



**HAL**  
open science

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

F.X. Simon, Th. Nguyen, M. Schmutz, G. Decher, J.F. Nicoud, Philippe J. Mésini

### ► To cite this version:

F.X. Simon, Th. Nguyen, M. Schmutz, G. Decher, J.F. Nicoud, et al.. Nitrochalcones as organogelators: evidence of the involvement of nitro groups and solvent in gel formation. *New Journal of Chemistry*, 2009, 33 (10), pp.2028-2033. 10.1039/b902444a . hal-00431723

**HAL Id: hal-00431723**

**<https://hal.science/hal-00431723v1>**

Submitted on 9 Jan 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# 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>

<sup>5</sup> Received (in XXX, XXX) Xth XXXXXXXXXX 200X, Accepted Xth XXXXXXXXXX 200X

First published on the web Xth XXXXXXXXXX 200X

DOI: 10.1039/b000000x

New 4-alkoxynitrochalcones have been synthesized and been shown to be organogelators; the dodecyloxy derivative/benzyl alcohol gels has been studied by freeze fracture electron microscopy,  
 10 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

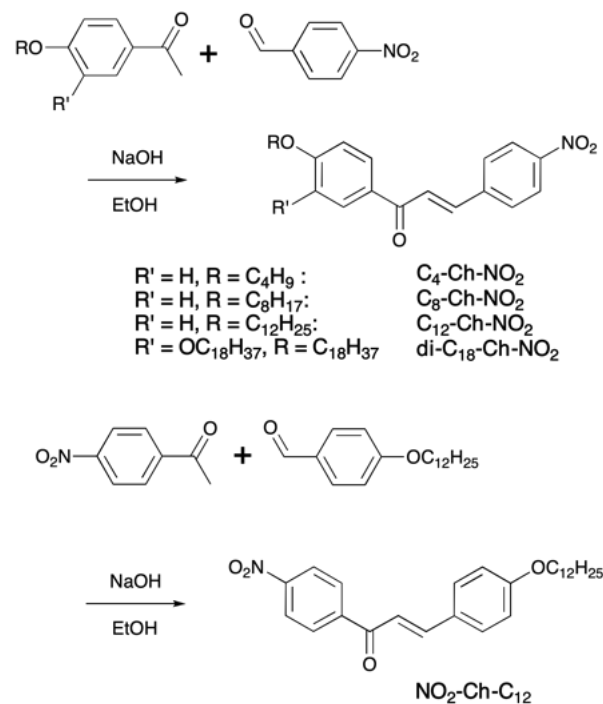
Low mass organogelators<sup>1-5</sup> (LMOG) are a growing class of compounds able to form gels with organic solvents at low concentration (typically a few % per weight). This macroscopic property expresses the ability at the microscopic level to self-assemble into three dimensional fibrillar networks. Beside fundamental aspects, these gels receive an increasing attention due to their potential applications in nanotechnology, photovoltaics,<sup>6</sup> pollution control as oil spill recovery<sup>7</sup> or toxics remediation devices,<sup>8</sup> biomedical field 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 of the known gelators possess H-bonding groups. The gelators able to self-assemble without H-bonds and only with 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 has extensively studied<sup>22</sup> oligophenylvinylidene as gelators and has shown that these compounds form gels only if they have either H-bonding group such as alcohol or polar groups 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 two benzene rings linked together by a conjugated enone and does not show any aggregation itself. Herein we demonstrate that the introduction of a nitro group on one side and an alkoxy group on the opposite side leads to the aggregation of the resulting molecules in various solvents. We explored 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<sub>n</sub>-Ch-NO<sub>2</sub> denotes 4'-alkoxy-4-

nitrochalcones with different alkyl chain lengths (Scheme 1). For 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>, that bears two side chains have also been synthesized.



**Scheme 1** Synthesis and structure of the studied compounds.

The synthesis, described in scheme 1, proceeds through the condensation of alkoxyacetophenone with 4-nitrobenzaldehyde in ethanol (C<sub>n</sub>-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 catalyst, according to a described method.<sup>23</sup> The compounds were obtained pure with yield between 66 and 82 %. They all are solids at room temperature and are soluble in solvents such as CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, toluene and EtOAc (table 1). In alcohols, the 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 of the 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 in respect with the alkyl chain is decisive in the packing of the molecules to form gels.

