Accepted Manuscript

Research paper

Electrocatalytic Hydrogen Evolution Reaction with a Supramolecular Cobalt(II)phthalocyanine Carrying Four Cobaloxime Moieties

İbrahim Özçeşmeci, Aykut Demir, Duygu Akyüz, Atıf Koca, Ahmet Gül

PII:	\$0020-1693(17)30425-5
DOI:	http://dx.doi.org/10.1016/j.ica.2017.07.024
Reference:	ICA 17747

To appear in: Inorganica Chimica Acta

Received Date:21 March 2017Revised Date:29 June 2017Accepted Date:12 July 2017



Please cite this article as: I. Özçeşmeci, A. Demir, D. Akyüz, A. Koca, A. Gül, Electrocatalytic Hydrogen Evolution Reaction with a Supramolecular Cobalt(II)phthalocyanine Carrying Four Cobaloxime Moieties, *Inorganica Chimica Acta* (2017), doi: http://dx.doi.org/10.1016/j.ica.2017.07.024

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Electrocatalytic Hydrogen Evolution Reaction with a Supramolecular

Cobalt(II)phthalocyanine Carrying Four Cobaloxime Moieties

İbrahim Özçeşmeci^a, Aykut Demir^a, Duygu Akyüz^b, Atıf Koca^b, Ahmet Gül^a*,

^a Department of Chemistry, Faculty of Science and Letters, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey

^b Department of Chemical Engineering, Engineering Faculty, Marmara University, 34722 Göztepe, Istanbul- Turkey.

Abstract

A supramolecular cobalt phthalocyanine (*CoPc*) bearing four redox active cobaloxime (*CoDMG*) substituents ((*CoDMG*)₄-*CoPc*) was synthesized and electrochemically characterized in order to determine its functionalities for practical usages as effective electrocatalysts. Voltammetric analyses of *CoDMG*, *CoPc*, and (*CoDMG*)₄-*CoPc* indicated redox activity of each compounds and supported substitution of *CoPc* with *CoDMG*. (*CoDMG*)₄-*CoPc* showed three CoPc based reduction processes and two *CoDMG* based reduction processes. While *CoDMG* showed two reduction and one oxidation processes, *CoPc* illustrated three reduction and two oxidation processes. Binding of *CoDMG* to *CoPc* increased the reduction processes to five. Multi-electron and metal and/or ring based redox processes showed worthy of the (*CoDMG*)₄-*CoPc* for using as an electrocatalyst. Shifting of the proton reduction reaction toward the positive potentials indicated electrocatalytic activities of the complexes for the hydrogen evolution reaction (*HER*). Among *CoDMG*, *CoPc*, and (*CoDMG*)₄-*CoPc*, modified glassy carbon electrode with (*CoDMG*)₄-*CoPc* illustrated the highest electrocatalytic activity and it decreased the over-potential of the bare electrode about 360 mV and increased the current density of the electrode about 10 fold.

Keywords: Supramolecule, Electrocatalyst, Hydrogen evolution reaction, Phthalocyanine *Corresponding authors Tel.: +90 212 285 68 27; Fax: +90 212 285 63 86

*E-mail address: ahmetg@itu.edu.tr (A. Gül)

1. Introduction

Supramolecular chemistry interests on well organized, synthetically built up molecular receptors for effecting molecular recognition, catalysis, light harvesting, transport processes and for setting up molecular devices. The use of macrocyclic structures like tetrapyrole was pushed by the need to achieve better control over the geometry of molecular receptors [1, 2]. Despite the great interest in terms of synthesis and reactivity of oximes and their metal complexes in medicinal and materials chemistry, there are very few studies with tetrapyrole/ cobaltdioxime combined systems on the production of H_2 in the literature [3, 4].

Metallophthalocyanines (MPcs) were used as functional materials in different electrochemical technologies due to their rich redox activities [5-7]. Redox activities of MPcs can be enhanced by incorporating redox active metal ions into the cavity of the Pc ring and/or by substituting with redox active moieties [8, 9].

MPcs having metal based electron transfer reaction generally behave as active species, thus a supramolecular cobalt phthalocyanine bearing four redox active cobaloxime substituents (*CoDMG*)₄-*CoPc* bearing redox active Co^{II} ions in both the Pc ring and four redox active *CoDMG* moieties was synthesized and tested as possible electrocatalyst for hydrogen evolution reaction (*HER*). Transition metal complexes with various ligands were extremely studied as homogeneous and/or heterogeneous electrocatalysts for *HER*, due to their rich redox properties [10-14]. In this context the complexes having metal-based reduction processes generally showed good electrocatalytic activity for *HER* [5, 6].

