

# Nitrochalcones as organogelators: evidence of the involvement of nitro groups and solvent in gel formation†

François-Xavier Simon,<sup>a</sup> Thi-Thanh-Tam Nguyen,<sup>a</sup> Marc Schmutz,<sup>a</sup> Gero Decher,<sup>a</sup> Jean-François Nicoud<sup>\*b</sup> and Philippe J. Mésini<sup>\*a</sup>

Received (in Montpellier, France) 5th February 2009, Accepted 21st April 2009

First published as an Advance Article on the web 26th May 2009

DOI: 10.1039/b902444a

New 4-alkoxynitrochalcones have been synthesized and shown to be organogelators; dodecyloxy/benzyl alcohol gels have been studied by freeze-fracture electron microscopy, DSC and FTIR. We show that the nitro group is involved in the formation of the gel and that the gelator co-assembles with solvent molecules.

## Introduction

Low mass organogelators<sup>1–5</sup> (LMOGs) are a growing class of compounds able to form gels with organic solvents at low concentrations (typically a few % per weight). This macroscopic property expresses the ability at the microscopic level to self-assemble into three-dimensional fibrillar networks. Besides the fundamental aspects, these gels have received increasing attention due to their potential applications in photovoltaics,<sup>6</sup> pollution control, as oil spill recovery<sup>7</sup> or toxicity remediation devices,<sup>8</sup> biomedical fields, as scaffolds for tissue repair<sup>9,10</sup> or drug-delivery systems,<sup>11,12</sup> mesoporous materials, as templates for silica nanotubes<sup>13</sup> or polymeric mesoporous materials.<sup>14–16</sup>

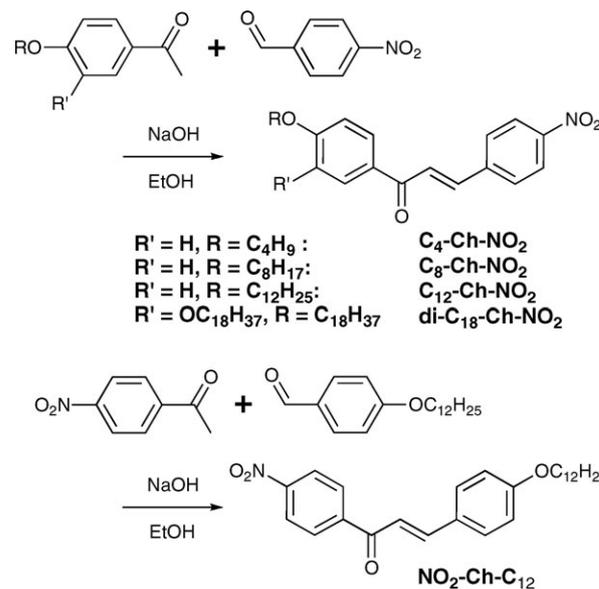
The self-association of gelators is achieved by a combination of non-covalent interactions, including H-bonds,  $\pi$ - $\pi$  stacking, metal coordination and van der Waals interactions. Most known gelators possess H-bonding groups. Gelators that are able to self-assemble without H-bonds and only by weaker interactions are rare. Among them, one can find alkoxyaromatic<sup>17,18</sup> compounds, azobenzene derivatives,<sup>19</sup> semifluoroalkanes<sup>20</sup> and even simple alkanes.<sup>21</sup> Ajayaghosh and Praveen<sup>22</sup> have extensively studied oligophenylvinylidene as gelators and have shown that these compounds form gels only if they bear either a H-bonding group, such as hydroxyl, or a polar group, such as nitrile or nitro. Derivatives lacking these groups provided only limited aggregation. Herein, we report the synthesis of new compounds based on the chalcone unit. Chalcone itself comprises of two benzene rings linked together by a conjugated enone and does not show any aggregation. We will demonstrate that the introduction of a nitro group on one side and an alkoxy group on the opposite leads to the aggregation of the resulting molecules in various

solvents. We explore the structure of the formed gels by electron microscopy. FT-IR measurements have been performed to examine the role of the nitro group in the self-association of the gelator.

## Results and discussion

New compounds incorporating the chalcone unit were synthesized (Scheme 1).  $C_n$ -Ch-NO<sub>2</sub> denotes 4'-alkoxy-4-nitrochalcones with different alkyl chain lengths (Scheme 1). For the sake of comparison, compounds O<sub>2</sub>N-Ch-C<sub>12</sub>, where the location of the nitro and alkyl groups are inverted, and di-C<sub>18</sub>-Ch-NO<sub>2</sub>, which bears two side chains, were also synthesized.

The synthesis described in Scheme 1 proceeds through the condensation of alkoxyacetophenone with 4-nitrobenzaldehyde in ethanol ( $C_n$ -Ch-NO<sub>2</sub>) or the condensation of 4-nitroacetophenone with 4-dodecyloxybenzaldehyde (O<sub>2</sub>N-Ch-C<sub>12</sub>), with NaOH as a catalyst, according to a previously described method.<sup>23</sup> The pure compounds were obtained with yields



Scheme 1 Synthesis and structure of the studied compounds.

