

Photochromism of dihydroindolizines Part X. Photo-responsive self-assembling organogelators based on photochromic dihydroindolizines and 11-aminoundecanoic acid (AUDA)[†]

Saleh A. Ahmed^{a*}, Ziad Moussa^b, Shaya Y. Al-Raqa^b and Saleh N. Alamry^c



Multi-addressable photophysical properties of new synthesized photochromic materials based on photochromic dihydroindolizine system (DHI) covalently linked to *N*-acyl-11 aminoundecanoic acid (AUDA) or to its sodium salt or to its ester, through an amidic or urethane linkage have been studied. The DHI skeleton in these compounds is substituted in both the fluorene part (region A) or in the heterocyclic base (region B) with the gelling moieties. These molecules have been designed to respond to their environment. Interestingly, they are shown to act as efficient gelators for polar organic fluids, water and obviously they exhibit a thermosensitive answer as low molecular mass organogelators. In these fluids, the aggregative properties are totally suppressed upon conversion to neutral carboxylic species. The gels of these carboxylate sodium salts are shown to be markedly affected by light irradiation. Supramolecular gelating assemblies can be disrupted by the photoinduced ring opening of the DHI subunit, so that the macroscopic flowing property is recovered. Upon a further thermal treatment, the system is reversibly converted back to the supramolecular network. Controlled gelation could be achieved using temperature, light, or acidity as external stimuli. These new synthesized photochromic gels with their multi-addressable properties will find their applications as super photoresponsive materials. Developing and tuning of the photophysical properties of the synthesized compounds by the amide and urethane substituents in the 4-position of the fluorene and pyridazine regions have been achieved. The absorption maxima (λ_{\max}) and the half-lives ($t_{1/2}$) of the colored betaines were detected in all cases using UV/VIS spectrophotometric measurements. Irradiation of DHI 12-20 in CH_2Cl_2 or in acetonitrile solutions at ambient temperature with polychromatic light leads to the formation of red to red-violet colored betaines 12'-20'. The kinetics of the bleaching process of betaines 12'-20' to DHIs 12-20 were found to take place in the second range (96-218 s) and fit well the first order thermal back reaction. Some of these DHIs showed a photostability higher than that of the standard one. These interesting photophysical properties will help this family of compounds to find useful applications. Copyright © 2008 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: photochromism; dihydroindolizines (DHIs); photostability; photoresponsive; gelation; organic fluids; super-gels

INTRODUCTION

Photochromism is a photoinduced reversible isomerization in a chemical species between two isomers that have distinct absorption spectra. The two isomers differ not only in their absorption spectra but also in other physical and chemical properties.^[1-5] The chemical bond reconstruction via photoexcitation induces not only changes in the absorption spectra but also in various physical and chemical properties such as fluorescence spectra, refractive indices, oxidation/reduction potentials, chiral properties, gelation abilities, and so on. The quick change of these properties induced by the photoexcitation has been attracting much attention^[1-23] from an application prospective to optoelectronic devices such as memories and switches. Also, from the basic viewpoint of the chemical reaction, the photochromic reaction can be regarded as an important chemical process investigation because the details of the reaction profiles occurring with the time origin at the photoexcitation can be precisely and

directly elucidated by using time-resolved measurements, so that we could acquire information on the detailed reaction

* Correspondence to: S. A. Ahmed, Chemistry Department, Faculty of Science, Taibah University, 30002, Al-Madana Al-Mounawara, Saudi Arabia.
E-mail: saleh_63@hotmail.com

[†] This article was published online on 3 December 2008. An error was subsequently identified. This notice is included in the online and print versions to indicate that both have been corrected (17 March 2009).

a S. A. Ahmed
Chemistry Department, Faculty of Science, Assiut University, 71516 Assiut, Egypt

b Z. Moussa, S. Y. Al-Raqa
Chemistry Department, Faculty of Science, Taibah University, 30002, Al-Madana Al-Mounawara, Saudi Arabia

c S. N. Alamry
Physics Department, Faculty of Science, Taibah University, 30002, Al-Madana Al-Mounawara, Saudi Arabia

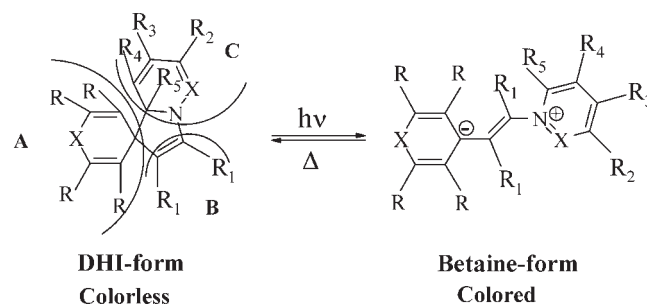
mechanisms that cannot be easily obtained for the usual thermal reaction processes. Among a number of photochromic molecules, the thermally reversible dihydroindolizines (DHIs) family undergoes ring opening to the colored betaine (opened form) form which thermally returned back to its colorless form (closed form) via 1,5-electrocyclization.^[1–5] This photochromic family is one of the most promising photochromic family because of their excellent fatigue resistance, rapid response, high sensitivity to irradiation, colorability, durability as well as many other and interesting properties like tune of the absorption spectra of the colored forms, half-lives, photostability, and solvatochromism by changing the substituents in the DHI regions.^[24–65] To the best of our knowledge, these unique sets of properties predominantly exist in the DHI family among other photochromic families which will help in finding new applications.

Molecular gels represent outstanding functional nanoscale materials with high potential in a wide range of advanced applications.^[66–74] Their formation stems from the spontaneous but controlled self-assembly of low molecular mass compounds into fibrous architectures, which, in turn, form entangled three-dimensional networks entrapping solvent molecules.^[66,72] In contrast to the case of their polymeric counterparts, molecular gels involve discrete molecular components with well-defined chemical structures. It is therefore possible, by introducing subtle changes in the chemical composition of the gelator backbone, to fine-tune the morphology, chirality, and size of the aggregates and, ultimately, the macroscopic properties of the gel.^[66–74] Arguably this unique feature largely contributes to motivate the great deal of activity toward the synthesis of new gelator molecules. When considering the data available in the literature over the last 20 years, it is amazing to realize that both kinds of molecular systems, either structurally sophisticated chemical entities or, on the other hand, simple compounds, can be found in the library of gelators. The former are generally multi-component molecular systems and they are appealing the gel materials with specific supramolecular functions, such as molecular recognition, photo- or electroactivity^[66–74] and for recent examples, see.^[75–83] However, as they are usually available in small amounts because their synthesis needs numerous synthetic steps, they are not often suited for large-scale applications. Structurally simple compounds, that can be obtained in gram scale quantities from cheap precursors in a limited number of synthetic steps, are also of great interest because they allow the production of nanostructured materials with thermoreversible properties at very moderate costs^[67] and for selected examples, see.^[84–89] Such systems can find applications as host matrices or media for a variety of applications, including sensing and separation technologies, catalysis, (bio)mineralization, etc. Recently, we reported in a preliminary communication the gelling behavior of a series of *N*-acyl-1, ω -amino acid derivatives^[90–92] Within the series, amide compounds including the 11-aminoundecanoic acid (AUDA) motif were proven very effective and versatile gelators of water and/or organic solvents.^[93,94]

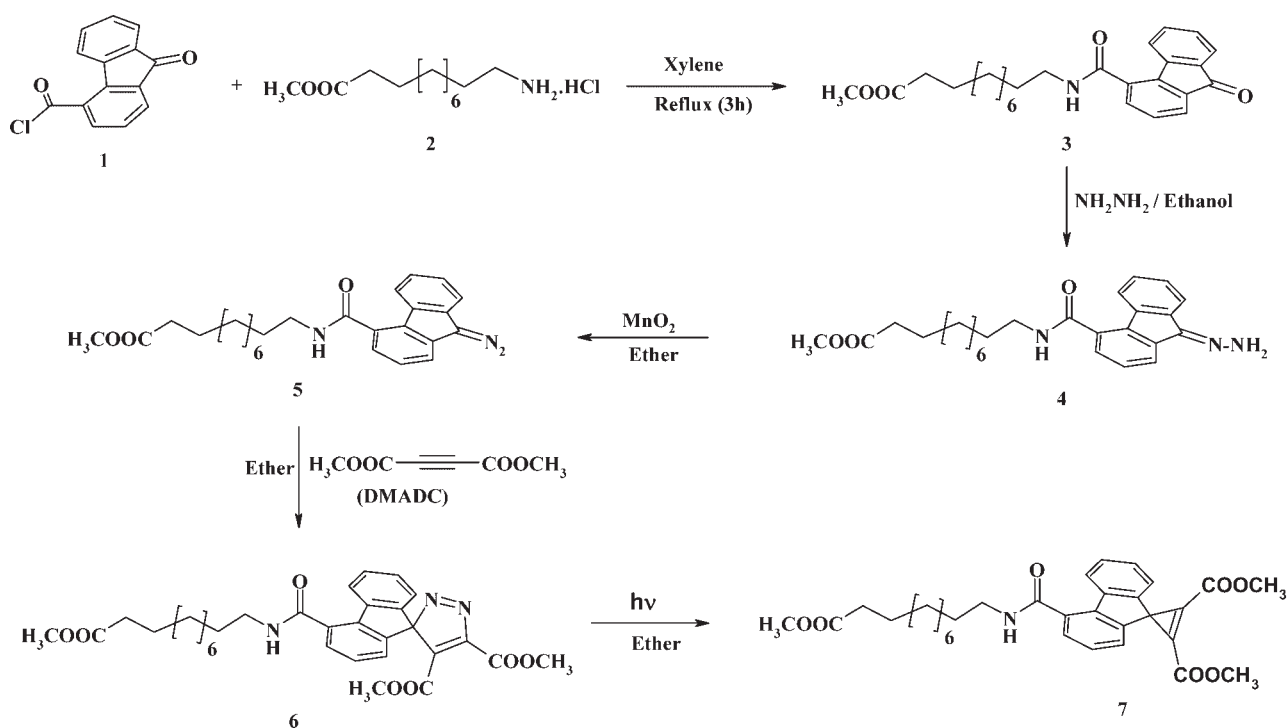
The construction of supramolecular architectures by the spontaneous self-assembly of molecules is currently a subject of great interest in areas that range from chemistry and biology to materials science.^[95–97] Of particular interest is the design of externally addressable molecules that contain self-assembled elements, as these can give rise to so-called smart materials.^[98–106] Such addressable molecules could include among others, photochromics, which can be used to bring about light-induced

changes in the self-assembly^[107–120] or environment-sensitive luminophores, which can provide valuable insight into the nature of the molecular aggregation within such assemblies.^[121] Low-molecular-weight (LMW) gelators have attracted much attention in recent years.^[122–124] Of particular interest for organogelator materials science are “smart gels”; i.e., gels whose properties can be controlled reversibly or irreversibly in response to changes in external chemical, photochemical, thermal stimuli, or sound.^[125] Such responsive systems are highly desirable in thermo- and mechano-responsive sensor materials or in applications like drug delivery or catalysis, or in nano- and mesoscopic assemblies with interesting optical and electronic properties and so on.^[126–128] Several groups exploited these features for the development of “smart” LMW organogelators.^[129–140] However, it is a tremendous challenging task to design controllable gelation systems based on reversible changes of a gelator molecule induced by external stimuli. Some organogelators with photochromic units including azobenzene, diaryl ethane, stilbene, naphthopyran, and DHI derivatives have been reported^[65,66,141–145] in which the gelation was controlled by heat, light, or acidity as external stimuli. Recently, we have reported the first attempts toward efficient organogelators based on photochromic DHI system. The previous work showed high gelation abilities of DHI connecting with 11-undecanoic acid derivatives units in some organic solvents at high temperature.^[64,65] These results motivated us to go further in these interesting properties of gel-based DHI systems by substitution with one or two gelling units (similar or different) in A or C regions (Scheme 1).

