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Synthesis, Crystal structure, Characterization of Pyrazine Diaminotriazine Based Complexes and their Systematic Comparative Study with Pyridyl Diaminotriazine Based Complexes for Light-Driven Hydrogen Production

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ABSTRACT: The present world has a dire need to increase its energy input in order to meet with the demands of growing population. Combining the most abundant renewable energy source such as sunlight with a clean fuel having the capacity to store and carry renewable energy *viz*. hydrogen is a promising alternative to control the detrimental effects of fossil fuels on our environment. A sunlight-triggered hydrogen evolution reaction (HER) would be an interesting approach for the production of pure hydrogen. Working towards this direction, we have synthesized complexes 8-10 by the reaction of 6-(pyrazin-2-yl)-1,3,5-triazine-2,4-diamine (PzDAT), with Co(II), Ni(II) and Cu(II) respectively. As indicated by single-crystal X-ray diffraction, the molecular organization of all the complexes is mainly dictated by the coordination modes of the ligands and the hydrogen bonds involving the DAT groups with reliable patterns. In conjunction with the synthesis and characterization, we investigated and compared the catalytic activities for HER of 8-10 with 5-7 (complexes of pyridine DAT (PyDAT) with Co(II), Ni(II) and Cu(II)) that we have reported previously. In the presence of triethanolamine (TEOA) as the sacrificial electron donor, $Ru^{(II)}(bpy)_3(PF_6)_2$ as the photosensitizer (PS) and aqueous HBF₄ as the proton source under blue light, the highest turnover number amongst 5-10 is observed for PyDAT copper complex 7 with TON of 72 moles of hydrogen per mole of PS. This value is higher compared to some Cu complexes reported in literature.

INTRODUCTION

The ever-increasing human population demands equally increasing energy resources. Until now fossil fuels have been the world's primary energy resource. However, their growing utility has caused a detrimental effect on our environment.^[1-3] In order to achieve a balance with our environment, the dependency on fossil fuels needs to be reduced. This can be done by increasing our dependency on renewable and environmentally friendly energy resources and finding a possible substitute for fossil fuels.^[4-7] Among the diverse renewable energy resources, sunlight is the predominant one which has the potential to fulfil all our energy demands. Hydrogen is a possible future alternative to fossil fuels as it is a clean fuel that can be used in near future to store renewable energy. Hence, sunlight and hydrogen are two clean and pollution free energy source and carrier, respectively, which can be combined to meet the present-day energy crisis and other environmental issues.^[8-10] Taking inspiration from natural photosynthesis, solar energy can be stored in high-density chemical bonds of hydrogen molecules. A sunlight-triggered hydrogen evolution reaction (HER) would be an interesting alternative to produce pure hydrogen.

Currently, one of the key challenges for HER is the development of efficient catalysts. Many of the studies reported so far have used platinum group metal *viz*. $Pt^{[11]}$, $Rh^{[12]}$, $Ir^{[13,14]}$ based complexes as catalysts and PSs for hydrogen evolution. However, photocatalysts based on first row transition metals are also being increasingly explored because of their low cost and good electrochemical stability. Although previously, researchers have used these low-cost metals *viz*. Co, Ni, Cu, $Zn^{[15-19]}$ as PSs and catalysts for H₂ production, there is an ever increasing need to synthesize more efficient and better improved catalytic systems for HER.^[20-23]

Considering the potential of transition metal complexes as catalysts for hydrogen production, we synthesized and studied the photocatalytic activity of complexes **5-10** which comprise of Co(II), Ni(II) and Cu(II) transition metals (denoted by M) in M(2,2-bipy)₂(NO₃)₂ framework functionalized with a diaminotriazinyl (DAT) and a pyrazinyl group by replacing one or two pyridyl rings (Chart 1). DAT-substituted pyridine and

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pyrazine complexes are called as tectoligands (**2** and **3**) and their self-assembly with metal ions forms metallotectons.^[24,25] The main advantages associated with the synthesis of coordination complexes using tectoligands are facile synthetic route and predictable intermolecular hydrogen bonding interactions along with simultaneous binding with metal ions to produce reliable patterns (Chart 2).^[26-32]



Chart 1. Molecular structure of ligands 1-3 and complexes 4-10

The investigation to prepare functionalized catalysts is an important task in order to modify their properties. Herein, we focus our work on the design, synthesis and characterization of DAT functionalized complexes **8-10** which are easy to obtain. As part of our ongoing research in the area of energy application, we studied and compared the catalytic activities of **5-10** for HER.^[33,34] In this work, along with the design and characterization of PzDAT complexes, a systematic comparative photocatalytic study of six complexes comprised of DAT groups (three PzDAT and three PyDAT) towards hydrogen evolution reaction has been presented.

EXPERIMENTAL SECTION

General Notes and Procedures for the Synthesis of complexes 8-10

6-pyridin-2-yl-[1,3,5]-triazine-2,4-diamine ligand **2**, 6-pyrazin-2-yl-[1,3,5]-triazine-2,4diamine ligand **3** and complexes **5-7** were synthesized by reported methods.^[35-37] Complexes **8-10** were prepared by the experimental procedure described below. Other chemicals were commercially available, purchased and used without any additional purification. A solid sample of ligand **3** (2.0 equiv) was added in small portions at 25 °C to the stirred solutions of $M(NO_3)_2 \cdot xH_2O$ (1 equiv) in MeOH (25 mL). The mixtures were refluxed for 12 h and the resulting homogeneous solutions were cooled to room temperature and subjected to crystallization by slow diffusion with diethyl ether.

Compound 8. The reaction of ligand 3 (0.05 g, 0.2644 mmol) with Co(NO₃)₂.6H₂O (0.038 g, 0.1322 mmol) according to the general procedure yielded 87% of pink crystals of complex 8 with the composition Co(3)₂·(NO₃)₂. FTIR (ATR): 3450.61, 3392.94, 3318.76, 3224.71, 3170.05, 1672.10, 1653.75, 1641.17, 1598.87, 1576.29, 1540.28, 1503.21, 1484.83, 1451.17, 1429.80, 1372.96, 1289.24, 1271.33, 1196.52, 1175.07, 1160.91, 1066.92, 1038.76, 1013.13, 989.38, 954.49, 910.94, 847.18, 824.22, 808.43, 770.55, 737.13, 697.28 cm⁻¹. HRMS (ESI) for [C₁₄H₁₄N₁₅O₃Co]⁺ m/e 499.0732, found 499.0731. Anal. calcd for C₁₄H₁₄CoN₁₆O₆: C, 29.96; H, 2.51; N, 39.93. Found: C, 30.05; H, 2.25; N, 39.40.

