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Photochromism of dihydroindolizines: part XIV. Synthesis and photophysical behavior of photochromic dihydroindolizine-tripodal linkers toward anchoring sensitizers to semiconductor nanoparticles

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Photochromic dihydroindolizines (DHIs) 4a,5-dihydropyrrolo[1,2-b]pyridazine based tripodal-linker systems with adamantane core and ethyl benzoate tripods as anchoring groups have been successfully synthesized. In addition, new spirocyclopropene precursors have been prepared through both chemical and photochemical processes. The photochromic properties of the newly synthesized DHIs derivatives have been optimized and fine-tuned by the incorporation of various substituents on the fluorene (region A) and pyridazine (region C) moieties. Several alternative routes for the synthesis of the DHIs under investigation have been established. The Sonogashira crosscoupling reaction was utilized for fragment coupling between DHIs and the phenylacetylene tether of the adamantane core. Several reaction conditions of this key reaction were surveyed to obtain optimal yields of a new series of coupling products targeted for anchoring to semiconductor nanoparticles. The chemical structures of the newly synthesized materials were elucidated by both analytical and spectroscopic tools. Irradiation of the photochromic DHIs with polychromatic light resulted in ring opened colored betaines which underwent cycloreversion reactions via thermal 1,5-electrocyclization processes. The kinetic of the thermal 1,5-electrocyclization was studied by using a UV/VIS/NIR spectrophotometer. The kinetic measurements showed the half-lives of the colored betaines to be in the second domain. A pronounced increase in the half-lives of betaines bearing dimethyl-substituted pyridazine was noted compared with non-substituted pyridazine betaines. A strong effect of solvent polarity on the λ_{max} and half-lives of the betaines was observed. The further adjustment of the absorption maxima and the kinetic properties via the manipulation of substituents on the fluorene (region A) and pyridazine moieties (region C) should yield more refined systems for application as supports onto metal-oxide surfaces which remains an active area of our ongoing research.

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

Keywords: anchoring groups; dihydroindolizines (DHIs); photochromism; photofatigue; Sonogashira coupling; tripodal linker

INTRODUCTION

The term photochromism derives from the Greek words "phos" (light) and "chroma" (color) and means the generation of color under the influence of light. When applied to the molecular world, this term implies a reversible photoinduced coloration of an ensemble of molecules in an amorphous, crystalline, or solution state.[1–7] It is well known that photochromic compounds support their activities in a reversible photochemical reaction induced by the absorption of electromagnetic radiation, mainly in the ultraviolet region to provoke a visible color change of the original colorless molecule. Throughout the last decade, photochromic compounds have been included in the development process of optoelectronic devices as integral active components.[8–10] An important characteristic of this optical change is the clear difference in the absorption spectra shown by these two species (colored and colorless forms). There exist several families of compounds that exhibit photochromism such as diarylethenes, spiropyrans, spirooxazines, fulgides, viologens, chromenes, azo compounds, and dihydroindolizines (DHIs). These photochromic families are appealing since they might find utility in electronic storage media as well as in optoelectronic devices.[11–13]

Several mandatory properties must be met for the organic photochromic compounds in order to be useful in photonic device applications such as erasable memory media and optical

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switching. Foremost are thermal irreversibility, photofatigue resistance, and high efficiency in rapid photoconversion processes.[1–7] An additional factor that cannot be downplayed is the ability to tailor the physical and chemical properties of the photochromic backbone in a facile, flexible, and modular manner. This can only be accomplished by designing photochromic compounds that possess many different locations on their molecular skeletons where functional groups can be anchored.[14,15] Moreover, π-aggregation of the attached chromophores is a known problem that changes or even suppresses the chromophore properties.[16,17] Recently, Tour,[18–24] Galoppini,[25–35] Rück- Braun,[36] and others[37–46] have developed three-dimensional linkers with tetrahedral core unit for sufficient control of the perpendicular shape and the head group to surface distance of the metal oxide nanoparticles. Additionally, it has been shown that tripods are feasible linkers that prevent π-stacking or dimerization of azobenzenes when adsorbed on gold or applied as AFM-tip.[36–46]

Photochromic DHIs which were discovered and developed by Dürr[47–57] are well-known photochromic materials that have been attracting much interest from the viewpoint of both fundamental elucidation of electrocyclization reactions and their potential applications to optical memories and switches.[58–73] This class of thermally reversible photochromic switches has been found to display excellent photochromic properties in solution as well as in the solid state: excellent fatigue resistance, short response time, high quantum yields, and large changes of absorption wavelength between the two isomers. This photochromic family which is based on the 1,5-electrocyclization between two distinct isomeric states, ring open form (betaine-form) and ring closed form (DHI-form), are promising candidates for optical storage media and electronic devices.[74,75] Recently we have synthesized some new photochromic DHIs bearing various acetylenic bridges in the fluorene part (region A of the DHI skeleton) under Sonogashira coupling conditions which may be useful in the application of electronic devices. In continuation of our research work dealing with the synthesis and photochromic behavior of photochromic DHIs, in this paper, we modified the DHI skeleton by substitution in 2- and 7-positions of the fluorene part (region A) with mono- and di-tripodal linker unit(s) which may be promising candidates toward anchoring onto metal oxide nanoparticles. Also, we reported the synthesis and photophysical properties of a tripodal-linker system with adamantane core and ethyl benzoate tripods as anchoring groups and photochromic DHIs bearing variously substituted pyridazines. Different synthetic outlines of palladium-mediated Sonogashira coupling will be described.

RESULTS AND DISCUSSION

Synthesis of mono- and dihalo-substituted spirocyclopropene precursors

The mono- and diiodo-substituted spirocyclopropenes **8a** and **8b** were prepared in six steps, starting with the precedented conversion of 2-nitro-9H-fluoren-9-one (**2a**) and 2,7-dinitro-9H-fluoren-9-one (**2b**) to the corresponding 2-amino-9H-fluoren-9-one **3a** and 2,7-diamino 9H-fluoren-9-one **3b** by reduction with stannous chloride in ethyl acetate (Scheme 1).[76,77] Treatment of compounds **3a**,**b** with sodium nitrite in concentrated sulfuric acid yielded the corresponding mono- and bis-diazonium salt, which upon treatment with potassium iodide gave the diiodoflourenones **4a**,**b** as yellow solids in moderate yield (65 and 72% yield, respectively).

When hydrazine hydrate was allowed to react with substituted fluorenone derivatives **4a**,**b** in boiling ethanol for 4 h, the corresponding hydrazones **5a**,**b** were obtained as white crystals in 82 and 89% yield, respectively. The hydrazone derivatives **5a**,**b** underwent oxidation with manganese dioxide in dry ether at room temperature in the absence of light to afford 9-diazo-2-iodo-9H-fluorene (**6a**) and 9-diazo-2,7-diiodo-9H-fluorene **(6b)** as red needles in moderate yield (56 and 67% yield, respectively). Cycloaddition of methyl acetylenedicarboxylate (MADC) to the 9-diazofluorene derivatives **6a**,**b** in dry ether under dark conditions for 12 h led to the formation of dimethyl 2-iodospiro-[fluorene-9,3′-pyrazole]-4′,5′-dicarboxylate (**7a**) in 46% yield and dimethyl 2,7-diiodospiro[fluorene-9,3′-pyrazole]-4′,5′-dicarboxylate (**7b**) in 52% yield as pale yellow crystals.

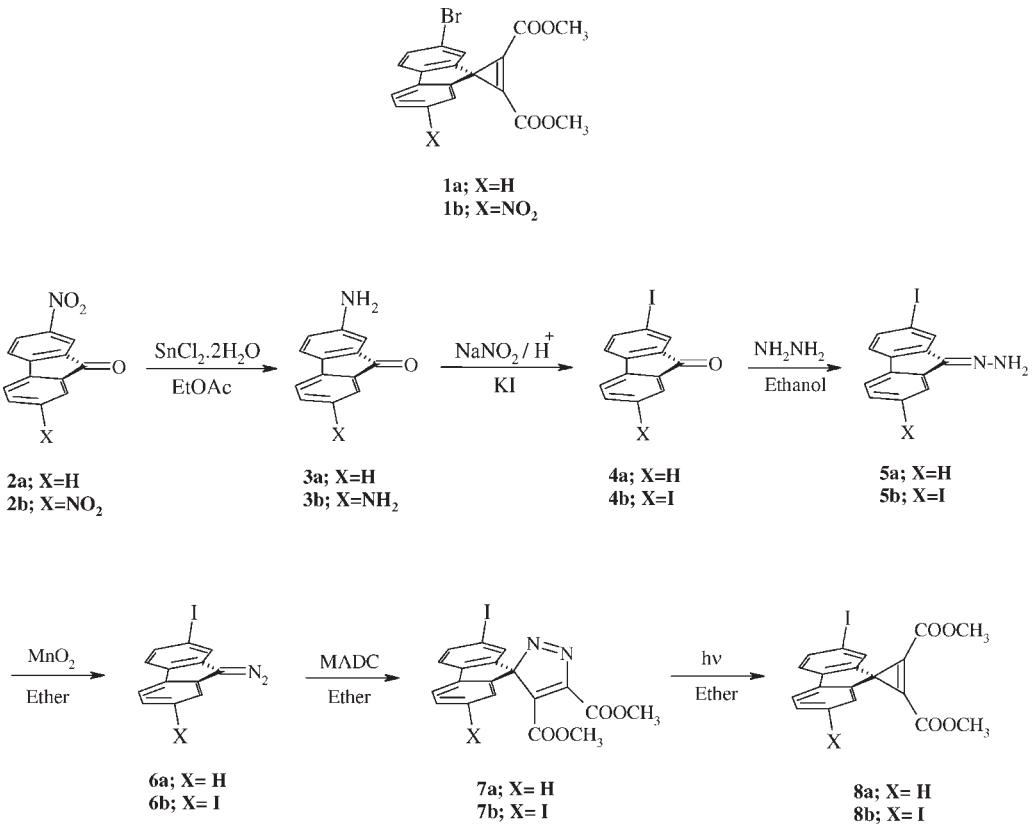
Photolysis of the pyrazole derivatives **7a**,**b** under inert atmosphere in dry ether solution for 3 h gave the target spirocyclopropene derivatives dimethyl 2′-iodospiro[cycloprop[2]ene-1,9′-fluorene]-2,3-dicarboxylate (**8a**) and dimethyl 2′,7′-diiodoospiro-[cycloprop[2]ene-1,9′-fluorene]-2,3-dicarboxylate (**8b**) in 32 and 46% yield, respectively. The chemical structures of the newly synthesized compounds **2a**,**b**–**8a**,**b** (Scheme 1) were confirmed and established by both spectroscopic (NMR, IR, and mass spectrometry) and analytical tools (all compounds gave satisfactory elemental analysis data). For example, the ^{1}HNMR (400 MHz, $CDCl_3$) of the spirocyclopropene precursor **8b** showed the following signals: δ 7.90–7.93 (d, $J = 1.76$ Hz, 2H, CH-arom.), 7.78–7.79 (d, $J = 1.32$ Hz, 2H, CH-arom.), 7.62–7.64 (d, $J = 8.9$ Hz, 2H, CH-arom.); 3.82 (s, 6H, 2′, 3′-CH_3) ppm.

