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ARTICLE

New Photocatalyst for Allylic aliphatic C-H Bond Activation and degradation of organic pollutants: Schiff's base Ti(IV) complexes

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The Schiff's base metal complexes have been concerned significantly due to their out-of-box applications in the environmental quantum leap by mineralization of the organic pollutants to fewer harmful byproducts and oxygen generation such as photosynthesis process. The Ti⁴⁺ complexes obtained from Schiff base ligands reacted with donor atoms such as S and N under solvothermal conditions. These complexes were characterized using the microanalysis, conductivity studies, and different spectral techniques. From these data reveals that the compound shows distorted octahedral geometry with ligands coordination via azomethine nitrogen and thiol sulfur atoms. Oxidation of allylic methyl group examined the photocatalytic activity of [Ti(L)O] under ambient conditions and oxidative and cyclization under visible light irradiation. Ti(DCMPPT)O complex is very efficient catalyst due to the very short span of time convert aldehydes from allylic compounds. Aldehydes ready to react with 2-aminophenol or 2-aminobenzenethiol to produce (E)-2-styrylbenzo[d]oxazoles and (E)-2-styrylbenzo[d]thiazoles. Due to the suitable of the bandgap energy of nature to the generation of •OH radicals during the catalytic reaction. For this reason, higher oxidation rate. [Ti(DCMPPT)O] as a very efficient photocatalyst for degradation of MB, due large surface area and that supports to lower recombination energy mechanism.

1. Introduction

Metal-organic oxides are very prominent and efficient catalysts for both oxidative coupling and C-H activation of organic compounds in organic synthesis.¹ Schiff's base complexes were used as catalysts for oxidation and whereas very rare for photodegradation of organic pollutants.² Photo-oxidation process of a broad range of organic pollutants over binary and ternary metal oxides has been studied throughout the past two decades.³ Due to highly pollutants are discharged from pharmaceutical or textile industrial effluents spoils the natural ecosystems in the surrounding of industrial areas and causes perturbations in the aquatic life.⁴ Most of these dyes are highly toxic and produce severe environmental pollution by discharging dangerous byproducts into the aqueous phase. Purification of industrial waste water as challenge task for the reusable techniques such as biological procedures, physical, chemical methods, and photocatalytic oxidation.⁵ However, these methods are highly expensive and not sensitive to degrade the toxic substances. Substantial work has been done on the photodegradation of dyes in the presence of metal oxides. However, depends on various factors such as phase purity, surface area, crystallite

size, amount of catalyst, nature of dopants and method of preparation.⁶ Even though, intrinsic semiconductor metal oxides exhibit poor efficiency due to their high bandgap energy, non-homogenous size of particles and high recombination energy.⁷ In the case of anionic or cationic doped metal oxide exhibits moderate to high photodegradation of dyes under visible light irradiation.⁸ In this mechanism of degradation of organic pollutants depends on •OH radicals stability and non-selectivity. Frequently, used method for purification of water is advanced oxidation processes (AOPs) due to produce •OH radicals under UV light irradiation, bicarbonate ions are present in water sample •OH radicals are unstable and very expensive. For this region, an altering of the method is required for purification of water under visible light conditions.

Heterocyclic moieties consisting of conjugated double bonds, hence transition metal ions are natural to complexation with hetero atoms. It is due to the flexibility in oxidation state and presence of unpaired electrons coordinated to metal ions through oxygenation process.⁹ For this reason, transition metal complexes are crucial for various fields such as biological, medicinal, chemical, photophysical and photochemical properties of the organic ligands. Hence, metal complexes concerning the degradation of dyes and C-H activation of organic compounds has been published from time to time.¹⁰ From the earlier information, it is noticed that most of the cases hydrogen peroxide acted a vital role to produce sensitive species such as •OH radical and used to mineralization of organic pollutants. However, a higher concentration of H₂O₂ is unsafe, and it is injurious to eyes, lungs and skin. Recently some of the Ni(II) Schiff base complexes used to degradation of MB and rhodamine-B in

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the absence of H_2O_2 as photocatalysts under visible light irradiation.^{2,11} These Schiff's base complexes are a pH dependent catalyst that is higher pH solution becomes strong basic then the catalysts are unstable and not reusable. Oxidation of benzhydrol and photodegradation of rhodamine-B in the presence of zeolite captured Ni(II) and Cu(II) complexes with N_2O_2 donor system of Schiff base ligands under visible light irradiation.¹² Lately published an article revealed that photocatalytic hydrogen evolution by a cobalt complex based on a tripodal iminopyridine ligand under visible light irradiation.¹³ Even some of the researchers are focused on metal-oxide frameworks are prepared and converted into respective metal oxide nanoparticles. Finally, metal oxide nanoparticles are used for photodegradation of dyes.¹⁴

In general, titanium base oxides are a significant contribution to the field of photocatalysis.¹⁵ TiO_2 and its doped materials (anionic and cationic) are semiconducting photocatalysts very frequently used for degradation of organic pollutants in UV and visible light irradiation conditions.¹⁶⁻¹⁸ However TiO_2 , the bandgap of 3.2 eV (for anatase) actual applications in the visible light region are very specific due to its wide bandgap energy. Recently, O=Ti consisting complexes have been proposed to be a photocatalyst for water splitting by a computational study.¹⁹ The ligand moiety assists as a probe for visible light and the O=Ti group exhibits the redox properties needed for the oxidation of water. A few studies of the electronic nature and structural properties of O=Ti porphyrins in water have been reported.²⁰ Ti (IV) complexes used for polymerization reactions,²¹⁻²³ but there are a few gaps found in the field such as degradation of dyes and C-H activation studies.²³ For this reason, Ti (IV) complexes are used towards the advancement of visible-light-sensitive photocatalysts. Hence, the pursuit of a more stability, recyclable, and affordable methodology still endures to avoid the researchers. Photocatalysis using Metal-organic complexes under visible light has attracted significant attention due to its prospective applications in eco-friendly remediation by degrading the organic pollutants to very safe byproducts due to absorption of toxic gasses.²⁴⁻²⁶ One such exploration, the new Schiff's base Ti (IV) complexes synthesized from N; S atoms coordinated and modification of absorption bands of shifted towards higher wavelength regions.

