Synthesis, Characterization, and Dielectric Properties of Phthalocyanines with Ester and Carboxylic Acid Functionalities

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Monomeric phthalocyanine pentylester derivatives containing Cu and Zn were synthesized via the cyclotetramerization of 4,5-dipentylphthalonitrile. Conversion of the pentylester derivatives by hydrolysis yielded the octacarboxylic acid phthalocyanine derivatives in high purity, without any contamination by oligomers. The dielectric properties of pressed pellets were investigated as a function of frequency. When exposing the phthalocyanine powders to water vapor, a high increase in the dielectric constant was found for the carboxylic acid derivatives, whereas the esters showed no effect. For Cu containing octacarboxylic acid phthalocyanine derivatives, the low-frequency dielectric constant of the pellets was raised from 12 to $>1 \times 10^5$ when going from a water content of 6.4 to 14.7 wt %, respectively. The concomitant sharp rise in conductivity was attributed to the protons released from the acid groups after water uptake. The present work clearly demonstrates that water uptake and not oxygen is the major factor for achieving surprisingly high dielectric constants in carboxylic acid phthalocyanine derivatives.

Introduction

The search for organic compounds exhibiting high dielectric constants ($\varepsilon > 1 \times 10^3$) has gained considerable attention because of their applicability in electric devices such as actuators, random access memories based on capacitive elements, and gate dielectrics for organic field effect transistors.[1] Since the discovery of the semiconducting property of phthalocyanines (Pc) in 1948 by Eley,[2] these compounds have become one of the most studied organic semiconductors[3] and have found applications in solar cells,[4,5] organic field effect transistors,[6] photovoltaic and fuel cells,[7−9] electroactive polymers,[10,11] and sensors.[12,13] Oligophthalocyanines (o-Pc), where at least one benzene ring is shared by two Pcs, have an extended π-conjugation and show a high ϵ and intrinsic electric conductivity (Scheme 1).[14−16] They became attractive components for actuator technology.[10,11] Often these o-Pcs have a transition metal like Cu, Fe, Co, or Zn as central atom. They are usually synthesized from pyromellitic anhydride (**A**) or 1,2,4,5-tetracyanobenzene (**B**) either in solution or in melt (Scheme 1).[17−21] In addition to the desired oligomers (**C**) consisting of fused Pcs only, the formation of byproduct was reported which contain units of both, Pc and isoindolenine, or triazine (structures not shown). Also, monomeric Pc (**1**) is contained in the mixture. Because of the low solubility of **1** and o-Pcs (**C**), the complex product mixtures could be neither sufficiently separated nor fully characterized.

The structural characterization rests only upon the data from elemental analysis and the IR as well as UV−vis spectra which are typically recorded in concentrated sulfuric acid. Polymerization degrees (P_n) could not be measured by solution techniques, but were rather estimated and are

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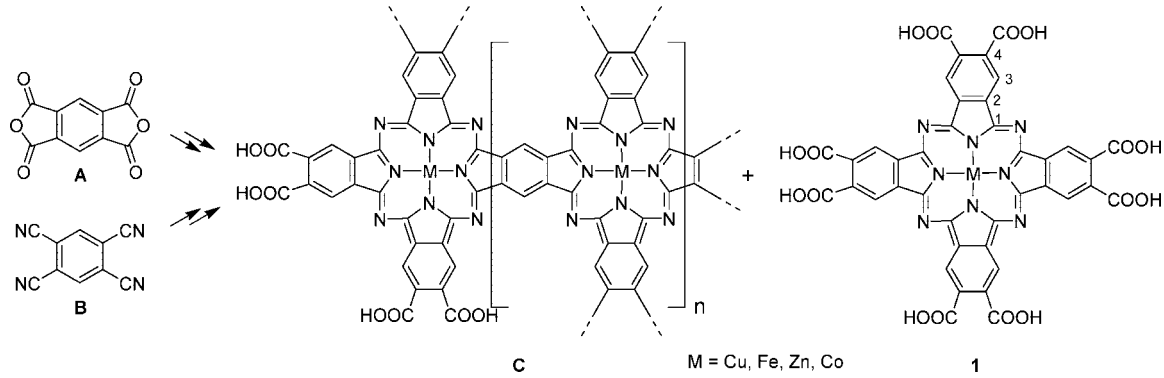
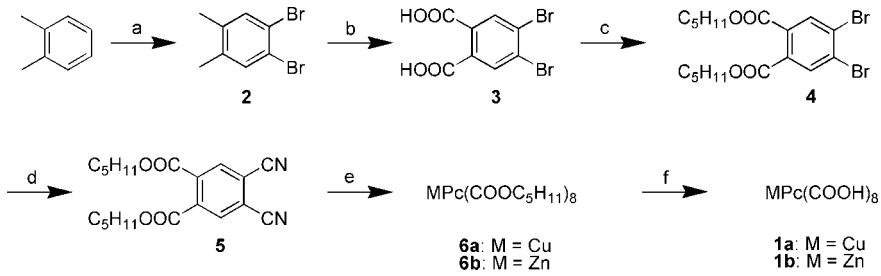
Scheme 1. Commonly Proposed Syntheses of Phthalocyanines Starting from Pyromellitic Anhydride (A) or 1,2,4,5-Tetracyanobenzene (B) Furnishing a Complex Mixture of the Monomeric Pc 1 and Oligomeric Products [o-Pc (C)]



