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Synthesis, Structure, Photochromism, Mesogenic property and DFT Computations of Silver(I) Complexes of Long Chain Alkyl Group Containing 1-Alkyl-2-(arylazo)imidazoles

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Abstract

The complexes $[Ag(Raai-C_nH_{2n+1})_2]ClO_4$ (where Raai- C_nH_{2n+1} refer 1-alkyl-2to (arylazo)imidazoles; R = H, Me and n = 4-22 (even numbers)) have been characterized by spectroscopic studies (UV-Vis, FT-IR, ¹H NMR). The X-ray structure of [Ag(Haai-C₂₂H₄₅)₂]ClO₄ confirms a distorted tetrahedral geometry. UV light irradiation (365-370 nm) of an acetonitrile solution of [Ag(Raai-C_nH_{2n+1})₂]ClO₄ shows E-to-Z (*trans*-to-*cis*) isomerization of the coordinated Raai- C_nH_{2n+1} group. The reverse transformation, Z-to-E (*cis*-to-*trans*), is very slow upon visible light irradiation, but becomes significantly faster on increasing the temperature (298-313 K). The rates and quantum yields ($\phi_{E\to Z}$) of the E-to-Z isomerization of the free ligands are higher than those of the complexes, which have proved the effect of rotor volume, rotor mass and the 1-alkyl chain length ($-C_nH_{2n+1}$). [Ag(Haai- $C_{18}H_{37}$)₂]ClO₄ shows a metallomesogenic property and undergoes phase transitions: the Cr (46.7 $^{\circ}$ C) – SmC (106.4 $^{\circ}$ C) – I phase sequence on heating and I (106.4 °C) – SmA (46.4 °C) - Cr on cooling. The SmC phase appears as the

typical fan-shaped texture. DFT computations on the optimized structure were carried out to explain the spectral properties.

Keywords: Silver(I)-arylazoimidazoles, structure, photochromism, liquid crystal, nematicisotropic phase transition, Smectic phase

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1. Introduction

Azobenzene, an interesting photochrome, undergoes a reversible E(trans)-Z(cis) isomerization [1-5] upon light irradiation. Such a property of molecules has been used in information storage, optical switching devices, surface relief gratings, non-linear optics etc [6-11]. Arylazopyridine, an azoheterocycle, has several advantages [12-14] over azobenzene. These compounds can bind M^{n+}/H^+ with the pyridyl-N and/or the azo-N donor centre(s), which can influence their properties. Binding with metal ions could minimize the problems of "fatigue" and low durability of the organic photochrome. We have used 1-alkyl-2-(arylazo)imidazoles to explore the coordination chemistry [15-20] and light stimulated properties [21-32]. The photoisomerization of arylazoimidazole was first reported in 2003 [33] by T. Majima and subsequent work had been done by us [21-32].

The synthesis of photosensitive liquid crystalline molecules [34, 35] is of present interest. The combination of photochromism and liquid crystalline properties in the same molecule provides an opportunity to explore a material which is useful for many practical applications including imaging technology, optical storage materials, integrated optical devices, laser optical

media and non-linear optical (NLO) materials [36-40]. However, the synthesis of such materials is challenging [41]. It is due to the loss of ordered orientation upon isomerisation of the rod-like E configuration to the bent Z configuration [40]. Liquid crystalline (LC) phases exist in between the three dimensionally ordered crystalline states and the disordered or isotropic fluid [37-41]. These are demanding problems in modern condensed matter chemistry and physics.

Recently, we have taken the initiative to include photochromism and liquid crystalline properties in a single molecule, like 1-alkyl-2-(arylazo)imidazoles [42] by substituting a long chain alkyl group at the imidazolyl part of the molecule. In this article, we wish to report the Ag(I)-coordination complexes of 1-alkyl-2-(arylazo)imidazoles, Raai- C_nH_{2n+1} (n = 4, 6, 8, 10, 12, 14, 16, 18, 20, 22). The characterisation has been carried out by spectroscopic data (IR, UV-Vis, NMR) and structural confirmation has been carried out in one case by a single crystal X-ray structure determination. Optical and thermal relaxation routes examine the photochromic properties. The liquid crystalline properties are examined by polarising optical microscopy and differential scanning calorimetry.

2. Experimental

2.1. Materials

AgClO₄ was purchased from E. Merck. The analytical reagent grades materials 1-iodo-nbutane, 1-bromo-n-hexane, 1-bromo-n-octane, 1-bromo-n-decane, 1-bromo-n-dodecane, 1bromo-n-tetradecane, 1-bromo-n-hexadecane, 1-bromo-n-octadecane, 1-bromo-n-icosane and 1bromo-n-docosane were purchased from Sigma-Aldrich and used as received. The 1-alkyl-2-(arylazo)imidazoles were synthesized by the reported procedure [42]. All other chemicals and solvents were reagent grade and used as received, and the solvents were purified before use by standard procedures [43].

2.2. Physical measurements

Microanalytical data (C, H, N) were collected on a Perkin-Elmer 2400 CHNS/O elemental analyzer. Spectroscopic data were obtained using the following instruments: UV-Vis spectra on a Perkin Elmer Lambda 25 spectrophotometer; IR spectra (KBr disk, 4000-400 cm⁻¹) on a Perkin Elmer RX-1 FTIR spectrophotometer; photo excitation using a Perkin Elmer LS-55 spectrofluorimeter; ¹H NMR spectra on a Bruker (AC) 300 MHz FTNMR spectrometer. The liquid crystalline properties were established by thermal microscopy (Nikon polarizing microscope LV100POL attached with a Linkam Temperature controlled stage model Examina-THMS600) and the phase transitions were confirmed by differential scanning calorimetry (Perkin Elmer Diamond DSC Pyris1 system).

2.2. The Synthesis of [Ag(Haai-C₈H₁₇)₂]ClO₄ (13a)

A solution of AgClO₄ (0.18 g, 1.06 mmol) in dry MeOH (10 ml) was added in drops to a stirred solution of Haai-C₈H₁₇ (0.40 g, 2.07 mmol) and the mixture was stirred in the dark for 2 h. A dark brown-red precipitate appeared. The mixture was further heated to dissolve the precipitate and it was then filtered hot through a G-4 sintered glass crucible. An aqueous solution of NaClO₄ (0.5 g in 5 ml) was added with constant stirring to this solution. The precipitate so obtained on cooling was collected by filtration, washed with water and recrystallised from 2-methoxyethanol-MeOH (1:3, v/v) mixture. It was dried in vacuum and preserved in the dark. Yield 0.54 g (66%).

Following identical procedures, the other $[Ag(Raai-C_nH_{2n+1})_2]ClO_4$ (11-20) complexes were prepared. Yield 60–75%.

The characterisation data of the complexes are as follows:

