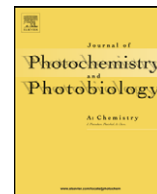




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Photochromism of dihydroindolizines Part IX First attempts towards efficient self-assembling organogelators based on photochromic dihydroindolizines and *N*-acyl-1, ω -amino acid units

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ABSTRACT

Six new photochromic materials **9–11**, **13–15** based on photochromic dihydroindolizine (DHI) system covalently linked to ester, acid or sodium *N*-acyl-11 aminoundecanoate through amidic or urethane linkage have been synthesized. These new compounds have been synthesized via nucleophilic addition of 11-methyl 4-pyridaizine aminoundecanoate **3** and methyl 11-methoxycarbonyl 4-pyridaizine aminoundecanoate **6** to spirocyclopropene **1**. Developing and tuning of the photophysical properties of the synthesized compounds by amide and urethane substitutes in the 4-position of the pyridazine base part 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 multichannel UV/vis spectrophotometric measurements. Irradiation of DHI **9**, **10**, **13** and **14** in CH_2Cl_2 solution at ambient temperature leads to the formation of red to red-violet colored betaines **8**, **10'**, **12** and **14'**, respectively. The kinetics of the bleaching process of betaines back to DHIs were found to take place in the second range in dichloromethane solution (53–96 s) and fit well the first order thermal back reaction. Some of these DHIs showed a higher photostability than the standard one. Interestingly, they are shown to act as efficient gelators for polar organic fluids, and obviously they exhibiting a thermosensitive response 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 chromene 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 photoresponsive materials and nanotechnology.

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1. Introduction

The term photochromism refers to the reversible transformation of a compound between two forms having different absorption spectra, with at least one of the reactions being driven by light [1,2]. If organic photochromic compounds are to find widespread use in photonic device applications such as erasable memory media and optical switching, several mandatory properties must be met. Fore-

most are thermal irreversibility, photofatigue resistance and high efficiency in rapid photoconversion processes [3–9]. An additional factor that cannot be downplayed is the ability to tailor the physical and chemical properties of the photochromic backbone in a facile, flexible and modular manner. This can only be accomplished by designing photochromic compounds that possess many different locations on their molecular skeletons where functional groups can be anchored.

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 [10]. Of particular interest is the design of externally addressable molecules that contain self-assembly elements, as these can give rise to so-called “smart materials” [11]. Such

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addressable molecules could include among others, photochromics, which can be used to bring about light-induced changes in the self-assembly [12,13] or environment-sensitive luminophores, which can provide valuable insight into the nature of the molecular aggregation within such assemblies [14]. Low-molecular weight (LMW) gelators have attracted much attention in recent years [15–17]. 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 [18]. 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 [19]. Several groups exploited these features for the development of “smart” LMW organogelators [20–25]. 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, diarylethene, stilbene or naphthopyran derivatives have been reported [9,26–28] in which the gelation was controlled by heat, light or acidity as external stimuli. Among various types of photochromic compounds, dihydroindolizine (DHI) which were developed by Dürr and co-workers [29,30] is one of the most promising photochromic families due to their excellent fatigue resistance and thermal stability in both isomeric forms, picosecond switching rate and high photochemical quantum yields [31,32]. Nowadays, it is possible to tune the absorption spectra of the colored forms, half-lives, photostability, colorability and solvatochromism by changing the substitution in the DHI regions [1,32–40]. To the best of our knowledge, this unique set of properties are advantages predominant exist in the DHI family among other photochromic families which will help to find applications.

In a continuation of our work dealing with the preparations and study the photochromic behavior of the dihydroindolizine systems, we present in this work for the first time the design of the photochromic organogelators that are based on the covalent association of a photostimulable dihydroindolizine and an acid-sensitive self-assembling unit. We report the synthesis and the gelation abilities of dihydroindolizine derivatives that incorporate an *N*-acyl-1,ω-amino acid moiety which have recently been reported to induce gelation of various organic fluids [9,27].