Scheme 2. (a) Br_2, 5−10 °C; (b) $KMnO_4/H_2O$ reflux; (c) pentanol, *p*-toluenesulfonic acid, toluene, reflux, 4 days, or pentanol, $SiCl_4$, 1 day, r.t.; (d) CuCN, DMF, reflux; (e) MCl_2, DBU, pentanol; (f) NaOH/pentanol/H_2O, reflux



therefore to be considered with great care.[22] Because of this unfortunate complexity of products, measured properties could not unequivocally be correlated with a concrete molecular structure. For example, it is not clear which of the factors, extended conjugation, aggregation due to hydrogen bonding, or an unintentional doping by some impurities contributes to the attractively high dielectric constants of $\varepsilon > 1 \times 10^3$ reported.[14−16] In addition, there is scarce information about the reproducibility of the reported ε-values. Impurities capable of doping Pcs may dramatically alter results from one batch to another. So far, no report on the dielectric constant of a monomeric Pc **1** free of any oligomers or defects is available. This is where the present work sets in. It describes a synthetic route to the monomeric Pc **1** that is based on a simple precursor concept avoiding any oligomer formation. The soluble and therefore fully characterizable Pcs **6a** and **6b** were synthesized, and only after their monomeric character and purity were confirmed were they converted into the desired target structures **1a** and **1b** (Scheme 2). The dielectric constant of these phthalocyanines was measured on pellets as a function of frequency and humidity. The results reveal that the ε values strongly depend on water content. A small amount of water contained in the Pcs **1a** and **1b** increases the dielectric constant by several orders of magnitude. The effect of water content on ε at relative humidities (RH) from 0 to 52% and at frequencies from 20 Hz to 1 MHz is reported.

Experimental Section

Materials. All chemicals were purchased from Aldrich and used as received. Solvents were purified and dried by standard procedures. Compounds o-Pcs (**C**),[19,21] **2**,[23] and **3**[24] were prepared according to literature methods. For the known **3**, analytical data are also given because they are not fully available in the literature. Compounds **1a** and **1b** are known[19] but were prepared by a different procedure. Column chromatography was carried out on silica gel 60 (Macherey-Nagel, 0.04−0.063 mm/230−400 mesh) as the stationary phase. Reactions were monitored by thin layer chromatography (TLC) with TLC silica-gel-coated aluminum plates (60 UV254, Macherey- Nagel) and visualized by ultraviolet light (λ = 254 and 366 nm).

Characterization. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance-400 spectrometer (^{1}H: 400 MHz and ^{13}C: 100 MHz at room temperature). MALDI MS spectra were recorded with an IonSpec Ultra Instrument. 2-[(2*E*)-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene] malonitrile (DCTB) and 3-hydroxypyridine-2-carboxylic acid (3-HPA) served as the matrix. MS spectra were obtained on a Bruker Autoflex using electron impact ionization (EI). The thermogravimetric analysis (TGA) was conducted with a Perkin-Elmer TGA7 at a heating rated of 20 °C min^{-1} under a nitrogen gas flow. The TGA-MS investigations were done with a Netzsch STA 409 with QMS 403 C skimmer coupling in a helium/oxygen flow with a heating rate of 10 °C min^{-1}. UV−vis absorption spectra were recorded with a Cary 50 spectrophotometer. FT-IR spectra were taken on a Bio-Rad FTS 6000 spectrometer.

Cyclic voltammetry (CV) measurements were recorded on a PGStat μ30 potentiostat (Autolab) using a standard three electrodes cell (Ar-purged). The working electrode was a rotating glassy carbon electrode (Ø = 0.3 cm), the counter-electrode was a platinum wire, and a water-free double junction Ag/AgCl reference electrode system separated by a ceramic and a sleeve diaphragma was used as reference (Methrom). Electrolyte of the inner system was a 0.1 M tetrabutyl ammonium chloride in acetonitrile, whereas the outer

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system was 0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile. Ferrocene/ferrocenium (Fc/Fc^+) was used as internal reference. A weighted amount of either **6a**, **6b**, **1a**, or **1b** was introduced into the electrochemical cell together with a 0.1 M solution of TBAP in DMSO or DCM and the compounds concentration was 0.5×10^{-3} M. The CV experiments were obtained with sweep rates in the 0.05−0.3 V/s range.

Dielectric constant measurements were done in the frequency range of 20 Hz to 1 MHz using an HP 4284A LCR meter. The amplitude of the probing ac electric signal applied to the samples was 1 V. The dielectric constant was determined from the capacitance $C = \varepsilon\varepsilon_0 A/d$, where A is the area, d is the thickness of the capacitor, and ε_0 is the vacuum permittivity, $\varepsilon_0 = 8.854 \times 10^{-12}$ $C^2\ N^{-1}\ m^{-2}$. The dielectric constants of **1a** and **1b** were measured at different RH. Before use, the samples were dried using a drying agent and are referred to as 0% RH specimens in the following. The humidity was increased from 0 up to 52% RH using the partial water pressure over a saturated aqueous salt solution. Equilibrium was monitored by weight measurements. When the weight no longer changed with time, the sample was considered to be in equilibrium. Pellets were then prepared by pressing at 9 tons (Ø = 13 mm or Ø = 3 mm) and were then covered with silver paste electrodes. All the samples were measured immediately after pellet preparation in order to avoid the changes in the water content.

