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Synthesis and solvent effects on the spectroscopic properties of octatosylamido phthalocyanines

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Octatosylamido-substituted metal-free, Ni(II) and Zn(II) phthalocyanines (pcs, **3a–c**) have been synthesized from 4,5-dicyano-*N*,*N*'-ditosyl-*o*-phenylenediamine (**2**, tosyl: toluene-*p*-sulfonyl) in the presence of an anhydrous metal salt and a strong base. The new compounds have been characterized by elemental analysis, IR and UV-vis spectroscopy, different NMR techniques (^{1}H, ^{13}C, ^{1}H–^{15}N HSQC, ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC) and mass spectroscopy. The influence of the solvent on the ^{1}H, ^{13}C NMR and UV-vis spectra has been determined. In chloroform, **3a–c** are able to form intramolecular hydrogen bonds between four NH and oxygen atoms from neighbouring tosyl units and two tosyl groups occur in one single molecule: while four tosyl units are in the pc plane, the other four are nearly vertical to it. They have different chemical environments because of the magnetic anisotropy of the pc ring. For this reason, in chloroform, each of the protons and carbon atoms gives two sets of signals in the ^{1}H and ^{13}C NMR spectra of pcs. In tetrahydrofuran, the intramolecular hydrogen bonding of pcs is disrupted and all tosyl units are located in the same environment. In the electronic spectra of **3a–c**, all bands change with the solvent. This solvatochromism is caused by solvent basicity. Compounds **3a–c** show rapid and reversible colour change upon addition of a base.

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Introduction

Phthalocyanines (pcs) have aroused extensive interest in the past decades since their unique properties led to their use in a wide number of applications in the area of materials science, such as chemical sensors, liquid crystals, catalysis, and nonlinear optics.[1–7] In addition, their properties have been considered to have potential applications in cancer photodynamic therapy (PDT).[8–10] Fundamental to their specific properties is the delocalized electronic nature of the pc ring system. Most of the applications of pcs are focused on the electronic properties of the π-electron system of the macrocycles. Strong light absorption by pcs to give clear blue or green colours led to their use as pigments and dyes, soon after their discovery, and these applications are still of immense commercial importance. Pcs show typical electronic spectra with strong absorption in two regions, the visible (Q band at 600–700 nm) and the ultraviolet [B (Soret) band at 300–350 nm]; the latter is generally much less intense. In the absorption spectra of pcs, the bands can be changed by changing the type of central metal ion and/or the nature of substituents.

The electronic spectra of some molecules can be influenced by the polarity (solvatochromism or perichromism[11]), temperature (thermochromism), light (photochromism), pressure, pH (acidichromism), *etc*., of the medium.[12] In acidichromism, the protonated form and the conjugate base may have distinctly different absorption spectra. This phenomenon, well-known for phenols and aromatic amines, has potential applications in pH or acid and base gas sensors, photo- and chemical-switching systems and gas-controlled reversible colour-change devices.[13]

One of our main aims is the synthesis of new pcs with various functional groups for potential applications such as chemical gas sensors, liquid crystals, PDT and catalysis.[14] Substituents play an important role in tailoring pcs for various applications. For example, aromatic diamines have interesting properties. They are less basic than aliphatic amines due to the delocalization of the electron pair on the nitrogen atom toward the π-orbitals of the aromatic ring, the electron density on the nitrogen atom available for bond formation thus being lower.[15] Thanks to their protonation-deprotonation properties, aromatic diamines are useful for many applications such as biosensors, mutagens, carcinogens and antitumor agents.[15–18] Substitution of amines confers promising properties onto pcs.[19] In this respect, we have now designed and synthesized octatosylamido-substituted metal-free, Ni(II) and Zn(II) pcs (**3a–c**, respectively). These new compounds have been characterized by elemental analysis, IR, NMR UV-vis and mass spectroscopy. The influence of the solvent on the ^{1}H, ^{13}C NMR and UV-vis spectra has been examined.

Experimental

Materials

4,5-Dibromo-*N*,*N*′-ditosyl-*o*-phenylenediamine (**1**) was prepared according to the literature[20] and spectroscopic results are given below. All other reagents and solvents were of

reagent grade quality from commercial suppliers and were dried before use as described in the literature.[21]

Measurements

Elemental analyses were obtained from a Carlo Erba 1106 instrument. Infrared spectra from KBr pellets were recorded on a Bio-Rad FTS 175C FT-IR spectrophotometer. UV-vis spectra were recorded on a Schimadzu 2001 UV PC spectrophotometer using 1 cm pathlength cuvettes at room temperature. The mass spectra were recorded on a VG Zab Spec GC-MS spectrometer using electronic impact (EI) method and on a LCQ ion trap (Thermofinnigan, San Jose, CA, USA), equipped with an electrospray ionization (ES) source. ES full scan spectra, in the range of *m*/*z* 50–2000 or 2000–3000 amu, were obtained by infusion through fused silica tubing at 2–10 μl min^{-1}. The solutions were analyzed in positive mode. The LCQ calibration (*m*/*z* 50–2000) was achieved according to the standard calibration procedure from the manufacturer (mixture of caffeine, MRFA and Ultramark 1621). An ES-Tuning Mix solution (Agilent) was used to calibrate the spectrometer between 2000 and 3000 amu. The temperature of the heated capillary of the LCQ was set in the range 180–200 °C, the ion spray voltage was in the range 1–7 kV with an injection time of 5–200 ms. ^{1}H and ^{13}C NMR spectra were recorded in deuterated chloroform, THF and DMSO solutions on a Bruker 500 MHz spectrometer using TMS as an internal reference.

The absorption spectra of **3a–c** were taken on 7.5×10^{-3} mol dm^{-3} concentration solutions in various solvents. Acid-base titrations of pcs were performed by addition of increasing concentrations of KOH or HCl solutions in MeOH to the fixed concentrations of pcs (3 ml; 7.5×10^{-6} mol dm^{-3}).