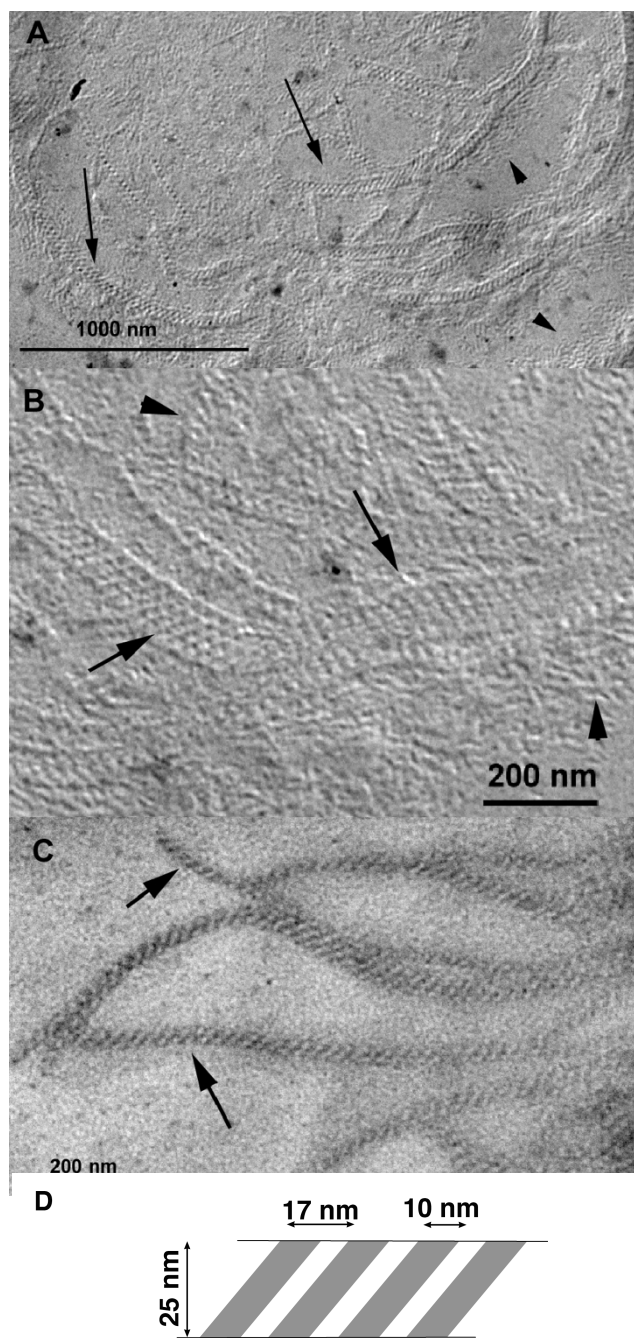
**Table 1** Gelation properties of the nitrochalcone with various solvents.<sup>a</sup>

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>	DiC <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>a</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>a</sup> opaque gel

The structures of the gels have been explored by electron microscopy. Studies have been performed with freeze fracture. This technique consists in a rapid freeze of the gel, which preserves the self-assemblies in an amorphous solvent surrounding. This method which is well-known in aqueous media has been implemented successfully to 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 gels from C<sub>12</sub>-Ch-NO<sub>2</sub> in BnOH, the fractures show oblong structures (Fig. 1A, arrows). Higher magnifications (Fig. 1B) show that these objects are made from the 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 show the same fibrils as in the gels, but less associated (arrows). The characteristic sizes of the structures have been measured both in gels and solutions on hundred of fibrils, and they were found to be identical in both states. The fibrils have a width of 25 ± 3 nm and exhibit a periodical structure with alternate shadowed strips and clear ones (Fig. 1D). The widths of the shadowed ones 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.



