Synthesis, spectroscopic characterization, photochromism of zinc(II)-iodo complexes of long chain 1-alkyl-2-(arylazo)imidazoles and the DFT correlative studies

Chandana Sen, Debashis Mallick[†], Sudipa Mondal and Chittaranjan Sinha*

Department of Chemistry, Inorganic Chemistry Section, Jadavpur University, Kolkata-700 032, India

E-mail : c_r_sinha@yahoo.com

Abstract : Zinc(II)-iodo complexes of 1-alkyl-2-(arylazo)imidazole (1-5), [Zn(Raai-C_nH_{2n+1})$_2I_2$] (6-10) (Raai-C_nH_{2n+1}, n = 10 (1/6), 12 (2/7), 14 (3/8), 16 (4/9), 18 (5/10)) have been characterized by spectroscopic studies (FT-IR, UV-Vis, ^{1}H NMR). The complexes, [Zn(Raai-C_nH_{2n+1})$_2I_2$], exhibit UV light assisted photoisomerisation (E(*trans*)-to-Z(*cis*)) in the solution phase. The Z-to-E (*cis*-to-*trans*), isomerisation is very slow with visible light irradiation and has been carried out under thermal treatment. The rate and quantum yield of photochromism are dependent on molar mass and chain length of -C_nH_{2n+1}. The activation energy (E_a) is also lower in the complexes than free ligand data. The spectral properties have been explained using DFT computation of optimized geometries of [Zn(Haai-$C_{10}H_{21}$)$_2I_2$].

Keywords : Zinc(II)-arylazoimidazoles, spectroscopic data, photochromism, DFT computation.

Introduction

Photochromism is a reversible structural change of a molecule upon irradiation of electromagnetic wave in which two isomers have distinguished spectral characteristics. G. S. Hartley reported the *cis-trans* isomerization of aromatic azo dyes in 1937 upon irradiation of UV light[1]. A large volume of work, since then, has been reported on the derivatives of azobenzene among the best characterized photoswitches[2–8]. The *cis-trans* (Z-to-E) isomerization of phenylazopyridines was reported by Ellis V. Brown and G. Richard Granneman in 1975[9]. Advantage of azopyridine derivatives is their coordination to a metal ion and hydrogen bonding through the pyridyl-*N* and/or the azo-N group[9,10]. In search of other azoheterocycles we have examined the effect of UV light irradiation on 1-alkyl-2-(arylazo)imidazoles (Scheme 1, Raai-C_nH_{2n+1}) and have found the photoisomerisation[11]. We have extended the photochromic activity of Raai-C_nH_{2n+1} in different medium by changing different innocent foreign molecules, micelles[12–15] and also the coordination of complexes of transition[16] and nontransition metal ions[17–20]. In this article, we wish to report Zn^{II}-coordination complexes of Raai-C_nH_{2n+1} (n = 10, 12, 14, 16, 18). The structural characterisation has been carried out by spectroscopic data (FT-IR, UV-Vis, ^{1}H NMR). Photochromic properties are examined by optical and thermal relaxation routes. DFT computation of optimised geometry of one of the complexes has been carried out and information has been used to explain the electronic and photochromic properties.
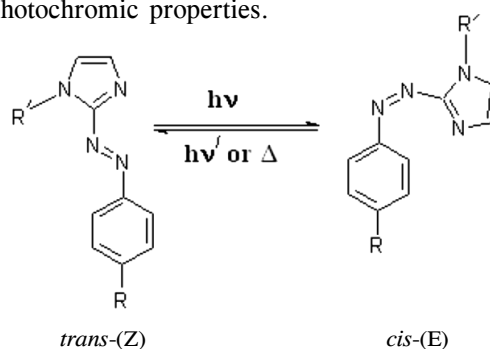
Scheme 1. Photoisomerisation of 1-alkyl-2-(arylazo)imidazoles, Raai-C_nH_{2n+1}.

Experimental

Materials :

1-Alkyl-2-(arylazo)imidazoles (Raai-C_nH_{2n+1}) were synthesized by reported procedure[21]. 1-Bromo-n-decane,

[†a]Present address : Department of Chemistry, Mrinalini Datta Mahavidyapith, Birati, Kolkata-700 051, India.

1-bromo-n-dodecane, 1-bromo-n-tetradecane, 1-bromo-n-hexadecane, 1-bromo-n-octadecane, 1-bromo-n-icosane, 1-bromo-n-docosane were purchased from Sigma-Aldrich and were of analytical reagent grade and used as received. All other chemicals and solvents were reagent grade and used as received and the solvents were purified before use by standard procedure[22].

Physical measurements :

Microanalytical data (C, H, N) were collected on Perkin-Elmer 2400 CHNS/O elemental analyzer. Spectroscopic data were obtained using the following instruments : UV-Vis spectra from a Perkin-Elmer Lambda 25 spectrophotometer; IR spectra (KBr disk, 4000–400 cm^{-1}) from a Perkin-Elmer RX-1 FTIR spectrophotometer; photo excitation has been carried out using a Perkin-Elmer LS-55 spectrofluorimeter and ^{1}H NMR spectra were recorded from a Bruker (AC) 300 MHz FTNMR spectrometer.

