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Vertically π-Expanded Coumarins: The Synthesis and Optical Properties

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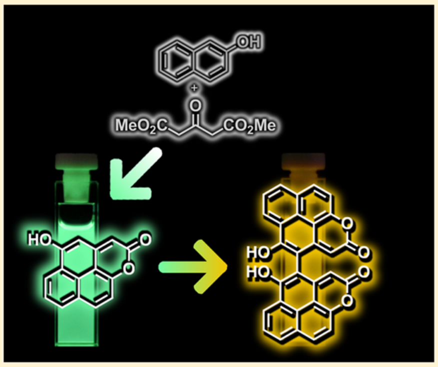
Supporting Information

ABSTRACT: A regioselective synthesis of naphtho[2,1,8-*def*]coumarins has been realized through a concise route that involves the intramolecular Friedel−Crafts reaction of benzo[*f*]coumarins. Tetracyclic, planar products were prepared starting from assembly of the suitably substituted coumarin via the Pechmann reaction of 2-naphthols with acetone-1,3-dicarboxylates, followed by an intramolecular Friedel−Crafts reaction. In contrast to earlier report, the main product of the condensation reaction performed at 130 °C was the corresponding sulfonic acid and not the phenol itself. The one-pot process afforded the desired phenol in 39% yield. This reaction has been extended to some naphthalenediols. The model 5-hydroxy-naphtho[2,1,8-*def*]coumarin was transformed into corresponding dimer using various pathways including intermolecular oxidative aromatic coupling. Photophysical studies revealed that 5-hydroxy-naphtho[2,1,8-*def*]coumarin has the most bathochromically shifted both absorption and emission among all π-expanded coumarins bearing one OH functionality. In general, all prepared coumarin-phenols as well as their hexyl ethers displayed moderate to strong greenish-yellow fluorescence, except of dimer that emits at 552 nm. The fluorescence of these dyes was strongly dependent on polarity of the solvent. Computational studies supported interpretation of optical properties for the selected compounds.



INTRODUCTION

Among many classes of heterocyclic compounds coumarins[1] and π-expanded coumarins[2] play a privileged role since their chemistry is under continuous development for over 100 years. Whereas initially biomedical activity was mainly studied,[1] the interest has been subsequently shifted toward exploration of their optical properties in such photonic applications as, e.g., laser dyes, sensing and light-emitting devices.[3]

The continuous interest in coumarins[4−6] stems mainly from the following factors: (1) pronounced fluorescence of derivatives possessing an electron-donating group in position 7 and an electron-withdrawing group at position 3 combined with their straightforward synthesis;[7] (2) useful two-photon absorption cross sections[8a] − coumarins found use as two-photon excited, photolabile protecting groups;[8b−d] and (3) large Stokes shifts (Δ*S*), which play decisive role in their use as optical whiteners and brighteners.[1,9]

Although Pechmann first synthesized π-expanded coumarins in 1884,[10] only in the past decade has this field started to burgeon and a number of new types of π-expanded coumarins have been synthesized (Figure 1).[11] Also recently, Ahn and co-workers revealed superb optical properties of benzo[*g*]-coumarins and employed them in fluorescence imaging.[12] Oxapyrenones represent one of many structural variations for π-expansion of the coumarin core. The skeleton of 4-oxapyren-2-one (naphtho[8,1,2-*cde*]chromen-5-one) is present in many plants (Figure 1).[13] Various synthetic pathways have been elaborated for this particular heterocycle.[14] Unlike naphtho[8,1,2-*cde*]chromen-5-one, its regioisomer naphtho[2,1,8-*def*]-coumarin (1-oxapyren-2-one) has been virtually unknown (Figure 1). More than a century ago, Dey reported that heating of ethyl 2-(3-oxo-3*H*-benzo[*f*]chromen-1-yl)acetate in