**Fig. 1** A: TEM of C<sub>12</sub>-Ch-NO<sub>2</sub>/BnOH gels (2 % wt) after freeze fracture. Arrows: periodical structures. Arrowhead: disordered structures. B: same objects with higher magnification. C: TEM of solution of C<sub>12</sub>-Ch-NO<sub>2</sub> in BnOH (1.9 % wt) after adsorption on carbon grids; short arrow: single fibril; long arrow: double fibers. D : scheme of the characteristic distances measured in the fibers (± 2 nm).

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

uncertainty.

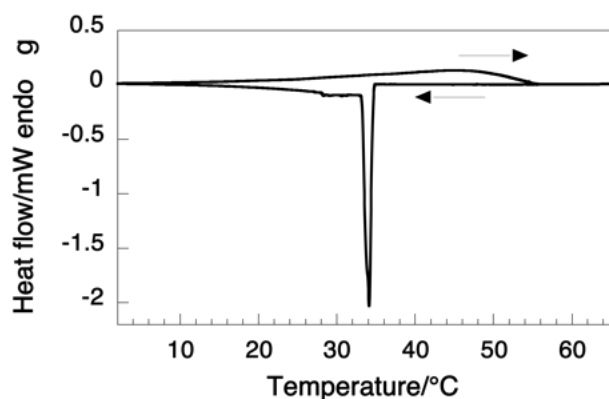


Fig. 2 Thermogram of  $C_{12}\text{-Ch-NO}_2/\text{BnOH}$  gel (2 % wt.). The measured enthalpy for the gel-to-sol transition is  $\Delta H = 48 \text{ kJ}\cdot\text{mol}^{-1}$ .

The transition was studied by FTIR at different temperatures. Most of the bands of the spectra show little or no evolution. The strongest evolution is found for the bands between 1510 and 1540  $\text{cm}^{-1}$ . This signal comprises one peak at 1521  $\text{cm}^{-1}$  and a set of two overlapping peaks at 1538 and 1534  $\text{cm}^{-1}$ .

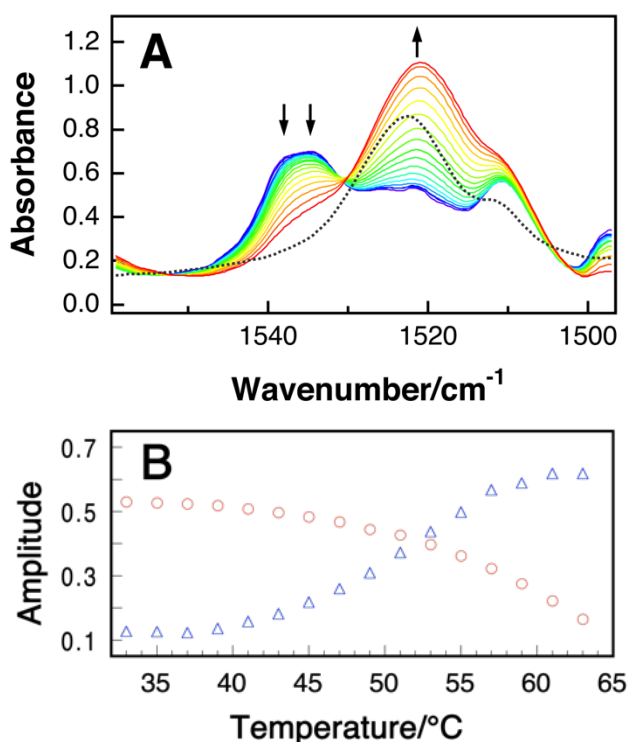


Fig. 3 FTIR of  $C_{12}\text{-Ch-NO}_2/\text{BnOH}$  gel (2 % wt.) in the  $\nu_{\text{as}} \text{NO}_2$  area, for temperatures varying from 32 to 65 °C (plain lines); dotted line :  $C_{12}\text{-Ch-NO}_2/\text{CHCl}_3$  solution. B : Amplitude of the bands at 1521  $\text{cm}^{-1}$  (O) and sum of the amplitudes of the bands at 1538 and 1534  $\text{cm}^{-1}$  ( $\Delta$ ).

