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Propargyl-functionalized single arm allied Anthracene based Schiff bases: Crystal structure, solvatochromism and selective recognition of Fe³⁺ ion

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ABSTRACT

An organic moiety exhibit specific behavior in electronic absorption spectra while accommodating various solvents or metal ions and that specificity depends on particular guest solvent molecules or metal ions. Herein, we report about the photophysical properties of newly synthesized Propargyl-functionalized anthracene based Schiff bases (PASB). The formulated compounds have been thoroughly characterized by elemental analysis, FT-IR, NMR (¹H and ¹³C) and UV-Vis spectroscopy, emphasized with Kamlet-Taft approach to explain the solvatochromic behavior of the synthesized compounds. PASBs were screened for the sensorial aptitude towards various metal ions which were found to act as an excellent UV-Vis probe for selective detection of Fe³⁺ ion with LOD 1.60×10^{-8} M. Additionally, coordination behavior of ligand with Fe³⁺ ion was examined through the change in magnetic property of Fe³⁺ ions by VSM (vibrating sample magnetism) study. Moreover, complete structure elucidation of compound 4b was achieved via X-ray crystallography. The binding sites of sensor conjugate 4b-Fe³⁺ are well supported by FT-IR spectroscopy and computational analysis following DFT approach. The reported contribution focused on the factors determining the ability of propargyl appended Schiff base to present structure, mental picture of solvatochromism and metal ion sensitivity.

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1. Introduction

The interactive nature of solute molecules with its surrounding solvent counterparts lies at the root of problems associated with our fundamental understanding of reactivity in solution or in physico-chemical nature of receptor binding sites. Hence the selectivity of solvents towards the receptor molecules is highly influenced by the solvatochromic nature of receptor. Moreover, the effect of solvent on the electronic absorption spectra of solute observed with change in the environment of different solvents has been a subject of interesting investigations.¹ For any compound, a solvent affects both ground and excited states differently. A change in solvent is always accompanied by a change in polarity and dielectric constant of the surrounding medium. The knowledge of polarity of ground and electronically excited states provides an insight of photophysical properties of solute. Therefore,

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https://doi.org/10.1016/j.molstruc.2020.129618 0022-2860/© 2020 Elsevier B.V. All rights reserved. solvatochromism is a type of fruitful interaction and has wide acceptance in theoretical and analytical chemistry.

Among various metal ions, iron (III) ion not only is an essential metal ion in living beings but also plays a key role in various biological processes like oxygen transport, DNA and RNA synthesis, cellular metabolism, electron transport, enzyme catalyses and so on.² In any organism both the deficiency and overload of iron (III) ions can lead to serious disorders like anemia, parkinsons and alzheimers, liver damage and hemochromatosis.³ Therefore selective and sensitive detection of iron (III) in biological and environmental system is very essential.

Propargyl group is a very interesting functionality due to its versatile reactivity which is utilized in many organic reactions for various transformations and functionalizations by researchers for decades.⁴ Propargyl reagents undergo "click reactions" i.e. 1,3-dipolar cycloaddition reactions designed by Huisgen.⁵ One of the very effective transformations to introduce propargyl functional group is the well known Williamson reaction. Propargyl functionalized compounds are of particular interest in the design of pharmaceutically active drugs like rasagiline (N-propargyl-1-(R)-

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Scheme 1. Synthetic route for propargyl-functionalized anthracene based schiff bases (PASB)

aminoindan), selegiline (L-deprenyl), ladostigil (TV-3,326), agrochemicals like clodinafop-propargyl and in the field of analytical and synthetic chemistry.⁶⁻¹¹ Moreover, Schiff bases are enjoying a special status in the field of chemistry which can be easily synthesized through a simple synthetic procedure and have good solubility in common solvents.^{12–13}

Usually solvatochromism have been studied for schiff bases having tautomerism but in present study positive solvatochromism is observed for synthesized compounds having no tautomerism which may be due to the solute-solvent interactions by the formation of hydrogen bonds between hydrogen-bond acceptor (HBA) solvent and propargyl moiety. Till date only a few examples of anthracene based Schiff bases are described.¹⁴ Nevertheless, to the best of our knowledge no report is available on the study of propargyl allied anthracene based schiff bases.

