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Influence of different transition metals in phthalocyanines on their interaction energies with volatile organic compounds: an experimental and computational study

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Abstract Experimental partition coefficients were determined for a series of volatile organic compounds (VOCs) (acetonitrile, *n*-butylamine, *n*-octane tetrachloroethene, and toluene) for the interaction with 2,3,9,10,16,17,23,24-octakis(octyloxy)-phthalocyaninato complexes, $\text{PcM}(\text{OR})_8$, with varying central metal atoms [$\text{M}=\text{H}_2$ (metal-free), Ni, Pd, Cu, Zn]. Large partition coefficients for toluene were observed in the case of the nickel and palladium phthalocyanines, whereas for the corresponding zinc-containing compound, interaction with *n*-butylamine resulted in a high value for the partition coefficient. Interaction energies for model coordination complexes were obtained at the ab initio LMP2/ LACVP* level of theory. The interaction of various small volatiles with the various $\text{PcM}(\text{OR})_8$ compounds was studied using the PM3 semiempirical Hamiltonian. Large values for interaction energies correspond to particularly strong partition coefficients, suggesting that coordination of the volatiles to the central metal dominates over the often discussed π -system stacking at the $\text{PcM}(\text{OR})_8$'s.

Keywords Chemical sensor · Phthalocyanine · Intercalation · Interaction energy

Introduction

Among various research topics and industrial applications, phthalocyaninato metal compounds (PcMs) have been studied for their use as sensor coatings in chemical-sensing devices. For a bibliographic compilation see, e.g., [1]. Their high chemical stability, caused by the aromaticity and

the high symmetry of the molecule, is very advantageous for gas-sensing applications. Another reason why PcMs are attractive for sensor applications is the variety of reversible interactions they exhibit toward target molecules. Because of their dense electron clouds, they interact with analyte molecules by strong dipolar attraction forces. Additionally, varying the metal atom allows coordinative interaction with small analytes. Some target molecules will possibly interact by a combination of these interaction forces. For this reason, it would be highly interesting to determine energies for the interaction of PcMs with different metal centers with various gases. Based on these findings, a better understanding of the driving forces for preferential hosting of gases will be gained.

Looking at earlier attempts to utilize PcMs as sensor coatings, there have been three main approaches and corresponding synthetic routes: Early PcM coatings were built from simple, i.e., nonsubstituted, molecules, which could be evaporated onto sensor substrates. The films obtained consisted of closely packed columns with a very short gap between the column-forming molecules, only 3.35 Å for example in the case of β -PcCu. [1] The gas molecules only enter surface interactions with these kinds of phthalocyanines [2]. Usually, the surface absorbency of the gases is indicated by (chemical) resistors, which transform the number of adsorbed molecules into electric signals. Appropriate computational approaches toward determining resistances are quite complex because of intricate contributions of the surface for semiconducting materials. Conductivity is influenced by morphology, particle size, and a lively surface chemistry resulting from humidity. Small impurities inside the bulk act as dopants and influence the electron mobility. Compact reviews concerning these research activities are given in [1] and [3]. The surface adsorption allows other transducer principles, e.g., Kelvin-probe measurements or field-effect transistors, to monitor the concentration of analytes by detecting the change in work function upon adsorption. A quantum chemical approach to the interaction of PcMs with NO/NO₂, e.g., demonstrates that the choice of central metal has no significant influence on the attraction

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strengths of the corresponding complexes because NO/NO₂ preferentially interacts with the metal center (Fietzek et al. 2006, submitted for publication). The second class of PcMs used for gas-sensing applications is Langmuir–Blodgett films [4]. These films often have a limited number of interacting molecules because they consist of mono- or multilayers. Thus, thermodynamic constants are especially difficult to determine. From a sensor device point of view, their interactions are rather sophisticated and difficult to interpret compared with unsubstituted PcMs.