Synthesis of photochromic dihydroindolizines DHIs 11e–h bearing mono- and diiodofluorene (region A) and substituted pyridazines 9a,b in the heterocyclic region (region B)

The synthesis of photochromic DHIs, namely, dimethyl-2,7-dibromo-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b](substituted)pyridazine]-6′,7′-dicarboxylate **11a**–**d** via nucleophilic addition of substituted pyridazines **9a**,**b** to spirocyclopropenes **1a**,**b** was previously reported by us [70–74]. Likewise, nucleophilic addition of substituted pyridazines **9a**,**b** to spirocyclopropenes **8a**,**b**[47–75] (Scheme 2) in dry ether at room temperature and under dry nitrogen and dark conditions (TLC-monitored using CH_2Cl_2 as an eluent) led to the formation of the photochromic DHIs **11e**–**h** in low to moderate yields (32–56%). The reaction involves the electrophilic addition of the electron-deficient spirocyclopropenes **8a**,**b** to the nitrogen of the *N*-heterocyclic pyridazines **9a**,**b** which leads to ring opening via the intermediacy of a cyclopropyl-allyl conversion of **10e**–**h** to the colored betaines **10e**–**h** (Scheme 2). A subsequent ring closure to DHIs **11e**–**h** results in a partially slow thermal 1,5-electrocyclization back reaction (Scheme 2) which can be reversed upon exposure to light. DHIs **11e**–**h** were obtained in pure form by column chromatography on silica gel using dichloromethane as an eluent.

Palladium-mediated Sonogashira coupling of photochromic DHIs 11a–f tripodal-linker 12 under different reaction conditions

The synthesis of the tripodal-linker system **12** was carried out according to well-known literature procedures.[36,78,79] In the

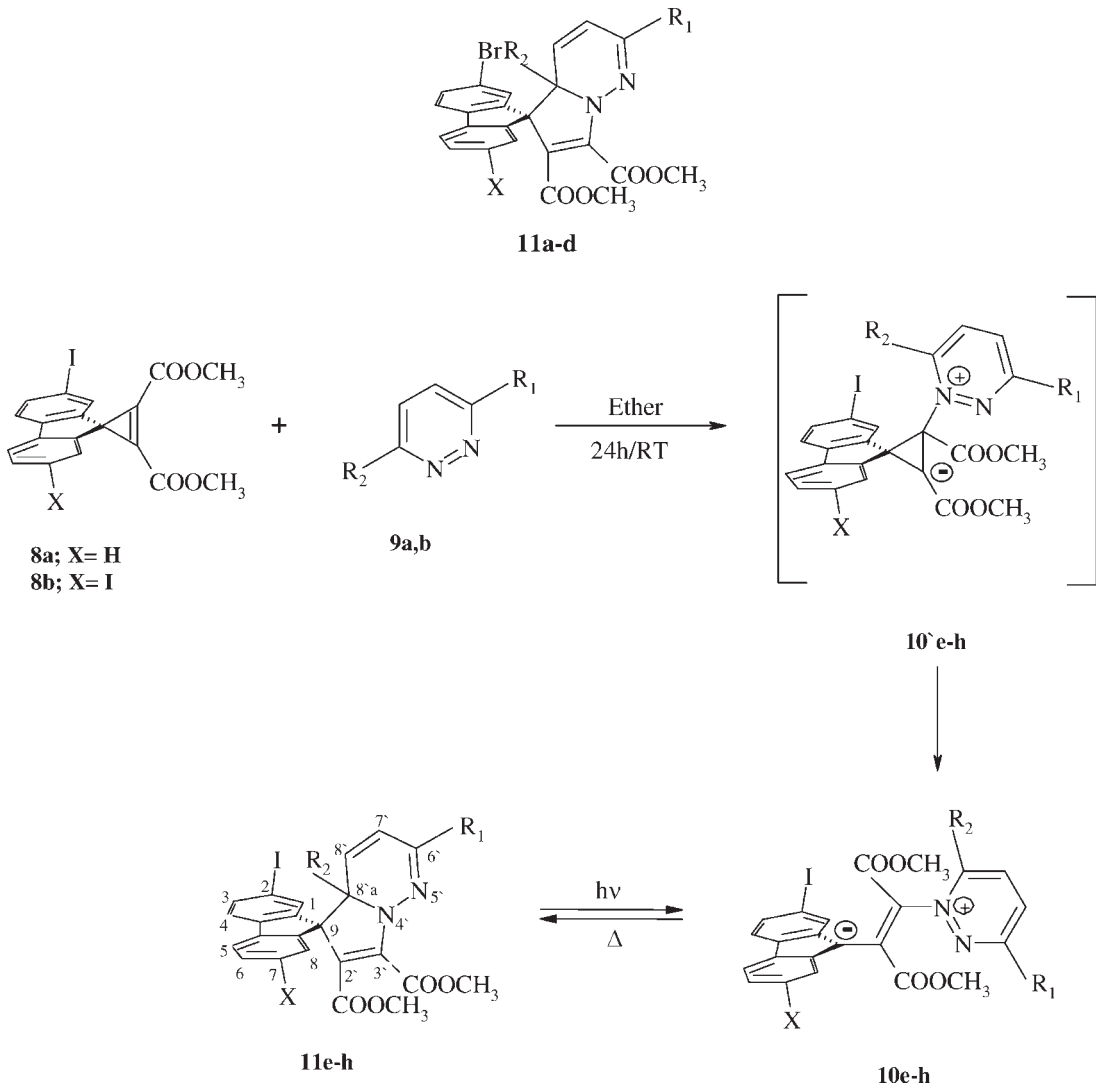


Scheme 1. Preparation of mono- and diiodo-substituted spirocyclopropenes **8a**,**b**

reaction of bromo-substituted DHIs **11a**–**d** with one or two moles of the tripodal-linker **12** under standard Sonogashira conditions (3% $Pd(PPh_3)Cl_2$, 10% PPh_3, 5% Cu_2I_2/ Et_3N, THF, 18 h at 45 °C, method A), low yields of coupling products **14a**–**d** were obtained (10–18% yield, method A; Scheme 3). Changing the reaction conditions of the Sonogashira coupling by using $Pd(OAc)_2/PPh_3$ and 10% Cu_2I_2, Et_3N, toluene, DMF, 24 h at 40 °C (method B) afforded the coupling products **14a**–**d** in slightly better yields (14–22%). Aiming to improve the chemical yields of DHIs **14a**–**d**, the reaction conditions were modified by using bis(dibenzylideneacetone)palladium (0) as a Pd(0) source, 10% Cu_2I_2, triphenylphosphine, DIEA in THF at 40 °C for 6 h (method C). Such conditions afforded the coupling products **14a**–**d** in 18–25% yields. In addition, coupling of photochromic DHIs **11a**–**d** with one or two moles of the linker **12** using 1,0-phenanthroline NaI, Cu_2I_2, DMF, and TEA at 110 °C (method D) did not show any improvement in the yields of **14a**–**d** and instead resulted in extensive decomposition. This suggests that the instability of the DHI system is due to high reaction temperatures and basic reaction conditions.[74,75]

On the other hand, the coupling reactions of DHIs **11a**–**d** and the linker **12** using $Pd(PPh_3)_4$ in dry pyrrolidine at 50 °C for 6 h (also RT and 40 °C were done) showed no evidence for the formation the coupling products **14a**–**d** (method E). In this method, copper-free reaction conditions were applied to avoid the homo-dimerization of the linker system. Attempts to improve the yield by increasing and decreasing the percentage of the palladium catalyst and the reaction time were unsuccessful in improving the yields in all of the preceding reactions.