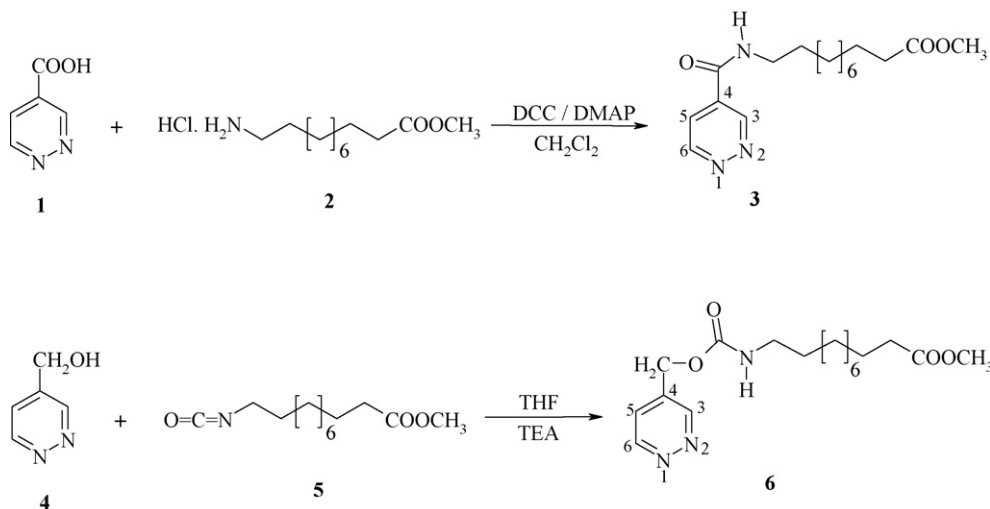
2. Results and discussion

2.1. Preparation of 11-aminoundecanoic acid pyridazine precursors **3**, **6**

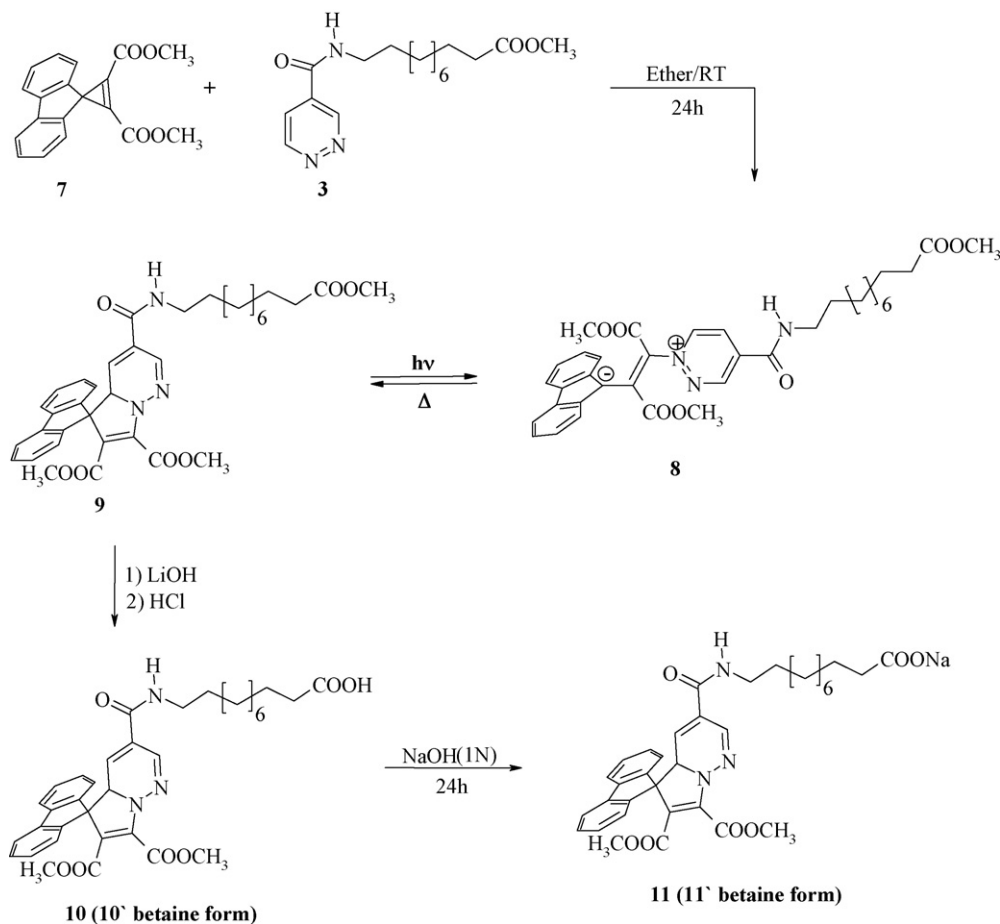
Pyridazine-4-carboxylic acid **1** and 4-hydroxymethyl pyridazine **4** were prepared following the published procedures [41,42]. Methyl 11-(pyridazine-4-carboxamido)undecanoate **3** was prepared according to the classic peptide coupling procedure in 26% yield via condensation of pyridazine 4-carboxylic acid **1** with methyl 11-aminoundecanoate hydrochloride **2** in CH₂Cl₂ at 0 °C and in presence of DCC and DMAP for 8 h (Scheme 1). On the other hand, addition of methyl 11-isocyanatoundecanoate **5** to pyridazine 4-methanol **4** in dry THF and presence of TEA at 73 °C for 22 h under nitrogen atmosphere, yielded the corresponding urethane derivative methyl 11-((pyridazin-4-ylmethoxy)carbonylamino)undecanoate **6** in 18% yield (Scheme 1). The pure heterocyclic bases **3** and **6** obtained via column chromatography using methylene chloride/hexane (3:7) as eluent. The chemical structure of **3** and **6** were established by both analytical and spectral tools. For example, the ¹H NMR spectra of the base **3** showed the following signals: multiplet at 1.31–1.76 ppm corresponding to the methylene protons between the amidic and ester groups. The two triplets at 2.54 and 3.01 ppm are due to the two CH₂ beside the ester and amidic groups, respectively. The two doublets at 8.12 and 8.96 ppm are corresponding to the pyridazine protons at 5 and 6 positions, respectively. On the other hand, the pyridazine proton at 3 position appears as a singlet at 9.20 ppm while the NH proton appears at 8.44 ppm.

2.2. Preparation of photochromic dihydroindolizines **9–11**, **13–15**

Electrophilic addition of spirocyclopropene **7** to methyl 11-(pyridazine-4-carboxamido)undecanoate **3** and methyl 11-((pyridazin-4-ylmethoxy)carbonylamino)-undecanoate **6** using the cyclopropene route [1] (Schemes 2 and 3) in dry ethereal solution at room temperature under dry nitrogen in the absence of light for 24 h led to the formation of the photochromic dihydroindolizines **9**, **13** in 34, 21% yield, respectively. The formation of DHIs **9** (Scheme 2), **13** (Scheme 3) proceeded by a cyclopropylallylanion rearrangement [29,30]. The dark colored betaines **8** (Scheme 2), **12** (Scheme 3) underwent 1,5-electrocyclization to give the corresponding DHIs **9**, **13**.



Scheme 1. Preparation outline of 11-methyl 4-pyridazine aminoundecanoate **3** and methyl 11-methoxycarbonyl 4-pyridazine aminoundecanoate **6**.



Scheme 2. Preparation outline of photochromic dihydroindolizines (DHIs) **9–11**.

Saponification of the ester DHIs **9**, **13** under mild condition using lithium hydroxide in ethanol yielded the corresponding acid DHIs **10**, **14** after mild acidification with HCl (pH 2–5). The sodium salt of DHIs **11**, **15** obtained via treatment of the corresponding acids DHIs **10**, **14** with 1NaOH in water/ethanol mixture at room temperature for 24 h.

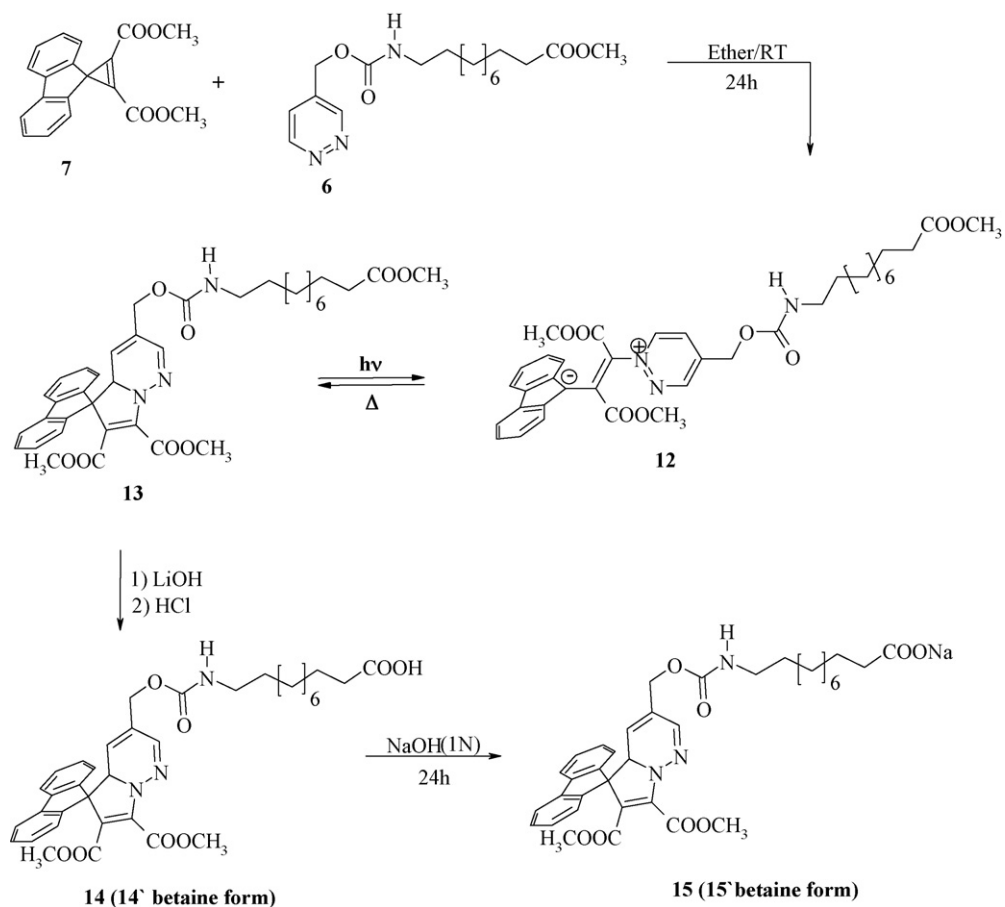
Characterizations of the new synthesized photochromic DHIs **9–11** and **13–15** were established by using spectral as well as analytical tools and they showed spectra fit well with the designed chemical structures. In addition, the chemical structure of DHI **13** was assigned by 2D-NMR spectroscopy. The ^1H - ^1H -correlation of DHI **13** was used to assign the protons of three region of DHI skeleton, especially the pyridazine ring (region C). The ^1H , ^1H -COSY spectrum both 2'- and 3'-methyl ester groups showed no coupling with other protons and appeared as two singlets 3.24 and 4.02 ppm. The 8'-CH signal was shifted to high field and appeared as a doublet of triplets at $\delta = 5.20$ ppm showing two coupling systems. The first is due to ^3J -coupling with the 8'a-CH, which appears as multiplet at $\delta = 4.33$ ppm, the second is due to ^4J -coupling with the CH_2 of the urethane group connected to the 6'-CH, which appears as a double doublet at $\delta = 5.90$ ppm. The higher field shift of the 8'a-CH to 5.33 ppm is attributed to the anisotropic effect of the fluorene moiety which makes this proton lie as a sandwich between the fluorene and pyridazine moieties. Interestingly, a ^5J -coupling at 5.28 ppm between 8'a-CH and CH_2 of the urethane group connected to the 6'-CH was recorded. These interesting ^4J and ^5J -couplings motivated us to study the NOESY spectra of some selected samples in this system. Further assignments of 8'CH, 8'a-CH as well as some other protons in the DHI skeleton were done by the aid of NOESY