Compound **9**. The reaction of ligand **3** (0.05 g, 0.2644 mmol) with Ni(NO₃)₂.6H₂O (0.038 g, 0.1322 mmol) according to the general procedure yielded 90% of cyan crystals of complex **9** with the composition [Ni(**3**)₂(MeOH)(NO₃)].NO₃. FTIR (ATR): 3427.54, 3383.71, 3330.85, 3158.68, 1662.55, 1622.82, 1602.10, 1574.52, 1515.64, 1486.09, 1459.67, 1378.07, 1277.62, 1212.06, 1175.03, 1166.50, 1043.71, 1014.14, 995.70, 914.10, 850.20, 807.10, 771.26, 731.53 cm⁻¹. HRMS (ESI) for $[C_{14}H_{14}N_{15}O_3Ni]^+$ m/e calcd

498.0765, found 498.052. Anal. calcd for C₁₅H₁₈N₁₆NiO₇: C, 30.38; H, 3.06; N, 37.79. Found: C, 29.82; H, 2.67; N, 38.12.

Compound **10**. The reaction of ligand **3** (0.05g, 0.2644 mmol) with Cu(NO₃)₂. 2.5H₂O (0.030 g, 0.1322 mmol) according to the general procedure yielded 92% green crystals of complex **10** with the composition Cu(**3**)₂·(NO₃)₂. FTIR (ATR): 3481.68, 3403.44, 3321.96, 3221.84, 3150.14, 1653.76, 1617.58, 1580.80, 1559.45, 1507.24, 1486.40, 1462.61, 1429.85, 1375.55, 1295.82, 1279.38, 1205.88, 1178.18, 1157.85, 1064.20, 1041.40, 994.75, 954.68, 944.62, 911.26, 871.13, 830.49, 818.92, 804.82, 714.27 cm⁻¹. HRMS (ESI) for $[C_{14}H_{14}N_{15}O_3Cu]^+$ m/e calcd for 503.0800, found 503.0684. Anal. calcd for $C_{14}H_{14}CuN_{14}O_6$: C, 29.71; H, 2.49; N, 39.60. Found: C, 29.98; H, 2.50; N 39.41.

Instrumentation

Crystallographic data were collected using a Bruker Venture Metaljet diffractometer with Ga Ka radiation. The structures were solved by intrinsic phasing using SHELXT,^[38] and non-hydrogen atoms were refined anisotropically with least-squares minimization.^[39] Hydrogen atoms were treated by first locating them from different Fourier maps, recalculating their positions using standard values for distances and angles, and then refining them as riding atoms. Microcrystalline powders were analyzed in transmissionmode geometry using a Bruker D8-Discover instrument (θ - θ geometry) equipped with a XYZ platform and a HI-STAR gas detector. X-rays were generated using a conventional sealed-tube source with a copper anode producing Cu K α radiation ($\lambda = 1.54178$ Å). The samples were gently ground and then mounted on a flat Kapton sample holder. The data collection involved acquisition of two different sections with increasing angular position, giving two different 2D frames. These frames were integrated and combined to produce the final one-dimensional powder X-ray diffraction pattern. Calculated powder X-ray diffraction patterns were generated from the structural data in the corresponding CIF resulting from single crystal analyses. The calculation was performed using MERCURY^[40] software of the Cambridge Crystallographic Data Center. A unique value of the full width at half maximum for the diffraction peaks was adjusted to get a better match between the

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resolution of the experimental and the calculated patterns. The determination of the total carbon, hydrogen, nitrogen and sulfur (C, H, N, and S) contents in the compounds was performed by using EA 1108 Fisons CHNS Element analyser by quantitative "dynamic flash combustion" method. The UV–Vis spectra were recorded on a Cary 5000 spectrometer. The crystals were gently ground and placed on quartz holders. The ATR–FTIR spectra were collected with a Nicolet iS 10 Smart FT-IR Spectrometer within $600-4000 \text{ cm}^{-1}$. The thermogravimetric analysis was performed using Mettler Toledo at 10° C/min, under N₂ gas.

Electrochemical measurements

Electrochemical measurements were performed with a BAS SP-50 potentiostat, in pure dimethylformamide purged with argon at room temperature. Glassy carbon electrode was used as a working electrode, the counter electrode was a Pt wire and silver wire was the pseudo-reference electrode. The reference of electrochemical potential was set using 1 mM ferrocene as an internal standard and the values of potentials are reported vs SCE.^[41] The concentrations of samples were 1mM. Tetrabutylammonium hexafluorophosphate (TBAP) (0.1 M) was used as supporting electrolyte. Cyclic voltammograms were obtained at a scan rate of 100 mV/s and current amplitude of 100 μ A.

Photocatalytic experiments

A PerkinElmer Clarus-480 gas chromatograph (GC) was used to measure hydrogen evolution for our complexes. The assembly of this chromatograph consists of a thermal conductivity detector, a 7-inch HayeSep N 60/80 pre-column, a 9-inch molecular sieve 13*45/60 column, a 2 mL injection loop and argon gas as carrier and eluent. DMF was the solvent of choice for our experiments. Three separate solutions of 1) sacrificial donor and proton source, 2) photosensitizer [Ru(bpy)₃] (PF₆)₂ and 3) catalyst were prepared in order to obtain 5 mL of sample solutions in standard 20 mL headspace vials. In DMF, the resulting molar concentration of photocatalytic components were: 1 M for triethanolamine (TEOA), 0.1 M for HBF₄ (proton source), 0.56 M for water, 0.1 mM for the photosensitizer