2. Experimental

2.1 Materials and equipment

FT-IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR (ATR sampling accessory) spectrometer and electronic spectra was obtained on a Scinco S-3100 spectrophotometer using 1cm path length cuvettes at room temperature. Mass spectra were

2

performed on a Bruker Microflex LT MALDI-TOF MS spectrometer. All reagents and solvents were of reagent grade quality obtained from commercial suppliers. Anhydrous metal salts were finely ground and dried at 100 °C. The purity of the products was tested in each step by thin-layer chromatography (TLC). The solvents were stored over molecular sieves. 4-(4-pyridyloxy)phthalonitrile (1) was prepared according to the literature [15] and chloro(pyridine)cobaloxime (*CoDMG*) complex was prepared according to reported procedures [16-17].

2.2 Synthesis

2.2.1. 2,9,16,23-tetrakis(4-pyridyloxy)phthalocyaninatocobalt (II) (CoPc)

A mixture of 4-(4-pyridyloxy)phthalonitrile (0.200 g, 0.900 mmol) and cobalt (II) chloride (0.039 g, 0.300 mmol) in N,N-(dimethylamino)ethanol (2 mL) was heated and stirred at 140 °C for 24 h under nitrogen atmosphere. After cooling to room temperature the crude product was precipitated by addition of hexane. The solid was washed several times with ethanol, chloroform, acetone, hexane, and diethyl ether and then dried in *vacuo*. Yield: 0.109 g (51.4%). Anal. calcd. for $C_{52}H_{28}CoN_{12}O_4C$, 66.18; H, 2.99; N, 17.81;%. Found: C, 66.24; H, 3.03; N, 17.78%. IR: v_{max} , cm⁻¹ 3060 (Ar–H), 1633, 1547, 1257 (C–O–C), 1189, 842. UV-Vis (DMF): λ max nm (log ε) 295 (4.20), 340 (3.96), 678 (4.26). (MALDI-TOF): m/z 944.84 [M+1]⁺

2.2.2. Pentanuclear supramolecular phthalocyanine (CoDMG)₄-CoPc)

A mixture of dimethylglyoxime (0.278 g, 2.400 mmol), dry CoCl₂ (0.156 g, 1.200 mmol) and CoPc (0.189 g, 0.200 mmol) was stirred in ethanol (20 mL) at reflux temperature and a very gentle stream of air is bubbled through the solution. After 24 h, the solvent was evaporated at reduced pressure. The solid was washed several times with chloroform, acetone, hexane, and diethyl ether and then dried in *vacuo*. Yield: 0.285 g (63.6%). Anal. calcd. for $C_{84}H_{84}Cl_4Co_5N_{28}O_{20}C$, 45.00; H, 3.78; N, 17.49 %. Found: C, 45.14; H, 3.83; N, 17.54%. IR:

v_{max}, cm⁻¹ 3045 (Ar–H), 1635, 1552, 1260 (C–O–C), 1232, 1189, 842. UV-Vis (DMF): λmax nm (log ε) 293 (4.40), 333(4.26), 675 (4.18). (MALDI-TOF): m/z 2242.31 [M+1]⁺

2.3 Chemicals and solutions

The experimental studies were carried on with high purity chemicals. Extra pure dichloromethane (DCM), and ultra-pure water (\geq 18 M_, Milli-Q, Millipore) were used as solvents. Electrochemical grade tetrabutylammonium perchlorate (TBAP), NaOH, NaCl, H₃PO₄, KH₂PO₄, LiClO₄, HCl, and other reagents were purchased from Aldrich and used without further purification. The buffer solutions were prepared by using 0.1 mol/dm³ H₃PO₄, and 0.1 mol/dm³ KH₂PO₄. The desired pH was obtained by addition of conjugate acids or 0.1 mol/dm³ NaOH solution.

2.4 Electrode modification

Glassy carbon working electrodes (GCE) were coated with *CoDMG*, *CoPc*, and $(CoDMG)_4$ -*CoPc* by using the cast film coating technique. During this modification process, 100 µL of 5.0 10⁻⁵ moldm⁻³ each complexes dissolved in DMSO was dropped on the active surface of GCE and then it was dried under vacuum at room temperature. Finally, the modified electrodes (GCE/*CoDMG*, GCE/*CoPc*, and GCE/(*CoDMG*)_4-*CoPc*) were washed with water and used as modified working electrode for HER in the phosphate buffer solution.

