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Synthesis and properties of photoswitchable bis(hemi-indigo) derivatives bearing elongated alkyloxy substitutents

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This article is dedicated to Prof. Dr. Thomas J. J. Müller for his outstanding contribution to organic chemistry

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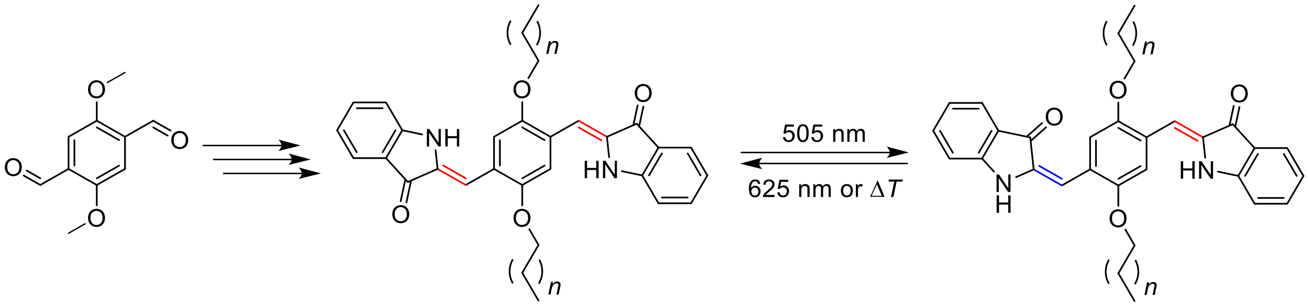
Abstract

In this work, two bis(hemi-indigo) derivatives bearing hexyloxy and octyloxy substitutents in the central ring were synthesized and their photophysical and photochemical properties were investigated by optical spectroscopy and real-time NMR spectroscopy with in situ irradiation. Importantly, the introduction of alkyloxy substituents significantly increased the solubility of bis(hemi-indigo) derivatives in many solvents, making it possible to study their properties in eight different solvents. It was found that the presence of the alkyloxy substituents significantly increased the conversion in the photostationary states and led to much higher photoisomerization quantum yields in comparison with the parent unsubstituted bis(hemi-indigo).



Keywords: Hemiindigo, photochromism, photoswitching, indigoid photoswitches, real-time NMR spectroscopy, in situ irradiation

Introduction

Indigoid photoswitches represent a class of photochromes that are based on the indigo dye.[1–4] The intense development of indigoid photoswitches has occurred mainly during the last 10 years although the synthetic methods towards the key representatives of indigoid dyes have been elaborated more than 100 years ago.[1–4] Indigoid photoswitches possess a range of practically valuable properties such as switching in both directions with visible light, high thermal bistability and controllable geometry changes.[1–4] One of the main sub-classes of the growing family of indigoid photoswitches are hemi-indigo derivatives.

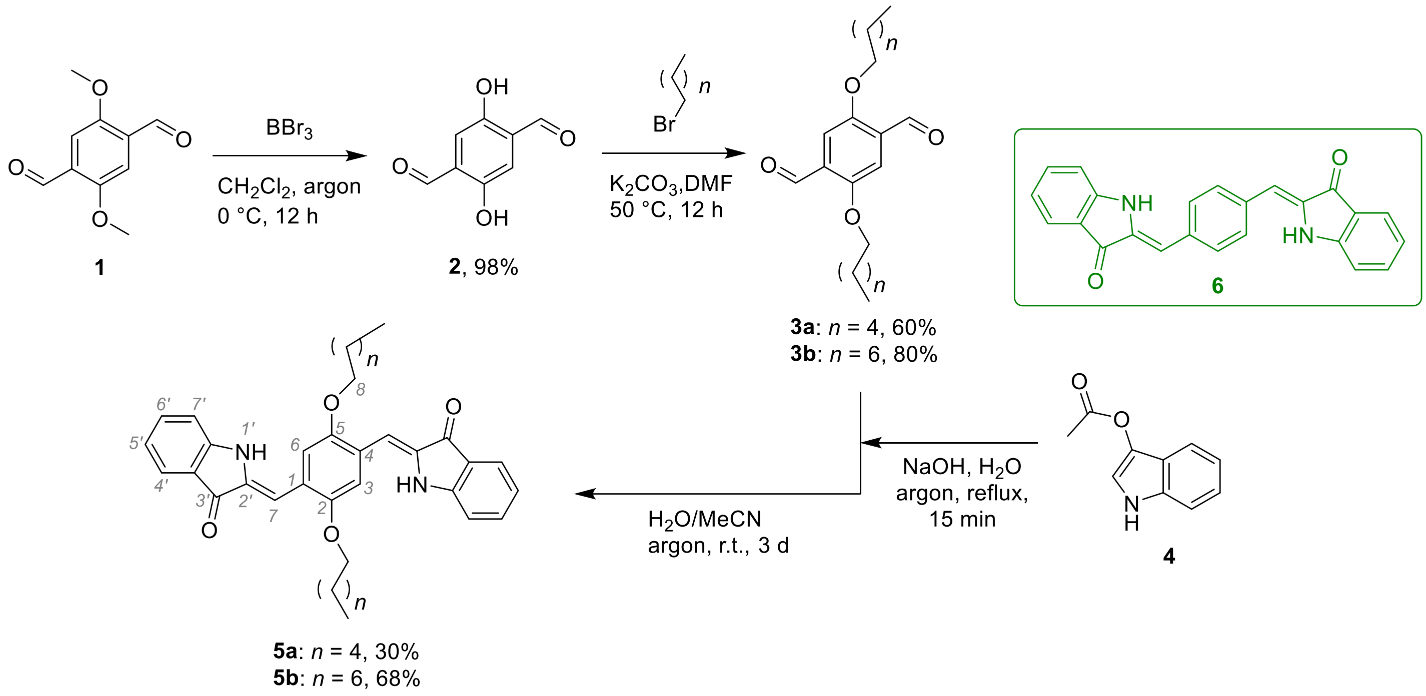
The hemi-indigo dyes were first synthesized by Adolf von Baeyer in 1883[5] and found their application as colorants. The first report on the photochromism of hemi-indigo was provided by Mostoslavski *et al.* in 1970th.[6] In 2003, Arai *et al*. described synthesis and photochemical studies of the hemi-indigos comprising pyrrole and pyridine residues.[7] Nevertheless, a systematic development of hemi-indigos as molecular photoswitches started from the publication by Dube *et al.* in 2017 describing the photochemical behavior of 4'-dialkylamino-substituted hemi-indigo derivatives.[8] Since then, a number of novel hemi-indigo derivatives have been reported, demonstrating valuable properties for applications in biology, supramolecular chemistry and materials science.[9–14] It is therefore surprising that systems combining two or more hemi-indigo units in a single molecule have been studied very little. To the best of our knowledge, there is only one publication so far devoted to bis(hemi-indigo) derivatives.[15]