At lower temperature, the band at 1538 and at 1534  $\text{cm}^{-1}$  are the dominant ones. When the temperature increases, their intensities decrease while the peak at 1521  $\text{cm}^{-1}$  increases and becomes the major one at higher temperature. All the mentioned peaks can be assigned to the antisymmetric  $\text{NO}_2$

stretching ( $\nu_{\text{as}} \text{NO}_2$ ).<sup>26</sup> This strong change in the FTIR spectra during the transition shows that the  $\text{NO}_2$  group is involved in the self-assembly and the packing of the compound  $C_{12}\text{-Ch-NO}_2$  in gel formation. In chloroform,  $C_{12}\text{-Ch-NO}_2$  does not form any gel and the IR spectra are similar to the spectrum in BnOH at higher temperature: one observes only a major peak at 1523  $\text{cm}^{-1}$  (Fig. 3A).

The evolution of the intensity at 1521  $\text{cm}^{-1}$  in regard with temperature is very slow, and half of the maximal intensity is reached for 50 °C (Fig. 3B). For gels in tert-butyl acetate and  $\text{CCl}_4$  the same complex bands can be observed (Suppl. Info) in the  $\nu_{\text{s}} \text{NO}_2$  area ( $^t\text{BuOAc}$  : 1538, 1534 and 1526  $\text{cm}^{-1}$ ;  $\text{CCl}_4$  : 1536 and 1526  $\text{cm}^{-1}$ ). The intensity band at 1526  $\text{cm}^{-1}$  increases with increasing temperature like the band at 1521  $\text{cm}^{-1}$  in BnOH. For the neat solid, only the peak at 1536 is observed. These results show that splitting of the  $\nu_{\text{as}} \text{NO}_2$  band is characteristic of the gel state. For the gels in BnOH, the spectral region between 3700 and 3500  $\text{cm}^{-1}$  exhibit two peaks after subtraction of the signal of the pure solvent. This spectral window does not comprise any bands of the gelator molecules and corresponds only to the OH stretching bands of the benzyl alcohol. In the gel state, these bands are clearly shifted toward higher frequencies than in the pure solvent (Fig. 4). Hence, for a small part of the benzyl alcohol molecules in the gel, the hydroxyl groups lead to H-bonds different from those existing the pure solvent. These bands also change when the gel melts, which shows the involvement of some BnOH molecules in the structure of the gel. It is possible that the hydroxyl interacts 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 gelators through van der Waals interactions and that this association results in looser H-bonds with the rest of the solvent than in the bulk solvent.

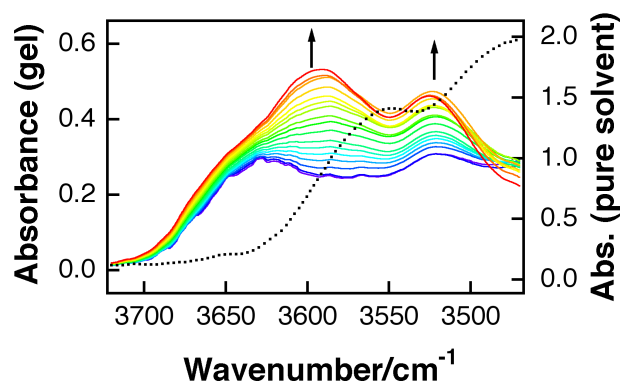


Fig. 4 Plain lines : FTIR of  $C_{12}\text{-Ch-NO}_2/\text{BnOH}$  gel (2 % wt.) in the OH stretching area, for temperature varying from 32 to 65 °C. Dotted line : IR spectra of pure BnOH.

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

only slightly, which shows that the other parts of the molecule play only a minor role as compared to the nitro group. For instance, the symmetric vibration of the CH<sub>2</sub> show a very weak increase from 2848 to 2849.5 cm<sup>-1</sup> that parallels the evolution of the NO<sub>2</sub> bands. The range of values indicates that the chains remain relatively well ordered and in an extended conformation in the sol phase.