Syntheses

4,5-Dibromo-*N*,*N*′-ditosyl-*o*-phenylenediamine (1). **1** was synthesized from *o*-phenylenediamine as described in the literature.[20] Yield 94%; m.p.: 218–220 °C; anal. calcd for $C_{20}H_{18}Br_2N_2O_4S_2$: C, 41.83; H, 3.16; N, 4.88; found: C, 41.92; H, 3.32; N, 4.59%; IR ν_{max}/cm^{-1}: 3520 (free NH), 3257 (H-bonded NH), 3096 (CH_{Ar}), 2924 (CH_3), 1597, 1503, 1468, 1426, 1391, 1361, 1335 (SO_2), 1321, 1264, 1185, 1163 (SO_2), 1118, 1090, 1018, 942, 900, 867, 835, 810, 723, 710, 676, 614, 589, 563, 483, 462; MS (EI) *m*/*z* (%): 576 (11) $[M]^+$ ($^{81}Br^{81}Br$), 574 (19) $[M]^+$ ($^{81}Br^{79}Br$), 572 (9) $[M]^+$ ($^{79}Br^{79}Br$), 420 (59) $[M - tosyl]^+$, 341 (25) $[M - (tosyl + Br)]^+$, 265 (19) $[M - 2tosyl]^+$, 185 (12) $[M - (2tosyl + Br)]^+$, 155 (79) $[M - (2tosyl + Br + 2NH)]^+$, 91 (100) $[M - (2tosyl + 2Br + NH)]^+$, 78 (48) $[M - (2tosyl + 2Br + 2NH)]^+$; ^{1}H NMR (DMSO-d_6) δ: 2.38 (s, 6H, CH_3), 7.27 (s, 2H, CH_{Ar}), 7.38 (d, 4H, CH_{Ar}), 7.61 (d, 4H, CH_{Ar}), 9.60 (br, 2H, NH); ^{13}C NMR (DMSO-d_6, APT) δ: 20.98 (CH_3), 125.80 (C_{Ar}–Br), 126.81 ($C_{Ar}H$–C–Br and $C_{Ar}H$–C–SO_2–), 129.81 ($C_{Ar}H$═C–CH_3), 130.67 (C_{Ar}–NH–), 136.08 (C_{Ar}–SO_2–), 143.78 (C_{Ar}–CH_3).

4,5-Dicyano-*N*,*N*′-ditosyl-*o*-phenylenediamine (2). A mixture of 25.41 g (44.24 mmol) of **1**, 12.32 g (137.56 mmol) of CuCN and 120 ml of anhydrous DMF were heated to 140 °C for 20 h under argon atmosphere. After cooling, the resulting dark brown mixture was mixed with aqueous NH_4OH (25%, 300 ml) and air was passed through the solution for 14 h. The brown precipitate was filtered off and washed with water until the filtrate was neutral. The solid product was recrystallized first from acetic acid and then from ethanol. Yield 7.02 g (34%); m.p.: 203–205 °C; anal. calcd for $C_{22}H_{18}N_4O_4S_2$: C, 56.64; H, 3.89; N, 12.01; found: C, 56.36; H, 3.52; N, 11.91%; IR ν_{max}/cm^{-1}: 3535 (free NH), 3262 (H-bonded NH), 3065 (CH_{Ar}), 2925 (CH_3), 2232 (CN), 1600, 1564, 1505, 1439, 1410, 1348, 1333 (SO_2), 1306, 1164 (SO_2), 1086, 1019, 915, 883, 815, 750, 670, 580, 550, 538. MS (EI) *m*/*z* (%): 469 (16) $[M + 2]^+$, 468 (15) $[M + 1]^+$, 467 (51) $[M]^+$, 312 (18) $[M - (tosyl)]^+$, 157 (25) $[M - 2tosyl]^+$, 155 (100) $[M - 2(tosyl + H)]^+$.

Octatosylamido phthalocyanine (3a). Freshly hexane-cleaned lithium, 0.11 g (25.72 mmol), was dissolved in 3 ml of *n*-pentanol and 0.4 g (0.86 mmol) of **2** were added to the solution. The mixture was heated to reflux for 60 h under argon atmosphere. The solvent was completely removed under reduced pressure and the crude product was washed with hexane several times, dissolved in 60 ml of a mixture of acetic acid–CH_2Cl_2 (1 : 5). Then, it was extracted with distilled water (4 × 100 ml), and the organic layer was isolated, dried over anhydrous Na_2SO_4 and the solvent removed. The dark green-blue crude product was purified by silica gel chromatography by elution with CH_2Cl_2. Yield 0.022 g (5.5%); anal. calcd for $C_{88}H_{74}N_{16}O_{16}S_8$: C, 56.58; H, 3.99; N, 12.00; found C, 56.94; H, 4.17; N 11.86%; IR ν_{max}/cm^{-1}: 3546 (free NH), 3234 (H-bonded NH), 3064 (CH_{Ar}), 2924 (CH_3), 1650, 1620 (C═N), 1597, 1496, 1453, 1403, 1333 (SO_2), 1291, 1263, 1161 (SO_2), 1089 1019, 912, 812, 752, 704, 666, 596, 547. MS (ES-MS) *m*/*z* (%): 1868 (100) $[M + 1]^+$, 1867 (91) $[M]^+$.

