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# Synthesis of Cyclophane-Like Porphyrin–Calix[4]pyrrole Conjugates

**O. M. Kulikova and N. Zh. Mamardashvili**

*Institute of Solution Chemistry, Russian Academy of Sciences, ul. Akademicheskaya 1, Ivanovo, 153045 Russia*
*e-mail: ngm@isc-ras.ru*

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**Abstract**—New cyclophane-like porphyrin–calix[4]pyrrole conjugates were synthesized on the basis of *meso*-ethynyloctaethylporphyrin, and their physicochemical properties were studied.

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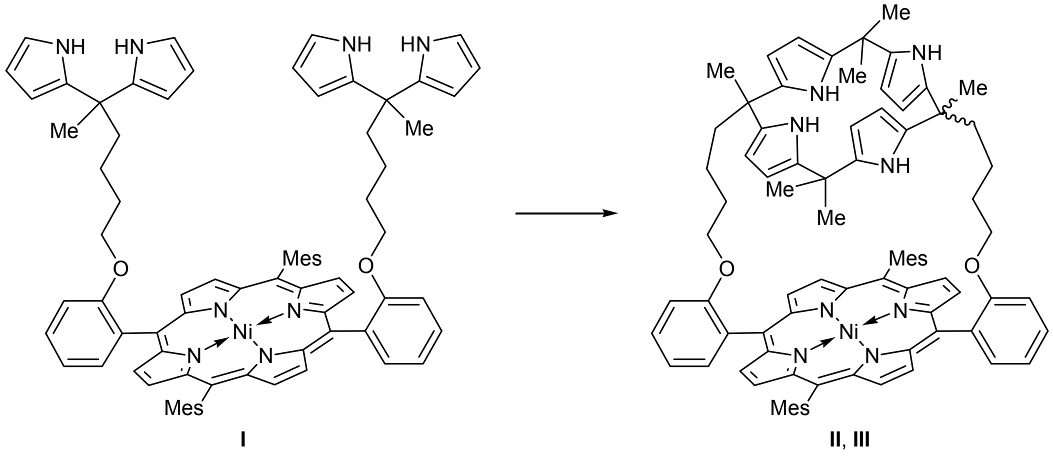
In the recent time, many compounds in which porphyrin fragments are covalently linked to crown ethers, cyclodextrins, and calixarenes were synthesized and found to possess interesting physicochemical properties [1–11]. We believed that new polyfunctional supramolecules, namely calix[4]pyrrole–bis-porphyrin conjugates, should be promising. The calix[4]pyrrole fragment in their molecules may be capable of acting simultaneously as complexing cavity (for selective binding of anions) and scaffold endowing the molecule with a definite geometric structure in which the reaction centers in the porphyrin fragments are fixed at a certain distance with respect to each other. The presence of tetrapyrrole chromophores in such supramolecules should considerably extend the set of spectral methods for analysis of a broad spectrum of intermolecular interactions.

We have found only one published example of synthesis of chemically bonded calix[4]pyrrole–porphyrin conjugates. The condensation of porphyrin–bis(dipyrromethane) (**I**) with acetone in the presence of boron trifluoride–ether complex in strongly dilute solution gave two stereoisomers **II** and **III** [12, 13] differing in the orientation of *meso*-methyl groups in the calix[4]pyrrole macroring relative to the porphyrin ring plane (Scheme 1). The yields of calix[4]pyrrole–porphyrins **II** and **III** were 5 and 7%, respectively.