 $[Ru(bpy)_3](PF_6)_2$ and 1 mM catalysts (pH apparent= 8, 9). (Aqueous HBF₄ solution acts as the proton source and TEOA as the sacrificial electron donor). This was followed by placing the vials on a panel of blue LED 10 W center at 445 nm in a thermostatic bath set at 20°C which was sealed with a rubber septum and two stainless-steel tubes pierced in it. Argon was carried in the first tube at a flow rate of 10 ml min⁻¹ (flow rate adjusted with a manual flow controller (Porter, 1000) and referenced with a digital flowmeter (Perkin Elmer Flow Mark)). The second stainless steel tube carried the flow to the GC sample loop passing through a 2 mL over flow protection vial and an 8-port stream select valve (VICCI). Timed injections were done by a microprocessor (Arduino Uno) coupled with a custom PC interface. Corresponding to a specific argon flow, H₂ production rate was calibrated. For calibration of H₂ production rate at a specific argon flow, a syringe pump (New Era Pump) equipped with a gas-tight syringe (SGE) and a 26s-gauge needle (Hamilton) was used to bubble different rates of pure hydrogen gas into the sample, to a minimum of 0.5 μ L/minute. For calibration testing, stock cylinders of known concentration of H₂ in argon replaced the argon flow (inserted at the pre-bubbler, to keep the same vapor matrix). The measured results independent of flow rate (under same pressure) can be easily converted into the rate of hydrogen using equation 1. The errors associated to the TON and TOF are estimated to be 10 %.^[42]

Equation 1

Rate of production of H_2 (μ L min⁻¹) = [H_2 standard] (ppm) x Ar flow rate (L min⁻¹)

RESULTS AND DISCUSSION

In comparison to a pyridine ring, the DAT group present in our synthesized compounds consists of a triazinyl ring and two $-NH_2$ groups. Located in *ortho* position of a coordination site, the DAT group can participate by binding with metal ions to produce functionalized transition metal complexes. As the catalytic properties can be severely altered depending upon the metal ion used and the functional groups attached to the catalysts, we examined the effect of DAT group for HER. We have previously reported the synthesis and the characterization of compounds $M(PyDAT)_2(NO_3)_2$ **5-7** obtained by coordination of 6-(pyridin-2-yl)-1,3,5-triazine-2,4-diamine (PyDAT) with earth-abundant

metal ions (M= Co(II), Ni(II) and Cu(II)).^[35] These complexes can be prepared easily in high yield and purity (Chart 1). Herein, we discuss the synthesis and the structural study of three novel complexes **8-10** obtained by the reaction of 6-(pyrazin-2-yl)-1,3,5-triazine-2,4-diamine (PzDAT) with Co^{II}, Ni^{II} and Cu^{II}. Moreover, we have studied the physicochemical properties of complexes **5-10** by thermogravimetric analysis (TGA), UV-Vis, infrared and cyclic voltammetry (CV). In this work, we also investigated the catalytic activities of **5-10** for HER.

Structural Analysis and Characterization of Complexes 8-10

Based on the coordination of 2,2'-bipy and related bidentate ligands, we expect ligand 3 to yield well established coordination motifs with transition metal ions and to further associate in solid-state by hydrogen bonding of DAT groups (Chart 2) to generate crystalline molecular materials. Complexes 8-10 were obtained by mixing ligand 3 (2 equiv) with $M(NO_3)_2.x(H_2O)$ (1 equiv) in methanol and purified by crystallization. Analyses by electrospray ionization mass spectrometry (ESI-MS) measurements confirm the presence of the metal ions in the complexes with the masses and isotope distribution patterns corresponding to that of $[M(pzDAT)_2(NO_3)]^+$ for complexes 8-10. The infrared spectra of 8-10 (Fig. S3) indicate the presence of the ligand 3 with typical broad bands characteristic of symmetric and asymmetric N-H stretching of the NH₂ group between 3500-3200 cm⁻¹. The band appearing between 1300-1200 cm⁻¹ that is not observed in the IR spectrum of the free ligand is assigned to NO_3^- group (Table S1). The compositions confirmed by elemental analysis (EA) for the samples are $M(pzDAT)_2(NO_3)_2$ for complexes 8 and 10 and $M(pzDAT)_2(MeOH)(NO_3)_2$ for complex 9 (see experimental section). Except for 8, we have studied the molecular organization in solid state by single-crystal X-ray diffraction (SCXRD).



Chart 2. Cyclic hydrogen bonding motifs I-III of diamino-1,3,5-triazinyl group (DAT).

1. Structure of 6-(pyridin-2-yl)-1,3,5-triazine-2,4-diamine 2 with $M(NO_3)_2.6(H_2O)$ (Complexes 5-7, M = Co(II), Ni(II) or Cu(II))

In the previous work, we have reported the single-crystal structures of compounds **5-7**.^[35] In order to facilitate a comparison of these known structures with new ones we summarized succinctly their supramolecular organization. Molecular structures of **5-7** are shown in Fig. 1. The chemical compositions of **5-7**, with 2:1 pyDAT -to- M ratio, are $M(PyDAT)_2(NO_3)_2$ (M = Co(II), Ni(II) or Cu(II)). Isostructural crystal structures were determined for **5** and **6** by single-crystal X-ray diffraction. A strongly distorted octahedral coordination geometry was observed for complexes **5-7**. The observed structures of **5-7** consist of enantiomeric metallotectons that are linked alternatively *via* N-H^{...}N hydrogen bonds of DAT groups to produce the three-dimensional supramolecular networks.



Fig. 1. Molecular structures of (a) **5** and **6** and (b) **7**. Unless stated otherwise, carbon atoms are shown in grey, hydrogen atoms in white, oxygen atoms in red, nitrogen atoms in blue, cobalt or nickel atoms in pink and copper atoms in green.

2. Structure of 6-(pyrazin-2-yl)-1,3,5-triazine-2,4-diamine 3 with Ni(NO₃)₂. $6(H_2O)$ (Complex 9). Ligand 3 chelates with Ni(II) in the ratio 2:1 to form a cationic complex 9. Crystals of this complex are grown in MeOH/Et₂O and belong to the triclinic space group $P\overline{1}$. Perspective views of the crystal structure are shown in Fig. 2 and other crystallographic data is provided in Table 1. As expected, the pyrazinyl-substituted diaminotriazine ligand **3** reacts with Ni(II) to form a mononuclear complex, which then engages in multiple directed in the hydrogen bonding part by DAT groups resulting in [Ni(pzDAT)₂(NO₃)(MeOH)].(NO₃) structure for complex 9 (Fig. S1). Ni(II) displays a distorted octahedral coordination geometry with the two DAT groups in trans conformation, and the nitrato and methanol in *cis* conformation. The Ni atom and one pair of coordinated N atoms from different DAT groups gives a N-Ni-N angle of 169.3(2)°. The other coordinated pair of N atoms of pyridine rings has N-Ni-N angle of 96.6(1)°. The pyrazinyl and DAT rings of one of the ligand is nearly coplanar and the other is distorted at an angle of 14.1(1)°. As anticipated, DAT groups engage in intermolecular N-H...N hydrogen bonding according to type I (Chart 2) (average distance = 3.058 Å) to produce tapes of alternating complexes (Δ and λ) (Fig. 2a). These tapes are further connected to form the three-dimensional structure by multiple hydrogen bonds involving bridging of nitrate and N-H^{...}O_{methanol} (Fig. 2b). Selected hydrogen bonds and angles are given in Table

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S2. It is worth noticing that intramolecular $N-H^{...}O$ hydrogen bonds involving the free hydrogen atom from $-NH_2$ group and oxygen atom from methanol reinforce the geometry of coordination of the complex. Moreover, the observed structure reflects intra- and intercomplex interactions which are strongly directed by the multiple hydrogen bonds involving DAT groups and nitrate counterions. However, unpredictably, a methanol molecule is coordinated to the nickel atom during the crystallization process.



