

Special
Collection

Spectroelectrochemical Behaviour of 1,4-Dimethoxypillar[5]arene (P5A) and its Monomer in Different Organic Solvents

Magdalena Z. Wiloch,* Ewelina Kuna, Sandra Kosiorek, Volodymyr Sashuk, and Martin Jönsson-Niedziółka*^[a]

This work is dedicated to Prof. Marcin Opałło on the occasion of his 65th birthday

The spectroelectrochemical response of the macrocyclic compound 1,4-dimethoxypillar[5]arene (P5A) and its monomer 1,4-dimethoxybenzene was investigated using cyclic voltammetry combined with UV-Vis spectroscopy. The influence of three different aprotic solvents, acetonitrile, dichloromethane, and dichloroethane, as well as supporting electrolyte, on the anodic behaviour of P5A were studied and discussed. The results indicate that the donor-acceptor Lewis-type interactions be-

tween tested compounds and the solvent molecules affect the oxidation processes and thus the formal potentials (E_f). In all solvents we see subsequent oxidation of P5A to P5A⁵⁺ followed at higher potential by an irreversible oxidation to the corresponding quinone. The results also show that small amounts of water can significantly influence the redox behaviour of the P5A.

1. Introduction

Supramolecular chemistry, which is a relatively new branch of chemistry, focuses on weak non-covalent interactions between molecules and/or ionic species.^[1] The non-covalent linkages allow for molecular self-assembling. Therefore, studying the nature of these interactions is essential to understand processes taking place in living organisms. Inspired by biological models, scientists obtained synthetic receptors like crown ethers, cyclodextrins, or calixarenes to investigate host-guest interactions. From 2008, when Ogoshi reported on 1,4-dimethoxypillar[5]arene (hereinafter called P5A), a new family of host macrocyclic molecules, pillar[n]arenes (P[n]A), emerged.^[2] Not surprisingly, since that time many derivatives of P[n]A, bearing other moieties have been synthesised.


P5A consists of 1,4-dimethoxybenzene subunits linked by methylene bridges.^[2] The presence of oxygen atoms in the P5A structure results in an electron-rich cavity of this phenolic macrocycle. Thus, the alkoxybenzene subunits might easily undergo oxidation to the corresponding benzoquinones, providing changes in the oxidation state of P5A, and hence in the corresponding absorption spectra. So far, the well-known structure and complexing properties of P[n]A as well its derivatives were mainly characterised by spectrochemical


analysis, including fluorescence techniques, UV-Vis, FTIR or NMR spectroscopy,^[3–5] whereas the electrochemistry of these P[n]A macrocycles still needs to be studied in detail.

Comparison of the electrochemical behaviour of pillar[n]arene and its model units has been an interesting approach to study their electrochemical response, and was initiated by Cheng and Kaifer.^[6] In that work, structures of pillar[5]quinone (P5Q) and its monomer p-xyloquinone (XQ) were examined by three different voltammetry techniques.^[6] It was shown that for measurements carried out in dichloromethane, which is an aprotic solvent, p-xyloquinone (XQ) underwent a subsequent reversible two-step reduction reaction. In the first step, p-xyloquinone was reversibly reduced, forming a radical anion, and then dianion. On the square wave voltammograms, two separate peaks appeared at potentials -0.67 V and -1.19 V vs Ag/AgCl. Provided that quinone groups in the macrocycle do not strongly influence each other, a similar cathodic electrochemical behaviour was expected for pillar[5]quinone. However, for P5Q, four consecutive peaks corresponding to 2, 1, 2, and 3 electron uptakes were observed in the square wave voltammogram. It is worth noting that the first reduction processes for P5Q took place at more positive potentials than for the monomer, -0.388 V and -0.596 V, followed by peaks at -0.800 V, and -1.080 V vs Ag/AgCl. This electrochemical response is most likely related to the pentagonal structure of P5Q where electrostatic repulsions of neighbouring units occur. Similar experiments for a series of 1,4-dimethoxypillar[m]arene-[n]quinones (P[m]A[n]Q) were performed by Liu *et al.* in acetonitrile.^[7] In this study, a correlation between a number of quinone units in macrocycle on the electrochemical behaviour was examined. In contrast to the previously described results for P5Q, only two reduction peaks have been observed.^[7] The discrepancy between the obtained results could be explained by the difference of solvent being used (ACN vs DCM).

The strong influence of the solvent effect on the electrochemical behaviour was also seen for pillar[5]arene, consisting

[a] Dr. M. Z. Wiloch, Dr. E. Kuna, S. Kosiorek, Dr. V. Sashuk, Dr. M. Jönsson-Niedziółka
Institute of Physical Chemistry Polish Academy of Sciences
Kasprzaka 44/52 01-224 Warsaw, Poland
E-mail: mwiloch@ichf.edu.pl
martinj@ichf.edu.pl

 An invited contribution to the Marcin Opałło Festschrift Supporting information for this article is available on the WWW under <https://doi.org/10.1002/celec.202100257>

 © 2021 The Authors. ChemElectroChem published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

of five hydroquinone rings, and for its hydroquinone form. The Evtugyn^[8,9] group recorded cyclic voltammograms on screen-printed carbon electrode in 50% acetone containing 0.1 M Na₂SO₄, whereas Yamagishi *et al.*^[10] performed experiments on a platinum electrode in a nonaqueous solvent - 0.1 M tetrabutylammonium hexafluorophosphate dissolved in acetonitrile. The comprehensive study shows that upon similar reaction conditions, at platinum electrodes in acetonitrile, hydroquinone undergoes an irreversible two-electron oxidation process to protonated quinone, resulting in one broad peak followed by irreversible two-electron reduction process on the cathodic sweep.^[11,12] Ogoshi *et al.*^[10] concluded that the shape of the curves obtained in acetonitrile for both compounds was similar, indicating that oxidation of the five hydroquinone in macrocycle appeared separately at the potential 1.02 V vs SCE. This kind of electrochemical response was not observed in 50% acetone containing 0.1 M Na₂SO₄. The redox activity of pillar[5] hydroquinone and hydroquinone were strongly dependent on their concentration and the concentration of their oxidation products. On cyclic voltammograms recorded for hydroquinone, in a wide range of potentials only one pair of peaks appeared under the potential of 0 V, while for the macrocycle, two pairs of oxidation and corresponding reduction steps were observed.^[8,9]