<sup>a</sup> Institut Charles Sadron, CNRS, 23 rue de Loess, BP 84047, 67034 Strasbourg Cedex 2, France. E-mail: mesini@ics.u-strasbg.fr; Fax: +33 (0)388 41 40 99; Tel: +33 (0)388 41 40 70

<sup>b</sup> Laboratoire de Biophotonique et Pharmacologie, CNRS UMR 7213, Faculté de Pharmacie, 74 route du Rhin, BP 60024, 67401 Illkirch Cedex, France. E-mail: Jean-Francois.Nicoud@pharma.u-strasbg.fr; Tel: +33 (0)390 24 42 76

† Electronic supplementary information (ESI) available: FTIR spectra of C<sub>12</sub>-Ch-NO<sub>2</sub> gels in *tert*-butyl acetate and CCl<sub>4</sub>, and C<sub>12</sub>-Ch-NO<sub>2</sub> solid. See DOI: 10.1039/b902444a

**Table 1** Gelation properties of the nitrochalcones with various solvents<sup>a</sup>

Solvent	C <sub>4</sub> -Ch-NO <sub>2</sub>	C <sub>8</sub> -Ch-NO <sub>2</sub>	C <sub>12</sub> -Ch-NO <sub>2</sub>	Di-C <sub>18</sub> -Ch-NO <sub>2</sub>	O <sub>2</sub> N-Ch-C <sub>12</sub>
C <sub>6</sub> H <sub>6</sub>	P	P	P	P	/
Et <sub>2</sub> O	P	S	G (4)	P	P
CCl <sub>4</sub>	P	P	G (2)	P	P
CHCl <sub>3</sub>	S	S	S	S	S
CH <sub>2</sub> Cl <sub>2</sub>	S	S	S	P	/
MeOH	G (4) <sup>b</sup>	P	P	I	P
BuOH	P	P	G (2)	G (4)	P
BnOH	S	Visc. S	G (2)	G (2)	S
Toluene	S	S	S	P	/
EtOAc	S	S	S	S	/
nBuOAc	S	S	G (2)	P	P
<sup>t</sup> BuOAc	G (4)	G (2)	G (2)	P	P

<sup>a</sup> P: precipitates, I: insoluble in boiling solvent, G: gel (minimal gel concentration in wt%), Visc. S: viscous solution. <sup>b</sup> Opaque gel.

between 66 and 82%. They all are solids at room temperature and are soluble in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, toluene and EtOAc (Table 1). In alcohols, their solubility properties depend on the alkyl chain length. In MeOH C<sub>4</sub>-Ch-NO<sub>2</sub> forms a gel, whereas longer chain analogues precipitate. In BuOH, the trend is the opposite: compounds C<sub>4</sub>-Ch-NO<sub>2</sub> and C<sub>8</sub>-Ch-NO<sub>2</sub> precipitate, whereas C<sub>12</sub>-Ch-NO<sub>2</sub> and di-C<sub>18</sub>-Ch-NO<sub>2</sub> form gels. In BnOH, the C<sub>4</sub> and C<sub>8</sub> analogues are soluble but longer chain analogues form gels. The reverse analogue, O<sub>2</sub>N-Ch-C<sub>12</sub>, differs from the other analogues since it precipitates in BuOH and is soluble in BnOH. This result suggests that the orientation of the chalcone with respect to the alkyl chain is decisive in the packing of the molecules to form gels.

The structures of the gels have been explored by electron microscopy. The studies were performed by freeze-fracture. This technique consists of rapid freezing of the gel, which preserves the self-assemblies in an amorphous solvent surrounding. This method, which is well-known for aqueous media, has been implemented successfully for organic solutions and gels, and has proved to be efficient for the direct observation of self-assembled structures.<sup>16,24,25</sup> The success of the technique depends on the ability of the solvent to remain amorphous when the sample is frozen. In our hands, only BnOH gave satisfactory results with the selected gelators; in the other systems, either the solvent crystallized during the freeze, which prevented the observation of structures, or the fracture planes displayed no objects.

For the gel from C<sub>12</sub>-Ch-NO<sub>2</sub> in BnOH, the fractures showed oblong structures (Fig. 1A, arrows). Higher magnifications (Fig. 1B) showed that these objects are made from an assembly of fibrillar structures that are ordered into bundles. Solutions of the same compounds (conc. 1.9 wt%) have been studied after deposition on carbon-coated grids and rotary shadowing (Fig. 1C). They showed the same fibrils as the ones observed in the gels, but less associated (arrows). The characteristic sizes of the hundreds of fibrils were measured and averaged, both in gels and solutions, and were found to be identical in both states. The fibrils have a width of 25 ± 3 nm and exhibit a periodic structure with alternate shadowed and clear strips (Fig. 1D). The widths of the shadowed strips are 10 ± 2 nm and the periodic distance between two consecutive strips is 17 ± 2 nm. They form an angle of 50° with the main