Fig. 2. Views of the crystal structure of the bis[6-(pyrazin-2-yl)-1,3,5-triazine-2,4-diamine](methanolato)(nitrato-*O*)Nickel(II) nitrate **9** grown from MeOH/Et₂O. Hydrogen bonds are represented by broken lines. Unless stated otherwise, carbon atoms are shown in grey, hydrogen atoms in white, oxygen atoms in red, nitrogen atoms in blue and nickel atoms in cyan. (a) Alternating arrangement of complex **9** and its enantiomer joined together by hydrogen bonding of DAT groups according to motif **I** and by free N-H^{...}O_{nitrate}. to generate chains (b) Chains are maintained together by hydrogen bonding involving bridging nitrates to form the three-dimensional structure. For clarity a chain is marked in green.

	9	10
Formula	[(Ni(C7H7N7)2(MeOH)(NO3)](NO3)	Cu(C7H7N7)2(NO3)2
Mr	593.16	565.95
Crystal size/mm ³	$0.15 \times 0.14 \times 0.1$	$0.17 \times 0.11 \times 0.06$
Crystal system	Triclinic	Triclinic
radiation	GaKα	GaKα
λ (Å)	1.34139	1.34139
F(000)	608.0	574.0
Space group	$P\overline{1}$	PĪ
<i>a</i> (Å)	7.9534(3)	8.3550(4)
<i>b</i> (Å)	10.3562(4)	10.4080(5)
<i>c</i> (Å)	14.6063(6)	12.2948(5)
α (deg)	100.637(2)	93.120(2)
β (deg)	104.771(2)	96.497(2)
γ (deg)	97.685(2)	97.972(2)
$V(\text{\AA}^3)$	1122.45(8)	1049.33(8)
Ζ	2	2
$ ho_{ m calc} g/cm^3$	1.755	1.791
<i>T</i> (K)	100	100
μ (mm ⁻¹)	5.175	6.058
Measured reflns	26335	36360
independent reflns	5040	3582
Rint	0.0691	0.0681
observed reflns $I > 2\sigma(I)$	4308	3410
$R_{l}, I \geq 2\sigma(I)$	0.0478	0.0623
R_1 , all data	0.0594	0.0642
$\omega R_2, I > 2\sigma (I)$	0.1144	0.1645
ωR_2 , all data	0.1243	0.1677
GoF	1.038	1.097

Table 1. Crystallographic Data for 9 and 10

2. Structure of 6-(pyrazin-2-yl)-1,3,5-triazine-2,4-diamine **3** with $Cu(NO_3)_2.(H_2O)$ (Complex **10**). In complex **9**, nitrate plays a structural role by serving as a counterion and by forming multiple hydrogen bonds to stack the tapes together. Moreover, we have seen that methanol molecule is not only playing as a solvent of crystallization but also as a ligand. To probe the importance of these effects, we prepared the 2:1 complex of ligand **3** with Cu(NO₃)₂.(H₂O) under the same conditions. Crystals of **10** were grown from MeOH/Et₂O and proved to belong to the triclinic space group $P\overline{1}$. Views of the crystal structure are shown in Fig. 3, and other crystallographic data are summarized in Table 1. The chemical composition of complex **10**, with 2:1 pzDAT-to-Cu ratio, is

[Cu(pzDAT)₂(NO₃)].(NO₃) (Fig. S2). In the structure, DAT groups of ligand **3** are positioned in *trans* conformation as expected and the nitrato is in an equatorial position creating a typical Cu(II) coordination geometry that can be described as a distorted bipyramid. The other nitrate ion is present outside the coordination sphere. The Cu atom and two coordinated N atoms from different DAT groups are almost linear with N-Cu-N angle of 177.5(2)°. The other coordinated pair of N atoms forms N-Cu-N angle of 128.7(6)°. The pyrazinyl and DAT rings of both ligands are nearly coplanar with an average torsional angle of 2.76°. As anticipated, complex 10 self-assembles to form tapes via hydrogen bonding of DAT groups according to the modified version of standard motif I (average distance N-H^{...}N = 3.109 Å) (Fig. 3a). The overall molecular organization involves N-H.^{..}O hydrogen bonding involving bridging of nitrato ligands and nitrate counterions and π - π stacking (3.835 Å) of pyrazinyl and DAT rings to generate the threedimensional structure (Fig. 3b). Details of the hydrogen bonds and their angles are provided in Table S3. Again, the results confirm that complex 10 can be obtained with predictable number of ligands **3** as well as a single well-defined constitution. The DAT groups and the counterions play a key role in directing molecular association by engaging in multiple hydrogen bonds. However, the topology of complexes can not be easily predicted owing to the diverse coordination geometries associated with Cu(II). As can be seen, in the structure of complex 10, methanol molecules used in the crystallization are not involved in coordination with the Cu(II).



Fig. 3. Views of the crystal structure of the bis[6-(pyrazin-2-yl)-1,3,5-triazine-2,4diamine](nitrato-*O*)Copper(II) nitrate 10 grown from MeOH/Et₂O. Hydrogen bonds are represented by broken lines. (a) Alternating arrangement of complex 10 and its enantiomer joined together by hydrogen bonding of DAT groups according to the modified version of motif I to generate tapes. Tapes are maintained together by hydrogen bonding involving bridging nitrate counterion and nitrato ligand to form the 3Dnetworks. Furthermore, π -stacking reinforce the structure. (b) View showing stacking of tapes to form the three-dimensional structure. Carbon atoms are shown in grey, hydrogen atoms in white, oxygen atoms in red, nitrogen atoms in blue and copper atoms in green.

