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Highly extended styrylstyrylcalix[4]arene assemblies: synthesis and optical properties

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Abstract

Novel highly extended, cone-conformed tetrakis-styrylstyryltetrapropoxycalix[4]arenes and bis-styrylstyryltetrapropoxycalix[4]arenes were synthesized by stereoselective Wadsworth–Emmons reactions. Intramolecular chromophoric interaction of these assemblies resulted in changes to optical properties relative to those of the corresponding monomers with fluorescence enhancement being observed for the assemblies end-capped with methylsulfonyl acceptors. © 2000 Elsevier Science Ltd. All rights reserved.

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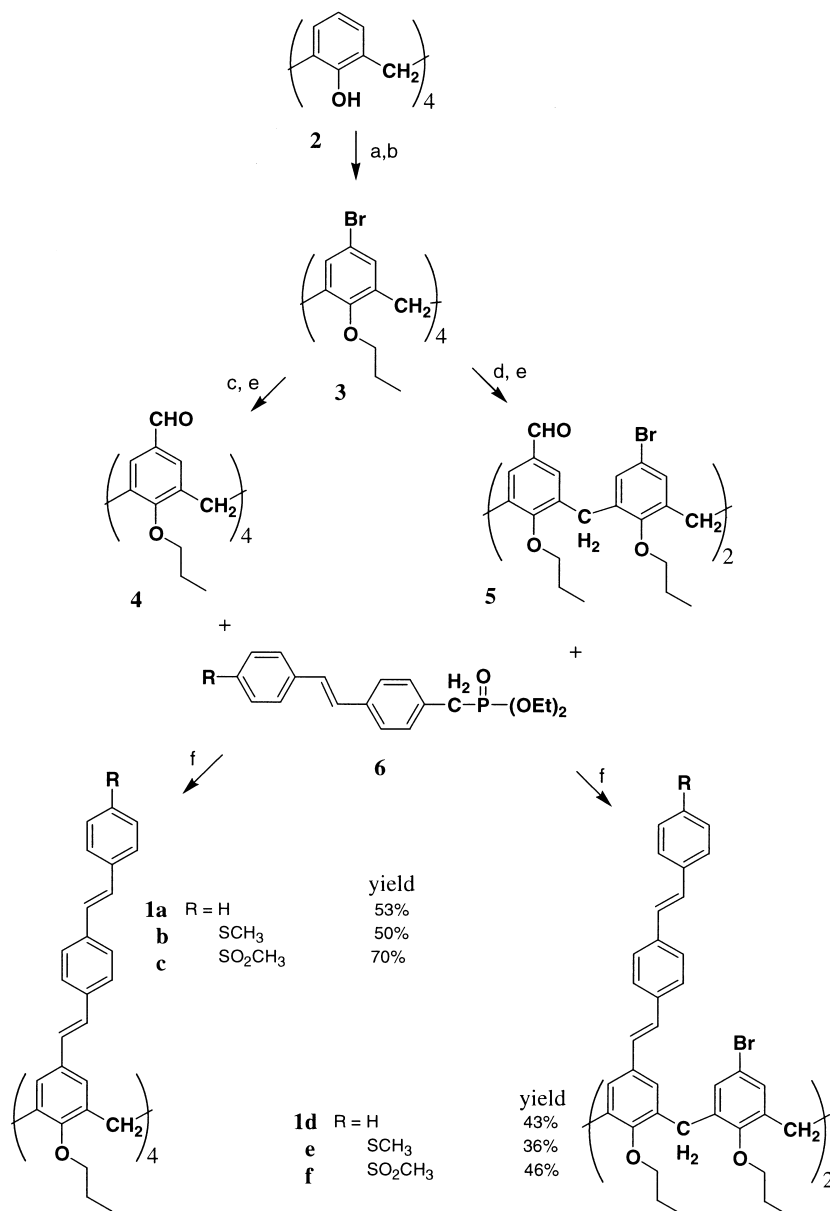
There has been increased interest into the investigation of intermolecular interactions as they play an important role in the optical and electronic properties of materials. It has been shown that there is a strong second harmonic signal generated from centrosymmetric squaraine dyes which is attributed to an intermolecular charge–transfer interaction.¹ In addition, the lower photoluminescence efficiency of a sexithiophene thin-film was attributed to the close packing of the sexithiophene molecules in the solid state when compared to those of β, β' -alkylsubstituted sexithiophenes.² There have been several theoretical studies^{3,4} addressing the influence of intermolecular interactions on various physical properties; however, only few experimental studies have been carried out so far. Therefore, an investigation of the intermolecular interactions in a pre-oriented and pre-defined multi-chromophoric system would be of interest.