Keeping the above perspectives in mind, herein we report the synthesis, spectral characterization, crystal structure of propargyl appended anthracene based Schiff bases (PASB) and focuses to elucidates the solvatochromism and selectively detection of Fe³⁺ ions. Additionally, metal ion and ligand coordination is also confirmed by VSM (vibrating sample magnetism) studies followed by theoretical studies using DFT/B3LYP/6-31G level. The motive behind the present work is to have a better visualization towards qualitative solvents effect and selective metal ion sensitivity.

2. Results and Discussion

2.1. Synthesis and characterization

A two step synthetic route, shown in scheme 1, was employed to synthesize PASBs (4a-4g). Firstly, 9-anthracenecarboxaldehyde (1) was made to undergo condensation reaction with aromatic amines (2a-2g) using ethanol as solvent to yield anthracene based Schiff bases (3a-3g). The obtained Schiff bases were then stirred in room temperature with propargyl bromide in DMF using potassium carbonate as base for 16 hours to give desired PSABs (4a-4g).

The structure and purity of all the compounds were inferred from their infrared and NMR (¹H and ¹³C) spectra. The FT-IR spectra of the newly synthesized compounds were recorded as neat spectra in the range of 4000-400 cm⁻¹. The absorption frequencies recorded were found to be in close agreement with the structure of the synthesized compounds. The typical bands observed for the terminal alkynes appeared near 2123-2110 cm⁻¹ and 3297-3180

cm⁻¹ corresponding to C≡C and C≡C-H bonds. The C=N stretching vibration of Schiff bases appears as a strong peak in the region of 1635-1605 cm⁻¹.¹⁵ The absorption band for the aromatic C=C vibrations and C-H stretching appears in the region of 1500-1600 cm⁻¹ and 3076-3060 cm⁻¹ respectively. For aryl alkyl ether asymmetric stretching band appears at 1271-1265 cm⁻¹ and symmetric stretching band appears at 1028-1100 cm⁻¹. Alkyl C-H stretching gives a medium absorption band around 2850 cm⁻¹ and aromatic C-H stretching gives absorption band in the region of 3076-3060 cm⁻¹. The ¹H NMR spectra of the synthesized compounds have demonstrated the symbolic peaks of allylic (-C=C-H) protons in the range of 2.55-2.50 ppm. Signals in the region of 7.60-6.40 ppm are assigned for aryl ring protons. Peaks in the region of 4.40-4.80 ppm are observed for alkyl protons (-O- CH_2 -). In all the compounds – HC=N- protons are observed in the region of 8.40-8.80 ppm. In ¹³C NMR spectra, peak corresponding to $-C \equiv C$ - group in the region of 75.06 to 85.07 ppm and for -C=N- group in the region of 160.02 to 162.07 ppm validate the product formation. Further, the most upfield peak was observed for -OCH₂ group in the region of 56.10 to 56.20 ppm. Moreover, the aromatic carbon peaks were seen in the region of 156.29 to 115.55.

2.2. Crystal structure

The ORTEP diagram and atom numbering scheme for empirical formula C₂₄H₁₇NO (4b) are given in (Fig. 1). Crystallographic data and structure determination parameters are summarized in (Table S2). X-ray studies disclose that the compound 4b has comparable structure, as is evident from the bond angles and bond parameters. Compound 4b crystallized in triclinic crystal system containing two molecules per unit cell with P-1 space group. Antheracene and Schiff base substituted aromatic ring are in parallel plane at 118.58(15)°. The propargyl group attached to aromatic ring assume to be lie above the plane at an angle of 124.89(15)° with an extended conformation which can be seen from the C19-O1-C22 torsion angles of 118.25(13). The propargyl group in crystal structure shows linear conformation which can be seen from the C22-C23-C24 at an angle of 178.5(2)°. The C1- N1 bond length is found to be 1.256(2) Å which is closer to theoretical (C=N) double bond length (1.25Å) than to C-N single bond length (1.47Ű).

