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Photochromism of dihydroindolizines part VII: multiaddressable photophysical properties of new photochromic dihydroindolizines bearing substituted benzo[i]phenanthridine as a fluorescing moiety†

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ABSTRACT: Sixteen benzo[i]phenanthridine derivatives **8a-p** were prepared via photocyclization of *cis-trans* substituted 4-styrylquinolines in low-to-moderate yields. The chemical structure of the photocyclized benzo[i]phenanthridine derivatives was unambiguously elucidated by means of both spectral and analytical tools. The photochromic (PC) dihydroindolizines (DHIs) **8a-p** based on benzo[i]phenanthridines were prepared in 19–57% yields via nucleophilic addition of benzo[i]phenanthridines **4a-p** to spirocyclopropenes **5**. The 1D, 2D, NOESY NMR spectra, mass spectrometry, and elemental analysis were used for characterization of the chemical structures of the newly synthesized DHIs **8a-p**. Developing and tuning of the photophysical properties of the synthesized compounds by substituents in the base part have been achieved. The absorption maxima (λ_{max}) and the half-lives ($t_{1/2}$) of the colored zwitterionic forms **7a-p** were detected in all cases by flash-photolysis measurements due to the fast 1,5-electrocyclization back to the DHI system. Irradiation of DHI **8a-p** in CH_2Cl_2 solution with polychromatic light leads to the formation of green to green–blue colored betaines **7a-p** after cooling with liquid nitrogen. The kinetics of the fast bleaching process of betaines **7a-p** to DHIs **8a-p**, studied by flash photolysis as well as low temperature FT-UV/VIS, were found to take place in the millisecond range (432–2675 ms) in dichloromethane solution and fitted well a first-order thermal back reaction. The fluorescence spectra as well as the fluorescence quantum yield were studied. Noticeable bathochromic and hypsochromic shifts in the emission spectra by changing the substituents in the base part were monitored. Interestingly, the photo-fatigue resistance of some studied betaines **7a-p** showed a higher t_{30}-value than the standard one (dicyanopyridazine DHI). Large solvatochromic effects on the absorption maxima (λ_{max}) as well as a substantial increase in the half-lives ($t_{1/2}$) with solvent polarity of betaines **7a-p** were also observed. The multiaddressable PC properties of DHIs **8a-p** will help these compounds to find applications.

KEYWORDS: photocyclization; photochromism; dihydroindolizines (DHIs); flash photolysis; fluorescence; photo-fatigue; solvatochromism

INTRODUCTION

In the recent years, the design and synthesis of organic photochromics (PCs)[1a] have attracted considerable attention because of their potential applications to molecular devices, such as high density optical memories[1–3] and photo-optical switching,[4–6] optically switchable gratings,[7–9] and non-linear optics.[10] Extensive research has been devoted to study the molecules whose physical properties can be reversibly switched using light. This is due to the possibility of such materials to give a high lateral resolution and short switching time as well as to have an almost instantaneous verification of written data and photo-optical technology.[4–8] The design of light-driven molecular switches is an active area of research, since they are crucial for devices that operate at the molecular and supramolecular levels,[11–17] A PC material is characterized by its ability to undergo reversible transitions between two states that have different optical properties. The transition in at least one direction should occur when the material is exposed to electromagnetic radiation while the transition in the other direction could be accomplished by either electromagnetic radiation of different wavelength or by some other processes (e.g., thermally).[1a]

Among various thermally reversible PC compounds, dihydroindolizine derivatives which were discovered and

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†This work is dedicated to Prof. Dr Heinz Dürr on the occasion of his 72nd birthday.

developed by Dürr[18,19] in 1979 are the most promising compounds because of their fatigue resistant and wide range lifetimes as well as absorption spectra of the colored betaine forms. 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 dihydroindolizines (DHI) regions.[1,20–26] To the best of our knowledge, this unique set of properties of the DHI family will help to find applications.

In a continuation of our work dealing with the preparation and PC behavior of the dihydroindolizine systems, the present work will shed more light on the multifunctional PC properties of a new type of PC dihydroindolizines bearing a substituted benzo[i]phenanthridine unit. The fluorescence spectra of this family will confer another important property[27–44] (S. A. Ahmed, C. Weber, Z. A. Hozien, Kh. M. Hassan, A. A. Abdel-Wahab, H. Dürr, unpublished results). In addition, the photocyclization of 4-styrylquinolines to substituted benzo[i]phenanthridines as precursors for the synthesis of the desired DHIs is studied.

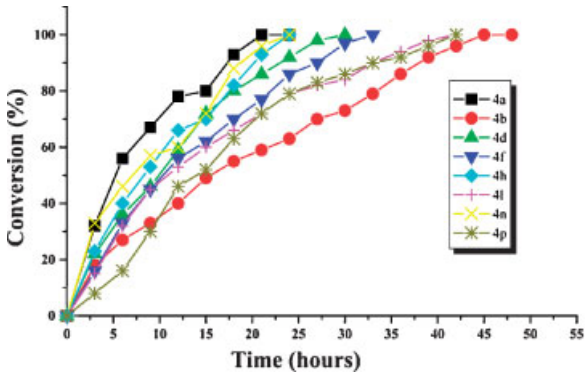


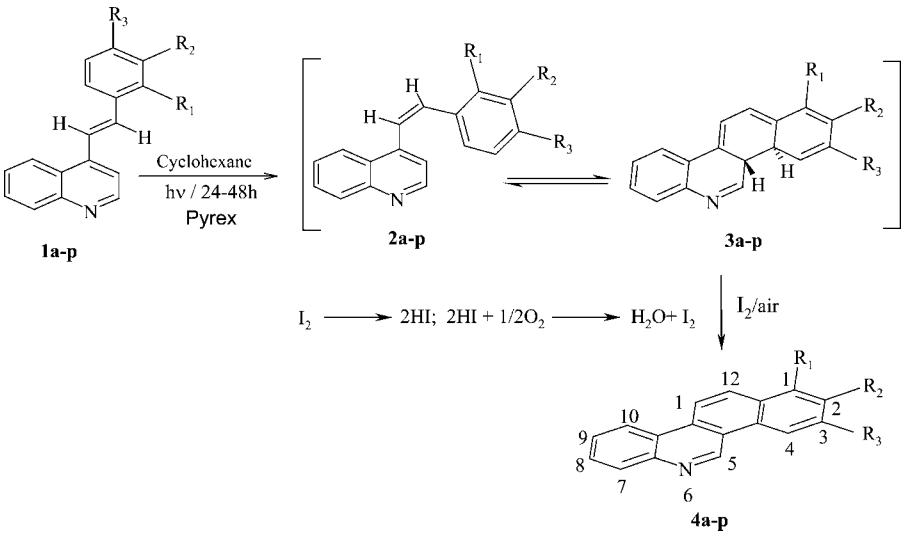
Figure 1. Kinetics of the photocyclization reaction of substituted 9-styrylquinolines **1a-p** to substituted benzo[i]phenanthridines **4a-p** recorded by gas chromatograph (GC). The cyclization rates depend on the experimental conditions.

RESULTS AND DISCUSSION

Synthesis of substituted benzo[i]phenanthridines 4a-p via photocyclization of 4-styrylquinolines 1a-p

Different substituted benzo[i]phenanthridines **4a-p** were prepared via photolysis of substituted 4-styrylquinolines **1a-p** in hexane solution in the presence of a catalytic amount of iodine (Scheme 1). The different substituted 4-styrylquinoline precursors **1a-p** were prepared previously in moderate-to-high yields (52–90%) via zinc chloride catalyzed aldol condensation of 4-methylquinoline with substituted benzaldehydes.[19,25,43–48] Irradiation of substituted 4-styrylquinolines **1a-p** in aerated cyclohexane solution by high pressure mercury lamp (125 W, Pyrex filter) for 24–48 h in the presence of iodine as a catalyst yielded the corresponding substituted benzoi]-phenanthridines **4a-p** in moderate yields (18–38%).

The kinetics of the photocyclization reaction through the decrease in the concentrations of the educts **1a-p** and the increase in the concentrations of the photocyclized products **4a-p** were monitored by gas chromatography (Fig. 1). The reaction kinetics were followed by injecting the irradiated reaction mixture at a concentration of 5×10^{-3} M every 3 h as well as thin layer chromatography (TLC). Even if the retention time of both educts **1a-p** and the photocyclized products **4a-p** are very close (the difference is about 0.10 min) because the difference in molecular weight between the starting materials and the products is only 2 (separation depends on the molecular weight), the reaction proceeding could be



Scheme 1. Photocyclization reaction of 9-styrylquinolines **1a-p** to benzo[i] phenanthridines **4a-p**

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Table 1. Substitutions, photolysis times, yields, and melting points of photocyclized benzo[i]phenanthridines **4a-p**

4	R_1	R_2	R_3	Photolysis time (h)	Yield (%)	Melting point (°C)
a	H	H	H	24	20	185[48]
b	H	H	OCH_3	48	22	97
c	H	H	$N(CH_3)$	48	18	103
d	H	F	H	30	30	124
e	H	H	F	35	26	116
f	Cl	H	H	36	38	136
g	H	Cl	H	24	34	123
h	H	H	Cl	24	30	111
i	Cl	H	Cl	24	28	141
j	H	Cl	Cl	24	32	153
k	H	NO_2	Cl	24	31	162
l	H	H	Br	42	23	128
m	NO_2	H	H	24	42	130
n	H	NO_2	H	24	41	149
o	H	H	NO_2	24	33	156
p	H	H	$COOCH_3$	45	23	89

followed and distinguished well between the starting materials and products (Table 1). In all cases, some non-identified products were detected.

The pure benzo[i]phenanthridines **4a-p** were obtained by column chromatography on silica gel and CH_2Cl_2–hexane (5:5) as the eluent. Interestingly, the photocyclized products benzo[i]phenanthridines **4a-p** showed a fluorescence emission upon UV-radiation in the column during purification as well as on TLC plates. This phenomenon helps to distinguish between the starting material and the desired products. Further chemical structure assignments for the products were well established on the basis of NMR. The NMR spectra of substituted benzo[i]phenanthridines showed the disappearance of the two doublets of the *trans*-styryl protons at around 6.22 and 6.98 ppm with coupling constant of 15.99 Hz and the appearance of two other doublets at 7.34 and 7.99 ppm (CH11, CH12) with coupling constant about 8.2 Hz which were assigned to the *cis*-styryl protons after the photocyclization process. The decrease in the coupling constant of the styryl protons by about 7.8 Hz is in good agreement with the conversion of *trans*-styryl to *cis*-cyclized products which is evidence for the formation of the photocyclization products **4a-p**. More details and structure description about the photocyclization products will be published elsewhere.

