

# Atomistic simulations of materials for optical chemical sensors: DFT-D calculations of molecular interactions between gas-phase analyte molecules and simple substrate models

Andrey A. Safonov · Elena A. Rykova ·  
Alexander A. Bagaturyants · Vyacheslav A. Sazhnikov ·  
Michael V. Alfimov

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**Abstract** The structures of complexes of some small molecules (formaldehyde, acetaldehyde, ammonia, methylamine, methanol, ethanol, acetone, benzene, acetonitrile, ethyl acetate, chloroform, and tetrahydrofuran, considered as possible analytes) with ethylbenzene and silanol ( $C_6H_5C_2H_5$  and  $SiH_3OH$ , considered as models of polystyrene and silica gel substrates) and with acridine ( $C_{13}H_9N$ , considered as a model of an indicator dye molecule of the acridine series) and the corresponding interaction energies have been calculated using the DFT-D approximation. The PBE exchange-correlation potential was used in the calculations. The structures of complexes between the analyte and the substrate were determined by optimizing their ground-state geometry using the SVP split-valence double-zeta plus polarization basis set. The complex formation energies were refined by single-point calculations at the calculated equilibrium geometries using the sufficiently large triple-zeta TZVPP basis set. The calculated interaction energies are used to assess the possibility of using dyes of the acridine series adsorbed on a polystyrene or silica substrate for detecting the small molecules listed above.

**Keywords** DFT-D · Molecular complexes · Optical chemosensors

## Introduction

Optical chemosensors are widely used in various environmental, biomedical, and industrial applications (see, e.g., the recent review [1]). An optical chemosensor is based on the molecular recognition of analyte molecules due to a change in the optical (mainly, fluorescence) properties of an indicator molecule upon its interaction with an analyte. Recently, we have developed a general strategy for the hierarchical design of nanostructured materials for optical chemosensors [2–7]. According to this strategy, an indicator dye molecule is adsorbed on the surface of a nanoparticle (which is used as a substrate). The nanoparticles are assembled into a sensing layer (sensor material), which can be used to construct a sensor array (see [2–7] for more details). An indicator dye molecule along with its local environment forms a functional supramolecular center, whose properties depend on both the indicator dye itself and its environment. The interaction of an analyte molecule with the supramolecular center generates an optical response of the material.

The predictive modeling of the properties of nanostructured materials is very important for designing sensitive and selective optical chemosensors. A rational approach to the design of optical chemosensor materials should be based on a consideration of intermolecular interactions between analytes, indicators, and matrices [3]. In a general case, all types of interactions between these components must be taken into account. It may be believed that the possibility of detecting an analyte by an indicator depends on the mode and strength of interaction between the analyte molecule and the indicator. For the successful detection of low concentrations of an analyte, this interac-

A. A. Safonov · E. A. Rykova · A. A. Bagaturyants (✉) ·  
V. A. Sazhnikov · M. V. Alfimov  
Photochemistry Center, Russian Academy of Sciences,  
ul. Novatorov 7a, b. 1,  
Moscow 119421, Russia  
e-mail: sasha@photonics.ru

tion should be stronger than the interaction of the analyte with the substrate.

As a first step of such a large-scale investigation, we consider here the interaction of some small molecules (possible analytes) with polystyrene and silica gel substrates and with an indicator dye molecule of the acridine series. The main goal of this work was to determine the mode of interaction and estimate the interaction energy between the adsorbed molecule, on the one hand, and the substrate and the indicator dye on the other hand. In this work we used simplified molecular models of the substrate surface and the indicator dye that include only the main active surface center (for the substrates) or the representative interacting fragment (for the dye molecule) responsible for the interaction with analyte molecules. The use of simplified models allowed us to consider simultaneously a rather large variety of analyte molecules. Calculations were performed using the DFT-D approach well established in the literature [8–10]. It should be noted here that similar simplified models were used rather long ago by Calderone, Lazzaroni, and Bredas [11] in modeling interactions at a polymer/polymer interface and more recently by Perez, Florez, Mark, and Lopez [12] in modeling interactions of nitrile, aromatic, and olefinic polymers with silica.