In a continuation of our work dealing with the synthesis and study of the photochromic behavior of the photochromic DHI systems with multi-addressable photophysical properties suitable for some applications, in this paper we present (a) the design of the photochromic organogelators that are based on the covalent association of a photostimulable DHI and an acid-sensitive self-assembling unit (one or more) in region A or C of the DHI skeleton, (b) the synthesis and the gelation abilities of DHI derivatives that incorporate an *N*-acyl-1, ω -amino acid moiety which have recently reported to induce gelation of various organic fluids,^[64,65,90–92] (c) the effects of the ionization state of the terminal carboxylic acid functionality (ester, acid, or salt), (d) the study of the physical properties of the network fibers and their chemical sensitivity to acid, base, and light in addition to their mechanical properties and (e) a comparison of the properties of the present organogelators with those published previously.^[64,65]



Scheme 1. Schematic representation of the photo-induced ring opening of the DHI (the three regions **A**, **B**, **C** are represented) to the corresponding colored betaine

Scheme 2. Preparation outline of spirocyclopropene precursor **7**

RESULTS AND DISCUSSION

Preparation of dimethyl 4'-(11-methoxy-11-oxoundecylcarbamoyl)spiro[cycloprop[2]ene-1,9'-fluorene]-2,3-dicarboxylate **7**

Dimethyl 4'-(11-methoxy-11-oxoundecylcarbamoyl)spiro[cycloprop[2]ene-1,9'-fluorene]-2,3-dicarboxylate **7** was prepared in five step (Scheme 2) as follow: Reaction of 9-fluorenone-4-acid chloride **1** with 11-methyl aminoundecanoate **2** in xylene under reflux condition for 3 h yielded the corresponding 9-fluorenone 4-AUDA methyl ester **3** in 92% yield. Condensation of compound **3** with hydrazine hydrate in absolute ethanol at reflux temperature gave the corresponding hydrazone derivative **4** in good yield (86%). Oxidation of the hydrazone **4** with yellow mercuric oxide or manganese dioxide in dry ether at room temperature in absence of light afforded the diazo fluorene derivative **5** in moderate yield (56%). Addition of methyl acetylenedicarboxylate (MADC) to the 9-diazo fluorene derivative **5** in dry ether in dark condition led to the formation of pyrazole derivative **6** in 47% yield.

Photolysis of the pyrazole derivative **6** with high pressure mercury lamp in dry ether solution for 3 h gave the spirocyclopropene derivative **7** in low yield (37%). The chemical structure of the newly synthesized compounds **3-7** were confirmed and established by both spectroscopic (NMR, IR, and mass spectrometry) and analytical tools (give satisfactory elemental analysis data). For example the ^1H NMR (400 MHz, CDCl_3) of the spirocyclopropene precursor **7** showed the following signals: δ 7.80–7.82 (dd, $J = 7.50$ Hz, 2H, CH-arom.), 7.55–7.56 (d, $J = 7.50$ Hz, 1H, CH-arom.), 7.47–7.52 (m, 4H, CH-arom.), 6.76 (t, $J = 4.9$ Hz, 1H, NH), 4.31 (s, 3H, 2'- CH_3), 3.75 (s, 3H, COOCH_3), 3.41 (s, 3H, 3'- CH_3), 3.27 (m, 2H, CH_2NH), 2.21 (t, $J = 7.2$ Hz,

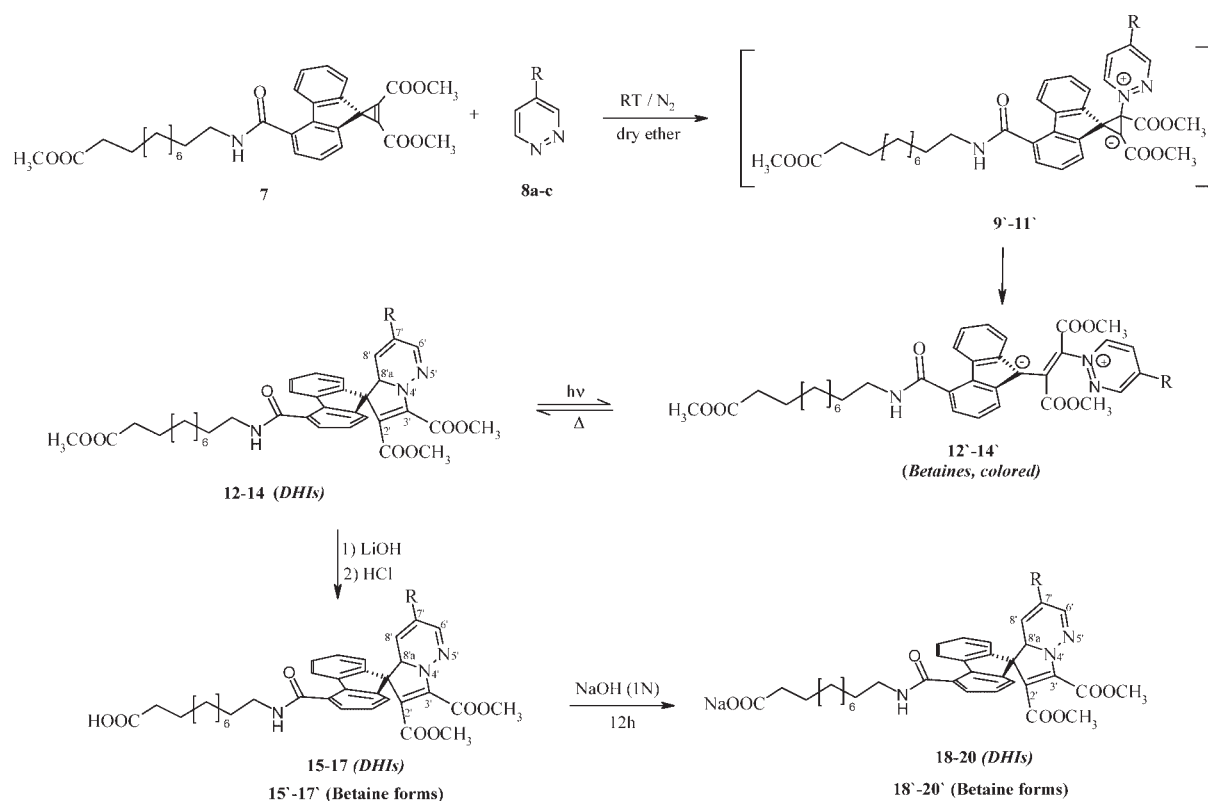
2H, $\text{CH}_2\text{—COOCH}_3$), 1.42–1.49 (m, 4H, $\text{CH}_2\text{CH}_2\text{COOCH}_3$ and $\text{CH}_2\text{CH}_2\text{NH}$), 1.37–1.43 (m, 12H, 6 \times CH_2) ppm.

Preparation of photochromic dihydroindolizines (DHIs) **12-20** bearing pyridazine **8a**, 11-methyl 4-pyridazineaminoundecanoate **8b** and methyl 11-methoxycarbonyl 4-pyridazine aminoundecanoate **8c**, respectively

Electrophilic addition of spirocyclopropene **7** to pyridazine **8a**, 11-Methyl 4-pyridazine aminoundecanoate **8b**^[64,65,146,147] and methyl 11-methoxycarbonyl 4-pyridazine aminoundecanoate **8c**^[64,65,148] precursors using the cyclopropene route (Scheme 3) in dry ether at room temperature under dry nitrogen in the absence of light (TLC-controlled using CH_2Cl_2 as eluent) led to the formation of the photochromic DHIs **12-14** in 53, 23, and 13% yield, respectively (Table 1).

The reaction occurs through the nucleophilic addition of pyridazine derivatives **8a-c** to the electron-deficient spirocyclopropenes **7**, which open via a cyclopropyl-allyl conversion **9'-11'** to the colored betaines **12'-14'**. A subsequent ring-closure to DHIs **12-14** results in a slow thermal 1,5-electrocyclization reaction (Scheme 2) which can be reversed upon exposure to light. Pure photochromic DHIs **12-14** were obtained in all cases by two successive column chromatography operations on silica gel using dichloromethane as the eluent.

Under mild conditions using lithium hydroxide in ethanol at room temperature, the ester DHIs **12-14** are easily saponified and yielded the corresponding DHIs-acid derivatives **15-17** after mild acidification with HCl (pH = 3–4) in high yield (94, 89, and 90%), respectively. The DHIs-sodium salt **18-20** obtained also in high yield (80, 81, 83% yield) via treatment of the corresponding



Scheme 3. Preparation outline of photochromic DHIs derivatives (**12-20**)

DHIs-acids **15-17** with 1NaOH in water/ethanol mixture at room temperature for 9–22 h (Scheme 3, Table 1). No chromatographic purification used in the cases of DHIs-sodium salt **18-20** due to their poor solubility in most of organic solvents and only washing with ether many times is enough to get the pure substances **18-20** to go further for studying all their high efficient gelation abilities in most organic fluids. The chemical structure of all new synthesized photochromic DHIs **12-20** were established on the basis of spectral and analytical tools and they showed spectra fitting well with the designed chemical structures and also give the satisfactory elemental analysis data.

Photophysical properties of the new photochromic DHIs **12-20** and their corresponding betaines **12'-20'** and in solutions

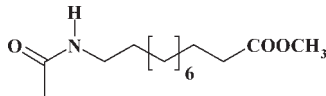
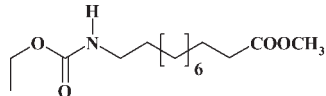
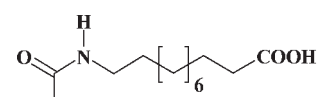
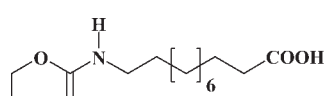
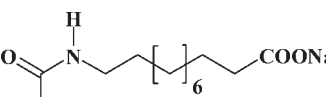
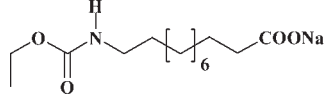
Absorption spectra of DHIs 12-20 and their corresponding betaines 12'-20' in dichloromethane and acetonitrile solutions.

