Volume 1 | Number 1 | Jan 2013 | Pages 1–100

PCCP

Physical Chemistry Chemical Physics
www.rsc.org/pccp

ROYAL SOCIETY OF CHEMISTRY

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard **Terms & Conditions** and the **Ethical guidelines** still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Journal Name

ARTICLE

Vertically π-expanded coumarin - the synthesis via the Scholl reaction and photophysical properties

Mariusz Tasior,[a] Irena Deperasińska,[c] Karolina Morawska,[b] Marzena Banasiewicz,[c] Olena Vakuliuk,[a,b] Bolesław Kozankiewicz*[c] and Daniel T. Gryko*[a,b]

A short and efficient access to a unique type of π-expanded coumarin is achieved. Strategic placement of naphthalene at the 4-position of coumarin allowed us to fuse these two moieties via aromatic dehydrogenation under Scholl conditions. The intriguing optical properties of this π-expanded coumarin are discussed on a basis of quantum chemical calculations. The fluorescence quantum yield (~20%) is significantly higher than for classical 7-hydroxycoumarin. The ratio of emission versus radiationless deactivation is governed by the following factors: decrease in the oscillator strength of the SS transition (vs. perylene), low yield of intersystem crossing and strong internal conversion originating from the activity of the number of vibronic states.

1 Introduction

Coumarins[1] are widespread both in chemical laboratories and in nature. They possess diversified biological activities.[2-5] The combination of suitable optical properties such as strong light absorption,[6,7] high fluorescence quantum yield (Φ_{fl}),[8] and large Stokes shift[9,10] have attracted considerable attention in various photonics applications.[11-15] The role of coumarins in optical brightening[16] and as fluorescent probes[17,18] directly stems from their advantageous properties. Coumarins' photophysics has been extensively studied with emphasis on the structure-property relationship.[10,19-21] Although coumarin chemistry is well developed, new synthetic methods are being continuously discovered.[22-24]

Various π-expanded coumarins[25-28] have been prepared and studied over the years such as benzo[*h*]coumarins (mostly *via* Pechmann reaction of corresponding naphthols[29]) and benzo[*c*]coumarins.[30] Ahn and co-workers improved the synthetic method for preparation of benzo[*g*]coumarin and employed this new approach in fluorescent imaging.[31,32] Among coumarins π-expanded at positions 4 and 5, a large number of 4-oxa-pyren-5-one analogs have been studied,[33-35] including the naturally occuring alkaloid santiagonamine.[36] On the other hand, the synthesis and photophysical properties of analogous systems corresponding to the perylene skeleton have not been studied yet. The only example bearing a slight

resemblance has been 1-oxa-5-oxocoronene, originally described by Zinke in 1953.[37] Such 'vertically π-expanded coumarins' are consequently the missing link in this area and their synthesis would broaden our understanding of the relationship between the structure and the optical properties in the coumarin family. As a part of a program in the chemistry of rylene's analogues, we have directed our research efforts towards the simplest representative of this family – vertically expanded coumarin bearing hydroxyl group at position 11 (i.e. an analogue of extensively studied 7-hydroxycoumarin).

2 Experimental

2.1 Synthetic procedures

(1-Naphthyl)-3-oxopropanoic acid ethyl ester (1). NaH (60% dispersion in mineral oil, 1.19 g, 29.75 mmol) was washed four times with dry toluene under an Ar atmosphere. Finally, dry toluene (4 mL) was added, followed by diethyl carbonate (3.32g, 0.028 mol) and the whole reaction mixture was heated under reflux. 1-Acetylnaphthalene (2.38 g, 0.014 mol) in dry toluene (5 mL) was slowly added and the resulting mixture was refluxed for 4 h. After that time, the dark-orange suspension was cooled to room temperature, poured into ice-water and acidified with acetic acid to pH=6. Ethyl acetate was added and the organic phase was separated, washed three times with water, and dried with MgSO4. After removal of the solvent, 3.4

g (100%) of desired product (mixture of keto- and enol- form) was obtained as a yellow oil, which was used in the next step without further purification. Analytical data were consistent with literature values.[38]

7-Hydroxy-4-(1-naphthyl)-2*H*-chromen-2-one (**3**). Methanesulfonic acid (3 mL) was slowly added to the mixture of ester **1** (2.24 g, 10 mmol) and resorcinol (1.1 g, 10 mmol). After stirring for 16 h at room temperature, the resulting dark brown mixture was poured into water and extracted with AcOEt. The organic phase was washed with water, dried with Na_2SO_4 and evaporated. Crystallization from EtOH gave 700 mg (24%) of the desired coumarin as an off-white powder. $R_f = 0.7$ (CDCl$_3$). M. p. > 240 °C. ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 10.43 (s, 1H, OH), 8.06 (dd, J = 24Hz, J = 8Hz, 2H, Ar), 7.66-7.44 (m, 5H, Ar), 6.84 (d, *J* = 2Hz, 1H, Ar), 6.66 (d, *J* = 9 Hz, 1H, Ar), 6.61 (dd, *J* = 9Hz, *J* = 2Hz, 1H, Ar), 6.24 (s, 1H, CH). ^{13}CNMR (125 MHz, DMSO-d$_6$) δ 161.5, 160.3, 155.3, 154.8, 133.1, 132.9, 130.4, 129.4, 129.4, 128.5, 128.3, 127.0, 126.5, 126.4, 125.6, 125.2, 113.3, 112.1, 102.6. HRMS (EI): m/z calculated for $C_{19}H_{12}O_3$ [M$^{·+}$] = 288.0772; found 288.0786.