Octatosylamido phthalocyaninato nickel(II) (3b). A mixture of 1.87 g (4.00 mmol) of compound **2**, 0.52 g (4.00 mmol) of anhydrous $NiCl_2$, 0.9 ml (6.00 mmol) of DBU and 6 ml of dried *n*-hexanol was heated to reflux for 18 h under argon atmosphere. The solvent was completely removed under reduced pressure and the crude product was washed with ethanol several times, dissolved in 70 ml of a mixture of acetic acid–CH_2Cl_2 (1 : 5). Then, it was extracted with distilled water (4 × 100 ml) and the organic solution was dried over anhydrous Na_2SO_4 and concentrated. The dark green-blue product was purified over silica gel with CH_2Cl_2 as the eluent. Yield 0.75 g (%39); anal. calcd for $C_{88}H_{72}N_{16}NiO_{16}S_8$: C, 54.91; H, 3.77; N, 11.64; found C, 54.63; H, 4.07; N 11.36%; IR ν_{max}/cm^{-1}: 3547 (free NH), 3233 (H-bonded NH), 3068 (CH_{Ar}), 2925 (CH_3), 1621 (C═N), 1598, 1534, 1468, 1438, 1402, 1338 (SO_2), 1294, 1161 (SO_2), 1090, 1055, 1020, 919, 812, 753, 706, 668, 546. MS (ES-MS), *m*/*z* (%): 1925 (100) $[M + 1]^+$, 1924 (88) $[M]^+$.

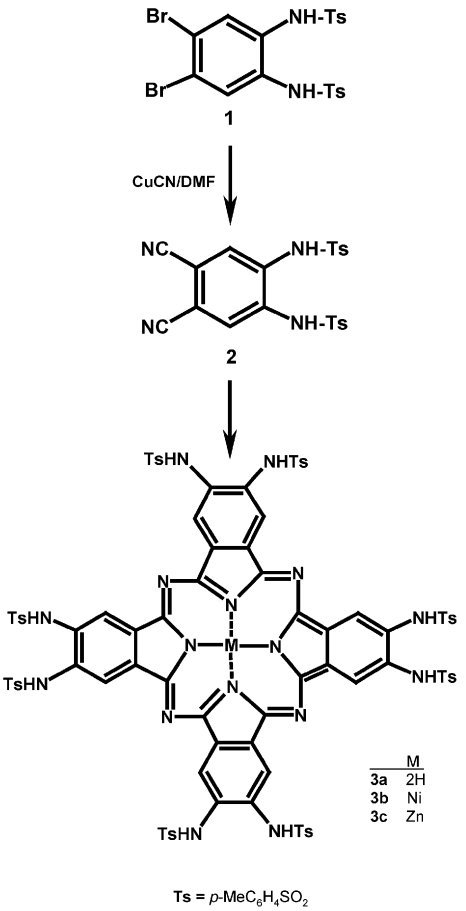
Octatosylamido phthalocyaninato zinc(II) (3c). The procedure is the same as above with 0.88 g (4.00 mmol) of anhydrous $Zn(OAc)_2$ (instead of $NiCl_2$) and 5 ml dried *n*-hexanol (instead of 6 ml). Yield 0.64 g (%33); anal. calcd for $C_{88}H_{72}N_{16}O_{16}S_8Zn$: C, 54.72; H, 3.76; N, 11.60; found C, 54.46; H, 4.07; N 11.41%; IR ν_{max}/cm^{-1}: 3449 (free NH), 3248 (H-bonded NH), 3070 (CH_{Ar}), 2927 (CH_3), 1619 (C═N), 1599, 1492, 1460, 1403, 1339 (SO_2), 1294, 1262, 1162 (SO_2), 1090, 1037, 919, 812, 746, 706, 669, 548. MS (ES-MS) *m*/*z* (%): 1931 (100) $[M + 1]^+$, 1930 (70) $[M]^+$.

Results and discussion

Synthetic procedure and characterization

Pcs (**3a–c**) were prepared by the route shown in Scheme 1. Commercially available *o*-phenylenediamine was employed as the starting material for the synthesis of the pcs. It was first tosylated, then brominated and converted into 4,5-dicyano-*N*,*N*′-ditosyl-*o*-phenylenediamine (**2**).

The synthesis of metal-free pc **3a** from **2** was accomplished through a dilithium pc intermediate followed by a proton-lithium exchange. In the synthesis of **3b** and **3c**, the best yields were obtained by a cyclotetramerization reaction in the presence of the metal salt and 8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) as a strong nitrogen base in *n*-hexanol at reflux of the



Scheme 1 Syntheses of the pc derivatives.

solvent. Silica gel column chromatography was employed to obtain the pure products. The intense green-blue powders were very soluble in a number of solvents such as chloroform, acetone, tetrahydrofuran (THF), ethyl acetate and slightly soluble in benzene, toluene, dimethyl sulfoxide (DMSO), methanol and *N*,*N*'-dimethyl formamide (DMF).

Elemental analysis results and a close investigation of the mass spectra of the intermediates (**1**, **2**) and pcs confirmed the proposed structures. Compound **1** gave $[M]^+$ isotope peaks (at 572, 574, 576) in the ratio 1 : 2 : 1, respectively, because of the presence of two bromine atoms. In the EI mass spectra of the intermediates, fragmentation ion peaks appeared to correspond to the stepwise loss of tosyl and NH groups from the molecules. In the mass spectra of pcs obtained by the relatively soft ES-MS technique, the molecule ion peaks were observed at *m*/*z* 1867 for **3a**, 1924 for **3b** and 1930 for **3c**. Another common point in all pcs mass spectra is the clear appearance of the small dimerization peaks.

Comparison of the IR spectra at each step gave some insights on the nature of the products. In the IR spectrum of **2**, C≡N was responsible for an absorption at 2232 cm^{-1}. This sharp peak disappeared in the IR spectra of pcs. The characteristic vibration of SO_2 groups appeared around 1335 and 1160 cm^{-1} in the spectra of all compounds. For all compounds the two NH groups gave rise to two bands around 3550 and 3235 cm^{-1}: the bands at *ca.* 3550 cm^{-1} correspond to free NH and the lower frequency bands at *ca.* 3235 cm^{-1} arise from the hydrogen-bonded NH.