The latest research on the redox properties of the fully alkylated pillar[5]arene: 1,4-dimethoxypillar[5]arene (P5A) and its analogues with one (P4AQ1) or two quinone units (P3AQ2) were conducted by Champness *et al.*, in dichloromethane containing 0.4 M tetrabutylammonium tetrafluoroborate as a supporting electrolyte.^[13] Cyclic voltammograms of P5A, recorded in the negative potential range, did not show any redox processes. However, in the positive range of potentials, three consecutive oxidation peaks and corresponding reduction peaks were observed. Based on spectroelectrochemical experiments, all these processes were described as chemically reversible.^[13] According to the authors of this work, the use of a dry aprotic solvent such as dichloromethane prevented oxidation of dimethoxybenzene units to their corresponding quinones. Various studies can be found in the literature relating to the solvent's influence on the obtained electrochemical response of dimethoxybenzene. The electrochemical oxidation process of dialkoxybenzene was examined in different organic media such as dry acetonitrile, wet acetonitrile, methanol, and a mixture of methylene chloride with trifluoroacetic acid.^[14–19] As reported, the dialkoxybenzene molecule undergoes oxidation *via* formation of aromatic radical cation which stability depends on the solvent nucleophilicity. Hydrated solvents, *i.e.*, wet acetonitrile or mixture of methylene chloride with trifluoroacetic acid, stabilised once formed radical cation affecting protonation equilibria and caused reversible oxidation process. While in the presence of other nucleophiles such as cyanide (CN⁻) and methoxide (OCH₃⁻) ions, decomposition of the radical cation was observed.^[16,20,21] Therefore, in the dry acetonitrile, the polymerisation process of dialkoxybenzene occurred.^[18] In other experiments performed in acetonitrile with 0.1 M lithium perchlorate at platinum electrodes, two-steps oxidation was registered. The first oxidation process occurred at 1.2–1.4 V (vs

Ag/AgCl) and was reversible, whereas the second step was irreversible and appeared at more positive potentials 1.4–1.9 V (vs Ag/AgCl).^[14] On the contrary, for the oxidation of dialkoxybenzene derivatives carried out on GC electrodes in methanol, the first oxidation step became irreversible. These data indicate higher stability of cation radical intermediates in acetonitrile than in methanol media.^[14] Furthermore, as pointed by Becker *et al.*, the electrochemical oxidation of dialkoxybenzene derivatives also depends on its substituents. For the oxidation reactions performed in the mixture of acetone with sulfuric acid, only monosubstituted derivatives were fully oxidised towards corresponding quinones whereas disubstituted derivatives underwent partial oxidation.^[14] As reported by Champness *et al.*, for the partial oxidated P5A derivatives, bearing one (P4AQ1) and two (P3AQ2) quinone units, two reversible oxidation process for P4AQ1 and one for P3AQ2 were observed in anodic potential range.^[13]

Apart from this study, there are relatively sparse data available concerning the electrochemical behaviour of P5A in different organic solvents. Consequently, in this work, we present the spectroelectrochemical response of 1,4-dimethoxypillar[5]-arene (P5A) and its monomer in different aprotic solvents, *i.e.*, in acetonitrile, dichloromethane, and dichloroethane.

2. Results and Discussion

In this article, we investigated the redox behaviour of 1,4-dimethoxypillar[5]arene (P5A) and 1,4-dimethoxybenzene (MET) in three different aprotic solvents as acetonitrile (ACN), dichloromethane (DCM), and dichloroethane (DCE) using TBAHPF as a supporting electrolyte. The concentration of the examined analyte was 0.1 mM, and supporting electrolyte TBAHPF was 0.1 or 0.2 M. High concentration of supporting electrolyte increase the conductivity of the used solutions and limits transport of electroactive species by ion migration in the electric field.

2.1. P5A and MET Electrochemistry in DCE Containing 0.1 M and 0.2 M TBAHPF

On the voltammogram (Figure 1A) registered for 0.1 mM MET dissolved in 0.1 M TBHAFP/DCM, only one pair of peaks corresponding to oxidation and reduction processes were present. The formal potential (E_f) of this process is 1.0837 V (vs Ag/AgNO₃), and peak separation (ΔE) is 0.0694 V. Since the separation of the peaks is slightly greater than 59 mV, and the ratio of oxidation and reduction currents (I_{ox}/I_{red}) is different from 1 (it is 0.8), the process could be described as quasi-reversible. It is worth noting that the values of both anodic and cathodic currents in each subsequent cycle do not change, which could mean that the cation-radical intermediate is stabilised in DCM.^[14] The polymerisation process, expected for very dry solvent (less than 10⁻³% H₂O) which results in an increase of the peaks current in each subsequent cycles, was not observed which may be related to the water concentration

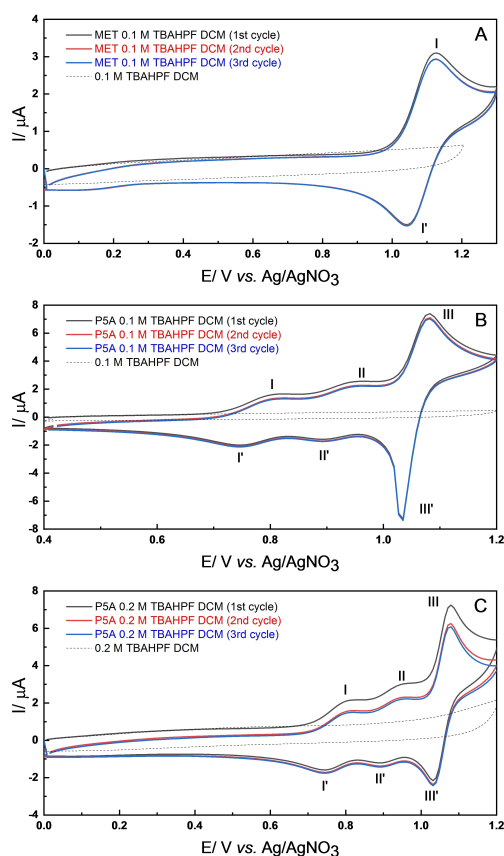


Figure 1. Cyclic voltammograms on glassy carbon of A) 0.1 mM MET and B, C) 0.1 mM P5A in DCM containing (A, B) 0.1 M TBAHFP or (C) 0.2 M TBAHFP as supporting electrolyte, $v = 100$ mV/s.

in DCM. For the electrochemical experiments, we used DCM with low water concentration ($\leq 0.01\%$). However, the water concentration could have increased slightly during sample preparation, since the solutions were prepared under a non-inert atmosphere. The effect of water concentration on the electrochemical response of MET in ACN was investigated by Ortis *et al.* The author suggested that the oxidation current does not change in relatively dry conditions (about 0.02% H₂O).^[30] Obtained electrochemical response may also be related to a very low MET concentration (0.1 mM).^[30] According to literature data, monomer concentration is a very important factor in a polymerisation process, for higher concentration (5 mM) polymerisation process occurs more easily than for lower concentration (0.5 mM).^[19] In the next subsections of this manuscript, we show results obtained in another strongly hydrophobic solvent as DCE, in which one electron quasi-

reversible process was also observed in this potential range 0–1.2 V vs Ag/AgNO₃. It is also worth noting that most of the studies related to the electrochemical behaviour of MET were carried out on platinum electrodes. There are reports in the literature showing the influence of the type of working electrode (Pt or GC) on the electrochemical response.^[16] The related data for MET obtained from voltammograms from all the investigated solvents are shown in Table 1. Additionally, we performed a series of cyclic voltammograms with increasing scan rate from 20 mV/s to 500 mV/s (Figure SI 1.1 A) to plot the peak currents vs square root scan rate and/or scan rate. Based on these results, both oxidation and reduction processes can be described as diffusion-controlled, since a linear dependence of the peak currents vs the square root of the scan rate was observed. (Figure SI 1.6).

