

New Calix[4]arene Based Hydroxystyryl Cyanine Dyes

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Abstract

Calix[4]arene derivatives bearing one or two hydroxystyryl cyanine chromophores at the wide rim of the macrocycle have been synthesized. The influence of bases and Li^+ on the UV–Vis spectra of the compounds obtained has been investigated.

Introduction

Calixarenes [1] are vase shaped macrocyclic compounds, which are readily obtained through carefully controlled condensation of *para*-substituted phenols with formaldehyde. They have been successfully used as molecular scaffolds for the construction of various supramolecular systems. Preorganization of several metal coordinating or hydrogen bonding fragments at the rims of the calixarenes afforded highly efficient and selective receptors for cations, anions and neutral molecules. Outstanding binding properties of calixarene-based receptors have been applied in sensors sensitive to various analytes [2]. The calixarenes have another interesting application in nonlinear optics [3]. Chromophoric functional calixarenes [4] have attracted a special attention because of their potential use in optical sensors. Calixarene derivatives bearing various chromophores have been synthesized [5–12] and characterized by UV–Vis spectroscopy. A number of highly sensitive optical sensors [13] for cations, anions and organic molecules (including chiral ones [8e]) have been devised on the basis of chromophoric calixarenes.

At present research we have been undertaken in order to combine binding properties calixarenes with optical properties of cyanine dyes, which have narrow intensive absorption bands and are very sensitive for some exo-influences [14, 15].

Experimental

Melting points are uncorrected. ^1H NMR spectra were recorded on a VXP 300 instrument operating at 300 MHz. The chemical shifts are reported from internal tetramethylsilane standard. Absorption spectra

were recorded on Shimadzu – 3100 spectrophotometer. IR spectra were recorded in KBr plates on a M 80 spectrometer.

5-((*E*)-2-(1-methylpyridinium-4-yl)-1-ethenyl)-25,27-dipropoxycalix[4]arene *p*-toluenesulfonate **3**

5-Formyl-25,27-dipropoxycalix[4]arene (0.1 g, 0.186 mmol) **1** and 1,4-dimethylpyridinium *p*-toluenesulfonate (0.26 g, 0.932 mmol) were dissolved in mixture of dry pyridine (3 ml), glacial acetic acid (0.6 ml) and piperidine (2 drops). Reaction mixture was refluxed for 72 h. Product was precipitated with dry ether. The crude product was recrystallized from EtOH. Orange solid: yield 27%, Mp 250 °C (decomp).

^1H NMR (DMSO- D_6), δ : 1.32 (t, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_3$, $J = 6.9$ Hz), 2.02 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 2.28 (s, 3H, ArCH_3), 3.49 (m, 4H, $\text{ArCH}_{2\text{eq}}$), 3.98 (t, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_3$, $J = 6.9$ Hz), 4.21 (m, 7H, $\text{ArCH}_{2\text{ax}}$ and NCH_3), 6.59 (t, 1H, ArH , $J = 7.5$ Hz), 6.82 (t, 2H, ArH , $J = 7.5$ Hz), 7.09 (m, 8H, ArH), 7.33 (d, 1H, CHCH , $J = 16.5$ Hz), 7.46 (d, 2H, ArH , $J = 7.8$ Hz), 7.64 (s, 2H, ArH), 7.84 (d, 1H, CHCH , $J = 16.5$ Hz), 8.11 (d, 2H, HetH , $J = 6.9$ Hz), 8.52 (s, 1H, OH), 8.76 (d, 2H, HetH , $J = 6.9$ Hz), 9.18 (s, 1H, OH). Anal. Found: C 73.68%; H 6.41%. Calc. for $\text{C}_{49}\text{H}_{51}\text{NO}_7\text{S}$: C 73.74%; H 6.45%.

5,17-Bis((*E*)-2-(1-methylpyridinium-4-yl)-1-ethenyl)-25,27-dipropoxycalix[4]arene bis(*p*-toluenesulfonate) **4**

5,17-Diformyl-25,27-dipropoxycalix[4]arene (0.5 g, 0.89 mmol) **2** and 1,4-dimethylpyridinium *p*-toluenesulfonate (0.52 g, 1.86 mmol) were dissolved in mixture of dry pyridine (12.5 ml), glacial acetic acid (2.5 ml) and piperidine (2 drops). Reaction mixture was refluxed for

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24 h. The crude product was filtered and recrystallized from EtOH. Orange solid: yield 40%, Mp 255 °C (decomp).

