

# Multiple Routes for the Synthesis of Dimerized 3-Substituted-2-Oxindoles Employing Proton-Coupled Electron Transfer

Harapriya Behera, Shivani Ahlawat, and Amit Paul\*

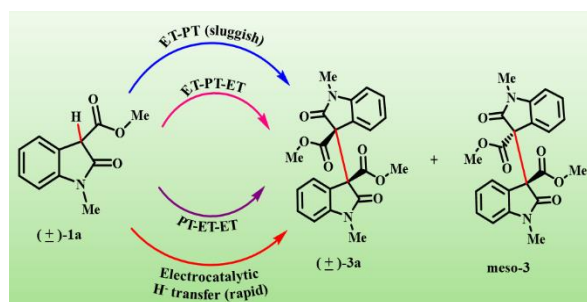
Department of Chemistry, Indian Institute of Science Education and Research (IISER), Bhopal, MP 462066

Email: apaul@iiserb.ac.in

Received: August 22, 2024 | Accepted: September 12, 2024 | Published online: September 18, 2024

## Abstract

We discussed four different synthetic routes for the dimerization of 3-carboxylate-2-oxindole (**1a**). The order of efficiency was: Stepwise electron transfer (ET)-proton transfer (PT) < Stepwise-ET-PT-ET < Stepwise-PT-ET-ET < TEMPO<sup>+</sup>-catalyzed hydride (H<sup>-</sup>) (2e<sup>-</sup> & H<sup>+</sup>) transfer. We also discussed dimerization of 3-alkyl-2-oxindole (**4a**), which followed a kinetically slower TEMPO<sup>+</sup>-catalyzed 1e<sup>-</sup> transfer mechanism, since pK<sub>a</sub> of pseudobenzyl proton of **4a** is significantly higher than that of **1a**.

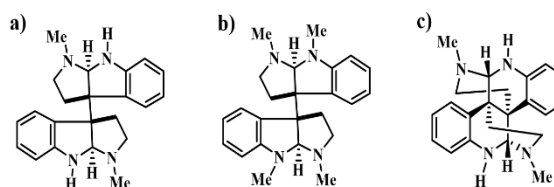


**Keywords:** Dimerization, Proton-Coupled Electron Transfer, Hydride Transfer, 3-Substituted-2-Oxindole

## 1. Introduction

Mother nature finds efficient routes for the synthesis of natural products, and a symphony can be found in natural product synthesis. Hence, scientists are always on the quest to understand nature. In this regard, dimeric hexapyrrolo[2,3-b] indole alkaloids such as chimonanthine, folicanthine, calycanthines are important natural products (Scheme 1).<sup>1</sup> A closer look at these natural products reveals that the dimerization of 3-substituted-2-oxindoles were an important component towards the synthesis of these natural products. On the other hand, Proton-Coupled Electron Transfer (PCET) was discovered by Thomas J. Meyer in 1980, wherein the key discovery was concerted electron (e<sup>-</sup>) and proton (H<sup>+</sup>) transfer in a single step.<sup>2, 3</sup> The beauty of this discovery lies in the fact that in this process, a neutral species is transferred, and a high-energy intermediate formation can be avoided for a reaction to occur. In due course, it was realized that nature exercises this process often to avoid excess activation barriers for a reaction to occur. Thereafter, the concept of PCET has now been expanded, and it involves different types of electron and proton transfer, such as stepwise electron transfer (ET) and proton transfer (PT), concerted electron-proton transfer

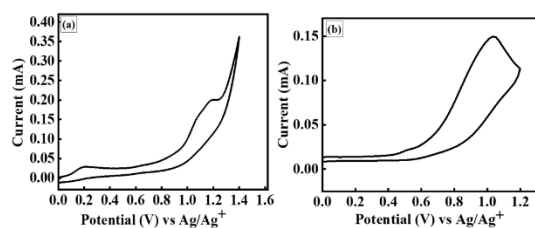
(EPT), hydrogen atom transfer (HAT), hydride (H<sup>-</sup>) transfer, multi-site electron-proton transfer (MS-EPT) etc.<sup>3,4</sup> Each of these pathways has its own advantages and disadvantages. Nevertheless, all these mechanisms are important to understand from a scientific point of view and, even more importantly, for our journey to unravel Mother Nature.