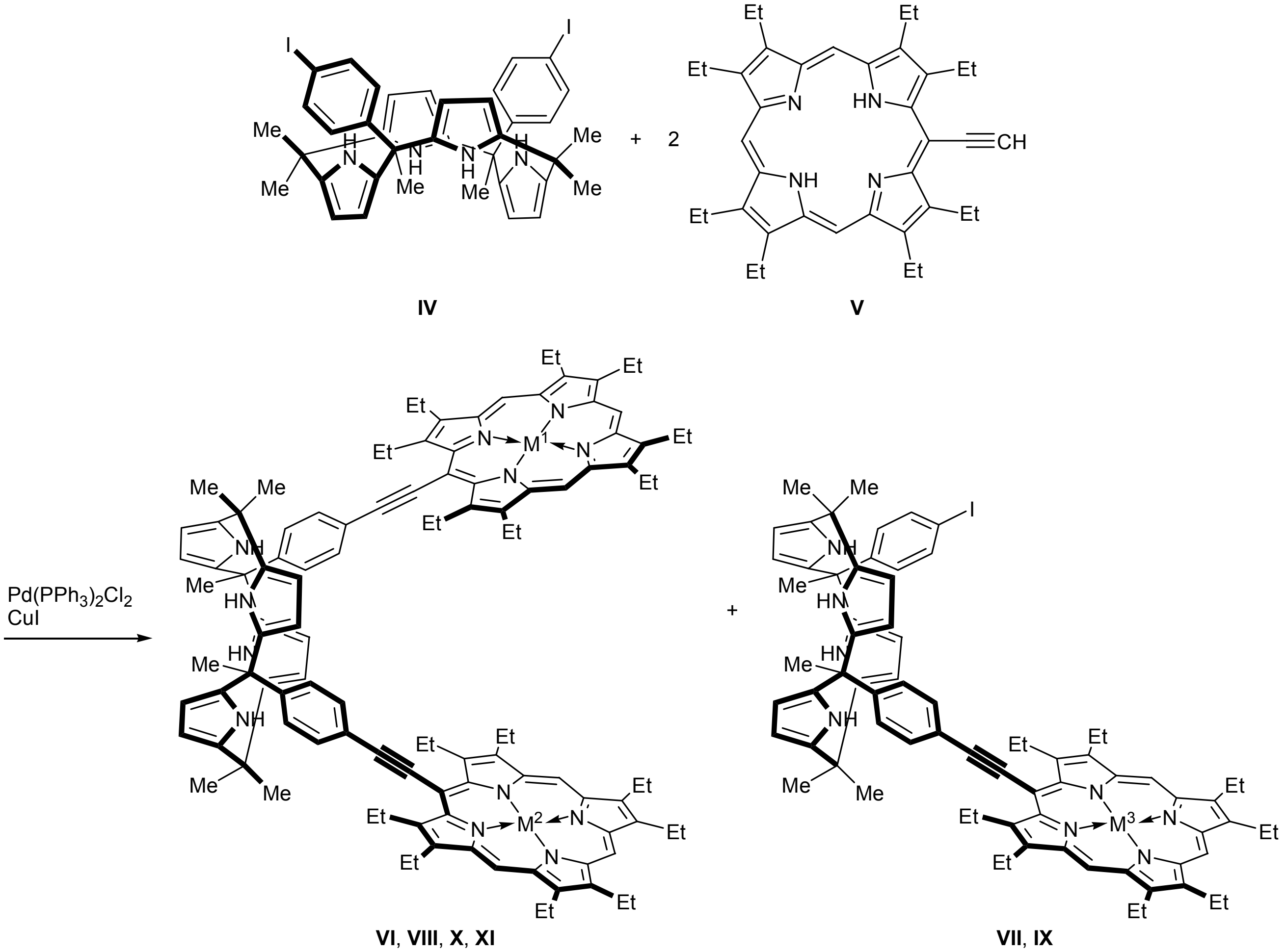
In the present work we synthesized cyclophane-like calix[4]pyrrole–porphyrin conjugates in which the calix[4]pyrrole fragment holds two porphyrin fragments in the face-to-face mode. The structure of the synthesized compounds was confirmed by their electronic absorption and $^{1}$H NMR spectra. The spectral data indicated strong mutual effect of π-electron systems in the neighboring porphyrin macrocycles.

By the Sonogashira reaction [14] of *meso*-hexamethylbis(4-iodophenyl)calix[4]pyrrole (**IV**) with 5-ethynyloctaethylporphyrin (**V**) we synthesized calix-

Scheme 1.