[Ag(Haai-C₄H₉)₂]ClO₄ (11a), Anal. found: C, 55.24; H, 5.77; N, 20.01. Calc. for AgC₂, H₂, N₂O₄Cl: C, 55.33; H, 5.67; N, 19.86%. **FTIR** (KBr disc, cm⁻¹): v(N=N), 1380; v(C=N), 1578. UV/Vis (MeCN) (λ_{max} , nm (10⁻³ ϵ , dm³ mol⁻¹ cm⁻¹): 280 (12.0), 364 (18.5), 380 (29.3), 448 (2.4). [Ag(Meaai-C₄H₉)₂]ClO₄ (11b), Anal. found: C, 56.89; H, 6.50; N, 20.01. Calc. for AgC₁₀H₂₆N₀O₄Cl: C, 56.77; H, 6.42; N, 18.92%. FTIR (KBr disc, cm⁻¹): v(N=N), 1384; v(C=N), 1580. UV/Vis (MeCN) (λ_{max} , nm (10⁻³ ϵ , dm³ mol⁻¹ cm⁻¹): 282 (13.1), 363 (18.2), 382 (16.0), 450 (3.4). [Ag(Haai-C₆H₁₃)₂]ClO₄ (12a), Anal. found: C, 58.00; H, 6.38; N, 17.95. Calc. for AgC₃₀H₄₀N₈O₄Cl: C, 58.08; H, 6.45; N, 18.07%. **FTIR** (KBr disc, cm⁻¹): v(N=N), 1380; v(C=N), 1576. UV/Vis (MeCN) (λ_{max} , nm (10⁻³ ϵ , dm³ mol⁻¹ cm⁻¹): 286 (12.5), 365 (2.5), 380 (27.5), 451 (3.6) 286 (12.5). [Ag(Meaai-C₆H₁₃)₂]ClO₄ (12b), Anal. found: C, 59.20; H, 7.15; N, 17.22. Calc. for AgC₂₂H₄₄N₆O₄Cl: C, 59.27; H, 7.10; N, 17.28%. FTIR (KBr disc, cm⁻¹): v(N=N), 1385; v(C=N), 1572. UV/Vis (MeCN) (λ_{max} , nm (10⁻³ ϵ , dm³ mol⁻¹ cm⁻¹): 288 (13.2), 369 (19.1), 382 (16.8), 450 (2.2). [Ag(Haai-C₈H₁₇)₂]ClO₄ (13a), Anal. found: C, 60.43; H, 7.15; N, 16.48. Calc. for AgC₂₄H₄₀N₆O₄Cl: C, 60.37; H, 7.10; N, 16.57%. FTIR (KBr disc, cm⁻¹): v(N=N), 1414; v(C=N), 1532. UV/Vis (MeCN) (λ_{max} , nm (10⁻³ ϵ , dm³ mol⁻¹ cm⁻¹): 285 (12.5), 368 (18.9), 381 (29.8), 451 (2.7). [Ag(Meaai-C₈H₁₇)₂]ClO₄ (**13b**), Anal. found: C, 61.35; H, 7.54; N, 15.87. Calc. for AgC₃₆H₅₀N₈O₄Cl: C, 61.38; H, 7.67; N, 15.91%. **FTIR** (KBr disc, cm⁻¹): v(N=N), 1384; v(C=N), 1568. UV/Vis (MeCN) (λ_{max} , nm (10⁻³ ϵ , dm³ mol⁻¹ cm⁻¹): 284 (13.5), 365 (18.5), 382 (16.5), 450 (3.5). [Ag(Haai-C₁₀H₂₁)₂]ClO₄ (14a), Anal. found: C, 62.24; H, 7.58; N, 15.28. Calc. for $AgC_{30}H_{50}N_{0}O_{1}Cl: C, 62.31; H, 7.65; N, 15.30\%$. **FTIR** (KBr disc, cm⁻¹): v(N=N), 1380; v(C=N), 1572. UV/Vis (MeCN) (λ_{max} , nm (10⁻³ ϵ , dm³ mol⁻¹ cm⁻¹): 285 (13.4), 366 (18.4), 381 (16.4), 452 (2.8). [Ag(Meaai-C₁₀H₂₁)₂]ClO₄ (14b), Anal. found: C, 63.10; H, 8.10; N, 14.46.

Calc. for AgC₄₀H₆₀N₈O₄Cl: C, 63.17; H, 8.16; N, 14.54%. **FTIR** (KBr disc, cm⁻¹), ν(N=N), 1385;

v(C=N), 1570. UV/Vis (MeCN) (λ_{max} , nm (10⁻³ ϵ , dm³ mol⁻¹ cm⁻¹): 286 (13.2), 367 (18.7), 384 (16.2), 453 (3.5). [Ag(Haai-C₁₂H₂₅)₂]ClO₄ (**15a**), Anal. found: C, 63.92; H, 8.10; N, 14.13. Calc. for AgC₄₂H₅₄N₈O₄Cl: C, 63.97; H, 8.12; N, 14.21. **FTIR** (KBr disc, cm⁻¹): v(N=N), 1376; v(C=N), 1578. UV/Vis (MeCN) (λ_{max} , nm (10⁻³ ϵ , dm³ mol⁻¹ cm⁻¹): 302 (9.1), 365 (17.6), 379 (16.1), 450 (1.4). [Ag(Meaai-C₁₂H₂₅)₂]ClO₄ (15b), Anal. found: C, 64.09; H, 8.16; N, 14.09. Calc. for AgC₄₄H₆₀N₆O₄Cl: C, 63.97; H, 8.12; N, 14.21%. FTIR (KBr disc, cm⁻¹): v(N=N), 1375; v(C=N), 1578. UV/Vis (MeCN) (λ_{max} , nm (10⁻³ ϵ , dm³ mol⁻¹ cm⁻¹): 296 (11.4), 368 (18.4), 383 (17.0), 454 (2.1). [Ag(Haai-C₁₄H₂₉)₂]ClO₄ (16a), Anal. found: C, 65.38; H, 8.48; N, 13.15. Calc. for AgC₄₆H₂₇N₈O₄Cl: C, 65.41; H, 8.53; N, 13.27%. FTIR (KBr disc, cm⁻¹): v(N=N), 1380; v(C=N), 1566. UV/Vis (MeCN) (λ_{max} , nm (10⁻³ ϵ , dm³ mol⁻¹ cm⁻¹): 285 (11.2), 367 (18.5), 382 (16.9), 453 (2.3). [Ag(Meaai-C₁₄H₂₉)₂]ClO₄ (16b), Anal. found: C, 66.00; H, 8.99; N, 12.74. Calc. for AgC₄₈H₇₆N₈O₄Cl: C, 66.07; H, 8.94; N, 12.84%. **FTIR** (KBr disc, cm⁻¹): ν (N=N), 1388; v(C=N), 1578. UV/Vis (MeCN) (λ_{max} , nm (10⁻³ ϵ , dm³ mol⁻¹ cm⁻¹): 284 (11.3), 366 (18.9), 381 (15.9), 452 (2.5). [Ag(Haai-C₁₆H₃₃)₂]ClO₄ (**17a**), Anal. found: C, 66.62; H, 8.97; N, 12.37. Calc. for AgC₅₀H₈₀N₈O₄Cl: C, 66.68; H, 8.89; N, 12.42%. **FTIR** (KBr disc, cm⁻¹): v(N=N), 1385; v(C=N), 1573. UV/Vis (MeCN) (λ_{max} , nm (10⁻³ ϵ , dm³ mol⁻¹ cm⁻¹): 302 (8.1), 365 (11.9), 378 (10.8), 456 (1.2). [Ag(Meaai-C₁₆H₃₃)₂]ClO₄ (17b), Anal. found: C, 67.18; H, 9.23; N, 12.00. Calc. for AgC₅₂H₆₄N₆O₄Cl: C, 67.25; H, 9.26; N, 12.07%. FTIR (KBr disc, cm⁻¹): v(N=N), 1381; v(C=N), 1568. UV/Vis (MeCN) (λ_{max} , nm (10⁻³ ϵ , dm³ mol⁻¹ cm⁻¹): 285 (8.9), 368 (17.2), 377 (16.8), 458 (2.2). [Ag(Haai-C₁₈H₃₇)₂]ClO₄ (**18a**), Anal. found: C, 67.70; H, 9.13; N, 11.64. Calc. for AgC₅₄H₆₆N₆O₄Cl: C, 67.79; H, 9.20; N, 11.71%. **FTIR** (KBr disc, cm⁻¹): v(N=N), 1387;