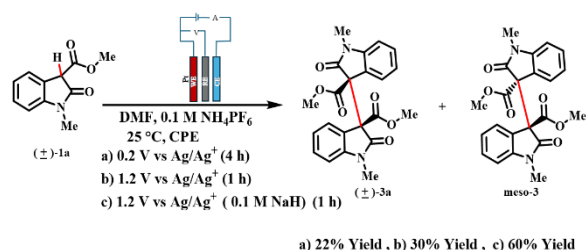
**Scheme 1:** Structures of (a) chimonanthine, (b) folicanthine, and (c) calycanthine.

Recently, electro-organic synthesis has been gaining momentum for organic molecules syntheses since electrode potential acts as an oxidant or reductant and hence avoids the necessity of chemical oxidants/reductants.<sup>5</sup> Furthermore, electro-organic syntheses avoid the use of toxic metals, atom-economical and green in nature. However, the advancement of electro-organic synthesis did not focus much on finding energy-efficient routes utilizing PCET, which may lead to enhancing our understanding about nature's way of natural product synthesis as well. From this

perspective, we summarized our effort to synthesize the dimerized 3-carboxylate-2-oxindoles (**1a**) in four different PCET pathways.<sup>6</sup> We also demonstrate the synthesis of dimerization of 3-alkyl-2-oxindole (**4a**) synthesis utilizing an electro-catalytic pathway.<sup>7,8</sup> The efficiency of these pathways can be arranged in chronological order by connecting the yield of the reaction and understanding of the PCET. The results for this manuscript have been taken from *J. Org. Chem.* **2020**, *85*, 14926; *ACS Catal.* **2023**, *13*, 2118; and partly from *Org. Biomol. Chem.* **2021**, *19*, 9390, wherein organic molecules syntheses were the focal point. However, this manuscript has been presented from a very different scientific viewpoint than that of previously published manuscripts from our group. Herein, the discussion is about the kinetics of different PCET pathways and understanding this viewpoint can enhance the yield of these type of reactions further in the near future.



**Figure 1:** Cyclic voltammetry of 3-carboxylate-2-oxindole (**1a**) (5 mM) at 100 mV/s scan rate on a glassy carbon electrode with 0.1 M  $\text{NH}_4\text{PF}_6$  in DMF. (a) In absence of NaH and (b) in presence of 5 mM NaH.

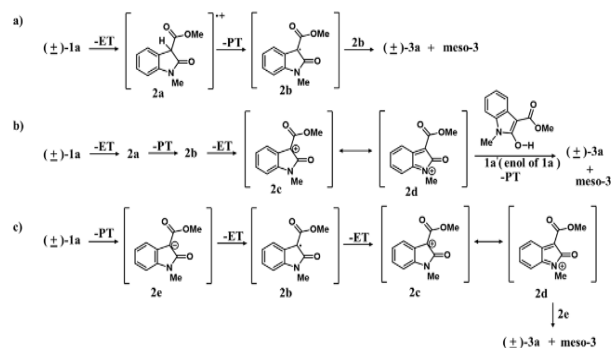


**Scheme 2:** Dimerization of 3-carboxylate-2-oxindole (**1a**) at different electrolysis conditions.

## 2. Results of Dimerization of 3-substituted-2-oxindoles

Dimerization of 3-carboxylate-2-oxindole (**1a**) was achieved by oxidation of **1a** directly on a platinum working electrode employing different electrolytic conditions, which will be discussed. Cyclic voltammetry (CV) of **1a** revealed two irreversible oxidation peaks at 0.17 and 1.14 V vs.  $\text{Ag}/\text{Ag}^+$  reference electrode in dimethyl formamide (DMF) solvent with 0.1 M  $\text{NH}_4\text{PF}_6$  supporting electrolyte (Figure 1a). **1a** also revealed two chemically irreversible oxidation peaks in CV at (+) 0.55 and (+) 1.15 V vs.  $\text{Ag}/\text{Ag}^+$  reference electrode in DMF with 5 mM NaH (base) in 0.1 M  $\text{NH}_4\text{PF}_6$  supporting