## Conclusions

New alkoxy-nitrochalcones were synthesized. These molecules are able to form gels in tert-butyl acetate at a few percent per weight. The dodecyl derivative is able to gel also BuOH, BnOH, ether and CCl<sub>4</sub>. 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. FTIR study in this solvent 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 has been very rarely observed in organogels. It 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 a 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 in Igor (Wavemetrics, Inc.). The complex signals were deconvoluted as follows: the maxima of the peaks were found with the second or forth derivatives of the spectra. Amplitudes and width of the peaks were fitted with Gaussian curves with the Igor built-in algorithm.

**DSC.** Thermograms were recorded with a microcalorimeter DSC III from Setaram. A first heating cycle was performed between 6 and 85 °C at a rate of 1 °C/min. The heat was measured in second and third scan at a rate of 0.1 °C/min. No difference was observed between the second and third scan.

**Freeze-fracture electron microscopy.** Transmission electron microscopy (TEM) was performed with 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 45° angle, and then carbon under a 90° angle respective to the surface. The sample was warmed to room temperature, and the replica was rinsed with chloroform and deposited on 400 mesh grids

**Synthesis.** The compounds were synthesized by the method of Murphy;<sup>23</sup> the typical procedure is described for the exemple below.

**4'-Dodecyloxy-4-nitrochalcone (C<sub>12</sub>-Ch-NO<sub>2</sub>):** 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 was separated with centrifugation, and re-suspended in fresh water and centrifuged twice. 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<sub>27</sub>H<sub>35</sub>NO<sub>4</sub>: C, 74.11; H, 8.06; N, 3.20%. δ<sub>H</sub>(400 Mhz, CDCl<sub>3</sub>): 8.28 (2H, d, ArNO<sub>2</sub> C3-H), 8.04 (2H, d, *J* 8.9, ArNO<sub>2</sub> C2-H), 7.83-7.77 (3H, m, CH=CH-CO and ArOR C2-H), 7.66 (1H, d, *J* 15.7, CH=CH-CO), 7.00-6.98 (2H, m, ArOR C4H), 4.05 (2H, t, *J* 6.5, ArOCH<sub>2</sub>), 1.82 (2H, p, *J* 7.0, ArOCH<sub>2</sub>CH<sub>2</sub>), 1.48 (2H, p, *J* 7.0, ArOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.38-1.24 (16H, m, CH<sub>2</sub>), 0.88 (3H, t, *J* 7.0, CH<sub>3</sub>). δ<sub>C</sub>(100 Mhz, CDCl<sub>3</sub>): 187.7 (CO), 163.5 (C4-O), 148.4 (C-NO<sub>2</sub>), 141.3 (C=C-CO), 140.5 (C1-ArNO<sub>2</sub>), 131.0 130.2 (C1 ArOR), 128.8 (C2- ArNO<sub>2</sub>), 125.7 (CO-CH=CH), 124.2 (C2-ArNO<sub>2</sub>), 114.5 (C3-ArOR), 68.4 (ArOCH<sub>2</sub>), 31.9 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 29.63, 29.60, 29.56, 29.53, 29.32, 29.1, 26.0 (ArOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 22.7 (CH<sub>2</sub>CH<sub>3</sub>), 14.1 (CH<sub>3</sub>). λ<sub>max</sub> (CHCl<sub>3</sub>)/nm 314 (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 12 900). ν/cm-1 (gel in BnOH) 2957, 2939, 2939, 2918, 2947, 1656 (ν CO), 1610, 1600, 1538 (ν<sub>as</sub> NO<sub>2</sub>), 1534 (ν<sub>as</sub> NO<sub>2</sub>), 1521 (ν<sub>s</sub> NO<sub>2</sub>), 1344, 1320 (ν<sub>s</sub> NO<sub>2</sub>), 1310 (ν<sub>s</sub> NO<sub>2</sub>), 1262, 1225, 1179, 855, 831, 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%); δ<sub>H</sub>(400 Mhz, CDCl<sub>3</sub>): 8.29 (2H, d, *J* 8.2, ArNO<sub>2</sub> C3-H), 8.06 (2H, d, *J* 8.4, 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, CH=CH-CO), 7.02 (2H, d, 8.5, ArOR C4H), 4.08 (2H, t, *J* 6.6, ArOCH<sub>2</sub>), 1.83 (2H, p, *J* 6.6, ArOCH<sub>2</sub>CH<sub>2</sub>), 1.55 (2H, m, ArOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 0.88 (3H, t, *J* 7.2, CH<sub>3</sub>). δ<sub>C</sub> (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 (ArNO<sub>2</sub> C1), 131.2 (C2 ArOR), 130.2 (C1 ArOR), 128.8 (ArOR C2), 125.7 (CH=CH-CO), 124.2 (ArNO<sub>2</sub> C3), 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>), 14.1 (CH<sub>3</sub>). ν/cm<sup>-1</sup> (ATR) 3079.4, 1657 (νCO), 1607, 1598, 1586, 1510 (s, ν<sub>as</sub> NO<sub>2</sub>), 1473, 1339 (s, ν<sub>s</sub> NO<sub>2</sub>), 1228, 1123, 1169 (s, ν CN), 1000, 833, 825, 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%; δ<sub>H</sub>(400 Mhz, CDCl<sub>3</sub>): 8.27 (2H, d, *J* 8.53, ArNO<sub>2</sub> C3-H, C5-H), 8.03 (2H, d, *J* 8.7, ArNO<sub>2</sub> C2-H and C6-H), 7.82-7.79 (3H, m, CH=CH-CO and ArOR C2-H C6-H), 7.65 (1H, d, *J* 15.7, CH=CH-CO), 6.99 (2H, d, *J* 8.7, ArOR C3'-H and C5'-H), 4.04 (2H, t, *J* 6.3, ArOCH<sub>2</sub>), 1.82 (2H, p, *J* 6.6, 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 (8 H, CH<sub>2</sub>), 0.89 (3H, t, *J* 7.2, CH<sub>3</sub>). δ<sub>C</sub> (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 (ArNO<sub>2</sub> C1), 131.3 (ArOR C2'), 130.6