4,5-Dibromophthalic Acid (3). A suspension of **2** (30 g, 114 mmol) and $KMnO_4$ (73 g, 462 mmol) in water (1000 mL) was heated to reflux for 48 h. The unreacted $KMnO_4$ was reduced with ethanol and the mixture was treated with a 2 N KOH solution to pH 9. After separation of MnO_2 by filtration, the solution was treated with a concentrated hydrochloric acid solution. A white precipitate was formed, filtrated, and washed with water. The compound is slightly soluble in water and well soluble in dimethylsulfoxide. ^{1}H NMR (d_6-DMSO, 400 Hz): δ 8.22 (s, 2 H, benzyl-H); ^{13}C NMR (d_6-DMSO, 100 Hz): δ 126.85 (CBr), 134.69 (C-COO), 135.75 (CH), 166.39 (COO). MS (EI, 80 eV) *m/z* (%): 323.84 (14.09), 307.83 (20.81), 305.83 (42.58), 303.84 (21.97), 154.93 (22.77), 152.93 (22.05), 74.01 (100). Elemental anal. Calcd for $C_8H_4O_4Br_2$ (323.92): C, 29.66; H, 1.24. Found: C, 28.18; H, 1.32.

4,5-Dibromo-dipentylphthalate (4). Route A: A mixture of **3** (7.58 g, 23.4 mmol), p-toluenesulfonic acid (4.02 g, 23.4 mmol), pentanol (100 mL), and toluene (100 mL) was heated to reflux for 4 days, while the water was removed using a Dean−Stark trap. The reaction mixture was neutralized with $NaHCO_3$ solution and washed with water. The phases were separated and the organic phase was dried over $MgSO_4$. The solvent was evaporated and the residue was separated by column chromatography on silica gel using hexane/ethylacetate (95: 5) as eluent to give **4** (5.97 g, 55%) as colorless liquid.

Route B:[25] A mixture of **3** (22.67 g, 70 mmol), $SiCl_4$ (59.5 g, 35 mmol), and pentanol (220 mL) was heated at 80 °C for 1 day. The reaction was allowed to cool to r.t. and triethylamine was added until pH 9 was reached, followed by water (200 mL) and toluene (200 mL). The organic phase was separated, washed with water, and dried over $MgSO_4$. The solvent was removed and the residue purified by column chromatography on silica gel using hexane/ethyl acetate (95:5) as eluent to give **4** (29.2 g, 90%) as a colorless liquid. R_f (hexane/ethylacetate 95:5) = 0.3. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.94 (t, 6H, CH_3), 1.39 (m, 8H, γ-, δ-CH_2), 1.74 (m, 4H, β-CH_2), 4.31 (t, 4H, α-CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.95 (CH_3), 22.31, 28.04, 28.14, 66.45 (O-CH_2), 127.97, 132.48, 133.79, 165.55 (COO). MS (EI, 80 eV) *m/z* (%): 463.99 (3.11), 394.93 (17.28), 308.84 (48.72), 306.84 (100), 304. 84 (50.89). Elemental anal. Calcd for $C_{18}H_{24}O_4Br_2$ (464.19): C, 46.58; H, 5.21; Br, 34.43. Found: C, 46.70; H, 5.27; Br, 34.18.

4,5-Dipentylphthalonitrile (5). A mixture of **4** (21.14 g, 45.56 mmol), CuCN (9 g, 101 mmol), and KI (200 mg) in 300 mL DMF was heated to reflux. The reaction was monitored by TLC and it was quenched after all **4** reacted (4 h). Water (300 mL) was added and the precipitate was isolated by filtration and dried. The residue was then dissolved in dichloromethane and filtered. The solvent was removed and the solid was purified by column chromatography through silica gel using hexane/ethylacetate (8:1) as eluent to give **4** (6.72 g, 41.4%) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.92 (t, 6H, CH_3), 1.37 (m, 8H, γ-, δ-CH_2), 1.74 (m, 4H, β-CH_2), 4.35 (t, 4H, α-CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.76 (CH_3), 22.12, 27.79, 27.91, 67.14 (CH_2−O), 113.91 (CN), 117.91, 133.69, 136.37, 164.02 (COO). MS (EI, 80 eV) *m/z* (%): 356.1 (30.15), 345 (60.29), 339 (64.71), 328.1(100). Elemental anal. Calcd for $C_{20}H_{24}N_2O_4$ (356.42): C, 67.40; H, 6.79; N, 7.86. Found: C, 67.36; H, 6.78; N, 7.84. Monoisotopic mass for $C_{20}H_{24}O_4N_2Na^+$. Calcd: 379.16. Found: 379.10. Special care must be taken when working with CuCN. In contact with acids it emits very toxic hydrogen cyanide gas.

Phthalocyanine 6. A suspension of **5** (2.89 g, 8.10 mmol), MCl_2 (M = Cu, Zn) (2.21 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (609 mg, 4 mmol) in 60 mL of pentanol was refluxed for 1 day. The solvent was evaporated and the solid washed several times with methanol. It was then purified by column chromatography on silica gel using hexane/ethylacetate (7:1) to remove some impurities and then the compound was washed out of the column using dichloromethane/methanol (8:2). The blue fraction was collected and the solvent was removed to give **6** as blue solid.

Phthalocyanine 6a. Yield **6a** (2.7 g, 90%). HR MALDI MS: $C_{80}H_{96}CuN_8O_{16}$: calcd, 1489.21; found, 1489. Elemental anal. Calcd for $C_{80}H_{96}CuN_8O_{16}$ (1489.21): C, 64.52; H, 6.50; N, 7.52. Found: C, 64.23; H, 6.51; N, 7.56. Because of paramagnetic nature of Cu^{2+}, no NMR can be given.

Phthalocyanine 6b. Yield **6b** (2.6 g, 86%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.93 (t, 24H, CH_3), 1.40 (m, 32H, γ-, δ-CH_2), 1.76 (br. m, 16H, β-CH_2), 4.24 (br. m, 16H, α-CH_2), 9.43 (s, 8H, Ph). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.02 (CH_3), 22.39, 28.09, 28.20, 66.60 (CH_2−O), 123.68 (C-2), 132.50 (C-4), 139.67 (C-3), 153.65 (C-1), 168.03 (COO), see Scheme 1. HR MALDI MS: $C_{80}H_{96}N_8O_{16}Zn$: calcd, 1491.05; found, 1492. Monoisotopic mass calcd for $C_{80}H_{97}O_{16}N_8Zn^+$: 1489.6308. Found: 1489.634.

