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*Short Communication*

# Metal-free Electrocatalyst for Hydrogen Production from Water

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Here we report organic metal-free catalyst − 9-phenyl-10-methylacridinium iodide (PhAcrI) for hydrogen evolution reaction (HER) from water at pH from 1 to 4. With increasing pH to 7 HER, according to the GA analysis of the HER is not observed. The catalytic nature of the reduction wave $PhAcr^+/PhAcr^{\cdot}$ was confirmed by controlled potential electrolysis experiments with a simultaneous quantitative detection of hydrogen evolved. PhAcrI at low pH reacts via protonation of an $PhAcr^{\cdot}$-intermediate that subsequently forms $H_2$ via a homolytic mechanism.

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**Keywords:** HER, Metal-free electrocatalyst, aqueous solution, 9-phenyl-10-methylacridinium iodide

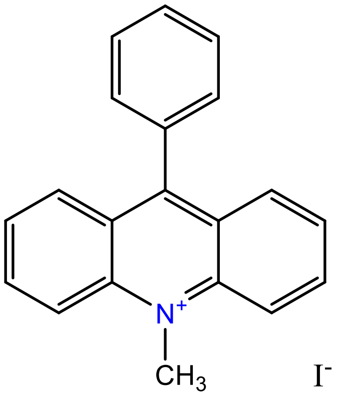
## 1. INTRODUCTION

Molecular hydrogen is considered by many a promising alternative to fossil fuels; however, it is currently produced by steam reforming from natural gas, which it neither sustainable nor environmentally friendly [1]. A technology that relies on renewable resources and has a great potential for a sustainable energy future is water electrolysis, now accounting for about 5% of world hydrogen production [2]. To make its use widespread, new catalysts of this process are needed to be designed that are superior to industrial noble metal catalysts (expensive and non-abundant), hydrogenases (expensive and unstable) or its molecular mimics (neither stable nor cheap or active enough)[3].

Many transition metal complexes have been designed as electrocatalysts for hydrogen production [4], some of them performed well in fully aqueous solutions [5-6] or showed turnover frequencies matching (or above) that of hydrogenases [7]. Despite all these efforts, no economically viable molecular electrocatalyst has emerged yet. In the ideal case, it should combine low working overpotential (as those for known molecular catalysts are still too large) [4] with availability, high activity and stability in water (whether pure or with impurities, as it occurs in nature), also at extreme pH and high temperatures (e.g., as in electrolyzers with Nafion membranes at pH 0 and 90°C that only noble metal catalysts can sustain [8]

Recently we have reported the metal-free electrocatalysts of generation of hydrogen from acidic organic media [9]. While the catalytic behavior of our fully organic compound in hydrogen evolution seems highly unusual and inspiring, its successful industrial applications are significantly more demanding and can hardly be viable as long as acetonitrile and perchloric acid are used as a solvent and a source of protons, respectively. PhAcrI is, however, highly soluble in water, in contrast to many metal-based molecular catalysts with poor solubility in this most abundant source of hydrogen.

Here we report the first metal-free electrocatalyst, a simple acridinium salt PhAcrI (Scheme 1.) that efficiently electrocatalyzes hydrogen production from water. The purely organic compounds have been never viewed as homogenous electrocatalysts for HER from water, although catalytic waves observed for some organic polysaccharides, such as chitosan [10]. The discovery of a simple organic electrocatalyst that efficiently produces hydrogen from water creates a new way in design of cheap, robust and economically viable (i.e. “good”) catalysts for hydrogen evolution [4]