Geometry optimization of the structure **3a** was done by means of the semi-empirical method AM1 (GAUSSIAN 03W program package) in the gas phase. As shown in Fig. 1, four N–H units were found close to oxygen atoms of neighbouring tosyls. Nitrogen atoms lead to rotation of hydrogen

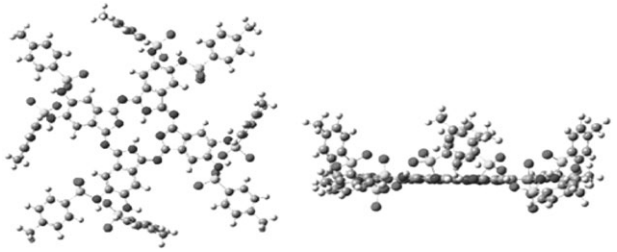


Fig. 1 Molecular structure of metal-free pc **3a**

and tosyl units. In order to form intramolecular hydrogen bonding, two different tosyl groups occured: while four tosyl units were at the pc plane, other four were nearly vertical to pc. This structure was confirmed in the IR and NMR spectra of pcs.

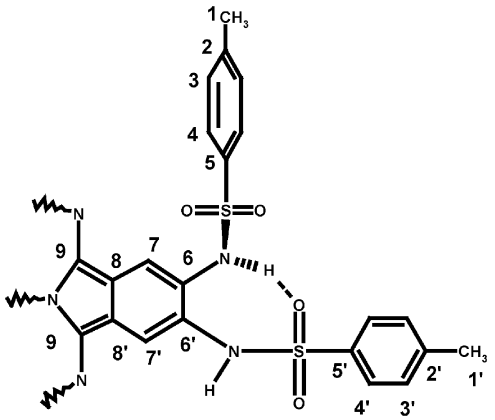
NMR spectra

The NMR spectra of compound **1** provided the characteristic chemical shifts and confirmed the proposed structure. DMSO-d_6 was used as the solvent owing to good solubility. The methyl signal was observed at 2.38 ppm as a singlet. Aromatic CH protons of tosyl units gave two doublets at 7.38 and 7.61 ppm and another aromatic CH proton gave a singlet signal at 7.27 ppm. The disappearance of the broad signal at 9.60 ppm upon addition of D_2O confirmed its attribution to the NH proton. In the ^{1}H NMR spectrum of compound **2** (Table 1) in DMSO-d_6 methyl protons gave a singlet chemical shift at 2.40 ppm. Aromatic protons of tosyl units gave two doublets at 7.40 and 7.70 ppm and other aromatic CH protons gave a singlet signal at 7.55 ppm. When chloroform-d was used as solvent for ^{1}H NMR spectroscopy of compound **2**, methyl protons gave rise to two singlet signals at 2.06 and 2.37 ppm and two NH signals, at 7.49 and 8.50 ppm, disappeared upon deuterium exchange. In the ^{13}C NMR spectra of these two compounds all of the carbon atoms showed the expected chemical shifts, as listed in the Experimental and Table 2.

These spectral data confirmed that compound **2** formed intramolecular hydrogen bonds in chloroform. In general, the formation of hydrogen bonds leads to significant shifts to low field. Hence, in the ^{1}H NMR spectrum of compound **2** in chloroform-d, two hydrogen-bonded and free NH protons appeared at two different chemical shifts. In the case of intramolecular hydrogen bonding, two different types of tosyl units occurred in one molecule: while one was in the same plane as benzene, the other was nearly vertical to it. The methyl protons of two tosyl units had different chemical environments because of the magnetic anisotropy of the benzene.

Figs. 2 and 3 show the ^{1}H and ^{13}C NMR spectra of **3b** in deuterated chloroform and THF. In $CDCl_3$, two NH signals disappeared by deuterium exchange and the ^{1}H–^{15}N HSQC (heteronuclear single quantum coherence) 2D NMR spectrum showed two signals. Table 1 summarizes the ^{1}H and ^{13}C NMR spectral data of **3a–c** in deuterated chloroform and THF. Similar to the nitrile derivative **2**, **3a–c** formed intramolecular hydrogen bonds as confirmed by IR spectroscopy, giving the special shown in Fig. 1. Here one of the NH groups forms a H-bridge with the neighbouring tosyl moiety while the other stays in the free form. Consequently, the chemical environments around the two tosylamido groups are totally different. The ^{1}H NMR spectra of phthalocyanines are known to show large diamagnetic ring current shifts due to the macrocyclic π-system. The signals of aromatic protons of pcs appear at low field. Protons of axially bonded groups show a large shift to higher field.[2,22] In the case of dinitrile derivative **2**, only the methyl protons showed two different chemical shifts. Interestingly, the ^{1}H and ^{13}C NMR spectra of pcs exhibited two sets of

Table 1 ^{1}H NMR spectral data for dinitrile (**2**) and pc derivatives (**3a–c**)