Phthalocyanine 1a and 1b. A solution of **6** (1 g, 0.67 mmol) and 1N KOH in a mixture of pentanol (200 mL) and tetrahydrofurane (20 mL) was refluxed for 10 min. Water (200 mL) was then added and the reaction was refluxed for another 15 min. The reaction is visually indicated by switching of the blue color from the organic to the aqueous phase. The phases were separated, the water phase was treated with an aqueous HCl (5% w/w) to pH 2, and the precipitate formed was filtered off. Because of the relatively high solubility of **1a** and **1b** in water at pH 5, it was impossible to remove the HCl by washing, if not much of the product was to be lost. Further purification was therefore achieved by a dialysis step using a cellulose membrane (ZelluTrans Roth, nominal filter rating 3500) in water, over 1 week. The solid was isolated by letting the water evaporate at room temperature to give **1a** and **1b** as blue solids.

Phthalocyanine **1a.** Yield **1a** (0.6 g, 95%). MS ESI *m/z* (%): 950.2 (12) $[M + Na]^+$, 928.1 (100) $[M + H]^+$, 910.1 (12) $[M - H_2O + H]^+$. Because Cu^{2+} is paramagnetic, no NMR data can be given for this compound. Unfortunately, because compound **1a**

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proved to be highly hygroscopic, no correct elemental analysis could be obtained.

Phthalocyanine **1b.** Yield **1b** (0.6 g, 95%). ^{1}H NMR ($(CD_3)_2SO$, 400 MHz): δ 9.73. ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): δ 123.96 (C-2), 134.83 (C-4), 138.72 (C-3), 151.91 (C-1), 168.77 (COO). MS ESI *m/z* (%): 951 (9) $[M + Na]^+$, 929.1 (100) $[M + H]^+$, 911.1 (13) $[M - H_2O + H]^+$.

Results and Discussions

Synthesis and Characterization. Phthalocyanines **1a** and **1b** were prepared on 3−10 g scale in six steps starting from *o*-xylene in 15% overall yield (Scheme 2). The *o*-xylene was converted to dibromide **2** as previously described[23] and oxidized to the dicarboxylic acid **3** by using $KMnO_4$ in water at reflux for 2 days.[24,26,27] For its esterification two different protocols were compared. First, a mixture of **3**, pentanol, and *p*-toluenesulphonic acid in toluene was heated to reflux for 4 days and the water removed using a water trap. Second, a suspension of **3** and $SiCl_4$ in pentanol was heated to 80 °C for 24 h.[25] Both reactions gave the desired dipentylester **4**; however, the second route required shorter reaction times and gave better yields (90% instead of 55%). In the next step, standard Rosenmund/von Braun-reaction conditions were used to convert the dibromide **4** into the corresponding dinitrile **5** using CuCN.[28] It should be noted that because of **5**'s high reactivity, some of it cyclotetramerized to the phthalocyanine **6a** already during this step. Under prolonged reaction times, compound **4** could even be completely converted into **6a** without isolating the intermediate **5**. Pure **5** could nevertheless be separated by column chromatography. The phthalocyanines **6a** and **6b** were obtained from **5** by cyclotetramerization in presence of DBU and the corresponding metal salt. For the final step, i.e., the conversion of the esters **6a** and **6b** into the carboxilic acids **1a** and **1b**, respectively, the solvent played an important role. When heated to reflux in 1N NaOH/tetrahydrofurane, **6a** and **6b** did not suffer any hydrolysis. By heating these compounds in 1N NaOH/pentanol/tetrahydrofurane at reflux, the conversion is finished in a few minutes, which is visually indicated by the shift of the blue color from the organic to the aqueous phase. To isolate **1a** and **1b**, we lowered the pH of the solution resulting from hydrolysis to 2 by adding aqueous HCl (5% w/w) and filtering off the formed precipitate. Because of the relatively high solubility of **1a** and **1b** in water at pH 5, it was difficult to remove the HCl by washing. This could be nevertheless removed by making a dialysis step in water using a cellulose membrane.

The structure of the products isolated from the tetramerization of **5** and the hydrolysis of **6a** and **6b** were established to be the phthalocyanines **6a** and **6b**, and **1a** and **1b**, respectively, on the basis of mass spectrometric, ^{1}H and ^{13}C NMR, MS, IR, and UV−vis spectroscopic analyses. It should be noted that NMR spectroscopy could only be applied to the nonparamagnetic compounds **6b** and **1b**. The MALDI-TOF mass spectra of compounds **6a** and **6b** shows the expected molecular ions at *m/z* = 1489 and 1491, respectively (see the Supporting Information). The ^{1}H NMR spectrum of **6b** exhibits a singlet at δ 9.43 ppm for the eight aromatic protons (Figure 1a); its ^{13}C NMR spectrum displays 10 signals, consistent with the symmetry of structure **6b** (see ESI). The ^{1}H NMR spectrum of its hydrolyzed product **1b** shows a singlet at δ 9.73 and no signals in the aliphatic region (Figure 1b).