electrolyte (Figure 1b). Each of these CV peaks was tentatively assigned for  $1e^-$  oxidation process of **1a**. Thereafter, three important control potential electrolysis experiments were performed. The first experiment was performed in a three-electrodes configuration at (+) 0.2 V vs.  $\text{Ag}/\text{Ag}^+$  (Reference electrode) for 4 h in DMF with 0.1 M  $\text{NH}_4\text{PF}_6$  without the addition of NaH (Scheme 2). Pt plate and Pt wire were taken as working and counter electrodes, respectively. The reaction yield was found to be only 22%. The second experiment was performed in a three-electrodes configuration at (+) 1.2 V vs  $\text{Ag}/\text{Ag}^+$  for 1 h in DMF with 0.1 M  $\text{NH}_4\text{PF}_6$  without the addition of base in the same electrochemical setup (Scheme 2). The yield for the reaction was found to be 30% suggesting higher efficiency than in the previous experiment. The third experiment was performed at (+) 1.2 V vs.  $\text{Ag}/\text{Ag}^+$  in the same setup but with 5 mM NaH (base) for 1 h (Scheme 2). The yield of the third experiment was found to be 60%, suggesting a significant increase in the kinetics of the reaction. At this point, we highlight that the last two yields in three-electrodes configuration were not reported in the original manuscript (*J. Org. Chem.* **2020**, *85*, 14926). Furthermore, an experiment was performed by performing control potential electrolysis at (+) 0.55 V vs  $\text{Ag}/\text{Ag}^+$  for 2 h without the addition of base in the presence of a radical scavenger DPPH (2,2-diphenyl-1-picrylhydrazyl). The experiment revealed the formation of DPPH-**2b** complex which was confirmed by the results of  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and HRMS.<sup>6</sup> This experiment confirmed the formation of a neutral radical species beyond the  $1^{\text{st}}$  peak of CV (Figure 1).



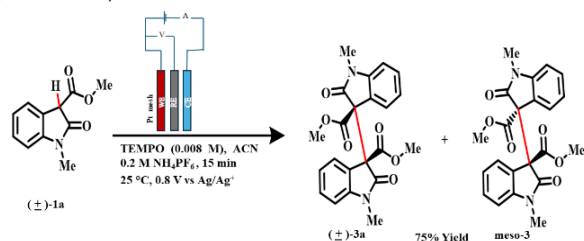
**Scheme 3:** Mechanisms of dimerization of 3-carboxylate-2-oxindole (**1a**) at three different conditions. (a) at (+) 0.2 V vs  $\text{Ag}/\text{Ag}^+$  in absence of base, (b) at (+) 1.2 V vs  $\text{Ag}/\text{Ag}^+$  in absence of base, and (c) at (+) 1.2 V vs  $\text{Ag}/\text{Ag}^+$  in presence of 5 mM NaH (Base).

Since the control experiment suggested the formation of neutral radical species beyond the  $1^{\text{st}}$  peak in CV, the proposed mechanism at (+) 0.2 V vs  $\text{Ag}/\text{Ag}^+$  can be explained as follows: First, an electron transfer (ET) to the electrode from **1a** generated a radical cation species (**2a**) (Scheme 3a). The  $\text{pK}_a$  of **2a** is significantly lower than that of **1a** due to high electron deficiency in **2a** compared to **1a**, and hence, it loses the proton (PT) at 3-position immediately to generate a neutral radical species (**2b**) (Scheme 3a). Thereafter, dimerization of **2b** produced the dimerized 3-

carboxylate-2-oxindole (**3a**) (22% yield after 4 h of electrolysis) (Scheme 3a). Hence, the mechanism for this reaction follows a stepwise ET-PT pathway, and the yield of the reaction was poor since neutral radical species (**2b**) were in-situ generated; and hence, the concentration of the species was low, which resulted in a lower yield.