The synthesis of [Zn(HaaiC$_{10}$H$_{21}$)$_2$I$_2$] (6a) :

To methanolic solution of Haai-C$_{10}$H$_{21}$ (0.85 g, 0.27 mmol) (20 ml) was added dropwise acetonitrile solution

(5 ml) of ZnI$_2$ (0.40 g, 0.13 mmol) and refluxed for 2 h. Orange-yellow precipitate appeared. The precipitate was collected by filtration, washed with cold MeOH and dried over CaCl$_2$ *in vacuo*. It was then recrystallized from acetonitrile solution by slow evaporation. The yield was 168 mg (64%).

All other complexes [Zn(Raai-C$_n$H$_{2n+1}$)$_2$I$_2$] (6-10) were prepared similarly and the yield varied from 60 to 70%. The characterisation data of the complexes were as follows : [Zn(HaaiC$_{10}$H$_{21}$)$_2$I$_2$] (6a) Anal. Found : C, 48.36; H, 5.93; N, 11.85%. Calcd. for C$_{38}$H$_{56}$N$_8$ZnI$_2$: C, 48.34; H, 5.94; N, 11.87%; FTIR (KBr disc) : ν(N=N), 1377; ν(C=N), 1592 cm^{-1}; UV/Vis (MeCN) (λ (nm) (10^{-4} ε (dm^3 mol^{-1} cm^{-1})) : 369 (4.2), 389 (3.67), 461 (0.47). [Zn(MeaaiC$_{10}$H$_{21}$)$_2$I$_2$] (6b) Anal. Found : C, 49.44; H, 6.21; N, 11.55%. Calcd. for C$_{40}$H$_{60}$N$_8$ZnI$_2$: C, 49.41; H, 6.18; N, 11.53%; FTIR (KBr disc) : ν(N=N), 1378; ν(C=N), 1603 cm^{-1}; UV/Vis (MeCN) (λ (nm) (10^{-4} ε (dm^3 mol^{-1} cm^{-1})) : 369 (4.00), 385 (3.49), 458 (0.47). [Zn(HaaiC$_{12}$H$_{25}$)$_2$I$_2$] (7a) Anal. Found :
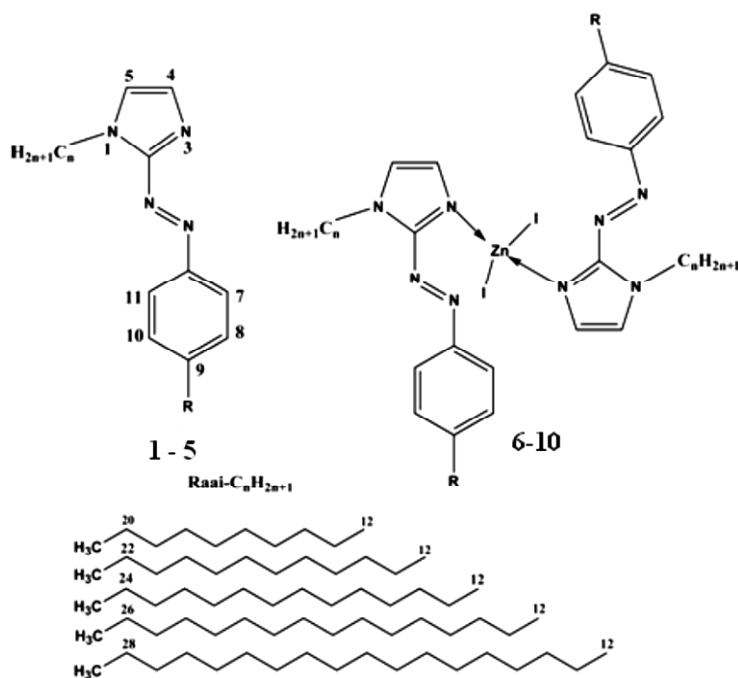
R = H, n = 10, (1a/6a); R = Me, n = 10, (1b/6b); R = H, n = 12, (2a/7a); R = Me, n = 12, (2b/7b); R = H, n = 14, (3a/8a); R = Me, n = 14, (3b/8b); R = H, n= 16, (4a/9a); R = Me, n = 16, (4b/9b); R = H, n = 18, (5a/10a); R = Me, n = 18, (5b/10b)

Scheme 2. The ligands, Raai-C$_n$H$_{2n+1}$ (1-5) and the complexes [Zn(Raai-C$_n$H$_{2n+1}$)$_2$I$_2$] (6-10).

