Synthesis and conformational studies of a series of 5,17-bis-aryl-25,26,27,28-tetrapropoxycalix[4]arenes: the influence of π–π interactions on the molecular structure

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Four 5,17-bis-aryl-25,26,27,28-tetrapropoxycalix[4]arenes were prepared *via* Negishi, Suzuki and Ullman type couplings [aryl = phenyl (**1**), 3-bromophenyl (**2**), 1-naphthyl (**3**) and carbazol-9-yl (**4**)]. The influence of the aryl groups on the structure was studied by X-ray crystallography, NMR, electronic absorption and fluorescence spectroscopy. The results show a drastic difference in conformation where **1** and **2** prefer to have the substituents away from each other while **3** and **4** have them in close contact. The photophysical properties of **3** and **4** exhibited a very solvent dependent fluorescence.

Introduction

Interactions between aromatic groups held in close proximity by molecular frameworks can be studied by spectroscopic and photophysical methods. Several papers have been published concerning the stereochemistry and photophysical properties of 1,8-diarylnaphthalenes[1–3] and 9,10-diarylphenanthrenes.[4,5] The phenyl groups in simple 1,8-diarylnaphthalenes can rotate around the aryl–aryl bonds in solution at room temperature according to NMR spectroscopy. The rotation can be inhibited by attaching appropriate substituents in the *ortho* position of the phenyl group,[6] or by attaching larger aromatic groups (*e.g.* 1- or 2-naphthyl or pyren-1-yl). These compounds can exist in a *cis* and *trans* conformation (atropisomerism) and some have been isolated.[3,6] Many of these compounds display interesting fluorescence properties such as excimer fluorescence.[4]

In this paper we wish to report on a series of calix[4]arene ethers disubstituted in the 5,17-positions with phenyl (**1**), 3-bromophenyl (**2**), 1-naphthyl (**3**) and carbazol-9-yl (**4**) groups which show similar behavior. Simple calix[4]arene ethers[7,8] in the so-called cone conformation with all four ether groups pointing in the same direction have been shown by temperature dependent NMR studies to exist in rapid equilibrium between two flattened cone structures with C_{2v} symmetry.[9] At ambient temperature the two forms are equilibrated so rapidly that the NMR spectra show an apparent C_{4v} symmetry. When acid groups or amide substituents are placed in the 5,17-positions (upper rim, opposite each other) the flattened cone structure with the substituents close together will be preferred due to hydrogen bonding and dipole interactions.[10] The aryl groups introduced in the 5,17-positions can interact as in the above mentioned diaryl-naphthalenes and -phenanthrenes, but have the added flexibility of the calix[4]arene producing very interesting bistable molecules that are suitable for studying weak supramolecular interactions. NMR and X-ray crystallography have been used to investigate these and the excited state was investigated by means of electronic spectroscopy.

Results and discussion

Synthesis

Preparation of the calixarenes **1** and **2** through a Negishi coupling procedure has been described previously.[11] The Suzuki cross-coupling reaction[12,13] of *cone*-5,17-dibromo-25,26,27,28-tetrapropoxycalix[4]arene with 1-naphthylboronic acid[14] in toluene and aqueous Na_2CO_3 with $Pd(PPh_3)_2Cl_2$ as catalyst gave the expected *cone*-5,17-bis(1-naphthyl)-25,26,27,28-tetrapropoxycalix[4]arene **3** in 89% yield after column chromatography. Analogously, we synthesized 1-(3,5-dimethyl-4-propoxyphenyl)naphthalene **6** in 80% yield *via* a Suzuki reaction from 4-bromo-2,6-dimethyl-1-propoxybenzene **5** and 1-naphthylboronic acid under the same reaction conditions as mentioned above. Compound **5** was synthesized in 80% yield from the commercially available 4-bromo-2,6-dimethylphenol by standard alkylation with *n*-propyl bromide and anhydrous K_2CO_3 in MeCN. *Cone*-5,17-bis(9*H*-carbazol-9-yl)-25,26,27,28-tetrapropoxycalix[4]arene **4** and 9-(3,5-dimethyl-4-propoxyphenyl)-9*H*-carbazole **7** were prepared by an Ullman type coupling from the 5,17-dibromocalixarene or bromodimethylphenyl ether **5** with carbazole and Cu_2O in *s*-collidine at reflux. The syntheses are outlined in Scheme 1.

X-Ray structure analysis

Crystal data for **1**–**4** are shown in Table 1. Compounds **1** and **2** are isostructural and both crystallize in spacegroup *C*2/*c* with the molecules stacking *head*-to-*tail* along the crystallographic two-fold axis as shown for **1** in Fig. 1. The stacking arrangement is similar to the stacking arrangement observed in styryl substituted calixarenes[15] but the inter-stack arrangement is different in the sense that the substituent parts of the molecules in adjacent stacks do not interdigitate. Instead the propoxy groups of molecules in neighboring stacks fill the gaps between the substituents within the same stack. This effect is more pronounced for **1** than for **2** where the larger torsion angle and the steric effect of the bromine atom come into play. The molecular conformations are similar in both instances where the planes of the phenyl and 3-bromophenyl substituents are twisted with respect to the plane of the aromatic ring in the calixarene moiety bearing the substituent, thus forming a torsion angle of 33.40(16)° and 46.26(18)° respectively; the increase in torsion angle for compound **2** as