**Scheme 2.**



**VI**, $M^1 = M^2 = H_2$, **VIII**, $M^1 = M^2 = Cu$; **VII**, $M^3 = H_2$; **IX**, $M^3 = Cu$; **X**, $M^1 = Cu$, $M^2 = H_2$; **XI**, $M^1 = Cu$, $M^2 = Zn$.

[4]pyrrole–bisporphyrin conjugate **VI** with the calix[4]pyrrole scaffold having 1,3-*alternate* conformation (Scheme 2). The reaction was carried out in thoroughly dried toluene in the presence of CuI, $Pd(PPh_3)_2Cl_2$, and triethylamine. The product was purified by chromatography on aluminum oxide, followed by recrystallization from methylene chloride–methanol (1 : 1); the yield of **VI** was 30%. Calix[4]pyrrole–porphyrin conjugate **VII** having only one porphyrin fragment was formed as by-product. The reactions of compounds **VI** and **VII** with copper acetate in dimethylformamide gave the corresponding copper porphyrin complexes **VIII** and **IX** in 95% yield.

In the porphyrin chemistry, of particular interest are dimeric porphyrin complexes having different metal cations in the coordination centers of the tetrapyrrole macrorings. Such compounds can be successfully synthesized following the above approach. The reaction of equimolar amounts of calix[4]pyrrole–porphyrin **IX** with 5-ethynyloctaethylporphyrin (**V**) gave 25% of calix[4]pyrrole–bisporphyrin **X**. Complex formation of the latter with zinc acetate in dimethylformamide afforded bisporphyrinate **XI** in which the tetrapyrrole macrorings contain zinc and copper cations.

The $^1$H NMR spectra of calix[4]pyrrole–porphyrins **VI**–**XI** contained signals from protons in the calix[4]pyrrole and porphyrin fragments. Interactions between π-electron systems in the neighboring tetrapyrrole fragments in molecules **VI**, **VIII**, **X**, and **XI** gave rise to upfield shift of signals from protons in the *meso* positions ($\delta\Delta \approx 0.2$ ppm) and β-ethyl groups ($\delta\Delta \approx 0.08$–$0.25$ ppm) relative to the corresponding signals in the spectra of conjugates **VII** and **IX** having only one porphyrin macroring. The observed shifts are consistent with face-to-face orientation of the porphyrin fragments in conjugates **VI**, **VIII**, **X**, and **XI**.

Protons in the *p*-phenylene fragments resonated in the $^1$H NMR spectra as two doublets at δ ~6.55 (*ortho*) and ~6.30 ppm (*meta*). The signals from bisporphyrin conjugates **VI**, **VIII**, **X**, and **XI** were located in a stronger field than those of compounds **VII** and **IX**. The NH protons in the calix[4]pyrrole fragment of **VI**–**XI** gave rise to a broadened singlet at δ 7.2 ppm. All CH protons in the pyrrole rings of the calix[4]pyrrole macroring appeared as one well-resolved doublet at about δ ~5.70 ppm.

The electronic absorption spectra of calix[4]pyrrole–bisporphyrins **VI**, **VIII**, **X**, and **XI** were characterized by a blue shift ($\Delta\lambda = 4.5$ nm), reduced intensity, and considerable broadening of the Soret band as compared to monoporphyrin analogs **VII** and **IX**. These findings also indicate fairly strong interaction between π-electron systems of the porphyrin fragments. In going from methanol to toluene solution, the Soret band in the electronic absorption spectra of calix[4]pyrrole–bisporphyrins **VI**, **VIII**, **X**, and **XI** is appreciably displaced to longer wavelength ($\Delta\lambda \approx 12$ nm). Presumably, effective solvation of aromatic porphyrin fragments by toluene molecules is accompanied by increase in the distance between the tetrapyrrole macrorings and weakening of interaction between their π-electron system. The effect of solvent on the position of absorption maxima in the electronic absorption spectra of porphyrin analogs **VII** and **IX** is minimal.