Cyclic voltammetry was applied to investigate the anodic electrochemical behaviour of 0.1 mM P5A dissolved in DCM containing in 0.1 M TBAHFP (Figure 1B; SI 1.1B). The obtained results indicate three consecutive oxidation processes. These data seem to be in good agreement with the available literature.^[13] Champness *et al.*^[13] reported a similar electrochemical behaviour of 1 mM P5A in DCM and 0.4 M tetrabutylammonium tetrafluoroborate (TBATFB) salt, although the relative peak currents seem to differ. Based on these electrochemical and spectroelectrochemical studies, the first two anode processes can be described as a reversible or quasi-reversible one-electron process. The peak separation for the first pair of signals was $\Delta E = 0.054$ V which is very close to the theoretical value of 0.059 V. Interestingly, the ΔE values for these two subsequent processes were lower (0.046 V and 0.044 V, respectively). The significantly higher current for the 3rd peak suggests that more than 1 electron is involved in this process. To determine the exact number of electrons involved in the processes electrochemical measurements (CV and DPV; Table 2) were supplemented with computer simulations in the program Comsol (Figure 2B, details on the simulations in the SI). As expected, two first anodic steps could be defined as a single electron process forming P5A⁺ and P5A²⁺, respectively. During the third oxidation step, three electrons are involved leading to the P5A⁵⁺ oxidised form. Cheng and Kaifer reported the sequential 5 electron uptake for pentagonal symmetry of P5Q,^[6] therefore, a loss of 5 electrons of P5A appears to be possible.

The main differences between the CVs recorded here, and those described by Champness' group^[13] are the interpretation of the electron numbers for the three oxidation steps and the shape of the third reduction peak (Figure 1B; SI 1.1B) marked as III'. The sharpness of this peak could be attributed to an

Table 1. Potential value and peak width (calculated from CV curves), $b_{1/2}$ -peak width at the half-height from (calculated from DPV curves) for MET in three different solvents. All values were given in [V] vs Ag/AgNO₃. The error is the standard deviation for three measurements.^[a]

100 mV/s		E_{ox} [V]	E_{red} [V]	E_f	ΔE	$b_{1/2}$
MET	ACN	1.008 ± 0.009	0.938 ± 0.002	0.973 ± 0.005	0.069 ± 0.005	0.094
	DCM	1.118 ± 0.004	1.048 ± 0.005	1.084 ± 0.004	0.069 ± 0.004	0.098
	DCE	1.110 ± 0.004	1.041 ± 0.002	1.075 ± 0.002	0.069 ± 0.004	0.098

[a] E_{ox}/E_{red} : anodic/cathodic peak potential; ΔE : the difference between anodic and cathodic potential ($E_{ox} - E_{red}$); E_f : formal potential.

Table 2. The potential value and peak width (calculated from CV curves), $b_{1/2}$ -peak width at the half-height from (calculated from DPV curves) for P5A in DCM containing 0.1 or 0.2 M TBAHPF as a supporting electrolyte. All values were given in [V] vs Ag/AgNO₃. The error is the standard deviation for three measurements.^[a]

PA5 DCM 0.1 M TBAHPF						
Step	E _{ox} [V]	E _{red} [V]	E _f	ΔE	E _{ox} (DPV)	b _{1/2} (DPV)
1	0.806 ± 0.002	0.752 ± 0.004	0.779 ± 0.002	0.054 ± 0.004	0.773 ± 0.004	0.074 ± 0.001
2	0.951 ± 0.004	0.905 ± 0.006	0.928 ± 0.005	0.046 ± 0.004	0.916 ± 0.008	0.0647 ± 0.004
3	1.086 ± 0.006	1.042 ± 0.005	1.064 ± 0.002	0.044 ± 0.010	1.055 ± 0.004	0.0480 ± 0.004
4	1.408 ± 0.011	–	–	–	1.314 ± 0.020	0.085 ± 0.009
PA5 DCM 0.2 M TBAHPF						
Step	E _{ox} [V]	E _{red} [V]	E _f	ΔE	E _{ox} (DPV)	b _{1/2} (DPV)
1	0.803 ± 0.007	0.744 ± 0.003	0.773 ± 0.005	0.059 ± 0.004	0.764 ± 0.003	0.074 ± 0.001
2	0.942 ± 0.003	0.896 ± 0.006	0.919 ± 0.004	0.045 ± 0.004	0.906 ± 0.005	0.066 ± 0.002
3	1.079 ± 0.006	1.037 ± 0.006	1.060 ± 0.004	0.039 ± 0.011	1.046 ± 0.003	0.047 ± 0.001
4	1.426 ± 0.025	–	–	–	1.365 ± 0.021	0.098 ± 0.002

[a] E_{ox}/E_{red}: anodic/cathodic peak potential; ΔE: the difference between anodic and cathodic potential (E_{ox}-E_{red}); E_f: formal potential.

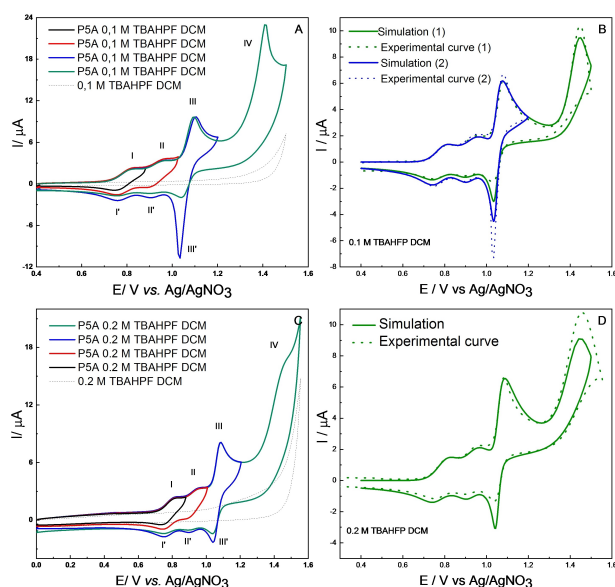


Figure 2. Cyclic voltammograms registered in various ranges of potentials on glassy carbon of 0.1 mM P5A in DCM containing A) 0.1 M TBAHPF or C) 0.2 M TBAHPF as supporting electrolyte, $v = 100$ mV/s. B, D) Comparison of 0.1 mM P5A cyclic voltammogram with simulation curves (B) 0.1 M TBAHPF/DCM and (D) 0.2 M TBAHPF/DCM.