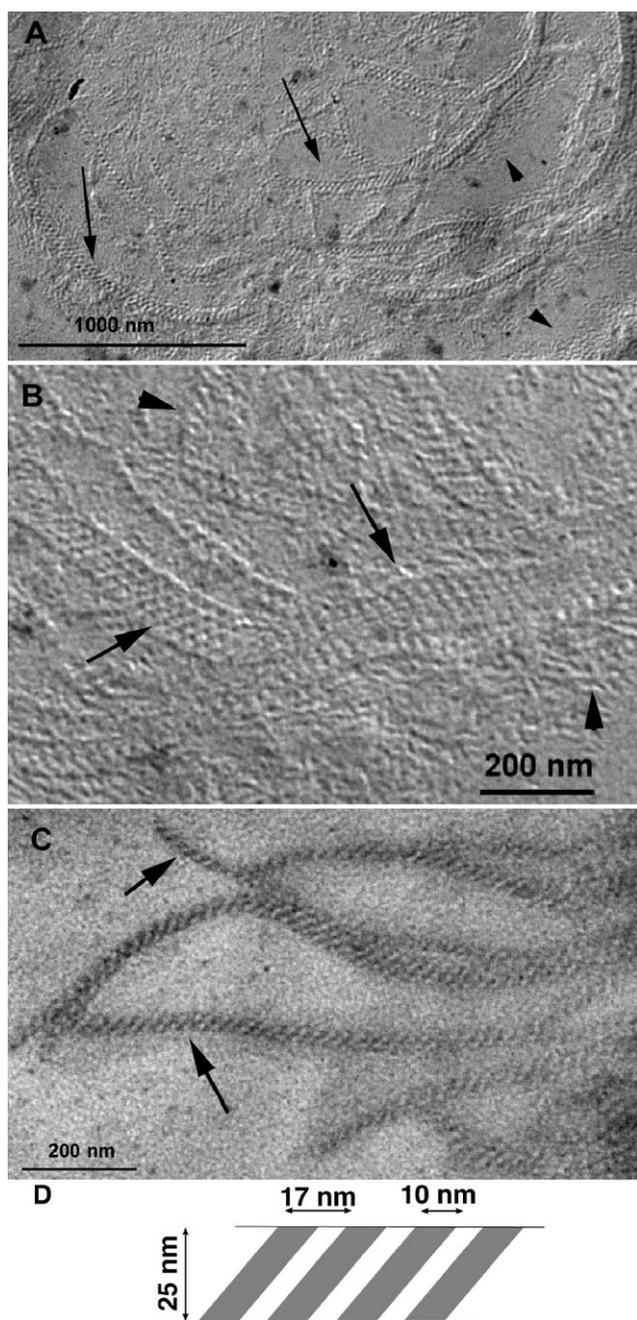
axis of the fibers. In the gels, the ordered fibers are surrounded by disordered and shorter arrays (Fig. 1A and 1B, arrowhead). In close vicinity to the main bundles, these shorter structures are arranged parallel to the fibers, but the alignment decreases when their distance from the bundles increases.

The gel-to-sol transition was studied by DSC (Fig. 2). The thermograms clearly showed a first order and endothermic transition upon melting. The transition was very broad, with an onset as low as 6 °C and a maximum at 45 °C. The enthalpy value was found to be 48 kJ mol<sup>-1</sup>. When the mixture was cooled back down, a sharp exothermic transition was observed. Both endothermic and exothermic peaks yielded the same absolute value of heat within 2% of experimental uncertainty.

The transition was also studied by FTIR at different temperatures. Most of the bands of the spectra showed little or no evolution. The strongest evolution was found for the bands between 1510 and 1540 cm<sup>-1</sup>. These signals comprised of one peak at 1521 cm<sup>-1</sup>, and a set of two overlapping peaks at 1538 and 1534 cm<sup>-1</sup>.

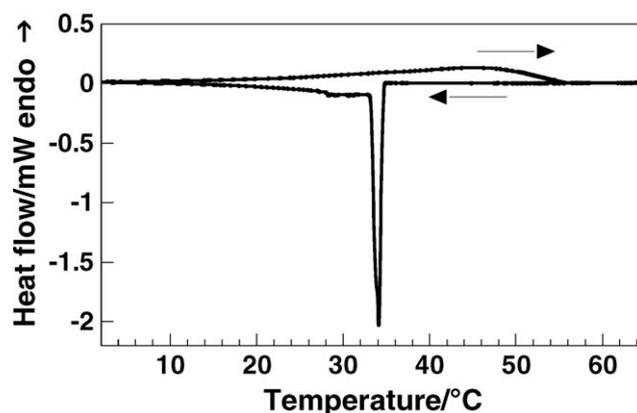
At lower temperatures, the bands at 1538 and 1534 cm<sup>-1</sup> were the dominant ones. When the temperature was increased, their intensities decreased, while the peak at 1521 cm<sup>-1</sup> increased and became the major one. All of these peaks could be assigned to antisymmetric NO<sub>2</sub> stretching ( $\nu_{as}(\text{NO}_2)$ ).<sup>26</sup> This strong change in the FTIR spectrum during the transition shows that the NO<sub>2</sub> group is involved in the self-assembly and packing of C<sub>12</sub>-Ch-NO<sub>2</sub> during gel formation. In chloroform, C<sub>12</sub>-Ch-NO<sub>2</sub> did not form a gel, and its IR spectrum was similar to that in BnOH at a higher temperature: only a major peak at 1523 cm<sup>-1</sup> (Fig. 3A) being observed.

The evolution of the intensity of the band at 1521 cm<sup>-1</sup> with temperature was very slow, and half of the maximum intensity was reached at 50 °C (Fig. 3B). For gels in *tert*-butyl acetate and CCl<sub>4</sub>, the same complex bands could be observed (see ESI†) in the  $\nu_s(\text{NO}_2)$  region (<sup>t</sup>BuOAc: 1538, 1534 and 1526 cm<sup>-1</sup>; CCl<sub>4</sub>: 1536 and 1526 cm<sup>-1</sup>). The intensity of the band at 1526 cm<sup>-1</sup> increased with increasing temperature, like the band at 1521 cm<sup>-1</sup> in BnOH. For the neat solid, only one peak at 1536 cm<sup>-1</sup> was observed. These results show that the splitting of the  $\nu_{as}(\text{NO}_2)$  band is characteristic of the gel state. For the gels in BnOH, the spectral region between 3700 and 3500 cm<sup>-1</sup> exhibited two peaks after subtracting the signal of

