylquinolino)porphyrazine **69** (Table 3) [33]. In general, however, this method provides Pcs of lower purity compared with those obtained from the complexation of the corresponding *o*-dinitriles. All above mentioned soluble compounds were chromatographed on alumina or silica gel, with purification being less cumbersome compared with the multistep synthesis of the corresponding hard-to-get dinitriles.

Preparing the copper(II) complexes of tetra-6,7-(2-*tert*-butyl)quinoxalinoporphyrazine **79** [46] and tetra-2,3-quinoxalinoporphyrazine **73** (Table 3) [28] via the reaction of 2-*tert*-butyl-6,7-dibromoquinoxaline and 2,3-dichloroquinoxaline with copper(I) cyanide in diphenylformamide respectively can be considered as an atypical synthesis of azaNcs (Scheme 4, Method 4).



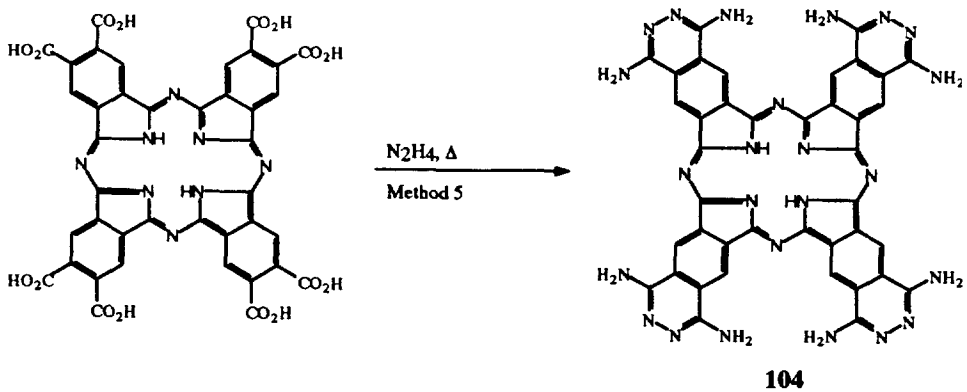
Scheme 3



Scheme 4

Only one example exists whereby the substituted Pc is directly converted into an azaNc, i.e. the synthesis of tetra-6,7-(1,4-diaminophthalazino)porphyrazine **104** from octacarboxyPc (Scheme 5, Method 5) [73].

Pure azaPcs and azaNcs are deeply coloured crystalline solids which decompose without melting upon heating over 550 °C. Unlike Pcs, the azaanalogs cannot be purified by sublimation, even in high vacuum. The unsubstituted azaPcs are less soluble in common organic solvents compared with Pcs and thus they are difficult to purify by chromatography or recrystallization. Reprecipitation from conc. sulfuric



104

Scheme 5

acid followed by extensive extraction of impurities with hot organic solvents in a Soxlet apparatus are the most common methods to purify the azaPcs. Owing to the presence of exocyclic nitrogen atoms, which are more basic than the meso-atoms of the porphyrazine macroring, precipitation of the complexes requires much less concentrated acid compared with the corresponding Pcs [46]. The increased basicity of the azaanalogs permits reprecipitation from conc. HCl or a mixture of phenol–trichlorobenzene (1:1 by weight). The UV–vis spectra of azaPcs are indicative of the degree of purity. Heating the unsubstituted complexes in organic solvents, such as 1-chloronaphthalene, quinoline or dimethyl sulfoxide (DMSO) provides approximate 10^{-6} M solutions, which is sufficiently concentrated for spectral measurements. During purification the electronic spectrum changes substantially: the long-wave band (Q-band) becomes narrower (half-width of the peak ca. 570 cm^{-1}), the vibrational peaks resolve, and an absorbance in the area 400–500 nm gradually disappears.

It is well known that Pc heteroanalogs readily form hydrates [18,42]. Thus, the tetrapyridino- and tetrapyrazinoporphyrazines were obtained as hydrates containing one to four molecules of water, but no correlation was observed between the structure of the molecule and number of water molecules retained in the hydrate. Even heating the azaPc hydrates in vacuo in the presence of dehydrating agents failed in many cases to afford anhydrous compounds [24,46]. The dehydration can be performed more efficiently by heating the samples in acetic anhydride [28,34].