## Models and methods

The ethylbenzene molecule (Fig. 1a) was chosen as the simplest model of polystyrene, which includes its main constituent moieties (phenyl ring and alkyl chain) and represents an elementary link of its polymer chain. The silanol molecule  $\text{SiH}_3\text{OH}$  (Fig. 1b) was selected as the simplest model of a silanol group on the silica surface. The acridine molecule (Fig. 1c) was taken as the main fragment of an acridine dye responsible for interaction with analyte molecules.

This suggestion is correct for acridine dyes like 9-(diphenylamino)acridine (DPAA) or its analog, 2,7-dimethyl-9-(ditolylamino)acridine (DTAA), which was investigated experimentally in our previous works [2, 3]. It should be also noted that the first electronic transition in DPAA was shown to be associated with electron density transfer from the diphenylamino group to the acridine moiety [13].

As the analyte molecules, we considered formaldehyde, acetaldehyde, ammonia, methylamine, methanol, ethanol,

acetone, benzene, acetonitrile, ethyl acetate, chloroform, and tetrahydrofuran, and calculated their interaction energies with the ethylbenzene, silanol, and acridine molecules, considered, as indicated above, as models for polystyrene and silica gel substrates and for an acridine indicator dye.

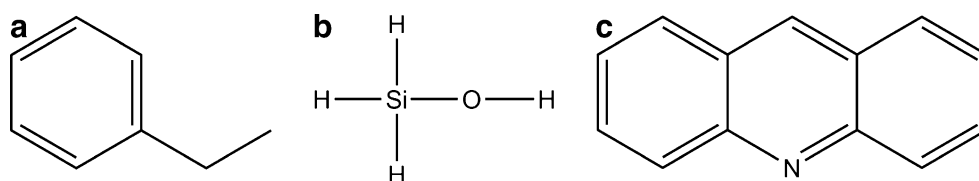
The interaction energies were estimated as the formation energies of intermolecular analyte–substrate and analyte–indicator model complexes. In most cases, the possible mutual arrangement of the molecules in the complexes was evident, and the starting geometry for the geometry optimization of the intermolecular model complexes was unambiguously selected. In some cases, several starting trial structures were tested, and the most favorable optimized structure was chosen.

Quantum-chemical calculations were made by density functional theory supplemented with an empirical correction for dispersion interactions (DFT-D) using the ORCA program [8, 9, 14]. The PBE exchange–correlation potential was used in the calculations [15]. The structures of complexes between the analyte and the substrate were determined by optimizing their ground-state geometry using the SVP split-valence double-zeta plus polarization basis set from [16]. The complex formation energies were refined by single-point calculations at the calculated equilibrium geometries using the sufficiently large triple-zeta TZVPP basis set [17] containing three sets of polarization functions. Geometry optimization with the TZVPP basis set required a very large computer time and did not lead to substantial changes in the complex formation energy. Such calculations were performed for some selected systems, and the resulting change in energy (as compared to that calculated with the geometry optimized using the SVP basis set) did not exceed  $0.5 \text{ kcal mol}^{-1}$ . Therefore, the use of the geometries optimized with the SVP basis set seems to be quite reasonable.