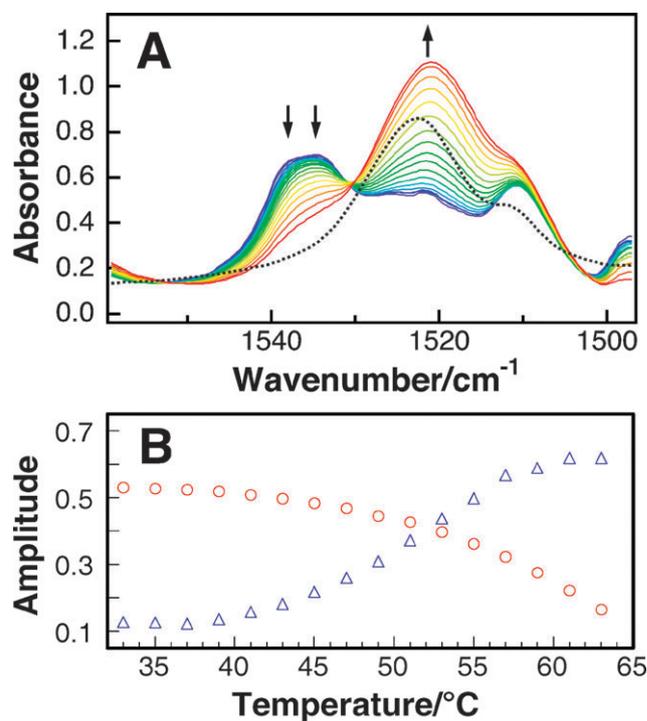


**Fig. 1** A: TEM of  $C_{12}$ -Ch- $NO_2$ /BnOH gels (2 wt%) after freeze-fracture. Arrows: periodic structures. Arrowhead: disordered structures. B: The same objects with a higher magnification. C: TEM of a solution of  $C_{12}$ -Ch- $NO_2$  in BnOH (1.9 wt%) after adsorption onto carbon grids. Short arrow: single fibril. Long arrow: double fibers. D: Scheme of the characteristic distances measured in the fibers ( $\pm 2$  nm).

the pure solvent. This spectral window does not comprise any bands for the gelator molecules and corresponded only to OH stretching bands of the benzyl alcohol. In the gel state, these bands were clearly shifted towards higher frequencies than in the pure solvent (Fig. 4). Hence, for a small proportion of the benzyl alcohol molecules in the gel, the hydroxyl groups lead to H-bonds different from those in the pure solvent. These bands also change when the gel melts, which shows the involvement of this fraction of BnOH molecules in the



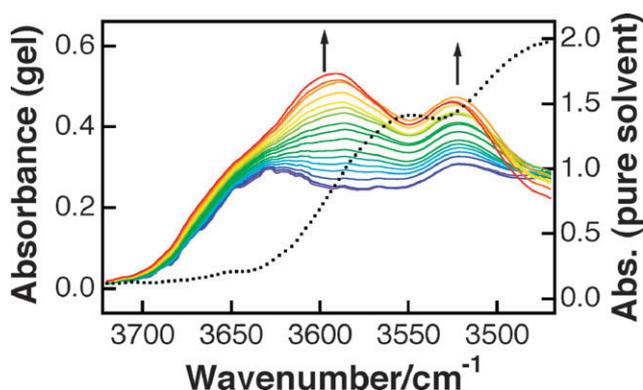
**Fig. 2** The thermogram of the  $C_{12}$ -Ch- $NO_2$ /BnOH gel (2 wt%). The measured enthalpy for the gel-to-sol transition was  $\Delta H = 48 \text{ kJ mol}^{-1}$ .



**Fig. 3** FTIR spectra of the  $C_{12}$ -Ch- $NO_2$ /BnOH gel (2 wt%) in the  $\nu_{\text{as}}(\text{NO}_2)$  region for temperatures varying from 32 to 65 °C (plain lines) (dotted line:  $C_{12}$ -Ch- $NO_2$ /CHCl<sub>3</sub> solution). (B) Amplitude of the band at 1521  $\text{cm}^{-1}$  (○) and sum of the amplitudes of the bands at 1334 and 1338  $\text{cm}^{-1}$  (△).

structure of the gel. It is possible that the hydroxyl groups interact directly with the gelator, either by an H-bond with the nitro group, as observed in solid state,<sup>27–29</sup> or by the formation of a  $\pi$ -adduct between the OH and the gelator.<sup>30,31</sup> It is also possible that these BnOH molecules are associated with the gelator through van der Waals interactions, and that this association weakens their H-bonds with the rest of the solvent.

The presence of isosbestic points proves that the system evolves through a two-state equilibrium, which corroborates the calorimetric data and indicates that the transition is a first-order one. The intensity of the peak at 1521  $\text{cm}^{-1}$  evolves slowly over a large temperature range, in the same way as the



**Fig. 4** Solid lines: FTIR spectra of the  $C_{12}$ -Ch- $NO_2$ /BnOH gel (2 wt%) in the OH stretching region for temperatures varying from 32 to 65 °C. Dotted line: IR spectrum of pure BnOH.

transition proceeds. The other bands in the spectrum vary only slightly, which shows that the other parts of the molecule play only a minor role compared to the nitro group. For instance, the symmetric vibration of the  $CH_2$  groups show a very weak increase from 2848 to 2849.5  $cm^{-1}$  in parallel to the evolution of the  $NO_2$  bands. The range of values indicates that the alkyl chains remain relatively well ordered and in an extended conformation in the sol phase.

## Conclusions

Several new 4-alkoxynitrochalcones have been synthesized. These molecules were able to form gels in *tert*-butyl acetate at a few wt%. The dodecyl derivative was also able to gel in BuOH, BnOH, diethyl ether and  $CCl_4$ . The introduction of the polar nitro group into soluble chalcones transforms them into self-associating compounds. Freeze-fracture TEM allowed the visualization of the fibrillar structure formed by self-association. An FTIR study in BnOH confirmed the strong implication of the nitro group in the formation of the gel. The same studies also showed the involvement of solvent molecules in the structure of the gel. This phenomenon is very rarely observed in organogels, and can be considered as an extension of the case of two-component gelators<sup>32</sup> such as AOT/phenol.<sup>32–35</sup> In those cases, a mixture of two molecules is required to form the gel. Therefore, despite their modest gel concentration, this new family of gelators has an original structure. Further structural studies are in progress to gain new insights into these self-assemblies and to increase their gelation abilities.

