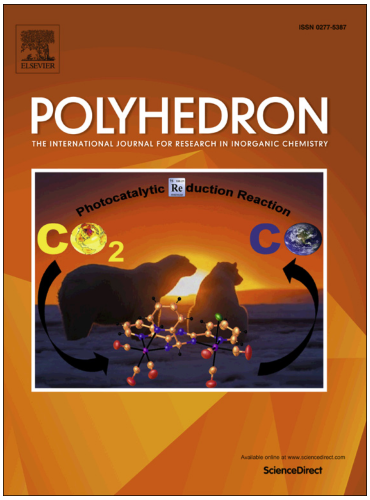

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Exploration of photocatalytic activity of an end-on azide bridged one-dimensional cadmium(II) Schiff base complex for the degradation of organic dye in visible light

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Abstract: A one-dimensional polynuclear end-on azide bridged octahedral cadmium(II) Schiff base complex, $[\{CdL(\mu\text{-}1,1\text{-}N_3)\}_2Cd(\mu\text{-}1,1\text{-}N_3)_2\cdot 1.76CH_3OH]_n$ {HL = 2-(3-(dimethylamino)propyliminomethyl)-6-ethoxyphenol} has been synthesized and characterized by X-ray crystallography. The complex crystallizes in monoclinic space group *C*2/*c* with cell dimensions, a = 21.4706(8) Å, b = 9.9542(4) Å, c = 19.3257(7) Å, β = 103.7819(11)°. Extended supra-molecular assemblies were generated through weak non-covalent interactions. The energetic features of these interactions have also been studied by means of DFT calculations.

The complex exhibits good photoluminescence in DMSO medium. The application of the complex as a photocatalyst for the decomposition of organic dye in visible light has been explored.

Keywords: Cadmium(II); Schiff base; End-on Azide; Crystal structure; Photocatalyst; DFT study.

1. Introduction

Cadmium was thought to be a toxic element for long. It is a very challenging task till date to develop appropriate chelating ligands for the treatment of cadmium intoxication [1,2]. However, following the discovery of cadmium(II) containing enzyme, carbonic anhydrase [3,4], this group 12 metal is currently not considered as biologically untouchable. On the other hand, as a result of the d^{10} configuration of cadmium(II) with no CFSE in any geometry, cadmium(II) complexes may adopt varieties of structures thereby attracting the attention of the 'crystal engineers' [5,6]. They are also known to have interesting photochemical and photophysical properties with potential applications as light-emitting diodes, luminescent probes and photovoltaic devices [7-10]. Supramolecular systems based on cadmium(II) complexes have also received much attention because of their potential use in material science [11-13]. A new emerging application of cadmium(II) complexes as photocatalytic for the degradation of organic dyes in UV light was established in recent years [14,15]. The environmental contamination caused by several organic dyes, e.g. methylene blue (MB) [which is widely used in the textile, printing and paper industries], has caused serious pollution with increasing industrialization and population and the synthesis and characterization of new photocatalysts is a hot research topic for their applications in the purification of water and air by thoroughly decomposing those organic compounds [16-18]. It is to be noted here that there is no report of the application of cadmium(II) Schiff base complexes in photocatalysis using visible light.

In the present work, a tetradentate N_2O_2 donor salicylaldimine Schiff base has been used to prepare an end-on azide bridged polynuclear cadmium(II) complex. The X-ray crysytal structure determination confirms that the complex contains a trinuclear building block with $\{Cd(\mu\text{-}1,1\text{-}N_3)\}_2Cd$ core. The complex has been shown to have good photocatalytic activity to decompose methylene blue in visible light. Herein, we would like to report the synthesis characterization, self assembly and photocatalytic activity of a polynuclear end-on azide bridged cadmium(II) complex with a salicylaldimine Schiff base.

2. Experimental

2.1. Preparations

Methylene Blue was purchased from Loba chemie and used without further purification. All other starting materials and solvents were commercially available, reagent grade, and used as purchased from Sigma-Aldrich without further purification.

2.1.1. Synthesis of $[\{CdL(\mu\text{-}1,1\text{-}N_3)\}_2Cd(\mu\text{-}1,1\text{-}N_3)_2\cdot 1.76CH_3OH]_n$

A methanol solution of 3-ethoxysalicylaldehyde (1 mmol, 0.166 g) and N,N-dimethyl-1,3-diaminopropane (1 mmol, 0.125 ml) was refluxed for 1 h to prepare a tetradentate N_2O_2 donor Schiff base, 2-(3-(dimethylamino)propyliminomethyl)-6-ethoxyphenol (HL). A methanol solution of cadmium(II) acetate dihydrate (1 mmol, 0.266 g) was added drop wise to the methanol solution of Schiff base followed by addition of aqueous methanol solution of sodium azide (1 mmol, 0.065 g) with constant stirring. The stirring was continued for additional 30 min.

Block shaped yellow coloured crystals, suitable for X-ray diffraction, were obtained after few days on slow evaporation of the solution in open atmosphere.

Yield: 0.76 g (72%). Anal. Calc. for $C_{29.76}H_{49.04}Cd_3N_{16}O_{5.76}$, (FW 1060.26): C, 33.71; H, 4.76; N, 21.13; Found: C, 33.65; H, 4.71; N, 21.19 %. IR (KBr, cm^{-1}): 1636 ($\upsilon_{C=N}$), 2072, 2038 (υ_{N3}), 3518-3374 (υ_{OH}), 2993-2842 (υ_{CH}). UV-Vis, λ_{max} (nm), [ε_{max} (L mol^{-1} cm^{-1})] (DMSO), 266 (2.1×10^4), 332 (5.8×10^3), 421 (1.1×10^3).

2.2. Physical measurements

Elemental analysis (carbon, hydrogen and nitrogen) was performed on a Perkin-Elmer 240C elemental analyzer. Infrared spectrum in KBr (4000-400 cm^{-1}) was recorded using a PerkinElmer Spectrum Two FTIR spectrophotometer. Electronic spectrum in DMSO (800-200 nm) was recorded on a PerkinElmer Lambda 35 UV-Vis spectrophotometer. Fluorescence spectrum in DMSO was obtained on a Hitachi F-7000 Fluorescence spectrophotometer at room temperature. Lifetime measurement was recorded using Hamamatsu MCP photomultiplier (R3809) and was analyzed by using IBHDAS6 software.

