PERKIN 2

Synthesis and photochromic properties of ferrocenyl substituted benzo- and dibenzochromenes

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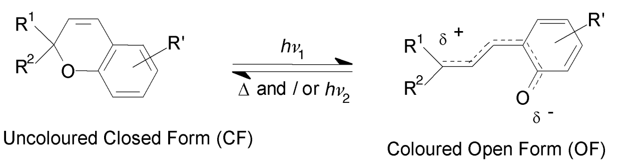
The synthesis, photochromic behaviour, photodegradation parameters and fluorescence spectra of a range of benzo- and dibenzochromenes substituted by a ferrocenyl group in the 2-position have been investigated. The ferrocenyl group leads to two absorption bands in the visible spectrum of the photomerocyanine species, in contrast to the single band observed with corresponding phenyl substituted derivatives. It also increases the thermal rate of bleaching of the photomerocyanine.

Introduction

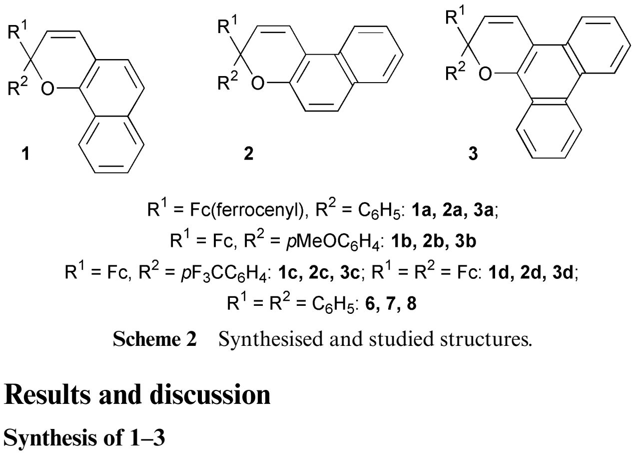
Under UV irradiation, 2*H*-chromenes (elsewhere called 2*H*-benzopyrans) undergo cleavage of a C–O bond leading to an open form,[1] which is often referred as the photomerocyanine form.[2] On opening, the absorption range of this class of compound is shifted towards longer wavelengths, from the UV to the visible region. The back closure of the photomerocyanine to the starting 2*H*-chromenes is generally a thermal process but one that can also be induced by irradiation in the visible range (Scheme 1).



Scheme 1 General photochromic equilibrium.

The photochromic behaviour of such compounds is characterised by several factors: the wavelength at which maximum absorption occurs (λ_{max}) for the OF in the visible region, the bleaching kinetic constant (k_Δ) and the colorability A_∞ (absorbance at λ_{max} observed at the photostationary equilibrium between OF and CF).

The photochromic properties of the 2*H*-chromenes are greatly influenced by the nature of the substituents R^1 and R^2 located in the 2-position[3] and also by the type of the annelation (5–6 or 7–8) on the aromatic moiety. Previous works[4,5] have shown that, when a ferrocenyl group replaces a phenyl group in the 2-position, the photochromic properties are modified. Two λ_{max} values are observed and the appearance of the second λ_{max} value results in an extended absorption range in the visible region. Furthermore, the back closure process is accelerated. In this work, we describe the synthesis and the photochromic properties of different benzo- and dibenzochromenes substituted by one ferrocenyl (Fc) group and one phenyl or two ferrocenyl groups in the 2-position (Scheme 2).



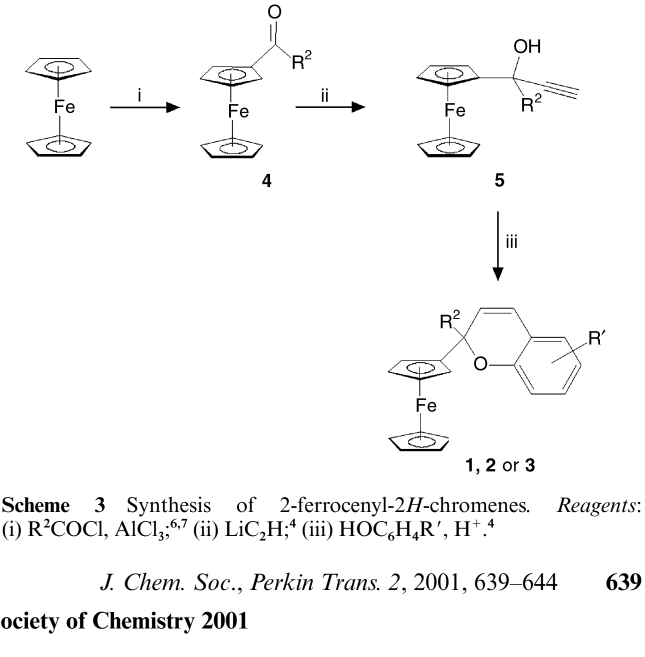
R^1 = Fc(ferrocenyl), R^2 = C_6H_5: **1a, 2a, 3a**;
R^1 = Fc, R^2 = *p*MeOC_6H_4: **1b, 2b, 3b**
R^1 = Fc, R^2 = *p*$F_3CC_6H_4$: **1c, 2c, 3c**; R^1 = R^2 = Fc: **1d, 2d, 3d**;
R^1 = R^2 = C_6H_5: **6, 7, 8**

Scheme 2 Synthesised and studied structures.

Results and discussion

Synthesis of 1–3

Compounds **1**–**3** are synthesised in three steps from ferrocene (Scheme 3).



