The Synthesis of Diquinone and Dihydroquinone Derivatives of Calix[4]arene and Electrochemical Characterization on Au(111) surface

Boštjan Genorio

University of Ljubljana, Faculty of Chemistry and Chemical Technology, Večna pot 113, 1000 Ljubljana, Slovenia

* Corresponding author: E-mail: bostjan.genorio@fkkt.uni-lj.si
Tel: +386 1 479 8586

***In the memory of Janez (Janko) Jamnik, my doctoral advisor who taught me that everything can be done
and built if there is a vision and a will.***

Abstract

Several new electroactive diquinone and dihydroquinone derivatives of calix[4]arene bearing anchor functional groups were designed, synthesized and characterized. A method for selective protection of the hydroquinone –OH groups with trimethylsilyl groups (TMS) either on lower-rim or on upper-rim was developed. Four selected molecules – with sulfide anchor groups and carboxylic anchor groups – were adsorbed onto Au(111) single crystal surface using *ex-situ* and *in-situ* self-assembly methods. Adsorbed molecules were then electrochemically probed with cyclic voltammetry. All adsorbed molecules showed redox response which changed during cycling. After conditioning CVs stabilized and showed two distinct current peaks for all molecules. Synthesized and electrochemically probed molecules are of interest to: Li-ion batteries (as cathode materials and overcharge protection), beyond Li-ion batteries and redox-flow batteries.

Keywords: Electroactive molecules, calixarene, quinone, hydroquinone, electrochemistry

1. Introduction

World energy consumption is continuously growing with electrical energy being the single largest consumer. Today roughly 68% of electrical energy is generated from the fossil fuels.[1] It is predicted that consumption of electrical energy will double in the next 30 years. Considering the limited natural resources and the environmental impact of the fossil fuels and its combustion products, the alternative sources of electrical energy together with electrochemical energy storage should be taken into account. Batteries, being the main representative of electrochemical energy storage, will play a key role in the future energy consumption cycle.

Over the past decades a tremendous work has been done on the field of the batteries. In particular, Li-ion batteries experienced the biggest boom among them, due to high specific energy (energy per unit weight) and high energy density (energy per unit volume).[2] However, recently the research was being diverted to the other battery chemistries too, in order to increase energy density and decrease

the cost of the final product.[3] One of the revived fields is the use of redox active organic molecules in the battery systems. Advantages of the redox active organic molecules are low cost, high specific capacity, abundance, flexibility, safety, recyclability and sustainability. Up to date, redox active organic molecules were used as: redox shuttles in Li-ion batteries,[4] active cathode materials,[5,6] and active anode materials.[7] Depending on the nature of the system, redox active organic molecules can be: a) dissolved in the organic solvents – redox shuttles and redox-flow batteries,[8,9] b) grafted to the solid support – solid cathode in Li-ion batteries,[10–13] or c) free standing cathode material.[14] Redox active organic molecules are chemically divided into:[6] organosulfur molecules,[15] organic free radical compounds,[16] and carbonyl compounds.[17] The latter, having a quinone/hydroquinone as a key representative, are playing a significant role in electroactivity relevant to biochemistry, medicine and electrochemistry. Quinone derivatives were tested as cathode materials in Li-ion batteries[10–12,18] and redox-flow batteries.[19] Although it was demonstrated that quinones are promising candidates for

the use in energy storage, the field is still in its infancy. Motivated by above mentioned and the fact that there is a lack of fundamental understanding, we have focused on design of new quinone derivatives and electrochemical characterization.

In the present study, we examined several synthetic routes in order to synthesize quinone derivatives of calix[4]arene which could be then bound to the electrode materials and electrochemically tested. Calix[4]arene,[20] which was used as starting compound, is in particularly interesting for electrochemical applications, due to inherently opened cavities in the macrocycle. Cavities are potential sites for sieving cations with small ionic radius such as H^{+} or Li^{+}.[21–23] The letter is relevant to the enhanced accessibility of the active species in the energy conversion and storage systems. The crucial step in synthetic routes was the introduction of anchor functional groups. We have introduced carboxylic and sulfur containing anchor functional group. The latter is advantageous due to strong sulfur – noble metal interaction. Both, "short" anchors where redox active center would be close to the electrode surface and "long" anchors where center is further away from the electrode surface were introduced. By variation of the length we were hoping to investigate electrochemical reaction mechanisms. Successfully synthesized organic molecules were then anchored to the Au(111) single crystal surface using self-assembly protocol[24] and electrochemically probed.

2. Results and Discussion

The synthesis scheme is summarized in the Scheme 1. In the first attempt we have tried to introduce "short" sulfur based functional groups to the upper rim of the calix[4]arene macrocycle. We hypothesized that using "short" functional groups would bring electroactive centers of the molecule closer to the electrode material and thus mitigate electron transfer. Following the scheme we started from the basic calix[4]arene which was selectively protected with *n*-propyl groups on sites 26 and 28. Protected product **1b** was then oxidized to quinone derivative **2b** and bromine was introduced to the unoccupied sites. We tried to substitute the bromine on compound **3b** with thioacetyl anchor group but reaction conditions used, did not furnish desired product. We believe that side reaction is occurring on the carbonyl groups of quinone center. To avoid possible side reactions, we reduced **3b** to hydroquinone **4b**. In the next step, we tried to protect hydroxyl groups of hydroquinone with trimethylsilyl groups (TMS). Interestingly, on compound **5b**, upper-rim hydroxyl groups were protected only, while lower-rim stayed intact when using either *N,O*-bis(trimethylsilyl)acetamide (BSA) or trimethylsilyl chloride (TMSCl) (in the presence of triethylamine (TEA) or bis(trimethylsilyl)amine (HMDS)). On the other hand, TMSCl in the

presence of the NaH yielded **6b** where lower-rim OH groups were selectively protected, while upper-rim groups stayed intact. This interesting phenomenon is probably a combination of steric effects and non-covalent interactions of Na^{+} cations with calix[4]arene macrocycle. Despite the fact that we have failed to protect the hydroxyl groups of **4b** with TMS, we have shown new selective synthesis strategy, which can be used in designing new molecules. However, the protection of –OH groups on **4b** was successful when using less bulky *n*-propyl groups, yielding compound **7b$_1$** or methyl groups yielding **7b$_2$**. In the next step we introduced thioacetyl anchor groups and obtain compound **8**. The product **8** was then subject to oxidation in order to obtain redox-active quinone centers. Standard oxidation procedures did not furnish desired product, so the synthetic path was abandoned.

Using alternative synthetic path, we targeted the introduction of sulfide anchor functional groups. We again started from calix[4]arene, which was selectively protected with benzyl groups to furnish compound **1a**. Protected compound was then brominated on positions 5 and 17 to isolate product **9a**. In the next step we protected remaining two hydroxyl groups on the lower-rim, which yielded product **10a$_1$**. Bromine functional groups on upper-rim were then substituted with methylsulfide group using an exchange protocol. The product **11a$_1$** with –SMe anchor groups was then subject to deprotection of benzyl groups at lower-rim using trimethylsilyl bromide (TMSBr). The attempt to oxidize the deprotected product **12a$_1$** and synthesize quinone derivative failed. Although the synthesis of the designed molecules did not yield the desired products, the intermediate products could be in the future tested for other applications such as redox shuttles.

After two unsuccessful trials of introducing sulfur anchor groups to the upper-rim of calix[4]arene, we decided to introduce sulfur anchor groups to the lower-rim. Once again we started with calix[4]arene, which was selectively protected with functional groups already bearing sulfur containing anchor groups. We have successfully introduced three different functional groups containing sulfide anchor centers – **1d–g**. All three compounds were then oxidized to final quinone derivative **2d–g** in 10% to 58% yields.

For electrochemical comparison, the molecules with carboxyl functional groups at the lower-rim were also synthesized (Scheme 1). Slightly modified previously published method[25] yielded selectively protected calix[4]arene **1c** with protected carboxyl groups. In the next step phenolic units were oxidized to yield the molecule **2c** with quinone redox centers. In order to obtain carboxylic anchor groups, the *tert*-butyl groups were removed from **2c** and molecule **13** was isolated. For electrochemical comparison, a reduced version – hydroquinone **14** was also synthesized from **13**, applying Na$_2$S$_2$O$_4$ as a reducing agent.