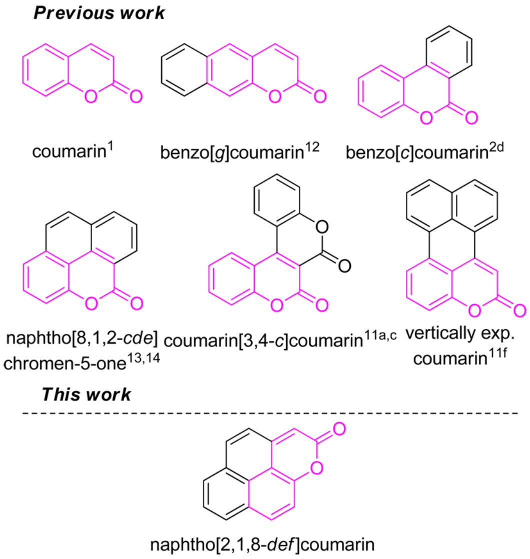


Figure 1. Structures of various π-expanded coumarins.

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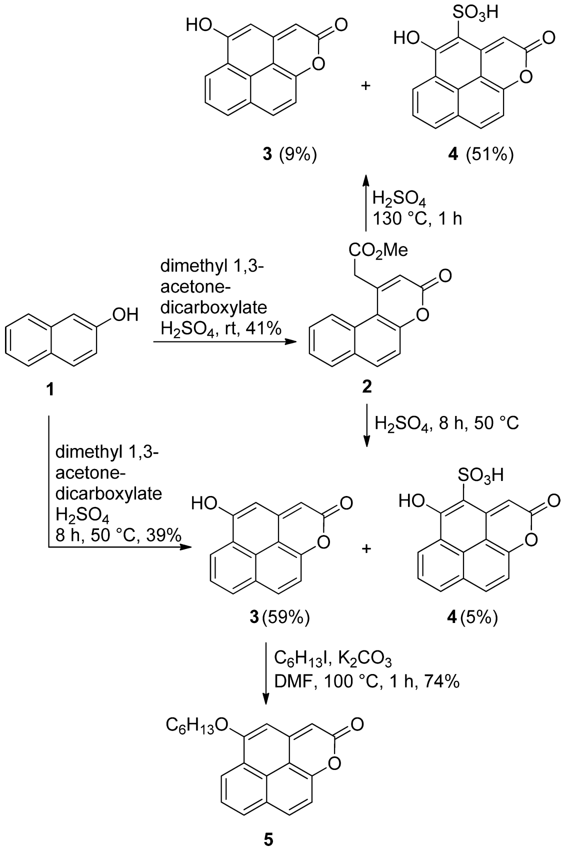
concentrated sulfuric acid at both 50 and 130 °C gave yellow crystals.[15] On the basis of elemental analysis, the structure of this product was ascribed as 5-hydroxy-naphtho[2,1,8-*def*]-coumarin.[15] Given the facts that (a) no other analytical methods were known at that time and that (b) not a single paper has ever appeared in the literature about compounds bearing that skeleton, the structure of Dey's product remains to be confirmed. The unusual skeleton and the potential for interesting and useful optical properties inclined us to repeat this reaction to reconfirm the structure assignment and to explore this chemistry both synthetically and photophysically. Herein, we present results of our investigation.

■ RESULTS AND DISCUSSION

The Pechmann reaction of β-ketoesters with 2-naphthol is well-known not to be regioselective and it leads to a mixture of benzo[*f*]coumarin and benzo[*g*]coumarin.[16] The ratio depends also on the structure of the ester[17] and we were able to prepare the intermediate **2** via Pechmann reaction of 2-naphthol with dimethyl acetone-1,3-dicarboxylate in good yield (Scheme 1).