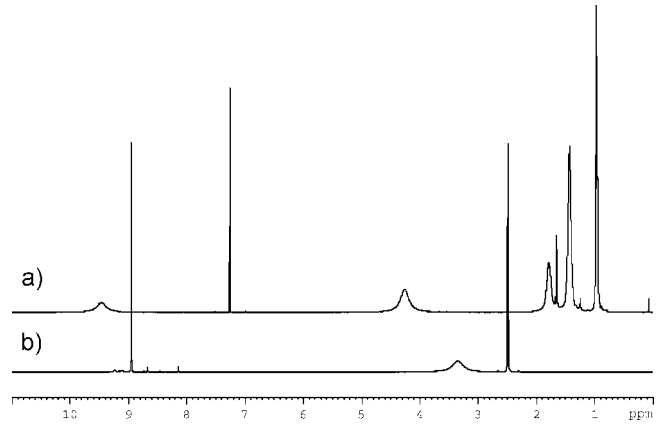

Figure 1. ^{1}H NMR spectra of (a) **6b** ($CDCl_3$) and (b) **1b** in [d_6-DMSO] at room temperature. The signals due to the pentyl group of **6b** have completely disappeared in the spectrum of **1b**.

The absence of aliphatic signals was also observed in the ^{13}C NMR spectrum, which confirms a complete hydrolysis of the ester groups (see ESI). Though NMR spectroscopy could not be applied to **1a**, the fact that it did not contain any residual ester functionality could nevertheless be proven by ESI mass spectrometry. The corresponding spectrum of **1a** as well as that of **1b** shows the molecular ions $[M+H]^+$ at 928 and 921, and $[M+Na]^+$ at 950 and 951, respectively, and no signals at higher masses indicative of any residual ester groups (see ESI). It was also observed that by heating the latter Pcs in vacuum above 40 °C the carboxylic acid function starts to self-condense with formation of anhydride units. This process was easily monitored by IR spectroscopy where increasing signals at 1775 and 1837 cm^{-1} typical of anhydrides were observed. Already by exposing these materials to the humidity of air these anhydrides hydrolyzed completely back to the acids. The UV−vis spectra of **6a** and **6b** display typical features of Pcs with a Soret band at 350 nm and a Q-band at 687 nm, with a weak shoulder at 618 nm (Figure 2).[29] The UV−vis spectra in aqueous NaOH of **1a** and **1b** were similar to that of the corresponding esters. If the UV−vis spectra of Pcs **1a** and **1b** were recorded in conc. H_2SO_4, a solvent typically used for low soluble o-Pcs (**C**), λ_{max} was bathochromically shifted to approximately λ = 750 nm, much the same as was reported for o-Pcs in the same solvent.[17] We also prepared Pc **1** (M = Co) according to the classical procedure,[19,20] which is supposed to yield **1** in a complex mixture with o-Pcs and other compounds (see above). In this case the UV−vis spectrum in H_2SO_4 exhibited another absorption band at λ = 954 nm in addition to the band at λ = 750 nm (see ESI). To our knowledge, such

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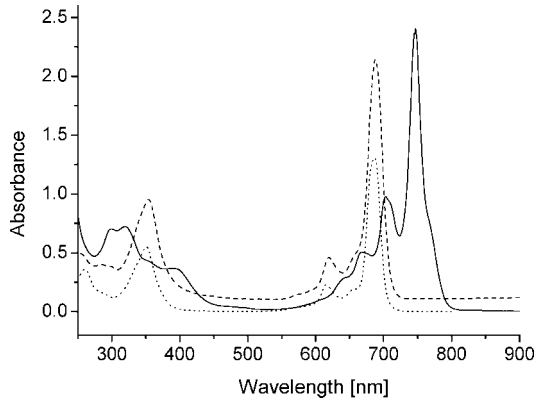

Figure 2. UV−vis spectra of **6a** in CH_2Cl_2 (dotted line), **1a** in aqueous NaOH (dashed line), and **1a** in conc. H_2SO_4 (full line).

absorption has not yet been reported for o-Pcs. In order to get an assignment, the product mixture was analyzed by mass spectrometry. Besides the expected molecular ion at *m*/*z* the ESI-MS also showed a signal at $m/z = 795$ which was proven to be a doubly charged species and thus indicates the presence of a Pc dimer (see ESI). Since no higher oligomers were detected, the λ_{max} at 954 was tentatively assigned to the dimer. This assignment in turn means that the H_2SO_4-soluble part of the o-Pc mixture reported to contain oligomers, does not even have significant amounts of dimer. Increasing bathochromic shifts of o-Pcs with increasing numbers of conjugated Pc units is a well-studied effect.[30] There are reports in the literature according to which this bathochromic shift may be prevented in H_2SO_4 because of a proposed protonation of the phenyl ring that connects the Pc units in o-Pc and thus hinders the conjugation.[22] The $\lambda_{max} = 954$ observed in the present study is in disagreement with this proposal which is also supported by the chemical shifts of the benzene rings under consideration, which indicate a low electron density and, thus, reduced propensity to undergo protonation.[30]

To evaluate the thermal stability of these phthalocyanines, we carried out TGA-MS investigations (Figure 3). This technique was also used to study the decomposition products. The samples were heated from 20 to 600 °C in a helium/oxygen flow with a heating rate of 10 °C min^{-1}. The gases formed during the decomposition were analyzed using a mass spectrometer. Up to 250 °C a total weight loss of 13.5% was observed which was due to loss of water. As can be seen from the gas detection curve in Figure 3, this loss has two different reasons: physically adsorbed water which was set free upon temperature increase and water which was formed by chemical reaction between the carboxylic acid functions resulting in anhydride formation. This latter interpretation is in agreement with the above IR-spectroscopic investigation in which the formation of anhydride units was observed. Above 210 °C compound **1a** started to decarboxylate and CO_2 was detected by the mass spectrometer. Above approximately 330 °C the Pc ring started to decompose which was not further investigated.