spectrum of **13**. Herein, we observed that 8'a-CH at $\delta = 4.89$ ppm is close in space to both 8'-CH at $\delta = 5.20$ ppm, CH_2 of the urethane group connected to the 6'-CH and 1-CH of the fluorene moiety at $\delta = 7.74$ ppm. This observation proves that 8'a-CH is in 8'a-position and not at 8'-position. Indeed, the connectivity between 8'-CH, CH_2 of the urethane group connected to the 6'-CH and 8-CH of the fluorene part at $\delta = 7.65$ ppm was observed. This vicinity of 8'-CH with 8-CH proves the ^4J -coupling with the CH_2 of the urethane group connected to the 6'-CH and the pyridazine moiety is perpendicular to the fluorene skeleton as proved by a molecular modeling calculation of DHI **13**. It showed that the distance between both 8'a-CH, 8'-CH, CH_2 of the urethane group connected to the 6'-CH and 1-CH, 8-CH of the fluorene moiety is $<3 \text{ \AA}$ (Fig. 1).

2.3. Photophysical properties of the new photochromic DHIs **9**, **10** and **13**, **14** and their corresponding betaines **8**, **10'** and **12**, **14'** in solutions

2.3.1. Absorption spectra of DHIs **9**, **10** and **13**, **14** and their corresponding betaines **8**, **10'** and **12**, **14'**

Photophysical data pertinent to their photochromic properties were obtained from the absorption features of photochromic DHIs **9**, **10** and **13**, **14**. The DHIs **11**, **15** were not studied due to solubility in CH_2Cl_2 . Electronic spectra of the newly synthesized DHIs **9**, **10** and **13**, **14** were measured in dichloromethane solution using a UV/vis spectrophotometer with concentration of 1×10^{-4} mol/l at 23°C . All studied DHIs **9**, **10** and **13**, **14** are colorless to pale yellow in both the solid state and in dichloromethane solution (Table 1). The intensities ($\log \epsilon$) of these bands were found to be



Scheme 3. Preparation outline of photochromic dihydroindolizines (DHIs) **13**–**15**.

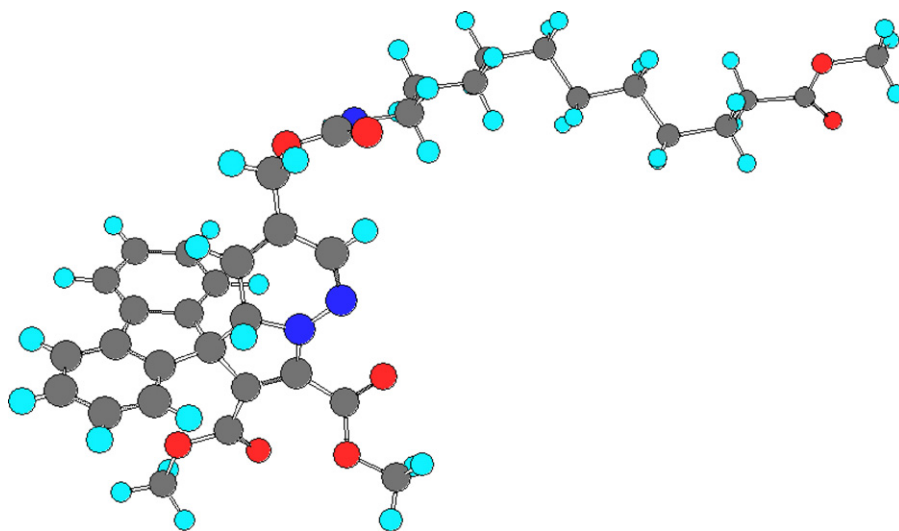


Fig. 1. Representation of the optimized (MM2) structure of DHI **13** (optimized energy = 36.85 kcal/mol).

Table 1
UV/vis absorption DHIs **9**, **10** and **13**, **14** and their corresponding betaines **8**, **10'** and **12**, **14'** and kinetic data of betaines **8**, **10'** and **12**, **14'** in the (s) range (recorded by multichannel UV/vis spectrophotometer) in CH_2Cl_2 solution (23 °C, $c = 1 \times 10^{-4}$ mol/l)

	λ_{max} DHI (nm)	$\log \epsilon$	λ_{max} betaine (nm)	k ($\times 10^{-3} \text{ s}^{-1}$)	$t_{1/2}$ (s)	Color of betaine
8/9	361	4.79	561	11.18	62	Red
10'/10	363	4.81	564	7.22	96	Red
12/13	346	4.30	553	13.07	53	Red-violet
14'/14	344	4.31	551	8.87	78	Red-violet

