

A reactivity index study to monitor the role of solvation on the interaction of the chromophores with amino-functional silanol surface for colorimetric sensors

Abhijit Chatterjee^{a,*}, Tatineni Balaji^b, Hideyuki Matsunaga^b, Fujio Mizukami^b

^a *Accelrys, Nishishinbashi TS Bldg. 11F, 3-3-1 Nishishinbashi, Minato-ku, Tokyo 105-0003, Japan*

^b *Research Center for Compact Chemical Process, National Institute of Advanced Industrial Science and Technology, AIST Tohoku, 4-2-1 Nigatake, Miyagino-ku, Sendai 983-8551, Japan*

Received 13 October 2005; received in revised form 16 December 2005; accepted 19 December 2005

Available online 19 January 2006

Abstract

Amino-functional silanol surface are mostly used for the immobilization of inorganic ions, molecules, organic or biochemical molecules onto the mesopore surface. In analytical chemistry, the metal ion uptake was visualized through colorimetric sensors using chromophore molecules. One needs to know the structure–property correlation between the chromophore and silylating agent while choosing chromophore, which is very important to design the sensors. We have used two chromophores representative of hydrophobic and hydrophilic type. We used density functional calculation on all the interacting molecules in both the unsolvated phase and solvated medium within the domain of hard soft acid base principle (HSAB) to look at the localized activity of the interacting atoms of these reacting molecules to formulate a priori rule to choose of the best chromophore. We have as well postulated the mechanism of interaction between chromophore and the silylating agent. The results were compared with experiment and it is observed that solvation plays a detrimental role in the binding of chromophore with silylating agent. The results also show that, the range of reactivity index can be used as a suitable property to scale activity of chromophore molecules suitable for the sensing process. It is observed that the hydrophobic chromophore binds stronger with both the metal and the silylating agent; whereas for the hydrophilic one, it binds only with the silylating agent when solvated and in all cases the metal ion binding is weaker compared to that of the hydrophobic one.

© 2005 Elsevier Inc. All rights reserved.

Keywords: Chromophore; Silylating agent; Density-functional calculations; Reactivity index; Solvent effect

1. Introduction

The emerging field of functionalized material resulted from the combination of the structural aspect of inorganic lattice with the intrinsic chemical reactivity of organic component, is recently demanding attraction for its various possible applications. Colorimetric sensor is one of these functional materials whose design is important for innumerable applications. Generally, the mesoporous material is used as the inorganic lattice and tetra-alkoxysilane or organoalkoxysilanes are typically used to synthesize these materials [1–4]. The synthesis of mesoporous materials [5], with large surface area like SBA-15, with well-defined pore size and pore shapes [6] have a great

potential in advanced materials designing. However, applications such as adsorption, sensing, ion exchange and catalysis, require the materials to have specific attributes such as binding sites, stereo chemical configuration, charge density and acidity, which is discussed in a review by Sayari [7]. There is an exhaustive study with the chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal atoms [8]. These materials find a broad application in analytical extractions [9]. In analytical science, there is always need to use different techniques for selective separation of metal ions. Colorimetric sensors (naked eye sensors) one of such method, which do not require the use of any sophisticated instrumentation and are particularly attractive due to the simplicity, quick analysis in measuring the presence of analyte. Here, we wish to explore the interaction between these chromophores and the silylating agents responsible for the binding of specific metals to design a sensor for a particular

* Corresponding author. Tel.: +81 3 3578 3861; fax: +81 3 3578 3873.

E-mail address: achatterjee@accelrys.com (A. Chatterjee).

usage. The binding of silylating agent with mesopores is well studied, but the interaction of the silylating agent and the chromophore is not at all studied. If that interaction is proposed right in terms of the active site of the interacting species, this can foresee the binding nature of the chromophore with the silylating agent and as well the metal ions; to complete designing of a specific sensor. We also wish to monitor the role of solvent in this interaction process, which is detrimental to use these hybrid materials for analytical sensors. It is well known that, the reactivity of a chemical species depends on the solvent associated around the molecules [10,11]. The effect of hydration on the molecular charge distribution of cations, anions and neutral molecules [12–14] are shown by numerous theoretical studies mainly with Meirtus–Scrocco–Tomasi self-consistent reaction field method. Generally, it is observed that, the solvent environment alters the charge distribution of a molecule and there is an increase in the dipole moment, compared to a gas phase calculation. Water enhances the intrinsic reactivity of polar molecules towards nucleophilic and electrophilic attack [11]. Self-consistent reaction field study was performed recently to rationalize the selective formation of 3, 7 dimethyloctanal by hydrogenation of citral (3,7-dimethyl 2, 6-octadienal) exclusively in supercritical carbon dioxide medium. This study shows the importance of solvent in a particular reaction [15].

The hard soft acid–base (HSAB) principles classify the interaction between acids and bases in terms of global softness [16]. Pearson also suggested a principle of maximum hardness (PMH) [17], which states that, for a constant external potential, the system with the maximum global hardness is most stable. In recent days, density functional theory (DFT) has gained widespread use in quantum chemistry. Some DFT-based local properties, e.g., Fukui functions and local softness [18], have already been used for the reliable predictions in various types of electrophilic and nucleophilic reactions in case of zeolites and clay materials [19–23]. A recent review by Geerlings et al. [24] on conceptual DFT discusses on chemically relevant concepts and principles.

In the present article, we wish to monitor the localized reactivity of the silylating agent *N*-trimethoxysilylpropyl *N*, *N*, *N*-trimethyl ammonium chloride (TMAC), which is used for the organic monolayer formation over mesoporous material SBA-15 and two representative chromophores 4-(2-pyridylazo)-resorcinol (PAR) and 2-[1-(2-hydroxy-5-sulphonyl)-3-phenyl-5 formazano] benzoate (ZINCON), respectively both in the gas phase and in the presence of solvent. From the localized reactivity descriptors, a probable interaction is to be postulated. These proposed interactions from the localized reactivity index will then be validated by the interaction energy calculations for the TMAC–chromophore complex in blank and as well in presence of metal ion. The results were validated with the experimental results. A priori rule was formulated to design the sensors.

2. Theory

In DFT, hardness (η) is defined as [16]

$$\eta = \frac{1}{2}(\mathrm{d}^2E/\mathrm{d}N^2)_v(r) = \frac{1}{2}(\mathrm{d}\mu/\mathrm{d}N)_v$$

where E is the total energy, N the number of electrons of the chemical species and μ is the chemical potential.

The global softness, S , is defined as the inverse of the global hardness, η .

$$S = 1/2\eta = (\mathrm{d}N/\mathrm{d}\mu)_v$$

Using the finite difference approximation, S can be approximated as

$$S = 1/(\mathrm{IE} - \mathrm{EA}) \quad (1)$$

where IE and EA are the first ionization energy and electron affinity of the molecule, respectively.

The Fukui function $f(r)$ is defined by [25]

$$f(r) = [\delta\mu/\mathrm{d}v(r)]_N = [\delta\rho(r)/\delta N]_v \quad (2)$$

The function f is thus a local quantity, which has different values at different points in the species, N is the total number of electrons, μ is the chemical potential and v is the potential acting on an electron due to all nuclei present. Since $\rho(r)$ as a function of N has slope discontinuities, Eq. (1) provides the following three reaction indices [25]:

$$f^-(r) = [\delta\rho(r)/\delta N]_v^- \text{ (governing electrophilic attack),}$$

$$f^+(r) = [\delta\rho(r)/\delta N]_v^+ \text{ (governing nucleophilic attack),}$$

$$f^0(r) = \frac{1}{2}[f^+(r) + f^-(r)] \text{ (for radical attack)}$$

In a finite difference approximation, the condensed Fukui function of an atom, say x , in a molecule with N electrons are defined as

$$f_x^+ = [q_x(N+1) - q_x(N)] \text{ (for nucleophilic attack),}$$

$$f_x^- = [q_x(N) - q_x(N-1)] \text{ (for electrophilic attack),}$$

$$f_x^0 = [q_x(N+1) - q_x(N-1)]/2 \text{ (for radical attack)} \quad (3)$$

where, q_x is the electronic population of atom x in a molecule.

