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# Novel thiophosphorylated calix[4]resorcinol Mannich bases and their electrochemical behavior in hydrogen evolution reaction

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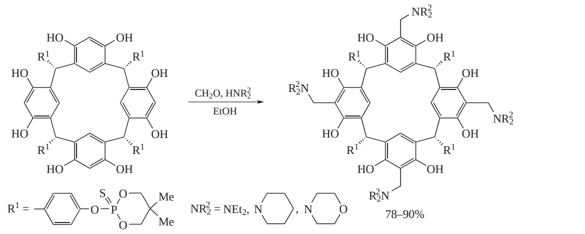
**Aminomethylation of thiophosphorylated calix[4]resorcinol with formaldehyde and secondary amines affords the novel Mannich base derivatives possessing better solubility. The nickel complex of morpholinomethyl derivative exhibits a good catalytic activity in hydrogen evolution decreasing potential of direct acid reduction on glassy carbon electrode to 1.3 V.**




Calix[4]resorcinols are available macrocyclic compounds which can be further functionalized at *ortho*-position of aromatic rings, hydroxyl groups of the upper rim, and functional groups of the calixarene framework.[1,2] Structural modification of calixarenes with different functional substituents allows one to vary their binding selectivity and efficiency of various substrates in a broad range. One of the most facile methods for the modification of calixarene framework is the Mannich condensation, which occurs with the formation of new C–C bonds and introduces additional functional groups.[3] Based on Mannich-amino-derivatized calix[4]arenes, the copper(II)-induced ‘turn-off’ fluorescence and ‘naked eye’ chemosensors,[4] efficient ionophores for the extraction of dichromate anions from an aqueous phase into an organic one at lower pH,[5] effective phase-transfer catalysts for esterification reaction,[6] polymer systems and magnetic nanoparticles serving as selective extractants of toxic and carcinogenic water-soluble azo-dyes and aromatic amines from aqueous solution were obtained.[7,8] The one-pot high dilution Mannich condensation of calix[4]resorcinols with piperazine and excess formaldehyde results in covalently linked dimers of two calix[4]resorcinols connected *via* four piperazine bridges, which can encapsulate small guest molecules by adapting the cavity according to the guest size.[9] The similar tetrakis(dimethylamino)-substituted derivative was used to produce a new promising calix[4]arene-embedded polysulfone membrane capable of $HCr_2O_7^-$ transporting due to its efficient complexation behavior.[10]

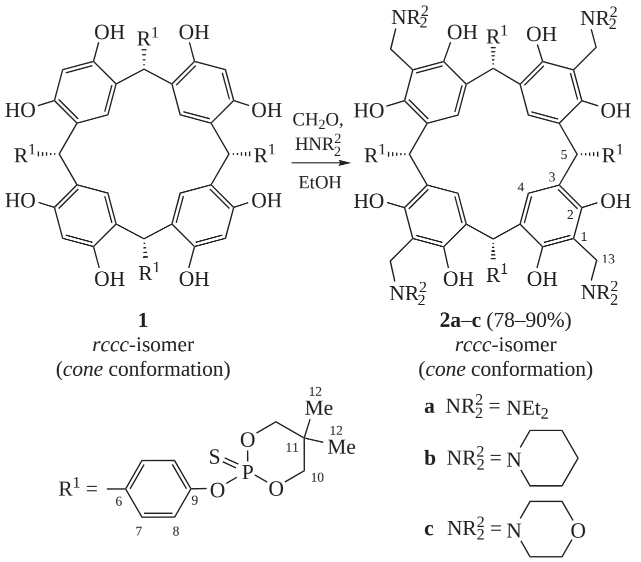
We have previously shown that phosphorus-containing calix[4]resorcinols can also be easily modified *via* Mannich approach,[11] and the resulting polyfunctional macrocyclic compounds exhibit surface-active behavior, which is superior to that of known surfactants, while at low concentrations they represent effective dispersing agents of carbon nanotubes in water.[12] In addition, their self-associated supramolecular structures demonstrate high catalytic activity in the hydrolysis of phosphoric acid esters and phosphorylation of polyethylenimines.[13,14] It was also noted that the Mannich adducts of calixarenes possess better solubility in organic solvents and water.[11,15,16]

In this work, we chose calix[4]resorcinol in *cone* conformation with *rccc*-arrangement of four thiophosphorylated substituents **1** for the Mannich modification. Compound **1** was synthesized by acid-catalyzed condensation of resorcinol with 2-(4-formylphenoxy)-5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinane.[17] Its nickel complex was found to effectively catalyze electrochemical processes of hydrogen generation from acid solutions.[18] However, macrocycle **1** possesses a low solubility, which significantly restricts its potential application. We suggested that the functionalization of the upper rim of calixarene **1** using Mannich reaction would both increase the solubility of the products and improve their catalytic properties in electrochemical hydrogen evolution reactions.