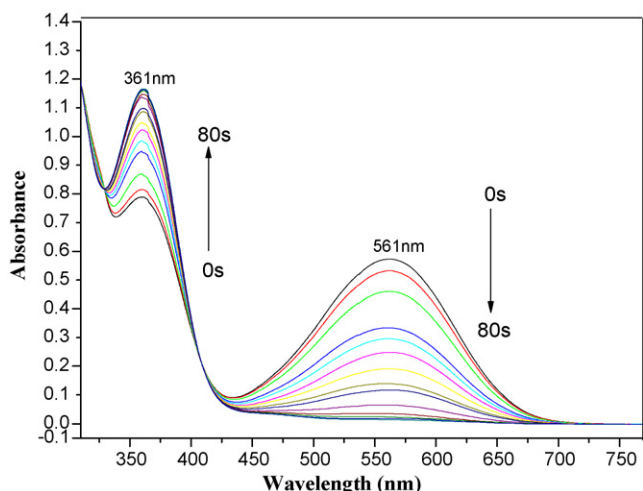


Fig. 2. Kinetic FT-UV/vis spectrum of the thermal fading of betaine **8** to DHI **9** (cycle time = 5 s, run time = 80 s) in CH_2Cl_2 ($c = 1 \times 10^{-4}$ mol/l at 253 K).

between 4.30 and 4.79. The absorption of DHIs **9**, **10** and **13**, **14** were observed in the UV-region and showed absorption maxima lied between 346 and 363 nm (Table 1). It is noticeable that the absorption is depending on the type of substitutions in the 4-position of the pyridazine part. When the amidic carbonyl connected directly to the pyridazine as in case of DHIs **9**, **10**, a bathchromic shift of about 18 nm compared with the DHIs **13**, **14** was recorded. This may be attributed to the electron attracting effect of the carbonyl group. On the other hand, the esters substituted DHIs **9**, **13** showed no pronounced effect compared with the acids DHIs **10**, **14**. As established previously [1], these absorption bands can be assigned to the locally excited π - π^* -transition (LE) located in the butadienyl-vinyl-amine chromophore [1,31–34] of the DHIs **5** (Table 1).

Irradiation of the DHIs **9**, **10**, **13** and **14** CH_2Cl_2 solution with polychromatic light led to respectively the formation of red to red-violet colored betaines **8**, **10'**, **12** and **14'**. The absorption maxima of the colored betaines **8**, **10'**, **12** and **14'** were found to be between 551 and 564 nm. A bathochromic shift of about 10 nm between betaines **8**, **10'** and **12**, **14'** which leads to color changes was recorded.

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 lie between 53 and 96 s. A pronounced increasing of the half-lives of the acid substituted betaines **10'**, **14'** than their corresponding ester betaines **8**, **12** by about 34 s was observed (Table 1). This is 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. The presence of the isobestic point proved that the thermal 1,5-electrocyclization follows the first order back reaction (Fig. 2).

2.3.2. Photo-fatigue resistance of photochromic DHIs **9**, **10** and **13**, **14** and their corresponding betaines **8**, **10'** and **12**, **14'** in dichloromethane solution ($c = 1 \times 10^{-4}$ mol/l) at 253 K

In studying the quality of a photochromic system or in other terms the thermal full reversibility of a specific photochromic molecule is the problem of carrying out a large number of colorization-decolorization cycles arises frequently. The gradual loss of ability to change color by exposure to visible or ultraviolet light in this context has been termed fatigue [1]. Gautron [43]

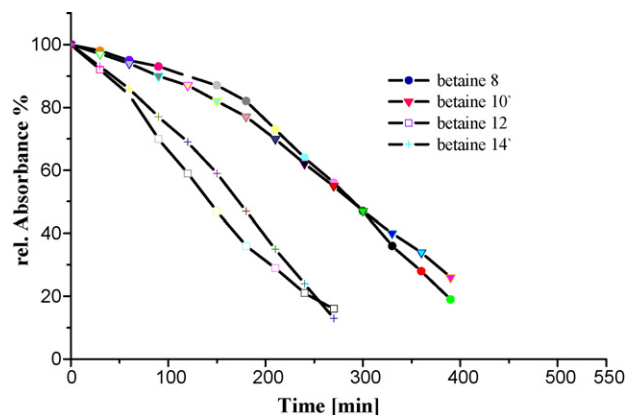


Fig. 3. Time-relative absorbance relationship of the photodegradation experiment for determination the t_{30} -value of betaines **8**, **10'**, **12**, **14'** in CH_2Cl_2 at ambient temperature.

has advanced a quantitative approach to measure the fatigue in photochromic systems.

Upon irradiation of DHIs **9**, **10**, **13** and **14** with polychromatic light ($\lambda = 200$ – 400 nm) in CH_2Cl_2 solution at room temperature, the colored betaines **8**, **10'**, **12** and **14'** were produced. When irradiation is continued they decompose after some time. However if oxygen is removed, these systems are noticeably more stable. It is possible that in the presence of oxygen, the betaines **8**, **10'** and **12**, **14'** acts as a sensitizer towards singlet oxygen [1].

The initial absorbance of pyridazine DHIs **9**, **10** and **13**, **14** was measured using a 3 ml quartz cell UV/vis spectrometer in degassed CH_2Cl_2 ($c = 1 \times 10^{-4}$ mol/l) solution. Before the start of the degradation experiment, the degassed DHIs **9**, **10** and **13**, **14** solutions were irradiated for 3 min to achieve equilibrium between DHIs and betaines.

At the beginning, 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 initial extinction (Fig. 3). This time is called in our work as t_{30} -value and the stability factor (F) can be recognized by the ratio of t_{30} -values of the measured compounds and the t_{30} -value of dicyanopyridazine-betaine, which used as standard [1,29–39].

From the photodegradation data represented in Table 2, it is clear that, the betaine form of the DHI **10'** ($t_{30} = 370$ min) is the most stable betaine under investigation and more stable than the standard dicyano-pyridazine DHI ($t_{30} = 243$ min) by a factor of 1.50. The betaines forms **12**, **14'** which based on urethane system showed a lower t_{30} -value than the amidic betaines **8**, **10'** by a factor of about 0.5. This is may be attributed to the weak urethane bond which can be easily cleaved with UV-irradiation compared with amidic betaines **8**, **10'**. In addition, the betaines **12**, **14'** showed a lower t_{30} -value by factor of 0.14 and 0.28 compared with the standard dicyano-pyridazine DHI.

Table 2

Photodegradation data of betaines **8**, **10'** and **12**, **14'** in dichloromethane ($c = 1 \times 10^{-4}$ mol/l) at 23 °C

Betaines	$t_{1/2}$ (s)	λ_{max} betaine (nm)	t_{30} -betaine/DHI (min)	F
8	62	561	350	1.37
10'	96	564	370	1.50
12	53	553	176	0.72
14'	78	551	209	0.86
Standard	56.2	535	243	1.0

2.4. Multi-addressable gelation abilities of new synthesized photochromic DHIs **9**, **10**, **13** and **14** in organic fluids

Successful synthesis of organized supramolecular assemblies is the fundamental step on the way to new materials or functional supramolecular devices [44–46]. Recently, thermoreversible physical gels generated from relatively low molecular mass organic molecules [47] have emerged as a fascinating new class of self-assembling organic materials which opens up new prospects in elaborating nanostructured materials and devices. Although many aspects of gelation remain unclear [48] and the variety of low molecular mass organogelators is still increasing [10], it is usually stated that gel formation relies on the spontaneous self-recognition of individual organic gelators into fiberlike structures, which in turn assemble into larger aggregates. Thus, solvents when entrained within the interstices of a network, became immobilized by surface tension. Aggregation of low molecular mass organogelators is usually driven by specific noncovalent 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 [49]. 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 [50,51]. Organic photochromes [51,52] 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 [52].