The mechanism at (+) 1.2 V vs Ag/Ag<sup>+</sup> in the absence of base has been shown in Scheme 3b. First, an electron transfer (ET) from **1a** to the electrode generated the radical cation species **2a** and thereafter, **2a** lost the proton (PT) to generate **2b**. The second CV peak in Figure 1a was due to the loss of another electron transfer (ET) from **2b**, which resulted in the formation of a cationic species **2c**. **2c** can also be present in another resonance form **2d**. **2c/2d** then reacted with enol form of **1a** (**1a'**), which was present in large excess to form dimeric 3-carboxylate 2-oxindole (**3a**) after losing a proton. Hence, this mechanism was described as a stepwise ET-PT-ET pathway, and this pathway was significantly more efficient than the stepwise ET-PT pathway.

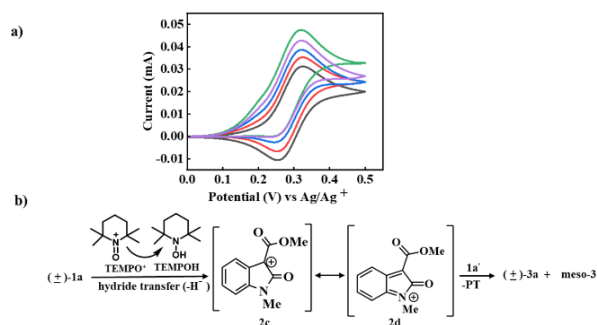
The mechanism in the presence of a base (NaH) at (+) 1.2 V vs. Ag/Ag<sup>+</sup> has been described in Scheme 3c. The strong base removed the proton of **1a** to generate an anionic species **2e** since the pK<sub>a</sub> of **1a** was estimated to be low (~18). The **2e** undergoes two successive ET steps to generate cation species **2c/2d**, and thereafter **2c/2d** reacts with **2e** and results in the formation of a dimeric product (**3a**). The excess potential ((+) 0.4 V) required for the first electron transfer in the presence of base compared to in the absence of base (Figure 1) was due to the excess energy requirement for the removal of an electron from a negatively charged species (**2e**). The overall mechanism in the presence of base can be summarized as a stepwise PT-ET-ET pathway, which is kinetically more facile than that of the previous two pathways (Scheme 3c).



**Scheme 4:** TEMPO<sup>+</sup>-catalyzed dimerization of 3-carboxylate-2-oxindole (**1a**) in acetonitrile (ACN) solvent with 0.2 M NH<sub>4</sub>PF<sub>6</sub> as electrolyte.

Next, an electrocatalytic pathway for the dimerization of **1a** was attempted. In this pathway, **1a** was oxidized at a significantly lower potential ((+) 0.8 V vs. Ag/Ag<sup>+</sup>) than that of direct oxidation of **1a** ((+) 1.2 V vs. Ag/Ag<sup>+</sup>) on the electrode surface by an in-situ generated catalyst, i.e. TEMPO<sup>+</sup> generated from TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy). As shown in Scheme 5, dimerization of **1a** was achieved in acetonitrile (ACN) solvent with 0.008 M

TEMPO and 0.2 M NH<sub>4</sub>PF<sub>6</sub> on Pt mesh working electrode without the addition of any base. 75% yield was obtained in only 15 min of electrolysis without addition of any base. The 0.4 V lowering of potential