We believe the PcMs bearing voluminous substituents at the rim of the PcM ring result in a third class of PcMs. [5, 6] The substitution at all 16 rim atoms causes an irregular arrangement resulting in isolated PcMs, whereas PcMs with lower degrees of substitution follow special self-association arrangements [7]. As demonstrated by X-ray diffraction (XRD) [8] and extended X-ray absorption fine structure (EXAFS) measurements [9], the distance between cofacially arranged PcM(OR)_{*n*} (*n*=4,8) increases to almost 5 Å, allowing for analyte intercalation into the columns and, as a consequence, to take advantage of the PcM bulk material. Sensing layers of these PcM(OR)₈ can be used for mass-sensitive transducer principles, as realized in microbalances such as cantilevers [10, 11] or quartz-crystal microbalances (QCMs). [12] The analyte gases are allowed full access to the central metal atoms of the PcM(OR)₈, permitting a wide complex chemistry with metals. Examples for analytes of interest in gas sensing applications are aromatics and amines. The first class is used for monitoring air pollution, the second for food-quality applications. Both undergo coordinative interactions. In these interactions, the choice of the central metal atom allows for tuning the selectivity.

The substituents at the PcM(OR)₈ offer channels for quick absorption and desorption processes inside the films because the high mobility of the chain segments permits passing of analyte molecules. The response time to reach equilibrium signals is very short. For example, in the case of the quartz crystal microbalances, the response time for a

film thickness of 200 nm is below 10 s [12]. For such equilibrium states, the dimension-free partition coefficient is defined by

$$K = \frac{c_{solid}}{c_{liquid}} \quad (1)$$

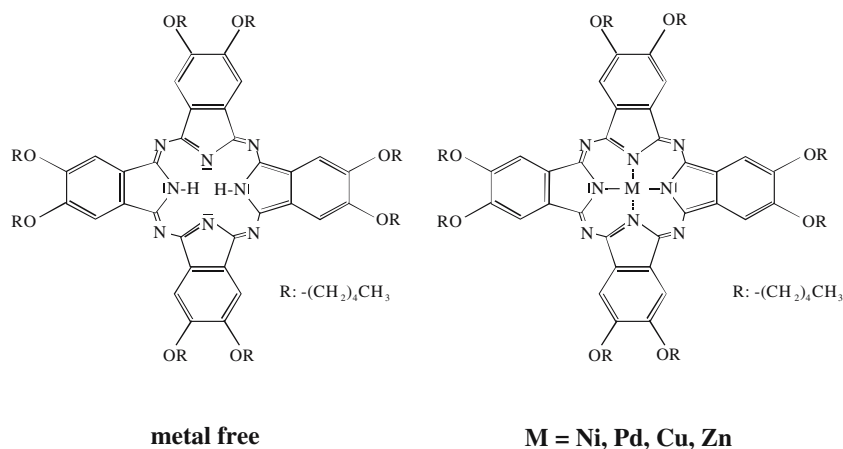
Experimentally, they can be determined easily, e.g., by QCM measurements [13]. From a thermodynamic point of view, the partition coefficient *K* is determined by the temperature *T*, the universal gas constant *R*, and the Gibbs free energy ΔG . Following the Gibbs–Helmholtz equation, we obtain:

$$\ln K = -\frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (2)$$

The entropic contribution ΔS to the free energy is usually smaller than the enthalpy term ΔH [14]. As the reaction mechanism and molecular arrangement are assumed to be the same for the interactions in question, the entropic contribution is neglected in this work, and the enthalpic contribution only is used to evaluate the strength of the interaction.

Interaction energies for complexes of the PcM(OR)₈ compounds [M=H₂ (metal-free), Ni, Pd, Cu, Zn] with various volatile organic molecules (*n*-octane, tetrachloromethane, ethylamine, benzene, and toluene) were calculated using the PM3 semiempirical Hamiltonian. To check the reliability of these energy values, ab initio calculations at the LMP2/LACVP* were performed for the model compounds NiCl₂, PdCl₂, CuCl₂, and ZnCl₂ interacting with the same analytes. These theoretical results are then compared to the experimental partition coefficients to gain further insight into the interaction mechanisms of small volatile organic compounds (VOCs) toward PcM(OR)₈ molecules containing different transition metal centers.