$^1\text{H NMR}$ (DMSO- D_6), δ : 1.32 (t, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_3$, $J = 6.9$ Hz), 2.02 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 2.28 (s, 6H, ArCH_3), 3.54 (d, 4H, $\text{ArCH}_{2\text{eq}}$, $J = 13.2$ Hz), 4.01 (t, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_3$, $J = 6.9$ Hz), 4.21 (m, 10H, $\text{ArCH}_{2\text{ax}}$ and NCH_3), 6.84 (t, 2H, ArH , $J = 7.8$ Hz), 7.12 (m, 8H, ArH), 7.33 (d, 2H, CHCH , $J = 16.2$ Hz), 7.48 (d, 4H, ArH , $J = 7.8$ Hz), 7.66 (s, 4H, ArH), 7.83 (d, 2H, CHCH , $J = 16.2$ Hz), 8.09 (d, 4H, HetH , $J = 6.9$ Hz), 8.76 (d, 4H, HetH , $J = 6.9$ Hz), 9.13 (s, 2H, OH). Anal. Found: C 70.53%; H 6.13%; S 5.85%. Calc. for $\text{C}_{64}\text{H}_{66}\text{N}_2\text{O}_{10}\text{S}_2$: C 70.68%; H 6.13%; S 5.90%.

Compounds **5** and **6** were synthesized by the condensation of 5,17-diformyl-25,27-dipropoxycalix[4]arene **2** with the 1-ethyl-2-methylbenzo[*c,d*]indolium tetrafluoroborate or with 1,2,3,3-tetramethyl-3H-indolium tetrafluoroborate, respectively, using the same procedure.

*5,17-Bis((E)-2-(1-ethylbenzo[*c,d*]indolium-2-yl)-1-ethenyl)-25,27-dipropoxycalix[4]arene bis(tetrafluoroborate) 5*

Black solid: yield 58%, Mp > 300 °C.

$^1\text{H NMR}$ (DMSO- D_6), δ : 1.36 (t, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_3$, $J = 6.9$ Hz), 1.56 (t, 6H, NCH_2CH_3 , $J = 6.5$ Hz), 2.06 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 3.67 (d, 4H, $\text{ArCH}_{2\text{eq}}$, $J = 13.5$ Hz), 4.09 (t, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_3$, $J = 6.9$ Hz), 4.31 (d, 4H, $\text{ArCH}_{2\text{ax}}$, $J = 13.5$ Hz), 4.85 (qu, 4H, NCH_2CH_3 , $J = 6.5$ Hz), 6.94 (t, 2H, ArH , $J = 7.8$ Hz), 7.24 (d, 4H, ArH , $J = 7.8$ Hz), 7.90 (m, 4H, HetH and CHCH), 8.25 (m, 10H, ArH and HetH), 8.72 (m, 4H, HetH and CHCH), 9.28 (d, 4H, HetH , $J = 7.2$ Hz), 9.74 (s, 2H, OH).

5,17-Bis((E)-2-(1,3,3-trimethyl-3H-indolium-2-yl)-1-ethenyl)-25,27-dipropoxycalix[4]arene bis(tetrafluoroborate) 6

Orange solid: yield 48%, Mp 265 °C (decomp).

$^1\text{H NMR}$ (DMSO- D_6), δ : 1.35 (t, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_3$, $J = 6.9$ Hz), 1.77 (s, 12H, HetCH_3), 2.04 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 3.62 (d, 4H, $\text{ArCH}_{2\text{eq}}$, $J = 13.5$ Hz), 4.09 (m, 10H, $\text{OCH}_2\text{CH}_2\text{CH}_3$ and NCH_3), 4.27 (d, 4H, $\text{ArCH}_{2\text{ax}}$, $J = 13.5$ Hz), 6.91 (t, 2H, ArH , $J = 7.8$ Hz), 7.22 (d, 4H, ArH , $J = 7.8$ Hz), 7.53 (m, 6H, HetH and CHCH), 7.84 (m, 4H, HetH), 8.19 (s, 4H, ArH), 8.28 (d, 2H, CHCH , $J = 16.2$ Hz), 9.67 (s, 2H, OH).

