

Synthesis and QCM gas-sensing properties of 3,4-dialkoxyphenyl tosylamino-substituted phthalocyanines

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Dedicated to Professor Roberto Paolesse on the occasion of his 60th birthday.

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ABSTRACT: Octa-substituted metallophthalocyanines [M = Ni(II), Zn(II), Co(II), and Cu(II)] carrying 3,4-dialkoxyphenyl tosylamino groups at the peripheral positions have been synthesized from 1,2-dicyano-4,5-*bis*[(3,4-dialkoxyphenyl-tosylamino)methyl]benzene in the presence of the corresponding anhydrous metal salt. Next to the metal ion center, the length of the alkyl chains in the dialkoxyphenyl moiety (n = 4, 5, 6, and 12) was varied. In total, sixteen soluble phthalocyanines have been characterized by elemental analysis, FT-IR and ¹H-NMR spectroscopy as well as mass spectrometry. Furthermore, the gas sensing properties of these new compounds have been studied using quartz crystal microbalance transducers. The sensing properties are described on the basis of sensor responses to nine different test analytes comprising volatile organic compounds, toxic gases, and chemical warfare agent simulants. The influence of the metal ion center and substituents on sensor selectivity and sensitivity is discussed. The compounds show good performance in the gas-sensing experiments with diverse responses to the analytes. Phthalocyanine species with pronounced selectivity for polar analytes, hydrocarbons or amines have been identified among the set of sensors with the help of multivariate data exploration methods. The results reveal that quite a high diversity in terms of selectivity is introduced through the minute variations to the phthalocyanine structure.

KEYWORDS: phthalocyanine, gas sensing, QCM, volatile organic compounds, toxic gases, CWA simulants.

INTRODUCTION

Sorption-based chemical sensors are most adequate for gas sensing applications targeting vapors of volatile organic compounds (VOCs) and similar compounds. Generally, for analyte detection and classification several partially selective but complementary sensing materials on a suitable transducer, *e.g.* mechanical, optical or electrical, are combined to form a sensor array. Acoustic devices such as the quartz crystal microbalance (QCM) and surface acoustic wave sensors are attractive transducer technologies for chemical sensor testing and application, as they are easy to use, reliable, and suitable for many types of sensitive materials. The performance of these chemical sensors highly depends on the chemical and physical properties of the sensitive material. A common compound for sensitive sorption layers in chemical gas sensors is phthalocyanines (Pcs). They have proven their excellent sensing capabilities already in many gas sensing applications with acoustic transducers including the QCM [1].

The growing use of phthalocyanines as advanced functional materials has encouraged research on the synthesis of new compounds which differ from one another in the central metal ion or in the peripheral substituents. Since they are usually applied as thin films, soluble derivatives are preferred to allow easy deposition

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or coating from solution. This trivial but important prerequisite has to be considered in the design of new sensitive compounds in addition to the expected sensing properties. This factor restricts the choice of potential substituents, as not all possible compounds have enough solubility in solvents suitable for the coating process.

Unsubstituted Pcs are insoluble in organic solvents, but the solubility can be enhanced by introducing certain functional groups to the peripheral benzene rings of the phthalocyanine structure such as alkyl [2, 3], alkoxy [4,5], alkoxymethyl [6] or poly(oxyethylene) [7,8] groups. Amino-substituted metallophthalocyanine derivatives are found to be promising, since these functional groups are known to enhance solubility and can be modified with different moieties to alter the analyte sorption properties. Such derivatives have been previously synthesized mostly for the preparation of inks, dyes and pigments [9–11]. Tosylamino-substituted phthalocyanines without further substituents were previously studied as gassensing materials with FT-IR spectroscopy and the QCM, providing evidence of many active centers for analyte-Pc interactions [12]. They have also been studied in the liquid phase as sensing materials with total internal reflection ellipsometry [13] and UV-vis spectroscopy [14, 15].

In this work, in total sixteen nickel (NiPc), zinc (ZnPc), copper (CuPc) and cobalt (CoPc) phthalocyanines having tosylamino substituents with 3,4-dialkoxyphenyl moieties of different alkyl chain lengths (n = 4, 5, 6, and 12) are presented and investigated in their gas sensing properties using the QCM. The synthesis and chemical characterization of the new compounds is described. For assessment of the gas sensing performance the sensors have been exposed to nine selected test analytes. The influence of the metal ion center and substituents on sensor selectivity and sensitivity is examined using multivariate sensor data.

EXPERIMENTAL

Chemical characterization

Elemental analyses were obtained using a Thermo Finnigan (now Thermo Fisher Scientific) Flash 1112 instrument. Infrared spectra were recorded on a Perkin Elmer Spectrum BX FT-IR system. ¹H-NMR spectra were recorded in CDCl₃ solution on a Bruker or Varian 500 MHz spectrometer. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) measurements were performed on a Bruker Daltonics MicrOTOF. Positive ion and linear mode MALDI-TOF MS spectra of the compounds were obtained in 2,5-dihydroxy benzoic acid (DHB) or a dithranol MALDI matrix using a nitrogen laser accumulating 50 laser shots.

Phthalocyanine synthesis

Detailed experimental procedures and conditions and the characterization of the compounds 1-4 can be found in

the Supporting information. All intermediate compounds have been purified *via* column chromatography and thoroughly characterized prior to the next reaction step. The procedures for all other compounds including the final phthalocyanines are given below:

Preparation of 1,2-dibromo-4,5-bis[(3,4-dialkoxy phenyl-tosylamino)methyl]benzene (5a-5d). A solution of N-[3,4-bis(dodecyloxy)phenyl]-4-methylbenzenesulfonamide (4a) (16 g, 0.026 mol) in anhydrous DMF (200 ml) containing finely ground anhydrous K₂CO₃ (8.60 g, 0.062 mol) was heated under argon for 1 h at 30-40 °C. A solution of 1,2-dibromo-4,5-bis(bromomethyl)benzene (5.49 g, 0.013 mol) in anhydrous DMF (200 ml) was added dropwise over a period of 1 h. The reaction mixture was stirred under argon at 50-60°C for 5 days. It was then poured into ice water (150 g) and extracted with dichloromethane. The extract was dried over Na_2SO_4 and the solvent was evaporated. Recrystallization from ethanol gave a pure product of white crystals. The compound is soluble in *n*-hexane, chloroform, ethanol, acetone, DMF, and THF. Yield 12 g (62%), mp 80 °C. Found: C 67.00; H 8.35; N 1.88; Anal. calcd for C₈₂H₁₂₆Br₂N₂O₈S₂: C 66.10; H 8.38; N 1.90; IR μ_{max} (cm⁻¹): 2921–2853 (CH₂), 1595, 1511, 1349 (O=S=O), 1164, 1091, 813, 738, 662. ¹H-NMR (CDCl₃), δ (ppm): 7.48–7.47 (d, 4H, Ar-H), 7.29 (s, 2H, Ar-H), 7.23-7.21 (d, 4H, Ar-H), 6.58-6.56 (d, 2H, Ar-H), 6.31 (d, 2H, Ar-H), 6.29 (s, 2H, Ar-H), 4.61 (s, 4H, CH₂), 3.84–3.83 (t, 4H, CH₂-O), 3.67–3.64 (t, 4H, CH₂-O), 2.36 (s, 6H, Tosyl- Ar-CH₃), 1.72–1.69 (p, 4H, CH₂-CH₂-O), 1.64-1.61 (p, 4H, CH₂-CH₂-O), 1.37–1.29 (m, 72H, CH₂), 0.8 (t, 12H, CH₃); MS (FAB), (m/z): 1513 $[M + Na]^+$.

5b, **5c**, and **5d** were synthesized according to **5a**.

5b: Yield 62%, mp 100 °C. Found: C 59.57; H 6.64; N 2.77; Anal. calcd for $C_{58}H_{78}Br_2N_2O_8S_2$: C 60.37; H 6.81; N 2.43; IR, μ_{max} (cm⁻¹): 2949–2868 (CH₂), 1593, 1513, 1345 (O=S=O), 1165, 1090, 851, 813, 714, 658. ¹H-NMR (CDCl₃), δ (ppm): 7.47–7.45 (d, 4H, Ar-H), 7.39 (s, 2H, Ar-H), 7.23–7.19 (d, 4H, Ar-H), 6.58–6.57 (d, 2H, Ar-H), 6.32 (d, 2H, Ar-H) 6.30 (s, 2H, Ar-H), 4.61 (s, 4H, CH₂), 3.86–3.83 (t, 4H, CH₂-O), 3.68–3.65 (t, 4H, CH₂-O), 2.37 (s, 6H, Tosyl-Ar-CH₃), 1.74–1.68 (p, 4H, CH₂-CH₂-O), 1.66–1.60 (p, 4H, CH₂-CH₂-O), 1.27 (m, 24H, CH₂), 0.84 (t, 12H, CH₃); MS (FAB), (m/z): 1177 [M + Na]⁺.

5c: Yield 60%, mp 113 °C. Found: C 58.95; H 6.40; N 2.57; Anal. calcd for $C_{54}H_{70}Br_2N_2O_8S_2$: C 59.01; H 6.42; N 2.55; IR, μ_{max} (cm⁻¹): 2953–2870 (CH₂), 1592, 1511, 1339 (O=S=O), 1163, 1089, 889, 816, 708, 658. ¹H-NMR (CDCl₃), δ (ppm): 7.58–7.56 (d, 4H, Ar-H), 7.39 (s, 2H, Ar-H), 7.32–7.28 (d, 4H, Ar-H), 6.68 (d, 2H, Ar-H), 6.66–6.41 (d, 2H, Ar-H) 6.39 (s, 2H, Ar-H), 4.70 (s, 4H, CH₂), 3.95–3.93 (t, 4H, CH₂-O), 3.77–3.74 (t, 4H, CH₂-O), 2.25 (s, 6H, Tosyl-Ar-CH₃), 1.82–1.79 (p, 4H, CH₂-CH₂-O), 1.78–1.74 (p, 4H, CH₂-CH₂-O), 1.42–1.21 (m, 16H, CH₂), 0.87 (t, 12H, CH₃); MS (FAB), (m/z):1099.

5d: Yield 60%, mp 127 °C. Found: C 57.00; H 6.00; N 2.77; Anal. calcd for $C_{50}H_{62}Br_2N_2O_8S_2$: C 57.44; H 6.17; N 2.68; IR, μ_{max} (cm⁻¹): 2958–2867 (CH₂), 1597, 1511, 1336 (O=S=O), 1166, 1090, 883, 816, 709, 658. ¹H-NMR (CDCl₃), δ (ppm): 7.36–7.34 (d, 4H, Ar-H), 7.17 (s, 2H, Ar-H), 7.13–7.06 (d, 4H, Ar-H), 6.46 (d, 2H, Ar-H), 6.46–6.44 (d, 2H, Ar-H) 6.19 (s, 2H, Ar-H), 4.48 (s, 4H, CH₂), 3.72–3.70 (t, 4H, CH₂-O), 3.56–3.53 (t, 4H, CH₂-O), 2.30 (s, 6H, Tosyl-Ar-CH₃), 1.60–1.54 (p, 4H, CH₂-CH₂-O), 1.51–1.45 (p, 4H, CH₂-CH₂-O), 1.31–1.19 (m, 8H, CH₂), 0.78 (t, 12H, CH₃); MS (FAB), (m/z): 1077 [M + Na + H₂O]⁺.

Preparation of 1,2-dicyano-4,5-bis[(3,4-dialkoxyphenyl-tosylamino)methyl]benzene (6a-6d). 5a (9 g, 6.04 mmol), CuCN (1.66 g, 18.5 mmol), and anhydrous DMF (26 ml) were refluxed and stirred at 175 °C for 9 h under argon. After cooling down to room temperature, the dark brown mixture was poured into 25% aqueous NH₄OH (132 ml) and air was passed through the solution for 24 h. It became dark blue and a reddish brown precipitate formed. The reddish brown precipitate was purified by column chromatography on silica gel with hexane-dichloromethane (5:2 v/v) to obtain a beige product after evaporation. The compound is soluble in *n*-hexane, chloroform, ethanol, acetone, DMF, and THF. Yield 3 g (72%), mp 89 °C. Found: C 73.00; H9.19; N 4.05; Anal. calcd for C₈₄H₁₂₆N₄O₈S₂: C 72.91; H 9.11; N 4.32; IR, μ_{max} (cm⁻¹): 2921–2852 (CH₂), 2233 (C=N), 1595, 1467, 1344, 1165 (O=S=O), 1090, 942, 660. ¹H-NMR (CDCl₃), δ (ppm): 7.55 (s, 2H, Ar-H), 7.48–7.46 (d, 4H, Ar-H), 7.25–7.23 (d, 4H, Ar-H), 6.59–6.57 (d, 2H, Ar-H), 6.32 (d, 2H, Ar-H), 6.32 (s, 2H, Ar-H), 4.81 (s, 4H, CH₂), 3.85-3.83 (t, 4H, CH₂-O), 3.66-3.64 (t, 4H, CH₂-O), 2.38 (s, 6H, Tosyl-Ar-CH₃), 1.77–1.73 (p, 4H, CH₂-CH₂-O), 1.67–1.63 (p, 4H, CH₂-CH₂-O), 1.19 (m, 72H, CH₂), 0.8 (t, 12H, CH₃); MS (FAB), (m/z): 1407 [M + Na]⁺.