## EXPERIMENTAL

*meso*-Hexamethylbis(4-iodophenyl)calix[4]pyrrole (**IV**) was synthesized according to the procedure described in [15], and 2,3,7,8,12,13,17,18-octaethyl-5-ethynylporphyrin (**V**) was prepared as reported in [16]. Individual compounds were isolated by column chromatography on neutral aluminum oxide using toluene–hexane (1 : 2) as eluent. Organic solvents were purified by standard methods [17]. The progress of reactions was monitored by TLC on Silufol UV-254 plates. The $^1$H NMR spectra were recorded on a Bruker VC-200 spectrometer (200 MHz) using benzene-$d_6$ as solvent and tetramethylsilane as internal reference. The mass spectra (electron impact, 70 eV) were obtained on an MKh-1310 instrument (ion source temperature 150–200°C). The electronic absorption spectra were measured from solutions in toluene and methanol on a Varian Cary 100 spectrophotometer.

**10,20-Bis[4-(2,3,7,8,12,13,17,18-octaethylporphyrin-5-ylethynyl)phenyl]-5,5,10,15,15,20-hexamethylporphyrinogen (VI).** Triethylamine, 5 ml, was added under argon to a solution of 78.0 mg (0.14 mmol) of compound **V** and 47.11 mg (0.07 mmol) of bis(4-iodophenyl)calix[4]pyrrole **IV** in 5 ml of toluene, the mixture was stirred for 5 min, 4.76 mg (0.01 mmol) of dichlorobis(triphenylphosphine)palladium(II) and 1.62 mg (0.01 mmol) of copper(I) iodide were added, and the mixture was stirred for 24 h at 50°C. The solvent was distilled off under reduced pressure, the residue was dissolved in methylene chloride, and the organic phase was washed twice with water, dried over sodium sulfate, and evaporated to dryness under reduced pressure. The residue was subjected to chromatography on aluminum oxide using methylene chloride–hexane (2 : 1) as eluent. The eluate was evaporated under reduced pressure, and the product was recrystallized from methylene chloride–methanol (1 : 1). Yield 29.1 mg (30%), $R_f$ 0.53 ($Al_2O_3$, $CH_2Cl_2$–$C_6H_{14}$, 2 : 1). Electronic absorption spectrum, $\lambda_{max}$, nm (logε): in toluene: 623.4 (3.58), 571.4 (3.72), 540.2 (3.62), 505.3 (4.01), 421.1 (4.97); in methanol: 618.8 (3.49), 565.3 (3.59), 539.2 (3.58), 502.1 (4.12), 411.8 (4.92). $^1$H NMR spectrum, δ, ppm: –3.23 br.s (4H, NH), –0.41 s (6H, *meso*-$CH_3$), 0.44 s (12H, *meso*-$CH_3$), 1.40 t (12H, $CH_2\mathbf{CH_3}$), 1.52 t (36H, $CH_2\mathbf{CH_3}$), 3.71 m (8H, $\mathbf{CH_2}CH_3$), 3.29 q (24H, $\mathbf{CH_2}CH_3$), 5.51 d (4H, β-CH), 5.72 d (4H, β-CH), 6.23 d (4H, $H_{arom}$), 6.53 d (4H, $H_{arom}$), 7.23 br.s (4H, NH), 9.83 s (2H, *meso*-H), 10.04 s (4H, *meso*-H). Mass spectrum: *m*/*z* 1665.1 $[M]^+$. Found, %: C 82.17; H 7.62; N 10.04. $C_{114}H_{128}N_{12}$. Calculated, %: C 82.21; H 7.69; N 10.10.