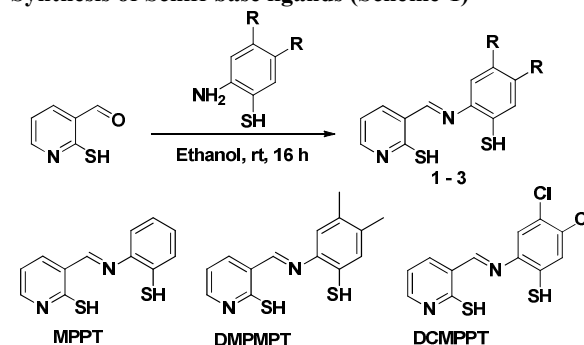
Experimental

All reagents were purchased from Sigma-Aldrich and used without further purification such as tetraisopropoxytitanium, 2-aminobenzenethiol, 2-iodo-4,5-dimethylaniline, 4,5-dichloro-2-iodoaniline, toluene and other solvents. 2-thioxo-1,2-dihydropyridine-3-carbaldehyde was obtained by Synocule Research Lab Pvt. 2-iodo-4,5-dimethylaniline and 4,5-dichloro-2-iodoaniline are converted into 2-amino-4,5-dimethylbenzenethiol and 2-amino-4,5-dichlorobenzenethiol as per literature procedure.^{27,28}

In our attempts to syntheses of Schiff base ligands using aldehyde and amines. The prepared new ligands i.e. (E)-3-(((2-mercaptophenyl)imino)methyl)pyridine-2-thiol (MPPT), (E)-3-(((2-mercapto-4,5-dimethylphenyl)imino)methyl)

pyridine-2-thiol (DMPMPT) and (E)-3-(((4,5-dichloro-2-mercaptophenyl)imino)methyl)pyridine-2-thiol (DCMPPT) containing two thiols and one imine groups have characterized by mass, SEM, IR, Raman, UV and NMR spectral investigations. Ti(IV) complexes are prepared using Schiff base ligands, characterize and photocatalytic oxidative cyclization and photodegradation of MB were studied, and all the experimental procedures presented in Supplementary information.

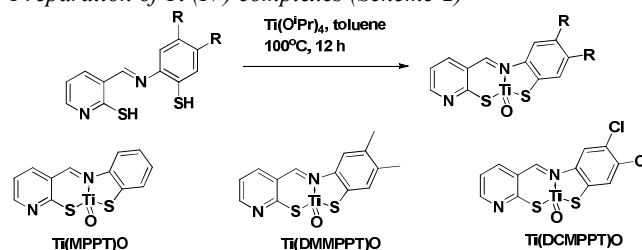
Synthesis of Schiff base ligands (Scheme-1)



Preparation of Schiff's base ligands

Addition of 2-aminobenzenethiol / 2-amino-4,5-dimethylbenzenethiol / 2-amino-4,5-dichloro-benzenethiol (25 mmol) to a solution of 2-mercaptopyridine-3-carbaldehyde (25 mmol) and piperidine (5 mmol) in toluene (100 mL) at room temperature. The resulting reaction solution was allowed to reflux for 16 h. The reaction mixture cooled and removed the solvent to give a residue followed by a standard aqueous workup, affording the corresponding ligand above scheme-1.

Preparation of Ti (IV) complexes (Scheme-2)



The Schiff's base ligand (MPPT, DMPMPT and DCMPPT) (1.00 mmol) and $\text{Ti}(\text{O}i\text{Pr})_4$ (0.30 ml, 1.00 mmol) dissolved in toluene (30 ml) then heated at 80°C under solvothermal conditions for 8 h. The solvent was evaporated under reduced pressure and recrystallized to yield microcrystalline materials 4 – 6 with a yield of the materials 48 - 54%.

Characterization of photocatalysts

CHN analyzes are estimated by using Elemental Analyzer Flash EA 1112. The conductance of the metal complexes measured on Digisun digital conductivity meter model DI-909. Mass spectra data collected by HR -EI systems on JMS-700 double focusing mass spectrometer (JEOL, Tokyo, Japan). Thermograms of all the samples were obtained using Shimadzu differential thermal analyzer (DTG-60H) with a heating rate of $10^\circ\text{C min}^{-1}$. The SEM-EDS images obtained on HITACHI SU-1500 variable pressure scanning electron

microscope (VP-SEM). The X-ray photoelectron spectroscopic (XPS) measurements were performed on a KRATOS AXIS165 X-ray photoelectron spectrometer using excitation energy of 1253.6 eV (Mg Ka) and pass energy of 80 eV. FT-IR spectra were recorded using Shimadzu spectrometer in the form of KBr pellets. Infrared (IR; KBr disc) has registered with a PerkinElmer BX series; Fourier transforms infrared spectrophotometer. Raman spectra were recorded using a 632.81 nm line from a He-Ne laser and the scattered light was analyzed using HORIBA JOBIN YVON HR800. The laser was focused on a spot of ~3 μm , and a 109 lens was used for the collection of backscattered Raman signal. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra recorded on a Bruker AV400 MHz Spectrometer with chemical shifts referenced using the ^1H resonance of residual CHCl_3 . Melting points verified on a Cintex apparatus. The electronic spectra obtained in chloroform solutions on a JASCO V-650 UV-Vis spectrophotometer. Brunauer-Emmett-Teller (BET) surface areas were determined by nitrogen adsorption-desorption isotherm measurements at 77 K on a Quantachrome autosorb automated gas sorption system. The photoluminescence (PL) spectra of the catalysts were recorded on Cary Eclipse Fluorescence Spectrophotometer and the samples were excited at their respective absorption maxima.