Herein, we describe synthesis and photoswitching of two novel bis(hemi-indigo) derivatives containing two elongated alkyloxy chains in the central ring. Optical spectroscopy and real-time NMR experiments with in situ irradiation provide a detailed understanding of the structural, photophysical, and photochemical characteristics of these compounds. Particular attention is paid to the analysis of the photochemical isomerization of bis(hemi-indigo) derivatives in different solvents.

Results and Discussion

Synthesis

The synthesis of novel bis(hemi-indigo) derivatives **5a** and **5b** bearing the hexyloxy and octyloxy substituents in the central ring was performed in three steps (Scheme 1). In the first step, 2,5-dimethoxyterephthalaldehyde (**1**) was demethylated in the reaction with BBr_3 yielding 2,5-dihydroxyterephthalaldehyde (**2**) in 98% yield. Compound **2** subsequently interacted with 1-bromohexane or 1-bromooctane in the presence of K_2CO_3 in dry DMF yielding two corresponding 2,5-bis(alkyloxy)terephthalaldehydes **3a** (60%) and **3b** (80%). The dialdehydes **3a** and **3b** were finally condensed with two indoxyl molecules obtained in situ upon hydrolysis of commercially available indoxyl acetate (**4**) under basic conditions in the inert gas atmosphere giving the bis(hemi-indigo) derivatives **5a** (30%) and **5b** (68%). It is noteworthy that the condensation reaction should be carried out strictly under oxygen-free conditions to avoid formation of a by-product, indigo, resulting from the rapid dimerization of deprotected indoxyl molecules in the presence of oxygen. The overall yield of the reaction sequence over three steps was 18% for **5a** and 53% for **5b**. This difference in overall reaction efficiencies can be explained by incomplete oxygen removal during the synthesis of **5a**, which involves two oxygen-sensitive intermediates, namely 2,5-dihydroxyterephthalaldehyde (**2**) and deprotected indoxyl acetate (**4**). In the synthesis of **5b**, these issues were addressed and oxygen-free conditions were improved, resulting in the increase of the overall yield. All known intermediary products were identified by comparison of the melting points and ^{1}H NMR chemical shifts with the reported data. Novel compounds **5a** and **5b** were purified by recrystallization and fully characterized by 1D and 2D NMR spectroscopy (^{1}H, ^{13}C, COSY, HSQC, HMBC), elemental analysis, and electrospray ionization mass spectrometric analysis (ESI-MS) (cf. Supporting Information).



Scheme 1. Synthesis of bis(hemi-indigo) derivatives **5a** and **5b** and the structure of compound **6** used for comparison.

Optical properties

Optical properties of the bis(hemi-indigo) derivatives **5a** and **5b** were studied in eight solvents of different polarity, namely, 1,4-dioxane, toluene, chloroform, ethyl acetate, ethanol, methanol, acetonitrile, and DMSO (Table 1). It is noteworthy that the introduction of the alkyloxy substituents in **5a** and **5b** significantly increased their solubility in many solvents compared to the unsubstituted parent compound **6**, which was only soluble in DMSO and DMF.[15] In all solvents, compounds **5a** and **5b** show characteristic long-wavelength absorption bands centered at 519–562 nm (Table 1, Figure 1) which corresponds to red and purple color. The positions of the absorption maxima of **5a** and **5b** are significantly influenced by the solvent polarity resulting in the positive solvatochromism (Table 1). Thus, the red-shift of the absorption maximum between the less polar solvent (dioxane) and the most polar one (DMSO) is $\Delta\lambda$ = 35 nm for **5a** and $\Delta\lambda$ = 29 nm for **5b**.