Molecules **2f**, **2g**, **13** and **14** were then attached to the Au(111) single crystal surface using *ex-situ* (**2f** and
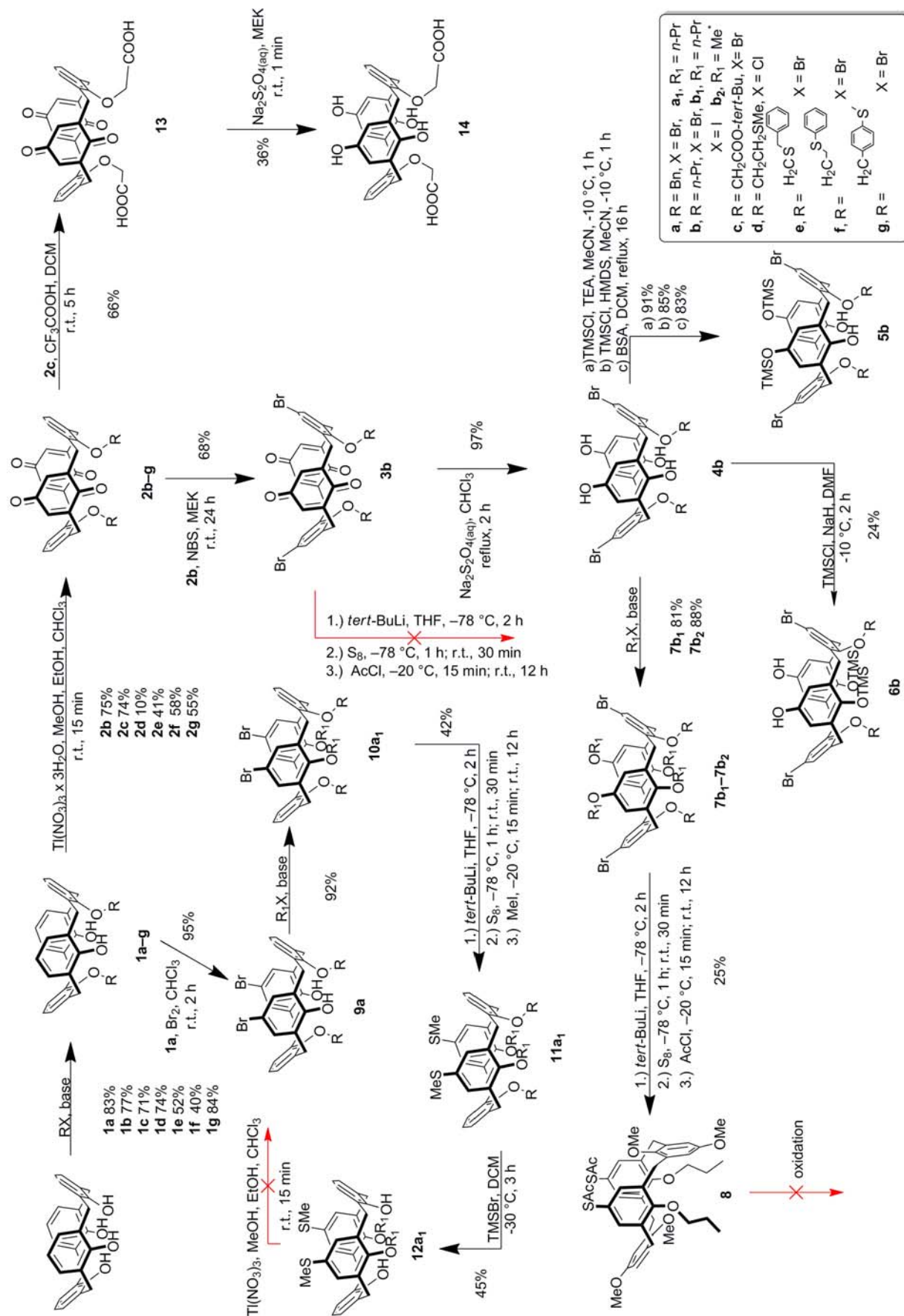
Scheme 1. Synthesis of electroactive diquinone derivatives of calix[4]arene with anchoring functional groups.
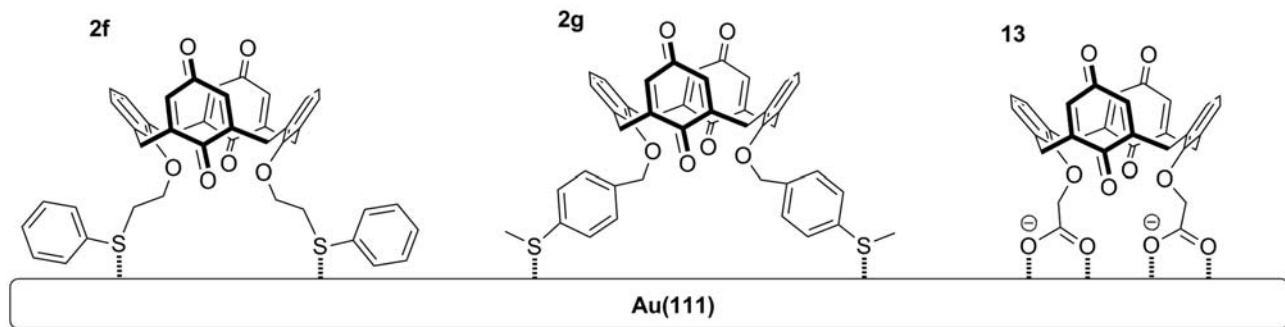
Figure 1. Self-assembled molecules at Au(111) single crystal surface. **2f** and **2g** were attached to the surface using *ex-situ* self-assembly method, **13** was attached using *in-situ* self-assembly method.

2g) and *in-situ* (**13** and **14**) self-assembly methods (Figure 1). Sulfide anchor groups in **2f** and **2g** were expected to bind to the gold through a dative bond. It was shown previously that sulfur can interact with Au(111) single crystal surfaces by donating the electron pair to the unoccupied Au orbitals.[26] On the other hand in the case of the carboxyl anchor groups (**13**, **14**), ion-metal interaction was expected. In this respect, pH of self-assembly system and surface charge of the metal surface are playing significant role, thus *in-situ* self-assembly method was applied. Adsorption of the carboxylates has also been extensively studied over the past decades where several successful grafting methods were shown,[27] including adsorption of electroactive anthraquinone-2-carboxylic acid on gold surface.[28]

To evaluate the electrochemical response of the adsorbed molecules on the Au(111) single crystal surface, cyclic voltammetry (CV) was used. Molecules **2f**, **2g**, **13**, and **14** on Au(111) were tested and their faradaic currents were measured. All chemically modified Au(111) electrodes showed specific faradaic response. Molecule **2f** with long and bulky sulfide anchor groups showed stable redox activity in the potential region from 0.1V to 1.15V vs. reversible hydrogen electrode (RHE). The reaction is quasi-reversible (Figure 2). In the first cycle (Figure 2, black line) the anodic scan shows at least two peak potentials (Ep_a) at 0.65V and 0.88V while cathodic scan shows three peak potentials (Ep_c) at 0.77V, 0.56V, and 0.43V. Redox

mechanisms of diquinone derivatives of cali[4]arene in aprotic organic solvents have been studied previously.[29] Authors suggest that there are two consecutive one-electron transfers followed by simultaneous concerted two-electron transfer, giving the ionized hydroquinone (Scheme 2). Another study noticed change of the mechanism in the presence of water to concerted four-electron transfer per two quinone units.[30] According to above mentioned and recorded CV, we can presume that the mechanism of the **2f** on Au(111) electrode could follow two consecutive one-electron transfers followed by concerted two-electron transfer in the first cycle.

However, after several cycles the shape of the CVs changed dramatically. Ep_a at 0.88V lost intensity, while Ep_a at 0.65V substantially increased. Similar was observed for the cathodic scan. Ep_c at 0.43V diminished while Ep_c at 0.56V increased. The reasons for the CV changes are unclear. One of the reasons could be, that the molecules on the Au(111) are rearranging and position of the redox centers are, in respect to the electrode, changing. Similar is happening with the molecules **2g** on Au(111) surface.

Scan in the anodic direction reveals single Ep_a at 0.88V while the reverse scan in the cathodic direction, single peak Ep_c at 0.33V (Figure 3). After cycling in the defined potential window the Ep_a shifted to 0.67V and Ep_c to 0.56V. This was the most pronounced when we held the potential at –0.1V for 1h. The peak potential separation ΔEp is becoming smaller, thus one can conclude that reac-
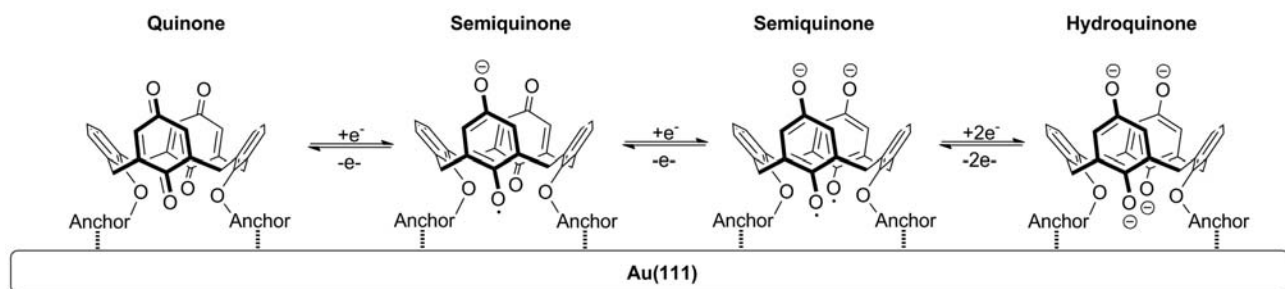
Scheme 2. Redox mechanism of electroactive diquinone derivatives of calix[4]arene with anchoring functional groups.
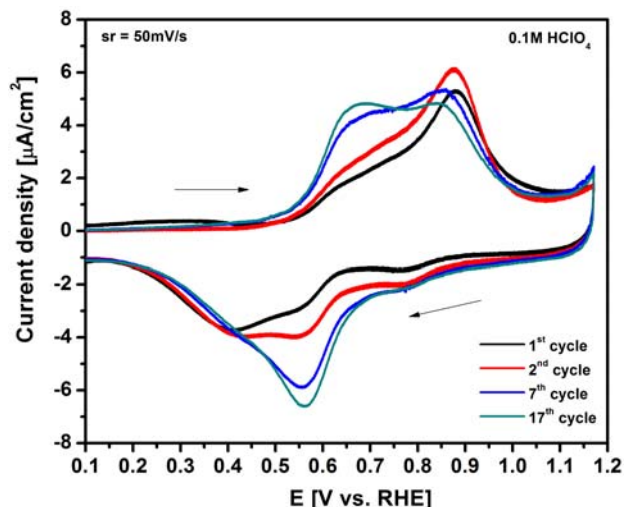
Figure 2. CVs of **2f** bound to Au(111). Black line – 1st cycle, red line – 2nd cycle, blue line – 7th cycle, and green line – 17th cycle. Conditions: 0.1M HClO$_4$, at room temperature, applying 50 mV/s scan rate. Arrows indicate direction of CV scan.

tion is getting more reversible. As mentioned above, the reason could be; the rearrangement of the self-assembled layer of the molecules on the Au(111) surface and change of the mechanism from two consecutive one-electron transfers followed by simultaneous concerted two-electron transfer to concerted four-electron transfer. In order to confirm that, extensive studies should be done, however, this is beyond the scope of this work.