The photochromic reactions of 1,2-bis-thienylcyclopentenes functionalized with two amide groups have been reported to largely influence the medium viscosity [50]. However, incorporation of diarylethene does not guarantee photoswitchable macroscopic phase transition as reported recently in two very elegant studies. In fact these derivatives covalently linked to a chiral moiety have been shown to reversibly control supramolecular chirality switching between different chiral aggregates in the gel phase [10] and multi-switchable cholesterol-based gelators have been reported to be photochromic without any phase changes [9]. Various compounds based on 11-aminoundecanoic acid, hereafter denoted by 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 [9]. As an attempt to obtain new functional organogelators with multiple-switch applications, we have rationally designed, for the first time, photochromic organogelators based on dihydroindolizine containing AUDA in the pyridazine part of DHI skeleton.

In this study, photochromic organogelators that are based on the covalent association of a photostimulable dihydroindolizines and an acid-sensitive self-assembling unit. We report the gelation abilities of DHI derivatives that incorporate an *N*-acyl-1, ω -amino acid moiety various organic fluids [9].

Both amide and urethane ester substituted DHIs **9** and **13** showed a high solubility in most organic fluids and no gelation abil-

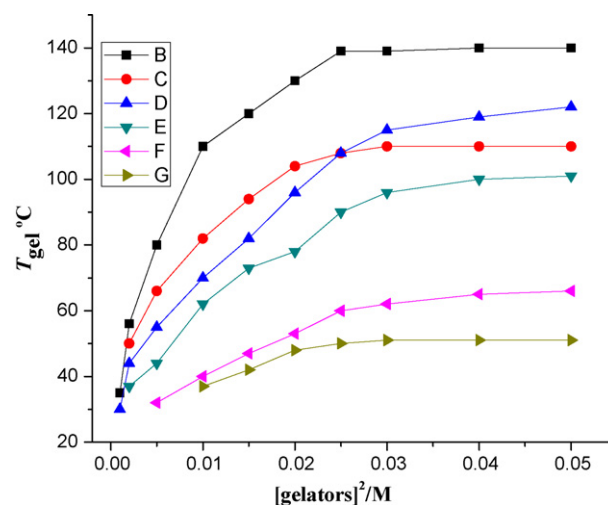


Fig. 4. T_{gel} of (B) **11**-Na in DMF, (C) **15**-Na in DMF, (D) **11**-Na in DMSO, (E) **15**-Na in DMSO, (F) **11**-H in toluene and (G) **14**-H in toluene as a function of organogelator concentration.

ities were observed. The acid substituted DHIs **10** and **14** showed gelation abilities in toluene (Figs. 4 and 5) and some of higher alcohols (C8–C12). These acids are completely soluble in DMF and DMSO and no gelation abilities in these fluids were observed. The gelation behavior was first investigated via the inverted test tube method [9,13,14]. DMF and DMSO 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 [9]. Furthermore, compounds **11**-Na and **15**-Na are insoluble in most of the usual organic fluids. They are insoluble in DMF and DMSO, but upon heating at 80–150 °C and sonication, they gradually dissolved. Upon cooling to ambient temperature, gels are readily obtained which are then stable for months (Fig. 6a and b). Both chromenic derivatives were found to gelate these fluids over a wide range of concentration.

The gel-to-sol phase transition temperatures (hereafter denoted T_{gel}) of DMF gels in a concentration of 1 wt%/vol are 141 and 117 °C for **11**-Na and **15**-Na, respectively, which could be considered to act as a supergelator. The neutral carboxylic acid derivatives **10** and **14** were found to be very soluble in DMF and DMSO at 25 °C but they showed gelation ability in toluene with T_{gel} of 71 and 64 °C for 10-H, 14-H, respectively. Upon addition of sodium hydroxide, they rapidly convert to the gel state. So, for the targeted dihy-

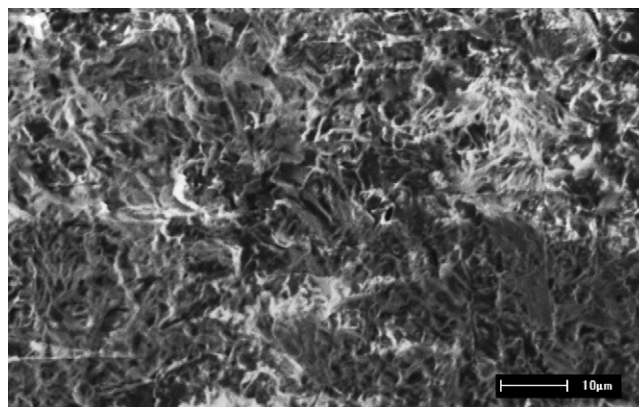


Fig. 5. Electron scan microscope (ESM) of the free acid substituted DHI **14** after gelation in toluene.