C, 50.46; H, 6.42; N, 11.18%. Calcd. for $C_{42}H_{64}N_8ZnI_2$: C, 50.43; H, 6.40; N, 11.21%; FTIR (KBr disc) : $\nu(N=N)$, 1376; $\nu(C=N)$, 1592 cm^{-1}; UV/Vis (MeCN) (λ (nm) (10^{-4} ε (dm^3 mol^{-1} cm^{-1})) : 367 (3.74), 387 (3.44), 457 (0.49). [$Zn(MeaaiC_{12}H_{25})_2I_2$] (**7b**) Anal. Found : C, 51.37; H, 6.66; N, 10.92%. Calcd. for $C_{44}H_{68}N_8ZnI_2$: C, 51.39; H, 6.62; N, 10.90%; FTIR (KBr disc) : $\nu(N=N)$, 1375; $\nu(C=N)$, 1586 cm^{-1}; UV/ Vis (MeCN) (λ (nm) (10^{-4} ε (dm^3 mol^{-1} cm^{-1})) : 36 (4.5), 389 (3.96), 460 (0.39). [$Zn(HaaiC_{14}H_{29})_2I_2$] (**8a**) Anal. Found : C, 52.29; H, 6.79; N, 10.63%. Calcd. for $C_{46}H_{72}N_8ZnI_2$: C, 52.30; H, 6.82; N, 10.61%; FTIR (KBr disc) : $\nu(N=N)$, 1375; $\nu(C=N)$, 1593 cm^{-1}; UV/ Vis (MeCN) (λ (nm) (10^{-4} ε (dm^3 mol^{-1} cm^{-1})) : 368 (4.20), 383 (3.89), 463 (0.42). [$Zn(MeaaiC_{14}H_{29})_2I_2$] (**8b**) Anal. Found : C, 53.19; H, 6.98; N, 10.31%. Calcd. for $C_{48}H_{76}N_8ZnI_2$: C, 53.17; H, 7.02; N, 10.34%; FTIR (KBr disc) : $\nu(N=N)$, 1378; $\nu(C=N)$, 1587 cm^{-1}; UV/ Vis (MeCN) (λ (nm) (10^{-4} ε (dm^3 mol^{-1} cm^{-1})) : 369 (4.1), 386 (3.74), 459 (0.43). [$Zn(HaaiC_{16}H_{33})_2I_2$] (**9a**) Anal. Found : C, 54.02; H, 7.22; N, 10.86%. Calcd. for $C_{50}H_{80}N_8ZnI_2$: C, 53.99; H, 7.21; N, 10.88%; FTIR (KBr disc) : $\nu(N=N)$, 1379; $\nu(C=N)$, 1593 cm^{-1}; UV/ Vis (MeCN) (λ (nm) (10^{-4} ε (dm^3 mol^{-1} cm^{-1})) : 366 (4.20), 384 (3.74), 455 (0.42). [$Zn(MeaaiC_{16}H_{33})_2I_2$] (**9b**) Anal. Found : C, 54.74; H, 7.35; N, 9.85%. Calcd. for $C_{52}H_{84}N_8ZnI_2$: C, 54.77; H, 7.37; N, 9.83%; FTIR (KBr disc) : $\nu(N=N)$, 1381; $\nu(C=N)$, 1601 cm^{-1}; UV/Vis (MeCN) (λ (nm) (10^{-4} ε (dm^3 mol^{-1} cm^{-1})) : 368 (3.85), 382 (3.62), 454 (0.44). [$Zn(HaaiC_{18}H_{37})_2I_2$] (**10a**) Anal. Found : C, 55.53; H, 7.51; N, 9.62%. Calcd. for $C_{54}H_{88}N_8ZnI_2$: C, 55.51; H, 7.54; N, 9.59%; FTIR (KBr disc) : $\nu(N=N)$, 1379; $\nu(C=N)$, 1594 cm^{-1}; UV/ Vis (MeCN) (λ (nm) (10^{-4} ε (dm^3 mol^{-1} cm^{-1}) : 367 (3.86), 386 (3.43), 459 (0.37). [$Zn(MeaaiC_{18}H_{37})_2I_2$] (**10b**) Anal. Found : C, 56.19; H, 7.71; N, 9.35%. Calcd. for $C_{56}H_{92}N_8ZnI_2$: C, 56.22; H, 7.70; N, 9.37%; FTIR (KBr disc) : $\nu(N=N)$, 1377; $\nu(C=N)$, 1589 cm^{-1}; UV/ Vis (MeCN) (λ (nm) (10^{-4} ε (dm^3 mol^{-1} cm^{-1})) : 365 (4.34), 387 (4.01), 459 (0.37).

Photometric measurements :

The absorption spectra were taken using Perkin-Elmer Lambda 25 UV/Vis spectrophotometer in a 1 × 1 cm quartz optical cell maintained at 25 °C with a Peltier thermostat. The light source of a Perkin-Elmer LS 55 spectrofluorimeter was used as an excitation light, with a slit width of 10 nm. An optical filter was used to cut off overtones when necessary. The absorption spectra of the *cis* isomers were obtained by extrapolation of the absorption spectra of a *cis*-rich mixture for which the composition is known from ^{1}H NMR integration. Quantum yields (ϕ) were obtained by measuring initial E-to-Z (*trans*-to-*cis*) isomerization rates (ν) in a well-stirred solution within the above instrument using the relation, $\nu = (\phi I_0/V)(1-10^{-Abs})$ where I_0 is the photon flux at the front of the cell, V is the volume of the solution, and Abs is the initial absorbance at the irradiation wavelength. The value of I_0 was obtained by using azobenzene ($\phi = 0.11$ for π-π* excitation[23]) under the same irradiation conditions.

The thermal *Z*-to-*E* (*cis*-to-*trans*) isomerisation rates were obtained by monitoring absorption changes intermittently for a *Z*-rich solution kept in the dark at constant temperatures (*T*) in the range from 298–313 K. The activation energy (E_a) and the frequency factor (A) were obtained from $\ln k = \ln A - E_a/RT$, where k = rate constant, R = gas constant and T is temperature. The values of activation free energy (ΔG^*) and activation entropy (ΔS^*) were obtained through the relationships, $\Delta G^* = E_a - RT - T\Delta S^*$ and $\Delta S^* = [\ln A - 1 - \ln (k_B T/h)]/R$, where k_B and h are Boltzmann's and Plank's constants, respectively.