2.3. X-ray crystallography

Single crystal of complex having suitable dimension, was used for data collection using a Bruker SMART APEX II diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 100 K. The molecular structure was solved by direct method and refined by full-matrix least squares on F^2 using SHELXL-2014/7 [19]. X-ray intensity data were measured. The frames were integrated with the Bruker SAINT Software package using a wide-frame algorithm. Non hydrogen atoms were refined anisotropically. Hydrogen atoms attached to oxygen were located by difference Fourier maps and were kept at fixed positions. Others hydrogen atoms were placed in their geometrically idealised positions and constrained to ride on their parent atoms. Numerical and/or multi-scan absorption corrections were applied to the data using the program SADABS [20]. The crystallographic and refinement data of complex are summarized in Table 1.

2.4. Photocatalytic Measurement

A photocatalytic experiment in aqueous solution was carried out in a typical process [14]. A 36 W Hg vapour lamp was used as the visible light source, and the catalytic degradation was carried out with 100 mL of Methylene Blue solution (10 mg L^{-1}) with the complex using as catalyst. The mixture was stirred for 10 min in a dark environment to get a balance between adsorption and desorption. Then, the solution was stirred constantly. A 4 mL sample was taken from the reaction system in an interval of 10 min and the supernatant liquid obtained by centrifugation was used for collecting the UV-Visible spectrum. The characteristic peak for methylene blue at $\lambda = 607$ nm was employed to monitor the photocatalytic degradation.

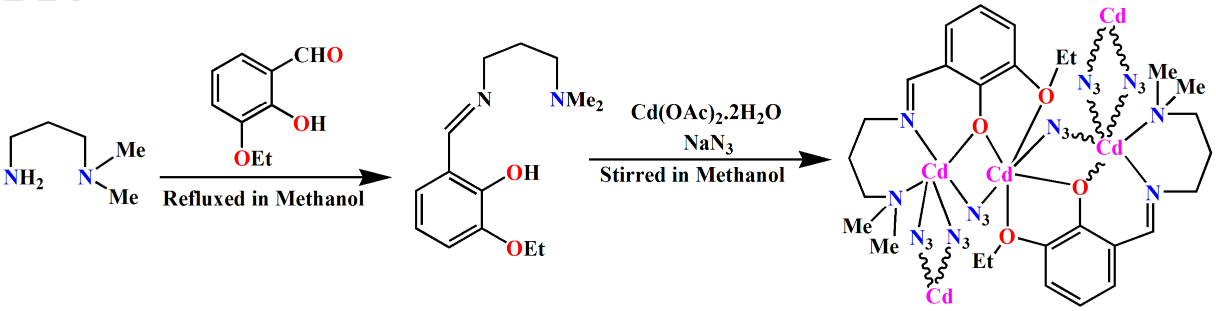
2.5. Theoretical methods

The calculations of non-covalent interactions were carried out using the TURBOMOLE version 7.0 [21], using the BP86-D3/def2-TZVP level of theory. To evaluate the interactions in the solid state, we have used the crystallographic coordinates. This procedure and level of theory have been successfully used to evaluate similar interactions [22-25]. Interaction energies were computed by calculating the difference between the energies of isolated monomers and their assembly. The interaction energies were corrected for the Basis Set Superposition Error (BSSE) using the counterpoise method [26]. The NCI plot is a visualization index based on the electron density and its derivatives, and enables identification and visualization of non-covalent interactions efficiently. The isosurfaces correspond to both favorable and unfavorable interactions, as differentiated by the sign of the second density Hessian eigen value and defined by the isosurface colour. NCI analysis allows an assessment of host-guest complementarities and the extent to which weak interactions stabilize a complex. The information provided by NCI plots is essentially qualitative, i.e. which molecular regions interact. The color scheme is a red-yellow-green-blue scale with red for ρ^{+}_{cut} (repulsive) and blue for ρ^{-}_{cut} (attractive). Yellow and green surfaces correspond to weak repulsive and weak attractive interactions, respectively [27].

3. Results and discussions

3.1. Synthesis

Schiff base ligand HL was prepared by the condensation of N,N-dimethyl-1,3-diaminopropane with 3-ethoxysalicylaldehyde following the literature method [28,29]. The ligand was not isolated and the methanol solution of ligand was used directly for preparation of the complex. The methanol solution of HL was reacted with methanol solution of cadmium(II) acetate dihydrate followed by the addition of sodium azide under stirring condition to produce the complex. The tetradentate Schiff base, HL, occupies four sites of the octahedral cadmium(II). Exploiting bridging capacity phenoxo oxygen atoms and azides, a one-dimensional coordination polymer, $[\{CdL(\mu\text{-}1,1\text{-}N_3)\}_2Cd(\mu\text{-}1,1\text{-}N_3)_2\cdot 1.76CH_3OH]_n$ is formed. Synthesis of the complex is shown in scheme 1.



Scheme **1:** Preparation of complex.

3.2. Description of structure

3.2.1. [{CdL(μ-1,1-N$_3$)}$_2$Cd(μ-1,1-N$_3$)$_2$·1.76CH$_3$OH]$_n$

It crystallizes in the monoclinic space group *C2/c*. The asymmetric unit of complex consists of a dinuclear cadmium(II) moiety { Cd(1) and Cd(2)} with a deprotonated tetradentate Schiff base (L)$^-$ along with two end-on bridged azides. A lattice solvent molecule (MeOH) is also present in the asymmetric unit near the origin of the unit cell and has been refined with occupancy 1.76. It assumes chain structure having trinuclear cadmium(II) moieties as the building blocks, in which the cadmium(II) centres {Cd(1)^a, Cd(2) and Cd(1)} possess distorted octahedral geometries. The perspective view of the trinuclear moiety is shown in Figure 1. The Cd(2) is coordinated by two phenoxo oxygen atoms, O(5) and O(5)^a, two ethoxy oxygen atoms, O(6) and O(6)^a, from two different tetradentate deprotonated Schiff bases and two end-on bridged azide nitrogen atoms, N(1Z) and N(1Z)^a {Symmetry transformation ^{a} = 1-x,y,1/2-z}. The environment around Cd(1)^a centre is very similar to that of the Cd(1) centre. Cd(1)^a is coordinated by two nitrogen atoms, N(1)^a and N(5)^a, and an oxygen atom, O(5)^a, of a tetradentate deprotonated Schiff base and two end-on bridging azide nitrogen atoms, N(4Z)^a and N(1Z)^a. On the other hand, Cd(1) is coordinated by two nitrogen atoms, N(1) and N(5), and an oxygen atom, O(5), of a second molecule of tetradentate deprotonated Schiff base and two end-on bridged azide nitrogen atoms, N(4Z) and N(1Z). Symmetry related nitrogen atoms, N(4Z)^b and N(4Z)^c, from two different end-on bridged azides, coordinate Cd(1)^a and Cd(1), respectively to grow the polymer (Figure 2). {Symmetry transformations ^{b} = x,1-y,-1/2+z; ^{c} = 1-x,1-y,1-z}. Selected bond lengths and angles are gathered in Tables 2 and 3, respectively.