**10-(4-Iodophenyl)-20-[4-(2,3,7,8,12,13,17,18-octaethylporphyrin-5-ylethynyl)phenyl]-5,5,10,15,-15,20-hexamethylporphyrinogen (VII).** Yield 5%, $R_f$ 0.56 ($Al_2O_3$, $CH_2Cl_2$–$C_6H_{14}$, 2 : 1). Electronic absorption spectrum, $\lambda_{max}$, nm (logε): in toluene: 625.1 (3.60), 572.3 (3.70), 542.1 (3.63), 507.1 (4.22), 424.6 (5.07); in methanol: 623.5 (3.53), 570.5 (3.65), 541.9 (3.61), 505.7 (4.20), 422.9 (5.01). $^1$H NMR spectrum, δ, ppm: –2.97 s (2H, NH), –0.29 s (6H, *meso*-$CH_3$), 0.59 s (12H, *meso*-$CH_3$), 1.54 t (6H, $CH_2\mathbf{CH_3}$), 1.59 t (18H, $CH_2\mathbf{CH_3}$), 3.38 q (12H, $\mathbf{CH_2}CH_3$), 3.98 q (4H, $\mathbf{CH_2}CH_3$), 5.54 d (4H, β-CH), 5.73 d (4H, β-CH), 6.32 d (4H, $H_{arom}$), 6.65 d (4H, $H_{arom}$), 7.29 br.s (4H, NH), 10.05 s (1H, *meso*-H), 10.27 s (2H, *meso*-H). Mass spectrum: *m*/*z* 1259.3 $[M]^+$. Found, %: C 80.95; H 6.52; N 8.81. $C_{78}H_{83}IN_8$. Calculated, %: C 81.00; H 6.59; N 8.90.

**10,20-Bis[4-(2,3,7,8,12,13,17,18-octaethylporphyrin-5-ylethynyl)phenyl]-5,5,10,15,15,20-hexamethylporphyrinogen dicopper(II) complex (VIII).** Yield 40.1 mg (95%), $R_f$ 0.62 ($Al_2O_3$, $CH_2Cl_2$–$C_6H_{14}$, 2 : 1). Electronic absorption spectrum, $\lambda_{max}$, nm (logε): in toluene: 425.6 (4.82), 549.9 (3.87), 592.3 (3.35); in methanol: 413.1 (4.76), 550.1 (3.81), 587.5 (3.36). $^1$H NMR spectrum, δ, ppm: –0.38 s (6H, *meso*-$CH_3$), 0.43 s (12H, *meso*-$CH_3$), 1.38 t (12H, $CH_2C\mathbf{H}_3$), 1.50 t (36H, $CH_2C\mathbf{H}_3$), 3.30 q (24H, $C\mathbf{H}_2CH_3$), 3.70 m (8H, $C\mathbf{H}_2CH_3$), 5.50 d (4H, β-CH), 5.73 d (4H, β-CH), 6.21 d (4H, $H_{arom}$), 6.52 d (4H, $H_{arom}$), 7.22 br.s (4H, NH), 9.82 s (2H, *meso*-H), 10.02 s (4H, *meso*-H). Mass spectrum: *m/z* 1788.3 $[M]^+$. Found, %: C 76.49; H 6.89; N 9.33. $C_{114}H_{124}Cu_2N_{12}$. Calculated, %: C 76.55; H 6.94; N 9.40.

**(2,3,7,8,12,13,17,18-Octaethyl-5-{4-[15-(4-Iodophenyl)-5,10,10,15,20,20-hexamethylporphyrinogen-5-yl]phenylethynyl}porphyrinato)copper(II) (IX).** Yield 37.3 mg (91%), $R_f$ 0.49 ($Al_2O_3$, $CH_2Cl_2$–$C_6H_{14}$, 2:1). Electronic absorption spectrum, $\lambda_{max}$, nm (logε): in toluene: 420.9 (4.89), 547.2 (3.93), 594.2 (3.39); in methanol: 419.7 (4.85), 546.5 (3.90), 593.6 (3.41). $^1$H NMR spectrum, δ, ppm: –0.25 s (6H, *meso*-$CH_3$), 0.56 s (12H, *meso*-$CH_3$), 1.52 t (6H, $CH_2C\mathbf{H}_3$), 1.57 t (18H, $CH_2C\mathbf{H}_3$), 3.36 q (12H, $C\mathbf{H}_2CH_3$), 3.97 q (4H, $C\mathbf{H}_2CH_3$), 5.52 d (4H, β-CH), 5.69 d (4H, β-CH), 6.30 d (4H, $H_{arom}$), 6.61 d (4H, $H_{arom}$), 7.31 br.s (4H, NH), 10.06 s (1H, *meso*-H), 10.28 s (2H, *meso*-H). Mass spectrum: *m/z* 1320.5 $[M]^+$. Found, %: C 70.87; H 6.10; N 8.43. $C_{78}H_{81}CuIN_8$. Calculated, %: C 70.93; H 6.14; N 8.49.