In order to increase the reactivity of DHIs **11a**–**d** toward the coupling with the tripod **12** under Sonogashira coupling conditions, the mono- and diiodo-substituted DHIs **11e**–**h** (Scheme 3) were synthesized. The DHIs **11e**–**h** were allowed to react with the linker **12** under Sonogashira coupling conditions aiming to get better coupling product yields. The above-mentioned reaction conditions have been applied during the reaction of DHI **11e**–**h** with one or two moles of the linker **12** in order to improve the product yield of the coupling products **14a**–**d**. The best reaction conditions with optimized yields were found to be with bis(dibenzylideneacetone)palladium (0), Cu_2I_2, triphenylphosphine, DIEA in THF at 40 °C for 6 h (method C) which led to the formation of the coupling products **14a**–**d** in 52–69% yield. All of the preceding various coupling conditions (Methods A–E) for the synthesis of DHIs **14a**–**d** were applied to mono- and diiodo-substituted DHIs **11e**–**h** and the yields were measured (Method A, 22–29%; Method B, 30–37%; Method D, 7–10%, and Method E, 9–12%). Pronounced improvements in reaction yields using mono- and diiodo-substituted DHIs **11e**–**h** compared with mono- and dibromo-substituted DHIs **11a**–**d** were noted. The yields of DHIs **14a**–**d** using the reaction conditions of methods D and E were still low, albeit better than those obtained in the coupling reactions with DHIs **11a**–**d** bearing mono- and dibromo-substituted DHIs using the same methods. The chemical structures of all newly synthesized photochromic DHIs **14a**–**d** were established on the basis of spectral and analytical tools as they showed spectral data corroborating the suggested chemical structures and also gave the satisfactory elemental analyses data. For instance, assignments of 8′-CH, 8′a-CH as well as some other diagnostic protons in the DHI skeleton were done by the aid of NOESY spectrum of **14c**. Herein, we observed that 8′a-CH at $\delta = 4.83$ ppm is close in space to 8′-CH at $\delta = 5.07$ ppm, and 1-CH of the fluorene moiety at $\delta = 7.63$ ppm. This shows that 8′a-CH is



Scheme 2. Structures of known DHIs **11a–d** and synthetic outline to the new photochromic dihydroindolizines **11e–h** (**11e**, $R_1{=}R_2{=}X{=}H$; **11f**, $R_1{=}R_2{=}CH_3$, $X{=}H$; **11g**, $R_1{=}R_2{=}H$, $X{=}I$; **11h**, $R_1{=}R_2{=}CH_3$, $X{=}I$)

in 8′a-position and not at 8′-position. Indeed, the connectivity between 8′-CH and 8-CH of the fluorene part at $\delta = 7.54$ ppm was observed. This close proximity of 8′-CH with 8-CH suggests that the pyridazine moiety is perpendicular to the fluorene skeleton. This observation is also supported by molecular modeling calculation of DHI **14a** (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).

Photophysical properties of the newly synthesized photochromic DHIs 11e–h and 14a–d and their corresponding betaines 10e–h and 13a–d in dichloromethane solution at ambient temperature

Absorption spectra of DHIs **11e–h** *and* **14a–d** *and their corresponding betaines* **10e–h** *and* **13a–d** *in solution*

The absorption spectra of DHIs **11a–d** and their corresponding betaines **10a–d** were previously studied by us.[63–75] Photophysical data pertinent to their photochromic properties were obtained from the absorption features of photochromic DHIs **11e–h** and **14a–d**. Electronic spectra of the newly synthesized DHIs **11e–h** and **14a–d** were measured in dichloromethane using a UV/VIS/NIR spectrophotometer with a concentration of 1×10^{-5} mol/L at 23 °C. All of the studied DHIs **11e–h** and **14a–d** are yellow in the solid state and in dichloromethane solution (Table 1). The intensities (log ε) of the absorption bands ranged between 3.96 and 4.49 depending on whether the fluorene is substituted by one or two iodine atoms (DHIs **11e–h**) as well as one or two tripodal units (DHIs **14a–d**). The absorption of DHIs **11e–h** and **14a–d** were observed in the far UV-region and showed maxima lying between 393 and 407 nm (Table 1). This absorption depends on the number of the tripodal units on the fluorene group (region A). No significant effect on the absorption of mono- and diiodo-substituted DHIs **11a–d** was recorded. A pronounced bathochromic shift of di-substituted tripodal-DHI **14c,d** by about 8 nm compared with mono-substituted tripodal-DHI was monitored. This may be attributed to the increase in extended conjugation in the DHI skeleton after the coupling reaction. Changing the substitution in the pyridazine region from un-substituted to substitution by two methyl groups could not

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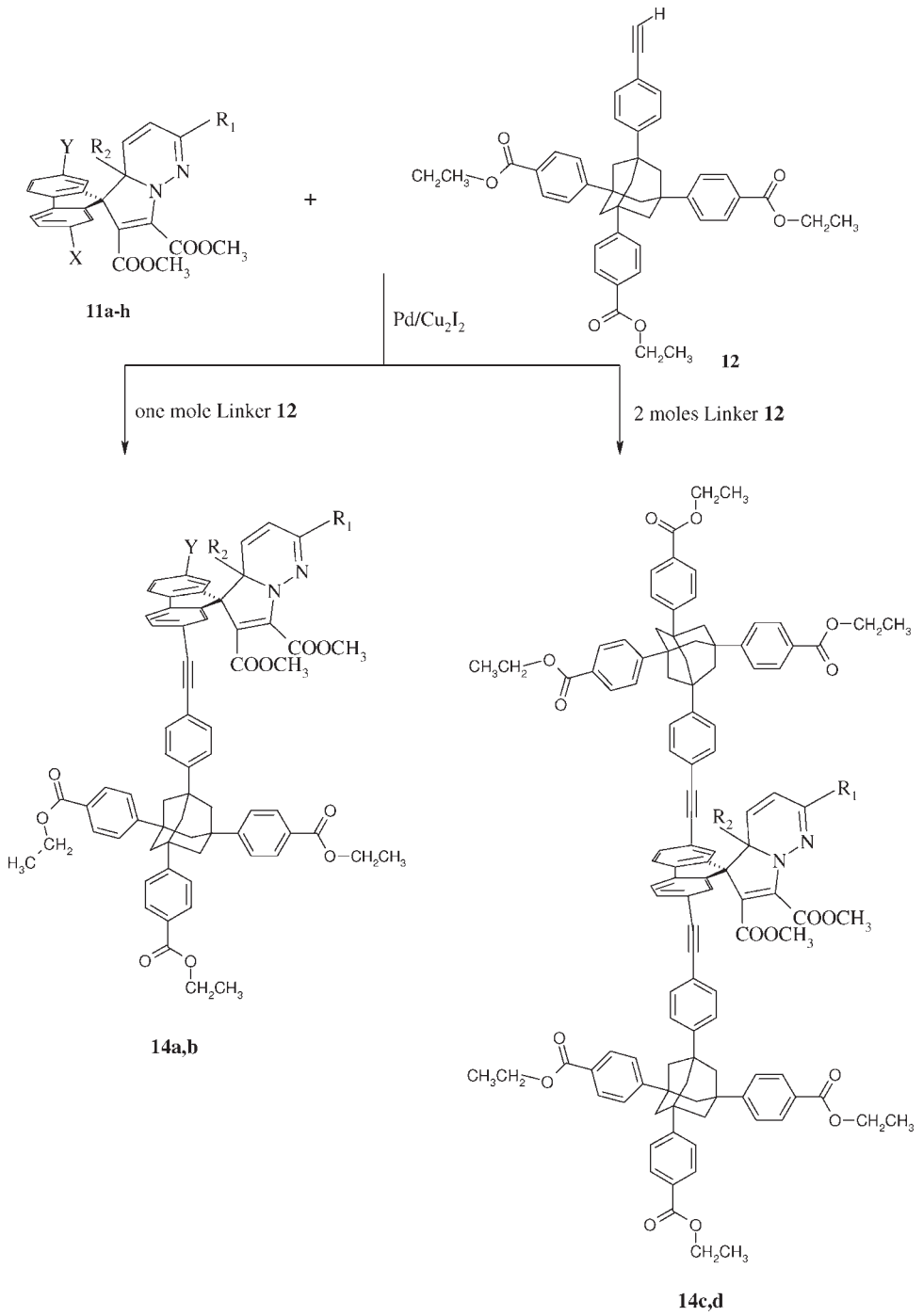

Scheme 3. Palladium-mediated Sonogashira coupling of DHIs **11a**–**h** and tripod-linker **12** for the synthesis of DHIs **14a**–**d** (**14a**, R_1═R_2═Y═H; **14b**, R_1═R_2═CH_3, Y═H; **14c**, R_1═R_2═H; **14d**, R_1═R_2═CH_3)

influence the absorption maxima of the DHI system. As established previously,[47–75] these absorption bands can be assigned to the locally excited π–π^*-transition (LE) located in the butadienyl-vinyl-amine chromophores of the DHIs **11e**–**h** and **14a**–**d** (Table 1).