2.5 Electrochemical measurements

The electrochemical measurements were performed with a GAMRY reference 600Potentiostat/Galvanostat/ZRA utilizing a three-electrode cell configuration at 25°C. For cyclic voltammetry (CV), linear sweep voltammetry (LSV), square wave voltammetry (SWV), controlled potential coulometry (CPC), chronoamperometry (CA), and

chronocoulometry (CC) measurements, the working electrode was a bare or modified GCE/*CoDMG*, GCE/*CoPc*, and GCE/(*CoDMG*)₄-*CoPc* electrodes with a surface area of 0.071 cm^2 . A Pt wire was used as the counter electrode. Ag/AgCl electrode was employed as the reference electrode. Both of the reference and counter electrodes were separated from the electrolyte with salt bridges. High purity N₂ was used to remove dissolved O₂ for at least 15 min prior to each run and to maintain a nitrogen atmosphere over the solution during the measurements. UV–vis absorption spectrum of the electrodes was measured with an Ocean Optics QE65000 diode array spectrophotometer.

3. Result and Discussion

3.1 Synthesis and characterization

Scheme 1 showed the synthetic route of pentanuclear supramolecular phthalocyanine (*CoDMG*)₄-*CoPc*). The synthesis of a new supramolecular phthalocyanine precursor bearing pyridyloxy substituent was achieved by base-catalyzed nucleophilic aromatic displacement of 4-nitrophtalonitrile and with 4-hydroxypyridine according to the literature [15]. Cobaloxime (*CoDMG*) complex was prepared according to reported procedures [16, 17]. Conversion of 4-(4-pyridyloxy)phthalonitrile into the corresponding cobalt (II) phthalocyanines (*CoPc*) was accomplished in a high-boiling N-donor solvent (N,N-(dimethylamino)ethanol) in the presence of the metal salt (CoCl₂).

The primary goal of this study was the construction of a supramolecular structure starting with a phthalocyanine molecule. Taking into account the ready coordination of *CoDMG* with four pyridine donors, these penta-coordinated complexes were preferred as the capping agents for tetra pyridine end-groups on each molecule to reach the penta nuclear supramolecular structure. The blue solid pentanuclear supramolecular product $(CoDMG)_4$ -(CoPc) was obtained in powder form. All of these new compounds were characterized by

elemental analysis, IR, UV–Vis and Mass spectroscopy techniques. The spectroscopic data of the new compounds were in accordance with the structures.

Scheme 1

Naturally, the phthalocyanine products synthesized during this work are a mixture of positional isomers while 4-(4-pyridyloxy)phthalonitrile carry a single substituent [18, 19]. The FT-IR spectra of *CoPc* and (*CoDMG*)₄-*CoPc*) confirmed the structures of target compounds by exhibiting the disappearance of C=N band at 2238 cm⁻¹ and the presence of aromatic CH stretching bands at 3060 and 3045 cm⁻¹, respectively. The IR spectra of these compounds showed aromatic C=C and C-O-C peaks around at 1635, 1260 cm⁻¹, respectively.

CoPc and (*CoDMG*)₄-*CoPc*) show typical electronic spectra with two strong absorption regions, one of them in the UV region at about 300-400 nm (B band) arising from the deeper π - levels \rightarrow LUMO transition and the other in the visible part of the spectrum around 600-700 nm (Q band) attributed to the π - π * transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc⁻² ring [20-22]. In the UV-Vis spectra of *CoPc* and (*CoDMG*)₄-*CoPc*) in DMF, the absorption peaks belonging to Q bands were observed at 678 and 675 nm and B bands at 340 and 333 nm, respectively (Fig. 1). The outcome of the presence of the *CoDMG* was an absorption band with a maximum at about 295 nm comparable in intensity with the B-bands of the (*CoDMG*)₄-*CoPc*). MALDI-TOF mass spectra of *CoPc* and (*CoDMG*)₄-*CoPc*) show the presence of the characteristic peaks at m/z = 944.84 [M+1]⁺ (**CoPc**) (Fig. S1) and 2242.31 [M+1]⁺ (*CoDMG*)₄-*CoPc*) (Fig. S2) confirming the proposed structures.

Figure 1

3.2. Electrochemistry of (CoDMG)₄-CoPc

In order to decide possible usage of a functional material, its redox behaviors should be investigated in detail [23-26]. Therefore, electrochemical behaviors of *CoDMG*, *CoPc*, and (*CoDMG*)₄-*CoPc* were determined with CV, SWV and in situ spectroelectrochemistry. The results were compared with each other in order to understand effects of each groups to the redox responses. Fig.2 shows CV and SWV responses of *CoDMG* in DMSO/TBAP electrolyte system. *CoDMG* illustrates two irreversible reduction processes at -0.47 V (E_c of Red_{1S}) and at -0.75 V ($E_{1/2}$ of Red_{2S}) and an oxidation at 1.24 V (E_a of Oxd_{1S}). Fig.3 illustrates CV and SWV responses of *CoPc* in DMSO/TBAP electrolyte system. *CoPc* gives a metal based reduction at -0.23 V ($E_{1/2}$ of Red_{1P}) and two Pc based reductions at -1.07 V ($E_{1/2}$ of Red_{2P}) and at -1.63 V ($E_{1/2}$ of Red_{3P}) respectively. Moreover, two oxidation processes are also observed at 0.61 V ($E_{1/2}$ of Oxd_{1P}) and 1.18 V ($E_{1/2}$ of Oxd_{2P}).