(C1' ArOR), 129.2 (ArNO<sub>2</sub> C2 and C6), 126.0 (CH=CH-CO), 124.5 (ArNO<sub>2</sub> C3 and C5), 114.8 (ArOR C3' and C5'), 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>), 14.4 (CH<sub>3</sub>).  $\nu/\text{cm}^{-1}$  (ATR) 2955 ( $\nu_{\text{as}}$  CH<sub>3</sub>), 2919 ( $\nu_{\text{as}}$  CH<sub>2</sub>), 2874 ( $\nu_{\text{s}}$  CH<sub>3</sub>), 2850 ( $\nu_{\text{s}}$  CH<sub>2</sub>), 1656 ( $\nu$  CO), 1610 ( $\nu_{\text{CCAr}}$ ), 1593 ( $\nu_{\text{C=C}}$  (enone)), 1534 (s,  $\nu_{\text{as}}$  NO<sub>2</sub>), 1511, 1467, 1342 (s,  $\nu_{\text{s}}$  NO<sub>2</sub>), 1259 (s,  $\nu_{\text{as}}$ , =C-O-C), 1221, 1178 (s,  $\nu$  CN), 1070 (s,  $\nu_{\text{s}}$ , =C-O), 1033, 988 (C-N stretching), 980, 780, 760, 733, 655, 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 (2 H, d, *J* 8.72, ArNO<sub>2</sub> C3-H), 7.82-7.77 (3 H, 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, ArOR C5-H), 4.09 (4 H, t, *J* 6.48, ArOCH<sub>2</sub>), 1.86 (4H, p, *J* 6.48, 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 (4 H, m, CH<sub>2</sub>CH<sub>3</sub>), 1.25 (52 H, CH<sub>2</sub>), 0.88 (6H, t, *J* 7.0, 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 (ArNO<sub>2</sub> C1), 130.8 (C1 ArOR), 129.2 (C2 ArNO<sub>2</sub>), 126.0 (CH=CH-CO), 124.5 (ArNO<sub>2</sub> C3), 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>), 14.5 (CH<sub>3</sub>).  $\nu/\text{cm}^{-1}$  (ATR) 2956 ( $\nu_{\text{as}}$  CH<sub>3</sub>), 2916 ( $\nu_{\text{as}}$  CH<sub>2</sub>), 2873 ( $\nu_{\text{s}}$  CH<sub>3</sub>), 2849 ( $\nu_{\text{s}}$  CH<sub>2</sub>), 1655 ( $\nu$  CO), 1578 ( $\nu_{\text{C=C}}$  (enone)), 1525 (s,  $\nu_{\text{as}}$  NO<sub>2</sub>), 1514, 1467, 1434 ( $\delta$  CH vinylo), 1343 (s,  $\nu_{\text{s}}$  NO<sub>2</sub>), 1278, 1267 (s,  $\nu_{\text{as}}$ , =C-O-C), 1217, 1177, 1153 (s,  $\nu$  CN), 1069 (s,  $\nu_{\text{s}}$ , =C-O), 995 (C-N stretching), 840, 813, 754, 721, 675, 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, ArNO<sub>2</sub> C3-H and C5-H), 8.12 (2H, d, *J* 8.2, ArNO<sub>2</sub> C2-H and C6-H), 7.81 (1H, d, *J* 15.2, CH=CH-CO), 7.60 (2H, d, *J* 8.4, ArOR C2-H and C6-H), 7.35 (1H, d, *J* 15.4, CH=CH-CO), 6.94 (2H, d, *J* 8.0, ArOR C3-H and C5-H), 4.02 (2H, t, *J* 6.3, ArOCH<sub>2</sub>), 1.81 (2H, p, *J* 6.6, ArOCH<sub>2</sub>CH<sub>2</sub>), 1.54-1.21 (18 H, CH<sub>2</sub>), 0.89 (3H, t, *J* 7.2, 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 (ArNO<sub>2</sub> C1), 143.9 (CH=CH-CO), 131.0 (ArNO<sub>2</sub> C2), 129.7 (ArOR C2 and C6), 127.1 (C1 ArOR), 124.2 (ArNO<sub>2</sub> C3 and C5), 119.1 (CH=CH-CO), 115.4 (ArOR C5 and C3), 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>), 14.5 (CH<sub>3</sub>).  $\nu/\text{cm}^{-1}$  (ATR) 2946 ( $\nu_{\text{as}}$  CH<sub>3</sub>), 2916 ( $\nu_{\text{s}}$  CH<sub>2</sub>), 2871 ( $\nu_{\text{s}}$  CH<sub>3</sub>), 2849 ( $\nu_{\text{s}}$  CH<sub>2</sub>), 1657 ( $\nu$  CO), 1587 ( $\nu_{\text{C=C}}$  (enone)), 1567, 1512 (s,  $\nu_{\text{as}}$  NO<sub>2</sub>), 1476, 1463, 1425, 1340 (s,  $\nu_{\text{s}}$  NO<sub>2</sub>), 1295, 1256 (s,  $\nu_{\text{as}}$ , =C-O-C), 1217, 1173 (s,  $\nu$  CN), 1061 (s,  $\nu_{\text{s}}$ , =C-O), 989 (C-N stretching), 832, 826, 767, 727, 703, 638.

