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ORIGINAL PAPER

Photochromism of dihydroindolizines. Part XV: Synthesis and photophysical properties of dihydroindolizine photoswitches bearing a conjugated aryleneethynylene tripodal linker system

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Abstract Different photochromic dihydroindolizines (DHIs) bearing conjugated aryleneethynylene tripodal linker systems were synthesized using several Sonogashira coupling reactions. The spirocyclopropene precursors incorporating different acetylenic bridge moieties at the 2-position of the fluorene moiety were synthesized via chemical and photochemical routes. Multiaddressable photochromic properties of the DHI derivatives substituted in the fluorene (region A) and pyridazine (region C) parts were studied. Optimization of the formation of the DHIs was also done by applying different palladium-mediated Sonogashira coupling reactions. Irradiation of the photochromic DHIs with polychromatic light led to colored betaines which undergo thermal 1,5-electrocyclization. The kinetics of the thermal 1,5-electrocyclization were studied by using a multichannel FT–UV–Vis spectrophotometer. A pronounced effect on the kinetic behavior of the 1,5-electrocyclization process of the betaines was observed by changing substitution from non-substituted to dimethyl-substituted pyridazines. Photodegradation experiments and the bleaching and fading cycles revealed high photostability of the betaines under investigation. These properties of betaines of tripodal linker conjugates will help these materials to find applications.

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Introduction

Photochromic molecules attract much attention both theoretically and practically because of their potential applications in optical devices, for example optical memories and switches [1–4]. These molecules find use in the fabrication of several optoelectronic devices, for example optical memories, switches, and holograms. Since the last decade, the development of such optoelectronic devices has included photochromic compounds as the active components [5]. It has been established that photochromic compounds support their activities in a reversible photochemical reaction induced by the absorption of electromagnetic radiation in the ultraviolet region, which provokes a visible color change of the original colorless molecule. Photochromic dihydroindolizines (DHIs), which were discovered and developed by H. Dürr [6–19], are well known photochromic materials that have attracted much interest from the standpoints of both fundamental elucidation of electrocyclization reactions and their potential applications to optical memories and switches [20–24, 38–44]. Because of a 1,5-electrocyclization photoisomerization between two distinct isomeric states, i.e., the ring-opened form (betaine form) and the ring-closed form (DHI form), these entities are promising candidates for optical storage media and electronic devices [38–47]. Photochromic DHIs have sufficient thermal stability in both the open and the closed forms, very high resistance to photofatigue, and their chromophores provide convenient distinctive groupings that absorb ultraviolet radiation and allow the

reaction to be easily monitored by UV–Vis spectroscopy [15–47].

Research on the synthesis of carbon-rich organic and organometallic compounds for widespread applications in the field of materials science has increased substantially. In this context, the use of π-conjugated rigid fluorenyl chromophores and their derivatives offers exciting perspectives for the design of new molecular oligomeric and polymeric materials for various optoelectronic applications [48–52]. Many molecular structures have been synthesized for use as molecular devices, including switches, wires, controllers, and gates [53–57]. Within contemporary acetylene chemistry [58], there is great interest in the synthesis of conjugated diyne and oligoyne molecules. These carbon-rich building blocks [59] are fundamentally important for molecular rods and cyclic frameworks and are active components in optoelectronic devices such as wires, switches, and nonlinear optics, etc. [60–64].

In continuation of our research on the synthesis and photochromic behavior of photochromic DHIs, we now describe the synthesis and photophysical properties of carbon-rich fluorenyl DHI tripodal linkers and report studies on their photochromic behavior in solution. Also, synthesis approaches and Sonogashira-mediated methodologies are described in detail.

Results and discussion

*Synthesis of fluorenylethynylene spirocyclopropene precursors **8a–8c***

Dimethyl 2′-iodospiro[cycloprop[2]ene-1,9′-fluorene]-2,3-dicarboxylate (**1**) has been previously prepared by us [65–67]. The spirocyclopropene precursors **8a** ($n = 0$), **8b** ($n = 1$), and **8c** ($n = 2$) were synthesized via a five-step sequence, starting with the known three-step conversion of 2-nitro-9*H*-fluoren-9-one to 2-iodo-9*H*-fluoren-9-one (**2**) in 64% yield [68, 69 and references therein] (Scheme 1). Sonogashira coupling of **2** with trimethylsilane derivatives **3a–3c** ($n = 0$, 1, 2) in the presence of $Pd(PPh_3)_2Cl_2$ (2.5%)/Cu_2I_2/Et_2NH in THF for 4 h afforded the coupling products **4a** ($n = 0$), **4b** ($n = 1$), and **4c** ($n = 2$) in 74, 67, and 59% yield, respectively. Condensation of the substituted fluorenones **4a–4c** with hydrazine hydrate in boiling ethanol for 3 h led to both condensation and desilylation with formation of **5a** ($n = 0$), **5b** ($n = 1$), and **5c** ($n = 2$) in 61, 54, and 42% yield, respectively.

The diazofluorene derivatives **6a–6c** were obtained in 53–76% yields after oxidation of hydrazones **5a–5c** with manganese dioxide in dry ether at room temperature in the absence of light. Addition of dimethyl acetylenedicarboxylate (DMAD) to **6a–6c** in dry ether under dark conditions for 8 h led to the formation of the pyrazole derivatives **7a–7c** in moderate yields (55, 52, and 49%).

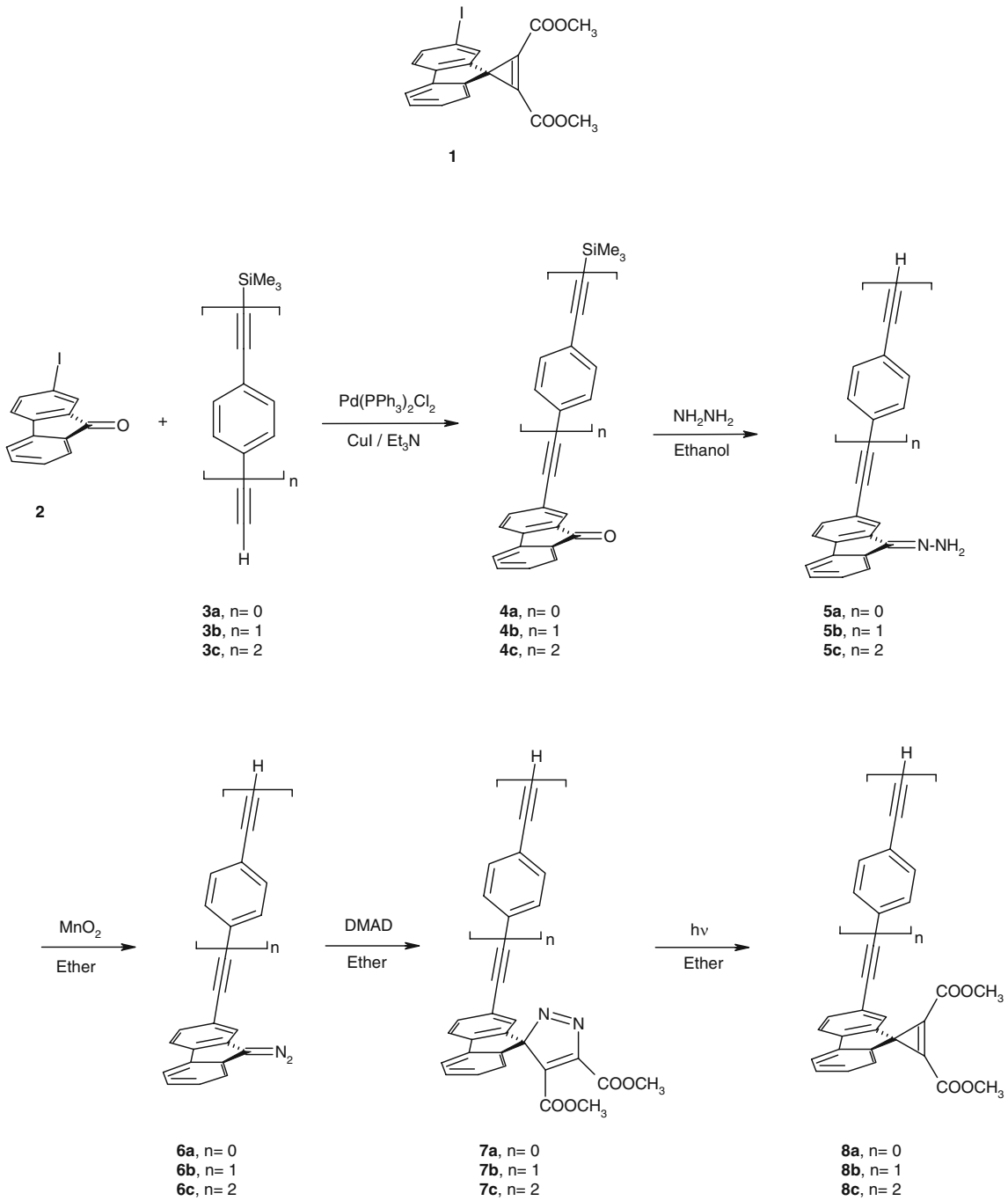
The target spirocyclopropene derivatives **8a–8c** were obtained in low yields ranging from 19 to 32% via photolysis of the pyrazole derivatives **7a–7c**. The photolysis was carried out in an inert and dry nitrogen atmosphere using a high pressure mercury lamp (125 W) in dry ether solution for 2 h. The chemical structures of the synthesized compounds **4–8** (Scheme 1) were confirmed and established by both spectroscopic (NMR, IR, and mass spectrometry) and elemental microanalytical data (elemental analysis data were satisfactory).

*Approaches to the synthesis of the π-conjugated photochromic dihydroindolizines **10a–10f***

Electrophilic addition of spirocyclopropenes **8a–8c** to pyridazine (**9a**) and 3,6-dimethylpyridazine (**9b**) using the cyclopropene route [11–47] (Scheme 2) under dry, dark, and inert conditions for 12 h (TLC monitored using CH_2Cl_2 as eluent) led to the formation of the photochromic DHIs **11a–11f** in poor yields (22–35%, method A). Formation of the photochromic DHIs **11a–11f** occurs through conjugate addition of one of the nitrogen atoms of pyridazines **9a**, **9b** to of the electron-deficient α,β-unsaturated spirocyclopropene diester **8a–8c**, which leads to ring opening via a cyclopropyl–allyl conversion to the colored betaines **10a–10f** (Scheme 2). A subsequent ring closure to DHIs **11a–11f** results in a partial, slow, thermal 1,5-electrocyclization back reaction (Scheme 2) which can be reversed upon exposure to UV light. The photochromic DHIs **11a–11f** were obtained in the pure form by purification on silica gel using dichloromethane as the eluent.

Alternatively, the target photochromic DHIs **11a–11f** could be synthesized via the multi-step synthesis route shown in Scheme 3. The palladium-mediated Sonogashira coupling of DHI **12a** and its dimethyl derivative **12b** [65–67] with compounds **3a–3c** (2.5% $Pd(PPh_3)_2Cl_2$, CuI/Et_3N, dry THF, 5 h) yielded the desired photochromic trimethylsilyl DHIs **13a–13f** through the betaines **14a–14f**, in 55–67% isolated yields. Purification was carried out by flash chromatography on silica gel with CH_2Cl_2 as eluent (method B). Subsequent desilylation of the DHIs **13a–13f** with tetrabutylammonium fluoride (TBAF) in dry THF for 4 h afforded the silyl-free products **15a–15f** obtained in good isolated yields (62–75%).