The electrochemical investigation of the molecule with carboxylate anchor groups **13** on the Au(111) surfaces showed even more pronounced redox changes during cycling (Figure 4). To highlight the response of the redox
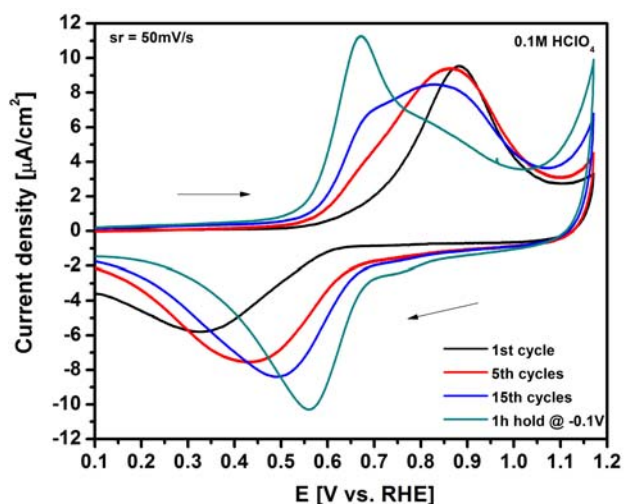
electrochemistry of **13** the CV of pure Au(111) is overlaid in the Figure 4. The first scan of **13** on Au(111) exhibited distinct electrochemical response with at least four peaks. Redox processes are reversible with Ep$_a$ at 0.53V, 0.63V, 0.70V, and 0.88V and Ep$_c$ at 0.50V, 0.57V, 0.71V, and 0.86V. After the third cycle, CVs stabilized and did not change significantly. However, the difference between first and third cycle is significant. In the third cycle only one Ep$_a$ at 0.70V can be seen and two Ep$_c$ at 0.55V, 0.56V. Interestingly, when CV of 3rd cycle of quinone derivative of calix[4]arene **13** was compared to CV of 1st cycle of reduced version – a hydoquinone derivative of calix[4]arene **14** (Figure 5c and 5d), the CVs almost overlapped. One would expect to see overlapping of the CVs in the first cycles since we are probing the same molecule but in different oxidation state. However, the molecules on the surface are immediately reduced when electrode is immersed at lower potential. From above mentioned observation we can deduct that molecule **13** is rearranging on the surface and making more accessible to the protons from the electrolyte which are protonating phenoxide anion of the hydroquinone molecules. Once the film is thermodynamically stable the electrochemical response give the same results for either oxidized quinone **13** or reduced hydroquinone **14**.

To evaluate the possible effect of the anchor groups, conditioned CVs of molecules **2f**, **2g**, **13** and **14** on Au(111) were compared (Figure 5). Surprisingly, all molecules exhibit similar electrochemical response with faradaic currents in anodic scan at Ep$_a$ – 0.67V and cathodic scan at Ep$_c$ – 0.56V. Although the ΔEp (0.11V) of the main electrochemical reaction is the same for all four compounds, there are differences between the CVs which indicate different mechanism either in the anodic scan for

Figure 3. CVs of **2g** bound to Au(111). Black line – 1st cycle, red line – 5th cycle, blue line – 15th cycle, and green line – 1h hold at –0.1V. Conditions: 0.1M HClO$_4$, at room temperature, applying 50 mV/s scan rate. Arrows indicate direction of CV scan.
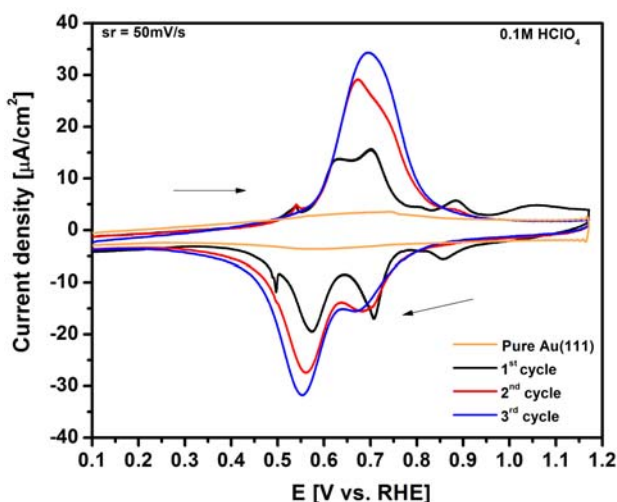

Figure 4. CVs of pure Au(111) (orange line) and **13** bound to Au(111). Black line – 1st cycle, red line – 2nd cycle, and blue line – 3rd cycle. Conditions: 0.1M HClO$_4$, at room temperature, applying 50 mV/s scan rate. Arrows indicate direction of CV scan.
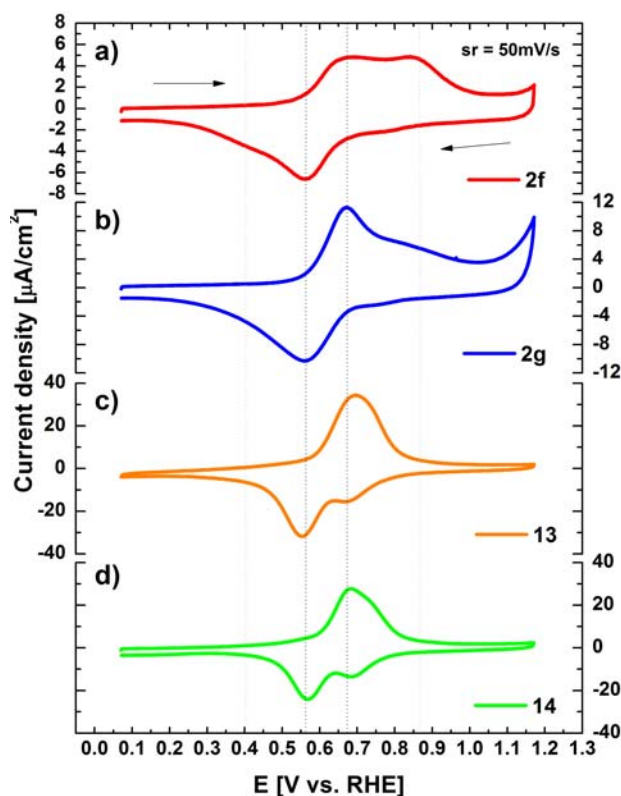
Figure 5. Comparison of stable CVs of quinone and hydroquinone derivatives of calix[4]arene: a) **2f** bound to Au(111), 17th cycle, b) **2g** bound to Au(111), 1h hold at –0.1V c) **13** bound to Au(111), 3rd cycle, and d) **14** bound to Au(111), 1st cycle. Conditions: 0.1M HClO$_4$, at room temperature, applying 50 mV/s scan rate. Arrows indicate direction of CV scan.

2f and **2g** or the cathodic scan for **13** and **14**. According to previously published results,[30] one would expect that the reduction of all four diquinone compounds would undergo a concerted four-electron reduction in acidic aqueous media. However, the conditioning of the chemically modified Au(111) electrodes shows that all the diquinones; **2f**, **2g**, and **13** bearing different anchor groups exhibit their unique electrochemical response with additional waves. One of the reasons for such behavior could be a specific steric effect of the molecules where one-electron transfer reactions followed by protonation are shielded and thus reaction intermediates are more stable. According to above mentioned we cannot draw any solid conclusions on the effect of the length of the anchor groups.

3. Conclusions

Specifically designed redox-active diquinone derivatives of calix[4]arene bearing various anchor functional were synthesized and fully characterized. Designed and synthesized electroactive molecules are particularly interesting for the energy conversion and storage systems

e.g. Li-ion and beyond Li-ion batteries (cathode materials, redox shuttles), and redox-flow batteries. In an attempt to introduce thiol anchor functional groups on the upper-rim of the calix[4]arene macrocycle, we have developed the method where selective protection of the hydroquinone –OH groups either on lower-rim (**6b**) or on upper-rim (**5b**) was achieved. Further, we have successfully synthesized new derivatives of calix[4]arene with 1,4-dimethoxybenzene moieties (**8**) and 1-methoxy-4-(methylthio)benzene moieties (**11a$_1$** and **12a$_1$**) that are in particular interest for the non-aqueous redox flow batteries and as an overcharge protection for Li-ion batteries. We have also successfully synthesized diquinone derivatives of calix[4]arene with sulfide (**2e**, **2f**, and **2g**) and carboxylate (**13** and **14**) anchor groups on lower-rim of the macrocycle. Above mentioned molecules could be used as an active cathode component of the Li-ion and beyond Li-ion batteries.

Molecules **2f**, **2g**, **13** and **14** were then attached to the Au(111) single crystal electrode using *ex-situ* and *in-situ* self-assembly methods and electrochemically characterized. All the analyzed molecules gave redox response in 0.1M HClO$_4$. It was noticed that electrochemical responses are changing during cycling for the molecules **2f**, **2g**, and **13**. The positions of the peak potentials; Ep$_a$ and Ep$_c$ are shifting, increasing and decreasing. However, after conditioning the peak potentials; Ep$_a$ and Ep$_c$ stabilized and CVs did not change substantially. The conditioned CVs of **2f**, **2g**, **13** and **14** on Au(111) revealed two common peak potentials; Ep$_a$ at 0.67V and Ep$_c$ at 0.56V with the peak potential separation ΔEp – 0.11V. The latter indicates that main redox mechanism of the different diquinone derivatives of calix[4]arene is similar while the presence of other peak potentials suggest that the full mechanism is complex and specific for the molecules tested.

4. Experimental

4. 1. Synthetic Materials and General Synthetic Procedures

Reactions were performed in dried glassware under Ar atmosphere, unless stated otherwise. Precursor calix[4]arene was prepared according to literature procedures.[31] Reagent grade tetrahydrofuran (THF) was distilled from Na and sodium benzophenone ketyl. Triethylamine (TEA) and N,N-dimethylformamide (DMF) were distilled over CaH$_2$. Reagent grade hexanes, CHCl$_3$, CH$_2$Cl$_2$ (DCM), MeOH, and ethyl acetate (EtOAc) were used without further distillation. Acetyl chloride (AcCl) was heated at reflux with PCl$_5$ and then distilled. tert-Butyllithium titrated before use (1.46 M solution in pentane) was obtained from Aldrich. All other commercially available reagents were used as received. Flash column chromatography was performed using 230–400 mesh silica gel from EM Science. Thin layer chromatography was performed using

glass plates pre-coated with silica gel 40 F_{254} purchased from Merck. [1]H spectra were taken at 400 or 300 MHz. ^{13}C NMR were recorded on the same instrument at 100.6 or 75.5 MHz, respectively. Proton chemical shifts (D) are reported in ppm downfield from tetramethylsilane (TMS). Carbon was referenced to CDCl$_3$ (77.23 ppm), except when specified otherwise. Infrared spectroscopy (IR) spectra were recorded on Nicolet Avatar FTIR instrument. High resolution mass spectrometry (HRMS) was recorded on Q-Tof Premier, Waters-Micromass spectrometer.