**Scheme 1.**

## 2. MATERIAL AND METHODS

### *2.1. Synthesis [9]*

9-phenyl-10-methylacridinium iodide (PhAcrI) was obtained as described previously [11] by quaternization of 9-phenylacridine with methyl iodide in a sealed tube for 10 hours. The purity of the compound, accessed by NMR and elemental analysis, was estimated as more than 99.6. *Anal.* calc. for $C_{20}H_{16}NI$ (%): C, 60.45; H, 4.03; N, 3.53. Found (%): C, 60.48; H, 4.04; N, 3.49. $^{1}H$ NMR ($CD_3CN$) δ 8.69 (d, $J$ = 9.2 Hz, 2H, *H4*), 8.42 (dd, $J$ = 9.2, 6.8 Hz, 2H, *H3*), 8.04 (d, $J$ = 8.5 Hz, 2H, *H1*), 7.94 – 7.83 (dd, $J$ = 8.5, 6.8 Hz, 2H, *H2*), 7.83 – 7.73 (m, 3H, *m-Ph, p-Ph*), 7.56 (d, $J$ = 7.2 Hz, 2H, *o-Ph*), 4.90 (s, 3H, *Me*). $^{13}C$ NMR ($CD_3CN$) $\delta$ (ppm): 161.65 (*C9*), 141.70 (*C12*), 138.74 (*C3*), 133.32 (*ipso-*

*Ph*), 130.25 (*p-Ph*), 130.18 (*C1*), 129.92(*o-Ph*), 128.89(*m-Ph*), 127.82 (*C2*), 126.21 (*C11*), 118.68 (*C4*), 39.15 (Me).

### 2.2. Materials

All the reagents, solvents and buffers were obtained commercially and used without further purification. Following buffer solutions were used: hydrochloric acid/potassium chloride buffer solution for pH 1.0 (Fluka), glycine buffer solution for pH 2.0 (Fluka), citric acid/sodium hydroxide/sodium chloride buffer solutions for pH 3.0 and pH 4.0 (Fluka), phthalate buffer solution for pH 5.0 (Fluka), phosphate buffer solution for pH 6.0 (Fluka), phosphate buffer solution for pH 7.0 (Sigma) [12].

### 2.3. Cyclic voltammetry .

Cyclic voltammetry experiments were carried out in water (with 1 M buffer solution) using a model Parstat 2273 with a conventional one-compartment three-electrode cell (10 ml of solution). Glass carbon electrode with an active surface area of 0.125 cm$^2$ was used as a working electrode. The electrode was thoroughly polished and rinsed before and between the measurements. A platinum counter electrode and a standard Ag/AgCl reference electrode were used. In the case of aqueous solutions, those are given versus normal hydrogen electrode (NHE), with the standard potential of the ferrocene/ferricinium (Fc/Fc$^+$) couple equal to +0.400 V versus NHE. All the solutions were thoroughly deaerated by passing argon through them before the cyclic voltammetry experiments and above them during the measurements [9].

Turnover numbers and turnover frequencies were determined based on the total charge passed through the electrochemical cell during the experiment. Note that while these values appear significantly lower than intrinsic TOF values obtained from the CV data, they are based on homogenous and not surface concentration of the catalyst and thus are more suitable for the assessment of catalytic activity from the practical standpoint.

### 2.4. Controlled potential electrolysis in water.

10 ml of 0.1 mM solution of PhAcrI in the corresponding 1M buffer were electrolyzed for 1 hour. Glass carbon electrodes with an active surface area of 0.125 cm$^2$ were used as working and counter electrodes. Turnover frequencies (TOF) were determined based on the total charge passed through the electrochemical cell during the experiment [12].

### 2.5. Gas chromatography

Gas chromatography analysis of gases evolved during the electrolysis was performed with a Varian 450 gas chromatograph equipped with a pulsed discharge helium ionization detector D-4-I-

VA38-R. Hydrogen production was quantitatively detected using a 30 m-in-length stainless steel column with inside diameter 250 µm at 120°C for the detector and at 80°C for the oven. The carrier gas was helium flowing at a rate of 40 ml min$^{-1}$. The injections (250 µL) were performed *via* a sampling loop. The retention time of gaseous $H_2$ was 2.48 min [12].

## 3. RESULTS AND DISCUSSION

Cyclic voltammograms of PhAcrI in aqueous buffers (Figure 1) feature the expected reduction wave PhAcr$^+$/PhAcr$^\bullet$ at −0.45 V as well as a reverse wave PhAcr$^\bullet$/ PhAcr$^+$, the latter being previously attributed to a relatively low water solubility of radical species leading to their physical adsorption on the electrode surface[11].

