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Synthesis and optical properties of new photochromic systems based on 1,2-bis(2-methylbenzo[b]thien-3yl) hexafluorocyclopentenes and 5,7-dihydro-1H-1,2,5,7,8-pentaazas-indacen-6-one or 1,7-dihydro-5thia-1,2,7,8-tetraaza-s-indacen-6-one derivatives

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Synthesis and optical properties of new photochromic systems based on 1,2-bis(2-methylbenzo[b]thien-3-yl) hexafluorocyclopentenes and 5,7-dihydro-1H-1,2,5,7,8-pentaaza-s-indacen-6-one or 1,7-dihydro-5-thia-1,2,7,8-tetraaza-s-indacen-6-one derivatives[†]

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New photochromic molecules based on 1,2-bis(2-methylbenzo[b]thien-3-yl)hexafluorocyclopentenes and fluorescent 5,7-dihydro-1H-1,2,5,7,8-pentaaza-s-indacen-6-one or 1,7-dihydro-5-thia-1,2,7,8-tetraaza-s-indacen-6-one derivatives were synthesized via nucleophilic substitution. Photochromic properties of the compounds and composite mixtures of fluorophores and photochrome were investigated.



Keywords: photochromes; bis(benzothienyl)hexafluorocyclopentenes; regioselective Friedel–Crafts acylation; FRET; fluorescent dyes

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[†]In blessed commemoration of Professor Alessandro Del'Innocenti

1. Introduction

Dihetarylethenes appear to be a class of very promising heterocyclic compounds because of a variety of plausible applications in the fields of photonics and molecular electronics.[1] In particular, compounds of this family have successfully been used for the design of light-sensitive recording media for ultra-high-density three-dimensional optical memory systems, polymers with photo- and electrically controlled conductivity, and optical switches.[2–5]

Nowadays, the design of new dihetarylethene skeletons with different aryl moieties is becoming an active and very promising area of research.[6] A great deal attention has recently been paid to the synthesis of asymmetrical structures.[7–10] Simultaneous incorporation of different functional fragments in dihetarylethene molecules serves to adjust their spectral properties for specific tasks and their use in various areas of science and technology. For example, introduction of benzothiophene fragments provides a basic photochromic dihetarylethene platform that is of great interest for the development of the fluorescence resonance energy transfer (FRET) system.[11]

Synthesis of unsymmetrical bis(benzothienyl)perfluorocyclopentenes by mono-modification of bis(benzothienyl)perfluorocyclopentene has not, for all practical purposes, been described to date. To the best of our knowledge, only a few examples of mononitro and monoformyl substituted derivatives of bis(benzothienyl) perfluorocyclopentene have been reported.[12–14] It is worth noting that reported synthesis of the above-mentioned compounds are not regioselective, and mixtures of isomers are formed.

In the previous work, we developed a method for regioselective introduction of only one substituent into 1,2-bis(2-methylbenzo[b]thien-3-yl)hexafluorocyclopentene **1** by using Friedel–Crafts acylation.[15] Acylation of **1** with bromoacetyl chloride allows one to obtain mono- or bis(bromoacetyl)dihetarylethenes depending on acylation conditions (Scheme 1). A variety of new monosubstituted or disubstituted dihetarylethenes were prepared by heterocyclization reactions involving bromoacetyl functionality.



Scheme 1. Acylation of 1,2-bis(2-methylbenzo[b]thien-3-yl)hexafluorocyclopentene with bromoacetyl chloride.

2. Results and discussion

In this paper, we report the synthesis of new photochromic systems **5** and **6** that incorporate fluorescent moieties derived from mono-and bis(bromoacetyl)dihetarylethenes **2** and **3**. The synthesis is based upon nucleophilic substitution of the reactive bromine in mono- or bisbromoacetyl bis(benzothienyl)perfluorocyclopentenes by amide nitrogen of previously synthesized fluorescent 5,7-dihydro-1H-1,2,5,7,8-pentaaza-s-indacen-6-one **4a** or 1,7-dihydro-5-thia-1,2,7,8-tetraaza-s-indacen-6-one **4b** derivatives (Scheme 2).

All compounds **5** and **6** exhibited good photochromic properties and can be switched between their ring-open (A) and ring-closed (B) forms by alternate irradiation with ultraviolet and visible light (Scheme 3).