## Notes and references

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

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

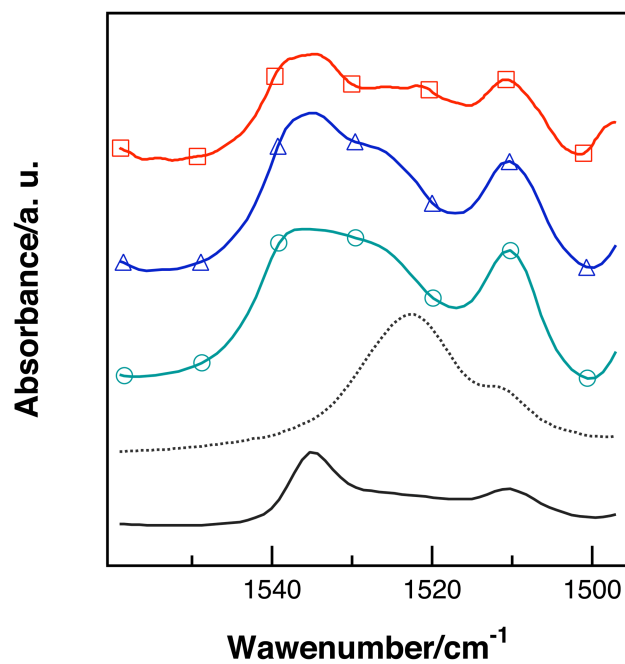
† Electronic Supplementary Information (ESI) available: FTIR spectra of C<sub>12</sub>-Ch-NO<sub>2</sub> gels in tert-butyl acetate and CCl<sub>4</sub> and C<sub>12</sub>-Ch-NO<sub>2</sub> solid. See DOI: 10.1039/b000000x/