Computational study :

DFT copmputation of [$Zn(HaaiC_{10}H_{21})_2I_2$] (**5a**) was performed by GAUSSIAN-03 program package[24]. Hybrid DFT-B3LYP functional was used throughout the calculations[25]. For C, H and N the 6-31G(d) basis set were assigned. Los Alamos effective core potential plus double zeta (LanL2DZ)[26] basis set along with the corresponding pseudo potential without any symmetry constrain for Zn and I were used. The vibrational frequencies of core groups were calculated to ensure that the optimized geometries represent the local minima. To assign the low lying electronic transitions in the experimental spectra, TD-DFT calculations of the complexes were done. We computed the lowest 25 singlet-singlet transition in methanol using the conductor-like polarizable continuum model and results of the TD-DFT calculations was qualitatively very similar. Gauss Sum[27] was used to

calculate the fractional contributions of various groups to each molecular orbital.

Results and discussion

Synthesis and formulation of the complexes :

1-Alkyl-2-(arylazo)imidazoles (Raai-C_nH_{2n+1}, **1-5**) of long chain 1-alkyl group (-C_nH_{2n+1} where n = 10 (**1**), 12 (**2**), 14 (**3**), 16 (**4**), 18 (**5**)) have been reacted with ZnI_2 in methanol solution of (2 : 1 molar ratio, Raai-C_nH_{2n+1} and ZnI_2 respectively) to synthesize [Zn(Raai-$C_nH_{2n+1})_2I_2$] (**6-10**) (Scheme 2). The complexes have been crystallized from 2-methoxyethanol-MeOH (1 : 3, v/v) mixture by slow evaporation. The compounds are non-conducting and their composition has been supported by microanalytical data. The complexes are hitherto unknown and have been characterized by microanalytical and spectroscopic data (vide Experimental section).

Spectral studies :

The bands in the FTIR spectra of the ligands and the complexes are assigned based on literature report[17-21]. In the complexes, moderately intense stretching at 1580–

1615 and 1370–1410 cm^{-1} are assigned to $v(C=N)$ and $v(N=N)$, respectively (vide Experimental section) which are shifted to lower frequency region by 30–50 cm^{-1}. Movement of infrared signals has been comparable with reported results[17-21].

The ^{1}H NMR spectra of the complexes are recorded in $CDCl_3$ and have been compared with free ligand data available in literature[21]. The alkylation of imidazolyl group is supported by the disappearance of δ(N–H) at ~10.35 ppm and the appearance of N(1)-alkyl signal at 0.80–4.40 ppm for ligands and complexes[15,21]; -N–CH_2–$(CH_2)n$–CH_3 shows a triplet for -CH_2- at 4.40 ppm, a triplet at 0.80 ppm for -CH_3 group and a multiplet for -$(CH_2)n$- at 1.20–1.86 ppm (Table 1). Imidazolyl 4- and 5-H appear as broad singlet at 7.27–7.30 and 7.10–7.16 ppm, respectively. Broadening may be due to rapid proton exchange between these imidazolyl protons. The aryl protons (7-H to 11-H) are upfield shifted on going from Haai- (**a**) to Meaai- (**b**) which may be due to +I effect of substituted -Me group. Important feature of the spectra is the shifting of imidazole protons 4-H and 5-H to lower δ-

Table 1. ^{1}H NMR spectral data of [Zn(Raai-$C_nH_{2n+1})_2I_2$] (**6-10**) in $CDCl_3$ at room temperature[a]

Compds.	4-H[s]	5-H[s]	7,11-H[d]	8,10-H	9-R	12-CH_2[t]	[L]CH_3-(CH_2)*-CH_2[bs]
[Zn(HaaiC$_{10}$H$_{21}$)$_2$I$_2$] (**6a**)	7.77	7.25	7.82	7.51[m]	7.51	4.52	1.32–0.84
			(8.2)			(6.9)	
[Zn(MeaaiC$_{10}$H$_{21}$)$_2$I$_2$] (**6b**)	7.74	7.24	7.83	7.41	2.47	4.54	1.34–0.83
			(7.8)	(7.4)		(7.1)	
[Zn(HaaiC$_{12}$H$_{25}$)$_2$I$_2$] (**7a**)	7.78	7.27	7.83	7.52[m]	7.53	4.58	1.35–0.81
			(8.4)			(7.4)	
[Zn(MeaaiC$_{12}$H$_{25}$)$_2$I$_2$] (**7b**)	7.72	7.26	7.83	7.44	2.48	4.55	1.35–0.83
			(8.7)	(7.0)		(7.6)	
[Zn(HaaiC$_{14}$H$_{29}$)$_2$I$_2$] (**8a**)	7.71	7.25	7.84	7.53[m]	7.51	4.58	1.39–0.82
			(8.2)			(7.2)	
[Zn(MeaaiC$_{14}$H$_{29}$)$_2$I$_2$] (**8b**)	7.72	7.24	7.87	7.45	2.44	4.55	1.35–0.86
			(7.9)	(7.4)		(7.2)	
[Zn(HaaiC$_{16}$H$_{33}$)$_2$I$_2$] (**9a**)	7.74	7.25	7.85	7.52[m]	7.51	4.57	1.33–0.87
			(7.7)			(6.3)	
[Zn(MeaaiC$_{16}$H$_{33}$)$_2$I$_2$] (**9b**)	7.40	7.23	7.88	7.43	2.47	4.54	1.33–0.85
			(8.0)	(7.4)		(6.9)	
[Zn(HaaiC$_{18}$H$_{37}$)$_2$I$_2$] (**10a**)	7.43	7.26	7.86	7.52[m]	7.51	4.52	1.31–0.83
			(7.8)			(7.3)	
[Zn(MeaaiC$_{18}$H$_{37}$)$_2$I$_2$] (**10b**)	7.47	7.25	7.84	7.42	2.45	4.53	1.35–0.81
			(8.3)	(7.0)		(6.7)	