Scheme 3 Synthesis of 2-ferrocenyl-2*H*-chromenes. *Reagents*: (i) R^2COCl, $AlCl_3$;[6,7] (ii) LiC_2H;[4] (iii) HOC_6H_4R', H^+.[4]

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Table 1 Yields of **1**, **2**, **3**, **4** and **5**

R^2	**4** (Yield (%))	**5** (Yield (%))	**1** (Yield (%))	**2** (Yield (%))	**3** (Yield (%))
C_6H_5	**4a** (68)	**5a** (65)	**1a** (25)	**2a** (75)	**3a** (53)
pMeOC_6H_4	**4b** (55)	**5b** (23)	**1b** (37)	**2b** (75)	**3b** (18)
$p$$F_3CC_6H_4$	**4c** (39)	**5c** (26)	**1c** (44)	**2c** (82)	**3c** (32)
Fc	**4d** (20)	**5d** (52)	**1d** (17)	**2d** (16)	**3d** (26)

Table 2 Visible absorption maxima (λ_{max}/nm) of the photomerocyanine species derived from chromenes **1**–**3** and **6**–**8**

		1a	**2a**	**3a**	**1b**	**2b**	**3b**	**1c**	**2c**	**3c**	**1d**	**2d**	**3d**	**6**	**7**	**8**
Tol.	(1)[a]	467	450	447	464	438	440	482	457	454	466	[d]	460	472	427	425
	(2)[b]	600	602	600	604	604	591	607	608	583	606		601			
CH_3CN	(1)	450	452	444	459	453	440	482	444	450	457	431	462	471	430	415
	(2)	602	580	585	593	603	581	607	604	584	617		606			
EtOH	(1)	469	413	432	496	440	442	496	420	446	[c]	425	455	490	429	424
	(2)	618	622	590	617	625	596	600	642	587			598			

[a] First absorption band. [b] Second absorption band. [c] Not soluble. [d] Not photochromic.

In order to study the effect of the type of annelation, we used, in the third step, three different phenols: 1-naphthol, 2-naphthol and 9-phenanthrol which lead respectively to compounds **1**, **2** and **3**. Our results are reported in the Table 1.

Ketone **4d** was prepared starting from ferrocenylmethanoic acid which was reacted with PCl_5 and then with ferrocene in presence of $AlCl_3$.

The reaction between the propargylic† alcohols and the phenolic derivatives is usually catalysed by protic acids. However the use of such acids also induces a Meyer–Schuster rearrangement of the propargylic alcohol into a conjugated ketone and thus decreases the yield of the pyran derivative. As it is known that a ferrocenyl group is able to stabilise a carbocation in an α-position on the side chain of a cyclopentadienyl framework, we thought that the acidity of the phenolic derivatives could be sufficient to catalyse the reaction. Indeed, the yields given in Table 1 were observed without addition of an extra acid and are better than the ones we obtained in the presence of toluene-*p*-sulfonic acid.

Spectrokinetic properties of 1–3

The studies were performed under continuous irradiation with a xenon lamp (150 W).[8] A UV–visible spectrophotometer was used for determination of λ_{max} in the OF and the decrease in absorbance when the irradiation is stopped. From these results, the bleaching kinetic constants k_Δ were calculated using PC Software (Grafit 3.0). The studies were realised in three different solvents: toluene (Tol.), acetonitrile (CH_3CN) and ethanol (EtOH).

In order to quantify the effect of the ferrocenyl substituent, the photochromic properties were compared with those of the three 2,2-diphenyl benzannelated chromenes **6**, **7** and **8** (Scheme 2).[9,10] The results concerning the visible spectra are reported in Table 2.

The most important phenomenon evidenced in Table 2 is the presence of two absorption bands for compounds **1**–**3** substituted by a ferrocenyl group while only one is observed for the reference compounds **6**, **7** and **8** (Fig. 1). The appearance of two absorption maxima may be explained by manifestation of two π-electron conjugated chains including phenyl or ferrocenyl substituents.

The presence of these two absorption bands results in an extended absorption range (400–600 nm), which could be obtained, before, only by mixing two photochromic compounds belonging to different families (chromene and spironaphthoxazine for instance).

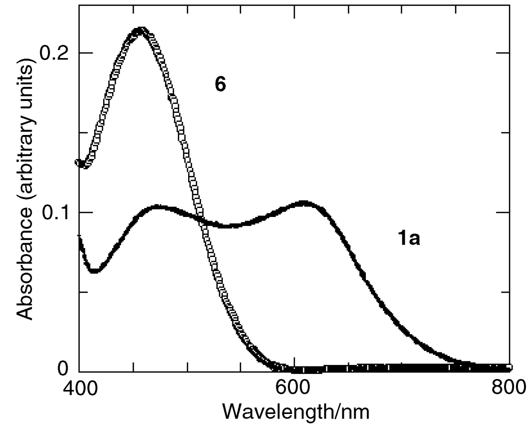

Fig. 1 Visible absorption spectra of compounds **6** and **1a**.

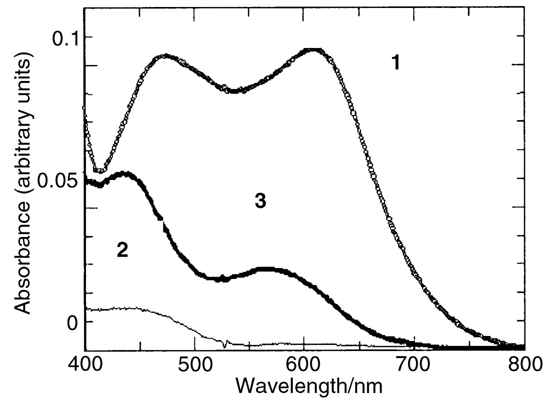

Fig. 2 Absorbance for the **1**, **2** and **3** series (at the same concentration).

It can be seen that the absorbances for compounds **1**–**3** are lower than those for **6**–**8**. However it must be noted that the sum of two integrated curves for these compounds bearing a ferrocenyl group is higher than those for **6**–**8**.

Within the **1**–**3** series the optical density depends on the type of annelation (Fig. 2) and is maximum for 7–8 annelated substrates. It can also be noted that for the long wavelength absorption band the relative absorbance increases greatly from the 5–6 annelated substrates to the 7–8 ones.

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† The IUPAC name for propargyl is prop-2-ynyl.