Electrochemical Properties. The redox behavior of Pcs **6a** and **6b** as well as **1a** and **1b** was investigated by cyclic voltammetry in DCM and DMSO, respectively, and is illustrated in Figure 4. The half-wave potentials referenced to (Fc/Fc^+) are summarized in table 1. The phthalocyanines **6a** and **6b** exhibited one reversible oxidation and four reversible reduction steps, attributed to ligand-based redox processes.[29] The cyclovoltammogram of **1a** exhibited two reversible reduction waves at $E_{1/2} = -0.91$ and -1.26 V, and a reversible oxidative one at $E_{1/2} = 0.64$ V. The oxidation/reduction behavior of compound **1b** was similar to that of **1a**; however, a reduction wave was also observed at $E_{1/2} = -1.83$ V. The voltammograms could be repeatedly scanned many cycles without a change in the redox characteristics. The electron-withdrawing effect of the carboxylic groups at the periphery decreases the charge density in the phthalocyanine ring and thus shifts the reduction potentials to more positive values as compared to the noncarboxylated Pcs. Similar effects were previously observed for octacyano Zn and Cu phthalocyanines.[31,32]

Dielectric Properties. The dielectric constants of the Pcs **6** and **1** were estimated by measuring the capacitance of a pressed pellet using the sandwich architecture Ag/Pc derivative/Ag in the frequency range of 20 Hz to 1 MHz (see experimental part). Pcs **6a** and **6b** have a small dielectric constant of approximately 9 at all frequencies, as expected from the literature.[33] However, a different behavior was observed for the hydrolyzed Pcs **1a** and **1b**, although their conjugated system is similar to that of **6**. For different batches largely varying ε values were observed. At first glance this may be surprising considering the fact that the Pcs **1a** and **1b** samples contained no oligomers and were also free of other organic impurities. In order to exclude that any remaining traces of HCl may have caused the ϵ values to scatter, the powder samples were thoroughly dialyzed with ultrapure water (see Experimental Section). After this treatment, they showed higher ε values, which were still scattered over a wide range. This raised the suspicion that adsorbed water might be responsible for the widespread of measured values. Therefore, the samples were dried in such a way that anhydride formation was prevented, by exposing them to drying agents at room temperature for one week. These samples recovered after this treatment were considered to have a relative humidity (RH) of 0%. Thereafter, the samples were exposed to different levels of RH at 23 °C. The following RH values (in %) were chosen: RH = 0, 20, 43, and 52. To assess whether the exposure of the samples to these controlled humidity conditions had led to an equilibrium state, their weights were monitored until they reached constant levels. After removal from this controlled atmosphere, the powder samples were immediately pressed into pellets and the dielectric constants measured in air. Thermogravimetric analysis was used in order to determine the water content in the samples exposed to different RH. The powders were heated in a He flow at a rate of 20 °C min^{-1}

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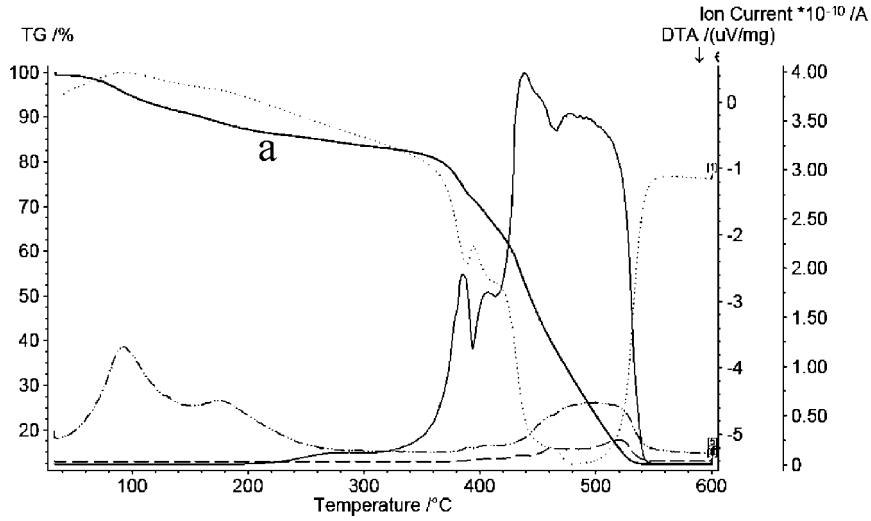

Figure 3. TGA thermogram of **1a** (a) heated at a rate of 10 °C min^{-1} in a helium/oxygen flow. The evolved gases were identified using a MS spectrometer H_2O (dashed dot dot line), CO_2 (full line), NO (dashed line).

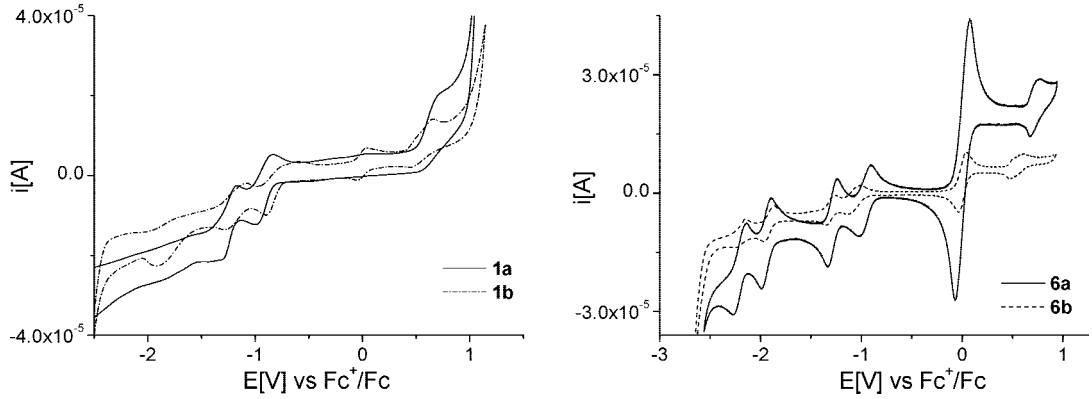

Figure 4. Cyclic voltammograms of **1** and **6** in DMSO and DCM containing 0.1 M TBAP as supporting electrolyte.