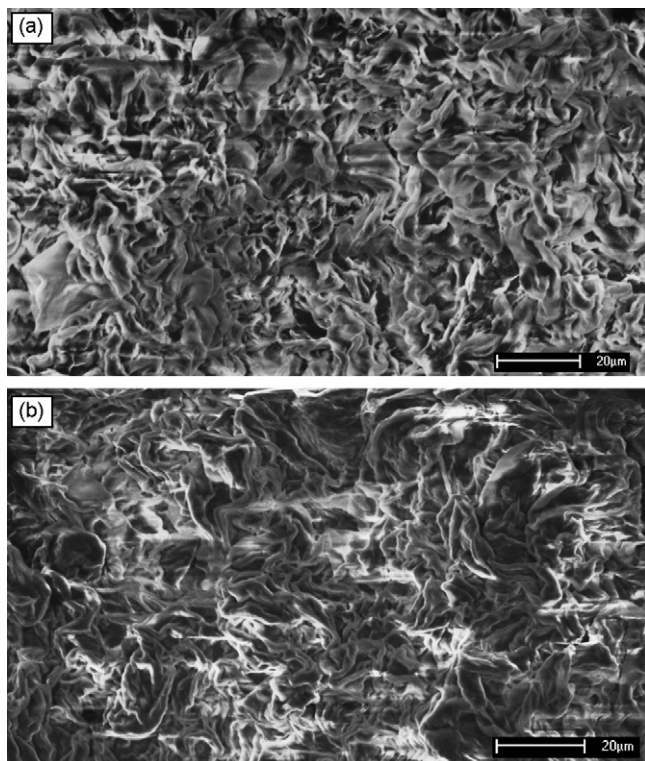


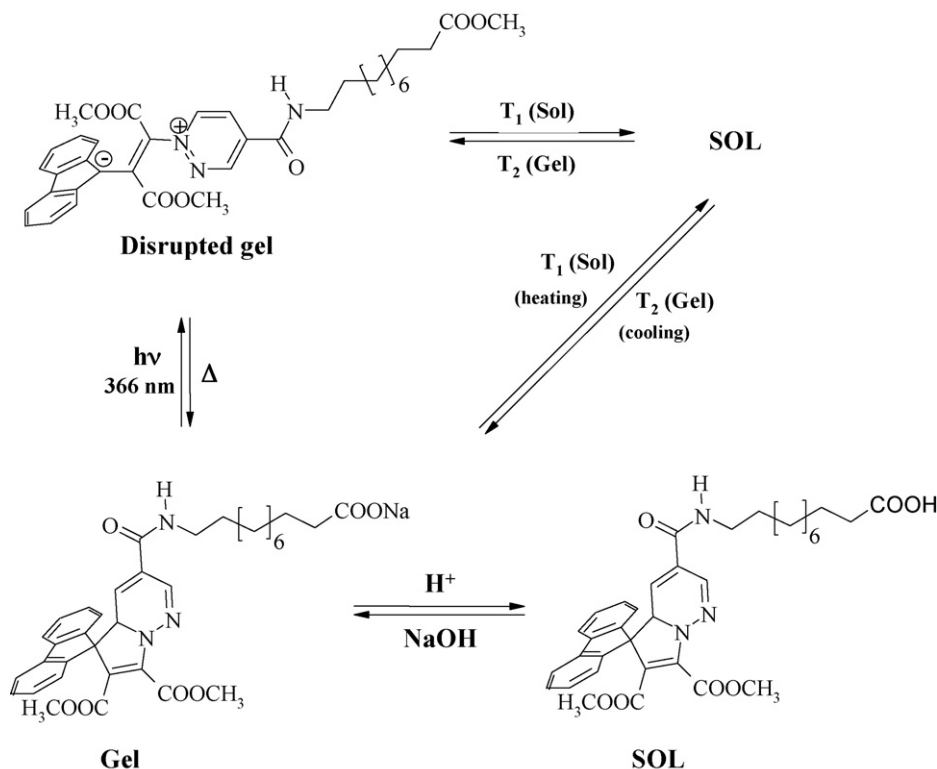
Fig. 6. Electron scan microscope (ESM) of the gels: (a) **11-Na** in DMF and (b) **15-Na** in DMSO.

droindolizines, the interesting gelation ability is retained and the presence major 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 **11-Na** and **15-Na** are formed (Fig. 6a and b). The morphology of gels was based on long fibers which form an entangled network. The diameter of the smallest entities which can be distinguished is 60–80 nm. This represents several gelator lengths. 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 amides I and II regions. The maxima of these peaks are characteristics for the presence of the hydrogen-bonded amide group [53].

Alternative evidence supporting the self-aggregation of dihydroindolizines in DMF_{gel} was provided by rheological measurements [54]. The frequency sweep experiment shows that the elastic modulus G' and the loss modulus G'' are fairly independent of frequency over more than three decades. Typical values are here reported for 1.5 wt%/vol of **15-Na** in DMF. The G' value (1×10^4 Pa) was observed to be one order of magnitude higher than that of G'' (1×10^3 Pa) indicating that the system still exhibits a solid like behavior.

2.5. Irradiation of gels

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 an inverted cell set up. One can observe the appearance of



Scheme 4. Illustration of interconversion between the different molecular species and corresponding macroscopic states upon external stimuli in **10-H** and **11-Na** DHIs. Similar behavior was observed in case of **14-H** and **15-Na** DHIs.

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 is taking place. The primary photoinduced ring opening event 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 to the T_{gel} values which are invariable.

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 and DMF, and more interestingly this transformation is accompanied by the gel-to-sol phase transition within 4 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. 1 mM). UV-irradiation ($\lambda > 530$ nm) of the photoinduced sols gave rise to the photocycloreversion to reform **11**-Na and **15**-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).

3. Conclusions

We have succeeded in building a photoresponsive DHs unit based on the sodium *N*-acyl-11-aminoundecanoate scaffold. This modification does not suppress the gelation ability. 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 photoinduced structural changes of the photochromic subunit. Upon addition of sodium hydroxide, the DMF and DMSO homogeneous solutions of neutral carboxylic species are reversibly converted into gels. As expected, the multi-addressable molecular switches operate at supramolecular scale, the phase changes among gel and sol being independently driven by acidity, light and temperature. These systems represent example of smart super gel which display the ability to respond to various changes of their environment. These multi-addressable photochromic properties of newly synthesized dihydroindolizines will makes it promising applications in the fields of opto and electronic smart materials, logic gate and other molecular photonic devices. All these applications will open a new era in the field of sensor materials as will as in nanotechnology.

4. Experimental

The solvents used (Aldrich or Merck were spectroscopic grade) were dried, according to standard procedures [55], 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 **7** was obtained via photolysis of the corresponding pyrazoles prepared according to reported procedures [1,29,30]. Photolysis was carried out in the photochemical reactor of Schönberg [56] made from Pyrex ($\lambda > 290$ nm). The source of irradiation was a high-pressure mercury lamp (Philips HPK 125W). 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 Brüker DRX 500 spectrometer (500 MHz) in $CDCl_3$ using TMS as the internal standard. Chemical shifts (δ) are reported in ppm. FT-IR measurements were performed using a PerkinElmer 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-dihydroxy-benzoic acid in dioxane as matrix. Microanalyses were determined in the microanalytical laboratory at the CNRS, Vernaison. 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. Mass spectra were recorded on a Mat-90, FINNIGAN MAT mass spectrometer. UV-spectra were recorded using FT-UV/vis HP 6543 computer-spectrometer. The experimental details and full characterizations for all synthesized DHs **9–11** and **13–15** are described below. Further structural modifications and gelation abilities of DHs based gelators will be presented in the forthcoming paper [57].

4.1. Dimethyl-[11-methyl-7'-carbonylamino undecanoate]-1'H-spiro [fluorene-9,1'-pyrrolo[1,2-b] pyradazine]-2',3'-dicarboxylate (**9**)