Comparing the structures of compounds **5-7** and **8-10**, we note that their structures are similar to each other and the association of these complexes is mainly dictated by the self-assembly *via* hydrogen bonds of the DAT groups with typical association motifs. In the conditions of preparation of complexes **8-10**, the nitrogen atom of the pyrazinyl ring in the DAT group does not participate in coordination to metal ions. Within the six crystal structures analyzed by SCXRD, methanol molecules are observed only in the crystal structure of complex **9**. In this case, methanol not only acts as a solvent of crystallization but also as a ligand which participates in the first nickel coordinating sphere.

The phase purity of complexes **9** and **10** were evaluated by powder X-ray diffraction (PXRD) which confirmed the absence of secondary phase. Fig. S4 shows the comparison of the measured PXRD (in black) and the simulated patterns (in red) obtained from the

SCXRD. As can be seen the two patterns are matching well which confirms the phase purity of the bulk samples **9** and **10**. Together, the SCXRD and PXRD demonstrate that samples **9** and **10** can be prepared in a single phase.

Thermal behaviours of complexes **8-10** were studied by thermogravimetric analysis (TGA). The TG curves of these compounds are shown in Fig. S5. Compounds **8-10** show similar decomposition curves with two main weight loss steps in the range of \sim 32-39% at 300-306 °C and 36-46% at 305-795 °C which are attributed to the de-coordination of the nitrates and ligands to produce the final residue. In the case of complex **9**, an additional step is observed in the range 45-107 °C with net mass loss of \sim 3 % that is assigned to the loss of methanol.

UV-visible Spectroscopy and Cyclic Voltammetry

For successful utilization of the synthesized complexes as photocatalysts in HER, they must show absorption in the visible region of the spectrum and must be able to accept an electron from the excited photosensitizer. To better understand the electronic properties of compounds 2-10, we measured their UV-Vis and cyclic voltammetry (CV). UV-Vis spectra of these compounds were measured at room temperature in DMF solutions at concentration 8.8 x 10⁻⁶ M (Fig. 4). The UV-Vis spectra in DMF solution of the free ligands 2 and 3 displayed two absorption bands between 200-350 nm which can be attributed to the π - π * electronic transitions of aromatic rings. In the case of complexes 5-10, the presence of transition metal ions produced significant variation in the intensities of the absorption bands in the UV region of the spectra but only a slight shift towards lower energy as compared to the absorption bands of free ligands. This red shift is well supported by literature.^[43] The transitions in the visible region (400-900 nm) are attributed to weak d-d transitions. Selected data (maximum absorption wavelengths, λ_{max} , molar absorption coefficients, ε) are summarized in Table 2. As d-d transitions are weak, we also recorded the UV-Vis of **5-10** at room temperature in DMF solutions at concentration $8.8 \times 10^{-3} \text{ M}$ to be able to see clearly the absorption bands (see inset Fig. 4).

Parameters	DMF			
	Conc = 8.8 x 10 ⁻⁶ From 250 to 900 nm		Conc = 8 x 10 ⁻³ From 350 to 900 nm	
Sample	λ _{max} (nm)	ε (mol ⁻¹ dm ³ cm ⁻¹)	$\lambda_{max}(nm)$	ε (mol ⁻¹ dm ³ cm ⁻¹)
2	268	$1.21 \mathrm{x} \ 10^4$		
	288(sh)	6.17 x 10 ³		
3	274	2.49 x 10 ⁴		
	320(sh)	$4.19 \ge 10^3$		
5	273	3.21 x 10 ⁴	404	60
	310(sh)	1.35 x 10 ⁴	444	49
	350(sh)	$4.97 \ge 10^3$		
6	275	2.90 x 10 ⁴	492	6
	311(sh)	1.09 x 10 ⁴	685	2
			882	10
7	275	2.17 x 10 ⁴	658	19
	304(sh)	8.59 x 10 ³		
	275	4.09 x 10 ⁴	405	26
8	302(sh)	1.95 x 10 ⁴	553	3
	393(sh)	2.36 x 10 ³		
9	279	4.39 x 10 ⁴	514	4
	314(sh)	1.87 x 10 ⁴	701	1
10	275	4.24 x 10 ⁴	412	4
	308	$1.50 \ge 10^4$	663	5

Table 2. UV-Vis spectroscopy data of 2 and 3 and 5-10 in DMF solution

sh: shoulder



Fig. 4. UV-Vis spectra of **2-3** and **5-10** in DMF solution at room temperature at a concentration of 8.8 x 10^{-6} M. Inset is shown the visible region (450-800 nm) at a concentration 8 x 10^{-3} M (a) **2** and **5-7** and (b) **3** and **8-10**.

The electrochemical behavior of ligands 2 and 3 and complexes 5-10 were measured using CV in DMF solutions at a concentration of 1 mM for ligands and complexes with 1 M TBA-PF₆ (tetrabutylammonium hexafluorophosphate) as supporting electrolyte at a scan rate 100 mV/s (Fig. 5). A summary of the wave peaks of these compounds are provided in Table 3. Cyclic voltammograms of the complexes exhibit oxidation and reduction peaks, which are attributed to the different redox states of the metal ions and reduction of the ligands.

Cyclic voltammograms (CV) of ligands **2** and **3** shows two reversible redox waves at -2.22 and -2 V, and -2.31 and -1.72 V versus the Saturated Calomel Electrode (SCE), respectively. These redox signals can be assigned as the two consecutive one electron redox reaction of ligands. The CV of complex **5** shows three sequential redox waves at -2, -1.34 and at -1.15 V out of which, the first and the third redox waves are reversible. The first redox signal can be assigned to be ligand based and the third signal can be of a Co^{VII} couple. In the CV of **8**, there are four reversible redox waves occurring at -1.89, -1.71, -1.54 and -0.93 V, from which the second wave is indistinguishable due to overlapping of waves. The first and the second redox signal can be assigned as ligand based and the third and fourth

signal are for Co^{I/0} and Co^{II/1} couple respectively. ^[44] The CV of complexes **6** and **9** with nickel (II) metal ion shows two quasi-reversible redox waves at -1.30 and -1.05 V, and -1.54 and -0.88 V versus SCE, respectively. These redox signals can be assigned to a first ligand reduction and a Ni^{VII} couple, respectively. In case of the complexes **7** and **10** with copper (II) metal ion, only the ligand based redox waves at -1.96 and -1.19 V respectively, appears to be quasi reversible but its not completely distinct due to overlapping of the waves. Whereas in case of the metal ion, no quasi reversible redox waves were observed. However, Cu (II) metal ions gets reduced at 0.0063 and 0.089 V for **7** and **10** respectively, it further undergoes oxidation at 0.32 and 0.42 V respectively, Vs SCE. This might be due to the dimerization of copper complexes. ^[45] These values have been found comparable to those of 2,2'-bipyridine complexes reported in literature (Table S4).^[44, 46, 47] The possibility of multiple redox states for our complexes indicates their ability to be employed as redox catalysts especially for HER.