In molecular lattice arrangement of compound 4b along a-axis, molecules are packed via strong intermolecular hydrogen-bonding interactions (N•••H-C) 2.564(2) Å and (O•••H-C) 2.630(2) involv-

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Fig. 1. ORTEP diagram of 4b with thermal ellipsoids at 40% probability, selected bond length (Å) and angle (°) 01-C19 = 1.3736(18), 01-C22 = 1.4218(19), N1-C16 = 1.420(2), N1-C1 = 1.256(2), C19-C20 = 1.377(2), C22-C23 = 1.465(3), C23-C24 = 1.167(2), C19-O1-C22 = 118.25(13), C1-N1-C16 = 118.58(15), O1-C19-C20 =124.89(15), 01-C19-C18 = 115.46(14), 01-C22-C23 = 113.14(14), C24-C23-C22 = 178.5(2)

Table	1

UV	spectral	data	$\bar{\upsilon}max$	(103	cm-1) of	compounds	(4a-4g).
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	Analyte $\bar{v}_{max}(10^3 \text{ cm}^{-1})$						
Solvent	4a	4b	4c	4d	4e	4f	4g
CH₃CN	25.44	25.18	25.38	25.25	25.25	25.83	25.18
CHCl₃	25.00	25.38	25.00	25.00	25.00	25.00	25.18
DMF	25.12	25.00	25.12	25.00	25.06	25.25	27.79
MeOH	25.64	25.44	25.90	25.83	25.38	26.10	25.25
EtOH	25.38	25.51	25.44	25.44	25.06	26.04	25.06
DMSO	24.93	24.69	25.00	25.00	25.00	25.00	27.17
THF	25.25	25.00	25.18	25.00	25.25	25.00	27.47
Acetone	25.38	25.51	25.31	25.18	25.31	25.06	27.77

ing imine group (N1) of one molecule and H24 of adjacent propargyl moiety and furthermore, O1 of one propargyl moiety linked with H18 of aromatic ring of adjacent molecule and overall packing looks like a staircase pattern (Fig. 2a). The pair of molecules in unit cell are joined by non-classical interactions of (C-H•••O) type between H18 of one propargyl moiety and O1 of another moiety with bond length of 3.168 Å. The propargyl fragment prevents close contact between molecules leading to an open structure packing, which shows that there are no intramolecular interactions. Moreover, the propargyl fragment is clearly twisted out of the plane with respect to the same fragment of the other molecule in the unit cell (centrosymmetric dimer) due to head to head steric hindrance represented in Fig. 2b and parallel anthracene units are showing formation of layers with weak π - π interactions (Fig. 2c).

2.3. UV-Vis spectral study

Preliminary investigations of the synthesized compounds under UV-Visible spectroscopy were recorded in the range of 200-600 nm in acetonitrile with 10 μ M concentration of the compounds (Fig. 3). The spectral data of the synthesized PASB are summarized in Table 1. The absorbance in the range of 380-430 can be attributed to π - π * transitions. Analysis of absorption spectra shows appreciable difference with change in substitution position and presence of different heteroatoms. While comparing spectral shifts from ortho to para-isomer, a red shift was observed which may be due to the planarity differences as Ortho-isomer (4a) being less planar then para-isomer (4b) in structural configuration.

Moreover, high molar absorptivity of ortho-isomer may be the consequence of high electron density. Slight increase in absorption of compound 4c bearing methyl at *meta*-position is may be due to electron releasing effect of methyl group while decrease in the absorption of compound 4d is may be due to Cl-atom with a slight red shift. It is noteworthy to mention that substituent at o- and pposition having oxygen atom shows more absorption compared to substituent having sulfur atom which may be attributed to energy difference in HOMO of sulfur and LUMO of conjugated backbone.

It is wide accepted that solvent can influence UV-Vis absorption spectra and can alter the shape, intensity and position of the absorption band. Later the term "solvatochromism" introduced by Hantzsch described this phenomenon, the effect of solvents polarity and their interactions with the solute molecules.¹⁶ The study of solvatochromism is important as it simply paves a way to study the effect of environment on solute molecules under examination. It has been known that solvent effect mostly depends on the variation of dipolar characteristics of any solute when promoted to excited state and the resulting interactions of the solvent depends upon the change in the dipolar characteristics between the ground and excited state of the solute molecules.¹⁷ The changes observed with varying polarity of the solvents depends on the overall solvation capability of the solvents which is the summative effect of all solvent-solute interactions viz. relative polarities of ground and excited states, H-bonding interactions and π -conjugated backbone excluding some chemical reactions like oxidation, reduction, protonation, complexation etc. leading to chemical changes in the solute molecules.¹⁸ It is recognized that the propargyl moiety of all templates form an intermolecular hydrogen bond solvated molecular complex with HBA (hydrogen bond acceptor) solvent (Scheme 2).