The local softness $s(r)$ can be defined as

$$s(r) = (\delta\rho(r)/\delta\mu)_v \quad (4)$$

Eq. (3) can also be written as

$$s(r) = [\delta\rho(r)/\delta N]_v[\delta N/\delta\mu]_v = f(r)S \quad (5)$$

Thus, local softness contains the same information as the Fukui function $f(r)$ plus additional information about the total molecular softness, which is related to the global reactivity with respect to a reaction partner, as stated in HSAB principle. Atomic softness values can easily be calculated by using Eq. (4), namely:

$$\begin{aligned} s_x^+ &= [q_x(N+1) - q_x(N)]S, & s_x^- &= [q_x(N) - q_x(N-1)]S, \\ s_x^0 &= S[q_x(N+1) - q_x(N-1)]/2 \end{aligned} \quad (6)$$

3. Computational methodology

Condensed Fukui functions for chromophore molecules and the silylating agent at gas phase and in solvents have been calculated in the framework of DFT within the helm of hard soft acid base (HSAB) principle. The calculations were performed using the DMol³ program [26–28] of Accelrys Inc.. The geometry of all the interacting molecules in all the cases were optimized using the double numerical with polarization basis set DNP [29] which is equivalent to the 6-311G** basis set of Gaussian and with BLYP as the exchange correlation functional [30,31]. This has also been used for Cd considering the *d* electrons. Basis set superposition error (BSSE) was also calculated for the current basis set in nonlocal density approximation (NLDA) using the Boys–Bernardi method [32]. Single point calculations of the cation and anion of the chromophore molecule and the silylating agent, both in gas phase and in solvent medium, at the optimized geometry of the neutral molecule were also carried out to evaluate Fukui function, global and local softness. The condensed Fukui function and atomic softness were evaluated using Eqs. (3) and (6), respectively. The gross atomic charges were evaluated using the technique of electrostatic potential (ESP) driven charges. In order to consider the effect of solvent, we employed the conductor-like screening model (COSMO) solvation method within the DFT formalism as in the program DMol³ of Accelrys Inc. [33]. In this method, the solute molecules form a cavity within the dielectric continuum of permittivity ϵ that represents the solvent. The charge distribution of the solute polarizes the dielectric medium. The response of the dielectric medium is described by the generation of screening (or polarization) charges on the cavity surface. The cavity surface is obtained as a superimposition of spheres centered at the atoms, discarding all parts lying on the interior part of the surface. The spheres are represented by a discrete set of points, the so-called basic points; eliminating the parts of the spheres that lie within the interior part of the molecule thus amounts to eliminate the basic grid points that lie in the interior of the molecule. The radii of the spheres are determined as the sum of the van der Waals radii of the atoms of the molecule and of the probe radius. The surviving basic grid points are then scaled to lie on the surface generated by the spheres of van der Waals radii alone. The basic points are then collected into segments, which are also represented as discrete points on the surface. The screening charges are located at the segment points. The interaction energy calculations were performed with all electrons relativistic which includes all electrons explicitly and introduces some relativistic effects into the core. This is to handle the 5d metal system Cd.

4. Results and discussion

First the global softness values of the TMAC as well as the interacting chromophore molecules were calculated in the gas phase. All the calculations were repeated to consider the solvation model, where each molecule is put into a spherical cavity of water with definite radius and solvated. The results are shown in Table 1.

Table 1

Global softness (a.u.) and the dipole moment (Debye) for the chromophores studied and the silylating agent

System	Dipole moment (Debye)	Global softness (a.u.)
4-(2-pyridylazo) –resorcinol (PAR)	1.2799	0.1243
Solvated PAR	2.8844	0.8960
2-[1-(2-hydroxy-5-sulphenyl)-3-phenyl –5-formazeno benzoic acid and monosodium salt (ZINCON)	10.5119	0.0455
Solvated ZINCON	11.1256	0.5163
<i>N</i> -trimethoxysilyl – <i>N,N,N</i> -trimethyl ammonium chloride (TMAC)	10.9687	1.1368
Solvated TMAC	13.5787	3.4314

The values of nucleophilic and electrophilic condensed local softness, condensed Fukui function, of all the constituent atoms of the interacting molecules (TMAC and the chromophores) both for the unsolvated and solvated phases obtained through ESP technique at the DFT level are shown in Tables 2–7. A semi quantitative activity order is proposed. This is followed by the interaction energy calculation of the individual chromophore with the TMAC to justify the proposed order. The trends observed in these two sets of results were compared. Finally, an interaction model involving metal ion and chromophore, to compare the experimental results, were studied to verify the methodology. The analytical experimental results were compared with the results obtained by the calculations.

4.1. The global information about the interacting molecules

The dipole moment, global softness values for the independent chromophore molecules and the silylating agent are shown in Table 1. It is observed from Table 1 that the global softness of the silylating agent TMAC is higher than the values for the chromophore molecules both in the solvated and in unsolvated form. There is a consistent increase in the global softness after solvation and the trend is same as that for unsolvated situation. The order of activity remains ZINCON < PAR, where as TMAC has the highest global softness value. An important correlation between the dipole moment and global softness is obtained from Table 1. Here, we are considering two different set of molecules (1) chromophore and (2) the silanol surface. If we look at the trend for the chromophores it shows that while dipole moment is increasing for the chromophores the global softness is decreasing, after solvation. Comparing the dipole moment of all the interacting molecules it is observed that the dipole moment is lowest for PAR and is highest for TMAC for both solvated and unsolvated situation. We know that the dipole moment reflects the charge distribution of a molecule. It is defined by the following equation:

$$\mu = \sum qr$$

A larger dipole moment means that the solvent molecules can interact favorably with charged solute molecules by screening their charges. Consequently, a high dipole moment

usually implies a high dielectric constant. A high dielectric constant, such as that found in water, is important because the forces between charges are attenuated. The values of dielectric constant are again related with the hydro-phobicity/-philicity of a system. The results therefore propose that chromophore PAR is hydrophobic and the other chromophore ZINCON together with the silylating agent TMAC is hydrophilic, which need further verification in terms of the localized interaction. Let us now compare the values of global softness with the dipole moment; the trend of dipole moment is as well not influenced by solvation, for both the cases the dipole moment changes in the order $\text{TMAC} > \text{ZINCON} > \text{PAR}$. Though we have put together the TMAC with the chromophores in the trend for comparison but actually TMAC should be excluded from the comparison as it is not the chromophore. This trend is different from that observed with the global softness except for TMAC. To resolve this anomaly we need to look at the localized interaction carefully to extract the reason of this behavior.

4.2. Localized activity of the constituent atoms present in TMAC, PAR and ZINCON both when solvated and unsolvated

In the current study, we want to monitor the localized activity of chromophores and the silylating agent, which is

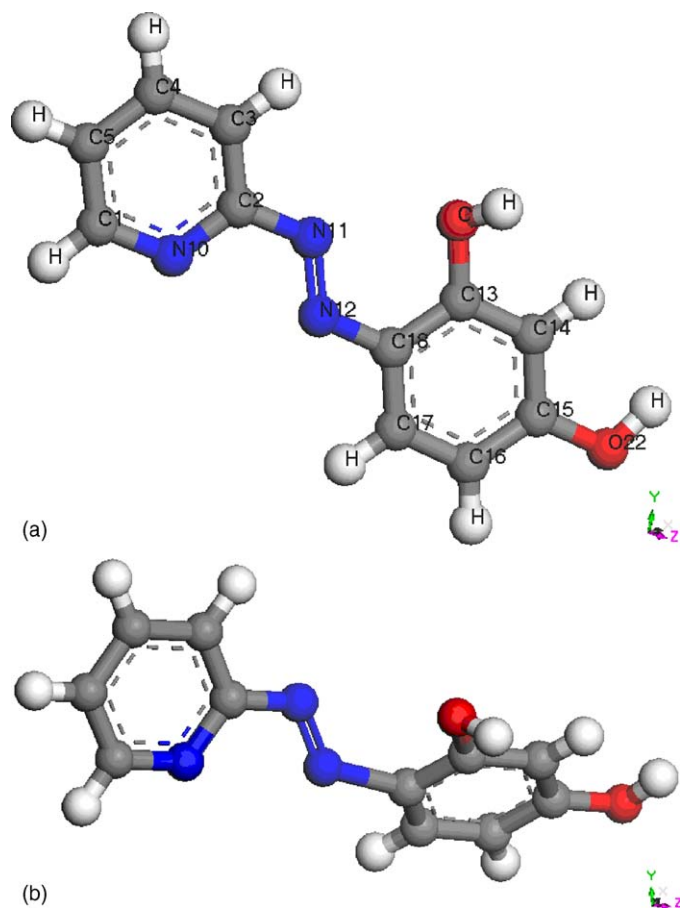


Fig. 1. (a) Optimized geometry of 4-(2-pyridylazo)-resorcinol (PAR) at unsolvated condition with all the constituent atoms labeled. (b) Optimized geometry of 4-(2-pyridylazo)-resorcinol (PAR) at solvated condition.