v(C=N), 1568. UV/Vis (MeCN) (λ_{max} , nm (10⁻³ ϵ , dm³ mol⁻¹ cm⁻¹): 289 (9.6), 365 (17.9), 375 (16.7), 450 (2.5). [Ag(Meaai-C₁₈H₃₇)₂]ClO₄ (18b), Anal. found: C, 68.23; H, 9.50; N, 11.29. Calc. for AgC₅₆H₁₀N₆O₄Cl: C, 68.30; H, 9.55; N, 11.38%. **FTIR** (KBr disc, cm⁻¹): v(N=N), 1377; v(C=N), 1577. UV/Vis (MeCN) (λ_{max} , nm (10⁻³ ϵ , dm³ mol⁻¹ cm⁻¹): 287 (11.2), 367 (18.2), 378 (16.8), 457 (2.3). [Ag(Haai-C₂₀H₄₁)₂]ClO₄ (**19a**), Anal. found: C, 68.75; H, 9.45; N, 11.00. Calc. for AgC₅₀H₀₆N₂O₄Cl: C, 68.78; H, 9.48; N, 11.06%. FTIR (KBr disc, cm⁻¹): v(N=N), 1414; v(C=N), 1572. UV/Vis (MeCN) (λ_{max} , nm (10⁻³ ϵ , dm³ mol⁻¹ cm⁻¹): 290 (12.2), 366 (2.4), 382 (27.3), 458 (3.3). [Ag(Meaai-C₂₀H₄₁)₂]ClO₄ (19b), Anal. found: C, 69.17; H, 9.88; N, 10.69. Calc. for AgC₆₀H₁₀₀N₈O₄Cl: C, 69.24; H, 9.80; N, 10.77%. **FTIR** (KBr disc, cm⁻¹): ν (N=N), 1379; v(C=N), 1574. UV/Vis (MeCN) (λ_{max} , nm (10⁻³ ϵ , dm³ mol⁻¹ cm⁻¹): 288 (11.1), 366 (18.7), 383 (15.3), 450 (2.8). [Ag(Haai-C₂₂H₄₅)₂]ClO₄ (**20a**), Anal. found: C, 69.62; H, 9.65; N, 10.40. Calc. for AgC₆₂H₁₀₄N₈O₄Cl: C, 69.67; H, 9.73; N, 10.48%. FTIR (KBr disc, cm⁻¹): v(N=N), 1384; v(C=N), 1567. UV/Vis (MeCN) (λ_{max} , nm (10⁻³ ϵ , dm³ mol⁻¹ cm⁻¹): 288 (4.8), 367 (16.3), 381 (16.7), 453 (2.0). [Ag(Meaai-C₂₂H₄₅)₂]ClO₄ (**20b**), Anal. found: C, 70.00; H, 10.09; N, 10.12. Calc. for AgC₆₄H₁₀₈N₈O₄Cl: C, 70.08; H, 10.03; N, 10.22%. FTIR (KBr disc, cm⁻¹): v(N=N), 1380; v(C=N), 1573. UV/Vis (MeCN) (λ_{max} , nm (10⁻³ ϵ , dm³ mol⁻¹ cm⁻¹): 292 (15.1), 367 (16.0), 382 (14.1), 456 (1.5).

2.3. *X*-ray diffraction study

Crystals of $[Ag(Haai-C_{22}H_{45})_2]ClO_4$ (**20a**) (0.20 x 0.14 x 0.08 mm) were grown by slow diffusion of a dichloromethane solution into hexane at ambient conditions for a week. A suitable single crystal was mounted on a Siemens CCD diffractometer equipped with graphite monochromated Mo-K_{α} ($\lambda = 0.71073$ Å) radiation. The crystallographic data are shown in Table

1. Unit cell parameters and crystal-orientation matrices were determined from the least-squares method in the range $-12 \le h \le 12$, $-10 \le k \le 10$, $-40 \le l \le 40$ and angle varying in the range $1.87 < \theta < 24.80^\circ$. The intensity data were corrected for Lorentz and polarisation effects and an empirical absorption correction was also employed using the SAINT program. Data were collected applying the condition $I > 2\sigma(I)$. The structure was solved by direct methods and followed by successive Fourier and difference Fourier syntheses. Full matrix least squares refinements on F^2 were carried out using SHELXL-97 [44] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were constrained to ride on their respective carbon or nitrogen atoms with anisotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement of their parent atom in all cases. Complex neutral atom scattering factors were used throughout for all cases. The maximum (Δ_{max} , e Å⁻³) and minimum (Δ_{min} , e Å⁻³) electron densities are 0.942 and -0.613. All calculations and drawings were carried out using SHELXL 97 [44], SHELXS 97 [45], PLATON 99 [46] and ORTEP-3 [47] programs.

2.4. Photometric measurements

Absorption spectra were taken with a Perkin Elmer Lambda 25 UV/VIS spectrophotometer in a I x 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 ¹H NMR integration. Quantum yields (ϕ) were obtained by measuring the initial *trans*-to-*cis* isomerization rates (ν) in a well-stirred solution within the above instrument using the equation, $\nu = (\phi I_0/V)(1-10^{-Abs})$ where I₀ is the photon flux at the front of the cell, V is the volume of the solution, and Abs is the initial

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absorbance at the irradiation wavelength. The value of I_0 was obtained by using azobenzene ($\phi = 0.11$ for π - π * excitation [48]) under the same irradiation conditions.

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

2.5. Computational methods

All the calculations were carried out with the density functional theory (DFT) method as implemented in the GAUSSIAN 03 program package for the optimized geometry of [Ag(Haai-C₂₂H₄₅)₂]ClO₄ (**20a**) using the crystallographic information file [49]. The hybrid DFT-B3LYP functional was used in the calculations [50]. For C, H, N, O and Cl, the 6-31G(d) basis set was assigned. The Los Alamos effective core potential plus double zeta (LanL2DZ) [51] basis set along with the corresponding pseudo potential without any symmetry constrains were used for silver. A vibrational frequency calculation was also performed for two complexes to ensure that the optimized geometries represent the local minima and there are only positive Eigen values. To assign the low lying electronic transitions in the experimental spectra, TDDFT calculations of the complexes were done in the gas phase. We have attempted TD-DFT calculations in acetonitrile solvent using a conductor-like polarizable continuum model (CPCM) [52–54], however these failed due to the huge number of functional parameters for such a large molecule on a desktop computer. We computed the lowest 25 singlet-singlet transitions and the results of the TD-DFT

calculations were qualitatively very similar. GaussSum [55] was used to calculate the fractional contributions of various groups to each molecular orbital.

3. Results and Discussion

3.1. Synthesis and formulation

1-Alkyl-2-(arylazo)imidazole (Raai- C_nH_{2n+1}) has been synthesized by the alkylation of 2-(arylazo)imidazole (Raai-H) by controlled addition of alkyl halide ($C_nH_{2n+1}X$) in dry THF using NaH [42] (Scheme 1). Alkyl halides of varying carbon chain length (C_4 to C_{22}) have been used to synthesize Raai- C_nH_{2n+1} (R = H (a), Me (b); n = 4 (C_4H_9 , 1), 6 (C_6H_{13} , 2), 8 (C_8H_{17} , 3), 10 ($C_{10}H_{21}$, 4), 12 ($C_{12}H_{25}$, 5), 14 ($C_{14}H_{29}$, 6), 16 ($C_{16}H_{33}$, 7), 18 ($C_{18}H_{37}$, 8), 20 ($C_{20}H_{41}$, 9), 22 ($C_{22}H_{45}$, 10)). Raai- C_nH_{2n+1} has been used for the synthesis of silver(I) complexes [Ag(Raai- $C_nH_{2n+1})_2$](ClO₄) (11-20). The complexes were purified by diffusion of a dichloromethane solution into layered hexane. The molar conductance data (Λ_M , 120-160 Ω^{-1} mol⁻¹) correspond to 1:1 electrolyte character in acetonitrile solution and their composition has been supported by microanalytical data. The structural confirmation has been achieved by a single-crystal X-ray diffraction study of [Ag(Haai- $C_{22}H_{45})_2$]ClO₄ (20a). Other spectroscopic techniques (FTIR, UV-Vis, ¹H NMR) have been used to characterize the complexes. Mass spectral have not been collected due to the typical problem of the explosive nature of the complexes.