6b, 6c, and 6d were synthesized according to 6a.

6b: Yield 64%, mp 120 °C. Found: C 68.17; H 6.53; N 5.57; Anal. calcd for $C_{60}H_{78}N_4O_8S_2$: C 68.90; H 7.52; N 5.35; IR, μ_{max} (cm⁻¹): 2950–2868 (CH₂), 2220 (C=N), 1593, 1513, 1345 (O=S=O), 1165, 1090, 851, 813, 714, 658. ¹H-NMR (CDCl₃), δ (ppm): 7.55 (s, 2H, Ar-H), 7.51–7.46 (d, 4H, Ar-H), 7.25–7.19 (d, 4H, Ar-H), 6.59–6.57 (d, 2H, Ar-H), 6.32 (d, 2H, Ar-H) 6.30 (s, 2H, Ar-H), 4.81 (s, 4H, CH₂), 3.86–3.83 (t, 4H, CH₂-O), 3.66–3.64 (t, 4H, CH₂-O), 2.38 (s, 6H, Tosyl-Ar-CH₃), 1.74–1.68 (p, 4H, CH₂-CH₂-O) 1.66–1.61 (p, 4H, CH₂-CH₂-O), 1.25 (m, 24H, CH₂), 0.8 (t, 12H, CH₃). MS (FAB), (m/z): 1046 [M]⁺.

6c: Yield 75%, mp 135 °C. Found: C 67.75; H 7.10; N 5.70; Anal. calcd for $C_{56}H_{70}N_4O_8S_2$: C 67.86; H 7.12; N 5.65; IR, μ_{max} (cm⁻¹): 2931–2869 (CH₂), 2234 (C=N), 1674, 1594, 1510, 1346 (O=S=O), 1231, 1160, 857, 812, 706, 660. ¹H-NMR (CDCl₃), δ (ppm): 7.63 (s, 2H, Ar-H), 7.57–7.54 (d, 4H, Ar-H), 7.34–7.28 (d, 4H, Ar-H), 6.68–6.67 (d, 2H, Ar-H), 6.41 (d, 2H, Ar-H), 6.40 (s, 2H, Ar-H), 4.90 (s, 4H, CH₂), 3.77–3.74 (t, 4H, CH₂-O),

3.51–3.49 (t, 4H, CH₂-O), 2.47 (s, 6H, Tosyl-Ar-CH₃), 1.83–1.80 (p, 4H, CH₂-CH₂-O), 1.75–1.72 (p, 4H, CH₂-CH₂-O), 1.23 (m, 16H, CH₂), 0.96 (t, 12H, CH₃). MS (FAB), (m/z): 1077 [M]⁺. 3

6d: Yield 62%, mp 148 °C. Found: C 66.75; H 6.60; N 5.90; Anal. calcd for $C_{52}H_{62}N_4O_8S_2$: C 66.78; H 6.68; N 5.99; IR, μ_{max} (cm⁻¹): 2959–2869 (CH₂), 2236 (C=N), 1592, 1510, 1334 (O=S=O), 1165, 1090, 857, 816, 708, 658. ¹H-NMR (CDCl₃), δ (ppm): 7.64 (s, 2H, Ar-H), 7.58–7.47 (d, 4H, Ar-H), 7.49–7.47 (d, 4H, Ar-H), 6.60– 6.58 (d, 2H, Ar-H), 6.38–6.32 (d, 2H, Ar-H) 6.24 (s, 2H, Ar-H), 4.89 (s, 4H, CH₂), 3.96–3.94 (t, 4H, CH₂-O), 3.78–3.75 (t, 4H, CH₂-O), 2.47 (s, 6H, Tosyl-Ar-CH₃), 1.79–1.72 (p, 4H, CH₂-CH₂-O), 1.71–1.70 (p, 4H, CH₂-CH₂-O), 1.47 (m, 8H, CH₂), 0.97 (t, 12H, CH₃); MS (FAB), (m/z): 957 [M + Na]⁺.

Preparation of the nickel phthalocyanines (7a-7d). **6a** (0.500 g, 3.6 10^{-4} mol) and anhydrous NiCl₂ (0.116 g, 9.03 10^{-4} mol) were refluxed in dry quinoline (1.5 ml) and stirred at 170°C for 5 h. After cooling to room temperature, the reaction mixture was treated with ethanol (60 ml) and then the crude product was washed with water and ethanol to remove the unreacted organic material. The green product was dried with diethyl ether and purified by column chromatography (silica gel, 5:2 v/v; *n*-hexane:CH₂Cl₂). The compound is soluble in *n*-hexane, chloroform, DMF, and acetone. Yield 0.050 g (10%), mp > 200 °C. Found: C 71.01; H 8.95; N 3.92; Anal. calcd for C₃₃₆H₅₀₄N₁₆NiO₃₂S₈: C 72.14; H 9.04; N 4.00; IR, µ_{max} (cm⁻¹): 2921–2852 (CH₂), 1595, 1511, 1460, 1345, 1259, 1132 (O=S=O), 1090, 941, 860, 660. ¹H-NMR (CDCl₃), δ (ppm): 9.20 (s, 8H, Ar-H), 7.64– 7.47 (d, 16H, Ar-H), 7.35-7.19 (d, 16H, Ar-H), 6.71-6.69 (d, 8H, Ar-H), 6.59-6.55 (d, 8H, Ar-H) 6.32 (s, 8H, Ar-H), 5.33 (s, 16H, Ar-CH₂-N), 3.85–3.83 (t, 16H, CH₂-O), 3.72–3.61 (t, 16H, CH₂-O), 2.42 (s, 24H, Tosyl-Ar-CH₃), 1.74–1.70 (p, 16H, CH₂-CH₂-O), 1.65–1.62 (p, 16H, CH₂-CH₂-O), 1.19 (m, 288H, CH₂), 0.80 (t, 48H, CH₃); MS (FAB), (m/z): 5592 [M]⁺.