Irradiation of DHIs **11e**–**h** and **14a**–**d** with polychromatic light led to ring opened betaines (Figs. 2–4). The colored betaine forms **10e**–**h** and **13a**–**d** showed red to blue-green colors in CH_2Cl_2 solution (with a concentration of 1×10^{-5} mol/L) at room temperature because of their inherent sluggish 1,5-electrocyclization. The absorption maxima of the colored betaines **10e**–**h** and **13a**–**d** were found in the visible region lying between 520 (betaine **10a**) and 639 nm (betaine **13d**). The UV-spectra of the colored betaines containing non-substituted pyridazine as a heterocyclic moiety in region C as in betaines **10e**,**g** and **13a**,**c** (Fig. 3) exhibit red colored betaines and showed only one absorption maximum between 520 and 530 nm. On the other hand, the betaine forms which contain substituted dimethyl pyridazine in region C as in the case of betaines **10f**–**h** and **13b**,**d** (Figs 2 and 4) exhibited green-blue colored betaines and showed

Table 1. UV/VIS/NIR absorption DHIs **11e–h** and **14a–d** and their corresponding betaines **10e–h** and **13a–d** and kinetic data of betaines **10e–h** and **13a–d** in the second range (recorded by UV/VIS/NIR-spectrophotometer) in CH_2Cl_2 solution (23 °C, $c = 1 \times 10^{-5}$ mol/L)

DHI/betaine	λ_{max} (DHI) (nm)	log (ε)	λ_{max} (betaine) (nm)	k $\times 10^{-3}$ (s^{-1})	$t_{1/2}$ (s)	Color of betaine
11e/10e	393	3.96	520	5.25	132	Red
11f/10f	394	3.98	350, 444,627	0.62	1120	Blue-green
11g/10g	396	4.03	523	6.13	113	Red
11h/10h	398	4.11	354, 448,629	0.72	968	Blue-green
14a/13a	402	4.22	529	2.57	270	Red
14b/13b	403	4.34	353, 442,632	0.46	1513	Blue-green
14c/13c	405	4.39	530	1.95	356	Red
14d/13d	407	4.49	354, 443,635	0.39	1769	Blue-green

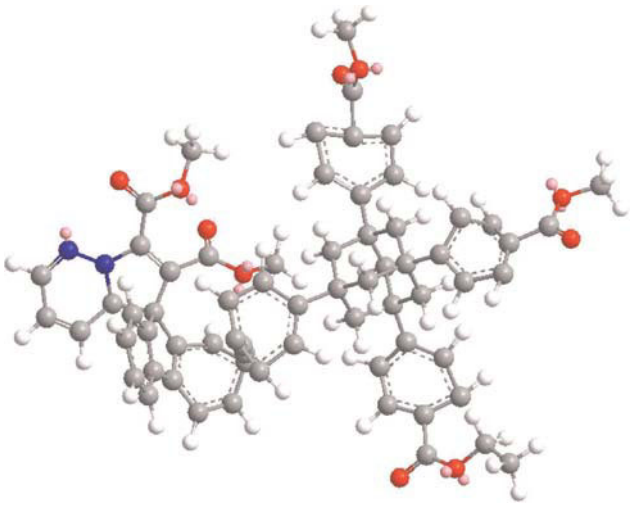

Figure 1. Representation of the optimized (MM2) structure of DHI **14a**.

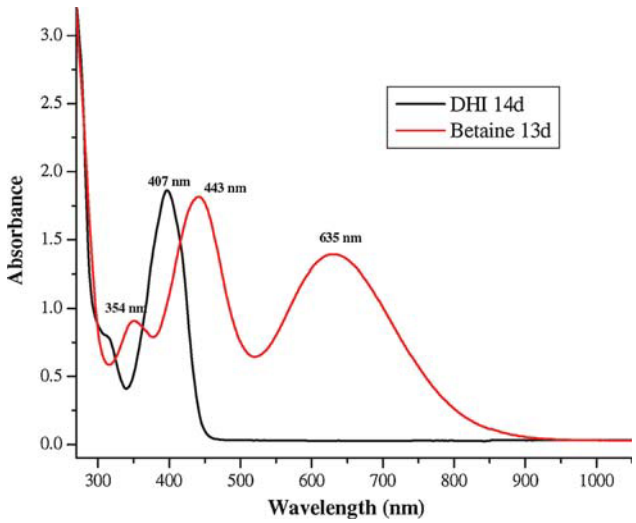

Figure 2. UV/VIS/NIR of photochromic DHI **14d** and the corresponding betaine form **13d** after UV irradiation in CH_2Cl_2 ($c = 1 \times 10^{-5}$ mol/L) at ambient temperature.

three absorption maxima with three isobestic points (Table 1, Figs 2 and 4). The existence of the three isobestic points proves that the thermal back reaction of the colored betaines follows first order. Interestingly, a bathochromic shift of the absorption of the betaines containing non-substituted pyridazines **10e**,**g** and **13a**,**c** by more than 110 nm in the visible region compared with the betaines with dimethyl-substituted pyridazines **10f–h**, **13b**,**d** was recorded. This wide-range bathochromic shift led to the change of the betaine colors from red to green-blue which can be attributed to the increase in the electron donating abilities of the two methyl groups to stabilize the zwitter ionic betaine forms[70,71,74,75] (Table 1). Furthermore, a noticeable bathochromic shift of about 3–4 nm accompanied the increase in the number of tripodal units from 1 to 2 which did not show any dependence on the substituted or non-substituted pyridazine. This may be attributed to the extended conjugation of the fluorene unit with the tripodal-acetylenic aromatic phenyl rings of the tripodal system. Further spectroscopic data related to the UV/VIS measurements of the colored betaines **10e–h** and **13a–d** are listed in Table 1.

The kinetics of the thermal 1,5-electrocyclization was studied by using a UV/VIS/NIR spectrophotometer (Figs. 3 and 4). The kinetic measurements showed that the half-lives of the colored betaines **10e–h** and **13a–d** are in the second domain and lie between 113 and 1769 s (Table 1, Figs. 3 and 4). A highly

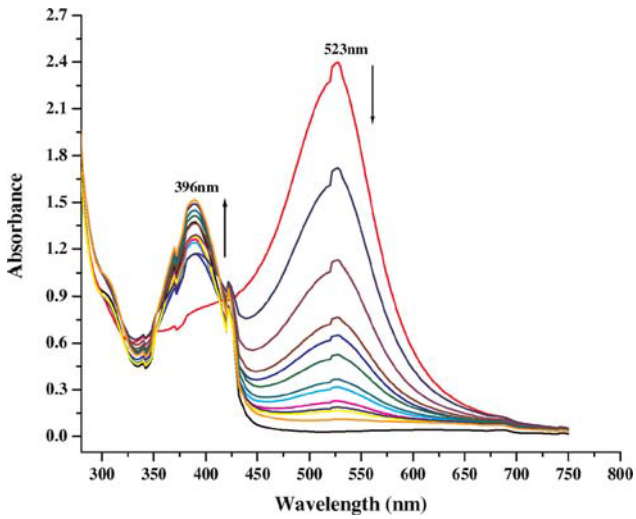

Figure 3. Kinetic UV/VIS/NIR spectrum of the thermal fading of betaine **10g** to DHI **11g** (cycle time = 30 s, run time = 400 s) in CH_2Cl_2 ($c = 1 \times 10^{-5}$ mol/L) at 253 K.

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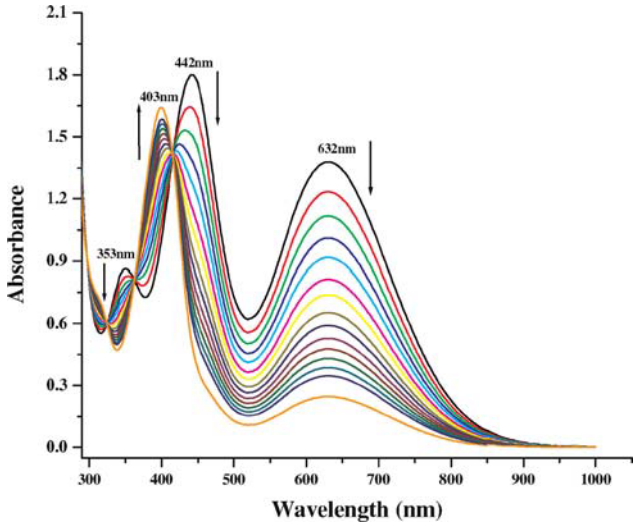

Figure 4. Kinetic UV/VIS/NIR spectrum of the thermal fading of betaine **13b** to DHI **14b** (cycle time = 200 s, run time = 3000 s) in CH_2Cl_2 ($c = 1 \times 10^{-5}$ mol/L) at 253 K.

pronounced increase in the half-lives of the betaines bearing dimethyl-substituted pyridazine **10f**, **10h**, **13b**, and **13d** by approximately a factor of 7 compared with the half-lives of the betaines bearing non-substituted pyridazine **10e**, **10g**, **13a**, and **13c** is noted. This increase in the half-lives may be attributed to the stabilization of the positive and negative charges on the betaines forms by the electron-donating methyl groups. An increase in the half-lives of the betaine forms by increasing the number of the tripod linker from mono-substituted (**13b**) to di-substituted (**13d**) tripod-DHIs by approximately a factor of 1.30 was observed. Also, a noticeable increase in the half-lives of the betaines coupled with tripodal molecules as in **13a**–**d** compared

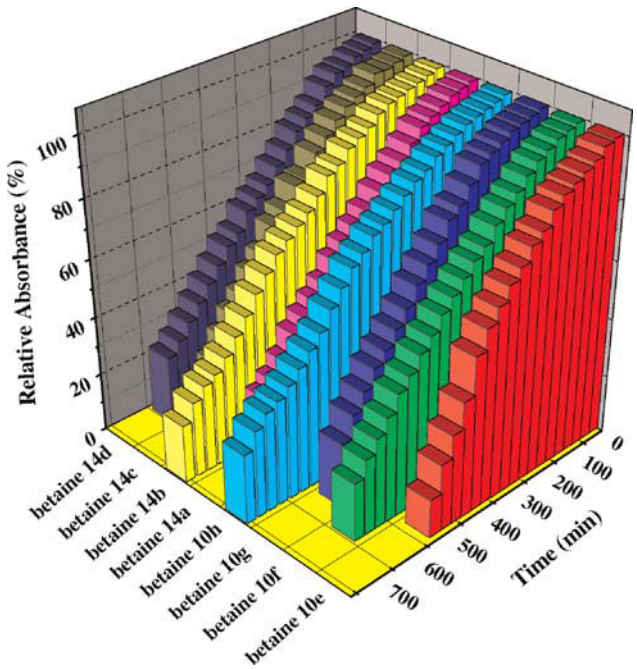

Figure 5. Balcony diagram representing the time-relative absorbance relationship of the photodegradation experiment for determination the t_{30}-value of the betaines **10e**–**h** and **13a**–**d** in CH_2Cl_2 ($c = 1 \times 10^{-5}$ mol/L) at ambient temperature.