	Solvent	1, 1′	3, 3′	4, 4′	7, 7′	NH	Other
2	$CHCl_3$-d	2.06 (s, 3H)	7.25 (d, 4H)	7.59 (d, 4H)	7.32 (s, 2H)	7.49 (s, 1H)	—
		2.37 (s, 3H)				8.50 (s, 1H)	
2	DMSO-d_6	2.40 (s, 6H)	7.40 (d, 4H)	7.70 (d, 4H)	7.55 (s, 2H)	Not observed	—
3a	$CHCl_3$-d	2.11 (s, 12H)	6.67 (d, 8H)	7.10 (d, 8H)	8.16 (s, 4H)	7.92 (s, 4H)	−3.46 (s, 2H, NH)
		2.93 (s, 12H)	7.79 (d, 8H)	8.04 (d, 8H)	8.80 (s, 4H)	8.89 (s, 4H)	
3b	$CHCl_3$-d	2.13 (s, 12H)	6.69 (d, 8H)	7.09 (d, 8H)	8.05 (s, 4H)	7.90 (s, 4H)	—
		2.90 (s, 12H)	7.76 (d, 8H)	8.00 (d, 8H)	8.67 (s, 4H)	8.82 (s ,4H)	
3b	THF-d_8	2.38 (s, 24H)	7.39 (d, 16H)	7.92 (d, 16H)	9.04 (s, 8H)	9.30 (br, 8H)	—
3c	$CHCl_3$-d	2.19 (s, 12H)	6.71 (d, 8H)	7.15 (d, 8H)	8.25 (s, 4H)	7.99 (s, 4H)	—
		2.97 (s, 12H)	7.82 (d, 8H)	8.08 (d, 8H)	8.85 (s, 4H)	8.86 (s, 4H)	

signals for all protons and carbons except carbon atoms of the pc core in chloroform-d but only one set of signals was observed in THF-d_8. The reason for this is that the benzene ring in **2** possesses a smaller magnetic anisotropic effect than the pc ring of **3a–c**. All carbon signals obtained from ^{13}C (APT) NMR were determined by ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC (heteronuclear multiple bond coherence) 2D NMR techniques (Table 2).

The hydrogen-bonding capability of the solvent is very important in the NMR spectra of these compounds. Chloroform is a weak hydrogen-acceptor solvent so it is not capable of disrupting the intramolecular hydrogen bonds of dissolved molecules. For this reason, when chloroform-d was used as the solvent, the unexpected splitting of almost all bands was observed in the NMR spectra of compounds **2** and **3a–c**. However, THF and DMSO are electron-donor (H-acceptor) solvents so they break up the intramolecular hydrogen bonds of the molecules, thereby leaving all tosyl units in the same chemical environment.

Electron absorption spectra

The blue-green phthalocyanines show typical electronic spectra with two strong absorption bands: an ultraviolet Soret (B) band around 300–350 nm and a visible Q band around 600–700 nm. In the case of metal-free phthalocyanine, the Q band splits into two bands arising from its lower symmetry (D_{2h}) compared with that of metal phthalocyanines (D_{4h}). The splitting of the metal-free phthalocyanine is lost on deprotonation, using a strong base to form the pc^{2-} anion, which also has D_{4h} symmetry.[1,2]

The colour of **3a–c** changed in different solvents. In THF and ethyl acetate they were green, in chloroform, benzene and

Table 2 ^{13}C (APT) NMR spectral data[a] for dinitrile (**2**) and pc derivatives (**3a–c**)

		CH_3	Aromatic CH[b]			Aromatic C[c]					
	Solvent	1, 1′	3, 3′	4, 4′	7, 7′	2, 2′	5, 5′	6, 6′	8, 8′	9	Other
2	$CHCl_3$-d	21.73	130.33	127.50	127.50	145.79	134.29	133.95	112.78	—	114.45 (CN)
2	DMSO-d_6	21.50	130.49	127.36	124.95	144.8	136.31	133.98	110.33	—	115.92 (CN)
3a	$CHCl_3$-d	20.60	128.52	125.96	122.22	142.99	135.82	133.11	135.42	145.10	—
		21.44	130.01	126.26	123.42	145.02	136.07	133.59	135.60		
3b	$CHCl_3$-d	20.61	128.53	125.97	121.46	142.99	135.73	132.71	133.79	145.03	—
		21.41	129.98	126.21	122.62	144.58	135.84	133.60	134.29		
3b	THF-d_8	21.37	129.84	128.13	118.16	144.67	137.08	133.07	134.04	146.04	—
3c	$CHCl_3$-d	20.60	128.45	125.89	121.87	142.80	135.54	132.11	135.06	151.79	—
		21.42	129.89	126.29	123.10	144.88	135.95	133.80	135.76		

[a] Numbering of the atoms as shown in Table 1. [b] Determined by ^{1}H-^{13}C HSQC 2D NMR technique. [c] Determined by ^{1}H-^{13}C HMBC 2D NMR technique.