Synthesis of PC dimethyl spiro[fluorene-9,1′-pyrrolo[1,2-f] benzo[i]phenanthridines]-2′,3′-dicarboxylate 8a-p.

Spirocyclopropene **5** was obtained via the pyrazole route[27–44] by photolysis of the substituted fluorene pyrazole using a 125 W high pressure mercury lamp in dry ether at room temperature under nitrogen atmosphere; it was used in the following without further purification. Electrophilic addition of spirocyclopropene **5** to substituted benzo[i]phenanthridines **4a-p** in dry ether at ambient temperature for 24 h under dry nitrogen atmosphere in the absence of light afforded the new PC dimethyl spiro[fluorene- 9,1′-pyrrolo[1,2-f]benzo [i]phenanthridine]-2′,3′-dicarboxylate (DHIs) **8a-p** (Scheme 2) in poor-to- moderate yields (19–57%) (Table 2).

The reaction occurs through the nucleophilic addition of the nitrogen of *N*-heterocyclic benzo[i]phenanthridines **4a-p** to the electron-deficient spirocyclopropene **5**, which ring-opens via cyclopropyl–allyl conversions **6a-p** to the colored betaines **7a-p**. A subsequent ring-closure to DHIs **8a-p** results in a fast thermal 1,5-electrocyclization back reaction (Scheme 2) which can be reversed upon exposure to light. Pure PC DHIs **8a-p** were obtained in all cases by two successive column chromatography operations on silica gel using dichloromethane as the eluent.

The chemical structures of all the synthesized DHIs **8a-p** were established by elemental analysis, ^{1}H, ^{13}C, ^{1}H, ^{1}H-COSY, ^{1}H, ^{13}C-COSY and ^{1}H, ^{1}H-NOESY NMR experiments, mass and IR spectroscopy (see the Section Experimental). For example, it is worth commenting upon some typical features of the NMR spectra, illustrated by that of **8c**. In addition, the chemical structure of **8c** was assigned by 2D-NMR spectroscopy. The ^{1}H-^{1}H-correlation of **8c** was used to assign the protons of the benzo[i]phenanthridine moiety as well as the 15′c-CH proton (region C). The ^{1}H, ^{1}H-COSY spectra of **8c** showed that both $N(CH_3)_2$, 2′- and 3′-methyl ester groups showed no coupling with other protons and appeared as three singlets at 2.84, 3.15, and 4.32 ppm, respectively. Interestingly, the 15c′-CH signal was shifted to high field and appeared as a double doublet at $\delta = 6.04$ ppm showing two coupling systems. The first is due to ^5J-coupling with the 14′-CH, which appears as doublet at $\delta = 7.22$ ppm, the second coupling is due to ^5J-coupling with the 1-CH of fluorene which appears as a double doublet at $\delta = 7.46$ ppm. A ^3J-coupling by 8.26 Hz at 7.38, 7.92 ppm for the doublet of 9′ and 10′-CH was recorded. Further assignments of 14′CH and 1-CH of fluorene and 15′c-CH were done by the aid of the NOESY spectrum of **8c**. Its noticeable that 15′c-CH at $\delta = 6.04$ ppm is close in space to both 14′-CH at $\delta = 7.22$ ppm and 1-CH of the fluorene moiety at $\delta = 7.46$ ppm. Additionally, the connectivity between 14′-CH and 8-CH of the fluorene part at $\delta = 7.52$ ppm was observed. This vicinity of 14′-CH with 8-CH proved that the benzo[i]phenanthridine moiety is perpendicular to the fluorene skeleton as suggested by a molecular modeling calculation[24,25] of **8c** (Fig. 2). It showed that the distance between both 15′c-CH, 14′-CH and 1-CH, 8-CH of the fluorene moiety is <3 Å. Indeed, probably 6′-CH and 3′-CH_3 of the ester group at $\delta = 4.32$ ppm are close in space to each other.

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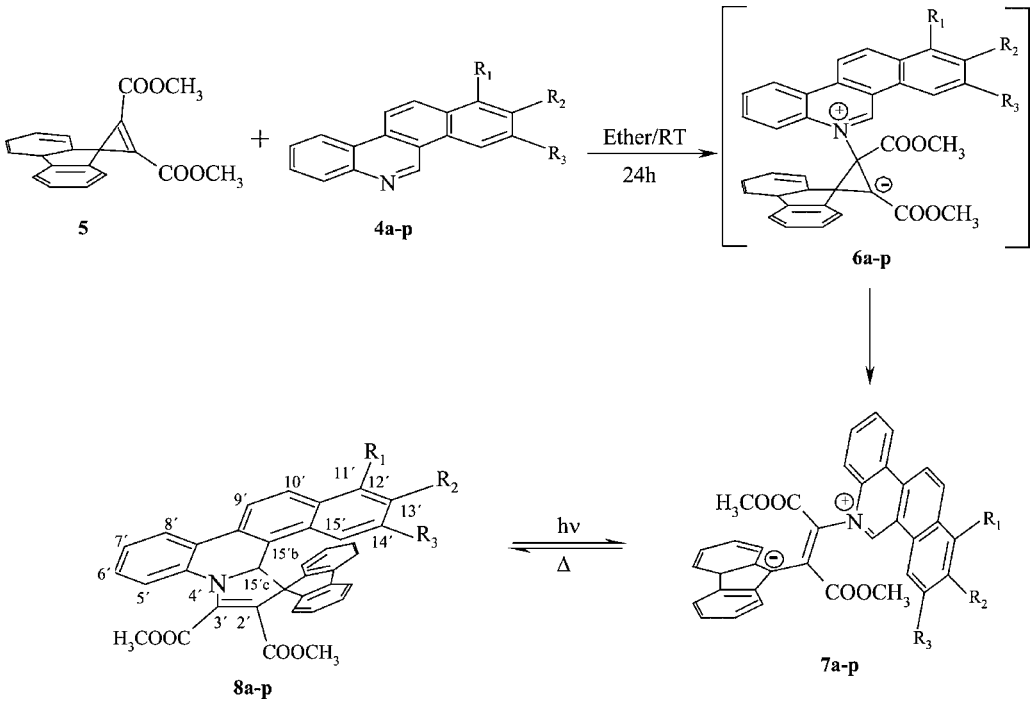

Scheme 2. Preparation outline of photochromic DHIs **8a-p** bearing benzo[i]phenanthridine moiety

Photophysical properties of the new PC DHIs 8a-p and their corresponding betaines 7a-p in solutions

Absorption spectra of DHIs 8a-p and their corresponding betaines 7a-p. Photophysical data pertinent to their PC properties were obtained from the absorption features of PC DHIs **8a-p**. Electronic spectra of the newly synthesized DHIs **8a-p** were measured in dichloromethane solution with concentration of 0.5×10^{-5} M at 23 °C using a UV/VIS spectrophotometer. All studied DHIs **8a-p** are colorless to pale yellow in both the solid state and in dichloromethane solution. The intensities (logε) of these bands were found to be between 4.25 and 4.46. Absorptions of DHIs **8a-p** were observed in the UV-region and showed absorption maxima between 360 and 378 nm (Table 3). This absorption is depending on the type of substitutions in the benzo[i]phenanthridine part. Substitution with electron-withdrawing groups, as in case of DHIs **8m-o**, caused about 12 nm bathochromic shift compared with the unsubstituted DHI **8a**. Substitution with halogens showed no pronounced effect compared with the unsubsituted DHI **8a**. Due to the increase in the aromaticity (the presence of the phenanthridine moiety) of the conjugated DHI skeleton, a shift of around 25 nm was recorded compared with our work on 9-styryl DHI system.[19,25] As established previously,[1] these absorption

Table 2. Substitution pattern of the synthesized DHIs **8a-p**, their melting points, and reaction yields

DHIs **8**	R1	R2	R3	Yield (%)	Melting point (°C)
a	H	H	H	45	254
b	H	H	OCH_3	52	216
c	H	H	$N(CH_3)$	36	234
d	H	F	H	57	219
e	H	H	F	49	225
f	Cl	H	H	46	210
g	H	Cl	H	36	221
h	H	H	Cl	41	234
I	Cl	H	Cl	46	266
j	H	Cl	Cl	51	247
k	H	NO_2	Cl	45	271
l	H	H	Br	55	231
m	NO_2	H	H	19	213
n	H	NO_2	H	27	236
o	H	H	NO_2	39	240
p	H	H	$COOCH_3$	43	199

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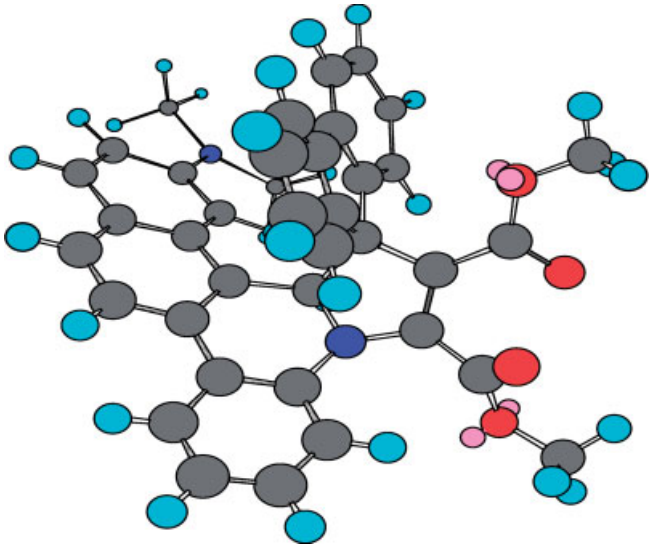

Figure 2. Representation of the optimized (MM2) structure of DHI **8c** (optimized energy = 38.23 kcal/mol).

bands can be assigned to the locally excited π–π^*-transition (LE) located in the butadienyl-vinyl-amine chromophore[1,17–25] of DHIs (Table 3).