Differences between Pcs and azaPcs owing to the presence of additional exocyclic N atoms is also displayed in their UV–vis spectra in acidic media. Thus, protonation of Pcs, dissolved in conc. sulfuric acid, causes substantial changes in the absorption spectra, including a strong bathochromic shift of the long-wavelength maximum (about 100 nm) [47,48]. This shift of the Q-band is due to the protonation of the N meso-atoms, which strongly affects the adjacent C atoms included in the a_{1u} orbital [49]. The bathochromic shift of the absorption maxima in the spectra of tetra-2,3-pyridino-, tetra-2,3-pyrazino- and tetra-2,3-quinoxalinoporphyrazines in conc. sulfuric acid never exceeds 30 nm [46,50,51,62]. It has been suggested that the protonation of azaPc affects the exocyclic N atoms and only slightly influences the

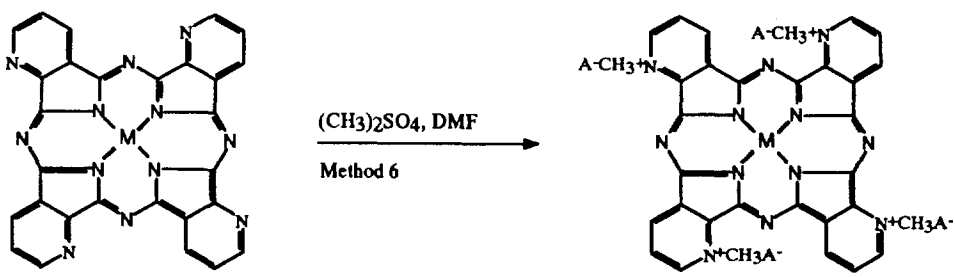
charge density on C atoms of the porphyrazine ring. Therefore, the Q-band, corresponding to the $a_{1u} \rightarrow e_g$ transition [52], taken in acidic media, is hardly shifted compared with the spectra recorded in organic solvents.

3.2. *Water soluble azaPc*

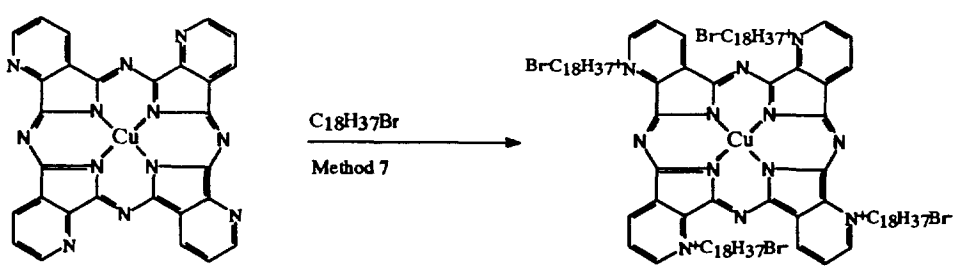
The presence of additional N atoms in the molecules of the azaPcs allows the formation of a water soluble cationic form of the complexes via quaternization with dimethyl sulfate (Scheme 6, Method 6) [36,39,53] or alkyl bromides (Scheme 7, Method 7) [54].

Complexes **18–23** (Table 1) are highly soluble in water and their UV–vis spectra are indicative of substantial monomerization. Their photoredox behavior [36], biological activity [55] and interaction with DNA in solutions [56] were studied. Compound **25** (Table 1) has a well-defined amphiphilic character and was shown to be particularly easy to handle by Langmuir–Blodgett methods, rendering it a useful material for basic studies on molecular electronics [54].

A novel class of water soluble azaPcs, functionalized on the macrocycle with carboxy substituents, was recently described by us [17]. Octaethoxycarbonyl tetrapyrazinoporphyrazines **55–58** (Table 2) were synthesized by complexation of 2,6-dicyano-5,6-diethoxycarbonylpyrazine with metal salts in quinoline. The ester



Scheme 6



Scheme 7

groups of compounds **57** and **58** were hydrolyzed with a mixture of three parts of NaOH saturated methanol and one part water, resulting in instantaneous dissolution of the complexes followed by precipitation of the salts of **59** and **60** (Table 2). The reaction was monitored by HPLC analysis of the redissolved precipitate. Complexes **59** and **60** were obtained as single compounds in quantitative yields. This type of compound constitutes an alternative class of photosensitizers for the photodynamic therapy of cancer, with a different pK_a compared with those currently available [32].