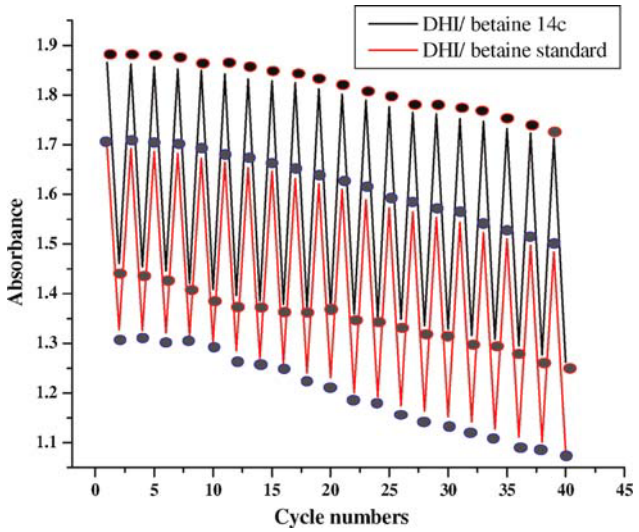

Figure 6. UV-Bleaching and thermal fading between betaine **13c** and DHI **14c** and the standard betaine/DHI system (irradiation/thermal fading/irradiation cycles) with irradiation time of 5 min at wavelength 530 nm in CH_2Cl_2 ($c = 1 \times 10^{-5}$ mol/L) at ambient temperature.

with non-coupled betaines **10e**–**h** by a factor of 1.5–2.0 was observed. These tunings of the absorption maxima and the kinetic properties by the changing of the substitution in the fluorene part (region A) as well as in the pyridazine part (region C) are important to develop the potential of such compounds toward applications.

Photo-fatigue resistance of photochromic DHIs **11e**–**h** *and* **14a**–**d** *and their corresponding betaines* **10e**–**h** *and* **13a**–**d** *in dichloromethane solution* ($c = 1 \times 10^{-5}$ *mol/L) at 253 K*

The photostability of the photochromic materials is a very important property for assessing their quality as suitable for applications. As such, in a photochromic system, the problem of carrying out a large number of coloration–decoloration cycles arises frequently. The gradual loss of the ability to change color by exposure to visible or ultraviolet light in this context has been termed

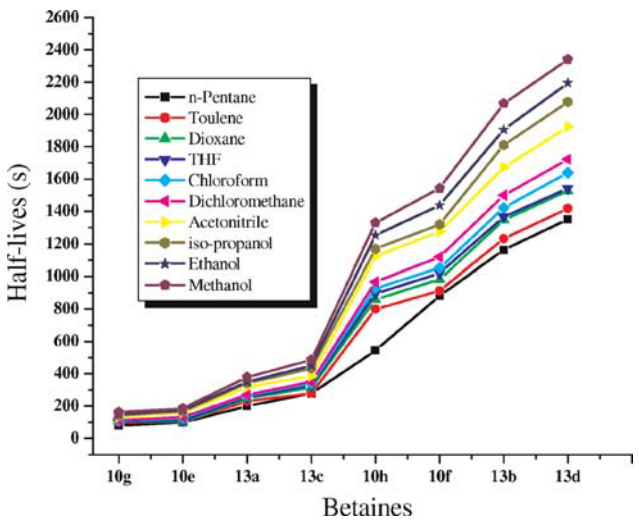

Figure 7. Influence of solvent polarity on the half-lives ($t_{1/2}$) of betaines **10e**–**h** and **13a**–**d** monitored by UV/VIS/NIR ($c = 1 \times 10^{-5}$ m/L) at 23 °C.

Table 2. Photodegradation data of betaines **10e–h** and **14a–d** in dichloromethane solution ($c = 1 \times 10^{-5}$ mol/L) at 23 °C

Betaines	t_{30}-betaine/ DHI (min)	F	Betaines	t_{30}-betaine/ DHI (min)	F
10e	425	1.75	**13a**	583	2.40
10f	649	2.67	**13b**	694	2.86
10g	502	2.07	**13c**	510	2.10
10h	717	2.95	**13d**	628	2.58
Standard	**243**	**1.00**	**243**	**243**	**1.00**

Table 3. Solvatochromic effect on the ($t_{1/2}$) of thermal 1,5-electrocyclization of selected betaines **10e–h** and **13a–d** and $E_T(30)$ values of ten different solvents recorded by kinetic UV/VIS/NIR technique ($c = 1 \times 10^{-5}$ mol/L) at ambient temperature

	Betaines $t_{1/2}$ (s)								
Solvents	**10e**	**10f**	**10g**	**10h**	**13a**	**13b**	**13c**	**14d**	$E_T(30)$
n-Pentane	98	882	79	545	201	1162	278	1351	32
Toluene	104	913	99	801	229	1231	281	1418	34
Dioxane	103	983	106	861	246	1346	316	1526	36
Tetrahydrofurane	110	1020	107	896	256	1367	328	1543	37
Chloroform	126	1052	111	929	267	1423	341	1640	39
Dichloromethane	132	1120	113	968	270	1500	350	1722	41
Acetonitrile	160	1276	132	1122	318	1673	386	1924	46
2-Propanol	167	1321	142	1168	342	1812	432	2079	49
Ethanol	176	1437	149	1253	349	1907	450	2195	52
Methanol	186	1543	162	1330	379	2067	486	2341	56

fatigue.[1–7] Gautron[80] has advanced a quantitative approach to measure the fatigue in photochromic systems.

Due to the slow thermal bleaching process of the betaines to DHIs, a temperature UV/VIS/NIR measurement was used in this case. Irradiation of the degassed dichloromethane solution of DHIs **11e–h** and **14a–d** at room temperature (23 °C) with polychromatic light ($\lambda = 200$–400 nm) led to the formation of the colored betaines **10e–h** and **13a–d**. Upon continued irradiation they decomposed after some time (irradiation time means the continuous irradiation of the colored betaines for a fixed duration of time). However, if oxygen is excluded, these systems are noticeably more stable. It is possible that in the presence of oxygen, the betaines **10e–h** and **13a–d** act as sensitizers toward singlet oxygen.[70,71]

The t_{30}-value is defined as the measure of the decrease in the initial absorbance by 70% with remaining 30% of the betaines absorbance at zero time of the photodegradation experiment. The factor in the photofatigue resistance is the relative value of the t_{30}-value of the measured compound and the t_{30}-value of the standard compound (dicyano-pyridazine DHI). From the photostability measurements listed in Fig. 5 and Table 2 it is clear that all betaines under investigation showed a higher photo-fatigue resistance than the standard dicyano-pyridazine DHI ($t_{30} = 243$ min) by a factor ranging between 1.75 as in the case of betaine **10e** and 2.95 as in the case of betaine **10h**. A pronounced increase of the t_{30}-values by substitution of the fluorene part by mono- and di-substituted tripod-units was observed. An increase in the t_{30}-values of the betaines incorporating two methyl pyridazine as in betaines **10f**, **10h**, **13b**, and **13d** compared with the betaines incorporating non-substituted pyridazine as in betaines **10e**, **10g**, **13a**, and **13c** by a factor of about 0.2 has been seen. Interestingly, the tripodal-betaines **13a–d** showed higher t_{30}-values compared with other betaines under investigation. Betaine **13b** ($t_{30} = 694$ min) substituted with two methyl groups in the pyridazine moiety showed the highest photo-fatigue resistance compared with other betaines **13a**,**c**,**d** and also by a factor of 1.86 compared with the standard betaine ($t_{30} = 243$ min). The high detectable photostability of these materials will help this family to find their applications.

Figure 6 represents an interesting property of the UV-bleaching/thermal fading of the DHI **13c** and DHI **14c** and the standard betaine dicyanopyridazine-DHI with irradiation time of 5 min and waiting for thermal fading for 1 h for 20 cycles (number of cycle means the bleaching and thermal fading which corresponds to one cycle). These cycles of DHI/betaine showed after irradiation and thermal fading no big evidence of any decomposition compared with the standard betaine product as recorded by the UV/VIS measurements.

Solvatochromism

It has been known that UV/VIS/NIR-absorption spectra of the 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 bands.[81–85] A strong effect of the solvent polarity on the λ_{max} and half-lives of betaines **10e–h** and **13a–d** was observed. Changing the solvent from tetrahydrofurane ($E_T(30) = 37$) to methanol ($E_T(30) = 56$) led to a hypsochromic shift ranged between $\Delta\nu \cong +820$ and $\Delta\nu \cong +$

1198 cm^{-1} in the 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 **10e**–**h** and **13a**–**d** was determined using UV/VIS technique at room temperature in ten different solvents (Table 3). A pronounced increase in the half-lives with increasing solvent polarity was recorded in all studied betaines **10e**–**h** and **13a**–**d** (Fig. 7). This is mainly attributed to the partial charge transfer from the betaine form to the solvent and vice versa, as a result of weak Coulombic-exchange effects. Therefore, the charged zwitterionic betaine structure was stabilized by increasing the solvent polarity due to the electrostatic interactions between them. The strong tuning of the half-lives in the different media polarities will help these compounds to select the solvent for suitable applications.