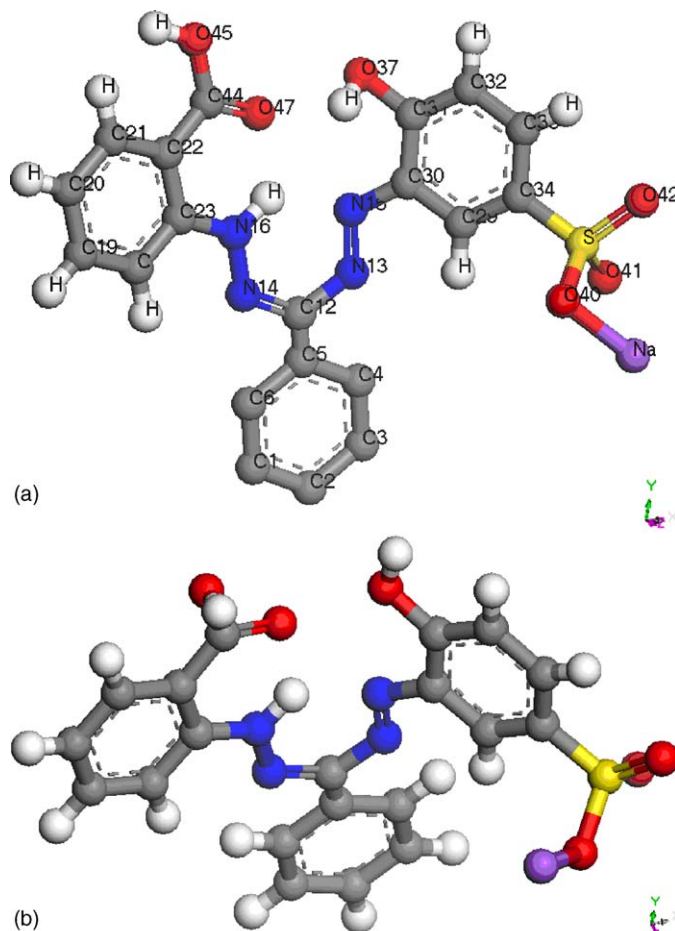


Fig. 2. (a) Optimized geometry of 2-[1-(2-hydroxy-5-sulphonyl)-3-phenyl-5 formazano] benzoate (ZINCON) at unsolvated condition with all the constituent atoms labeled. (b) Optimized geometry of 2-[1-(2-hydroxy-5-sulphonyl)-3-phenyl-5 formazano] benzoate (ZINCON) at solvated condition.

grafted over the mesoporous material used as support. The grafting and elucidation of that grafted structure is beyond the scope of this study. TMAC is chosen mainly for the presence of N^+ , which can be used for the ion pair interaction with the chromophores. The $-\text{NH}_3$ groups of the aminopropyl segments present in TMAC were converted into the $-\text{NH}_3^+$ groups on the SBA-15 surface showing that the $\text{SiO}^-/\text{H}^+ \text{NH}_3^+$ type structure was predominantly stabilized on the surface of silica gel. This is more about the binding of TMAC on SBA-15, which is again beyond the scope of this study. Experimentally, it is established that for a 1:1 loading of SBA-15 (mesoporous material) and TMAC, the pore size decreases from 7.1 to 5.4 nm and the surface area as well decreases from 897 to 620 m^2/g . Hence, the silylating agents TMAC must be present over or inside SBA-15. With that we will now explore the localized binding between TMAC and the chromophores with or without solvation. All the structures of the interacting systems were optimized independently at their neutral form. The optimized geometries of PAR, ZINCON and TMAC, both solvated (a) and unsolvated (b) are shown in Figs. 1–3, respectively. The results for the reactivity index values for the constituent atoms except the hydrogen atoms for unsolvated and solvated case for PAR are listed in

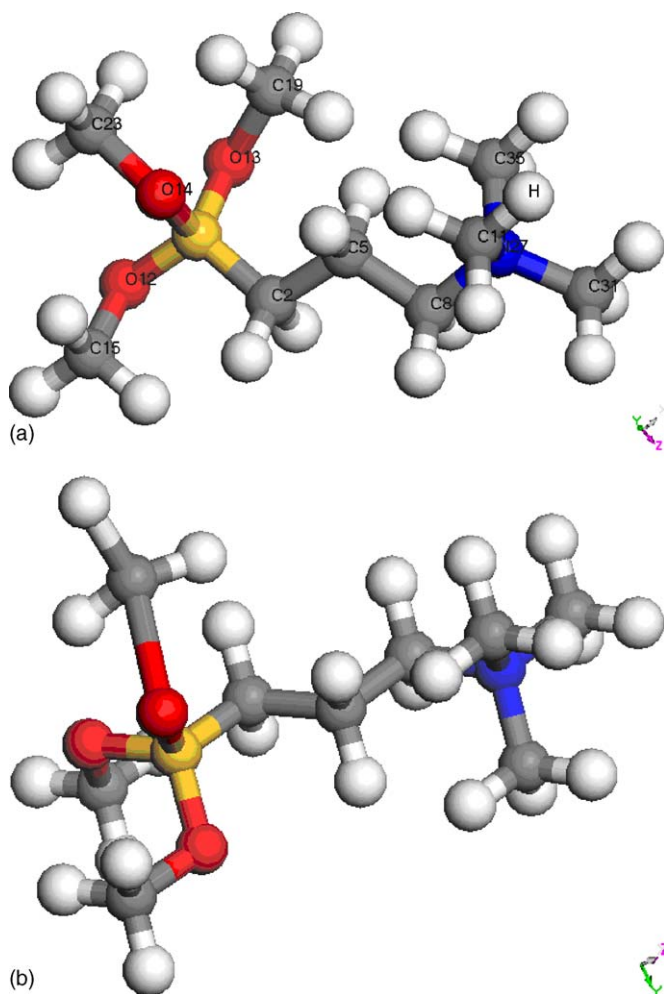


Fig. 3. (a) Optimized geometry of *N*-trimethoxysilylpropyl *N,N,N*-trimethyl ammonium chloride (TMAC) at unsolvated condition with all the constituent atoms labelled. (b) Optimized geometry of *N*-trimethoxysilylpropyl *N,N,N*-trimethyl ammonium chloride (TMAC) at solvated condition.

Tables 2 and 3, respectively. The results show that for intramolecular electrophilicity and nucleophilicity, there are some anomalous cases in which a specific atom shows both high electrophilicity and nucleophilicity, and hence it is more appropriate to rationalize this concept of relative electrophilicity/nucleophilicity. Relative nucleophilicity is the nucleophilicity of a site relative to its own electrophilicity, and vice versa for relative electrophilicity. The idea of relative nucleophilicity/electrophilicity was first proposed by Roy et al. [34] to predict intramolecular reactivity sequences of carbonyl compounds. We have used a similar ratio for the first time to find the best dioctahedral smectite for nitrogen heterocyclics adsorption in terms of intermolecular interaction [35] and as well for the adsorption property of para and meta substituted nitrobenzene [22]. Relative nucleophilicity and electrophilicity values are as well included in those tables. The coexistence of nucleophilic and electrophilic sites will result in intramolecular H-bonding, whereby the center of highest relative nucleophilicity interacts with the center of highest relative electrophilicity within the same molecule. Depending on the activity of the respective centers, the electron donor/

Table 2

Fukui function and local softness values for the constituent atoms of the chromophore PAR