Fig. 1 Chemical structure of the phthalocyanines investigated



Materials and methods

2,3,9,10,16,17,23,24-Octakis(octyloxy)-phthalocyaninato complexes investigated here are the metal-free phthalocyanine, as well as phthalocyanines with various central metal atoms (see Fig. 1). The side chains of these compounds consist of eight carbon units. The compounds were prepared according to standard procedures and checked for purity by ^1H NMR. Details of the preparation are given in [15, 16]. $\text{PcCu}(\text{OR})_8$ and $\text{PcZn}(\text{OR})_8$ were purchased from Aldrich-Chemie, Steinheim, Germany.

The polymer polyetherurethane (PEUT, Thermedics, Woburn, MA) was chosen as reference coating with nonspecific VOC binding properties (see Fig. 2).

Partition coefficients were determined using QCM measurements at a gas test station. Discrete quartz microbalances with gold electrodes operating in a thickness shear-mode resonance were used at a fundamental frequency of $f_0=30$ MHz (KVG, Quartz Crystal Technology GmbH, Germany). Details of the measurement setup are given in [17]. The measurement chamber was kept at a constant temperature of 313 K. The test gases were generated by temperature-controlled evaporation of the liquids (Aldrich-Chemie) [18].

The sensors were prepared by airbrush coating. Each $\text{PcM}(\text{OR})_8$ substance was dissolved in dichloromethane (approx. 3 mg ml^{-1}) and sprayed onto the cleaned surfaces of the QCM sensors using synthetic air as the carrier gas. During the coating process, the frequency change of the resonators was monitored. The process was stopped as soon as a shift of 40 kHz was reached on each side. An overall frequency shift of 80 kHz corresponds to a layer thickness of at least 160 nm per side, assuming a homogeneous layer of $\text{PcM}(\text{OR})_8$ and a density of 1.2 g mol^{-1} [8].

Signals were determined by the frequency difference Δf between gas exposure and purging with analyte-free air. For linear isotherms, the partition was calculated by [13]

$$K = \frac{\Delta f_{\text{solid}}[\text{Hz}] \rho_{\text{polymer}}[\text{g/mol}] R[\text{J/mol K}] T[\text{K}] 10^7}{\Delta f_{\text{liquid}}[\text{Hz}] M_{\text{analyte}}[\text{g/mol}] p_{\text{gas}}^i 0.98[\text{ppm Pa}]} \quad (3)$$

For strongly nonlinear isotherms, the partition coefficient is a function of the concentration. Thus, we used the partition coefficients for infinite concentration by applying a superposition of Henry and Langmuir adsorption (dual sorption model) [19]. This model allows a more precise determination of the partition coefficients.

The ab initio calculations at the local MP2 (LMP2) level of theory [20] were performed with the program Jaguar

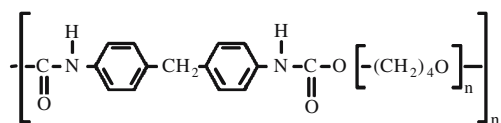


Fig. 2 Reference polymer polyetherurethane (PEUT)

[21] using the pseudopotential LACVP* basis set. [22] For the semiempirical quantum chemical calculations (PM3), the program Titan [23] was used. In all cases, the structures of the monomers (metal-containing compounds and analytes), as well as the structures of the 1:1 adducts $\text{MCl}_2/\text{PcM}(\text{OR})_8$ and volatiles, were fully optimized.

Results and discussion

Partition coefficients

The partition coefficients were determined on sensor coatings at 40°C for a set of analytes. Acetonitrile and *n*-butylamine represent polar molecules, whereas *n*-octane, tetrachloroethene, and toluene are nonpolar molecules with increasing polarization toward toluene.

The experimentally obtained partition coefficients are shown in Table 1. The values range from about a hundred, for acetonitrile, to several thousands for *n*-butylamine. The partition coefficients, therefore, strongly depend on the volatility of the VOC, as can be seen from Eq. 3: The higher the volatility and, thus, the saturation pressure of the analyte, the smaller are the partition coefficients. This is the reason why the especially volatile acetonitrile and *n*-butylamine exhibit rather low partition coefficients <500 .