7b, 7c, and 7d were synthesized according to 7a.

7b: Yield 10%, mp > 200 °C. Found; C 68.00; H 7.45; N 5.27; Anal. calcd for $C_{240}H_{312}N_{16}NiO_{32}S_8$: C 67.85; H 7.40; N 5.28; IR, μ_{max} (cm⁻¹): 2926–2858 (CH₂), 1595, 1511, 1467, 1342, 1258, 1158 (O=S=O), 1090, 1017, 940, 810, 706, 660. ¹H-NMR (CDCl₃), δ (ppm): 9.01 (s, 8H, Ar-H), 7.54–7.52 (d, 16H, Ar-H), 7.20–7.19 (d, 16H, Ar-H), 6.56–6.54 (d, 8H, Ar-H), 6.46–6.44 (d, 8H, Ar-H), 6.40 (s, 8H, Ar-H), 5.21 (s, 16H, Ar-CH₂-N), 3.71 (t, 16H, CH₂-O), 3.53–3.51 (t, 16H, CH₂-O), 2.28 (s, 24H, Tosyl-Ar-CH₃), 1.60–1.57 (p, 16H, CH₂-CH₂-O), 1.52–1.49 (p, 16H, CH₂-CH₂-O), 1.39 (m, 96H, CH₂), 0.90 (t, 48H, CH₃); MS (FAB), (m/z): 4246 [M]⁺.

7c: Yield 12%, mp > 200 °C. Found: C 66.85.; H 7.00.; N 5.57; Anal. calcd for C₂₂₄H₂₈₀N₁₆NiO₃₂S₈: C 66.87; H 7.02; N 5.57; IR, μ_{max} (cm⁻¹): 2930–2870 (CH₂), 1595, 1509, 1467, 1343, 1259, 1160 (O=S=O), 1090, 945, 811, 706, 660. ¹H-NMR (CDCl₃), δ (ppm): 9.23 (s, 8H, Ar-H), 7.76–7.64 (d, 16H, Ar-H), 7.56–7.34 (d, 16H, Ar-H), 6.79–6.77 (d, 8H, Ar-H), 6.27–6.63 (d, 8H, Ar-H) 6.42 (s, 8H, Ar-H), 5.43 (s, 16H, Ar-CH₂-N), 3.94–3.89 (t, 16H, CH₂-O), 3.76–3.70 (t, 16H, CH₂-O), 2.40 (s, 24H, Tosyl-Ar-CH₃), 1.65–1.59 (p, 32H, CH₂-CH₂-O), 1.28 (m, 64H, CH₂), 0.94 (t, 48H, CH₃); MS (FAB), (m/z):4023 [M]⁺.

7d: Yield 16%, mp > 200 °C. Found: C 65.70.; H 6.55; N 5.90; Anal. calcd for $C_{208}H_{248}N_{16}NiO_{32}S_8$: C 65.75; H 6.58; N 5.90; IR, μ_{max} (cm⁻¹): 2930–2871 (CH₂), 1595, 1508, 1465, 1342, 1258, 1162 (O=S=O), 1091, 1026, 937, 811, 706, 660. ¹H-NMR (CDCl₃), δ (ppm): 9.19 (s, 8H, Ar-H), 7.75–7.73 (d, 16H, Ar-H), 7.42–7.40 (d, 16H, Ar-H), 6.76–6.74 (d, 8H, Ar-H), 6.66–6.64 (d, 8H, Ar-H), 6.62 (s, 8H, Ar-H), 5.42 (s, 16H, Ar-CH₂-N), 3.70–3.68 (t, 16H, CH₂-O), 3.68–3.66 (t, 16H, CH₂-O), 2.50 (s, 24H, Tosyl-Ar-CH₃), 1.62–1.55 (p, 16H, CH₂-CH₂-O), 1.55–1.48 (p, 16H, CH₂-CH₂-O), 1.28 (m, 32H, CH₂), 0.9 (t, 48H, CH₃); MS (FAB), (m/z): 3799 [M]⁺.

Preparation of the zinc phthalocyanines (8a-8d). **6a** (1.35 g, 9.75 10^{-4} mol) and anhydrous Zn(OAc)₂ $(0.045 \text{ g}, 2.46 \text{ } 10^{-4} \text{ mol})$ in dry quinoline (0.9 ml) were heated and stirred at 170 °C for 5 h. After cooling to room temperature, the reaction mixture was treated with ethanol (60 ml) and then the crude product was washed with water and ethanol to remove the unreacted organic material. The green product was dried with diethyl ether and purified by column chromatography (silica gel, 1:20 v/v; MeOH:CH₂Cl₂). The compound is soluble in *n*-hexane, chloroform, DMF, and acetone. Yield 0.070 g (10%), mp > 200 °C. Found: C 71.70; H 9.00; N 4.23; Anal. calcd for C₃₃₆H₅₀₄N₁₆O₃₂S₈Zn: C 72.05; H 9.07; N 4.00; IR, μ_{max} (cm⁻¹): 2920–2851 (CH₂), 1596, 1560, 1466, 1343, 1231, 1133 (O=S=O), 1090, 940, 810, 673. ¹H-NMR (CDCl₂), δ (ppm): 9.50 (s, 8H, Ar-H), 7.55–7.50 (d, 16H, Ar-H), 7.48–7.29 (d, 16H, Ar-H), 6.59–6.57 (d, 8H, Ar-H), 6.55-6.51 (d, 8H, Ar-H) 6.36 (s, 8H, Ar-H), 5.42 (s, 16H, Ar-CH₂-N), 3.85–3.80 (t, 16H, CH₂-O), 3.66–3.58 (t, 16H, CH₂-O), 2.38 (s, 24H, Tosyl-Ar-CH₃), 1.74–1.67 (m, 32H, CH₂-CH₂-O), 1.19 (m, 288H, CH₂), 0.8 (t, 48H, CH₃); MS (FAB), (m/z): 5602 [M]⁺.

8b, 8c, and 8d were synthesized according to 8a.