4. Effect of azasubstitution and annelation on the electronic spectra of azaanalogs of Pc, Nc and anthracyanine

4.1. Azasubstitution of the Pc

There are four basic absorption bands in the wavelength range from 280 to 700 nm in the electronic spectra of tetraazaPc and octaazaPc metal complexes. The first two long-wave bands represent a Q-band and its vibrational satellite, similar to those observed with Pcs [52]. The less intense and wider B band, related to the Soret band of porphyrins, is located in the UV–vis region about 340 nm. Often this band is split (N band, ca. 300 nm), as in the spectra of tetrapyridinoporphyrazines **1**, **2**, **4–6**, **17–20** (Table 1) and tetrapyrazinoporphyrazines **39–41** (Table 2). The splitting can have a vibrational nature, since its magnitude is about 1500 cm^{-1}, but a superposition of several electronic transitions also can be considered [46].

Substitution of the CH groups of the Pc benzo rings adjacent to the porphyrazine macrocycle with N atoms, causes a remarkable hypsochromic shift in the visible part of the spectrum. The magnitude of this shift increases from tetraazaPcs (20–25 nm, 550–780 cm^{-1}) to the octaaza derivatives (40–60 nm, 870–1260 cm^{-1}, depending on the nature of the central metal atom) [28–30]. Comparing the spectra of metal-free tetra-2,3-(5-*tert*-butylpyrazino)porphyrazine **38** (Table 2) [30] and tetra-4-*tert*-butylPc [64,65] in organic solvents reveals, as similarly observed for the metal complexes, a strong blue shift of all long-wave bands, whereas the bands in the UV area remain at the same wavelengths.

It has been shown that the absorption spectrum of azaPc depends on the position of the heterocyclic N atoms in the benzo rings. Unlike the tetra-2,3-pyridinoporphyrazines, electronic spectra in the visible region of tetra-3,4-pyridinoporphyrazines are identical to the spectra of the corresponding Pcs [22].

Phenyl substituents, even when oriented out of plane of the molecule, contribute to the interaction with the exocyclic nitrogen atoms. Thus, the main absorption maximum of the vanadyl octaphenyl tetrapyrazinoporphyrazine **51** (Table 2) is at 656 nm [33] while the carbocyclic analog, i.e. octaphenylPcVO [68] exhibits a maximum at 720 nm (shift: 64 nm, 1350 cm^{-1}).

4.2. Azasubstitution of Nc and its annelated analogs

Tetraaza substitution of Ncs causes a strong hypsochromic shift of the main long-wave maxima, up to 1600 cm^{-1} in the case of the copper(II) tetra-2,3-quinolinoporphyrazine **66** (Table 3) [41], although values around 1000 cm^{-1} are more common for compounds in the series. It is interesting to note that 1-phenyl substitution hardly affects the sensitivity of the Nc aromatic system to the tetraaza substitution. Thus, vanadyl tetra-2,3-(4-phenylquinolino)porphyrazine **69** (Table 3) shows a maximum at 780 nm (in chloroform), whereas vanadyl tetra(1-phenyl)Nc absorbs at 850 nm [67] (70 nm, 1060 cm^{-1} blue shift). The magnitude of this shift far exceeds the analogous shifts for the above mentioned series of tetraazaPcs, i.e. tetra-2,3-pyridinoporphyrazines. Therefore, the larger the aromatic system, the more pronounced the effect of tetraazasubstitution on the absorption maximum of the complex.

Comparison of the spectral data in the visible region of the tetra-6-*tert*-butyl-2,3-NcCu [66] with those of the copper(II) octaazaNcs **73** and **79** (Table 3) shows that the long-wave band of NcCu at 782 nm and its vibrational satellite at 697 nm undergo a substantial hypsochromic shift to 712 and 645 nm for the tetra-2,3-quinoxalinoporphyrazine **73** and to 755 and 675 nm for *tert*-butyl-substituted 6,7-isomer **79**. Thus, octaaza substitution of 2,3-Nc, like in the Pc series, causes a hypsochromic shift of the Q-band maximum, which is more distinct when the CH groups adjacent to the porphyrazine macroring are substituted. Surprisingly, in contrast to the Pc, the magnitude of this shift is about the same for the tetraaza substituted Nc as for the octaaza substituted Nc (see Table 3, compounds **62–68** and **70–78**).