To eliminate the strong dependence on the volatility, the partition coefficients were divided by the saturation pressure at the measuring condition of 40°C [24]. The values for the corrected partition coefficients are listed in Table 2. They range from 0.3 ppm^{-1} for acetonitrile with $\text{PcNi}(\text{OR})_8$ to 144 ppm^{-1} for *n*-butylamine with $\text{PcZn}(\text{OR})_8$. The corrected values help to identify preferential interactions caused by a large interaction energy. Values $<1 \text{ ppm}^{-1}$ indicate that the chemical potential of the molecule in the appropriate matrix is smaller than in its liquid state. If the values are $>1 \text{ ppm}^{-1}$, the chemical potential for the molecule increased for a polymer or $\text{PcM}(\text{OR})_8$ -matrix. The obtained values for *n*-octane and PER vary between 8 and 18 ppm^{-1} , indicating that the chemical potential for these two compounds in $\text{PcM}(\text{OR})_8$ is higher than in the corresponding liquids. Looking at the enrichment of *n*-butylamine in $\text{PcZn}(\text{OR})_8$, a value of 144 ppm^{-1} is found to suggest an especially high affinity to the coating. This value is almost tenfold higher than those observed for *n*-octane and PER, both with the phthalocyanines and the PEUT. This indicates a rather stronger and even more specific interaction for *n*-butylamine with $\text{PcZn}(\text{OR})_8$.

For toluene, the corrected partition coefficient with the reference polymer and for the $\text{PcH}_2(\text{OR})_8$ and $\text{PcZn}(\text{OR})_8$ are in the range of simple preferential interactions. Exceptionally high values for toluene of approximately 50 ppm^{-1} are found for $\text{PcNi}(\text{OR})_8$ and $\text{PcPd}(\text{OR})_8$, indicating very strong interactions of toluene with $\text{PcNi}(\text{OR})_8$ and $\text{PcPd}(\text{OR})_8$. The values of *n*-butylamine for the $\text{PcCu}(\text{OR})_8$ and the $\text{PcZn}(\text{OR})_8$ coatings are higher than 100 ppm^{-1} , indicating a specific interaction for these pairs, while the values of the amine for the reference polymer and the other $\text{PcM}(\text{OR})_8$ are relatively small.

Table 1 Calculated saturation pressures and QCM-determined partition coefficients at 40°C

	p ⁰ 40°C (ppm)	Reference polymer PEUT	Phthalocyanines				
			PcH ₂ (OR) ₈	PcNi(OR) ₈	PcPd(OR) ₈	PcCu(OR) ₈	PcZn(OR) ₈
<i>n</i> -Octane	40,885	540	340	430	480	415	740
Tetrachloroethene (PER)	51,332	900	740	790	840	600	630
Toluene	234,771	950	1,190	4,600	4,770	1,920	850
<i>n</i> -Butylamine	246,615	470	8,860	2,250	3,510	25,050	35,600
Acetonitrile	77,917	480	110	70	95	117	100

Acetonitrile shows a value of 2.0 ppm⁻¹ for PEUT, which is higher than in its liquid, according to the definitions. However, the enrichment in all PcM(OR)₈ is poor, the values are below 1 for all the PcM(OR)₈. Unexpectedly, the values are very similar for all PcM(OR)₈, regardless of the central metals, and even for the metal-free PcH₂(OR)₈. This might be explained by a barrier effect for acetonitrile caused by the nonpolar chains surrounding the PcM(OR)₈. Such an effect could be beneficial for applications such as sensor coatings, as it discriminates interactions with polar analytes. It could also protect the metals from poisoning gases, like mercapto-functionalized molecules, which could block the metal function within the PcM(OR)₈.

In Fig. 3, all values are given in a 3-D plot to visualize the combinations with high interactions. The analyte/coating combinations amine/PcZn(OR)₈, toluene/PcNi(OR)₈, and toluene/PcPd(OR)₈ show strong interactions. The high affinity of amines toward zinc-containing compounds is quite well-known: Pure zinc phthalocyanines on graphite exposed to various vapors show a reversible interaction with amines and, therefore, are used for gas chromatography [25]. In the liquid phase, derivatives of zinc phthalocyanine show a high affinity toward malignancies, eventually due to the high affinity toward the amines, and, for this reason, have been investigated for antitumor purposes. Zinc-containing porphyrines have been described for optical detection of amines [26]; however, little is known on the use of zinc phthalocyanines as gas sensors.