Herein we have attempted a comprehensive study for possible interactions of PASB with a series of polar aprotic solvents viz. acetonitrile, chloroform, dimethyl sulfoxide, dimethyl formamide, tetrahydrofuran, acetone and polar protic solvents viz. methanol and ethanol by probing the corresponding absorption spectra (Fig. 4). Concentration-dependent absorption behavior was also investigated to avoid any interference with the results of solvatochromism and its interperation and evidently did not show any shift in UV-Vis absorption maxima value. Thus ensures that compounds do not self- aggregate and can be investigated for their solvatochromic properties.¹⁹

A large number of non-equivalent scales have been developed for achieving a correlation of experimental data with the empirical solvent parameters. Amongst them the multi parameters based linear regression approach successfully enunciated by Kamlet and Taft has been widely used for the quantitative treatment and estimation of various solute-solvent interactions.²⁰

In the present work, we have explored the empirical solvatochromic scale developed by Kamlet and Taft.²¹

$$\bar{\nu}_{max} = \bar{\nu}_{max,0} + s\pi^* + a\alpha + b\beta$$

Where $\bar{\upsilon}_{max}$ corresponds to UV-Vis absorption maxima wavelength of a solute in a particular solvent, $\bar{v}_{max,0}$, is the value of this property for the same solute in a hypothetical condition for which $\pi^* = \alpha = \beta = 0$. The parameter π^* , α and β reflects, respectively, the general solvent dipolarity/Polarizability, specific H-bond donating ability (HBD/acidity) and specific H-bond accepting ability (HBA/basicity) which are collected in Table 2. Where regression coefficients s, a and b are the respective susceptibility constants. The inclusive study of these analytical parameters is important as their sign and magnitude are the measure of type of solvatochromism exhibited by solute molecules.

The UV-Vis absorption spectra of all the compounds for both polar protic and polar aprotic solvents has been depicted in Fig. 4, while the absorption data of all the compounds in various solvents is represented in (Table 1) and λ_{max} and ϵ_{max} values of all the

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Fig. 2. (a) Molecular lattice arrangement for compound 4b along a-axis, (b) Pair of molecules joined by non-classical interactions of benzene ring H18 of one propargyl moiety and O1 of another moiety, (c) Shows weak π interactions between two molecules along b- axis



Fig. 3. Absorption spectra of propargyl-functionalized Anthracene Schiff base (PASB) ($10\mu M$) in CH₃CN.

compounds are summarized in **Table S1**. The data in **Table 3** shows the regression parameters of compounds 4a-4g as a function of Kamlet–Taft solvent scale. The data depicts the –ve sign of s-value for compounds 4a-4g except 4d and 4f, suggesting they have more polar excited state as compared to ground state and hence these compounds possess a positive solvatochromism. Moreover, further information can be deduced from coefficients 'a' and 'b' values which index HBD and HBA values of a solvent respectively. Inter-



Scheme 2. Possible Specific Interactions for PASB (4a-4g), Where α , β , and π^* Stand for Acidity, Basicity and Polarity/Polarizability Parameters in the Kamlet–Taft Solvent Scale.

esteingly, for compound 4g sign of 'a' comes out to be –ve, indicating the bathochromic shift with increase in solvent hydrogen-bond donor acidity and for compound 4a-4f 'a' comes out to be +ve indicating hypsochromic shift with increasing solvent hydrogenbond donor acidity. Also, for compound 4g coefficient 'b' has +ve value which can be attributed to its capability of forming strong Hbonding with HBA solvent because of acidic hydrogen of propagyl at *p*-position of aryl ring. Overall we can say that the percentage contribution of the three solvatochromic parameters for the investigated PASB show that the solvent effect on UV-vis spectra is very complex and depends on nature of substituents, position of substitution and its electronic behaviour and hence a simple generalization cannot be made (Table 4). Fig. 5 showing parcentage contribu-

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Fig. 4. Absorption spectra of PASB (4a-4g) in solvents of different polarity.

tion chart. Altogether we can say that exploring solvatochromism helps to get insight of physical and chemical properties of solute molecules.