A mixture spirocyclopropene **7** (306 mg, 1 mmol) in 75 ml dry ether and methyl 11-(pyridazine-4-carboxamido)undecanoate **3** (321 mg, 1 mmol) was stirred at room temperature under dry N_2 with exclusion of light for 24 h (TLC-controlled). Ether was removed under reduced pressure and the residue was chromatographed twice on silica gel (dichloromethane). The pure product was obtained (213 mg, 34% yield) after recrystallization from ethanol-hexane (1:1) as pale yellow crystals: mp = 147 °C; 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.76–7.75 (dd, $J = 7.50$ Hz, 2H, CH-arom.), 7.51–7.49 (d, $J = 7.50$ Hz, 1H, CH-arom.), 7.40–7.53 (m, 4H, CH-arom.), 7.16–7.18 (dd, $J = 7.50$ Hz, 1H, CH-arom.); 6.24 (t, $J = 4.9$ Hz, 1H, NH), 5.94–5.97 (t, $J = 2.2$ Hz, 1H, 6'-CH), 5.29–5.31 (t, $J = 2.2$ Hz, 1H, 8'a-CH), 4.88–4.91 (dt, $J = 2.2$ Hz, 1H, 8'-CH); 4.17 (s, 3H, 2'-CH₃), 3.65 (s, 3H, COOCH₃), 3.38 (s, 3H, 3'-CH₃), 3.23 (m, 2H, CH₂NH), 2.29 (t, $J = 7.2$ Hz, 2H, CH₂-COOCH₃), 1.50–1.60 (m, 4H, CH₂CH₂COOCH₃ and CH₂CH₂NH), 1.25–1.35 (m, 12H, 6 \times CH₂); IR (KBr): ν (cm^{-1}) = 3337 (NH), 3059 (C-H, arom.), 2840–2984 (C-H, aliph.), 1752 (3'-C=O), 1728 (7'-C=O); 1706 (2'-C=O), 1698 (11-C=O), 1615 (C=N), 1550 (C=C), 1444, 1398, 1340, 1284, 1229, 1133, 1031, 970, 861, 755; HR-MS *m/e* (%) 627.7324 [M^+]; elemental analysis for $C_{36}H_{41}N_3O_7$: Calc.: C, 68.88; H, 6.58; N, 6.69; found (%): C, 68.89; H, 6.57; N, 6.70.

4.2. Dimethyl-[11-carboxy-7'-carbonylamino undecanoic acid]-1'H-spiro [fluorene-9,1'-pyrrolo[1,2-b] pyradazine]-2',3'-dicarboxylate (**10**)

A mixture of compound **9** (614 mg, 1 mmol) and lithium hydroxide (150 mg, 6.25 mmol) were dissolved in 20 ml of methanol and 5 ml of water and then stirred at 20 °C for 6 h. Methanol was

removed, and the residue was dissolved in water and acidified to pH 2 with a 2 N hydrochloride solution and then stirred for 5 h. The product was extracted with dichloromethane (3 × 40 ml). The organic layer was dried over MgSO₄, and the residue was chromatographed on silica gel (7/3 dichloromethane/ethyl acetate as eluent) to yield a white solid (601 mg, 98%): mp 182 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.71–7.74 (dd, *J* = 7.50 Hz, 2H, CH-arom.), 7.54–7.57 (d, *J* = 7.50 Hz, 1H, CH-arom.), 7.48–7.56 (m, 4H, CH-arom.), 7.14–7.16 (dd, *J* = 7.50 Hz, 1H, CH-arom.); 5.94–5.97 (t, *J* = 2.2 Hz, 1H, 6'-CH), 5.29–5.31 (t, *J* = 2.2 Hz, 1H, 8'a-CH), 4.88–4.91 (dt, *J* = 2.2 Hz, 1H, 8'-CH); 4.32 (m, 1H, NH), 4.17 (s, 3H, 2'-CH₃), 3.44 (m, 2H, CH₂NH), 3.38 (s, 3H, 3'-CH₃), 2.32 (t, *J* = 7.2 Hz, 2H, CH₂COOH), 2.29 (t, *J* = 7.2 Hz, 2H, CH₂-COOCH₃), 1.50–1.60 (m, 4H, CH₂CH₂COOCH₃ and CH₂CH₂NH), 1.20–1.40 (m, 12H, 6xCH₂); IR (KBr): ν (cm⁻¹) = 3370 (br. OH), 3337 (NH), 3059 (C-H, arom.), 2840–2984 (C-H, aliph.), 1752 (3'-C=O), 1728 (7'-C=O); 1706 (2'-C=O), 1692 (11-C=O), 1619 (C=N), 1547 (C=C), 1440, 1398, 1347, 1281, 1233, 1138, 1027, 971, 865, 757; HR-MS *m/e* (%) 613.6764 [M⁺]; elemental analysis for C₃₅H₃₉N₃O₇: Calc.: C, 68.50; H, 6.41; N, 6.85; found (%): C, 68.47; H, 6.43; N, 6.87.

4.3. Dimethyl-[11-carboxy-7'-carbonylamino]undecanoic acid sodium salt]-1'-H-spiro [fluorene-9,1'-pyrrolo[1,2-b] pyridazine]-2',3'-dicarboxylate (**11**)

A mixture of **10** (307 mg, 0.5 mmol) and 500 mg of a 1 N sodium hydroxide solution was stirred in methanol (10 ml) at room temperature for 3 h. The solvent was removed under vacuum. The product was washed with diethyl ether and then dried under vacuum to yield a white solid (305 mg, 96%): mp (dec) 218 °C; ¹H NMR (400 MHz, CD₃OD) δ (ppm) 7.70–7.73 (dd, *J* = 7.50 Hz, 2H, CH-arom.), 7.53–7.56 (d, *J* = 7.50 Hz, 1H, CH-arom.), 7.48–7.52 (m, 4H, CH-arom.), 7.15–7.17 (dd, *J* = 7.50 Hz, 1H, CH-arom.); 5.93–5.95 (t, *J* = 2.2 Hz, 1H, 6'-CH), 5.30–5.32 (t, *J* = 2.2 Hz, 1H, 8'a-CH), 4.89–4.92 (dt, *J* = 2.2 Hz, 1H, 8'-CH); 4.34 (m, 1H, NH), 4.18 (s, 3H, 2'-CH₃), 3.46 (m, 2H, CH₂NH), 3.37 (s, 3H, 3'-CH₃), 3.27 (m, 2H, CH₂NH), 2.37 (t, *J* = 7.2 Hz, 2H, CH₂COONa), 1.51–1.57 (m, 4H, CH₂CH₂COONa and CH₂CH₂NH), 1.24–1.36 (m, 12H, 6xCH₂); IR (KBr): ν (cm⁻¹) = 3340 (NH), 3062 (C-H, arom.), 2844–2972 (C-H, aliph.), 1757 (3'-C=O), 1734 (7'-C=O), 1700 (2'-C=O), 1687 (11-C=O), 1623 (C=N), 1557 (C=C), 1441, 1383, 1344, 1287, 1239, 1134, 1034, 973, 878, 742; HR-MS *m/e* (%) 635.683676 [M⁺]; elemental analysis for C₃₅H₃₈N₃O₇Na: Calc.: C, 66.13; H, 6.03; N, 6.61; found (%): C, 66.15; H, 6.00; N, 6.60.