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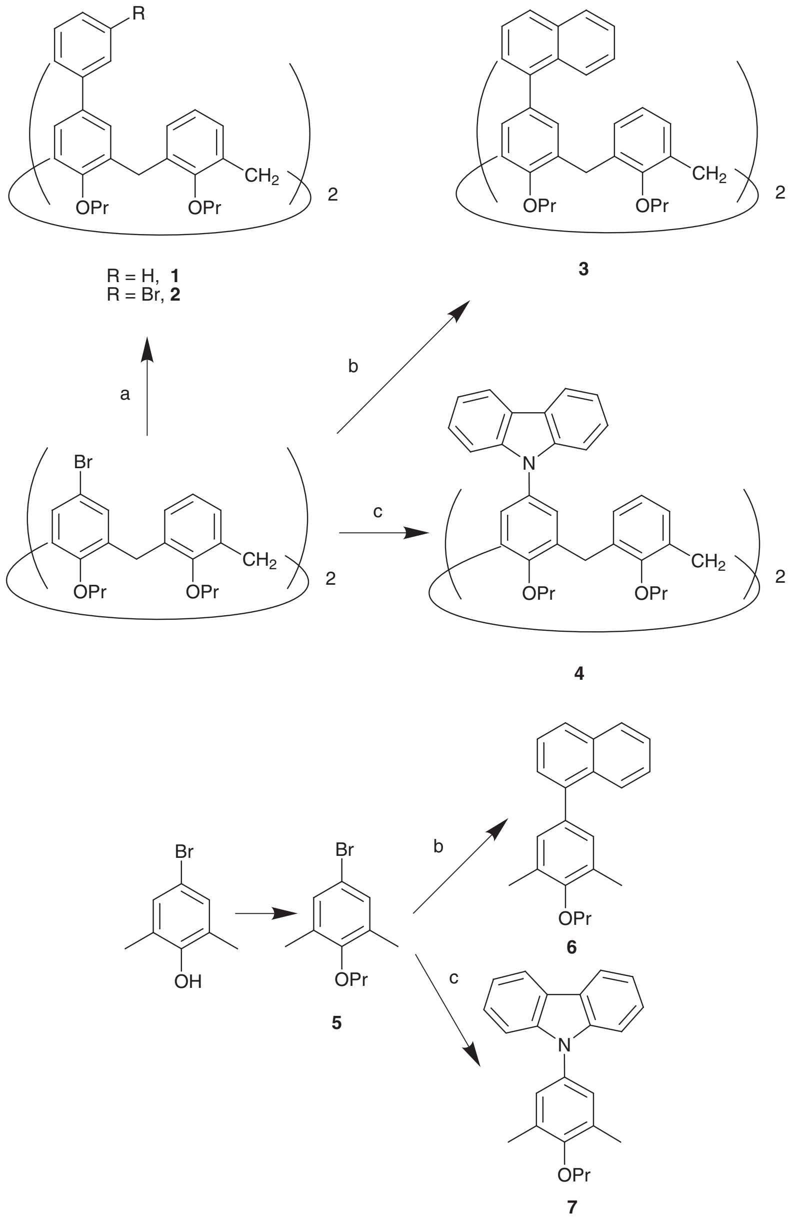
Table 1 Crystallographic data for the 5,17-diaryltetrapropoxycalix[4]arenes

Compound	1	2	3	4
Formula	$C_{52}H_{56}O_4$	$C_{52}H_{54}O_4Br_2$	$C_{60}H_{60}O_4\cdot\frac{1}{2}CH_3CN$	$C_{64}H_{62}O_4N_2$
Formula weight	744.97	902.77	865.60	923.16
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$C2/c$	$C2/c$	$P1$	$P\bar{1}$
Z	4	4	2	2
a/Å	24.645(5)	30.890(6)	10.854(2)	13.047(3)
b/Å	9.0580(18)	9.590(2)	12.946(3)	14.178(3)
c/Å	19.580(4)	18.151(4)	19.085(4)	15.207(3)
α (°)	90	90	109.39(3)	115.31(3)
β (°)	112.52(3)	123.02(3)	98.08(3)	96.69(3)
γ (°)	90	90	99.64(3)	95.82(3)
V/Å^3	4037.6(14)	4509(2)	2437.8(8)	2489.6(9)
μ/cm^{-1}	0.076	1.842	0.072	0.076
T/K	120(2)	120(2)	120(2)	120(2)
Number of reflections	20633	23294	25543	26791
Unique reflections (with $I > 2\sigma$)	2203	4597	7263	6567
R_{int}	0.1127	0.0382	0.0283	0.0433
$R(F)$, $R_w(F^2)$ (all data)	0.0730, 0.2080	0.0512, 0.1431	0.0512, 0.1431	0.0486, 0.1285



Scheme 1 a, Negishi coupling; b, Suzuki coupling; c, Ullman coupling.

compared to **1** is ascribed to the steric demands of the bromine atom (Fig. 2).

Compounds **3** and **4** are also isostructural and oppose compounds **1** and **2** both in packing arrangement and in molecular conformation. Both molecules crystallize in spacegroup $P\bar{1}$ and pack *head*-to-*head* and *tail*-to-*tail* in the crystal with slightly

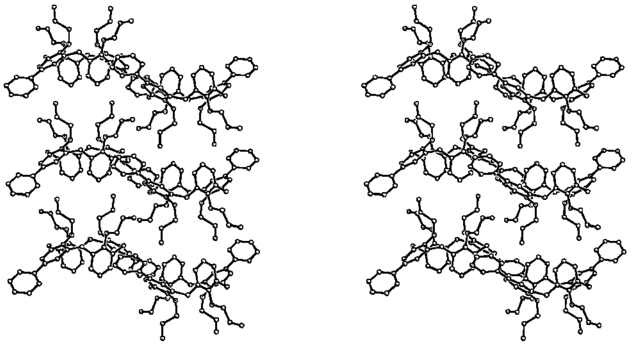


Fig. 1 Packing plot for compound **1** (also representative for compound **2**). The propoxy groups of the molecules in the neighboring stack fill in the gap between the phenyl substituents within the same stack. This effect is more pronounced for **1** than for **2**.

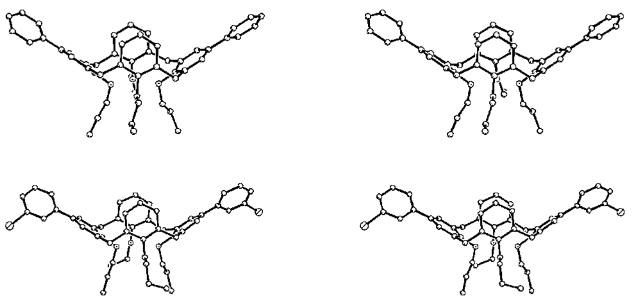


Fig. 2 Molecular stereo plots of compounds **1** and **2** show the similarities in the molecular conformation. The 3-bromophenyl substituent in **2** forms a larger torsion angle with the calixarene moiety than does **1**.

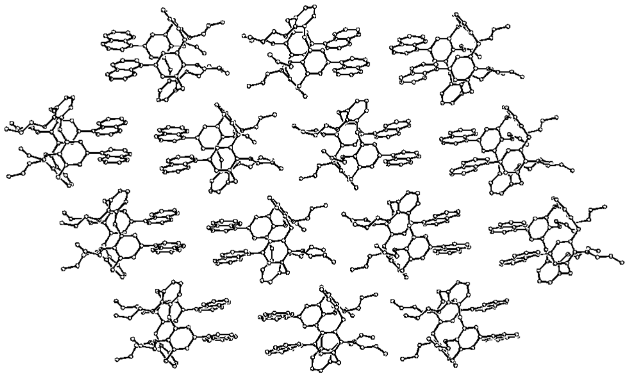


Fig. 3 Packing plot for compound **3** (also representative for compound **4**). The molecules pack in layers *head*-to-*head* and *tail*-to-*tail*. The acetonitrile molecules have been left out for clarity.

interdigitated naphthyl and carbazolyl substituents, respectively, as shown for **3** in Fig. 3. The average interplanar distance between the two substituents is 3.53(25) Å (shortest 3.32 Å, longest 3.78 Å) for **3** and 3.83(25) Å (shortest 3.34 Å, longest 4.25 Å) for **4**. The substituent planes are however not entirely coplanar as can be seen in the packing plot (Fig. 3) and this is ascribed to the packing arrangement. The torsion angles between the substituent and the aromatic ring bearing the substituent are 53.11(6)° and 56.55(6)° for **3** and 48.91(7)° and 53.03(6)° for **4**, where the differences again are ascribed to the packing arrangement, with no symmetry bounds upon the molecular conformation.