Scheme 2. Synthesis of new systems based on 1,2-bis(2-methylbenzo[b]thien-3-yl) hexafluorocyclopentenes and 5,7-dihydro-1H-1,2,5,7,8-pentaaza-s-indacen-6-one or 1,7-dihydro-5-thia-1,2,7,8-tetraaza-s-indacen-6-one derivatives.



Scheme 3. The photochromic interconversions of bis(benzothienyl)perfluoro-cyclopentenes.

The results of this study are presented in Table 1 and Figures 1–4. Asymmetric **5b** and symmetric **6b** dihetarylethenes containing fluorophor structural fragments exhibit photochromic transformations and photo-induced reversible fluorescence property changes (Table 1).

For example, photo-induced spectral changes for compound **6b** in toluene are shown in Figure 1.

Figure 1 shows that the initial colorless compound (Figure 1, Curve 1) is colored under UV irradiation (Figure 1, Curve 2) and is bleached under visible light (Figure 1, Curve 3). These photo-induced changes of absorption properties confirm that this compound is similar to another dihetarylethenes which experience known photochromic transformations from the open form (A) to cyclic from (B) as a result of valence photoisomerization (Scheme 3). The open form (A) of dihetarylethene possesses fluorescence (Figure 1, Curve 4). The fluorescence intensity changes in parallel with photochromic transformations. This assumes the reversible transition between the fluorescent open (A) and nonfluorescent cyclic (B) isomers. The fluorescence bands of photochromic dihetarylethenes **5b**, **6b** and fluorophore **4b** coincide. This indicates that the nature of the fluorescence bands is due to the introduction of the fluorescent fragments into the dihetarylethene structure.

Similar photo-induced changes of absorption and fluorescence spectra are shown by compound **5b** (Table 1).

The main distinction between compounds **5b** and **6b** consists in the bathochromic spectral shift of the absorption band for the cyclic form (B) of symmetrical dihetarylethene **6b** as compared with the asymmetric compound **5b**.

Compounds	$\lambda_A^{\max} (nm)^a$	$\varepsilon_{\mathrm{A}}, (\mathrm{M}^{-1}\mathrm{cm}^{-1})^{\mathrm{b}}$	$\lambda_B^{\max} (nm)^a$	$\Delta D_B^{\rm phot}/D_A^{\rm c}$	$\lambda_A^{\mathrm{flu.max}}$ (nm) ^d	$I_A^{\text{flu.max}}$ (a.u.) ^e	$I_A^{* \text{flu.max}}$ (a.u.) ^f
4a	335	5000	_	_	398	1245	1245
5a	290	29,000	542	0.04	403	20	200
	329	27,000					
6a	324	25,000	562	0.05	400	123	105
4b	335	10,000	-	_	387	715	715
5b	320	27,500	545	0.08	387	315	240
6b	324	27,500	562	0.08	382	182	99
7	322	15,000	542	0.36	-	-	-
7 + 4a	330	_	547	0.22	400	960	960
7 + 4b	320	-	547	0.20	387	390	390

Table 1. Absorption – kinetic and fluorescence characteristics of organic fluorophors and photochromic dihetarylethenes in toluene.

^aAbsorption maxima of the open-ring isomers in the UV region and absorption maxima of the closed-ring isomers in the visible region. ^bMolar extinction coefficients of the open-ring isomers at the absorption maxima in the UV region.

^cA value of a photo-induced change of optical density at the maximum of the absorption band for the closed-ring isomers that normalized the value of optical density at the maximum of open-ring isomers.

^dA wavelength of the fluorescence band maximum for open-ring isomers of dihetarylethene or fluorophor.

°Fluorescence intensity at the maximum of the fluorescence band for open-ring isomers of dihetarylethene or fluorophor.

 $^{\rm f}$ Fluorescence intensity at the maximum of the fluorescence band for open-ring isomers of dihetarylethene or fluorophor at the photostationary state after UV irradiation.



Figure 1. Absorption (1-3) and fluorescence (4-6) spectra for compound **6b** in toluene before (1, 4), after UV irradiation (2, 5) and subsequent influence of visible light (3, 6). Fluorescence is recorded during excitation by light with wavelength 330 nm.



Figure 2. Absorption (1, 2) and fluorescence (3-5) spectra for the compound **5a** in toluene before (1, 3), after subsequent UV irradiation (2, 4, 5). Fluorescence is recorded during excitation by light with wavelength 335 nm.