Scheme 1. Synthesis of Coumarins 2−5



Subsequently, the reaction originally described by Dey[15] was repeated under exactly the same conditions, i.e., ester **2** was subjected to conc. H_2SO_4 at 120−130 °C for 1 h. We found, however, that under such conditions, in addition to an intramolecular Friedel−Crafts reaction, sulfonation also occurred and acid **4** was isolated as the main product in 51% yield (Scheme 1). Phenol **3** was also isolated, albeit in low yield (9%, Scheme 1). In hindsight, this was not a surprising result, since sulfuric acid is well-known to have sulfonating properties. On the other hand, by using conc. H_2SO_4 at 50 °C for 8 h, we were able to reverse the ratio of the products—phenol **3** was obtained in 59% yield and acid **4** was a side-product (Scheme 1). Subsequently, in an attempt to optimize this reaction other types of acid catalysts were explored. The addition of a prototypical Lewis acid ($AlCl_3$, 2 equiv) at 130 °C did not lead to the full conversion, even after 8 h. Increasing the temperature from 130 to 170 °C made it possible to complete the transformation within 1 h. Needless to say acid **4** was not formed, but the yield of phenol **3** was only 39% (Table 1, entry 3). Replacing $AlCl_3$ with $In(OTf)_3$ resulted in even lower yield of coumarin **3** (Table 1, entry 4). We found that such acids as CF_3COOH and K-10 clay did not catalyze this reaction at all (Table 1, entries 5−6), whereas the use of benzenesulfonic acid resulted in the formation of coumarin **3** albeit in lower yield (Table 1, entry 7). We finally optimized the conditions for direct transformation of 2-naphthol with dimethyl acetone-1,3-dicarboxylate into compound **3** in 39% yield (50 °C, 16 h, Scheme 1).

Table 1. Optimization of the Transformation of Ester 2 into Phenol 3

entry	catalyst	catalyst (equiv)	time (h)	temp. (°C)	yield (%)[a]
1	H_2SO_4	excess	1	130	9
2	H_2SO_4	excess	8	50	59
3	$AlCl_3$	2	1	170	39
4	$In(OTf)_3$	0.1	8	170	19
5	TFA	5	16	80	0
6	K-10		16	170	0
7	$PhSO_3H$	0.5	8	170	31

[a] Isolated yields.

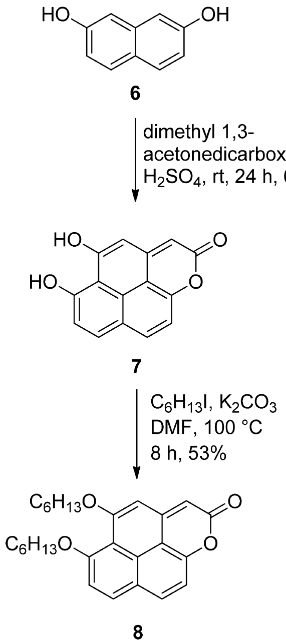
The key step is the intramolecular Friedel−Crafts reaction, which occurs quite efficiently in spite of the fact that the attacked position 8 of naphthalene did not have particularly high electron-density. We hypothesized that use of naphthalene-2,7-diol (**6**) as the starting material would lead to a benzo[*f*]coumarin possessing the activating OH group at the desired position. As expected, the intermediate product of Pechmann reaction was not isolated since reaction led directly to compound **7** in 61% yield (Scheme 2). Given that solubility of bis-phenol **7** was rather poor, for the purposes of both better identification and to studying the optical properties, phenols **3** and **7** were transformed into aryl-alkyl ethers **5** and **8** (Schemes 1 and 2).

Although the assignment and the identification of structures of compounds **3−5**, **7** and **8** was confirmed by analysis of ^1H, ^{13}C NMR, COSY, HSQC, HMBC and MS, we resolved to confirm the skeleton structure by X-ray crystallography (Figure 2). The X-ray quality crystals were obtained for compound **5**. X-ray analysis fully confirmed the structure and according to expectations, the polycyclic ring system of compound **5** was planar (Figure 2).

Encouraged by this synthetic success, we performed analogous tandem processes with naphthalene-1,6-diol (**9**). As anticipated, the presence of the second phenolic OH group did not increase the electron-density at the position 8, resulting in rather poor yield of product **10** (Scheme 3).