Table 1. Half-Wave Redox Potentials of Pc 1a,b (V versus Fc/Fc^+) in DMSO Containing 0.1 M TBAP

compd	$E_{1/2}^{I}$	$E_{1/2}^{II}$	$E_{1/2}^{III}$	$E_{1/2}^{IV}$	$E_{1/2}^{V}$
6a	+0.72	−0.96	−1.29	−1.94	−2.21
6b	+0.54	−1.07	−1.31	−1.92	−2.20
1a	+0.64	−0.91	−1.26		
1b	+0.56	−0.81	−1.18	−1.83	−

from room temperature to 180 °C and kept at this temperature until constant mass was reached (300 min). Because the dried substance was considered to be the anhydride (see TGA-MS), the water content was calculated according to the following formula

$$m_{wet} = m_{acid} + m_{water} = m_{anhydride} + 4M_{water}\frac{m_{anhydride}}{M_{anhydride}} + m_{water} \quad (1)$$

$$m_{water} = m_{wet} - m_{anhydride} - 4M_{water}\frac{m_{anhydride}}{M_{anhydride}} \quad (2)$$

$$c_{water}(\%) = 100\frac{m_{water}}{m_{wet}} \quad (3)$$

where: m_{wet} is the mass after the samples were exposed to different RH, m_{acid} is the mass of dried acid, m_{water} is the mass of adsorbed water, $m_{anhydride}$ is the mass of the samples after heating to 180 °C.

Table 2. Water Content (%) at Different RH

Pc	0% RH	20% RH	43% RH	52% RH
1a	6.4	7.8	9.7	14.7
1b	6.5	9.7	12.3	17.2

The water content at different RH is given in Table 2.

The dielectric response of the Pc's **1a** and **1b** are given in Figures 5 and 6, respectively. At lower frequencies, the dielectric constant increases strongly with increasing water content, exceeding 1×10^5 for compound **1a** having a water content of 14.7% wt, which was kept at 52% RH.

The AC conductivity is given by $\sigma = 2\pi\nu\varepsilon_0\varepsilon''$, where ε'' is the imaginary part of the dielectric constant, ε_0 is the permittivity of vacuum, and ν is the frequency. If the universal response function $\sigma(\nu) = A\nu^s$ is fitted to the measured AC conductivity (Figure 7), a frequency exponent between 0.8 and 0.2 is obtained, depending on the weight percent of adsorbed water.[34,35]

Clearly, a frequency exponent $s < 1$ suggests that non-Debye type relaxation caused by hopping or tunnelling of

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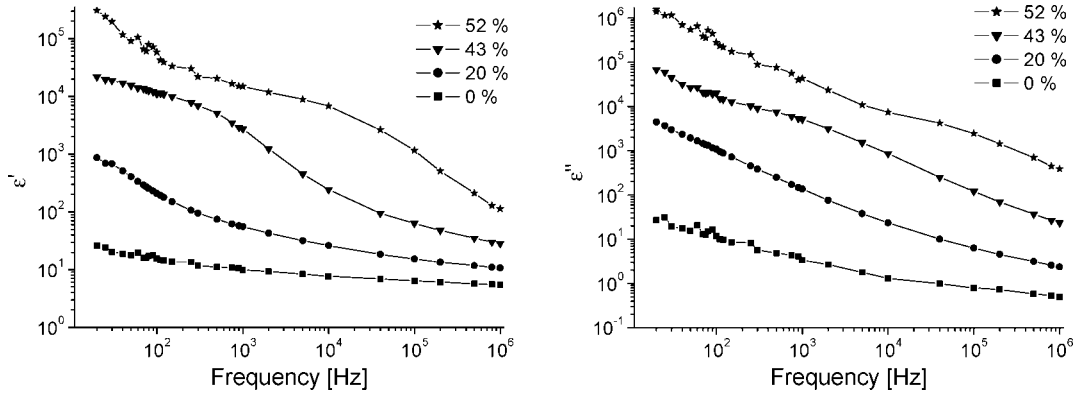

Figure 5. Dielectric constant (left) and dielectric loss (right) of **1a** as function of frequency under different relative humidity conditions and room temperature.

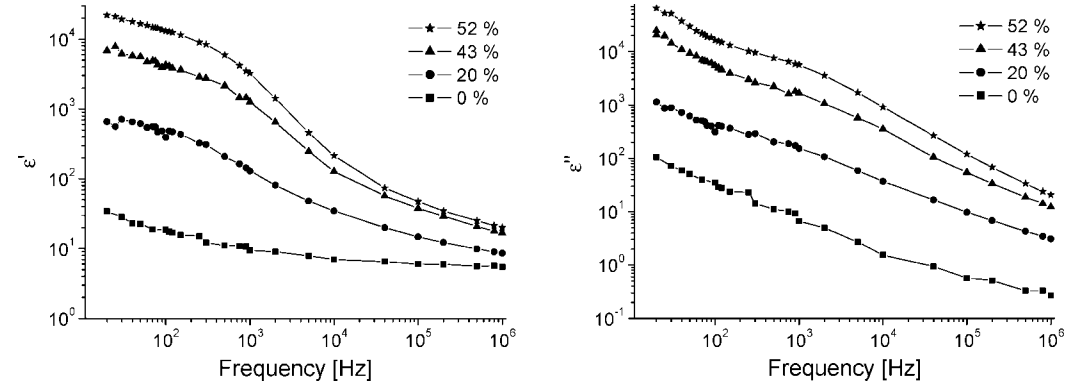

Figure 6. Dielectric constant (left) and dielectric loss (right) of **1b** as function of frequency under different relative humidity conditions and room temperature.