The angle between $Cd(1)^aO(5)^aN(1Z)^aCd(2)$ and Cd(2)O(5)Cd(1)N(1Z) rhombohedral plane is 74.44°. The $N(1)^a$-$Cd(1)^a$-$N(5)^a$ and N(1)-Cd(1)-N(5) angles are 81.45(5)° and are typical of a six membered chelate ring [30,31]. The Cd-N_{imine} distance {2.301(1) Å} is shorter than the Cd-N_{amine} {2.384(1) Å} distances, as were also observed in similar systems [30-33]. The distance between $Cd(1)^a\cdots Cd(2)$, $Cd(2)^a\cdots Cd(1)$ and $Cd(1)^a\cdots Cd(1)$ are 3.6499(4), 3.6499(4) and 6.6944(6) Å, respectively. The bridging azides are quasi-linear; the N-N-N angles are 179.0(2)º and 179.5(2)º, as were also observed in similar systems [32,33].

3.3. IR, electronic and fluorescence spectra

In IR spectrum of the complex, strong band corresponding to the azomethine (C=N) stretching vibration appears at 1636 cm^{-1}. The presence of bridging azides is indicated by the sharp bifurcated bands within 2072-2038 cm^{-1} range [34]. Bands in the range of 2993-2842 cm^{-1} are assigned due to alkyl C-H bond stretching vibrations are customarily noticed In IR spectrum of the complex [32,33]. Broad bands in the range of 3518-3374 cm^{-1} may be assigned as O-H stretching vibrations [35,36].

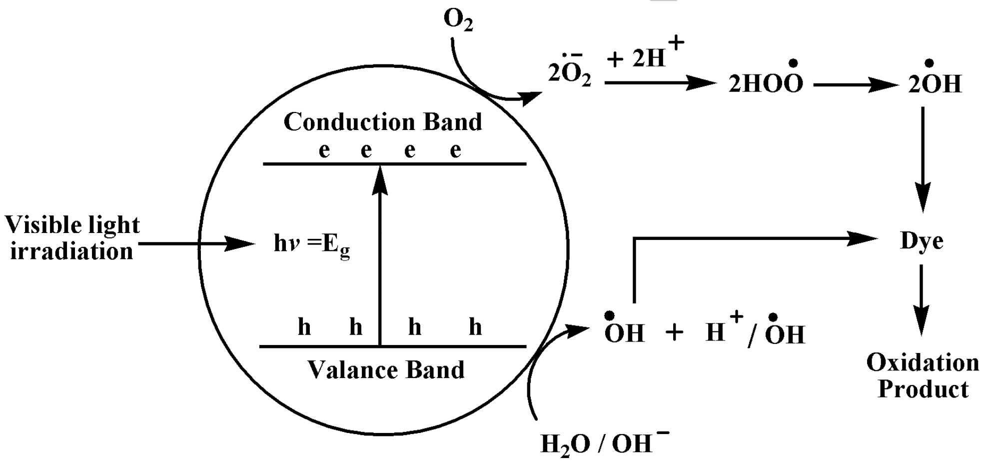
Electronic spectrum of complex exhibits three bands of which high energy bands around 266 and 332 nm may be attributed to π-π* and n-π* transitions and last band at 421 nm assigned as ligand to metal charge transfer transition (LMCT) [37,38]. The complex exhibits luminescence in DMSO medium at 332 nm on exciting at 394 nm, which may be assigned to the intra-ligand (π-π*) fluorescence [39]. The average lifetime of the excited state is 9.72 ns (Table 4) and decay profile is shown in Figure 3. Relative fluorescence quantum yield for the complex was measured following the literature method [35,40] and the value is found to be 0.1461.

3.4. Photocatalytic activity

The distinct performance on the photocatalytic degradation of an organic dye, methylene blue, was discovered in the complex in an aqueous solution under visible light irradiation. As shown in Figure 4, the residual concentration of the dye in an aqueous solution gradually decreased as a function of the increasing reaction time, indicating that the complex can degrade the organic dye. With increase in complex concentration, the rate of degradation was also increased (Figure 4).

The complex is highly efficient for the degradation of MB and the ratio of the degradation reaches about 68% using only 1 mg of the complex (Figure 4, curve **III**). Use of 3 and 4.8 mg of the complex, the ratio of the degradation reaches about 82 and 86 %, respectively (Figure 4, curves **IV**,**V**). The ratio of the degradation reaches about 99 % using 7 mg of the complex (Figure 4, curve **VI**). To prove the high photocatalytic efficiency of the complex to MB, comparative experiments without catalyst under visible light irradiation were performed, which showed only very little decomposition. We had also studied the photocatalytic activity of cadmium(II) acetate hexahydrate to MB under similar conditions (Figure 4, curve **II**), which showed that the rate of degradation was still very slow (only 16 % using 4 mg of bare cadmium(II). Again, as shown in Figure 5, it is shown that the intensity of the characteristic absorption peak of MB decreased with the increase of irradiation time in the degradation process. The reaction depends on 1st Order Kinetics and the details data on average rate constants for this degradation are given in Table 5. A probable mechanistic pathway for the photocatalytic degradation of organic dye is shown in Scheme 2. At first, electrons (e^-) of the complex were excited from the valence band (VB) to the conduction band (CB) which leads to equal amounts of positives vacancies (holes, h) left in VB. In the next step, oxygen (O_2) or hydroxyl (OH^-)

adsorbed on the surfaces of complex could interact with the electrons (e^{-}) on the CB or the hole (h) on the VB, respectively, which would probably lead to the formation of the hydroxyl radicals ($\dot{O}H$). Later on, the $\dot{O}H$ radicals could effectively degrade the methylene blue (MB) to carry out the process. Similar mechanism has also been proposed by other groups [15]. The stability of the complex as catalyst has been investigated by recording the IR spectrum of the complex after photocatalytic reaction. The IR spectrum of the complex at the end of photocatalytic degradation of MB is more or less identical with that of the original one (Figure 6), demonstrating the stability of the complex after the photocatalytic process.



Scheme 2: Probable mechanistic pathway for the degradation of organic dye (MB).