General Procedure for synthesis of partially alkylated calix[4]arene (1). Calix[4]arene (3 g, 7.07 mmol) and K$_2$CO$_3$ (1.07 g, 7.77 mmol) were suspended in MeCN (50 ml) and alkyl halide (2.15 ml, 14.21 mmol) was added. The reaction suspension was let to stir at the temperature of solvent boiling point, for 24 h. After 24 h MeCN was removed under reduced pressure, the remaining solid dissolved in CHCl$_3$ (50 ml), and washed with 1M HCl (50 ml) and saturated aqueous solution of NaCl (50 ml). Organic phase was then separated from the aqueous and dried with MgSO$_4$. Organic solvent was removed under reduced pressure and crude product purified by column chromatography (silica gel) or recrystallization.

General procedure for synthesis of diquinone derivative of calix[4]arene (2). A solution of Tl(NO$_3$)$_3$ × 3H$_2$O (20.97 g, 47.18 mmol) in solvent mixture, MeOH (480 ml) and EtOH (1440 ml) was slowly added to the solution of **1** (4 g, 7.86 mmol) in CHCl$_3$. Reaction mixture was let to stir for 15 min and then quenched by addition of H$_2$O (200 ml). 10% aqueous solution of HCl was then added dropwise until precipitate that formed during reaction did not dissolve. By applying reduced pressure, ~80% of the solvents were removed and CH$_2$Cl$_2$ (100 m) and H$_2$O (50 ml) were added. Organic phase was separated from the aqueous and dried with MgSO$_4$. Solvents were removed under reduced pressure and remaining solid purified by column chromatography (silica gel) or recrystallization.

General procedure for synthesis of alkoxy-calix[n]arene (7, 10). Compound **7** or **10** (8.50 mmol) was added to the suspension of NaH (1.4 g, 59.50 mmol) in DMF (37 ml) under inert atmosphere. Reaction mixture was let to stir at room temperature for 1 h and then alkyl halide (127.5 mmol) was added dropwise. Reaction mixture was then heated up to 60 °C and let to stir for 24 h. DMF was removed under reduced pressure and remaining solid suspended in CH$_2$Cl$_2$ (50 ml). This was shook with saturated solution of NH$_4$Cl (50 ml). Organic phase was separated from aqueous and dried with MgSO$_4$. CH$_2$Cl$_2$ was removed under reduced pressure and crude product purified by column chromatography or recrystallization.

Cone 26,28-bis(phenylmethoxy)-25,27-dihydroxycalix[4]arene (1a). Following the procedure for synthesis of partially alkylated calix[4]arene; calix[4]arene (3 g, 7.07 mmol), benzyl bromide (1.72 ml, 14.49 mmol), K$_2$CO$_3$ (1.11 g, 8.06 mmol) and MeCN (90 ml) were used. Recrystallization from solvent mixture, CHCl$_3$ – MeOH yields colorless crystalline product (3.56 g, 83% yield). ^{1}H NMR (300 MHz, CDCl$_3$): Δ 7.82 (s, 2H), 7.65 (m, 4H), 7.36 (m, 6H), 7.05 (d, *J* = 7.5 Hz, 4H), 6.88 (d, *J* = 7.5 Hz, 4H), 6.75–6.63 (m, 4H), 5.06 (s, 4H), 4.31 (d, *J* = 13.1 Hz, 4H), 3.34 (d, *J* = 13.1 Hz, 4H). The spectrum is in accordance with previously published results.[32]

Cone 26,28-di-*n*-propoxy-25,27- dihydroxycalix[4]arene (1b). Calix[4]arene (4 g, 9.42 mmol) was dissolved in DMF (87 ml) and BaO (8.41 g, 54.84 mmol), Ba(OH)$_2$ × 8H$_2$O (8.95 g, 28.36 mmol), and 1-bromopropane (4.28 ml, 47.11 mmol) were added. Reaction mixture was let to stir over night at 50 °C. After completion of reaction, 10% aqueous solution of HCl was added and extracted with CH$_2$Cl$_2$. Organic phase was separated from aqueous and dried with MgSO$_4$. The solvents were removed under reduced pressure and remaining solid was recrystallized from solvent mixture CHCl$_3$ – MeOH. Recrystallization yielded colorless crystalline product (3.68 g, 77% yield). ^{1}H NMR (300 MHz, CDCl$_3$): Δ 8.30 (s, 2H), 7.05 (d, *J* = 7.5 Hz, 4H), 6.91 (d, *J* = 7.5 Hz, 4H), 6.73–6.61 (m, 4H), 4.32 (d, *J* = 12.9 Hz, 4H), 3.97 (t, *J* = 6.3 Hz, 4H), 3.37 (d, *J* = 12.9 Hz, 4H), 2.07 (m, 4H), 1.31 (t, *J* = 7.4 Hz, 6H). The spectrum is in accordance with previously published results.[33]

Cone 26,28-bis[(*tert*-butoxycarbonyl)methoxy]-25,27-dihydroxycalix[4]arene (1c). Following the procedure for synthesis of partially alkylated calix[4]arene; calix[4]arene (1 g, 2.36 mmol), *tert*-butyl bromoacetate (0.71 ml, 4.83 mmol), K$_2$CO$_3$ (371 mg, 2.69 mmol) and MeCN (30 ml) were used. Recrystallization from solvent mixture, CHCl$_3$ – MeOH yields colorless crystalline product (1.09 g, 71% yield). ^{1}H NMR (300 MHz, CDCl$_3$): Δ 7.66 (s, 2H), 7.04 (d, *J* = 7.5 Hz, 4H), 6.88 (d, *J* = 7.5 Hz, 4H), 6.72–6.65 (m, 4H), 4.58 (s, 4H), 4.47 (d, *J* = 13.2 Hz, 4H), 3.37 (d, *J* = 13.2 Hz, 4H), 1.56 (s, 18H). The spectrum is in accordance with previously published results.[25]

Cone 26,28-bis[2-(methylsulfanyl)ethoxy]-25,27-dihydroxycalix[4]arene (1d). Following the modified procedure (NaI was also used) for synthesis of partially alkylated calix[4]arene; calix[4]arene (2.5 g, 5.89 mmol), 2-chloroethyl methyl sulfide (1.18 ml, 12.07 mmol), K$_2$CO$_3$ (928 mg, 6.71 mmol), MeCN (75 ml) and NaI (1.81 g, 12.07 mmol) were used. Column chromatography (CH$_2$Cl$_2$: *n*-hexane 2 : 1) followed by recrystallization from solvent mixture CHCl$_3$ – MeOH yielded colorless crystalline product (2.48 g, 74% yield). ^{1}H NMR (300 MHz, CDCl$_3$): Δ 7.56 (s, 2H), 7.07 (d, *J* = 7.5 Hz, 4H), 6.84 (d, *J* = 7.5 Hz, 4H), 6.71 (m, 4H), 4.35 (d, *J* = 13.1 Hz, 4H), 4.15 (t, *J* = 6.7 Hz, 4H), 3.39 (d, *J* = 13.1 Hz, 4H), 3.10 (t, *J* = 6.7 Hz, 4H), 2.29 (s, 6H). ^{13}C NMR (75.5

MHz, CDCl$_3$): Δ 153.5, 152.1, 133.4, 129.3, 128.9, 128.4, 125.7, 119.4, 75.8, 33.9, 31.7, 16.7. HRMS: calcd for C$_{34}$H$_{36}$O$_4$S$_2$ + H$^+$, 573.2133; found, 573.2125.

Cone 26,28-Bis[(benzylsulfanyl)methoxy]-25,27-dihydroxycalix[4]arene (1e). Following the procedure for synthesis of partially alkylated calix[4]arene; calix[4]arene (2 g, 4.71 mmol), bromomethyl benzyl sulfide (1.46 ml, 9.66 mmol), K$_2$CO$_3$ (742 mg, 5.37 mmol) and MeCN (60 ml) were used. Column chromatography (CH$_2$Cl$_2$: *n*-hexane 2 : 1) yielded white powder product (1.71 g, 52% yield). IR (KBr): 3372, 3060, 3025, 2925, 1591, 1462 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): Δ 7.68 (s, 2H), 7.38–7.24 (m, 10H), 7.09 (d, *J* = 7.5 Hz, 4H), 6.92 (d, *J* = 7.5 Hz, 4H), 6.76 (m, 4H), 5.08 (s, 4H), 4.45 (d, *J* = 13.2 Hz, 4H), 4.05 (s, 4H), 3.42 (d, *J* = 13.2 Hz, 4H). ^{13}C NMR (75.5 MHz, CDCl$_3$): Δ 153.6, 151.9, 137.6, 133.9, 129.8, 129.6, 129.1, 128.6, 127.7, 126.4, 119.7, 116.4, 113.0, 77.9, 36.1, 32.6. HRMS: calcd for C$_{44}$H$_{40}$O$_4$S$_2$ + Na$^+$, 719.2266; found, 719.2289.