Conclusion

Eight photochromic tripodal-DHI derivatives have been synthesized though multistep reactions. Palladium-mediated Sonogashira coupling reactions have been applied for mono-, di-bromo, and -iodosubstituted fluorene moieties of the DHI system for optimized reaction conditions and product yields. The coupling reactions have been carried out on the fluorene group (region A) with the flexible tripodal system having anchoring groups to help the extension of the photochromism of the target molecules for future applications by supporting them on the surfaces of metal-oxides nanoparticles. In addition, new mono- and di-iodosubstituted spirocyclopropenes and their corresponding DHIs have been synthesized. Different attempts toward optimizing conditions for the Sonogashira-mediated coupling of the DHI skeleton with the tripodal system and the adamantane core have been presented. Interesting photochromic properties with tuning of the chemical structure of the photochromic DHIs by changing the substitutions in the fluorene part and in the pyridazine region have been recorded. This pronounced influence of the substitutions in both A and C regions showed strong effects on the UV/VIS absorption of DHIs and betaines as well as on kinetic properties (half-lives). These newly synthesized photochromic DHIs and their corresponding betaines showed a very low ability to the photodegradation by direct irradiation or by cycling between opened and closed forms for 20 cycles. The solvent effect of ten solvents with different polarities on the photochromism of DHIs and their corresponding betaines has been observed. The tuning of the photochromic properties of the new DHIs and their corresponding betaines will help to find suitable applications. More studies on the anchoring of these compounds onto the surface of metal oxides will be discussed in details in the ongoing research work.

EXPERIMENTAL

Photolysis of the corresponding pyrazole derivatives **7a**,**b** has been done in the photochemical reactor of Schenck[86] made from Pyrex ($\lambda > 290$ nm) according to reported procedures.[86] The source of irradiation was a high pressure mercury lamp Philips-HPK (125 W) and the photolysis time is 3 h. Photochromic DHIs **11a**–**d** were previously prepared by us.[70,71,74,75] The tripod-linker system **12** was prepared following the reaction procedures published by Galoppini[25–35] and Rück-Braun.[36] Full characterization of spirocyclopropenes **8e**–**h** will be given in details in the forthcoming paper.[87] Solutions to be photolyzed were flushed with dry nitrogen for 30 min before switching on the UV lamp. Progress of the reaction and purity of the products isolated were monitored using thin layer chromatography (TLC). Separation and purification of all synthesized photochromic materials were carried out using column chromatography (80 cm length × 2 cm diameter) on silica gel and CH_2Cl_2 as an eluent. Melting points were determined on an Electrothermal Eng. Ltd melting point apparatus and are uncorrected. Some procedures are indispensable to obtain high quality analytical results such as (1) the purifications of the DHIs were done by two or three times column chromatography till showing NMR highly pure spectra, (2) the obtained samples after chromatographic purifications were vacuum dried for 48 h at 45 °C, (3) the samples to be analyzed were weighed in a moisture free atmosphere, and (4) the analysis process was repeated for at least three times and the average values were taken.[88–93] All NMR spectra were collected on a Bruker DRX 400 spectrometer (400 MHz) in $CDCl_3$ using TMS as the internal standard. Chemical shifts (δ) are reported in ppm. FT-IR measurements were performed using a Perkin Elmer Paragon 1000 instrument. Mass spectra were recorded on a VG AutoSpec apparatus using electronic impact at 70 eV. MALDI-MS spectra were recorded in the positive mode by using a 2,5-dihydroxy-benzoic acid in dioxane as a matrix. IR spectra were measured on a BIO-Rad Excalibur series, FTS 3000. UV-spectra were recorded on a UV/VIS/NIR JASCO V-570 computerized spectrophotometer. Experimental details, procedures, and full characterizations of the new synthesized DHIs **11e**–**h** and **14a**–**d** are described below.

Synthesis of photochromic dihydroindolizines 11e–f: General procedure

A mixture of spirocyclopropenes **8a**,**b** (1 mmol) in 50 ml dry ether and pyridazine **8a** and 2,6-dimethyl pyridazine (1.5 mmol) was stirred at room temperature under dry N_2 with exclusion of light for 24 h (TLC-controlled). Ether was removed under reduced pressure and the residues were purified by column chromatography on silica gel and dichloromethane as an eluent. The pure product was obtained after crystallization from the proper solvents to afford the products as yellow crystals.

Dimethyl 2-iodo-4d′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate **11e**: $R_1{=}R_2{=}X{=}H$, yield = 45%, mp = 98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22–8.24 (d, J = 8.00 Hz, 1H, CH-arom.), 7.93–7.94 (d, J = 8.00 Hz, 1H, CH-arom.), 7.76–7.78 (d, J = 7.20 Hz, 1H, CH-arom.), 7.60–7.66 (dd, J = 7.20, J = 7.60 Hz, 2H, CH-arom.), 7.41–7.48 (m, 2H, CH-arom.), 6.95–6.98 (dd, J = 1.76, J = 1.76, 1H, 6′-CH), 5.64–5.67 (m, 1H, 7′-CH), 5.13–5.17 (t, J = 2.2 Hz, 1H, 8′-CH), 4.86–4.98 (dt, J = 8.00 Hz, J = 2.00 Hz, 8a′-CH), 3.84 (s, 3H, 3′-CH_3), 3.49 (s, 3H, 2′-CH_3) ppm. ^{13}CNMR (400 MHz, $CDCl_3$) δ 164.25 (3′-CO), 162.31 (2′-CO), 149.82, 148.85, 142.52, 139.13, 138.62, 138.34, 133.61, 133.37, 130.06, 127.64, 124.16, 123.78, 124.25, 122.01, 121.39, 118.82, 105.86, 65.24 (8′a-C), 63.28 (spiro-C), 53.79 (3′-CH_3), 51.46 (2′-CH_3) ppm; IR (KBr): ν = 3136−3097 (C-H, arom.), 2832–2990 (C—H, aliph.), 1740 (3′-C═O), 1692 (2′-C═O), 1584 (C═N), 1446 (C═C), 1329, 1243, 1182, 1084, 957, 880, 772 cm^{-1}; HR-MS m/e (%) 512.02 [M^+]; Elemental Analysis for $C_{23}H_{17}IN_2O_4$: C, 53.92; H, 3.34; N, 5.47; Found %: C, 53.93; H, 3.33; N, 5.46.

Dimethyl 2-iodo-2′,4a′-dimethyl-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate **11f**: $R_1{=}R_2{=}CH_3$, X = H, yield = 32%, mp = 72 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17– 8.20 (d, *J* = 8.00 Hz, 1H, CH-arom.), 7.90–7.93 (d, *J* = 8.00 Hz, 1H, CH-arom.), 7.81–7.83 (d, *J* = 7.20 Hz, 1H, CH-arom.), 7.66–7.69 (dd, *J* = 7.20, *J* = 7.60 Hz, 2H, CH-arom.), 7.44–7.50 (m, 2H, CH-arom.), 5.67–5.92 (d, *J* = 9.73 Hz, 1H, 7′-CH), 5.10–5.13 (d, *J* = 9.72 Hz, 1H, 8′-CH), 3.87 (s, 3H, 3′-CH_3), 3.32 (s, 3H, 2′-CH_3), 2.12 (s, 3H, 6′-CH_3), 1.54 (s, 3H, 8′-CH_3) ppm. ^{13}CNMR (400 MHz, $CDCl_3$) δ 164.03 (3′-CO), 162.12 (2′-CO), 149.23, 147.48, 144.32, 139.75, 138.01, 132.72, 131.43, 131.73, 129.54, 127.73, 121.17, 121.35, 121.08, 119.24, 101.46, 67.23 (8′a-C), 66.85 (spiro-C), 53.27 (3′-CH_3), 51.19 (2′-CH_3), 22.47 (6′-CH_3), 21.27 (8′-CH_3) ppm; IR (KBr): ν = 3121 (C—H, arom.), 2912–2998 (C—H, aliph.), 1740 (3′-C═O), 1687 (2′-C═O), 1615 (C═N), 1533 (C═C), 1449, 1363, 1278, 1154, 1101, 949, 880, 767 cm^{-1}; HR-MS m/e (%) 540.05 [M^+]; Elemental Analysis for $C_{25}H_{21}IN_2O_4$: C, 55.57; H, 3.92; N, 5.18; Found %: C, 55.56; H, 3.92; N, 5.17.