To achieve the best sensing performance, ionochromic studies were performed at room temperature and sufficient time was provided for the solutions to become consistent before recording the spectra. The sensing ability of compounds were investigated with the help of UV-visible experiments in the presence of various metal cations Na⁺, K⁺, Rb⁺, Ca²⁺, Mg²⁺, Ni²⁺, Fe³⁺, Co²⁺, Zn²⁺, Ba²⁺, Hg²⁺, Ce²⁺, La²⁺ and NH₄⁺ and as their chlorides in 10 μ M

acetonitrile (Fig. 6). Significant changes were observed in the absorption spectra only upon the addition of Fe^{3+} ions. The solution of analyte 4b exhibited one absorption band at 393 nm. Upon addition of Fe^{3+} ions two strong bands were appeared at 355 nm and 480 nm. Also, color change was observed from pale yellow to orange red which is evident from the fact that new peak at 480 nm lies in visible range.

To gain an insight into the sensing properties, a titration experiment was carried out with consequent addition of Fe^{3+} ions (0-1.6 equiv.) to 10μ M solution of analyte 4b in acetonitrile. As depicted

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Table 2 Kamlet-Taft parameters and physical properties of the employed solvents.

Solvent	Solvent E	n	param A	eters β	π^*	$\mu^{a} D$
CH₃CN	35.94	1.34	0.19	0.40	0.75	3.53
CHCl ₃	4.81	1.44	0.20	0.10	0.58	1.15
DMF	36.7	1.43	0.00	0.69	0.88	3.24
MeOH	32.7	1.33	0.98	0.66	0.60	2.87
EtOH	24.5	1.36	0.86	0.75	0.54	1.66
DMSO	46.45	1.47	0.00	0.76	1.00	4.06
THF	7.58	1.40	0.00	0.55	0.58	1.75
Acetone	20.56	1.35	0.08	0.48	0.71	2.69

 \mathcal{E} = relative permittivity; n= refractive index; α = solvents HBD acidity; β = solvents HBA basicity; π^* = solvents polarizability/dipolarity, μ^a D = dipole moment



Fig. 5. Percentage Contribution chart of the Solvatochromic Effects for (4a-4g)

Table 3



Fig. 7. Change in UV-vis absorption spectrum of 4b upon addition of increasing amounts of Fe $^{+3}$ (0.2,0.4,0.6,0.8,1.0,1.2,1.4,1.6 equiv.,respectively) in CH₃CN solution. Insets: the LOD plots for Fe $^{3+}$ ions

in Fig. 7 gradual increase in the absorption bands were observed centered at 355nm and 480 nm with increase in the concentration of Fe^{3+} ions. However, no prominent changes were observed in the absorbance for metal ion concentration greater than 1.6 equiv. Furthermore, Job's continuous variation method was employed to evaluate the stoichiometry of the complex. The stoichiometry of the complex formed between 4b and Fe^{3+} would be 1:1 as evident from the maxima at 0.5 (see Fig. 8a). To further explore the

Analyte	$\bar{\upsilon}_0 \ (10^3 cm^{-1})$	s (10 ³ cm ⁻¹)	a (10 ³ cm ⁻¹)	$b (10^3 cm^{-1})$	R ²	F-statics
a	25.38	-0.396	0.286	0.147	0.479	1.22
b	25.77	-0.602	0.397	-0.449	0.694	3.03
с	25.09	-0.050	0.586	0.120	0.688	4.24
d	24.81	0.280	0.762	-0.040	0.856	7.95
e	25.34	-0.334	0.012	0.962	0.130	0.20
f	24.66	0.524	1.208	-0.015	0.766	6.33
g	27.94	-2.498	-3.435	3.952	0.780	4.96

 $\bar{\upsilon}0$, a, s and b (in cm-1) and correlation coefficient (R²) obtained from the Kamlet-Taft fitting of



Fig. 6. (a) absorption spectra of 4b ($10\mu M$) in the presence of various metal ions ($10\mu M$) in acetonitrile; (b) Bar diagram showing the change in the absorbance of the analyte 4b at $\lambda max = 393$ nm.