adsorption process on the electrode surface. In the literature, the adsorption phenomenon in the electrochemical system for other compounds, *e.g.* viologens, is well described.^[31,32] Adsorption can also explain the discrepancy between the simulations and the experiments, as this was not taken into account in the computer model. To confirm the adsorptive character of peak III', a series of cyclic voltammograms were recorded at different scan rates (Figure SI 1 B). For the third reduction peak (III'') we did not observe a linear relationship neither for cathodic peak heights as a function of the scan rate nor as a function of the square root of the scan rate, which indicates a mixed process (Figure SI 1.7). For the rest of anodic (I, II, III) and cathodic (I', II') process we have obtained a linear relationship of the square root of the scanning rate which means that these processes are diffusion controlled. (Figure SI 1.7). To finally verify that the

adsorption process occurs, we performed additional experiments where a CV was registered for a clean electrode in an electrolyte solution (0.1 M TBAHPF DCM), showing no Faradaic processes, and then the electrode was transferred to a solution containing 0.1 mM P5A in 0.1 M TBAHPF DCM in which chronoamperometry was carried out by applying a potential of 1.1 V for 300 seconds. After the CA, cyclic voltammetry was again done in the clean electrolyte solution. The reduction peaks that appeared are evidence of weak adsorption on the electrode surface (Figure SI 1.5). The ongoing adsorption process may be caused, among other reasons, by the interaction of P5A with the solvent^[33] or with the salt TBAHPF *via* formation of ion pairs.^[34] Another possibility is the formation of oxidation side products that deposit on the GC electrode. To better understand the nature of this adsorption phenomena, we have increased the TBAHPF concentration from 0.1 to 0.2 M (Figure 1C; 2 C). The positions of all recorded peaks hardly change (Table 2), but, importantly, under these measuring conditions, the third reduction peak III', previously identified with the adsorption process, turned into a peak mainly corresponding to a diffusion-controlled process. (Figure SI 1.8). This may suggest that the oxidized P5A⁵⁺ macromolecules are less soluble in a low polarity solvent like DCM compared with P5A. We assume that a higher concentration of supporting electrolyte can partially or totally prevent precipitation of P5A⁵⁺ macromolecules. Possibly the higher concentrations of larger supporting electrolyte anions lead to ion-pairing with the P5A⁵⁺ species, thus favouring their solubility in the nonpolar medium.

Extending the potential range towards higher positive values (Figures 2A; B) revealed a 4th, irreversible, oxidation process. This is consistent with the literature data because for the monomer MET where and the additional irreversible oxidation process is also observed.^[14,19] Based on simulations made in COMSOL, we determined that 5 electrons are involved in this oxidation process. As reported, coulometric determination of the oxidation stoichiometry performed for P5A showed 10 electrons per one P5A molecule.^[8,9] In order to clarify the product of this process, we have also performed spectroelectrochemical studies. These confirmed that the appearance of

the 4th peak is related to the oxidation of P5A⁵⁺ towards a corresponding quinone (see section Results and Discussion 3). In contrast to measurements carried out in 0.2 M TBAHPF/DCM (Figure 2C), a sharp-edge IV peak profile was observed under 0.1 M TBAHPF/DCM measuring conditions (Figure 2A). However, this effect is visible only when the background current is not subtracted (Figure 2B). As expected, this 4th oxidation peak (marked as IV) significantly influenced the current of the 3rd reduction peak (marked as III') causing its decrease. Contrary to our results, no quinone formation was observed by Pearce *et al.*^[13] Control experiments in a glove box under dry conditions showed the same initial three peaks, but the fourth, irreversible, peak disappeared (Figure S1.10). This shows that even the minute amount of water absorbed during preparation of the electrolyte can change the oxidation of P5A. Keeping in mind that the addition of water could influence the current response, we have registered series of CV experiments adding water before and after each measurements. To 5 ml of 0.1 mM P5A in 0.1 M TBAHPF/DCM or 0.2 M TBAHPF/DCM we added 5 μ l or 45 μ l of water, affording 0.1% and 1% water content, respectively. These results are presented in the SI (Figure SI 1.3A–D). The shape of obtained CV curves do not change when measurements are performed immediately after first addition of water. For the experiments carried out about 30 minutes after addition, the current response changed slightly. We assume that this time is sufficient for an hydrolysis reaction to take place. When the measurement was carried out in a potential range of 0–1.2 V, a decrease of the current intensity of peak III' was observed. An additional peak in the range of 0.5–0.7 V (vs Ag/AgNO₃), was observed for the wider range of potentials (0–1.55 V) but only after the first cycle (SI 1.1D). The addition of 1% water significantly changed the anodic behaviour of P5A. Under these reaction conditions additional redox processes appear at potentials less positive than 0.7 V (vs Ag/AgNO₃). As a control we added water to the electrolyte solution itself and measured CVs without any P5A. No Faradaic responses were recorded in this case, which indicates that the addition of water causes additional reactions related to the P5A oxidation process. Similar pre-peaks in the CVs were observed for 8-hydroxyquinoline. The authors of that study suggest that they

appear as a consequence of a quite complex electro-oxidation process that leads to dimerisation or polymerisation taking place on the electrode surface.^[35]

Additionally, the presence of water leads to a shift of peak IV to less positive values. This means that in the presence of water, the oxidation of P5A⁵⁺ to the corresponding quinone is favoured, but that the results from the original experiments are likely not significantly affected by the minute water content possibly present in the solutions.

2.2. P5A and MET Electrochemistry in DCE and ACN Containing 0.1 M TBAHPF

To compare the anodic behaviour of P5A and its monomer in different organic solvents, we performed additional experiments in ACN and DCE. In ACN successive anodic process took place at lower potential compared to the DCM and DCE (Table 3), which indicated that the tested compounds' oxidation process is more favourable in ACN. A similar dependence was observed for the ferrocene oxidation process, where donor-acceptor Lewis-type interactions could explain the shift in E_f potentials.^[28] The electrochemical oxidation of P5A and MET corresponds to the formation of cation radicals, which acts as a Lewis electron-pair acceptor, whereas solvent molecule act as Lewis electron-pair donor. The strength of the interaction between cation and solvent molecule influenced donor number (DN) of the solvent. The donor number (DN) of ACN is 59.0 kJ/mol while DCE is 0 kJ/mol.^[28,36] Consequently, the weaker electron contribution of the solvent (DCM and DCE) to the cations resulted in increasing the E_f value.