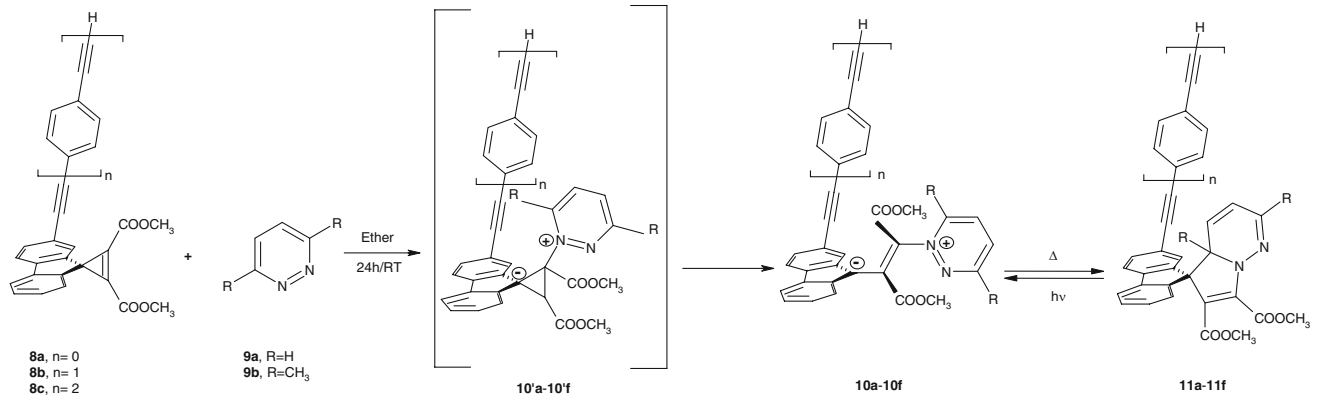
The treatment of DHIs **13a–13f** with hydrazine hydrate in ethanol at 0 °C for 1 h afforded the desilylated photochromic DHIs **11a–11f** in 45–59% yield (method C), which is similar to results for compounds **4a–4c**. The products obtained from the three different routes gave the same analytical and spectroscopic data and the same melting points and mixed melting points.



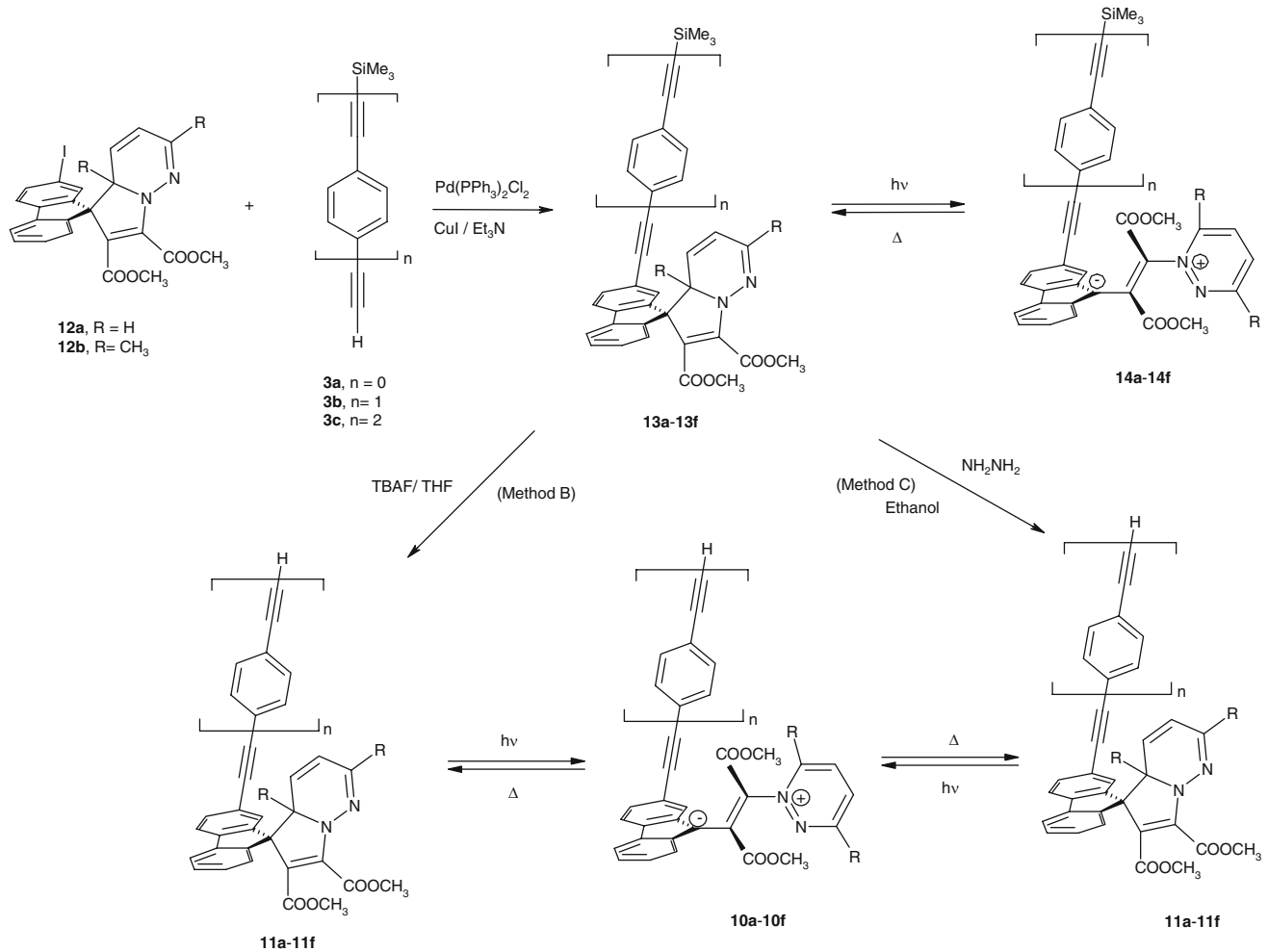
Scheme 1

*Palladium-mediated Sonogashira coupling of photochromic DHIs **11a–11f** with the tripodal linker **15** under different coupling conditions*

The tripodal linker **15** was prepared in six steps and 29% overall yield in accordance with the methods reported by Galoppini and coworkers [70–80] and Zarwell and Rück-Braun [81]. The final fragment coupling of the photochromic DHIs **11a–11f** to the tripodal linker system **15** was surveyed, via a Sonogashira cross-coupling reaction, under different reaction conditions for optimization purposes (Scheme 4). Reaction of **11a–11f** with **15** under standard Sonogashira coupling conditions (2% $Pd(PPh_3)_2Cl_2$, 1% PPh_3, CuI/Et_3N, THF, 15 h at 45 °C, method A) led to low conversion of DHIs **11a–11f** to the coupling products **17a–17f** (22–28%). The conditions of the Sonogashira coupling were varied by using $Pd(OAc)_2/Ph_3P$ with CuI/Et_3N, toluene/DMF and stirring for 12 h at 40 °C (method B). In this case, the

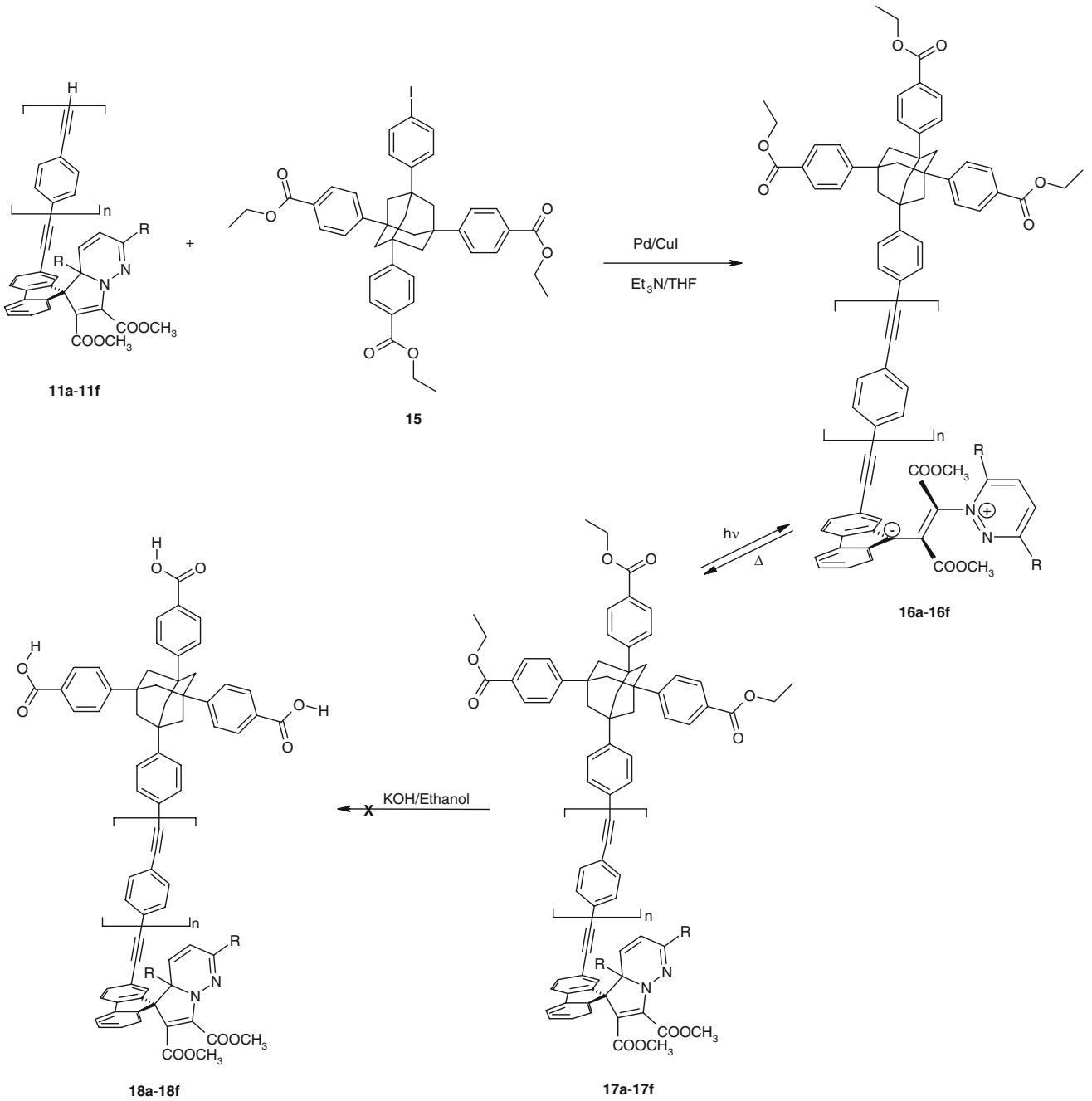


Scheme 2



Scheme 3

coupling products **17a–17f** were obtained in slightly better yields (31–52%). With the objective of further improving the yields of **17a–17f**, the reaction conditions were modified to include bis(dibenzylideneacetone)palladium(0) as the new palladium source, CuI, and DIEA as the base (method C), which led to the formation of the coupling products **17a–17f** in 52–68% yield. In addition, coupling of photochromic DHIs **11a–11f** with the tripod system **15** using 2.5 or 5%



Scheme 4

$Pd(PPh_3)_2Cl_2$, 1% 1,10-phenanthroline, 5% NaI, CuI/Et_3N, DMF at 90 °C (method D) did not afford the coupling products **17a**–**17f** and, instead, decomposition of the reaction mixtures was observed.

Also the coupling reaction of DHIs **11a**–**11f** and the tripodal linker **15** using $Pd(PPh_3)_4$ in dry pyrrolidine at 45 °C for 8 h (RT and 60 °C were also used) showed no evidence of the formation of the coupling products **17a**–**17f** (method E). This copper-free method was investigated to circumvent the homo-dimerization of the DHI system. Attempts to improve the yield by manipulating the percentage of the palladium catalyst and reaction times were unsuccessful in all of the above mentioned coupling reactions. Interestingly, the photochromic DHIs **17a** and **17d** were previously synthesized by us [67] via a Sonogashira cross-coupling reaction by coupling of halo-substituted DHI with an acetylenic tripodal system which resulted in exactly the same chemical structures.