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Table 4

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% Contribution of solvatochromic parameter for analyte 4a-4g. 10⁴ L mol⁻¹ % Contribution of solvatochromic parameter $\epsilon_{max}~\times$ Compound $\Lambda max (nm)$ P_{π} P_{β} cm-Pα 47.76 34.49 А 400 4.75 17.73 В 394 3.0 41.57 27.41 31.00 С 400 2.86 06.61 77.51 15.87 D 400 0.99 25.87 70.42 03.69 E 400 7.48 25.53 9.35 73.54 400 4.85 29.99 69.14 08.58 F 397 2.04 25.27 G 34.74 39.97 11



Fig. 8. (a) Job's plot for the complexation of 4b with Fe3+ showing 1:1 stoichiometry in CH3CN at nm; (b) B-H plot for 1:1 complexation.

concentration limit that the compound 4b can detect, the limit of detection (LOD) was calculated from UV-Vis titration of 4b with Fe³⁺ ions. By employing the equation LOD = $3\sigma s^{-1}$, where σ is standard deviation of the response and s is slope of the curve obtained and the value comes out to be 1.60×10^{-8} M (see inset Fig. 7). The curve exhibited good linear relationship between the absorbance or 4b and Fe³⁺ ion concentration with correlation coefficient of R² = 0.975.

An attempt was made to further explore the binding mechanism, by applying Benesi-Hildebrand (B-H) method, to calculate association constant (K_a) and stoichiometry of complexation assuming a 1: n complex formation.²² The equilibrium is given by the Equation 1.

$$4b + nFe^{3+} \Longrightarrow \left[4b \bullet Fe^{3+}\right]_n \tag{1}$$

$$K_a \frac{\left[4b \, F e^{3+}\right]_n}{\left[4b\right] \left[F e^{3+}\right]^n}$$

The estimation of UV-Vis titration plot is made in a way to have linearity of regression in the plot of $[A-A_0]^{-1}$ vs $[Fe^{3+}]^n$, where $[A-A_0]$ is the change in the intensity of absorbance of compound in the presence of metal ions recorded at particular wavelength. The graph of $[A-A_0]^{-1}$ vs $[Fe^{3+}]^n$ comes out to be linear with a high regression coefficient (R = 0.997), which illustrates that the stoichiometry of the complexation of 4b with Fe³⁺ ion is 1:1. The association constant (K_a), a measure of strength of interaction between the probe and Fe³⁺, was determined from the B-H plot. A significant value of K_a was obtained 2.6 \times $10^8~M^{-1},$ indicating strong binding ability of probe with Fe^{3+} ion.

2.4. Vibrating sample magnetism (VSM)

Additionally, we have also investigated the magnetic behavior (M) of bare ligand 4b, Fe^{3+} ion and complex $[4b+Fe^{3+}]$ as a function of applied field H (hysteresis loop) at room temperature in order to analyze the possible contribution on magnetic properties of the complex. The values of coercivity (Hc) and remanent magnetization (Mr) for ligand 4b was found to be in the range of 150 Oe and 5 \times 10⁻⁴ emu/g respectively. Further very high values of saturation magnetization (Ms) were obtained. The results obtained indicated that bare ligand 4b shows clear signature of ferromagnetic nature at room temperature (Fig. 9a). The slope of M-H curve is a measure of magnetic permeability (μ), where μ = M/H, and has a finite value for free space, $\mu_0 = 4\pi \times 10^{-7}$ or 1.257 $\times 10^{-6}$ Hm⁻¹. In case of Fe³⁺ ion magnetization moment increases linearly with applied field and it is found that slope >1 which is a indicative feature of paramagnetism but in the case of complex $[4b + Fe^{3+}]$ value of slope is <1 indicating its diamagnetic behavior (see Fig. 9b). Hence, change in magnetic behavior provides a clear evidence that ligand 4b is responsible for pairing electrons in Fe^{3+} ion and coordinate with metal ion to form complex.

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Fig. 9. (a) Magnetization curves recorded at room temperature: (a) the magnetization curve of 4b (b) Fe³⁺ and [4b + Fe³⁺] complex.