11-Hydroxy-1-oxaperylene-2-one (**4**). 7-Hydroxy-4-(1-naphthyl)-2*H*-chromen-2-one (**3**; 166 mg; 0.576 mmol), sodium chloride (377 mg; 6.46 mmol) and aluminum chloride (2000 mg; 15.00 mmol) were placed in the flask under a continuous argon stream. The reaction mixture was heated at 140 °C for 4 h and cooled down. Subsequently, water and ethyl acetate were added and the phases were separated. The organic phase was washed with water and dried (MgSO$_4$). The filtrate was evaporated under reduced pressure with Celite and chromatography (DCVC) was performed (SiO$_2$, CH$_2$Cl$_2$/hexanes) to obtain desired product **4** as yellow powder in 26% yield (44 mg). R_f =0.7 (DCM : EtOAc=2 : 1); mp >240 °C; ^{1}H NMR (600 MHz, DMSO d$_6$) 10.63 (s, 1H), 8.52 (d, 1H, 7Hz), 8.25 (d, 1H, 8Hz), 8.09 (d, 1H, 8Hz), 7.94 (d, 1H, 8Hz), 7.63- 7.58 (m, 2H), 7.51 (d, 1H, 2Hz), 6.92 (s, 1H), 6.67 (d, 1H, 2Hz); ^{13}C NMR (600 MHz, DMSO d$_6$) 161.7, 161.4, 156.2, 145.3, 133.7, 133.3, 132.8, 130.4, 127.6, 127.4, 127.03, 126.98, 126.2, 125.5, 123.8, 107.9, 106.6, 102.8, 101.9; HR MS [M+H$^+$] m/z calcd. for (C$_{19}$H$_{10}$O$_3$) 286.0638; m/z found 286.0630.

2.2 Materials and methods

Absorption and fluorescence spectra of **4** in liquid acetonitrile (spectroscopic grade) were measured at room temperature using a PerkinElmer UV/VIS Spectrometer Lambda 35, and a Perkin-Elmer 512 Fluorescence Spectrometer, respectively.

Absorption spectra at low temperature (5 K) were measured in single-beam configuration with the aid of a homemade cuvette in which a solution was frozen between two quartz windows separated by a 1.5 mm Teflon ring. The light from a xenon lamp transmitted through the sample was dispersed with a McPherson 207 monochromator and detected with an EMI96659 photomultiplier operating in photon counting mode. Fluorescence spectra in solid matrices at 5 K were measured with a photon sampling technique by using a McPherson 207 monochromator, an EMI96659 photomultiplier and a Stanford

Research SR259 boxcar averager. We used a Lambda Physics LPX100 excimer laser as the excitation source (λ$_{exc}$=308 nm).

All calculations were done with aid of the Gaussian 09 package.[39] Optimization of the molecular geometry in the electronic ground (S$_0$) and lowest excited (S$_1$) states were done with the DFT and TD DFT B3LYP/6-31G(d,p) methods. For all energy minima, both in the ground and excited states, a full set of positive frequencies of vibrations has been found. The transitions energies for molecules in solutions were calculated with use of a simple polarizable-continuum model (PCM), included in the Gaussian package. Simulations of spectra for the calculated electronic transitions were obtained with Gaussian profile (fwhm=3000 cm^{-1}) according to the GaussSum program.[40] Vibrational structures of the electronic spectra was calculated with a procedure included in Gaussian 09, which uses the Franck-Condon factors and the Duchinsky matrix.[41,42]

3 Results and discussion

Our target was naphthalene-fused coumarin **4** (Scheme 1). We assumed that dehydrogenation of the molecule containing both coumarin and naphthalene linked at positions 4 could lead to formation of intramolecular C-C bond. Starting 1-naphthyl-7-hydroxycoumarin (**3**) was prepared using the Pechmann reaction from ester **1** and resorcinol (**2**) (Scheme 1).[43,44] This compound was first described by Pillon with conc. H$_2$SO$_4$ as the condensing agent.[45] We found that replacing sulfuric acid with methanesulfonic acid led to higher yield of coumarin **3** (Scheme 1). The coupling reaction was initially attempted under typical oxidative coupling conditions[46] (FeCl$_3$,CH$_2$Cl$_2$/MeNO$_2$), but reactions led only to the recovery of starting material.

We therefore employed the classical Scholl conditions in the Neumann version.[47,48] Subjecting coumarin **3** to a mixture of melted AlCl$_3$ and NaCl at 140 °C afforded naphthalene-coumarin **4** in 26% yield as yellow crystals (Scheme 1). This structural assignment was further confirmed by analysis of ^{13}C NMR, COSY, HSQC, HMBC and MS. We have also studied the possibility of performing both these transformations as one-pot process, as AlCl$_3$ facilitates both Pechmann and Scholl reaction. Therefore we mixed resorcinol and ethyl 1-naphthoylacetate in melted AlCl$_3$/NaCl mixture at 140 °C, however, we could not detect any traces of desired coumarin.

The structural novelty of π-expanded coumarin **4** as well as its visible fluorescence, prompted us to study its optical properties. For structural reasons, **4** can be compared with perylene, one of the most frequently studied (especially in the area of photophysics) organic dye.[49-52] On the other hand, **4** can be considered as complex and new relative of 7-hydroxycoumarin (7-HC), which has been also extensively studied.[53-58]

Photophysical properties of perylene are well known - the (0, 0) frequency of this compound in *n*-nonane matrix is located at 22533 cm^{-1} (443.8 nm),[59] the Stokes shift between the absorption and emission bands in liquid solvents at room temperature is small and the fluorescence quantum yield (Φ$_{fl}$) amounts to 96%.[50] Photophysical properties of both component

moieties of **4** differ markedly from those of perylene. Naphthalene is a weakly emitting molecule ($\Phi_{fl} \approx 0.23$)[50] and its (0,0) transition (in *n*-pentane at 20 K) is located at 31750 cm^{-1} (315 nm).[60] Different properties of perylene and naphthalene result from different type of the emitting states, which are L_a in perylene and L_b in naphthalene.[52] The photophysics of 7-HC are also well known. The Stokes shift between the absorption (maximum at about 325 nm) and emission (maximum at about 400 nm) bands is relatively large, amounting to about 5500 cm^{-1}, and the fluorescence quantum yield $\Phi_{fl} \approx 8\%$.[54]
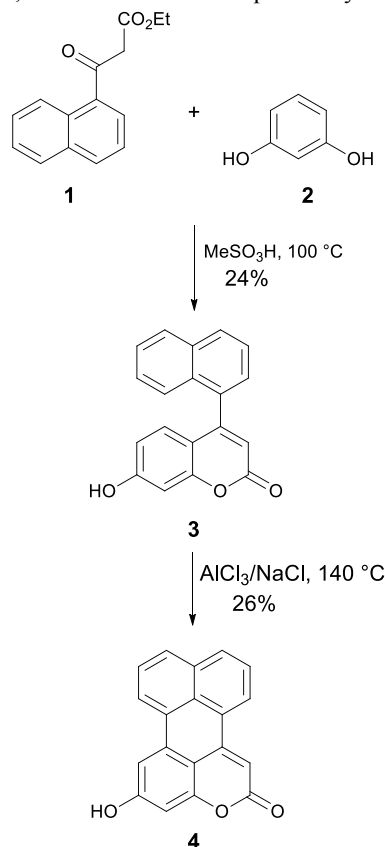
Scheme 1 The synthesis of vertically π-expanded coumarin **4**.

