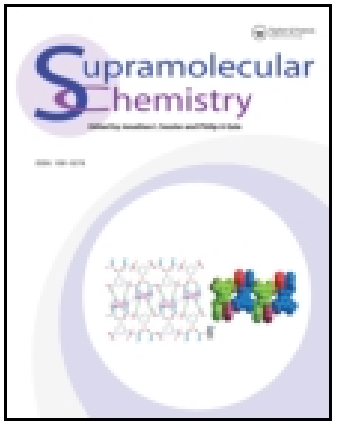

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Synthesis of a phloroacetophenon[4]arene consisting of four isomers via the one-pot, acid-catalysed condensation of phloroacetophenone with benzaldehyde

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Synthesis of a phloroacetophenon[4]arene consisting of four isomers via the one-pot, acid-catalysed condensation of phloroacetophenone with benzaldehyde

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A phloroacetophenon[4]arene (**3**) consisting of four isomers was synthesised for the first time via the condensation of phloroacetophenone and benzaldehyde in a one-pot reaction with refluxing toluene in the presence of catalytic amounts of $TsOH{\cdot}H_2O$ for a maximum yield of 64%. The conformational elucidation of four isomers (**3a**–**d**) by ^1H NMR spectroscopy and X-ray crystal structure analysis showed them to be cone, partial cone, 1,3-alternate and 1,2-alternate types of conformations, respectively.

Keywords: phloroacetophenon[4]arene; four isomers; conformational elucidation; hydrogen bonding

1. Introduction

There are many reports (*1*) on the synthesis and the functionality of cyclic oligomers consisting of a phenol analogue, whereby the compounds taking a calix structure are referred to as 'calixarene'. These were mainly synthesised by the condensation between phenols such as *p-tert*-butylphenol (*2*) or resorcinol (*3*) or pyrogallol (*4*) and an alkyl- and aryl aldehyde such as formaldehyde or benzaldehyde (*5*). Although there are many reports on the chemical modification of a *p-tert*-butylcalix[4]arene or resorcin[4]arene, there are no reports on the synthesis of cyclic oligomers that consist of a phloroglucinol (benzene 1,3,5-triol). We previously reported the first synthesis of a cyclic tetramer and hexamer (**1** and **2**, Figure 1) with alternately arranged phloroglucinols and *p-tert*-butylphenols, and explored the chemical and inclusion properties of **1** (*6*). It appeared that the phloroglucinol moiety in **1** had partially taken a keto-form under alkaline conditions (*6a*). However, despite many efforts, the synthesis of a cyclic oligomer that is consisting only of phloroglucinol has not been achieved because oligomerisation proceeded preferentially because of a high reactivity at the 2,4,6-positions. It could not be synthesised by the same approach as resorcin[4]arene, which is achieved by acid-catalysed condensation between resorcinol and aldehyde (*3*). Based on the reasons given earlier, we formulated our hypothesis on the reactivity of the phloroglucinol as follows: if one of the 2,4,6-positions of phloroglucinol is acylated, its C-alkylated site will decrease to two from three, one of the three phenolic hydroxyls will form a chelation with an acyl–carbonyl group, and because taking a keto-form is difficult, the C-acylated phloroglucinol, phloroacetophenone would behave like a resorcinol in the reaction.

On the basis of this hypothesis, we attempted the synthesis of a cyclic oligomer consisting of only phloroacetophenone. We describe here the first one-pot synthesis of a cyclic tetramer **3** (Figure 1) consisting of phloroacetophenone and benzaldehyde, which hereafter will be called a 'phloroacetophenon[4]arene'.