Atom	f_x^+	s_x^+	f_x^-	s_x^-	s_x^+/s_x^-	s_x^-/s_x^+
C1	0.047	0.005	0.069	0.008	0.625	1.600
C2	0.2	0.248	0.310	0.038	6.526	0.153
C3	0.507	0.088	0.752	0.093	0.946	1.057
C4	0.27	0.033	0.296	0.037	0.891	1.121
C5	0.336	0.042	0.064	0.007	6.000	0.166
N10	0.769	0.096	0.694	0.086	1.116	0.896
N11	0.711	0.088	0.592	0.073	1.205	0.829
N12	0.548	0.068	0.320	0.040	1.700	0.588
C13	0.051	0.006	0.160	0.020	0.300	3.333
C14	0.392	0.049	0.436	0.054	0.907	1.102
C15	0.007	0.008	0.004	0.004	2.000	0.500
C16	0.003	0.003	0.174	0.022	0.136	7.333
C17	0.726	0.090	0.678	0.084	1.071	0.933
C18	0.111	0.013	0.114	0.014	0.928	1.077
O22	1.149	0.143	1.026	0.128	1.117	0.895
O24	1.246	0.155	1.116	0.139	1.115	0.897

acceptor property will vary. The center with highest electrophilicity will have a tendency to combine with a center with highest nucleophilicity resulting in intermolecular interaction. For the systems studied, both intra and intermolecular H-bonding is an issue, which will be detrimental in the molecular level interaction between the silylating agent and the chromophore. Now, from Table 2 it is observed that C2 has the highest electrophilicity and as well the highest relative electrophilicity for the chromophore PAR. The second highest electrophile center present in PAR is O24 but in terms of relative electrophilicity it is C5. Again in terms of nucleophilicity O24 and O22 have the highest value, but it differs in terms of relative nucleophilicity. The most active atom in terms of relative nucleophilicity is C16, followed by C13. Let us see the situation when PAR is solvated. The results are shown in Table 3. C2 is showing most electrophilicity and nucleophilicity when solvated, which falls in the anomaly we warned before.

Table 3

Fukui function and local softness values for the constituent atoms of the solvated chromophore PAR

Atom	f_x^+	s_x^+	f_x^-	s_x^-	s_x^+/s_x^-	s_x^-/s_x^+
C1	0.306	0.274	0.002	0.018	15.222	0.065
C2	1.283	1.149	1.430	1.281	0.897	1.146
C3	0.086	0.077	0.141	0.126	1.638	1.638
C4	0.719	0.644	0.778	0.697	0.924	1.082
C5	0.081	0.073	0.113	0.101	1.394	1.395
N10	0.713	0.639	0.585	0.524	1.219	0.820
N11	0.399	0.357	0.176	0.158	2.267	0.441
N12	0.618	0.554	0.235	0.211	2.629	0.380
C13	0.283	0.254	0.196	0.176	1.444	0.692
C14	0.083	0.074	0.025	0.022	3.321	0.301
C15	0.469	0.420	0.508	0.455	0.923	1.083
C16	0.025	0.022	0.161	0.144	0.155	6.440
C17	0.966	0.866	0.962	0.862	1.004	0.996
C18	0.025	0.022	0.091	0.081	0.275	3.640
O22	1.213	1.087	1.090	0.977	1.113	0.898
O24	1.239	1.110	1.143	1.024	1.084	0.922

In terms of relative electrophilicity C1 is the most active center, while C16 is the atom with highest relative nucleophilicity when solvated. Here, all the calculations were carried out considering that, the whole system is neutral. This calculation is followed by cationic and anionic calculation with reducing or adding one electron to calculate the localized reactivity index. Hence, the picture obtained from here will guide us to propose the interaction site of TMAC and chromophores to interact favorably. This effect of charge delocalization is the key factor for the interaction of the chromophore with the other interacting molecule (silylating agent and/or metal ion).

The localized reactivity index results for ZINCON both for unsolvated and solvated situation are shown in Tables 4 and 5, respectively. The results show that, in terms of localized electrophilicity and nucleophilicity C12 has the highest activity; whereas C20 is having highest relative electrophilicity; whereas C34, O37 and O42 show a similar activity in terms of relative nucleophilicity. In the solvated situation the results changes, the C31 atom center has the highest localized electrophilicity and nucleophilicity. In terms of relative electrophilicity the trend matches with that of unsolvated case and the most active atom with highest relative electrophilicity is C20, whereas in terms of relative nucleophilicity the most

Table 4

Fukui function and local softness values for the constituent atoms of the chromophore ZINCON

Atom	f_x^+	s_x^+	f_x^-	s_x^-	s_x^+/s_x^-	s_x^-/s_x^+
C1	0.118	0.005	0.086	0.003	1.666	0.600
C2	0.131	0.006	0.172	0.007	0.857	1.166
C3	0.310	0.014	0.286	0.013	1.076	0.928
C4	0.059	0.002	0.136	0.006	0.333	3.000
C5	1.292	0.058	1.277	0.058	1.000	1.000
C6	0.032	0.001	0.064	0.002	0.500	2.000
C12	1.586	0.072	1.597	0.072	1.000	1.000
N13	0.127	0.006	0.251	0.011	0.545	1.833
N14	0.166	0.007	0.339	0.015	0.466	2.142
N15	0.193	0.009	0.303	0.014	0.642	1.555
N16	0.464	0.021	0.500	0.022	0.954	1.047
C18	0.69	0.031	0.813	0.037	0.837	1.193
C19	0.686	0.031	0.703	0.032	0.968	1.032
C20	0.081	0.003	0.014	0.001	3.000	0.333
C21	0.513	0.023	0.504	0.023	1.000	1.000
C22	0.939	0.043	1.044	0.047	0.915	1.093
C23	0.702	0.032	0.669	0.030	1.066	0.937
C28	0.679	0.031	0.73	0.033	0.939	1.064
C29	0.914	0.041	0.874	0.040	1.025	0.976
C30	0.946	0.043	0.869	0.039	1.102	0.907
C31	0.929	0.042	0.960	0.043	0.976	1.023
C32	0.264	0.012	0.329	0.015	0.800	1.250
C33	0.028	0.001	0.098	0.004	0.250	4.000
C34	0.033	0.001	0.107	0.005	0.200	5.000
O37	0.018	0.001	0.124	0.005	0.200	5.000
S39	0.200	0.009	0.183	0.008	1.125	0.888
O40	0.082	0.004	0.056	0.002	2.000	0.500
O41	0.016	0.001	0.043	0.002	0.500	2.000
O42	0.030	0.001	0.103	0.005	0.2.00	5.000
Na43	0.286	0.013	0.308	0.014	0.928	1.076
C44	0.553	0.025	0.565	0.026	0.961	1.040
O45	0.124	0.005	0.179	0.008	0.625	1.600
O47	0.021	0.001	0.005	0.001	1.000	1.000

Table 5

Fukui function and local softness values for the constituent atoms of the solvated chromophore ZINCON

Atom	f_x^+	s_x^+	f_x^-	s_x^-	s_x^+/s_x^-	s_x^-/s_x^+
C1	0.035	0.018	0.234	0.121	0.149	6.711
C2	0.057	0.029	0.098	0.051	0.582	1.717
C3	0.060	0.031	0.053	0.027	1.131	0.883
C4	0.051	0.026	0.082	0.042	0.621	1.608
C5	0.736	0.380	0.172	0.089	4.269	0.233
C6	0.020	0.010	0.406	0.210	0.048	21.000
C12	0.801	0.413	0.494	0.255	1.621	0.616
N13	0.358	0.185	0.291	0.150	1.230	0.812
N14	0.282	0.145	0.063	0.032	4.531	0.221
N15	0.126	0.065	0.297	0.153	0.424	2.354
N16	0.176	0.091	0.222	0.115	0.791	1.264
C18	0.248	0.128	0.941	0.486	0.263	3.803
C19	0.038	0.020	0.247	0.127	0.154	6.505
C20	0.044	0.023	0.001	0.001	23.000	0.043
C21	0.040	0.021	0.053	0.027	0.751	1.330
C22	0.301	0.155	0.702	0.362	0.428	2.333
C23	0.001	0.001	0.058	0.030	0.033	30.000
C28	0.333	0.172	0.683	0.353	0.487	2.052
C29	0.675	0.348	1.828	0.944	0.369	2.713
C30	0.408	0.211	0.521	0.269	0.783	1.276
C31	0.954	0.492	1.193	0.616	0.799	1.250
C32	0.275	0.142	0.411	0.212	0.669	1.495
C33	0.058	0.030	0.098	0.051	0.592	1.729
C34	0.046	0.024	0.087	0.045	0.592	1.729
O37	0.009	0.005	0.125	0.064	0.078	12.800
S39	0.089	0.046	0.149	0.077	0.597	1.675
O40	0.007	0.004	0.028	0.014	0.250	4.000
O41	0.016	0.008	0.038	0.020	0.400	2.500
O42	0.021	0.011	0.053	0.027	0.407	2.454
Na43	0.013	0.007	0.011	0.006	1.175	0.851
C44	0.199	0.103	0.645	0.333	0.308	3.241
O45	0.001	0.001	0.055	0.028	0.036	28.000
O47	0.105	0.054	0.125	0.064	0.843	1.185