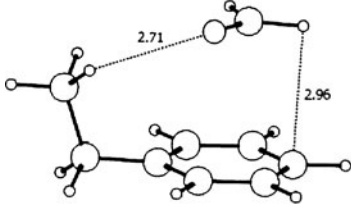
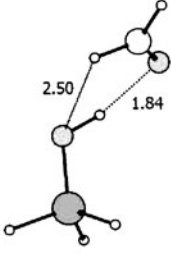
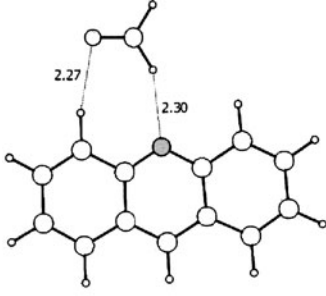
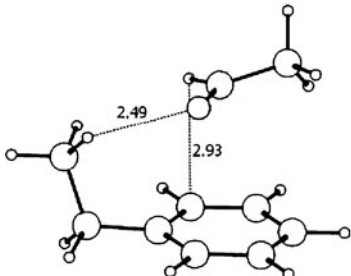
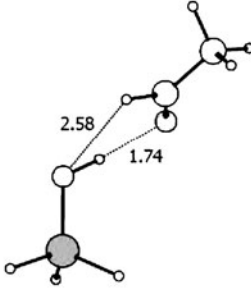
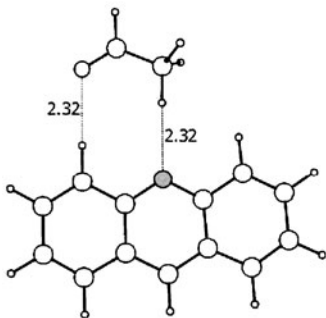
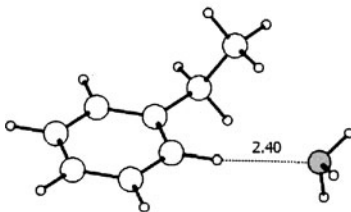
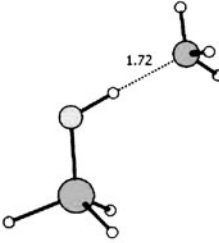
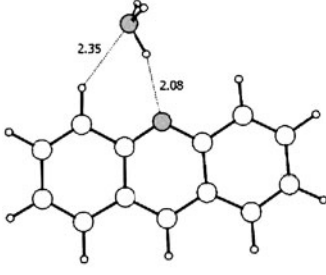
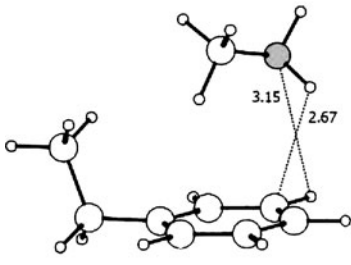
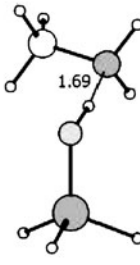
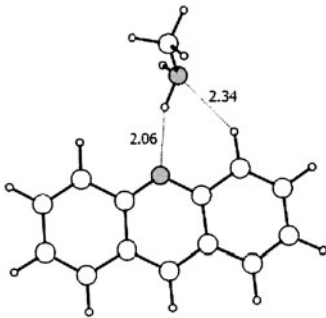
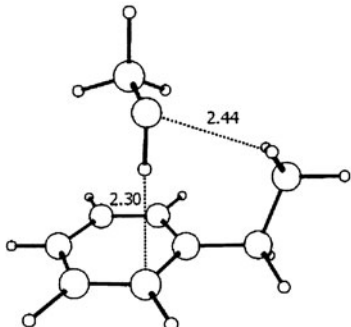
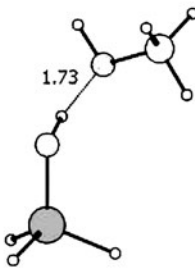
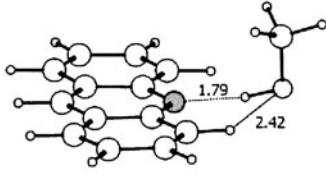
## Results and discussion

The calculated structures of complexes and the lengths of shortest contacts between the analyte molecule and the substrate in the calculated intermolecular complexes are presented in Table 1. The formation energies of the complexes are given in Table 2. The short contacts between the molecule and the substrate in the complexes are shown in dotted lines along with their lengths indicated at these

**Fig. 1** Structural formulas of molecules selected as models of the substrates and the indicator dye: (a) ethylbenzene, (b) silanol, and (c) acridine