Attempted hydrolysis of the methyl ester groups of DHIs **17a**–**17f** using KOH in ethanol or THF at room

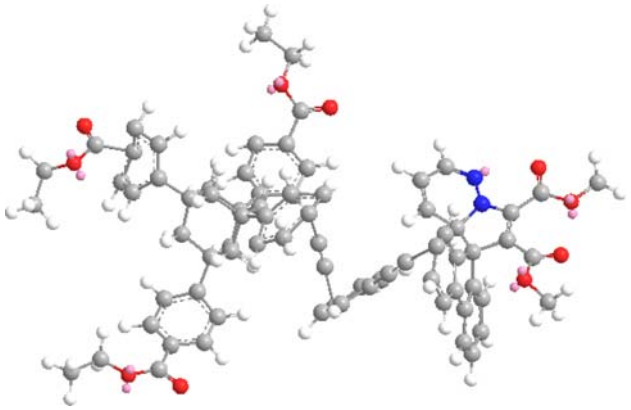


Fig. 1 Representation of the optimized (MM2) structure of DHI **17c**

temperature and at 50 °C afforded no product and instead decomposition of the DHIs was observed. All subsequent attempts to obtain the tricarboxylic acids **18a–18f** by changing base concentration (4–8 M) and reaction times (from RT to 72 h, in ethanol or in THF) were met with failure. The chemical structures of all photochromic DHIs **11a–11f**, **13a–13f**, and **17a–17f** were established on the basis of spectral and analytical data which corroborated the suggested chemical structures. For example, the chemical structure of DHI **17c** was assigned by 2D NMR spectroscopy. Further assignments of 8′-CH, 8′a-CH, and some other protons in the DHI skeleton were achieved with the aid of a NOESY spectrum of **17c**. We observed that 8′a-CH at $\delta = 4.94$ ppm is proximal to 8′-CH at $\delta = 5.35$ ppm and 1-CH of the fluorene moiety at $\delta = 7.68$ ppm. This suggests that 8′a-CH is in the 8′a-position and not the 8′-position. Indeed, the connectivity between 8′-CH and 8-CH of the fluorene part at $\delta = 7.54$ ppm was observed. This vicinity of 8′-CH with 8-CH indicates that the pyridazine moiety is perpendicular to the fluorene skeleton. This observation is also supported by molecular modeling calculation of DHI **17a** (Fig. 1). The molecular mechanics calculation (MM2) showed that the distance between both 8′a-CH and 8′-CH connected to 6′-CH and 1-CH of the fluorene moiety is <3 Å, which is in good agreement with the NMR results (Fig. 1).

*Absorption spectra of DHIs **11a–11f**, **13a–13f**, and **17a–17f**, and their corresponding betaines **10a–10f**, **14a–14f**, and **16a–16f***

The photophysical properties pertinent to their photochromic properties were obtained from the absorption features of photochromic DHIs **11a–11f**, **13a–13f**, and **17a–17f**. The absorption spectra of the synthesized DHIs **11a–11f**, **13a–13f**, and **17a–17f** were measured in dichloromethane solution, at a concentration of 1×10^{-5} mol dm^{-3}, at 23 °C, using a UV–Vis spectrophotometer. The photochromic DHIs **11a–11f**, **13a–13f**, and **17a–17f** showed yellow color in dichloromethane solution and in the solid state (Table 1). The intensities (log ε) of the absorption of these bands were found to lie between 3.80 and 4.67 depending on the number of aryleneethynylene groups. The absorption of DHIs **11a–11f**, **13a–13f**, and **17a–17f** were observed in the far UV region and showed absorption maxima between 390 and 405 nm (Table 1). This absorption depends on the number of aryleneethynylene groups substituting the aromatic fluorene (region A). A pronounced bathchromic shift of about 6 nm was recorded after coupling of DHIs **11a–11f** with the tripodal system **15**, as in DHIs **17a–17f**. This may be attributed to the increase in extended conjugation of the DHI skeleton following coupling. Exchanging the proton on the pyridazine with a methyl substituent led to a bathochromic shift of about 3 nm of the DHIs **17d–17f**. These absorption bands can be assigned to the locally excited π–π*-transition (LE) located in the butadienyl-vinylamine chromophores [11–47] of the photochromic DHIs **11a–11f**, **13a–13f**, and **17a–17f** (Table 1).

Polychromatic light irradiation of DHIs **11a–11f**, **13a–13f**, and **17a–17f** led to the ring-opened betaines **10a–10f**, **14a–14f**, and **16a–16f** (Fig. 2). The colored betaine forms **10a–10f**, **14a–14f**, and **16a–16f** changed from red to blue-green in CH_2Cl_2 solution, at a concentration of 1×10^{-5} mol dm^{-3}, at room temperature because of their slower 1,5-electrocyclization. All absorption maxima of the colored betaines **10a–10f**, **14a–14f**, and **16a–16f** were found in the visible region between 522 nm (betaine **11a**) and 635 nm (betaine **17f**). The UV spectra of the colored betaines containing a non-substituted pyridazine as a heterocyclic moiety, as in betaines **10a–10c**, **14a–14c**, and **16a–16c** (Fig. 2), exhibit a red-violet color and show only one absorption maximum ranging between 522 and 534 nm. On the other hand, the betaines containing a dimethylpyridazine in region C (**10d–10f**, **14d–14f**, and **16d–16f**) showed a green–blue color and three absorption maxima with three isobestic points (Table 1). Interestingly, a bathochromic shift by more than 110 nm was observed in the absorption spectra of the betaines containing non-substituted pyridazines **10a–10c**, **14a–14c**, and **16a–16c** compared with the dimethyl analogs **10d–10f**, **14d–14f**, and **16d–16f**. This large shift led to the change of the colored forms from red to green–blue, which is attributed to the hyper-conjugation bestowed by the two methyl groups which imparts stability to the zwitterionic betaines leading to a bathochromic shift [65–67] (Table 1). Furthermore, a noticeable bathochromic shift of about 7–9 nm was noted by increasing the number of bridged phenyl acetylenic groups from $n = 0$ to $n = 2$ which showed no dependence on the substitution pattern of the pyridazine. This may be attributed to an increase in the conjugation of the fluorene unit via hyperconjugation with the aromatic

Table 1 Absorption spectra of DHIs **11a–11f**, **13a–13f**, and **17a–17f** and their corresponding betaines **10a–10f**, **14a–14f**, and **16a–16f**, and kinetic data of betaines **10a–10f**, **14a–14f**, and **16a–16f** in the second range (monitored by UV spectrophotometry) in CH_2Cl_2 solution (23 °C, $c = 1\times10^{-5}$ mol dm^{-3})

DHI/Betaine	λ_{max} (DHI) (nm)	log (ε)	λ_{max} (betaine) (nm)	$k \times10^{-3}$ (s)	$t_{1/2}$ (s)	Color of betaine
11a/10a	385	3.82	522	3.50	198	Red–violet
11b/10b	386	3.85	523	3.22	215	Red–violet
11c/10c	387	4.96	523	3.04	228	Red–violet
11d/10d	398	4.02	354, 444, 626	1.03	675	Green–blue
11e/10e	399	4.09	355, 445, 628	0.69	995	Green–blue
11f/10f	401	4.13	355, 448, 630	0.64	1,083	Green–blue
13a/14a	391	3.87	527	6.54	106	Red–violet
13b/14b	393	3.89	529	5.10	136	Red–violet
13c/14c	394	3.96	532	3.96	175	Red–violet
13d/14d	395	4.03	355, 449, 627	1.11	624	Red–violet
13e/14e	399	4.07	357, 445, 626	8.22	843	Green
13f/14f	402	4.13	352, 445, 634	7.40	937	Green
17a/16a[a]	402	4.22	529	2.57	270	Red–violet
17b/16b	403	4.28	532	2.42	287	Red–violet
17c/16c	405	4.35	534	2.31	300	Red–violet
17d/16d[a]	406	4.34	353, 442, 632	0.49	1,413	Green–blue
17e/16e	407	4.46	355, 447, 632	0.46	1,521	Green–blue
17f/16f	407	4.52	355, 448, 635	0.41	1,678	Green–blue

[a] The photochromic data of DHIs **17a**, **17d** have been reported elsewhere [65–67] and are cited here for comparison

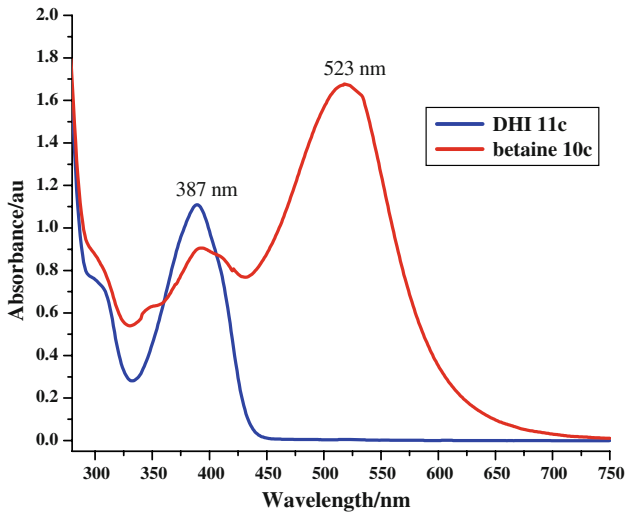


Fig. 2 UV–Vis of photochromic DHI **11c** and the corresponding betaine form **10c** after UV irradiation in CH_2Cl_2 ($c = 1\times10^{-5}$ mol dm^{-3}) at ambient temperature

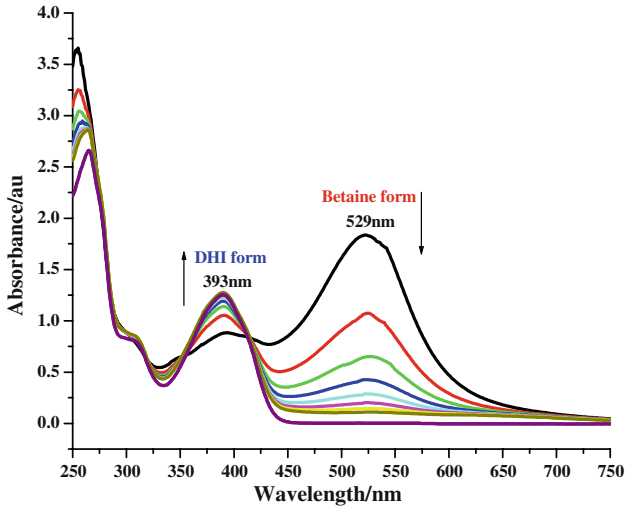


Fig. 3 FT–UV–Vis kinetic spectra of the 1,5-electrocylization of the betaine **14b** to DHI **13b** (cycle time = 50 s, run time = 400 s) in CH_2Cl_2 ($c = 1\times10^{-5}$ mol dm^{-3} at 253 K)

phenyl rings through the bridged acetylenic bond. Indeed, a bathochromic shift of about 10 nm of the absorption of the betaines **16a–16f** incorporating the tripod linker conjugate compared with the betaines **10a–10f** and **14a–14f** incorporating no tripodal linker conjugates was detected. More spectroscopic data about the UV–Vis measurements of the colored betaines under investigation are listed in Table 1.