Result and Discussion

All the ligands and complexes are analytical data presented in Table 1 and the data agreement with the calculated values. The ligands MPPT, DMPMPT, and DCMPT synthesized from the aldehyde reacts with various amino-thiols compounds in methanol media and the high yields propose the reaction conditions were correct. The ligands are highly stable and fairly soluble in polar organic solvents, such as EtOH, MeOH, and CH_3CN due to presence thiol and azomethine groups. The metal complexes synthesized are stable at room temperature and soluble in DMSO and DMF. The morphology of all ligands and Ti - complexes was acquired by scanning electron microscopy (SEM). This technique is supportive to organize the discrete morphology of ligands and Ti(IV) complexes. The SEM metaphors of the ligand and complexes (Ti(MPPT)O, Ti(DMPMPT)O and Ti(DCMPPT)O) as shown in Figure S1 and Figure 1 respectively. The surface morphology of the parent Ti(MPPT)O, Ti(DMPMPT)O and Ti(DCMPPT)O samples is characterized by densely packed particles with considerable agglomeration, whereas the Ti^{4+} ions complexation to produced complexes were smaller than those of respective ligand.²⁹ The different morphology of Ti(IV) complexes is noticeable the manifestation of the new product. The morphologies of Ti(IV) complexes are established in distinct dimensions and profiles. Nevertheless, they are synthesized from a single ligand. The morphology of Ti(MPPT)O complex (Figure 1a and Figure S1) is found cube type form as well as appeared like a stack of blocks, whereas MPPT ligand is mixed forms. Similarly, Ti(DMPMPT)O and Ti(DCMPPT)O morphologies are cubes and hexagonal type profiles (Figure 1b and 1c). However ligand DMPMPT and DCMPT are found as mixture shapes and plate type profile (Figure S1).

The molar conductance of the metal complexes is measured for 10^{-3}M solution in DMF and presented in Table 1. Complexes have Ω_{m} values in the range 10.0 – 12.0 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ that fall within the range of non-electrolytes.³⁰ All the Ti(IV) complexes dried under vacuum and heated at 120°C for two hours. All the complexes were thermally stable up to 250°C and underwent the decomposition in one step (Figure S2). The single step of decomposition (endothermic) ensues between 250 and 580°C with a weight loss of corresponds to the loss of the ligand molecule.^{31,32} The weight of the residue remain in the crucible was signifying the formation of TiOS. The residue obtained from TGA is examined the XPS.

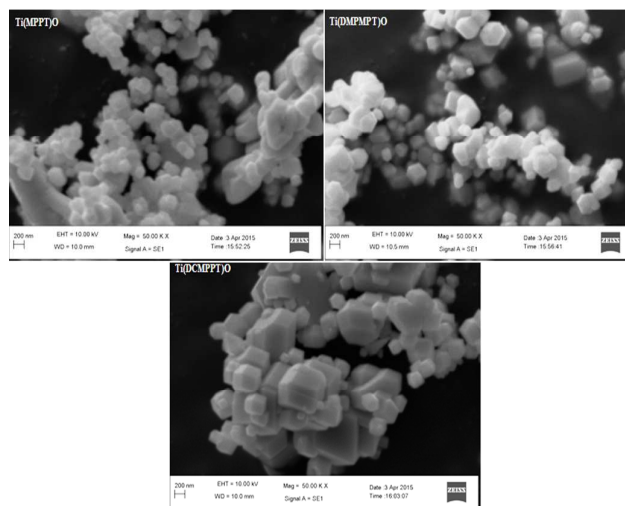
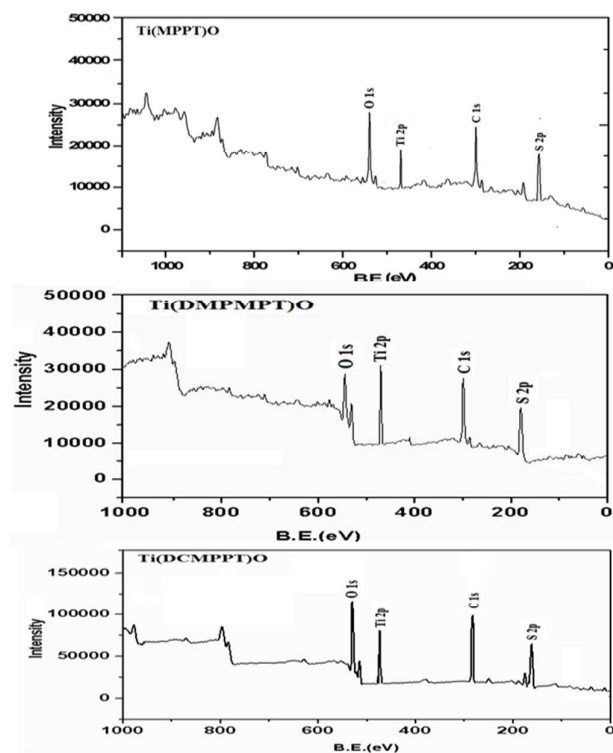


Fig. 1 SEM images of Ti(MPPT)O, Ti(DMPMPT)O and Ti(DCMPPT)O

The XPS data for all the residues in the complexes are revealed the same pattern, as shown in Figure 2, the peaks present in the spectrum of each complex, has same positions. The XPS explains that Ti (IV) complexes give a significant information for complex formation through S, N and O atoms. Ti 2p, O 1s, C 1s and S 2p peaks. The XPS spectrum of Ti 2p is unchanged with varying of ligands but very small change in S 2p peak position as compared with Ti(MPPT)O complex as shown in figure 2 due both donating and week withdrawing groups present in ligands of other two complexes.³³ Spectral data gives the significant information of the complexes i.e. 1:1 ratio of ligand and Ti – metal ion and supports to TGA and elemental analysis data. The mass spectral studies of the ligands and Ti(IV) complexes were recorded, and obtained data coincide with calculated data are given in the Supplementary information (Figure S3).