The photochromic DHIs **12-20** are colorless or yellow in the solid state or in dichloromethane solutions ($\lambda_{\max} = 370\text{--}392$ nm). The sodium salts of DHIs **18-20** were studied in acetonitrile solution and under ultra-sonication conditions due to the poor solubility of these compounds in dichloromethane. An example of absorption maxima is given in Fig. 2. The absorption of the DHIs under investigation lie between 370 and 392 nm with concentration of 1×10^{-4} mol/L at room temperature (Fig. 1). An increasing of the λ_{\max} of the closed form of non-substituted pyridazine DHI **12** compared with substituted DHIs **13**, **14** by 6

and 9 nm, respectively was recorded (Table 2). A decrease in the absorption maxima of the acid in the gelling part in both fluorene and pyridazine parts **14-17** by 2–4 nm compared with the ester substituted DHIs **12** was noticed. The logarithm of the molar absorptivity (ϵ) of all DHIs under studies varies between 3.75 (**17**) and 4.07 (**12**). The presence of the substituents in both A and B region of the DHI skeleton does not greatly influence the energy of the absorption maximum. Substitutions in pyridazine and fluorene parts by the 11-AUDA derivatives showed a small effect on the molar absorptivity of the photochromic DHI system. As established previously,^[1-5] these absorption bands can be assigned to the locally excited $\pi\text{-}\pi^*$ -transition (LE) located in the butadienyl-vinyl-amine chromophore^[24-65] of the DHIs **12-20**.

Irradiation of DHIs **12-20** with polychromatic light leads to ring opening betaines **12'-20'** (Figs 2 and 3). The colored betaine forms **12'-18'** is obvious in CH_2Cl_2 solution with concentration of 1×10^{-4} mol/L at room temperature because of their slower 1,5-electrocyclization. All the absorption maxima of the colored betaines **12'-20'** found to be in the visible region and lie between 518 (betaine **14'**) and 527 nm (betaine **12'**). The UV-spectra of the colored betaines **12'-20'** exhibit two absorption maxima; between 341 and 342 nm and between 518 and 527 nm (Figs 2 and 3). The color of betaines varied from red to red-violet, which strangely depends on the position of the substitution with the gelling group in both fluorene part (region A) and heterocyclic part (region C) as well as the conversion of the gelling group from ester to acid and then to sodium salt. A bathochromic shift of about 8 nm between betaines **12'-14'** and **15'-17'** which leads to color changes was recorded.

Table 1. Substituent pattern in the pyridazine part (region B) of the prepared 9 DHIs derivatives, their melting points and reaction yields

DHI	R	Reaction time (h)	Mp (°C)	Yield (%)
12	H	24	146	53
13		38	159	23
14		24	133	13
15	H	40	172	94
16		48	180	89
17		25	167	90
18	H	12	207	90
19		24	220	81
20/20'		9	181	83

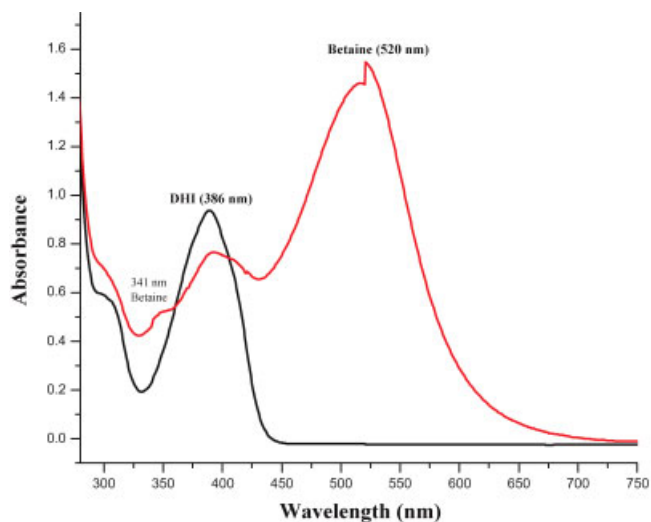
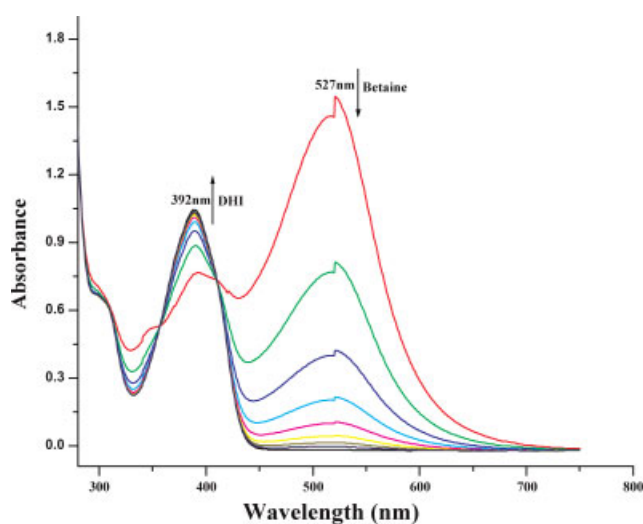
**Figure 1.** UV/VIS of photochromic DHI 13 and the corresponding betaine form 13' after UV irradiation in CH_2Cl_2 ($c = 1 \times 10^{-4}$ mol/L) at ambient temperature. This figure is available in colour online at www.interscience.wiley.com/journal/poc**Figure 2.** Kinetic FT-UV/VIS spectrum of the thermal fading of betaine 12' to DHI 12 (cycle time = 30 s, run time = 300 s) in CH_2Cl_2 ($c = 1 \times 10^{-4}$ mol/L at 253 K). This figure is available in colour online at www.interscience.wiley.com/journal/poc

Table 2. UV/Vis absorption and kinetic data of the thermal 1,5-electrocyclization of betaines **12'**-**20'** to their corresponding DHIs **12-20** in CH₂Cl₂ solution (23 °C, $c = 1 \times 10^{-4}$ mol/L)

DHI/ betaine	λ_{\max} DHI (nm)	Log(ϵ) DHI	λ_{\max} betaine (nm)	k (1/s) $\times 10^{-3}$ (betaine)	$t_{1/2}$ (s) (betaine)	Color of betaine
12/12'	392	4.07	342,527	4.88	143	red
13/13'	386	3.90	341,520	7.07	98	red
14/14	383	3.83	342,518	7.22	96	red-violet
15/15'	390	3.97	343,526	4.44	218	red
16/16'	388	3.80	342,523	5.55	183	red-violet
17/17'	389	3.75	342,522	5.78	169	red-violet
18/18' *	388	3.95	342,527	3.30	156	red
19/19' *	380	3.82	341,522	3.92	112	red-violet
20/20' *	384	3.77	342,519	4.59	106	red-violet

* Measurements were carried out in acetonitrile solution ($c = 1 \times 10^{-4}$ mol/L) at ambient temperature.

The kinetic of the thermal 1,5-electrocyclization was studied by using multichannel UV-Vis. The kinetic measurements showed that the half-lives of the colored betaine **12'**-**20'** in second domain lie between 96 and 218 s (Table 2, Fig. 3). A pronounced increasing in the half-lives of the acid substituted betaines **15'**-**17'** than their corresponding ester betaines **12'**-**14'** by about 25 s was observed (Table 2). This maybe attributed to the formation of hydrogen bond in case of the acids which will lead to stabilization of the betaine forms in the addition to the stabilization of the positive charge on the nitrogen atom of the base part of the DHI skeleton. Further strong evidence stemmas by the comparison the half-life time of betaine **12'**, **15'**, **18'** (143, 218, 156 s) containing one substitution in fluorene part with those containing two acidic functions with substitution with two gelling parts. These tuning of the absorption maxima and the kinetic properties by the changing of the substitution in both fluorene part (region A) and pyridazine part (region C) will help this family to find many sounding applications.

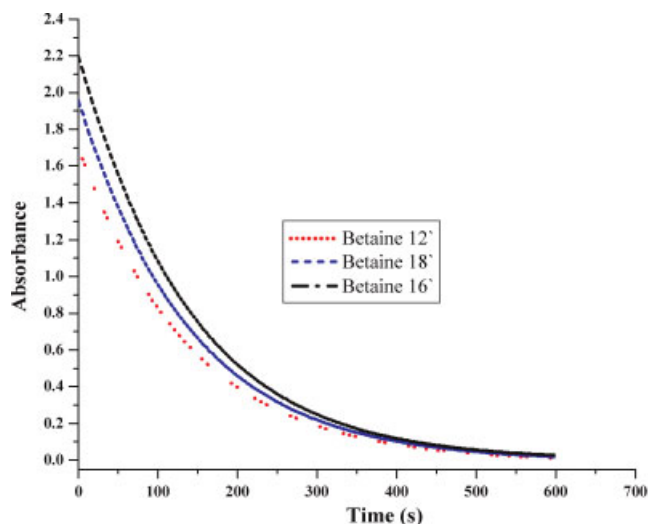


Figure 3. Time-absorbance relationship for the 1,5-electrocyclization of betaine **12'**, **16'**, and **18'** for determination the half-lives of the colored betaine forms. This figure is available in colour online at www.interscience.wiley.com/journal/poc

Photo-stability of photochromic DHIs **12-20** and their corresponding betaines **12'-20'** in dichloromethane and acetonitrile solutions ($c = 1 \times 10^{-4}$ m/L) at 253 K

One of the most important properties of photochromic materials to find their sounding applications is the efficiency of these materials for photodegradation. In studying the quality of a photochromic system, or in other terms the thermal full reversibility of a specific photochromic molecule, the problem of carrying out a large number of colorization-decolorization cycles arises frequently. The gradual loss of the ability to change color by exposure to visible or ultraviolet light in this context has been termed fatigue.^[1-5] Gautron^[149] has advanced a quantitative approach to measure the fatigue in photochromic systems. In the present work, the study of the photodegradation is important factor since the photochromic compounds will be converted into many forms by different treatments such as light, heat, and acid-base effect.

The photo-stability measurements were carried out by irradiation of DHIs **12-20** with polychromatic light ($\lambda = 200-400$ nm, 400 W xenon lamp) at room temperature in degassed CH₂Cl₂ solution except in case of photochromic sodium salt **18-20** which measured in acetonitrile solution due to the poor solubility of the salts in dichloromethane solution. After irradiation, at room temperature, the colored betaines **12'-20'** were produced which upon continuous irradiation, decomposes after some time. However if oxygen is excluded, these systems are noticeably more stable. It is possible that in the presence of oxygen, the betaines **12'-20'** acts as a sensitizer toward singlet oxygen.^[1-5] The initial absorbance of pyridazine DHIs **12-20** was measured using a 3 ml quartz cell UV/Vis spectrometer in degassed CH₂Cl₂ ($c = 1 \times 10^{-4}$ mol/L) solution. Before starting the photodegradation experiment, the degassed DHIs **12-20** solutions were irradiated for 3 min to achieve equilibrium between DHIs and betaines.