5,17-Bis((E)-2-(3-(1-pyridinio)propan-1-sulfonate-4'-yl)-1-ethenyl)-25,27-dipropoxycalix[4]arene 7

5,17-Diformyl-25,27-dipropoxycalix[4]arene (0.5 g, 0.89 mmol) **2** and 3-(4-methyl-1-pyridinio)propan-1-sulfonate (0.4 g, 1.86 mmol) were dissolved in mixture

of dry pyridine (8 ml), glacial acetic acid (3 ml) and piperidine (5 drops). The reaction mixture was refluxed for 24 h. The crude product was filtered and recrystallized from acetic acid. Yellow solid: yield 26%, Mp 260 °C (decomp).

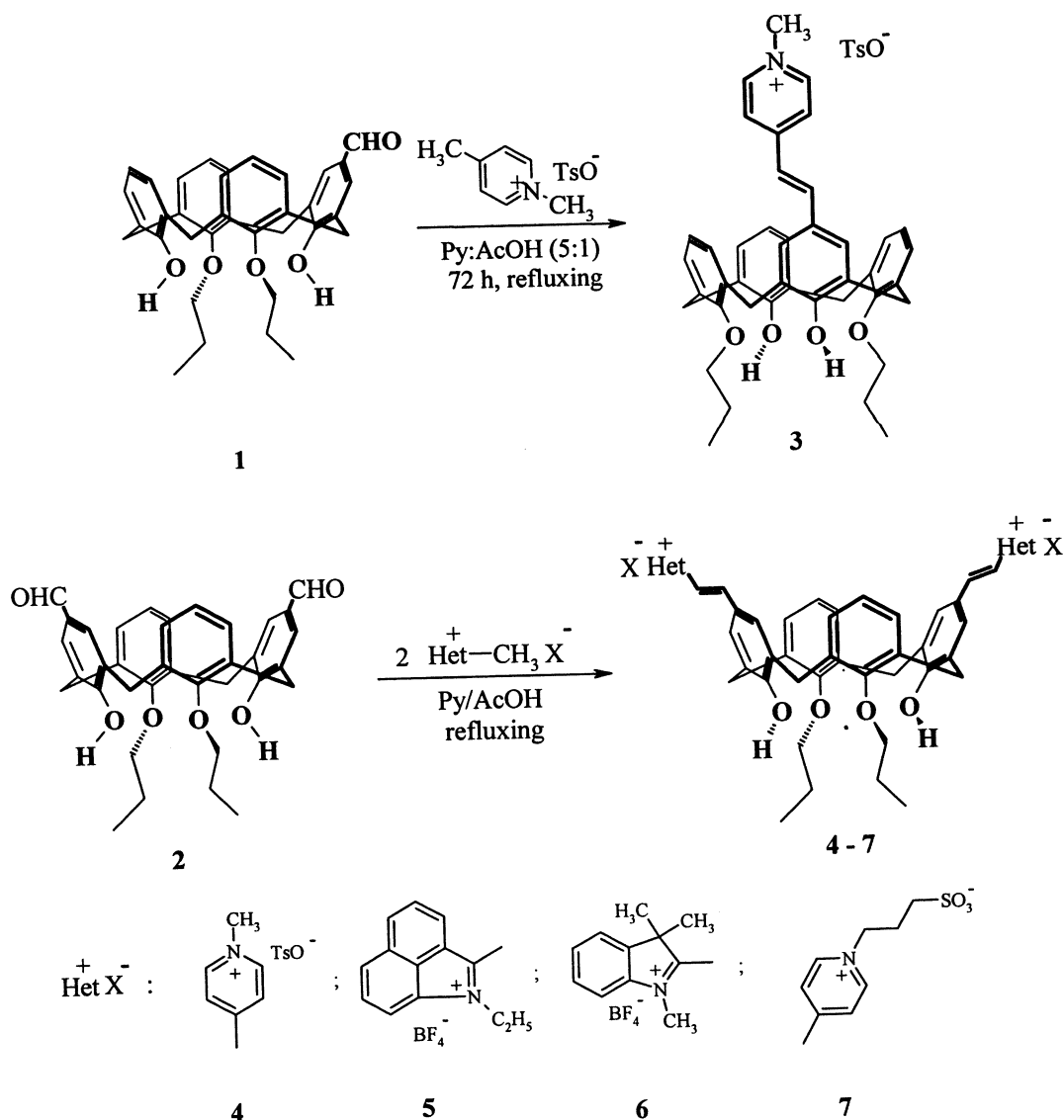
$^1\text{H NMR}$ (DMSO- D_6), δ : 1.32 (t, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_3$, $J = 6.9$ Hz), 2.02 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 2.22 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{SO}_3$), 2.44 (t, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{SO}_3$, $J = 5.6$ Hz), 3.56 (d, 4H, $\text{ArCH}_{2\text{eq}}$, $J = 13.2$ Hz), 4.01 (t, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_3$, $J = 6.9$ Hz), 4.24 (d, 4H, $\text{ArCH}_{2\text{ax}}$, $J = 13.2$ Hz), 4.62 (t, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{SO}_3$, $J = 5.6$ Hz), 6.85 (t, 2H, ArH , $J = 7.8$ Hz), 7.13 (d, 4H, ArH , $J = 7.8$ Hz), 7.32 (d, 2H, CHCH , $J = 16.5$ Hz), 7.65 (s, 4H, ArH), 7.84 (d, 2H, CHCH , $J = 16.5$ Hz), 8.10 (d, 4H, HetH , $J = 6.3$ Hz), 8.85 (d, 4H, HetH , $J = 6.3$ Hz), 9.08 (s, 2H, OH). Anal. Found: C 67.58%; H 6.1%; S 6.68%; Calc. for $\text{C}_{54}\text{H}_{58}\text{N}_2\text{O}_{10}\text{S}_2$: C 67.61%; H 6.11%; S 6.69%.