2. Results and discussion

2.1 Synthesis

Although our attempts towards the synthesis of a cyclic oligomer that consisted of only a phloroglucinol have been unsuccessful, an acid-catalysed condensation of phloroacetophenone with benzaldehyde on the base of the previously mentioned hypothesis gave the desired cyclic tetramer. Because one of the three reaction sites of phloroglucinol was filled with an acetyl group, it was assumed that phloroacetophenone behaved like resorcinol. This reaction was achieved with a normal and practical concentration (0.5 M) and reaction time (10 min) using equimolar amounts of phloroacetophenone and benzaldehyde in refluxing toluene in the presence of a catalytic amount (0.15 equiv.) of *p*-toluenesulfonic acid monohydrate ($TsOH{\cdot}H_2O$), whereas compounds **1** and **2** were synthesised by stepwise synthesis. The substrates disappeared after 5 min, and the reaction mixture was readily separable to only the corresponding cyclic tetramer from some chained oligomers by silica gel column chromatography (solvent: chloroform), which

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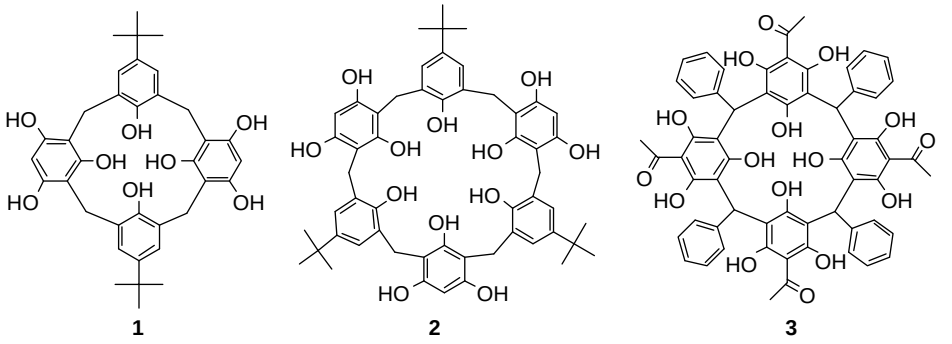
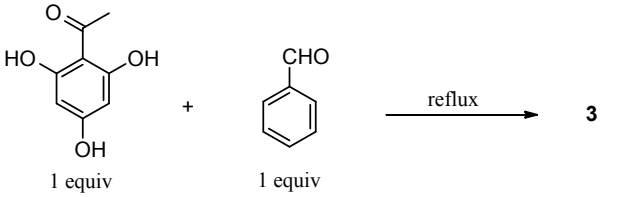


Figure 1. The synthesised cyclic oligomers containing phloroglucinol.

was afforded in a yield of 35% (Table 1). Phloroacetophenone also reacted with *p*-anisaldehyde or 2-naphthaldehyde to give the corresponding phloroacetophenon[4]arene in the same yields. However, it did not react with the other benzaldehydes such as *p*-hydroxybenzaldehyde, *p*-phenylbenzaldehyde, *o*-nitrobenzaldehyde or 1-naphthaldehyde, or with any aliphatic aldehydes such as formaldehyde or alkylaldehyde. Benzaldehyde reacted neither with phloroacetophenone derivatives in which a hydroxyl group was protected nor with alkylated phloroglucinols such as those containing an ethyl group in place of an acetyl group.

The use of either HCl or ytterbium(III) trifluoromethanesulfonate [$Yb(OTf)_3$], which was used as a catalyst in the synthesis of resorcinarene (*3f*), was never successful. The use of sulfonic acid derivatives like H_2SO_4, CH_3SO_3H or CF_3SO_3H in the place of $TsOH{\cdot}H_2O$ afforded **3** in the same yield. The use of protic solvents such as ethanol or aprotic polar solvents such as acetonitrile and 1,4-dioxane gave no or little yield (Table 2). Aprotic non-polar solvents with high-boiling temperatures such as toluene, ethylbenzene or chlorobenzene gave higher yields.

Table 1. Synthesis of **3** in the presence of some catalysts.



Run	Catalyst (equiv.)	Solvent	Concentration (mM)	Time	Yield (%)
1	*p*-$TsOH{\cdot}H_2O$ (0.15)	Toluene	500	5 min	35
2	$Yb(OTf)_3$ (0.15)	Toluene	500	20 min	0
3	Concentrated HCl (1.92)	Ethanol	1000	16 h	0

Next, optimum amount of a catalyst *p*-$TsOH{\cdot}H_2O$ was examined (Table 3). When the amount of *p*-$TsOH{\cdot}H_2O$ was doubled (0.30 equiv.), the yield was improved to 40%; however, the use of more amount (0.50 equiv.) decreased the yield to 30%. The change in the amounts of *p*-$TsOH{\cdot}H_2O$ had no significant influence on the yield.