Before starting the photodegradation experiments, the extinction was set as 100%. The analysis was carried out from absolute destruction time (every 15 min.). At the fixed point recommended the absorbance of betaine form through irradiation decreased by 30% of the beginning extinction (Fig. 4). This time called in our work as t_{30} -value and the stability factor (F) can be recognized by

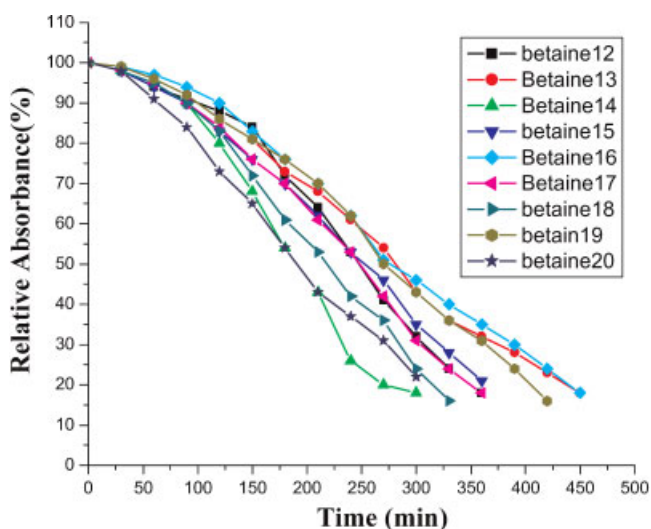


Figure 4. Time-relative absorbance relationship of the photodegradation experiment for determination of the t_{30} -value of betaines **12'–20'** in CH_2Cl_2 and acetonitrile at ambient temperature ($c = 1 \times 10^{-4}$ mol/L). This figure is available in colour online at www.interscience.wiley.com/journal/poc

the ratio of t_{30} -values of the measured compounds and the t_{30} -value of dicanopyridazine-betaine, which was used in the earlier studies.^[24–65]

The photodegradation data represented in Table 3 showed that, the betaine form of the DHI **16'** ($t_{30} = 391$ min) is the most stable betaine structure under investigation and more stable than the standard dicyano-pyridazine DHI ($t_{30} = 243$ min) by a factor of 1.61. A general notice is that all the betaines **12'–20'** showing a high t_{30} -value than the standard compounds except in the case of the urethane structure **14'**. The urethane-based photochromic gels **14', 17', 20'** showed a lower t_{30} -value than the amidic betaines **13', 16', 19'** by factor ranged between 0.4–0.6. This is may be attributed to the weakness of the urethane bond which can be easily cleaved with UV-irradiation compared with amidic betaines **13', 16', 19'**. Indeed, the acid based photochromic gels showed a high stability compared to both the ester and sodium salt derivatives under investigation. These results will help in the multi-addressable conversions of these compounds in presence of light, heat, and pH conditions.

Multi-addressable gelation abilities of new synthesized photochromic DHIs 12-20 ganic fluids

Aggregation of low molecular mass organogelators is usually driven by specific non-covalent intermolecular forces, and several examples have been reported based on hydrogen bond formation, hydrophobic interactions, dipole–dipole interactions, charge transfer, van der Waals interactions, or metal coordination bond formation. The control by external stimuli of the gelation process, which is a macroscopic expression of self-assembling, remains a tremendous challenging task.^[150,151] A promising approach toward such smart gels is the introduction of an addressable function into the supramolecular building blocks. Different approaches using cation complexation or pH variation have already been proven successful but were reported to slightly modulate the gelling abilities or the medium viscosity.^[150,151] Organic photochromes^[152] could offer the possibility to modify the self-assembly process of the individual molecules and also the resulting supramolecular network by means of light. Indeed, photochromic systems display two different molecular states in terms of their respective absorption spectra. More interestingly, the light-induced transformation causes reversibly important structural and physicochemical changes. Photoswitchable hydrogen-bonded in self-organized cylindrical peptide systems have been successfully prepared, the *E/Z* isomerization of the azobenzene moiety allowing the reversible interconversion of inter- to intramolecular hydrogen bonding.^[152]

Various compounds based on 11-AUDA have been shown to act as potent organogelators or hydrogelators, furthermore the presence of a sodium carboxylate has been exploited to alter the self-assembling process and thus to largely modify the gel formation upon acidic conditions.^[84–89]

Recently, we reported for the first time the efficient gelation ability of a series of *N*-acyl-1, ω -amino acid derivatives based on photochromic DHI.^[64,65] Within the series, amide and urethane compounds including the 11-AUDA and photochromic DHI motif were proven very effective and versatile gelators of some organic solvents which motivated us to continue working in this series. In this paper, we focus on a series of mono and di-1, ω -amino acids substituted the photochromic DHIs in both fluorene and pyridazine parts with expecting to show more gelation abilities in many organic fluids. As an attempt to obtain new functional organogelators with multiple-switch applications, we have

Table 3. Photodegradation data of betaines **12'–20'** in dichloromethane and acetonitrile solutions ($c = 1 \times 10^{-4}$ mol/L) at 23 °C

Betaines	$t_{1/2}$ (s)	λ_{max} Betaine(nm)	t_{30} -betaine/ DHI (min)	F
12'	143	534	298	1.23
13'	98	523	367	1.51
14'	96	519	228	0.94
15'	218	526	310	1.28
16'	183	517	391	1.61
17'	169	515	297	1.22
18'*	156	529	288	1.19
19'*	112	511	367	1.51
20'*	106	519	272	1.12
Standard	56.2	535	243	1.0

* Measurements carried out in acetonitrile solutions.

rationally designed photochromic organogelators based on DHI containing mono and di- AUDA in fluorene and the pyridazine part of DHI Skelton. Herein, we report the gelation abilities of DHI derivatives that incorporate one or two *N*-acyl-1, ω -amino acid moiety in various organic fluids.^[84–89]

The gelation behavior was first investigated via the inverted test tube method^[84–89,95–106] DMF, DMSO, alcohols, and water were selected as fluids according to the minimum gelation concentrations which were found in the millimolar range for some sodium salts of *N*-acyl amino acids.^[84–89] The gelation behavior of the prepared compounds **12–20** were investigated in water and in various organic solvents. The methyl ester derivative **12–14** was found to be soluble in almost all of the organic solvents tested (Table 4). The acid–DHIs **15–17** showed efficient gelation abilities in toluene and some higher alcohols (C5–C8), especially the amide-acid–DHI **16**. These acids are completely soluble in DMF and DMSO and no gelation abilities in these fluids were observed. Introduction of a metal ion like Na⁺ into the acid–DHIs **17–20** resulted in a poor solubility of these compounds. Furthermore, **18-Na**, **19-Na**, and **20-Na** are insoluble in most of the usual organic fluids. They are insoluble in DMF and

DMSO, but upon heating at 90–150 °C and sonication, they gradually dissolved. Upon cooling to ambient temperature, gels are readily obtained which are then stable for months (Fig. 6a,b). Both chromenic derivatives were found to gelate these fluids over a wide range of concentration. Interestingly, the DHI **19** shows high efficient gelation abilities not only in DMF and DMSO but also in water which can be considered as super photochromic gel.

The gel-to-sol phase transition temperatures (hereafter denoted T_{gel}) of DMF gels in a concentration of 1% wt/vol are 121, 145, and 132 °C for **18-Na**, **19-Na**, and **20-Na**, respectively, which could be considered to act as a supergelator (Fig. 5b). The neutral carboxylic acid derivatives **15**, **16**, and **17** were found to be very soluble in DMF and DMSO at 25 °C but they showed gelation ability in toluene with T_{gel} of 94, 120, and 105 °C for 15-H, 16-H, and 17-H, respectively (Fig. 5a). More interesting is to find the high gelation abilities of both acids–DHIs **15–17** and sodium salt–DHIs **18–20** in higher alcohols such as heptanol and octanol with T_{gel} of 80, 125 and 100 °C for acids–DHIs **15–17** in octanol (Fig. 6a). Upon addition of sodium hydroxide, the acids–DHIs **15–17** rapidly convert to the gel state. So, for the targeted DHIs, the interesting gelation ability is retained and the presence major

Table 4. Gelation abilities of photochromic DHIs **15–20** expressed as minimal gel concentration of tested compounds at room temperature^a

Solvents	15	16	17	18	19	20
Toluene	G	G	G	I	I	I
Ethyl acetate	I	I	I	I	I	I
THF	S	S	S	I	I	I
Methanol	S	P	P	P	P	P
Ethanol	S	P	P	P	P	P
Butanol	VS	VS	P	VS	VS	P
Pentanol	VS	GL	VS	VS	GL	GL
Heptanol	G	G	VS	G	G	G
Octanol	G	G	G	G	G	G
DMF	S	S	S	G	G	G
DMSO	S	S	S	G	G	G
Water	I	I	I	S	G	S

^a Gelator concentration 50 mM (room temperature). G, gel; GL, gel-like; S, solution; VS, viscous solution; P, precipitate; I, insoluble when heated.

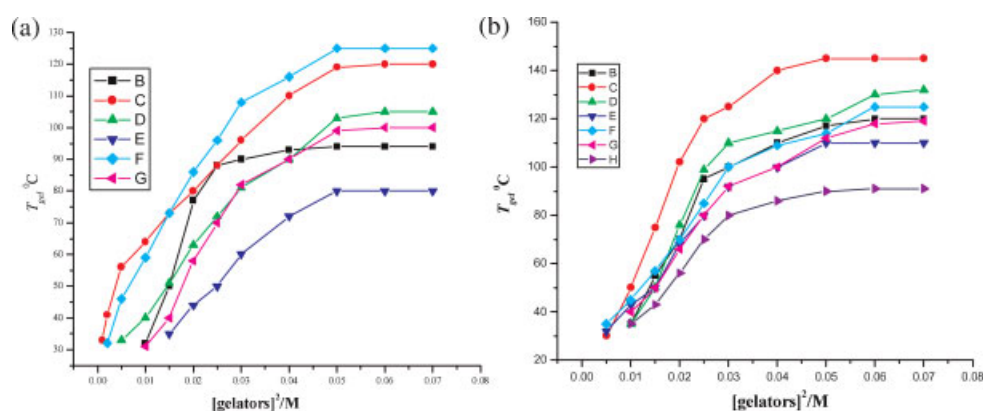


Figure 5. (a) T_{gel} of (B) 15-H in toluene, (C) 16-H in toluene, (D) 17-H in toluene, (E) 15-H in octanol, (F) 15-H in octanol and (G) 15-H in octanol; (b) T_{gel} of (B) 18-Na in DMF, (C) 19-Na in DMF, (D) 20-Na in DMF, (E) 18-Na in DMSO, (F) 19-Na in DMSO (G) 20-Na in DMSO and (H) 19-Na in water; as a function of organogelator concentrations