3.5. DFT study on supramolecular interactions

The polymeric chain formed by the complex in the solid state is also common in many cadmium(II) complexes. These polymeric chains can be viewed as trinuclear $[Cd_3L_2(N_3)_2]^{2+}$ discrete units connected by azide bridges. In Figure 7, a fragment of the crystal structure is showed where it is highlighted how these polymeric one-dimensional chains interact to each other forming two-dimensional layers. Remarkably, the aromatic hydrogen atoms of ligands (highlighted in Figure 7) are interacted by means of weak hydrophobic interactions with the aliphatic groups of ligands belonging to the neighbour one-dimensional chain. Moreover, the presence of MeOH molecules from the solvent is also important for connecting these polymeric one-dimensional chains which also help to estabilise hydrogen bonding interactions, as further described below. The purpose of this theoretical study is to emphasize the contribution of weak long range interactions in the formation of the two-dimensional layer represented in Figure 7.

A discrete dimer has been taken from the X-ray structure where the infinite chains have been reduced to the trinuclear $[Cd_3L_2(N_3)_2]^{2+}$ repeating unit and have been computed by means of DFT calculations (BP86-D3/def2-TZVP) (see Figure 8). Moreover, two azide ligands belonging to the double azide bridge have been included to compensate the positive charge. The octahedral coordination environment of the cadmium atom has been completed by neutral HCN ligand (see small arrows in Figure 8b). The interaction energy of this dimer (ΔE_1 = -10.0 kcal/mol) is considerably large taking into consideration that only weak C-H···H-C and other long range van der Waals (vdW) interactions are present. In order to evaluate the role of the MeOH molecules connecting the one-dimensional chains, The interaction energy of this dimer has also been computed with two methanol molecules. Each MeOH molecule has established two hydrogen bonding interactions (see red dashed lines in Figure 8c), one as donor (with the azide ligand) and other as acceptor (with an aromatic C-H). The binding energy that results from the interaction of this dimer with two solvent molecules is ΔE_2 = -21.8 kcal/mol that corresponds to the contribution of the four hydrogen bonds. As expected, the role of the MeOH is crucial connecting the one-dimensional chains; however the long range interactions (ΔE_1) are not negligible and they are also important to explain the final solid state architecture of the polymer.

In order to characterize the weak van der Waals interactions shown in Figure 8b, the non-covalent interaction (NCI) plot of this model dimer has been computed also. The NCI plot is a visualization index that enables identification and visualization of non-covalent interactions efficiently. The representation of the NCI plot computed for the dimer of the complex is shown in Figure 9. An extended region can be observed between the aromatic and aliphatic C-H bonds. The presence of this extended region explains the large interaction energy, since it includes the contribution of many weak long range C-H···H-C contacts.

4. Summary

In conclusion, we have synthesized a polynuclear end-on azide bridged octahedral cadmium(II) Schiff base complex and characterized by elemental, spectral and single crystal X-ray diffraction analysis. The complex exhibits extremely highly efficient photocatalytic decomposition of methylene blue in visible light. This is the first example of any ray characterized cadmium(II) Schiff base complex with photocatalytic application. These results provide an opening into a promising new field of the highly efficient photocatalytic degradation of organic pollutant. We are now working hard to get better yield of the reaction and to synthesize other photocatalytic cadmium(II) complexes.

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Appendix A. Supplementary data

Crystallographic data for the analysis have been deposited with the Cambridge Crystallographic data Centre, CCDC No 1478964. The data can be obtained free of charge from CCDC via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] O. Andersen, Chem. Rev. 99 (1999) 2683-2710.

[2] J. Schubert, S. K. Derr, Nature 275 (1978) 311-313.

[3] T. W. Lane, F. M. M. Morel, Proc. Natl. Acad. Sci. U. S. A. 97 (2000) 4627-4631

[4] Y. Xu, L. Feng, P. D. Jeffrey, Y. Shi, M. M. Morel, Nature 452 (2008) 56-62.

[5] Z. Su, K. Cai, J. Fan, S. -S. Chen, M.-S. Chen, W. -Y. Sun, CrystEngComm 12 (2010) 100-108.

[6] J. -C. Dai, X. -T. Wu, Z. -Y. Fu, C. -P. Cui, S. -M. Hu, W. -X. Du, L. -M. Wu, H. -H. Zhang, R. -Q. Sun, Inorg. Chem. 41 (2002) 1391-1396.

[7] R. Kumar, P. Bhargava, R. Srivastava, Adv. Sci. Lett. 20 (2014) 1001-1004.

[8] G. -Y. Wang, C. Song, D. -M. Kong, W.-J. Ruan, Z. Chang, Y. Li, J. Mater. Chem. A 2 (2014) 2213-2220.

[9] Y. Wu, Y. Lin, F. Wei, M. Hu, L. Liu, P. Zhou, Q. Hu, J. Nanosci. Nanotechnol. 14 (2014) 3976-3982.

[10] P. K. Santra, P. V. Kamat, J. Am. Chem. Soc. 135 (2013) 877-885.

[11] D. Singh, C. M. Nagaraja, Cryst. Growth Des. 15 (2015) 3356-3365

[12] O. R. Evans, W. Lin, Acc. Chem. Res. 35 (2002) 511-522

[13] J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, Chem. Soc. Rev. 38 (2009) 1450-1459.

[14] W. Meng, Z. Xu, J. Ding, D. Wu, X. Han, H. Hou, Y. Fan, Cryst. Growth Des. 14 (2014) 730-738.

[15] L. Liu, J. Ding, C. Huang, M. Li, H. Hou, Y. Fan, Cryst. Growth Des.14 (2014) 3035-3043.

[16] T. Wen, D. -X. Zhang, J. Zhang, Inorg. Chem. 52 (2013) 12-14.

[17] A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J. -M. Herrmann, Appl. Catal. B-Environ. 31 (2001) 145-157

[18] W. Cui, W. An, L. Liu, J. Hu, Y. Liang, J. Hazard. Mater. 280 (2014) 417-427.

[19] G. M. Sheldrick, ActaCryst.,A64 (2008) 112-122.

[20] G. M. Sheldrick, SADABS: Software for Empirical Absorption Correction, University of Gottingen, Institute fur AnorganischeChemiederUniversitat, Gottingen, Germany, 1999-2003.

[21] R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, Chem. Phys. Lett. 162 (1989) 165-169.

[22] A Bauzá, A Terrón, M Barceló-Oliver, A García-Raso, A. Frontera, Inorg. Chim. Acta. 2015, DOI: 10.1016/j.ica.2015.04.028.

[23] D Sadhukhan, M Maiti, G Pilet, A Bauzá, A Frontera, S. Mitra, Eur. J. Inorg. Chem. 11 (2015) 1958-1972.