Results and discussion

The general procedure for the synthesis of hydroxystyryle dyes [16] consists of the condensation of methylsubstituted heterocyclic salts with derivatives of *ortho*- or *para*-hydroxybenzaldehydes. *para*-Formylhydroxycalixarenes **1**, **2** are easily available [17]; therefore, we used the above procedure to synthesize the dyes **3–7**.

Calixarene **3** bearing one hydroxystyryle fragment at the wide rim was obtained in 27% yield by the condensation of calix[4]arene aldehyde **1** with 1,4-dimethylpyridinium *p*-toluenesulfonate. A similar condensation of calix[4]arene dialdehyde **2** with 1,4-dimethylpyridinium *p*-toluenesulfonate, 1-ethyl-2-methylbenzo[*c,d*]indolium tetrafluoroborate, 1,2,3,3-tetramethyl-3H-indolium tetrafluoroborate and 3-(4-methyl-1-pyridinio)propan-1-sulfonate afforded corresponding bishydroxystyryl derivatives **4–7** in 26–58% yields (Scheme 1). The model *para*-hydroxystyrylbezaldehyde based dyes **8–11** [16] and their meroforms **8A–11A** [18] were synthesized, according to Scheme 2.

The $^1\text{H NMR}$ spectra of compounds **3–7** measured in CDCl_3 contain AB doublets for the methylene protons of the bridges ($J_{\text{HH}} = 13$ Hz), which are separated by 0.7–0.9 ppm. This pattern is characteristic for the stereochemically rigid *pinched cone* conformation, stabilized with the intramolecular hydrogen bonds OH–OPr [19]. In IR-spectra, the OH-groups band was observed at 3220 cm^{-1} , which confirms the intramolecular hydrogen bonds [19]. For the *pinched cone* conformation, characterized by C_{2v} symmetry of the macrocyclic skeleton, propylated benzene rings are almost perpendicular to the main plain of the macrocycle formed by four methylene links with the other two hydroxystyryl fragments flattened. Compounds **3–7** have E-configuration as indicated by the coupling constant $^3J_{\text{HH}} = 16.5$ Hz between the protons of double bond.