Figure 2

Figure 3

Binding of *CoDMG* to *CoPc* extends the redox processes from five to seven processes as shown in Fig.4. (*CoDMG*)₄-*CoPc* shows five reduction and two oxidation processes. The *CoPc* and *CoDMG* based processes are observed clearly as shown in this figure. While the peaks at -0.22 V ($E_{1/2}$ of Red_{1P}), -1,06 V ($E_{1/2}$ of Red_{2P}), -1.66 ($E_{1/2}$ of Red_{3P}), and -1.83 V ($E_{1/2}$ of Red_{3P}) are easily assigned to the reduction of *CoPc* part of (*CoDMG*)₄-*CoPc*, the wave at -0.71 V ($E_{1/2}$ of Red_{1S}) and -1.19 V ($E_{1/2}$ of Red_{2S}) are assigned to the reduction of *CoDMG* groups of (*CoDMG*)₄-*CoPc* complex. During the oxidation reactions, (*CoDMG*)₄-*CoPc* illustrates two oxidations. When compared with the voltammetric responses of *CoDMG*

and *CoPc*, the first oxidation process at 0.27 V ($E_{1/2}$ of Oxd_{1P}) can be easily assigned to the oxidation of CoPc center of the complex. The wave at 1.18 V is most propably due to the overlap of the oxidation of *CoDMG* and *CoPc* groups of the complex. When compared with the similar complexes in the literature, it can be easily stated that the first oxidation (Oxd_{1P}) and the first reduction processes (Red_{1P} and Red_{1S}) of (*CoDMG*)₄-*CoPc* should be metal based processes. Since MPcs having Co^{II}, Mn^{III}, Fe^{III} and etc. gives metal-based reduction and oxidation reactions firstly in polar coordination solvents due to the d orbital positions between the HOMO and LUMO orbital of Pc ring [1, 27]. Peak assignments of (*CoDMG*)₄-*CoPc* were also performed with in situ spectroelectrochemical measurements discussed below.

NP

Figure 4

3.3. in situ Spectroelectrochemistry of (CoDMG)₄-CoPc

In order to decide the redox assignments, *in situ* spectroelectrochemical measurements of *CoPc* and (*CoDMG*)₄-*CoPc* were performed and compared with each other. As shown in Fig. 5 and 6 there are very slight differences between the spectral changes of *CoPc* and (*CoDMG*)₄-*CoPc*. During the spectral changes of CoPc under -0.50 V applied potential application, while the Q band shifts from 662 to 704 nm, anew band is observed at 488 nm (Fig. 5a). These spectral changes are characteristic changes for $[Co^{II}Pc^{2-}]/[Co^{I}Pc^{2-}]^{1-}$ process. The spectral changes given in Fig. 5b are the characteristic changes for a Pc based reduction, thus this process is assigned to $[Co^{IP}c^{2-}]^{1-}/[Co^{IP}c^{3-}]^{2-}$ process. During the oxidation reaction, the Q band shift to longer wavelengths with increase in absorption intensity. These changes are characteristic for $[Co^{II}Pc^{2-}]/[Co^{III}Pc^{2-}]^{1+}$ process (Fig. 5c). $(CoDMG)_4$ -*CoPc* shows similar spectral changes with slight differences. $(CoDMG)_4$ -*CoPc* shows a metal based reduction reaction for $[(Co^{II}-DMG)_4$ -*Co^{II}Pc*^{2-}]/[(Co^{II}-DMG)_4-*Co^IPc*^{2-}]^{1-} process under -0.50 V

potential application (Fig. 6a) [28-31]. Similarly, spectral changes assigned to a Pc based reduction are observed at -1.25 V applied potential. The main difference is the changes on the band at around 488 nm. While the bad at 488 nm shift towards the longer wavelength with slight decrease in intensity for **CoPc**, this band increases with shift to 503 nm for (*CoDMG*)₄-*CoPc* during the second reduction reaction. Moreover, the band at 805 nm is only observed during the second reduction reaction of **CoPc**. These spectral differences may be resulted from the electron transfer reactions of *CoDMG groups of* (*CoDMG*)₄-*CoPc* in addition to the electron transfer reactions of *CoPc* center. Distinctive color changes are observed during the reductions for both complexes as shown in the chromaticity diagram of the complex (Fig. 5d and 6d). The color changes of these complexes have same trend. The cyan color (of the neutral species turns to yellow and then to orange during the reduction reactions and a light blue color is observed for the monocationic species.