Table 3 Thermal bleaching constants k_Δ for different absorption wavelengths (T = 25 °C)

	Toluene		Acetonitrile		Ethanol	
	$\lambda_{k\Delta}$/nm	k_Δ/s^{-1}	$\lambda_{k\Delta}$/nm	k_Δ/s^{-1}	$\lambda_{k\Delta}$/nm	k_Δ/s^{-1}
1a	467	2.0×10^{-3} 1.0×10^{-4}	450	1.2×10^{-2}	396 469	4.0×10^{-4} 1.9×10^{-3}
2a	450	2.1×10^{-1} 3.0×10^{-3}	452	1.3×10^{-1} 1.0×10^{-4}	413	4.0×10^{-4}
3a	447	4.0×10^{-2}	444	2.2×10^{-2} 9.0×10^{-4}	432	6.1×10^{-3} 6.0×10^{-4}
1b	482	4.8×10^{-3}	482 607	3.7×10^{-2} 4.0×10^{-2} 6.0×10^{-4}	403 496	5.0×10^{-4} 1.8×10^{-2}
2b	457	9.6×10^{-2} 6.1×10^{-3}	444	2.0×10^{-1} 1.8×10^{-3}	420	5.0×10^{-4}
3b	454	1.4×10^{-2}	450	4.0×10^{-2} 1.0×10^{-3}	446	3.3×10^{-2} 1.7×10^{-3}
1c	464	1.7×10^{-3}	459	9.1×10^{-3}	410 496	6.0×10^{-4} 3.3×10^{-3}
2c	438	1.5×10^{-1} 6.3×10^{-3}	453	2.2×10^{-1} 6.0×10^{-4}	440	2.4×10^{-2} 2.4×10^{-3}
3c	440	6.3×10^{-3}	440	3.8×10	442	1.4×10^{-2} 2.7×10^{-3}
1d	466	1.7×10^{-2} 5.0×10^{-4}	457	2.6×10^{-2} 1.5×10^{-3}		Not soluble
2d	Not photochromic for determination of k_Δ					
3d	460	3.7×10^{-2}	462	1.1×10^{-1} 2.0×10^{-4}	455	3.6×10^{-2} 6.0×10^{-4}
6	472	5.0×10^{-4}	471	4.0×10^{-4}	490	5.0×10^{-4}
7	432	1.0×10^{-1} 10^{-1}	430	7.1×10^{-2} 2.0×10^{-4}	429	2.8×10^{-2} 4.0×10^{-4}
8	425	2.6×10^{-3}	415	3.9×10^{-3}	424	1.9×10^{-3}

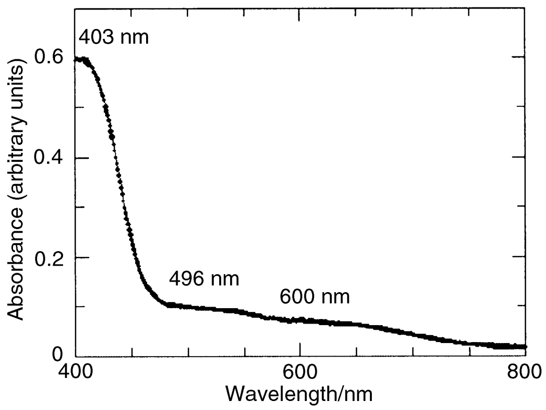

Fig. 3 UV–visible spectrum of compound **1c** in ethanol.

Solvent effects on λ_{max} depend on the annelation type and also on the substituent. When considering the first absorption band (1), in most cases, on going from the **1** to the **3** series, within a group (**a**, **b** or **c**) and for a given solvent, a hypsochromic effect is observed except for the three series in ethanol. However in all cases a larger absorption wavelength is observed for the 7–8 annelation framework, and a shorter one for the 5–6 annelated series.

We can also observe, for the first absorption band, on going from acetonitrile to ethanol, a bathochromic effect for the **1** series ($\Delta\lambda_{max}$: **1a**/**1b**/**1c**: 19/37/14), a hypsochromic effect for the **2** series ($\Delta\lambda_{max}$: **2a**/**2b**/**2c**: −39/−13/−20), and a very small hypsochromic effect in the **3** series ($\Delta\lambda_{max}$: **3a**/**3b**/**3c**: −12/2/−4).

In going from toluene to acetonitrile, the effects are not so clear. In the **1** series, a hypsochromic effect is observed for **1a** and **1b**. No significative effects are observed for the **3** series while small bathochromic and hypsochromic effects can be seen in the **2** series.

When considering the second long wavelength absorption band (2) (≈600 nm), the annelation type and the nature of the substituent do not have a marked influence while a small bathochromic effect can be observed in most cases when toluene or acetonitrile are replaced by ethanol.

On replacing a phenyl substituent by a ferrocenyl (comparing **1a**, **2a**, **3a** with **1d**, **2d**, **3d**), we observed a bathochromic effect on the two absorption bands, except for **2d** (no photochromic properties) and **1d** (not soluble in EtOH).

It must be noted that a third absorption band around 400 nm is observed in ethanol for the **1** series (**1a**: 396 nm, **1b**: 410 nm, and **1c**: 403 nm) (Fig. 3) with a very large absorbance compared to the two other λ_{max} values. The thermal bleaching constants k_Δ measured at each λ_{max} wavelength at 25 °C, are given in Table 3.

The k_Δ values of ferrocenyl compounds (**1a**, **2a**, **3a**) are increased by comparison with those of the reference compounds **6**, **7** and **8**. Moreover the k_Δ values are a function of the type of annelation and increase in the order: series **2** > series **3** > series **1**.

When substituents are introduced in the *para* position of the phenyl substituents (**1b**, **2b**, **3b** and **1c**, **2c**, **3c**), the k_Δ values are increased. The same effect is also observed when two ferrocenyl groups are in the 2-position. It must be noted that these k_Δ values are nearly the same at the two λ_{max} wavelengths (verified here for **1b** in acetonitrile).