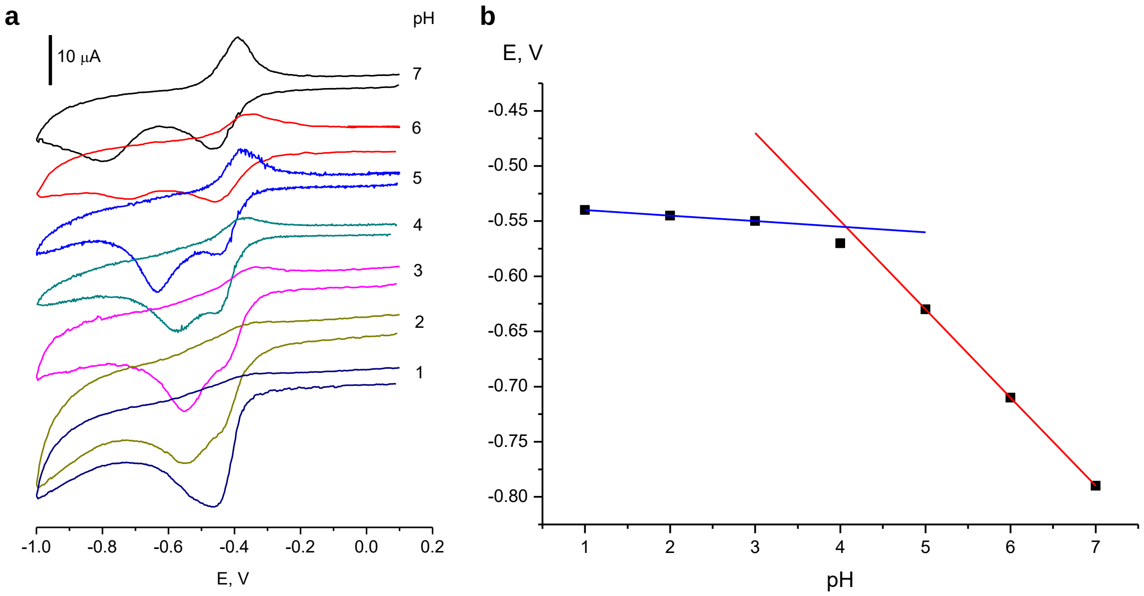


**Figure 1**. Electrochemical data for aqueous solutions of PhAcrI. **a,** Cyclic voltammograms for 0.5 mM solution of PhAcrI at different pH. **b**, pH-dependence of the second reduction peak vs $E_{red}$.

Lowering of pH increases the catalytic current (which is slightly lower than in a perchloric acid solution as a result of much lower concentrations of H$^+$ ions in aqueous media) with a simultaneous decrease in the reverse peak current, implying that at lower pH the radical protonation is fast enough to prevent any adsorption. Note that the values reported for cyclic voltammograms are the experimental peak potentials; the potentials at half of the catalytic current are used below to calculate overpotentials [13] and to perform electrolysis experiments[9].

As shown in figure 1a the catalytic current a maximum value reaches at pH 1, and at higher pH it decreases. At pH higher than 4, the current varies slightly. A controlled potential electrolysis experiment at range pH from 5 to 7, according to the gas chromatographic analysis of the production of molecular hydrogen is not observed. The catalytic nature of the reduction wave PhAcr$^+$/PhAcr$^\bullet$ (from 1 to 4) was confirmed by controlled potential electrolysis experiments with a simultaneous quantitative detection of hydrogen evolved. A series of one-hour electrolyzes (at different pH) was performed using a glass carbon electrode at the potentials at half of the catalytic current at a given pH (Figure 1a). The Faradaic yield in the region of pH 1 to 4 is 41±5% at pH 1, 39±5% at pH 2, 37±5% at pH 3, 35±5% at pH 4. The low Faradaic yield, as in the case [9] due of side electrochemical or chemical reactions. A TOF value when moving from pH 1 to 4 is markedly decreased: 2.5, 1.8, 1.3 and 0.55 per mol cat. $h^{-1}$ at pH 1, 2, 3 and 4, respectively. The resulting value TOF for PhAcrI is higher than that for some complexes, so the cobalt complex bearing the $Py_5Me_2$ ligand in HER shows a TOF of ~0.3 $s^{-1}$ at an overpotential of −900 mV on a mercury electrode [14]. Furthermore, TOF of ~0.07 $s^{-1}$ have been reported for carbon-supported $[Mo_3S_4]^{4+}$ clusters [15].