Dimethyl 2,7-diiodo-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate **11g**: $R_1{=}R_2{=}H$, X = I, yield = 56%, mp = 127 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34– 8.37 (d, *J* = 8.00 Hz, 1H, CH-arom.), 7.95–7.96 (d, *J* = 8.00 Hz, 1H, CH-arom.), 7.72–7.74 (d, *J* = 7.20 Hz, 1H, CH-arom.), 7.53–7.56 (dd, *J* = 7.20, *J* = 1.76 Hz, 1H, CH-arom.), 7.47–7.50 (m, 2H, CH-arom.), 6.95–6.98 (dd, *J* = 1.76, *J* = 1.76, 1H, 6′-CH), 5.60–5.64 (m, 1H, 7′-CH), 5.17–5.20 (t, *J* = 2.2 Hz, 1H, 8′-CH), 4.90–4.93 (dt, *J* = 8.00 Hz, *J* = 2.00 Hz, 8a′-CH), 3.81 (s, 3H, 3′-CH_3), 3.52 (s, 3H, 2′-CH_3) ppm. ^{13}CNMR (400 MHz, $CDCl_3$) δ 164.75 (3′-CO), 162.97 (2′-CO), 150.12, 148.64, 142.73, 139.64, 138.74, 138.30, 133.94, 133.22, 129.12, 127.87, 124.27, 123.45, 124.78, 121.67, 121.20, 118.87, 105.86, 65.20 (8′a-C), 63.35 (spiro-C), 53.87 (3′-CH_3), 51.57 (2′-CH_3) ppm; IR (KBr): ν = 3101–3087 (C—H, arom.), 2898–2982 (C—H, aliph.), 1737 (3′-C═O), 1687 (2′-C═O), 1580 (C═N), 1441 (C═C), 1330, 1241, 1178, 1088, 960, 875, 762 cm^{-1}; HR-MS m/e (%) 637.92 [M^+]; Elemental Analysis for $C_{23}H_{16}I_2N_2O_4$: C, 43.29; H, 2.53; N, 4.39; Found %: C, 43.30; H, 2.54; N, 4.40.

Dimethyl 2,7-diiodo-2′,4a′-dimethyl-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate **11h**: $R_1{=}R_2{=}CH_3$, X = I, yield = 39%, mp = 103 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20–8.23 (d, *J* = 8.00 Hz, 1H, CH-arom.), 7.96–7.99 (d, *J* = 8.00 Hz, Hz, 1H, CH-arom.), 7.73–7.76 (d, *J* = 7.20 Hz, 1H, CH-arom.), 7.61–7.64 (dd, *J* = 7.20, *J* = 7.60 Hz, 2H, CH-arom.), 7.41–7.43 (m, 2H, CH-arom.), 5.64–5.66 (d, *J* = 9.73 Hz, 1H, 7′-CH), 5.17–5.20 (d, *J* = 9.72 Hz, 1H, 8′-CH), 3.84 (s, 3H, 3′-CH_3), 3.36 (s, 3H, 2′-CH_3), 2.10 (s, 3H, 6′-CH_3), 1.57 (s, 3H, 8′-CH_3) ppm. ^{13}CNMR (400 MHz, $CDCl_3$) δ 163.64 (3′-CO), 161.98 (2′-CO), 148.64, 147.34, 144.46, 139.77, 138.13, 132.28, 131.48, 131.75, 129.63, 127.75, 121.10, 121.32, 121.12, 119.25, 101.57, 67.34 (8′a-C), 66.67 (spiro-C), 53.22 (3′-CH_3), 51.24 (2′-CH_3), 22.41 (6′-CH_3), 21.31 (8′-CH_3) ppm; IR (KBr): ν = 3097 (C—H, arom.), 2914–2983 (C—H, aliph.), 1746 (3′—C═O), 1681 (2′—C═O), 1635 (C═N), 1520 (C═C), 1442, 1360, 1266, 1146, 1118, 976, 878, 760 cm^{-1}; HR-MS m/e (%) 665.95 [M^+]; Elemental Analysis for $C_{25}H_{20}I_2N_2O_4$: C, 45.07; H, 3.03; N, 4.20; Found %: C, 45.06; H, 3.05; N, 4.19.

Sonogashira-mediated coupling for the synthesis of photochromic DHIs-tripodal-linker 14a–d: General procedure (Best conditions)

To an oven-dried screw cap tube or a round bottom flask equipped with a water cooled west condenser and a magnetic stir bar were added the mono- and dihalo-substituted fluorene DHIs **11a–h** (3 mmol), bis(dibenzylideneacetone)palladium(0) (86 mg, 0. 15 mmol), copper(I) iodide (72 mg, 0.3 mmol), triphenylphosphine (157 mg, 0.06 mmol) to 1-(ethynylphenyl)-3,5,7- tris(4-carboethoxy)adamantane **12** (1.49 mmol). The vessel was then sealed with a rubber septum, evacuated, and backfilled with nitrogen (three times). A co-solvent system of freshly distilled THF (20 ml) followed by DIEA (2.1 ml, 12 mmol) were added. The reaction mixture was stirred in a 40 °C oil bath for 6 h (TLC-controlled) until the reaction is completed. The reaction vessel was cooled to room temperature and the mixture quenched with water or a saturated solution of NH_4Cl. The organic layer was diluted with CH_2Cl_2 and washed with a saturated solution of NH_4Cl (3 × 30 ml). The combined aqueous layers were extracted with CH_2Cl_2 (3 × 30 ml). The combined organic layers were dried over anhydrous $MgSO_4$ and the solvent removed under reduced pressure. The crude products were then purified by twice column chromatography on silica gel and CH_2Cl_2 as an eluent. The pure products were obtained with highly purity as yellow needles. Full characterizations of the coupling products **14a–d** are cited below:

Dimethyl 2-(ethynylphenyl)-3,5,7-tris(4-carboethoxy)adamantyl-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate **14a:** From DHI **11a**; $R_1{=}R_2{=}H$, method A, yield = 13%, mp = 137 °C; method B, yield = 12%, mp = 136 °C; method C, yield = 20%, mp = 136–137 °C; from DHI **11e**: $R_1{=}R_2{=}H$, method A, yield = 25%, mp = 136 °C; method B, yield = 31%, mp = 137 °C; method C, yield = 54%, mp = 136 °C; method D, yield = 8%, mp = 136 °C; method E, yield = 10%, mp = 137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46– 8.49 (d, *J* = 8.00 Hz, 1H, CH-arom.), 8.15–8.17 (d, 6H, *J* = 8.72 Hz), 8.08–7.13 (d, *J* = 8.00 Hz, 1H, CH-arom.), 7.65–7.68 (d, *J* = 7.20 Hz, 1H, CH-arom.), 7.53–7.54 (dd, *J* = 7.20, *J* = 7.60 Hz, 2H, CH-arom.), 7.43–7.47 (d, 6H, *J* = 8.72 Hz), 7.36–7.40 (d, 2H, *J* = 8.60 Hz), 7.16–7.19 (d, 2H, *J* = 8.60 Hz), 7.08–7.14 (m, 2H, CH-arom.), 6.92–6.95 (dd, *J* = 1.76, *J* = 1.76, 1H, 6′-CH), 5.60–5.62 (m, 1H, 7′-CH), 5.20–5.23 (t, *J* = 2.2 Hz, 1H, 8′-CH), 4.97–5.01(dt, *J* = 8.00 Hz, *J* = 2.00 Hz, 8a′-CH), 4.46–4.50 (q, 6H, *J* = 7.12 Hz), 3.90 (s, 3H, 3′-CH_3), 3.42 (s, 3H, 2′-CH_3), 2.16 (two overlapping, s, 12H), 1.42 (t, 9H, *J* = 7.12 Hz) ppm. ^{13}CNMR (400 MHz, $CDCl_3$) δ 167.25 (3′-CO), 165.31 (2′-CO), 163.15 (CO-ethyl ester), 153.9, 149.82, 148.85, 148.65, 147.7, 142.70, 142.52, 139.13, 138.62, 138.34, 136.09, 136.01, 133.61, 133.37, 131.87, 130.06, 129.97, 128.83, 127.64, 124.25, 124.16, 123.91, 123.78, 122.01, 121.95, 121.39, 118.82, 117.71, 112.64, 105.86, 93.41 (acetylenic-C), 89.34 (acetylenic-C), 88.17, 65.67 (8′a-C), 63.38 (spiro-C), 61.53, 52.65 (3′-CH_3), 51.40 (2′-CH_3), 46.91, 39.73, 30.08, 26.24, 24.94, 23.80, 22.86, 22.14, 14.57, 12.20 ppm; IR (KBr): ν = 3017−3067 (C—H, arom.), 2887–2981 (C—H, aliph.), 2211 (acetylenic bond), 1751 (3′-C═O), 1709 (CO-ester), 1691 (2′-C═O), 1588 (C═N), 1454 (C═C), 1348, 1261, 1183, 1118, 956, 895, 767 cm^{-1}; HR-MS m/e (%) 1064.42 [M^+]; Elemental Analysis for $C_{68}H_{60}N_2O_{10}$: C, 76.67; H, 5.68; N, 2.63; Found %: C, 76.65; H, 5.69; N, 2.64.