Comparison of the main absorption maxima (in chloroform) of bis(tri-*n*-hexylsiloxy)-silicon Pc (λ_{max} 668 nm) [74] vs. its octaaza analog **37** (Table 2, λ_{max} 624 nm), and of the bis(tri-*n*-hexylsiloxy)silicon Nc (λ_{max} 772 nm) [74] vs. its octaaza derivative **77** (Table 3, λ_{max} 704 nm), show that the magnitude of the blue shift due to octaaza substitution increases from 1080 cm^{-1} for the azaPc to 1250 cm^{-1} for the azaNc. Similar values have been observed for a variety of unsubstituted and *tert*-butyl-substituted metal complexes of Pc, Nc and their octaaza analogs [28–30]. Furthermore, comparing the spectral data for the quinoline solutions of NcVO (λ_{max} 819 nm) [63,69] vs. vanadyl tetra-2,3-quinoxalinoporphyrazine **71** (Table 3, λ_{max} 725 nm), we observe an even more remarkable hypsochromic shift of 1580 cm^{-1}. In contrast, comparison of condensed Nc analogs such as vanadyl anthracyanine (λ_{max} 932 nm) [63] vs. the tetra-2,3-benzo[*g*]quinoxalinoporphyrazine **100** (Table 6, λ_{max} 830 nm, 1320 cm^{-1} blue shift due to the octaaza substitution) or vanadyl tetra-4,5-(9,10-phenanthro)Pc (λ_{max} 776 nm) [68] vs. its octaaza analog **86** (Table 4, λ_{max} 706 nm, 1280 cm^{-1} blue shift) suggests that the electron-buffering effect of the aromatic Nc does not render this system more sensitive to octaaza substitution upon annelation.

4.3. Linear annelation of azaPcs

Comparison of the UV–vis spectra of linearly annelated octaazaPcs, tetra-2,3-pyrazinoporphyrazines (Table 2), tetra-2,3-quinoxalinoporphyrazines

(Table 3) and tetra-2,3-benzo[*g*]quinoxalinoporphyrazines (Table 6) reveals that each additional benzo ring causes a strong bathochromic shift of the Q-band (80–100 nm, 1500–2000 cm^{-1}) [28–30]. The same rule applies to the series of tetraazaPcs, i.e. tetra-2,3-pyridinoporphyrazines (Table 1) and tetra-2,3-quinolinoporphyrazines (Table 3), where the red shift due to the additional benzo ring averages about 1550 cm^{-1}. This displacement of absorption maxima with the sequential annelation, which does not change the symmetry of molecule, is due to the extension of the aromatic system of the macrocycle. This correlation was first noticed in the series of Pc azaanalogs; subsequently it was also found in the sequence porphyrazine – Pc – 2,3-Nc [70] – anthracyanine [71] and adopted as a common feature of the Pc class of compounds.

4.4. Angular annelation of octaazaPcs

How does the angular annelation affect the spectral properties of the azaanalogs? This is not an easy question to answer since insolubility of condensed azaPcs and strong aggregation in solutions needs to be circumvented. Thus, the absorption maximum of the vanadyl tetra-2,3-(benzo[*f*]-quinoxalino)porphyrazine **80** (Table 4) is located at 700 nm, whereas the vanadyl tetra-2,3-[5,6-(9,10-phenanthro)]porphyrazine **86** (Table 4) absorbs at 706 nm and vanadyl tetra-2,3-quinoxalinoporphyrazine **71** (Table 3) at 725 nm (all spectra in quinoline). Therefore, the first angularly annelated benzo ring causes a hypsochromic shift of the Q-band, whereas the second condensed ring hardly affects the absorption pattern. Aggregation of Pc molecules in solution strongly affects the position of the long-wave maxima, and in general increases with the size of the molecule [72]. In order to accurately study the spectral properties of the angularly annelated azaNcs, the aggregation phenomenon needed to be eliminated. This was approached in two ways: *tert*-butyl substitution on the periphery of the macrocycle (Table 5) [34] and synthesis of the axially-substituted silicon complexes **77** (Table 3), **84** and **93** (Table 4) [35]. The latter compounds appeared to be particularly useful since they allowed comparison of the spectral properties of fully monomerized derivatives of tetraazaNc, containing the same central atom, in the same solvent, i.e. chloroform. Comparison of the spectra of complex **77** (λ_{max} 704 nm) and its angularly annelated analogs **84** (λ_{max} 688 nm) and **93** (λ_{max} 679 nm) suggests that each angularly condensed benzo ring causes a hypsochromic shift of 10–15 nm. It should be noted that for the series of unsubstituted carbocyclic analogs it was difficult to conclude anything concerning their spectral properties due to their extremely low solubility and strong aggregation in organic solvents [68]. Furthermore, *tert*-butyl-substituted (or any other soluble) derivatives of tetra(9,10-phenanthro)Pc are unknown.

5. Conclusions

Synthetic methods for preparing the azaPcs and their spectral properties are described and compared with those of their carbocyclic analogs. This basic informa-

tion is essential for the design of new materials with 'tuned' absorption maxima and selected solubility, derived from different Pc-related structures containing at least one heterocyclic ring per molecule.

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