Table 1: Analytical and Physicochemical data of Ti(IV) complexes

Compound	Mol.wt	m/z [M ⁺ +1]	% Yield	Surface area ((m ² g ⁻¹)/ Bandgap energy (eV)	Mp/Dc. (°C) ±2	%C	%H	%N	%Cl	S%	% Ti	Λ _m (ohm ⁻¹ mol ⁻¹ cm ²)
MPPT	246.35	247.3	85	16 / 3.26	142	58.46 (58.51)	4.06 (4.09)	11.42 (11.37)	--	23.28 (23.37)	--	12.4
DMPMPT	270.40	271.4	78	11 / 3.39	163	61.25 (61.28)	5.12 (5.14)	10.27 (10.21)	--	20.26 (20.37)	--	11.6
DCMPPT	315.24	316.2	81	21 / 3.17	186	45.66 (45.72)	2.51 (2.56)	8.91 (8.89)	22.53 (22.49)	20.29 (20.34)	--	10.1
Ti(MPPT)O	308.20	309.1	48	31 / 2.99	252	63.13 (46.76)	2.58 (2.62)	9.17 (9.09)	--	20.73 (20.81)	15.39 (15.53)	10.9
Ti(DMPMPT)O	336.26	337.26	51	23 / 3.12	318	49.96 (50.01)	5.54 (3.60)	8.23 (8.33)	--	18.98 (19.07)	14.06 (14.24)	11.1
Ti(DCMPPT)O	377.09	378.09	54	43 / 2.64	334	38.15 (38.22)	1.63 (1.60)	7.36 (7.43)	18.59 (18.80)	16.94 (17.01)	12.49 (12.69)	10.8

**Fig. 2** XPS images of Ti(MPPT)O, Ti(DMPMPT)O and Ti(DCMPPT)O

The high-resolution mass spectra of the ligands show molecular ion peak as well as a base peak at 246 (MPPT), 274 (DMPMPT) and 315 (DCMPPT) (M)⁺. Confirms that the formulae of the ligands are C₁₂H₁₀N₂S₂ (MPPT), C₁₄H₁₄N₂S₂ (DMPMPT) and C₁₂H₈Cl₂N₂S₂ (DCMPPT). The peaks shown in the mass spectra are equivalent to the ligand and its metal

complexes to Schiff base fragmentation. The mass spectrum of the complexes shows molecular ion peak ([M]⁺, 100%) at m/z 308.1 [Ti(MPPT)O], 336.26 [Ti(DMPMPT)O] and 377.32 [Ti(DCMPPT)O]. For this reason, all the complexes composed with 1:1 ratios of Ti and ligands.³⁰ The surface area of ligands and complexes were measured and presented in Table-1. The order of the surface area is DMPMPT < MPPT < DCMPPT < Ti(DMPMPT)O < Ti(MPPT)O < Ti(DCMPPT)O. Therefore, Ti(DCMPPT)O exhibits good photocatalytic activity other than two complexes. The IR spectra of all the ligands have the two common functional groups are present, such as azomethine and thiol respectively. The spectra of ligands exhibit two significant bands nearly at 3090 and 1614 cm⁻¹ are due to the stretching vibration of -SH group and azomethine ν(C=N) group for ligands MPPT, DMPMPT, and DCMPPT. The IR spectra of the complexes were equated with those of the ligands to define the coordination positions that may involved in chelation. There are some significant peaks in the spectra of the ligands, which were cooperative in achieving this complexation. The location and/or the intensities of these peaks are expected to change upon the chelation. The bands shifted to lower wavenumber region by a range of 10 to 15 cm⁻¹ in all the complexes.³⁴ That is representing the participation of the azomethine nitrogen. The new band as appeared in spectra all the complexes are. ν (Ti-N) and (Ti-S). The most characteristic bands revealed in the spectra of the complexes in the areas 392, 388 and 374 (thiophenyl S). These new absorption peaks are assigned to ν (Ti-S) stretching vibration modes for Ti(IV) complexes. The other prominent bands at 422, 416 and 412 in MPPT, DMPMPT and DCMPPT of Ti (IV) complexes,³⁵ respectively, have been consigned to ν(M-N) mode. For this reason, from the IR spectra, it is established that the MPPT, DMPMPT, and DCMPPT behaves as tridentate ligands coordinated to the Ti ions via azomethine-N pyridine-S and thiophenyl-S and Ti-O band also revealed. However, this band presented in the range of TiO band at 1022 cm⁻¹, which indicated that all the complexes consist Ti=O bond³⁶ (Figure S4a – c). For this region, all complexes are 1:1 ratios of Ti and ligands nature from molar conductivity data, TGA, mass

and IR studies. Raman spectra of all the Ti(IV) complex shown Figure 3. The O=Ti stretching mode of O=Ti (IV) was also consigned, which has described in O=Ti contain -porphyrins.^{20c,37} The O=Ti bond is considered to result from the σ -donor between the filled O^{2-} p_z orbital and empty Ti^{4+} d_z^2 orbital, and the π -donor interactions between the filled p_x and p_y orbitals and the vacant d_{xz} and d_{yz} orbitals. Then the builds a strong O=Ti bond, which is reflected in the high stretching frequency at 920 cm^{-1} . Raman data of all the complexes shows that the phenyl ring, azomethine, Pyridine-N and Aryl-S peaks are identified as per reported data.³⁸

The UV-Visible spectra of ligands L_1 to L_3 recorded in methanol show a sharp and broad absorption bands nearly at 362 and 294 nm. The first lowest energy band arises because of the $n \rightarrow \pi^*$ transition from the central ring to aromatic ring. The higher energy band observed at 232 nm due to the $\pi \rightarrow \pi^*$ transitions (Figure S5). In all the spectra of ligands, L_1 to L_3 bands is onset at 365 to 391 nm, which indicates that the bandgap of the ligands was between 3.39 to 3.17 eV. For this reason, the reaction between the aldehyde and aromatic amines to give Schiff's base and donating group is present HOMO as shifted downwards, and withdrawn group is present LUMO shifted direction downwards. Theoretical calculations studied by K. Kaleta et.al³⁹ and bands shifted to higher wavelength region depends on small dipoles groups present on the system.

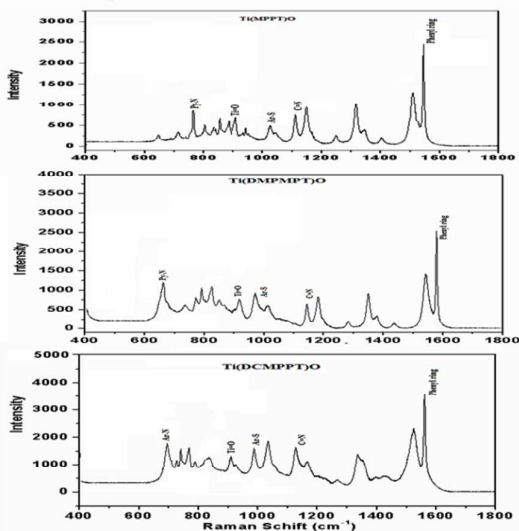


Fig. 3 Raman spectra of Ti(MPPT)O, Ti(DMPMPT)O and Ti(DCMPPT)O

In the complexes with the metal (Ti(IV)) $n - \pi^*$ transition slightly shift to the lower value signifying the coordination of the ligand to metal and bands is onset towards longer wavelength region.⁴⁰ The change in the onset values of the complexes, which indicating that bandgap energies of the complexes are marginal change than ligands as shown in Figure 4. Since Ti^{4+} ion has d^0 arrangement, so there is no chance of d-d transition. The wideness of the band can be taken as a suggestion of distorted octahedral geometry.