The calixarene moieties adopt a pinched *cone* conformation in all instances, the conformation of the calix[4]arene molecules observed in the solid state being similar to the conformation in solution as established by NMR for **1**, **2**, **3** and **4**. The conformations of **1** and **2** differ from the conformations of **3** and **4** in the arrangement of the aryl substituents. In **1** and **2** the substituents are splayed outwards, whereas for **3** and **4** the aryl substituents are pinched towards each other, giving rise to significant π–π overlap; this is summarized in Figs. 2 and 4. The interplanar angles defining the pinched cone conformation of the calix[4]arene are, for the benzene rings bearing the aromatic substituent, 109.6(1)°, 109.7(1)°, −7.8(1)° and −9.3(1)° (respectively for **1**, **2**, **3** and **4**). The planes of the unsubstituted aromatic rings of the calix[4]arene unit form angles of −20.3(1)°, −26.2(1)°, 85.7(1)° and 89.9(1)° (respectively for **1**, **2**, **3** and **4**) with each other. These values for compounds **3** and **4** compare quite well with other values found in the literature[9,16–18] where values range from 90° to 106° and 20° to −15°, respectively. For compound **2** however the conformation is very pinched and is to the best of our knowledge the most pinched conformation ever reported for a calix[4]arene. This is ascribed to packing effects.

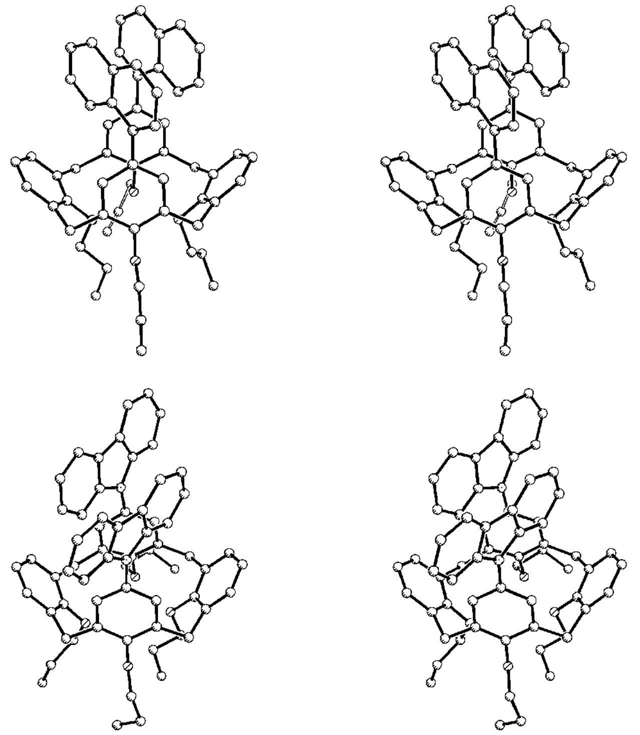


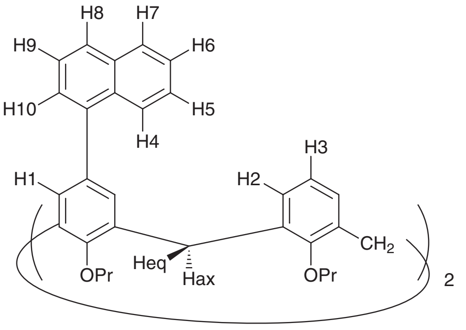
Fig. 4 Molecular stereo plots of compounds **3** and **4** show the near identical molecular conformation for the two molecules. The acetonitrile molecule in **3** has been left out for clarity. The large aromatic substituents give rise to a significant π–π overlap.

NMR analysis

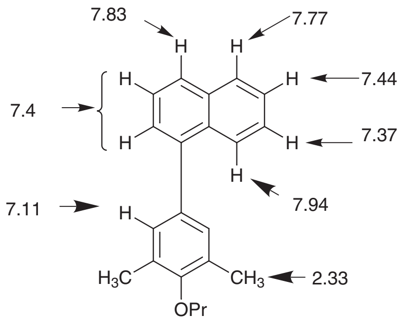
Proton NMR can be used to distinguish between the two possible flattened cone structures in solution. The signals of the protons on the calix[4]arene rings which are pinched together experience a larger shift towards higher field than the signals of the other two ring protons pointing outwards. This is due to ring current effects. The flattened cone also gives rise to two sets of signals arising from the propoxy groups. In particular, the signals from the OCH_2 groups can be used as a rough estimate of the equilibrium between the two conformations in the rapid exchange regime. If chemical shift changes due to substituents in the 5 and 17 positions can be ignored a complete superposition of these signals indicates an equal mixture while a difference of about 0.4 ppm shows that one conformer is clearly favored.

Bisphenylcalixarenes 1 and 2. In the ^1H NMR spectrum at 300 K in $CDCl_3$ of 5,17-bis(phenyl)calixarene **1** two sets of propoxy groups appear, but the difference between the signals from the OCH_2 groups is only 0.14 ppm, indicating a slight excess of the conformation with the phenyl groups splayed outwards compared to the one where they are pinched together. On cooling to 275 K this difference increased slightly to 0.17

Table 2 Proton NMR data for bisnaphthylcalixarene **3** and "monomer" **6** at 240 and 400 K



3



6

	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
240 K	6.61	7.2	6.88	5.75	6.06	6.47	6.99	7.11–7.21		6.99
400 K	6.92	6.93	6.76	6.81	7.01–7.07		7.51	7.51	7.20	7.08

	Hax	Heq	Propyl-1			Propyl-2		
240 K	4.58	3.29	4.15	2.23	0.99	3.77	2.01	1.12
400 K	4.73	3.36	4.18	2.15	1.17	4.08	2.12	1.22

ppm. If the equilibrium had been dominated by π–π interactions between the aryl groups one would have expected that the difference between the OCH_2 signals would have gone through a minimum, with a larger difference expected for the conformer with the phenyl groups pinched together. Since this is not the case other interactions, perhaps with the solvent, must make the conformation seen in the solid state more stable also in solution. For 5,17-bis(3-bromophenyl)calixarene **2** the difference between the OCH_2 signals almost disappears (0.03 ppm at 300 K and 0.07 ppm at 250 K). Again the conformation with the substituents splayed outwards as in the X-ray structure seems slightly more stable.