Compound	E0x1/2 [V]	Ered1 _{1/2} [V]	Ered2 _{1/2} [V]	Ered3 _{1/2} [V]	Ered4 _{1/2} [V]
2		-2	-2.22		
3		-1.72(74)	-2.31(38)		
5		-1.15(18)	-1.34(02)		
6		-1.05(20)	-1.30(32)	-1.74(56)	-1.99(68)
7	0.13(24)	-1.04(20)	-1.55(52)		
8		-0.93(96)	-1.54(04)	-1.71(99)	-1.89(02)
9		-0.88(91)	-1.54(39)	-1.90(61)	
10	0.09(95)	-0.57(27)	-0.85(80)		

Table 3. Redox data of the ligands 2 and 3 and the complexes 5-10 in DMF solution



Conditions: 1 M TBA-PF₆ as supporting electrolyte, scan rate: 100 mV/s, glassy carbon working electrode (1 mm diameter), Pt counter electrode and Ag wire as the pseudo-reference electrode.

Catalytic Hydrogen Evolution

In order to study the effect of substituent and metal ion on the suitability of complexes **5**-**10** as photocatalysts for hydrogen production, we examined their photocatalytic properties. The hydrogen production displayed by 1 mM of each complex **5**-**10** in DMF using 1 M triethanolamine (TEOA) as the sacrificial electron donor, $0.1 \text{ mM Ru}^{(II)}(\text{bpy})_3(\text{PF}_6)_2$ as the photosensitizer (PS) and aqueous 0.1M HBF₄ as the proton source at an apparent pH between 8-9 was recorded (Fig. 6). The experiment was conducted for 15 hours (after which no further change in photocatalytic activity is observed) and the hydrogen production rate, TON and TOF have been reported in millimoles per hour (mmol/h), moles of hydrogen per moles of PS and mmol of hydrogen per mole of PS per minute^[33,48], respectively, for each compound (Table 4).

In the visible region, under blue irradiation (445 nm) the production of H₂ starts after turning on the light. This irradiation wavelength is sufficient to excite the photosensitizer $[Ru^{II}(bpy)_3](PF_6)_2$. The proposed mechanism for the process is shown in Fig. S7. ^[49,50] Benjamin Probst and group studied the effect of pH on the photocatalytic production of hydrogen, under different pH conditions using reference catalyst $[Co(dmgH)_2]$. It was observed that although acetic acid was the main proton source, but photocatalysis also occurred without acetic acid, at a very slow rate, due to the residual protons coming from water present in the system and the decomposition of TEOA. Similarly, we can deduce that in the current photocatalysis experiment, HBF₄ is the major source of proton while water and TEOA are acting as a subsidiary proton source.^[51] Control experiments were conducted in the presence of PS/TEOA alone with and without light and no H₂ production was recorded which was consistent with the previous results.^[52] We also conducted blank experiments with Co(NO₃)₂. 6H₂O, Ni(NO₃)₂. 6H₂O, Cu(NO₃)₂. 2.5H₂O, **2** (pyDAT) and **3** (pzDAT) which displayed TON's of 9.96, 18.54, 0.58, 5.25 and 0.12 mol_{H2} mol_{PS}⁻¹ respectively (Fig. S9, S10). Amongst the synthesized complexes, Cu complex **7** and Co

complex **8** display TON's of 72 and 37 $\text{mol}_{\text{H2}} \text{mol}_{\text{PS}}^{-1}$. However, the remaining complexes don't prove to be efficient photocatalysts towards HER.

The replacement from the pyDAT (complex 5) to pzDAT (complex 8) significantly modifies the capacity of Co(II) complexes in the production of H₂ with TONs that almost increase to three times. However, for copper complexes 7 and 10, pyDAT based Cu(II) complex 7 has TON almost thirty five times higher, than its pzDAT analogue complexes 10. Since, different combinations of metals and ligands result in different TONs and TOFs, we can suggest that the combined effect of the metal ion and the ligand leads to the overall hydrogen production. Hence, the variation of substituent/ligand and the metal ion affects the hydrogen production rate in photocatalytic experiments. The maximum TON and hydrogen production rate of 72 mol_{H2} mol_{PS}⁻¹ and 0.48mmol of H₂ per hour, respectively, observed for complex 7, is moderately higher than the TON and the H₂ production rate of the literature standard cobaloxime catalyst, which has 68 and 0.45 mmol/h values, respectively (Fig. 6).

Amid all the tested complexes, Cu and py-DAT proved to be the most effective combination as a photocatalyst to produce hydrogen. This can be due to the inherent nature of Cu metal which displays diverse valence states, well-defined coordination chemistry and special d-d spin-allowed transitions. ^[53,54] However, Cu complex **10** with pzDAT doesn't display good H₂ production. This indicates that for H₂ production along with the metal, the organic part of the complex also plays a major role and the combined effect of the two leads to the final TON and TOF values. The values obtained for hydrogen production are better than some of the previously reported copper based photocatalysts. For instance, Wu and coworkers synthesized { $[Cu^{I}Cu^{II}_{2}-(DCTP)_{2}]NO_{3}\cdot 1.5DMF$ }_n 3D framework where DCTP = 4' - (3,5 - dicar - boxyphenyl) - 4,2':6',4'' - terpyridine and observed its photocatalyticactivity in UV-visible light in the presence of methanol as sacrificial agent and H₂PtCl₆ as co-catalyst. 0.032 mmol/g/h was the observed hydrogen production rate.^[55] Song and group synthesized C₄₂H₄₆CuN₆O₂₁S₄ compound, the hydrogen production rate of 0.006 mmol/h was observed in visible light using TEOA as sacrificial agent.^[56] The same group later synthesized $C_{21}H_{21}CuN_3O_{10}S_2$ metal organic framework and observed a hydrogen production rate of 0.073mmol/h using TEOA as sacrificial electron donor and platinum as co-catalyst in visible light.^[57] Majee and coworkers synthesized [Cu(DQPD)]₂ photocatalyst (where DQPD = deprotonated N2,N6-di(quinolin-8-yl)pyridine-2,6-dicarboxamide) that produced 427 μ mol H₂/h/ μ mol PS, using a PS (fluorescein) concentration of 2 mM and TEA as a sacrificial electron donor.^[58]