Scheme 1.

Absorption spectra data for compounds **3–11** are listed in the Table 1. Hydroxystyryls shown broad, symmetric bands with $\lambda_{\text{max}} = 380\text{--}540$ nm (Figure 1a). The absorption maxima of calixarenes **3–7** are shifted to longer wavelength ($\Delta\lambda_{\text{max}} = 20\text{--}25$ nm) and show nearly two-fold increase of absorption intensity compared with compounds **8–11**.

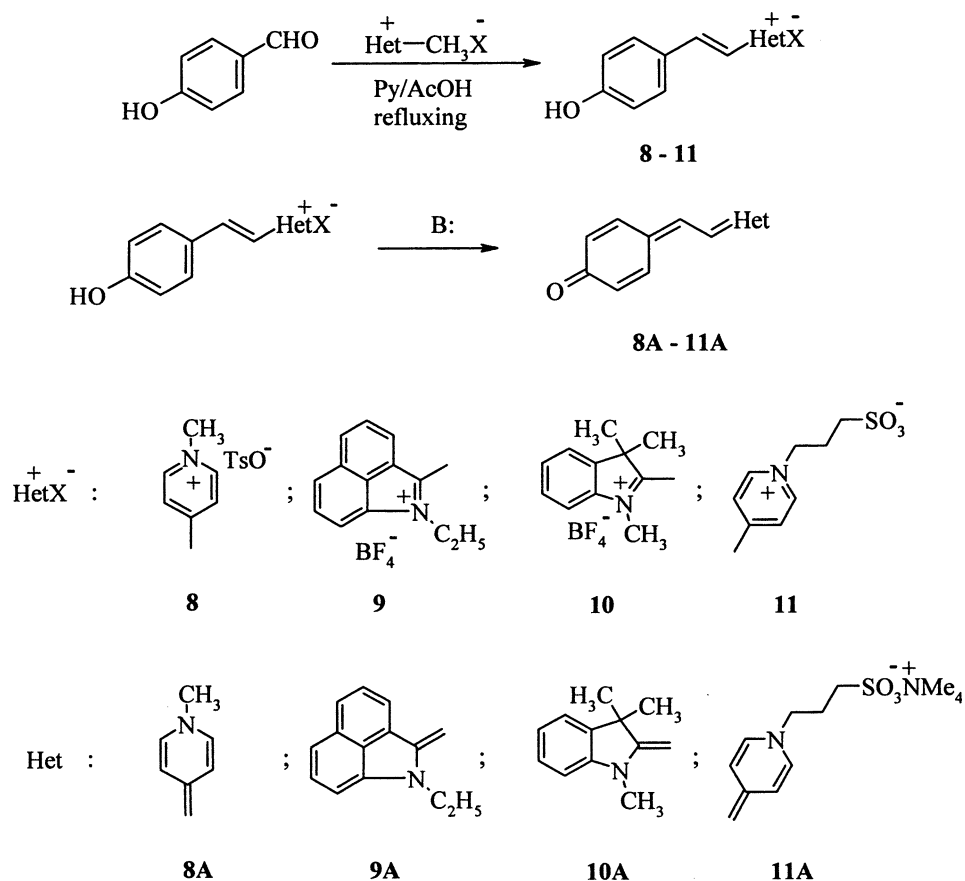
The formation of the merocyanine forms **8A–11A** are characterized with bathochromic shifts of absorption maxima for $\Delta\lambda_{\text{max}} = 100\text{--}140$ nm and at least in 1.5 times increase in intensity (Table 1, Figure 1b) [20].

Hydroxystyryl calix[4]arenes **3–7** were transformed into their merocyanine forms **3A–7A** by the treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Scheme 3) [21].