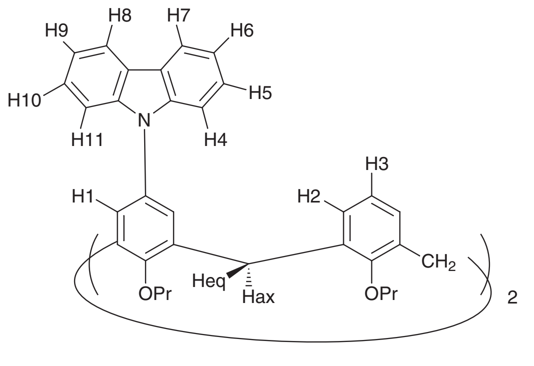
Bisnaphthylcalixarene 3. The ^1H NMR spectrum of **3** in $CDCl_3$ at 300 K shows a typical pinched cone conformation with two different sets of propoxy groups, but the signals in the low field region are very broad. This is interpreted as a sign of hindered rotation around the naphthyl–calixarene bonds. To study this phenomenon the ^1H NMR spectrum of **3** has been investigated as a function of temperature from 240 to 300 K in $CDCl_3$ and from 300 to 400 K in $C_2D_2Cl_4$. The signals in the low field region became narrow at both low and high temperature indicating that the slow and fast exchange regimes were reached. COSY spectra at 240 and 400 K have been used to assign the proton resonances, as given in Table 2. The ^1H NMR spectrum of **6** in $CDCl_3$ at 300 K is included as a reference. The most dramatic change is observed for the AA′XX′ system (H4–H7) in the naphthyl groups of compound **3**. At 240 K the signals for these protons occur at 5.75, 6.06, 6.48 and 6.99 ppm indicating that they are in a fixed position and shielded to a high degree by the nearby aromatic rings. The shielding is greatest for H4 and falls off to H7. This is in agreement with the X-ray structure where it is seen that the AA′XX′ systems are situated directly above the calixarene benzene residues that are pinched outward (see Fig. 4). At higher temperature these protons are less shielded and move to lower field by 0.5–1 ppm. This dramatic change indicates that these parts of the naphthyl groups are now allowed to swing outside the calixarene bowl. At 240 K the distance between the OCH_2 signals are 0.38 ppm while at 400 K it is only 0.10 ppm, indicating a much higher proportion of the pinched cone with the phenyl groups carrying the naphthyl groups splayed outwards at high temperature. This conformation of course allows the rotation of the naphthyl groups. The coalescence temperature for the H4 protons is 290 K and corresponds to a $\Delta G^‡$ of 56 kJ mol^{-1}.[19] In conclusion the low temperature ^1H NMR spectrum can be assigned to the structure observed by X-ray crystallography where the naphthyl groups are in close contact due to favorable π–π interactions, while at higher temperature increasing amounts of the other pinched cone is present.

Biscarbazolylcalixarene 4. A similar temperature dependence was observed for the ^1H NMR spectrum of 5,17-dicarbazolylcalix[4]arene **4**. The resonances due to the carbazole groups almost disappeared at 325 K, but became sharper at lower or higher temperatures. COSY spectra at 250 and 400 K have been used together with the ^1H NMR spectrum of the "monomer" **7** to assign the proton resonances, as given in Table 3. As in the case of compound **2**, the most remarkable shift changes occur in the AA′XX′ system of the carbazolyl groups. At 250 K the H4/H11 protons resonate at 5.20 and 7.4 ppm respectively, while at 400 K the signals have coalesced at 6.53 ppm. The low temperature chemical shift of H11 is very close to the value observed for the "monomer" **7** indicating that it is outside the calixarene cavity. H4 on the contrary is shielded to a large extend (2.2 ppm) by the neighboring aryl groups in the cavity. Similar but progressively smaller effects are seen for H5/H10–H6/H9 and H7/H8. The protons on the calixarene part (H1–H3) show very little temperature dependence indicating that the flattened cone conformation with the carbazolyl groups pinched together is preferred over the whole temperature range. Also the difference in the OCH_2 signals changes from 0.39 ppm at 250 K to 0.27 ppm at 400 K, again indicating the preference for one conformer. Since one carbazolyl group cannot rotate 180° due to its neighbor the equilibration of proton resonances observed at high temperature must be due to a smaller concerted rotation of the two aryl groups. This seesaw motion is depicted in Fig. 5. The coalescence temperature for the signals due to the carbazole groups is 325 K and corresponds to a $\Delta G^‡$ of 61 kJ mol^{-1}.[19]

Electronic absorption and fluorescence spectra

The calixarenes **3** and **4** are composed of four aromatic

Table 3 Proton NMR data for biscarbazolylcalixarene **4** and "monomer" **7** at 250 K and at 400 K



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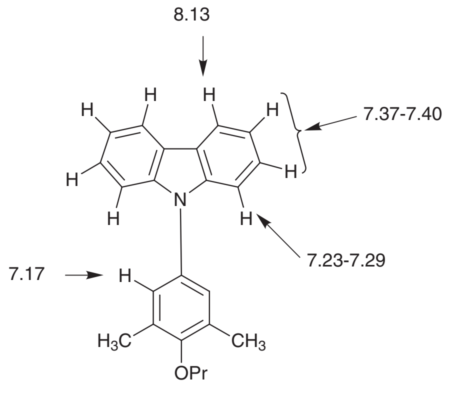

7

	H1	H2	H3	H4	H11	H5	H10	H6	H9	H7	H8
250 K	6.63	7.17	6.88	5.20	7.4	5.84	7.15	6.05	7.3	7.4	7.78
400 K	6.81	7.11	6.88	6.53			6.74			7.65	

	Hax	Heq	Propyl-1			Propyl-2		
250 K	4.62	3.32	4.16	2.22	0.99	3.81	2.02	1.18
400 K	4.74	3.39	4.27	2.21	1.13	4.00	2.07	1.24

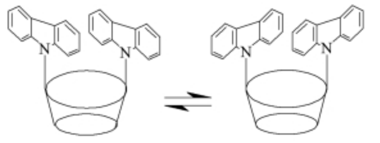

Fig. 5 A seesaw type motion that becomes rapid above 325 K can explain the temperature dependence of the ^{1}H NMR spectrum of compound **4**.

chromophores. Two of these can be represented by 2,6-dimethyl-1-propoxybenzene in both compounds. In **3** the other two can be represented by 1-(3,5-dimethyl-4-propoxyphenyl)-naphthalene (**6**) while **4** is partly composed of units resembling 9-(3,5-dimethyl-4-propoxyphenyl)-9*H*-carbazole (**7**). Compared to **6** and **7** (*vide infra*) 2,6-dimethyl-1-propoxybenzene absorbs only weakly (λ_{max}^{ABS} = 267 nm, ε = 343 M^{-1} cm^{-1}, cyclohexane, spectrum not shown). Thus, this chromophore does not contribute significantly to the absorption spectra of **3** and **4**, nor to their photophysical properties. Any observations made in the electronic spectra will therefore reflect the supramolecular implications experienced by the naphthyl and carbazolyl substituents, respectively. In the solid state the average distance between the naphthyl groups in **3** was found to be only 3.53 Å while a slightly longer distance (3.85 Å) was found between the carbazolyl groups in **4** (*vide supra*). The question arises as to what extent this proximity is retained in solution at room temperature and whether it manifests itself in the photophysical properties of **3** and **4**. Solvent effects were investigated by obtaining the spectra in cyclohexane, benzene and chloroform.