Dimethyl 2-(ethynylphenyl)-3,5,7-tris(4-carboethoxy)adamantyl-2′,4a′-dimethyl-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate **14b**: From DHI **11b**; $R_1{=}R_2{=}CH_3$, method A, yield = 10%, mp = 122 °C; method B, yield = 16%, mp = 123 °C; method C, yield = 18%, mp = 122 °C; from DHI **11f**: $R_1{=}R_2{=}CH_3$, method A, yield = 22%, mp = 123 °C; method B, yield = 34%, mp = 123 °C; method C, yield = 52%, mp = 122 °C; method D, yield = 7%, mp = 121 °C; method E, yield = 9%, mp = 121 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32–8.36 (d, *J* = 8.00 Hz, 1H, CH-arom.), 8.09–8.11 (d, 6H, *J* = 8.72 Hz), 8.07–7.10 (d, *J* = 8.00 Hz, 1H, CH-arom.), 7.76–7.80 (d, *J* = 7.20 Hz, 1H, CH-arom.), 7.60–7.63

(dd, $J = 7.20$, $J = 7.60$ Hz, 2H, CH-arom.), 7.40–7.43 (d, 6H, $J = 8.72$ Hz), 7.32–7.36 (d, 2H, $J = 8.60$ Hz), 7.16–7.19 (d, 2H, $J = 8.60$ Hz), 7.05–7.09 (m, 2H, CH-arom.), 5.68–5.72 (m, 1H, 7′-CH), 5.11–5.17 (dt, $J = 8.00$ Hz, $J = 2.00$ Hz, 8′-CH), 4.50–4.53 (q, 6H, $J = 7.12$ Hz), 3.94 (s, 3H, 3′-CH_3), 3.49 (s, 3H, 2′-CH_3), 2.19 (two overlapping, s, 12H), 2.12 (s, 3H, 6′-CH_3), 1.62 (s, 3H, 8′-CH_3), 1.42 (t, 9H, $J = 7.12$ Hz) ppm. ^{13}CNMR (400 MHz, $CDCl_3$) δ 167.65 (3′-CO), 165.35 (2′-CO), 163.28 (CO-ethyl ester), 152.99, 150.34, 148.65, 148.79, 147.56, 142.62, 142.37, 139.63, 138.68, 138.67, 136.10, 136.85, 133.63, 133.47, 131.22, 130.19, 129.85, 128.64, 127.78, 124.61, 124.10, 124.02, 123.75, 122.18, 121.87, 121.46, 118.76, 117.26, 112.50, 105.81, 93.76 (acetylenic-C), 89.79 (acetylenic-C), 88.28, 65.41 (8′a-C), 63.40 (spiro-C), 61.87, 52.41 (3′-CH_3), 51.23 (2′-CH_3), 46.89, 39.65, 30.18, 26.17, 24.85, 23.64, 22.37, 22.76 (6′-CH_3), 22.43, 21.13 (8′-CH_3), 14.13, 12.58, ppm; IR (KBr): $\nu = 3069-3021$ (C—H, arom.), 2895–2976 (C—H, aliph.), 2228 (acetylenic bond), 1748 (3′-C═O), 1702 (CO-ester), 1687 (2′-C═O), 1586 (C═N), 1450 (C═C), 1379, 1261, 1175, 1136, 950, 887, 746 cm^{-1}; HR-MS m/e (%) 1092.46 [M$^+$]; Elemental Analysis for $C_{70}H_{64}N_2O_{10}$: C, 76.90; H, 5.90; N, 2.56; Found %: C, 76.89; H, 5.94; N, 2.58.

Dimethyl 2,7-((bis(ethynylphenyl)-3,5,7-tris(4-carboethoxy) adamanty)l-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b]pyridazine]-6′,7′-dicarboxylate **14c**: From DHI **11c**; $R_1 = R_2 = H$, method A, yield = 18%, mp = 146 °C; method B, yield = 14%, mp = 147 °C; method C, yield = 23%, mp = 146 °C; from DHI **11g**: $R_1 = R_2 = H$, method A, yield = 29%, mp = 145 °C; method B, yield = 37%, mp = 146 °C; method C, yield = 69%, mp = 145 °C; method D, yield = 10%, mp = 146 °C; method E, yield = 12%, mp = 145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22–8.24 (d, $J = 8.00$ Hz, 1H, CH-arom.), 8.10–8.14 (d, 12H, $J = 8.72$ Hz), 8.04–7.07 (d, $J = 8.00$ Hz, 2H, CH-arom.), 7.60–7.63 (d, $J = 7.20$ Hz, 2H, CH-arom.), 7.49–7.55 (dd, $J = 7.20$, $J = 7.60$ Hz, 3H, CH-arom.), 7.46–7.9 (d, 12H, $J = 8.72$ Hz), 7.20–7.26 (d, 2H, $J = 8.60$ Hz), 7.02–7.05 (d, 2H, $J = 8.60$ Hz), 7.08–7.14 (m, 2H, CH-arom.), 6.99–7.01 (dd, $J = 1.76$, $J = 1.76$, 1H, 6′-CH), 5.72–5.73 (m, 1H, 7′-CH), 5.36–5.40 (t, $J = 2.2$ Hz, 1H, 8′-CH), 5.06–5.08 (dt, $J = 8.00$ Hz, $J = 2.00$ Hz, 8a′-CH), 4.42-4.48 (q, 12H, $J = 7.12$ Hz), 3.92 (s, 3H, 3′-CH_3), 3.40 (s, 3H, 2′-CH_3), 2.19 (two overlapping, s, 24H), 1.48 (t, 18H, $J = 7.12$ Hz) ppm. ^{13}CNMR (400 MHz, $CDCl_3$) δ 166.98 (3′-CO), 165.76 (2′-CO), 164.01 (CO-ethyl ester), 153.91, 150.02, 148.95, 148.64, 148.02, 144.35, 143.67, 141.68, 140.27, 138.95, 138.20, 136.11, 136.11, 134.03, 133.87, 132.16, 131.64, 129.90, 128.84, 127.50, 125.67, 124.78, 123.05, 122.48, 121.17, 121.02, 118.24, 117.36, 112.13, 105.78, 93.87 (acetylenic-C), 89.01 (acetylenic-C), 88.46, 65.34 (8′a-C), 63.57 (spiro-C), 61.43, 52.46 (3′-CH_3), 51.47 (2′-CH_3), 46.87, 40.21, 31.64, 26.38, 24.78, 23.34, 22.78, 22.24, 14.67, 12.29 ppm; IR (KBr): $\nu = 3117-3041$ (C—H, arom.), 2887–2981 (C—H, aliph.), 2209 (acetylenic bond), 1748 (3′-C═O), 1711 (CO-ester), 1685 (2′-C═O), 1567 (C═N), 1450 (C═C), 1354, 1268, 1178, 1106, 949, 887, 751 cm^{-1}; HR-MS m/e (%) 1742.72 [M$^+$]; Elemental Analysis for $C_{113}H_{102}N_2O_{16}$: C, 77.82; H, 5.89; N, 1.61; Found %: C, 77.81; H, 5.88; N, 1.62.

Dimethyl 2,7-((bis(ethynylphenyl)-3,5,7-tris(4-carboethoxy) adamanty)l-2′,4a′-dimethyl-4a′H-spiro[fluorene-9,5′-pyrrolo[1,2-b] pyridazine]-6′,7′-dicarboxylate **14d**: From DHI **11d**; $R_1 = R_2 = CH_3$, method A, yield = 14%, mp = 126 °C; method B, yield = 22%, mp = 126 °C; method C, yield = 25%, mp = 127 °C; from DHI **11h**: $R_1 = R_2 = CH_3$, method A, yield = 25%, mp = 126 °C; method B, yield = 36%, mp = 125 °C; method C, yield = 64%, mp = 126 °C; method D, yield = 8%, mp = 126 °C; method E, yield = 11%, mp = 125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22–8.24 (d, $J = 8.00$ Hz, 1H, CH-arom.), 8.32–8.36 (d, 12H, $J = 8.72$ Hz), 8.12–7.15 (d, $J = 8.00$ Hz, 2H, CH-arom.), 7.67–7.70 (d, $J = 7.20$ Hz, 2H, CH-arom.), 7.51–7.54 (dd, $J = 7.20$, $J = 7.60$ Hz, 3H, CH-arom.), 7.61–7.64 (d, 12H, $J = 8.72$ Hz), 7.26–7.32 (d, 2H, $J = 8.60$ Hz), 7.10–7.13 (d, 2H, $J = 8.60$ Hz), 7.06–7.08 (m, 2H, CH-arom.), 5.88–5.92 (m, 1H, 7′-CH), 5.18–5.23 (dt, $J = 8.00$ Hz, $J = 2.00$ Hz, 8′-CH), 4.49–4.53 (q, 12H, $J = 7.12$ Hz), 3.86 (s, 3H, 3′-CH_3), 3.44 (s, 3H, 2′-CH_3), 2.17 (two overlapping, s, 24H), 2.16 (s, 3H, 6′-CH_3), 1.53 (s, 3H, 8′-CH_3), 1.47 (t, 18H, $J = 7.12$ Hz), ppm. ^{13}CNMR (400 MHz, $CDCl_3$) δ 166.43 (3′-CO), 165.98 (2′-CO), 164.16 (CO-ethyl ester), 153.94, 150.18, 148.79, 148.32, 148.47, 144.31, 143.63, 141.79, 140.36, 138.74, 138.30, 136.18, 136.03, 134.46, 133.74, 132.30, 131.79, 130.62, 127.50, 125.67, 123.16, 122.48, 122.00, 121.32, 118.38, 117.57, 112.21, 105.89, 93.47 (acetylenic-C), 89.35 (acetylenic-C), 88.67, 65.32 (8′a-C), 63.52 (spiro-C), 61.64, 52.51 (3′-CH_3), 51.97 (2′-CH_3), 46.53, 40.28, 31.64, 26.31, 24.70, 23.18, 22.65 (6′-CH_3), 22.28, 21.16 (8′-CH_3), 14.85, 12.34, ppm; IR (KBr): $\nu = 3100-3032$ (C—H, arom.), 2910–2997 (C—H, aliph.), 2216 (acetylenic bond), 1742 (3′-C═O), 1713 (CO-ester), 1685 (2′-C═O), 1567 (C═N), 1452 (C═C), 1355, 1261, 1185, 1134, 947, 868, 751 cm^{-1}; HR-MS m/e (%) 1770.75 [M$^+$]; Elemental Analysis for $C_{115}H_{106}N_2O_{16}$: C, 77.94; H, 6.03; N, 1.58; Found %: C, 77.93; H, 6.05; N, 1.57.

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