The bis(hemi-indigo) derivatives **5a** and **5b** demonstrate pronounced fluorescence emission in all aprotic solvents (Table 1, Figure 1). At the same time, fluorescence in alcohols is almost completely quenched. The possible reason for this is fast prototropic equilibria that occur between the protic solvents and the NH groups of bis(hemi-indigo) in the excited state. The fluorescence maxima of **5a** and **5b** cover the range of 568–612 nm (Table 1) which corresponds to yellow, orange and red emission colors. As in the case of absorption, the positions of the emission maxima depend on the solvent polarity resulting in positive fluorosolvatochromism. The red-shift of the fluorescence maximum between the less polar solvent (dioxane) and the most polar one (DMSO) is $\Delta\lambda$ = 41 nm for **5a** and $\Delta\lambda$ = 38 nm for **5b**.

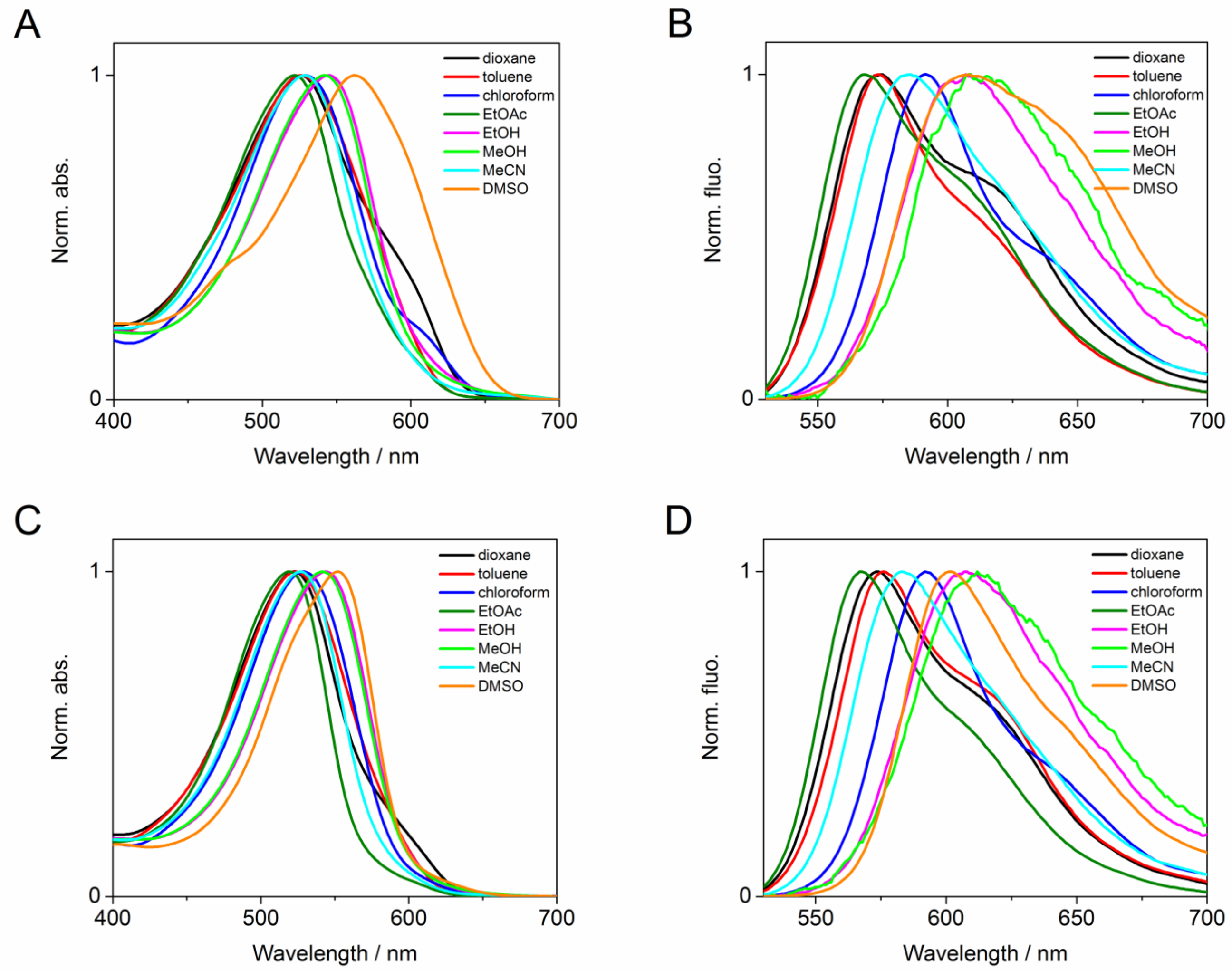


Figure 1. Normalized absorption spectra of compounds **5a** (A) and **5b** (C) and normalized fluorescent spectra of compounds **5a** (B) and **5b** (D) (λ_{ex} = 520 nm) in different solvents, *c* = 30 μM.