As in case of model compounds **8A–11A**, the transformation of the hydroxystyryl calixarenes into their merocyanine forms **3A–7A** is accompanied by bathochromic shifts and the increase of molar coefficient of absorption (Table 1). However, in contrast to **8A–11A**, absorption spectra of calix[4]arene derivatives **3A**, **4A**, **6A**, **7A**

contain two maxima separated by 36–52 nm [22] (Table 1, Figure 1b). Complication of the spectral curve may be caused by the conformational mobility of the calixarene-based merocyanine molecule, as a consequence of loss of intramolecular hydrogen bonds OH–OPr after transformation of the hydroxystyryl into a merocyanine. Owing to the free rotation of quinonemethine fragments around Ar–CH₂–Ar bonds, the molecule can adopt the *cone*, the *partial cone* and the *1,3-alternate* conformations [23]. Thus, the superposition of the bands of different conformers is observed in the absorption spectra.

In principle, the doubling of the absorption maxima may result from the intramolecular interaction of two distal chromophores [24] in the *cone* or the *1,3-alternate* conformations (Figure 2). Semiempirical calculations of these conformers showed that the energy of these conformers differ by 2–3 kcal mol⁻¹. This implies the conformers can easily interconvert at ambient temperature.



Scheme 2.

Calculations of calix[4]arene based merocyanine **4A** has shown the distance between heterocyclic fragments of two chromophores equal 1.5 nm – value, allowing their interaction [24]. However, absorption spectra,

recorded in the presence of 10-fold excess of LiClO₄, have demonstrated only one maximum ($\lambda_{\text{max}} = 580 \text{ nm}$, $\epsilon = 156400 \text{ l mol}^{-1} \text{ cm}^{-1}$) for merocyanine **3A**. In the case of bismerocyanines **4A–7A**, increase of long-wave

Table 1. Absorption spectra data of hydroxystyryls **3–11** and merocyanines **3A–11A** in acetonitrile at 295 K

Compound	Hydroxystyryls 3–11		Merocyanines 3A–11A			
	λ_{max} (nm)	$\epsilon \times 10^{-5}$ (l mol ⁻¹ cm ⁻¹)	In absence of LiClO ₄		In Presence of LiClO ₄	
			λ_{max} (nm)	$\epsilon \times 10^{-5}$ (l mol ⁻¹ cm ⁻¹)	λ_{max} (nm)	$\epsilon \times 10^{-5}$ (l mol ⁻¹ cm ⁻¹)
3/3A	403	0.173	583	0.653	580	0.771
			619	0.793		
4/4A	404	0.631	570	1.357	603	1.564
			622	1.685		
5/5A	537	0.641	559	0.908	650	1.274
					711	1.349
6/6A	450.5	0.606	518	0.895	521	0.902
			563	0.971	576	1.606
7/7A	404	0.628	568	1.344	603	1.736
			616	1.643		
8/8A	383	0.321	571	0.837	570	0.836
			9/9A	513		
10/10A	424	0.358	665	0.298	664	0.299
			511	0.645	510	0.644
11/11A	378 ^a	0.218	539	0.954	538	0.955
			452 ^a	0.247	452 ^a	0.247

^aIn water.