Exploration of the optimum concentration of phloroacetophenone and benzaldehyde on the reaction in refluxing toluene in the presence of *p*-$TsOH{\cdot}H_2O$ (0.15 equiv.) showed that the more dilute concentration gave a higher yield (Table 4, runs 4 and 5). When the concentration used was 34 mM, the yield was maximum 63%, and when with 3.4 mM, the yield was about the same, at 64%.

To summarise the reaction conditions, it appeared that phloroacetophenon[4]arene was produced in a 64% yield after the 4-h refluxing of a concentration of 3.4 mM substrates in toluene in the presence of 0.15 equiv. of *p*-$TsOH{\cdot}H_2O$. Although the yield of **3** was changed by a change in either the solvent or catalyst, the product ratio of the four isomers was scarcely changed from *ca.* **3a**:**3b**:**3c**:**3d** = 13:61:12:14, as determined by HPLC analysis [column: silica gel, solvent system: toluene–AcOEt–AcOH = 65:30:5, flow rate: 1 ml/min, detection: UV310 nm, R_t: 1.97 min (**3a**), 4.39 min (**3b**), 6.38 min (**3c**) and 16.91 min (**3d**)].

Table 2. Synthesis of **3** catalysed by *p*-$TsOH{\cdot}H_2O$ (0.15 equiv.) in some refluxing solvents.

Run	Solvent	Concentration (mM)	Time (min)	Yield (%)
1	Toluene	500	10	35
2	Ethanol	500	10	0
3	CH_3CN	500	60	Trace
4	1,4-Dioxane	500	30	Trace
5	Benzene	500	10	17
6	Ethylbenzene	500	10	23
7	Xylenes	500	10	10[a]
8	Chlorobenzene	500	10	38

[a] *p*-$TsOH{\cdot}H_2O$ (0.30 equiv.).

Table 3. Synthesis of **3** in the presence of catalytic amount of *p*-TsOH·H_2O in a refluxing toluene.

Run	*p*-TsOH·H_2O (equiv.)	Concentration (mM)	Time (min)	Yield (%)
1	0.15	500	10	35
2	0.30	500	5	40
3	0.50	500	5	30