In most cases, two bleaching kinetic constants can be measured. This reflects the fact that after opening of the starting compounds, two or more stereoisomers of the OF are formed. These forms differ by the relative stereochemistry of the polyenic system that is formed.

It can also be seen that the fastest first bleaching kinetic constants are observed for the **2** series (**2a**, **2b** and **2c**) when they are measured in toluene and acetonitrile while the slowest ones are observed in the **1** series whatever the nature of the solvent. This reflects the influence of the annelation type on the k_Δ value, which is related to the steric hindrance in the photomerocyanine form. It must also be noted that the k_Δ values measured for the λ_{max} wavelength around 400 nm for **1a**, **1b** and **1c** in ethanol are very small. This indicates strong stabilisation by the solvent of particular photomerocyanines forms. This has been already noted in another series of 2-ferrocenyl-2-methyl-

Table 4 Fluorescence wavelength maxima of photomerocyanines in toluene

	Chromene					
	1a	**2a**	**3a**	**6**	**7**	**8**
Excitation wavelength (λ_{exc}/nm)	300	300	300	300, 550	480	300, 480
Fluorescence (λ_{max}/nm)	485	[a]	520	640	535	530

[a] Fast thermal bleaching.

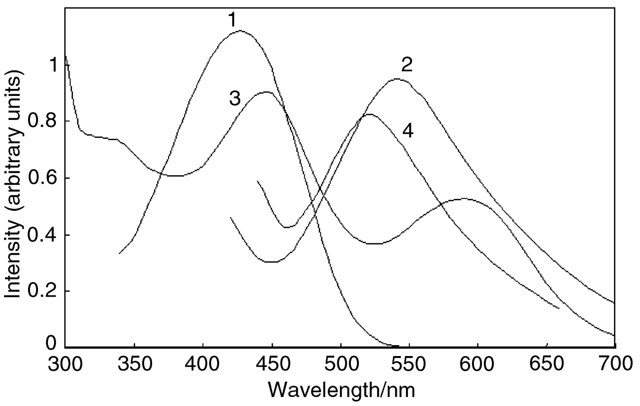

Fig. 4 Absorption (1, 3) and fluorescence (2, 4) spectra of the photoinduced form of chromenes **8** (1, 2) and **3a** (3, 4) in toluene.

2*H*-benzochromenes in which permanent photomerocyanines are observed.[11]

Fluorescence properties of benzochromenes

The diphenyl substituted benzochromenes exhibit fluorescence properties in their initial and photoinduced forms (Fig. 4).

The strong effect of the substituent is exhibited in fluorescence characteristics of investigated naphthopyrans (Table 4). These data show that the positions of the maxima in absorption and fluorescence spectra depend on the molecular structure. We suppose that the observed difference is due to the change of the conjugation chain. It is interesting to note that the fluorescence characteristics are sharply changed after replacement of the phenyl substituent by the ferrocenyl fragment. For the diphenyl substituted chromenes absorption and luminescence spectra with a single maximum are observed (Fig. 4, curves 1 and 2). The replacement of one of the two phenyl groups by a ferrocenyl one gives a photoinduced absorption spectrum with two maxima (Fig. 4, curve 3) but a fluorescence spectrum with only a single band (Fig. 4, curve 4) as is also the case for the diphenyl-containing compounds. The presence of only one emission band in the fluorescence spectrum is surprising and suggests that the photomerocyanines are a mixture of two different species, one with λ_{max} at 450 nm and the other with λ_{max} at about 600 nm. The observed fluorescence originates from the first species as it is very unusual for a compound to fluoresce at a shorter wavelength than its absorption wavelength. This could be an example of allopolar isomerism.[12] The keto chromophoric system is in conjugation with the ferrocenyl group in one of the species (λ_{max}: 600 nm) and with the phenyl group in the other one (λ_{max}: 450 nm).

Photodegradation

The effect of the introduction of a ferrocenyl substituent instead of a phenyl group is exhibited by the difference of photodegradation stability for the investigated compounds (Fig. 5 and Table 5).

As a rule, changing the phenyl groups for ferrocenyl ones leads to an increased photostability of the benzochromenes. This effect for the ferrocenyl-containing compounds is two or three times as large as that for the diphenyl ones. This is in concordance with the effect of ferrocene on photostabilization of a spiropyran solution.[13] The effect was explained by the influence of the metal on intramolecular deactivation of reactive excited states of photochromic molecules.

Table 5 Photodegradation stability for the investigated compounds in toluene

	Chromene						
	1a	**2a**	**3a**	**3d**	**6**	**7**	**8**
$T_{0.5}^{deg}$/min[a]	110	105	150	>240	35	45	>240

[a] $T_{0.5}^{deg}$/min: irradiation time after which the absorbance is divided by two.

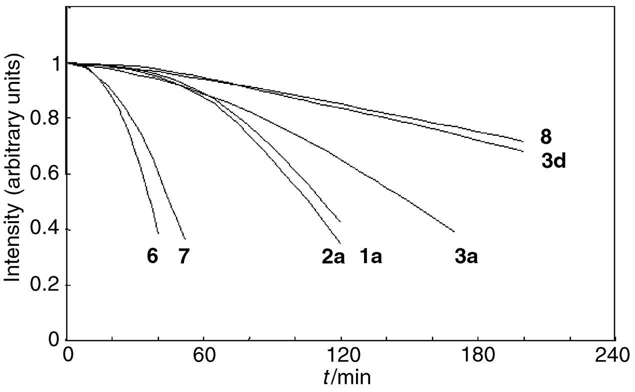

Fig. 5 Kinetics curves for photodegradation of studied chromenes

The one exception to the behaviour of these chromenes is compound **8**, which is characterised by a high stability against irreversible photochemical and thermal transformation. This effect may be associated with the greater rigidity in the structure of the photoinduced form as compared with other diphenyl substituted benzochromenes.