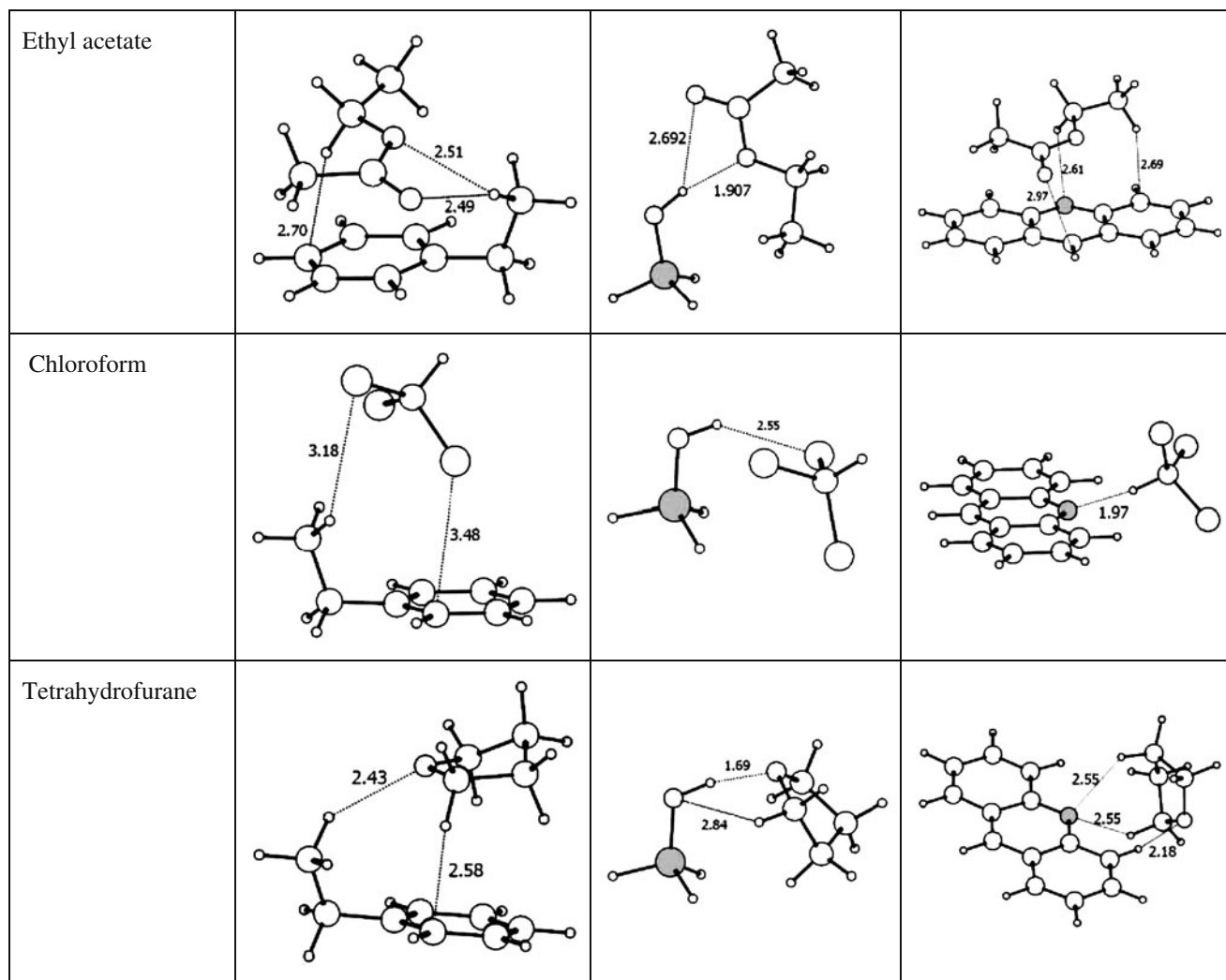


**Table 1** Structures of ethylbenzene, silanol, and acridine complexes with various analyte molecules

Molecule	Ethylbenzene	Silanol	Acridine
Formaldehyde			
Acetaldehyde			
Ammonia			
Methylamine			
Methanol			

**Table 1** (continued)

Ethanol			
Acetone			
Benzene			
Acetonitrile			

**Table 1** (continued)**Table 2** Intermolecular interaction energies  $-\Delta E$  (kcal mol<sup>-1</sup>) in ethylbenzene, silanol, and acridine complexes with various analyte molecules

Molecule	$\Delta E$		
	Ethylbenzene complex	Silanol complex	Acridine complex
Formaldehyde	4.2	6.9	4.7
Acetaldehyde	4.0	7.8	4.4
Ammonia	2.8	10.9	6.2
Methylamine	3.8	12.0	6.5
Methanol	6.6	8.6	11.1
Ethanol	6.3	9.6	10.9
Acetone	6.3	9.6	4.8
Benzene	4.2	4.5	5.5
Acetonitrile	5.5	6.9	5.2
Ethyl acetate	6.9	6.7	9.0
Chloroform	3.2	3.1	8.1
Tetrahydrofuran	5.0	10.6	6.2

lines in Å. It is evident from the calculated structures that the modes of interaction between the analyte molecules and the substrates are mainly determined by short contacts  $H^{\delta+}-X^{\delta-}$  between a positively charged H atom of one molecule and a negatively charged atom X (X=C, N, or O) of the other counterpart of the complex. All the obtained structures can be conditionally classified as belonging to the lateral or stacking type as will be described below.