The purity of the ligands (MPPT, DMPMPT, and DCMPPT) also one of the evidence from 1H NMR spectra recorded in d_6 -DMSO (Figure S6). In these ligands, two

important characteristic peaks are present one azomethine, and another one is thiol protons respectively. The most typical and characteristic signals revealed by all the ligands spectra at δ values in the range as 8.9, 7.2 – 8.5, 5.8 – 6.2 and 3.4 ppm. Due to the existence of the protons of -CH=N, Ar-Hs, pyridine-SH, and phenolic-SH respectively. The signal exposed at δ 2.42 ppm attributed to the methyl group protons present in ligand DMPMPT. The ^{13}C -NMR spectra of all the ligands are exhibits one standard carbon atom nearly at ~ 160 ppm that supports the above NMR data, and this carbon atom is azomethine group. Another important peak present in each spectrum of the ligand is a functional group attached to the various aromatic carbon atoms that are Py-C-SH and Ar-C-SH at 180 and 125 ppm respectively. In all the ligands spectra shown peaks from 125 to 156 ppm, these peaks are belonged to aromatic ring carbon atoms.

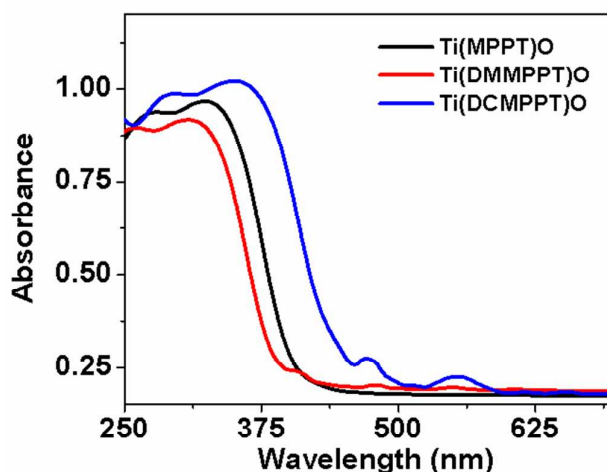


Fig. 4 Kubelka-Munk-transformed diffuse reflectance spectra (DRS) of all the Complexes.

The NMR spectra of complexes are compared with ligands (SH's) one of the characteristic peaks are absent that result in the formation of Ti-S bonds (Figure S7). Because azomethine nitrogen atoms participated into the complexation with Ti(IV) ions, then protons of azomethine shielded in complex spectra.⁴¹ Finally, remaining aromatic protons also moved towards lower ppm values. From these data revealed that the Schiff's base ligands are complexation with $Ti(O^iPr)_4$ and all the complexes distorted octahedral geometry.

Oxidative cyclization

In Allylic Oxidations very frequently used catalyst is SeO_2 .⁴²⁻⁴⁴ However, purification of the final products very lengthy process due to Se reacts with substrate forms unwanted byproducts. Therefore, metal-organic frameworks act as solid heterogeneous catalysts for the synthesis of nitrogen atom enclosing heterocycles.⁴⁵ Oxidative cyclization is one of the most significant reactions in organic synthesis. Benzoxazole and benzothiazole are crucial scaffolds in various fields of research such as medicinal and material chemistry.⁴⁶⁻⁵⁰ Styryl group containing systems are a mimic structure with stilbenes and for this region, styryl substituted heterocycles used as cis – trans molecular switches under UV-visible light.^{51,52}

Synthesis of new analogues of stilbenes is essential for the development of the molecular electronics. Synthetic conditions critical for the preparation of materials which is not affect the environment (both aquatic & soil), sustainability of the catalyst for number cycles in the solvent medium and utilize the green energy sources. For this region, we are focusing on better conditions, a modest catalyst based on Ti (IV) complexes. The product formation of the reaction monitored through UV-Visible spectra of reaction mixture continuously for every 10 min as shown in Figure 5.

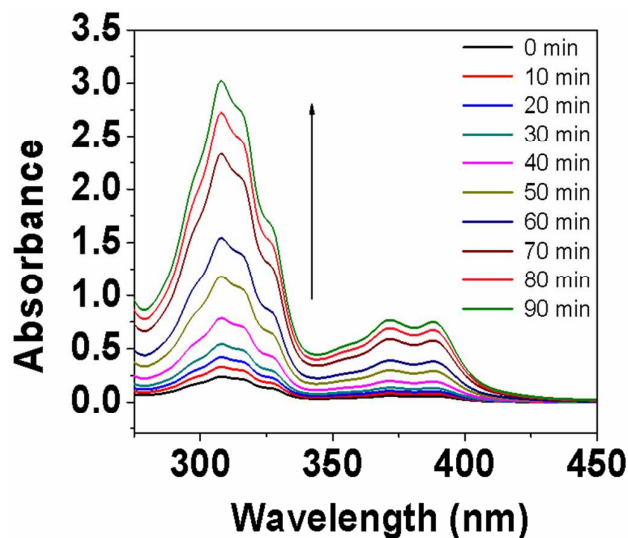


Fig. 5 Temporal Absorbance spectral pattern of reaction mixture during oxidative cyclization process on Ti(DCMPPT)O

All the substrates can converted to the corresponding products with excellent yields with a moderate reaction time in the presence of Ti(DCMPPT)O complex compared with remaining complexes. All the reactions were run same time intervals by optimization with the substrate as prop-1-en-1-ylbenzene represented in the scheme 3 in supplementary data. The yields usually ranged between 76 and 95% with respect to Ti(IV) complex. The product was isolated and purified using a simple recrystallization from ethanol, resulting in a still quite impressive isolated yield of 80%.