8b: Yield 12%, mp > 200 °C. Found: C 67.00; H 7.35; N 5.00; Anal. calcd for $C_{240}H_{312}N_{16}O_{32}S_8Zn$: C 67.74; H 7.39; N 5.27; IR, μ_{max} (cm⁻¹): 2934–2853 (CH₂), 1596, 1504, 1344, 1230, 1158 (O=S=O), 1090, 811, 756, 660. ¹H-NMR (CDCl₃), δ (ppm): 9.28 (s, 8H, Ar-H), 7.70–7.61 (d, 16H, Ar-H), 7.36–7.25 (d, 16H, Ar-H), 6.66 (d, 8H, Ar-H), 6.56–6.55 (d, 8H, Ar-H) 6.36 (s, 8H, Ar-H), 4.88 (s,16H, Ar-CH₂-N), 3.83–3.80 (t, 16H, CH₂-O), 3.66–3.64 (t, 16H, CH₂-O), 2.38 (s, 24H, Tosil-Ar-CH₃), 1.71–1.61 (m, 32H, CH₂-CH₂-O), 1.21 (m, 96H, CH₂), 0.8 (t, 48H, CH₃). MS (FAB), (m/z):4252 [M]⁺.

8c: Yield 11%, mp > 200 °C. Found: C 66.80; H 7.00; N 5.55; Anal. calcd for C₂₂₄H₂₈₀N₁₆O₃₂S₈Zn: C 66.87; H 7.02; N 5.57; IR, μ_{max} (cm⁻¹): 2930–2868 (CH₂), 1595, 1507, 1468, 1344, 1229, 1156 (O=S=O), 1090, 811, 660. ¹H-NMR (CDCl₃), δ (ppm): 8.47 (s, 8H, Ar-H), 7.78–7.49 (d, 16H, Ar-H), 7.32–7.15 (d, 16H, Ar-H), 7.05–6.87 (d, 8H, Ar-H), 6.52–6.45 (d, 8H, Ar-H) 6.37 (s, 8H, Ar-H), 4.03 (s, 16H, Ar-CH₂-N), 3.98–3.97 (t, 16H, CH₂-O), 3.67–3.62 (t, 16H, CH₂-O), 1.49 (s, 24H, Tosil-Ar-CH₃), 1.41–1.36 (m, 32H, CH₂-CH₂-O), 1.28 (m, 64H, CH₂), 0.9 (t, 48H, CH₃). MS (FAB), (m/z): 4029 [M]⁺.

8d: Yield 12%, mp > 200 °C. Found: C 65.60; H 6.55; N 5.80; Anal. calcd for $C_{208}H_{248}N_{16}O_{32}S_8Zn$: C 65.63; H 6.57; N 5.88; IR, μ_{max} (cm⁻¹): 2928–2857 (CH₂), 1595, 1507, 1469, 1341, 1232, 1160 (O=S=O), 1090, 811, 570, 660. ¹H-NMR (CDCl₃), δ (ppm): 8.35 (s, 8H, Ar-H), 7.75–7.49 (d, 16H, Ar-H), 7.30–7.15 (d, 16H, Ar-H), 6.90–6.75 (d, 8H, Ar-H), 6.55–6.45 (d, 8H, Ar-H) 6.35 (s, 8H, Ar-H), 4.25 (s, 16H, Ar-CH₂-N), 3.95–3.90 (t, 16H, CH₂-O), 3.70–3.65 (t, 16H, CH₂-O), 1.45 (s, 24H, Tosil-Ar-CH₃), 1.40–1.35 (m, 32H, CH₂-CH₂-O), 1.25 (m, 32H, CH₂), 0.85 (t, 48H, CH₃). MS (FAB), (m/z): 3963 [M + DHB (matrix)]⁺.

Preparation of the copper phthalocyanines (9a-9d). A mixture of **5a** (0.500 g, 2.62 10⁻⁴ mol), CuCN (0.060 g, 6.81 10⁻⁴ mol) and 1-methyl-2-pyrrolidone (0.2 ml) was heated and stirred at 177 °C under argon for 5 h. After cooling to room temperature, the reaction mixture was treated with NaCN to precipitate the blue product and filtered. The product was washed several times successively with hot water, hot ethanol, hot methanol and then with diethyl ether. The green product was purified by column chromatography (silica gel, 1:20 v/v; MeOH:CH₂Cl₂). The compound is soluble in n-hexane, chloroform, acetone, DMF, and THF. Yield 0.040 g (10%), mp > 200 °C. Found: C 71.61; H 9.00; N 3.9; Anal. calcd for C₃₃₆H₅₀₄CuN₁₆O₃₂S₈: C 72.00; H 9.07; N 4.00; IR, µ_{max} (cm⁻¹): 2921–2852 (CH₂), 1595, 1511, 1344, 1232, 1162 (O=S=O), 1017, 941, 800, 660. MS (FAB), (m/z): 5609 [M]⁺.

9b, 9c, and 9d were synthesized according to 9a.

9b: Yield 12%, mp > 200 °C. Found: C 67.00; H 7.20; N 5.04; Anal. calcd for $C_{240}H_{312}CuN_{16}O_{32}S_8$: C 67.77; H 7.39; N 5.27; IR, μ_{max} (cm⁻¹): 2928–2857 (CH₂), 1595, 1507, 1341, 1238, 1162 (O=S=O), 1090, 920, 811, 706, 660. MS (FAB), (m/z): 4257 [M]⁺.

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9d: Yield 10%, mp > 200 °C. Found: C 65.65; H 6.50; N 5.80; Anal. calcd for $C_{208}H_{248}CuN_{16}O_{32}S_8$: C 65.67; H 6.57; N 5.89; IR, μ_{max} (cm⁻¹): 2957–2870 (CH₂), 1595, 1506, 1470, 1341, 1258, 1160 (O=S=O), 1090, 937, 809, 706, 660. MS (FAB), (m/z): 3804 [M]⁺.

Preparation of the cobalt phthalocyanines (10a– 10d). 6a (1.40 g, 1.01 mmol), anhydrous CoCl_2 (0.033 g, 2.49 10^{-4} mol), and ethylene glycol (5.2 ml) were heated and stirred at 175 °C for 5.5 h. After cooling to room temperature, the reaction mixture was treated with ethanol to precipitate the blue product and filtered. The product was washed several times successively with hot water, hot ethanol and purified by column chromatography (silica gel, 1:20 v/v; MeOH:CH₂Cl₂). The compound is soluble in *n*-hexane, chloroform, acetone, and THF. Yield: 0.140 g (10%), mp > 200 °C. Found: C 71.70; H 9.00; N 4.00; Anal. calcd for $C_{336}H_{504}CoN_{16}O_{32}S_8$: C 72.13; H 9.08; N 4.00; IR, μ_{max} (cm⁻¹): 2921–2852 (CH₂), 1594, 1511, 1343, 1231, 1090 (O=S=O), 1090, 940, 660. MS (FAB), (m/z): 5619 [M + Na]⁺.