In the case of ethylbenzene, most calculated structures correspond to the stacking type, in which the analyte molecule is located over the plane of the phenyl ring. The only exception is the ammonia complex. In this complex, the ammonia molecule is coordinated with ethylbenzene through a C–H...N bond, which lies approximately in the plane of the phenyl ring.

The lengths of short contacts in the ethylbenzene complexes vary from 2.16 Å (with ethanol) to 3.18 Å (with chloroform). Generally, interaction energies (Table 2) are higher in ethylbenzene complexes with oxygen-containing molecules. Ethyl acetate exhibits the highest interaction energy with ethylbenzene among the studied molecules. It is seen from Table 1 that two oxygen atoms of ethyl acetate interact with an H–C bond of the ethylbenzene CH<sub>3</sub> group and that one of the ethyl acetate C–H groups interacts with an atom C of the ethylbenzene phenyl ring. In the case of alcohols, high interaction energies can be attributed to the fact that their OH group simultaneously participates in the two hydrogen bonds: O–H...C and O...H–C. On the other hand, the low interaction energy of ammonia reflects the fact that ammonia forms only one short contact with ethylbenzene. It might be seen that there is no direct correlation between the lengths of short contacts in the complexes (Table 1) and the interaction energies (Table 2). Hence, in the case of complexes between a small analyte molecule and ethylbenzene, two factors determine the interaction energy: the number of short contacts between the molecules in the complex and their length.

The situation is different in the case of complexes with silanol. All complexes are formed through an Si–O–H...X hydrogen bond, where X is a heteroatom (N or O) of the analyte. All these structures can be classified as lateral. The interaction energy in the silanol complexes nicely correlates with the H...X distance; so that, the shorter the distance, the higher the interaction energy. From this qualitative picture, it may be concluded that electrostatic interactions determine the structure and energy of the analyte complexes with silanol. Generally, almost all the interaction energies with silanol are higher than with ethylbenzene. The exceptions are presented by ethyl acetate and chloroform, for which the interaction energies with silanol are, on the contrary, slightly lower than with ethylbenzene.

Most complexes with acridine have a lateral structure in which an H(analyte)...N(acridine) hydrogen bond is formed.

An additional interaction H(acridine)...X(analyte) is also present in almost all the lateral complexes with acridine. An exception is chloroform, in which its geometry does not permit the formation of the second short contact. Two molecules, benzene and ethyl acetate, form stacking-type complexes in which the lengths of short contacts indicate that dispersion interactions dominate here. The parallel-displaced geometry of the benzene–acridine complex is rather typical for aromatic benzene complexes [18–20].

The complexes with methanol, ethanol, and chloroform are of a lateral type with the shortest H(analyte)...N(acridine) contacts (see Table 1), while, as was already mentioned, the acridine complex with ethyl acetate is of a stacking type. The shortest contact in this complex (H(analyte)...N(acridine)) is longer than any H(analyte)...N(acridine) distance in the lateral acridine complexes. The intermolecular separation in this complex indicates that, notwithstanding the polar nature of the ethyl acetate molecule, the structure of its complex with acridine is governed by dispersion interactions.

It is interesting to compare our theoretical results with rather scarce experimental data on heats of adsorption found in the literature. The direct comparison of the calculated interaction energies with the experimental heats of adsorption is not reasonable, because the nature of the adsorbed state might be rather complicated. Actually, an adsorbed molecule can simultaneously interact with more than one surface group, especially, in the case of a porous adsorbent. However, such a comparison may still shed some light on the possible structure of the adsorbed molecule on the corresponding surface.