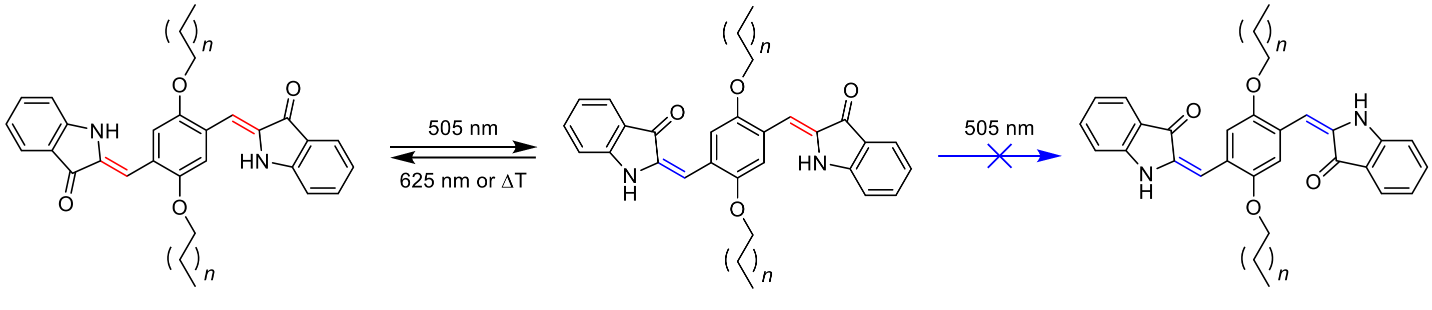
Table 1. Absorption and emission properties of derivatives **5a** and **5b**.

	5a			**5b**		
Solvent[a]	λ_{abs} / nm[b]	ε / mol L^{-1} cm^{-1}	λ_{fl} / nm[d]	λ_{abs} / nm[b]	ε / mol L^{-1} cm^{-1}	λ_{fl} / nm[d]
1,4-Dioxane	527	20440	575	523	25935	574
Toluene	525	18110	573	524	26890	576
$CHCl_3$	530	23750	592	530	30130	592
EtOAc	522	22360	568	519	28840	567
EtOH	544	16975	607	544	29200	608
MeOH	543	18865	609	542	22950	612
MeCN	528	18245	586	528	23020	583
DMSO	562	21755	608	552	32515	602

[a] Solvents arranged in order of increasing dielectric constant values. [b] Absorption maxima, *c* = 30 μM. [c] Molar extinction coefficient. [d] Fluorescence maxima, *c* = 30 μM, λ_{ex} = corresponds to the absorption maxima.

Photoswitching

The photoswitching of bis(hemi-indigos) **5a** and **5b** was studied in detail in DMSO using optical spectroscopy and real-time NMR spectroscopy with in situ irradiation.[16] The compounds possess two C–C double bonds that can potentially isomerize (Scheme 2). Initially, the molecules **5a** and **5b** adopt the thermodynamically stable *Z,Z*-configuration. Irradiation of the *Z,Z*-isomers of **5a,b** by cyan light (λ = 505 nm) results in the decrease of the initial absorption along with formation of new red-shifted bands (Figure 2). Under similar conditions, the photoreaction of **5a** (t = 48 s) bearing hexyloxy chains occurs ca. 3 times faster than that of **5b** (t = 131 s) with longer octyloxy chains. The isomerization of **5a** and **5b** is reversible upon irradiation with red light (λ = 625 nm) or heating. The backward *E*–*Z* photoreaction of bis(hemi-indigos) proceeds slower that the direct one. Thus, the *E*–*Z* photoisomerization of the hexyloxy derivative **5a** is ca. 7 times slower (t = 323 s) than the direct *Z*–*E* reaction. The backward *E*–*Z* photoreaction of the octyloxy derivative **5b** is only 1.5 time slower (t = 199 s) than the forward one. This observation indicates an important role of the alkyl chain length in the kinetics of the photoreaction, since the photoactive units are identical in both compounds. The photoinduced forms of bis(hemi-indigos) show good stabilities in DMSO with half-lives of $\tau_{1/2}$ = 17 days for **5a** and $\tau_{1/2}$ = 104 days for **5b**. These values are generally consistent with most reported half-lives of mono- and bis(hemi-indigo) in DMSO, but are significantly shorter than those of the parent unsubstituted bis(hemi-indigo) **6** ($\tau_{1/2}$ = 4 years).[15]



Z,Z-**5a,b** *E,Z*-**5a,b** *E,E*-**5a,b**

Scheme 2. Photoswitching of bis(hemi-indigo) derivatives **5a** and **5b**.