## Experimental

### FTIR

Spectra were recorded on a Bruker Vertex 70 spectrophotometer equipped with a thermostatic cell holder and a temperature-controlling unit (Specac West 6100+). The gels were placed in an NaCl cell with an optical path of 0.1 mm. The samples were visually checked after a heating period to ensure that no loss of solvent occurred. The curves were processed and fitted using Igor (Wavemetrics, Inc.). The complex signals were deconvoluted as follows: the maxima of the peaks were found with the second or fourth derivatives of

the spectra. The amplitudes and widths of the peaks were fitted with Gaussian curves using the built-in Igor algorithm. The spectra of the pure solids were measured by attenuated total reflection (ATR) over a diamond crystal.

### DSC

Thermograms were recorded using a microcalorimeter DSC III from Setaram. A first heating cycle was performed between 6 and 85 °C at a rate of 1 °C  $min^{-1}$ . The heat was measured in the second and third scan at a rate of 0.1 °C  $min^{-1}$ . No differences were observed between the second and third scan.

### Freeze-fracture electron microscopy

Transmission electron microscopy (TEM) was performed using a Philips CM12 microscope operating at 120 kV. The gel samples were placed between two copper holders and rapidly frozen in liquid nitrogen. The sample was kept frozen and transferred into a freeze-fracture apparatus (developed by Dr J.-C. Homo), where the sample was cleaved. Pt was evaporated onto the sample under a 45° angle, and then carbon under a 90° angle with respect to the surface. The sample was warmed to room temperature, and the replica was rinsed with chloroform and deposited on a 400 mesh grid.

### Synthesis

The compounds were synthesized by the method of Wattanasin and Murphy.<sup>23</sup> A typical procedure is described for the example below.

**4'-Dodecyloxy-4-nitrochalcone ( $C_{12}$ -Ch- $NO_2$ ).** 4-Nitrobenzaldehyde (100.2 mg, 0.66 mmol) and 4-dodecyloxyacetophenone (201.6 mg, 0.66 mmol, 1 equiv.) were added to a solution of NaOH in EtOH (0.1 M, 10 mL). The reaction mixture was stirred at 25 °C for 24 h. Water (150 mL) was added and the resulting precipitate separated by centrifugation, re-suspended in fresh water and centrifuged twice more. The dried precipitate was recrystallized from cyclohexane to yield the pure compound as a yellow powder (191 mg, 66% yield). M.p. 103.5 °C. Found: C, 73.88; H, 8.30; N, 3.22. Calc. for  $C_{27}H_{35}NO_4$ : C, 74.11; H, 8.06; N, 3.20%.  $\delta_H$ (400 MHz,  $CDCl_3$ ): 8.28 (2H, d, Ar $NO_2$  C3-H), 8.04 (2H, d,  $J$  = 8.9 Hz, Ar $NO_2$  C2-H), 7.83–7.77 (3H, m, CH=CH-CO and ArOR-C2-H), 7.66 (1H, d,  $J$  = 15.7 Hz, CH=CH-CO), 7.00–6.98 (2H, m, ArOR-C4-H), 4.05 (2H, t,  $J$  = 6.5 Hz, ArOCH $_2$ ), 1.82 (2H, p,  $J$  = 7.0 Hz, ArOCH $_2$ CH $_2$ ), 1.48 (2H, p,  $J$  = 7.0 Hz, ArOCH $_2$ CH $_2$ CH $_2$ ), 1.38–1.24 (16H, m, CH $_2$ ) and 0.88 (3H, t,  $J$  = 7.0 Hz, CH $_3$ ).  $\delta_C$ (100 MHz,  $CDCl_3$ ): 187.7 (CO), 163.5 (C4-O), 148.4 (C- $NO_2$ ), 141.3 (C=C-CO), 140.5 (C1-Ar $NO_2$ ), 131.0 and 130.2 (C1-ArOR), 128.8 (C2-Ar $NO_2$ ), 125.7 (CO-CH=CH), 124.2 (C2-Ar $NO_2$ ), 114.5 (C3-ArOR), 68.4 (ArOCH $_2$ ), 31.9 (CH $_2$ CH $_2$ CH $_3$ ), 29.63, 29.60, 29.56, 29.53, 29.32, 29.1, 26.0 (ArOCH $_2$ CH $_2$ CH $_2$ ), 22.7 (CH $_2$ CH $_3$ ) and 14.1 (CH $_3$ ).  $\lambda_{max}$ (CHCl $_3$ /nm): 314 ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ : 12900).  $\nu_{gel}$  in BnOH/ $cm^{-1}$ ): 2957, 2939, 2939, 2918, 2947, 1656 ( $\nu$ (CO)), 1610, 1600, 1538 ( $\nu_{as}$ ( $NO_2$ )), 1534 ( $\nu_{as}$ ( $NO_2$ )), 1521 ( $\nu_s$ ( $NO_2$ )), 1344, 1320 ( $\nu_s$ ( $NO_2$ )), 1310 ( $\nu_s$ ( $NO_2$ )), 1262, 1225, 1179, 855, 831 and 816.