Conclusion

In this work, we have synthesised ten new 2-ferrocenyl-2*H*-chromenes. In most cases, these compounds are prepared in three steps in good yields.

Studies of the photochromic properties have shown original spectrokinetic properties for these 2-ferrocenyl-2*H*-chromenes. These compounds are very interesting compounds because of the extension of the absorption area, the increase of the closure back process (k_Δ), the strong stabilisation by ethanol of particular photomerocyanine forms for 7–8 annelated structures and also adequate resistance to photodegradation.

Experimental

Solvents were purified by distillation over P_2O_5 (CH_2Cl_2) or C_6H_5MgBr (THF). Column chromatography (CC): silica gel 60 Merck (0.063–0.200 mm). Melting points: Electrothermal 9100 apparatus with capillary tubes. IR spectra in $CHCl_3$: Perkin-Elmer 297 spectrophotometer. ^1H- and ^{13}C-NMR spectra in $CDCl_3$: Bruker-AC-250 spectrometer; chemical shifts δ in ppm downfield from $SiMe_4$, coupling constants *J* in Hz; for trifluoromethylated compounds the C of CF_3 was not detected because of its long relaxation time. UV and spectrokinetic parameters: Beckman DU-7500 spectrophotometer, irradiation with Oriel 150 W high pressure xenon lamp, and guide to the thermostated quartz cell by an optical fiber, the photochromic solutions ($c = 5 \times 10^{-4}$ mol L^{-1}) were prepared in anhydrous toluene (SDS France) and were studied at 25 °C.

Fluorescence spectra were measured with a SHIMADZU KA-5000 spectrofluorometer. Thoroughly purified toluene, ethanol and other solvents were used in luminescence investigations. The concentration of photochromic compounds in solution was usually $c = 2 \times 10^{-4}$ M.

Comparative investigation of the efficiency of the benzochromenes' photodegradation was carried out in toluene, under aerobic conditions (in order to simulate the usual conditions of photochromic compounds' utilization), using monochromatic irradiation ($\lambda = 365$ nm) selected by filters from light of a mercury lamp with a power of 250 W.

Ferrocenyl ketones 4

Ferrocenyl ketones **4** were prepared according to ref. 6 and 7.

Compound 4a: ferrocenyl phenyl ketone. 68%; mp 105 °C (lit.,[6] 107 °C); IR: ν 1600 cm^{-1}; ^1H-NMR (250 MHz): 4.2 (5H, s), 4.5 (2H, t, *J* 1.8), 4.8 (2H, t, *J* 1.8), 7.4 (3H, m), 7.8 (2H, dd, *J* 6.6 and 2.8); ^{13}C-NMR (62.8 MHz): 70.2 (CH), 72.1 (CH), 72.9 (CH), 79.0 (C), 127.3 (CH), 128.1 (CH), 133.6 (CH), 140.1 (C), 198.2 (C).

Compound 4b: ferrocenyl *p*-methoxyphenyl ketone. 55%; mp 85 °C (lit.,[6] 83 °C); IR: ν 2900, 1600 cm^{-1}; ^1H-NMR (250 MHz): 3.7 (3H, s), 4.1 (5H, s), 4.4 (2H, m), 4.8 (2H, m), 6.9 (2H, d, *J* 7.5), 7.8 (2H, d, *J* 7.5); ^{13}C-NMR (62.8 MHz): 55.4 (CH_3), 70.1 (CH), 71.5 (CH), 72.1 (CH), 78.7 (C), 113.4 (CH), 130.4 (CH), 132.3 (C), 162.4 (C), 197.3 (C).

Compound 4c: ferrocenyl *p*-trifluoromethylphenyl ketone. 39%; mp 113 °C (decomp.); IR: ν 2900, 1600 cm^{-1}; ^1H-NMR (250 MHz): 4.15 (5H, s), 4.6 (2H, m), 4.8 (2H, m), 7.9 (2H, d, *J* 8.2), 8.2 (2H, d, *J* 8.2); ^{13}C-NMR (62.8 MHz): 69.7 (CH), 70.9 (CH), 71.8 (CH), 79.0 (C), 127.3 (CH), 128.1 (CH), 133.2 (C), 146.4 (C), 198.8 (C).

Compound 4d: diferrocenyl ketone. 55%; mp 208 °C (lit.,[5] 204 °C); IR: ν 1610 cm^{-1}; ^1H-NMR (250 MHz): 4.15 (10H, s), 4.45 (4H, m), 4.95 (4H, m); ^{13}C-NMR (62.8 MHz): 70.0 (CH), 70.6 (CH), 71.5 (CH), 81.0 (C), 199.2 (C).

Ferrocenylpropynols 5

To a solution of lithium acetylide (7.5 mmol) in 100 mL of anhydrous THF, cooled to 0 °C (ice bath), a solution of **4** (1.5 mmol) in 100 mL of anhydrous THF was slowly added. The mixture was stirred for 2 h 30 min then hydrolysed with saturated aqueous NH_4Cl. The organic phase was filtered on Celite, washed with H_2O, dried with $MgSO_4$ and evaporated. The residue was rapidly chromatographed (silica gel, hexane–ether: 75 : 15).

Compound 5a: 1-ferrocenyl-1-phenylprop-2-ynol. 65%; mp 56 °C; IR: ν 3560, 3300, 2100 cm^{-1}; ^1H-NMR (250 MHz): 2.7 (1H, s), 3.1 (1H, s), 4.05 (1H, m), 4.15 (1H, m), 4.2 (5H, s), 7.2 (3H, m), 7.5 (2H, d, *J* 7.9); ^{13}C-NMR (62.8 MHz): 65.3 (CH), 68.5(CH), 68.7 (CH), 69.3 (CH), 71.4 (C), 71.4 (C), 73.3 (CH), 87.0 (C), 96.8 (C), 125.7 (CH), 127.9 (CH), 128.3 (CH), 143.9 (C).

