



J. Indian Chem. Soc.,
Vol. 96, August 2019, pp. 1037-1048

Synthesis, characterisation, photochromic study of cadmium(II) halide complexes of 1-alkyl-2-methyl-4-(*p*-nitro-phenylazo)imidazole and DFT computation

Debashis Mallick^{a*}, Chandana Sen^b, Mrinal Kanti Paira^c, Basudeb Dutta^d, Suman Kundu^e and Chittaranjan Sinha^f

^aDepartment of Chemistry, Mrinalini Datta Mahavidyapith, Kolkata-700 051, India

E-mail: dmchemmdm51@gmail.com

^bDepartment of Chemistry, Sripat Singh Collge, Murshidabad-742 123, West Bengal, India

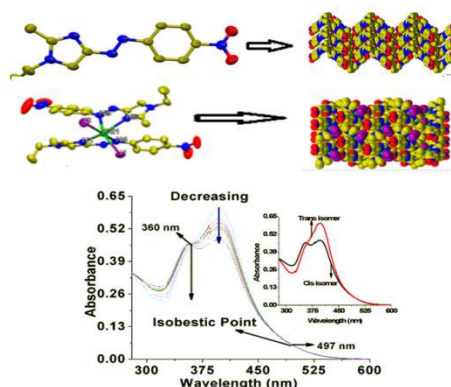
^cDepartment of Chemistry, Raja N. L. Khan College, Gope Palace, Paschim Medinipur-721 102, West Bengal, India

^dDepartment of Chemistry, Aliah University, New Town, Kolkata 700 156, India

^eDepartment of Chemistry, Ramakrishna Mission Residential College, Kolkata-700 103, India

^fDepartment of Chemistry, Jadavpur University, Kolkata-700 032, India

Manuscript received online 16 June 2019, revised and accepted 10 July 2019



1-Alkyl-2-methyl-4-(*p*-nitro-phenylazo)imidazole complexes of Cd(II), Cd[{*p*-NO₂-aai(Me)R}₂]₂X₂ (**2-4**) [{*p*-NO₂-aai(Me)R = 1-alkyl-2-methyl-4-(*para*-nitro-phenylazo)imidazole}, {R = -CH₃ (**1a**), -C₂H₅ (**1b**)} (X = Cl, Br, I)] have been synthesized and characterized by spectral (UV-Vis, IR, ¹H NMR) data and have been confirmed by single crystal X-ray diffraction study in the case *p*-NO₂-aai(2-Me)1-C₂H₅ (**1b**) and Cd[{*p*-NO₂-aai(2-Me)1-C₂H₅]₂I₂] (**4b**). Both ligands and complexes undergo *E*(*trans*)-to-*Z*(*cis*) isomerization when irradiated with UV light. The reverse *Z*(*cis*)-to-*E*(*trans*) isomerization can be driven thermally in the dark. The rates and quantum yields (φ_{E→Z}) of *E*-to-*Z* isomerisation are higher for free ligand, **1**, than their complexes, **2-4**. The activation energies (*E*_a) and activation entropies (Δ*S*) of the *Z*-to-*E* isomerization are calculated by controlled temperature experiment (298–313 K). Effect of halides on the rate and quantum yields of photochromism is established and has been supported by DFT computation of optimized structures. Slow rate of photoisomerisation of coordinated ligands compare to the free ligands may be due to increased mass and rotor volume of the complexes. The rate of isomerization follows the sequence Cd[{*p*-NO₂-aai(2-Me)1-C₂H₅]₂Cl₂] < Cd[{*p*-NO₂-aai(2-Me)1-C₂H₅]₂Br₂] < Cd[{*p*-NO₂-aai(2-Me)1-C₂H₅]₂I₂].

Keywords: Cd(II) complexes, ligand, X-ray structures, photoisomerisation, DFT computation.