In fact, the Mannich condensation of thiophosphorylated calix[4]resorcinol **1** with paraformaldehyde and secondary amines, such as diethylamine, piperidine, and morpholine, gave new aminomethylated derivatives **2a–c** in yields up to 90% (Scheme 1). The products appear as pink powders and really possess higher solubility as compared to their precursor **1**; they are soluble not only in DMSO and DMF, but also in most organic solvents. Their structures were proved by NMR spectroscopy ($^1$H, $^{31}$P), mass spectrometry (MALDI-MS) and elemental analysis. Importantly, the Mannich reaction proceeds with the retention of conformational features of the starting macrocycle **1** and products **2a–c** also possess cone conformation with *rccc*-configuration of P=S-containing aromatic substituents.†

Recently, new effective catalytic systems for hydrogen evolution and oxidation reactions were extensively investigated.[19–21] We

† Calix[4]resorcinol **2c** was obtained as a slightly pink powder by heating calix[4]resorcinol **1** (0.15 g, 0.10 mmol) and paraformaldehyde (0.02 g, 0.80 mmol) in morpholine (5 ml) at 75 °C for 12 h. Yield 0.17 g (90%), mp > 200 °C (decomp.). $^1$H NMR (600.1 MHz, DMSO-$d_6$) $\delta$: 1.44 (s, 12 H, H-12), 1.77 (s, 12 H, H-12), 2.97 (br. m, 16 H, $NCH_2$), 4.10 (br. m, 16 H, $OCH_2$), 4.25 (s, 8 H, H-13), 4.57 (m, 8 H, H-10), 4.95 (m, 8 H, H-10), 6.29 (s, 4 H, H-5), 6.91 (s, 4 H, H-4), 7.43 (d, 8 H, H-7, $^3J_{HH}$ 8.17 Hz), 7.59 (d, 8 H, H-8, $^3J_{HH}$ 8.17 Hz). $^{31}$P NMR (242.9 MHz, DMSO-$d_6$) $\delta$: 54.2. IR ($\nu$/cm$^{-1}$): 828 (P=S), 970, 1004 (P–O–C), 3100–3600 (OH). MS (MALDI), *m/z*: 1909.0 [M + H]$^+$ (calc., *m/z*: 1908.0). Found (%): C, 57.82; H, 5.74; N, 2.94; P, 6.51; S, 6.42. Calc. for $C_{92}H_{112}N_4O_{24}P_4S_4$ (%): C, 57.86; H, 5.87; N, 2.94; P, 6.50; S, 6.71. For the synthesis and characteristics of compounds **2a**,**b**, see Online Supplementary Materials.




**Scheme 1**

previously reported that nickel complexes of thiophosphorylated calix[4]resorcinols including compound **1** are effective catalysts for electrochemical hydrogen generation and oxygen reduction.[18,22] Their aminomethylated derivatives **2a–c** were found to retain the complexation ability toward nickel(II) ions, which indicates a promising activity in hydrogen evolution. Investigation of the effect of additional amino groups at the upper rim of thiophosphorylated ligand on the catalytic efficiency of its nickel complex in electrocatalytic reaction of hydrogen production as compared to unsubstituted counterpart **1** seemed interesting.

For these purposes, the appropriate nickel complex was prepared by analogy with the previously described procedure[18] of *in situ* reaction of equimolar amounts of new ligand **2c** with $Ni(BF_4)_2$. It is known that nickel(II) tetrafluoroborate in DMF is intrinsic for irreversible two-electron reduction peak at the potential of –1.17 V (*vs.* Ag/AgCl), which corresponds to $Ni^{II} \rightarrow Ni^0$ transition (Figure 1).[23] The nickel complex is characterized by two irreversible reduction peaks at the potentials of –0.9 and –1.1 V in voltammogram, which indicates binding of ligand with metal. Assuming that calix[4]resorcinols do not possess their own reduction and oxidation peaks in the potential range under study, new peaks can be attributed to redox-transitions of the nickel center, namely, $Ni^{II/I/0}$. According to published data,[18] the reduction of hydrogen from trifluoroacetic acid (TFA) without catalyst occurs at the potential of –2.1 V (*vs.* Ag/AgCl). Gradual addition of TFA as a proton source[24] to the nickel complex solution leads to small anodic shift of the first reduction potential of catalyst to –0.8 V and catalytic current enhancement at this potential (Figure 2). In this case, gas bubbles are observed on the surface of