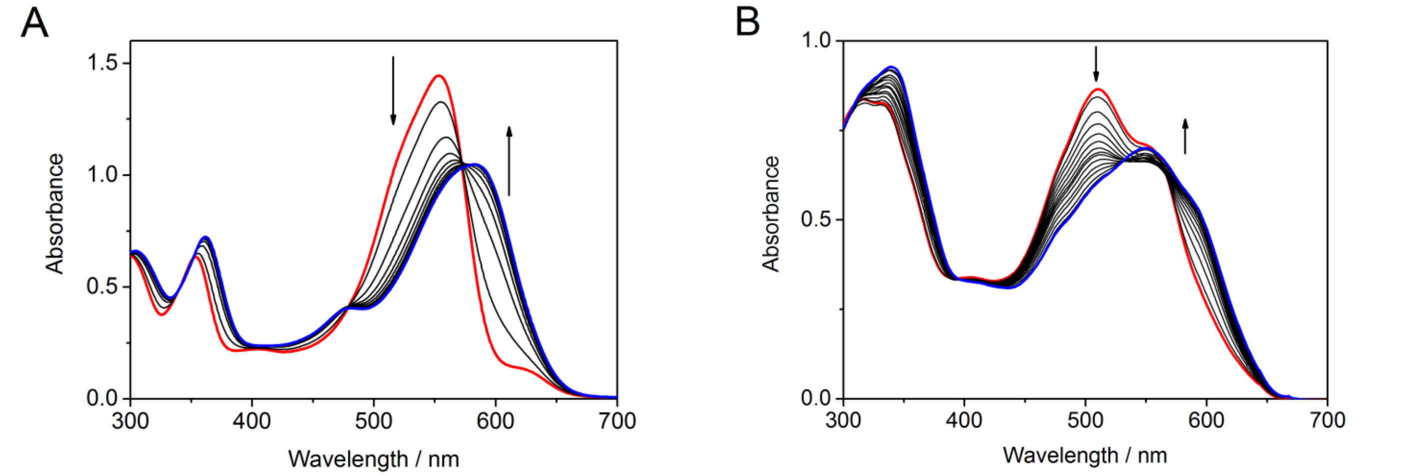


Figure 2. Changes of the absorption of (A) **5a** and (B) **5b** during irradiation with cyan light (λ_{ex} = 505 nm), c = 30 µM in DMSO, arrows indicate the development of the absorption bands with increasing irradiation time.

The detailed information of the structural changes during the photoisomerization of bis(hemi-indigo) derivatives **5a** and **5b** was obtained by real-time NMR experiments with in situ irradiation in DMSO-d_6 (Figure 3, Figure S1, Supporting Information). The light inside the spectrometer was provided by our home-modified

NMR probe with a LED insert.[16] The direct photoreaction was carried out upon irradiation with green light (λ = 520 nm), the follow-up backward isomerization was performed upon irradiation with red light (λ = 625 nm).