Irradiation of DHIs **8a-p** in dichloromethane solution with polychromatic light at *room temperature* did not lead to any color change due to the fast 1,5-electrocyclization of betaines **7a-p** back to DHI **8a-p**. However, red colored **7c** and green colored **7a,b,d-p** betaines were observed after irradiation at 253 K using a *FT-UV/VIS* spectrophotometer (Fig. 3 for betaine **7c** and Fig. 4 for betaine **7m**). In addition, a millisecond flash-photolysis technique was used to determine the absorption of the colored betaine, as well as the kinetics of the fast electrocyclic process (Figs 5–7 for betaine **7o**). The absorption maxima of the colored betaines **7a-p** were found to be between 450 and 500, 675 and 725 nm. An interesting exception is that of betaine **7c** bearing the *N*,*N*-dimethyl group in the benzo[i]phenanthridine moiety which showed only one absorption maximum at 550 nm exhibiting a red colored betaine with the strongest colorability of all studied betaines. This could be attributed to the strong electron-donating ability of the $N(CH_3)_2$ group, a push–pull system being formed. This exception is in good agreement with our former studies of the DHI system.[17,25] Irradiating DHIs **8a-p** in CH_2Cl_2 *at 77 K* (liquid nitrogen) gave green and red colors immediately. The resulting betaines **7a-p** could be stored at this temperature *for several weeks* without color decay. Compared to styryl-DHIs, betaines **7a-p** showed only absorption in the visible region (a tailing in the near-IR) without any detection of absorption in the IR-region as in the cases of the formerly studied on styryl-DHIs. This is good evidence for the tunable photophysical properties by changing the structure of **7** and formerly studied styryl-DHI system.[17,25]

Kinetic measurements of the 1,5-electrocyclization of betaines 7a-p to their corresponding DHIs 8a-p in dichloromethane solution. The kinetics of the fast 1,5-electrocyclization were studied by using both millisecond flash photolysis and FT-UV/VIS. The millisecond flash-photolysis technique showed that the half-lives of the colored betaines lie between 2695 and 432 ms. A pronounced effect of the substituents in the benzo[i]phenanthridine part on the half-life times of the betaine form was recorded (Table 3, Figs 6 and 7). As a general notice, introducing electron-donating groups as in betaines **7b,c** led to an increase in the half-lives of the colored form and this may be attributed to the stabilization of the positive charge on the nitrogen atom of the base part of the betaine. The higher $t_{1/2}$ value of the betaine **7c** by a factor of 1.75 is in keeping with stabilization of betaine form by the electron-donating *N*,*N*-dimethyl group. An increase in the

Table 3. UV/VIS absorption of DHIs **8a-p** and their corresponding betaines **7a-p** and kinetic data of betaines **7a-p** recorded by millisecond flash photolysis in CH_2Cl_2 solution (23 °C, $c = 0.5 \times 10^{-5}$ M)

7/8	λ_{max}(DHI) (nm)	log(ε)	λ_{max} (betaine) (nm)	$k \times 10^3$ (s^{-1})	$t_{1/2}$ (ms)	Color of betaine
a	368	4.28	475, 675	4.10	1543	Green
b	364	4.33	475,675	6.13	1896	Green
c	382	4.46	550	2.24	2695	Red
d	360	4.37	500, 675	6.42	1361	Green
e	360	4.34	450, 675	9.12	1436	Green
f	361	4.32	450, 675	4.03	1654	Green
g	361	4.31	450, 700	8.06	1432	Green
h	362	3.30	475, 700	4.65	1249	Green
i	360	4.42	475, 700	15.40	1199	Green
j	364	4.45	450, 700	5.98	1569	Green
k	363	4.38	500, 700	9.00	563	Green
l	362	4.36	500, 700	12.60	981	Green
m	380	4.25	475, 725	5.73	671	Green
n	378	4.26	475, 725	8.56	465	Green
o	376	4.27	475, 725	13.33	432	Green
p	365	4.43	450, 675	5.10	1840	Green

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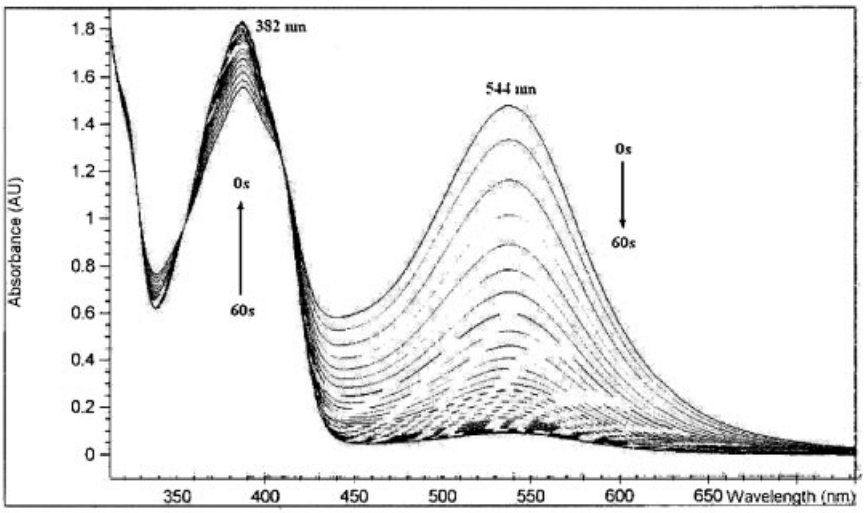

Figure 3. Kinetics (FT-UV/VIS spectrum) of the thermal fading of betaine **7c** to DHI **8c** (cycle time = 2 s, run time = 60 s) in CH_2Cl_2 ($c = 0.5 \times 10^{-5}$ M at 253 K)

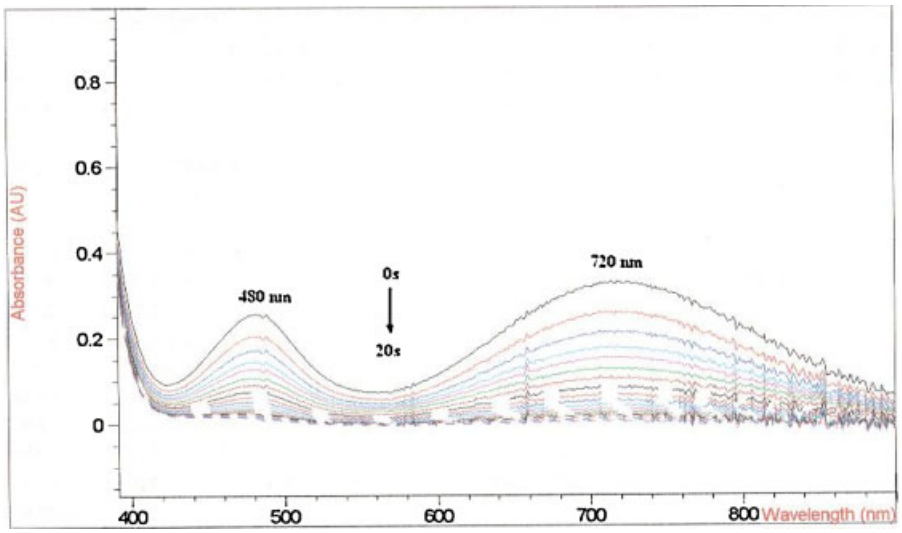

Figure 4. Kinetics (FT-UV/VIS spectrum) of the thermal fading of betaine **7m** to DHI **8m** (cycle time = 1 s, run time = 20 s) in CH_2Cl_2 ($c = 0.5 \times 10^{-5}$ M at 253 K). This figure is available in colour online at www.interscience.wiley.com/journal/poc

half-lives of the colored betaines by enlarging the halogen atom size and decreasing the electronegativity from fluorine to bromine was observed. Changing the substitution from 12′ to 14′ position in the benzo[i]phenanthridine moiety led to a large increase in the half-life times of the corresponding betaine forms. This may be attributed to the steric hindrance of the substitution in position 14′ with the fluorene part because they are close in space to each other as well as the base part lying perpendicular to the fluorene part. A drastic decrease in the $t_{1/2}$ of the nitro-substituted benzo[i]phenanthridines **7m-o** compared to other substituents is noted. This may be attributed to the electron-withdrawing effect which destabilizes the positive charge of the nitrogen atom of the betaine **7**.

Fluorescence emission spectroscopy of the newly synthesized PC DHIs 8a-p in dichloromethane solution ($c = 5 \times 10^{-6}$ M) at 273 K. To the best of our knowledge, only a few PC materials such as anthracenes,[1] spiropyrans,[36] and fulgimides[41,42] show fluorescence emission. For instance, no emission has been reported for spiroindolinooxazines[41] although the quantum yield of the ring-opening of the spiro skeleton is *ca*. 0.50.[41] The only spiro derivatives for which a fluorescence emission has been reported with a quantum yield of about 0.001 belong to the dihydroindolizine series.[41] For this reason, the determination of the singlet lifetime from the fluorescence decay of such spiro derivatives can give an evaluation of the different rate constants of the

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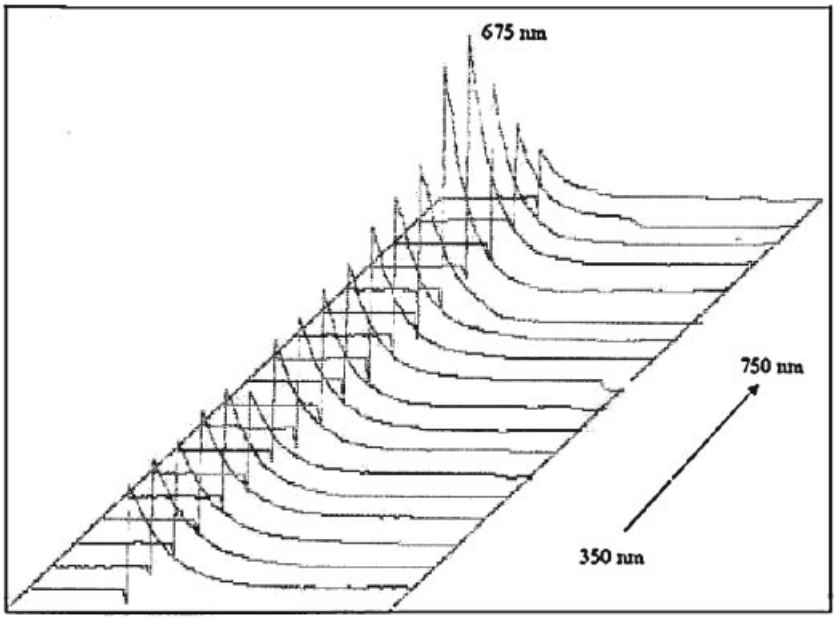

Figure 5. Millisecond flash-photolysis spectrum of betaine **7o**. Absorbance decay curves and half-life determination at different wavelengths (350–750 nm every 25 nm)

processes which deactivate the singlet excited state, including that of the formation of the opened betaine form. For a potential application in information recording or as optical switches, a very fast ring-opening of the spiro molecule to the betaine-type structure is desirable.