10b, **10c**, and **10d** were synthesized according to **10a**. **10b**: Yield 12%, mp > 200 °C. Found: C 67.50; H 7.40; N 5.20; Anal. calcd for $C_{240}H_{312}CoN_{16}O_{32}S_8$: C 67.92; H 7.41; N 5.28; IR, μ_{max} (cm⁻¹): 2927–2858 (CH₂), 1595, 1510, 1343, 1232, 1160 (O=S=O), 1091, 920, 811, 660. MS (FAB), (m/z): 4248 [M]⁺.

 $\label{eq:solution} \begin{array}{l} \mbox{10c: Yield 13\%, mp} > 200 \ ^{\circ}\mbox{C. Found: C 66.80; H 7.00;} \\ \mbox{N 5.50.; Anal. calcd for: $C_{224}H_{280}\mbox{CoN}_{16}\mbox{O}_{32}\mbox{S}_8$: C 66.87; H $7.01; $N 5.57; $IR, μ_{max} (cm^{-1})$: $2926\mbox{-}2860$ (CH_2)$, 1595, 1509, 1343, 1259, 1160 (O=S=O)$, 1094, 944, 809, 660. MS (FAB)$, (m/z): 4023 [M]^+. } \end{array}$

10d: Yield 10%, mp > 200 °C. Found: C 65.70; H 6.40; N 5.90; Anal. calcd for: $C_{208}H_{248}CoN_{16}O_{32}S_8$: C 65.75; H 6.58; N 5.90; IR, μ_{max} (cm⁻¹): 2930–2871 (CH₂), 1595, 1558, 1507, 1345, 1233, 1158 (O=S=O), 1090, 937, 811, 660. MS (FAB), (m/z): 4244 [M+2 Dithranol(matrix)]⁺.

Sensor preparation and test procedures

AT-cut QCMs with a fundamental frequency of 10 MHz (Klove B.V., NL) were used as transducers. Solutions of the sensitive materials were prepared by dissolving the Pcs (1 mg per 1 ml solvent) in analytical grade chloroform or acetone. The solution was then sprayed on the electrodes of a QCM using a jet-spray system. During the coating process the frequency of the QCM was monitored online and coating of the electrode was ceased at a frequency shift of 11 kHz per side.

The gas streams containing the analyte vapors were generated from thermostatted bubblers (at -10 °C) with synthetic air as carrier gas. The gas stream was then diluted with pure air to achieve the desired vapor concentration at a constant total flow rate (200 ml/min). Flow rates of all channels are controlled by computer-driven mass flow controllers (Sierra Instruments, NL). Typical experiments consist of repeated exposure to analyte vapor (1200 s) and subsequent purging with pure air (1200 s) to reset the baseline.

The sensing materials were characterized using the VOCs acetonitrile (ACN, 945–4720 ppm), *n*-heptane (*n*C7, 385–1930 ppm), *n*-propanol (*n*PrOH, 130–655 ppm), toluene (TLN, 245–1210 ppm), tetrachloroethylene (TCE, 145–730 ppm), triethylamine (Et3N, 70–720 ppm) as well as the CWA simulants di(propylene glycol) methyl ether (DPGME, 4–19 ppm) and dimethyl methylphosphonate (DMMP, 0.3–3 ppm) and the fumigant and historical CWA chloropicrin (CP, 20–205 ppm). All solvents used

to produce the vapors were of high purity and used as obtained from the manufacturer. The VOCs were selected to represent common chemical classes and to cover a wide range of chemical properties as expressed in their linear solvation energy relationship (LSER) parameters [16]. The LSER parameters of the test analytes can be found in the Supporting information. During the measurements, the temperature of the sensor chamber was kept at 22 °C at all times. The sensors were prepared and tested in duplicate and the measurements were repeated at least once to assess reproducibility and repeatability.

Hierarchical cluster analysis (HCA) and principal component analysis (PCA) were performed with the help of the R statistical programming language and the FactoMineR package (V1.41) on the sensor response data after normalization and centering. For HCA, Euclidian distance was used as a dissimilarity measure and cluster linkage was based on the averaging method.

RESULTS AND DISCUSSION

Synthesis and characterization

The Pcs under investigation are unique in their substituents having a 3,4-dialkoxyphenyl tosylamino moiety which is attached to the Pc at peripheral positions *via* methylene groups. To create a manifold of sensing materials, the alkyl group has been varied from *n*-butyl to *n*-dodecyl and the inner hydrogen atoms of the Pc core replaced by four different metal ions. In this way, sixteen different octa-substituted phthalocyanine derivatives have been obtained.

The code numbers for the individual compounds specify metal type (NiPc 7, ZnPc 8, CuPc 9, CoPc 10) and alkyl chain type (*n*-dodecyl **a**, *n*-hexyl **b**, *n*-pentyl **c**, *n*-butyl **d**). The full list of materials and their identification codes are given in Fig. 1.

A common method of Pc synthesis is to start with the substituted phthalonitrile (compounds 6a-6d) obtained from the dibromide (5a-5d) as shown in the scheme of Fig. 1. The phthalonitrile was prepared in several steps as follows: First, the 1,2-dialkyloxybenzenes (1a-1d) were prepared using a reaction of catechol in absolute DMF in the presence of potassium carbonate with the respective 1-bromoalkane. In the next step, a nitro group was introduced to the aromatic system using 65%-HNO₃ and then reduced to the amine using palladium-activated charcoal. The N-[3,4bis(alkyloxy)phenyl]-4-methylbenzenesulfonamide (4a–4d) were synthesized in anhydrous pyridine using *p*-toluenesulfonyl chloride. Then, 1,2-dibromo-4,5-bis(bromomethyl)benzene was added to 4a-4d in anhydrous DMF in the presence of anhydrous potassium carbonate to obtain the 1,2-dibromo-4,5bis[(3,4-dialkoxyphenyl-tosylamino)methyl]benzenes (5a–5d) [17]. The phthalonitriles (6a–6d) were obtained



Fig. 1. Scheme of the synthetic pathway for the preparation of the substituted phthalonitriles **6a–6d** and the final phthalocyanines **7a–7d** to **10a–10d**

in a reaction with CuCN and anhydrous DMF by stirring at an elevated temperature of 175 °C. The reaction product was poured into 25% aqueous NH₄OH and air was passed through the solution for 24 h. The Pc metal ion complexes **7a–7d**, **8a–8d**, and **10a–10d** of nickel, zinc and cobalt were produced in a cyclotetramerization reaction in a high boiling anhydrous solvent (*e.g.* quinoline or ethylene glycol) from the corresponding anhydrous metal salt. **5a–5d** were converted into the CuPcs **9a–9d** directly through their reaction with CuCN in 1-methyl-2-pyrrolidone.