2.2 Conformation analysis

The FAB-MS and elemental analysis of the four products (**3a**–**3d**) gave 1025 $(M + H)^+$ and $C_{60}H_{48}O_{16}$. Each ^{1}H NMR spectrum showed characteristic chemical shifts (Figure S1 of the Supporting Information, available via the article webpage) as follows: from one to four singlet peaks for the four acetyl–methyl groups at *ca.* 2.6 ppm, from one to three singlet peaks for the four triphenylmethanes at *ca.* 6.5 ppm and as each from one to four singlet peaks for the three phenolic hydroxyls at 9.6, 10 and 16 ppm. They were elucidated to be a cyclic tetramer where four phloroacetophenones and four benzaldehydes were alternatively condensed. The four isomers of the cyclic tetramer were expected, as ordered from high to low, in the following R_f-values of the silica gel thin layer chromatography (TLC) [toluene:AcOEt:AcOH = 5:2:0.5, R_f-value: 0.70 (**3a**), 0.25 (**3b**), 0.18 (**3c**) and 0.10 (**3d**)], to be cone (**3a**), partial cone (**3b**), 1,3-alternate (**3c**) and 1,2-alternate (**3d**) (see Figure 2), as with a *p-tert*-butylcalix[4]arene (*7*). In isomer **3a**, all peaks, with the exception of the phenyl-aromatic protons derived from benzaldehyde, were observed as a singlet peak: at 2.6 ppm derived from four C-acetyl groups; at 6.5 ppm derived from triphenylmethanes; at 9.7 and 10 ppm derived from eight phenolic hydroxyls and at 16 ppm derived from four phenolic hydroxyls chelated to carbonyl groups. In the ^{1}H NMR spectrum of **3c**, two singlet peaks for four chelated hydroxyls, two singlet peaks for the four upper hydroxyls and one singlet peak for four lower hydroxyls and two singlet peaks for four acetyl–methyl residues were observed, respectively. Therefore, **3c** was assumed from their symmetry to have taken a 1,3-alternative conformation. In the ^{1}H NMR spectra of **3b** and **3d**, four signals for each proton were observed with the exception of the observation of one singlet peak with four hydroxyls on the lower side. In the signal from the four chelated hydroxyls, however, **3b** was separated to one and three other singlet peaks and **3d** was separated to two and two singlet peaks, respectively. From the above analysis, it was assumed that **3b** had taken a partial cone-type conformation and **3d** a 1,2-alternate-type conformation, respectively. Because the peaks derived from the four phenolic hydroxyls on the lower side were observed as a singlet in all isomers, it was assumed that the structure of the three isomers, with the exception of **3a**, taken in $CDCl_3$ was not examples of the perfect-reverse models depicted in Figure 2 (*7*), but was of half-reverse models where a hydrogen-bonding ring network at the lower side was not broken. Further, X-ray crystal structure analysis showed that **3a** also adopted a cone-type conformation (see Figure 3) and that an acetone molecule had bonded via four intermolecular hydrogen bonds between the carbonyl oxygen of acetone and the four hydroxyl groups of the lower side of **3a**. Also possible was four CH–π interactions between the two methyl groups of acetone and the four benzene rings on the lower side of **3a**. Although the crystal of **3a** was fragile, X-ray crystal structure analysis showed that one of the four isomers, **3a**, had taken a calix structure and that a new characteristic structure of the lower and upper rims had hydrogen-bonding networks like those of *p-tert*-butylcalix[4]arene and resorcinarene, respectively. Also, the lower rim had a shallow calix structure with four benzene rings bonded at the lower side for the triphenylmethyl carbon with a small molecular structure similar to that of an acetone included.

Finally, a change in the UV–vis spectra resulting from a change in the solution pH (7–13) of phloroglucinol and a major isomer **3b** was measured (Figures S6 and S7 of the Supporting Information, available via the article webpage). The UV–vis spectra of cyclic compound **1**, in which phloroglucinol and *p-tert*-butylphenol had bonded alternatively, were changed together with a change in pH, as was phloroglucinol (*6a*). However, the UV–vis spectra of **3b** did not change until pH 13 was reached due to the strong intramolecular hydrogen bonding, whereas that of phloroacetophenone was changed with any change in pH.

Four isomers were unstable under basic conditions to give some non-cyclic products. They were party cleaved and afforded some degradation products even under refluxing in xylenes.

There are well-known reports of various species from a neutral small molecule such as organic solvents (*8*) to metal ions (*9*) and a large molecule such as C60 (*10*) that were included as guests, and, recently, an alcohol that was included selectively under competitive conditions (*11*). A study on selective inclusion using **3a** is now in progress.

Table 4. Synthesis of **3** in some concentrations of phloroacetophenone and benzaldehyde in refluxing toluene in the presence of *p*-TsOH·H_2O.

Run	*p*-TsOH·H_2O (equiv.)	Concentration (mM)	Time	Yield (%)
1	0.15	500	10 min	35
2	0.15	1000	10 min	24
3	0.15	100	4 h	42
4	0.15	34	4 h	63
5	0.15	3.4	4 h	64

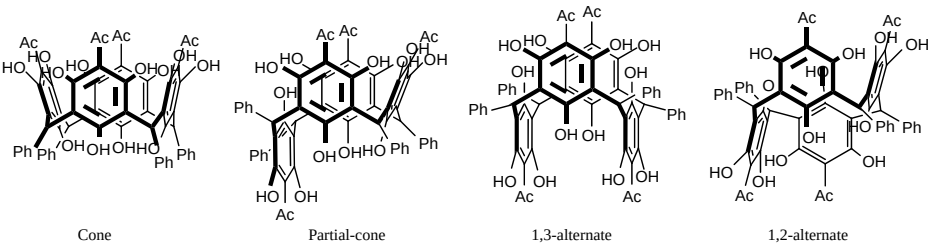


Figure 2. The four possible conformers for **3**.