Similar photochromic transformations were found for symmetrical **6a** µ and asymmetrical **5a** dihetarylethenes containing fluorophor **4a** (Table 1). However, the sensitivity of these compounds to UV irradiation was lower as compared with compounds **5b** and **6b**. The symmetric derivative



Figure 3. Absorption spectra for dihetarylethene 7 in toluene before (1) and after (2) UV irradiation.



Figure 4. Absorption (1-3) and fluorescence (5) spectra of equimolar solution of the compound **7** and fluorophore **4b** in toluene before (1, 5), after UV irradiation (2, 5) and subsequent visible light irradiation (3, 5). Fluorescence is recorded during excitation by light with wavelength 335 nm.

6a as well as dihetarylethenes **5b** and **6b** shows reversible changes of fluorescence intensity during photochromic transformations (Table 1). Unlike the compound **6a**, asymmetric dihetarylethene **5a** manifests irreversible photo-induced increasing fluorescence intensity under UV irradiation (Figure 2). Thus, the position of the appearing fluorescence band practically coincides with the position of the same band of fluorophor **4a**.

The observed difference of fluorescent properties for symmetric **6a** and nonsymmetric **5a** dihetarylethenes can be explained by a photo-induced detachment of a fluorescent fragment from compound **5a** during UV excitation. The formation of fluorescent and non-fluorescent photoproducts is confirmed by a chromatography study carried out by us. The reason for similar distinction is unclear and will be studied elsewhere.

For comparison to photochromes **6a** and **6b**, we obtained the non-fluorescent analogue **7**, as shown in Scheme 4 and also studied the spectral properties of the composite mixture of **7** and **4b** (Scheme 4).

Figure 3 shows the change in optical density during photochromic transformations.

This compound as well as the above-investigated nonsymmetrical dihetarylethenes are characterized by a long-wave absorption band with a maximum at 542 nm for the photo-induced cyclic form (B) (Table 1). Unlike **6a** and **6b**, dihetarylethene **7** possesses UV sensitivity that it is possible to explain in the absence of fluorescence.



Scheme 4. Synthesis of 1,2-bis(5-(2-imidazolylacetyl)-2-methylbenzo[b]thien-3-yl)-hexafluo-rocyclopentene.

The spectral-luminescent study of equimolar solutions of dihetarylethene 7 and fluorophor (**4a** or **4b**) in toluene shows the lack of the photo-induced change of fluorescence intensity for fluorophores during photochromic transformations (Table 1, Figure 4). It testifies to practical absence of the FRET from fluorophore to the cyclic form (B) of dihetarylethene (FRET effect) despite some overlap of absorption bands of the dihetarylethelene cyclic form (B) and fluorescence bands of fluorophores.

3. Conclusion

New photochromic compounds including fluorophor fragments have been synthesized. All synthesized dihetarylethenes exhibit photochromic properties. For compounds **6a**, **5b** and **6b** containing fluorescent fragments, photo-induced reversible changes of fluorescence intensity for the open form (A) according to photochromic transformations between open (A) and cyclic (B) photoisomers were found. Dihetarylethene **5a** showing photochromic transformations undergoes allegedly irreversible photodissociation with the formation of fluorescent fragments.

4. Experimental

All reagents and solvents were used as received. Column chromatography was performed on silica gel (Merck Kieselgel 60 H). Analytical thin-layer chromatography was carried out on aluminumbacked plates coated with Merck Kieselgel 60 F254 that were visualized under UV light (at 254 or 365 nm). ¹H NMR, ¹⁹F NMR and ¹³C NMR spectra were recorded on Bruker AM-300 (300 MHz) and Bruker Avance II 300 (75 MHz) spectrometers, respectively. Chemical shifts in CDCl₃ are reported downfield from TMS (= 0) as the internal reference. ESI spectra were measured on a Kratos MS-30 instrument.

Spectral absorption and fluorescent measurements of synthesized compounds were carried out in toluene (Aldrich) with the use of the spectrophotometer "Cary 50 bio" (Varian) and the spectrofluorimeter "Ñary Eclipse" (Varian), accordingly. Working concentration of compounds in toluene made $C = 4.10^{-5}$ M. Quartz cuvette of 1 cm thickness was used for measurements.

Kinetic investigations of photocoloration and photobleaching processes were carried out with the use of the spectrophotometer "Cary 50 bio" (Varian). Working concentration of compounds in toluene made $C = 2.10^{-4}$ M. Quartz cuvette of 0.2 cm thickness was used for measurements.

During photochemical experiments, filtered irradiation from the lamp of LC-4 (Hamamatsu) was used which was passed via light filters UFS-1 (photocoloration) and JS-16 (photobleaching). Intensities of irradiation made 12 and 190 mW/cm², accordingly.