Column chromatography with silica gel was used to obtain the pure products from the reaction mixtures. The intense green-blue Pcs are very soluble in a number of solvents such as chloroform, acetone or dichloromethane.

In the IR spectra, a confirmation of successful phthalocyanine formation from the phthalonitrile is the disappearance of the sharp and intense C=N vibration at 2220 cm⁻¹. Other than that, the spectra of the Pcs are similar to those of **4a–4d**, **5a–5d**, and **6a–6d** including the characteristic vibrations corresponding to the tosyl moieties at around 1160 and 1340 cm⁻¹ and CH₂ vibrations around 2880 cm⁻¹ [18].

In the ¹H-NMR spectra of the NiPcs (7a-7d) and ZnPcs (8a-8d), the aromatic protons of the Pc core appear at 9.50 and 8.35 ppm as singlets and those of

the tosyl groups appear as two doublets at around 7.64 and 6.42 ppm. Methylene protons (Ar-CH₂-N) appear as singlets around at 5.33-4.03 ppm. Tosyl Ar-CH₃ appears as a singlet at around 2.50-2.28 ppm. The observed sharp peaks indicate that the bulky peripheral substituents prevent aggregation [19]. However, peaks in the spectra of **9a–9d** and **10a–10d** are very broad due to the paramagnetic Cu(II) and Co(II) ions.

General gas sensing properties

The QCM sensors prepared with the sixteen Pc metal complexes were studied in their responses to vapors of nine test analytes to evaluate the gas sorption and sensing properties of the new materials. In Fig. 2 (top) the transient responses of two QCMs coated with 8a measured in parallel during exposure to vapors of TCE, *n*C7, CP, and ACN in five increasing concentration steps alternating with analyte-free carrier gas are depicted as a typical example for the performance of the sensitive compounds. Generally, the gas-sensing characteristics of the compounds in terms of baseline stability, response and recovery times, and repeatability are good. Equilibrium responses and a full recovery of the baseline are easily reached within the 20 min exposure window and consecutive purging phase. The sensor responses increase with increasing analyte concentration.



Fig. 2. Transient responses of two QCM sensors with 8a during exposure to vapors of TCE, *n*C7, ACN, and CP (top) and sensor response curves for all test analytes (bottom). Next to the analyte label, the slope of the best fit line to the data as the sensor sensitivity (in Hz/ppm) and *r*2 values are included

The graph in Fig. 2 (bottom) illustrates the obtained response curves of the two sensors with the same sensitive material to all test analytes. The two specimens were repeatedly measured under the same conditions. To better compare the responses to analytes of very different saturation vapor pressures, relative concentrations $p_i/p_{i,0}$ are used, where p_i is the actual analyte vapor pressure and p_{i0} is the saturation vapor pressure of the respective analyte at measurement temperature. The responses increase linearly with concentration and no saturation effects can be observed in the arranged vapor pressure ranges. The responses of the sensors vary notably in their magnitude for the different analytes. For all compounds and analytes the sensitivities span a range of 0.5 Hz/ ppm for TCE and CP to around 0.006 Hz/ppm for the analyte ACN. The DMMP and DPGME sensitivities are an order of magnitude higher and reach values between 2 and 13 Hz/ppm and 1 and 3 Hz/ppm, respectively. All sensitivity values are for valid for the used 10 MHz QCM with a total of 22 kHz of coating.

The gas-phase-sensitive material partition coefficient K is a good descriptor of the performance of a sensitive material, as it describes the degree of enrichment of an analyte in the sensitive material independent of transducer sensitivity and other factors such as layer thickness. It is defined as the ratio of the concentration of a chemical compound in the sorbent phase and the gas phase. High K values represent a high number of absorbed molecules



Fig. 3. Heatmap of relative (indicated by colors) and absolute partition coefficient values (grey numbers) for all sixteen Pcs grouped by substituent. Green color and red color indicate positive and negative deviation from the respective NiPc reference (three levels for deviations larger than 50, 25, and 5%, respectively)

in the sensitive layer and are an indicator of high sensor responses. From the sensor sensitivity as the slope of the best fit line to the response data the partition coefficients K were calculated as previously reported [20]. The full list of partition coefficients of the compounds obtained in the gas exposure experiments in dry air is given in Fig 3. The values span a wide range from 220 for ACN to 6 000 for DPGME, while the values for DMMP are between 24000 and 157000. Among all tested materials, the NiPcs **8a**, **8b**, and **8d** show the highest overall responses and partition coefficients.

The Pcs in the K matrix of Fig. 3 are grouped by the substituent in four blocks to illustrate the influence of the central metal ion. The respective NiPc is chosen as reference for each block. The colors indicate relative deviations of the individual K values from the reference: green color indicates a higher K, whereas red color a lower K than the NiPc reference. The influence of the metal ion center is different for the four substituents and is found to depend on the analyte, as well. In the case of Pcs with the substituent **b** and **d**, metal ion centers other than Ni produce higher K values, whereas in the case of Pcs with a and c substituents the opposite is true, as in most cases the partition coefficients for the NiPcs 7a and 7c are the highest. Even though the change of the metal ion center is known to be an effective way to alter the sorption properties of Pcs [21], the resulting effect is strongly dependent on the substituents, as shown by the results. The same metal ion center can introduce a decrease and increase in sensitivity in an unpredictable way for a certain analyte when different substituents are attached to the Pcs. Consequently, the sorption preference and accordingly the sensor selectivity of a Pc after change of central metal ion cannot be anticipated.

The chain length of the substituents is the other influential parameter to change the sensor response characteristics of the Pcs. Figure 4 illustrates the chain length dependency of the partitioning for Pcs having the same metal ion center. The plot depicts the relative partition coefficient for all analytes for each sensing material relative to the respective compound with the substituent **a**. Mostly, a decrease in K with decreasing



Fig. 4. Heatmap of relative (indicated by colors) partition coefficients for all sixteen Pcs grouped by metal ion center. Green color and red color indicate positive and negative deviation from the respective reference (Pcs with substituent **a**). The data is encoded in three levels for deviations larger than 50, 25, and 5%, respectively

chain length was observed. However, as for the metal center influences, there is no general rule.