Figure 5

Figure 6

3.4. Electrocatalytic hydrogen evolution on GCE/(CoDMG)₄-CoPc electrode

It is well known that for practical application, an electrocatalyst should be coated on an electrode, and this catalyst should behave as heterogeneous active catalyst for HER [32, 33]. *GCE/CoDMG*, *GCE/CoPc* and *GCE/(CoDMG)*₄-*CoPc* electrodes were constructed with cast film coating technique and used as electrocatalyst for *HER*. Electrocatalytic activities of the electrode are examined with different LSV technique. LSV is performed for the bare Pt and GCE and *GCE/CoDMG*, *GCE/CoPc* and *GCE/(CoDMG)*₄-*CoPc* modified electrode in order to compare catalytic activities of the electrodes (Fig. 7). While onset potential of HER on GCE is observed at -0.72 V, it is shifted to -0.22 V on Pt working electrode. If the onset potential closes to that on Pt electrode, it has possibilities to be used as practical catalyst for

HER. As shown in Fig. 7, onset potential of HER shifts up to -0.65 V on *GCE/CoPc* -0.62 V on *GCE/CoDMG* and -0.36 V on *GCE/(CoDMG)₄-CoPc* modified electrode. These results indicated that binding of *CoDMG* to *CoPc* enhance the electrocatalytic activity of CoPc and the highest catalytic activity is observed with $GCE/(CoDMG)_4$ -CoPc modified electrode. Onset potential of HER on $GCE/(CoDMG)_4$ -CoPc electrode closes to that of Pt electrode, which shows $GCE/(CoDMG)_4$ -CoPc electrode can be used instead of Pt electrode in the water electrolyzers. Under -0.50 V constant applied potential hydrogen gas evolving can be seen easily on the surface of $GCE/(CoDMG)_4$ -CoPc electrode with naked eyes. As shown in the figure, positive potential shifts of *HER* onset potentials and enhancing in the current density of *HER* process and overpotentials of HER decrease about 360 mV on $GCE/(CoDMG)_4$ -CoPc modified electrode with respect to those on bare GCE at pH 3.40. In addition to the small overpotential of these electrodes, approximately 77-fold enchantment of the current density of HER indicates superior catalytic activities of the electrode.

Figure 7

Tafel plots are used to determine mechanism of the catalytic reaction [34]. During HER in acidic media, an initial step involves the reduction of a proton in solution followed by adsorption of intermediate H_{ads} to the electrode surface as follows (Eq. 1):

 $H_{3}O^{+} + e^{-} + EC \rightarrow EC - H_{ads} + H_{2}O$ (1) (Volmer reaction) A Tafel slope of approximately 120 mV dec⁻¹ is associated with this reaction step. This is followed by desorption of H₂ by either of the following reactions (Eq. 2 and 3): $EC - H_{ads} + H_{3}O^{+} + e^{-} \rightarrow EC + H_{2} + H_{2}O$ (2) (Heyrovsky reaction) $EC - H_{ads} + EC - H_{ads} \rightarrow 2EC + H_{2}$ (3) (Tafel reaction)

The latter reaction has a Tafel slope of approximately 30 mV dec⁻¹. While Tafel slope of Pt electrode is around 130 mV dec⁻¹ at higher overpotentials, these values are around 200

mV dec⁻¹ for other electrodes except *GCE/(Co-DMG)₄-CoPc*. Tafel plot of *GCE/(Co-*DMG)₄-CoPc electrode shows two linear ranges. At small overpotential, it gives Tafel slope of approximately 79 mVdec⁻¹ and at higher overpotentials, Tafel slope of approximately 137 $mVdec^{-1}$ is observed. These data indicate that HER occurs via Volmer–Hevrovsky equation with different efficiency at small and higher over potentials respectively. Although only one linear range were reported with electrocatalytic HERs with MPcs [35]. LSV and Tafel plot of GCE/(Co-DMG)₄-CoPc electrode is different than the previous once. This difference may be resulted from the presence of redox active *Co-DMG* groups on (*Co-DMG*)₄-*CoPc* complex. Most probable both of the *Co-DMG* groups and Co^{II} metal center of the Pc ring of (*Co-*DMG)₄-CoPc complex catalyze the HER. Protonation of Co-DMG groups catalyzes HER at small overpotentials (between -0.36 and -0.57 V). After that potential current response of the electrode reach to a steady state and then it starts to change its trend due to the catalyzing HER with Co^{II} metal center of the Pc ring at higher overpotentials (after -0.57 V). Stability of the (*CoDMG*)₄-*CoPc* electrode was tested with consecutive 50 LSVs and only 17.8% current losses was observed, which showed suitable stability of the electrode for practical usage. During the repetitive LSV measurement, LSV intensely changed and reach to a steady state after the 10th LSV. During the first LSV, the current increases at -0.32 V and reaches to a steady state at around -0.42 V. Then after -0.60 V the current sharply increases again. However, during the consecutive LSVs the current linearly increases after the onset potential of -0.36 V (Fig. 7). After this point it gives a stable response. it loses 17.8% of its current response until the 50th LSV.