Compounds 3 and 6. The electronic spectra of **3** and **6** are shown in Fig. 6 except for the absorption spectra in benzene and chloroform. The numerical data are collected in Table 4, from which it is seen that the solvent influence on the absorption spectra of both **3** and **6** is negligible. The fluorescence maximum of **6** is red-shifted by *ca.* 850 cm^{-1} when going from cyclohexane to chloroform. Concomitantly, the fluorescence quantum yield is reduced to 34%. Intermediate values are found in benzene. Rather than dipole–dipole forces, dispersive interaction between the fluorophore and the solvent is believed to be the main reason for this solvatochromism (*vide infra*). A solvent influence is also observed in the fluorescence spectra of **3**, but in this case the highest fluorescence energy and efficiency is observed in benzene, followed by cyclohexane and chloroform.

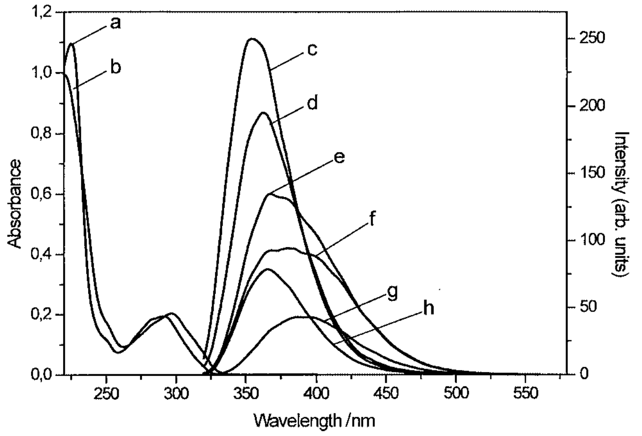

Fig. 6 Electronic absorption spectra of **6** in c-C_6H_{12} (trace a, 2.0×10^{-5} M) and **3** (trace b, 1.0×10^{-5}) and fluorescence spectra (λ_{ex} = 300 nm) of **6** (2.0×10^{-6} M) in c-C_6H_{12} (trace c), C_6H_6 (trace d), $CHCl_3$ (trace g) and **3** (1.0×10^{-6} M) in C_6H_6 (trace e), c-C_6H_{12} (trace f), $CHCl_3$ (trace h). The integrated intensities reflect the relative quantum efficiencies.

The fluorescence from a 0.105 M solution of **6** in aerated cyclohexane was recorded using front-face illumination and compared with the spectrum obtained from a 1×10^{-6} M solution obtained with the same sample geometry. The two spectra were superimposable, thus leaving no indication of emission from excimers eventually formed.

A modest bathochromic shift is observed in the absorption spectra when going from **6** to **3**. It is greatest in cyclohexane (580 cm^{-1}) which indicates some π–π interactions between the ground state naphthalene groups in this solvent. However, the occurrence of stronger dispersive forces between the naphthyl groups in the excited singlet state of **3** can be deduced from the fluorescence spectra of **6** and **3**. The fluorescence maximum of **3** is invariably red-shifted compared to that of **6** and the

Table 4 Electronic spectroscopy parameters for compounds **3** and **6** in c-C_6H_{12}, C_6H_6 and $CHCl_3$

	Compound **3**			Compound **6**		
	c-C_6H_{12}	C_6H_6	$CHCl_3$	c-C_6H_{12}	C_6H_6	$CHCl_3$
$\lambda_{max}{}^{ABS}$/nm	297	298	298	292	294	295
ε^a/M^{-1} cm^{-1}	20000	20000	19500	9500	9500	9500
$\lambda_{max}{}^{FLU}$/nm	381	367	387, 391 (min), 395^b	355	362	366
FWHM^c/cm^{-1}	5850	5150	4850	4050	3950	4050
Stokes shift^d/cm^{-1}	7400	6300	8000	6100	6400	6550
$\Phi_f{}^e$	0.63	0.78	0.25	1	0.82	0.34

^{a} Absorption coefficient. ^{b} The top of the spectrum is almost flat; the Stokes shift is measured from 391 nm. ^{c} Full width at half maximum in cm^{-1}, rounded to nearest 50 cm^{-1}. ^{d} The distance from $\lambda_{max}{}^{ABS}$ to $\lambda_{max}{}^{FLU}$ rounded to nearest 50 cm^{-1}. ^{e} Fluorescence quantum yield relative to **6** in cyclohexane.

bandwidth (FWHM, Table 4) is always greater in the case of **3**. The differences are most noticeable in cyclohexane and chloroform. Further, the emission efficiency in cyclohexane is reduced by 37% when going from **6** to **3**, while only small effects are observed in benzene and chloroform.

Even though no excimer emission was detectable from a concentrated solution of **6** in cyclohexane the fixed geometry of the calixarene might induce excimer-like emission from the naphthyl moieties. However, the greatest shift between the maxima of the fluorescence spectra of **6** and **3** is observed in cyclohexane, but amounts to only *ca.* 1900 cm^{-1}. This value is less than that expected from a completely relaxed naphthalene excimer, since the corresponding shift observed between monomer and excimer fluorescence of 1-methylnaphthalene in *n*-heptane is 6500 cm^{-1}.[20] Rather, the excitation energy seems to be localized on one of the 1-(3,5-dimethyl-4-propoxyphenyl)-naphthalene units of the calixarene, but the spectral output is perturbed by dispersive interaction with the other naphthyl group to a varying extent. Dispersive forces are known to produce spectral shifts to lower energy.[21–22]

In **3** the interaction energy must depend on the relative orientation of the naphthyl groups and consequently on the conformation of the calixarene framework of which they are parts. The distribution of conformers, however, seems to vary in the three solvents investigated. A weak fine structure is discernible in the calixarene fluorescence spectra (Fig. 6, traces e, f and g), an observation which alone would exclude the participation of a relaxed excimer as the emitting species. When examined with greater scrutiny, the local maxima of the fine structure occur at the same wavelengths in all three spectra, albeit with different intensities. The short wavelength components decrease in relative intensity when going through the series benzene/cyclohexane/chloroform, thus causing the overall maximum to undergo a bathochromic shift.