Table 4 Turnover number and Turnover frequency maximal for complexes 5-10

Compound	Molecular Formula	H ₂ production (mmol/hour)	TON _{max}	TOF _{max} (min ⁻¹)
std.*	[Co(dmgH) ₂ (py)Cl]	0.45	68	1892
5	Co(pyDAT) ₂ (NO ₃) ₂	0.11	16	307
6	Ni(pyDAT) ₂ (NO ₃) ₂	0.14	21	793
7	Cu(pyDAT) ₂ (NO ₃) ₂	0.48	72	314
8	Co(pzDAT) ₂ (NO ₃) ₂	0.25	37	841
9	Ni(pzDAT) ₂ (MeOH)(NO ₃) ₂	0.06	9.1	215
10	$Cu(pzDAT)_2(NO_3)_2$	0.01	2.1	90

*std. stands for literature standard *viz*. cobaloxime; TON is reported in moles of hydrogen per mole of PS and TOF in mmol of hydrogen per mole of PS per minute.



Fig. 6. Turn-over number with respect to PS for hydrogen evolution reaction of complexes **5-10** and literature standard (**std:** [Co(dmgH)₂(py)Cl]).

CONCLUSIONS

A series of functionalized transition metal ion complexes 8-10, $M(PzDAT)(NO_3)_2$, with molecular structures that resemble $M(bpy)_2(NO_3)_2$ was easily prepared by a facile procedure. The solid-state structures of complexes 8-10 reveals that all cation complexes have 2:1 ligand to metal ion ratio. In the solid-state the molecular organization of the complexes is mainly dictated by the coordination modes of the ligands and the hydrogen bonds involving the DAT groups with reliable patterns. An analysis of the thermal stability and electronic properties of complexes 8-10 synthesized herein and pyridine DAT based complexes 5-7, $(pyDAT)(NO_3)_2$ previously synthesized indicates the complexes to be stable up to ~300 °C and their ability to be employed as redox catalysts for HER respectively. An investigation on the effect of substituent and metal ion on the catalytic activity of complexes **5-10** for hydrogen evolution reaction designates copper complex **7** to the best displaying the highest TON viz. 72 moles of hydrogen per mole of PS suggesting Cu and py-DAT to be the best amongst the synthesized combinations of ligands and metal ions. This value observed for complex 7 (0.48mmol/h) is higher compared to some previously reported Cu based catalysts (0.032 mmol/g/h, 0.006 mmol/h, 0.073 mmol/h, 427 μmol H₂/h/μmol PS) ^[55-58].

ASSOCIATED CONTENT

Appendix A. Supplementary data

CCDC 1918901-1918902 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or email: deposit@ccdc.cam.ac.uk.

Supporting Information. Supporting Information. The supporting Information is available free of charge via the internet at Elsevier Publications website at DOI:

Infrared data, additional crystallographic details, PXRD patterns, TGA curves, Cyclic voltammograms and Emission spectrum.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- [1] N. S. Lewis, D. G. Nocera, Proc. Natl. Acad. Sci. 103 (2006) 15729.
- [2] M. Wang, L. Chen, L. Sun, Energy Environ. Sci. 5 (2012) 6763.
- [3] M. Serra, J. Albero, H. García, ChemPhysChem 16 (2015) 1842.
- [4] J. A. Turner, Science 305 (2004) 972.
- [5] J. Barber, Chem. Soc. Rev. 38 (2009) 185.

[7] Y. Sun, J. P. Bigi, N. A. Piro, M. L. Tang, J. R. Long, C. J. Chang, J. Am. Chem. Soc. 133 (2011) 9212.

^[6] T. R. Cook, D. K. Dogutan, S. Y. Reece, Y. Surendranath, T. S. Teets, D. G. Nocera, Chem. Rev. 110 (2010) 6474.

[8] H. B. Gray, Nat. Chem. 1 (2009) 112.

[9] J. R. McKone, S. C. Marinescu, B. S. Brunschwig, J. R. Winkler, H. B. Gray, Chem. Sci. 5 (2014) 865.

[10] A. J. Esswein, D. G. Nocera, Chem. Rev. 107 (2007) 4022.

[11] M. G. Pfeffer, T. Kowacs, M. Wächtler, J. Guthmuller, B. Dietzek, J. G. Vos, S. Rau, Angew. Chem. 54 (2015), 6627.

[12] J. Xie, C. Li, Q. Zhou, W. Wang, Y. Hou, B. Zhang, X. Wang, Inorg. Chem. 51 (2012)6376.

[13] C. L. Pitman, A. J. Miller, ACS Catal. 4 (2014), 2727.

[14] P. N. Curtin, L. L. Tinker, C. M. Burgess, E. D. Cline, S. Bernhard, Inorg. Chem. 48 (2009) 10498.

[15] A. Fihri, V. Artero, M. Razavet, C. Baffert, W. Leibl, M. Fontecave, Angew. Chem.47 (2008) 564.

[16] T. M. McCormick, B. D. Calitree, A. Orchard, N. D. Kraut, F. V. Bright, M. R. Detty, R. Eisenberg, R., J. Am. Chem. Soc.132 (2010), 15480.

[17] M. Nippe, R. S. Khnayzer, J. A. Panetier, D. Z. Zee, B. S. Olaiya, M. Head-Gordon,

C. J. Chang, F. N. Castellano, J. R. Long, Chem. Sci. 4 (2013) 3934.

- [18] M. P. McLaughlin, T. M. McCormick, R. Eisenberg, P. L. Holland, ChemComm 47 (2011) 7989.
- [19] M. A. Gross, A. Reynal, J. R. Durrant, E. Reisner, J. Am. Chem. Soc. 136 (2013) 356.

[20] E. Rousset, I. Ciofini, V. R. Marvaud, G. S. Hanan, Inorg. Chem. 56 (2017) 9515.

[21] A. Jacques, O. Schott, K. Robeyns, G. S. Hanan, B. Elias, Eur. J. Inorg. Chem. 2016 (2016) 1779.

[22] E. Rousset, D. Chartrand, I. Ciofini, V. Marvaud, G. S. Hanan, ChemComm 51 (2015)9261.