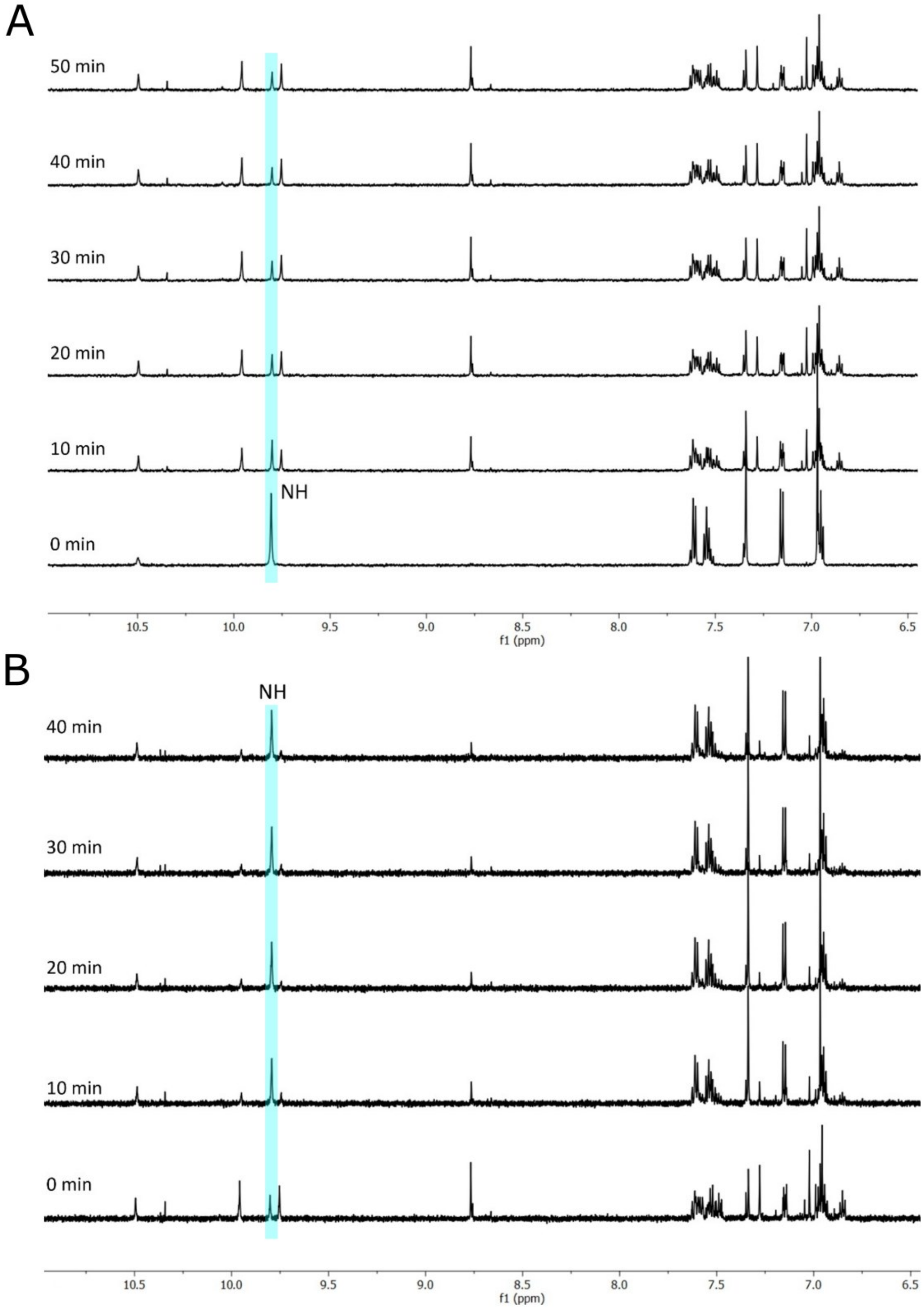


Figure 3. Real-time ^{1}H NMR spectroscopic monitoring with in situ irradiation of (A) the forward *Z,Z–E,Z* isomerization of **5a** upon irradiation at λ = 520 nm and (B) the follow-up backward *E,Z–Z,Z* isomerization of **5a** upon irradiation at λ = 625 nm (*c* = 3 mM) in DMSO-d_6. The characteristic signals of the NH groups are highlighted in blue.

Before irradiation, compounds **5a** and **5b** adopted the *Z,Z*-configuration and showed one distinctive signal for the two NH group at δ = 9.79 ppm (Figure 3A, Figure S1, Supporting Information). In the course of irradiation, this signal split into two new signals with the chemical shifts of δ = 9.96 ppm and 9.75 ppm indicating isomerization of one out of two C–C double bonds and formation of the *E,Z*-isomer. The ratio of the two isomers was determined from the signals at δ = 9.79 ($NH^{Z,Z}$) and 9.75 ($NH^{Z,E}$) and gave the values of *Z,Z*-**5a**/*Z,E*-**5a** = 24:76 and *Z,Z*-**5b**/*Z,E*-**5b** = 27:73. Further irradiation with cyan light did not result in the isomerization of the second C–C double bond, which is in accordance with our previous studies (Scheme 2).[15] The reason for this behavior is the inaccessibility of the corresponding conical intersection (CI) associated with the *E,Z*–*E,E* isomerization of bis(hemi-indigo) on the potential energy surface in the excited state.[15] The backward *E,Z*–*Z,Z* isomerization of the obtained photostationary mixture was accomplished upon irradiation with red light (λ = 625 nm) and, again, followed by the changes of the NH group signals (Figure 3B, Figure S1, Supporting Information). Thus, the split signals of the *E,Z*-isomer at δ = 9.79 ($NH^{Z,Z}$) and 9.75 ($NH^{Z,E}$) merged into one signal at δ = 9.79 ppm corresponding to the *Z,Z*-isomer. The backward *E,Z*–*Z,Z* photoisomerization proceeded almost quantitatively. It should be noted that both direct and backward photoreactions were accompanied by slight destruction as indicated by formation of small signals in the NMR spectra that cannot be assigned to the bis(hemi-indigo) scaffold.

The *Z,Z*–*E,Z* conversion of bis(hemi-indigo) derivatives **5a** and **5b** was additionally studied upon irradiation with light of different wavelengths in DMSO (Figure 4A, Table S1, Supporting Information). The conversions (%) of the *Z,Z*-isomers were calculated by the integration of the corresponding NMR proton signals for the 520-nm light (Figure 3, Figure S1, Supporting Information) as well as from the optical spectroscopy data for other irradiation wavelengths. The *Z,Z*–*E,Z* photoisomerization of both compounds **5a** and **5b** showed clear dependency on the irradiation wavelength and the most complete conversions of 86% for **5a** and 78% for **5b** were achieved upon irradiation with cyan light (λ = 505 nm). Comparison with the data obtained previously for the unsubstituted bis(hemi-indigo) **6** clearly indicated that the introduction of alkoxy