Raai- $C_n H_{2n+1}$ (1 -10)

 $[Ag(Raai-C_nH_{2n+1})_2]^+$ (11-20)

 $R = H (a), Me (b); C_{n}H_{2n+1} \text{ for } n = 4 (1), 6 (2), 8 (3), 10 (4), 12 (5), 14 (6), 16 (7), 18 (8), 20 (9), 22 (10); [Ag(Haai-C_{4}H_{9})_2]ClO_4 (11a), [Ag(Meaai-C_{4}H_{9})_2]ClO_4 (11b), [Ag(Haai-C_{6}H_{13})_2]ClO_4 (12a), [Ag(Meaai-C_{6}H_{13})_2]ClO_4 (12b), [Ag(Haai-C_{8}H_{16})_2]ClO_4 (13a), [Ag(Meaai-C_{8}H_{16})_2]ClO_4 (12a), [Ag(Meaai-C_{6}H_{13})_2]ClO_4 (12b), [Ag(Haai-C_{8}H_{16})_2]ClO_4 (13a), [Ag(Meaai-C_{8}H_{16})_2]ClO_4 (13b), [Ag(Meaai-C_{10}H_{21})_2]ClO_4 (14a), [Ag(Meaai-C_{10}H_{21})_2]ClO_4 (14b), [Ag(Meaai-C_{12}H_{25})_2]ClO_4 (15a), [Ag(Meaai-C_{12}H_{25})_2]ClO_4 (15b), [Ag(Haai-C_{14}H_{29})_2]ClO_4 (16a), [Ag(Meaai-C_{14}H_{29})_2]ClO_4 (16a), [Ag(Meaai-C_{16}H_{33})_2]ClO_4 (17a), [Ag(Meaai-C_{16}H_{33})_2]ClO_4 (17b), [Ag(Haai-C_{18}H_{37})_2]ClO_4 (18a), [Ag(Meaai-C_{18}H_{37})_2]ClO_4 (18b), [Ag(Meaai-C_{20}H_{41})_2]ClO_4 (19a), [Ag(Meaai-C_{20}H_{41})_2]ClO_4 (19b), [Ag(Meaai-C_{22}H_{45})_2]ClO_4 (20a), [Ag(Meaai-C_{22}H_{45})_2]ClO_4 (20b)$

Scheme 1. Raai- C_nH_{2n+1} (1-10) and $[Ag(Raai-C_nH_{2n+1})_2]ClO_4$ (11-20)

3.2. Molecular structures

The molecular structure of $[Ag(Haai-C_{22}H_{45})_2]ClO_4$ (**20a**) is shown in Fig. 1. The bond parameters are listed in Table 2. Haai-C₂₂H₄₅ acts as an N,N[/]-chelating ligand where N and N[/]

refer to N(imidazole) and N(azo) donor centres and the chelate angle $\begin{bmatrix} A_{g}^{\dagger}(-N=N-C=N^{-})\end{bmatrix}$ of $67.44(12)^{\circ}$ is close to reported data [56,57]. The constituents of the chelate plane Ag(1)–N(2)– C(1)-N(3)-N(4) show torsion angles in the range 2.2-4.0°. The two chelate planes about Ag(I) are inclined at 52.55(16)°. Other bond angular values are $\angle Ag(1)-N(2)-C(1)$, 120.0(3)° and $\angle Ag(1)-N(4)-N(3)$, 111.7(2)°. The Ag-N(imidazolyl) bond length (2.146(4) Å) is shorter than the Ag-N(azo) bond length (2.650(4) Å), which reflects the stronger interaction between Ag(I) and N(imidazolyl). The Ag-N(imidazolyl) distances in this example are longer than previously reported data of $[Ag(\alpha-NaiEt)_2]ClO_4$ (α -NaiEt = 1-ethyl-2-(naphthyl- α -azo)imidazole; Ag-N(imidazolyl), 2.124(5)/2.128(5) Å) while the Ag-N(azo) bond length is shortened by 0.3 Å compared to the reported result (2.851(5) Å) [57]. The pendant phenyl ring is no longer planar with the chelate plane of Ag(1)-N(2)-C(1)-N(3)-N(4) and is inclined at an angle of $13.6(2)^{\circ}$. Imidazolyl-H (3-H) forms a hydrogen bond with O-ClO₃⁻ to give a supramolecule (C(3)–H(3)---O(2): H(3)---O(2), 2.490(3) Å; C(3)---O(2), 3.262(11) Å and \angle C(3)-H(3)---O(2), 141.00°; symmetry, -1+x, 1+y, z). The packing view shows interdigitation of alkyl C-H bonds of the long chain alkyl group and the dispersion force may hold these units together (Fig. 2). The DFT calculated optimized structure of the E-isomer (20a) shows structural compatibility with the experimentally determined structure (Table 2). We could not isolate a crystal of the Z-isomer (20a[']), however the structural parameters from optimized geometry (DFT technique) show elongation of bond lengths and angles, which may be due to the structural strain developed in the arrangement.

3.3. The spectral characterization

The infrared spectral bands of the -N=N- and -C=N- groups of Raai- C_nH_{2n+1} appear at 1400-1410 and 1620-1625 cm⁻¹ respectively. The complexes $[Ag(Raai-C_nH_{2n+1})_2]ClO_4$ show moderately intense stretches at 1565-1580 and 1370-1385 cm⁻¹ which are due to v(C=N) and v(N=N), respectively. DFT computation of the optimized structure of $[Ag(Haai-C_{22}H_{45})_2]ClO_4$ has been carried out and a vibrational frequency calculations were performed; the main frequencies have been compared between the calculated and experimental data. The stretching frequencies shifting to a lower frequency region in the complexes are in support of coordination of the azo-N and imine-N atoms to Ag(I) [57].

The ¹H NMR spectra of the complexes were recorded in CDCl₃. The atom numbering pattern is shown in Scheme 1. The alkylation of the imidazolyl motif at 2-(arylazo)imidazole is supported by the disappearance of δ (N–H) at ~10.30 ppm and the appearance of an N(1)-alkyl signal at 0.85- 4.40 ppm; -N–CH₂ –(CH₂)_n –CH₃ shows a triplet for –CH₂– at 4.40 ppm and multiplet for –(CH₂)_n– at 1.22-1.90 ppm [42]. The imidazolyl 4- and 5-H protons appear as broad singlets at 7.24-7.28 and 7.14-7.17 ppm, respectively. Broadening may be due to rapid proton exchange between these protons. The aryl protons (7-H to 11-H) are upfield shifted on going from Haai-C_nH_{2n+1} (**1a-10a**) to Meaai-C_nH_{2n+1} (**1b-10b**), which may be due to the +I effect of the Me group in the aryl part. The data (Table 3) reveal that the signals in the spectra of the complexes are shifted downfield relative to the free ligand values. This supports the coordination of the ligand to Ag(I) [56,57]. The imidazolyl protons (4-H and 5-H) suffer downfield shifting by 0.3-0.4 ppm compared to the free ligand positions. This supports the strong preference of imidazolyl-N binding to Ag(I).

3.4. The absorption spectra and photochromism

The absorption spectra were recorded in MeOH solution for the ligands and in MeCN solution (because of the sparing solubility of the complexes in MeOH) for the complexes, over the wavelength range 200-600 nm. The absorption spectra of the ligands Raai- C_nH_{2n+1} show transitions at 270-290 and 360-390 nm (ϵ , 10⁴ M⁻¹ cm²) and a tail with a weak band at 450-460 nm. The intense absorption band at 270-290 nm corresponds to π - π * transitions localized on the phenyl group, the band at 360 nm originates from symmetry-allowed π - π * transitions and the band at 450 nm corresponds to an n- π * transition [21]. In the solution spectra of [Ag(Raai- $C_nH_{2n+1})_2$]ClO₄ (**11-20**), the absorption maxima (λ_{max}) are shifted to a longer wavelength region by 4-10 nm compared to the free Raai- C_nH_{2n+1} data. This defines the coordination of Raai- C_nH_{2n+1} to Ag(I) [57]. The effect of the chain length of the alkyl group (- C_nH_{2n+1}) on the transition wavelength is difficult to rationalize, however there is a general trend that λ_{max} increases with an increase in the number of earbon atoms (n) in the chain of - C_nH_{2n+1} in the ligand.