Compound 5b: 1-ferrocenyl-1-(*p*-methoxyphenyl)prop-2-ynol. 23%; mp 67 °C; IR: ν 3340, 3300 cm^{-1}; ^1H-NMR (250 MHz): 2.7 (1H, s), 3.1 (1H, s), 3.7 (3H, s), 4.05 (1H, m), 4.15 (1H, m), 4.2 (5H, s), 4.2 (1H, m), 4.3 (1H, m), 6.7 (2H, d, *J* 8.7), 7.4 (2H, d, *J* 8.7); ^{13}C-NMR (62.8 MHz): 55.3 (CH_3), 65.1 (CH), 68.3 (CH), 68.5 (CH), 69.1 (CH), 70.9 (C), 73.0 (CH), 87.0 (C), 96.6 (C), 113.4 (CH), 126.9 (CH), 136.2 (C), 159.1 (C).

Compound 5c: 1-ferrocenyl-1-(*p*-trifluoromethylphenyl)prop-2-ynol. 26%; mp 96 °C; IR: ν 3350, 3300 cm^{-1}; ^1H-NMR (250 MHz): 2.8 (1H, s), 3.2 (1H, s), 4.05 (1H, m), 4.15 (2H, m), 4.4 (1H, m), 7.4 (2H, d, *J* 8.3), 7.6 (2H, d, *J* 8,3); ^{13}C-NMR (62.8 MHz): 65.0 (CH), 68.8 (CH), 69.1 (CH), 69.3 (CH), 71.7 (C), 73.8 (CH), 87.0 (C), 96.0 (C), 125.3 (CH), 125.7 (CH), 126.0 (CH), 128.0 (C), 147.0 (C).

Compound 5d: 1,1-diferrocenylprop-2-ynol. 52%; mp 127 °C; IR: ν 3540, 3300 cm^{-1}; ^1H-NMR (250 MHz): 2.7 (1H, s), 3.1 (1H, s), 4.1 (4H, m), 4.2 (10H, s), 4.3 (4H, m); ^{13}C-NMR (62.8 MHz): 65.6 (CH), 67.4 (CH), 67.9 (CH), 68.1 (CH), 69.0 (C), 69.1 (CH), 71.6 (CH), 81.0 (C), 94.9 (C).

Ferrocenyl-2*H*-chromenes 1, 2 and 3

A solution of the appropriate alcohol (1 mmol) in a minimum amount of CH_2Cl_2 was added to a solution of the phenol (4 mmol) in a minimum amount of CH_2Cl_2. The mixture was stirred until total consumption of propargyl alcohol. The organic phase was washed with H_2O, dried and reduced under vacuum. The residue was chromatographed (silica gel, 100% hexane).

Compound 1a: 2-ferrocenyl-2-phenyl-2*H*-benzo[*h*]chromene. 25%; mp 131 °C (Found: C 78.7, H 5.0. Calc. for $C_{29}H_{22}OFe$: C 78.74, H 5.01%); UV: λ 347, 364 nm; ^1H-NMR (250 MHz): 4.0 (5H, s), 4.1 (3H, m), 4.4 (1H, m), 6.2 (1H, d, *J* 8.8), 6.6 (1H, d, *J* 8.8), 7.1 (4H, m), 7.3 (1H, m), 7.5 (4H, m), 7.7 (1H, d, *J* 1.1), 7.8 (1H, d, *J* 1.1); ^{13}C-NMR (62.8 MHz): 66.0 (CH), 66.5 (CH), 68.0 (CH), 68.1(CH), 69.1 (CH), 81.0 (C), 96.0 (C), 116.0 (C), 120.2 (CH), 122.0 (CH), 122.4 (CH), 124.2 (C), 124.8 (CH), 125.6 (CH), 125.7 (CH), 126.4 (CH), 126.7 (CH), 127.3 (CH), 127.9 (CH), 128.0 (CH), 134.8 (C), 139.0 (C), 146.0 (C).

Compound 1b: 2-ferrocenyl-2-(*p*-methoxyphenyl)-2*H*-benzo-[*h*]chromene. (37%); mp 72 °C (Found: C 76.0, H 6.6. Calc. for $C_{30}H_{24}O_2Fe$: C 76.30, H 6.35%); UV: λ 328, 354 nm; ^1H-NMR (250 MHz): 3.6 (3H, s), 3.95 (5H, s), 4.05 (3H, m), 4.4 (1H, m), 6.2 (1H, d, *J* 9.8), 6.5 (1H, d, *J* 9.8), 6.6 (1H, d, *J* 8.9), 7.1 (2H, d, *J* 8.9), 7.3 (5H, m), 7.6 (1H, d, *J* 8.5), 8.3 (1H, d, *J* 8.5); ^{13}C-NMR (62.8 MHz): 55.3 (CH_3), 66.1 (CH), 66.4 (CH), 68.0 (CH), 68.1 (CH), 69.2 (CH), 80.8 (C), 95.7 (C), 113.4 (CH), 115.3 (C), 120.3 (CH), 122.1 (CH), 122.4 (CH), 124.8 (C), 124.85 (CH), 125.7 (CH), 126.4 (CH), 126.9 (CH), 127.1 (CH), 128.0 (CH), 134.9 (C), 138.6 (C), 148.3 (C), 158.9 (C).