[a]^{1}H NMR spectra of Raai-C_nH_{2n+1} are reported in reference [21].

values, in general, relative to aryl protons (7-H–11-H). Imidazole protons suffer downfield shifting by 0.2–0.4 ppm compared to the free ligand position[21]. The complexes [Zn(Raai-C_nH_{2n+1})$_2I_2$]$_2$ show downfield shifting of aryl protons (7-11-H) by 0.05–0.15 ppm. It may suggest monodentate imidazolyl-N donor nature of Raai-C_nH_{2n+1} in the complexes. The coordination of two Raai-C_nH_{2n+1} to Zn^{II} may result steric crowding which may inhibit the chelation of azo-N.

UV-Vis spectra and photochromism :

The absorption spectra of Raai-C_nH_{2n+1} show strong absorption at 340–380 nm (π-π*) and a weak band at 450–455 nm (n-π*)[21]. The absorption spectra of complexes were reorded in MeOH in the wavelength range 200–900 nm (Fig. 1). The UV light irradiation to a MeOH solution of [Zn(Raai-C_nH_{2n+1})$_2I_2$]$_2$ (6-10) shows the E-to-Z (*trans*-to-*cis*) isomerization of coordinated Raai-C_nH_{2n+1}[15-20]. It is observed that upon irradiation with UV light E-to-Z photoisomerisation proceeds and the Z-molar ratio is reached to ∼85%. The complexes show little sign of degradation upon repeated irradiation at least upto 15 cycles in each case. The quantum yields were measured for the E-to-Z ($\phi_{E\rightarrow Z}$) photoisomerisation of these ligands and complexes in MeOH on irradiation of UV wavelength (Table 2; Fig. 2). The $\phi_{E\rightarrow Z}$ values are dependent mainly on molar mass of the complexes and also nature of substituents. The Me substituent at azoaryl group (Haai-C_nH_{2n+1} to Meaai-C_nH_{2n+1}) and substituents (-$C_{10}H_{21}$ to -$C_{22}H_{45}$) at N(1)-position both reduce

$\phi_{E\rightarrow Z}$ values. Increased mass of the molecule reduces the rate of E-to-Z isomerisation. In the complexes, the $\phi_{E\rightarrow Z}$ values are significantly less than that of free ligand data[21]. In addition to mass of the molecule the stereochemical orientation of coordinated Raai-C_nH_{2n+1} about Zn^{II} may interfere with the motion of the -N=N-Ar moiety. Besides, the photo bleaching efficiency of iodide may snatch out energy from π-π* state which may cause very fast deactivation other than photochromic route.

Thermal Z-to-E isomerisation was followed by UV-Vis spectroscopy at 298–313 K. The Eyring plots gave a linear graph from which the activation energy was ob-
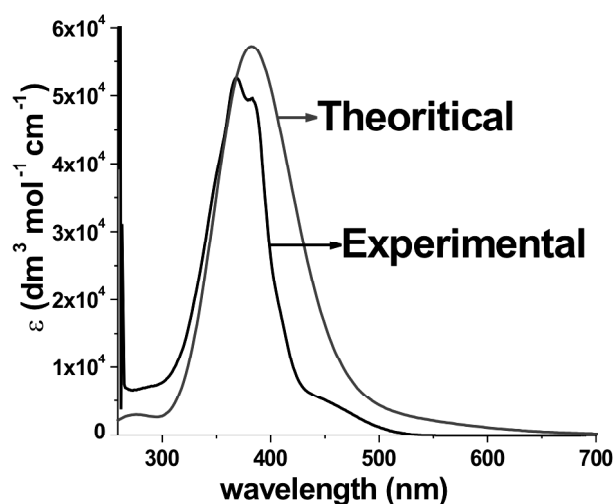

Fig. 1. Theoretical and experimental UV-Vis spectra of [Zn(MeaaiC$_{10}$H$_{21}$)$_2$I$_2$] (6b).

Table 2. Results of photochromism, rate of conversion and quantum yields upon UV light irradiation[a]

Compds.	$\lambda_{\pi,\pi*}$ (nm)	Isosbestic point (nm)	Rate of E→Z conversion × 10^8 (s^{-1})	$\phi_{E\rightarrow Z}$
[Zn(HaaiC$_{10}$H$_{21}$)$_2$I$_2$] (6a)	369	329, 440	1.90	0.109 ± 0.002
[Zn(MeaaiC$_{10}$H$_{21}$)$_2$I$_2$] (6b)	369	328, 443	1.87	0.108 ± 0.003
[Zn(HaaiC$_{12}$H$_{25}$)$_2$I$_2$] (7a)	366	330, 438	1.85	0.107 ± 0.001
[Zn(MeaaiC$_{12}$H$_{25}$)$_2$I$_2$] (7b)	367	328, 442	1.79	0.105 ± 0.003
[Zn(HaaiC$_{14}$H$_{29}$)$_2$I$_2$] (8a)	368	328, 441	1.75	0.101 ± 0.003
[Zn(MeaaiC$_{14}$H$_{29}$)$_2$I$_2$] (8b)	370	332, 442	1.70	0.099 ± 0.001
[Zn(HaaiC$_{16}$H$_{33}$)$_2$I$_2$] (9a)	366	329, 443	1.66	0.096 ± 0.002
[Zn(MeaaiC$_{16}$H$_{33}$)$_2$I$_2$] (9b)	368	333, 444	1.59	0.091 ± 0.001
[Zn(HaaiC$_{18}$H$_{37}$)$_2$I$_2$] (10a)	366	334, 438	1.50	0.088 ± 0.003
[Zn(MeaaiC$_{18}$H$_{37}$)$_2$I$_2$] (10b)	367	329, 442	1.45	0.083 ± 0.001

[a]Photochromism of Raai-C_nH_{2n+1} are reported in reference [21].