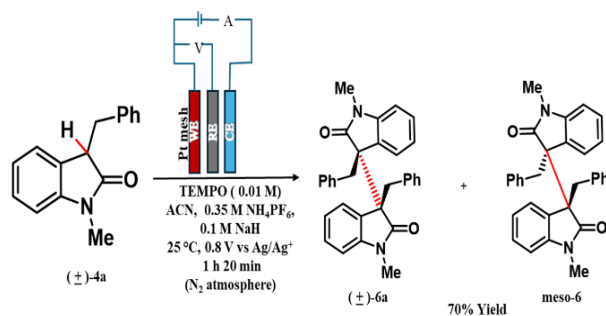
**Scheme 5:** (a) CV of TEMPO at 10 mVs<sup>-1</sup> scan rate on Pt disk electrode in ACN solvent with 0.5 M NH<sub>4</sub>PF<sub>6</sub> electrolyte (0.5 mM) with increasing concentration of **1a** (0 (black), 15 (red), 20 (blue), 25 (purple), and 30 mM (green)) in presence of N<sub>2</sub>, and (b) TEMPO<sup>+</sup> catalyzed mechanism for dimerization of **1a**.

translates to an 9.2 kcal/mol decrease in the energetics of the reaction (calculated from the relation between the Gibbs Free Energy and emf). This remarkable improvement in the kinetics of dimerization of **1a** was not only attributed to the involvement of the electrocatalytic pathway but also due to the avoidance of electrode passivation during electrocatalysis compared to direct oxidation on the electrode surface. Scheme 5a shows a reversible CV for TEMPO in the same solvent and electrolyte (Black curve). During the forward scan, TEMPO (nitroxyl radical) oxidizes to TEMPO<sup>+</sup> (oxoammonium cation) in a chemically reversible process since the peak intensities for forward and reverse scans were same. However, the CVs show that with the increasing addition of **1a**, the oxidation peak intensity increased systematically while the reverse reduction peak decreased. These electrochemical features represent that in-situ generated TEMPO<sup>+</sup> oxidized **1a** and simultaneously TEMPO<sup>+</sup> was reduced to TEMPOH (hydroxylamine) through a hydride transfer (H<sup>-</sup>) mechanism, which was confirmed by further experiments (*vide infra*). During a CV scan for a reversible reaction, at a particular potential, the concentration of [TEMPO<sup>+</sup>]/[TEMPO] is maintained following the Nernst equation. However, consumption of TEMPO<sup>+</sup> due to reaction with **1a** decreases the concentration of TEMPO<sup>+</sup> at the electrode surface, and the electrode tries to regenerate TEMPO<sup>+</sup> by oxidizing excess TEMPO present in the solution. This phenomenon increases the current, and this enhanced current is known as catalytic current. This discussion suggests that the current enhancement during the CV scan is dependent on the reaction kinetics between TEMPO<sup>+</sup> and **1a**. CVs in Scheme 5a show that with increasing concentration of **1a**, current enhances due to 1<sup>st</sup> order dependence of reaction kinetics with **1a**. The data obtained from Scheme 5a and further scan rate-dependent results, the second-order rate