The irradiation of UV light at λ_{max} (selected from the π -- π * band of the UV-Vis spectra) to a MeOH solution of the ligands, and an acetonitrile solution of the complexes gives the spectral change shown in Fig. 3. Ag(I) compounds are, in general, sensitive to light and undergo photoreduction to metallic Ag [58]. However, in many coordination complexes with delocalized π -electrons or accessible molecular vibration or rotation, the photon energy (hv) may be used for these additional activities instead of the photoredox reaction [56,57]. The spectra of irradiated solutions show that the intense peak at λ_{max} decreases, and this is accompanied by a slight increase at the tail portion of the spectra, around 525 nm, until a stationary state is reached. The state is defined as photostationary state I (PSS-I) activated by the π -- π * transition. Subsequent irradiation at the newly appeared longer wavelength peak reverses the course of the reaction

slowly and the original spectra are recovered up to a point, which is another photostationary state II (PSS-II, n-- π^* transition) under irradiation at the longer wavelength peak. The quantum yields of the E-to-Z photoisomerization were determined using those of azobenzene [48] as a standard and the results are tabulated in Table 4. The photoisomerisation of the ligands in the complexes is dependent on the nature of metal ion, its oxidation state and the structural state [21-26]. It is observed that upon UV light irradiation the E-to-Z photoisomerisation proceeds and a Z molar ratio reaches ~ 75%. The absorption spectra of the E-isomers have changed, with isosbestic points upon excitation (Fig. 3), into the Z-isomer. The ligands and the complexes show little sign of degradation upon repeated irradiation with up to at least 15 cycles in each case. The quantum yields were measured for the *trans*-to-*cis* ($\phi_{t\to c}$) photoisometisation of complexes in acetonitrile on irradiation with UV wavelength light (Table 4). The $\phi_{E \rightarrow Z}$ values are significantly dependent on the chain length, -C_nH_{2n+1}; an increase in the chain length decreases the rate of E-to-Z isomer transformation. The Me substituent at the azoaryl group (Haai-C_nH_{2n+1} to Meaai-C_nH_{2n+1}) and substituents at the N(1)-position both reduce the $\varphi_{E\to Z}$ values. In general, an increase in mass of the molecule reduces the rate of isomerisation. In the complexes, the $\varphi_{E \to Z}$ values are significantly less than those of the free ligand data. It may be argued that the reasons for this decrement are (i) the presence of a coordinated Ag(I) motif which increases the molar mass of the unit and may interfere with the motion of the -N=N-Ar moiety and (ii) the increase of the alkyl chain length N(1)-CnH2n+1 which interferes with the motion of the -N=N-Ar moiety, in addition to the small increase in molar mass (14 per -CH2- unit). The rotor volume has significant influence on the isomerisation rate and quantum yields [21-32].

Thermal isomerisation was carried out in the dark by UV-Vis spectroscopy in MeOH (ligand) and in MeCN (complexes) at varied temperatures, 298-308 K. The Eyring plots gave a

linear graph from which the activation energy was obtained (Table 5, Fig. 4). In the complexes, the E_a values are severely reduced, which means faster Z-to-E thermal isomerisation. The entropies of activation (ΔS^*) are more highly negative in the complexes than in the free ligands. This is also in support of an increase in rotor volume in the complexes. The activation energy (E_a) deceases significantly with an increase in alkyl chain length (Fig. 5).



Scheme 2. Plausible mechanism of the photoisomerisation of coordinated Raai- C_nH_{2n+1} in $[Ag(Raai-C_nH_{2n+1})_2]^+$

A plausible mechanism for photoisomerisation may be accounted for by cleavage of the Ag-N(azo) bond, retaining the Ag-N(imidazolyl) bond, followed by rotation of the excited state about the free -N=N- bond (Scheme 2). Sustenance of the Ag-N(imidazolyl) bond may be supported by the photostability of these complexes, even after prolonged irradiation in the solution phase [58]. The DFT calculated results of the optimized geometries of representative complexes, the E-isomer of $[Ag(E-Haai-C_{22}H_{45})_2]ClO_4$ (**20a**) and Z-isomer of $[Ag(Z-Haai-C_{22}H_{45})_2]ClO_4$ (**20a**[/]), have been used to interpret the absorption spectra in the gas phase and to

explain the photoisomerisation. The optimized structure of the E-isomer is more stable than the Z-isomer by 125.51 Kcal mol⁻¹ (Fig. 6). In the case of the E-isomer, the HOMO (highest occupied molecular orbital) (-8.26 eV), HOMO-1 (-8.26 eV); HOMO-2 (-8.82 eV), HOMO-3 (-8.82 eV); HOMO-4 (-8.88 eV), HOMO-5 (-8.88 eV) (Fig. 7) are degenerately paired; other lower energetic filled MOs are closely spaced (Supplementary Material, Fig. S1). The LUMO (lowest unoccupied molecular orbital) (-5.48 eV) and LUMO+1 (-5.47 eV) are also nearly degenerate. There is a large energy gap between LUMO+1 (-5.47 eV) and LUMO+2 (-2.80 eV), and other LUMO+m (m = 3, 4 5 etc) appear within -2.8 to -2.4 eV (Supplementary Materials; Fig. S2). The MOs of the Z-isomer are distributed as follows: HOMO (-7.75 eV), HOMO-1 (-7.86 eV), HOMO-2 (-8.29 eV), LUMO (-5.82 eV), LUMO+1 (-5.68 eV), LUMO+2 (-3.23 eV) etc (Supplementary Materials; Fig. S3). The HOMO is stabilized by 0.51 eV (11.76 Kcal) in the E-isomer, while the LUMO is stabilized by 0.34 eV (7.84 Kcal) in the Z-isomer. The carbon of the alkyl chain $(-C_{22}H_{45})$ partly contributes to the HOMO and HOMO-1 (99%) of the E-isomer, while HOMO-3, HOMO-4 and others are comprised of the 2-(phenylazo)imidazolyl (Haai-) motif (> 80%) (Supplementary Material, Table S1). The unoccupied MOs (LUMO, LUMO+1 etc.) are composed mainly of the Haai- motif. The composition and energy of the MOs are given in the Supplementary Material (Figs. S1, S2, Tables S1, S2). High intense bands calculated at 430.83 (oscillator strength f, 0.0166), 384.4 (f, 0.1694), 382.04 (f, 0.6257) and 379.11 nm (f, 0.4894) are referred to the HOMO-3 \rightarrow LUMO, HOMO-4 \rightarrow LUMO+1, HOMO-3 \rightarrow LUMO+1 and HOMO-6 \rightarrow LUMO+1 transitions, respectively, and have been assigned mainly to intraligand charge transfer (ILCT) bands. The transition at 379.64 nm (f, 0.0366) is assigned to the HOMO-5 \rightarrow LUMO+1 transition, and refers to CRCT (chain to ring charge transfer). The HOMO \rightarrow LUMO+6 transition at 322 nm is assigned to a ligand-to-metal charge transfer

(LMCT) transition. Higher energy transitions < 300 nm are associated with ClO_4^- and the Haaimotif (*Supplementary Materials, Tables S3*). The HOMO-LUMO energy separation ($\Delta E = 0.85$ eV or 19.60 Kcal mol⁻¹) also indicates the generation of a low energy band (~420 nm) upon UV light irradiation, which indicates a population increment for the Z-isomer (Fig. 3).

In the photochromic process irradiation with UV light isomerizes the more stable *trans*isomer (E) to the *cis*-isomer (Z). Irradiation in the UV region causes a $\pi \rightarrow \pi^*$ transition which is responsible for cleavage of the Ag-N(azo) bond and opening of the chelate ring, followed by the $E \rightarrow Z$ geometry change. The LMCT (ligand-to-metal charge transition) or CRCT (chain-to-ring charge transition) are lower energetic transitions and are insufficient to perform bond cleavage and isomerisation. Conversely, the metallated ligand may perform a charge transition in a secondary (LMCT or CRCT) process, which is responsible for deactivation of the excited species and regulates the rate of isomerisation and quantum yields (Table 4).