Subsequently, we set ourselves the goal of obtaining the product of intermolecular oxidative aromatic coupling[18] of compound **3**. Since its structure bears some resemblance to 2-naphthol, we first attempted to use classical oxidant, i.e., iron(III) chloride[19] (Scheme 4). Poor solubility of dye **3** in

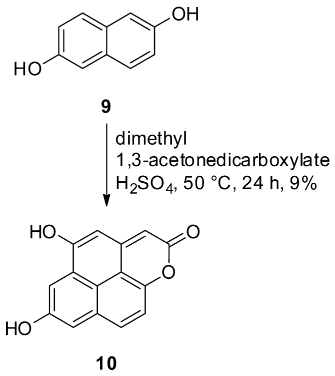
Scheme 2. Synthesis of Coumarins 7 and 8



CH_2Cl_2 resulted in no conversion and prompted us to use a higher boiling solvent, i.e., 1,2-dichlorobenzene. Unexpectedly, instead of compound **15** we isolated product **11** resulting from the bis-chlorination of phenol **3** (Scheme 4). The chlorination of phenols in the presence of $FeCl_3$ was first observed by Niementowski,[20] and later on by others for various electron-rich aromatic compounds.[21] The unsuccessful attempts to use $FeCl_3$ in combination with other reagents were summarized in Table 2. The use of classical Scholl conditions (Table 2, entry 6) led to negative results as well.

Consequently, we designed a longer synthetic strategy. The first attempt of bromination of phenol **3** with Br_2 or NBS caused the formation of a complex and inseparable product mixture. Eventually, phenol **3** was brominated in the presence of copper(I) bromide[22] and the resulting bromophenol **12** was subjected to tandem Suzuki reaction in the presence of bis-pinacoloborane[23] to obtain bis-phenol **15** in 21% yield (Scheme 4). The low yield of the last step can be associated with the presence of a free OH group. We then performed methylation of phenol **12** to obtain compound **13** in 79% yield (Scheme 4). Compound **13** underwent tandem homocoupling under the same conditions leading to product **14** in 69% yield. Cleavage of alkyl-aryl ethers mediated by aluminum(III) chloride gave us desired phenol **15** in overall yield 45% from phenol **3**. Although the last result was satisfactory, we kept trying to obtain bis-phenol **15** directly from compound **3**. By the use of recently published conditions consisting of a catalytic amount of iron chloride and a stoichiometric amount of (t-BuO)$_2$, we successfully achieved this transformation.[24] Bis-phenol **15** was obtained in 73% yield (Scheme 4, Table 2, entries 7–8).

Scheme 3. Synthesis of Coumarin 10



We subsequently studied the effects of structural variations on photophysical properties for compounds **3**–**5**, **7**, **8** and **10**–**15** in 2-MeTHF (for the sake of solubility of all dyes which allowed for their comparison, Table 3, Figures 3–5). These spectral characteristics were compared to those of the known coumarins and π-expanded coumarins possessing phenolic OH groups. All examined dyes possessed absorption bands, which were typically located between 370 and 500 nm. All investigated π-expanded coumarins have emission maxima in