The kinetics of the thermal 1,5-electrocyclization of the betaine forms **10a–10f**, **14a–14f**, and **16a–16f** were studied by use of a multichannel FT–UV–Vis spectrophotometer (Figs. 3, 4). The thermal fading back reaction measurements showed that the half-lives of the colored betaines **10a–10f**, **14a–14f**, and **16a–16f** lie in the second domain and were found to be between 106 and 1,678 s (Table 1

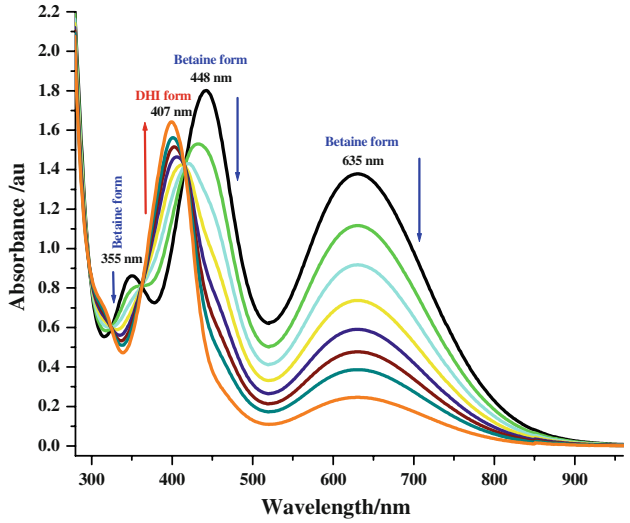


Fig. 4 FT–UV–Vis kinetic spectra of the 1,5-electrocyclization of the betaine **16f** to DHI **17f** (cycle time = 500 s, run time = 4,000 s) in CH_2Cl_2 ($c = 1\times10^{-5}$ mol dm^{-3} at 253 K)

and Figs. 3, 4). A pronounced increase in the half-lives of the betaines bearing a dimethylpyridazine **10d–10f**, **14d–14f**, and **16d–16f** by approximately a factor of 7 compared with the half-lives of the betaines bearing a non-substituted pyridazine **10a–10c**, **14a–14c**, and **17a–17c** was observed. As previously discussed [65–67], the detected increase in the half-lives may be attributed to the stabilization of the positive and negative charges on the betaine forms leading to enhancement of the half-lives of the betaine structures by the electron-donating methyl groups. Elongation of the half-lives of the betaine forms by increasing the number of acetylenic units in the bridge by approximately a factor of 1.30 was recorded. Also, a noticeable rise in the half-lives of the betaines coupled with tripodal linker system as in **16a–16f** compared with non-coupled betaines **10a–10f** and **14a–14f** was observed. These increases and tuning of the absorption spectra and half-lives of the tripodal DHIs will help these materials to be supported on metal oxide nanoparticles.

*Photo-degradation resistance of photochromic DHIs **11a–11f, 13a–13f, 17a–17f** and their corresponding betaines **10a–10f, 14a–14f, 16a–16f***

The gradual loss of the ability to change color by exposure to visible or ultraviolet light in this context has been termed fatigue [1–4, 11–14]. Gautron [82] has advanced a quantitative approach to measure fatigue in photochromic systems. Because of the slow thermal bleaching process of the betaines to DHIs, FT–UV–Vis measurement at room temperature was used to study the photo-fatigue of the DHIs and betaines under investigation. Irradiation of degassed dichloromethane solution of DHIs **11a–11f**, **13a–13f**, **17a–17f** at room temperature (23 °C) with polychromatic light (λ = 200–400 nm) led to the ring-opened colored betaines **10a–10f**, **14a–14f**, and **16a–16f**. Upon continued irradiation they decomposed after some time. The time in which the absorbance reaches 30% of its initial value is called t_{30} value.

Table 2 Photodegradation data of some selected betaines **10a–10f**, **14a–14f**, and **16a–16f** in dichloromethane solution ($c = 1 \times 10^{-5}$ mol dm^{-3}) at 23 °C

Betaine	t_{30} betaine/DHI	F	Betaine	t_{30} betaine/DHI	F
10a	518	2.13	**14d**	498	2.05
10b	464	1.91	**14e**	451	1.86
10c	419	1.72	**14f**	436	1.79
10d	559	2.30	**16a**[a]	583	2.40
10e	520	2.14	**16b**	533	2.19
10f	499	2.05	**16c**	461	1.90
14a	461	1.90	**16d**[a]	694	2.86
14b	433	1.78	**16e**	599	2.47
14c	362	1.49	**19f**	512	2.11
Standard	243	1.00	Standard	243	1.00

[a] The photodegradation data of betaines **16a**, **16d** have been reported previously [65–67] and are cited here for comparison. The factor F is the ratio between the t_{30} value of the betaine under investigation and the standard betaine (dicyanopyridazine DHI)

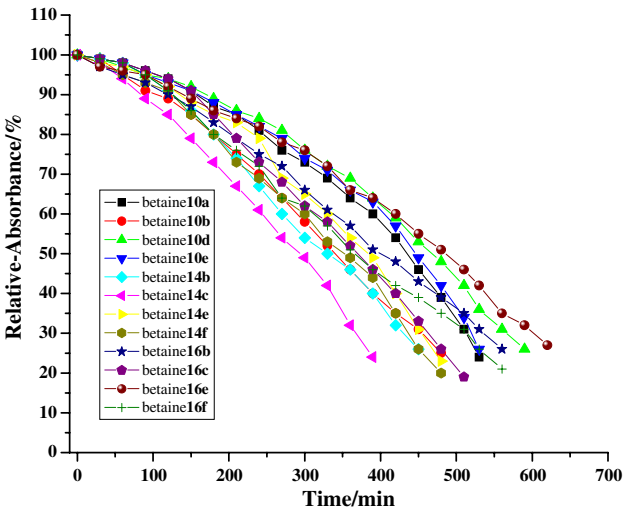


Fig. 5 Photodegradation experiment for determination of the t_{30}-value of selected betaines **10a–10f**, **14a–14f**, and **16a–16f** in CH_2Cl_2 ($c = 1\times10^{-5}$ mol dm^{-3}) at ambient temperature

The photodegradation data represented in Table 2 and Fig. 5 show that most of the selected betaines under investigation showed a higher photo-fatigue resistance than the standard dicyano-pyridazine DHI (t_{30} = 243 min) by a factor between 1.72 as in the case of betaine **10c** and 2.86 as in the case of betaine **16d**. A noticeable decrease in the

t_{30} values by increasing the number of acetylenic bridges in both betaines bearing two methyl groups and the non-substituted pyridazines was recorded. A highly pronounced increase in the t_{30} values of the betaines incorporating dimethylpyridazine as in betaines **10d–10f**, **14d–14f**, and **16d–16f** compared with the betaines incorporating a non-substituted pyridazine as in betaines **10a–10c**, **14a–14c**, and **16a–16c** by factor of about 0.1–0.3 has been observed. Interestingly, betaines **16a–16f** incorporating a tripodal linker showed the highest t_{30} values compared with other betaines under investigation. This interesting phenomenon will help these promising compounds find their applications. Betaine **16d** ($t_{30} = 694$ min) substituted with two methyl groups in the pyridazine moiety showed the highest photo-fatigue resistance amongst the other studied betaines and more than the standard betaine ($t_{30} = 243$ min) by a factor of 2.86.

The irradiation and thermal fading measurements presented in Fig. 6 show that the DHI/betaine **17e/16e** bearing the tripod linker system is more stable than the DHI/betaine **13e/14e** in terms of bleaching the thermal fading processes. The 20 bleaching and thermal fading cycles studied revealed no evidence of any decomposition product of the DHI/betaine **17e/16e**, as indicated by the UV–Vis measurements. These results have been further supported by NMR measurements which showed superimposable NMR spectra (coupling, δ values, and intensities) of the DHIs before irradiation and after 20 cycles of irradiation with no detection of any decomposition products.

In conclusion, we have described different palladium-mediated Sonogashira coupling reactions to optimize the coupling reactions with different acetylenic bridges and with the tripod linker system. Carbon-rich molecules and tripodal linker conjugate based photochromic DHI derivatives were synthesized successfully through different pathways to optimize reaction conditions and yields. Many coupling reactions were done on the fluorene part (region A) with different phenyl acetylenic bridges to help the extension of the photochromism of target molecules for future applications in electronic devices, molecular wires, and solar energy conversion using different alternative routes. Interesting photochromic properties with tuning of the chemical structures of the photochromic DHIs by changing the number of acetylenic bridges in the fluorene part and substitutions in the pyridazine region were detected. The photodegradation measurements of the photochromic DHIs and their corresponding betaines under investigation showed a higher photo-fatigue resistance by direct irradiation or by cycling between colored and colorless forms than the standard dicyano-DHI system. The multi-addressable photochromic properties of the new studied photochromic DHIs and their corresponding betaines are expected to be helpful in finding suitable applications.

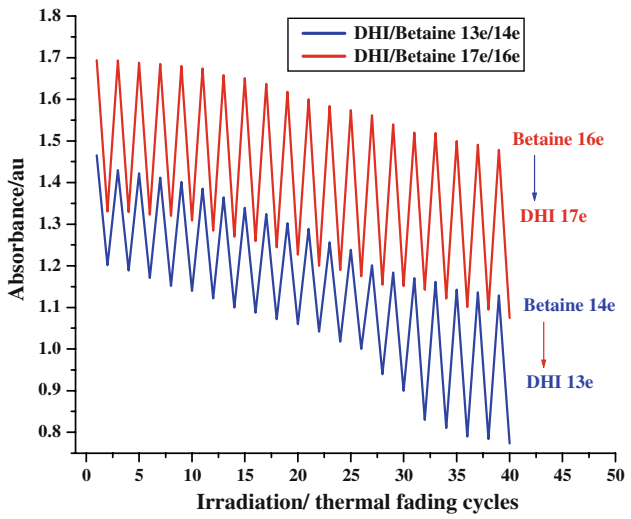


Fig. 6 Irradiation and thermal fading of DHI/betaine **14e/13e** and DHI/betaine **17e/16e** (irradiation/thermal fading/irradiation cycles) in CH_2Cl_2 ($c = 1\times10^{-5}$ mol dm^{-3}) at ambient temperature

Experimental

Fluorenespirocyclopropene derivatives **8a–8c** were obtained via photolysis of the corresponding pyrazoles in the photochemical reactor of Schenck [83] made from Pyrex ($\lambda > 290$ nm) according to reported procedures [15–53]. A high-pressure mercury lamp Philips–HPK (125 W) was used as a source of irradiation and the photolysis time was 4 h. Photochromic DHIs **17a** and **17d** were previously prepared by us [65–67]. The tripod linker system was prepared following the reaction procedures published by Galoppini and coworkers [70–80] and Zarwell and Rück-Braun [81]. Trimethylsilyl acetylene derivatives **2a–2c** were prepared following the reaction procedures published by Rodriguez et al. [48–50, 68, 69]. 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 (100 × 2 cm) on silica gel and CH_2Cl_2 as eluent. An Electrothermal Engineering melting-point apparatus was used to determine melting points. All NMR spectra were collected on a Bruker DRX 400 spectrometer (400 MHz) in $CDCl_3$ using TMS as the internal standard. Chemical shifts (δ) are reported in ppm. FT-IR measurements were performed using a Shimadzu FT-IR-8400S Fourier-transform infrared spectrophotometer. Mass spectra were recorded on a VG AutoSpec apparatus using electron impact at 70 eV. MALDI-MS spectra were

recorded in the positive mode using 2,5-dihydroxybenzoic acid in dioxane as matrix. UV-spectra were recorded on a Jasco V-570 FT-UV–Vis computerized spectrophotometer. All synthesized compounds gave satisfactory elemental analysis data. Compounds **17a** and **17d** are identical with those reported in Refs. [65–67].

*General procedures for the synthesis of dimethyl 2-[ethynyl(phenylethynyl)$_n$]spiro[9H-fluorene-9,5′(4′aH)-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylates **11a–11f***

Method A. A solution of spirocyclopropenes **8a–8c** (0.5 mmol) in 30 cm^3 dry ether and pyridazine (**9a**) or 3,6-dimethylpyridazine (**9b**) (0.7 mmol) were stirred at room temperature under dry N_2 in the absence of light for 12 h (TLC controlled). Ether was removed under reduced pressure and the products were purified by twice repeated column chromatography on silica gel using dichloromethane as eluent; finally recrystallization from the appropriate solvents afforded the products as pale yellow crystals.