3. Conclusion

The first synthesis of phloroacetophenon[4]arene (**3**) was accomplished via the Bronsted-catalysed one-pot condensation of phloroacetophenone and benzaldehyde, and it consisted of four isomers. One of the four isomers, **3a**, adopted a characteristic structure with a calyx structure on the upper side and a small calix structure on the lower side where a small molecule can be included, as shown by the X-ray crystal structure. Phloroacetophenon[4]arene (**3**) showed no change in the structure that had taken a keto-form, such as a phloroacetophenone in an alkaline solution as shown by the UV–vis spectra.

4. Experimental section

The solvents used in this study were purified by distillation. Reactions were monitored by TLC on 0.25-mm Silica Gel F254 plates using UV light and either a 5% ethanolic solution of ferric chloride or a 7% ethanolic solution of phosphomolybdic acid with heat as a colouration agent. For separation and purification, flash column chromatography was performed on silica gel (40–50 μm). IR spectra were recorded on a Fourier transform infrared spectrophotometer using a KBr disk. The NMR spectra were recorded on a 500-MHz spectrometer using Me_4Si as the internal standard. Fast-atom bombardment mass spectral data were measured using 3-nitrobenzyl alcohol or glycerol as a matrix on a FAB-MS instrument. Elemental analyses were performed on an elemental analysis instrument.

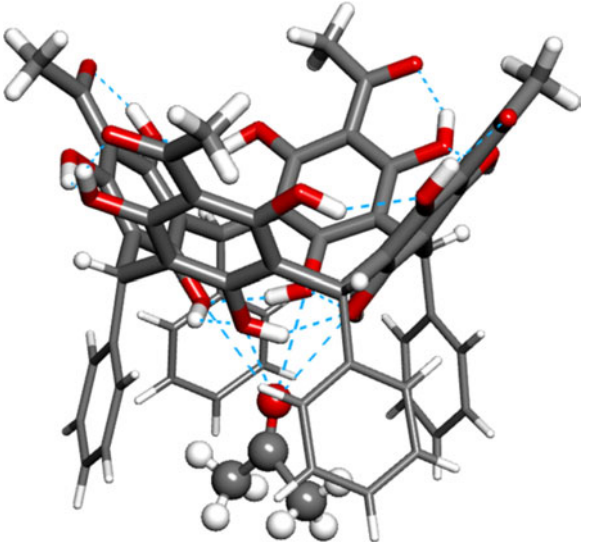


Figure 3. (Colour online) X-ray structure of **3a**. Dotted lines represent the intra- and intermolecular hydrogen bonds.

5. Synthesis (typical procedure for the synthesis of 3)

To a stirred solution of phloroacetophenone (672 mg, 4 mmol) and *p*-TsOH·H_2O (114 mg, 0.15 equiv.) in dried toluene (5 ml), benzaldehyde [406 μl (424 mg), 4 mmol] in toluene (3.5 ml) was added, and the resultant mixture was refluxed in an oil bath at 140°C for 15 min. The colour of the reaction mixture was changed from yellow to red. After cooling at room temperature, the reaction mixture was poured into a 0.5N-HCl solution (*ca.* 30 ml). The mixture was extracted twice with AcOEt. The organic extract was washed with water and brine and dried over anhydrous Na_2SO_4. After evaporation, the residue was purified by silica gel column chromatography ($CHCl_3$) to give **3** (410 mg, Y: 40%) as a pale yellow powder. Separation of four isomers of **3** was conducted using preparative silica gel TLC (solvent system: toluene–AcOEt–AcOH = 5:2:0.5) or silica gel column chromatography (solvent system: $CHCl_3$–EtOH, or/and toluene–AcOEt–AcOH).