The above mentioned data concerning the compounds "parent" for the compound **4** and the data obtained within the framework of present work for the compound **4** (details will be described later) are collected in Table 1. Complementary information from literature on the energy of triplet state and/or phosphorescence are added.

Absorption and fluorescence spectra of compound **4** in solution at room temperature were composed of dispersed bands with traces of the structure (Fig. 1). The maximum of absorption of the lowest energy band is located at ~425nm, while the maximum of fluorescence occurred at ~465 nm. The positions of these bands depended only weakly on the solvent polarity (the only exception was the fluorescence spectrum of **4** in MeOH, but this case can be attributed to a complex formation). The spectra of compound **4** are in the spectral region close to the absorption and emission spectra of perylene.

Table 1. Photophysical data for the compound **4**, determined in this work (see below), and the data for molecules of perylene, naphthalene and 7-HC, taken from literature. v_{00} – energy of the (0,0) transition between the ground S_0 and electronically excited S_1 state, Δ_{Stokes} – Stokes shift between the absorption and emission spectra, ϕ_{fl} – quantum yield of fluorescence, v_{phosph} - transition energy for phosphorescence.

molecule	v_{00} (cm^{-1})	Δ_{Stokes} (cm^{-1})	ϕ_{fl}	v_{phosph} (cm^{-1})
4	~22222	~3000	0.19	
perylene	22533	1370	0.96	12884[a]
naphthalene	31750	1850	0.26	21203[b]
7-HC	~28000	~5500	0.08	~21322[c]

[a] phosphorescence of perylene is usually difficult to detect, weak phosphorescence in a matrix of anthracene crystal [61] results from intermolecular intersystem crossing [62]. [b] ref. [63]. [c] population of the triplet state of 7-HC [55] and phosphorescence of this compound [64-66] is not well recognized.
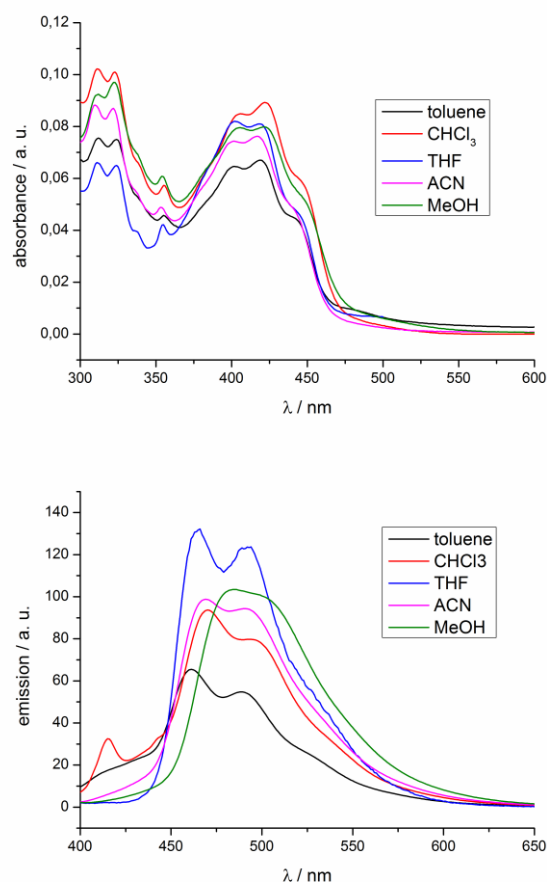
Fig. 1 Absorption (upper panel) and fluorescence (lower panel) spectra of compound **4** in toluene, chloroform (CHCl₃), tetrahydrofuran (THF), acetonitrile (ACN) and methanol (MeOH) at room temperature. For the fluorescence spectra, the excitation wavelength was 400 nm.

To further examine the photophysical properties of **4** we measured the fluorescence quantum yield of this compound in acetonitrile and methanol using perylene as the reference. The quantum yields were found to be 19.2 % in acetonitrile and 21.9 % in methanol. These values fell between those for 7-HC (Φ_{fl}=8 %) and perylene (96 %).

Table 2. Properties of the isolated isomers of compound **4** according to the quantum chemical calculations. f indicates oscillator strength of the transition.

	isomer A	isomer B
structure		
	ground electronic state S_0	
energy of the ground state S_0 *(provided in respect to the energy of more stable isomer A)*	0	223 cm^{-1}
energy barrier between both isomers in the S_0 state	1746 cm^{-1}	
dipole moment in the ground S_0 state	5.12 D	7.59 D
energy and oscillator strength of the $S_0 \rightarrow S_1^{FC}$ absorption transition	24503 cm^{-1} (408.1 nm) f = 0.2631	24290 cm^{-1} (411.7 nm) f = 0.2555
	excited electronic state S_1	
energy of the lowest excited state S_1 *(provided in respect to the energy of more stable, in this state, conformer B)*	5 cm^{-1}	0
energy barrier between both isomers in the S_1 state	1659 cm^{-1}	
dipole moment in the excited S_1 state	5.96 D	8.11 D
energy and oscillator strength of the $S_1 \rightarrow S_0^{FC}$ fluorescence transition	21649 cm^{-1} (461.9 nm) f = 0.2480	21407 cm^{-1} (467.1 nm) f = 0.2396
the (0, 0) energy	22214 cm^{-1} (450.2 nm)	22032 cm^{-1} (453.9 nm)
	triplet states T_i	
transition energies to the lowest triplet states (all in cm^{-1})	13778 20576 25172	13798 21050 25046

Molecules of compound **4** were not soluble in nonpolar *n*-alkanes and we were not able to discuss high resolution absorption and emission spectra of this compound at a low temperature Shpol'skii matrix. Therefore, in this work we used room temperature spectra together with the results of quantum chemical calculations as the basis for characterizing the photophysical properties of **4**.