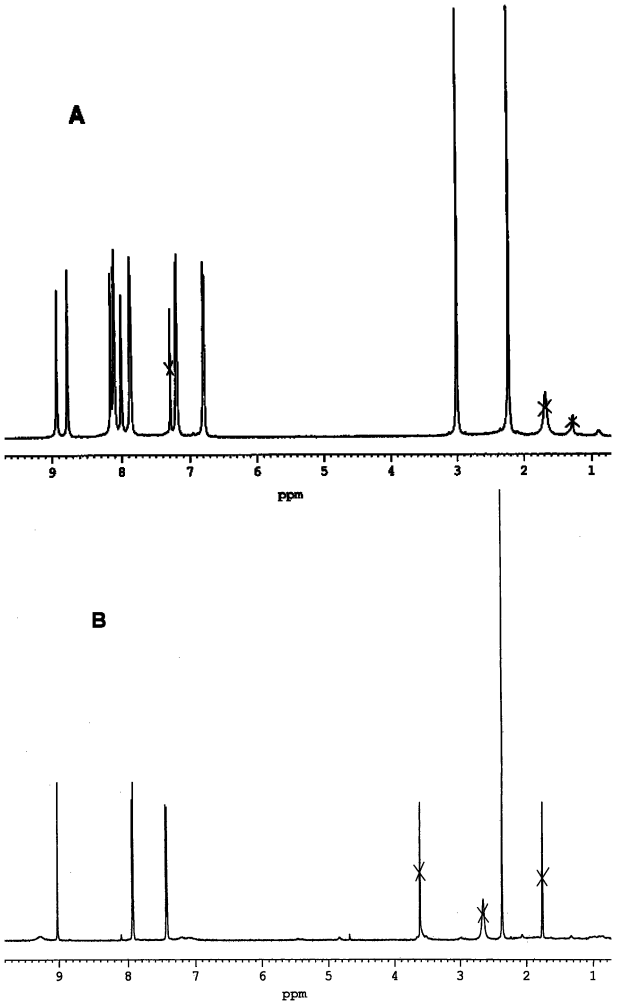


Fig. 2 ^{1}H NMR spectra of **3b** in (A) $CHCl_3$-d and (B) THF-d_8

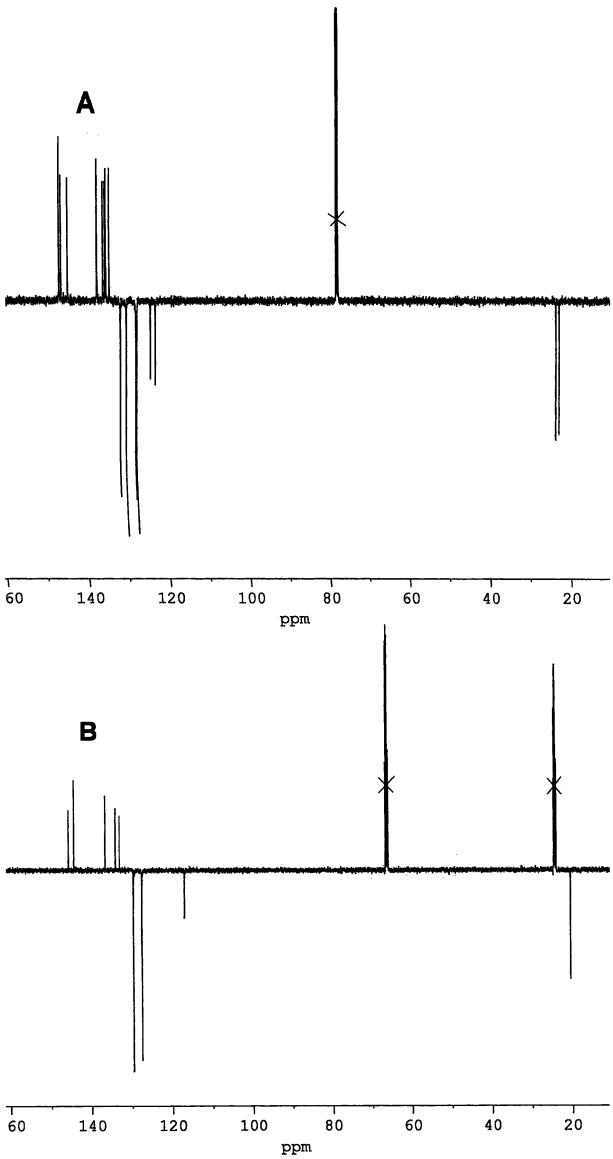


Fig. 3 ^{13}C (APT) NMR spectra of **3b** in (A) $CHCl_3$-d and (B) THF-d_8

toluene blue, and reddish-brown in pyridine, DMF and DMSO. This is demonstrated in Fig. 4, which shows the absorption spectra of compounds **3a–c** in THF, chloroform and DMSO. In the case of THF, metal-free pc **3a** gave a split Q band at 710 and 681 nm as a result of the D_{2h} symmetry. The smaller two bands at shorter wavelengths (at 647 and 615 nm) are vibrational progressions of the Q bands, which usually appear in spectra of metal-free pcs.[23] The nickel(II) pc **3b** and zinc(II) pc **3c** exhibit intense Q bands at 683 and 687 nm, respectively.

Electronic absorption spectra of **3a–c** gave two Q bands in chloroform: a monomeric Q band around 680 nm together with a blue-shifted intense band around 640 nm corresponding to aggregated species. In the case of most pcs, aggregation is closely related to the concentration of the solution; any dilution usually results in lowering the intensity of the higher energy band corresponding to aggregated species, together with a relative increase in the lower energy band of the monomers.[24] When solvents such as chloroform, benzene, toluene and nitromethane were used to obtain the UV-vis spectra of pcs **3a–c**, dilution brought out no appreciable change in the relative intensities of both Q bands and the absorbance values closely followed the Lambert–Beer law. This means that there should be some additional interaction among the pc units, so that they are kept in close contact even at very low concentrations. Taking into account the usual spectra obtained in the case of highly basic solvents (*e.g.*, THF, methanol, acetone, ethyl acetate, 1,4-dioxane), we expect an interaction of the tosylamido groups of neighbouring pc molecules, similar to the intramolecular H-bridge formation shown in Fig. 1.

In the absorption spectra of pcs **3a–c** in DMSO, Q bands were appreciably shifted to the red and also the splitting of the Q band of metal-free pc **3a** disappeared. In addition to the Q and B bands, a relatively weaker and broad new band appeared around 500–550 nm. DMSO is basic enough to deprotonate pcs *via* the NHTs (Ts = tosyl) units, which produces the anionic form and increases the number of lone pair electrons on the nitrogen atoms. When this occurs, the new band around 500–550 nm appears, which is attributable to a n-π* transition. Also, this new band is observed in the deprotonation of pc derivatives in the presence of bases (KOH).

All these spectral changes are a result of the intermolecular solute-solvent interaction forces. The ambitious approach of Catalan *et al.* to quantify solvent effects on electronic absorption spectra includes comprehensive scales of solvent polarity/polarizability (SPP), solvent basicity (SB), and solvent acidity (SA).[25] Table 3 summarizes the Q bands of **3a–c** in various solvents. In our case, solvatochromism is caused by a combination of hydrogen bonding and deprotonation of the NHTs units and it closely depends on the solvent basicity. Fig. 5 shows the relation between the peak wavelength of the Q band maximum of compound **3b** in various solvents on the SB scale.