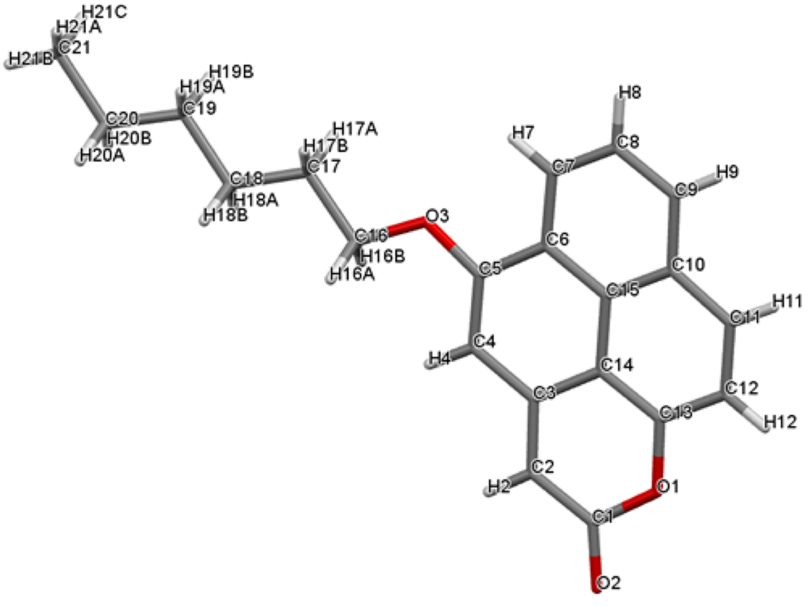


Figure 2. Molecular structure of compound **5**.

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Scheme 4. Synthesis of Coumarins 11−15

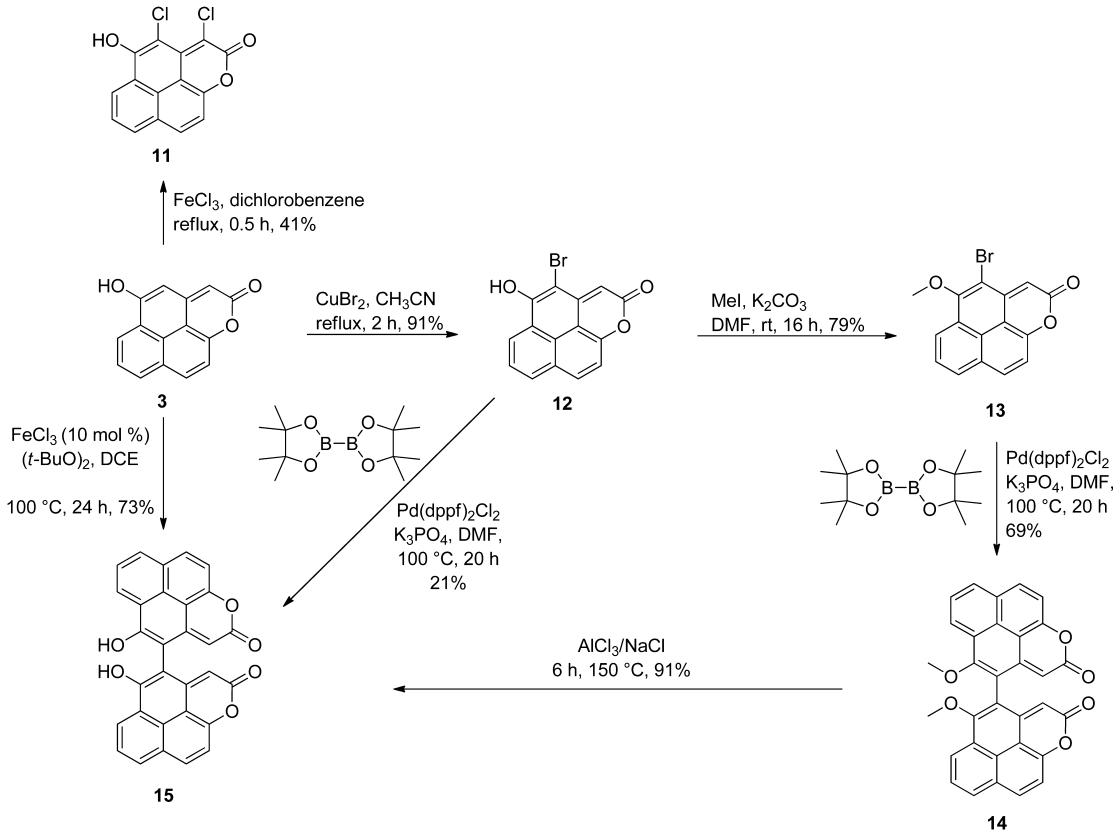

Table 2. Optimization of the Conversion of Coumarin 3 into Compound 15 via Oxidative Aromatic Coupling