Compound 1c: 2-ferrocenyl-2-(*p*-trifluoromethylphenyl)-2*H*-benzo[*h*]chromene. 44%; mp 82 °C (Found: C 70.4, H 9.3. Calc. for $C_{30}H_{21}OF_3Fe$: C 70.60, H 9.00%); UV: λ 324, 345 nm; ^1H-NMR (250 MHz): 4.0 (1H, m), 4.05 (5H, s), 4.1 (2H, m), 4.4 (1H, m), 6.2 (1H, d, *J* 9.7), 6.6 (1H, d, *J* 9.7), 7.1 (3H, m), 7.3 (1H, m), 7.5 (4H, m), 7.7 (1H, m), 8.3 (1H, m); ^{13}C-NMR (62.8 MHz): 66.5 (CH), 66.6 (CH), 68.4 (CH), 69.2 (CH), 79.9 (C), 94.8 (C), 116.1 (C), 120.2 (CH), 122.0 (CH), 124.2 (C), 124.8 (CH), 125.6 (CH), 125.7 (CH), 126.4 (CH), 126.7 (CH), 127.3 (CH), 127.9 (CH), 128.0 (CH), 134.8 (C), 139.4 (C), 146.3 (C), 147.8 (C).

Compound 1d: 2,2-diferrocenyl-2*H*-benzo[*h*]chromene. 17%; mp 153 °C (decomp.) (Found: C 71.8, H 8.6. Calc. for $C_{33}H_{26}OFe_2$: C 72.00, H 8.36%); UV: λ 340, 356 nm; ^1H-NMR (250 MHz): 3.9 (10H, s), 4.1 (4H, m), 4.3 (2H, m), 6.0 (1H, d, *J* 10.1), 6.5 (1H, d, *J* 10.1), 7.1 (1H, d, *J* 10.0), 7.3 (1H, d, *J* 10.0), 7.4 (2H, m), 7.7 (1H, m), 8.2 (1H, m); ^{13}C-NMR (62.8

MHz): 65.3 (CH), 66.5 (CH), 68.0 (CH), 68.3 (CH), 69.0 (CH), 77.9 (C), 94.3 (C), 115.2 (C), 120.0 (CH), 122.2 (CH), 122.3 (CH), 124.8 (CH), 125.0 (C), 125.5 (CH), 126.3 (CH), 127.9 (CH), 128.5 (CH), 134.9 (C), 148.1 (C).

Compound 2a: 3-ferrocenyl-3-phenyl-3*H*-benzo[*f*]chromene. 75%; mp 149 °C (Found: C 78.8, H 10.6. Calc. for $C_{29}H_{22}OFe$: C 78.70, H 10.40%); UV: λ 351, 363 nm; ^{1}H-NMR (250 MHz): 4.05 (1H, m), 4.05 (5H, s), 4.1 (2H, m), 4.3 (1H, m), 6.3 (1H, d, *J* 10.1), 7.1 (5H, m), 7.2 (1H, d, *J* 10.1), 7.4 (3H, m), 7.6 (2H, m), 7.9 (1H, m); ^{13}C-NMR (62.8 MHz): 66.7 (CH), 68.2 (CH), 69.2 (CH), 80.2 (C), 95.1 (C), 113.7 (C), 118.3 (CH), 121.3 (CH), 123.6 (CH), 126.1 (CH), 127.2 (CH), 127.4 (CH), 127.8 (CH), 128.7 (CH), 129.4 (C), 129.8 (CH), 130.0 (C), 145.5 (C), 151.2 (C).

Compound 2b: 3-ferrocenyl-3-(*p*-methoxyphenyl)-3*H*-benzo[*f*]chromene. 75%; mp 134 °C (Found: C 76.2, H 6.5. Calc. for $C_{30}H_{24}O_2Fe$: C 76.27, H 6.35%); UV: λ 303, 316 nm; ^{1}H-NMR (250 MHz): 3.7 (3H, s), 4.0 (1H, m), 4.05 (5H, s), 4.1 (2H, m), 4.3 (1H, m), 6.3 (1H, d, *J* 10.0), 6.7 (2H, d, *J* 8.8), 7.2 (3H, m), 7.35 (3H, m), 7.6 (2H, m), 7.9 (1H, d, *J* 8.6); ^{13}C-NMR (62.8 MHz): 55.1 (CH_3), 66.5 (CH), 67.9 (CH), 68.9 (CH), 80.1 (C), 95.0 (C), 112.9 (CH), 113.5 (C), 118.0 (C), 118.2 (CH), 121.1 (CH), 123.3 (CH), 126.5 (CH), 127.1 (CH), 127.2 (CH), 128.5 (CH), 129.1 (C), 129.5 (CH), 129.8 (C), 137.5 (CH), 151.0 (C), 158.6 (C).

Compound 2c: 3-ferrocenyl-3-(*p*-trifluoromethylphenyl)-3*H*-benzo[*f*]chromene. 82%; mp 129 °C (Found: C 70.4, H 9.2. Calc. for $C_{30}H_{21}OF_3Fe$: C 70.60, H 9.00); UV: λ 303, 316, 346 nm; ^{1}H-NMR (250 MHz): 4.05 (1H, m), 4.1 (5H, s), 4.2 (2H, m), 4.3 (1H, m), 6.4 (1H, d, *J* 9.8), 7.2 (5H, m), 7.6 (5H, m), 7.9 (1H, d, *J* 8.9); ^{13}C-NMR (62.8 MHz): 29.9 (C), 66.5 (CH), 66.5 (CH), 68.4 (CH), 69.2 (CH), 80.0 (C), 95.0 (C), 116.9 (C), 118.0 (CH), 119.1 (CH), 121.3 (CH), 124.8 (CH), 124.9 (C), 126.3 (CH), 126.9 (CH), 128.6 (CH), 129.2 (C), 129.9 (C), 130.1 (CH), 147.3 (C), 151.2 (C).