Method B. To a solution of 2-iodopyridazine DHIs **12a** or **12b** (0.55 mmol) and trimethylsilylacetylene (**3a**), ((4-ethynylphenyl)ethynyl)trimethylsilane (**3b**), or ((4-((4-ethynylphenyl)ethynyl)phenyl)ethynyl)trimethylsilane (**3c**) (1.25 mmol) in 20 cm^3 dry THF and 50 cm^3 freshly distilled triethylamine under argon atmosphere at 50 °C was added dichlorobis(triphenylphosphine) palladium (19 mg, 0.026 mmol) and copper iodide (1.1 mg, 0.008 mmol). The mixture was stirred for 5 h, then the amine and THF were removed under reduced pressure. The crude residue was washed with saturated aqueous ammonium chloride solution (3 × 20 cm^3) with a small amount of KCN (200 mg), and extracted with dichloromethane (3 × 20 cm^3). The extracts were dried over anhydrous sodium sulfate and the solvent was removed to give a brown solid, which was purified by column chromatography to afford the trimethylsilylated DHIs **13a–13f**. The DHIs **13a–13f** (0.14 mmol) were dissolved in 10 cm^3 freshly distilled dry THF and treated with a solution of tetrabutylammonium fluoride (TBAF, 0.150 g, 1.1 mmol) in 5 cm^3 freshly distilled THF at room temperature under nitrogen atmosphere. The reaction mixture was stirred for 4 h, then 10 cm^3 water was added. The mixture was extracted with ethyl acetate (3 × 20 cm^3) and the residue was purified by column chromatography using dichloromethane as eluent to afford the required compounds **11a–11f** as yellow solids.

Method C. A solution of DHIs **13a–13f** (0.25 mmol) and hydrazine hydrate (99%, 0.1 cm^3, 2 mmol) in 10 cm^3 absolute ethanol was cooled to 0 °C and stirred at this temperature for 1 h. The solvent was removed, the product was extracted three times with 20 cm^3 ethyl acetate, and the residue was purified by column chromatography using dichloromethane as eluent to afford the required compounds **11a–11f** as yellow solids.

Dimethyl 2-ethynylspiro[9H-fluorene-9,5′(4′aH)-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate (**11a**, $C_{25}H_{18}N_2O_4$)
Method A: yield 35%, m.p.: 177 °C; method B: yield 75%, m.p.: 177 °C; method C: yield 75%, m.p.: 176 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91–7.92 (d, J = 2.4 Hz, 1H, CH arom.), 7.87–7.89 (d, J = 2.4 Hz, 1H, CH arom.), 7.75–7.76 (d, J = 1.89 Hz, 1H, CH arom.), 7.49–7.52 (d, J = 2.4 Hz, 1H, CH arom.), 7.45–7.47 (d, J = 2.4 Hz, 1H, CH arom.), 7.40–7.42 (dd, J = 1.76 Hz, J = 1.98 Hz, 1H, 6′-CH), 7.30–7.33 (dt, J = 2.4 Hz, J = 0.88 Hz, 1H, CH arom.), 7.21–7.23 (dt, J = 2.4 Hz, J = 0.88 Hz, 1H, CH arom.), 5.72–5.74 (m, 1H, 7′-CH), 4.99–5.02 (t, J = 2.2 Hz, 1H, 8′-CH), 4.71–4.74 (dt, J = 9.60 Hz, J = 1.76 Hz, 8′-CH), 4.09 (s, 1H, acetylenic H), 3.87 (s, 3H, 3′-CH_3), 3.45 (s, 3H, 2′-CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.42 (3′-CO), 161.79 (2′-CO), 149.23, 146.22, 142.97, 141.03, 140.19, 138.43, 136.02, 132.99, 130.62, 128.67, 126.76, 123.32, 122.46, 121.84, 120.34, 118.38, 104.48, 82.46 (acetylenic C), 81.34 (acetylenic C), 62.31 (8′a-C), 59.34 (spiro-C), 53.34 (3′-CH_3), 51.46 (2′-CH_3) ppm; IR (KBr): $\bar{\nu}$ = 3,076–3,043 (C–H, arom.), 2,887–2,972 (C–H, aliph.), 2,162 (acetylenic bond), 1,741 (3′-C=O), 1,694 (2′-C=O), 1,585 (C=N), 1,432 (C=C), 1,357, 1,252, 1,179, 1,080, 953, 875, 760 cm^{-1}; MS: m/z = 410.13 [M$^+$].

Dimethyl 2-[(4-ethynylphenyl)ethynyl]spiro[9H-fluorene-9,5′(4′aH)-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate (**11b**, $C_{33}H_{22}N_2O_4$)
Method A: yield 28%, m.p.: 164 °C; method B: yield 57%, m.p.: 165 °C; method C: yield 52%, m.p.: 163 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88–7.90 (d, J = 2.4 Hz, 1H, CH arom.), 7.87–7.89 (d, J = 2.4 Hz, 1H, CH arom.), 7.75–7.76 (d, J = 1.89 Hz, 1H, CH arom.), 7.56–7.58 (d, J = 7.98 Hz, 2H, CH arom.), 7.50–7.53 (d, J = 7.98 Hz, 2H, CH arom.), 7.45–7.47 (d, J = 2.4 Hz, 1H, CH arom.), 7.42–7.43 (d, J = 2.4 Hz, 1H, CH arom.), 7.39–7.41 (dd, J = 1.76 Hz, J = 1.98 Hz, 1H, 6′-CH), 7.29–7.32 (dt, J = 2.4 Hz, J = 0.88 Hz, 1H, CH arom.), 7.23–7.25 (dt, J = 2.4 Hz, J = 0.88 Hz, 1H, CH arom.), 5.70–5.73 (m, 1H, 7′-CH), 4.96–4.98 (t, J = 2.2 Hz, 1H, 8′a-CH), 4.70–4.73 (dt, J = 9.60 Hz, J = 1.76 Hz, 8′-CH), 4.05 (s, 1H, acetylenic H), 3.82 (s, 3H, 3′-CH_3), 3.42 (s, 3H, 2′-CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.42 (3′-CO), 161.79 (2′-CO), 149.23, 146.22, 142.97, 141.03, 140.19, 138.43, 136.02, 132.99, 131.56, 130.62, 128.67, 126.76, 123.32, 122.46, 121.84, 120.34, 118.38, 104.48, 93.12 (acetylenic C), 89.65 (acetylenic C), 82.46 (acetylenic C), 81.31 (acetylenic C), 62.30 (8′a-C), 59.35 (spiro-C), 53.39

(3′-CH_3), 51.41 (2′-CH_3) ppm; IR (KBr): $\bar{\nu}$ = 3,100–3,025 (C–H, arom.), 2,890–2,987 (C–H, aliph.), 2,154 (acetylenic bonds), 1,739 (3′-C=O), 1,692 (2′-C=O), 1,581 (C=N), 1,437 (C=C), 1,349, 1,254, 1,172, 1,081, 953, 877, 757 cm^{-1}; MS: m/z = 510.16 [M^+].

Dimethyl 2-[[4-[(4-ethynylphenyl)ethynyl]phenyl]ethynyl]-spiro[9H-fluorene-9,5′(4′aH)-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate (**11c**, $C_{41}H_{26}N_2O_4$)
Method A: yield 27%, m.p.: 144 °C; method B: yield 65%, m.p.: 143 °C; method C: yield 50%, m.p.: 143 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.86 (d, J = 2.4 Hz, 1H, CH arom.), 7.86–7.88 (d, J = 2.4 Hz, 1H, CH arom.), 7.74–7.75 (d, J = 1.89 Hz, 1H, CH arom.), 7.56–7.58 (m, 6H, CH arom.), 7.50–7.53 (d, J = 7.98 Hz, 2H, CH arom.), 7.44–7.46 (d, J = 2.4 Hz, 1H, CH arom.), 7.40–7.42 (d, J = 2.4 Hz, 1H, CH arom.), 7.36–7.38 (dd, J = 1.76 Hz, J = 1.98 Hz, 1H, 6′-CH), 7.30–7.33 (dt, J = 2.4 Hz, J = 0.88 Hz, 1H, CH arom.), 7.24–7.25 (dt, J = 2.4 Hz, J = 0.88 Hz, 1H, CH arom.), 5.71–5.74 (m, 1H, 7′-CH), 4.95–4.97 (t, J = 2.2 Hz, 1H, 8′a-CH), 4.75–4.78 (dt, J = 9.60 Hz, J = 1.76 Hz, 8′-CH), 4.07 (s, 1H, acetylenic H), 3.84 (s, 3H, 3′-CH_3), 3.45 (s, 3H, 2′-CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.36 (3′-CO), 161.85 (2′-CO), 149.13, 146.01, 143.10, 141.63, 140.23, 138.68, 136.00, 132.95, 131.95, 131.51, 130.69, 128.60, 126.79, 123.30, 122.44, 121.91, 120.37, 118.36, 104.54, 93.23 (acetylenic C), 89.77 (acetylenic C), 82.47 (acetylenic C), 81.43 (acetylenic C), 62.37 (8′a-C), 59.36 (spiro-C), 53.43 (3′-CH_3), 51.46 (2′-CH_3) ppm; IR (KBr): $\bar{\nu}$ = 3,100–3,019 (C–H, arom.), 2,890–2,982 (C–H, aliph.), 2,157 (acetylenic bonds), 1,749 (3′-C=O), 1,694 (2′-C=O), 1,576 (C=N), 1,476 (C=C), 1,353, 1,257, 1,136, 1,088, 967, 871, 763 cm^{-1}; MS: m/z = 610.19 [M^+].

Dimethyl (4′aS)-2-ethynyl-2′,4′a-dimethylspiro[9H-fluorene-9,5′(4′aH)-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate (**11d**, $C_{27}H_{22}N_2O_4$)
Method A: yield 26%, m.p.: 146 °C; method B: yield 63%, m.p.: 145 °C; method C: yield 54%, m.p.: 144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95–7.97 (d, J = 2.4 Hz, 1H, CH arom.), 7.84–7.86 (d, J = 2.4 Hz, 1H, CH arom.), 7.73–7.75 (d, J = 1.89 Hz, 1H, CH arom.), 7.50–7.54 (d, J = 2.4 Hz, 1H, CH arom.), 7.47–7.49 (d, J = 2.4 Hz, 1H, CH arom.), 7.37–7.40 (dt, J = 2.4 Hz, J = 0.88 Hz, 1H, CH arom.), 7.18–7.22 (dt, J = 2.4 Hz, J = 0.88 Hz, 1H, CH arom.), 5.60–5.63 (m, 1H, 7′-CH), 4.78–4.81 (dt, J = 9.60 Hz, J = 1.76 Hz, 8′-CH), 4.06 (s, 1H, acetylenic H), 3.84 (s, 3H, 3′-CH_3), 3.44 (s, 3H, 2′-CH_3), 2.11 (s, 3H, 6′-CH_3), 1.43 (s, 3H, 8′a-CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.00 (3′-CO), 161.98 (2′-CO), 149.26, 146.46, 143.89, 141.64, 140.19, 138.76, 136.36, 133.06, 130.66, 128.46, 126.76, 123.47, 122.63, 121.88, 120.42, 118.37, 104.52, 82.42 (acetylenic C), 81.36 (acetylenic C), 63.26 (8′a-C), 59.31 (spiro-C), 53.39 (3′-CH_3), 51.25 (2′-CH_3), 22.46 (6′-CH_3), 21.22 (8′-CH_3) ppm; IR (KBr): $\bar{\nu}$ = 3,091–3,013 (C–H, arom.), 2,846–2,979 (C–H, aliph.), 2,167 (acetylenic bond), 1,747 (3′-C=O), 1,693 (2′-C=O), 1,585 (C=N), 1,438 (C=C), 1,363, 1,250, 1,187, 1,082, 950, 878, 766 cm^{-1}; MS: m/z = 438.16 [M^+].