All the Ti(IV) complexes of MPPT, DMPMPT, and DCMPPT used a catalyst for the oxidation of prop-1-en-1-ylbenzene converted into cinnamaldehyde. Cinnamaldehyde condensation with 2-aminophenol and finally dehydrogenation to give respective styryl derivatives.⁵³ For ease of evaluation with other catalytic systems, we conceded out the oxidation on a millimole scale using 0.5 mol % catalysts added. For the establishment of the reaction conditions in the presence of the catalyst also studied. For this, in the presence of Ti(MPPT)O, Ti(DMPMPT)O and Ti(DCMPPT)O used as catalysts and also 1:1 ratio of ethanol and water as a solvent for establish the system. All the reactions monitored by TLC. Within 90 min of the termination of the reaction, the yield of the corresponding product shown from TLC and no further reaction is observed.

Theoretically, only two equivalents of $\cdot\text{OH}$ radicals consumed for the oxidation of allyl methyl group to get primary alcohol. After one more hydroxyl radical attached to primary alcohol to obtaining aldehyde, under solar light irradiation in-situ production of hydroxyl radicals. For this region, our method is eco-friendly, and stability of the catalysts is reusable nature. The catalyst used for the preparation of various functional groups present on (E)-prop-1-en-1-ylbenzene to give styryl product as shown in Table S1. The oxidative cyclization reaction was continuously monitored by using UV-visible spectra as illustrated in figure 5. From this spectrum indicates that passing of time increased the intensity of the new absorption band up to 90 min. Further, photoreaction is continuous for 180 minutes no change in the absorption band and stability of the product high under solution. For all the final products confirmed from $^1\text{H-NMR}$ spectra as shown in Figure S8a & S8b.

Photodegradation of methylene blue (MB)

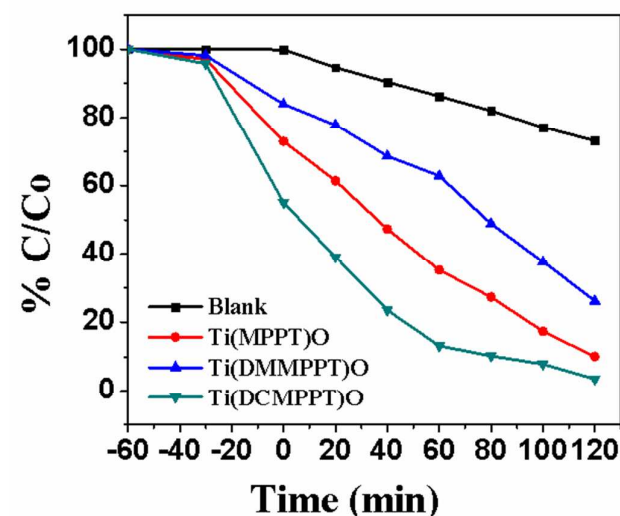
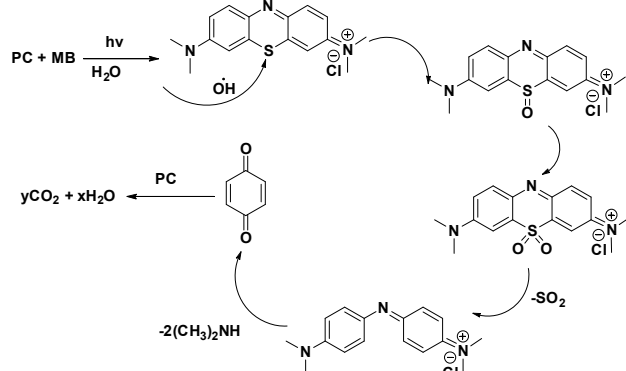


Fig. 6 Degradation curves of Methylene Blue solution under visible light irradiation overall photocatalysts

MB is an extensively used as an indicator for acid – base titrations in laboratory and textile industry as an organic dye. All the organic dyes exceptionally used for dyeing agents in various applications in daily life due to vigorous soluble in water. At the same time, aquatic pollution enhances, for this region degradation of dyes are very crucial to saving the environment.⁵⁴ Here, we examine the photoactivity of the catalyst for MB as a pollutant. Therefore, we have selected MB as the model contaminant to evaluate the photocatalytic ability of Ti(MPPT)O, Ti(DMPMPT)O and Ti(DCMPPT)O, under visible light irradiation. Experiments were carried out in presence and absence of light. The dark experiments were conducted to create the adsorption-desorption equilibrium. After the one-hour dark test, the reaction was exposed to light irradiation and observed the decrement of the concentration of aqueous MB dye over catalysts with increasing time intervals. With the rise of time, the color of MB disappeared progressively. Figure 6 reveals the characteristic

photodegradation efficiencies of Ti(MPPT)O, Ti(DMPMPT)O and Ti(DCMPPT)O. From the figure 6, it could be clearly seen that the Ti(DCMPPT)O have exhibited higher activity than that of their parent analogous. The extent of MB degradation by Ti(MPPT)O, Ti(DMPMPT)O and Ti(DCMPPT)O up to 120 min of visible light irradiation is found to be 88%, 78% and 94% respectively. It is well-known that an aqueous solution of MB undergoes self-photolysis under visible light irradiation. To distinguished between the photocatalysis and photolysis of MB, experiments were carried out in the presence and absence of catalysts under identical conditions. The degradation curve obtained without the addition of the photocatalyst (Figure 6, MB Photolysis) show about 25% degradation only. Therefore, the results indicate that the degradation of MB increases considerably in the presence of catalysts due to photodegradation only and not due to the photosensitization of MB. After 20 min. of visible light irradiation passed into the sample was subjected to mass spectral analysis. The data revealed that the some significant fragment peaks are identified and proposed a degradation path as followed (Figure S9).