Cone 26,28-bis[2-(phenylsulfanyl)ethoxy]-25,27-dihydroxycalix[4]arene (1f). Following the procedure for synthesis of partially alkylated calix[4]arene; calix[4]arene (2 g, 4.71 mmol), 2-bromoethyl phenyl sulfide (1.46 ml, 9.66 mmol), K$_2$CO$_3$ (742 mg, 5.37 mmol) and MeCN (60 ml) were used. Column chromatography (CH$_2$Cl$_2$: *n*-hexane 2 : 3) followed by recrystallization from solvent mixture CH$_2$Cl$_2$ – MeOH yielded colorless crystalline product (1.3 g, 40% yield). ^{1}H NMR (300 MHz, CDCl$_3$): Δ 7.75 (s, 2H), 7.44–7.17 (m, 10H), 7.05 (d, *J* = 7.5 Hz, 4H), 6.85 (d, *J* = 7.5 Hz, 4H), 6.67 (m, 4H), 4.30 (d, *J* = 13.1 Hz, 4H), 4.16 (t, *J* = 7.2 Hz, 4H), 3.56 (t, *J* = 7.2 Hz, 4H), 3.35 (d, *J* = 13.1 Hz, 4H). ^{13}C NMR (75.5 MHz, CDCl$_3$): Δ 153.5, 151.8, 135.6, 133.5, 130.2, 129.5, 129.3, 128.9, 128.7, 128.5, 126.9, 125.8, 119.5, 74.7, 33.3, 31.7. HRMS: calcd for C$_{44}$H$_{40}$O$_4$S$_2$ + Na$^+$, 719.2266; found, 719.2280. The data is in accordance with previously published results.[34]

Cone 26,28-Bis[(4-methylthio)benzyl]-25,27-dihydroxycalix[4]arene (1g). Following the procedure for synthesis of partially alkylated calix[4]arene; calix[4]arene (1 g, 2.36 mmol), 4-(methylthio)benzyl bromide (1.05 g, 4.83 mmol), K$_2$CO$_3$ (371 mg, 2.69 mmol) and MeCN (30 ml) were used. Recrystallization from solvent mixture CH$_2$Cl$_2$ – MeOH yielded colorless crystalline product (1.38 g, 84% yield). IR (KBr): 3406, 3022, 2921, 2858, 1595, 1462 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): Δ 7.78 (s, 2H), 7.56 (d, *J* = 8.3 Hz, 4H), 7.25 (d, *J* = 8.3 Hz, 4H), 7.04 (d, *J* = 7.5 Hz, 4H), 6.87 (d, *J* = 7.5 Hz, 4H), 6.67 (m, 4H), 5.02 (s, 4H), 4.28 (d, *J* = 13.1 Hz, 4H), 3.33 (d, *J* = 13.1 Hz, 4H). ^{13}C NMR (75.5 MHz, CDCl$_3$): Δ 153.6, 152.2, 138.9, 133.9, 133.6, 129.4, 128.9, 128.4, 128.3, 127.0, 125.8, 119.4, 78.3, 31.8, 16.2. HRMS: calcd for C$_{44}$H$_{40}$O$_4$S$_2$ + Na$^+$, 719.2266; found, 719.2250.

Cone 11,26,23,28-tetraone-25,27-dipropoxycalix[4] arene (2b). Following the procedure for synthesis of diquinone derivative of calix[4]arene; compound **1b** (4 g, 7.86 mmol), Tl(NO$_3$)$_3$ × 3H$_2$O (20.97 g, 47.18 mmol), MeOH (480 ml), EtOH (1440 ml), CHCl$_3$ (400 ml) and H$_2$O (200 ml) were used. Recrystallization from solvent mixture CH$_2$Cl$_2$ – MeOH at 4 °C, yielded orange crystalline product (3.16 g, 75% yield). ^{1}H NMR (300 MHz, CDCl$_3$): Δ 6.80 (d, *J* = 7.4 Hz, 4H), 6.63 (m, 6H), 3.81 (d, *J* = 12.7 Hz, 4H), 3.65 (t, *J* = 7.1 Hz, 4H), 3.32 (d, *J* = 12.7 Hz, 4H), 1.81 (m, 4H), 1.00 (t, *J* = 7.5 Hz, 6H). The spectrum is in accordance with previously published results.[35]

Cone 11,26,23,28-tetraone-25,27-bis[(*tert*-butoxycarbonyl)methoxy]-calix[4]arene (2c). Following the procedure for synthesis of diquinone derivative of calix[4]arene; compound **1c** (500 mg, 0.77 mmol), Tl(NO$_3$)$_3$ × 3H$_2$O (2.04 g, 4.60 mmol), MeOH (60 ml), EtOH (180 ml), CHCl$_3$ (50 ml) and H$_2$O (25 ml) were used. Column chromatography (CH$_2$Cl$_2$: EtOAc 3 : 1) yielded orange powder product (386 mg, 74% yield). ^{1}H NMR (300 MHz, CDCl$_3$): Δ 6.82 (d, *J* = 7.4 Hz, 4H), 6.74 (s, 4H), 6.66 (m, 2H), 4.34 (s, 4H), 3.96 (d, *J* = 12.4 Hz, 4H), 3.36 (d, *J* = 12.4 Hz, 4H), 1.49 (s, 18H). The spectrum is in accordance with previously published results.[25]

Cone 11,26,23,28-tetraone-25,27-bis[2-(methylsulfanyl)ethoxy]-calix[4]arene (2d). Following the procedure for synthesis of diquinone derivative of calix[4]arene; compound **1d** (50 mg, 0.09 mmol), Tl(NO$_3$)$_3$ × 3H$_2$O (233 mg, 0.52 mmol), MeOH (6 ml), EtOH (18 ml), CHCl$_3$ (5 ml) and H$_2$O (2.5 ml) were used. Column chromatography (CH$_2$Cl$_2$: EtOAc 10 : 1) yielded orange powder product (5 mg, 10% yield). IR (KBr): 3063, 2921, 2866, 1656, 1459, 1292, 1200 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): Δ 6.81 (d, *J* = 7.4 Hz, 4H), 6.65 (m, 6H), 3.90 (m, 8H), 3.33 (d, *J* = 12.9 Hz, 4H), 2.85 (t, *J* = 6.5 Hz, 4H), 2.18 (s, 6H). ^{13}C NMR (75.5 MHz, CDCl$_3$): Δ 188.5, 186.2, 148.4, 132.5, 130.2, 123.9, 93.2, 74.2, 46.0, 34.2, 31.7. HRMS: calcd for C$_{34}$H$_{32}$O$_6$S$_2$ + H$^+$, 601.1719; found, 601.1738.

Cone 11,26,23,28-tetraone-25,27-bis[(benzylsulfanyl)methoxy]-calix[4]arene (2e). Following the procedure for synthesis of diquinone derivative of calix[4]arene; compound **1e** (500 mg, 0.72 mmol), Tl(NO$_3$)$_3$ × 3H$_2$O (1.91 g, 4.30 mmol), MeOH (60 ml), EtOH (180 ml), CHCl$_3$ (50 ml) and H$_2$O (25 ml) were used. Column chromatography (CH$_2$Cl$_2$: EtOAc 15 : 1) yielded orange powder product (215 mg, 41% yield). IR (KBr): 3060, 3028, 2923, 1653, 1459, 1293 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): Δ 7.35–7.15 (m, 10H), 6.79–6.66. (m, 10H), 4.91 (s, 4H), 4.05 (d, *J* = 13.0 Hz, 4H), 3.73 (s, 4H), 3.23 (d, *J* = 13.0 Hz, 4H). ^{13}C NMR (75.5 MHz, CDCl$_3$): Δ 188.9, 187.9, 187.6, 151.4, 148.8, 148.7, 148.1, 137.7, 133.3, 129.5, 129.1, 128.5, 127.0, 126.3, 121.7, 64.5, 34.4, 30.7.

HRMS: calcd for $C_{44}H_{36}O_6S_2$ + H$^+$, 725.2032; found, 725.2058.

Cone 11,26,23,28-tetraone-25,27-bis[2-(phenylsulfanyl)ethoxy]-calix[4]arene (2f). Following the procedure for synthesis of diquinone derivative of calix[4]arene; compound **1f** (500 mg, 0.72 mmol), Tl(NO$_3$)$_3$ × 3H$_2$O (1.91 g, 4.30 mmol), MeOH (60 ml), EtOH (180 ml), CHCl$_3$ (50 ml) and H$_2$O (25 ml) were used. Column chromatography (CH$_2$Cl$_2$: EtOAc 20 : 1) yielded orange powder product (300 mg, 58% yield). IR (KBr): 3056, 2957, 2923, 2868, 1656, 1459, 1288 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): Δ 7.35–7.15 (m, 10H), 6.74–6.56. (m, 10H), 3.87–3.83 (m, 8H), 3.25–3.21 (m, 8H). ^{13}C NMR (75.5 MHz, CDCl$_3$): Δ 188.5, 186.1, 155.9, 148.3, 135.6, 132.6, 130.3, 130.1, 129.7, 129.4, 126.9, 124.0, 73.1, 33.9, 31.8. HRMS: calcd for $C_{44}H_{36}O_6S_2$ + Na$^+$, 747.1851; found, 747.1847.

Cone 11,26,23,28-tetraone-25,27-bis[(4-methylthio)benzyl]-kaliks[4]aren (2g). Following the procedure for synthesis of diquinone derivative of calix[4]arene; compound **1g** (500 mg, 0.72 mmol), Tl(NO$_3$)$_3$ × 3H$_2$O (1.91 g, 4.30 mmol), MeOH (60 ml), EtOH (180 ml), CHCl$_3$ (50 ml) and H$_2$O (25 ml) were used. Column chromatography (CH$_2$Cl$_2$: EtOAc 10 : 1) yielded orange powder product (288 mg, 55% yield). IR (KBr): 3026, 2960, 2921, 2859, 1656, 1459, 1293 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): Δ 7.24–7.17 (m, 8H), 6.79. (d, J = 7.5 Hz, 4H), 6.65 (t, J = 7.5 Hz, 2H), 6.48 (s, 4H), 4.75 (s, 4H), 3.65 (d, J = 12.6 Hz, 4H), 3.14 (d, J = 12.6 Hz, 4H), 2.49 (s, 6H). ^{13}C NMR (75.5 MHz, CDCl$_3$): Δ 188.5, 186.2, 156.1, 148.2, 139.2, 133.7, 132.4, 130.6, 129.9, 129.2, 126.8, 123.9, 76.2, 32.1, 16,0. HRMS: calcd for $C_{44}H_{36}O_6S_2$ + Na$^+$, 747.1851; found, 747.1879.