Compound **3a**: Pale yellow powder. m.p. = >250°C (dec.). IR ν 3255, 3058, 3027, 2935, 1604, 1494, 1446, 1365, 1299 cm^{-1}. UV–vis ($CHCl_3$) λ (log ε): 391 (3.03), 330 (3.97), 282 (4.71), 241 (4.62) nm. ^1H NMR ($CDCl_3$) δ 2.78 (s, 12H, CH_3 ×4), 6.34 (s, 4H, >CH— ×4), 7.13 (d, 8H, J = 7.5, ArH), 7.19–7.22 (m, 12H, ArH), 9.52 (s, 4H, OH ×4), 9.88 (s, 4H, OH ×4), 16.43 (s, 4H, OH ×4). ^{13}C NMR ($CDCl_3$) δ 33.5 (×4), 34.3 (×4), 107.1 (×4), 108.2 (×4), 109.5 (×4), 126.7 (×4), 127.0 (×8), 128.1 (×8), 136.5 (×4), 157.8 (×4), 160.2 (×4), 162.1 (×4), 206.2 (×4). FAB-MS (*m*/*z*) 1025 $(M + H)^+$. Anal. calcd for $C_{60}H_{48}O_{16}·H_2O$: C69.09, H4.83; found: C69.20, H4.73.

Compound **3b**: Pale yellow powder. m.p. = >250°C (dec.). IR ν 3226, 3058, 3027, 2933, 1604, 1494, 1446, 1365, 1301 cm^{-1}. UV–vis ($CHCl_3$) λ (log ε): 391 (3.12),

330 (4.04), 282 (4.73), 241 (4.72) nm. ^{1}H NMR ($CDCl_3$) δ 2.66, 2.73, 2.79 and 2.80 (each s, 3H, CH_3 × 4), 5.90 (s, 1H, > CH—), 6.36 (s, 2H, > CH— × 2), 6.40 (br s, 1H, > CH—), 7.17–7.38 (m, 20H, ArH × 20), 9.48, 9.52, 9.56 and 9.59 (each s, 1H, OH × 4), 9.81 (br s, 4H, OH × 4), 16.11, 16.41, 16.45 and 16.47 (each s, 1H, OH × 4). ^{13}C NMR ($CDCl_3$) δ 33.4, 33.4 (× 2), 33.6, 34.2, 34.3, 34.4, 35.1, 107.0, 107.1, 107.1, 107.2, 107.3, 107.9, 108.0, 108.2, 108.3, 108.9, 109.2, 109.4, 126.8 (× 2), 126.9 (× 2), 126.9 (× 6), 127.1 (× 2), 128.1 (× 2), 128.2 (× 2), 128.3 (× 2), 128.3 (× 2), 136.2, 136.4, 136.5, 136.7, 157.7, 157.8, 157.9, 157.9, 159.7, 160.1 (x2), 160.2, 161.3, 161.8, 162.1 (× 2), 206.1, 206.1, 206.2 (× 2). FAB-MS (*m*/*z*) 1025 $(M + H)^+$. Anal. calcd for $C_{60}H_{48}O_{16}$: C70.30, H4.72; found: C69.91, H4.75.

Compound **3c**: Pale yellow powder. m.p. = >250°C (dec.). IRν 3247, 3058, 3027, 2931, 1602, 1494, 1446, 1365, 1301 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.67, 2.74 (each s, 6H, CH_3 × 4), 6.02 and 6.38 (each s, 2H, > CH— × 4), 7.22–7.40 (m, 20H, ArH × 20), 9.42 and 9.53 (each s, 2H, OH × 4), 9.61 (br s, 4H, OH × 4), 16.11 and 16.40 (each s, 2H, OH × 4). ^{13}C NMR ($CDCl_3$) δ 33.5 (× 2), 33.7 (× 2), 34.7 (× 2), 35.2 (× 2), 107.0 (× 2), 107.3 (× 2), 107.4 (× 2), 108.1 (× 2), 108.3 (× 2), 109.0 (× 2), 126.6 (× 2), 127.1 (× 2), 127.2 (× 4), 127.3 (× 4), 128.4 (× 4), 128.7 (× 4), 136.4 (× 2), 136.7 (× 2), 157.9 (× 2), 158.4 (× 2), 159.9 (× 2), 160.2 (× 2), 161.5 (× 2), 161.9 (× 2), 206.3 (× 4). FAB-MS (*m*/*z*) 1025 $(M + H)^+$. Anal. calcd for $C_{60}H_{48}O_{16}$: C70.30, H4.72; found: C70.27, H5.04.