Dimethyl (4′aS)-2-[(4-ethynylphenyl)ethynyl]-2′,4′a-dimethylspiro[9H-fluorene-9,5′(4′aH)-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate (**11e**, $C_{35}H_{26}N_2O_4$)
Method A: yield 24%, m.p.: 133 °C; method B: yield 68%, m.p.: 134 °C; method C: yield 49%, m.p.: 133 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.87 (d, J = 2.4 Hz, 1H, CH arom.), 7.82–7.81 (d, J = 2.4 Hz, 1H, CH arom.), 7.71–7.74 (d, J = 1.89 Hz, 1H, CH arom.), 7.57–7.61 (d, J = 7.98 Hz, 2H, CH arom.), 7.54–7.56 (d, J = 7.98 Hz, 2H, CH arom.), 7.44–7.46 (d, J = 2.4 Hz, 1H, CH arom.), 7.40–7.43 (d, J = 2.4 Hz, 1H, CH arom.), 7.30–7.34 (dt, J = 2.4 Hz, J = 0.88 Hz, 1H, CH arom.), 7.24–7.26 (dt, J = 2.4 Hz, J = 0.88 Hz, 1H, CH arom.), 5.76–5.80 (m, 1H, 7′-CH), 4.74–4.77 (dt, J = 9.60 Hz, J = 1.76 Hz, 8′-CH), 4.04 (s, 1H, acetylenic H), 3.80 (s, 3H, 3′-CH_3), 3.47 (s, 3H, 2′-CH_3), 2.14 (s, 3H, 6′-CH_3), 1.42 (s, 3H, 8′a-CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.58 (3′-CO), 161.92 (2′-CO), 149.26, 146.20, 143.03, 141.13, 140.34, 138.45, 136.12, 132.87, 131.54, 130.56, 128.64, 126.71, 123.31, 122.44, 121.83, 120.34, 118.33, 104.44, 93.10 (acetylenic C), 89.64 (acetylenic C), 82.44 (acetylenic C), 81.37 (acetylenic C), 62.32 (8′a-C), 59.37 (spiro-C), 53.30 (3′-CH_3), 51.47 (2′-CH_3), 22.45 (6′-CH_3), 21.29 (8′a-CH_3) ppm; IR (KBr): $\bar{\nu}$ = 3,096–3,012 (C–H, arom.), 2,880–2,981 (C–H, aliph.), 2,150 (acetylenic bonds), 1,743 (3′-C=O), 1,690 (2′-C=O), 1,582 (C=N), 1,440 (C=C), 1,352, 1,250, 1,167, 1,089, 950, 889, 765 cm^{-1}; MS: m/z = 538.19 [M^+].

Dimethyl (4′aS)-2-[[4-[(4-ethynylphenyl)ethynyl]phenyl]-ethynyl]-2′,4′a-dimethylspiro[9H-fluorene-9,5′(4′aH)-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate
(**11f**, $C_{43}H_{30}N_2O_4$)
Method A: yield 22%, m.p.: 121 °C; method B: yield 62%, m.p.: 120 °C; method C: yield 45%, m.p.: 120 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88–7.91 (d, J = 2.4 Hz, 1H, CH arom.), 7.85–7.87 (d, J = 2.4 Hz, 1H, CH arom.), 7.76–7.78 (d, J = 1.89 Hz, 1H, CH arom.), 7.54–7.59 (m, 6H, CH arom.), 7.51–7.53 (d, J = 7.98 Hz, 2H, CH arom.), 7.42–7.45 (d, J = 2.4 Hz, 1H, CH arom.), 7.38–7.41 (d, J = 2.4 Hz, 1H, CH arom.), 7.32–7.35 (dt, J = 2.4 Hz, J = 0.88 Hz, 1H, CH arom.), 7.20–7.24 (dt, J = 2.4 Hz, J = 0.88 Hz, 1H, CH arom.), 5.78–5.82 (m, 1H, 7′-CH), 4.72–4.76 (dt, J = 9.60 Hz, J = 1.76 Hz, 8′-CH), 4.04 (s, 1H, acetylenic H), 3.82 (s, 3H, 3′-CH_3), 3.44 (s, 3H, 2′-CH_3), 2.18 (s, 3H, 6′-CH_3), 1.44 (s, 3H, 8′a-CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.45 (3′-CO), 161.84 (2′-

CO), 149.13, 146.09, 143.18, 141.62, 140.18, 138.67, 136.05, 132.97, 131.98, 131.50, 130.73, 128.69, 126.83, 123.37, 122.42, 121.87, 120.43, 118.38, 104.53, 93.22 (acetylenic C), 89.74 (acetylenic C), 82.42 (acetylenic C), 81.40 (acetylenic C), 62.34 (8′a-C), 59.43 (spiro-C), 53.48 (3′-CH_3), 51.46 (2′-CH_3), 22.40 (6′-CH_3), 21.34 (8′a-CH_3) ppm; IR (KBr): $\bar{\nu}$ = 3,089–3,023 (C–H, arom.), 2,898–2,983 (C–H, aliph.), 2,152 (acetylenic bonds), 1,743 (3′-C=O), 1,689 (2′-C=O), 1,571 (C=N), 1,473 (C=C), 1,355, 1,253, 1,142, 1,067, 962, 885, 764 cm^{-1}; MS: m/z = 638.22 [M^+].

Dimethyl 2-[(trimethylsilyl)ethynyl]spiro[9H-fluorene-9,5′(4′aH)-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate (**13a**, $C_{28}H_{26}N_2O_4Si$)

Yield 55%, m.p.: 121 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87–7.90 (d, J = 2.4 Hz, 1H, CH arom.), 7.83–7.86 (d, J = 2.4 Hz, 1H, CH arom.), 7.73–7.75 (d, J = 1.89 Hz, 1H, CH arom.), 7.44–7.46 (d, J = 2.4 Hz, 1H, CH arom.), 7.40–7.43 (d, J = 2.4 Hz, 1H, CH arom.), 7.36–7.39 (dd, J = 1.76 Hz, J = 1.98 Hz, 1H, 6′-CH), 7.32–7.35 (dt, J = 2.4 Hz, J = 0.88 Hz, 1H, CH arom.), 7.18–7.22 (dt, J = 2.4 Hz, J = 0.88 Hz, 1H, CH arom.), 5.69–5.72 (m, 1H, 7′-CH), 4.94–4.96 (t, J = 2.2 Hz, 1H, 8′a-CH), 4.70–4.73 (dt, J = 9.60 Hz, J = 1.76 Hz, 8′-CH), 3.86 (s, 3H, 3′-CH_3), 3.47 (s, 3H, 2′-CH_3), 0.94 (s, 9H, Si(CH_3)$_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.37 (3′-CO), 161.85 (2′-CO), 149.20, 146.36, 142.87, 141.26, 140.37, 138.47, 136.36, 132.90, 130.97, 128.64, 126.78, 123.32, 122.43, 121.58, 120.36, 118.21, 104.78, 82.37 (acetylenic C), 81.30 (acetylenic C), 62.46 (8′a-C), 59.57 (spiro-C), 53.30 (3′-CH_3), 51.27 (2′-CH_3), 13.85 (Si(CH_3)$_3$) ppm; IR (KBr): $\bar{\nu}$ = 3,098–3,028 (C–H, arom.), 2,880–2,987 (C–H, aliph.), 2,149 (acetylenic bond), 1,745 (3′-C=O), 1,689 (2′-C=O), 1,578 (C=N), 1,424 (C=C), 1,363, 1,254, 1,182, 1,036, 964, 870, 767 cm^{-1}; MS: m/z = 482.17 [M^+].

Dimethyl 2-[[4-[(trimethylsilyl)ethynyl]phenyl]ethynyl]-spiro[9H-fluorene-9,5′(4′aH)-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate (**13b**, $C_{36}H_{30}N_2O_4Si$)

Yield 58%, m.p.: 149 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95–7.98 (d, J = 2.4 Hz, 1H, CH arom.), 7.88–7.90 (d, J = 2.4 Hz, 1H, CH arom.), 7.77–7.79 (d, J = 1.89 Hz, 1H, CH arom.), 7.52–7.55 (d, J = 7.98 Hz, 2H, CH arom.), 7.49–7.51 (d, J = 7.98 Hz, 2H, CH arom.), 7.44–7.46 (d, J = 2.4 Hz, 1H, CH arom.), 7.43–7.45 (d, J = 2.4 Hz, 1H, CH arom.), 7.38–7.42 (dd, J = 1.76 Hz, J = 1.98 Hz, 1H, 6′-CH), 7.31–7.34 (dt, J = 2.4 Hz, J = 0.88 Hz, 1H, CH arom.), 7.20–7.24 (dt, J = 2.4 Hz, J = 0.88 Hz, 1H, CH arom.), 5.76–5.79 (m, 1H, 7′-CH), 4.93–4.96 (t, J = 2.2 Hz, 1H, 8′a-CH), 4.68–4.72 (dt, J = 9.60 Hz, J = 1.76 Hz, 8′-CH), 3.81 (s, 3H, 3′-CH_3), 3.46 (s, 3H, 2′-CH_3), 0.91 (s, 9H, Si(CH_3)$_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.65 (3′-CO), 161.68 (2′-CO), 149.20, 146.37, 142.85, 141.11, 140.23, 138.47, 136.08, 132.87, 131.50, 130.76, 128.64, 126.64, 123.37, 122.54, 121.97, 120.30, 118.57, 104.36, 93.04 (acetylenic C), 89.53 (acetylenic C), 82.38 (acetylenic C), 81.37 (acetylenic C), 62.28 (8′a-C), 59.37 (spiro-C), 53.46 (3′-CH_3), 51.74 (2′-CH_3), 13.79 (Si(CH_3)$_3$) ppm; IR (KBr): $\bar{\nu}$ = 3,098–3,029 (C–H, arom.), 2,890–2,978 (C–H, aliph.), 2,155 (acetylenic bonds), 1,745 (3′-C=O), 1,689 (2′-C=O), 1,580 (C=N), 1,441 (C=C), 1,356, 1,257, 1,178, 1,064, 950, 887, 751 cm^{-1}; MS: m/z = 582.20 [M^+].

Dimethyl 2-[[4-[[4-[(trimethylsilyl)ethynyl]phenyl]ethynyl]-phenyl]ethynyl]spiro[9H-fluorene-9,5′(4′aH)-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate (**13c**, $C_{44}H_{34}N_2O_4Si$)

Yield 61%, m.p.: 163 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.87 (d, J = 2.4 Hz, 1H, CH arom.), 7.81–7.84 (d, J = 2.4 Hz, 1H, CH arom.), 7.70–7.74 (d, J = 1.89 Hz, 1H, CH arom.), 7.51–7.54 (m, 6H, CH arom.), 7.46–7.49 (d, J = 7.98 Hz, 2H, CH arom.), 7.43–7.45 (d, J = 2.4 Hz, 1H, CH arom.), 7.40–7.42 (d, J = 2.4 Hz, 1H, CH arom.), 7.35–7.37 (dd, J = 1.76 Hz, J = 1.98 Hz, 1H, 6′-CH), 7.32–7.35 (dt, J = 2.4 Hz, J = 0.88 Hz, 1H, CH arom.), 7.26–7.28 (dt, J = 2.4 Hz, J = 0.88 Hz, 1H, CH arom.), 5.70–5.73 (m, 1H, 7′-CH), 4.98–5.01 (t, J = 2.2 Hz, 1H, 8′a-CH), 4.73–4.75 (dt, J = 9.60 Hz, J = 1.76 Hz, 8′-CH), 3.80 (s, 3H, 3′-CH_3), 3.45 (s, 3H, 2′-CH_3), 0.89 (s, 9H, Si(CH_3)$_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.45 (3′-CO), 161.88 (2′-CO), 149.12, 146.34, 143.18, 141.57, 140.20, 138.76, 136.08, 132.79, 131.35, 131.50, 130.76, 128.58, 126.84, 123.36, 122.47, 121.87, 120.36, 118.34, 104.53, 93.64 (acetylenic C), 89.76 (acetylenic C), 82.23 (acetylenic C), 81.10 (acetylenic C), 62.27 (8′a-C), 59.31 (spiro-C), 53.47 (3′-CH_3), 51.52 (2′-CH_3), 13.81 (Si(CH_3)$_3$) ppm; IR (KBr): $\bar{\nu}$ = 3,087–3,021 (C–H, arom.), 2,894–2,978 (C–H, aliph.), 2,152 (acetylenic bonds), 1,745 (3′-C=O), 1,691 (2′-C=O), 1,573 (C=N), 1,477 (C=C), 1,352, 1,254, 1,122, 1,046, 960, 877, 763 cm^{-1}; MS: m/z = 682.23 [M^+].