active atom is C23, followed by O45, C6 and O37, with a decreasing order of activity. The results show that there is drastic change in the order of relative nucleophilicity for the ZINCON molecule, when solvated. To explain this behavior, we looked into the geometry of ZINCON molecule as shown in Fig. 2. The presence of neighboring nitrogen influences the electron donor–acceptor scenario resulting in the activity of the C20 atom site as also observed in case of PAR. Now, from the dipole moment values we have predicted that ZINCON is more hydrophilic than PAR. To explain the enhanced activity of C23 we find that it has oxygen as its nearest neighbor. This oxygen is interactive when solvated, that causes the drastic difference in presence of the solvent. This again proposes that the localized descriptors bring forward the activity of the atomic sites in terms of their electron donor acceptor capability, which will guide the interaction process.

Finally, the calculations were performed on TMAC molecule, which is the silylating agent. The results for the unsolvated and solvated situations were presented in Tables 6 and 7, respectively. In terms of localized electrophilicity/nucleophilicity, it is observed that for unsolvated case the activity for electrophilicity lies with C2 and the nucleophilicity with C5 atom. This order is very different when we consider the relative electrophilicity/nucleophilicity order. In terms of

Table 6
Fukui function and local softness values for the constituent atoms of the TMAC

Atom	f_x^+	s_x^+	f_x^-	s_x^-	s_x^+/s_x^-	s_x^-/s_x^+
Si1	0.016	0.018	1.239	1.408	0.013	78.222
C2	0.959	1.089	1.529	1.737	0.627	1.594
C5	0.020	0.023	1.633	1.855	0.012	80.652
C8	0.031	0.035	1.149	1.306	0.027	37.314
N11	0.102	0.116	0.071	0.081	1.435	0.696
O12	0.020	0.023	0.004	0.005	4.600	0.194
O13	0.004	0.005	0.018	0.020	0.213	4.000
O14	0.004	0.005	0.032	0.036	0.121	7.200
C15	0.011	0.012	0.102	0.115	0.104	9.583
C19	0.002	0.002	0.164	0.186	0.013	93.000
C23	0.001	0.001	0.020	0.023	0.045	23.000
C27	0.040	0.045	0.123	0.140	0.321	3.111
C31	0.020	0.023	0.174	0.198	0.114	8.601
C35	0.050	0.057	0.068	0.077	0.733	1.363
Cl39	0.760	0.863	0.132	0.150	5.753	0.173

relative electrophilicity the most active atom is Cl39 followed by O12; where as in terms of relative nucleophilicity the atom with the highest value is C19, followed by C5 and Si1, in a decreasing order. The results for the calculation with solvation show that in terms of localized electrophilicity the most active atom is C2 same as with the unsolvated case. The atom with highest local nucleophilicity is Cl39, which is different from that of the unsolvated situation. The trend totally changes in terms of the relative electrophilicity/nucleophilicity. The active atom in terms of relative electrophilicity is Si1 followed by C19 and C23 in a decreasing order. In terms of relative nucleophilicity the center with the highest value is C5, which is close to the result obtained for the unsolvated situation. There is a drastic anomaly in the results, the relative electrophilicity was highest for Cl39 when unsolvated, whereas Si1 becomes the atom with highest relative electrophilicity when solvated.

From the above results, one thing seems obvious that there is a role of solvent in the activity of the constituent atoms of the individual molecules. The activity change dramatically in case of hydrophilic chromophores (ZINCON) and silylating agent

(TMAC). It is also observed that except for the relative nucleophilicity values of PAR there is an increase in the activity of the constituent atoms when the molecules were solvated. Hence, solvation is playing a crucial role in the activity of the interacting molecules. The results also proposes that each molecule has couple of close range active centers which can either way help the formation of intra or inter molecular bonding scenarios.

4.3. Reactivity index scale

We will consider the results of relative electrophilicity/nucleophilicity only, as relative nucleophilicity, and relative electrophilicity, by definition can depict the intrinsic activity of the atom center more quantitatively compared to its localized term. We calculated the reactivity index from the non-protonated moiety to propose their activity while protonated resulted due to the intramolecular H-bonding. The intramolecular H-bonding will be resulted from the interaction between the nucleophilic site with an electrophilic site as a combination of electron donor and acceptor site to favor a pseudo bond formation process inside the molecule. And at the same time for a situation, where there is a possibility to interact with other molecule, then these molecules may interact with their active centers to form intermolecular bonding. Hence, a center with highest nucleophilicity will go to react with a center with highest relative electrophilicity, and vice versa. Depending on the activity of the respective centers electron donor acceptor property will vary. We have used this methodology successfully to explain the inter-molecular and intra-molecular H-bonding for fluorophore sensor [36].

In terms of global softness the order of activity for the chromophores both when solvated and unsolvated is as follows: PAR > ZINCON. PAR shows much higher global softness than ZINCON, even compared to that of TMAC. In terms of dipole moment ZINCON shows greater hydrophilicity compared to TMAC when unsolvated. But TMAC is more hydrophilic than the ZINCON when solvated. At the same time it shows the greater hydrophobicity for PAR. We will now compare the atomic center of the silylating agent with highest relative electrophilicity/nucleophilicity to match with the counter active atom from chromophore with highest nucleophilicity/electrophilicity for pseudo bond formation. We are considering the interaction of TMAC with PAR and ZINCON, while the TMAC is bonded with the SBA-15 surface. From the results it is observed that, when the molecules are unsolvated Cl39 of TMAC interacts with C16 of PAR and C34/O37/O42 of ZINCON. In reality, the reaction is carried out in solvated medium. So at the solvated situation, Si1 of TMAC interacts with same C16 of PAR and may interact with C23/O45 of ZINCON. The second option, O45 looks more reasonable apart from that of PAR. But we have seen from the results of dipole moment that PAR is hydrophobic so the solvent does not influence the binding, whereas for O45, which is the free oxygen present in ZINCON will guide itself toward Si1 of TMAC. These results were obtained in terms of the highest electrophilic site of TMAC. That site is interacting with highest

Table 7
Fukui function and local softness values for the constituent atoms of the solvated TMAC

Atom	f_x^+	s_x^+	f_x^-	s_x^-	s_x^+/s_x^-	s_x^-/s_x^+
Si1	0.543	1.863	0.003	0.010	186.300	0.005
C2	0.851	2.920	0.047	0.161	11.925	0.055
C5	0.001	0.003	0.220	0.755	0.004	251.667
C8	0.083	0.284	0.267	0.916	0.310	3.225
N11	0.022	0.075	0.179	0.614	0.122	8.196
O12	0.241	0.827	0.016	0.055	15.036	0.066
O13	0.032	0.110	0.002	0.007	15.714	0.060
O14	0.210	0.721	0.027	0.093	7.752	0.129
C15	0.047	0.161	0.010	0.034	4.735	0.212
C19	0.196	0.672	0.002	0.007	96.000	0.096
C23	0.187	0.641	0.002	0.007	91.571	0.010
C27	0.113	0.388	0.067	0.230	1.687	0.604
C31	0.022	0.075	0.030	0.103	0.738	1.354
C35	0.022	0.075	0.012	0.041	1.86	0.538
Cl39	0.013	0.045	0.765	2.625	0.017	58.333

nucleophilic site of the chromophore molecule, considering that the interaction is taking place between two neutral center with the delocalized charge inside. Now to compare these binding situations, with the experimental results one needs to look at the interaction of this TMAC–chromophore complex with the metal ion. The experimental results found that TMAC binds both PAR and ZINCON while solvated. So the results obtained for the unsolvated case using reactivity index cannot be verified. As well experimentally it is not possible to compare the strength of binding between the chromophore and TMAC unless one does a study for metal ion interaction, which is detrimental to figure out which chromophore acts better than the other.