**4'-Butyloxy-4-nitrochalcone (C<sub>4</sub>-Ch-NO<sub>2</sub>).** M.p. 125 °C. Found: C, 69.95; H, 6.05; N, 4.12. Calc. for C<sub>19</sub>H<sub>19</sub>NO<sub>4</sub>: C, 70.14; H, 5.89; N, 4.31%.  $\delta_{\text{H}}$ (400 MHz, CDCl<sub>3</sub>): 8.29 (2H, d,  $J = 8.2$  Hz, ArNO<sub>2</sub>-C3-H), 8.06 (2H, d,  $J = 8.4$  Hz, ArNO<sub>2</sub>-C2-H), 7.84–7.79 (3H, m, CH=CH-CO and ArOR-C2-H), 7.67 (1H, d,  $J = 15.5$  Hz, CH=CH-CO), 7.02 (2H, d, 8.5, ArOR-C4-H), 4.08 (2H, t,  $J = 6.6$  Hz, ArOCH<sub>2</sub>), 1.83 (2H, p,  $J = 6.6$  Hz, ArOCH<sub>2</sub>CH<sub>2</sub>), 1.55 (2H, m, ArOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>) and 0.88 (3H, t,  $J = 7.2$  Hz, CH<sub>3</sub>).  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>): 187.7 (CO), 163.6 (C4-O), 148.4 (C-NO<sub>2</sub>), 141.3 (CH=CH-CO), 140.5 (C1-ArNO<sub>2</sub>), 131.2 (C2-ArOR), 130.2 (C1-ArOR), 128.8 (C2-ArOR), 125.7 (CH=CH-CO), 124.2 (C3-ArNO<sub>2</sub>), 114.5 (C3-ArOR), 68.1 (ArOCH<sub>2</sub>), 31.1 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 19.2 (CH<sub>2</sub>CH<sub>3</sub>) and 14.1 (CH<sub>3</sub>).  $\nu$ (ATR, solid/cm<sup>-1</sup>): 3079.4, 1657 ( $\nu$ (CO)), 1607, 1598, 1586, 1510 (s,  $\nu_{\text{as}}(\text{NO}_2)$ ), 1473, 1339 (s,  $\nu_{\text{s}}(\text{NO}_2)$ ), 1228, 1123, 1169 (s,  $\nu$ (CN)), 1000, 833, 825 and 760.

**4'-Octyloxy-4-nitrochalcone (C<sub>8</sub>-Ch-NO<sub>2</sub>).** M.p. 106 °C. Found: C, 72.22; H, 7.31; N, 3.82. Calc. for C<sub>27</sub>H<sub>35</sub>NO<sub>4</sub>: C, 72.42; H, 7.13; N, 3.67%.  $\delta_{\text{H}}$ (400 MHz, CDCl<sub>3</sub>): 8.27 (2H, d,  $J = 8.53$  Hz, ArNO<sub>2</sub>-C3-H and -C5-H), 8.03 (2H, d,  $J = 8.7$  Hz, ArNO<sub>2</sub>-C2-H and -C6-H), 7.82–7.79 (3H, m, CH=CH-CO and ArOR-C2-H and -C6-H), 7.65 (1H, d,  $J = 15.7$  Hz, CH=CH-CO), 6.99 (2H, d,  $J = 8.7$  Hz, ArOR-C3'-H and -C5'-H), 4.04 (2H, t,  $J = 6.3$  Hz, ArOCH<sub>2</sub>), 1.82 (2H, p,  $J = 6.6$  Hz, ArOCH<sub>2</sub>CH<sub>2</sub>), 1.59 (2H, m, ArOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.47–1.20 (8H, CH<sub>2</sub>) and 0.89 (3H, t,  $J = 7.2$  Hz, CH<sub>3</sub>).  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>): 188.1 (CO), 163.9 (C4-O), 148.8 (C-NO<sub>2</sub>), 141.7 (CH=CH-CO), 140.9 (C1-ArNO<sub>2</sub>), 131.3 (C2'-ArOR), 130.6 (C1'-ArOR), 129.2 (C2- and C6-ArNO<sub>2</sub>), 126.0 (CH=CH-CO), 124.5 (C3- and C5-ArNO<sub>2</sub>), 114.8 (C3'- and C5'-ArOR), 68.7 (ArOCH<sub>2</sub>), 32.1 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 29.7 (ArOCH<sub>2</sub>CH<sub>2</sub>), 29.5 (ArO(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>), 29.4 (ArO(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>), 26.3 (ArO(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 23.0 (CH<sub>2</sub>CH<sub>3</sub>) and 14.4 (CH<sub>3</sub>).  $\nu$ (ATR, solid/cm<sup>-1</sup>): 2955 ( $\nu_{\text{as}}(\text{CH}_3)$ ), 2919 ( $\nu_{\text{as}}(\text{CH}_2)$ ), 2874 ( $\nu_{\text{s}}(\text{CH}_3)$ ), 2850 ( $\nu_{\text{s}}(\text{CH}_2)$ ), 1656 ( $\nu$ (CO)), 1610 ( $\nu$ (CC<sub>Ar</sub>)), 1593 ( $\nu$ (C=C<sub>enone</sub>)), 1534 (s,  $\nu_{\text{as}}(\text{NO}_2)$ ), 1511, 1467, 1342 (s,  $\nu_{\text{s}}(\text{NO}_2)$ ), 1259 (s,  $\nu_{\text{as}}(\text{C-O-C})$ ), 1221, 1178 (s,  $\nu$ (CN)), 1070 (s,  $\nu_{\text{s}}(\text{C-O})$ ), 1033, 988 ( $\nu$ (C-N)), 980, 780, 760, 733, 655 and 631.