Dimethyl (4′aS)-2′,4′a-dimethyl-2-[(trimethylsilyl)ethynyl]spiro[9H-fluorene-9,5′(4′aH)-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate (**13d**, $C_{30}H_{30}N_2O_4Si$)

Yield 67%, m.p.: 112 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96–7.99 (d, J = 2.4 Hz, 1H, CH arom.), 7.88–7.92 (d, J = 2.4 Hz, 1H, CH arom.), 7.76–7.78 (d, J = 1.89 Hz, 1H, CH arom.), 7.54–7.53 (d, J = 2.4 Hz, 1H, CH arom.), 7.44–7.47 (d, J = 2.4 Hz, 1H, CH arom.), 7.39–7.42 (dt, J = 2.4 Hz, J = 0.88 Hz, 1H, CH arom.), 7.20–7.24 (dt, J = 2.4 Hz, J = 0.88 Hz, 1H, CH arom.), 5.72–5.74 (m, 1H, 7′-CH), 4.80–4.83 (dt, J = 9.60 Hz, J = 1.76 Hz, 8′-CH), 3.84 (s, 3H, 3′-CH_3), 3.44 (s, 3H, 2′-CH_3), 2.11 (s, 3H, 6′-CH_3), 1.43 (s, 3H, 8′a-CH_3), 0.90 (s, 9H, Si(CH_3)$_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.89 (3′-CO), 161.94 (2′-CO), 149.30, 146.21, 143.85, 141.63, 140.27,

138.26, 136.33, 133.09, 130.57, 128.42, 126.61, 123.46, 122.60, 121.74, 120.39, 118.46, 104.57, 82.41 (acetylenic C), 81.22 (acetylenic C), 63.32 (8′a-C), 59.21 (spiro-C), 53.46 (3′-CH_3), 51.23 (2′-CH_3), 22.41 (6′-CH_3), 21.28 (8′-CH_3), 13.86 ($Si(CH_3)_3$) ppm; IR (KBr): $\bar{\nu}$ = 3,098–3,008 (C–H, arom.), 2,842–2,976 (C–H, aliph.), 2,165 (acetylenic bond), 1,745 (3′-C=O), 1,685 (2′-C=O), 1,581 (C=N), 1,442 (C=C), 1,359, 1,257, 1,178, 1,081, 958, 877, 763 cm^{-1}; MS: m/z = 510.20 [M^+].

Dimethyl (4′aS)-2′,4′a-dimethyl-2-[[4-[(trimethylsilyl)-ethynyl]phenyl]ethynyl]spiro[9H-fluorene-9,5′(4′aH)-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate
(**13e**, $C_{38}H_{34}N_2O_4Si$)
Yield 64%, m.p.: 125 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.86 (d, J = 2.4 Hz, 1H, CH arom.), 7.80–7.83 (d, J = 2.4 Hz, 1H, CH arom.), 7.75–7.79 (d, J = 1.89 Hz, 1H, CH arom.), 7.52–7.55 (d, J = 7.98 Hz, 2H, CH arom.), 7.48–7.51 (d, J = 7.98 Hz, 2H, CH arom.), 7.40–7.44 (d, J = 2.4 Hz, 1H, CH arom.), 7.36–7.39 (d, J = 2.4 Hz, 1H, CH arom.), 7.32–7.37 (dt, J = 2.4 Hz, J = 0.88 Hz, 1H, CH arom.), 7.21–7.23 (dt, J = 2.4 Hz, J = 0.88 Hz, 1H, CH arom.), 5.69–5.74 (m, 1H, 7′-CH), 4.71–4.74 (dt, J = 9.60 Hz, J = 1.76 Hz, 8′-CH), 3.84 (s, 3H, 3′-CH_3), 3.42 (s, 3H, 2′-CH_3), 2.11 (s, 3H, 6′-CH_3), 1.47 (s, 3H, 8′a-CH_3), 0.87 (s, 9H, $Si(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.46 (3′-CO), 161.87 (2′-CO), 149.32, 146.28, 143.46, 141.78, 140.36, 138.41, 136.10, 132.74, 131.68, 130.26, 128.64, 126.77, 123.26, 122.47, 121.82, 120.27, 118.46, 104.48, 93.11 (acetylenic C), 89.54 (acetylenic C), 82.47 (acetylenic C), 81.36 (acetylenic C), 62.29 (8′a-C), 59.37 (spiro-C), 53.28 (3′-CH_3), 51.47 (2′-CH_3), 22.46 (6′-CH_3), 21.31 (8′a-CH_3), 13.78 ($Si(CH_3)_3$) ppm; IR (KBr): $\bar{\nu}$ = 3,110–3,043 (C–H, arom.), 2,895–2,981 (C–H, aliph.), 2,152 (acetylenic bonds), 1,741 (3′-C=O), 1,692 (2′-C=O), 1,588 (C=N), 1,446 (C=C), 1,375, 1,263, 1,146, 1,087, 955, 896, 761 cm^{-1}; MS: m/z = 610.23 [M^+].

Dimethyl (4′aS)-2′,4′a-dimethyl-2-[[4-[[4-[(trimethylsilyl)ethynyl]phenyl]ethynyl]phenyl]ethynyl]spiro[9H-fluorene-9,5′(4′aH)-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate (**13f**, $C_{46}H_{38}N_2O_4Si$)
Yield 61%, m.p.: 143 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98–8.03 (d, J = 2.4 Hz, 1H, CH arom.), 7.92–7.94 (d, J = 2.4 Hz, 1H, CH arom.), 7.81–7.85 (d, J = 1.89 Hz, 1H, CH arom.), 7.50–7.55 (m, 6H, CH arom.), 7.46–7.50 (d, J = 7.98 Hz, 2H, CH arom.), 7.40–7.43 (d, J = 2.4 Hz, 1H, CH arom.), 7.26–7.30 (d, J = 2.4 Hz, 1H, CH arom.), 7.20–7.24 (dt, J = 2.4 Hz, J = 0.88 Hz, 1H, CH arom.), 7.16–7.19 (dt, J = 2.4 Hz, J = 0.88 Hz, 1H, CH arom.), 5.85–5.49 (m, 1H, 7′-CH), 4.70–4.74 (dt, J = 9.60 Hz, J = 1.76 Hz, 8′-CH), 3.87 (s, 3H, 3′-CH_3), 3.44 (s, 3H, 2′-CH_3), 2.13 (s, 3H, 6′-CH_3), 1.42 (s, 3H, 8′a-CH_3), 0.86 (s, 9H, $Si(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.46 (3′-CO), 161.72 (2′-CO), 149.27, 146.16, 143.36, 141.84, 140.28, 138.60, 136.16, 133.13, 131.85, 131.49, 130.73, 128.67, 126.75, 123.32, 122.40, 121.79, 120.52, 118.46, 104.79, 93.29 (acetylenic C), 89.58 (acetylenic C), 82.46 (acetylenic C), 81.42 (acetylenic C), 62.79 (8′a-C), 59.41 (spiro-C), 53.36 (3′-CH_3), 51.54 (2′-CH_3), 22.28 (6′-CH_3), 21.34 (8′a-CH_3), 13.81 ($Si(CH_3)_3$) ppm; IR (KBr): $\bar{\nu}$ = 3,085–3,013 (C–H, arom.), 2,898–2,967 (C–H, aliph.), 2,145 (acetylenic bonds), 1,746 (3′-C=O), 1,678 (2′-C=O), 1,564 (C=N), 1,458 (C=C), 1,351, 1,247, 1,136, 1,067, 960, 879, 763 cm^{-1}; MS: m/z = 710.26 [M^+].

*General procedure for the synthesis of photochromic DHIs–tripodal linker **17b**, **17c**, **17e**, and **17f***

Method A. To an oven-dried screw-cap tube or a round-bottomed flask equipped with a water cooled West condenser and a magnetic stir bar the 2-iodosubstituted fluorene DHIs **11b, 11c, 11e**, and **11f** (3 mmol), 20 mg palladium di(triphenylphosphine) dichloride (0.06 mmol), 78 mg triphenylphosphine (0.03 mmol), and 36 mg CuI (0.15 mmol) were added to 1-(4-iodophenyl)-3,5,7-tris[4-(ethoxycarbonyl)phenyl]adamantane **15** (3 mmol). The vessel was then sealed with a rubber septum, evacuated, and backfilled with nitrogen (three times). A co-solvent system of 20 cm^3 freshly distilled THF and 0.83 cm^3 triethylamine (6 mmol) was added. The reaction mixture was stirred in an oil bath at 45 °C for 15 h (TLC monitored) until the reaction was complete. The reaction vessel was cooled to room temperature and the mixture quenched with water or a saturated solution of NH_4Cl (20 cm^3). The organic layer was diluted with CH_2Cl_2 and washed with a saturated solution of NH_4Cl (3 × 30 cm^3). The combined aqueous layers were extracted with CH_2Cl_2 (3 × 30 cm^3), dried over anhydrous $MgSO_4$, and the solvent removed in vacuo. The crude products were then purified by twice repeated column chromatography on silica gel using CH_2Cl_2 as eluent. The pure products were obtained as yellow needles.

Method B. In comparison with method A 13.5 mg palladium diacetate (0.06 mmol) was used instead of 20 mg palladium di(triphenylphosphine) dichloride (0.06 mmol) and 20 cm^3 toluene and 3 cm^3 DMF replaced 20 cm^3 THF.

Method C. In comparison with method A 43 mg bis(dibenzylideneacetone)palladium(0) (0.07 mmol) was used instead of 20 mg palladium di(triphenylphosphine) dichloride (0.06 mmol) and 1 cm^3 DIEA (6 mmol) replaced 0.83 cm^3 triethylamine (6 mmol).

Dimethyl 2-[[4-[3,5,7-tris[4-(ethoxycarbonyl)phenyl]-1-adamantyl]phenyl]ethynyl]spiro[9H-fluorene-9,5′(4′aH)-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate (**17a**)
Method A: yield 25%; method B: yield 31%; method C: yield 54%; analytical data were identical with those published in Ref. [67].