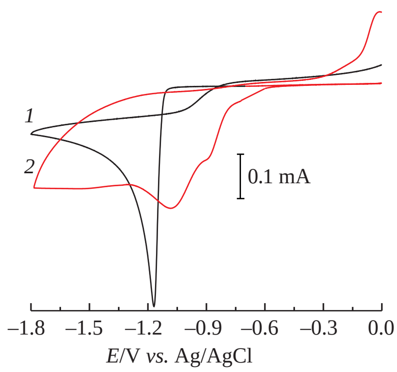



**Figure 1** CVs of 5 mM $Ni(BF_4)_2$ in DMF (*1*) in the absence and (*2*) in the presence of **2c** (1 : 1) . Glassy carbon working electrode, Pt counter electrode, $Bu_4NBF_4$, scan rate 0.1 V $s^{-1}$.

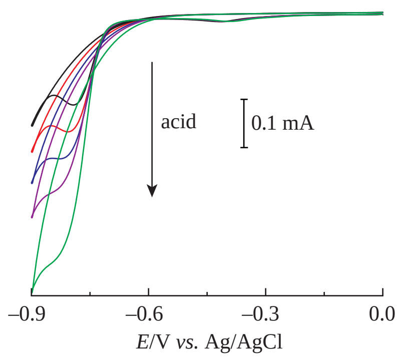



**Figure 2** CVs of 5 mM $Ni(BF_4)_2$ with **2c** (1 : 1) in DMF in the presence of increasing amounts of TFA. Glassy carbon working electrode, Pt counter electrode, $Bu_4NBF_4$, scan rate 0.1 V $s^{-1}$.

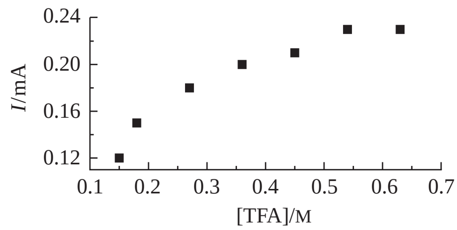



**Figure 3** Current *vs.* TFA concentration during its reduction in the presence of $Ni(BF_4)_2 \cdot$**2c**.

working electrode. Note that catalysis potential is more anodic for functionalized aminomethylated thiosphosphorylated calix[4]resorcinol **2c** as compared to potential of precursor **1** (–0.8 *vs.* –1.0 V).[18] The use of nickel complex with calix[4]resorcinol **2c** provides a decrease in the potential of direct reduction of TFA on electrode thus facilitating the reduction by 1.3 V. The maximum $i_{cat}/i_p$ = 4.5 is reached at 0.46 M concentration of the acid (Figure 3).[‡]

Hence, the introduction of amino groups to the upper rim of thiophosphorylated ligands (calix[4]resorcinols) *via* Mannich approach facilitates the reduction of their complexes at nickel center and also provides catalytic hydrogen evolution at more positive potentials (as compared to the potential of unmodified precursor **1**). The energy gap between direct acid reduction potential on GC electrode and catalytic potential is 0.95 V (*vs.* 1.10 V for calix[4]resorcinol **1**). Thus, on the example of aminomethylated thiosphosphorylated calix[4]resorcinol **2c**, we have shown that the proposed modification of the calixarene matrix allows one to create new prospective highly efficient catalytic systems for the hydrogen evolution reactions.

*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.09.022.

## References


1 I. S. Antipin, E. K. Kazakova, W. D. Habicher and A. I. Konovalov, *Russ. Chem. Rev.*, 1998, **67**, 905 (*Usp. Khim.*, 1998, **67**, 995).
2 I. R. Knyazeva, A. R. Burilov, M. A. Pudovik and W. D. Habicher, *Russ. Chem. Rev.*, 2013, **82**, 150.
3 Y. Matsushita and T. Matsui, *Tetrahedron Lett.*, 1993, **34**, 7433.
4 B. Tabakci and A. Yilmaz, *J. Mol. Struct.*, 2014, **1075**, 96.
5 A. Sap, B. Tabakci and A. Yilmaz, *Tetrahedron*, 2012, **68**, 8739.
6 E. Akceylan and M. Yilmaz, *J. Macromol. Sci.*, *Pure Appl. Chem.*, 2012, **49**, 911.
7 E. Akceylan, M. Bahadir and M. Yılmaz, *J. Hazard. Mater.*, 2009, **162**, 960.