To further study the electronic structure, NBO calculations on the optimized geometry of the Z-isomer of $[Ag(Haai-C_{22}H_{45})_2]ClO_4$ (**20a**) have been performed. The polarity of the bonds is accounted for by Natural Bond Orbital (NBO) analysis (*Supplementary Table S5*). The Ag-N bonds have one natural bond orbital; the NBO charge of the Ag centre is 0.624, which is lower than the +1 formal oxidation state. The charges on imidazolyl-N are -0.400 (N(1)) and -0.643 (N(2)), while the N(azo) atoms show charges of -0.266 (N(3)) and -0.219 (N(4)). The data imply that a stronger interaction exists between Ag and imidazoly-N, than between Ag and azo-N. The preferential cleavage of the Ag-N(azo) bond upon light irradiation may thus be rationalized.

3.5. Metallomesogenic properties

The thermal properties of $[Ag(Raai-C_nH_{2n+1})_2]ClO_4$ were examined using polarized light optical microscopy (POM) and differential scanning calorimetry (DSC). The mesogenic property of Raa-C_nH_{2n+1} has been reported by us [42]. Haai-C_{18}H_{37} exhibits a nematic (N) texture at 55 °C and Haai-C_{22}H_{45} shows an unknown Smectic (Sm) phase at 62 °C. On cooling, the isotropic phase of Haai-C_{18}H_{37} transforms to the 'Schlieren' phase.

A textural analysis of $[Ag(Raai-C_nH_{2n+1})_2]ClO_4$ has been performed by polarizing optical microscopy (POM). A significant response was observed for $[Ag(Haai-C_{18}H_{37})_2]ClO_4$ (**18a**) (Fig. 8). Complex **18a** shows the phase sequence Cr – SmC- I. On cooling, the isotropic phase of **18a** shows the phase sequence I – SmA- Cr. The SmC phase appears as a typical fan-shaped texture [34,37,41] (Fig 8b) when placed in a thin cell with a cell gap of d = 5 ± 0.2 µm under homogeneous planar boundary conditions. On cooling the isotropic liquid, the Smectic phase forms a fan-shaped texture, which is more reminiscent of a SmA phase than a SmC phase (Fig. 8d). The other complexes do not show any mesomorphic phase sequences.

Differential scanning calorimetry (DSC) was used to measure the phase transition energy. In case of complex **18a**, a large value of Δ H (160.97 J/g) was observed, which occurs at a phase transition at 106.4 °C. This peak clearly indicates that a transition takes place from the SmC phase to an isotropic phase. A small peak arises at 46.7 °C, where Δ H is very low (6.3 J/g), indicating a transition from a crystal phase to the SmC phase (Fig. 9). Upon cooling, the complex shows a phase transition around 46.4 °C to the SmA phase and here the enthalpy is (5.3 J/g). From the above information it is clear that both exothermic and endothermic changes take place.

Conclusions

The complexes $[Ag(Raai-C_nH_{2n+1})_2]ClO_4$ have been structurally established. Raai- C_nH_{2n+1} shows E(trans)-to-Z(cis) isomerisation upon UV-light irradiation both in the free and coordinated states. Photochromism of the complexes show a weaker response compared to the free ligand data. The rates and quantum yields of the E-to-Z isomerisation of the complexes are lower than the free ligands. The Z-to-E isomerisation is a thermally driven process. The activation energies (E_as) are found to be lower and ΔS^* more highly negative in the complexes than the free ligands. The slow rate of isomerisation in the complexes may be due to a higher rotor volume and mass than for the free ligands. One of the complexes, $[Ag(Haai-C_{18}H_{37})_2]ClO_4$, shows a metallomesogenic property and undergoes phase transitions: the Cr (46.7 °C) – SmC (106.4 °C) – I phase sequence on heating and I (106.4 °C) – SmA (46.4 °C) – Cr on cooling. The SmC phase appears with a typical fan-shaped texture.

Supplementary material

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 967552. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (e-mail, deposit@ccdc.cam.ac.uk or www, htpp://www.ccdc.cam.ac.uk).

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	20a	
Empirical formula	$C_{62}H_{104}N_8O_4ClAg$	
Formula weight	1168.85	
Temperature (K)	293(2)	
Crystal system	Monoclinic	
Space group	P2/c	
a (Å)	10.927(5)	
b (Å)	8.656(5)	
c (Å)	34.203(5)	
β(°)	92.778(5)	
$V(Å)^3$	3231(2)	
Ζ	2	
μ (MoK _{α}) (mm ⁻¹)	0.402	
D _{calc} (Mg m ⁻³)	1.201	
Refine parameters	344	
Total reflections	42980	
Unique reflections	5516	
R_{1}^{a} [I > 2 σ (I)]	0.0658	
wR ₂ ^b	0.1926	
Goodness of fit	1.037	
$a \mathbf{D} - \mathbf{\Sigma}$ E E / \S E b ₁	${}^{2}P = [\Sigma_{W}(E^{2} E^{2})^{2}/\Sigma_{W}(E^{2})^{2}]^{1/2} = 1/[\sigma^{2}(E^{2})^{2}]^{1/2}$	$(0.11210)^{2}$

Table 1. Summarized crystallographic data for $[Ag(Haai-C_{22}H_{45})_2]ClO_4$ (20a)

^a R= Σ | F_o| - F_c | / Σ | F_o|. ^bwR₂ = [Σ w(F_o²-F_c²)²/ Σ w(F_o²)²]^{1/2}, w = 1/[σ ²(F₀)²+ (0.1121P)²] where P = (F₀² + 2F_c²) / 3.

Table 2. Experimental and theoretical bond distances (Å) and angles (°) of some selected bonds in $[Ag(E-Haai-C_{22}H_{45})_2]ClO_4$ (**20a**) and $[Ag(Z-Haai-C_{22}H_{45})_2]ClO_4$ (**20a**)^{\neq}

Во	ond distance	l distances (Å) Bond angles (°)					
	20a		20a'	2	20a		20a'
Bonds	Expm	Theo	Theo	Angles	Expm	Theo	Theo
N(1)-C(1)	1.352(6)	1.382	1.403	C(4)-C(5)-C(6)	113.0(4)	111.618	113.251
N (1)-C(3)	1.354(6)	1.384	1.407	C(5)-C(6)-C(7)	111.6(4)	112.627	116.549
C(2)-C(3)	1.362(6)	1.395	1.415	C(22)-C(23)-C(24)	115.4(4)	113.319	120.322
Ag(1)–N(2)	2.146(4)	2.197	2.214	C(23)-C(24)-C(25)	115.0(5)	113.012	115.210
Ag(1)-N(4)	2.650(4)	2.728	2.845	Ag(1)-N(2)-C(1)	120.0(3)	118.597	122.609
N(2)–C(1)	1.314(6)	1.357	1.385	Ag(1)-N(4)-N(3)	111.7(2)	109.589	112.895
N(3)–C(1)	1.390(6)	1.390	1.410	N(2)-Ag(1)-N(4)	67.44(12)	68.006	64.667
N(4)–N(3)	1.273(5)	1.296	1.326				

^{*≠*} Theoretically generated structure using the DFT computational technique.