- P. Terech and R. G. Weiss, *Chem. Rev.*, 1997, **97**, 3133-3159.
- J. H. Van Esch and B. L. Feringa, *Angew. Chem., Int. Ed. Engl.*, 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 Network*, 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. USA*, 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. USA*, 2006, **103**, 5054-5059.
- S. Murdan, T. Andrysek and D. Son, *Int J Pharm*, 2005, **300**, 113-124.
- S. Murdan, *Expert Opin. Drug Deliv.*, 2005, **2**, 489-505.
- K. J. C. van Bommel, A. Friggeri and S. Shinkai, *Angew. Chem., Int. Ed. Engl.*, 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.
- F. Placin, M. Colomes and J.-P. Desvergne, *Tetrahedron Lett.*, 1997, **38**, 2665-2668.
- J.-i. Mamiya, K. Kanie, T. Hiyama, T. Ikeda and T. Kato, *Chem. Commun.*, 2002, 1870-1871.
- R. J. Twieg, T. P. Russell, R. Siemens and J. F. Rabolt, *Macromolecules*, 1985, **18**, 1361-1362.
- D. J. Abdallah and R. G. Weiss, *Langmuir*, 2000, **16**, 352-355.
- A. Ajayaghosh and V. K. Praveen, *Acc. Chem. Res.*, 2007, **40**, 644-656.
- S. Wattanasin and W. S. Murphy, *Synthesis*, 1980, 647-650.
- N. Diaz, F. X. Simon, M. Schmutz, M. Rawiso, G. Decher, J. Jestin and P. J. Mesini, *Angew. Chem., Int. Ed. Engl.*, 2005, **44**, 3260-3264.
- R. Schmidt, F. B. Adam, M. Michel, M. Schmutz, G. Decher and P. J. Mesini, *Tetrahedron Lett.*, 2003, **44**, 3171-3174.
- J. F. Brown, *J. Am. Chem. Soc.*, 1955, **77**, 6341-6351.
- M. Harrand, *J. Raman Spectrosc.*, 1975, **4**, 53-73.
- M. Harrand, *J. Raman Spectrosc.*, 1979, **8**, 161-164.
- 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.
- M. R. Basila, E. L. Saier and L. R. Cousins, *J. Am. Chem. Soc.*, 1965, **87**, 1665-1669.
- Z.-I. Yoshida and E. Osawa, *J. Am. Chem. Soc.*, 1966, **88**, 4019-4026.
- A. R. Hirst and D. K. Smith, *Chem. Eur. J.*, 2005, **11**, 5496-5508.
- 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.
- M. Tata, V. T. John, Y. Y. Waguespack and G. L. McPherson, *J. Am. Chem. Soc.*, 1994, **116**, 9464-9470.
- M. Tata, V. T. John, Y. Y. Waguespack and G. L. McPherson, *J. Phys. Chem.*, 1994, **98**, 3809-3817.

## Supplementary Information

### 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>



**Fig. S2** FTIR of C<sub>12</sub>-Ch-NO<sub>2</sub>/BnOH gel (2 % wt.) in the  $\nu_s$  NO<sub>2</sub> area.  $\square$  : gel in BnOH (2 % wt.); dotted line :  $\Delta$  : gel in <sup>t</sup>BuOAc (2 % wt.);  $\circ$  : gel in CCl<sub>4</sub> (4% wt.); dotted line in solution in CHCl<sub>3</sub> (0.17 % wt.); plain line : solid (ATR-IR).