Compound **3d**: Pale yellow powder. m.p. = >250°C (dec.). IRν 3232, 3060, 3027, 2929, 1602, 1494, 1446, 1365, 1301 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.61, 2.67, 2.75 and 2.81 (each s, 3H, CH_3 × 4), 5.98 and 6.00 (each s, 1H, > CH— × 2), 6.42 (br s, 1H, > CH—), 7.26–7.37 (m, 20H, ArH × 20), 9.54, 9.56, 9.60 and 9.66 (each s, 1H, OH × 4), 9.98 (br s, 4H, OH × 4), 16.13, 16.15, 16.48 and 16.53 (each s, 1H, OH × 4). ^{13}C NMR ($CDCl_3$) δ 33.36, 33.39, 33.48, 33.56, 34.33, 34.48, 35.67, 35.72, 107.08, 107.21, 107.28, 107.36, 107.39, 107.49, 107.83, 108.22, 108.24, 108.37, 108.96, 109.30, 126.46, 126.49, 126.75, 126.78, 126.97 (× 4), 127.02 (× 4), 128.15 (× 2), 128.19 (× 2), 128.34 (× 2), 128.39 (× 2), 136.25, 136.40, 136.63, 136.73, 157.69, 157.72, 158.09 (× 2), 159.66, 159.81, 160.16, 160.19, 161.30, 161.35, 161.89, 162.21, 206.09, 206.22, 206.27, 206.32. FAB-MS (*m*/*z*) 1025 $(M + H)^+$. Anal. calcd for $C_{60}H_{48}O_{16}\cdot H_2O$: C69.09, H4.83; found: C69.26, H4.87.

5.1 X-ray crystallographic structure determination

X-ray diffraction data for **3a** were collected on a Rigaku *R*-axis Rapid diffractometer with Cu Kα radiation (λ = 1.54187 Å) at 93 K. Single crystals of **3a** [$C_{60}H_{48}O_{16}\cdot C_3H_6O$, M_w = 1083.06] suitable for X-ray analysis were grown by slowly cooling a hot chloroform/acetone (5 ml/5 ml) solution of **3a** (5.0 mg) to ambient temperature, and a pale yellow crystal with dimensions 0.20 mm × 0.20 mm × 0.05 mm was selected for intensity measurements. The unit cell was monoclinic with the space group $P2_1/c$. Lattice constants with $Z = 4$, $D_{calcd} = 1.376$ g cm^{-3}, $\mu = 0.890$ mm^{-1}, $F(000) = 2272$ and $2\theta_{max} = 136.5°$ were $a = 12.2930(3)$, $b = 25.1174(8)$, $c = 17.6902(5)$ Å, $\alpha = 90°$, $\beta = 105.4385(14)°$, $\gamma = 90°$ and $V = 5265.1(3)$ Å^3. In total, 58,369 reflections were collected, of which 9484 reflections were independent ($R_{int} = 0.1305$). The structure was refined to final $R_1 = 0.1698$ for 6910 data [$I > 2\sigma(I)$] with 725 parameters and $wR_2 = 0.3949$ for all data, goodness-of-fit on $F^2 = 1.060$ and residual electron density max/min = 0.713/−0.467 eÅ^{-3}. Data collection, cell refinement and data reduction were conducted using the CrystalStructure (*12*) crystallographic software package. The structure was solved by direct methods using the program SHELXS-97 (*13*) and refined by full-matrix least squares methods on F^2 using SHELXL-97 (*13*). All non-hydrogen atoms were refined anisotropically except for the solvent molecule. The positions of all hydrogen atoms were calculated geometrically and refined as a riding model. Crystallographic data are deposited at the Cambridge Crystallographic Data Centre (CCDC; No. 943290). The data can be obtained free of charge from the CCDC via http://www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information

^{1}H and ^{13}C NMR and UV–vis spectra data: available on the article webpage.

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