**3',4'-Diocetadecyloxy-4-nitrochalcone (di-C<sub>18</sub>-Ch-NO<sub>2</sub>).** M.p. 120 °C. Found: C, 77.38; H, 10.74; N, 1.85. Calc. for C<sub>27</sub>H<sub>35</sub>NO<sub>4</sub>: C, 77.52; H, 10.59; N, 1.77%.  $\delta_{\text{H}}$ (400 MHz, CDCl<sub>3</sub>): 8.27 (2H, d,  $J = 8.72$  Hz, ArNO<sub>2</sub>-C3-H), 7.82–7.77 (3H, m, ArNO<sub>2</sub>-C2-H and CH=CH-CO), 7.67–7.61 (3H, m, ArOR-C6-H and CH=CH-CO), 6.92 (1H, d,  $J = 8.52$  Hz, ArOR-C5-H), 4.09 (4H, t,  $J = 6.48$  Hz, ArOCH<sub>2</sub>), 1.86 (4H, p,  $J = 6.48$  Hz, ArOCH<sub>2</sub>CH<sub>2</sub>), 1.57 (4H, m, ArOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.48 (4H, m, CH<sub>2</sub>CH<sub>3</sub>), 1.25 (52H, CH<sub>2</sub>) and 0.88 (6H, t,  $J = 7.0$  Hz, CH<sub>3</sub>).  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>): 188.1 (CO), 154.4 (C4-OR), 149.7 (C-NO<sub>2</sub>), 148.8 (CH=CH-CO), 140.8 (C1-ArNO<sub>2</sub>), 130.8 (C1-ArOR), 129.2 (C2-ArNO<sub>2</sub>), 126.0 (CH=CH-CO), 124.5 (C3-ArNO<sub>2</sub>), 123.7 (C6-ArOR), 113.3 (C2-ArOR), 111.9 (C5-ArOR), 69.7 (ArOCH<sub>2</sub>-R'), 69.5 (ArOCH<sub>2</sub>-R), 32.3 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 27.3 (ArOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 23.0 (CH<sub>2</sub>CH<sub>3</sub>) and 14.5 (CH<sub>3</sub>).  $\nu$ (ATR, solid/cm<sup>-1</sup>): 2956 ( $\nu_{\text{as}}(\text{CH}_3)$ ), 2916 ( $\nu_{\text{as}}(\text{CH}_2)$ ), 2873 ( $\nu_{\text{s}}(\text{CH}_3)$ ),

2849 ( $\nu_{\text{s}}(\text{CH}_2)$ ), 1655 ( $\nu$ (CO)), 1578 ( $\nu$ (C=C<sub>enone</sub>)), 1525 (s,  $\nu_{\text{as}}(\text{NO}_2)$ ), 1514, 1467, 1434 ( $\nu$ (CH<sub>vinyl</sub>)), 1343 (s,  $\nu_{\text{s}}(\text{NO}_2)$ ), 1278, 1267 (s,  $\nu_{\text{as}}(\text{C-O-C})$ ), 1217, 1177, 1153 (s,  $\nu$ (CN)), 1069 (s,  $\nu_{\text{s}}(\text{C-O})$ ), 995 ( $\nu$ (C-N) stretch), 840, 813, 754, 721, 675 and 630.

**4-Dodecyloxy-4'-nitrochalcone (O<sub>2</sub>N-Ch-C<sub>12</sub>).** M.p. 108 °C. Found: C, 73.92; H, 8.24; N, 3.25. Calc. for C<sub>27</sub>H<sub>35</sub>NO<sub>4</sub>: C, 74.11; H, 8.06; N, 3.20%.  $\delta_{\text{H}}$ (400 MHz, CDCl<sub>3</sub>): 8.34 (2H, d,  $J = 8.4$  Hz, ArNO<sub>2</sub>-C3-H and -C5-H), 8.12 (2H, d,  $J = 8.2$  Hz, ArNO<sub>2</sub>-C2-H and -C6-H), 7.81 (1H, d,  $J = 15.2$  Hz, CH=CH-CO), 7.60 (2H, d,  $J = 8.4$  Hz, ArOR-C2-H and -C6-H), 7.35 (1H, d,  $J = 15.4$  Hz, CH=CH-CO), 6.94 (2H, d,  $J = 8.0$  Hz, ArOR-C3-H and C5-H), 4.02 (2H, t,  $J = 6.3$  Hz, ArOCH<sub>2</sub>), 1.81 (2H, p,  $J = 6.6$  Hz, ArOCH<sub>2</sub>CH<sub>2</sub>), 1.54–1.21 (18H, CH<sub>2</sub>) and 0.89 (3H, t,  $J = 7.2$  Hz, CH<sub>3</sub>).  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>): 189.4 (CO), 162.3 (C4-O), 162.25 (C-NO<sub>2</sub>), 147.2 (C1-ArNO<sub>2</sub>), 143.9 (CH=CH-CO), 131.0 (C2-ArNO<sub>2</sub>), 129.7 (C2- and C6-ArOR), 127.1 (C1-ArOR), 124.2 (C3- and C5-ArNO<sub>2</sub>), 119.1 (CH=CH-CO), 115.4 (C5- and C3-ArOR), 68.7 (ArOCH<sub>2</sub>), 32.3 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 26.3 (ArOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 23.0 (CH<sub>2</sub>CH<sub>3</sub>) and 14.5 (CH<sub>3</sub>).  $\nu$ (ATR/cm<sup>-1</sup>): 2946 ( $\nu_{\text{as}}(\text{CH}_3)$ ), 2916 ( $\nu_{\text{as}}(\text{CH}_2)$ ), 2871 ( $\nu_{\text{s}}(\text{CH}_3)$ ), 2849 ( $\nu_{\text{s}}(\text{CH}_2)$ ), 1657 ( $\nu$ (CO)), 1587 ( $\nu$ (C=C<sub>enone</sub>)), 1567, 1512 (s,  $\nu_{\text{as}}(\text{NO}_2)$ ), 1476, 1463, 1425, 1340 (s,  $\nu_{\text{s}}(\text{NO}_2)$ ), 1295, 1256 (s,  $\nu_{\text{as}}(\text{C-O-C})$ ), 1217, 1173 (s,  $\nu$ (CN)), 1061 (s,  $\nu_{\text{s}}(\text{C-O})$ ), 989 ( $\nu$ (C-N) stretch), 832, 826, 767, 727, 703 and 638.