In the present work, we successfully prepared such systems which have a quantum yield of almost 0.09 in certain cases. Figure 8 represents the excitation and emission spectra of DHI **8b** in dichloromethane solution. The selection of dichloromethane as a solvent in the fluorescence measurements is due to its moderate polarity ($E_T(30) = 41$).

From the data listed in Table 4, it is clear that most compounds show improved fluorescence quantum yields which vary from 0.13×10^{-3} (**7o**) to 9.87×10^{-3} (**7d**). In dichloromethane solutions the fluorescence maxima lie between 516 and 586 nm. A noticeable bathochromic shift by about 20 nm is observed when the benzo[i]phenanthridine ring is substituted with electron-donating groups such as methoxy and *N*,*N*-dimethyl groups compared with the unsubsituted DHI **8a**. A hypsochromic shift by about 5–15 nm by changing the position of the same substituent in the benzo[i]phenanthridine, as in cases of **7d-o**, was recorded. Due to the strong

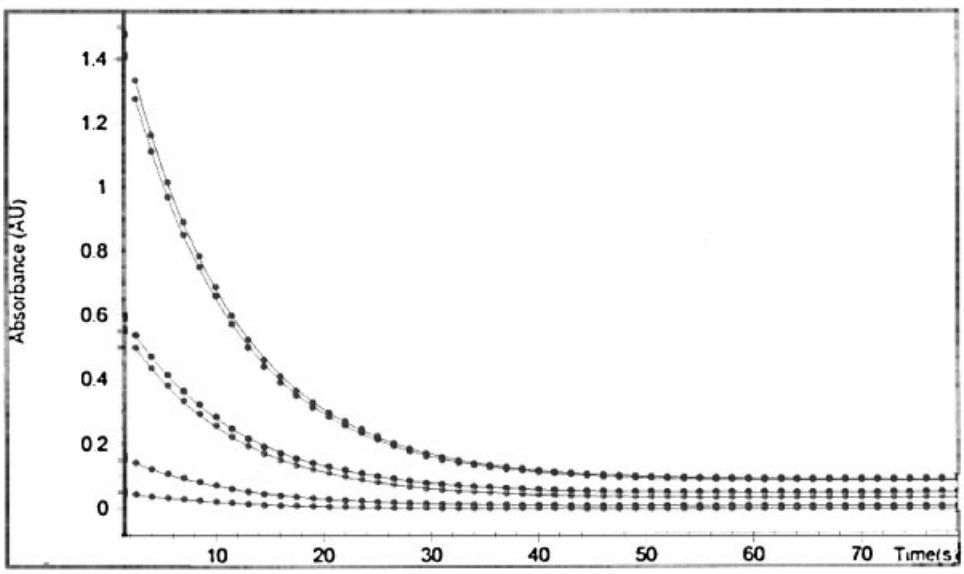

Figure 6. Absorbance–time relationship for the kinetic thermal fading of betaine **7c** at different wavelengths (400, 450, 500, 550, 600, and 750 nm) for determination of the electrocyclization rate constant *k* at 253 K

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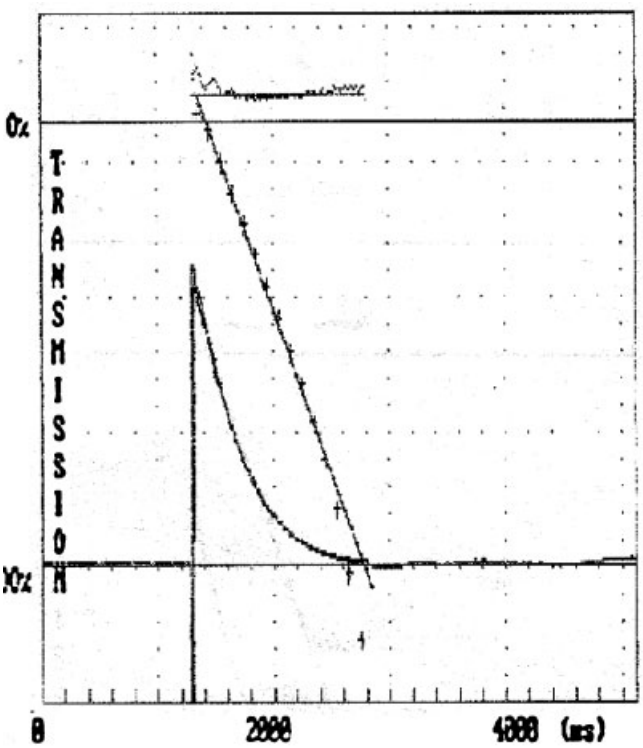

Figure 7. Analysis of the curve at 675 nm ($t_{1/2} = 432$ ms with correlation coefficient = 0.9998) of betaine **7o** recorded by millisecond flash photolysis

electron-attracting nitro-group, a pronounced hypsochromic shift by about 40 nm compared with the unsubstituted DHI **8a** was observed. An increase in the fluorescence quantum yield (about 0.01), compared with the other compounds of this family was observed. The detection of the fluorescence emission for these DHIs can be explained by the formation of *free resonance energy transfer (FRET)* from the conjugated benzo[i]phenanthridine to the DHI skeleton.[17]

However, it is surprising to observe that the fluorescence emission, which should originate from one of the two orthogonal moieties (each being independent of the other), can be shifted from the absorption maximum in different DHIs by 140–230 nm. It has been already pointed out that, for compounds related to those studied here and by comparison of the radiative lifetime measured experimentally with the radiative lifetime calculated from Strickler and Berg's equation, the excited state that fluoresces is different from the one which absorbed light.[49] One possibility would be the formation of a twisted intramolecular charge-transfer state, since the two entities of the molecule have the ideal geometry. However, if this had been the case, then one would not expect a lifetime in the picosecond timescale. Details about the fluorescence lifetimes of these compounds will be discussed in a forthcoming paper.

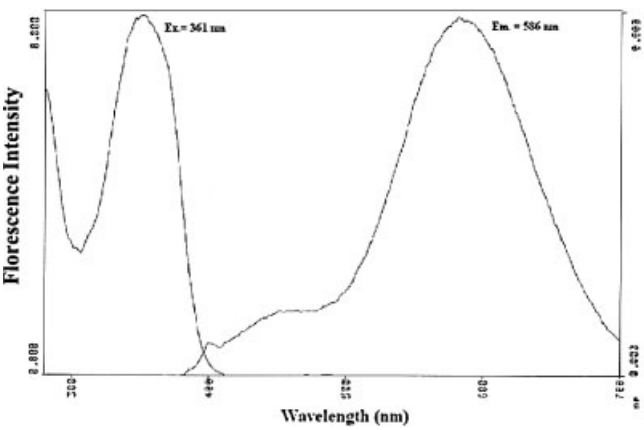

Figure 8. Fluorescence emission spectrum of DHI **8b** in dichloromethane solution ($c = 1 \times 10^{-6}$ M) at 23 °C

Solvatochromism. It has been known that UV/VIS-absorption spectra of chemical compounds may be influenced by the surrounding medium and that solvents can bring about a change in the position, intensity, and shape of absorption.[50,51] The term 'solvatochromism'[1a] is, however, so well established in the literature that it would be difficult to convince the scientific community to change this term to 'perichromism', which is certainly a more general expression for the spectroscopic phenomena under consideration (perichromism is meant to indicate a change in color due to the environment (peri) of the molecule.

A strong effect of the solvent polarity on λ_{max} and half-lives of betaines **7a-p** were observed. For example, changing the solvent from tetrahydrofuran to methanol leads to a hysochromic shift of $\Delta\nu \cong +750\,cm^{-1}$ in the first absorption and about $\Delta\nu \cong +980\,cm^{-1}$ for the second absorption in visible region. These two solvatochromic shifts are ascribable to π–π^*-transitions in the visible region.

A pronounced solvent influence on the half-lives ($t_{1/2}$) of the selected betaines **7a-p** was determined using the flash-photolysis technique in 10 different solvents (Table 5). A strong increase in the half-lives with increasing solvent polarity was recorded in all studied betaines **7a-p** (Fig. 9). This is mainly attributed to the partial charge transfer from the betaine form to the solvent and vice-versa, as a result of a weak Coulombic-exchange effects. Therefore, the charged zwitterionic betaine structure was stabilized by increasing the solvent polarity due to electrostatic interactions between them.

Photo-fatigue resistance of PC DHIs 8a-p and their corresponding betaines 7a-p in dichloromethane solution ($c = 0.5 \times 10^{-5}$ M) at 253 K

In studying the quality of a PC system 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

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Table 4. Excitation (λ_{Ex}) and emission (λ_{Em}) wavelengths and fluorescence quantum yield (ϕ_F) of DHIs **8a-p**

8	λ_{Ex} (nm)	λ_{Em} (nm)	$\phi_F \times 10^3$
a	364	568	3.56
b	361	586	6.89
c	366	580	4.20
d	364	559	9.87
e	363	556	8.9
f	360	552	4.38
g	362	551	4.20
h	364	549	4.01
I	359	557	3.68
j	367	555	3.90
k	364	536	1.39
l	366	544	3.36
m	379	530	0.99
n	377	521	0.35
o	375	516	0.13
p	364	566	5.6

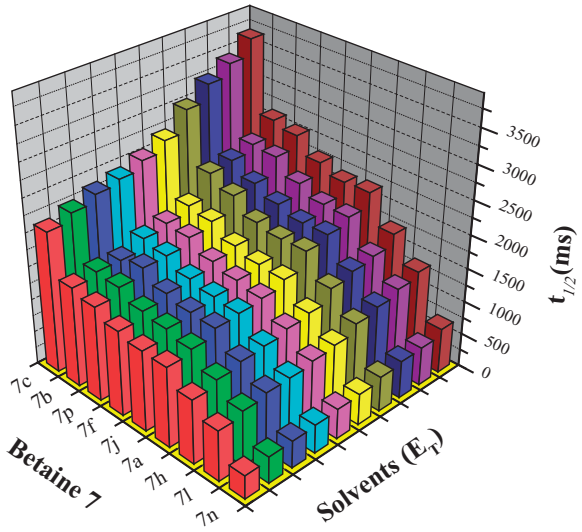

Figure 9. Balcony diagram representing the influence of differing solvent polarity on the half-lives ($t_{1/2}$) of betaines **7a-c,f,h,j,l,n,p** recorded by millisecond flash photolysis technique ($c = 0.5 \times 10^{-5}$M/l) at 23°C.

or ultraviolet light in this context has been termed fatigue.[1] Gautron[52] has advanced a quantitative approach to measure the fatigue in PC systems.