Conclusions

In this study, *CoPc* bearing redox active four *CoDMG* groups ((*CoDMG*)₄-*CoPc*) was synthesized and electrochemically characterized in order to determine its functionalities for practical usages as effective electrocatalysts. Electrochemical and spectroelectrochemical

11

characterization of *CoPc* and (*CoDMG*)₄-*CoPc* complexes showed that both (*CoDMG*) groups and CoPc center of (*CoDMG*)₄-*CoPc* complex were redox active. Multi-electron transfer reactions of the complex showed possible usage of the complex as electrocatalysts for *HER* reactions. Coating of GCE electrode with (*CoDMG*)₄-*CoPc* decreased the over potential up to 360 mV when compared with the bare GCE. Observation of the onset potential of HER on *GCE*/(*CoDMG*)₄-*CoPc* electrode very close to that of Pt and enhanced current density of HER on *GCE*/(*CoDMG*)₄-*CoPc* electrode indicated usability of this complex as active electrocatalyst for water splitting reactions.

Acknowledgments

This work was supported by the Research Funds of the TÜBİTAK (Project No: 113M991) and Technical University of Istanbul. AG and AK thank Turkish Academy of Sciences (TUBA) for partial support.

References

- C.C. Leznoff and ABP. Lever, *Phthalocyanines: Properties and Applications*, vols. 1–
 4. New York: VCH, 1989.
- [2] N.B. McKeown, *Phthalocyanine Materials Synthesis, Structure and Function*, Cambridge University Press, 1998.
- [3] J.C. Manton, C. Long, J.G. Vos, M.T. Pryce, Dalton Trans. 43 (2014) 3576-3583.
- [4] T. Lazarides, M. Delor, I.V. Sazanovich, T.M. McCormick, I. Georgakaki, G.
 Charalambidis, J.A. Weinstein, A.G. Coutsolelos, Chem. Commun. 50 (2014) 521-523.
- [5] S. Losse, J.G. Vos S. Rau, Coord. Chem. Rev. 254 (2010) 2492-504.
- [6] F. Zhao, J. Zhang, T. Abe, D. Wöhrle and M Kaneko, J. Mol. Catal. A: Chem. 145 (1999) 245-256.

- J.H. Zagal, S. Griveau, K.I. Ozoemena, T. Nyokong, F. Bedioui, J. Nanosci. Nanotechnol. 9 (2009) 2201-2214.
- [8] J.H. Zagal, S. Griveau, J.F. Silva, T. Nyokong, F. Bedioui, Coord. Chem. Rev. 254 (2010) 2755-2791.
- [9] C. Alexiou, A. Lever, Coord. Chem. Rev. 216 (2001) 45-54.
- [10] K. Zeng, D. Zhang, Prog. Energ. Combust. Sci. 36 (2010) 307-326.
- W.M. Singh, T. Baine, S. Kudo, S. Tian, X.A.N. Ma, H. Zhou, N.J. DeYonker, T.C
 Pham, J.C. Bollinger, D.L. Baker, B. Yan, C.E. Webster, X. Zhao, Angew. Chem. Int.
 Ed. 124 (2012) 6043-6046.
- [12] A. Koca, Int. J. Hydrogen Energy 34 (2009) 2107-2112.
- [13] Ö.A. Osmanbaş, A. Koca, M. Kandaz, F. Karaca, Int. J. Hydrogen Energ. 33 (2008) 3281-3288.
- [14] A. Koca, M.K. Şener, M.B. Koçak, A. Gül, Int J Hydrogen Energ. 31 (2006) 2211 2216.
- [15] I. Scalise, E.N. Durantini, Bioorg. Med. Chem. 13 (2005) 3037–3045.
- [16] P. F. Roussi and D. A. Widdowson, J. Chem. Soc., Perkin Trans. 1 (1982) 1025-1028.
- [17] P. J. Toscano, L. G. Marzilli, Prog. Inorg. Chem. 31 (1984) 105–204.
- [18] İ. Özçesmeci, S. Güner, A.İ Okur, A. Gül, J. Porphyr. Phthalocyanines 11 (2007) 531– 536.
- [19] İ. Özçesmeci, İ. Sorar, A. Gül Inorg. Chem. Commun. 14 (2011) 1254–1257.
- [20] M. Özçeşmeci, J. Organomet. Chem. 767 (2014) 16–21.
- [21] M. Hanack, Z. Iqbal, A. Lyubimtsev, İ. Özcesmeci, M. Özcesmeci, T. Ziegler,J. Porphyr. Phthalocyanines 13 (2009) 312-321.
- [22] İ. Özçesmeci, İ. Sorar, A. Gül, Philos. Mag. 96 (2016) 2986–2999.