The following differential heats of adsorption on porous polystyrene were found for benzene (15 kcal mol<sup>-1</sup>), chloroform (13 kcal mol<sup>-1</sup>), acetonitrile (11 kcal mol<sup>-1</sup>), acetone (13 kcal mol<sup>-1</sup>), and ethyl acetate (13 kcal mol<sup>-1</sup>) [21]. These values exceed the calculated interaction energies between these molecules and ethylbenzene, which may be considered as a model of a unit link of a polystyrene chain, by a factor of 2 to 4. Because our calculated values must give a quite reasonable estimate for the corresponding interaction energies, we may conclude that, when adsorbed on porous polystyrene, these molecules interact with two (ethyl acetate, acetonitrile, and acetone) or even with three or four (benzene, chloroform) polymer links.

There are also some experimental estimates for the heat of adsorption on various silicas for ammonia (9–11 kcal mol<sup>-1</sup> [22]), for acetone (two forms 10–15 and 16–17 kcal mol<sup>-1</sup> in [23], and 10–17 kcal mol<sup>-1</sup> in [24]), and for ethyl acetate (15.5 [25]). While the value for ammonia and the lower values for acetone are in good agreement with our theoretical estimates, the higher values for acetone and the value for ethyl acetate considerably

exceed the theoretical estimate, indicating that these molecules can participate in additional interactions with the silica surface (see discussion in the cited papers).

For sensing applications, it is interesting to compare the calculated interaction energies between the analyte molecules and the substrate and indicator models. Firstly, as it was indicated above, the interaction energies with silanol are generally higher than with ethylbenzene. From this point of view, for acridine dyes, polystyrene might be considered as a more versatile substrate than silica gel.

Methanol, ethanol, ethyl acetate, and chloroform most strongly interact with acridine. The complexes that these molecules form with acridine are stronger than their complexes with both ethylbenzene and silanol. Hence, the use of either polystyrene or silica substrate can be recommended for the detection of these molecules using an acridine dye.

Next, it is seen that the interaction of acetone and acetonitrile with acridine is weaker than with both substrate components. This fact may indicate that the dyes of the acridine series are not promising indicator molecules for low concentrations of acetone and acetonitrile when polystyrene or silica is used as the substrate. For all other analyte molecules, polystyrene can be considered a suitable substrate for an acridine dye indicator. Finally, silica might be considered a suitable substrate for the detection of methanol, ethanol, benzene, ethyl acetate, and chloroform using an acridine dye.

The properties of the nanoparticles used as chemosensing materials can be improved by increasing the coverage of nanoparticles with indicator dye molecules so as to decrease the available free surface of the substrate.

## Conclusions

The structures of complexes of some small molecules (formaldehyde, acetaldehyde, ammonia, methylamine, methanol, ethanol, acetone, benzene, acetonitrile, ethyl acetate, chloroform, and tetrahydrofuran) with ethylbenzene ( $C_6H_5C_2H_5$ ), silanol ( $SiH_3OH$ ), and acridine ( $C_{13}H_9N$ ) molecules and the corresponding interaction energies have been calculated using the DFT-D approximation, which gives rather reasonable results for the structure and energy of various molecular complexes. The calculated lengths of shortest contacts in these complexes have been used to analyze the corresponding coordination modes, while the interaction energies have been used to compare the possibilities of detecting these small molecules, considered as analytes, using an acridine dye adsorbed on the surface of a polystyrene or silica gel substrate.

Most complexes of ethylbenzene exhibit a stacking structure in which the analyte molecule is located over the

plane of the phenyl ring with the only exception for the ammonia complex. In the latter, the lateral coordination mode is preferable. All complexes of silanol and most complexes of acridine have a lateral structure formed through an  $Si-O-H...X$  hydrogen bond (X is an analyte heteroatom) or an  $H(analyte)...N(acridine)$  hydrogen bond.

The available experimental data on the heats of adsorption on polystyrene and silica gel for some of the considered analytes indicate that the adsorbed molecules can interact simultaneously with more than one surface group.