## References

- P. Terech and R. G. Weiss, *Chem. Rev.*, 1997, **97**, 3133–3159.
- J. H. Van Esch and B. L. Feringa, *Angew. Chem., Int. Ed.*, 2000, **39**, 2263–2266.
- L. A. Estroff and A. D. Hamilton, *Chem. Rev.*, 2004, **104**, 1201–1218.
- N. M. Sangeetha and U. Maitra, *Chem. Soc. Rev.*, 2005, **34**, 821–836.
- R. G. Weiss and P. Terech, *Molecular Gels: Materials with Self-Assembled Fibrillar Networks*, Springer, Dordrecht, The Netherlands, 2006.
- W. Kubo, K. Murakoshi, T. Kitamura, S. Yoshida, M. Haruki, K. Hanabusa, H. Shirai, Y. Wada and S. Yanagida, *J. Phys. Chem. B*, 2001, **105**, 12809–12815.
- S. Bhattacharya and Y. Krishnan-Ghosh, *Chem. Commun.*, 2001, 185–186.
- S. Kiyonaka, K. Sugiyasu, S. Shinkai and I. Hamachi, *J. Am. Chem. Soc.*, 2002, **124**, 10954–10955.
- T. C. Holmes, S. de Lacalle, X. Su, G. Liu, A. Rich and S. Zhang, *Proc. Natl. Acad. Sci. U. S. A.*, 2000, **97**, 6728–6733.
- R. G. Ellis-Behnke, Y.-X. Liang, S.-W. You, D. K. C. Tay, S. Zhang, K.-F. So and G. E. Schneider, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 5054–5059.
- S. Murdan, T. Andrysek and D. Son, *Int. J. Pharm.*, 2005, **300**, 113–124.
- S. Murdan, *Expert Opin. Drug Delivery*, 2005, **2**, 489–505.
- K. J. C. van Bommel, A. Friggeri and S. Shinkai, *Angew. Chem., Int. Ed.*, 2003, **42**, 980–999.
- R. J. H. Hafkamp, B. P. A. Kokke, I. M. Danke, H. P. M. Geurts, A. E. Rowan, M. C. Feiters and R. J. M. Nolte, *Chem. Commun.*, 1997, 545–546.
- G. Tan, M. Singh, J. He, V. T. John and G. L. McPherson, *Langmuir*, 2005, **21**, 9322–9326.
- F. X. Simon, N. S. Khelfallah, M. Schmutz, N. Diaz and P. J. Mesini, *J. Am. Chem. Soc.*, 2007, **129**, 3788–3789.
- T. Brotin, R. Utermohlen, F. Fages, H. Bouas-Laurent and J. P. Desvergne, *J. Chem. Soc., Chem. Commun.*, 1991, 416–418.

- 18 F. Placin, M. Colomes and J.-P. Desvergne, *Tetrahedron Lett.*, 1997, **38**, 2665–2668.
- 19 J.-i. Mamiya, K. Kanie, T. Hiyama, T. Ikeda and T. Kato, *Chem. Commun.*, 2002, 1870–1871.
- 20 R. J. Twieg, T. P. Russell, R. Siemens and J. F. Rabolt, *Macromolecules*, 1985, **18**, 1361–1362.
- 21 D. J. Abdallah and R. G. Weiss, *Langmuir*, 2000, **16**, 352–355.
- 22 A. Ajayaghosh and V. K. Praveen, *Acc. Chem. Res.*, 2007, **40**, 644–656.
- 23 S. Wattanasin and W. S. Murphy, *Synthesis*, 1980, 647–650.
- 24 N. Diaz, F. X. Simon, M. Schmutz, M. Rawiso, G. Decher, J. Jestin and P. J. Mésini, *Angew. Chem., Int. Ed.*, 2005, **44**, 3260–3264.
- 25 R. Schmidt, F. B. Adam, M. Michel, M. Schmutz, G. Decher and P. J. Mésini, *Tetrahedron Lett.*, 2003, **44**, 3171–3174.
- 26 J. F. Brown, *J. Am. Chem. Soc.*, 1955, **77**, 6341–6351.
- 27 M. Harrand, *J. Raman Spectrosc.*, 1975, **4**, 53–73.
- 28 M. Harrand, *J. Raman Spectrosc.*, 1979, **8**, 161–164.
- 29 D. Graham, A. R. Kennedy, C. J. McHugh, W. E. Smith, W. I. F. David, K. Shankland and N. Shankland, *New J. Chem.*, 2004, **28**, 161–165.
- 30 M. R. Basila, E. L. Saier and L. R. Cousins, *J. Am. Chem. Soc.*, 1965, **87**, 1665–1669.
- 31 Z.-I. Yoshida and E. Osawa, *J. Am. Chem. Soc.*, 1966, **88**, 4019–4026.
- 32 A. R. Hirst and D. K. Smith, *Chem.–Eur. J.*, 2005, **11**, 5496–5508.
- 33 B. A. Simmons, C. E. Taylor, F. A. Landis, V. T. John, G. L. McPherson, D. K. Schwartz and R. Moore, *J. Am. Chem. Soc.*, 2001, **123**, 2414–2421.
- 34 M. Tata, V. T. John, Y. Y. Waguespack and G. L. McPherson, *J. Am. Chem. Soc.*, 1994, **116**, 9464–9470.
- 35 M. Tata, V. T. John, Y. Y. Waguespack and G. L. McPherson, *J. Phys. Chem.*, 1994, **98**, 3809–3817.