At all pH the wave reduction $PhAcr^+/PhAcr^\bullet$ occurs at the same potential, as expected from the absence of an electron-coupled proton transfer step. It is known that the proton-coupled electron transfer (PCET) has dependence pH vs the redox potential [16-17]. However, it is observed only when both transfer processes (i.e. for electron and proton) are localized at the same center [16]. In the proposed catalytic mechanism (Figure 2) [9], electron and proton transfer processes are not coupled, as they occur at different centers: the electron transfer involves the 9 position of the acridinium cation, and the nitrogen atom is protonated (**II**) (Figure 2).

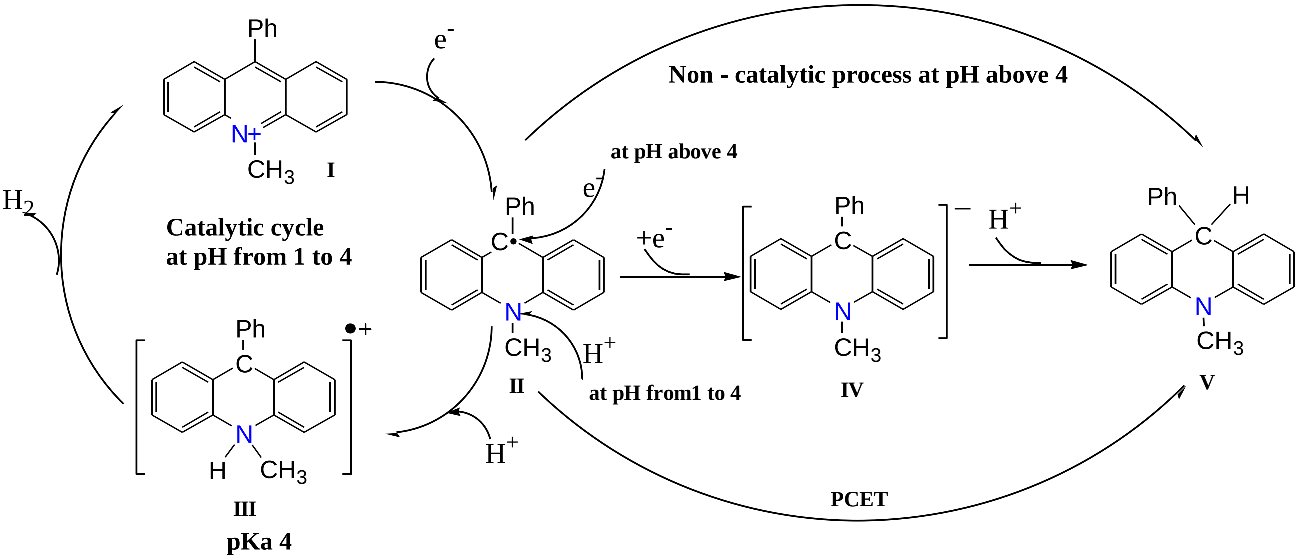


**Figure 2**. Probable catalytic mechanism for HER by PhAcrI from water at different pH ;

As these sites are separated by three chemical bonds, their impact on each other is very small. This results in the experimentally observed weak pH-dependence of the first reduction peak in water. However a second, more negative peak observed in the cyclic voltammograms of PhAcrI in aqueous buffers at the potential that clearly depends on the pH value (Figure 1b). This dependence has two separate linear regions intersecting at pH 4, which corresponds to the $pK_a$ of the cation-radical $PhAcrH^{+\bullet}$ **III** (Figure 2). At pH above 4 the potential of this peak shifts negatively by 68 mV with an increase per pH unit corresponding to the one-electron process that involves one $H^+$ ion [17]. This corresponds of the second reduction of the radical $PhAcr^\bullet$ at 9 position that is immediately followed by the protonation of the resulting anion $PhAcr^-$ (**IV**) (the PCET process), which eventually leads to the catalytically non-active 9-phenyl-10-methyl-9-hydroacridine (**V**). This behavior agrees with observed if the controlled potential electrolysis is performed at the potential that is low enough to cause the second reduction, which eventually leads to the catalytically non-active 9-phenyl-10-methyl-9-hydroacridine. At pH lower than 4 the protonation of the radical $PhAcr^{\bullet}$ is fast enough for the reaction to proceed by the ECEC pathway [9], so further decrease in pH does not change the potential of the second peak. Thus a key step of HER in the presence of PhAcrI from water is the protonation