The shape of P5A cyclic curves also changed depending on the solvent used. As shown in the corresponding voltammograms, the characteristic oxidation peaks in both DCM and DCE (Figure 1B; 3B) are well separated, while in ACN the individual peaks are not so well-defined (Figure 3A). Neither increasing nor decreasing the scan rate resulted in better separation of the peaks (Figure SI 1.2 A). Moreover, for CVs registered in DCE, the third reduction peak has the highest current intensity, similar to in DCM (Figure 1B), and it disappears almost entirely in ACN

Table 3. Potential value and peak width (calculated from CV curves), $b_{1/2}$ -peak width at the half-height from (calculated from DPV curves) for P5A in DCE or ACN containing 0.1 TBAHPF as a supporting electrolyte.^[a,b]

P5A ACN 0.1 M TBAHPF						
Step	E_{ox} [V]	E_{red} [V]	E_f	ΔE	E_{ox} (DPV)	$b_{1/2}$ (DPV)
1	0.763 ± 0.002	0.717 ± 0.004	0.740 ± 0.002	0.046 ± 0.004	0.718 ± 0.016	0.075 ± 0.010
2	0.867 ± 0.002	0.827 ± 0.002	0.847 ± 0.002	0.040 ± 0.002	0.827 ± 0.015	0.052 ± 0.002
3	1.052 ± 0.009	0.963 ± 0.015	1.008 ± 0.012	0.089 ± 0.008	0.990 ± 0.015	0.086 ± 0.006
4	1.469 ± 0.022	–	–	–	1.385 ± 0.021	0.166 ± 0.009
P5A DCE 0.1 M TBAHPF						
Step	E_{ox} [V]	E_{red} [V]	E_f	ΔE	E_{ox} (DPV)	$b_{1/2}$ (DPV)
1	0.847 ± 0.003	0.801 ± 0.003	0.824 ± 0.002	0.046 ± 0.004	0.813 ± 0.003	0.074 ± 0.002
2	0.970 ± 0.002	0.926 ± 0.002	0.948 ± 0.001	0.044 ± 0.005	0.937 ± 0.001	0.059 ± 0.001
3	1.087 ± 0.003	1.047 ± 0.003	1.067 ± 0.001	0.039 ± 0.006	1.056 ± 0.002	0.043 ± 0.003
4	1.407 ± 0.023	–	–	–	1.365 ± 0.020	0.134 ± 0.003

[a] All values were given in [V] vs Ag/AgNO₃. The error is the standard deviation for three measurements. [b] E_{ox}/E_{red} : anodic/cathodic peak potential; ΔE : the difference between anodic and cathodic potential ($E_{ox}-E_{red}$); E_f : formal potential.

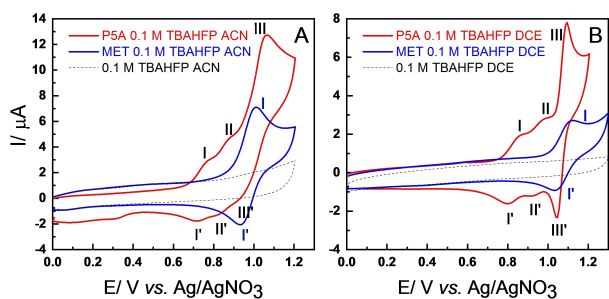


Figure 3. Cyclic voltammograms on glassy carbon of 0.1 mM P5A (red curve) or 0.1 mM MET (blue curve) in A) ACN containing 0.1 M TBAHFP as supporting electrolyte, $v = 100$ mV/s, B) DCE containing 0.1 M TBAHFP as supporting electrolyte, $v = 100$ mV/s.

(Figure 3A; SI 1.2 A). The change in the electrochemical response for macrocycles dissolved in ACN solution was already highlighted in an article by Liu *et al.*^[7] As reported, ACN has approximately 2-fold higher dipole moment value (3.71 D),^[37] in comparison with DCM (1.60 D)^[38] and DCE (1.80 D),^[39] as well as the lowest density (0.786 g/ml) and viscosity (0.334 mPa·s). Densities of DCM and DCE are 1.325 and 1.256 g/ml,^[40] respectively, and their viscosity is 0.410 mPa·s and 0.78 mPa·s, respectively.^[19] Consequently, one could assume that the difference observed in the electrochemical response is affected by the solvent's polarity, which influences the charge separation, and its viscosity that influences the rate of diffusion of charge carriers.^[41,42] Formation of inclusion complexes between P5A (host) and solvent molecules (guest) could also influence the shape of the electrochemical response. Literature data show that acetonitrile is more likely to interact with P5A than is DCM. The P5A-ACN complex association constant (29.8 M^{-1}) is higher than that of P5A-DCM (7.9 M^{-1}). The more substantial binding ability towards ACN is related to dipole-dipole interactions, multiple C–H...N interactions, dispersion forces, and the size-fit effects.^[43,44]

As noticed with DCM, extending the potential range to more positive values shows the 4th anodic peak with no corresponding reduction peak in neither ACN nor DCE media. This shows the irreversible nature of P5A^{5+} oxidation to a quinone (Figure 4 A, B) in all investigated solvents. In contrast to DCM, the fourth peak remained in ACN also under water-free conditions in a glovebox. (Figure SI1.10) The electrochemical

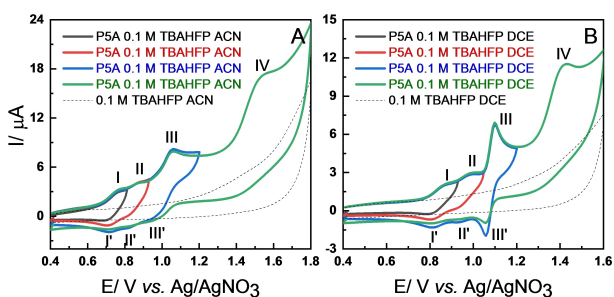


Figure 4. Cyclic voltammograms on the glassy carbon of 0.1 mM P5A in A) ACN containing 0.1 M TBAHFP as supporting electrolyte, B) DCE containing 0.1 M TBAHFP as supporting electrolyte, $v = 100$ mV/s.

studies performed for the monomer (MET) in ACN and DCE, in the investigated potential range 0–1.3 V, revealed a one-electron oxidation step in a diffusion-controlled process (Figures SI 1.2, SI 1.6) with a second irreversible oxidation step visible in more positive potential ranges (Figures SI 1.4).

2.3. Spectroelectrochemical Studies

The absorption spectra of 1,4-dimethoxypillar[5]arene, registered in DCM and TBAHFP as supporting electrolyte, exhibits a characteristic absorption band at 295 nm. Changes in the absorption spectrum occur gradually with an increase in the magnitude of applied potential. Increasing the applied potential from 0.4 V to 1.6 V results in new absorption bands with maxima at 443 nm/464 nm and 260 nm and a slight decrease of the intensity band at 295 nm. As reported by Champness,^[13] the new absorption band, in the region 400–500 nm, corresponds to various oxidised states of P5A. The band at 260 nm, generated from $n-\pi^*$ transition, is assigned to the corresponding 1,4-dimethoxypillar[n]arene[5-n]quinones.^[13] The oxidation of P5A to the corresponding quinones undergoes gradually through the mixed-valent intermediates in a multistep electron-transfer process and depends mainly on the reaction conditions.^[45] To better understand this process's mechanism, a series of chronoamperometric measurements were carried out at an applied potential of 0.83 V, 0.98 V, 1.15 V, and 1.45 V (vs Ag/AgNO₃) for up to 300 sec.