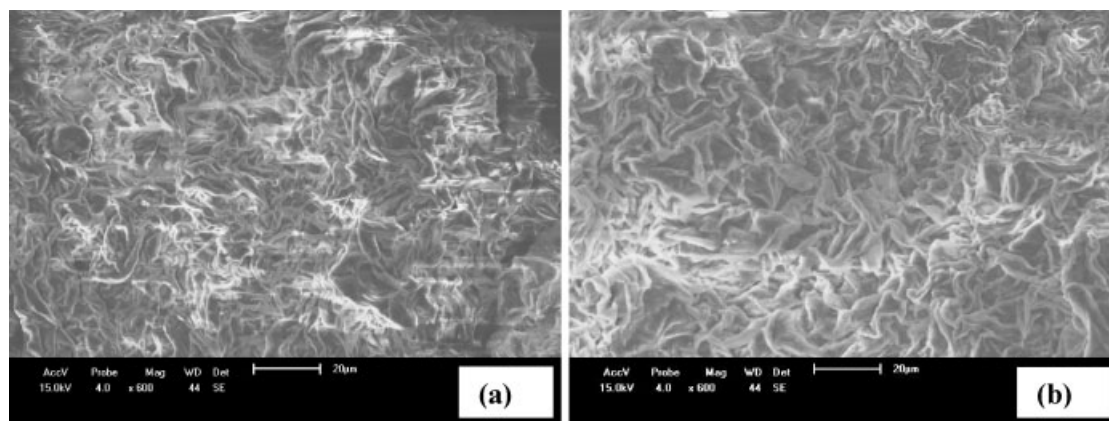
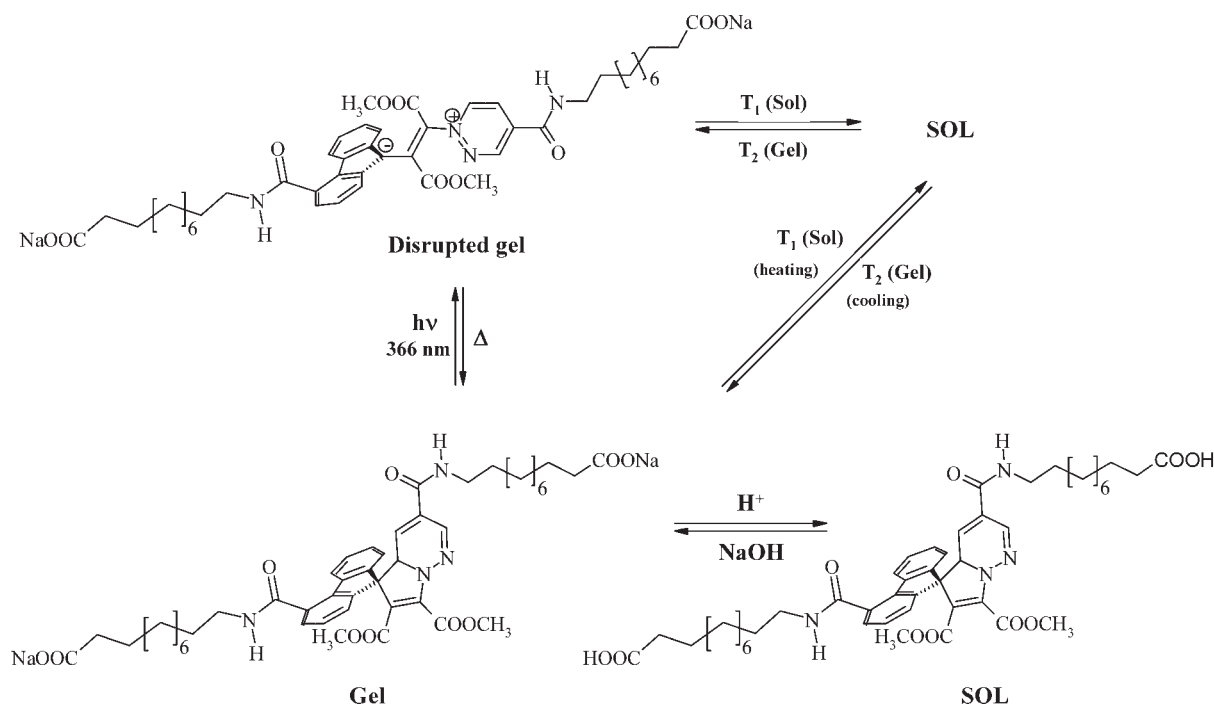


Figure 6. Electron scan microscope (ESM) of the free acids gel (a): DHI **15** after gelation in toluene and (b) DHI **17** after gelation in octanol



Scheme 4. Illustration of interconversion between the different molecular species and corresponding macroscopic states upon external stimuli in 16-H and 19-Na DHIs. (similar behavior was observed in case of 15-H, 17-H and 18-N, 20-Na DHIs)

importance since the addition of acid could suppress the gel formation (Scheme 4). TEM observations give direct evidence for the microscopic organization formed in DMF, DMSO, and toluene. Numerous juxtaposed and intertwined fibrous aggregates of low molecular mass gelators of acids (Fig. 8) and salts **18-Na**, **19-Na**, and **20-Na** are formed (Figs 7 and 8). The morphology of gels was based on long fibers which form an entangled network (Figs 6–8). The diameter of the smallest entities which can be distinguished is 20–40 nm. This represents several gelator lengths. Interestingly, the sodium salt of DHI **20** found be gelate also in water and the network fiber of the gel shown in Fig. 8. The network fiber formation through the hydrogen bond and van der Waals interactions represented in Fig. 9.

These gels were further studied by infrared spectroscopy. For such purpose, deuterated dimethylsulfoxide was used as the solvent in order to avoid strong peaks in the NH-stretch and in amide I and II regions. The maxima of these peaks are characteristics for the presence of the hydrogen-bonded amide group^[153] which is responsible for the gelation abilities forming the network fibers.

Alternative evidence supporting the self-aggregation of DHIs in DMF_{gel} was provided by rheological measurements.^[153] Frequency sweep experiment shows that the elastic modulus G' and the loss modulus G'' are fairly independent of frequency over more than 3 decades. Typical values are here reported for 1.5% wt/vol of **19-Na** in DMF. The G' value (1×10^4 Pa) was observed to

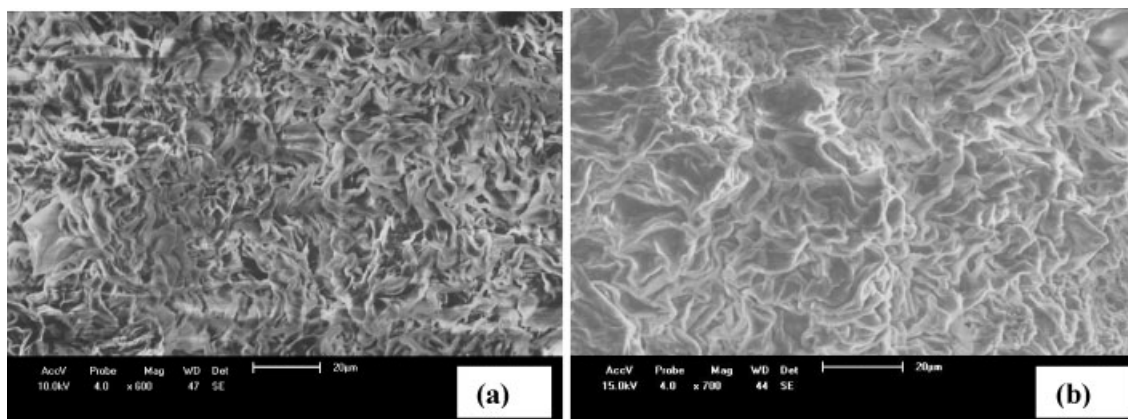


Figure 7. Electron scan microscope (ESM) of the sodium salt gels: (a) DHI **20** in DMF and (b) DHI **20** in DMSO

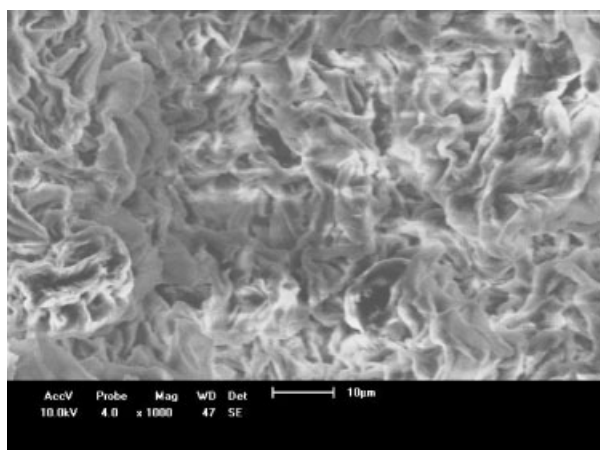


Figure 8. Electron scan microscope (ESM) of the DHI-sodium salt **19** after gelation in water

be 1 order of magnitude higher than that of G'' (1×10^3 Pa) indicating that the system still exhibits a solid like behavior.

Irradiation of gels

The photochromic gels **15–20** are showing multi-addressable photophysical properties due to their high sensitivity to light, acid–base, and heat. Photochromic gels have been studied in thermostated cells with a 1 mm optical pathway allowing one to follow coloration and subsequent decoloration by UV–vis measurements and to keep homogeneity within the samples. Upon irradiation using a 366 nm lamp, gels become rapidly colored and then begin to flow as we have set up an inverted cell. One can observe the appearance of yellow colored liquid areas within the sample along with aggregate zones. The shape of the absorption band displayed by the irradiated gel is totally superimposable with those arising from irradiated acid indicating that the conversion of some gelator molecules into open forms takes place. The primary photoinduced ring opening event

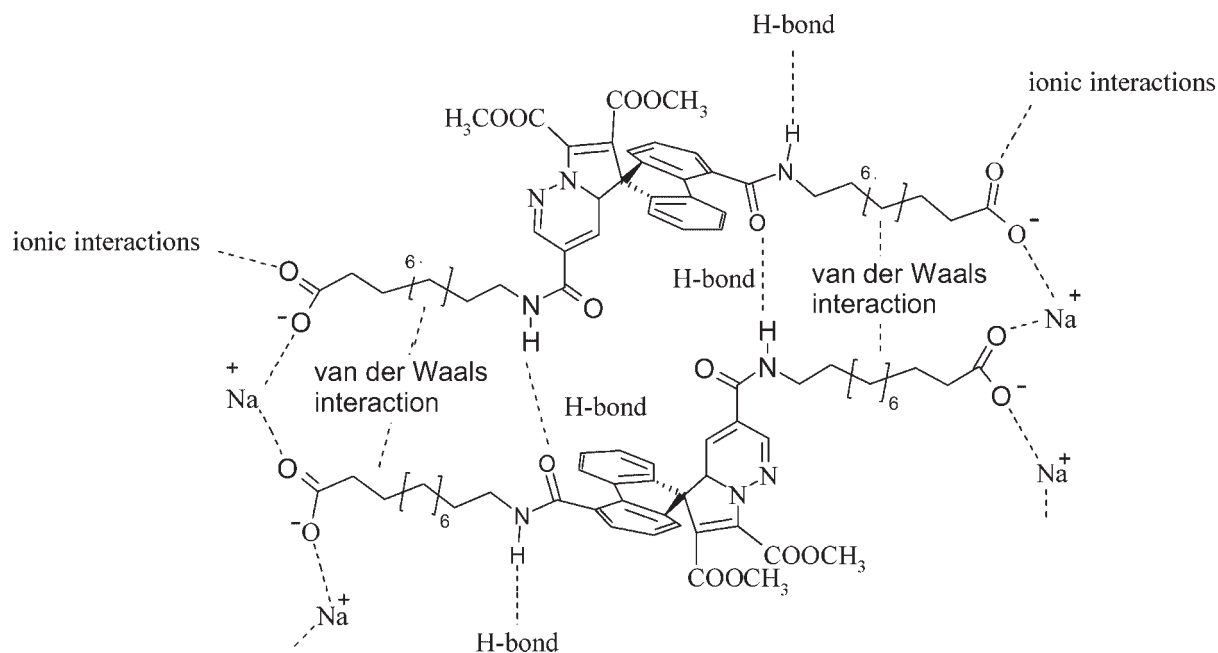


Figure 9. One-dimensional aggregate model of photochromic DHI–Na in the gel phase