Due to the fast thermal bleaching process of the betaines to DHIs, a low temperature *FT-UV/VIS* measurement was used in this case. Irradiation of the degassed dichloromethane solution of DHIs **8a-p** at low temperature (−20 °C) with polychromatic light ($\lambda = 200$–400 nm), produced the colored betaines **7a-p**. Upon continued irradiation they decomposed after some time. However, if oxygen is excluded, these systems are noticeably more stable. It is possible that in the presence of oxygen, betaines **7a-h** and **7j** act as sensitizers towards singlet oxygen.[1]

From the photodegradation data represented in Table 6 and Fig. 10, it is clear that most of the betaines under investigation showed a higher photo-fatigue resistance than the standard dicyanopyridazine *DHI* ($t_{30} = 542$ min) by factors between 1.13 and 1.47. In all cases, betaines **7d-j** bearing a fluoro- or chloro-substituent in the phenanthridine moiety showed an improved stability compared with the other substituents as well as the standard betaine by factors of 1.31 and 1.47. Betaine **7i**

Table 6. Photodegradation data of selected betaines **7** in dichloromethane ($c = 0.5 \times 10^{-5}$ M) at −20 °C

7	$t_{1/2}$ (ms)	t_{30}-betaine/DHI (min)	F
a	2653	610	1.13
b	3031	465	0.86
c	3839	450	0.83
d	2523	710	1.30
e	2559	690	0.79
f	2790	715	1.32
g	2588	716	1.32
h	2412	712	1.31
i	2359	798	1.47
j	2679	781	1.44
p	2979	401	0.74
Standard	4230	542	1.0

Table 5. Half-lives ($t_{1/2}$) of thermal 1,5-electrocyclization of selected betaines **7a-p** and $E_T(30)$ values of 10 different solvents recorded by millisecond flash photolysis ($c = 0.5 \times 10^{-5}$ M) at 23 °C

	Betaines $t_{1/2}$ (ms)									
Solvents	**7a**	**7b**	**7c**	**7f**	**7h**	**7j**	**7l**	**7n**	**7p**	$E_T(30)$
n-Pentane	1198	1498	2123	1278	956	1209	749	349	1422	32
Toluene	1263	1564	2241	1389	1043	1342	824	397	1532	34
Dioxane	1376	1590	2353	1466	1109	1394	879	406	1643	36
Tetrahydrofurane	1405	1722	2420	1506	1138	1443	892	426	1652	37
Chloroform	1443	1789	2546	1589	1201	1507	943	451	1760	39
Dichloromethane	1543	1896	2695	1654	1249	1569	981	465	1840	41
Acetonitrile	1789	2230	3009	1845	1433	1782	1112	523	2071	46
2-Propanol	1870	2279	3249	1960	1512	1861	1179	562	2100	49
Ethanol	1968	2377	3422	2118	1567	1978	1267	576	2351	52
Methanol	2137	2604	3659	2284	1733	2157	1349	647	2529	56

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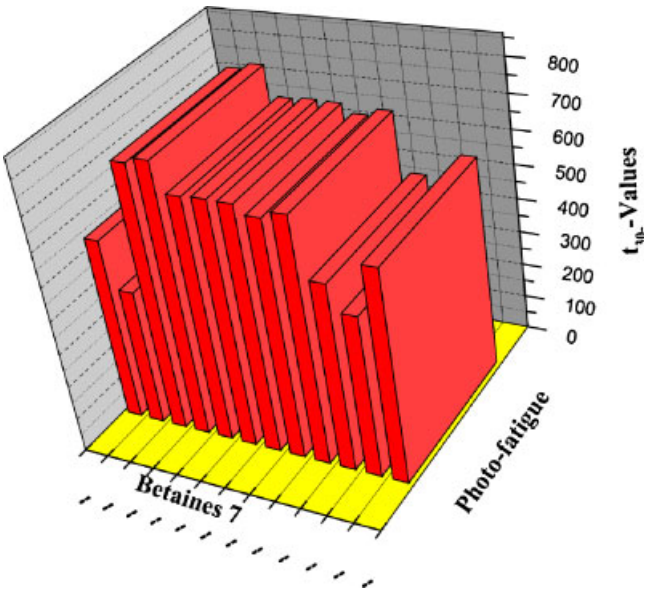

Figure 10. Balcony diagram showing the t_{30}-values of some selected betaines recorded from the photo-fatigue experiments in CH_2Cl_2 ($c = 0.5 \times 10^{-5}$ M) at −20 °C. This figure is available in colour online at www.interscience.wiley.com/journal/poc

bearing dichloro-substituted phenanthridine shows the highest stability ($t_{30} = 798$ min). This improved photostabilty of the colored forms is promising for applications.

SUMMARY AND CONCLUSION

New PC dihydroindolizines bearing a substituted phenanthridine moiety were prepared. The main important factors which should exist in any PC material for their applications have been designed through their multiaddressable PC behavior. The new PC compounds **8a-p** derived from substituted phenanthridine DHIs showed a fast 1,5-electrocylization. The absorption maxima of their corresponding betaines were determined using a FT-UV/VIS as well as the millisecond flash-photolysis technique. It is stressed that betaine **7c** bearing the *N*,*N*-dimethyl group in the benzo[i]phenanthridine moiety showing an absorption at 550 nm exhibits a red color with the strongest colorability of all betaines studied. This could be attributed to the strong electron-donating ability of the $N(CH_3)_2$ group. These compounds have potential for *non-linear optical materials*. Due to their fluorescence and high photo-fatigue resistance, the betaines **7a-p** could be used as *fluorescing recording or storage materials at 77 K* for several weeks without any color decay.

EXPERIMENTAL

The solvents used (Aldrich or Merck, spectroscopic grade) were dried, according to standard procedures,[53] over sodium for diethyl ether and P_2O_5 for CH_2Cl_2, 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. Photolysis was carried out in the photochemical reactor of Schenck made of Pyrex ($\lambda > 290$ nm).[54] The source of irradiation was a high pressure mercury lamp Philips HPK 125 W. When necessary, 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 isolated products were monitored using TLC. Separation and purification of all synthesized PC materials were carried out using column chromatography (80 cm length × 2 cm diameter) on silica gel and CH_2Cl_2 as eluent. Melting points were measured on a Gallenkamp- or a Büchi (Smp-20) melting point apparatus and are uncorrected.

All NMR spectra were recorded on a Bruker DRX 500 spectrometer (500 MHz) in $CDCl_3$ using TMS as the internal standard. Chemical shifts (δ) are reported in ppm. IR spectra were measured on a BIO-Rad Excalibur series, FTS 3000. Mass spectra were recorded on a Mat-90, FINNIGAN MAT mass spectrometer. Elemental analysis (CHN) was carried out on a LECO CHNS-932-analyzer. UV-spectra were recorded on a FT-UV/VIS HP 6543 computer–spectrometer. Millisecond flash photolysis was carried out with a 12 V (50 W) halogen lamp, Photoflash (METZ 32 Z-1). A detailed description of the experimental setup has been published.[25–27] The experimental details and characterization of the substituted benzo[i]-phenanthridines **4a-p** will be published elsewhere. A general procedure and full spectroscopic and elemental analysis data of the synthesized DHIs **8a-p** are listed below.

Preparation of dimethyl spiro[fluorene-9,1′-pyrrolo-[1,2-f]benzo[i]phenanthridine]-2′,3′-dicarboxylates 8a-p

General procedure. To a solution of spirene **5** (0.001 mol) in dry diethyl ether (50 ml), a solution of substituted-1,2,3-benzo[i]phenanthridines **4a-p** (0.001 mol) in dry diethyl ether (10 ml) over 15 min was added under dry nitrogen atmosphere. The mixture was stirred in the dark at room temperature for about 24 h (TLC-controlled). After the reaction was completed, the solvent was evaporated under reduced pressure and the pure products were obtained by column chromatography on silica gel using CH_2Cl_2 as eluent and recrystallized from the appropriate solvent to give DHIs **8a-p** as white to yellow needles in 19–57% yield.

Dimethyl spiro[fluorene-9,1′-pyrrolo[1,2-f]benzo[i]phenanthridine]-2′,3′-dicar boxylate (8a). Reactants: 375 mg (0.001 mol) spirene **5**, 229 mg (0.001 mol) benzo[i]phenanthridine **4a**; yield 241 mg

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(45%) as pale yellow crystals from ether-CH_2Cl_2 (7:3); m.p. 254 °C. ^{1}H NMR (DMSO-d_6): $\delta = 8.16–8.17$ (d, $J = 1.54$ Hz, 1H, CH-arom.); 7.74–7.75 (m, 4H, CH-arom.), 7.27–7.33 (m, 4H, CH-arom.), 7.00–7.09 (m, 3H, CH-arom.), 6.92–6.96 (t, $J = 7.80$, 2H, CH-arom.), 6.60–6.63 (t, $J = 7.52$, 2H, CH-arom.), 6.09 (s, 1H, 15′c-H), 5.70–5.73 (dd, $J = 7.87$ Hz, 2H, CH-arom.), 3.97 (s, 3H, 3'-CH_3), 3.22 (s, 3H, 2'-CH_3) ppm. ^{13}C NMR (DMSO-d_6): $\delta = 163.27$ (3'-CO), 162.69 (2'-CO), 69.34 (15'a-C), 62.59 (spiro-C), 52.98 (3'-CH_3), 50.87 (2'-CH_3) ppm. MS (70 eV): *m/z* (%) = 535.56 [M^+] (12.64), 247.00 [B^+] (100). IR (KBr): $\nu = 3059$ (C—H, arom.), 2836–2979 (C—H, aliph.), 1752 (3'-C═O), 1696 (2'-C═O), 1582 (C═C), 1496, 1263, 1200, 1164, 1131, 936, 753, 674 cm^{-1}. Elemental analysis for $C_{36}H_{25}NO_4$ (M. Wt = 535.36): calc. %: C, 80.76; H, 4.71; N, 2.62; found C, 80.77; H, 4.70; N, 2.62.