The calculated interaction energies indicate that the dyes of the acridine series adsorbed on a polystyrene or silica substrate are not promising indicator molecules for acetone and acetonitrile. For all other analyte molecules, polystyrene can be considered a suitable substrate for an acridine dye indicator. Finally, silica might be considered a suitable substrate for the detection of methanol, ethanol, benzene, ethyl acetate, and chloroform using an acridine dye as a molecular sensor.

The properties of the nanoparticles used as chemosensing materials can be improved by increasing the coverage of nanoparticles with indicator dye molecules.

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## References

- McDonagh C, Burke CS, MacCraith BD (2008) *Chem Rev* 108:400–422
- Plotnikov VG, Sazhnikov VA, Alfimov MV (2007) *High Energy Chem* 41(5):299–311
- Sazhnikov VA, Alfimov MV (2008) *Chem Eng Trans* 15:267–274
- Khlebunov A, Ionov D, Aristarkhov V, Sazhnikov V, Alfimov M (2008) *Chem Eng Trans* 15:293–300
- Khlebunov AA, Ionov DS, Komarov PV, Aristarkhov VM, Sazhnikov VA, Petrov AN, Alfimov MV (2009) *Prib Tekh Eksperim* 1:145–150, *Instr Experim Techn* (2009) 1:132–136
- Alfimov MV, Bagaturyants AA, Safonov AA, Scherbinin AV, Vladimirova KG, Belousov SA, Bogdanova MV, Valuev IA, Deinega AV, Lozovik YE, Potapkin BV (2010) *Russ Nanotekhnologii* (3–4):84
- Grigoriev FV, Romanov AN, Laikov DN, Zhabin SN, Yu A, Golovacheva I, Oferkin V, Sulimov AV, Basilevsky MV, Bagaturyants AA, Sulimov VB, Alfimov MV (2010) *Russ Nanotekhnologii* (5–6):47
- Grimme S (2004) *J Comput Chem* 25:1463–1476
- Grimme S (2006) *J Comput Chem* 27:1787–1799
- Grimme S, Antony J, Schwabe T, Muck-Lichtenfeld C (2007) *Org Biomolec Chem* 5:741–758
- Calderone A, Lazzaroni R, Bredas JL (1998) *Synth Met* 95:1–15
- Perez LD, Florez E, Mark JE, Lopez BL (2009) *Polym Int* 58:811–816
- Safonov AA, Bagaturyants AA, Sazhnikov VA, Alfimov MV (2010) *Atomistic Simulations of Materials for Optical Chemical Sensors: DFT Calculations of absorption spectra of 9-(Diphenyl-*

- lamino) acridine indicator and its complexes with some analyte molecules. *High Energy Chem* (in press)
14. The program ORCA is a modern electronic structure program package written by Neese F, with contributions from Becker U, Ganiouchine D, Kößmann S, Petrenko T, Riplinger C and Wennmohs F. <http://www.thch.uni-bonn.de/tc/orca/>
  15. Perdew JP, Burke K, Ernzerhof M (1996) *Phys Rev Lett* 77:3865–3868
  16. Schäfer A, Horn H, Ahlrichs RJ (1992) *J Chem Phys* 97:2571–2577
  17. Weigend F, Ahlrichs R (2005) *Phys Chem Chem Phys* 7:3297–3305
  18. Arnstein SA, Sherrill CD (2008) *Phys Chem Chem Phys* 10:2646–2655
  19. Jha PC, Rinkevicius Z, Agren H, Seal P, Chakrabarti S (2008) *Phys Chem Chem Phys* 10:2715–2721
  20. Kannemann FO, Becke AD (2010) *J Chem Theor Comput* 6:1081–1088
  21. Lanin SN, Pashkova EB, Kovaleva NV, Lanina KS (2009) *Russ Chem Bull (Inter Edn)* 58:729–732
  22. Civalleri B, Ugliengo P (2000) *J Phys Chem B* 104:9491–9499
  23. Ya DV (2000) Adsorption on Silica Surfaces. In: Papirer E (ed) *Adsorption on Silica Surfaces*. Dekker, New York, pp 63–118
  24. Crocella V, Cerrato G, Magnacca G, Morterra C (2009) *J Phys Chem C* 113:16517–16529
  25. Natal-Santiago MA, Hill JM, Dumesic JA (1999) *J Mol Catal A* 140:199–214