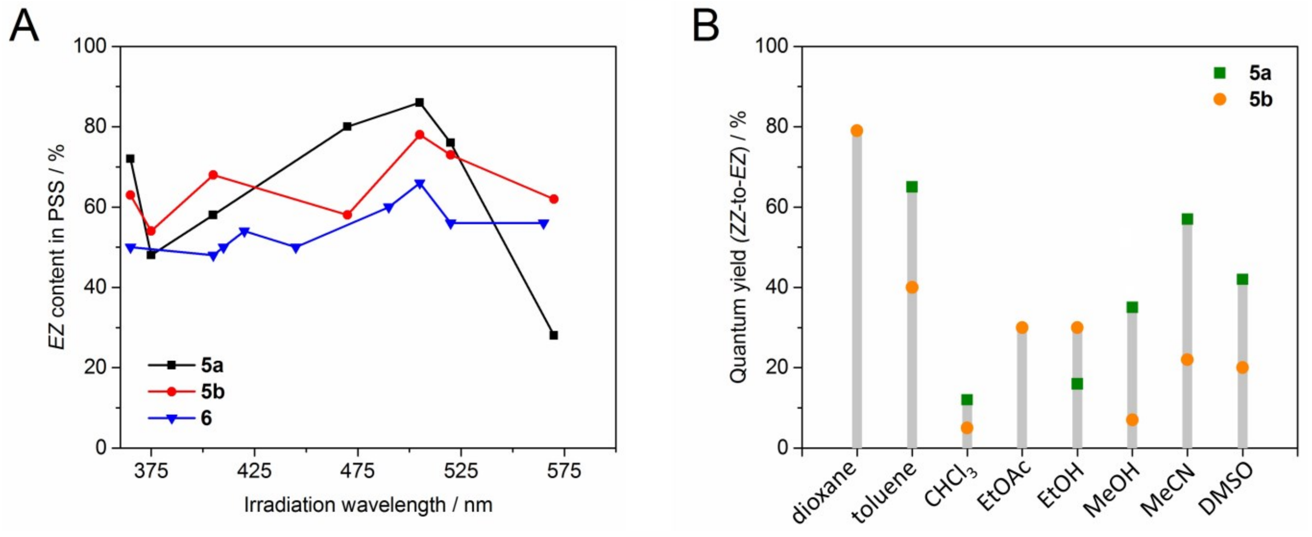


Figure 4. (A) Composition of photostationary states (conversion (%) of starting isomer) of **5a** and **5b** obtained upon irradiation at different wavelengths in DMSO (c = 30 µM, the data for compound **6** are taken from ref. 15 and plotted on the same graph for better comparison) and (B) dependence of the *Z,Z*–*E,Z* photoisomerization quantum yields of **5a** and **5b** (λ_{ex} = 505 nm) on the solvent, the solvents are arranged in order of increasing dielectric constant values from left to right, the quantum yields for **5a** in dioxane and EtOAc were not determined.

substituents in the central ring in **5a** and **5b** significantly improved the *Z,Z–E,Z* conversion at almost all applied irradiation wavelengths (Figure 4A). The maximum conversion compared to compound **6** (66% upon irradiation with the 505-nm light)[15] increased by 20% for compound **5a** and by 12% for compound **5b**.

Another important characteristic of a photochromic system is the photoisomerization quantum yield reflecting the efficiency and rate of the switching. To study the influence of the medium on the photoisomerization of bis(hemi-indigos), the *Z,Z–E,Z* photoisomerization quantum yields of **5a** and **5b** were measured in eight different solvents (Figure 4B, Table S3, Supporting Information). Thus, the photoisomerization quantum yields show significant dependence on the solvent polarity, however, the development trends for each derivative are not homogeneous. For both compounds, the highest quantum yields were achieved in non-polar solvents (toluene, dioxane). The lowest values were obtained in $CHCl_3$ that is probably caused by specific interactions with the halogen-containing solvent. The photoisomerization quantum yields of **5a** and **5b** in polar and protic solvents follow the opposite trends (Figure 4B). Thus, for the hexyloxy derivative **5a**, the quantum yield values show pronounced increase with increasing solvent polarity from EtOH to MeCN. The quantum yield of **5a** in DMSO is deviating from this trend, probably, due to the higher viscosity of DMSO, which hinders the rotation during the isomerization. At the same time, the photoisomerization quantum yields of the octyloxy derivative **5b** decrease with increasing solvent polarity from EtOAc to DMSO (Figure 4B). In most cases, bis(hemi-indigo) **5a** bearing shorter alkyl chains showed significantly higher photoisomerization quantum yields than compound **5b** containing longer alkyl chains. This effect may arise from more pronounced self-assembly of derivative **5b** resulting from the non-covalent interactions between the alkyl chains. Importantly, the introduction of the alkyloxy chains allowed to significantly increase the *Z,Z–E,Z* photoisomerization quantum yields of **5a** and **5b** (42% and 20% in DMSO, respectively) in comparison with the unsubstituted bis(hemi-indigo) **6** (5.2% in DMSO).[15]

Conclusions

To sum up, two novel bis(hemi-indigo) derivatives **5a** and **5b** bearing elongated alkyloxy chains in the central ring were synthesized and fully characterized. The photophysical and photochemical properties of these compounds were studied by optical spectroscopy and real-time NMR spectroscopy with in situ irradiation. It was found that only one C–C bond out of two underwent the photoswitching, while the second one remained photoinert. Several important characteristics such as photoisomerization quantum yields and solvatochromic behavior, were investigated and compared in eight different solvents. The presence of the alkyloxy substituents in **5a** and **5b** led to the significant increase of the conversion in the PSSs and the much higher photoisomerization quantum yields in comparison with the parent unsubstituted bis(hemi-indigo) **6**. However, the half-lives of the photoinduced isomers decreased from 4 years for compound **6** to 17–104 days for derivatives **5a**,**b**.