Fig. 10. Comparison of IR spectra of 4b (black spectra) and 4b with 1 equiv. Fe3+ ions (red spectra).

2.5. Mode of binding

The mode of binding was confirmed through FT-IR spectroscopy. The IR spectra of 4b clearly reveals that the peak at 1028 cm⁻¹, the characteristic frequency for the C-O-C group, shifts to 1008 cm⁻¹ on coordination to the Fe³⁺ ions, in presence of 1.0 equiv. of metal ions. Moreover, downward shift of the band from 3187 cm-1to 2980 cm-1 implies the participation of propargyl group in the bonding. Bands at 1617 cm-1 corresponding to Schiff base (-C=N-) remains intact after complexation, suggesting no contribution to bonding (Fig. 10).and possible mode of interaction shown in Fig. 11.

2.6. Theoretical study and computational details

Quantum chemical calculations at DFT level were studied for ligand 4b and its complex with Fe^{3+} ion. Energy optimization for



Fig. 11. plausible mode of intraction

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LUMO of 4b + Fe3+ LUMO of 4b ΔE = 0.110 eV $\Delta E = 0.049 \text{ eV}$ HOMO of 4b + Fe3+ HOMO of 4b



4b+Fe³⁺ complex was done with B3LYP in combination with 6-31+G(d,p) basis set for H,C,N and O atoms and LANL2DZ basis set for Fe atom. The energy minimized structure clearly evident that ligand 4b afforded a suitable cavity resulting from preorganization of ligating sites i.e electronically rich O atom and C=C moiety of propargyl group (Fig. S18). At the same level of theory, frontier molecular orbitals were also evaluated and it is found that in ligand 4b the electron density at HOMO is distributed all over the ligand but in case of LUMO it is located more over the anthracene part. Moreover in 4b+Fe³⁺ complex, the HOMO is distributed over anthracene and imine part.Whereas LUMO is located over Fe³⁺ complex. This indicates that this is a ligand to metal electron transfer Fig. 12. Furthermore, from the computed result, it can be clearly seen that the energy gap between HOMO and LUMO in case of complex is lowered by 0.049 eV as compared to bare ligand this pointed out the greater stability of the complex as compared to ligand. This lowering of energy band gap is corroborated with the bathochromic shift in UV-vis absorption spectra as observed by sequential addition of Fe³⁺ and publicizes the higher stability of complex generated.

3. Conclusion

We have been able to elaborate the facile and proficient methodology for the synthesis of Propargyl-functionalized anthracene based Schiff bases (PASB). The key focal points of this report involve solvatochromic study emphasized with Kamlet-Taft approach along with UV-Vis spectroscopy revealing positive solvatochromic shift in wavelength of PASB with no tautomerism. It is recognized that the propargyl moiety of all templates form an intermolecular hydrogen bond solvated molecular complex with HBA (hydrogen bond acceptor) solvents. Through an integrated UVvisible experiments and vibrating sample magnetic study (VSM), the results demonstrated that PASB (4b) acted as a remarkable chromogenic probe for the selective detection of Fe³⁺ ions with good LOD 1.60 \times 10⁻⁸ M. Delightfully, VSM study gave better visualization of binding nature of ligand with metal ions besides UV-Vis sensing. The molecular structure of the compound 4b is authenticated by single crystal X-ray diffraction analysis and shows a centrosymmetric dimer with an open packing structure which has great importance in many photophysical studies. FT-IR and com-

putational study following DFT approach pointed out that propargyl group of PASB is the main binding site Schiff base (-C=N-) made no contribution towards bonding with metal ion. In brief, the present contribution opens a promising approach to reliably explain the surrounding environment effect on electronic absorption spectra of solute and design propargyl based sensor for Fe³⁺ ion. This will probably be useful under more practical condition and provides a wider scope in the future.

Declaration of Competing Interest

There are no conflict to declare.

CRediT authorship contribution statement

Gurjaspreet Singh: Supervision, Conceptualization. Pawan: Investigation, Writing - original draft. Akshpreet Singh: Methodology. Shilpy: Writing - review & editing. Diksha: Resources. Suman: Data curation. Geetika Sharma: Validation. Subash Chandra Sahoo: Investigation. Amarjit Kaur: Supervision, Project administration.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2020.129618.

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