Cone 5,17-dibromo-11,26,23,28-tetraone-25,27-dipropoxycalix[4]arene (3b). Compound **2b** (2 g, 3.73 mmol) and *N*-bromosuccinimide NBS (2.26 g, 12.67 mmol) were dissolved in 2-butanone (MEK) (90 ml) and catalytic amount of 48% HBr (60 μl) was added. The reaction mixture was let to stir at room temperature in a dark place for 24 h. The reaction mixture was quenched by addition of 10% NaHSO$_3$ $_{(aq)}$ (75 ml) and let to stir for 10 min. CH$_2$Cl$_2$ (100 ml) and organic phase was separated from aqueous. The latter was extracted with additional CH$_2$Cl$_2$ (3 × 25 ml). Combined organic phases were dried with MgSO$_4$ and then solvents were removed under the reduce pressure. Crude product purified by column chromatography (CH$_2$Cl$_2$: EtOAc 15 : 1) and recrystallized from solvent mixture (CHCl$_3$ – MeOH) to yield orange crystalline product (1,77g, 68% yield). IR (KBr): 2966, 2931, 2876, 1657, 1460, 1294, 1204 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): Δ 7.01 (s, 4H), 6.64 (s, 4H), 3.79 (d, J = 13.3 Hz, 4H), 3.63 (t, J = 7.1 Hz, 4H), 3.28 (d, J = 13.3 Hz, 4H), 1.80 (m, 4H), 0.99 (t, J = 7.4 Hz, 6H). ^{13}C NMR (75.5

MHz, CDCl$_3$): Δ 188.3, 185.7, 156.1, 147.3, 133.1, 132.4, 116.4, 32.0, 23.9, 10.9. HRMS: calcd for $C_{34}H_{30}O_6Br_2$ + H$^+$, 693.0487; found, 693.0510.

Cone 5,17-dibromo-11,26,23,28-tetrahydroxy-25,27-dipropoxycalix[4]arene (4b). Compound **3b** (1.15 g, 1.65 mmol) was dissolved in CHCl$_3$ (287 ml) and heated up to 70 °C. Then NaHSO$_3$ $_{(aq)}$ (2.3 g, 13.2 mmol in 34 ml of H$_2$O) was added. Reaction mixture was let to stir at boiling point for 1.5 h. Reaction mixture was then cooled down to room temperature and H$_2$O (20 ml) was added. Organic phase was separated from aqueous and dried with MgSO$_4$. Solvents were removed under reduced pressure and remaining solid recrystallized from solvent mixture (CHCl$_3$ – *n*-hexane) to yield colorless crystalline product (1.12 g, 97% yield). IR (KBr): 3376, 2963, 2928, 2874, 1656, 1460, 1204 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): Δ 7.79 (s, 2H), 7.08 (s, 4H), 6.55 (s, 4H), 4.34 (s, 2H) 4.24 (d, J = 12.9 Hz, 4H), 3.92 (t, J = 6.4 Hz, 4H), 3.24 (d, J = 12.9 Hz, 4H), 2.04 (m, 4H), 1.27 (t, J = 7.4 Hz, 6H). ^{13}C NMR (75.5 MHz, CDCl$_3$): Δ 151.7, 148.4, 147.4, 135.9, 132.3, 128.6, 118.1, 115.7, 79.1, 31.7, 23.7, 11.2. HRMS: calcd for $C_{34}H_{34}O_6Br_2$ + H$^+$, 697.0800; found, 697.0816.

Cone 5,17-dibromo-26,28-dihydroxy-11,23-bis[4-(trimethylsiloxy)]-25,27-dipropoxycalix[4]arene (5b). Compound **4b** (200 mg, 0.29 mmol) was suspended in mixture of MeCN (10 ml) and triethylamine (TEA) (0.4 ml, 2.86 mmol). Reaction mixture was then cooled down to –10 °C and trimethylsilyl chloride (TMSCl) (0.36 ml, 2.86 mmol) was slowly added. After 10 min of stirring at -10 °C a precipitate formed, this was filtrated and washed with MeOH to yield analytically pure product (220 mg, 91% yield). IR (KBr): 3369, 3060, 3023, 2926, 1591, 1464, 1263, 1215 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): Δ 7.84 (s, 2H), 7.07 (s, 4H), 6.55 (s, 4H), 4.23 (d, J = 12.9 Hz, 4H), 3.91 (t, J = 6.2 Hz, 4H), 3.24 (d, J = 12.9 Hz, 4H), 2.03 (m, 4H), 1.29 (t, J = 7.4 Hz, 6H), 0.24 (s, 18H). ^{13}C NMR (75.5 MHz, CDCl$_3$): Δ 151.5, 148.0, 147.3, 135.8, 132.1, 127.9, 120.3, 117.9, 78.8, 31.6, 23.6, 11.1, 0.3. HRMS: calcd for $C_{40}H_{50}O_6Si_2Br_2$ + Na$^+$, 863.1410; found, 863.1434.

Cone 5,17-dibromo-11,23-dihydroxy-26,28-bis[4-(trimethylsiloxy)]-25,27-dipropoxycalix[4]arene (6b). NaH (96 mg, 4.01 mmol) was suspended in DMF (7 ml) and **4b** (280 mg, 0.40 mmol) was slowly – in parts – added to the suspension. After completed addition the reaction mixture was cooled down to –10 °C and let to stir for 15 min. TMSCl (1.02 ml, 8.02 mmol) was then slowly added to the mixture and let to stir at room temperature for 2 h. After 2 h the DMF was removed under reduced pressure, the remaining solid dissolved in CH$_2$Cl$_2$ and shook with H$_2$O. Organic phase was separated from aqueous, dried with MgSO$_4$ and then solvents removed under reduced pressure. Column chromatography (EtOAc : *n*-hexane 1 :

3) yielded white powder product (80 mg, 24% yield). IR (KBr): 3333, 2961, 2920, 2875, 1598, 1459, 1288, 1252, 1215 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): Δ 7.23 (s, 4H), 5.58 (s, 4H), 4.78 (br s, 2H), 4.25 (d, *J* = 13.7 Hz, 4H), 3.89 (m, 4H), 2.97 (d, *J* = 13.7 Hz, 4H), 1.83 (m, 4H), 0.85 (t, *J* = 7.4 Hz, 6H), 0.21 (s, 18H). ^{13}C NMR (75.5 MHz, CDCl$_3$): Δ 157.5, 148.6, 144.8, 139.4, 131.9, 131.7, 115.5, 114.5, 76.6, 32.2, 23.4, 9.9, 0.5. HRMS: calcd for C$_{40}$H$_{50}$O$_6$Si$_2$Br$_2$ + NH$_4^+$, 858.1856; found, 858.1888.

Cone 5,17-dibromo-11,23,25,26,27,28-hexapropoxy-calix[4]arene (7b$_1$). Following the general procedure for synthesis of alkoxy-calix[n]arene; compound **4b** (670 mg, 0.96 mmol), NaH (207 mg, 8.63 mmol), 1-bromo-propane (0.79 ml, 8.63 mmol) and DMF (9 ml) were used. Recrystallization from solvent mixture CHCl$_3$ – MeOH yielded colorless crystalline product (676 mg, 81% yield). IR (KBr): 2962, 2924, 2874, 1597, 1461, 1212 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): Δ 6.67 (s, 4H), 6.36 (s, 4H), 4.37 (d, *J* = 13.2 Hz, 4H), 3.84–3.72 (m, 12H), 3.05 (d, *J* = 13.2 Hz, 4H), 1.93–1.84 (m, 8H), 1.75 (m, 4H), 1.05–0.92 (m, 18H). ^{13}C NMR (75.5 MHz, CDCl$_3$): Δ 155.7, 154.3, 151.0, 136.9, 136.0, 130.9, 115.3, 114.8, 70.1, 31.6, 23.7, 23.4, 23.1, 11.0, 10.9, 10.6. HRMS: calcd for C$_{46}$H$_{58}$O$_6$Br$_2$ + Na$^+$, 887.2498; found, 887.2515.

Partial-cone 5,17-dibromo-11,26,23,28-tetramet-hoxy-25,27-dipropoxycalix[4]arene (7b$_2$). Following slightly modified (as a solvent mixture of THF – DMF was used) general procedure for synthesis of alkoxy-ca-lix[n]arene; compound **4b** (158 mg, 0.23 mmol), NaH (87 mg, 3.62 mmol), MeI (0.31 ml, 4.98 mmol), THF (5 ml), and DMF (0.5 ml) were used. Recrystallization from solvent mixture CH$_2$Cl$_2$ – MeOH yielded colorless crystalline product (150 mg, 88% yield). IR (KBr): 2964, 2925, 2872, 1595, 1464, 1212 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): Δ 7.09–6.44 (m, 8H) 4.31–2.99 (m, 24H), 1.91–1.84 (m, 4H), 1.16–1.05 (m, 6H). ^{13}C NMR (75.5 MHz, CDCl$_3$): Δ 155.8, 155.3, 155.2, 155.0, 154.2, 152.9, 152.5, 152.0, 137.2, 136.0, 135.8, 134.0, 133.8, 132.1, 130.8, 130.3, 116.5, 115.5, 115.0, 114.5, 114.3, 76.4, 61.3, 60.2, 59.7, 55.9, 55.8, 36.0, 31.2, 24.3, 24.1, 11.3, 11.2. HRMS: calcd for C$_{38}$H$_{42}$O$_6$Br$_2$ + H$^+$, 753.1426; found, 753.1448.