The situation is complicated by the fact that—on top of conformational differences—the position and intensity of the fluorescence spectrum are also strongly dependent on dispersive interactions between the fluorophore and the solvent. This conclusion can be deduced from the solvent influence on the spectra of **6** (Fig. 6, traces c, d and h). In cyclohexane and chloroform a pronounced increase in the Stokes shift is observed when going from **6** to **3** (Table 4). In benzene, the Stokes shift is the same for both **6** and **3**, indicating that *on average* no additional dispersion interaction from the "other" naphthyl group in **3** occurs in the excited state. Greater FWHM values are also observed for **3** compared with **6** in all three solvents, from which one can conclude that more than one geometry of the calixarene is present in solution.

As indicated by the data for **6**, cyclohexane is the least influential solvent of the three. Still, a relatively big reduction in fluorescence quantum yield and an increased Stokes shift are observed in this solvent when going from **6** to **3**. The exceptional FWHM value for **3** indicates that the widest distribution among different calixarene conformers exists in this medium. On average, however, the conformational distribution in cyclohexane is more favorable for dispersive interactions between the naphthyl groups than that occurring in benzene. These results for **3** in cyclohexane also imply that dispersive forces rather than dipole-dipole interactions are determining for the solvatochromism observed in the spectra of **6** (*vide supra*).

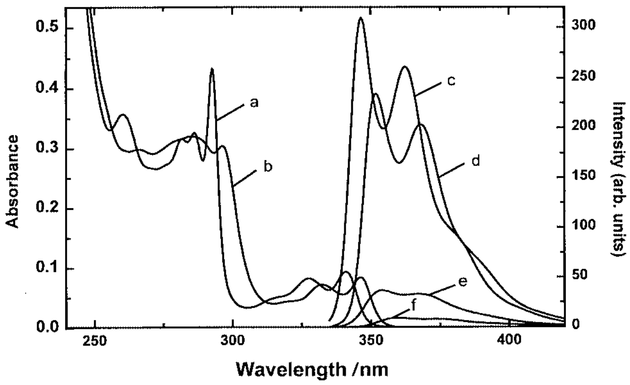

Fig. 7 Electronic absorption spectra of **7** in c-C_6H_{12} (trace a, 2.05×10^{-5} M) and **4** (trace b, 1.11×10^{-5} M). Fluorescence spectra ($\lambda_{ex} = 330$ nm) of **7** in c-C_6H_{12} (trace c, 2.05×10^{-5} M) and in $CHCl_3$ (trace e, 1.96×10^{-5} M). Fluorescence spectra of **4** in c-C_6H_{12} (trace d, 1.11×10^{-5} M) and in $CHCl_3$ (trace f, 1.11×10^{-5} M). The integrated fluorescence intensities reflect relative quantum yields. Fluorescence spectra in benzene are omitted for clarity.

The greatest Stokes shift and the smallest quantum efficiencies are observed in chloroform, indicating that dispersive forces are acting efficiently between the fluorophore and the solvent as well as intramolecularly. The relatively narrow bandwidth implies that the excited molecule enjoys conformational freedom and can relax to a geometry which promotes non-radiative decay particularly well in this solvent.

Compounds 4 and 7. In terms of shape and position, the long wavelength absorption and fluorescence spectra of **7** in cyclohexane are identical to those reported for 9-phenyl-9*H*-carbazole.[24] The profiles are characterized by a well resolved vibrational structure falling off from the peak 0–0 bands. The mirror-image symmetry between absorption and fluorescence is excellent. A slightly smaller absorption coefficient is observed for **7**, which might be tolerated within the general experimental uncertainties. Regarding the Stokes shift, though, a noticeable change is observed when going from 9-phenyl-9*H*-carbazole (*ca.* 200 cm^{-1})[24] to **7** (500 cm^{-1}, Table 5) in cyclohexane, which hints at the participation of the propoxy oxygen lone pairs in the LUMO orbitals. Accordingly, the Stokes shift increases when going to benzene and chloroform since these solvents are more strongly dispersing.

Interaction between the carbazolyl units in the ground state of **4** is revealed when comparing the absorption spectra of **7**

Table 5 Electronic spectroscopy parameters for compounds **4** and **7** in C_6H_6, c-C_6H_{12} and $CHCl_3$

	Compound **4**			Compound **7**		
	C_6H_6	c-C_6H_{12}	$CHCl_3$	C_6H_6	c-C_6H_{12}	$CHCl_3$
λ_{max}^{ABS}/nm	348	346	348	342	341	343
$\Delta\nu_{max}^{ABS}$ (**7**/**4**)^a/cm^{-1}	500	400	400			
ε^b/M^{-1} cm^{-1}	7400	7500	6600	4200	4500	4150
λ_{max}^{FLU}/nm	356	352	360	352	347	354
FWHM^c/cm^{-1}	2500	2300	2650	2500	2250	2700
Stokes shift^d/cm^{-1}	650	500	950	850	500	900
Φ_f^e	0.85	0.81	0.035	1.00	0.96	0.14
$\Delta\nu_{max}^{FLU}$ (**7**/**4**)^f/cm^{-1}	300	400	500			
Φ_f (**7**/**4**)^g	1.18	1.18	4.0			

[a] Distance in cm^{-1} between absorption maxima of **7** and **4**, rounded to nearest 50 cm^{-1}. [b] Absorption coefficient for the 0–0 band in the long wavelength band. [c] Full width at half maximum in cm^{-1}, rounded to nearest 50 cm^{-1}. [d] 0–0 Distance rounded to nearest 50 cm^{-1}. [e] Fluorescence quantum yield relative to **7** in benzene. [f] Distance in cm^{-1} between fluorescence maxima of **7** and **4**, rounded to nearest 50 cm^{-1}. [g] Ratio between relative quantum yields of **7** and **4**.

and **4** in cyclohexane (Fig. 7, traces a and b, respectively). In addition to a bathochromic shift of all transitions (*ca.* 400 cm^{-1}, Table 5) the detailed structure observed in the 250–300 nm region of the absorption spectrum of **7** is smeared out in the case of **4**. The fine structure is better preserved in the 340 nm region, but the maximum absorption coefficient of **4** is 20% less than twice the value observed for **7**. Completely parallel observations can be made in benzene and chloroform (spectra not shown) where the reduction of the maximum absorption coefficient amounts to 14% and 26%, respectively (Table 5).