4.4. Interaction energy results

We first compared the interaction energy for the complex between TMAC and PAR/ZINCON both when solvated and unsolvated. To study the interaction between the TMAC and the chromophores. We have used the results of the reactivity index to propose the starting configuration of the interactions. The PAR and ZINCON molecules were oriented in such a way that the highest electrophilic center of the chromophores faces the highest nucleophilic center of the TMAC. Here, we consider the relative electrophilicity/nucleophilicity results. We have chosen the initial geometry from the results of the localized reactivity index; that means we have placed the chromophore with its most active site facing the active site of the TMAC to interact. We have also tried with other options from the results of the reactivity index and then performed the interaction energy calculation. The point of doing a localized reactivity index is to find out the active site which will guide us to choose the correct conformation for the interaction energy calculation. From the results, it is observed that, when the molecules were unsolvated C139 of TMAC will interact with C16 of PAR and C34/O37/O42 of ZINCON. In reality, the reaction is carried out in solvated medium. So at the solvated situation, Si1 of TMAC interacts with same C16 of PAR and may interact with C23/O45 of ZINCON. The optimized geometry of the ZINCON and PAR molecule with TMAC in their unsolvated (a) and solvated (b) form is shown in Figs. 4 and 5, respectively. At the starting geometry the interacting species were kept at a distance of 2.5 Å. The calculations were repeated for various initial distances starting from 2.0 to 4.0 Å, and from the potential energy surface generated there forth, 2.5 Å distance was chosen for the interaction energy calculation. We have as well varied the interacting centers with comparable activity to visualize which center will really be dominant in the interaction process. Or in other words, we will compare the interaction energy for different centers to compare and then propose the most favorable interaction. The results show that when unsolvated TMAC + PAR complex is more stable than that of TMAC + ZINCON complex by 47.23 kcal/mol; whereas when solvated the ZINCON complex is more stable than the solvated PAR complex with TMAC by 23.17 kcal/mol. It shows that with all the options studied, the O45 center of zincon binds more favorably with the Si1 center of TMAC, while solvated;

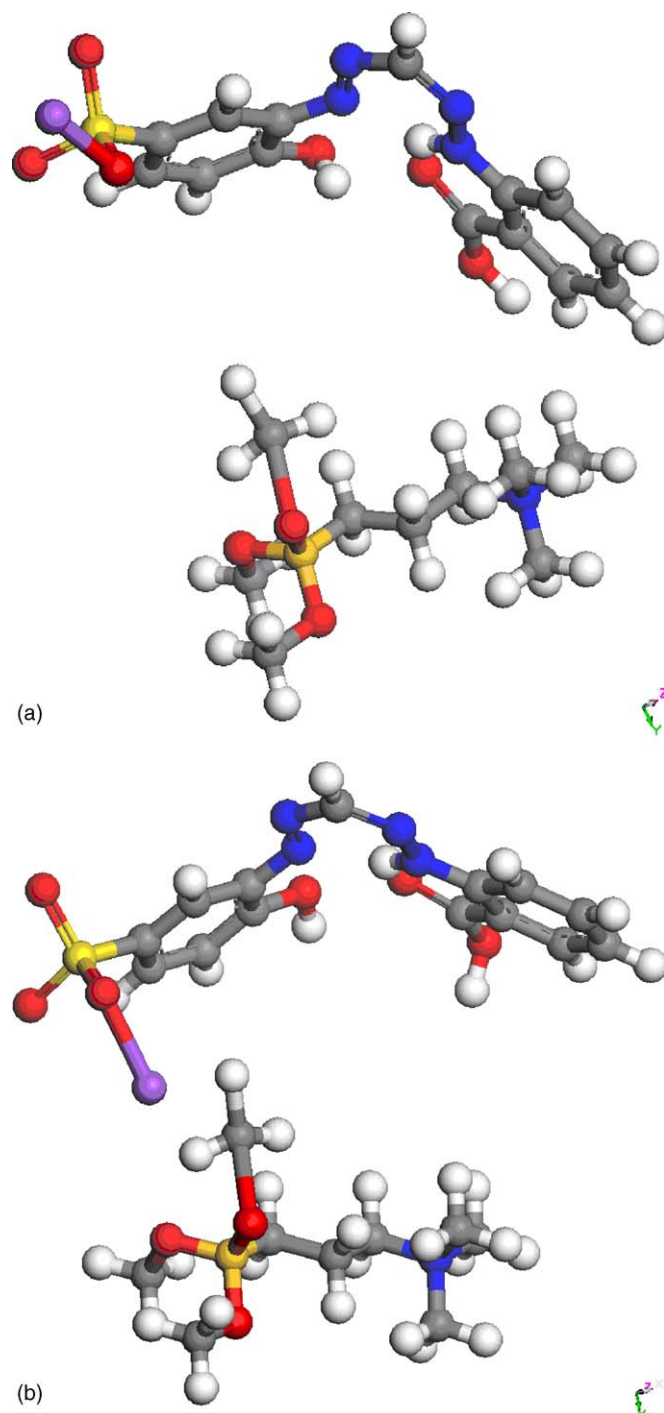


Fig. 4. Interaction between *N*-trimethoxysilylpropyl *N,N,N*-trimethyl ammonium chloride (TMAC) and 2-[1-(2-hydroxy-5-sulphonyl)-3-phenyl-5 formazano] benzoate (ZINCON). (a) Unsolvated. (b) Solvated.

whereas in the unsolvated situation C139 of TMAC binds strongly with PAR. The results show that ZINCON binds more strongly with TMAC when solvated. This brings us to look at the situation when a metal ion binds with the chromophore. We have chosen cadmium as the metal ion to be interacted with the chromophores. To study this interaction, we have placed Cd over PAR and ZINCON at a distance of 2.5 Å. The calculations were performed for both the unsolvated and solvated situation.

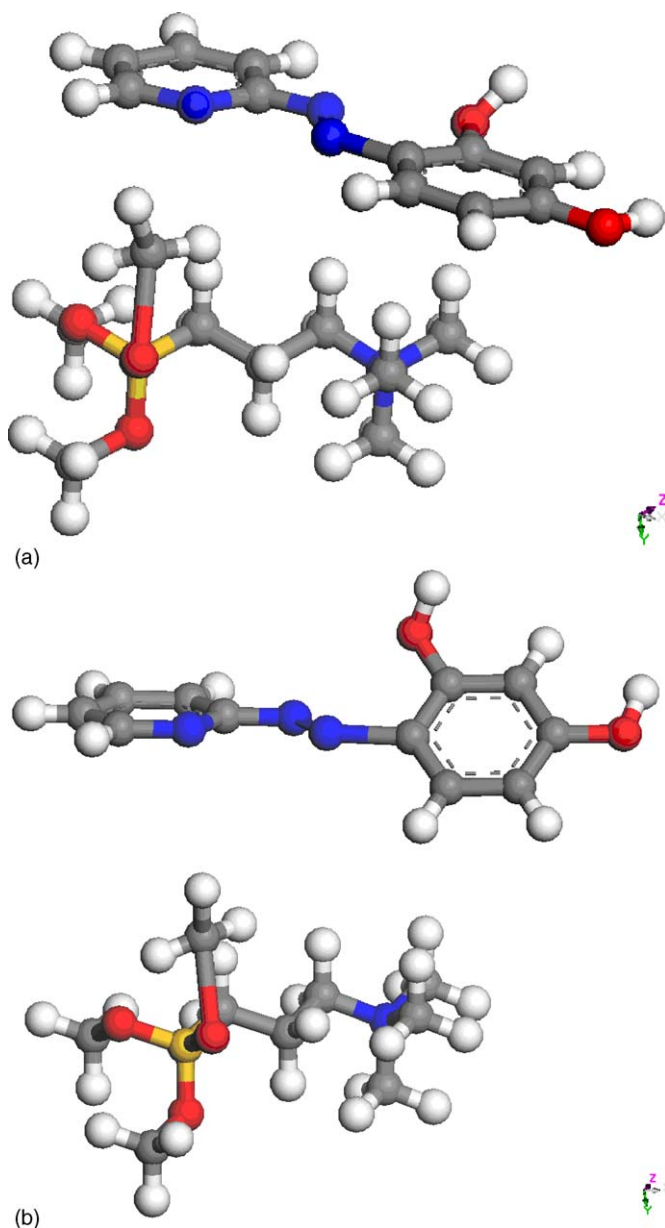


Fig. 5. Interaction between *N*-trimethoxysilylpropyl *N,N,N*-trimethyl ammonium chloride (TMAC) and 4-(2-pyridylazo)-resorcinol (PAR). (a) Unsolvated. (b) Solvated.