Compound **4** may exist in two isomeric forms (see Table 2) which differ by orientation of the -OH groups with respect to the skeleton of the molecule. The existence of two isomeric forms of this type (named also as cis/trans rotamers), whose electronic origins are separated by 200-400 cm-1, has been previously observed in the high resolution fluorescence excitation spectra of 1- and 2-hydroxynaphthalenes[67,68] and 7-hydroxyquinoline[69] recorded under experimental conditions of supersonic jet expansion. Two isomers were also taken into consideration in the theoretical calculation of vibrational spectra of 7-HC.[57] The structures of both stable isomers of **4**, which we called A and B, and their basic calculated properties, such as energies of the ground and excited electronic states and dipole moments, are presented in Table 2.

Calculated energies of both isomers and energies of electronic transitions between S_0 and S_1 states are illustrated in Fig. 2. Clearly, both isomers of **4** have similar energies and properties and under ambient conditions it is practically impossible to distinguish their spectra. This is shown in Fig. 3., where we present the simulated electronic spectra of both isomers of **4**, broadened by the Gaussian profiles. Calculated electronic transitions were $S_0 \rightarrow S_i$ (i = 1,2,…) for the absorption and $S_1 \rightarrow S_0$ for the fluorescence (details in Table S1 of Supporting Informations). Overlap of slightly different spectra leads to the blurred structure of the really observed spectra and thus can cause problems with their detailed analysis. It is also seen from Fig.3. that the calculated absorption and fluorescence spectra of both isomers, A and B, remarkably well approximate the spectral positions of the main experimentally observed bands. Good agreement between the calculated and experimental spectra entitled us to conduct more detailed analyses of the obtained results.

Molecules of **4**, unlike those of perylene and due to their 7-HC moiety, have a relatively high dipole moment in the ground (S0) and in the lowest excited (S1) electronic states (see Table 1). These moments are tilted with respect to the long molecular axis of this compound by 48 and 40.2 degree in the S0 for isomers A and B, respectively, and by 62.3 and 58.0 degree in the S1 states of the isomers A and B, respectively. Thus, although both of these dipole moments are large, they are not very different. Therefore, according to the models of solvent effect on the electronic spectra,[70-73] the positions of the absorption and fluorescence spectra of compound **4** would be expected to depend only weakly on the solvent polarity (results of the corresponding calculations are given in Table S2 of Supporting Information), as was experimentally observed (see Fig. 1).

Transition between the S0 and S1 states is dominated by the HOMO and LUMO electronic configurations (π,π^* character) and the transition moment created with the main (long) molecular axis an angle of 19° and 24° in the isomers A and B,
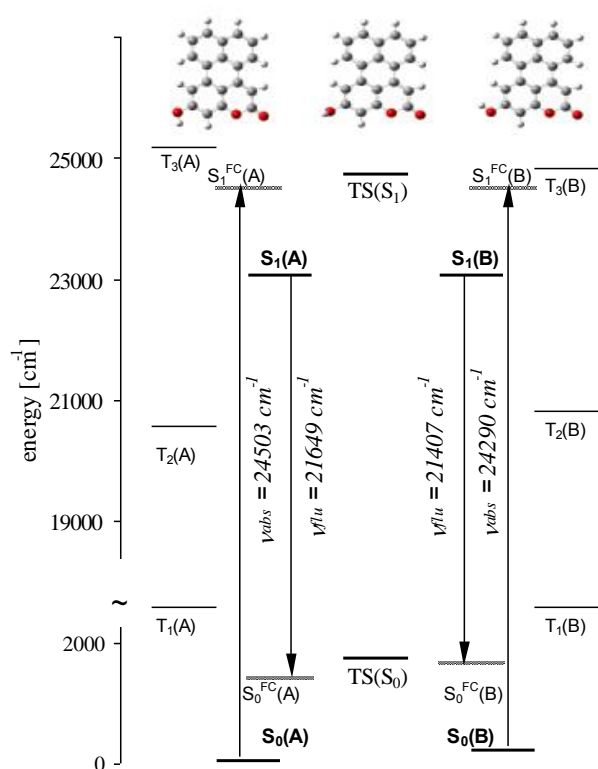
Fig. 2 Visualization of the structure and electronic transitions between the ground (S_0) and lowest excited (S_1) states of the two isomers of compound **4**. Absorption transition leads from the relaxed S_0 state to the Franck-Condon S_1^{FC} state (during optical transition the original positions of the nuclei are preserved); the molecule then relaxes to the equilibrated S_1 state (where the positions of the nuclei are adopted the new minimum energy in the excited state). Fluorescence emission proceeds from the relaxed S_1 state to the Franck-Condon state S_0^{FC}, which then relaxes to the S_0. The TS (transition state) corresponds to the barrier between the two isomers. The scheme also presents the ladders of triplet states, $T_i(A)$ and $T_j(B)$, for both isomers.

respectively (see Fig. 4. for the isomer A). The shapes of the HOMO and LUMO orbitals of compound **4** are perylene-like, but deformed due to the presence of the 7-HC moiety. Loss of the symmetry, as compared with the D2h symmetry of perylene, and the tilting of the transition moment from the long axis direction, decreased the oscillator strength of the S0 → S1 transition and thus is considerably smaller in compound **4** than in perylene. Nevertheless, this oscillator strength is rather large, comparable to the oscillator strength of the S0→S1 transition in 7-HC.