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Compound	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}
$[Ag(Haai-C_4H_9)_2]ClO_4$ (11a)	7.39	7.21	7.71	7.47 ^m	7.50 ^m	4.55	1.40-1.10
			(8.2)			(6.4)	
$[Ag(Meaai-C_4H_9)_2]ClO_4(11b)$	7.40	7.20	7.76	7.35	2.44	4.57	1.42-1.23
				(- 0)		2	
			(7.6)	(7.0)		(7.0)	
$[A\sigma(Haai-C_{\ell}H_{12})_{2}]C[O_{\ell}(12a)]$	7.41	7.22	7.71	7.49 ^m	7.58	4.62	1.43-1.12
[//g///////////////////////////////////							
		5.00	(8.2)	G		(6.4)	1 40 1 00
$[Ag(Meaai-C_6H_{13})_2]ClO_4(12b)$	7.44	7.22	7.86	7.42	2.40	4.55	1.42-1.23
			(7.6)	(7.0)		(7.0)	
$[Ag(Haai-C_8H_{17})_2]ClO_4$ (13a)	7.46	7.22	7.72	7.51 ^m	7.59	4.61	1.45-1.10
		1	(8.1)			(6.3)	
			(011)			(0.0)	
$[Ag(Meaai-C_8H_{17})_2]ClO_4(13b)$	7.43	7.21	7.96	7.41	2.42	4.58	1.43-1.02
			(7.9)	(7.0)		(7.1)	
			(1.))	(7.0)		(7.1)	
$[Ag(Haai-C_{10}H_{21})_2]ClO_4$ (14a)	7.47	7.20	7.72	7.52 ^m	7.59	4.60	1.46-1.03
			(9.1)			(6.8)	
			(0.1)			(0.8)	
$[Ag(Meaai-C_{10}H_{21})_2]ClO_4(14b)$	7.44	7.21	7.99	7.41	2.45	4.53	1.45-1.03
			(7,0)	(7, 4)		(7,1)	
			(7.8)	(7.4)		(7.1)	
$[Ag (Haai-C_{12}H_{25})_2]ClO_4 (15a)$	7.48	7.23	7.73	7.53 ^m	7.58	4.59	1.48-1.24
	7.42	7 22	(8.5)	7 20	2.47	(7.4)	1 47 1 24
$[Ag(Meaai-C_{12}H_{25})_2]CIO_4(15D)$	7.42	1.22	7.99	1.38	2.47	4.34	1.4/-1.24
			(8.7)	(7.0)		(7.5)	
	7.41	7.05	7.74	7.50 ^m	7.50	4.50	1 40 1 04
$[Ag(Haai-C_{14}H_{29})_2]ClO_4$ (16a)	7.41	7.25	1.14	7.52	7.59	4.58	1.49-1.04
			(8.1)			(7.2)	
$[Ag(Meaai-C_{14}H_{29})_2]ClO_4(16b)$	7.42	7.20	7.95	7.35	2.46	4.52	1.48-1.1
			(7.9)	(7.4)		(7.1)	
$[Ag(Haai-C_{16}H_{33})_2]ClO_4(17a)$	7.44	7.23	7.75	7.54 ^m	7.61	4.57	1.51-1.14
			(7.8)			(63)	
			(1.0)			(0.5)	

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Table	3.	'H NMR s	pectral	data o	f the	com	plexes	in	CDCl ₃	at room	temp	erature

		-					
$[Ag(Meaai-\overline{C_{16}H_{33}})_2]ClO_4(17b)$	7.40	7.22	7.98	7.33	2.48	4.51	1.52-1.24
			(8.0)	(7.4)		(6.9)	
[Ag(Haai-C ₁₈ H ₃₇) ₂]ClO ₄ (18a)	7.43	7.22	7.76	7.53 ^m	7.58	4.57	1.52-1.21
			(7.8)			(7.1)	
$[Ag(Meaai-C_{18}H_{37})_2]ClO_4(18b)$	7.47	7.21	7.98	7.32	2.47	4.49	1.51-1.11
			(8.1)	(7.0)		(6.8)	
$[Ag(Haai-C_{20}H_{41})_2]ClO_4$ (19a)	7.44	7.21	7.79	7.54 ^m	7.62	4.56	1.53-1.42
			(73)			(6.9)	
$[Ag(Meaai-C_{20}H_{41})_2]ClO_4$ (19b)	7.48	7.19	7.95	7.54	2.49	4.48	1.55-1.35
			(7,0)	(7.4)		(7.2)	
$[Ag(Haai_CaaH_{12})a]C[O_1(20a)]$	7.48	7.17	(7.8)	(7.4)	7.62	(7.3)	1.58-1.23
[//g(11aa1-C221145)2]C1O4 (20a)	/110	,,,,,,		G			
$[A \sim (Maaai C, U, a)]ClO(20b)$	7 47	7.18	(8.3)	7 35	2.48	(6.3)	1 57 1 25
$[Ag(Meaai-C_{22}H_{45})_2]CiO_4(20D)$	/.4/	7.10	1.90	1.33	2.40	4.47	1.37-1.23
e			(8.2)	(7.4)		(6.6)	
Singlet;							
^d Doublet:							
^t Triplet;							
Broad Singlet;							
^m Multiplet.							
C							
~							

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	1	1	1	
Compound	λ_{π,π^*} (nm)	Isosbestic	Rate of $E \rightarrow Z$	$\phi_{E \to Z}$
		point (nm)	conversion x 10^9 (s ⁻¹)	conversion x 10 ⁹
11a	365	336, 443	17.58	1.21
11b	367	334, 445	17.10	1.07
12a	366	336, 438	17.21	1.01
12b	369	339, 455	16.91	0.99
13a	365	335, 442	16.58	0.91
13b	368	338, 445	15.97	0.89
14a	367	332, 441	16.10	0.88
14b	369	337, 442	15.12	0.85
15a	365	333, 438	16.01	0.86
15b	368	332, 448	15.03	0.83
16a	367	334, 443	15.94	0.84
16b	368	335, 441	14.97	0.82
17a	367	335, 438	14.79	0.81
17b	369	337, 445	13.25	0.79
18a	365	336, 441	14.01	0.78
18b	368	338, 446	13.04	0.76
19a	366	332, 442	13.21	0.75
19b	367	334, 445	12.45	0.74
20a	366	333, 443	12.30	0.71
20b	368	325, 440	11.54	0.69

Table 4. Results of photochromism, rate of conversion $(E \rightarrow Z)$ and quantum yields upon UV light irradiation to a complex solution in acetonitrile

Compound	Temp	Rate of thermal	Ea	ΔH^*	ΔS^*	ΔG^*
	(K)	$Z \rightarrow E$ conversion x	kJ mol ⁻¹	kJ mol ⁻¹	J mol ⁻¹ K ⁻¹	kJ mol ⁻¹
		$10^3 (s^{-1})$				R
11a	298	0.190(1)	72.60 ± 0.34	70.10 ± 0.35	-80.81± 1.07	94.58±0.02
	303	0.325(2)				
	308	0.490(3)			9	
	313	0.825(5)				
11b	298	0.183(4)	74.14±0.84	71.63 ± 0.84	-75.77±2.65	94.62±0.03
	303	0.327(8)				
	308	0.483(4)				
	313	0.823(6)				
12a	298	0.200(1)	71.51 ± 0.05	69.00 ± 0.06	-83.92±0.22	94.42±0.01
	303	0.355(2)				
	308	0.510(3)				
	313	0.845(5)				
		CV CV				
	(6				

Table 5. Rate and activation parameters for $Z(cis) \rightarrow E(trans)$ thermal isomerisation of $[Ag(Raai-C_nH_{2n+1})_2]ClO_4$

12b	298	0.213(4)	68.63±0.47	66.11±0.22	-93.11±2.16	94.32±0.03
	303	0.367(8)				
	308	0.523(4)				
	313	0.853(6)				
1 3 a	298	0.210(2)	70.30± 0.86	67.77±0.86	-87.62±2.88	94.32±0.02
	303	0.364(8)				
	308	0.521(9)				
	313	0.865(9)				
13b	298	0.234(5)	62.88± 1.10	60.36± 1.10	-111.72± 3.53	94.22±0.03
	303	0.376(5)				
	308	0.533(2)				
	313	0.896(7)				
1 4 a	298	0.229(2)	66.80± 0.14	64.28±0.14	-98.67±0.44	94.17±0.03
	303	0.389(8)				
	308	0.549(6)				
	313	0.886(7)				
		C				
		0				

14b	298	0.234(5)	67.08±0.89	64.56±0.89	-97.55 ± 2.83	94.12±0.03
	303	0.397(6)				
	308	0.563(4)				
	313	0.897(9)				R
15a	298	0.236(7)	66.12±1.87	63.61±1.87	-100.67 ± 6.01	94.11±0.03
	303	0.399(7)			C	
	308	0.564(5)			9	
	313	0.899(7)				
15b	298	0.265(4)	64.40±0.23	61.89± 0.23	-105.60 ± 0.68	93.88±0.03
	303	0.423(5)				
	308	0.616(7)				
	313	0.954(6)				