Dimethyl spiro[fluorene-9,1′-pyrrolo[1,2-f]-(14′methoxy)-benzo[l]phenanthridine]-2′,3′-dicarboxylate (8b). Reactants: 375 mg (0.001 mol) spirene **5**, 247 mg (0.001 mol) 2-methoxybenzo[i]phenanthridine **4b**; yield 288 mg (52%) as pale yellow crystals from ether-CH_2Cl_2 (8:2); m.p. 216 °C. ^{1}H NMR ($CDCl_3$): $\delta = 8.12–8.14$ (d, $J = 1.54$ Hz, 1H, CH-arom.); 7.72–7.73 (m, 3H, CH-arom.), 7.22–7.29 (m, 4H, CH-arom.), 7.06–7.012 (m, 3H, CH-arom.), 6.94–6.98 (t, $J = 7.86$, 2H, CH-arom.), 6.60–6.63 (t, $J = 7.52$, 2H, CH-arom.), 6.12 (s, 1H, 15′c-H), 5.73–5.77 (dd, $J = 7.80$ Hz, 2H, CH-arom.), 3.97 (s, 3H, 3'-CH_3), 3.73 (s, 3H, OCH_3) 3.26 (s, 3H, 2'-CH_3) ppm. ^{13}C NMR (CDCl3): $\delta = 163.29$ (3'-CO), 162.63 (2'-CO), 69.37 (15'a-C), 62.63 (spiro-C), 55.43 (OCH_3), 52.94 (3'-CH_3), 50.91 (2'-CH_3) ppm. MS (70 eV): *m/z* (%) = 553.58 [M^+] (13.90), 247.00 [B^+] (100). IR (KBr): $\nu = 3052$ (C—H, arom.), 2820–2969 (C—H, aliph.), 1749 (3'-C = O), 1692 (2'-C═O), 1579 (C═C), 1491, 1269, 1204, 1160, 1134, 943, 752, 679 cm^{-1}. Elemental analysis for $C_{37}H_{27}NO_5$ (M. Wt = 553.58): calc. %: C, 80.27; H, 4.92; N, 2.53; found C, 80.27; H, 4.91; N, 2.54.

Dimethyl spiro[fluorene-9,1′-pyrrolo[1,2-f]-(14′-*N,N*-dimethyl)-benzo[l]phenanthridine]-2′,3′-dicarboxylate (8c). Reactants: 375 mg (0.001 mol) spirene **5**, 272 mg (0.001 mol) 2-*N,N*-dimethoxybenzo[i]phenanthridine **4c**; yield 208 mg (36%) as pale yellow crystals from ether-CH_2Cl_2 (6:4); m.p. 234 °C. ^{1}H NMR ($CDCl_3$): $\delta = 8.00–8.3$ (d, $J = 1.54$ Hz, 1H, CH-arom.); 7.70–7.71 (m, 3H, CH-arom.), 7.44–7.46 (m, 4H, CH-arom.), 7.20–7.23 (m, 3H, CH-arom.), 6.94–6.97 (t, $J = 7.86$, 2H, CH-arom.), 6.59–6.62 (t, $J = 7.52$, 2H, CH-arom.), 6.04 (dd, 1H, 15′c-H), 5.70–5.74 (dd, $J = 7.86$ Hz, 2H, CH-arom.), 4.32 (s, 3H, 3'-CH_3), 3.15 (s, 3H, 2'-CH_3), 2.84 (s, 3H, $N(CH_3)_2$ ppm. ^{13}C NMR (CDCl3): $\delta = 162.29$ (3'-CO), 162.69 (2'-CO), 69.39 (15'a-C), 62.68 (spiro-C), 55.49 (OCH_3), 52.94 (3'-CH_3), 50.97 (2'-CH_3); 40.09 ($N(CH_3)_2$) ppm. MS (70 eV): *m/z* (%) = 578.63 [M^+] (27.64), 272.00 [B^+] (100). IR (KBr): $\nu = 3057$(C—H, arom.), 2880–2920 (C—H, aliph.), 1752 (3'-C═O), 1703 (2'-C═O), 1574 (C═C), 1494, 1272, 1204, 1164, 1136, 947, 759, 682 cm^{-1}. Elemental analysis for $C_{38}H_{30}N_2O_4$ (M. Wt = 578.63): calc. %: C, 78.87; H, 5.22; N, 4.84; found C, 78.89; H, 5.21; N, 4.86.

Dimethyl spiro[fluorene-9,1′-pyrrolo[1,2-f]-(13′-iodo)benzo[i]phenanthridine]-2′,3′-dicarboxylate (8d). Reactants: 375 mg (0.001 mol) spirene **5**, 247 mg (0.001 mol) 2-iodo benzo[i]phenanthridine **4d**; yield 241 mg (57%) as pale yellow crystals from ether-CH_2Cl_2 (7:3); m.p. 219 °C. ^{1}H NMR ($CDCl_3$): $\delta = 8.00–8.06$ (d, $J = 1.54$ Hz, 1H, CH-arom.); 7.79–7.82 (m, 3H, CH-arom.), 7.25–7.28 (m, 4H, CH-arom.), 7.09–7.18 (m, 3H, CH-arom.), 6.91–6.97 (t, $J = 7.84$, 2H, CH-arom.), 6.67–6.69 (t, $J = 7.80$, 2H, CH-arom.), 6.02 (s, 1H, 15′c-H), 5.73–5.76 (dd, $J = 7.87$ Hz, 2H, CH-arom.), 3.94 (s, 3H, 3'-CH_3), 3.21 (s, 3H, 2'-CH_3) ppm. ^{13}C NMR (DMSO-d_6): $\delta = 163.22$ (3'-CO), 162.75 (2'-CO), 69.37 (15'a-C), 62.55 (spiro-C), 52.94 (3'-CH_3), 50.82 (2'-CH_3) ppm. MS (70 eV): *m/z* (%) = 553.56 [M^+] (19.34), 247.00 [B^+] (100). IR (KBr): $\nu = 3054$ (C—H, arom.), 2833–2989 (C—H, aliph.), 1747 (3'-C═O), 1699 (2'-C═O), 1584 (C═C), 1486, 1267, 1208, 1169, 1138, 939, 750, 672 cm^{-1}. Elemental analysis for $C_{36}H_{24}FNO_4$ (M. Wt = 553.56): calc. %: C, 78.11; H, 4.37; N, 2.53; found C, 78.12; H, 4.37; N, 2.55.

Dimethyl spiro[fluorene-9,1′-pyrrolo[1,2-f]-(13′-iodo)benzo[i]phenanthridine]-2′,3′-dicarboxylate (8e). Reactants: 375 mg (0.001 mol) spirene **5**, 247 mg (0.001 mol) 3-iodo benzo[i]phenanthridine **4e**; yield 207 mg (49%) as pale yellow crystals from ether-CH_2Cl_2 (7:3); m.p. 225 °C. ^{1}H NMR ($CDCl_3$): $\delta = 8.01–8.05$ (d, $J = 1.54$ Hz, 1H, CH-arom.); 7.78–7.81 (m, 3H, CH-arom.), 7.26–7.29 (m, 4H, CH-arom.), 7.11–7.19 (m, 3H, CH-arom.), 6.93–6.94 (t, $J = 7.84$, 2H, CH-arom.), 6.69–6.72 (t, $J = 7.80$, 2H, CH-arom.), 6.06 (s, 1H, 15′c-H), 5.73–5.75 (dd, $J = 7.80$ Hz, 2H, CH-arom.), 3.93 (s, 3H, 3'-CH_3), 3.24 (s, 3H, 2'-CH_3) ppm. ^{13}C NMR (DMSO-d_6): $\delta = 163.27$ (3'-CO), 162.72 (2'-CO), 69.32 (15'a-C), 62.57 (spiro-C), 52.91 (3'-CH_3), 50.87 (2'-CH_3) ppm. MS (70 eV): *m/z* (%) = 553.56 [M^+] (19.34), 247.00 [B^+] (100). IR (KBr): $\nu = 3057$ (C—H, arom.), 2887–2990 (C—H, aliph.), 1742 (3'-C═O), 1677 (2'-C═O), 1587 (C═C), 1482, 1261, 1200, 1178, 1128, 934, 751, 677 cm^{-1}. Elemental analysis for $C_{36}H_{24}FNO_4$ (M. Wt = 553.56): calc. %: C, 78.11; H, 4.37; N, 2.53; found C, 78.11; H, 4.36; N, 2.52.

Dimethyl spiro[fluorene-9,1′-pyrrolo[1,2-f]-(12′-chloro)benzo[i]phenanthridine]-2′,3′-dicarboxylate (8f). Reactants: 375 mg (0.001 mol) spirene **5**, 264 mg (0.001 mol) 1-chloro benzo[i]phenanthridine **4f**; yield 262 mg (46%) as pale yellow crystals

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from ether-CH_2Cl_2 (8:2); m.p. 210 °C. ^{1}H NMR ($CDCl_3$): $\delta = 8.00$–8.04 (d, $J = 1.54$ Hz, 1H, CH-arom.); 7.77–7.80 (m, 3H, CH-arom.), 7.25–7.27 (m, 4H, CH-arom.), 7.10–7.18 (m, 3H, CH-arom.), 6.91–6.93 (t, $J = 7.81$, 2H, CH-arom.), 6.68–6.71 (t, $J = 7.86$, 2H, CH-arom.), 6.01 (s, 1H, 15′c-H), 5.73–5.75 (dd, $J = 7.86$ Hz, 2H, CH-arom.), 3.94 (s, 3H, 3'-CH_3), 3.27 (s, 3H, 2'-CH_3) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 163.29$ (3'-CO), 162.68 (2'-CO), 69.37 (15'a-C), 62.52 (spiro-C), 52.87 (3'-CH_3), 50.80 (2'-CH_3) ppm. MS (70 eV): *m/z* (%) = 570.06 [M^+] (27.98), 264.01 [B^+] (100). IR (KBr): $\nu = 3045$ (C—H, arom.), 2883–2990 (C—H, aliph.), 1756 (3'-C═O), 1698 (2'-C═O), 1580 (C═C), 1488, 1264, 1207, 1189, 1134, 937, 748, 667 cm^{-1}. Elemental analysis for $C_{36}H_{24}ClNO_4$ (M. Wt = 570.06): calc. %: C, 75.84; H, 4.24; N, 2.46; Cl, 6.22; found C, 75.85; H, 4.25; N, 2.44; Cl, 6.32.