Deprotonation of pcs was also investigated in basic conditions. The colour of **3a–c** changed upon addition of a base to

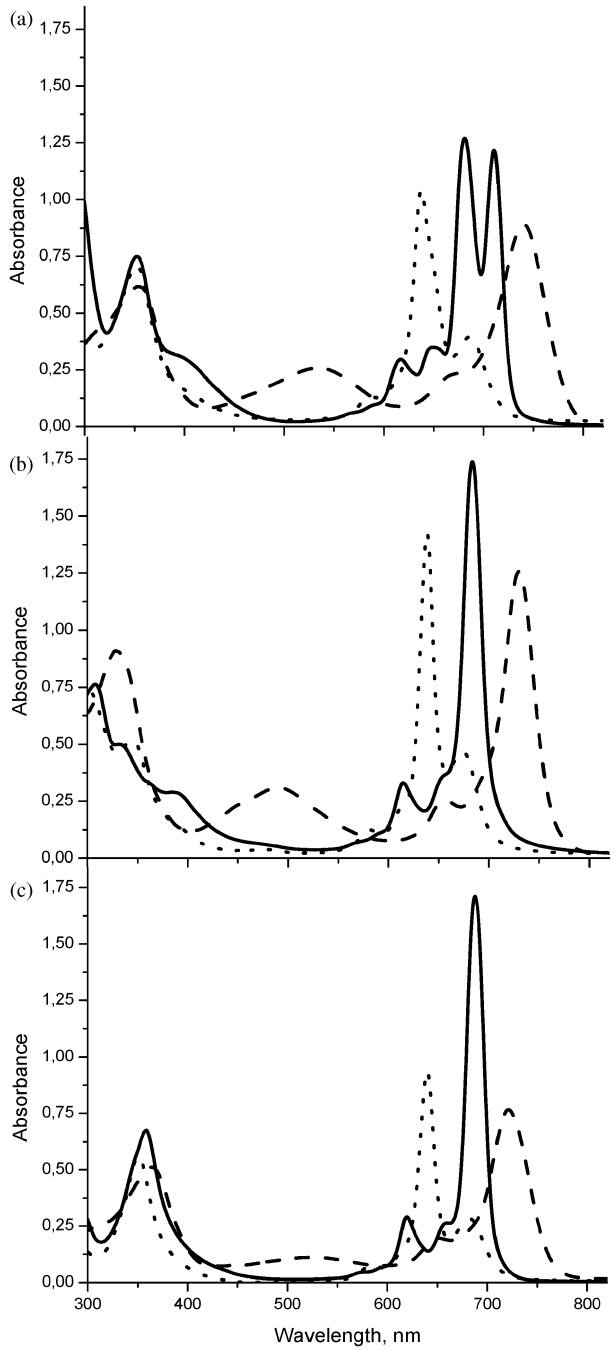


Fig. 4 Electronic spectra of 7.5×10^{-6} M solutions of metal-free pc (**3a**), NiPc (**3b**). ZnPc (**3c**) in THF (—), $CHCl_3$ (···) and DMSO (--).

the THF solutions, from green to red-brown. On the successive addition of an acid to the basic solution, the colour turned back to the original green. This colour change, which is caused by deprotonation of the NHTs units, could be followed by UV spectroscopy. Fig. 6 shows the evolution of the UV spectrum of **3b** upon addition of first KOH (A), then HCl (B). Portionwise addition of KOH (methanol solution) to the THF solution of pc caused a red shift of all bands and the appearance of a new band at around 500 nm. Addition of HCl to this solution reversed this step-by-step back to the original spectrum. In order to eliminate the possibility of any effect of MeOH, blank tests were applied but no appreciable change was observed. The bathochromic shift of the Q band in basic conditions can be attributed to extension of the aromatic π-system of pc owing to deprotonation of the NHTs units. Deprotonation of pcs *via* the NHTs units by treatment with strong bases produces the anionic form. In this case, the lone pair electrons of the

Table 3 Location of the Q bands (in nm) of pc derivatives **3a–c** in different solvents.

Solvent	Solvent basicity (from ref. 25)	**3a**	**3b**	**3c**
Chloroform	0.071	686, 637	673, 638	682, 640
Benzene	0.124	687, 639	674, 639	685, 643
Toluene	0.128	687, 639	673, 639	684, 643
Nitromethane	0.236	681, 637	674, 637	685, 643
1,4-Dioxane	0.444	717	683	688
Acetone	0.475	708, 682	681	686
Ethyl acetate	0.542	708, 678	681	686
Methanol	0.545	710	694	696
THF	0.591	710, 681	683	687
Pyridine	0.581	722	712	710
DMF	0.613	734	727	721
DMSO	0.647	740	730	721

nitrogen atoms expand the delocalized π-system of the pcs, resulting in the Q band shift to the red. The weaker broad absorption band around 500–550 nm is possibly due to an n-π* transition. A similar band (called the W band) has previously been reported for pcs with peripheral alkoxy or alkylthio groups as a broad band with intermediate intensity at *ca.* 400–500 nm and has been assigned to the involvement of ether oxygen or thioether sulfur lone pairs.[26]

When increasing concentrations of HCl was added to THF solutions of **3a** and **3b**, the colour and spectra did not change. But an additional new band was observed at a longer wavelength (at 730 nm) and the intensity of the Q band decreased in the absorption spectrum of ZnPc (**3c**, Fig. 7). In order to eliminate the possibility of any effect of MeOH, a blank test were run but no appreciable change was observed. The formation of this new band, which disappeared upon addition of a base, can be attributed to protonation of the nitrogen atoms of the pc ring. Metallated azaporphyrins have four meso nitrogen atoms, which exhibit basic properties and are able to participate in acid-base interaction with an acid.[27,28] Recently, spectral changes consisting of shifts of the Q band to the red with successive protonation of ZnPc complexes have been reported.[29]