Mass spectral studies of methylene blue after 20 minutes



The efficiency and sustainability of all the Ti-complexes depend on its chemical and photostability after the photoreaction, its capability to catalyze the MB in several cycles. As revealed in Figure 7, the photocatalysts exhibit the identical performance even after the third cycle. The 1H-NMR of Ti(DCMPPT)O pattern matched with unused Ti(DCMPPT)O after the three cycles indicating the stability of the complex (Figure 8). Whereas other two complexes are not performed the same amount of degradation as compared with the first cycle and even 1H-NMR spectra of recovered material not equivalent pattern and very complex nature. For this region, Ti(DCMPPT)O is better than other two Ti-complexes due to high surface area and low bandgap energy. Due to DCMPPT ligand consists of chlorine atoms, which handle increased the photocatalytic activity due to electron affinity is increased the electronic coupling increased then recombination energy decreased.⁵⁵

Mechanistic Studies of photodegradation process

The oxidative cyclization process is one of the most significant methods for process development. However, the mechanistic study of product formation in the presence of solar energy is essential for material designing, in which

either $\bullet\text{OH}$ or $\text{O}_2^{\bullet-}$ radicals handle the both oxidative cyclization and degradation of the pollutants.⁵⁶ The production of $\bullet\text{OH}$ radicals in a photoreaction is as follows: at the same time the incident light energy is larger or equivalent to bandgap energy of the Ti (IV) complex. Electrons will be transferred from the valence band to the conduction band, creating a hole in the valence band (equation-1). Both excited electrons and holes move to the surface of the Ti-complex and interact with adsorbed O_2 and water to produce $\text{O}_2^{\bullet-}$ and $\bullet\text{OH}$ radicals respectively (equation-3).

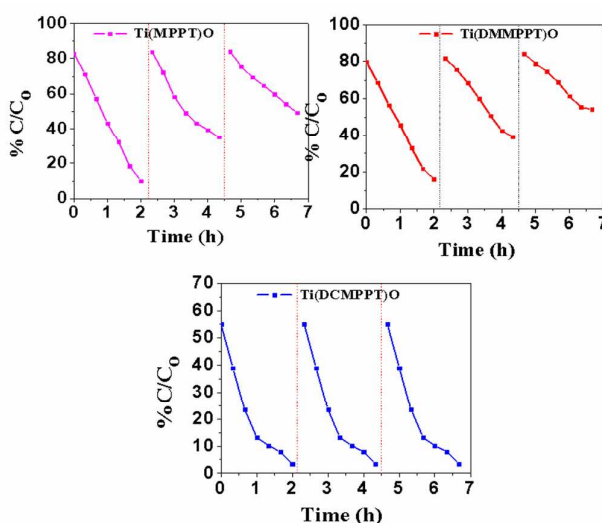


Fig. 7 Recyclability of the Ti(IV) complexes for the photodegradation of MB under visible light irradiation

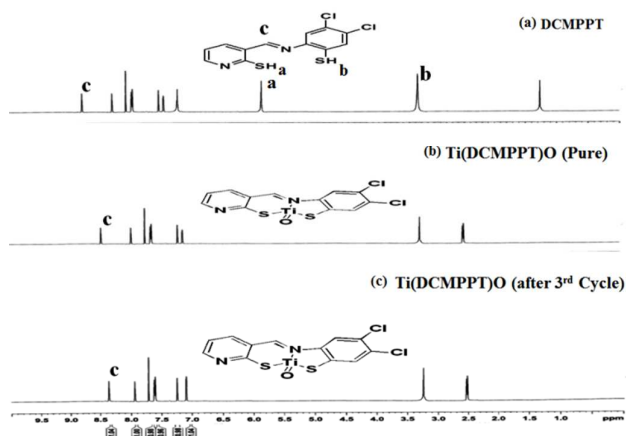
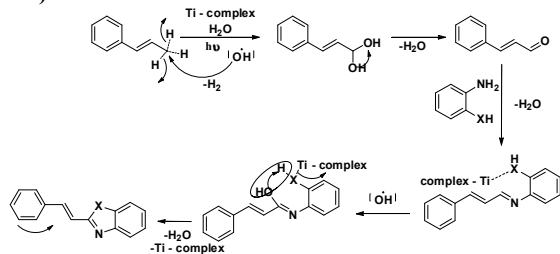


Fig. 8 1H-NMR spectra of (a) Ligand DCMPPT; (b) pure Ti(DCMPPT)O and (c) after third cycle

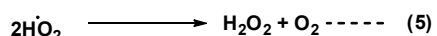
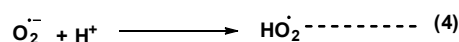
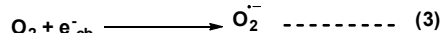
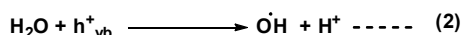
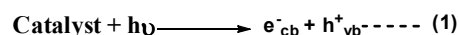
H^+ ion very fast reacts with $\text{O}_2^{\bullet-}$ radicals are natural to form HO_2^{\bullet} (equation-4) species that react among themselves and form H_2O_2 and O_2 (equation-5). The subsequently H_2O_2 decomposes to form $\bullet\text{OH}$ radicals (equation-6) that react allylic position to obtained aldehydes, Schiff's base, and cyclization as shown in proposed mechanism pathway – 1. In

the case of dye molecules $\bullet\text{OH}$ radical interact non-selectively and non-direction with dye (MB) and decompose into simple mineralization. The mechanistic pathway – 1 and 2 shown below

Proposed mechanism for Oxidative cyclization (Pathway – 1)



Possible degradation mechanism of MB (Pathway – 2)



For the proposed mechanism evidence is major consent for hydroxyl radicals interact with the dye or C-H activation. For this region, we choose the photocatalytic hydroxylation of terephthalic acid (TA) as further evidence of the facility of the photocatalysts to create $\bullet\text{OH}$ radicals.⁵⁷ It is well-known that the $\bullet\text{OH}$ radical attacked the TA to form a 2-hydroxy terephthalic acid (TAOH), which radiates a unique fluorescence signal at 440 nm. Photocatalytic test with TA was conceded out in the presence of Ti-complexes (Figure 9). Indications the fluorescence intensity of 2-hydroxy terephthalic acid produced in the photoreaction, in the presence of a Ti-complex catalyst under solar light irradiation. It observed that with continuous irradiation of light periodically, the intensity of fluorescence signals improved. Gradually, signifying enhanced concentration of $\bullet\text{OH}$ radicals in the photocatalytic reaction that are accountable for the enriched photocatalytic activity of Ti-complexes. Thus, the increase in the photoactivity of Ti-complex against the oxidative cyclization and MB degradation can be recognized to intensification in the $\bullet\text{OH}$ radical generation.