- [23] G. Lalande, R. Côté, G. Tamizhmani, D. Guay, J.P. Dodelet , L. Dignard-Bailey, L.T. Weng, P. Bertrand, Electrochim. Acta. 40 (1995) 2635-2646.
- [24] M. Sadakane, E. Steckhan, Chem. Rev. 98 (1998) 219-238.
- [25] E. Guerrini, S. Trasatti, *Electrocatalysis in Water Electrolysis, in Catalysis for Sustainable Energy Production* (eds P. Barbaro and C. Bianchini), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2009.
- [26] E. Gileadi, *Physical Electrochemistry: Fundamentals, Techniques and Applications*,
 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2011.
- [27] F. Bedioui, S. Griveau, T. Nyokong, A.J. Appleby, C.A. Caro, M. Gulppi, G. Ochoa, J.H. Zagal, Phys. Chem. Chem. Phys. 9 (2007) pp. 3383-3396.
- [28] W. A. Nevin, M. R. Hempstead, W. Liu, C. C. Leznoff, A. B. P. Lever, Inorg. Chem. 26 (1987) pp. 570-577.
- [29] W.A. Nevin, W. Liu, M. Melník, A.B.P. Lever, J. Electroanal. Chem. Interfacial. Electrochem. 213 (1986) 217–234.
- [30] G.K. Karaoğlan, G. Gümrükçü, A. Koca, A. Gül, U. Avcıata Dyes Pigm. 90 (2011)11-20.
- [31] H.P. Karaoğlu, A. Koca, M.B. Koçak, Dyes Pigm. 92 (2012) 1005-1017.
- [32] M. Croissant, T. Napporn, J-M. Léger, C. Lamy, Electrochim. Acta 43 (1998) 2447-2257.
- [33] X. Hu, B.S. Brunschwig, J.C. Peters, J. Am. Chem. Soc. 129 (2007) 8988-8998.
- [34] L. Chen, A. Lasia, J. Electrochem. Soc. 138 (1991) 3321-3328.
- [35] D. Akyüz, B. Keskin, U. Şahintürk, A. Koca, Appl. Catal., B. 188 (2016) 217-226.

Figures and Scheme captions:

Figure 1. Absorption spectra of the **CoPc** and $(CoDMG)_4$ -CoPc $(5x10^{-5} \text{ M})$ in DMF. (İnsert: Absorption spectrum of the CoDMG $(1x10^{-4} \text{ M})$ in DMF.)

Figure 2. CV and SWV of *CoDMG* $(5.0 \times 10^{-4} \text{ mol dm}^{-3})$ at various scan rates on GCE in DMSO/TBAP electrolyte system.

Figure 3. CV and SWV of *CoPc* $(5.0 \times 10^{-4} \text{ mol dm}^{-3})$ at various scan rates on GCE in DMSO/TBAP electrolyte system.

Figure 4. CV and SWV of $(CoDMG)_4$ -CoPc $(5.0 \times 10^{-4} \text{ mol dm}^{-3})$ at various scan rates on GCE in DMSO/TBAP electrolyte system.

Figure 5. In situ UV-Vis spectral changes of *CoPc* $(5.0 \times 10^{-4} \text{ mol dm}^{-3})$ in DMSO /TBAP. **a**) $E_{app} = -0.50 \text{ V}$. **b**) $E_{app} = -1.25 \text{ V}$. **c**) $E_{app} = = 0.80 \text{ V}$. **d**) Chromaticity diagram (each symbol represents the color of electro-generated species; O: $[Co^{II}Pc^{-2}]$, $\Box: [Co^{IP}c^{-2}]^{-1}$; $\Delta: [Co^{IP}c^{-3}]^{-2}$; $\bigstar: [Co^{II}Pc^{-1}]^{+1}$.