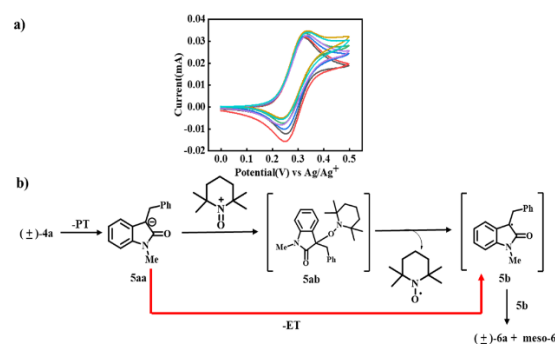
constant for the reaction between TEMPO<sup>+</sup> and **1a** was obtained, and a modest rate constant of 1.2 M<sup>-1</sup> s<sup>-1</sup> was obtained considering 2e<sup>-</sup> transfer process for the catalytic reaction. These kinetic analyses suggested even with modest kinetics, an excellent conversion of **1a** was obtained, and further improvement of reaction kinetics is possible. Next, the mechanism for this reaction was investigated. Electrochemical results ruled out the possibility of a radical intermediate generation. In-situ spectroelectrochemical results confirmed the presence of TEMPOH during the reaction. Based on this evidences, the mechanism for the reaction was proposed wherein a hydride (H<sup>-</sup>) transfer from **1a** to TEMPO<sup>+</sup> results in the formation of TEMPOH and a radical cation intermediate **2c/2d** (Scheme 5b). Thereafter, **2c/2d** reacts with the enol form of **1a** (**1a'**) to form **3a** after losing a proton (PT) (Scheme 5b). The hydride transfer can be viewed as a 2e<sup>-</sup> transfer process since hydride is composed of a proton and 2e<sup>-</sup>.

In summary, four different pathways for the dimerization of 3-carboxylate-2-oxindole (**1a**) have been demonstrated and based on the yields of these pathways with reaction time information, the order of kinetic efficiency can be summarized. They were stepwise ET-PT (1e<sup>-</sup> transfer radical pathway, in absence of base) < stepwise ET-PT-ET (2e<sup>-</sup> transfer cationic intermediate pathway, in the absence of base) < stepwise PT-ET-ET (2e<sup>-</sup> transfer cationic intermediate pathway, in the presence of base) < Electrocatalytic hydride transfer pathway (2e<sup>-</sup> transfer pathway catalyzed by TEMPO<sup>+</sup>).

The dimerization of 3-alkyl-2-oxindole (**4a**) was attempted through an electrocatalytic route. The pK<sub>a</sub> of the pseudobenzylic proton of **4a** was estimated to be in the range of 21-24, which is significantly higher than that of 3-carboxylate-2-oxindole (**1a**). The dimerized product **6a** was obtained in 70% yield in ACN solvent having 0.35 M NH<sub>4</sub>PF<sub>6</sub> electrolyte and 0.01 M TEMPO at the applied potential of 0.8 V Ag/Ag<sup>+</sup> in N<sub>2</sub> atmosphere (Scheme 6). However, the reaction time was enhanced to 1 h 20 min, besides 0.1 M NaH (base) was also needed.



**Scheme 6:** TEMPO<sup>+</sup>-catalyzed dimerization of 3-alkyl-2-oxindole (**4a**) in acetonitrile (ACN) solvent with 0.2 M NH<sub>4</sub>PF<sub>6</sub> as electrolyte and 0.1 M NaH in N<sub>2</sub> atmosphere.



**Scheme 7:** (a) CV of 0.004 M TEMPO at 10 mVs<sup>-1</sup> scan rate on Pt disk electrode in ACN solvent with 0.5 M NH<sub>4</sub>PF<sub>6</sub> electrolyte (0.5 mM) with increasing concentration of **4a** with 30 mM NaH in presence of N<sub>2</sub> (b) TEMPO<sup>+</sup>-catalyzed mechanism for dimerization of **4a**.