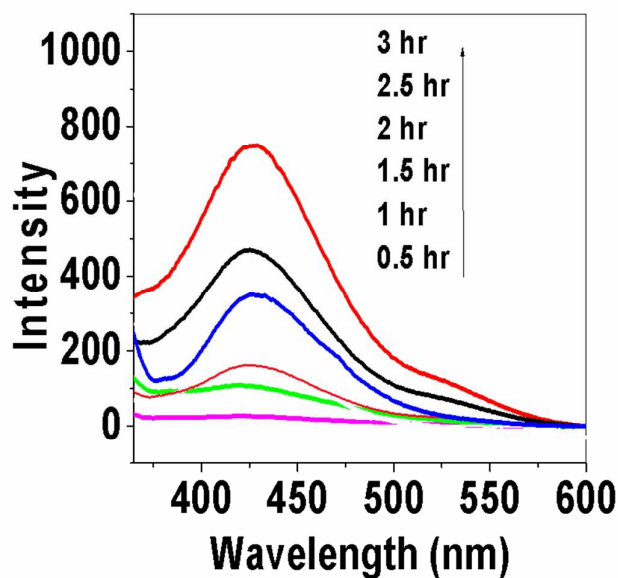


Fig. 9 PL spectral variations under visible light irradiation regular intervals of time on Ti(DCMPPT)O sample in TA solution

Conclusion

Ti (IV) complexes of (E)-3-(((2-mercaptophenyl)imino)methyl)pyridine-2-thiol, (E)-3-(((2-mercapto-4,5-dimethyl phenyl)imino)methyl)pyridine-2-thiol and (E)-3-(((4,5-dichloro-2-mercaptophenyl)imino)methyl)pyridine-2-thiol were syntheses and characterized by numerous spectroscopy techniques. The photocatalytic activity and oxidative cyclization of prepared complexes for MB and (E)-prop-1-en-1-ylbenzene were studied analytically under visible light irradiation. The photocatalytic activity was originated to be more efficient in the presence of Ti(DCMPPT)O complexes than the other two complexes and more stable after three cycles. Photo-oxidation and degradation exposed that these metal complexes with greater photocatalytic efficacy will be a prospective postulant for green cleansing under visible light at room temperature conditions. The prepared metal complexes in this work may find other applications similar to attempting a full diversity of reactants containing organic dye pollutants and aromatization of polycyclic hydrocarbons.

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Notes and references

Supplementary Information contains all the experimental process for oxidative cyclization, photodegradation of methylene blue and mechanistic studies of hydroxyl radicals by terephthalic acid. Some of the spectral data also included.

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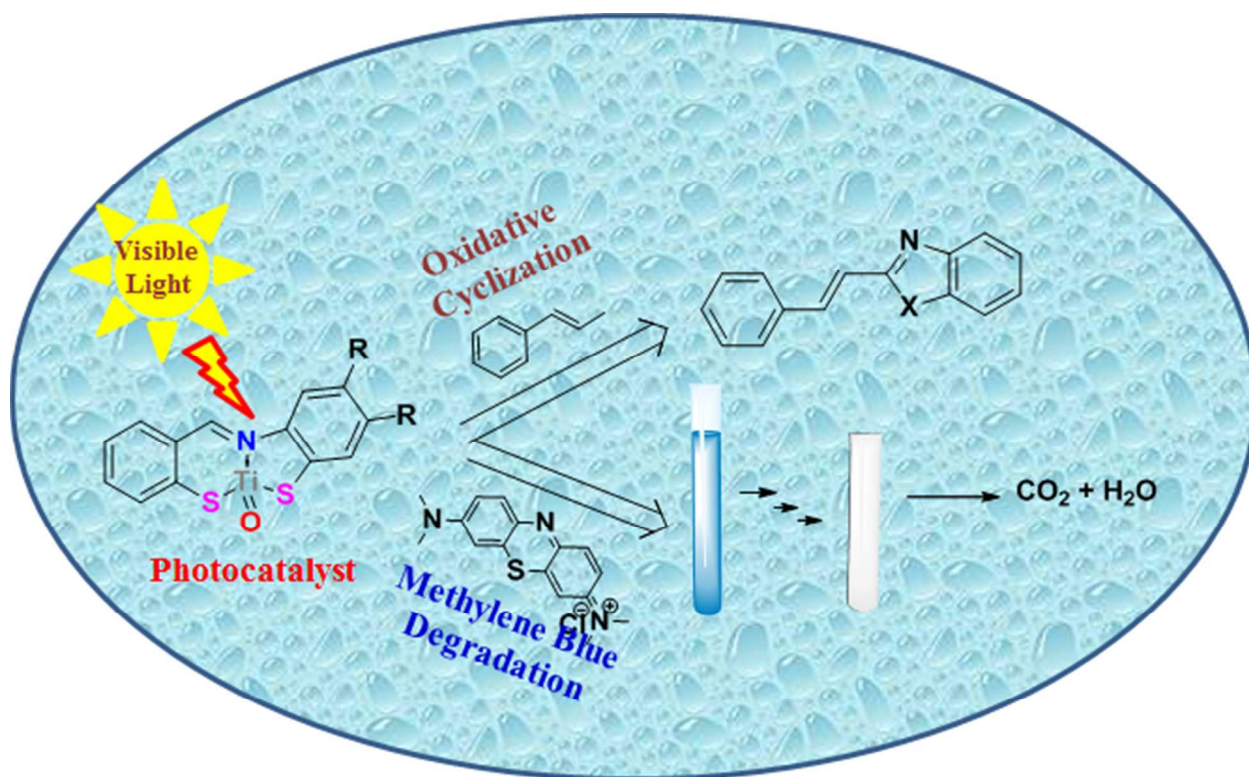
New Photocatalyst for Allylic aliphatic C-H Bond Activation and degradation of organic pollutants: Schiff's base Ti(IV) complexes

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Ti(IV) Schiff base complex oxide photocatalysts with high stability, oxidative – cyclization and photodegradation of methylene blue dye under visible light irradiation