Cd molecule is placed in the vicinity of the different active centers of the interacting species. We have chosen the optimized complex between TMAC and chromophore as obtained from the previous set for the calculation with Cd both in solvated and unsolvated situation. For the unsolvated case, all the atoms of the complex except the C16 of PAR, C139 of TMAC and C33 of ZINCON is relaxed; whereas for the solvated case Si1 of TMAC, C16 of PAR and O45 of ZINCON is kept fixed. The complex is formed through a virtual bonding between the activated atoms of the TMAC and the chromophores. Initially, we looked at the local complexation of PAR and ZINCON with the metal ion for both the condition of solvation. We see that in absence of solvent Cd forms a more stable complex with PAR (21.24 kcal/mol) compared to

ZINCON, for the same center. The situation does not change even when the molecules are solvated. After solvation Cd–ZINCON complex is less stable than the complex of Cd and PAR (17.09 kcal/mol). The geometry of the optimized structures for the Cd–PAR complex and the Cd–ZINCON complex for both unsolvated and solvated situation are shown in Figs. 6 and 7, respectively. It is observed that there is a dramatic change in the location of Cd, the Cd in the solvated situation comes closer to the PAR surface within a bonding distance of say 2.39, from 3.26 in the unsolvated case. In case of ZINCON, the nature of bonding explains the lower stability of Cd; in the unsolvated case the Cd is closer to the double bonded oxygen present on the ZINCON surface (2.72), but goes further away from the nitrogen centers due to the steric repulsions resulted from the proximity of other centers. The situation worsens in presence of solvent as the Cd atom moves behind the surface with a change in Cd–N distance of about 3.56. This forces us to look at the situation when TMAC, chromophore and cadmium, all are present in the reaction. Due to the complexity of the situation we were unable to include the figure for these cases. It is observed that for unsolvated case TMAC + Cd + PAR is more stable than the respective ZINCON complex by 18.76 kcal/mol. The situation for ZINCON worsens when it is solvated; the complex is less stable than the compatriot PAR complex. This result matches well with the experimental observation. In experiment, we have seen that PAR is the best performer for selective complexation with Cd in comparison to that with ZINCON. This is may be due to the fact

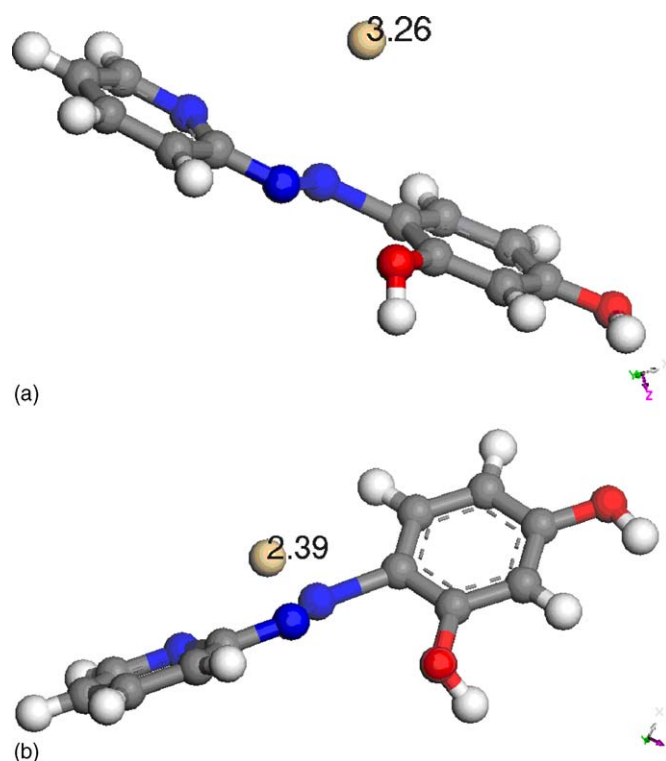


Fig. 6. (a) Optimized geometry of the complex formed between Cd and 4-(2-pyridylazo)-resorcinol (PAR) at unsolvated condition. (b) Optimized geometry of 4-(2-pyridylazo)-resorcinol (PAR) and Cd, at solvated condition. The numbers are the distances between Cd and the nearest neighboring atom.

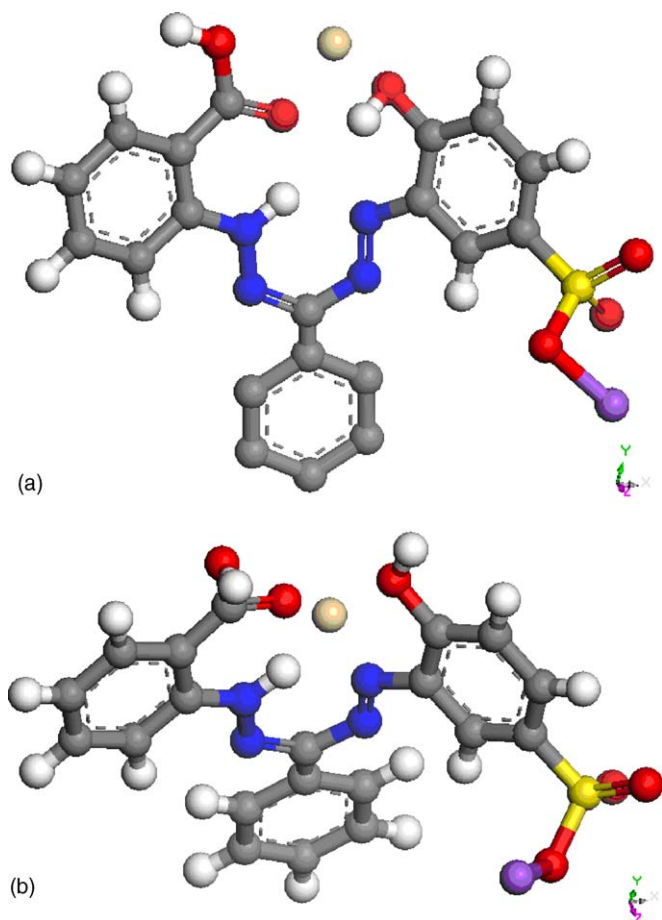


Fig. 7. (a) Optimized geometry of 2-[1-(2-hydroxy-5-sulphonyl)-3-phenyl-5 formazano] benzoate (ZINCON) at unsolvated condition with Cd. (b) Optimized geometry of 2-[1-(2-hydroxy-5-sulphonyl)-3-phenyl-5 formazano] benzoate (ZINCON) and Cd at solvated condition. The numbers are the distances between Cd and the nearest neighboring atom.

that Cd–PAR distribution coefficient is much higher than that of ZINCON–Cd. Here, ZINCON has no favorable interaction with Cd compared to that of PAR hence, it cannot bind Cd strongly enough and again at the same time its binding with TMAC when solvated is stronger than the metal ion and hence the metal chromophore complex cannot hold. The situation may change for interaction with other metal ion. Hence, chromophores can be selectively used for metal identification and separation and reactivity index method can be successfully used to design colorimetric sensor to address a specific analytical problem. This is a first study to show the applicability of reactivity index in analytical chemistry domain.