**10,20-Bis[4-(2,3,7,8,12,13,17,18-octaethylporphyrin-5-ylethynyl)phenyl]-5,5,10,15,15,20-hexamethylporphyrinogen copper(II) complex (X).** Triethylamine, 5 ml, was added under argon to a solution of 87.6 mg (0.07 mmol) of compound **IX** and 39.5 mg (0.07 mmol) of porphyrin **V** in 5 ml of toluene, the mixture was stirred for 5 min, 2.38 mg (0.005 mmol) of dichlorobis(triphenylphosphine)palladium(II) and 0.81 mg (0.005 mmol) of copper(I) iodide were added, and the mixture was stirred for 24 h at 50°C. The solvent was distilled off under reduced pressure, the residue was dissolved in methylene chloride, and the solution was washed twice with water, dried over sodium sulfate, and evaporated to dryness under reduced pressure. The residue was subjected to chromatography on aluminum oxide using $CH_2Cl_2$–$C_6H_{14}$ (2:1) as eluent. The eluate was evaporated under reduced pressure, and the product was recrystallized from $CH_2Cl_2$–MeOH (1:1). Yield 25.7 mg (25%), $R_f$ 0.44 ($Al_2O_3$, $CH_2Cl_2$–$C_6H_{14}$, 2:1). Electronic absorption spectrum, $\lambda_{max}$, nm (logε): in toluene: 423.6 (4.85), 506.3 (4.07), 548.3 (3.73), 586.1 (3.53), 622.4 (3.50); in methanol: 414.7 (4.80), 506.9 (4.01), 547.0 (3.70), 585.7 (3.51), 622.1 (3.49). $^1$H NMR spectrum, δ, ppm: –3.21 s (2H, NH), –0.34 s (6H, *meso*-$CH_3$), 0.47 s (12H, *meso*-$CH_3$), 1.47 t (12H, $CH_2C\mathbf{H}_3$), 1.53 t (36H, $CH_2C\mathbf{H}_3$), 3.32 q (24H, $C\mathbf{H}_2CH_3$), 3.70 m (8H, $C\mathbf{H}_2CH_3$), 5.50 d (4H, β-CH), 5.73 d (4H, β-CH), 6.27 d (4H, $H_{arom}$), 6.52 d (4H, $H_{arom}$), 7.20 br.s (4H, NH), 9.85 s (2H, *meso*-H), 10.07 s (4H, *meso*-H). Mass spectrum: *m/z* 1726.6 $[M]^+$. Found, %: C 79.22; H 7.23; N 9.68. $C_{114}H_{126}CuN_{12}$. Calculated, %: C 79.28; H 7.30; N 9.74.

**10,20-Bis[4-(2,3,7,8,12,13,17,18-octaethylporphyrin-5-ylethynyl)phenyl]-5,5,10,15,15,20-hexamethylporphyrinogen copper(II) zinc(II) complex (XI).** Compound **X**, 30 mg, was dissolved in 70 ml of dimethylformamide, 10 equiv of zinc acetate was added, and the mixture was heated for 30 min under reflux. The mixture was cooled, diluted with an equal volume of water, and filtered. The residue was dried and subjected to chromatography on aluminum oxide using $CH_2Cl_2$–$C_6H_{14}$ (1:1) as eluent. The eluate was evaporated under reduced pressure, and the product was recrystallized from $CH_2Cl_2$–MeOH (1:1). Yield 26.2 mg (85%), $R_f$ 0.67 ($Al_2O_3$, $CH_2Cl_2$–$C_6H_{14}$, 1:1). Electronic absorption spectrum, $\lambda_{max}$, nm (logε): in toluene: 427.8 (4.77), 552.3 (3.77), 586.9 (3.33); in methanol: 418.2 (4.71), 551.9 (3.73), 585.5 (3.30). $^1$H NMR spectrum, δ, ppm: –0.32 s (6H, *meso*-$CH_3$), 0.50 s (12H, *meso*-$CH_3$), 1.43 t (12H, $CH_2C\mathbf{H}_3$), 1.50 t (36H, $CH_2C\mathbf{H}_3$), 3.23 q (24H, $C\mathbf{H}_2CH_3$), 3.76 q (8H, $C\mathbf{H}_2CH_3$), 5.53 d (4H, β-CH), 5.70 d (4H, β-CH), 6.31 d (4H, $H_{arom}$), 6.56 d (4H, $H_{arom}$), 7.25 br.s (4H, NH), 9.84 s (2H, *meso*-H), 10.07 s (4H, *meso*-H). Found, %: C 76.41; H 6.88; N 9.33. $C_{114}H_{124}CuN_{12}Zn$. Calculated, %: C 76.47; H 6.93; N 9.39.