The synthesis of **6a** from **4a** revealed a comparatively slower kinetics compared to the dimerization of **1a**. Thereafter, CVs were collected for **4a** in the presence of 0.004 M TEMPO with 30 mM NaH and 0.5 M NH<sub>4</sub>PF<sub>6</sub> in ACN solvent. CV of TEMPO had reversible peaks, and with increasing concentration of substrate (**4a**), the peaks became somewhat irreversible since the oxidation current increased while the reduction current declined (Scheme 7a). These results clearly suggested that TEMPO<sup>+</sup> can catalyze the oxidation of **4a**; however, comparing the CVs shown in Scheme 5 for **1a**, it can be speculated that the kinetics of **4a** oxidation by TEMPO<sup>+</sup> was significantly slower and indeed the electrochemical analysis revealed a rate constant of only 0.29 M<sup>-1</sup>s<sup>-1</sup>, considering electrocatalytic process was a 1e<sup>-</sup> transfer process, which was confirmed by further experiments (*vide infra*). The electrochemical CV comparison of TEMPO<sup>+</sup>-catalyzed **4a** oxidation provided a higher current in the N<sub>2</sub> environment compared to the O<sub>2</sub> environment, which suggested the presence of a radical species during the reaction. Furthermore, in-situ UV-vis results during the electrolysis revealed that TEMPOH was not generated and indicated that the catalytic cycle was limited between TEMPO and TEMPO<sup>+</sup>. Furthermore, a radical intermediate was trapped by a radical scavenger (DPPH). These results clearly suggested one-electron transfer oxidation of **4a** by TEMPO<sup>+</sup>. The mechanism for **4a** oxidation has been shown in Scheme 7b. First, the strong base NaH abstracted the proton (PT) from **4a** to generate an anionic species **5aa**. Thereafter, **5aa** reacted with TEMPO<sup>+</sup> to generate **5ab**, which homolytically cleaved to generate TEMPO and radical intermediate **5b**. Overall, this process involves 1e<sup>-</sup> transfer from TEMPO<sup>+</sup> to **4a**, which is contrary to 2e<sup>-</sup> transfer reaction mechanism for **1a** discussed earlier. Thereafter, two radical intermediates reacted to obtain dimerized 3-alkyl-2-oxindole (**6a**). These results are interesting because the same catalyst changed



the mechanism for oxidation based on the difficulty of molecules to oxidize.

### 3. Conclusions and Future directions

In conclusion, we summarized the dimerization of 3-carboxylate-2-oxindole (**1a**) and 3-alkyl-2-oxindoles (**4a**) employing direct electrode oxidation and electrocatalytic pathways. 3-carboxylate-2-oxindole (**1a**) was oxidized in four different pathways, and the efficiency of these pathways was significantly different. The electrocatalytic TEMPO<sup>+</sup>-catalyzed 2e<sup>-</sup> hydride transfer (H<sup>-</sup>) mechanism was kinetically most efficient, which was not only due to the kinetics but also because of the avoidance of electrode passivation during the reaction. Thereafter, three direct electrode oxidation mechanisms followed the following trend: stepwise PT-ET-ET> stepwise ET-PT-ET> stepwise ET-PT (radical intermediate). It is important to highlight that the cationic intermediate generation provided a higher yield compared to the radical intermediate pathway since the radical intermediate pathway required two in-situ generated radical intermediates to couple, while the cationic intermediate can react with the monomer present in a large excess to provide the product. However, more insights for this observation can be obtained from theoretical investigations since 3-carboxylate-2-oxindole (**1a**) molecules are sterically hindered and C3a-C-3a' bonds are significantly longer than that of normal C-C single bonds (1.54 Å). 3-alkyl-2-oxindole (**4a**) was much more difficult to oxidize, and TEMPO<sup>+</sup>-catalyzed reaction with 3-alkyl-2-oxindole (**4a**) followed a one-electron transfer radical intermediate mechanism, which required a significantly longer time and the presence of a base for the reaction to complete. These syntheses provided important insights into the reaction kinetics of dimerization of 3-substituted-2-oxindoles. Indeed, following this direction, future research directed towards electrochemical synthesis of natural products may bring important breakthroughs towards improving the efficiency of reactions employing the understanding about PCET.

### 4. Acknowledgements

We sincerely thank IISER Bhopal for its generous funding. The authors sincerely thank Dr. Sulekha Sharma for providing important insights to prepare this manuscript. We thank Prof. Alakesh Bisai, IISER Kolkata and his group members for their important collaboration in this research project.