Dimethyl spiro[fluorene-9,1′-pyrrolo[1,2-f]-(13′-chloro)benzo[i]phenanthridine]-2′,3′-dicarboxylate (8g). Reactants: 375 mg (0.001 mol) spirene **5**, 264 mg (0.001 mol) 2-chloro benzo[i]phenanthridine **4g**; yield 205 mg (36%) as pale yellow crystals from ether-CH_2Cl_2 (8:2); m.p. 221 °C. ^{1}H NMR ($CDCl_3$): $\delta = 8.05$–8.08 (d, $J = 1.54$ Hz, 1H, CH-arom.); 7.72–7.78 (m, 3H, CH-arom.), 7.24–7.26 (m, 4H, CH-arom.), 7.14–7.17 (m, 3H, CH-arom.), 6.90–6.92 (t, $J = 7.88$, 2H, CH-arom.), 6.64–6.68 (t, $J = 7.82$, 2H, CH-arom.), 6.06 (s, 1H, 15′c-H), 5.72–5.76 (dd, $J = 7.86$ Hz, 2H, CH-arom.), 3.90 (s, 3H, 3'-CH_3), 3.23 (s, 3H, 2'-CH_3) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 163.35$ (3'-CO), 162.76 (2'-CO), 69.42 (15'a-C), 62.57 (spiro-C), 52.78 (3'-CH_3), 50.87 (2'-CH_3) ppm. MS (70 eV): *m/z* (%) = 570.06 [M^+] (27.98), 264.01 [B^+] (100). IR (KBr): $\nu = 3035$ (C—H, arom.), 2899–2990 (C—H, aliph.), 1752 (3'-C═O), 1670 (2'-C═O), 1587 (C═C), 1487, 1260, 1204, 1196, 1137, 932, 747, 660 cm^{-1}. Elemental analysis for $C_{36}H_{24}ClNO_4$ (M. Wt = 570.06): calc. %: C, 75.84; H, 4.24; N, 2.46; Cl, 6.22 found C, 75.84; H, 4.24; N, 2.48, Cl, 6.19.

Dimethyl spiro[fluorene-9,1′-pyrrolo[1,2-f]-(14′-chloro)benzo[i]phenanthridine]-2′,3′-dicarboxylate (8h). Reactants: 375 mg (0.001 mol) spirene **5**, 264 mg (0.001 mol) 3-chloro benzo[i]phenanthridine **4h**; yield 233 mg (41%) white crystals from ether-CH_2Cl_2 (7:3); m.p. 234 °C. ^{1}H NMR ($CDCl_3$): $\delta = 8.02$–8.04 (d, $J = 1.57$ Hz, 1H, CH-arom.); 7.77–7.71 (m, 3H, CH-arom.), 7.27–7.31 (m, 4H, CH-arom.), 7.15–7.18 (m, 3H, CH-arom.), 6.92–6.96 (t, $J = 7.88$, 2H, CH-arom.), 6.62–6.67 (t, $J = 7.82$, 2H, CH-arom.), 6.04 (s, 1H, 15′c-H), 5.77–5.79 (dd, $J = 7.82$ Hz, 2H, CH-arom.), 3.91 (s, 3H, 3'-CH_3), 3.27 (s, 3H, 2'-CH_3) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 163.34$ (3'-CO), 162.77 (2'-CO), 69.38 (15'a-C), 62.67 (spiro-C), 52.83 (3'-CH_3), 50.82 (2'-CH_3) ppm. MS (70 eV): *m/z* (%) = 570.06 [M^+] (27.98), 264.01 [B^+] (100). IR (KBr): $\nu = 3030$ (C—H, arom.), 2940–2990 (C—H, aliph.), 1757 (3'-C═O), 1677 (2'-C═O), 1587 (C═C), 1484, 1275, 1203, 1179, 1120, 987, 736, 678 cm^{-1}. Elemental analysis for $C_{36}H_{24}ClNO_4$ (M. Wt = 570.06): calc. %: C, 75.84; H, 4.24; N, 2.46; Cl, 6.23 found C, 75.89; H, 4.21; N, 2.42; Cl, 6.30.

Dimethyl spiro[fluorene-9,1′-pyrrolo[1,2-f]-(12′,14′dichloro)benzo[i]phenanthridine]-2′,3′-dicarboxylate (8i). Reactants: 375 mg (0.001 mol) spirene **5**, 299 mg (0.001 mol) 1,3-dichloro benzo[i]phenanthridine **4i**; yield 278 mg (46%) white crystals from ether-CH_2Cl_2 (7:3); m.p. 266 °C. ^{1}H NMR ($CDCl_3$): $\delta = 8.20$ (s,1H, CH-arom.); 7.72–7.75 (m, 3H, CH-arom.), 7.27–7.29 (m, 3H, CH-arom.), 7.15–7.18 (m, 3H, CH-arom.), 6.92–6.96 (t, $J = 7.88$, 2H, CH-arom.), 6.62–6.67 (t, $J = 7.82$, 2H, CH-arom.), 6.07 (s, 1H, 15′c-H), 5.79–5.82 (dd, $J = 7.80$ Hz, 2H, CH-arom.), 3.98 (s, 3H, 3'-CH_3), 3.24 (s, 3H, 2'-CH_3) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 163.30$ (3'-CO), 162.85 (2'-CO), 69.37 (15'a-C), 62.61 (spiro-C), 52.87 (3'-CH_3), 50.84 (2'-CH_3) ppm. MS (70 eV): *m/z* (%) = 606.56 [M^{+2}] (53.12), 300.01 [B^+] (100). IR (KBr): $\nu = 3054$ (C—H, arom.), 2947–2992 (C—H, aliph.), 1753 (3'-C═O), 1689 (2'-C═O), 1581 (C═C), 1487, 1275, 1200, 1198, 1117, 980, 778, 665 cm^{-1}. Elemental analysis for $C_{36}H_{23}Cl_2NO_4$ (M. Wt = 604.56): calc. %: C, 71.52; H, 4.00; N, 2.32; Cl, 11.72; found C, 71.59; H, 3.99; N, 2.36; Cl, 11.74.

Dimethyl spiro[fluorene-9,1′-pyrrolo[1,2-f]-(13′,14′dichloro)benzo[i]phenanthridine]-2′,3′-dicarboxylate (8j). Reactants: 375 mg (0.001 mol) spirene **5**, 299 mg (0.001 mol) 2,3-dichloro benzo[i]phenanthridine **4j**; yield 308 mg (51%) white crystals from ether-CH_2Cl_2 (6:4); m.p. 247 °C. ^{1}H NMR ($CDCl_3$): $\delta = 8.19$ (s,1H, CH-arom.); 7.70–7.73 (m, 3H, CH-arom.), 7.22–7.26 (m, 3H, CH-arom.), 7.14–7.17 (m, 3H, CH-arom.), 6.90–6.94 (t, $J = 7.88$, 2H, CH-arom.), 6.60–6.64 (t, $J = 7.80$, 2H, CH-arom.), 6.03 (s, 1H, 15′c-H), 5.75–5.80 (dd, $J = 7.80$ Hz, 2H, CH-arom.), 4.03 (s, 3H, 3'-CH_3), 3.54 (s, 3H, 2'-CH_3) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 163.45$ (3'-CO), 162.72 (2'-CO), 69.43 (15'a-C), 62.58 (spiro-C), 52.72 (3'-CH_3), 50.74 (2'-CH_3) ppm. MS (70 eV): *m/z* (%) = 605.56 [M^{+1}] (39.42), 300.01 [B^+] (100). IR (KBr): $\nu = 3054$ (C—H, arom.), 2940–2989 (C—H, aliph.), 1754 (3'-C═O), 1693 (2'-C═O), 1587 (C═C), 1481, 1289, 1212, 1178, 1112, 998, 767, 634 cm^{-1}. Elemental analysis for $C_{36}H_{23}Cl_2NO_4$ (M. Wt = 604.56): calc. %: C, 71.52; H, 4.00; N, 2.32; Cl, 11.74; found C, 71.54; H, 3.94; N, 2.33; Cl, 11.81.

Dimethyl spiro[fluorene-9,1′-pyrrolo[1,2-f]-(13′-chloro-14′-nitro)benzo[i]-phenanthridine]-2′,3′-dicarboxylate (8k). Reactants: 375 mg (0.001 mol) spirene **5**, 309 mg (0.001 mol) 2-chloro-3-nitrobenzo[i]phenanthridine **4k**; yield 247 mg (45%) pale

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yellow crystals from ether-CH_2Cl_2 (5:5); m.p. 271 °C. ^{1}H NMR ($CDCl_3$): $\delta = 8.06$ (s,1H, CH-arom.); 7.77–7.74 (m, 3H, CH-arom.), 7.20–7.24 (m, 3H, CH-arom.), 7.17–7.19 (m, 3H, CH-arom.), 6.92–6.97 (t, $J = 7.88$, 2H, CH-arom.), 6.61–6.64 (t, $J = 7.87$, 2H, CH-arom.), 6.00 (s, 1H, 15′c-H), 5.74–5.80 (dd, $J = 7.82$ Hz, 2H, CH-arom.), 4.08 (s, 3H, 3'-CH_3), 3.62 (s, 3H, 2'-CH_3) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 163.44$ (3'-CO), 162.77 (2'-CO), 69.49 (15'a-C), 62.51 (spiro-C), 52.71 (3'-CH_3), 50.77 (2'-CH_3) ppm. MS (70 eV): *m/z* (%) = 616.05 [M^{+1}] (16.30), 309.01 [B^+] (100). IR (KBr): $\nu = 3058$ (C—H, arom.), 2948–2989 (C—H, aliph.), 1748 (3'-C═O), 1683 (2'-C═O), 1574 (C═C), 1480, 1245, 1278, 1136, 1113, 947, 769, 623 cm^{-1}. Elemental analysis for $C_{36}H_{23}ClN_2O_6$ (M. Wt = 615.05): calc. %: C, 70.30; H, 3.77; N, 4.55; Cl, 5.77; found C, 70.28; H, 3.75; N, 4.79; Cl, 5.81.