The Stokes shift (which is an indicator of the differences between the geometries of molecule in the ground and excited state) between absorption and fluorescence of **4** is relatively large, ~3000 cm-1, according to the spectra presented in Fig. 3. Another kind of measure of the differences between the geometries of a molecule in the ground and excited state is the vibrational structure of the electronic spectrum. Taking into consideration not only the purely electronic states, but also the vibrational motions in a molecule, the absorption as well as the fluorescence spectra are compose of multiple, so called vibronic transitions. The bigger the difference in the molecule

geometry in the two electronic states participating in the transition, the more extended is the spectrum.
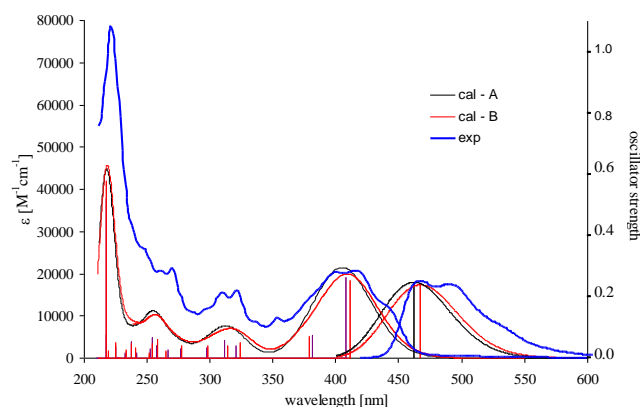

Fig. 3 Experimentally observed absorption and fluorescence spectra of **4** in acetonitrile (blue line) at room temperature and the simulated electronic spectra of isolated isomers A (black line) and B (red line) of **4** - (structures of the isomers are presented in Table 1 and in Fig. 2). The calculated spectra were obtained with the aid of TDDFT B3LYP/6-31G(d,p) method by taking into account the purely electronic transitions (to the Franck-Condon state, whose spectral positions are indicated by the vertical lines with the heights proportional to the oscillator strengths – numerical values are collected in Table S1 of Supplementary Information. The calculated spectra (black and red lines) were broadened with the Gaussian profile (fwhm=3000 cm-1) according to the GaussSum program.[40] For the fluorescence spectra, the excitation wavelength was 400 nm.
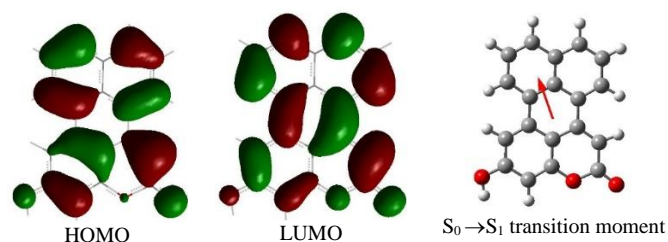

Fig. 4 The HOMO and LUMO configurations and direction of the transition moment of isomer A of compound **4**.

In Fig. 5. we consider the room temperature fluorescence spectrum of **4** in acetonitrile. This spectrum contains two bands, with the maxima at ~465 and ~490 nm. The separation between these two bands, 1600 cm-1, is greater than 200-300 cm-1, the energy difference between isomers A and B (compare Table 2 and Fig. 2). Therefore, these two bands may reflect common vibronic structure of the fluorescence of both isomers of **4**. We also present the calculated Franck-Condon factors for vibronic states contributing to the S1→S0 transition for both isomers. It is seen that the trace of the structure observed in the experimental fluorescence spectrum can be attributed to molecular vibrations with the highest Franck-Condon (FC) factors (numerical values are shown at the bottom of Fig. 5.): one with frequency 350-360 cm-1 and a second with frequency 1620-1630 cm-1. Both of these vibrations represent stretching along the long axis of the molecule. The shape of these dominating vibrations are graphically presented in Table S5;

they closely resemble the vibrations dominating the spectrum of the parent compound perylene.[49] The activity of the mentioned vibrations in the electronic transition between the ground S0 and excited S1 states is associated with characteristic shortening of the C-C bonds between the two moieties in compound **4**: naphthalene and 7-HC. According to our calculations, the lengths of these bonds are shorter by 0.03 and 0.04 Å in the S1 state as compared with their lengths in the S0 state. This effect is similar to the changes observed in the CC bond lengths in perylene and in larger oligorylenes.[74]
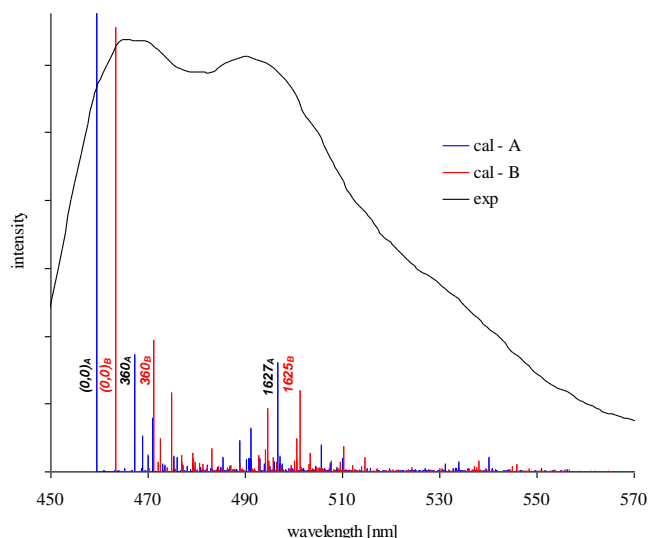

Fig. 5 Comparison of fluorescence spectrum of **4** in acetonitrile (room temperature, excitation wavelength 308 nm) with the simulated vibrational structure. Black and red lines show the Franck-Condon factors calculated for the $S_1 \rightarrow S_0$ emission spectra for isomers A and B.

The fluorescence quantum yield of compound **4** is larger than that for 7-HC and lower in comparison to perylene. Therefore, vertical π-expansion of 7-HC results in an increase of the quantum yield of fluorescence, but this yield does not reach that of perylene. Fluorescence quantum yield is determined by relative efficiency of the S1 state non-radiative energy relaxation by the intersystem crossing and internal conversion with respect to the radiative emission ($\Phi_{fl} = k_f/(k_f + k_{isc} + k_{ic})$, where k_f, k_{isc} and k_{ic} are the rate constants of the radiative, intersystem crossing, and internal conversion transitions, respectively). Internal conversion in classical interpretation is radiationless transition by which electronic energy is dissipated into vibrational motion of molecule. However, due to increasingly problem of dark structures in radiationless transitions,[75] this concept is expanded, and takes into account the electronic nature of this radiationless process. Such issues emerged in relation to deactivation of the S1 state of 7-HC.[55] Previous research on the photophysics of coumarins[54,55] indicated the important (although not entirely explained) role played by the nπ* states. However, in the case of compound **4,** this problem is of minor importance. Our calculations, performed with optimization of the molecule geometry in the nπ* states, showed that the energy of the lowest energy state of

this character is higher by about 935 cm^{-1} than the energy of the S$_1$(ππ*) state.