The preferential sorption of aromatics on PcM(OR)₈ for gas-phase sensing applications has been described [12].

LMP2/LACVP* calculations

Simple hypothetical valence state II metal chlorides were used as model compounds for calculating the interaction energy of the various metal atoms (Ni, Pd, Cu, Zn) toward

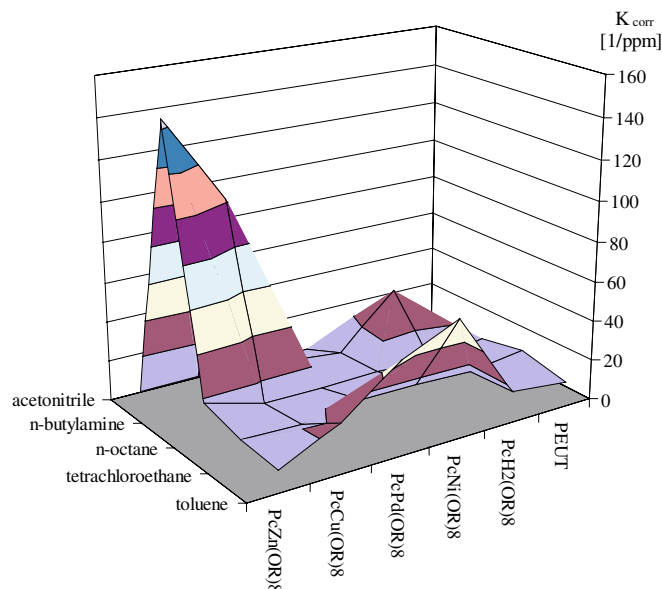


Fig. 3 3-D plot for the corrected partition coefficients of all analyte/PcM(OR)₈ combinations. High coefficient values indicate analyte/PcM(OR)₈ combinations with high interaction energies

different gases. Chloride ions were chosen to saturate the free valences of the metal atoms, resulting in the corresponding binary chloride complexes. Within this simplified scenario, no model compound exists for the metal-free phthalocyanines. The calculated interaction energies for the metal complexes with the various analyte molecules are shown in Table 3.

Equation 3 allows a comparison of the energies thus obtained with the experimental partition coefficients from Table 2, as the calculated values correlate with the experimental partition coefficients. As a result of the calculations, no attracting forces toward the chlorides were determined for *n*-octane and tetrachloromethane. Regarding the aromatics toluene and benzene, no interaction

Table 2 Saturation-pressure corrected partition coefficients from Table 1

<i>K</i> corr (ppm ⁻¹)	PEUT	PcH ₂ (OR) ₈	PcNi(OR) ₈	PcPd(OR) ₈	PcCu(OR) ₈	PcZn(OR) ₈
<i>n</i> -Octane	13.2	8.3	10.5	9.8	10.2	18.1
Tetrachloroethene (PER)	17.5	14.4	15.4	15.6	11.7	12.3
Toluene	12.2	15.3	59.0	46.6	24.6	10.9
<i>n</i> -Butylamine	1.9	35.9	9.1	12.2	101.6	144.4
Acetonitrile	2.0	0.5	0.3	0.3	0.5	0.4

Table 3 Calculated energies for the interaction of various volatile organics with different metal chlorides (LMP2/LACVP*)

E (kcal mol ⁻¹)	NiCl ₂	PdCl ₂	CuCl ₂	ZnCl ₂
<i>n</i> -Octane	0.0	0.0	0.0	0.0
Tetrachloromethane	0.0	0.0	0.0	0.0
Ethylamine	-51.1	-51.7	0.0	-16.0
Benzene	-11.1	-18.3	0.0	0.0
Toluene	-8.4	-16.1	0.0	0.0

energy was observed toward ZnCl₂. However, toluene and benzene show a considerable enthalpy in coordination with group VIIIb transition metals. Values for benzene are slightly larger than for toluene. The overall tendency increases toward palladium. For ethylamine, the calculations result in a high binding affinity toward the ZnCl₂ molecule. In general, the LMP2/LACVP* results support the experimental values and indicate an underlying model of metal coordination.