Figure 6. In situ UV-Vis spectral changes of $(CoDMG)_4$ -CoPc $(5.0 \times 10^{-4} \text{ mol dm}^{-3})$ in DMSO /TBAP. **a**) $E_{app} = -0.50 \text{ V}$. **b**) $E_{app} = -1.25 \text{ V}$. **c**) $E_{app} = 0.80 \text{ V}$. **d**) Chromaticity diagram (each symbol represents the color of electro-generated species; $O: [Co^{II}Pc^{-2}], \Box$: $[Co^{IP}c^{-2}]^{-1}$; $\bigstar: [Co^{II}Pc^{-1}]^{+1}$.

Figure 7. a) LSVs and b) Tafel plots of Pt, GCE, and GCE/*CoDMG*, GCE/*CoPc*, and GCE/(*CoDMG*)₄-*CoPc* electrodes recorded at 10 mV s⁻¹ scan rate in PBS containing 0.1 M LiClO₄ at pH 3.40.

Figure 8. Repetitive LSVs of GCE/(*CoDMG*)₄-*CoPc* electrode recorded at 10 mV s⁻¹ scan rate in PBS containing 0.1 M LiClO₄ at pH 3.40.

Scheme 1. The syntheses of CoPc and (*CoDMG*)₄-*CoPc*.

Figures and Scheme:



Figure 1. Absorption spectra of the **CoPc** and (*CoDMG*)₄-*CoPc* (5x10⁻⁵ M) in DMF. (İnsert: Absorption spectrum of the CoDMG (1x10⁻⁴ M) in DMF.)



Figure 2. CV and SWV of *CoDMG* $(5.0 \times 10^{-4} \text{ mol dm}^{-3})$ at various scan rates on GCE in DMSO/TBAP electrolyte system.

17



Figure 3. CV and SWV of *CoPc* $(5.0 \times 10^{-4} \text{ mol dm}^{-3})$ at various scan rates on GCE in DMSO/TBAP electrolyte system.



Figure 4. CV and SWV of $(CoDMG)_4$ -CoPc $(5.0 \times 10^{-4} \text{ mol dm}^{-3})$ at various scan rates on GCE in DMSO/TBAP electrolyte system.



Figure 5. In situ UV-Vis spectral changes of *CoPc* $(5.0 \times 10^{-4} \text{ mol dm}^{-3})$ in DMSO /TBAP. **a**) $E_{app} = -0.50 \text{ V}$. **b**) $E_{app} = -1.25 \text{ V}$. **c**) $E_{app} = = 0.80 \text{ V}$. **d**) Chromaticity diagram (each symbol represents the color of electro-generated species; O: $[Co^{II}Pc^{-2}]$, $\Box: [Co^{I}Pc^{-2}]^{-1}$; $\Delta: [Co^{IP}c^{-3}]^{-2}$; $\Delta: [Co^{II}Pc^{-1}]^{+1}$.



Figure 6. In situ UV-Vis spectral changes of $(CoDMG)_4$ -CoPc ($5.0 \times 10^{-4} \text{ mol dm}^{-3}$) in DMSO /TBAP. **a**) $E_{app} = -0.50 \text{ V}$. **b**) $E_{app} = -1.25 \text{ V}$. **c**) $E_{app} = 0.80 \text{ V}$. **d**) Chromaticity diagram (each symbol represents the color of electro-generated species; O: $[Co^{II}Pc^{-2}]$, \Box : $[Co^{IP}c^{-2}]^{-1}$; \bigstar : $[Co^{II}Pc^{-1}]^{+1}$.



Figure 7. a) LSVs and b) Tafel plots of Pt, GCE, and GCE/*CoDMG*, GCE/*CoPc*, and GCE/(*CoDMG*)₄-*CoPc* electrodes recorded at 10 mV s⁻¹ scan rate in PBS containing 0.1 M LiClO₄ at pH 3.40.



Figure 8. Repetitive LSVs of GCE/(*CoDMG*)₄-*CoPc* electrode recorded at 10 mV s⁻¹ scan rate in PBS containing 0.1 M LiClO₄ at pH 3.40.



Scheme 1. The syntheses of CoPc and (*CoDMG*)₄-*CoPc*.

RCC

Graphical abstract Pictogram

Electrocatalytic Hydrogen Evolution Reaction with a Supramolecular Cobalt(II)phthalocyanine Carrying Four Cobaloxime Moieties



Research highlights

- > A symmetrical phthalocyanine with Pyridyl substituents has been prepared.
- ➤ It is converted to pentanuclear supramolecule by interaction with CoDMG
- Electrochemical properties of the supramolecule and the precursors have been investigated.
- Multi-electron transfer reactions of the supramolecule showed possible usage as electrocatalysts for *HER* reactions.