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16a	298	0.256(7)	63.65 ± 1.07	61.13±1.07	-108.39 ± 3.43	93.98 ± 0.03
	202	0.412(5)				
	303	0.413(5)				
	308	0.589(6)				
	313	0.912(3)				~
16b	298	0.265(7)	69.40± 0.89	66.89±0.89	-88.60± 2.82	93.73±0.04
	303	0.476(7)				
	308	0.657(8)			6	
	313	0.954(5)				
17a	298	0.278(9)	61.06± 1.12	58.54± 1.12	-116.30± 3.67	93.78±0.04
	303	0.456(7)		5		
	308	0.618(9)				
	313	1.098(9)				
17b	298	0.257(7)	68.11±1.10	65.60±1.10	-93.39±3.52	93.90±0.04
	303	0.424(7)				
	308	0.627(6)				
	313	0.957(1)				
	I					<u> </u>
		0				

18a	298	0.346(7)	59.72±0.60	57.20±0.60	-118.35±2.17	93.26±0.03
	202	0.556(7)				
	303	0.556(7)				
	308	0.756(7)				
	313	1.456(7)				Q
18b	298	0.453(4)	52.37±0.01	49.52±0.47	-141.40±0.09	92.70±0.02
	303	0.698(9)				
	308	0.899(8)			6	
	313	1.967(5)				
19a	298	0.564(3)	60.21±0.75	57.66±0.32	-114.45±2.14	92.33±0.02
	303	0.768(6)		~		
	308	0.798(5)				
	313	2.015(4)				
19b	298	0.456(9)	49.88±0.86	47.37±0.89	-149.75±2.79	92.74±0.03
	303	0.678(9)				
	308	0.876(5)				
	313	1.987(6)				
		6				
	V					

20a	298	0.481(7)	52.58±.0.66	50.01±0.65	-140.14±2.11	92.53±0.01
	303	0.754(1)				
	308	0.957(4)				
	313	2.427(1)				
20b	298	0.714(0)	43.38±0.15	40.86±0.15	-166.45±2.42	91.80±0.01
	303	0.924(7)				
	308	1.261(3)			6	
	313	3.729(2)				
A CERTINA						

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Fig.1. The crystal structure of $[Ag(Haai-C_{22}H_{45})_2]ClO_4$ (20a)



Fig. 2. The packing view of the molecules shows interdigitation of the long alkyl chains of adjacent molecules



Fig. 3. Spectral changes of $[Ag(Haai-C_{22}H_{45})_2]ClO_4$ (20a) in acetonitrile upon repeated irradiation at 368 nm after 5 min intervals at 25 °C. Inset figure shows the spectra of the *cis* (Z) and *trans* (E) isomers of the complex.

X



Fig. 4. The Eyring plot of the rate constants of the Z-to-E (*cis*-to–*trans*) thermal isomerisation of $[Ag(Haai-C_{22}H_{45})_2]ClO_4$ (**20a**) at different temperatures

R



Fig. 5. Plot of n of (Haai- C_nH_{2n+1}) *vs.* activation energy (E_a) for the thermal isomerisation of [Ag(Haai- C_nH_{2n+1})₂]ClO₄



Fig. 6. DFT generated structures of the E- and Z-isomers of $[Ag(Haai-C_{22}H_{45})_2]^+$, showing a better stability of the E-isomer by 125.51 Kcal



Fig. 7. HOMO-LUMO energy gap comparison between the E- and Z-isomers of [Ag(Haai-C₂₂H₄₅)₂]ClO₄



Fig. 8. Texture of $[Ag(Haai-C_{18}H_{37})_2]ClO_4$ (18a) under crossed polarizers, heating (b) and cooling (d) phase, magnification 100X.



Fig. 9. DSC of $[Ag(Haai-C_{18}H_{37})_2]ClO_4$ (18a) at the rate of 2° C min⁻¹

GRAPHICAL ABSTRACT

Synthesis, Structure, Photochromism and Mesogenic properties and

DFT computations of Silver(I) Complexes of Long Chain Alkyl Group

Containing 1-Alkyl-2-(arylazo)imidazoles

Abhijit Nandi, Chandana Sen, Debasish Mallick, Randhir Sinha, Tapan Kumar Mondal, Chittaranjan Sinha^{*}

 $[Ag(Raai-C_nH_{2n+1})_2]ClO_4 (Raai-C_nH_{2n+1} = 1-alkyl-$ 2-(arylazo)imidazole, R = H, Me and n = 4-22) have been characterized. The X-ray structure of $[Ag(Haai-C_{22}H_{45})_2]ClO_4$ confirms the structure. UV light irradiation (365-370 nm) of a solution of the complexes shows E-to-Z isomerisation of the coordinated ligand. The reverse transformation, Zto-E, is a thermal process (298-313 K). The rates and the quantum yields $(\phi_{E\to Z})$ of E-to-Z isomerisation of the free ligands are higher than those of the complexes. The activation energy is much lower and ΔS^* is highly negative in the complexes. $[Ag(Haai-C_{18}H_{37})_2]ClO_4$ shows the Cr $(46.7 \ ^{\circ}C)$ - SmC $(106.4m \ ^{\circ}C)$ - I phase sequence on heating and I (106.4 °C) - SmA (46.4 °C) - Cr on cooling. The SmC phase appears as a typical fan-shaped texture.



PICTORIAL ABSTRACT

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Synthesis, Structure, Photochromism and Mesogenic property and DFT computation of Silver(I) Complexes of long chain alkyl group containing 1-alkyl-2-(arylazo)imidazoles

Avijit Nandi, Chandana Sen, Suman Roy, Debasish Mallick, Randhir Sinha, Tapan Kumar Mondal and Chittaranjan Sinha^{*}



Raai- C_nH_{2n+1} (1 -10) [Ag(Raai- C_nH_{2n+1})₂]⁺ (11-20)

 $R = H (a), Me (b); C_nH_{2n+1} \text{ for } n = 4 (1), 6 (2), 8 (3), 10 (4), 12 (5), 14 (6), 16 (7), 18 (8), 20 (9), 22 (10); [Ag(Haai-C_4H_9)_2]ClO_4 (11a), [Ag(Meaai-C_4H_9)_2]ClO_4 (11b), [Ag(Haai-C_6H_{13})_2]ClO_4 (12a), [Ag(Meaai-C_6H_{13})_2]ClO_4 (12b) , [Ag(Haai-C_8H_{16})_2]ClO_4 (13a), [Ag(Meaai-C_8H_{16})_2]ClO_4 (13b), [Ag(Haai-C_{10}H_{21})_2]ClO_4 (14a), [Ag(Meaai-C_{12}H_{25})_2]ClO_4 (15a), [Ag(Meaai-C_{12}H_{25})_2]ClO_4 (15b),$

 $[Ag(Haai-C_{14}H_{29})_2]ClO_4$ (16a), $[Ag(Meaai-C_{14}H_{29})_2]ClO_4$ (16b), $[Ag(Haai-C_{16}H_{33})_2]$ ClO_4 (17a), $[Ag(Meaai-C_{16}H_{33})_2]ClO_4$ (17b), $[Ag(Haai-C_{18}H_{37})_2]ClO_4$ (18a), $[Ag(Meaai-C_{16}H_{37})_2]ClO_4$ (18a), $[Ag(Meaai-C_{16}H_{37$ $C_{18}H_{37}_{2}$ ClO₄ (18b), [Ag(Haai-C₂₀H₄₁)₂]ClO₄ (19a), [Ag(Meaai-C₂₀H₄₁)₂]ClO₄ (19b), $[Ag(Haai-C_{22}H_{45})_2]ClO_4$ (**20a**), $[Ag(Meaai-C_{22}H_{45})_2]ClO_4$ (**20b**)

Scheme 1. Raai- C_nH_{2n+1} (1 -10) and [Ag(Raai- $C_nH_{2n+1})_2$]ClO₄ (11 - 20)