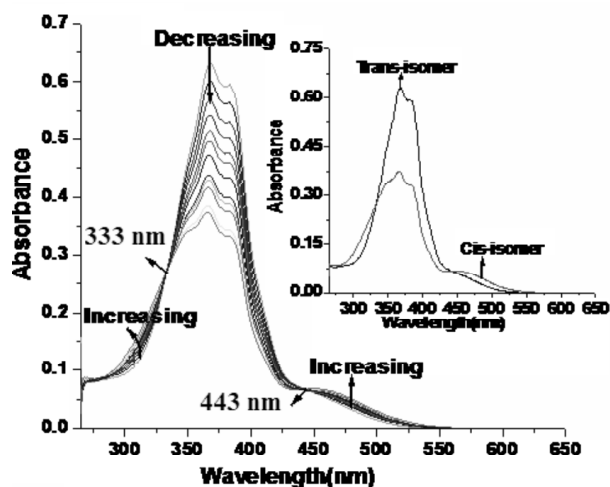**Fig. 2.** Spectral changes of [Zn(MeaaiC$_{10}$H$_{21}$)$_2$I$_2$] (**8b**) in MeOH upon repeated irradiation at 365 nm at 3 min interval at 25 °C. Inset figure shows the spectra of *cis* and *trans* isomers of [Zn(MeaaiC$_{10}$H$_{21}$)$_2$I$_2$] (**8b**).

tained (Table 3, Fig. 3). In the complexes, the E_as are severely reduced which means faster Z-to-E thermal isomerisation of the complexes. The entropy of activation (ΔS^*) are high negative in the complexes than that of free ligand. This is also in support of increase in rotor volume in the complexes.

Computational study :

The DFT and TD-DFT computation have been performed using optimized structure [Zn(HaaiC$_{10}$H$_{21}$)$_2$I$_2$] (**5a**). The energy of HOMO is –4.93 eV and is much higher than HOMO-1 (E$_{HOMO-1}$, –5.11 eV) and HOMO-2 (E$_{HOMO-2}$, –5.13 eV). The HOMO, HOMO-1 and HOMO-2 are mainly composed of iodide (>90%) and Haai-C$_{10}$H$_{21}$ contributes only 1–3% (Fig. 4). The reversal of contribution is observed on and from HOMO-6 where major contribution from Haai-C$_{10}$H$_{21}$ (99%). The

Table 3. Rate and activation parameters for Z(*cis*) → E(*trans*) thermal isomerisation of [Zn(Raai-C$_n$H$_{2n+1}$)$_2$I$_2$] in methanol^a

Compds.	Temp. (K)	Rate of thermal Z→E conversion × 10^4 (s^{-1})	E_a (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (J mol^{-1} K^{-1})	ΔG^{*c} (kJ mol^{-1})
6a	298	1.610	29.65	27.11	–225.87	96.12
	303	2.385				
	308	2.599				
	313	2.951				
6b	298	1.706	27.73	25.20	–231.96	96.06
	303	2.394				
	308	2.601				
	313	3.007				
7a	298	1.701	27.62	25.09	–232.37	96.08
	303	2.387				
	308	2.591				
	313	2.991				
7b	298	2.268	25.32	22.79	–238.13	95.51
	303	2.737				
	308	3.299				
	313	3.668				
8a	298	1.896	24.96	22.44	–240.77	95.98
	303	2.324				
	308	2.650				
	313	3.102				
8b	298	1.422	24.89	22.35	–243.98	96.89
	303	1.516				
	308	1.791				
	313	2.301				
9a	298	2.368	23.60	21.06	–243.69	95.52

Table-3 (contd.)

	303	2.737				
	308	3.095				
	313	3.778				
9b	298	2.395	23.16	20.62	−245.02	95.49
	303	2.813				
	308	3.158				
	313	3.792				
10a	298	2.325	22.22	19.67	−248.41	95.57
	303	2.694				
	308	3.158				
	313	3.553				
10b	298	1.699	21.82	19.28	−252.40	96.37
	303	1.956				
	308	2.265				
	313	2.585				

[a]Photochromism of Raai-C_nH_{2n+1} are reported in reference [21].
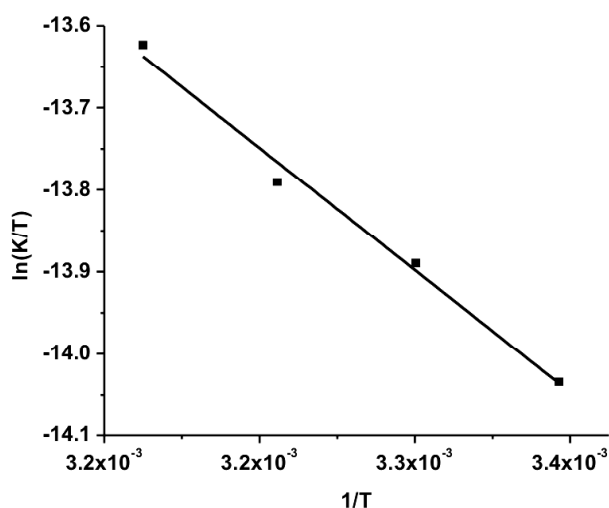
Fig. 3. The Eyring plots of rate constants of Z-to-E isomerisation of [Zn(MeaaiC$_{16}$H$_{33}$)$_2$I$_2$] (**11b**) in MeOH at different temperatures 298–313 K.

unoccupied MOs have > 95% Haai-$C_{10}H_{21}$ characteristics.