Efficiency of relaxation by an internal conversion channel is determined by changes in the molecular geometry when the molecule relaxes from the excited S$_1$ state to the ground S$_0$ electronic state.[75] The analysis of the fluorescence spectrum shape (which is almost entirely structureless band) performed in this work and results of the corresponding calculations (non-zero Franck-Condon factors for a large number of vibrations) indicate that these changes are large in compound **4**, reflecting the activity of the number of vibronic states. The result is reduction of the fluorescence quantum yield of **4** in comparison to perylene ("parent" molecule with similar energy parameters and sizes - compare Table 1).

To discuss efficiency of the intersystem crossing pathway, we tried to measure phosphorescence spectrum of **4** and calculated the energies of the excited triplet states of compound **4** (see Table 1 and Fig. 2.). According to the obtained results, the triplet states T$_1$ and T$_2$ (for both conformers of **4**) are located more than 2000 cm^{-1} below the S$_1$ state, whereas the T$_3$ state is more than 1000 cm^{-1} above. Such a high separation of energy suggests that the radiationless transitions by intersystem crossing would not be an effective relaxation channel.

Our effort to monitor phosphorescence of compound **4** appeared to be unsuccessful (although we studied compound **4** dissolved in acetonitrile and *n*-nonane and froze the samples to temperature as low as 5 K, the experiment was performed with Parker type phosphorimeter operating with mechanically choppered excitation light from a 445 nm, 100 mW laser, and photons were detected by a sensitive EM CCD camera). It should be noted, however, that the lack of phosphorescence is not a conclusive evidence of open or closed intersystem crossing channel. We should note however, that intersystem crossing channel is virtually negligible in both "parent" molecules, in perylene and in 7-HC.[55] Therefore, we expect that the main relaxation channel in compound **4** is internal conversion, and that it is responsible for a fluorescence quantum yield lower than in perylene.

It has to be said that the results of investigation presented here are only a guideline, and do not resolve the problem of various possible channels of excitation energy deactivation. Review of the literature dedicated to hydroxycoumarins[53-55,64-66,77,78] shows that their fluorescence is highly sensitive to the influence of solvents and that for interpretation of the observed effects may be necessary to consider formation of complexes with the specific stoichiometric ratio's between compound **4** and solvent molecules. Such the interactions can change both, radiative and nonradiative, channels of the excited state deactivation.

Compound **4** is difficult to dissolve in liquid *n*-alkanes and thus we were not able to monitor the absorption (as well as emission) spectrum of the monomers of this compound in *n*-nonane, even with prolonged hand-shaking of a mixture. In order to increase solubility, we treated a solution with ultrasonication, which broke the **4** material into smaller pieces, and then the obtained mixture was quickly frozen to 5 K. The

absorption and emission spectra of the solution of **4** in *n*-nonane, prepared in this way, are presented in Fig. 6.
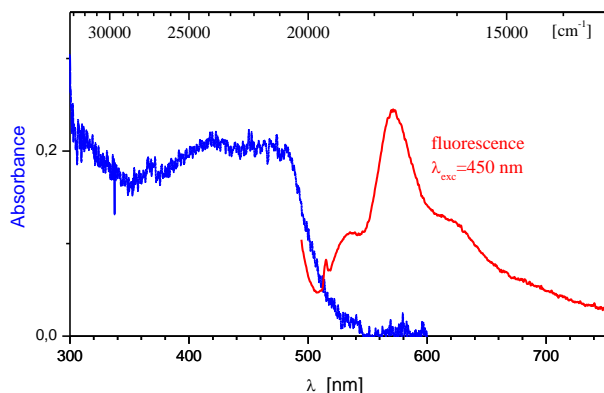

Fig. 6 Absorption and emission (its intensity in arbitrary units) spectra of **4** in *n*-nonane at 5 K. These spectra we attribute to microcrystals.

The beginnings of the spectra are shifted to lower energy as compared with the spectra of **4** in acetonitrile. Such a red spectral shift confirms that in the *n*-nonane matrix, microcrystals of **4** contribute to the spectra, and the spectra do not reflect the presence of monomers of this compound (compare the results of the calculations obtained for dimers of **4** shown in Supporting Information in Table S3 and Fig. S1). In the fluorescence spectrum, we observed a small peak at around 515 nm (~19400 cm^{-1}), which we attributed to the (0, 0) line of the microcrystals. Assuming that the energy of the (0, 0) line of a monomer of **4** is located at ~460 nm (21700 cm^{-1}), we may estimate that the crystal shift energy is ~2300 cm^{-1}. This energy is in reasonably good agreement with ~1600 cm^{-1}, the value obtained for the parent compound perylene.[79]

Conclusions

The moderate electron density of naphthalene and at position 5 of 7-hydroxycoumarin makes it possible to perform intramolecular dehydrogenation in the presence of strong Lewis acid. The various mechanisms, hence electronic requirements of oxidative aromatic coupling and Scholl reaction are responsible for drastically different results of dehydrogenation under various conditions. The π-expansion of 7-hydroxycoumarin (7-HC) to the compound **4** is associated with a large (approaching ~9000 cm^{-1}) reduction of the transition energy between the S_0 and S_1 states, and a threefold increase of the fluorescence quantum yield. This transition takes place between the HOMO and LUMO electronic configurations, both orbitals being of the ππ* type. The HOMO and LUMO orbitals are extended throughout the whole molecule and their shapes are perylene-like. Compound **4** retains a large dipole moment characteristic for 7-HC. The vibronic structure of the $S_0{\rightarrow}S_1$ transition is built on the perylene-like vibrations, but it is obscured by many more vibrations due to the lower symmetry of compound **4**. The nπ*, and also the triplet, states of

compound **4** appear to not play a significant role in energy relaxation from the lowest excited S_1 state. An open issue is extension of characterization of compound 4 in its specific intermolecular interactions, taking into account its different ionic forms.