PM3 calculations

The semiempirical PM3 method allows molecules of more than 200 atoms, like the phthalocyanines studied here, to be calculated in an adequate computational time. For this reason, the PcM(OR)₈ molecules investigated experimentally and their interaction energies toward the volatiles were calculated. The metal-free phthalocyanine, with hydrogen atoms saturating the valences of the inner ring, was also considered and compared to the metal-containing PcM(OR)₈ compounds.

For a first estimation of the quality of the theoretical results, some geometric parameters for PcZn(OR)₈ and PcNi(OR)₈ as predicted by the calculations, were compared to EXAFS measurements on tetra(alkyloxy)-phthalocyaninatonicel and -zinc complexes [9]. Although the number of substituents in the latter compound is smaller, the results are expected to be similar, especially because the inductive effect of the alkyloxy substituents is relatively small. A planar structure results for the ring atoms, both from the calculations and the experiment. Some key values are listed for comparison in Table 4. In agreement with the experimental data, the position of the nickel atom is located in the molecular plane, whereas the zinc atom is out of plane. The interatomic distances, as predicted by the calculations, are slightly larger than the experimental ones. This is probably due to missing interactions to the adjacent molecules as compared to the bulk-phase situation.

In general, the agreement of EXAFS and PM3 with respect to these structural parameters confirm the assumptions made for the basic calculations. Another criterion for realistic assumptions is the theoretically obtained structure of the resulting complexes: The molecules are closely attached to each other. Benzene and toluene especially exhibit a coplanar arrangement to the PcM(OR)₈s.

The interaction energies, as predicted by the PM3 approach, are listed in Table 5. It is obvious that almost all interaction energies for the metal-free PcH₂(OR)₈ are quite small, i.e., in the range of -1.0 kcal mol⁻¹, with the exception of -9.3 kcal mol⁻¹ for *n*-octane. Similar behavior is observed for PcCu(OR)₈, in which case all energies are smaller than -1.0 kcal mol⁻¹. For PcNi(OR)₈ and PcPd(OR)₈, the interaction energies are all larger than 10 kcal mol⁻¹. The behavior of PcZn(OR)₈ is different. In the case of the interaction with amines, the energies amount to about 18 kcal mol⁻¹. For the aliphatic and aromatic compounds investigated, almost no binding interaction was obtained.

The model of Lewis acid–base complexes helps explain the behavior toward the metal-containing phthalocyanines. This holds for the analytes with binding electrons of strong Lewis-base character, which are favored to coordinate to a metal center of high Lewis acidity. *n*-Octane, which has the lowest Lewis acidity of the analytes studied here, also exhibits lower interaction energies as compared to the VOCs with high Lewis acidity. The same holds for the metal-free PcH₂(OR)₈, which possesses the lowest Lewis acidity and, consequently, shows a low interaction energy toward all analytes. The exceptionally high interaction energy of PcH₂(OR)₈ toward *n*-octane might be explained by the high flexibility of the linear molecule, leading to stronger van der Waals forces. The strength of Lewis acid–base interactions can be predicted qualitatively by the coordination model of Hard and Soft Acids and Bases, as proposed by Pearson. The very soft palladium interacts strongly with the soft aromatics. The interaction with the rather hard amines is not so strong.