Partial-cone 5,17-bis(thioacetyl)-11,26,23,28-tetramet-hoxy-25,27-dipropoxycalix[4]arene (8). Following pre-viously published method;[21] compound **7b$_2$** (100 mg, 0.14 mmol), THF (12 ml), *tert*-BuLi (0.51 ml, 1.46 M in penta-ne, 0.86 mmol), sulfur (28 mg, 0.86 mmol) and AcCl (0.1 ml, 1.44 mmol) were used. Column chromatography (EtOAc : *n*-hexane 1 : 5) yielded white powder product (25 mg, 25% yield). IR (KBr): 2959, 2928, 2874, 2834, 1697, 1601, 1477, 1457, 1234, 1207 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): Δ 7.00–6.36 (m, 8H), 4.34–3.04 (m, 24H),

2.25 (s, 3H), 2.13 (s, 3H), 1.89 (m, 4H), 1.05 (m, 6H). ^{13}C NMR (75.5 MHz, CDCl$_3$): Δ 196.1, 156.1, 137.2, 135.4, 134.8, 134.4, 133.8, 116.4, 114.2, 114.0, 76.2, 61.2, 31.0, 30.2, 24.2, 11.1. HRMS: calcd for C$_{42}$H$_{48}$O$_8$S$_2$ + H$^+$, 745.2869; found, 745.2878.

Cone 5,17-dibromo-26,28-bis(phenylmethoxy)-25,27-dihydroxycalix[4]arene (9a). Compound **1a** (3.9 g, 6.45 mmol) was dissolved in CHCl$_3$ (130 ml) and Br$_2$ (0.66 ml, 12.96 mmol) solution in CHCl$_3$ (130 ml) was slowly ad-ded in 2h at 0 °C. The reaction mixture was let to warm up to room temperature and stirred for additional 2 h. The solvent was then removed under reduced pressure and re-maining solid recrystallized. Recrystallization from sol-vent mixture CHCl$_3$ – MeOH yielded colorless crystalline product (4.65 g, 95% yield). ^{1}H NMR (300 MHz, CDCl$_3$): Δ 7.86 (s, 2H), 7.61–6.80 (m, 22H), 5.03 (s, 4H), 4.23 (d, *J* = 13.2 Hz, 4H), 3.27 (d, *J* = 13.2 Hz, 4H). The spectrum is in accordance with previously published results.[36]

Cone 5,17-dibromo-26,28-bis(phenylmethoxy)-25,27-dipropoxycalix[4]arene (10a$_1$). Following the general procedure for synthesis of alkoxy-calix[n]arene; com-pound **9a** (4.91 g, 6.45 mmol), NaH (541 mg, 22.56 mmol), 1-bromopropane (2.05 ml, 22.56 mmol) and DMF (60 ml) were used. Recrystallization from solvent mixture CH$_2$Cl$_2$ – MeOH yielded colorless crystalline product (5.01 g, 92% yield). ^{1}H NMR (300 MHz, CDCl$_3$): Δ 7.42–7.32 (m, 10H), 7.02 (s, 4H), 6.47–6.38 (m, 6H), 4.82 (s, 4H), 4.33 (d, *J* = 13.3 Hz, 4H), 3.74 (m, 4H), 3.04 (d, *J* = 13.3 Hz, 4H), 1.65 (m, 4H), 0.64 (t, *J* = 7.4 Hz, 6H). The spectrum is in accordance with previously published re-sults.[37]

Cone 5,17-bis(thioacetyl)-26,28-bis(phenylmethoxy)-25,27-dipropoxycalix[4]arene (11a$_1$). Following slightly modified (AcCl was replaced by MeI) previously publis-hed method;[21] compound **10a$_1$** (2 g, 2.36 mmol), THF (96 ml), *tert*-BuLi (16.67 ml, 1,46 M solution in pentane, 28.34 mmol), sulfur (1.06 g, 33.07 mmol) and MeI (2.35 ml, 37.79 mmol) were used. Column chromatography (CH$_2$Cl$_2$: *n*-hexane 2 : 3) and recrystallization from sol-vent mixture (CHCl$_3$ – MeOH) yielded colorless crystalli-ne product (780 mg, 42% yield). IR (KBr): 3024, 2961, 2917, 2871, 1582, 1456, 1372, 1212, 1195 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): Δ 7.46–7.43 (m, 4H), 7.35–7.32 (m, 6H), 6.92 (s, 4H), 6.37–6.29 (m, 6H), 4.78 (s, 4H), 4.38 (d, *J* = 13.2 Hz, 4H), 3.76 (m, 4H), 3.07 (d, *J* = 13.2 Hz, 4H), 2.44 (s, 6H), 1.64 (m, 4H), 0.60 (t, *J* = 7,4 Hz, 6H). ^{13}C NMR (75.5 MHz, CDCl$_3$): Δ 155.9, 154.7, 137.6, 137.0, 133.4, 130.0, 129.1, 128.2, 128.0, 127.9, 127.8, 122.5, 76.6, 31.1, 22.8, 17.3, 9.5. HRMS: calcd for C$_{50}$H$_{52}$O$_4$S$_2$ + H$^+$, 781.3385; found, 781.3378.

Cone 5,17-bis(thioacetyl)-26,28-dihydroxy-25,27-di-propoxycalix[4]arene (12a$_1$). Compound **11a$_1$** (89 mg,

0.11 mmol) was dissolved in CH_2Cl_2 (15 ml) and molecular sieves were added. Mixture was cooled down to –30 °C and trimethylsilyl bromide (TMSBr) (0.12 ml, 0.91 mmol) was added and let to stir for 3 h. Reaction mixture was then poured into saturated aqueous $NaHCO_3$ solution and organic phase was separated. The organic phase was then extracted with H_2O and dried with $MgSO_4$. Solvents were removed under reduced pressure and crude product purified by column chromatography (CH_2Cl_2 : n-hexane 1 : 1) followed by recrystallization from solvent mixture ($CHCl_3$ – MeOH) to yield colorless crystalline product (31 mg, 45% yield). IR (KBr): 3330, 2959, 2921, 2862, 1583, 1464, 1436, 1203 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): Δ 8.33 (s, 2H), 7.02 (d, $J = 7.5$ Hz, 4H), 6.84 (s, 4H), 6.62 (t, $J = 7.5$ Hz, 2H), 4.28 (d, $J = 12.9$ Hz, 4H), 3.95 (t, $J = 6.2$ Hz, 4H), 3.34 (d, $J = 12.9$ Hz, 4H), 2.31 (s, 6H), 2.05 (m, 4H), 1.31 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$): Δ 153.4, 150.0, 134.1, 133.6, 128.6, 127.7, 127.5, 119.2, 78.5, 31.5, 23.5, 16.2, 10.9. HRMS: calcd for $C_{36}H_{40}O_4S_2 + H^+$, 601.2446; found, 601.2451.

Cone 11,26,23,28-tetraone-25,27-bis-[(hydroxycarbonyl)methoxy]-calix[4]arene (13). To a solution of **2c** (190 mg, 0.28 mmol) in CH_2Cl_2 (3 ml), trifluoroacetic acid (0.6 ml, 7.53 mmol) was slowly added and then let to stir at room temperature under inert atmosphere for 5 h. Reaction was quenched by addition of cold H_2O (0 °C). Organic phase was separated from aqueous and dried with $MgSO_4$. Solvent was concentrated under reduced pressure and product precipitated as a yellow crystalline substance (105 mg, 66% yield). ^{1}H NMR (300 MHz, DMSO-d$_6$, 2.50): Δ 6.83 (s, 4H), 6.75 (d, $J = 7.5$ Hz, 4H), 6.64 (t, $J = 7.5$ Hz, 2H), 4.41 (s, 4H), 3.83 (d, $J = 13.1$ Hz, 4H), 3.33 (d, $J = 13.1$ Hz, 4H). The spectrum is in accordance with previously published results.[25]

Cone 11,26,23,28-tetrahydroxy-25,27-bis-[(hydroxycarbonyl)methoxy]-calix[4]arene (14). Compound **13** (50 mg, 0.09 mmol) was dissolved in MEK (4 ml) and aqueous solution of $Na_2S_2O_4$ (122 mg, 0.70 mmol in 2 ml of H_2O) was added. Yellow color of reaction mixture disappeared during stirring (1 min). Organic phase was separated from aqueous and dried with $MgSO_4$. After addition of $CHCl_3$ (5 ml) to the dried organic phase, a precipitate formed. This was filtered off using PTFE filter (0.2 μm) and dried. The product was isolated as a pale yellow powder (18 mg, 36% yield). IR (KBr): 3434, 2932, 1739, 1609, 1464, 1440, 1242, 1193 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d$_6$, 2.50): Δ 7.00 (d, $J = 7.6$ Hz, 4H), 6.78 (t, $J = 7.6$ Hz, 2H), 6.47 (s, 4H), 4.68 (s, 4H), 4.36 (d, $J = 12.8$ Hz, 4H), 3.25 (d, $J = 12.8$ Hz, 4H). ^{13}C NMR (75.5 MHz, DMSO-d$_6$, 39.52): Δ 170.5, 153.1, 149.7, 144.5, 133.9, 129.0, 128.9, 125.0, 114.9, 72.1, 31.0. HRMS: calcd for $C_{32}H_{28}O_{10} + Na^+$, 595.1580; found, 595.1568.

4. 2. Preparation of Au(111) Substrate.

Au(111) single crystal (MaTecK) was annealed in UHV at 550 °C after ion bombardment with 1 kV Ar$^+$ ions at 5×10^{-6} mbar. The cycle was repeated at least two times. Au(111) single crystal was then transferred to a homemade annealing apparatus and annealed at 700 °C in 3% H_2/Ar atmosphere for 30 min. The surface of the Au(111) single crystal was protected with H_2O droplet (30μL) and transferred to a vial for self-assembly.

4. 3. Self-assembly

»Ex-situ« method. Au(111) was immersed into ~80 μM solution (solvent mixture CH_2Cl_2 : EtOH 1 : 9) of adsorbate molecules **2f** and **2g** at room temperature for 30 min. Adsorbate solutions; were always freshly prepared. After self-assembly the Au(111) was removed from the solution and washed with EtOH, i-PrOH in Milli-Q H_2O, and dried in Ar atmosphere.

»In-situ« method. The surface of Au(111) single crystal was immersed into an electrochemical cell with 0.1 M $HClO_4$ with ~80 μM concentrations of **13** and **14**. The system was hold at 0.2 V vs Ag/AgCl for 10 min.