Dimethyl spiro[fluorene-9,1′-pyrrolo[1,2-f]-(14′-bromo)benzo[i]-phenanthridine]-2′,3′-dicarboxylate (8l). Reactants: 375 mg (0.001 mol) spirene **5**, 308 mg (0.001 mol) 3-bromo-benzo[i]phenanthridine **4l**; yield 338 mg (55%) pale yellow crystals from ether-CH_2Cl_2 (7:3); m.p. 231 °C. ^{1}H NMR ($CDCl_3$): $\delta = 8.12$ (d, J = 1.64 Hz, 1H, CH-arom.); 7.70–7.73 (m, 3H, CH-arom.), 7.21–7.24 (m, 4H, CH-arom.), 7.16–7.20 (m, 4H, CH-arom.), 6.90–6.94 (t, $J = 7.80$, 2H, CH-arom.), 6.67–6.62 (t, $J = 7.82$, 2H, CH-arom.), 6.12 (s, 1H, 15′c-H), 5.74–5.78 (dd, $J = 7.80$ Hz, 2H, CH-arom.), 4.12 (s, 3H, 3'-CH_3), 3.58 (s, 3H, 2'-CH_3) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 163.35$ (3'-CO), 162.72 (2'-CO), 69.47 (15'a-C), 62.47 (spiro-C), 52.57 (3'-CH_3), 50.82 (2'-CH_3) ppm. MS (70 eV): *m/z* (%) = 616.55 [M^{+2}] (23.45), 300.79 [B^+] (100). IR (KBr): $\nu = 3056$ (C—H, arom.), 2958–2982 (C—H, aliph.), 1742 (3'-C═O), 1680 (2'-C═O), 1568 (C═C), 1473, 1237, 1260, 1176, 1136, 944, 779, 646 cm^{-1}. Elemental analysis for $C_{36}H_{24}BrN_2O_4$ (M. Wt = 614.55): calc. %: C, 70.35; H, 3.94; N, 4.59; Br, 13.02; found C, 70.41; H, 3.88; N, 4.61; Br, 13.12.

Dimethyl spiro[fluorene-9,1′-pyrrolo[1,2-f]-(12′-nitro)benzo[i]-phenanthridine]-2′,3′-dicarboxylate (8m). Reactants: 375 mg (0.001 mol) spirene **5**, 274 mg (0.001 mol) 1-nitrobenzo[i]phenanthridine **4m**; yield 110 mg (19%) yellow crystals from ether-CH_2Cl_2 (4:6); m.p. 213 °C. ^{1}H NMR ($CDCl_3$): $\delta = 8.00$ (d, $J = 1.68$ Hz, 1H, CH-arom.); 7.73–7.76 (m, 3H, CH-arom.), 7.20–7.25 (m, 4H, CH-arom.), 7.10–7.19 (m, 4H, CH-arom.), 6.92–6.96 (t, $J = 7.88$, 2H, CH-arom.), 6.60–6.64 (t, $J = 7.86$, 2H, CH-arom.), 6.01 (s, 1H, 15′c-H), 5.70–5.77 (dd, $J = 7.80$ Hz, 2H, CH-arom.), 4.14 (s, 3H, 3'-CH_3), 3.52 (s, 3H, 2'-CH_3) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 163.45$ (3'-CO), 162.63 (2'-CO), 69.51 (15'a-C), 62.42 (spiro-C), 52.64 (3'-CH_3), 50.87 (2'-CH_3) ppm. MS (70 eV): *m/z* (%) = 580.56 [M^+] (19.37), 274.21 [B^+] (100). IR (KBr): $\nu = 3040$ (C—H, arom.), 2934–2979 (C—H, aliph.), 1753 (3'-C═O), 1698 (2'-C═O), 1556 (C═C), 1470, 1247, 1268, 1167, 1120, 979, 777 644 cm^{-1}. Elemental analysis for $C_{36}H_{24}N_2O_6$ (M. Wt = 580.56): calc. %: C, 74.47; H, 4.17; N, 4.83; found C, 74.43; H, 4.09; N, 4.19.

Dimethyl spiro[fluorene-9,1′-pyrrolo[1,2-f]-(13′-nitro)benzo[i]- phenanthridine]-2′,3′-dicarboxylate (8n). Reactants: 375 mg (0.001 mol) spirene **5**, 274 mg (0.001 mol) 2-nitrobenzo[i]phenanthridine **4n**; yield 156 mg (27%) yellow crystals from ether-CH_2Cl_2 (4:6); m.p. 236 °C. ^{1}H NMR ($CDCl_3$): $\delta = 8.08$ (d, $J = 1.62$ Hz, 1H, CH-arom.); 7.72–7.75 (m, 3H, CH-arom.), 7.21–7.24 (m, 4H, CH-arom.), 7.12–7.17 (m, 4H, CH-arom.), 6.94–6.98 (t, $J = 7.82$, 2H, CH-arom.), 6.61–6.65 (t, $J = 7.80$, 2H, CH-arom.), 6.06 (s, 1H, 15′c-H), 5.71–5.75 (dd, $J = 7.88$ Hz, 2H, CH-arom.), 4.10 (s, 3H, 3'-CH_3), 3.59 (s, 3H, 2'-CH_3) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 163.49$ (3'-CO), 162.67 (2'-CO), 69.57 (15'a-C), 62.47 (spiro-C), 52.67 (3'-CH_3), 50.80 (2'-CH_3) ppm. MS (70 eV): *m/z* (%) = 580.56 [M^+] (19.37), 274.21 [B^+] (100). IR (KBr): $\nu = 3032$ (C—H, arom.), 2989–2999 (C—H, aliph.), 1750 (3'-C═O), 1694 (2'-C═O), 1550 (C═C), 1477, 1244, 1262, 1161, 1130, 962, 783; 636 cm^{-1}. Elemental analysis for $C_{36}H_{24}N_2O_6$ (M. Wt = 580.56): calc. %: C, 74.47; H, 4.17; N, 4.83; found C, 74.58; H, 4.11; N, 4.13.

Dimethyl spiro[fluorene-9,1′-pyrrolo[1,2-f]-(14′-nitro)benzo[i]-phenanthridine]-2′,3′-dicarboxylate (8o). Reactants: 375 mg (0.001 mol) spirene **5**, 274 mg (0.001 mol) 3-nitrobenzo[i]phenanthridine **4o**; yield 225 mg (39%) yellow crystals from ether-CH_2Cl_2 (4:6); m.p. 240 °C. ^{1}H NMR ($CDCl_3$): $\delta = 8.19$ (d, $J = 1.78$ Hz, 1H, CH-arom.); 7.70–7.73 (m, 3H, CH-arom.), 7.27–7.29 (m, 4H, CH-arom.), 7.14–7.18 (m, 4H, CH-arom.), 6.88–6.92 (t, $J = 7.80$, 2H, CH-arom.), 6.62–6.64 (t, $J = 7.82$, 2H, CH-arom.), 6.18 (s, 1H, 15′c-H), 5.71–5.75 (dd, $J = 7.82$ Hz, 2H, CH-arom.), 4.19 (s, 3H, 3'-CH_3), 3.67 (s, 3H, 2'-CH_3) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 163.53$ (3'-CO), 162.62 (2'-CO), 69.67 (15'a-C), 62.67 (spiro-C), 52.78 (3'-CH_3), 50.91 (2'-CH_3) ppm. MS (70 eV): *m/z* (%) = 580.56 [M^+] (19.37), 274.21 [B^+] (100). IR (KBr): $\nu = 3030$ (C—H, arom.), 2890–2645 (C—H, aliph.), 1756 (3'-C═O), 1687 (2'-C═O), 1545 (C═C), 1484, 1239, 1278, 1164, 1147, 968, 775; 689 cm^{-1}. Elemental analysis for $C_{36}H_{24}N_2O_6$ (M. Wt = 580.56): calc. %: C, 74.47; H, 4.17; N, 4.83; found C, 74.52; H, 4.18; N, 4.10.

Dimethyl spiro[fluorene-9,1′-pyrrolo[1,2-f]-(14′-carboxymethyl)benzo[i]-phenanthridine]-2′,3′-dicarboxylate (8p). Reactants: 375 mg (0.001 mol) spirene **5**, 287 mg (0.001 mol) 3-carboxymethylbenzo[i]phenanthridine **4p**; yield 255 mg (43%) white crystals from ether-CH_2Cl_2 (7:3); m.p. 199 °C. ^{1}H NMR ($CDCl_3$): $\delta = 8.22$ (d, $J = 1.78$ Hz, 1H,

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CH-arom.); 7.78–7.82 (m, 3H, CH-arom.), 7.24–7.26 (m, 4H, CH-arom.), 7.12–7.15 (m, 4H, CH-arom.), 6.82–6.84 (t, $J = 7.86$, 2H, CH-arom.), 6.63–6.67 (t, $J = 7.88$, 2H, CH-arom.), 6.12 (s, 1H, 15′c-H), 5.74–5.77 (dd, $J = 7.82$ Hz, 2H, CH-arom.), 4.12 (s, 3H, 3'-CH_3), 3.86 (s, 3H, $COOCH_3$), 3.62 (s, 3H, 2'-CH_3) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 163.46$ (3'-CO), 162.57 (2'-CO), 69.62 (15'a-C), 62.64 (spiro-C), 52.74 (3'-CH_3), 52.27 ($COOCH_3$); 50.75 (2'-CH_3) ppm. MS (70 eV): *m/z* (%) = 593.60 [M^+] (36.27), 274.21 [B^+] (100). IR (KBr): $\nu = 3020$ (C—H, arom.), 2920–2842 (C—H, aliph.), 1754 (3'-C═O), 1681 (2'-C═O), 1544 (C═C), 1479, 1242, 1279, 1175, 1150, 960, 774; 693 cm^{-1}. Elemental analysis for $C_{38}H_{27}NO_6$ (M. Wt = 593.60): calc. %: C, 76.88; H, 4.58; N, 2.36; found C, 76.81; H, 4.63; N, 2.44.

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