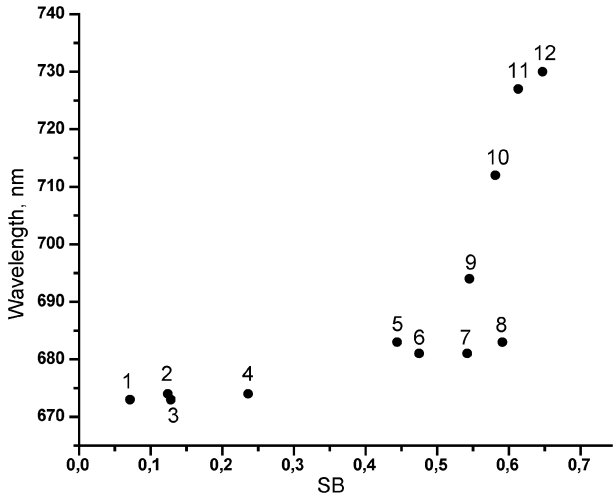


Fig. 5 Variation of the Q band wavelength of NiPc (**3b**) in different solvents with the solvent basicity (SB) value.[25] (1: chloroform, 2: benzene, 3: toluene, 4: nitromethane, 5: 1,4-dioxane, 6: acetone, 7: ethyl acetate, 8: THF, 9: methanol, 10: pyridine, 11: DMF, 12: DMSO.)

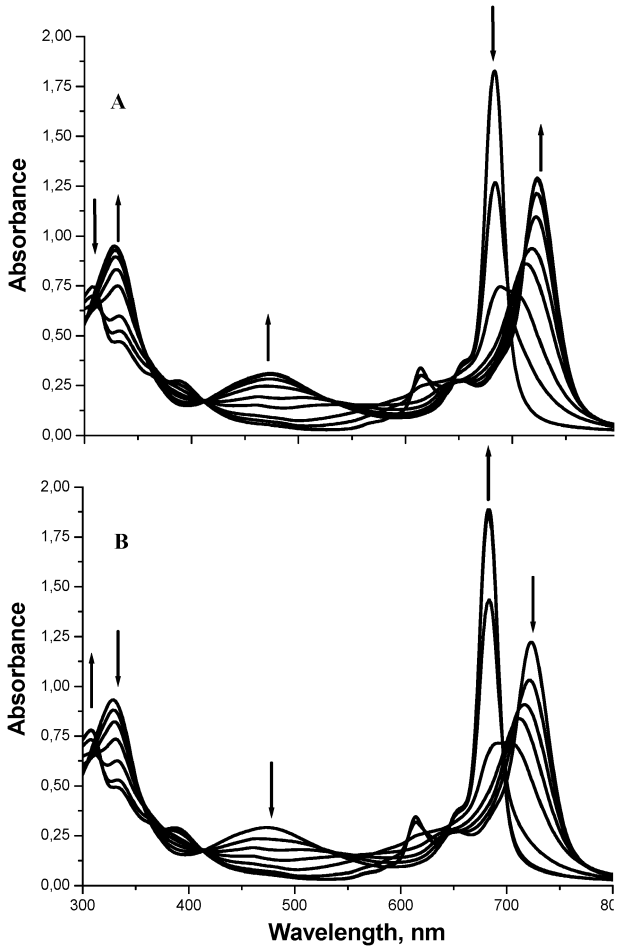


Fig. 6 Spectral changes in a NiPc **3b** solution (3 ml, 7.5×10^{-6} M in THF) upon addition of increasing amounts of KOH in MeOH (2.25×10^{-3} M): 0, 10, 20, 30, 40, 50, 60, 70, 80 µl (A), followed by addition of increasing amounts of HCl in MeOH (2.25×10^{-3} M): 10, 20, 30, 40, 50, 60, 70, 80 µl (B).

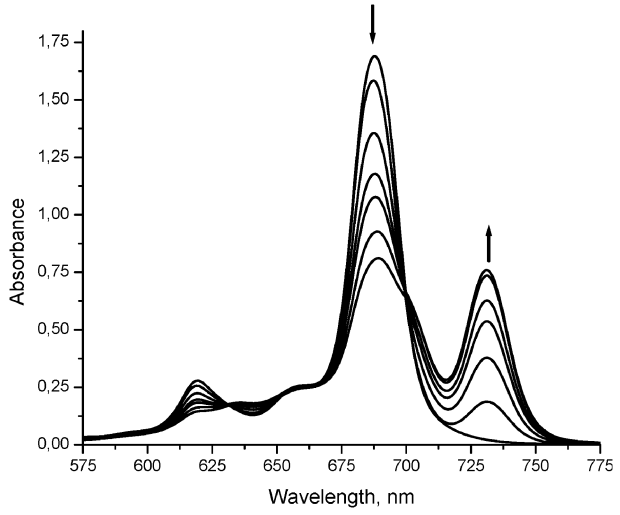


Fig. 7 Absorption spectral changes of zinc pc (**3c**) in THF (3 cm^3, 7.5×10^{-6} M) upon addition of increasing amounts of HCl in MeOH (2.25×10^{-2} M): 0, 8, 16, 24, 32, 40, 48 µl.

Conclusion

In this work, the synthesis of new octatosylamido-substituted metal-free, Ni(II) and Zn(II) pcs were described and the compounds were characterized by standard methods. All proton and carbon atoms, except core carbons, gave two sets of signals in the ^1H and ^{13}C NMR spectra of pcs in chloroform, but only one set in THF. Solutions of **3a–c** showed rapid and reversible colour changes upon addition of a base. Because of the hydrogen bonding and deprotonation of pcs *via* NHTs, these compounds show solvatochromic features. These spectral properties will be developed by modification of the substituents and future investigations will focus on the chemical sensor properties of these compounds.

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