The corresponding electrochemical data (Figure 1B) indicate consecutive one-electron oxidation processes at potentials 0.83 V and 0.98 V (vs Ag/AgNO₃). Therefore, once formed, P5A^+ and P5A^{2+} intermediates are correlated with new absorption bands with the maximum at 443 nm and 464 nm (Figure 5A; B), assigned to $n-\pi$, $\pi-\pi^*$ transitions.^[46] Further increase in an absorption intensity in the region 400–500 nm (Figure 5C) and a progressive broadening of the peak at 295 nm is related to the three-electron oxidation process at 1.15 V (vs Ag/AgNO₃), which resulted in the formation of P5A^{5+} . Such spectroscopic behaviour (observed in Figure 5A–C) is explained by the cation-

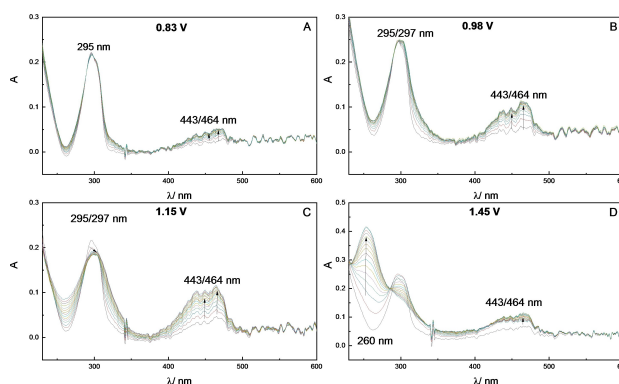


Figure 5. The absorption spectra of 0.1 mM P5A registered at an applied potential of A) 0.83 V; B) 0.98 V; C) 1.15 V, and D) 1.45 V. Spectra recorded in DMC containing 0.1 M TBAHFP at 22 °C. The time between each spectrum is 20 s.

states geometry changes, where the transitions are allowed due to vibronic coupling.^[47,48] Nevertheless, no definite emission spectra for these various oxidised forms can be easily registered. A significant spectral change occurs; an additional absorption band arises at 260 nm when the potential of 1.45 V is applied (vs Ag/AgNO₃) (Figure 5D). This band's intensity increases linearly with time, whereas the progressive displacement of the absorption at 295 nm with an isosbestic point at 286 nm is observed. The point corresponds closely to the cross-over point in the oxidation of P5A toward quinone derivatives.

As noticed, the absorption spectra indicate fully reversible changes when a reducing potential is applied, after the first (0.83 V), second (0.98 V), and third (1.15 V) oxidation step, pointing to a chemically reversible electron transfer (E mechanism). The absorption spectra of P5A registered at 1.45 V (vs Ag/AgNO₃) indicates irreversible changes. Hence, a chemically irreversible electron transfer in which the redox event is followed by a chemical reaction (EC mechanism).^[49] This complementary spectroscopic data is in good agreement with changes observed on the CV scans (Figure 2A).

In Figure 6 we can follow the kinetics of the growth of the new bands over time depending on the applied potentials. For 464 nm (Figure 6A), the kinetic profiles show changes in the absorption intensity corresponding to the various oxidised forms (*i.e.*, P5A⁺, P5A²⁺, P5A⁵⁺), and hence the differences in their concentration during electrochemical measurements. As is expected, the concentration of these oxidised forms increasing quickly with the increasing potential applied, reaching a plateau concentration after approximately first 60–120 sec of reaction, depending on the potential value. This steady-state concentration profile indicates the diffusion-controlled process. For the potential 1.45 V, a rapid decrease in the concentration of the intermediate oxidised forms is observed after the first 60 seconds that correlates with the conversion of P5A⁵⁺ into corresponding quinones. The formation of quinones is assigned to the increased absorption at 260 nm at 1.45 V (vs Ag/AgNO₃), (as shown in Figure 6 B). As mentioned before, an increase in the absorption intensity observed at lower potential values is due to strongly overlapped absorption bands of oxidised intermediates. The reaction rate towards intermediates and quinones is altered for experiments carried out in acetonitrile and dichloroethane and depends on the solvent and applied potential (SI 3.4; 3.5; 3.6). It can be clearly seen that the

oxidation reaction rate towards P5Q was faster in DCM and ACN media and slower in DCE. Whereas the oxidation reaction towards intermediates oxides forms (P5A⁺, P5A²⁺, P5A⁵⁺) was faster in DCE. Nevertheless, in both cases oxidation process follows the above-mentioned E/EC mechanism (SI 3.5; 3.6).

3. Conclusions

We have carried out spectroelectrochemical studies of the oxidation P5A and its monomer in three common aprotic solvents to understand the differences in electrochemical behaviour in acetonitrile, dichloromethane and dichloroethane. These solvents differ from each other in polarity, viscosity, and donor-acceptor Lewis properties.^[28] Lewis-type interactions seem to have had the most significant impact on the shift of oxidation potentials. Due to electron-donating properties of ACN, oxidation of both compounds P5A and MET appeared at less positive potentials compared to DCM and DCE. Our study also indicates a significant effect of host-guest interactions between the macrocycle molecules and solvent molecules. It is likely that the stronger interaction of ACN compared to DCM and DCE with P5A affected the shape of the recorded current responses.^[43,44] However, in all three solvents the oxidation of P5A showed three (quasi-)reversible reaction steps corresponding to two one-electron reactions and the third peak a three-electron oxidation, leading to P5A⁵⁺. The electron numbers here differ from the ones presented earlier by the Champness group. If scanned to higher potentials a fourth irreversible peak appears indicating the oxidation of P5A to its quinone-form P5Q. It has also been observed that the behaviour of tested structures is related to water concentration. In very dry aprotic solvents, oxidation of pillar[5]arene to their corresponding quinones does not take place.^[13] While in relatively dry conditions (less than 0.02 % H₂O), this process appears for all solvents, it disappears using water-free DCM in a glovebox under dry conditions.

This study shows the sequential charging of a pillar[5]arene and its subsequent irreversible oxidation. It also underlines the influence of solvent on the redox process for organic compounds^[50] and that the presence of even minute amounts of water can have substantial effect on the redox behaviour of pillararenes.