Compound 2d: 3,3-diferrocenyl-3*H*-benzo[*f*]chromene. 16%; mp 170 °C (decomp.) (Found: C 72.1, H 8.5. Calc. for $C_{33}H_{26}OFe_2$: C 72.00, H 8.36); UV: λ 347, 369 nm; ^{1}H-NMR (250 MHz): 4.0 (10H, s), 4.05 (2H, m), 4.1 (4H, m), 4.3 (2H, m), 6.1 (1H, d, *J* 11.2), 7.05 (1H, m), 7.1 (1H, m), 7.3 (1H, m), 7.45 (1H, m), 7.6 (1H, m), 7.7 (1H, m), 8.0 (1H, m); ^{13}C-NMR (62.8 MHz): 65.8 (CH), 66.7 (CH), 67.5 (CH), 67.7 (CH), 68.9 (CH), 79.9 (C), 95.1 (C), 112.9 (C), 117.1 (CH), 118.0 (CH), 120.9 (CH), 123.0 (CH), 126.2 (CH), 127.9 (CH), 128.4 (CH), 129.0 (C), 129.3 (CH), 129.9 (C), 151.0 (C).

Compound 3a: 2-ferrocenyl-2-phenyl-2*H*-dibenzo[*f,h*]chromene. 53%; mp 173 °C (Found: C 80.3, H 6.9. Calc. for $C_{33}H_{24}OFe$: C 80.50, H 6.70%); UV: λ 341, 373 nm; ^{1}H-NMR (250 MHz): 4.0 (5H, s), 4.1 (2H, m), 4.15 (1H, m), 4.5 (1H, m), 6.4 (1H, d, *J* 10.0), 7.1 (3H, m), 7.2 (1H, d, *J* 10.0), 7.4 (4H, m), 7.6 (2H, m), 8.0 (1H, d, *J* 8.1), 8.5 (4H, m); ^{13}C-NMR (62.8 MHz): 66.2 (CH), 66.8 (CH), 68.2 (CH), 68.4 (CH), 69.3 (CH), 70.6 (C), 96.4 (C), 110.1 (C), 118.8 (CH), 122.1 (CH), 122.8 (CH), 123.0 (CH), 123.3 (CH), 124.5 (CH), 125.7 (CH), 126.6 (CH), 127.1 (CH), 127.3 (CH), 127.4 (CH), 127.5 (CH), 128.0 (C), 128.1 (CH), 129.8 (C), 132.1 (C), 134.9 (C), 139.0 (C), 145.1 (C).

Compound 3b: 2-ferrocenyl-2-(*p*-methoxyphenyl)-2*H*-dibenzo[*f,h*]chromene. 18%; mp 91 °C (decomp.) (Found: C 78.0, H 6.8. Calc. for $C_{34}H_{26}O_2Fe$: C 78.16, H 6.51%); UV: λ 341, 373 nm; ^{1}H-NMR (250 MHz): 3.6 (3H, s), 4.0 (5H, s), 4.1 (2H, m), 4.15 (1H, m), 4.5 (1H, m), 6.3 (1H, d, *J* 10.0), 7.1 (2H, m), 7.2 (1H, d, *J* 10.0), 7.4 (3H, m), 7.7 (2H, m), 8.0 (1H, d, *J* 8.1), 8.5 (4H, m); ^{13}C-NMR (62.8 MHz): 55.4 (CH_3), 66.2 (CH), 66.8 (CH), 68.2 (CH), 68.4 (CH), 69.3 (CH), 70.6 (C), 96.4 (C), 110.1 (C), 118.8 (CH), 122.8 (CH), 123.0 (CH), 123.3 (CH), 124.5 (CH), 125.7 (CH), 126.6 (CH), 127.1 (CH), 127.3 (CH), 127.4 (CH), 127.5 (CH), 128.0 (C), 128.1 (CH), 129.8 (C), 132.1 (C), 134.9 (C), 139.0 (C), 145.1 (C), 146.9 (C).

Compound 3c: 2-ferrocenyl-2-(*p*-trifluoromethylphenyl)-2*H*-dibenzo[*f,h*]chromene. 32%; mp 174 °C (Found: C 72.0, H 6.2. Calc. for $C_{34}H_{23}OF_3Fe$: C 72.85, H 6.07%); UV: λ 340, 372 nm; ^{1}H-NMR (250 MHz): 4.0 (5H, s), 4.1 (2H, m), 4.15 (1H, m), 4.5 (1H, m), 6.6 (1H, d, *J* 10.0), 7.2 (3H, m), 7.4 (3H, m), 7.6 (2H, m), 8.0 (1H, m), 8.5 (4H, m); ^{13}C-NMR (62.8 MHz): 30.1 (C), 66.3 (CH), 66.8 (CH), 68.2 (CH), 68.5 (CH), 69.3 (CH), 77.2 (C), 97.4 (C), 110.1 (C), 122.1 (CH), 122.8 (CH), 123.0 (CH), 123.3 (CH), 124.5 (CH), 125.7 (CH), 126.6 (CH), 127.1 (CH), 127.3 (CH), 127.4 (CH), 127.5 (CH), 127.9 (C), 128.1 (CH), 129.8 (C), 132.1 (C), 134.9 (C), 139.0 (C), 145.1 (C), 148.1 (C).

Compound 3d: 2,2-diferrocenyl-2*H*-dibenzo[*f,h*]chromene. 26%; mp 203 °C (decomp.) (Found: C 73.9, H 5.7. Calc. for $C_{37}H_{28}OFe_2$: C 74.00, H 5.66%); UV: λ 342, 377 nm; ^{1}H-NMR (250 MHz): 4.0 (4H, m), 4.1 (10H, s), 4.3 (4H, m), 5.8 (1H, d, *J* 10.0), 7.0 (1H, d, *J* 10.0), 7.3 (4H, m), 8.1 (1H, d, *J* 8.1), 8.3 (1H, m), 8.5 (2H, d, *J* 8.7); ^{13}C-NMR (62.8 MHz): 66.1 (CH), 67.2 (CH), 68.3 (CH), 68.5 (CH), 69.0 (CH), 78.9 (C), 99.9 (C), 115.1 (C), 118.4 (CH), 122.5 (CH), 122.9 (CH), 123.6 (CH), 123.8 (C), 124.6 (CH), 126.5 (CH), 127.1 (CH), 128.3 (CH), 129.1 (C), 135.2 (C), 139.0 (C), 146.9 (C).

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