The electronic transitions in the complexes may be associated with intra-ligand π(azoimine) → π*(azoimine), I → π*(azoimine) and d(Zn) → π*(azoimine) charge transfer transitions (Table 4). Strong π–π* transitions (HOMO-6/HOMO-10/HOMO-13 → LUMO; HOMO-9 → LUMO+1) may appear around 280–410 nm. HOMO-5 → LUMO/LUMO+1 may observe at 392.7 nm who are assigned to the admixture of I → π*(azoimine) and d(Zn) → π*(azoimine) transitions. Theoretically generated spectrum is compared with experimental spectrum in Fig. 1.

UV light is irradiated to perform E-to-Z transformation of coordinated Raai-C_nH_{2n+1}. The irradiation is carried out for a fixed time which will enforce to isomerise

Table 4. TD-DFT computed assignment of electronic transition of [Zn(Haai-C$_{10}$H$_{21}$)$_2$I$_2$] (**6a**)

Excitation energy (eV)	Wavelength (nm)	Oscillation frequency (*f*)	Key transitions	Character
3.0228	410.16	0.0272	(22%) HOMO-6→LUMO	ILCT
3.1573	392.69	0.3432	(33%) HOMO-5→LUMO	XLCT, MLCT
3.2490	381.60	0.9361	(59%) HOMO-5→LUMO+1	XLCT, MLCT
3.4525	359.11	0.0507	(54%) HOMO-9→LUMO+1	ILCT
3.5382	350.42	0.1031	(78%) HOMO-10→LUMO	ILCT
4.3281	286.46	0.0243	(40%) HOMO-13→LUMO	ILCT

ILCT : Intra-ligand (π--π*) charge transfer; XLCT : Iodide-to-π*(azoimine) charge transfer; MLCT : d(Zn)-to--π*(azoimine) charge transfer.