Dimethyl 2-[[4-[[4-[3,5,7-tris[4-(ethoxycarbonyl)phenyl]-1-adamantyl]phenyl]ethynyl]phenyl]ethynyl]spiro[9H-fluorene-9,5′(4′aH)-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate (**17b**, $C_{76}H_{64}N_2O_{10}$)
Method A: yield 28%, m.p.: 164 °C; method B: yield 57%, m.p.: 162 °C; method C: yield 52%, m.p.: 163 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49–8.52 (d, J = 8.00 Hz, 1H, CH arom.), 8.22–8.42 (d, J = 8.72 Hz, 6H, CH arom.), 8.08–7.12 (d, J = 8.00 Hz, 1H, CH arom.), 7.72–7.75 (d, J = 7.20 Hz, 1H, CH arom.), 7.53–7.54 (dd, J = 7.20 Hz, J = 7.60 Hz, 4H, CH arom.), 7.45–7.49 (d, 8H, J = 8.72 Hz, CH arom.), 7.30–7.35 (d, 2H, J = 8.69 Hz), 7.10–7.14 (d, 2H, J = 8.60 Hz, CH arom.), 7.01–7.10 (m, 2H, CH arom.), 6.84–6.89 (dd, J = 1.76 Hz, J = 1.76 Hz, 1H, 6′-CH), 5.69–5.76 (m, 1H, 7′-CH), 5.34–5.67 (t, J = 2.2 Hz, 1H, 8′-CH), 4.90–5.94 (dt, J = 8.00 Hz, J = 2.00 Hz, 8′a-CH), 4.53–4.57 (q, 6H, J = 7.12 Hz, $3CH_2$ ethyl ester), 3.95 (s, 3H, 3′-CH_3), 3.41 (s, 3H, 2′-CH_3), 2.14 (two overlapping s, 12H), 1.41 (t, 9H, J = 7.12 Hz, $3CH_3$ ethyl ester) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.46 (3′-CO), 165.22 (2′-CO), 163.15 (CO ethyl ester), 154.06, 149.68, 148.63, 148.60, 146.98, 142.78, 141.58, 138.97, 138.46, 138.12, 136.85, 136.67, 133.37, 133.25, 131.70, 130.13, 129.82, 128.79, 127.43, 124.79, 124.36, 123.75, 123.36, 122.07, 121.64, 121.38, 118.07, 116.79, 113.63, 109.83, 94.43 (acetylenic C), 93.45 (acetylenic C), 89.76 (acetylenic C), 89.34 (acetylenic C), 88.36, 64.63 (8′a-C), 63.20 (spiro-C), 61.51, 52.36 (3′-CH_3), 51.46 (2′-CH_3), 46.48, 39.65, 30.36, 26.20, 24.67, 23.38, 22.84, 22.10, 14.41, 12.12 ppm; IR (KBr): $\bar{\nu}$ = 3,098–3,032 (C–H, arom.), 2,895–2,980 (C–H, aliph.), 2,223 (acetylenic bond), 1,746 (3′-C=O), 1,706 (CO ester), 1,646 (2′-C=O), 1,584 (C=N), 1,451 (C=C), 1,346, 1,252, 1,181, 1,127, 968, 891, 766 cm^{-1}; MS: m/z = 1,164.46 [M^+].

Dimethyl 2-[[4-[[4-[[4-[3,5,7-tris[4-(ethoxycarbonyl)-phenyl]-1-adamantyl]phenyl]ethynyl]phenyl]ethynyl]phenyl]ethynyl]spiro[9H-fluorene-9,5′(4′aH)-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate
(**17c**, $C_{84}H_{68}N_2O_{10}$)
Method A: yield 27%, m.p.: 143 °C; method B: yield 65%, m.p.: 141 °C; method C: yield 50%, m.p.: 144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56–8.59 (d, J = 8.00 Hz, 1H, CH arom.), 8.32–8.40 (d, J = 8.72 Hz, 6H, CH arom.), 8.11–7.15 (d, J = 8.00 Hz, 1H, CH arom.), 7.70–7.74 (d, J = 7.20 Hz, 1H, CH arom.), 7.52–7.55 (dd, J = 7.20 Hz, J = 7.60 Hz, 6H, CH arom.), 7.44–7.48 (d, 10H, J = 8.72 Hz, CH arom.), 7.33–7.36 (d, 2H, J = 8.69 Hz), 7.15–7.19 (d, 2H, J = 8.60 Hz, CH arom.), 7.12–7.16 (m, 2H, CH arom.), 6.80–6.86 (dd, J = 1.76 Hz, J = 1.76 Hz, 1H, 6′-CH), 5.76–5.84 (m, 1H, 7′-CH), 5.33–5.37 (t, J = 2.2 Hz, 1H, 8′-CH), 4.96–5.99 (dt, J = 8.00 Hz, J = 2.00 Hz, 8′a-CH), 4.56–4.60 (q, 6H, J = 7.12 Hz, $3CH_2$ ethyl ester), 3.91 (s, 3H, 3′-CH_3), 3.43 (s, 3H, 2′-CH_3), 2.13 (two overlapping s, 12H), 1.45 (t, 9H, J = 7.12 Hz, $3CH_3$ ethyl ester) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.99 (3′-CO), 164.36 (2′-CO), 162.98 (CO ethyl ester), 153.16, 149.48, 148.37, 148.56, 146.85, 142.69, 141.32, 138.87, 138.36, 138.10, 136.71, 136.63, 133.37, 133.54, 131.36, 130.28, 129.87, 128.71, 127.40, 124.96, 124.37, 123.84, 123.30, 122.11, 121.87, 121.29, 118.64, 116.73, 113.64, 109.52, 94.39 (acetylenic C), 93.43 (acetylenic C), 89.76 (acetylenic C), 89.32 (acetylenic C), 88.26, 64.64 (8′a-C), 63.21 (spiro-C), 61.54, 52.34 (3′-CH_3), 51.48 (2′-CH_3), 46.47, 39.63, 30.48, 26.21, 24.60, 23.76, 22.81, 22.13, 14.54, 12.17 ppm; IR (KBr): $\bar{\nu}$ = 3,089–3,019 (C–H, arom.), 2,890–2,979 (C–H, aliph.), 2,219 (acetylenic bond), 1,743 (3′-C=O), 1,708 (CO ester), 1,643 (2′-C=O), 1,587 (C=N), 1,449 (C=C), 1,343, 1,252, 1,180, 1,132, 967, 895, 760 cm^{-1}; MS: m/z = 1,264.49 [M^+].

Dimethyl (4′aS)-2′,4′a-dimethyl-2-[[4-[3,5,7-tris[4-(ethoxycarbonyl)phenyl]-1-adamantyl]phenyl]ethynyl]-spiro[9H-fluorene-9,5′(4′aH)-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate (**17d**)
Method A: yield 22%; method B: yield 34%; method C: yield 52%; analytical data identical with those published in Ref. [67].

Dimethyl (4′aS)-2′,4′a-dimethyl-2-[[4-[[4-[3,5,7-tris[4-(ethoxycarbonyl)phenyl]-1-adamantyl]phenyl]ethynyl]-phenyl]ethynyl]spiro[9H-fluorene-9,5′(4′aH)-pyrrolo-[1,2-b]pyridazine]-6′,7′-dicarboxylate
(**17e**, $C_{78}H_{68}N_2O_{10}$)
Method A: yield 24%, m.p.: 134 °C; method B: yield 68%, m.p.: 133 °C; method C: yield 49%, m.p.: 134 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37–8.39 (d, J = 8.04 Hz, 1H, CH arom.), 8.11–8.19 (d, 6H, J = 8.72 Hz), 8.06–8.09 (d, J = 8.00 Hz, 1H, CH arom.), 7.78–7.81 (d, J = 7.20 Hz, 1H, CH arom.), 7.65–7.66 (dd, J = 7.20 Hz, J = 7.60 Hz, 4H, CH arom.), 7.55–7.61 (d, 8H, J = 8.72 Hz, CH arom.), 7.42–7.45 (d, 2H, J = 8.60 Hz), 7.11–7.17 (d, 2H, J = 8.60 Hz), 7.00–7.08 (m, 2H, CH arom.), 5.69–5.73 (m, 1H, 7′-CH), 5.13–5.15 (dt, J = 8.00 Hz, J = 2.00 Hz, 8′-CH), 4.53–4.56 (q, 6H, J = 7.12 Hz, $3CH_2$ ethyl ester), 3.95 (s, 3H, 3′-CH_3), 3.51 (s, 3H, 2′-CH_3), 2.17 (two overlapping s, 12H), 2.13 (s, 3H, 6′-CH_3), 1.60 (s, 3H, 8′-CH_3), 1.45 (t, 9H, J = 7.12 Hz, $3CH_3$ ethyl ester) ppm; ^{13}C NMR (100 MHz, $CDCl_3$):

$\delta = 167.62$ (3′-CO), 165.42 (2′-CO), 163.36 (CO ethyl ester), 152.85, 150.33, 148.72, 148.78, 147.54, 142.56, 142.30, 139.68, 138.63, 138.67, 136.14, 136.81, 133.66, 133.47, 131.26, 130.09, 129.79, 128.76, 127.63, 124.46, 124.19, 124.49, 123.36, 122.28, 121.79, 121.53, 118.39, 117.47, 112.49, 105.80, 94.89 (acetylenic C), 93.59 (acetylenic C), 89.98 (acetylenic C), 89.62 (acetylenic C), 88.38, 65.67 (8′a-C), 63.45 (spiro-C), 61.81, 52.46 (3′-CH_3), 51.27 (2′-CH_3), 46.95, 39.64, 30.20, 26.37, 24.57, 23.60, 22.23, 22.74 (6′-CH_3), 22.44, 21.16 (8′-CH_3), 14.16, 12.62 ppm; IR (KBr): $\bar{\nu} = 3{,}079$–$3{,}006$ (C–H, arom.), 2,893–2,967 (C–H, aliph.), 2,225 (acetylenic bond), 1,749 (3′-C=O), 1,706 (CO ester), 1,685 (2′-C=O), 1,583 (C=N), 1,454 (C=C), 1,382, 1,273, 1,175, 1,136, 957, 886, 747 cm^{-1}; MS: $m/z = 1{,}192.49$ [M^+].

Dimethyl (4′aS)-2′,4′a-dimethyl-2-[[4-[[4-[[4-[3,5,7-tris-[4-(ethoxycarbonyl)phenyl]-1-adamantyl]phenyl]ethynyl]-phenyl]ethynyl]phenyl]ethynyl]spiro[9H-fluorene-9,5′(4′aH)-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate
(**17f**, $C_{86}H_{72}N_2O_{10}$)

Method A: yield 22%, m.p.: 121 °C; method B: yield 62%, m.p.: 119 °C; method C: yield 45%, m.p.: 119 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.49$–8.53 (d, $J = 8.04$ Hz, 1H, CH arom.), 8.25–8.29 (d, 6H, $J = 8.72$ Hz), 8.17–8.22 (d, $J = 8.00$ Hz, 1H, CH arom.), 7.84–7.86 (d, $J = 7.20$ Hz, 1H, CH arom.), 7.64–7.68 (dd, $J = 7.20$ Hz, $J = 7.60$ Hz, 6H, CH arom.), 7.50–7.56 (d, 8H, $J = 8.72$ Hz, CH arom.), 7.45–7.49 (d, 2H, $J = 8.60$ Hz), 7.10–7.16 (d, 2H, $J = 8.60$ Hz), 7.04–7.07 (m, 2H, CH arom.), 5.70–5.75 (m, 1H, 7′-CH), 5.06–5.09 (dt, $J = 8.00$ Hz, $J = 2.00$ Hz, 8′-CH), 4.50–4.53 (q, 6H, $J = 7.12$ Hz, 3CH_2 ethyl ester), 3.91 (s, 3H, 3′-CH_3), 3.46 (s, 3H, 2′-CH_3), 2.19 (two overlapping s, 12H), 2.11 (s, 3H, 6′-CH_3), 1.64 (s, 3H, 8′-CH_3), 1.44 (t, 9H, $J = 7.12$ Hz, 3CH_3 ethyl ester) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 167.64$ (3′-CO), 165.40 (2′-CO), 163.36 (CO ethyl ester), 152.76, 150.29, 148.64, 148.76, 147.50, 142.47, 142.29, 139.76, 138.65, 138.58, 136.09, 136.76, 133.63, 133.45, 131.27, 130.03, 129.84, 128.87, 127.60, 124.46, 124.23, 124.54, 123.38, 122.46, 121.85, 121.46, 118.76, 117.28, 112.46, 105.76, 94.68 (acetylenic C), 93.43 (acetylenic C), 89.82 (acetylenic C), 89.60 (acetylenic C), 88.36, 65.46 (8′a-C), 63.67 (spiro-C), 61.78, 52.40 (3′-CH_3), 51.36 (2′-CH_3), 46.84, 39.60, 30.28, 26.45, 24.50, 23.64, 22.19, 22.69 (6′-CH_3), 22.40, 21.17 (8′-CH_3), 14.16, 12.46 ppm; IR (KBr): $\bar{\nu} = 3{,}088$–$3{,}022$ (C–H, arom.), 2,890–2,961 (C–H, aliph.), 2,221 (acetylenic bond), 1,745 (3′-C=O), 1,703 (CO ester), 1,682 (2′-C=O), 1,583 (C=N), 1,451 (C=C), 1,388, 1,270, 1,167, 1,146, 958, 882, 743 cm^{-1}; MS: $m/z = 1{,}292.52$ [M^+].

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