4.4. Dimethyl-[11-methyl-(7'-yl-acetamido)undecanoate]-1'-H-spiro [fluorene-9,1'-pyrrolo[1,2-b] pyridazine]-2',3'-dicarboxylate (**13**)

A mixture spirocyclopropene **7** (306 mg, 1 mmol) in 75 ml dry ether methyl 11-((pyridazin-4-ylmethoxy)carbonylamino)undecanoate **6** (351 mg, 1 mmol) was stirred at room temperature under dry N₂ with exclusion of light for 24 h (TLC-controlled). Ether was removed under reduced pressure and the residue was chromatographed twice on silica gel (dichloromethane). The pure product was obtained (138 mg, 21 yield) after recrystallization from ethanol–hexane (2:8) as pale yellow crystals: mp = 78 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.76–7.73 (dd, *J* = 7.50 Hz, 2H, CH-arom.), 7.68–7.63 (d, *J* = 7.50 Hz, 1H, CH-arom.), 7.46–7.51 (m, 4H, CH-arom.), 7.17–7.19 (dd, *J* = 7.50 Hz, 1H, CH-arom.); 6.20 (t, *J* = 4.9 Hz, 1H, NH), 5.88–5.92 (t, *J* = 2.2 Hz, 1H, 6'-CH), 5.32–5.34 (t, *J* = 2.2 Hz, 1H, 8'a-CH), 5.28 (s, 2H, CH₂O), 5.19–5.21 (dt, *J* = 2.2 Hz, 1H, 8'-CH); 4.70 (m, 1H, CH₂NHCO), 4.02 (s, 3H, 3'-CH₃), 3.64 (s, 3H, COOCH₃), 3.24 (s, 3H, 2'-CH₃), 3.20 (m, 2H, CH₂NH), 3.18 (m, 2H, CH₂NH), 2.36 (t, *J* = 7.5 Hz, 2H, CH₂COOCH₃), 1.44–1.56 (m,

4H, CH₂CH₂COOCH₃ and CH₂CH₂NH), 1.27–1.32 (m, 12H, 6xCH₂); IR (KBr): ν (cm⁻¹) = 3342 (NH), 3040 (C-H, arom.), 2865–2999 (C-H, aliph.), 1754 (3'-C=O), 1728 (8-C=O), 1700 (2'-C=O), 1694 (11-C=O), 1617 (C=N), 1534 (C=C), 1456, 1395, 1344, 1270, 1237, 1120, 1046, 950, 886, 751; HR-MS *m/e* (%) 657.7278 [M⁺]; elemental analysis for C₃₇H₄₃N₃O₈: Calc.: C, 67.56; H, 6.59; N, 6.39; found (%): C, 67.59; H, 6.61; N, 6.36, 3370.

4.5. Dimethyl-[11-(7'-yl-acetamido)undecanoic acid]-1'-H-spiro [fluorene-9,1'-pyrrolo[1,2-b] pyridazine]-2',3'-dicarboxylate (**14**)

A mixture of ester **13** (329 mg, 0.5 mmol) and lithium hydroxide (150 mg, 6.25 mmol) was dissolved in 10 ml of methanol and 3 ml of water and then stirred at 20 °C for 6 h. Methanol was removed, and the residue was dissolved in water and acidified to pH 2 with a 2 N hydrochloride solution and then stirred for 5 h. The product was extracted with dichloromethane (3 × 30 ml). The organic layer was dried over MgSO₄ and concentrated. The resulting residue was chromatographed on silica gel (9/1 dichloromethane/ethyl acetate as eluent) to yield a white solid (148 mg, 46%): mp 119–121 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.71–7.75 (dd, *J* = 7.50 Hz, 2H, CH-arom.), 7.73–7.76 (d, *J* = 7.50 Hz, 1H, CH-arom.), 7.44–7.50 (m, 4H, CH-arom.), 7.19–7.21 (dd, *J* = 7.50 Hz, 1H, CH-arom.); 6.24–6.26 (t, *J* = 4.9 Hz, 1H, NH), 5.85–5.98 (t, *J* = 2.2 Hz, 1H, 6'-CH), 5.31–5.33 (t, *J* = 2.2 Hz, 1H, 8'a-CH), 5.34 (s, 2H, CH₂O), 5.21–5.24 (dt, *J* = 2.2 Hz, 1H, 8'-CH); 4.71–4.74 (m, 1H, CH₂NHCO), 4.10 (s, 3H, 3'-CH₃), 3.24 (s, 3H, 2'-CH₃), 3.24 (m, 2H, CH₂NH, CH₂NH), 2.32 (t, *J* = 7.5 Hz, 2H, CH₂COOH), 1.40–1.64 (m, 4H, CH₂CH₂COOH and CH₂CH₂NH), 1.20–1.30 (m, 12H, 6xCH₂); IR (KBr): ν (cm⁻¹) = 3366 (br. OH), 3340 (NH), 3032 (C-H, arom.), 2860–2980 (C-H, aliph.), 1734 (3'-C=O), 1719 (8-C=O); 1690 (2'-C=O), 1694 (11-C=O), 1609 (C=N), 1586 (C=C), 1458, 1402, 1364, 1271, 1238, 1127, 1036, 961, 884, 744; HR-MS *m/e* (%) 643.7324 [M⁺]; elemental analysis for C₃₆H₄₁N₃O₈: Calc.: C, 67.17; H, 6.42; N, 6.53; found (%): C, 67.18; H, 6.40; N, 6.55.

4.6. Dimethyl-[11-(7'-yl-acetamido)undecanoic acid sodium salt]-1'-H-spiro [fluorene-9,1'-pyrrolo[1,2-b] pyridazine]-2',3'-dicarboxylate (**15**)

A mixture of acid **14** (322 mg, 0.5 mmol) and 500 mg of 1 N NaOH was stirred in methanol (10 ml) at room temperature for 3 h. The solvent was removed under vacuum, and the product was washed with diethyl ether and dried to yield a white solid (320 mg, 96%): mp (dec) 152–154 °C; ¹H NMR (400 MHz, CD₃OD) δ 7.70–7.73 (dd, *J* = 7.50 Hz, 2H, CH-arom.), 7.70–7.74 (d, *J* = 7.50 Hz, 1H, CH-arom.), 7.39–7.45 (m, 4H, CH-arom.), 7.10–7.15 (dd, *J* = 7.50 Hz, 1H, CH-arom.); 6.27–6.29 (t, *J* = 4.9 Hz, 1H, NH), 5.80–5.88 (t, *J* = 2.2 Hz, 1H, 6'-CH), 5.27–5.28 (t, *J* = 2.2 Hz, 1H, 8'a-CH), 5.30 (s, 2H, CH₂O), 5.22–5.24 (dt, *J* = 2.2 Hz, 1H, 8'-CH); 4.74–4.78 (m, 1H, CH₂NHCO), 4.17 (s, 3H, 3'-CH₃), 3.26 (s, 3H, 2'-CH₃), 3.20 (m, 2H, CH₂NH), 2.37 (t, *J* = 7.5 Hz, 2H, CH₂COONa), 1.47–1.61 (m, 4H, CH₂CH₂COONa and CH₂CH₂NH), 1.22–1.28 (m, 12H, 6xCH₂); IR (KBr): ν (cm⁻¹) = 3321 (NH), 3043 (C-H, arom.), 2868–2989 (C-H, aliph.), 1731 (3'-C=O), 1710 (8-C=O); 1697 (2'-C=O), 1691 (11-C=O), 1600 (C=N), 1581 (C=C), 1460, 1411, 1370, 1262, 1230, 1124, 1037, 963, 890, 757; HR-MS *m/e* (%) 665.6941 [M⁺]; elemental analysis for C₃₆H₄₀N₃O₈Na: Calc.: C, 64.95; H, 6.06; N, 6.31; found (%): C, 64.97; H, 6.04; N, 6.33.

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