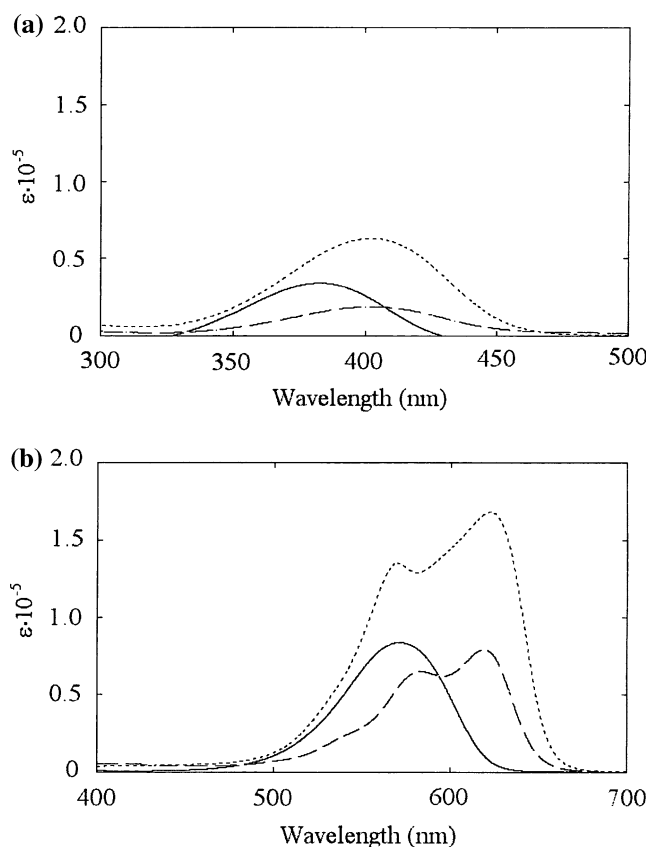


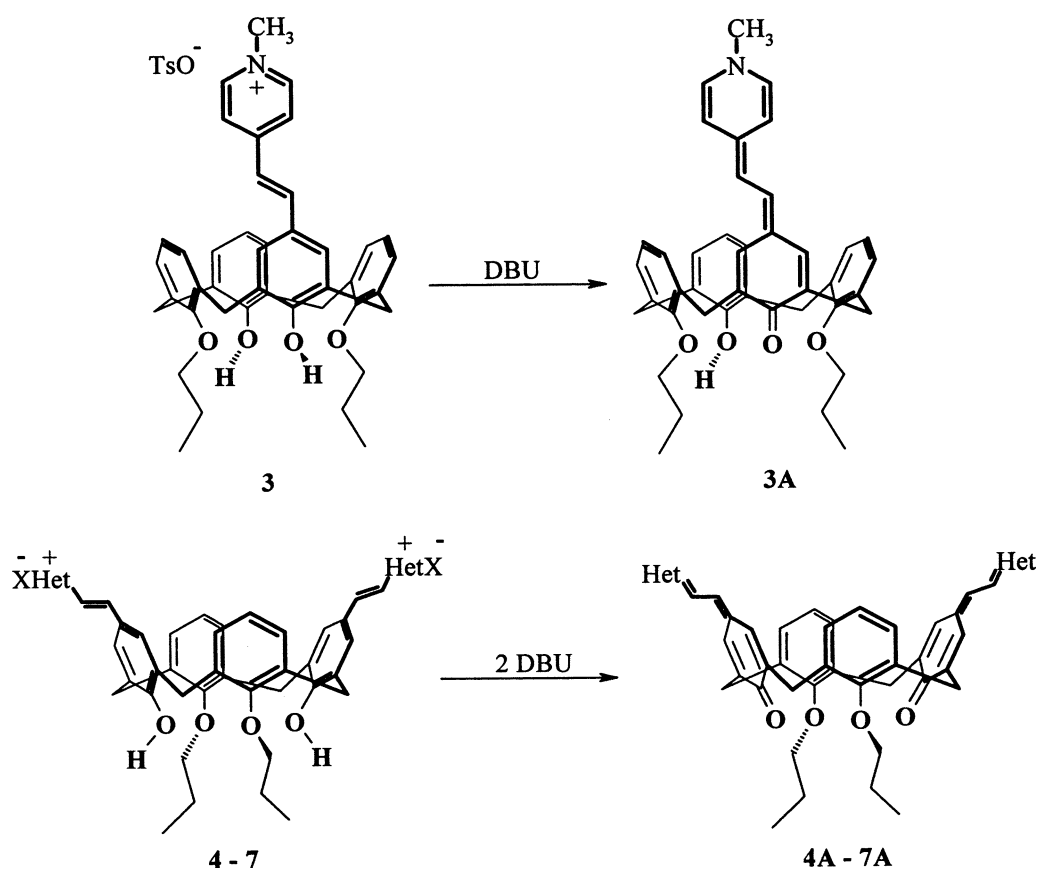
Figure 1. Absorption spectra of hydroxystyryls **3** (---), **4** (...), **8** (—) (a) and their merofoms **3A** (---), **4A** (...), **8A** (—) (b) in acetonitrile.

component of the band was observed after LiClO_4 addition (Figure 3).

This degeneration of the absorption maxima could be caused by the stabilization of the *cone* conformation through the coordination of Li^+ with oxygen atoms of the lower rim. The rotation of quinonemethine fragments is restricted by the complexation and only *cone* conformer band appears in the absorption spectra. Complementarity of the calix[4]arene lower rim dimension to Li^+ cation (ionic radius ca 0.134 nm) [25] and also the high electron density on the oxygen atoms of the merocyanine fragments [26] could be the reasons of the complex formation.