[24] M Mirzaei, H Eshtiagh-Hosseini, Z Bolouri, Z Rahmati, A. Esmaeilzadeh, A. Hassanpoor, A. Bauza, P. Ballester, M. Barceló-Oliver, J. T Mague, Behrouz Notash, A. Frontera, Cryst. Growth Des. 15 (2015) 1351-1361.

[25] P. Chakraborty, S. Purkait, S. Mondal, A. Bauzá, A. Frontera, C. Massera, D. Das, CrystEngComm 17 (2015) 4680-4690.

[26] S. F. Boys, F. Bernardi, Mol. Phys. 19 (1970) 553-566.

[27] J. Contreras-García,. E. R. Johnson, S.Keinan, R. Chaudret, J. -P. Piquemal, D. N. Beratan, W. Yang, J. Chem. Theory Comput. 7 (2011) 625-632.

[28] S. Roy, P. K. Bhaumik, K. Harms, S. Chattopadhyay, Polyhedron 75 (2014) 57-63.

[29] S. Bhattacharya, S. Roy, S. Chattopadhyay, J. Coord. Chem. 69 (2016) 915-925.

[30] P. K. Bhaumik, S. Roy, K. Harms, S. Chattopadhyay, Polyhedron 81 (2014) 168-179.

[31] W. -X. Cai, X. -Y. Zheng, H. Sua, Y. -L. Feng, Acta Cryst. E63 (2007) m2828-m2829.

[32] S. Roy, P. K. Bhaumik, S. Chattopadhyay, Inorg. Chim. Acta 427 (2015) 155-161.

[33] S. Roy, K. Harms, S. Chattopadhyay, Polyhedron 91 (2015) 10-17.

[34] J. -Y. Tsao, J. -D.Tsai, C. Yang, Dalton Trans.45 (2016) 3388-3397.

[35] S. Roy, S. Chattopadhyay, Inorg. Chim. Acta, 433 (2015) 72-77.

[36] K. Nakamoto, Infrared and Raman Spectra of Inorganic and CoordinationCompounds, third ed., Wiley-Interscience, New York, 1978.

[37] A. Golcu, M. Tumer, H. Demirelli, R. A. Wheatley, Inorg. Chim. Acta 358 (2005) 1785-1797.

[38] A. Guha, J. Adhikary, T. K. Mondal, D. das, Indian J. Chem. 50A (2011) 1463-1468.

[39] S. Basak, S. Sen, C. Marschner, J. Baumgartner, S. R. Batten, D. R. Turner, S. Mitra, Polyhedron 27 (2008) 1193-1200.

[40] R. A. Velapoldi, K. D. Mielenz; Standard Reference Materials: A Fluorescence Standard Reference Material: Quinine Sulfate Dihydrate, National Bureau of Standards Special Publication 260-64, National Bureau of Standards, Washington, DC (1980).

Table 1: Crystal data and refinement details of complex.

Formula	$C_{29.76}H_{49.04}Cd_3N_{16}O_{5.76}$
Formula Weight	1060.40
Temperature (K)	100
Crystal system	Monoclinic
Space group	*C*2/*c*
a(Å)	21.4706(8)
b(Å)	9.9542(4)
c(Å)	19.3257(7)
β(°)	103.7819(11)
Z	4
d_{calc} (g cm^{-3})	1.756
μ(mm^{-1})	1.637
F(000)	2118.7
Total Reflections	40107
Unique Reflections	4629
Observed data[I >2 σ (I)]	4298
No. of parameters	279
R(int)	0.024
R1, wR2 (all data)	0.0188, 0.0392
R1, wR2 [I > 2 σ (I)]	0.0163, 0.0382

Table 2: Selected bond lengths (Å) of complex**.**

Cd(1)–O(5)	2.3290(11)
Cd(1)–N(1)	2.3845(13)
Cd(1)–N(1Z)	2.3448(14)
Cd(1)–N(4Z)	2.333(2)
Cd(1)–N(5)	2.3015(14)
Cd(1)–N(4Z)[c]	2.318(2)
Cd(2)–O(5)	2.2187(11)
Cd(2)–O(6)	2.3941(11)
Cd(2)–N(1Z)	2.2854(13)
Cd(2)–O(5)[a]	2.2187(11)
Cd(2)–O(6)[a]	2.3941(11)
Cd(2)–N(1Z)[a]	2.2854(13)

Symmetry transformations [a] = 1-x,y,1/2-z; [c] = 1-x,1-y,1-z.

Table 3: Selected bond angles (°) of complex**.**

O(5)–Cd(1)–N(1)	100.13(4)
O(5)–Cd(1)–N(1Z)	72.90(4)
O(5)–Cd(1)–N(4Z)	168.15(6)
O(5)–Cd(1)–N(5)	77.38(4)
O(5)–Cd(1)–N(4Z)[c]	93.55(6)
N(1)–Cd(1)–N(1Z)	92.99(5)
N(1)–Cd(1)–N(4Z)	91.38(6)
N(1)–Cd(1)–N(5)	81.45(5)
N(1)–Cd(1)–N(4Z)[c]	164.97(6)
N(1Z)–Cd(1)–N(4Z)	103.89(7)
N(1Z)–Cd(1)–N(5)	148.29(5)
N(1Z)–Cd(1)–N(4Z)[c]	97.00(7)
N(4Z)–Cd(1)–N(5)	107.42(7)
N(4Z)–Cd(1)–N(4Z)[c]	75.36(7)
N(4Z)[c]–Cd(1)–N(5)	95.61(7)
O(5)–Cd(2)–O(6)	68.79(4)
O(5)–Cd(2)–N(1Z)	76.10(4)
O(5)–Cd(2)–O(5)[a]	178.56(4)
O(5)–Cd(2)–O(6)[a]	112.43(4)
O(5)–Cd(2)–N(1Z)[a]	103.05(4)
O(6)–Cd(2)–N(1Z)	138.47(4)
O(5)[a]–Cd(2)–O(6)	112.43(4)
O(6)–Cd(2)–O(6)[a]	75.77(4)
O(6)–Cd(2)–N(1Z)[a]	98.72(4)
O(5)[a]–Cd(2)–N(1Z)	103.05(4)
O(6)[a]–Cd(2)–N(1Z)	98.72(4)
N(1Z)–Cd(2)–N(1Z)[a]	110.46(5)
O(5)[a]–Cd(2)–O(6)[a]	68.79(4)
O(5)[a]–Cd(2)–N(1Z)[a]	76.10(4)
O(6)[a]–Cd(2)–N(1Z)[a]	138.47(4)

Symmetry transformations [a] = 1-x,y,1/2-z; [c] = 1-x,1-y,1-z.

Table 4: The details data of the photoluminescence and time-resolved photoluminescence decays of the complex.