Acknowledgements

Notes and references

[a] Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, Warsaw, Poland.
[b] Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, Warsaw, Poland.
[c] Institute of Physics, Polish Academy of Sciences, Poland.
E-mail: dtgryko@icho.edu.pl
kozank@ifpan.edu.pl

Electronic Supplementary Information (ESI) available: [details of DFT calculations, spectroscopic data and copies of NMR spectra]. See DOI: 10.1039/b000000x/

1   R. O. Kennedy and R. D. Thornes, *Coumarins: Biology, Applications and Mode of Action*; Wiley and Sons: Chichester, **1997**.
2   M. A. Al-Haiza, M. S. Mustafa and M. Y. El-Kady, *Molecules*, 2003, **8**, 275-286.
3. Y. Takeuchi, L. Xie, L. M. Cosentino and K. H. Lee, *Bioorg. Med. Chem. Lett.* 1997, **7**, 2573-2578.
4   M. A. Musa, M. Omar, F. Khan and J. S. Cooperwood, *Lett. Drug Des. Discv.* 2009, **6**, 133-138.
5   H. Zhao, N. Neamati, H. Hong, A. Mazumder, S. Wang, S. Sunder, G. W. Milne, Y. Pommier and T. R. Burke, *J. Med. Chem.* 1997, **40**, 242-249.
6   R. M. Christie, K. M. Morgan and M. S. Islam, *Dyes Pigm.* 2008, **76**, 741-747.
7   X. Luo, X. Naiyun, L. Cheng and D. Huang, *Dyes Pigm.* 2001, **51**, 153-159.
8   M.-S. Peng, and J. Cai, *Dyes Pigm*. 2008, **79**, 270–272.
9   C. Murata, T. Masuda, Y. Kamochi, K. Todoroki, H. Yoshida, H. Nohta, M. Yamaguchi and A. Takadate, *Chem. Pharm. Bull*. 2005, **53**, 750-758.
10 A. Elangovan, J.-H. Lin, S.-W. Yang, H.-Y. Hsu and T.-I. Ho, *J. Org. Chem*. 2004, **69**, 8086- 8092.
11 A. R. S. Koefod and K. R. Mann, *Inorg. Chem.* 1989, **28**, 2285-2290.
12 B. S. Tasch, C. Brandstatter, F. Meghdadi, G. Leising, G. Froyer and L. Athouel, *Adv. Mater.* 1997, **9**, 33-36.
13 A. Adronov, S. L. Gilat, J. M. J. Fréchet, K. Ohta, F. V. R. Neuwahl and G. R. Fleming, *J. Am. Chem. Soc.* 2000, **122**, 1175-1185.
14 M. Tasior, D. T. Gryko, D. Pielacińska, A. Zanelli and L. Flamigni, *Chem. Asian J*. 2010, **5**, 130-140.
15 J. M. Serin, W. Brousmiche and M. T. Fréchet, *Chem. Commun.* 2002, **38**, 2605-2607.
16 C. A. E. Siegrist, H. Hefti, H. R. Mayer and E. Schmidt, *Rev. Prog. Coloration*, 1987, **17**, 39-55.

17   S. Uchiyama, K. Takehira, T. Yoshihara, S. Tobita and T. Ohwada, *Org. Lett*. 2006, **8**, 5869-5872.

18   T. Hirano, K. Hiromoto and H. Kagechika, *Org. Lett*. 2007, **9**, 1315-1318.

19   D. J. Yee, V. Balsanek and D. Sames, *J. Am. Chem. Soc*. 2004, **126**, 2282-2283.

20   K. Sivakumar, F. Xie, B. M. Cash, S. Lung, H. N. Barnhill and Q. A. Wang, *Org. Lett*. 2004, **6**, 4603-4606.

21   M.-S. Schiedel, C. A. Briehn and P. Bäuerle, *Angew. Chem. Int. Ed*. 2001, **40**, 4677-4680.

22   M. Min and S. Hong, *Chem. Commun*. 2012, **48**, 9613-9615.

23   Z. Shao, L. Xu, L. Wang, H. Wei and J. Xiao, *Org. Biomol. Chem.*, 2014, **12**, 2185-2188.

24   J. Ferguson, F. Zeng and H. Alper, *Org. Lett*. 2012, **14**, 5602-5605.

25   M. K. Węcławski, M. Tasior, T. Hammann, P. J. Cywiński and D. T. Gryko, *Chem. Commun*. 2014, **50**, DOI:10.1039/C4CC03078H.

26   T. Högberg, M. Vora, S. D. Drake, L. A. Mitscher and D. T. W. Chu, *Acta Chem. Scand. B*, 1984, **38**, 359-366.

27   Y. M. Poronik, M. P. Shandura and Y. P. Kovtun, *Chem. Heterocycl. Compd.* 2006, **42**, 410-411.

28   M. Tasior, R. Voloshchuk, Y. M. Poronik, T. Rowicki and D. T. Gryko, *J. Porphyrins Phthalocyanines* 2011, **15**, 1011-1023.

29   O. S. Wolfbeis, *Monatsh. Chem.* 1978, **109**, 1413-1421.

30   P. L. Nandaluru and G. J. Bodwell, *Org. Lett*. 2012, **14**, 310.

31   I. Kim, D. Kim, S. Sambasivan and K. H. Ahn. *Asian J. Org. Chem.* 2012, **1**, 60-64.

32   D. Kim, S. Singha, T. Wang, E. Seo, J. H. Lee, S.-J. Lee, K. Kim and K. H. Ahn, *Chem. Commun*. 2012, **48**, 10243-10245.

33   S. A. Glover, S. L. Golding, A. Goosen and C. W. McCleland, *J. Chem. Soc. Perkin Transactions 1* 1981, 842-848.

34   S. Abdel-Baky, C. Sotiriou-Leventis and R. W. Giese, *Tetrahedron* 1991, **47**, 5667-5672.

35   E. Lee-Ruff, H. Kruk and M. Katz, *J. Org. Chem.* 1984, **49**, 553-555.

36   M. D. Markey, Y. Fu and T. R. Kelly, *Org. Lett*. 2007, **9**, 3255-3257.

37   O. Zinke, *Monatsh. Chem.* 1953, **84**, 1131-1139.

38   T. Lu, B. Tomczuk, L. V. LaFrance, T. P. Markotna, J. J. M. Sanchez, V. J. Marder, C. U'Prichard, B. M. Anaclerio, Z. Guo, W. Pan and K. A. Leonard, U.S. Pat. Appl. 2007/0219233 A1 Sep. 20, 2007.