Conclusion

In conclusion, the calix[4]arene based hydroxystyryl cyanine dyes are readily obtained by the condensation of methylsubstituted heterocyclic salts with mono- or bis-formylcalix[4]arenes. The hydroxystyryl cationic dyes transform into uncharged merofoms upon treatment with DBU. The merofoms mark out with narrow bands at 520–710 nm and with high molar coefficients of absorption. The calixarene-based merocyanines change their spectral properties upon the complexation with Li^+ cation.



Scheme 3.

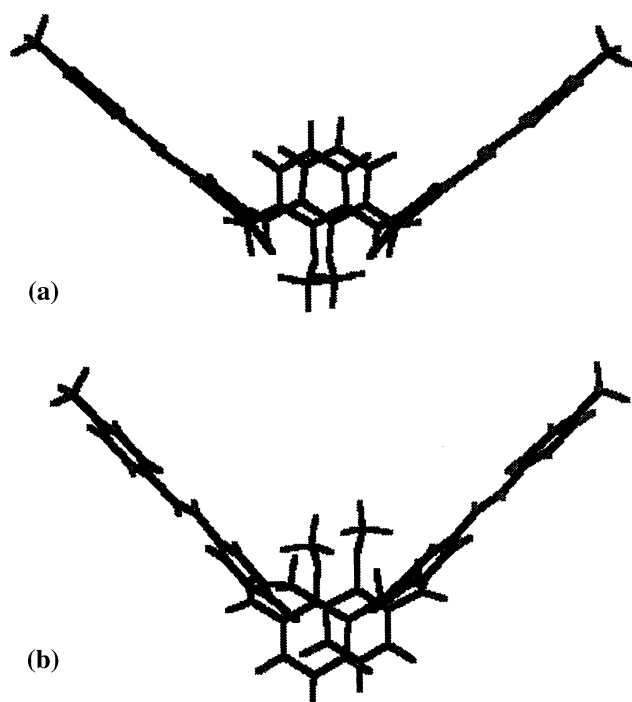


Figure 2. Energy minimized structures of the conformers cone (a) and 1,3-alternate (b) of meroform 4A in accordance with semiempirical calculations (AM1 method in HyperChem 6.00, propyl groups are substituted for methyl ones for clarity).

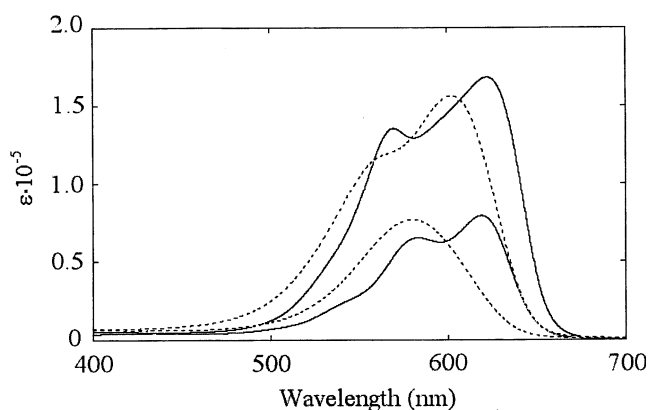


Figure 3. Absorption spectra of compounds 3A (lower bands) and 4A (upper bands) in the absence (—) and the presence (...) of 10-fold excess of LiClO₄ in acetonitrile.

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- Absorption spectra of meroforms 8A–11A recorded for the samples synthesized by previously reported method [18] and generated *in situ* by the addition of DBU to solution of hydroxystyryls 8–11 are identical.
- Calix[4]arene based merocyanines 3A–7A were not isolated as individual compounds. Therefore, their absorption spectra were recorded for samples generated *in situ* by the addition of DBU to solution of hydroxystyryls 3–7.
- Expression of the splitting value through energetical parameters shows that the both maxima have nonvibrational nature (3A – 998 cm⁻¹, 4A – 1467 cm⁻¹, 6A – 1543 cm⁻¹, 7A – 1372 cm⁻¹).
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