λ_{ex}(nm)	λ_{em}(nm)	A_1(%)	τ_1(ns)	A_2(%)	τ_2(ns)	τ_{av}(ns)	χ^2
332	394	90.14	10.01	9.86	3.62	9.72	1.0188

Table 5: The details data of the rate constants for the degradation of organic dye.

Amount of complex (mg) taken in 10 mg L^{-1} aqueous solution of MB	Average rate constant
1	3.56×10^{-3}
3	5.07×10^{-3}
5	5.39×10^{-3}
7	4.81×10^{-3}

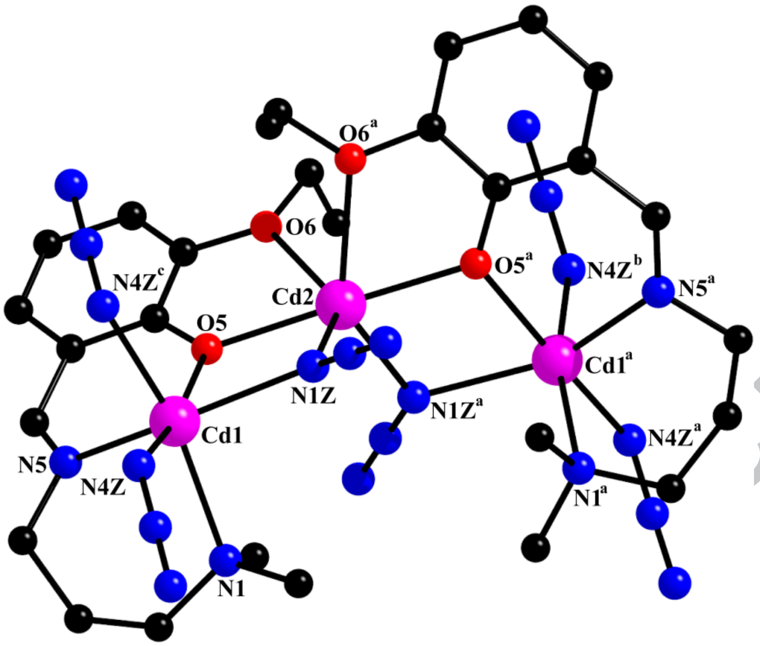


Figure 1: Trinuclear moiety of complex with selective atom-numbering scheme. Non-coordinated methanol molecule and hydrogen atoms are omitted for clarity. Symmetry transformations ^{a} = 1-x,y,1/2-z; ^{b} = x,1-y,-1/2+z; ^{c} = 1-x,1-y,1-z.

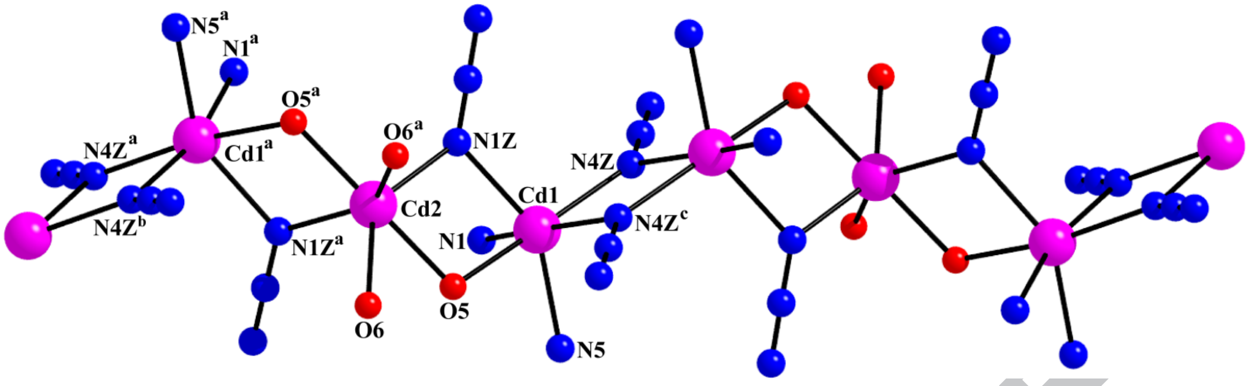


Figure 2: Polymeric chain of the complex with selective atom-numbering scheme showing only the coordinated atoms and bridging azides. Symmetry transformations ^{a} = 1-x,y,1/2-z; ^{b} = x,1-y,-1/2+z; ^{c} = 1-x,1-y,1-z.

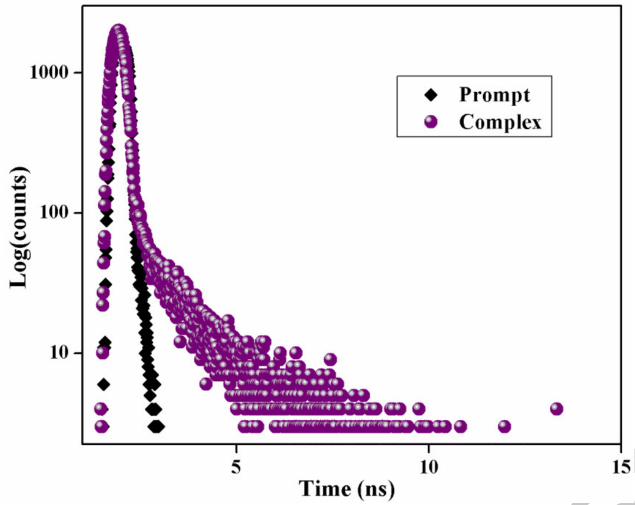


Figure 3: Lifetime decay profile of the complex.

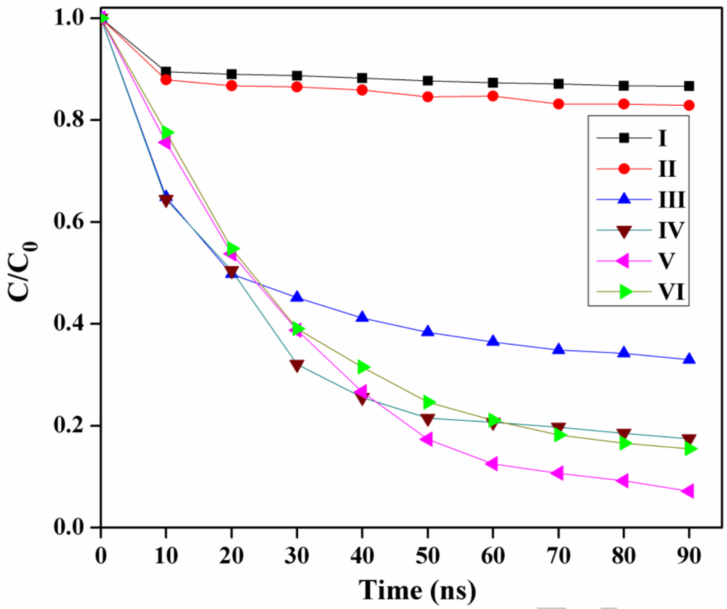


Figure 4: Changes in concentration of MB as a function of reaction time in the presence of different amount of complex (curves **III-VI**), without complex (curve **I**), and with Cadmium-salt (curve **II**), under visible light irradiation.