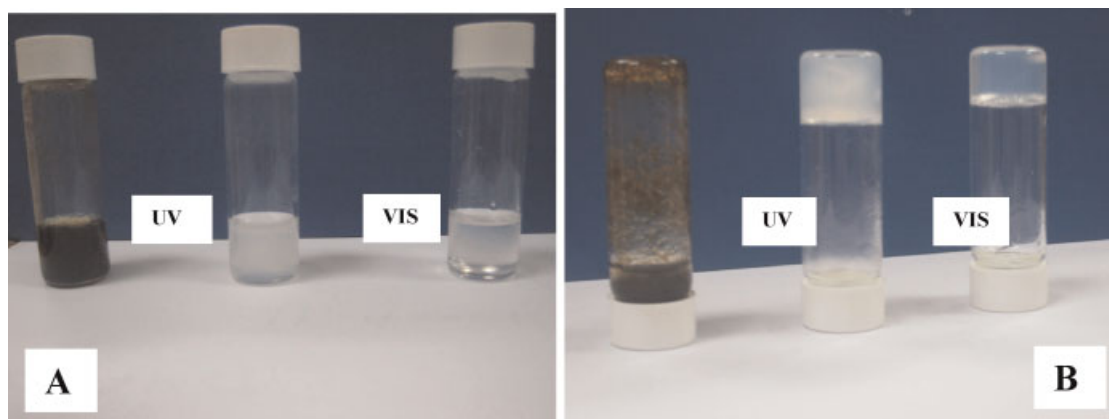


Figure 10. Photocontrolled gel-to-sol phase transition of 19-Na DMF gel/19-Na sol. (A) Left: 19'-Na sol after irradiation, middle: 19-Na gel before irradiation, and right: photoregenerated 19-Na DMF gel; (B) represents A more clearly in inverted form respectively

clearly diminishes the strength of the network which is not totally suppressed. Indeed, the strongly colored open forms could act as an internal filter preventing total conversion. When irradiation ceases, the coloration progressively disappears to yield a colorless viscous solution which does not revert spontaneously into a gel. This could be simply achieved upon heating and then cooling. This complete interconversion process between gel state, viscous liquid, and isotropic solution has been cycled 20 times without any detectable degradation side products. This can be unambiguously assigned due to the T_{gel} values which are invariable (Fig. 5)

When diluted DMF and DMSO (0.2 mM) solutions are exposed to UV-light, similar large absorption bands are obtained whose maxima do not exhibit any significant shift. When gels are irradiated, superimposable maxima have been found for DMSO, DMF, toluene, and other organic fluids. More interestingly this transformation is accompanied by the gel-to-sol phase transition within 3 min. The absorption intensity of the photoinduced sols is noticeably lower in comparison to expected values. This indicates that some photochromic units are still embedded within small remaining aggregates. In both solvents macroscopic gelation could be photodisrupted. For further investigation DMF was chosen because of the excellent stability of the translucent gel and the minimum gelation concentration (*ca.* 2 mM). UV-irradiation ($\lambda > 520$ nm) of the photoinduced sols gave rise to the photocycloreversion to reform **18-Na**, **19-Na**, and **20-Na**, which in turn gave birth to the gel phase. This represents one of the rare examples of a gel-to-sol phase transition that could be photoswitched in both directions using appropriate wavelength (Scheme 4). Switching the photochromic compounds between sol-gel and vice versa using light, pH, and heat for more than 20 cycles show no evidence for any decomposition of the gels. Pictures of the three steps of one cycle is depicted in Fig. 10. This interesting switching process will help these compounds to find their applications as nanostructured materials.

CONCLUSIONS

New spirocyclopropene derivative has been synthesized through chemical and photochemical reactions. Conversion of the spirocyclopropene to photochromic DHI-based gelators has been achieved through combination of one or two similar

and different versatile aggregative unit derived from a synthetic amino acid as gelling parts connected to the fluorene and/or pyridazine parts in photochromic DHI skeleton. The constructing of a photoresponsive DHIs unit on the sodium *N*-acyl-11-aminoundecanoate scaffold does not suppress the gelation ability in various organic fluids in addition to water. It exhibits excellent photochromic properties and defined thermo reversible properties in an organogel system. On the other hand, the formation of intermolecular hydrogen bonds, and thereafter the supramolecular aggregates, is strongly affected by photo-induced structural changes of the photochromic subunit. The multi-addressable molecular switches operate at supramolecular scale, the phase changes between gel and sol being independently driven by acidity, light, and temperature. The multi-addressable self-assembling organogelators are excellent building blocks for the development of functional materials and devices. These systems represent example of smart super-gel which display the ability to respond to various changes of their environment. The presence of two amidic gelling unites in both fluorene and pyridazine (region A and C) have strong influence for the DHIs to gelate in many organic fluids as well as in water and can be consider as a super-gels. A pronounced increasing in the gelation temperatures (T_{gel}) of the DHI-based gelators are present in this paper than the previous work, especially with two amidic linkages has been recorded. The multi-addressable gelation abilities of photochromic DHI will makes it promising application in the fields of opto-smart materials, logic gate, and sensor materials.

EXPERIMENTAL

The solvents used (Aldrich or Merck were spectroscopic grade) were dried, according to standard procedures,^[154,155] over sodium for diethyl and toluene, P_2O_5 for CH_2Cl_2 , CaH_2 for DMF, and DMSO and were all stored over sodium wire or molecular sieve (5 Å) in brown bottles under a nitrogen atmosphere.

Spirocyclopropene derivatives were obtained via photolysis of the corresponding pyrazoles prepared according to reported procedures^[1-5,8-20]. Photolysis was carried out in the photochemical reactor of Schenck^[156] made from Pyrex ($\lambda > 290$ nm). The source of irradiation was a high pressure mercury lamp Philips HPK 125 W. Solutions to be photolyzed were flushed with

dry nitrogen for 30 min before switching on the UV lamp. The progress of the reaction and the purity of the products isolated were monitored using TLC. Separation and purification of all synthesized photochromic materials were carried out using column chromatography (80 cm length \times 2 cm diameter) on silica gel and CH_2Cl_2 as eluent. Melting points were determined on an Electrothermal Eng. Ltd. melting point apparatus and are uncorrected. All NMR spectra were collected on a Bruker DRX 400 spectrometer (400 MHz) in CDCl_3 using TMS as the internal standard. Chemical shifts (δ) are reported in ppm. FT-IR measurements were performed using a Perkin Elmer Paragon 1000 instrument. Mass spectra were recorded on a VG AutoSpec apparatus using electronic impact at 70 eV. MALDI-MS spectra were recorded in the positive mode by using a 2,5-dihydroxybenzoic acid in dioxane as matrix. SEM was performed using Tapping Mode (Nanoscope Ila, Digital Instruments, Inc.) with a pyramidal Si_3N_4 tip. IR spectra were measured on a BIO-Rad Excalibur series, FTS 3000. UV-spectra were recorded on a FT-UV/VIS/NIR JASCO V-570 spectrometer. Experimental details and procedures for the synthesis of dimethyl 4'-(11-methoxy-11-oxoundecylcarbonyl)spiro[cycloprop[2]ene-1,9'-fluorene]-2,3-dicarboxylate **7** will be published elsewhere^[55]. The experimental details and full characterizations for all synthesized DHIs **12-20** are described as supplementary materials.

Acknowledgements

S. A. Ahmed is highly indebted to Alexander von Humboldt foundation for financial support of his AvH fellowship. Many thanks to Prof. Dr Heinz Dürr (University of Saarland, Saarbrücken, Germany), Prof. Dr Henri Bouas-Laurent, Prof. Dr Jean-Luc Pozzo for their continuous helpful discussions and measurements. The financial support from Taibah University (project number: 48/427), AvH, and CNRS (Supramolecular Chemistry Project D11/0015/99) is gratefully acknowledged.