5. Conclusion

This is the first study to monitor the interaction between amino-functional silanol surface and the chromophore to look into the naked eye sensing mechanism. We have used two chromophore molecules representing hydrophobic and hydrophilic type. We used density functional calculation on all the interacting molecules both in the unsolvated phase and in solvated medium within the domain of hard soft acid base

principle (HSAB) to look at the localized activity of the interacting atoms of these molecules to formulate a priori rule for the choice of the best chromophore. The results were comparable with experiment and it is observed that solvation plays a detrimental role in the binding of chromophore with silylating agent. As well, the results show that, the range of reactivity index can be used as a suitable property to scale activity of chromophore molecules suitable for a specific sensing process. The result shows that the hydrophobic chromophore binds stronger with the metal and the silylating agent; whereas the hydrophilic one binds well with the silylating agent when solvated but not with the metal chosen. This shows that chromophores can be selectively used for metal identification and separation.

References

- [1] K. Moller, T. Bein, Internal modification of ordered mesoporous hosts, *Stud. Surf. Sci. Catal.* 117 (1998) 53–64.
- [2] C.E. Fowler, B. Lebeau, S. Mann, Covalent coupling of an organic chromophore into functionalized MCM-41 mesophases by template-directed co-condensation, *Chem. Commun.* 17 (1998) 1825–1826.
- [3] M.C. Burleigh, M.A. Markowitz, M.S. Spector, B.P. Gaber, Direct synthesis of periodic mesoporous organosilicas: functional incorporation by co-condensation with organosilanes, *J. Phys. Chem. B.* 105 (2001) 9935–9942.
- [4] T. Asefa, C. Yoshina-Ishii, M.J. MacLachlan, G.A. Ozi, New nanocomposites: putting organic function “inside” the channel walls of periodic mesoporous silica, *J. Mater. Chem.* 8 (2000) 1751–1756.
- [5] B.J. Scott, G. Wirnsberger, G.D. Stucky, Mesoporous and mesostructured materials for optical applications, *Chem. Mater.* 13 (2001) 3140–3150.
- [6] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Triblock copolymer syntheses of mesoporous silica with periodic 50–300 Å pores, *Science* 279 (1998) 548–552.
- [7] A. Sayari, Catalysis by crystalline mesoporous molecular sieves, *Chem. Mater.* 8 (1996) 1840–1852.
- [8] P.K. Jal, S. Patel, B. Mishra, Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions, *Talanta* 62 (2004) 1005–1028.
- [9] J.G. Hou, Q. Ma, X.Z. Du, H.L. Deng, J.Z. Gao, Inorganic/organic mesoporous silica as a novel fiber coating of solid-phase microextraction, *Talanta* 62 (2004) 241–246.
- [10] R.G. Pearson, *Symmetry Rules for Chemical Reactions: Orbital Topology and Elementary Process*, Wiley-Interscience, New York, 1976, p. 213.
- [11] D. Sivanesan, R. Amutha, V. Subramanian, B.U. Nair, T. Ramasami, Assessment of the importance of the solvent in the calculation of condensed Fukui function: a self-consistent reaction field calculation study, *Chem. Phys. Lett.* 308 (1999) 223–228.
- [12] F.J. Luque, S.R. Gadre, P.K. Bhadane, M. Orozco, The effect of hydration on the molecular charge-distribution of cations an ab initio SCRF study, *Chem. Phys. Lett.* 232 (1995) 509–517.
- [13] F.J. Luque, S.R. Gadre, P.K. Bhadane, M. Orozco, Effect of solvation on the shapes, sizes, and anisotropies of polyatomic anions via molecular electrostatic potential topography – an ab initio self-consistent reaction field approach, *J. Chem. Phys.* 100 (1994) 6718–6726.
- [14] F.J. Luque, S.R. Gadre, P.K. Bhadane, M. Orozco, SCRF calculation of the effect of hydration on the topology of the molecular electrostatic potential, *J. Phys. Chem.* 97 (1993) 9380–9384.
- [15] A. Chatterjee, M. Chatterjee, Y. Ikushima, F. Mizukami, The role of solvent on selective hydrogenation of conjugated and isolated C=C of citral (3,7-dimethyl 2,6-octadienal) – a self-consistent reaction field study, *Chem. Phys. Lett.* 395 (2004) 143–149.
- [16] R.G. Parr, R.G. Pearson, Absolute hardness – companion parameter to absolute electronegativity, *J. Am. Chem. Soc.* 105 (1983) 7512–7516.

- [17] R.G. Pearson, Recent advances in the concept of hard and soft acids and bases, *J. Chem. Edu.* 64 (1987) 561–567.
- [18] R.G. Parr, W.T. Yang, Density functional-approach to the frontier-electron theory of chemical-reactivity, *J. Am. Chem. Soc.* 106 (1984) 4049–4050.
- [19] P. Geerlings, F. De Proft, HSAB principle: applications of its global and local forms in organic chemistry, *Int. J. Quant. Chem.* 80 (2000) 227–235.
- [20] A. Chatterjee, T. Iwasaki, T. Ebina, Reactivity index scale for interaction of heteroatomic molecules with zeolite framework, *J. Phys. Chem. A* 103 (1999) 2489–2494.
- [21] L.T. Nguyen, T.N. Le, F. De Proft, A.K. Chandra, W. Langenaeker, M.T. Nguyen, P. Geerlings, Mechanism of [2 + 1] cycloadditions of hydrogen isocyanide to alkynes: molecular orbital and density functional theory study, *J. Am. Chem. Soc.* 121 (1999) 5992–6001.
- [22] A. Chatterjee, T. Ebina, T. Iwasaki, F. Mizukami, Intermolecular reactivity study to scale adsorption property of para- and meta-substituted nitrobenzene over 2: 1 dioctahedral smectite, *J. Chem. Phys.* 18 (2003) 10212–10220.
- [23] A. Chatterjee, T. Ebina, Y. Onodera, F. Mizukami, Effect of exchangeable cation on the swelling property of 2:1 dioctahedral smectite – a periodic first principle study, *J. Chem. Phys.* 120 (2004) 3414–3424.
- [24] P. Geerlings, F. De Proft, W. Langenaeker, Conceptual density functional theory, *Chem. Rev.* 103 (2003) 1793–1873.
- [25] W. Yang, W.J. Mortier, The use of global and local molecular-parameters for the analysis of the gas-phase basicity of amines, *J. Am. Chem. Soc.* 108 (1986) 5708–5711.
- [26] B. Delley, An all-electron numerical-method for solving the local density functional for polyatomic-molecules, *J. Chem. Phys.* 92 (1990) 508–517.
- [27] B. Delley, Analytic energy derivatives in the numerical local-density-functional approach, *J. Chem. Phys.* 94 (1991) 7245–7250.
- [28] B. Delley, From molecules to solids with the DMol(3) approach, *J. Chem. Phys.* 113 (2000) 7756–7764.
- [29] B. Delley, Modern density functional theory: a tool for chemistry, in: J.M. Seminario, P. Politzer (Eds.), *Theoretical and Computational Chemistry*, vol. 2, Elsevier Science, Amsterdam, 1995.
- [30] A.D. Becke, A multicenter numerical-integration scheme for polyatomic-molecules, *J. Chem. Phys.* 88 (1988) 2547–2553.
- [31] C.T. Lee, W.T. Yang, R.G. Parr, Development of the colle-salvetti correlation-energy formula into a functional of the electron-density, *Phys. Rev. B* 37 (1988) 785–789.
- [32] S.F. Boys, F. Bernardi, *Mol. Phys.* 19 (1970) 553.
- [33] A. Klamt, G. Schüürmann, COSMO: a new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient, *J. Chem. Soc. Perkin Trans. 2* (1993) 799.
- [34] R.K. Roy, S. Krishnamurti, P. Geerlings, S. Pal, Local softness and hardness based reactivity descriptors for predicting intra- and intermolecular reactivity sequences: Carbonyl compounds., *J. Phys. Chem. A* 102 (1998) 3746–3755.
- [35] A. Chatterjee, T. Ebina, T. Iwasaki, Best dioctahedral smectite for nitrogen heterocyclics adsorption – a reactivity index study, *J. Phys. Chem. A* 105 (2001) 10694–10701.
- [36] A. Chatterjee, T.M. Suzuki, Y. Takahashi, D.A.P. Tanaka, A density functional study to choose the best fluorophore for photon-induced electron-transfer (PET) sensors, *Chem. Eur. J.* 9 (2003) 3920.