The fluorescence spectra from 0.1 M solutions of **7** in aerated cyclohexane and chloroform were recorded using front-face illumination and compared with the spectra obtained from the 10^{-6} M solutions. The spectra obtained from the concentrated solutions were superimposable on those from the dilute solutions, thus leaving no indication of emitting excimers eventually formed. However, when framed in the calixarene structure of **4** the interaction observed between the carbazolyl units in the ground state is also detected in the excited state. Thus, considering the fluorescence in cyclohexane (Fig. 7), a bathochromic shift of the same magnitude as that observed in absorption is seen when going from **7** to **4** (Fig. 7, traces c and d, respectively). The relative fluorescence quantum yield is concomitantly reduced by 20%, *i.e.* roughly the same decrease as observed when comparing the absorption coefficients. This coincidence may indicate that the reciprocal action of the carbazole chromophores in the calixarene framework implies a smaller transition dipole moment for the lowest singlet–singlet transition. The same parallel decrease in transition probabilities is observed in benzene when going from the isolated chromophore to the supermolecule (Table 5, spectra not shown). The mechanism by which this phenomenon occurs cannot be discussed on the basis of these preliminary data.

Likewise, it is not clear why the fluorescence quantum yields of **7** and—in particular—**4** are so drastically reduced in chloroform. Thus, the fluorescence of **7** is seven times less efficient in $CHCl_3$ compared with cyclohexane. This quenching effect of $CHCl_3$ must tentatively be attributed to specific interactions between the solvent molecules and the 9-phenyl-9*H*-carbazole chromophore. Even more pronounced, the fluorescence efficiency of calixarene **4** is reduced by a factor of 23 when going from cyclohexane to chloroform. In Fig. 7 the fluorescence spectra in cyclohexane and chloroform (those in benzene are omitted for clarity) are displayed with an intensity reflecting the relative quantum yields. However, when the spectra are normalized (not shown) it is clear that the spectral profile is maintained in all three solvents for both compounds. There is no indication of any excimer emission. In addition, this result provides no support for assuming a solvent dependent equilibrium between different conformations as the origin of the reduced quantum yield for **4** in chloroform. An identical conclusion can be deduced from the constant FWHM values observed for all the fluorescence spectra (Table 5). Therefore, on top of the quenching effect observed for the isolated fluorophore in **7**, chloroform must promote the π–π interaction between the carbazolyl units in the excited state of **4**. Whether this leads to a relaxed state which can be characterized as a (non-emitting) excimer remains to be elucidated by further investigations.

Supramolecularly imposed reciprocal action of the 5,17-substituents have been demonstrated in the ground states as well as the lowest excited singlet states of **3** and **4**. However, the systems behave differently as evidenced by the spectroscopic results.

In **3**, the naphthalene units interact moderately in the ground state but more strongly in the excited state. The dispersive forces between the chromophores depend on the overall conformation of the molecule which again depends on the solvent. Consequently, the width of the fluorescence spectra (FWHM) is increased relative to **6** in all solvents. Likewise, a bigger Stokes shift is observed (except in benzene).

The carbazolyl units in **4** interact moderately in the ground state and the magnitude of the effect is maintained at the same level in the excited state when the solvent is cyclohexane or benzene. Only in chloroform is an increased interaction observed in the excited state. There is no indication of different conformations in any of the solvents.

The diverging behavior of **3** and **4** can possibly be traced back to the different electronic structures of the naphthalene and carbazole units, respectively. Further elucidation of these matters must await forthcoming investigations.

Experimental

The mass spectrum of compound **3** was recorded on a MALDI-TOF MS instrument with 2,5-dihydroxybenzoic acid as matrix. NMR spectra were recorded on a 250 MHz instrument with TMS as internal standard and at 300 K unless otherwise stated. *J* Values are given in Hz. All chemicals and solvents were purchased from commercial sources and used without further purification. 5,17-Dibromo-25,26,27,28-tetrapropoxycalix[4]arene was synthesized by the method described previously.[25] Chromatographic separations were performed on silica gel 60 (SiO_2, particle size 0.040–0.063 mm, 230–240 mesh).

General procedure for the Suzuki cross coupling reaction

A mixture of toluene (50 cm^3) and 2 M Na_2CO_3 (4 cm^3) was flushed with argon for 10 min. 5,17-Dibromo-25,26,27,28-tetrapropoxycalix[4]arene or compound **5** (1.50 mmol or 3.00 mmol, respectively), 1-naphthylboronic acid (0.69 g, 4 mmol) and $Pd(PPh_3)_2Cl_2$ (90 mg, 9 mol%) were added and the mixture was refluxed under an argon atmosphere for 12 h. The black mixture was cooled and diluted with CH_2Cl_2 (100 cm^3), and the organic phase was washed with 1 M NaOH (100 cm^3) and 1 M hydrochloric acid (100 cm^3), dried (Na_2SO_4) and evaporated to dryness on a rotary evaporator. The residue was purified by column chromatography on silica with *n*-hexane–$CHCl_3$ (3 : 1, v/v) as eluent.

5,17-Bis(1-naphthyl)-25,26,27,28-tetrapropoxycalix[4]arene 3

$R_f \approx 0.66$ (*n*-hexane–$CHCl_3$, 1 : 1, v/v). Recrystallization from CH_2Cl_2–MeCN (1 : 1) gave **3** as colorless crystals in 89% yield; mp 249–250 °C (uncorr) (Found: C, 85.65; H, 7.39. $C_{60}H_{60}O_4$ requires C, 85.27; H, 7.16%); δ_H(250.1 MHz) (see Table 2); δ_C(62.9 MHz, $CDCl_2CDCl_2$, 360 K) 10.3, 10.8, 23.3, 23.6, 31.3, 76.7, 77.5, 122.4, 124.6, 124.7, 124.9, 125.7, 126.0, 126.8, 127.1, 128.7, 130.1, 130.6, 133.3, 133.8, 134.0, 136.2, 139.8, 155.3, 157.1; MALDI-TOF MS *m*/*z* 846 ($M + H^+$), 868 ($M + Na^+$), 884 ($M + K^+$).

1-(3,5-Dimethyl-4-propoxyphenyl)naphthalene 6

$R_f \approx 0.25$ (*n*-hexane–$CHCl_3$, 2 : 1, v/v). Compound **3** was obtained as a colorless oil in 74% yield (Found: C, 86.65; H, 7.56. $C_{21}H_{22}O$ requires C, 86.85; H, 7.64%); δ_H(250.1 MHz, $CDCl_3$) 1.10 (3H, t, *J* 7.4), 1.95–1.80 (2H, m), 2.33 (6H, s), 3.79 (2H, t, *J* 6.6), 7.11 (2H, s), 7.50–7.35 (4H, m), 8.00–7.80 (3H, m); δ_C(62.9 MHz, $CDCl_3$) 10.7, 16.4, 23.7, 73.9, 125.3, 125.6, 125.8, 126.2, 126.7, 127.3, 128.1, 130.4, 130.7, 131.8, 133.8, 135.9, 140.2, 155.4; MS *m*/*z* (EI, 70 eV) 290 (M^+, 50%), 248 (100).