- [23] O. Schott, A. K. Pal, D. Chartrand, G. S. Hanan, ChemSusChem 10 (2017) 4436.
- [24] A. Duong, A. V. Métivaud, T. Maris, J. D. Wuest, Cryst. Growth Des. 11 (2011) 2026.
- [25] S. G. Telfer, J. D. Wuest, Cryst. Growth Des. 9 (2009) 1923.
- [26] A. Duong, V. Métivaud, T. Maris, J. D. Wuest, Cryst. Growth Des. 11 (2011), 2026.
- [27] A. Duong, T. Maris, J. D. Wuest, Inorg. Chem. 50 (2011) 5605.
- [28] A. K. Pal, A. Duong, J. D. Wuest, G. S. Hanan, Polyhedron. 108 (2016) 100.

[29] A. Duong, S. Rajak, A. A. Tremblay, T. Maris, J. D. Wuest, Cryst. Growth Des. 19 (2019) 1299.

[30] J. Wu, J. Jung, P. Zhang, H. Zhang, J. Tang, B. Le Guennic, Chem. Sci. 7 (2016) 3632.

[31] R-R Duan, L. Wang, W-Q. Huo, S. Chen, X-H. Zhou, J. Coord. Chem. 67 (2014) 2765.

[32] K. E. Maly, E. Gagnon, T. Maris, J. D. Wuest, J. Am. Chem. Soc. 129 (2007) 4306.

[33] S. Rajak, O. Schott, P. Kaur, T. Maris, G. S. Hanan, A. Duong, RSC Adv. 9 (2019)28153.

[34] S. Rajak, O. Schott, P. Kaur, T. Maris, G. S. Hanan, A. Duong, Int. J. Hydrog. Energy. https://doi.org/10.1016/j.ijhydene.2019.11.141.

[35] S. Rajak, M. Mohan, A. A. Tremblay, T. Maris, S. Leal do Santos, E. C. Venancio, S.Ferreira Santos, A. Duong, ACS Omega 4 (2019) 2708.

[36] F. H. Case, E. Koft, J. Am. Chem. Soc. 81 (1959), 905.

[37] C-W. Chan, D. M. P. Mingos, A. J. White, D. J. Williams, Polyhedron 15 (1996), 1753.

[38] G. M. Sheldrick, Acta Cryst. A 71 (2015) 3.

[39] G. M. Sheldrick, Acta Cryst. C 71 (2015) 3.

[40] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock,

L. Rodriguez-Monge, R. Taylor, J. V. D. Streek, P. A. Wood, J. Appl. Crystallogr. 41 (2008) 466.

[41] N. G. Connelly, W. E. Geiger, Chem. Rev. 96 (1996) 877.

[42] C. D. Lentz, O. Schott, T. Auvray, G. S. Hanan, B. Elias, Inorg. Chem. 56 (2017), 10875.

[43] F. Gärtner, D. Cozzula, S. Losse, A. Boddien, G. Anilkumar, H. Junge, T. Schulz, N. Marquet, A. Spannenberg, S. Gladiali, Chem.: Eur. J. 17 (2011) 6998.

[44] S-P. Luo, L-Z. Tang, S-Z. Zhan, Inorg. Chem. Commun. 86 (2017) 276.

[45] Z. Guo, F. Yu, Y. Yang, C. F. Leung, S. M. Ng, C. C. Ko, C. Cometto, T. C. Lau, M. Robert, ChemSusChem 10 (2017) 4009.

[46] B. J. Henne, D. E. Bartak, Inorg. Chem. 23 (1984) 369.

[47] H-J. Park, J-H. Kwon, T-S. Cho, J. M. Kim, H. H. In, C. Kim, S. Kim, J. Kim, S. K. Kim, J. Inorg. Biochem. 127 (2013) 46.

[48] T. Auvray, R. Sahoo, D. Deschênes, G. S. Hanan. Dalton Trans. 48 (2019) 15136.

[49] V. Artero, M. Chavarot-Kerlidou, M. Fontecave, Angew. Chem. 50 (2011) 7238.

[50] N. Queyriaux, R. T. Jane, J. Massin, V. Artero, M. Chavarot-Kerlidou, Coord. Chem. Rev. 304-305 (2015) 3.

- [51] B. Probst, C. Kolano, P. Hamm, R. Alberto, Inorg. Chem. 48 (2009) 1836.
- [52] R. W. Hogue, O. Schott, G. S. Hanan, S. Brooker, Chem. Eur. J. 24 (2018) 9820.
- [53] H. T. Lei, H. Y. Fang, Y. Z. Han, W. Z. Lai, X. F. Fu, R. Cao, ACS Catal. 5 (2015)5145.
- [54] L. Li, S. Zhu, R. Hao, Jia-Jun Wang, En-Cui Yang, Xiao-Jun Zhao, Dalton Trans. 47 (2018) 12726.
- [55] Z. L. Wu, C. H. Wang, B. Zhao, J. Dong, F. Lu, W. H. Wang, W. C. Wang, G. J. Wu,
- J. Z. Cui, P. Cheng, Angew. Chem. Int. Ed. 55 (2016) 4938.
- [56] T. Song, L. Zhang, P. Y. Zhang, J. Zeng, T. T. Wang, A. Ali, H. P. Zeng, J. Mater. Chem. A 5 (2017) 6013.
- [57] T. Song, P. Y. Zhang, J. Zeng, T. T. Wang, A. Ali, H. P. Zeng, Int. J. Hydrogen Energy 42 (2017) 26605.
- [58] K. Majee, J. Patel, B. Das, S. K. Padhi, Dalton Trans. 46 (2017) 14869.

Graphical Abstract - Pictogram



Graphical Abstract Synopsis

Design, synthesis and characterization of pyrazinyl diaminotriazine complexes and their comparison with pyridyl diaminotriazine based complexes for photocatalytic activity towards hydrogen evolution reaction.

Credit Author Statement

Adam Duong: Supervision, Project administration, Conceptualization, Methodology, Writing- original draft

Sanil Rajak: Synthesis, Investigation, Interpretation of results

Olivier Schott: Supervision of Hydrogen Evolution Reaction (HER) study and analysis of the associated data

Prabhjyot Kaur: Writing- Reviewing and Editing, Analysis of results

Thierry Maris: Single Crystal X-ray Diffraction (SCXRD) data collection

Garry S. Hanan: Provided his laboratory facility to conduct HER and CV (Cyclic Voltammetry) studies