### 5. Notes and References

- Munda, M.; Niyogi, S.; Shaw, K.; Kundu, S.; Nandi, R.; Bisai, A., Electrocatalysis as a key strategy for the total synthesis of natural products. *Org. Biomol. Chem* **2022**, *20*, 727-748.
- Huynh, M. H. V.; Meyer, T. J., Proton-Coupled Electron Transfer. *Chem. Rev.* **2007**, *107*, 5004-5064.

- Weinberg, D. R.; Gagliardi, C. J.; Hull, J. F.; Murphy, C. F.; Kent, C. A.; Westlake, B. C.; Paul, A.; Ess, D. H.; McCafferty, D. G.; Meyer, T. J., Proton-Coupled Electron Transfer. *Chem. Rev.* **2012**, *112*, 4016-4093.
- Mallick, S.; Mandal, T.; Kumari, N.; Roy, L.; De Sarkar, S., Divergent Electrochemical Synthesis of Indoles through pK<sub>a</sub> Regulation of Amides: Synthesis and Mechanistic Insights. *Chem. Eur. J.* **2024**, *30*, e202304002.
- Zhu, C.; Ang, N. W. J.; Meyer, T. H.; Qiu, Y.; Ackermann, L., Organic Electrochemistry: Molecular Syntheses with Potential. *ACS Cent. Sci.* **2021**, *7*, 415-431.
- Sharma, S.; Roy, A.; Shaw, K.; Bisai, A.; Paul, A., Electrochemical Synthesis of Dimeric 2-Oxindole Sharing Vicinal Quaternary Centers Employing Proton-Coupled Electron Transfer. *J. Org. Chem.* **2020**, *85*, 14926-14936.
- Shaw, K.; Sharma, S.; Khatua, A.; Paul, A.; Bisai, A., Oxidative electro-organic synthesis of dimeric hexahydropyrrolo-[2,3-b]indole alkaloids involving PCET: total synthesis of (±)-folicanthine. *Org. Biomol. Chem.* **2021**, *19*, 9390-9395.
- Sharma, S.; Shaheeda, S.; Shaw, K.; Bisai, A.; Paul, A., Two-Electron- and One-Electron-Transfer Pathways for TEMPO-Catalyzed Greener Electrochemical Dimerization of 3-Substituted-2-Oxindoles. *ACS Catal.* **2023**, *13*, 2118-2134.

### 6. About the author(s)

Amit Paul received his B.Sc. from Jadavpur University, M.Sc. from IIT Bombay, and PhD from the University of Pittsburgh with Prof. David H. Waldeck in 2008. He was then a postdoctoral research associate as a part of the Energy Frontier Research Center (EFRC) at the University of North Carolina at Chapel Hill with Prof. Thomas J. Meyer. In October 2011, he joined the Indian Institute of Science Education and Research (IISER), Bhopal as an Assistant Professor and was subsequently promoted to Professor in December, 2023. He was awarded a DAE young scientist in 2013 and a Bronze medal by Chirantan Rasayan Sanstha (CRS) in 2024. His group is interested in electrochemical applications such as electrochemical supercapacitor, heterogeneous water oxidation, electro-organic synthesis, etc. He is particularly interested in understanding structure-property relations in energy applications.



Ms Harapriya Behera is currently pursuing a PhD in the Department of Chemistry at the Indian Institute of Science Education and Research, Bhopal, under the supervision of Prof. Amit Paul. In 2022, she graduated with a master's degree from the National Institute of Technology in Rourkela. Her studies are centred on investigating electro-organic synthesis.



Shivani Ahlawat is currently pursuing a PhD in the Department of Chemistry at IISER Bhopal, under the guidance of Prof. Amit Paul. She completed her master's degree from Jamia Millia Islamia, New Delhi in 2020. Her research work focuses on Electro-Organic synthesis and proton-coupled electron transfer reactions.



**Article Note:** A collection of invited papers based on *Invited Lecture* presentations in the International Symposium *Science Beyond Boundary: Invention, Discovery, Innovation and Society 'Rasayan 19'* held at IISER Kolkata during July 29-30, 2024.