Experimental Section

General. 2,5-Dimethoxyterephthalaldehyde (**1**) and indoxyl-3-acetate (**4**) were obtained from commercial sources and used as received. 2,5-Dihydroxyterephthalaldehyde (**2**), 2,5-bis(hexyloxy)terephthalaldehyde (**3a**), and 2,5-bis(octyloxy)terephthalaldehyde (**3b**) were prepared and characterized according to reported procedures.[17,18]

Synthesis of bis(hemi-indigo) derivatives 5a and 5b (general procedure). A solution of indoxyl-3-acetate (**4**) (44.0 mg, 0.82 mmol) in Ar-degassed aq. NaOH (1.5 M, 4.5 mL) was heated under argon atmosphere at 100 °C for 15 min. Then the mixture was cooled down to 0 °C and the corresponding dialdehyde **3** (0.37 mmol) dissolved in Ar-degassed MeCN (5.0 mL) was added. After addition of **3** was completed, the mixture was slowly warmed up to ambient temperature and stirred under argon atmosphere for 3 days. The reaction was stopped by addition of the stoichiometric amount of Ar-degassed aq. HCl (1 M) to completely neutralize NaOH. The crude was filtered off and re-dissolved in EtOH. The solution was then passed through a paper filter to remove the by-product, indigo, after which the solvent was removed under reduced pressure.

(2*Z*,2’*Z*)-2,2’-((2,5-bis(hexyloxy)-1,4-phenylene)bis(methanylylidene))bis(indolin-3-one) (5a). Recrystallized from EtOH, then recrystallized from THF, dark violet solid (63 mg, 0.11 mmol, 30%); mp 238–240 °C (dec.). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.80 (s, 1 H, NH), 7.60 (d, ^3J = 7.7 Hz, 2 H, H-7’), 7.54 (ddd, ^3J = 8.3 Hz, ^3J = 7.1 Hz, ^4J = 1.4 Hz, 2 H, H-5’), 7.34 (s, 2 H, H-3), 7.15 (d, ^3J = 8.1 Hz, 2 H, H-4’), 6.97–6.95 (m, 4 H, H-7, H-6’), 4.20 (t, ^3J = 6.3 Hz, 4 H, H-8), 1.82–1.79 (m, 4 H, H-9), 1.54–1.48 (m, 4 H, H-10), 1.37–1.34 (m, 8 H, H-11, H-12), 0.88 (t, ^3J = 6.8 Hz, 6 H, H-13). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 186.6 (C-3’), 154.4 (C-3a’), 152.3 (C-5), 136.8 (C-5’), 135.6 (C-2’), 125.3 (C-1), 124.6 (C-7’), 120.9 (C-7a’), 120.5 (C-6’), 114.0 (C-6), 113.3 (C-4’), 104.7 (C-7), 69.5 (C-8), 31.5 (C-ali.), 29.3 (C-9), 25.9 (C-10), 22.6 (C-ali.), 14.4 (C-13). El. anal. for $C_{36}H_{40}N_2O_4$ (565), calc. C 76.57, H 7.14, N 4.96, found C 75.75, H 6.96, N 5.18. ESI-MS in MeCN, *m/z*: calcd. 564.3; found 563.3 [**5a**–H]$^-$.

(2*Z*,2’*Z*)-2,2’-((2,5-bis(octyloxy)-1,4-phenylene)bis(methanylylidene))bis(indolin-3-one) (5b). Recrystallized from EtOH, dark violet solid (156 mg, 0.25 mmol, 68%); mp 186–188 °C (dec.). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.79 (s, 1 H, NH), 7.60 (d, ^3J = 7.5 Hz, 2 H, H-7’), 7.54 (ddd, ^3J = 8.4 Hz, ^3J = 7.2 Hz, ^4J = 1.4 Hz, 2 H, H-5’), 7.34 (s, 2 H, H-3), 7.15 (d, ^3J = 8.1 Hz, 2 H, H-4’), 6.96 (s, 2 H, H-7), 6.95 (ddd, ^3J = 7.8 Hz, ^3J = 7.2 Hz, ^4J = 0.8 Hz, 2 H, H-6’), 4.20 (t, ^3J = 6.3 Hz, 4 H, H-8), 1.82-1.79 (m, 4 H, H-9), 1.51-1.48 (m, 4 H, H-10), 1.36-1.23 (m, 16 H, H-11, H-12, H-13, H-14), 0.84 (t, ^3J = 6.9 Hz, 6 H, H-15). ^{13}C NMR (125 MHz, DMSO-d_6) δ = 186.1 (C-3’), 153.9 (C-3a’), 151.7 (C-5), 136.2 (C-5’), 135.1 (C-2’), 124.7 (C-1), 124.1 (C-7’), 120.4 (C-7a’), 119.9 (C-6’), 113.5 (C-6), 112.7 (C-4’), 104.1 (C-7), 68.9 (C-8), 31.2 (C-ali.), 28.7 (C-9), 28.7 (C-ali.), 25.7 (C-10), 22.1 (C-ali.), 13.9 (C-15). El. anal. for $C_{40}H_{48}N_2O_4$ (621), calc. C 77.39, H 7.79, N 4.51, found C 77.04, H 7.74, N 4.61. ESI-MS in MeCN, *m/z*: calcd. 620.8; found 619.3 [**5b**–H]$^-$.

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Supplementary Material

Supplementary materials (SI) available: ^{1}H, ^{13}C, COSY, HSQC and HMBC NMR spectra of bis(hemi-indigo) derivatives **5a** and **5b**, details of photochemical experiments.

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