Calixarenes are one of the most useful building blocks for constructing supramolecular systems and have been widely used in the preparation of artificial receptors for neutral and ionic molecules. Recently, there has been some interest in the exploitation of extended calix[4]arenes for cavity-enlarged receptors,⁵ second-order nonlinear optical materials⁶ and liquid crystals.⁷ One of the unique features of these calix[4]arene derivatives is that they can exist in a relatively rigid and stable cone structure, in which four functionalized phenolic units, oriented in the same direction are linked at their *ortho*-positions by methylene bridges. With chromophores built onto this framework, the arrangement and orientation of the chromophores may well be pre-defined and pre-organized and the chromophores may be close enough to interact. This assembly may be interesting enough for an investigation of the intra-chromophoric interactions.

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To enhance the chromophoric interaction, a larger interacting area would be favourable. Here we report the first synthesis and optical properties of a novel class of highly extended, cone-conformed calix[4]arene assemblies, tetrakis-styrylstyrylcalix[4]arenes, **1a–c** and bis-styrylstyrylcalix[4]arenes, **1d–f**.

Stereoselective Wadsworth–Emmons reactions were used to construct the all-*trans* *p*-styrylstyryl units as summarized in Scheme 1. Calix[4]arene **2** was alkylated with bromopropane using



Scheme 1. Syntheses of tetrakis-styrylstyryltetrapropoxycalix[4]arenes and bis-styrylstyryltetrapropoxycalix[4]arenes. Conditions: (a) NaH, PrBr, DMF, 50°C; (b) NBS, acetone–CH₂Cl₂ reflux; (c) *t*-BuLi, THF, –78°C; (d) *n*-BuLi, THF, –78°C; (e) *N*-formylmorphine, then HCl; (f) NaH, DME, room temperature

NaH as a base in DMF.⁸ Bromination of tetrapropoxycalix[4]arene with NBS in mixed solvent (acetone-CH₂Cl₂) afforded the bromocalixarene **3**. Exhaustive lithiation of **3** using *tert*-butyl lithium in THF⁹ followed by quenching with *N*-formylmorphine and hydrolysis afforded tetraformyl-tetrapropoxycalix[4]arene **4**. On the other hand, selective 1,3-formylation of **3** was accomplished using *n*-butyllithium as a lithiation agent. Styrylbenzyl-phosphonates were prepared either by a literature procedure¹⁰ or via Wadsworth–Emmons reactions of terephthalaldehyde monodiethylacetal and the benzyl-phosphonates followed by acidic work up which afforded the styrylbenzaldehydes. Reduction of styrylbenzaldehyde by NaBH₄, treatment of the alcohol with SOCl₂ and finally reaction with neat P(OEt)₃ gave the required phosphonates. The Wadsworth–Emmons reactions of **4** or **5** with the corresponding styrylbenzyl-phosphonates **6** gave the desirable tetrakis-styrylstyrylcalix[4]arenes, **1a–c** or bis-styrylstyrylcalix[4]arenes, **1d–f** in good to moderate yields, respectively.¹¹

It has been shown that in solution two rapidly inter-convertible and C_{2v} symmetry related pinched cone conformers of calixarenes are present.¹² The cone conformation of the highly extended tetrakis-styrylstyrylcalix[4]arenes in CDCl₃ has been confirmed by ¹H NMR measurements. On the other hand, the bis-styrylstyryl-calix[4]arenes exist in a pinched cone conformation with the highly extended *p*-styrylstyryl units stretched out which was also found to be the optimized geometry as calculated by the MM2 forcefield.¹³