REFERENCES

- [1] H. Bouas-Laurent, H. Dürr, *Pure. Appl. Chem.* **2001**, *73*, 639–665.
- [2] H. Dürr, In *Photochromism-Molecules and Systems*, (Ed.: H. Dürr, H. Bouas-Laurent), Elsevier, Amsterdam, (1990, 2003).
- [3] H. Dürr, In *Organic Photochromic and Thermochromic Compounds*, Vol. 1, (Eds.: J. C. Crano, R. J. Guglielmetti), Plenum Press, New York, **1999**, 223–266.
- [4] (Eds.: J. C. Crano, R. J. Guglielmetti), *Photochromic and Thermochromic Compounds*, Vol 1 and 2, Plenum Press, New York, **1999**.
- [5] G. H. Brown, *Photochromism*, Wiley-Interscience, New York, **1971**.
- [6] E. Fisher, Y. Hirshberg, *J. Chem. Soc.* **1952**, 4522.
- [7] G. J. Ashwell, *Molecular Electronics*, John Wiley & Sons Inc, New York, **1992**.
- [8] M. Irie, *Chem. Rev.* **2000**, *100*, 1685–1716.
- [9] G. Berkovic, V. Krongauz, V. Weiss, *Chem. Rev.* **2000**, *100*, 1741–1753.
- [10] S. Kawata, Y. Kawata, *Chem. Rev.* **2000**, *100*, 1777–1788.
- [11] S. L. Gilat, S. H. Kawai, J.-M. Lehn, *J. Chem. Soc., Chem. Commun.* **1993**, 1439–1442.
- [12] T. Saika, M. Irie, T. Shimidzu, *J. Chem. Soc., Chem. Commun.* **1994**, 2123–2124.
- [13] S. L. Gilat, S. H. Kawai, J.-M. Lehn, *Chem. Eur. J.* **1995**, *1*, 275–284.
- [14] G. M. Tsivgoulis, J.-M. Lehn, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1119–1122.
- [15] S. H. Kawai, S. L. Gilat, R. Ponsinet, J.-M. Lehn, *Chem. Eur. J.* **1995**, *1*, 285–293.
- [16] G. M. Tsivgoulis, J.-M. Lehn, *Chem. Eur. J.* **1996**, *2*, 1399–1406.
- [17] M. Irie, *Bull. Chem. Soc., Jpn.* **1998**, *71*, 985–996.
- [18] M. Takeshita, M. Irie, *Tetrahedron Lett.* **1999**, *40*, 1345–1348.
- [19] S. H. Kawai, S. L. Gilat, J.-M. Lehn, *Eur. J. Org. Chem.* **1999**, 2359–2366.
- [20] T. Yamagushi, T. Inagawa, H. Nakazumi, S. Irie, M. Irie, *Chem. Mater.* **2000**, *12*, 869–871.
- [21] L. N. Lucas, J. Van Esch, R. M. Kellogg, B. L. Feringa, *Chem. Commun.* **2001**, 759–760.
- [22] T. Kawai, T. Sasaki, M. Irie, *Chem. Commun.* **2001**, 711–712.
- [23] Ed.: B. L. Feringa, *Molecular Switches*, Wiley-VCH, Darmstadt, **2001**.
- [24] G. Hauck, H. Dürr, *Angew. Chem.* **1979**, *91*, 1010–1011; Int Ed 1979; 18: 945–946.
- [25] H. Dürr, G. Hauck, *Deutsche Offenlegungs Schrift.* **1979**, 29 06 193.
- [26] H. Dürr, H. Gross, G. Hauck, *Deutsche Offenlegungs Schrift.* **1983**, *116*, 856–8861.
- [27] S. A. Ahmed, Th. Hartmann, V. Huch, H. Dürr, A. A. Abdel-Wahab, *J. Phys. Org. Chem.* **2000**, *13*, 539–548.
- [28] Y. S. Tan, S. A. Ahmed, H. Dürr, V. Huch, A. A. Abdel-Wahab, *Chem. Commun.* **2001**, *14*, 1246–1247.
- [29] S. A. Ahmed, *Mol. Cryst. Liq. Cryst.* **2005**, *430*, 295–300.
- [30] S. A. Ahmed, H. Dürr, *Mol. Cryst. Liq. Cryst.* **2005**, *431*, 275–280 (or 575–580).
- [31] S. A. Ahmed, *Monatshefte für Chemie.* **2004**, *135*, 1173–1188.
- [32] S. A. Ahmed, A. A. Abdel-Wahab, H. Dürr, *J. Photochem. & Photobiol.* **2003**, *154*, 131–144.
- [33] S. A. Ahmed, *J. Phys. Org. Chem.* **2002**, *15*, 392–402.
- [34] S. A. Ahmed, *J. Phys. Org. Chem.* **19**, **2006**, 402–414.
- [35] R. Fromm, S. A. Ahmed, Th. Hartmann, V. Huch, A. A. Abdel-Wahab, H. Dürr, *Eur. J. Org. Chem.* **2001**, *21*, 4077–4080.
- [36] H. Dürr, C. Schommer, T. Münzmay, *Angew. Chem.* **1986**, *25*, 565–567 Int. Ed. 25(1986) 572–574.
- [37] H. Dürr, A. Thome, H. Kilburg, S. Bossmann, E. Blasius, K. Janzen, C. Kranz, *J. Phys. Org. Chem.* **5**, **1992**, 689–698.
- [38] H. Dürr, *Chimica.* **1994**, 514–515.
- [39] H. Dürr, M. Amlung, F. Rustemeyer, Y. S. Tan, *Deutsche Offenlegungs-Schrift Pat.* **1998**, 198, 349–408.
- [40] R. Fromm, S. A. Ahmed, Th. Hartmann, V. Huch, A. A. Abdel-Wahab, H. Dürr, *Eur. J. Org. Chem.* **2001**, *21*, 4077–4080.
- [41] C. Weber, F. Rustemeyer, H. Dürr, *Adv. Mater.* **1998**, *10*, 1348.
- [42] C. Andreis, H. Dürr, V. Wintgens, P. Valat, J. Kossanyi, *Chem. Eur. J.* **1997**, *3*, 509–5516.
- [43] S. A. Ahmed, A. A. Abdel-Wahab, H. Dürr, *CRC Handbook of Organic Photochemistry and Photobiology*, (Eds.: W. M. Horspool, F. Lenci), CRC press, New York, 2nd edn, Chapter 96, **2003**. 1–25.
- [44] H. Dürr, *Angew. Chem.* **1989**, *101*, 427–445 Int. Ed. Engl. 28 (1989) 413–438.
- [45] H. Dürr, *Wiss. Zeitschr. TH Leuna- Merseburg.* **1984**, *26*, 664–671.
- [46] H. Dürr, H. Gross, K. D. Zils, *Deutsche Offenlegungs Schrift Pat.* **1983**, 32 20 275 A 1.
- [47] H. Dürr, H. P. Jönsson, P. Scheidhauer, T. Münzmay, P. Spang, *Deutsche Offenlegungs Schrift Pat.* **1985**, 35214325.
- [48] H. Dürr, K. P. Janzen, A. Thome, B. Braun, *Deutsche Offenlegungs Schrift Pat.* **1988**, 35214325.
- [49] H. Dürr, H. Gross, K. D. Zils, G. Hauck, H. Hermann, *Chem. Ber.* **116**, **1983**, 3915–3925.
- [50] H. Dürr, P. Spang, *Deutsche Offenlegungs Schrift Pat.* **1984**, 32 20 2571.
- [51] S. A. Ahmed, C. Weber, Z. A. Hozien, M. Hassan, Kh, A. A. Abdel-Wahab, H. Dürr, Kluwer Academic Publishers, Plenum Press: New York.
- [52] S. A. Ahmed, *Ph.D Thesis*, Saarland-Assiut Universities, **2000**.
- [53] P. Burtscher, H. Dürr, V. Rheinberger, U. Salz, *German Pat D.* **1995**, 195200160.
- [54] H. Dürr, H. Gross, K. D. Zils, *Deutsche Offenlegungs Schrift Pat.* **1983**, 3220275A1.
- [55] H. Dürr, H. P. Jeonsson, P. Scheidhauer, T. Münzmay, P. Spang, *Deutsche Offenlegungs Schrift Pat.* **1985**, 35214325.
- [56] H. Dürr, K. P. Janzen, A. Thome, B. Braun, *Deutsche Offenlegungs Schrift Pat.* **1988**, 35214325.
- [57] Y. S. Tan, Th. Hartmann, V. Huch, H. Dürr, K. Kossanyi, *J. Org. Chem.* **2001**, *66*, 1130–1138.
- [58] C. Weber, F. Rustemeyer, H. Dürr, *Adv. Mater.* **1998**, *10*, 1348.
- [59] H. Dürr, M. Amlung, F. Rustemeyer, Y. S. Tan, *Deutsche Offenlegungs Schrift Pat.* **1998**, 198 349 408.
- [60] P. Burtscher, H. Dürr, V. Rheinberger, U. Salz, *Fa. IVOCLAR German Pat.* **1995**, 195200160.