Previously, Kilinc *et al.* reported that sensor response decreased with increasing the length of the alkyl chain for a group of Pcs in conductive sensors in some cases. However, no general relationship between sensor response and the length of alkyl chain could be established [22]. As the substituents used in this work are chemically very similar to each other, other factors than chemical properties of the substituents seem to play a role in the sorption. Thus, not only chemical interaction aspects [12, 23], but also sterical effects are thought to be influential [24].

Selectivity and sorption preferences

Some general observations can be obtained by inspection of the individual data, but the sensors' analyte preferences and selectivities can only be evaluated in detail using multivariable exploratory techniques, especially as the results have shown that the effects of metal ion centers and substituents are rather unsystematic. Accordingly, all sensitive compounds as a whole have been characterized with HCA and PCA. Based on the sensor responses, these methods allow exploration of similarities or dissimilarities among the individual sensitive materials and show the sorption preferences of individual sensors in comparison to the other materials. The selected analyte molecules have miscellaneous, very diverging physical and chemical properties, e.g. polarity can range from very polar to non-polar, and the molecules are capable of different chemical interactions such as van-der-Waals forces (permanent dipole-dipole interactions and induced dipole interactions, London forces), π - π interactions, and hydrogen bonding. The relevant analyte-sensitive materials interactions can be expressed with five LSFR parameters: the hydrogen-bond parameters α_2 and β_2 , the dispersion parameter logL₁₆ as well as parameters for dipolarity and polarizability π_2 and R_2 . The most dominant parameters for Et3N are logL₁₆ and β_2 , for DMMP π_2 , β_2 , and logL₁₆, for ACN π_2 and β_2 , and for *n*PrOH α_2 and β_2 . For both TLN and TCE the dominant parameters are $logL_{16}$ and R_2 , whereas *n*C7 has only a value for $\log L_{16}$.

In HCA the sensitive materials are clustered or separated according to their analyte responses, taking into account the whole sensor space (not a projection onto 2D as PCA), but the method does not give information on the actual similarities/dissimilarities between the resulting clusters. Potential preferences for any analytes are not disclosed. On the other hand, PCA does not directly provide a measure for the distance between data points and clusters as HCA, but illustrates well the relative positions in a 2D space and illustrates the sorption preferences of the materials in the space defined by the selected test analytes. Materials located in PCA in the same direction from the origin might appear



Fig. 5. Results of the hierarchical cluster analysis of the normalized and centered sensor data



Fig. 6. PCA biplot of loadings and scores for all sensors. Some sensor labels near the origin are omitted for clarity. The unlabeled sensors are part of the large group near 8a and 10c

in HCA in different subclusters, but are very similar in their sensing properties. Normalization eliminates concentration effects, but at the same time also saturation vapor pressure and molecular weight influences.

In Fig. 5, the result of HCA is depicted in a typical tree diagram. The data are separated in three: one main cluster with all but two materials which may be further divided into several subclusters and two compounds, namely **8b** and **8d**. The latter are fairly different from each other and the other sensors. In the main cluster the sensors **8a**, **9a**, **9d** and **10d** are quite distinct from the remaining sensors. It can be noted that the Pcs with the substituent **c** (**8c**, **9c**, **7c**, and **10c**) have the smallest diversity.

In Fig. 6, the PCA result is presented in a biplot of loadings and scores. The ellipses around clusters represent a 95% confidence region around the cluster mean (represented by open squares). The first two principal components contain about 77% of the total variance. In the PCA plot, dissimilar analytes are clearly separated from each other, whereas similar compounds *e.g.* TLN and TCE are close to each other. Similarity and dissimilarity is related to their preferred interactions with the sensitive materials as described above.

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The preferences of the sensor materials can be elucidated adequately in a projection onto two dimensions. All four compounds having the same substituent c but different metal centers form a close group, whereas Pcs with the substituent \mathbf{a} (7–10 \mathbf{a}) are located nearby, but notably separated from each other. In the case of the Pcs with the substituents **b** and **d**, one member of the two groups is quite different from the others. The large cluster located near the origin contains the compounds 7d, 9d, 10d as well as 7b, 9b, and 10b, but not the NiPcs 8b and 8d. While the former six compounds show few specific features in term of selectivity, the latter two are quite distinct sensor materials having pronounced selectivity for DMMP/ Et3N and polar compounds, respectively. The results show that a high degree of diversity can be introduced through a simple variation in the substituent, *i.e.* the alkyl chain length, and by changing the metal ion center. A small set of Pcs selected among the sixteen compounds shows enough variety to be allow for classifing the various analytes in a sensor array set-up. Only very similar analytes such as TCE and TLN cannot be separated easily.

The biplot in Fig. 7 is produced using only compounds identified as the most distinct in HCA and PCA. The compounds **8a**, **8b**, **8d**, and **9a** were found to have the highest diversity in their sorption preferences. The PCA result is nearly identical to the one obtained using all sensors. The possible use of other sensors, *e.g.* **7a** for **9a**, produces similar results, while the addition of more sensors was found to not improve the result.



Fig. 7. PCA using only selected sensors showing the best separation of the analytes in two dimensions

CONCLUSIONS

The synthesis of nickel, zinc, copper, and cobalt 3,4-dialkoxyphenyl tosylamino substituted phthalocyanines having alkyl chains of different lengths (n = 4, 5, 6 and 12) for the use in chemical gas sensors as sensitive compounds was achieved. The new compounds are characterized in their gas sensing properties with the QCM using selected test analyte including VOCs and CWA simulants. In a systematic approach, a total of 16 compounds have been tested in order to allow discussion of metal ion center and substituent effects on the gas sorption properties.

The Pcs exhibit generally good gas-sensing properties, as the observed responses to the analytes are high, with short response and recovery times. The QCM results reveal notable variations in the sensor responses and selectivity as a consequence of the alterations made to the substituents and Pc center. Even simple and minute variations, such as variations in the alkyl chain length on the substituent, are observed to have a large, but irregular, influence on the sensing characteristics of the compounds. The produced Pcs are diverse enough in their sensing properties to distinguish the analytes in a sensor array set-up. However, a general trend with carbon chain length is not apparent, as the effects depend much on the metal ion center, as well. Further studies including computational and experimental methods are needed to separate chemical and sterical factors that are influential in the gas sorption process in order to obtain a more systematic protocol in the search for new sensing materials with selectivity and sensitivity required for an envisaged application field.

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Supporting information

Synthesis and characterization of the compounds and LSER parameters of the test analytes are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

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