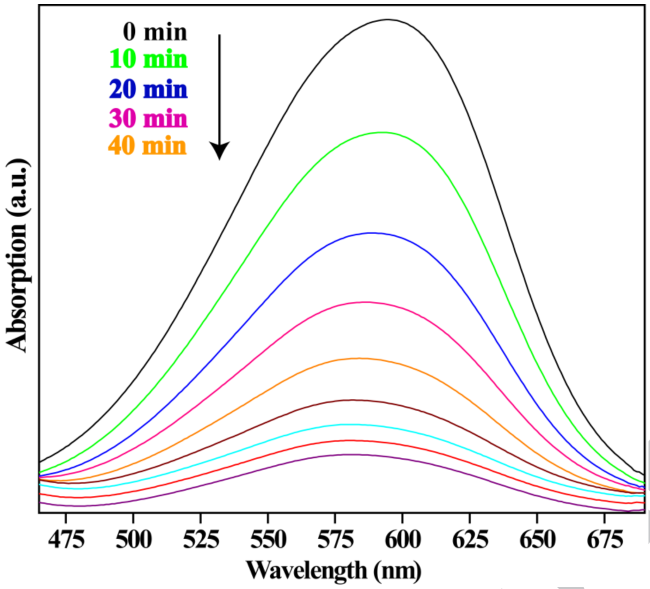


Figure 5: UV-VIS absorption spectra of MB solution with the complex (sample taken = 5 mg), used as a catalyst.

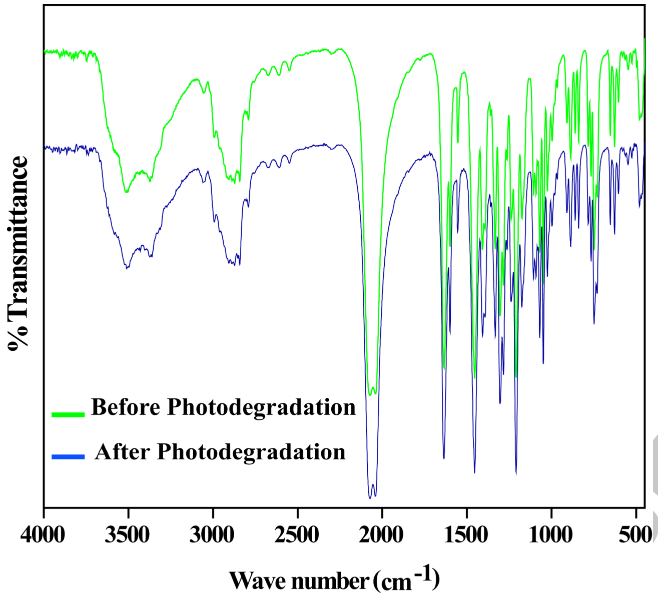


Figure 6: IR spectra of the complex before (green) and after photodegradation (blue) process

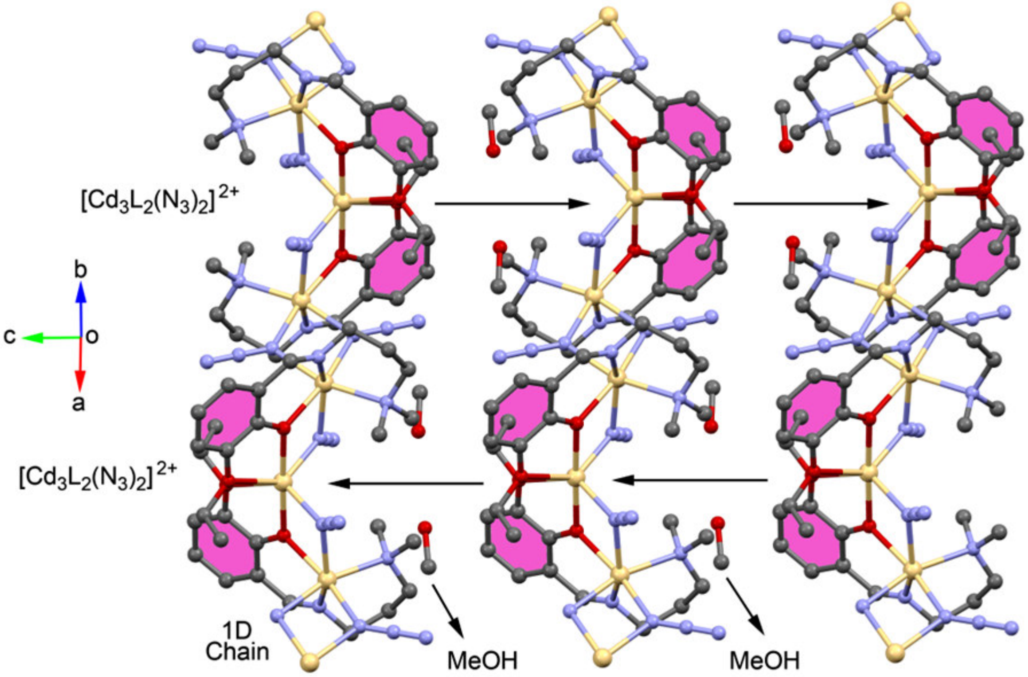


Figure 7: Two-dimensional layers of the complex.