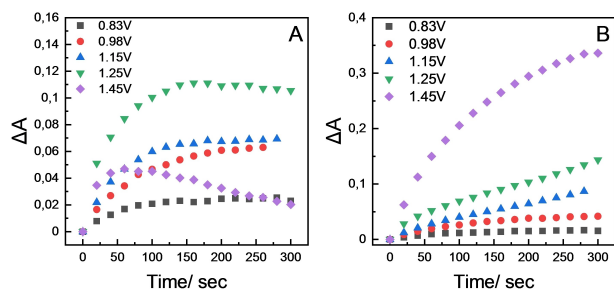


Figure 6. Changes in the absorption spectra of 0.1 mM P5A registered during the time for a given wavelength at A) $\lambda = 464$ nm and B) $\lambda = 260$ nm. Spectra recorded in DCM containing 0.1 M TBAHPF at 22 °C.

Experimental Section

Electrochemical methods

Cyclic voltammetry (CV), differential pulse voltammetry (DPV) and chronoamperometry (CA) experiments were performed using an Autolab potentiostat (Metrohm Autolab B.V., Netherlands) controlled by the NOVA software (version 2.1.2). CV measurements were performed at different scan rates, and at least 6 scans were recorded. Parameters for DPV measurements were as follows: step: 0.005 V, modulation amplitude 0.025 V, modulation time 0.05 s, and interval time 0.5 s. Each CA measurement was performed for 300 seconds, with a probing interval of 1 second. All experiments were

done in a three-electrode arrangement, with an Ag/AgNO₃ (0.01 M) in acetonitrile as the reference electrode, a platinum rod as the counter electrode, and a glassy carbon disk electrode (GCE from Mineral, Poland 0.0706 cm²) as the working electrode. The reference electrode potential was calibrated using a ferrocene (Fc) redox probe. Because the main measurements were carried out in three solvents, acetonitrile (ACN), dichloromethane (DCM), and dichloroethane (DCE), the formal potential of Fc/Fc⁺ was measured in these three solvents containing 0.1 M Bu₄NPF₆ (TBAHPF). The formal potential of Fc/Fc⁺ in 0.1 M TBAHPF in acetonitrile was 97 ± 4 mV,^[22–24] in 0.1 M TBAHPF in dichloromethane was 205 ± 8 mV,^[25,26] and in 0.1 M TBAHPF in dichloroethane was 201 ± 7 mV.^[25] The solvent dependence of the formal redox potentials of the ferrocene/ferrocenium couples is well known.^[23,25,27–29] The oxidation of ferrocene to the ferrocenium cation is shifted to the more positive potentials in DCM and DCE than for ACN solution due to donor-acceptor Lewis-type interactions.^[28] Argon was applied to deaerate the solution, and an argon blanket was maintained over the solution during the experiments carried out at room temperature (22 ± 2 °C). Prior to each voltammetric measurement, the GCE was polished on a Buehler polishing cloth to a mirror-like surface, using aqueous slurries of 0.05 μm alumina powder followed by 1 min acetonitrile ultrasonication to remove the remaining powder.

Spectroelectrochemical measurements

Redox properties of P5A were investigated by cyclic voltammetry and chronoamperometry, both combined with UV-Vis spectroscopic measurements. The measurements were performed using 0.1 mM P5A dissolved in DCM, DCE or ACN, containing 0.1 M TBAHPF as supporting electrolyte, at ambient temperature. The spectroelectrochemical experiments were carried out using a quartz photoelectrochemical cell with a 1 mm optical path length. A three-electrode configuration with Ag/AgNO₃ as the reference, a platinum wire as the counter, and platinum gauze working electrode were used in the cell. The absorption spectra were acquired using an Ocean Optics Flame-T spectrophotometer.

Chemicals and materials

Ferrocene (99%), 1,4-Dimethoxybenzene (hereinafter called MET) (99%) Tetrabutylammonium hexafluorophosphate (TBAHPF, for electrochemical analysis, ≥ 99.0%), Acetonitrile (ACN, for gas chromatography, ≥ 99.8% (GC), water: ≤ 0.05%), Dichloromethane (DCM, for gas chromatography, ≥ 99.8% (GC), water: ≤ 0.01%), 1,2-Dichloroethane (DCE, anhydrous, 99.8%) purity, were supplied by Sigma-Aldrich and used without further purification. Per-methylated pillar[5]arene was synthesised according to literature procedures.^[2] The purity of the compound was confirmed by NMR Spectroscopy (see SI 4). All electrochemical experiments were performed under inert atmosphere, using mother solutions degassed with argon prior to each measurement. The concentration of P5A and MET was 0.1 mM, whereas the supporting electrolyte concentration was equal to 0.1 M or 0.2 M for DCM solvent. Before measurements, all solutions were sonicated to ensure solubility of analytes.

Acknowledgements

The authors thank Dr. Emilia Witkowska Nery and Marta Podrażka for initial experiments and helpful discussions.

This work has been financially supported by the National Science Center Poland through the nr NCN 2015/18/E/ST4/00319 and by the Ministry of Science and Higher Education of Poland within a framework of Iuventus Plus III (nr IP2012 050772). E.K. would like to thank the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 847413 and note that this is scientific work published as part of an international co-financed project founded from the programme of the Minister of Science and Higher Education entitled "PMW" in the years 2020–2024; agreement no. 5005/H2020-MSCA-COFUND/2019/2.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: 1,4-dimethoxypillar[5]arene · 1,4-dimethoxybenzene · electrochemistry · spectroelectrochemistry · aprotic solvents