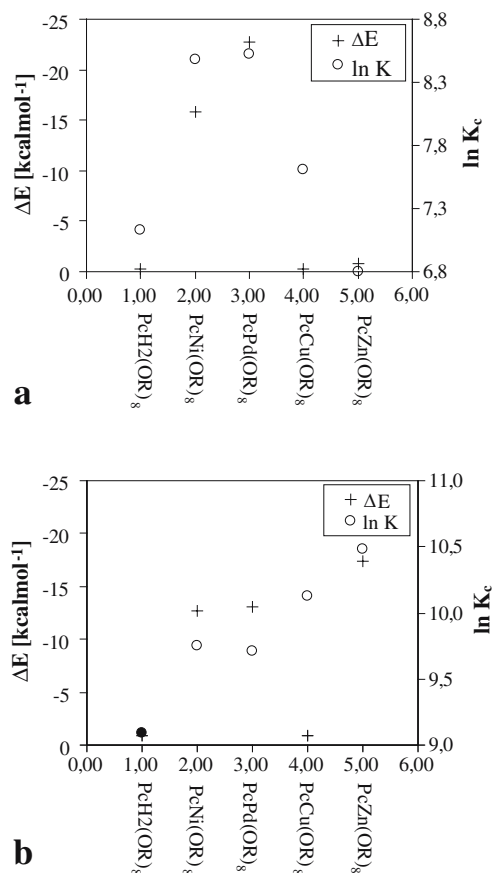
Table 4 Calculated (PM3) and experimental (EXAFS) distances [10] for alkoxy-substituted PcMs

Distance	PM3 (Å)	EXAFS (Å)
Ni–(N ₁)	1.90	1.89±0.02
Zn–(N ₁)	2.08	1.99±0.02
Ni to molecular plane	0	0
Zn to molecular plane	0.35	0.28

Table 5 Theoretically (PM3) obtained energies for the interaction of different volatile organics with phthalocyanine (1) and various phthalocyaninato metal complexes

E (kcal mol ⁻¹)	PcH ₂ (OR) ₈	PcNi(OR) ₈	PcPd(OR) ₈	PcCu(OR) ₈	PcZn(OR) ₈
<i>n</i> -Octane	-9.3	-11.7	-16.3	0.0	-0.6
Tetrachloroethene	-0.6	-10.4	-20.6	-0.1	-8.4
<i>n</i> -Butylamine	-0.9	-12.7	-13.1	-0.9	-17.4
Toluene	-0.2	-15.8	-22.8	0.0	-0.8
<i>m</i> -Xylene	0.0	-17.9	-23.0	0.0	0.0
Ethylamine	-0.9	-13.0	-14.7	-0.9	-18.3
Benzene	-0.5	-15.7	-22.1	0.0	-0.4

The PM3 calculations from this study predict qualitative values for the influence of the central metal atoms. According to Eq. 2, the values are directly proportional to $\ln K_c$ and allow a comparison with the experimentally observed differences resulting from varying the central metal atoms. Figure 4 compares the pattern of the calculated ΔE values for toluene and *n*-butylamine to the real-life partition coefficient $\ln K_c$. In the graphs, the lowest partition coefficient was taken as offset for the interaction energy of 0 kcal mol⁻¹. That offset is a guide to the eye and compensates for that part of the interaction of analytes and PcM molecule that is not caused by substitution with the central metal.

**Fig. 4** PM3 interaction energy ΔE compared to experimental partition coefficient $\ln K_c$ for different PcMs. **a** Values for toluene. **b** Values for *n*-butylamine

The comparison for the two analytes shows good agreement between experiment and theory for the phthalocyanines studied here. With the exception of PcCu(OR)₈, the theoretical values for the interaction energies correlate well with the experimentally determined partition coefficients. Weak or no interaction, as obtained by the PM3 approach in the case of the complexes PcCu(OR)₈/analyte, might be explained by the open-shell situation of these systems, which possess one unpaired electron. More sophisticated levels of theory are expected to lead to better results.

Conclusion

Thin films of heavily substituted soluble phthalocyanines proved to be especially suitable for the systematic investigation of the enrichment of VOCs into sorptive materials. With certain central metal atoms, a selective enrichment in closely limited material classes can be obtained, a behavior that cannot be achieved with conventional polymers. In the case of zinc-containing PcMs, a very strong enrichment of compounds with amines occurs. For PcMs containing Ni and Pd, a preferential sorption of aromatics could be demonstrated. High experimental partition coefficients, both for the preferential sorption of aromatics and of amines, correspond with particularly strong interaction energies as obtained by quantum chemical calculations. In the case of the complexes with aromatics, the theoretical results suggest that preferential enrichment is due to a strong interaction with the central metal atoms rather than to π -stacking. The integration of PcM sensors in arrays of conventional polymer sensors arises as a new and interesting option, especially for the detection of small concentrations down to the ppb region.

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