39   See the Supporting Information for more details.

40   N. M. O'Boyle, A. L. Tenderholt and K. M. Langner. *J. Comp. Chem.* 2008, **29**, 839-845.

41   V. Barone, J. Bloino, M. Biczysko and F. Santoro, *J. Chem. Theor. Comput.* 2009, **5**, 540-554.

42   J. Bloino, M. Biczysko, F. Santoro and V. Barone, *J. Chem. Theor. Comput.* 2010, **6**, 1256–1274.

43   H. Pechmann and C. Duisberg, *Ber. Dtsch. Chem. Ges.* 1883, **16**, 2119.

44   S. Sethna and R. Phadke, *Organic Reactions,* John Wiley & Sons Inc., **2004**, 1-58.

45   D. Pillon, *Bull. Soc. Chem. Fr.* 1955, 39-44.

46   J. Hassan, M. Sévignon, C. Gozzi, E. Schulz and M. Lemaire, *Chem. Rev.* 2002, **102**, 1359-1469.

47   M. Grzybowski, K. Skonieczny, H. Butenschön and D. T. Gryko, *Angew. Chem. Int. Ed*. 2013, **52**, 9900.

48   E. Clar, W. Kelly, D. G. Stewart and J. W. Wright, *J. Chem. Soc.* 1956, 2652-2656.

49   C. Joblin, F. Salama and I. Allamandola, *J. Chem. Phys.* 1999, **110**, 7287-7297.

50   I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, New York, **1971**.

51   J. N. Demas and G. A. Crosby, *J. Phys. Chem.* 1971, **75**, 991.

52   N. Nijegorodov and D. P. Winkoun, *Spectrochim. Acta, Part A* 1997, **53**, 2013-2022.

53   D. W. Fink and W. R. Koehler, *Anal. Chem.* 1970, **42**, 990-993.

54   N. Nizomov, A. U. Kholov, A. A. Ishchenko, V. V. Ishchenko and V. P. Khilya, *Journal of Appl. Spectrosc.* 2007, **74**, 626.

55   C. M. Krauter, J. Möhring, T. Buckup, M. Pernpointner and M. Motzkus, *Phys. Chem. Chem. Phys.* 2013, **15**, 17846-17861.

56   E. Gök, *J. Fluoresc.* 2013, **23**, 333–338.

57   S. Sebastian, S. Sylvestre, D. Jayarajan, M. Amalanathan, K. Oudayakumar, T. Gnanapoongothai and T. Jayavarthanan, *Spectrochim. Acta, Part A* 2013, **101**, 370–381.

58   T. J. Brett, J. M. Alexander and J. J. Stezowski, *J. Chem. Soc., Perkin Trans.* 1 2000, **2**, 1095–1103.

59   M. Pirotta, A. Renn, M. H. V. Werts and U. P. Wild, *Chem. Phys. Lett.* 1996, **250**, 576-582.

60   J. J. Dekkers, G. Ph. Hoornweg, C. Maclean and N. H. Velthorst, *Chem. Phys.* 1974, **5**, 393-407.

61   P. J. Walla, F. Jelezko, Ph. Tamarat, B. Lounis and M. Orrit, *Chem. Phys.* 1998, **233**, 117-125.

62   A. Nicolet, M. Kol'chenko, B. Kozankiewicz and M. Orrit, *J. Chem. Phys.* 2006, **124**, 164711.

63   E. B. Priestley and A. Haug, *J. Chem. Phys.* 1968, **49**, 622.

64   D. Jacquemin, E. A. Perpete, G. Scalmani, M. J. Frish, X. Assfeld, I. Ciofini and C. Adamo, *J. Chem. Phys.* 2006, **125**, 164324.

65   R. Graber, M. W. Grimes and A. Haug, *J. Chem. Phys.* 1969, **50**, 1623.

66   J. Seixas de Melo and P. F. Fernandes, *J. Mol. Struct.* 2001, **565/566**, 69-78.

67   J. R. Johnson, K. D. Jordan, D. F. Plusquellic and D. W. Pratt, *J. Chem. Phys.* 1990, **93**, 2258-2273.

68   T. Ebata, K. Kouyama and N. Mikami, *J. Chem. Phys.* 2003, **119**, 2947-2950.

69   F. Lahmani, A. Dodd, E. Breheret and A. Zehnacker-Rentien, *Chem. Phys. Lett.* 1994, **220**, 235-242.

70   H. Beens and A. Weller, *Organic Molecular Photophysics*, Birks, J., Ed.; Wiley: London, **1976**; p. 159; solvent effect p. 201.

71   I. Deperasinska and J. Dresner, *J. Mol. Struct. (THEOCHEM)* 1998, **422**, 205.

72   A. B. J. Parusel, *J. Photochem. Photobiol., B: Biol.* 2000, **55**, 188.

73   A. Makarewicz, A. Szemik-Hojniak, G. van der Zwan and I. Deperasinska, *J. Phys. Chem A*, 2009, **113**, 3438-3446.

74   S. Karabunarliev, M. Baumgarten and K. Müllen, *J. Phys. Chem. A*, 1998, **102**, 7029-7034.

75   R. Srinivasan, J. S. Feenstra, S. T. Park, S. Xu and A. H. Zewail, *Science*, 2005, **307**, 558 - 563.

76   A. Berces, M. Z. Zgierski and D.-S. Yang, *Computational Molecular Spectroscopy*; Jensen, P.; Bunker, P., Eds.; John Wiley: Chichester, U.K., **2000**; p. 119.

77 I. Georgieva, N. Trendafilova, A. Aquino and H. Lischka, *J. Phys. Chem. A*, 2005, **109**, 11860–11869.

78 J. R. Heldt, J. Heldt, M. Ston and H. A. Diehl, *Spectrochim. Acta Part A*, 1995, **51**, 1549-1563.

79 R. M. Hochstrasser, *Can. J. Chem.* 1961, **39**, 451-458.

For Table of Contents Only.

λ_{abs} = 420 nm
λ_{em} = 460 nm
Φ_{fl} = 19%