4.1. General procedure for the preparation of compounds 5a and 5b

To a solution of compounds 2 (50 mg, 0.085 mmol) and 4a (29 mg, 0.085 mmol) in DMF (0.5 ml) was added K₂CO₃ (12 mg, 0.085 mmol) and the mixture was stirred at RT for 24 h and poured

into H_2O . The precipitate was filtered, and purified on a chromatographic column (petroleum ether–EtOAc, 10:5).

(**5a**) Yield 53%, m.p. 129–131°C (EtOH). ¹H NMR (300 MHz, CDCl₃, δ, ppm): 1.52 (d, 6H, NCHCH₃CH₃, J = 7.1); 2.19 (s, 3H, CH₃); 2.53 (s, 3H, CH₃); 3.15 (s, 3H, NCH₃); 3.93 (s, 3H, OCH₃); 5.11 (quartet, 1H, NCHCH₃CH₃, J = 7.1); 5.56 (s, 2H, CH₂); 7.01–7.29 (m, 2H, ArH); 7.36–7.57 (m, 4H, Ar); 7.69–7.83 (m, 4H, Ar); 8.10 (m, 1H, ArH); 8.12 (s, 1H, imidazole). ¹³C NMR (50 MHz, CDCl₃, δ , ppm): 22.01 (CH₃); 29.69 (NCHCH₃CH₃); 32.00 (NCH₃); 46.30 (CH₂); 48.61 (NCHCH₃CH₃); 55.46 (OCH₃); 113.37; 114.00; 118.62; 122.10; 122.24; 122.29; 122.42; 123.09; 123.50; 124.31; 124.65; 124.73; 124.82; 125.47; 130.98; 131.10; 131.21; 138.27; 138.41; 144.90; 145.04; 155.17; 160.23; 191.04 (C=O). ¹⁹F NMR (280 MHz, CDCl₃, δ , ppm): –110.48 – (–111.25) (m, 4F, CF₂); 133.37 – (–133.54) (m, 2F, CF₂). HRMS (ESI) (*m*/*z*) [MH+] calc. for C₄₃H₃₃F₆N₅O₃S₂: 846.2002; found 846.1977.

(**5b**) Yield 50%, m.p. 130–134°C (EtOH).¹H NMR (300 MHz, CDCl₃, δ, ppm): 1.51 (d, 6H, NCHCH₃CH₃, J = 6.6); 2.26 (s, 3H, CH₃); 2.53 (s, 3H, CH₃); 3.96 (s, 3H, OCH₃); 4.00 (s, 3H, OCH₃); 5.11 (quartet, 1H, NCHCH₃CH₃, J = 6.6); 5.65 (s, 2H, CH₂); 7.01–7.29 (m, 1H, ArH); 7.36–7.57 (m, 4H, Ar); 7.69–7.83 (m, 4H, Ar); 7.92 (m, 1H, ArH); 8.04 (s, 1H, thiazole). ¹³C NMR (50 MHz, CDCl₃, δ, ppm): 21.97 (CH₃); 29.72 (NCHCH₃CH₃); 48.12 (CH₂); 48.95 (NCHCH₃CH₃); 56.10 (OCH₃); 56.14 (OCH₃); 110.90; 111.82; 112.20; 113.37; 114.00; 118.62; 122.10; 122.24; 122.29; 122.42; 123.09; 123.50; 124.31; 124.65; 124.73; 124.82; 125.47; 130.98; 131.10; 131.21; 138.27; 138.41; 144.90; 145.04; 155.17; 160.23; 191.05 (C=O). ¹⁹F NMR (280 MHz, CDCl₃, δ, ppm): -110.48 - (-111.25) (m, 4F, CF₂); 133.37 – (-133.54) (m, 2F, CF₂). HRMS (ESI) (*m*/*z*) [MH+] calc. for C₄₃H₃₂F₆N₄O₄S₃: 879.1563; found 876.1558.

4.2. General procedure for the preparation of compounds 6a, 6b and 7

To a solution of compounds **3** (50 mg, 0.07 mmol) and **4a** (47 mg, 0.014 mmol) in DMF (0.5 ml) was added K_2CO_3 (10 mg, 0.07 mmol) and the mixture was stirred at RT for 24 h and poured into H₂O. The precipitate was filtered, and purified on a chromatographic column (petroleum ether–EtOAc, 1:1).