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## REFERENCES

1. Hamilton, A., Lehn, J.M., and Sessler, J.L., *J. Chem. Soc., Chem. Commun.*, 1984, p. 311.
2. Hamilton, A., Lehn, J.M., and Sessler, J.L., *J. Am. Chem. Soc.*, 1986, vol. 108, p. 5158.
3. Kuroda, Y., Hiroshige, T., and Ogoshi, H., *J. Chem. Soc., Chem. Commun.*, 1990, p. 1594.
4. Weber, L., Imiolczyk, I., Haufe, G., Rehorek, D., and Hennig, H., *J. Chem. Soc., Chem. Commun.*, 1992, p. 301.
5. Kuroda, Y., Sera, T., and Ogoshi, H., *J. Am. Chem. Soc.*, 1991, vol. 113, p. 2793.
6. Arimura, T., Brown, C.N., Springs, S.L., and Sessler, J.L., *Chem. Commun.*, 1996, no. 19, p. 2293.

7. Fiammengo, R., Timmerman, P., de Jong, F., and Reinhoudt, D., *Chem. Commun.*, 2000, p. 2313.
8. Nagasaki, T., Fujishima, H., Takeuchi, M., and Shinkai, S., *J. Chem. Soc., Perkin Trans. 1*, 1995, p. 1883.
9. Arimura, T., Ide, S., Sugihara, H., Murata, S., and Sessler, J.L., *New J. Chem.*, 1999, p. 977.
10. Rudkevich, D.M., Verboom, W., and Reinhoudt, D., *Tetrahedron Lett.*, 1994, vol. 35, p. 7131.
11. Koifman, O.I., Mamardashvili, N.Zh., and Antipin, I.S., *Sinteticheskie retseptory na osnove porfirinov i ikh kon"yugatov s kaliks[4]arenami* (Synthetic Receptors Based on Porphyrins and Their Conjugates with Calix[4]arenes), Moscow: Nauka, 2006.
12. Panda, P.K. and Lee, C.-H., *Org. Lett.*, 2004, vol. 6, p. 671.
13. Panda, P.K. and Lee, C.-H., *J. Org. Chem.*, 2005, vol. 70, p. 3148.
14. Mori, A., Mohamed Ahmed, M.S., Sekiguchi, A., Masui, K., and Koike, T., *Chem. Lett.*, 2002, vol. 31, p. 756.
15. Kulikova, O.M., Mamardashvili, G.M., Mamardashvili, N.Zh., and Koifman, O.I., Abstracts of Papers, *III Konferentsiya molodykh uchenykh "Teoreticheskaya i eksperimental'naya khimiya zhidkofaznykh sistem"* (IIIrd Conf. of Young Scientists "Theoretical and Experimental Chemistry of Liquid-Phase Systems"), Ivanovo, 2008, p. 99.
16. Pognon, G., Mamardashvili, N., and Weiss, J., *Tetrahedron Lett.*, 2007, vol. 48, p. 6174.
17. Weissberger, A., Proskauer, E.S., Riddick, J.A., and Toops, E.E., Jr., *Organic Solvents: Physical Properties and Methods of Purification*, New York: Intersci., 1955, 2nd ed. Translated under the title *Organicheskie rastvoriteli*, Moscow: Inostrannaya Literatura, 1958, p. 518.