General procedure for the Ullman type coupling

Carbazole (2 or 1 equiv.), 5,17-dibromo-25,26,27,28-tetrapropoxycalix[4]arene or 4-propoxy-3,5-dimethyl-1-bromobenzene (2 or 10 mmol, respectively) and Cu_2O (3 g) were heated to reflux in *s*-collidine (30 cm^3) for 96 h under argon. The black mixture was poured onto ice (200 g) with conc. HCl (200 cm^3) and extracted with CH_2Cl_2 (200 cm^3). The organic phase was evaporated to oil that was triturated with hot ethanol (20 cm^3). A white solid precipitated from the cooled solution, which was filtered off and washed several times with ethanol.

5,17-(9*H*-Carbazol-9-yl)-25,26,27,28-tetrapropoxycalix[4]arene 4

Recrystallization from CH_2Cl_2–MeOH afforded the product as a colorless powder, yield 1.4 g (76%); mp >300 °C (Found: C, 82.39; H, 6.78; N, 3.18. $C_{64}H_{62}N_2O_4$ requires C, 82.26; H, 6.93; N, 3.03%); δ_H(250.1 MHz) (see Table 3); δ_C(62.9 MHz, $CDCl_3$) 10.3, 11.2, 23.5, 24.0, 76.9, 77.9, 109.4, 118.9, 123.2, 125.5, 129.4, 131.8, 134.9, 137.2, 153.8, 157.8.

9-(4-Propoxy-3,5-dimethylphenyl)-9*H*-carbazole 7

Recrystallized from ethanol. Yield 1.52 g (23%); mp 93–94 °C (Found: C, 83.60; H, 7.08; N, 4.34. $C_{23}H_{21}NO$ requires C, 83.86; H, 7.04; N, 4.25%); δ_H(250.1 MHz, $CDCl_3$) 1.13 (3H, t, *J* 7), 1.89 (2H, quin, *J* 7), 2.37 (6H, s), 3.85 (2H, t, *J* 7), 7.17 (2H, s), 7.23–7.29 (2H, m), 7.37–7.40 (4H, m), 8.13 (2H, d, *J* 8); δ_C(62.9 MHz, $CDCl_3$) 11.1, 16.9, 24.1, 74.4, 110.3, 120.0, 120.6, 123.5, 126.2, 127.7, 133.0, 133.1, 141.6.

4-Bromo-2,6-dimethyl-1-propoxybenzene 5

4-Bromo-2,6-dimethylphenol (100 g, 0.5 mol), anhydrous K_2CO_3 (69 g, 0.50 mol) and *n*-propyl bromide (55 cm^3, 0.55 mol) were stirred in dry MeCN (400 cm^3) for 18 h at 50 °C. The mixture was filtered and the filter cake was washed with MeCN (100 cm^3). The solvent was removed *in vacuo* and the resulting orange oil was distilled under reduced pressure yielding **5** (97 g, 80%) as a colorless liquid; bp 84–87 °C/0.15 mmHg (Found: C, 54.41; H, 6.32. $C_{11}H_{15}BrO$ requires C, 54.34; H, 6.22%); δ_H(250.1 MHz, $CDCl_3$) 1.05 (3H, t, *J* 7.9), 1.85–1.70 (2H, m), 2.22 (6H, s), 3.67 (2H, t, *J* 7.6), 7.11 (2H, s); δ_C(62.9 MHz, $CDCl_3$) 10.6, 16.1, 23.6, 73.9, 116.0, 131.3, 133.1, 155.2.

Crystallography methods

Crystals of compound **3** lost solvent upon exposure to air. Crystals of **1**, **2**, **3** and **4** were drawn directly from the mother liquor, coated with a thin layer of oil, mounted on a glass capillary using grease (Apiezon™) and transferred quickly to the cold nitrogen stream on the diffractometer. Data were collected on a Siemens SMART Platform diffractometer with a CCD area sensitive detector. Absorption corrections were made using SADABS.[26] Direct methods for the structure solution and full-matrix least-squares refinements were used. Hydrogen atoms were included in calculated positions but not refined. Programs used were SMART, SAINT and SHELXTL from Siemens.[27,28] The weighting schemes: $w = 1/[\sigma^2(F_o^2) + 0.0783P^2 + 7.7543P]$ for **1**, $w = 1/[\sigma^2(F_o^2) + 0.0540P^2 + 19.4637P]$ for **2**, $w = 1/[\sigma^2(F_o^2) + 0.0612P^2 + 1.2954P]$ for **3** and $w = 1/[\sigma^2(F_o^2) + 0.0589P^2 + 0.3769P]$ for **4** where $P = (F_o^2 + 2F_c^2)/3$ and with $\sigma(F_o)$ from counting statistics gave satisfactory agreement analysis. The structures were checked for overlooked symmetry using MISSYM and for voids using PLATON.[29] CCDC reference number 188/170. See http://www.rsc.org/suppdata/p2/1999/1749 for crystallographic data in .cif format.

For compound **1** all the propoxy groups were found to be disordered (two propoxy groups in the asymmetric unit). No disorder was observed for **2**. For compound **3** two of the propoxy groups were found to be disordered. Finally for **4** one propoxy group was found to be disordered. This was in all instances modeled as two mutually exclusive groups and refined with respect to the site occupancy factor (s.o.f.), which was found to be 0.77(3) and 0.776(14) respectively for **1**, and 0.482(8) and 0.529(7), respectively for **3** and 0.848(8) for **4**. Further the acetonitrile solvent molecule in **3** was found to lie close to the center of symmetry. It was treated as being disordered occupying either of the two positions given by inversion through the center of symmetry (*i.e.* the s.o.f. is 0.5).

Spectroscopic methods

Absorption spectra were recorded on a Perkin-Elmer UV-VIS Lambda 16 spectrophotometer. Fluorescence spectra were recorded on an LS 50B Perkin-Elmer luminescence spectrometer using solutions with $A < 0.05$ at the maximum absorbance. In all fluorescence spectra shown of compounds **3** and **6** excitation and emission bandpass were both 5 nm. In the case of compounds **4** and **7** excitation bandpass was 5 nm while the emission bandpass was reduced to 1 nm. All fluorescence spectra were corrected for any solvent background including Raman scattering. No correction was performed for the wavelength dependent response function of the detection system. Relative fluorescence quantum yields were estimated from the integrated fluorescence spectra and corrected for the small differences between absorbances (<5%) at the excitation wavelength ($\lambda_{ex} = 300$ nm for **3** and **6**, $\lambda_{ex} = 330$ nm for **4** and **7**) of the solutions. The fluorescence spectra displayed in Figs. 6 and 7 have been corrected accordingly and reflect the relative quantum yields.

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