4. 4. Electrochemistry

A standard three-compartment electrochemical cell containing 0.1 M $HClO_4$ (OmniTrace Ultra™ from EDM), Au wire as a counter electrode and Ag/AgCl as a reference electrode was used. In each experiment, the electrode was immersed (hanging meniscus technique) at 0.07 V in a solution saturated with Ar and cycled between 0.07 V and 1.17 V versus the reversible hydrogen electrode (RHE). The sweep rate for all measurements was 50 mVs^{-1}. Electrode potentials are given versus the RHE. Autolab potentiostat was used in the electrochemical measurements.

5. Acknowledgements

6. References

1. Yang, Z.; Zhang, J.; Kintner-Meyer, M. C. W.; Lu, X.; Choi, D.; Lemmon, J. P.; Liu, J. *Chem. Rev.* **2011**, *111*, 3577–3613 http://dx.doi.org/10.1021/cr100290v.

2. Goodenough, J. B.; Park, K. S. *J. Am. Chem. Soc.* **2013**, *135*, 1167–1176. http://dx.doi.org/10.1021/ja3091438

3. Noorden, R. Van *Nature* **2014**, *507*, 26–28.
http://dx.doi.org/10.1038/507026a

4. Chen, Z.; Qin, Y.; Amine, K. *Electrochim. Acta* **2009**, *54*, 5605–5613.
http://dx.doi.org/10.1016/j.electacta.2009.05.017

5. Song, Z.; Zhou, H. *Energy Environ. Sci.* **2013**, *6*, 2280.
http://dx.doi.org/10.1039/c3ee40709h

6. Liang, Y.; Tao, Z.; Chen, J. *Adv. Energy Mater.* **2012**, *2*, 742–769. http://dx.doi.org/10.1002/aenm.201100795

7. Sevov, C. S.; Brooner, R. E. M.; Chénard, E.; Assary, R. S.; Moore, J. S.; Rodríguez-López, J.; Sanford, M. S. *J. Am. Chem. Soc.* **2015**, *4*, jacs.5b09572.

8. Huang, Y.; Gu, S.; Yan, Y.; Li, S. F. Y. *Curr. Opin. Chem. Eng.* **2015**, *8*, 105–113.
http://dx.doi.org/10.1016/j.coche.2015.04.001

9. Pan, F.; Wang, Q. *Molecules* **2015**, *20*, 20499–20517.
http://dx.doi.org/10.3390/molecules201119711

10. Genorio, B.; Pirnat, K.; Cerc-Korosec, R.; Dominko, R.; Gaberscek, M. *Angew. Chem. Int. Ed.* **2010**, *49*, 7222–7224.
http://dx.doi.org/10.1002/anie.201001539

11. Pirnat, K.; Dominko, R.; Cerc-Korosec, R.; Mali, G.; Genorio, B.; Gaberscek, M. *J. Power Sources* **2012**, *199*, 308–314.
http://dx.doi.org/10.1016/j.jpowsour.2011.10.068

12. Pirnat, K.; Bitenc, J.; Jerman, I.; Dominko, R.; Genorio, B. *ChemElectroChem* **2014**, *1*, 2131–2137.
http://dx.doi.org/10.1002/celc.201402234

13. Genorio, B. *Acta Chim. Slov.* **2015**, *62*, 895–901.
http://dx.doi.org/10.17344/acsi.2015.1626

14. Chen, H.; Armand, M.; Demailly, G.; Dolhem, F.; Poizot, P.; Tarascon, J.-M. *ChemSusChem* **2008**, *1*, 348–355.
http://dx.doi.org/10.1002/cssc.200700161

15. Liu, M.; Visco, S. J.; De Jonghe, L. C. *J. Electrochem. Soc.* **1989**, *136*, 2570–2575.
http://dx.doi.org/10.1149/1.2097478

16. Nakahara, K.; Oyaizu, K.; Nishide, H. *Chem. Lett.* **2011**, *40*, 222–227. http://dx.doi.org/10.1246/cl.2011.222

17. Häupler, B.; Wild, A.; Schubert, U. S. *Adv. Energy Mater.* **2015**, *5*, 1402034–1402068.
http://dx.doi.org/10.1002/aenm.201402034

18. Wain, A. J.; Wildgoose, G. G.; Heald, C. G. R.; Jiang, L.; Jones, T. G. J.; Compton, R. G. *J. Phys. Chem. B* **2005**, *109*, 3971–3978. http://dx.doi.org/10.1021/jp040552u

19. Wang, W.; Xu, W.; Cosimbescu, L.; Choi, D.; Li, L.; Yang, Z. *Chem. Commun.* **2012**, *48*, 6669.
http://dx.doi.org/10.1039/c2cc32466k

20. Gutsche, C. D. *Calixarenes*; Stoddard, J. F., Ed.; Monographs in Supramolecular Chemistry; 2nd ed.; The Royal Society of Chemistry: Cambridge, 2008.

21. Genorio, B.; He, T.; Meden, A.; Polanc, S.; Jamnik, J.; Tour, J. M. *Langmuir* **2008**, *24*, 11523–11532.
http://dx.doi.org/10.1021/la802197u

22. Genorio, B.; Strmcnik, D.; Subbaraman, R.; Tripkovic, D.; Karapetrov, G.; Stamenkovic, V. R.; Pejovnik, S.; Marković, N. M. *Nat. Mater.* **2010**, *9*, 998–1003.
http://dx.doi.org/10.1038/nmat2883

23. Genorio, B.; Subbaraman, R.; Strmcnik, D.; Tripkovic, D.; Stamenkovic, V. R.; Markovic, N. M. *Angew. Chem. Int. Ed.* **2011**, *50*, 5468–72.
http://dx.doi.org/10.1002/anie.201100744

24. Love, J. C.; Estroff, L. a.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. *Self-assembled monolayers of thiolates on metals as a form of nanotechnology*; 2005; Vol. 105.

25. Chung, T. D.; Park, J.; Kim, J.; Lim, H.; Choi, M. J.; Kim, J. R.; Chang, S. K.; Kim, H. *Anal. Chem.* **2001**, *73*, 3975–80.
http://dx.doi.org/10.1021/ac001050p

26. Takiguchi, H.; Sato, K.; Ishida, T.; Abe, K.; Yase, K.; Tamada, K. *Langmuir* **2000**, *16*, 1703–1710.
http://dx.doi.org/10.1021/la981450w

27. Jadhav, S. a. *Cent. Eur. J. Chem.* **2011**, *9*, 369–378.
http://dx.doi.org/10.2478/s11532-011-0024-8

28. Han, S. W.; Joo, S. W.; Ha, T. H.; Kim, Y.; Kim, K. *J. Phys. Chem. B* **2000**, *104*, 11987–11995.
http://dx.doi.org/10.1021/jp002630t

29. Casnati, A.; Comelli, E.; Fabbi, M.; Bocchi, V.; Mori, G.; Ugozzoli, F.; Lanfredi, A. M. M.; Pochini, A.; Ungaro, R. *Recl. des Trav. Chim. des Pays-Bas* **1993**, *112*, 384–392.
http://dx.doi.org/10.1002/recl.19931120613

30. Kim, Y.-O.; Jung, Y. M.; Kim, S. Bin; Hong, B. H.; Kim, K. S.; Park, S.-M. *J. Phys. Chem. B* **2004**, *108*, 4927–4936.
http://dx.doi.org/10.1021/jp049864n

31. Gutsche, C. D.; Lin, L.-G. *Tetrahedron* **1986**, *42*, 1633–1640. http://dx.doi.org/10.1016/S0040-4020(01)87580-3

32. van Loon, J.-D.; Arduini, A.; Coppi, L.; Verboom, W.; Pochini, A.; Ungaro, R.; Harkema, S.; Reinhoudt, D. N. *J. Org. Chem.* **1990**, *55*, 5639–5646.
http://dx.doi.org/10.1021/jo00308a024

33. Arduini, A.; Fabbi, M.; Mantovani, M.; Mirone, L.; Pochini, A.; Secchi, A.; Ungaro, R. *J. Org. Chem.* **1995**, *60*, 1454–1457. http://dx.doi.org/10.1021/jo00110a055

34. Zeng, X.; Sun, H.; Chen, L.; Leng, X.; Xu, F.; Li, Q.; He, X.; Zhang, W.; Zhang, Z. Z. *Org. Biomol. Chem.* **2003**, *1*, 1073–1079. http://dx.doi.org/10.1039/b211381c

35. Lin, Y. L.; Yu, T. S.; Wang, W. Y.; Lin, L. G. *Tetrahedron* **2006**, *62*, 6082–6089.
http://dx.doi.org/10.1016/j.tet.2006.03.110

36. Shimizu, S.; Shirakawa, S.; Sasaki, Y.; Hirai, C. *Angew. Chemie – Int. Ed.* **2000**, *39*, 1256–1259.
http://dx.doi.org/10.1002/(SICI)1521-3773(20000403)39:7<1256::AID-ANIE1256>3.0.CO;2-F

37. Lai, S.; Chan, Q. K.-W.; Han, J.; Zhi, Y.; Zhu, N.; Che, C. *Organometallics* **2009**, *28*, 34–37.
http://dx.doi.org/10.1021/om800969z

Povzetek

Opisana je sinteza in karakterizacija novih elektroaktivnih dikinonskih in kinonskih derivatov kaliks[4]arena s sidrnimi funkcionalinimi skupinami. Razvita je bila tudi metoda selektivne zaščite hidrokinonskih –OH skupin s trimetilsililnimi skupinami (TMS) na spodnjem oz. zgornjem obroču makrocikla. Štiri molekule, s sulfidnimi oz. s karboksilnimi sidri so bile adsorbirane na površino monokristala Au(111), z uporabo *ex-situ* in *in-situ* metode samosestavljivosti. Adsorbirane molekule smo testirali s ciklično voltametrijo (CV). Vse testirane molekule so pokazale redox odziv, ki se je spreminjal med posameznimi cikli. Po kondicioniranju so se CV-ji ustalili in pokazali dva izrazita tokovna vrhova, podobna za vse testirane molekule. Sintetizirane in elektrokemijsko testirane molekule so zanimive za: Li-ionske baterije (kot katodni material oz. kot zaščita prenapetosti), baterije z novimi kemijami in redoks-pretočne baterije.