of the radicals $PhAcr^{\bullet}$ on the nitrogen atom with the formation of the cation-radical intermediate (Figure 2) that subsequently forms $H_2$ via a hemolytic pathway, presented earlier [9]. At pH above 4, the proton donor ability of the water becomes poor, which leads to the impossibility of the protonation of the radical $PhAcr^{\bullet}$.

## 4. CONCLUSIONS

In summary, we have presented the first purely organic electrocatalyst, a simple acridinium salt, demonstrates a promising catalytic activity in HER at low pH. Future studies will be directed towards PhAcrI modification for immobilization on electrode surfaces to further facilitate the (photo)electrocatalytic production of $H_2$ from water.

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## References

1. R. Navarro, M. Pena, J. Fierro, *Chem Rev*,107 (2007) 3952
2. N. Armaroli, V. Balzani, *ChemSusChem*, 49 (2011) 21.
3. J.A. Cracknell, K.A. Vincent, F.A. Armstrong, *Chem Rev*., 108 (2008) 2439.
4. V. Artero, M. Montecave, *Coord Chem Rev.,* 249 (2005) 1518.
5. E. Andreiadis, P. Jacques, P. Tran, A. Leyris, M. Chavarot-Kerlidou, B. Jousselme, M. Matheron, J. Pécaut, S. Palacin, M. Fontecave, V. Artero, *Nature Chemistry* , 5 (2013) 48.
6. H. Karunadasa, C. Chang, J. Long, *Nature* , 464 (2010) 1329.
7. M. Helm, M. Stewart, R. Bullock, M. DuBois, D. DuBois, *Science* , 333 (2011) 863.
8. L. Gandia, G. Arzamendi, P. Dieguez, Renewable hydrogen technologies: production, purification, storage, application and safety, Elsevier, Amsterdam, 2013.
9. A. Dolganov , B. Tanaseichuk, D. Moiseeva, V. Yurova, J. Sakanyan, N. Shmelkova, V. Lobanov, *Electrochem Commun*., 68 (2016) 59.
10. E. Paleček , L. Římánková, *Electrochem Commun.,* 44 (2014) 59.
11. N. Koper, S. Jonker, J. Verhoeve, *Recl Trav Chim Pays-Bas.,* 104 (1985) 296.
12. A. Dolganov, O. Tarasova, D. Moiseeva, E. Murymin, *Int J Hydrogen Energy*, 41 (2016) 9312
13. A. Appel, M. Helm, *ACS Catal*., 4 (2014) 630.
14. Y. Sun, P. Julian, N. Piro, M. Tang, J. Long, C. Chang, *J Am Chem Soc*., 133, (2011) 9212.
15. T. Jaramillo, J. Bonde, J. Zhang, B-L. Ooi, K. Andersson, *J Phys Chem* C., 112 (2008) 17492.
16. S. Hammes-Schiffer , A.A. Stuchebrukhov, *Chem Rev*., 110 (2010) 6937.

17. A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications. 2nd ed., 2001, John Wiley: New York.