‡ For the details of electrochemical studies, see Online Supplementary Materials.

8 A. A. Bhatti, M. Oguz and M. Yilmaz, *J. Chem. Eng. Data*, 2017, **62**, 2819.
9 N. Kodiah Beyeh, A. Valkonen and K. Rissanen, *Org. Lett.*, 2010, **12**, 1392.
10 M. S. Engin, S. Cay, S. Sayin, S. Eymur and T. Sardohan Koseoglu, *Supramol. Chem.*, 2017, **29**, 455.
11 I. R. Knyazeva, Yu. M. Sadykova, A. R. Burilov, M. A. Pudovik and A. I. Konovalov, *Russ. J. Gen. Chem.*, 2009, **79**, 2456 (*Zh. Obshch. Khim.*, 2009, **79**, 1930).
12 A. S. Lobach, I. S. Ryzhkina, N. G. Spitsina and E. D. Obraztsova, *Phys. Status Solidi B*, 2007, **244**, 4030.
13 G. A. Gainanova, E. P. Zhiltsova, L. A. Kudryavtseva, S. S. Lukashenko, I. R. Knyazeva, A. R. Burilov, V. I. Kovalenko, L. V. Avvakumova and A. I. Konovalov, *Russ. J. Gen. Chem.*, 2007, **77**, 40 (*Zh. Obshch. Khim.*, 2007, **77**, 45).
14 T. N. Pashirova, S. S. Lukashenko, E. M. Kosacheva, M. V. Leonova, I. R. Knyazeva, A. R. Burilov, L. A. Kudryavtseva and A. I. Konovalov, *Colloid J.*, 2008, **70**, 202.
15 R. R. Kashapov, L. Ya. Zakharova, M. N. Saifutdinova, E. L. Gavrilova and O. G. Sinyashin, *Tetrahedron Lett.*, 2015, **56**, 2508.
16 R. R. Kashapov, L. Ya. Zakharova, M. N. Saifutdinova, Y. S. Kochergin, E. L. Gavrilova and O. G. Sinyashin, *J. Mol. Liq.*, 2015, **208**, 58.
17 I. R. Knyazeva, V. I. Sokolova, M. Gruner, W. D. Habicher, V. V. Syakaev, V. V. Khrizanforova, B. M. Gabidullin, A. T. Gubaidullin, Yu. H. Budnikova, A. R. Burilov and M. A. Pudovik, *Tetrahedron Lett.*, 2013, **54**, 3538.
18 V. V. Khrizanforova, I. R. Knyazeva, V. I. Matveeva Sokolova, I. R. Nizameev, T. V. Gryaznova, M. K. Kadirov, A. R. Burilov, O. G. Sinyashin and Yu. H. Budnikova, *Electrocatalysis*, 2015, **6**, 357.
19 V. V. Khrizanforova, A. A. Karasik and Yu. H. Budnikova, *Russ. Chem. Rev.*, 2017, **86**, 298.
20 V. V. Khrizanforova, V. I. Morozov, A. G. Strelnik, Yu. S. Spiridonova, M. N. Khrizanforov, T. I. Burganov, S. A. Katsyuba, Sh. K. Latypov, M. K. Kadirov, A. A. Karasik, O. G. Sinyashin and Yu. H. Budnikova, *Electrochim. Acta*, 2017, **225**, 467.
21 V. V. Khrizanforova, V. I. Morozov, E. I. Musina, M. N. Khrizanforov, D. A. Mironova, D. R. Islamov, O. N. Kataeva, A. A. Karasik, O. G. Sinyashin and Y. H. Budnikova, *J. Organomet. Chem.*, 2015, **789**–**790**, 14.
22 M. K. Kadirov, I. R. Knyazeva, I. R. Nizameev, R. A. Safiullin, V. I. Matveeva, K. V. Kholin, V. V. Khrizanforova, T. I. Ismaev, A. R. Burilov, Yu. H. Budnikova and O. G. Sinyashin, *Dalton Trans.*, 2016, **45**, 16157.
23 V. V. Khrizanforova, I. R. Knyazeva, I. R. Nizamiev, T. V. Gryaznova, V. I. Sokolova, S. A. Krasnov, M. K. Kadirov, A. R. Burilov, Yu. G. Budnikova and O. G. Sinyashin, *Russ. J. Gen. Chem.*, 2013, **83**, 663 (*Zh. Obshch. Khim.*, 2013, **83**, 575).
24 V. Fourmond, P.-A. Jacques, M. Fontecave and V. Artero, *Inorg. Chem.*, 2010, **49**, 10338.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