- [1] D. N. Reinhoudt, *Supramolecular Chemistry and Heterocycles*, Elsevier Inc., 2013.
- [2] T. Ogoshi, S. Kanai, S. Fujinami, T. Yamagishi, Y. Nakamoto, *J. Am. Chem. Soc.* **2008**, *130*, 5022–5023.
- [3] Y. Wang, G. Ping, C. Li, *Chem. Commun.* **2016**, *52*, 9858–9872.
- [4] P. J. Cragg, K. Sharma, *Chem. Soc. Rev.* **2012**, *41*, 597–607.
- [5] B. Shi, K. Jie, Y. Zhou, J. Zhou, D. Xia, F. Huang, *J. Am. Chem. Soc.* **2016**, *138*, 80–83.
- [6] B. Cheng, A. E. Kaifer, *J. Am. Chem. Soc.* **2015**, *137*, 9788–9791.
- [7] H. Saba, J. An, Y. Yang, M. Xue, Y. Liu, *Chin. J. Chem.* **2016**, *34*, 861–865.
- [8] E. E. Stoikova, M. I. Sorvin, D. N. Shurpik, H. C. Budnikov, I. I. Stoikov, G. A. Evtugyn, *Electroanalysis* **2015**, *27*, 440–449.
- [9] V. A. Smolko, D. N. Shurpik, R. V. Shamagsumova, A. V. Porfireva, V. G. Evtugyn, L. S. Yakimova, I. I. Stoikov, G. A. Evtugyn, *Electrochim. Acta* **2014**, *147*, 726–734.
- [10] T. Ogoshi, Y. Hasegawa, T. Aoki, Y. Ishimori, S. Inagi, T. Yamagishi, *Macromolecules* **2011**, *44*, 7639–7644.
- [11] B. R. Eggins, J. Q. Chambers, *J. Chem. Soc. D* **1969**, *53*, 232.
- [12] B. R. Eggins, J. Q. Chambers, *J. Electrochem. Soc.* **1970**, *117*, 186.
- [13] N. Pearce, E. S. Davies, N. R. Champness, *Molecules* **2020**, *25*, 1627.
- [14] C.-C. Zeng, J. Y. Becker, *J. Org. Chem.* **2004**, *69*, 1053–1059.
- [15] Y. Martínez, R. Hernández, M. Kalaji, J. Márquez, O. P. Márquez, *Synth. Met.* **1998**, *93*, 9–15.
- [16] B. Fabre, K. Michelet, N. Simonet, J. Simonet, *J. Electroanal. Chem.* **1997**, *425*, 67–75.
- [17] R. P. Buck, D. E. Wagoner, *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *115*, 89–113.
- [18] V. Le Berre, L. Angely, J. Simonet, G. Mousset, M. Bellec, *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, *218*, 173–185.
- [19] M. Choy de Martinez, O. P. Márquez, J. Márquez, F. Hahn, B. Beden, P. Crouigneau, A. Rakotondrainibe, C. Lamy, *Synth. Met.* **1997**, *88*, 187–196.
- [20] S. Andreades, E. W. Zahnow, *J. Am. Chem. Soc.* **1969**, *91*, 4181–4190.
- [21] A. Nilsson, U. Palmquist, T. Pettersson, A. Ronlán, *J. Chem. Soc. Perkin Trans. 1* **1978**, *53*, 708–715.
- [22] J. W. Diggle, n.d.
- [23] Y. Wang, E. I. Rogers, R. G. Compton, *J. Electroanal. Chem.* **2010**, *648*, 15–19.
- [24] K. N. Jarzemska, R. Kamiński, K. Durka, M. Kubsik, K. Nawara, E. Witkowska, M. Wiloch, S. Luliński, J. Waluk, I. Glowacki, et al., *Dyes Pigm.* **2017**, *138*, 267–277.
- [25] I. Noviadri, K. N. Brown, D. S. Fleming, P. T. Gulyas, P. A. Lay, A. F. Masters, L. Phillips, *J. Phys. Chem. B* **1999**, *103*, 6713–6722.
- [26] K. Durka, I. Glowacki, S. Luliński, B. Łuszczynska, J. Smętek, P. Szczepanik, J. Serwatowski, U. E. Wawrzyniak, G. Wesela-Bauman, E. Witkowska, et al., *J. Mater. Chem. C* **2015**, *3*, 1354–1364.
- [27] J. R. Aranzas, M. C. Daniel, D. Astruc, *Can. J. Chem.* **2006**, *84*, 288–299.

- [28] N. G. Tsierkezos, *J. Solution Chem.* **2007**, *36*, 289–302.
- [29] N. G. Tsierkezos, U. Ritter, *J. Appl. Electrochem.* **2010**, *40*, 409–417.
- [30] O. P. Márquez, J. Márquez, M. Choy, R. Ortiz, *Electrochim. Acta* **1994**, *39*, 1927–1935.
- [31] K. Arihara, T. Ohsaka, F. Kitamura, *Phys. Chem. Chem. Phys.* **2002**, *4*, 1002–1005.
- [32] T. Lu, T. M. Cotton, J. K. Hurst, D. H. P. Thompson, *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *246*, 337–347.
- [33] C. Schönbeck, H. Li, B. H. Han, B. W. Laursen, *J. Phys. Chem. B* **2015**, *119*, 6711–6720.
- [34] M. Ni, Y. Guan, L. Wu, C. Deng, X. Hu, J. Jiang, C. Lin, L. Wang, *Tetrahedron Lett.* **2012**, *53*, 6409–6413.
- [35] M. C. Stević, L. M. Ignjatović, G. Ćirić-Marjanović, S. M. Stanišić, D. M. Stanković, J. Zima, *Int. J. Electrochem. Sci.* **2011**, *6*, 2509–2525.
- [36] Y. Marcus, *J. Solution Chem.* **1984**, *13*, 599–624.
- [37] J. R. Partington, E. G. Cowley, *Nature* **1935**, *135*, 474–474.
- [38] I. Capan, M. Bayrakci, M. Erdogan, M. Ozmen, *IEEE Sens. J.* **2019**, *19*, 838–845.
- [39] J. E. Mark, C. Sutton, *J. Am. Chem. Soc.* **1972**, *94*, 1083–1090.
- [40] G. Sivaramprasad, M. V. Rao, D. H. L. Prasad, *J. Chem. Eng. Data* **1990**, *35*, 122–124.
- [41] F. Wilkinson, A. A. Abdel-Shafi, *J. Phys. Chem. A* **1997**, *101*, 5509–5516.
- [42] R. L. Willson, C. A. Dunster, L. G. Forni, C. A. Gee, K. J. Kittridge, *Philos. Trans. R. Soc. London* **1985**, *311*, 545–563.
- [43] C. Schönbeck, H. Li, B.-H. Han, B. W. Laursen, *J. Phys. Chem. B* **2015**, *119*, 6711–6720.
- [44] L.-L. Tan, Y. Zhang, B. Li, K. Wang, S. X.-A. Zhang, Y. Tao, Y.-W. Yang, *New J. Chem.* **2014**, *38*, 845.
- [45] T. Li, L. Xing, W. Li, B. Peng, M. Xu, F. Gu, S. Hu, *J. Phys. Chem. A* **2011**, *115*, 4988–4994.
- [46] K. Piech, T. Bally, T. Ichino, J. Stanton, *Phys. Chem. Chem. Phys.* **2014**, *16*, 2011–2019.
- [47] M. H. Stockett, S. B. Nielsen, *Phys. Chem. Chem. Phys.* **2016**, *18*, 6996–7000.
- [48] Y. Honda, M. Hada, M. Ehara, H. Nakatsuji, *J. Phys. Chem. A* **2002**, *106*, 3838–3849.
- [49] C. Sandford, M. A. Edwards, K. J. Klunder, D. P. Hickey, M. Li, K. Barman, M. S. Sigman, H. S. White, S. D. Minteer, *Chem. Sci.* **2019**, *10*, 6404–6422.
- [50] P. S. Guin, S. Das, P. C. Mandal, *Int. J. Electrochem.* **2011**, *2011*, 1–22.

Manuscript received: February 25, 2021

Revised manuscript received: March 17, 2021

Accepted manuscript online: March 18, 2021