HOMO; E, –4.93 eV; I, 98%

HOMO-1; E, –5.11 eV; I, 98%; L, 02%

HOMO-2; E, –5.13 eV; Zn, 03%; I, 94%; L, 03%

LUMO; E, –3.2 eV; I, 2%; L, 98%

LUMO+1; E, –3.1 eV; I, 2%; L, 98%

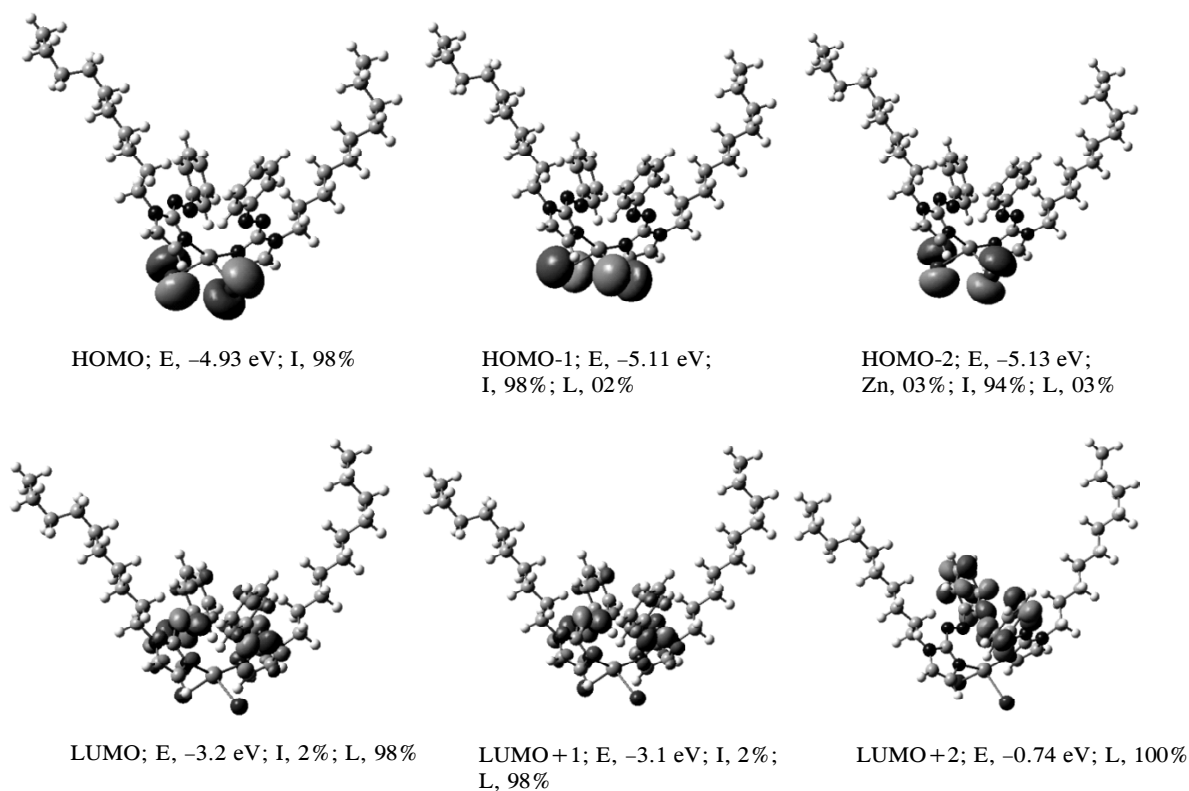LUMO+2; E, –0.74 eV; L, 100%

Fig. 4. Contour plots of some selected MOs; highest occupied MO (HOMO), lowest unoccupied MO (LUMO).

more stable *trans*-isomer to *cis*-isomer. Irradiation in the UV region (< 360 nm) causes $\pi \rightarrow \pi^*$ transition. The MLCT or XLCT are of lower energetic transition than π-π^* which may not capable to perform physical process like isomerisation. Conversely, the ligand in the complexes may assist charge transition in a secondary (MLCT or XLCT) process which is responsible for deactivation of excited species and regulates the rate of isomerisation and quantum yields.

Conclusion

[Zn(Raai-C_nH_{2n+1})$_2$I$_2$] (Raai-C_nH_{2n+1} where n = 10, 12, 14, 16, 18) were spectroscopically characterized. The complexes exhibit photochromism, E (*trans*)-to-Z (*cis*) and vice-versa of coordinated Raai-C_nH_{2n+1} about -N=N- bond upon UV light irradiation. The rate, quantum yields and activation energy (E_a) of isomerisation of coordinated Raai-C_nH_{2n+1} are lower than that of free ligand data. We will continue to account the effect of coordination of other ligands and other metal ions in such complexes.

References

1. G. S. Hartley, *Nature (London)*, 1937, 281.

2. H. Rau, in "Photochromism : Molecules and Systems", eds. H. Dürr and H. Bouas-Laurent, Elsevier, Amsterdam, 1990.

3. B. L. Feringa, "Molecular Switches",Wiley-VCH, Weinheim, 2001.

4. R. Guglielmetti, "Photochromism : Molecules and Systems", eds. H. Dürr, H. Bouas-Laurent, Elsevier, Amsterdam, 1990, pp. 314-466 and 855-878.

5. I. Willner and B. Willner, "Bioorganic Photochemistry", ed. H. Morrison, Wiley, New York, 1993, pp. 1-110.

6. R. C. Bertelson, "Organic Photochromic and Thermochromic Compounds", eds. J. C. Crano and R. Guglielmetti, Plenum Press, New York, 1999, pp. 11-83.

7. H. Knoll, in "CRC Handbook of Organic Photochemistry

and Photobiology", eds. W. Horspool and F. Lenci, CRC Press, Boca Raton, 2004, pp. 1-16.

8. "Photochromism : Memories and Switches (special issue)", *Chem. Rev.*, 2000, **100**, 1683.

9. E. V. Brown and G. R. Granneman, *J. Am. Chem. Soc.*, 1975, **97**, 621.

10. H. Yamagiwa and A. Sekine, *Bull. Chem. Soc. Jpn.*, 2013, **86**, 1028.

11. J. Otsuki, K. Suwa, K. Narutaki, C. Sinha, I. Yoshikawa and K. Araki, *J. Phys. Chem. (A)*, 2005, **109**, 8064.

12. P. Gayen and C. Sinha, *Spectrochim. Acta, Part A*, 2013, **104**, 477.

13. P. Gayen, K. K. Sarker and C. Sinha, *Coll. Surf. (A)*, 2013, **429**, 60.

14. P. Gayen and C. Sinha, *J. Indian Chem. Soc.*, 2013, **90**, 751.

15. P. Gayen, T. K. Misra and C. Sinha, *J. Spectrosc. Dyn.*, 2014, **4**, 27.

16. P. Pratihar, T. K. Mondal, A. K. Patra and C. Sinha, *Inorg. Chem.*, 2009, **48**, 2760.

17. S. Saha (Halder), P. Mitra and C. Sinha, *Polyhedron*, 2014, **67**, 321.

18. K. K. Sarker, D. Sardar, K. Suwa, J. Otsuki and C. Sinha, *Inorg. Chem.*, 2007, **46**, 8291.

19. S. Saha (Halder), P. Raghavaiah and C. Sinha, *Polyhedron*, 2012, **46**, 25.

20. D. Mallick, K. K. Sarker, P. Datta, T. K. Mondal and C. Sinha, *Inorg. Chim. Acta*, 2012, **387**, 352.

21. A. Nandi, C. Sen, D. Mallick, R. K. Sinha and C. Sinha, *Adv. Mater. Phys. Chem.*, 2013, **3**, 133.

22. A. I. Vogel, "A Text-Book of Quantitative Inorganic Analysis", 3rd ed., ELBS, Longman, 1975, 433.

23. G. Zimmerman, L. Chow and U. Paik, *J. Am. Chem. Soc.*, 1958, **80**, 3528.

24. Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery (Jr.), T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomas, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukud, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, P. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

25. B3LYP : A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

26. LanL2DZ : P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270.

27. N. M. O'Boyle and J. G. Vos, GaussSum 1.0, Dublin City University, Dublin, Ireland, 2005.