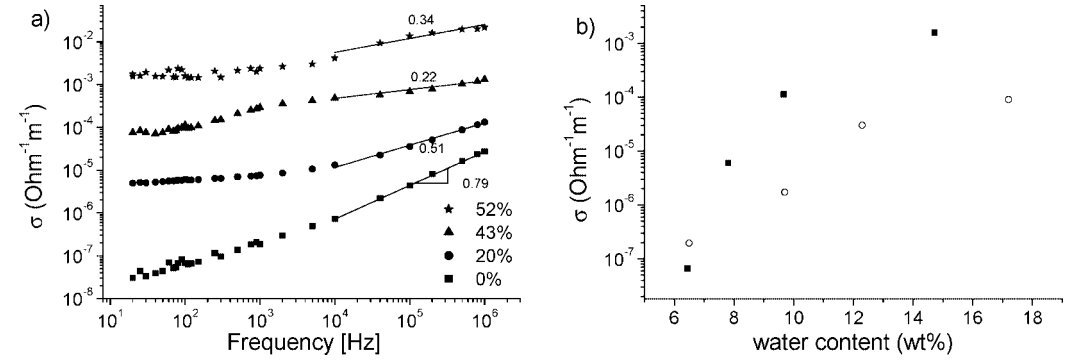

Figure 7. (a) Frequency dependence of the conductivity of **1a** under different relative humidity conditions at room temperature; (b) variation of the conductivity of **1a** (□) and **1b** (●) at 100 Hz with water content.

charges may be relevant for the dielectric response.[36] The trend that *s* decreases with increasing water uptake of the sample is characteristic for a system in which conductivity increases.[37] For all samples that have been exposed to water vapor the dielectric loss function $\varepsilon''/\varepsilon'$ shows a broad peak, which indicates the introduction of a new relaxation mechanism upon water uptake. Such a peak is absent in the dried samples for the investigated frequency range. The effect of water uptake on the dielectric constant and conductivity of organic and in particular biological materials has been given considerable attention.[38] Rosenberg suggested that the dipolar nature of water molecules lead to dielectric screening of electronic charges involved in the conduction.[39] The theory accounts for an exponential increase in the DC conductivity upon water uptake followed by saturation above certain water content. The low frequency conductivity for compounds **1a** and **1b** also shows a superlinear increase with increasing percentage of adsorbed water, and seems indeed to flatten off somewhat within the investigated range of water weight percentage (Figure 7b). Such an effect was also observed for a crown ether substituted lutetium bisphthalocyanine.[40] The hydration of the Pc samples leads to decreased activation energy and therefore to increased conductivity. In any case,

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this would require the presence of charge carriers in the Pc samples. In numerous metal phthalocyanines, oxygen has been shown to induce positive charge carriers due to its oxidizing action.[41] Previous investigations on the intrinsic dielectric properties of o-CuPc (**C**) suggested that the doping effect of oxygen induces giant ε values.[42] However, from the cyclic voltammetry data of compound **1** and **6**, it is clear that the high oxidation and reduction potentials render oxidation by oxygen very unlikely. Therefore, another mechanism operates in the generation and transport of mobile charge carriers. Carboxylic acid groups are ionized by water to an extent determined by their pK_a.[43] We therefore propose that protonic conduction rather than electronic conduction is the mechanism responsible for the giant effect on the dielectric constant induced by water uptake. As water is adsorbed, the carboxylic acid groups of **1a** and **1b** ionize releasing a high concentration of excess protons to the layers of adsorbed water. An increase in the DC conductivity has been explained by a percolation process, involving interconnection of water rich domains.[44] Within these hydrogen-bonded water domains, most efficient proton transport is likely to occur through tunnelling as described by the Grotthus mechanism,[45] which might explain the huge dielectric constants and sharp conductivity increase for carboxylic acid Pc **1** derivatives that have been exposed to water vapor. Further investigations are needed to determine the precise microscopic mechanism and structure.

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Conclusion

Soluble phthalocyanines containing Cu and Zn as central metal and having ester and carboxylic acid functionalities were synthesized. Employing a particular synthetic route these compounds were obtained in high purity, notably in the absence of any oligomeric species. This allowed to scrutinize the dielectric behavior of pellets based on pure materials and to clarify contradicting data in the literature. In particular, it was found that water and not oxygen is the main factor for increasing the dielectric constant upon atmospheric exposure. The dependence of the dielectric constant on the water uptake is striking for the carboxylic acid phthalocyanine derivatives, but is almost absent for the ester derivatives. For the former materials, giant values of the dielectric constant were obtained when the water uptake was substantial. Upon drying, the initial values were restored making these materials attractive for humidity sensing applications. The huge dielectric constants are very likely associated to mobile protons that are released from the carboxylic acid functional groups of the phthalocyanine derivatives. These materials might therefore find application in elastomeric composites for dielectric actuators, but could as well be of interest in proton-conducting fuel cell membranes.

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Supporting Information Available: MALDI-TOF mass spectra of **6a** and **6b**; MS spectra of **1a** and **1b**; ^{13}C NMR spectra of **6b** and **1b**;^{1}H NMR spectrum of **6b**; UV−vis spectra; MS spectrum of a complex mixture obtained from the reaction of PA with $CoCl_2$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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