- [61] G.-F. Masson, Th. Hartmann, H. Dürr, K. S. Booksh, *Optical Materials*. **2004**, *27*, 435–4439.
- [62] C. Andreis, H. Dürr, V. Wintgens, P. Valat, J. Kossanyi, *Chem. Eur. J.* **1997**, *3*, 509–516.
- [63] H. Bleisinger, P. Scheidhauer, H. Dürr, V. Wintgens, P. Valat, J. Kossanyi, *J. Org. Chem.* **1998**, *63*, 990–1000.
- [64] S. A. Ahmed, Th. Hartmann, H. Dürr, *J. Photochem. Photobiol.* **2008**, *200*, 50–56.
- [65] S. A. Ahmed, J.-L. Pozzo, *J. Photochem. Photobiol.* **2008**, *200*, 57–67.
- [66] P. Terech, R. G. Weiss, *Chem. Rev.* **1997**, *97*, 3133–3159.
- [67] D. J. Abdallah, R. G. Weiss, *Adv. Mater.* **2000**, *12*, 1237–1247.
- [68] L. A. Estroff, A. D. Hamilton, *Chem. Rev.* **2004**, *104*, 1201–1217.
- [69] J. H. van Esch, B. L. Feringa, *Angew. Chem., Int. Ed.* **2000**, *39*, 2263–2266.
- [70] N. M. Sangeetha, U. Maitra, *Chem. Soc. Rev.* **2005**, *34*, 821–836.
- [71] (Ed.: F. Fages), Low Molecular Mass Gelators: Design, Self-Assembly, Function, *Topics in Current Chemistry*, Springer, Berlin, **2005**. Vol. 256.
- [72] (Eds.: R. G. Weiss, P. Terech), *Molecular Gels: Materials with Self-Assembled Fibrillar Networks*, Springer, Dordrecht, **2005**.
- [73] M. de Loos, B. L. Feringa, J. H. van Esch, *Eur. J. Org. Chem.* **2005**, 3615–3631.
- [74] F. Fages, *Angew. Chem. Int. Ed.* **2006**, *45*, 1680–1682.
- [75] For recent examples, see: A. Ajayaghosh, C. Vijayakumar, R. Varghese, S. George, *Angew. Chem. Int. Ed.* **2006**, *45*, 456–460.
- [76] F. Camerel, L. Bonardi, M. Schmutz, R. Ziessel, *J. Am. Chem. Soc.* **2006**, *128*, 4548–4549.
- [77] S. Wang, W. Shen, Y. Feng, H. Tian, *Chem. Commun.* **2006**, 1497–1499.
- [78] M. Montalti, L. S. Dolci, L. Prodi, N. Zaccheroni, M. C. A. Stuart, K. J. C. van Bommel, A. Friggeri, *Langmuir* **2006**, *22*, 2299–2303.
- [79] A. Del Guerso, A. G. L. Olive, J. Reichwagen, H. Hopf, J.-P. Desvergne, *J. Am. Chem. Soc.* **2005**, *127*, 17984–17985.
- [80] S. Kawano, N. Fujita, S. Shinkai, *Chem. Eur. J.* **2005**, *11*, 4735–4742.
- [81] T. Akutagawa, K. Kakiuchi, T. Hasegawa, S. Noro, T. Nakamura, H. Hasegawa, S. Mashiko, J. Becher, *Angew. Chem. Int. Ed.* **2005**, *44*, 7283–7287.
- [82] T. Kitamura, S. Nakaso, N. Mizoshita, Y. Tochigi, T. Shimomura, M. Moriyama, K. Ito, T. Kato, *J. Am. Chem. Soc.* **2005**, *127*, 14769–14775.
- [83] M. de Loos, J. van Esch, R. M. Kellogg, B. L. Feringa, *Angew. Chem. Int. Ed.* **2001**, *40*, 613–616.
- [84] For selected examples, see: S. Bhattacharya, Y. Krishnan-Ghosh, *Chem. Commun.* **2001**, 185–186.
- [85] M. Jokic, J. Makarevic, M. Zinic, *Chem. Commun.* **1995**, 1723–1724.
- [86] A. Ballabh, D. R. Trivedi, P. Dastidar, *Chem. Mater.* **2003**, *15*, 2136–2140.
- [87] M. G. Page, G. G. Warr, *J. Phys. Chem. B* **2004**, *108*, 16983–16989.
- [88] M. George, S. L. Snyder, P. Terech, C. J. Glinka, R. G. Weiss, *J. Am. Chem. Soc.* **2003**, *125*, 10275–10283.
- [89] S. Kiyonaka, S. Shinkai, I. Hamachi, *Chem. Eur. J.* **2003**, *9*, 976–983.
- [90] S. A. Ahmed, X. Sallenave, F. Fages, G. Mieden-Gundert, W. M. Müller, U. Müller, F. Vögtle, J.-L. Pozzo, *Langmuir* **2002**, *18*, 7096–7101.
- [91] X. Sallenave, S. Delbaere, G. Vermeersch, S. A. Ahmed, J.-L. Pozzo, *Tetrahedron Lett.* **2005**, *46*, 3257–3259.
- [92] A. D'Aleo, J.-L. Pozzo, F. Fages, M. Schmutz, G. Mieden-Gundert, F. Vögtle, V. Caplar, M. Zinic, *Chem. Commun.* **2004**, 190–191.
- [93] M. Yamanaka, T. Nakagawa, R. Aoyama, T. Nakamura, *Tetrahedron* **2008**, *64*, 11558–11567.
- [94] G. Mieden-Gundert, L. Klein, M. Fischer, F. Vögtle, K. Heuze, J.-L. Pozzo, M. Vallier, F. Fages, *Angew. Chem., Int. Ed.* **2001**, *40*, 3164–3166.
- [95] B. L. Feringa, R. A. Van Delden, N. Koumura, E. M. Geertsema, *Chem. Rev.* **2000**, *100*, 1789–1816.
- [96] T. Yamada, K. Muto, S. Kobatake, M. Irie, *J. Org. Chem.* **2001**, *66*, 6164–6168.
- [97] M. Irie, *Supramolecular Science*. **1996**, *3*, 87–89.
- [98] P. Terech, R. G. Weiss, *Chem. Rev.* **1997**, *97*, 3133–3159.
- [99] D. J. Abdallah, R. G. Weiss, *Adv. Mater.* **2000**, *12*, 1237–1247.
- [100] L. A. Estroff, A. D. Hamilton, *Chem. Rev.* **2004**, *104*, 1201–1217.
- [101] J. H. van Esch, B. L. Feringa, *Angew. Chem. Int. Ed.* **2000**, *39*, 2263–2266.
- [102] N. M. Sangeetha, U. Maitra, *Chem. Soc. Rev.* **2005**, *34*, 821–836.
- [103] Ed.: F. Fages Low Molecular Mass Gelators: Design, Self-Assembly, Function, *Topics in Current Chemistry*, Vol 256, Springer, Berlin, **2005**.
- [104] (Eds.: R. G. Weiss, P. Terech), *Molecular Gels: Materials with Self-Assembled Fibrillar Networks*, Springer, Dordrecht, **2005**.
- [105] M. de Loos, B. L. Feringa, J. H. van Esch, *Eur. J. Org. Chem.* **2005**, 3615–3631.
- [106] F. Fages, *Angew. Chem. Int. Ed.* **2006**, *45*, 1680–1682.
- [107] A. Ajayaghosh, C. Vijayakumar, R. Varghese, S. J. George, *Angew. Chem. Int. Ed.* **2006**, *45*, 456–460.
- [108] F. Camerel, L. Bonardi, M. Schmutz, R. Ziessel, *J. Am. Chem. Soc.* **2006**, *128*, 4548–4549.
- [109] S. Wang, W. Shen, Y. Feng, H. Tian, *Chem. Commun.* **2006**, 1497–1499.
- [110] M. Montalti, L. S. Dolci, L. Prodi, N. Zaccheroni, M. C. A. Stuart, K. J. C. van Bommel, A. Friggeri, *Langmuir* **2006**, *22*, 2299–2303.
- [111] A. Del Guerso, A. G. L. Olive, J. Reichwagen, H. Hopf, J.-P. Desvergne, *J. Am. Chem. Soc.* **2005**, *127*, 17984–17985.
- [112] S. Kawano, N. Fujita, S. Shinkai, *Chem. Eur. J.* **2005**, *11*, 4735–4742.
- [113] T. Akutagawa, K. Kakiuchi, T. Hasegawa, S. Noro, T. Nakamura, H. Hasegawa, S. Mashiko, J. Becher, *Angew. Chem. Int. Ed.* **2005**, *44*, 7283–7287.
- [114] T. Kitamura, S. Nakaso, N. Mizoshita, Y. Tochigi, T. Shimomura, M. Moriyama, K. Ito, T. Kato, *J. Am. Chem. Soc.* **2005**, *127*, 14769–14775.
- [115] M. de Loos, J. H. van Esch, R. M. Kellogg, B. L. Feringa, *Angew. Chem. Int. Ed.* **2001**, *40*, 613–616.
- [116] Y. Bhattacharya, Y. Krishnan-Ghosh, *Chem. Commun.* **2001**, 185–186.
- [117] M. Jokic, J. Makarevic, M. Zinic, *Chem. Commun.* **1995**, 1723–1724.
- [118] A. Ballabh, D. R. Trivedi, P. Dastidar, *Chem. Mater.* **2003**, *15*, 2136–2140.
- [119] M. G. Page, G. G. Warr, *Phys. Chem. B* **2004**, *108*, 16983–16989.
- [120] S. Kiyonaka, S. Shinkai, I. Hamachi, *Chem. Eur. J.* **2003**, *9*, 976–983.
- [121] G. Mieden-Gundert, L. Klein, M. Fischer, F. Vögtle, K. Heuze, J.-L. Pozzo, M. Vallier, F. Fages, *Angew. Chem. Int. Ed.* **2001**, *40*, 3164–3166.
- [122] A. D'Aleo, J.-L. Pozzo, F. Fages, M. Schmutz, G. Mieden-Gundert, F. Vögtle, V. Caplar, M. Zinic, *Chem. Commun.* **2004**, 190–191.
- [123] V. Caplar, M. Zinic, J.-L. Pozzo, F. Fages, G. Mieden-Gundert, F. Vögtle, *Eur. J. Org. Chem.* **2004**, 4048–4059.
- [124] (Eds.: K. McGrath, D. L. Kaplan), *Protein-based Materials*, Birkhauser, Boston, **1997**.
- [125] O. Treager, S. Sowade, C. Beottcher, J.-H. Fuhrhop, *J. Am. Chem. Soc.* **1997**, *119*, 9120–9124.
- [126] K. Murata, M. Aoki, T. Suzuki, T. Harada, H. Kawabate, T. Komori, F. Ohseto, K. Ueda, S. Shinkai, *J. Am. Chem. Soc.* **1994**, *116*, 6664–6676.
- [127] P. Terech, D. Pasquier, V. Bordas, C. Rossat, *Langmuir* **2000**, *16*, 4485–4494.
- [128] F. M. Menger, S. J. Lee, *J. Am. Chem. Soc.* **1994**, *116*, 5987–5988.
- [129] J. Makarevic, M. Jokic, B. Peric, V. Tomisic, B. Kojic-Prodic, M. Zinic, *Chem. Eur. J.* **2001**, *7*, 3328–3341.
- [130] J. H. Fuhrhop, J. Keoning, *Membranes and Molecular Assemblies: The Syntkinetic Approach*, Royal Society of Chemistry, Cambridge, **1994**.
- [131] F. M. Menger, K. L. Caran, *J. Am. Chem. Soc.* **2000**, *122*, 11679–11691.
- [132] S. Heunig, W. Greassmann, V. Meurer, E. Leucke, W. Brenninger, *Chem. Ber.* **1967**, *100*, 3039–3044.
- [133] G. M. Clavier, J.-F. Bruggier, H. Bouas-Laurent, J.-L. Pozzo, *J. Chem. Soc. Perkin Trans.* **1998**, 2527–2534.
- [134] M. Lescanne, A. Colin, O. Mondain-Monval, F. Fages, J.-L. Pozzo, *Langmuir* **2003**, *19*, 2013–2020.
- [135] P. Terech, D. Pasquier, V. Bordas, C. Rossat, *Langmuir* **2000**, *16*, 4485–4494.
- [136] F. M. Menger, S. J. Lee, *J. Am. Chem. Soc.* **1994**, *116*, 5987–5988.
- [137] J. Makarevic, M. Jokic, B. Peric, V. Tomisic, B. Kojic-Prodic, M. Zinic, *Chem. Eur. J.* **2001**, *7*, 3328–3341.
- [138] J. H. Fuhrhop, J. Keoning, *Membranes and Molecular Assemblies: The Synthetic Approach*, Royal Society of Chemistry, Cambridge, **1994**.
- [139] F. M. Menger, K. L. Caran, *J. Am. Chem. Soc.* **2000**, *122*, 11679–11691.
- [140] S. Heunig, W. Greassmann, V. Meurer, E. Leucke, W. Brenninger, *Chem. Ber.* **1967**, *100*, 3039–3044.
- [141] G. M. Clavier, J.-F. Bruggier, H. Bouas-Laurent, J.-L. Pozzo, *J. Chem. Soc. Perkin Trans.* **1998**, 2527–2534.
- [142] M. Lescanne, A. Colin, O. Mondain-Monval, F. Fages, J.-L. Pozzo, *Langmuir* **2003**, *19*, 2013–2020.
- [143] S. Yagai, T. Karatsu, A. Kitamura, *Chem. Eur. J.* **2005**, *11*, 4054–4063.
- [144] G. Sevez, J. Gan, J. Pan, X. Sallenave, A. Colin, H. Saadoui, A. Saleh, F. Vögtle, J.-L. Pozzo, *J. Phys. Org. Chem.* **2007**, *20*, 888–893.
- [145] S. Miljanic, L. Frkanec, Z. Meic, M. Zinic, *Eur. J. Org. Chem.* **2006**, 1323–1334.
- [146] G. Heinisch, *Monatsh. Chem.* **1973**, *104*, 953.
- [147] G. Heinisch, *Monatsh. Chem.* **1973**, *104*, 1372.

- [148] G. Heinisch, *Monatsh Chem.* **1976**, 107, 799.
- [149] R. Gautron, *Bull Soc Chim France.* **1968**, 3190.
- [150] H. Hachisako, H. Ihara, T. Kamiya, C. Hirayama, K. Yamada, *Chem. Commun.* **1997**, 19–120.
- [151] J.-L. Pozzo, G. Clavier, F. Rustmeyer, H. Bouas-Laurent, *Mol. Cryst. Liq. Cryst.* **2000**, 344, 101.
- [152] FTIR absorption peaks for amid-Na in DMSO- d_6 gel: NH stretch, 3337 cm^{-1} ; amid I, 1621 cm^{-1} ; and amid II, 1576 cm^{-1} .
- [153] Rheological measurements were performed with a TA Instrument AR 1000 stress-controlled rheometer. A measuring cell with a cone and plate geometry (a diameter of 20 mm and a cone angle of 4°) was used. The heated solution was introduced in the cell regulated at 60°C and then cooled rapidly (environ $20^\circ\text{C}/\text{min}$) at 20°C . The elastic modulus G' and loss modulus G'' were measured as a function of angular frequency ω at 20°C . The oscillatory frequency was varied from 10 to 0.01 Hz.
- [154] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, (3rd edn). Pergamon Press, Oxford, **1988**.
- [155] H. G. O. Becker, R. Beckert, G. Domschke, E. Fanghanel, W. D. Habicher, P. Metz, D. Pavel, K. Schwetlich, *Organikum-Organisch-chemisches Grundpraktikum*, (21st edn). Wiley-VCH, Weinheim, Chapter F **2001**. 741–762.
- [156] A. Schönberg, *Präparative Organische Photochemie*. Chapter 1, Springer Verlag, Berlin **1958**.
- [157] S. A. Ahmed, Heinz Dürr, Jean Luc Pozzo, under preparations, **2008**.