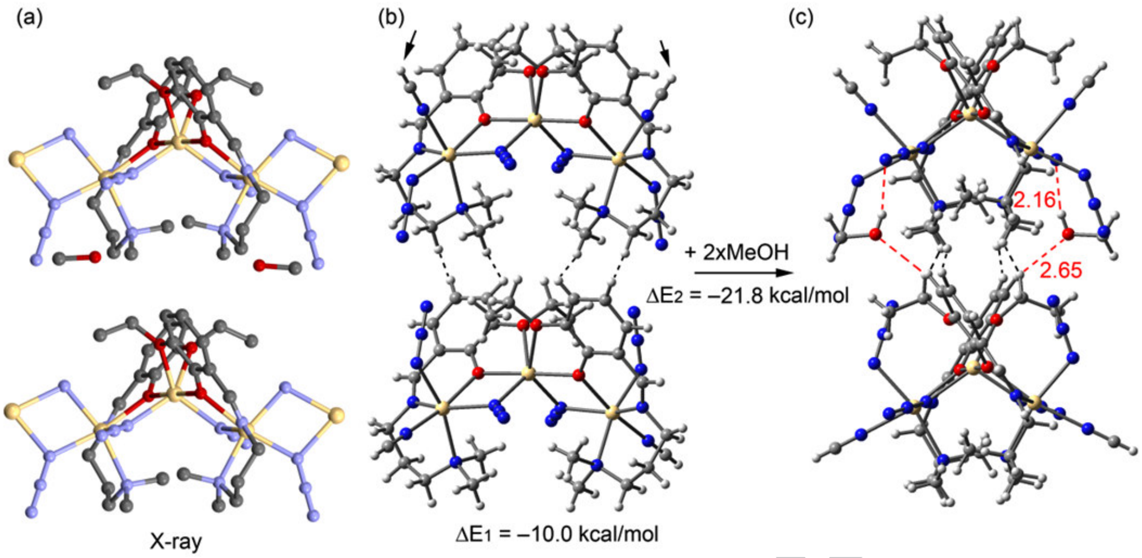


Figure 8: (a) Fragment of the X-ray structure of the complex; (b) Theoretical model of the dimer; (c) Hydrogen bonding interactions of the MeOH with the dimer. Distances in Å.

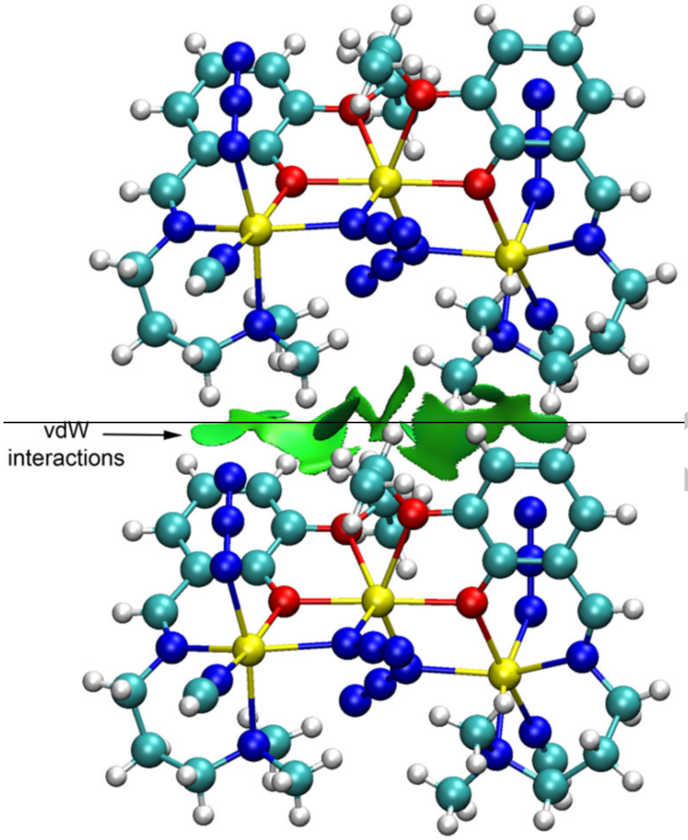
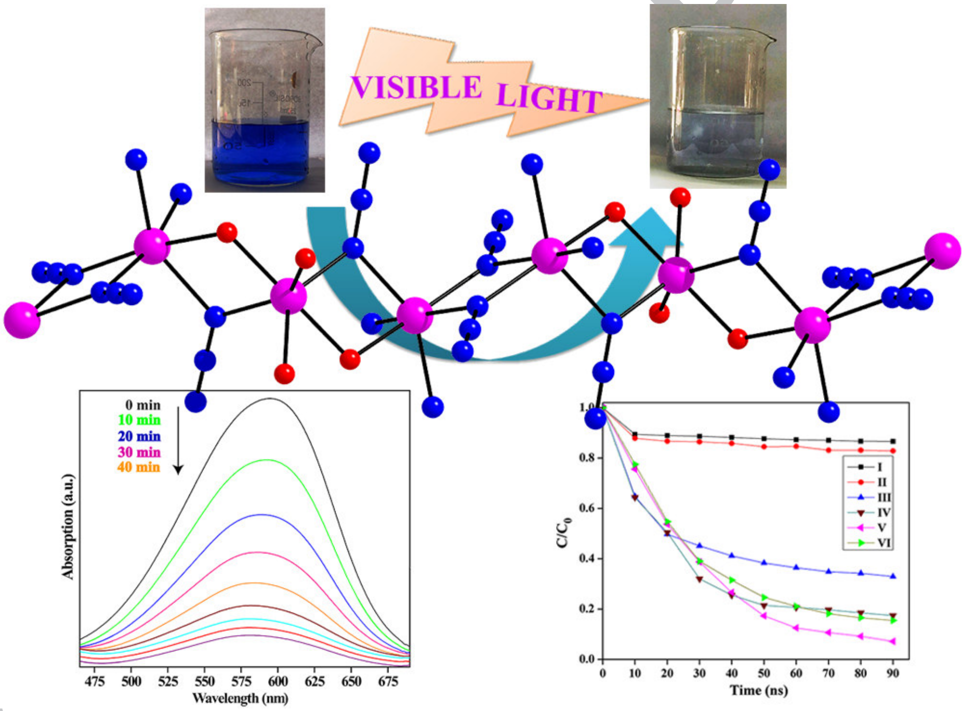


Figure 9: NCI plot of the self-assembled dimer of the complex. NCI plot only shows the intermolecular interactions.

Graphical Abstract (Pictogram)

Exploration of photocatalytic activity of an end-on azide bridged one-dimensional cadmium(II) Schiff base complex for the degradation of organic dye in visible light

Sumit Roy, Klaus Harms, Antonio Bauzá, Antonio Frontera, Shouvik Chattopadhyay



Graphical Abstract (synopsis)

Exploration of photocatalytic activity of an end-on azide bridged one-dimensional cadmium(II) Schiff base complex for the degradation of organic dye in visible light

Sumit Roy, Klaus Harms, Antonio Bauzá, Antonio Frontera, Shouvik Chattopadhyay

One new photo-luminescent polynuclear cadmium(II) complex with salicylaldimine Schiff base ligand and azide as co-ligand has been synthesized and characterized. The structure has been confirmed by single crystal X-ray analysis. Under visible light irradiation, the complex can acts as a highly efficient photocatalyst for the decomposition of organic dye.