(**6a**) Yield 40%, m.p. 151–155°C (EtOH). ¹H NMR (300 MHz, CDCl₃, δ , ppm): 1.52 (d, 12H, NCHCH₃CH₃, J = 7.1); 2.20 (s, 6H, CH₃); 3.16 (s, 6H, NCH₃); 3.94 (s, 6H, OCH₃); 5.11 (quartet, 2H, NCHCH₃CH₃, J = 7.1); 5.55 (s; 4H; CH₂); 7.00–7.28 (m, 2H, ArH); 7.35–7.58 (m, 4H, Ar); 7.69–7.83 (m; 4H; Ar); 8.10 (m, 2H, ArH); 8.15 (s, 2H, imidazole). ¹³C NMR (50 MHz, CDCl₃, δ , ppm): 22.02 (CH₃); 29.70 (NCHCH₃CH₃); 32.02 (NCH₃); 46.35 (CH₂); 48.62 (NCHCH₃CH₃); 55.45 (OCH₃); 113.39; 114.00; 118.65; 122.10; 122.25; 122.30; 122.45; 123.09; 123.50; 124.32; 124.65; 124.74; 124.83; 125.47; 130.98; 131.15; 131.22; 138.28; 138.42; 144.90; 145.05; 155.18; 160.23; 191.05 (C=O). ¹⁹F NMR (280 MHz, CDCl₃, δ , ppm): –110.48 – (–111.25) (m, 4F, CF₂); 133.37 – (–133.54) (m, 2F, CF₂). HRMS (ESI) (*m*/*z*) [MH+] calc. for C₆₂H₅₀F₆N₁₀O₆S₂: 1210.3003; found 1210.3000.

(**6b**) Yield 45%, m.p. 150–154°C (EtOH). ¹H NMR (300 MHz, CDCl₃, δ , ppm): 1.51 (d, 12H, NCHCH₃CH₃, J = 6.6); 2.28 (s, 6H, CH₃); 3.97 (s, 6H, OCH₃); 4.01 (s, 6H, OCH₃); 5.11 (quartet, 2H, NCHCH₃CH₃, J = 6.6); 5.65 (s, 4H, CH₂); 7.01–7.29 (m, 2H, ArH); 7.36–7.57 (m, 4H, Ar); 7.69–7.83 (m, 4H, Ar); 7.92 (m, 2H, ArH); 8.04 (s, 2H, thiazole). ¹³C NMR (50 MHz, CDCl₃, δ , ppm): 21.97 (CH₃); 29.73 (NCHCH₃CH₃); 48.15 (CH₂); 48.96 (NCHCH₃CH₃); 56.10 (OCH₃); 56.14 (OCH₃); 110.91; 111.83; 112.25; 113.39; 114.00; 118.62; 122.10; 122.24; 122.29; 122.42; 123.09; 123.50; 124.31; 124.65; 124.73; 124.82; 125.47; 130.99; 131.10; 131.23; 138.27; 138.41; 144.90; 145.04; 155.17; 160.23; 191.05 (C=O). ¹⁹F NMR (280 MHz, CDCl₃, δ , ppm): –110.48 – (–111.25) (m, 4F, CF₂); 133.37 – (–133.54) (m, 2F, CF₂). HRMS (ESI) (*m*/*z*) [MH+] calc. for C₆₃H₅₀F₆N₈O₈S₄: 1289.2611; found 1289.2607.

(7) Yield 50%, m.p. 140–144°C (EtOH).¹H NMR (300 MHz, CDCl₃, δ , ppm): 2.29 (s, 6H, CH₃); 5.36 (s, 4H, CH₂); 6.90 (m, 2H, imidazole); 7.12 (m, 2H, imidazole); 7.30–7.45 (m, 4H, Ar); 7.60 (m, 2H, imidazole); 7.92 (m, 2H, ArH). ¹³C NMR (50 MHz, CDCl₃, δ , ppm): 21.95 (CH₃); 48.10 (CH₂); 120.15; 120.30; 126.60; 129.60; 131.10; 134. 50; 138.27; 138.41; 150.17; 190.05 (C=O). ¹⁹F NMR (280 MHz, CDCl₃, δ , ppm): –110.49 – (–111.26) (m, 4F, CF₂); 133.36 – (–133.55) (m, 2F, CF₂). HRMS (ESI) (*m*/*z*) [MH+] calc. for C₃₃H₂₂F₆N₄O₂S₂: 685.6778; found 685.6770.

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