There is a consistent bathochromic shift of the absorption maxima of bis-styrylstyrylcalix[4]arenes (1–6 nm) and a significant hypsochromic shift of the absorption maxima of tetrakis-styrylstyrylcalix[4]arenes (6–14 nm) in various solvents when compared to those of the corresponding monomers. (Table 1) Therefore, such shifts in absorption maxima of styrylstyrylcalix[4]arenes are attributed to the excitonic interaction of proximate chromophores within the calix[4]arene assembly.¹⁴ The average proximity of two co-facial *p*-styrylstyryl units in tetrakis-styrylstyrylcalix[4]arenes is 3.4 Å, approximated from the MM2-optimized geometry of the pinched cone conformation, in which the absorption spectra are expected to shift hypsochromically according to the excitonic model. On the other hand, the oblique *p*-styrylstyryl units adopt a V-shaped arrangement in the pinched cone conformation of bis-styrylstyryl-calix[4]arenes resulting in a bathochromic shift of absorption maxima. The nearest van der Waals distance of the two stretched *p*-styrylstyryl units is about 5.5 Å in its MM2-optimized geometry.

In contrast to the electronic absorption behaviour, the emission maxima of all styrylstyrylcalix[4]arenes exhibit only bathochromic shifts (3–14 nm) in various solvents relative to those of the corresponding monomers. In addition, their emission maxima show significant solvatochromic effect particularly in the donor-acceptor series (Δ55 nm) which suggests that the emission states of these styrylstyrylcalix[4]arenes are relatively more polar than those of the corresponding monomers. The relative fluorescence quantum yields in chloroform were determined by the dilution method using the corresponding monomer as a reference as described by Parker et al.¹⁵ For styrylstyrylcalix[4]arenes end-capped with or without electron-donors (methylsulfanyl groups) the fluorescence quantum yields are generally lower than those of the corresponding monomers. (Table 1) The fluorescence quenching is likely to be due to the enhancement of the radiationless triplet intersystem crossing in the coupled excitonic states.¹⁴ The quenching effect is more detrimental to the bis-assembly than the tetrakis-assembly. However, styrylstyrylcalix[4]arenes end-substituted with methylsulfonyl groups, electron accepting, exhibit a consistent fluorescence enhancement in both the bis-assembly and tetrakis-assembly as compared to that of the monomer (Table 1). Such an enhancement is presumably due to the retardation of the radiationless triplet intersystem crossing in the coupled excitonic states.

Table 1

Summaries of physical measurements of tetrakis-styrylstyrylcalix[4]arenes, **1a–c**, bis-styrylstyrylcalix[4]arenes, **1d–f** and the corresponding monomers, 3,5-dimethyl-4-propoxydistyrylbenzene derivatives, **1g–i**^{a–c}

	λ_{abs} in dioxane (nm)	λ_{Fl} in dioxane (nm)	λ_{abs} in CHCl_3 (nm)	λ_{Fl} in CHCl_3 (nm)	λ_{abs} in DMSO (nm)	λ_{Fl} in DMSO (nm)	ϵ_{max} in CHCl_3 ($10^4 \text{ M}^{-1} \text{ cm}^{-1}$)	Relative Fluorescence Quantum yield ^d
1a	348	430	349	438	352	451	10.7	0.73
1b	359	440.5	360	444	360	451	10.4	0.94
1c	362	457	367	486	364	511	7.1	1.44
1d	364	426	363	428	367	442	7.7	0.65
1e	374	436	373	443	378	447	10.0	0.46
1f	374	451	373	470	377	507	5.9	1.15
1g	360	419	360	422	362	430	6.6	
1h	372	433	372	436	374	441	5.8	
1i	372	444	372	460	371	498	3.8	

^aAbsorption maxima, λ_{abs} . ^bEmission maxima, λ_{Fl} . ^cMolar extinction coefficient, ϵ_{max} at absorption maxima. ^dThe relative fluorescence quantum yields in chloroform determined by dilution method using the corresponding monomer as a reference.

In summary, a novel series of highly extended, cone-conformed tetrakis-styrylstyrylcalix[4]arenes and bis-styrylstyrylcalix[4]arenes has been synthesized for the investigation of intramolecular chromophoric interactions. Excitonic coupling has been evidenced in such assemblies resulting in a spectral shift and a change of fluorescence quantum yield. Those shifts and changes are greatly dependent upon the nature, arrangement and proximity of chromophores in these assemblies. Importantly, we have found that there is a fluorescence enhancement in the tetra-propoxy-styrylstyrylcalix[4]arene assemblies that are end-substituted with electron-accepting methylsulfonyl groups.

Acknowledgements

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