entry	oxid. (equiv)	addtive (equiv)	solv.	time (h)	temp. (°C)	yield (%)[a]
1	$FeCl_3$ (2)	–	–	8	50	0
2	$FeCl_3$ (2)	–	DCM	8	RT	0
3	$FeCl_3$ (1.2)	K_2CO_3 (1)	DCE	16	RT	0
4	$FeCl_3$ (0.1)	mCBPA (2)	DCE	16	RT	0
5	$FeCl_3$ (2)	–	DCE	0.5	150	0
6	$AlCl_3$ (26)	NaCl (11.14)	–	8	160	0
7	$FeCl_3$ (0.05)	$(t\text{-BuO})_2$ (2)	HFIP	16	45	39
8	$FeCl_3$ (0.05)	$(t\text{-BuO})_2$ (2)	DCE	16	70	73

[a] Isolated yields.

the range from 496 to 521 nm, which corresponds to green and yellow light. 1-Oxapyren-2-ones **5**, **8** and **13**, which possess MeO substituent(s) instead of free OH groups in their structure, exhibited markedly higher fluorescence quantum yield (Table 3), which for ethers **5** and **8** reached 0.74 and 0.83—the highest values ever reported for coumarins bearing alkoxy groups.[1a,2a] On the whole, although coumarins bearing free OH groups have lower Φ_{fl}, they were still higher than any other π-expanded coumarins possessing free OH group (Φ_{fl} = 0.20−0.52, except for compound **12** possessing a bromine atom, which decreased the fluorescence quantum yield via the heavy atom effect). As predicted, based on data related to coumarins, the hydroxy-substituted oxapyrenones **3**, **4** and **7** showed bathochromically shifted absorption vs dyes **5** and **8** possessing alkoxy groups. The same tendency should be observed for fluorescence, although the emission maximum of compound **7** possessing two hydroxy groups (i.e., 475 nm), was blue-shifted vs compound **8**. The addition of a second hydroxyl group to phenol **3**, caused small bathochromic shifts of both absorption and emission in bis-phenols **7** and **10**. Although the presence of SO_3H group, according to well-established knowledge,[25] has little influence on the optical properties, the fluorescence quantum yield decreased 2-fold from **3** to **4** (Table 3).

The presence of additional halogen atoms (phenols **11** and **12**) slightly shifted the absorption and emission maxima to the lower energy region of the spectrum. The exception was emission of coumarin **11** which had its maximum at 538 nm. Such a large shift is probably caused by distortion from planarity caused by the presence of two chlorine atoms in close proximity. Extension of the conjugation in this series of π-expanded coumarins resulted in ∼100 nm bathochromic shift of absorption vs 7-hydroxycoumarin. The charge-transfer character of 1-oxapyren-2-ones, which all possess electron-donating groups, may be responsible for this substantial shift. Absorption maxima were also red-shifted vs values reported for 11-hydroxy-1-oxaperylen-2-one,[11f] 3-hydroxycoumarino[3,4-*c*]-coumarin,[11c] and 3,9-dioxaperylene-2,8-diones.[11b] A distinct difference could be seen by comparison of λ_{abs} values of the dye **3** and 3-hydroxycoumarino[3,4-*c*]coumarin[11c] (also possessing four conjugated rings and one OH group) which equaled 468 and 374 nm, respectively (Figure 3, Table 3). Indeed, the absorption of compound **3** was the most red-shifted among all known π-expanded coumarins possessing the OH group.[2a]

π-Expanded bis-coumarins **14** and **15** represent a separate case. Their absorption maxima did not differ markedly from π-expanded monocoumarins **3** and **5**. The bathochromic shifts

Table 3. Optical Properties of Compounds 3−5, 7−8 and 10−15 in 2-MeTHF

compd	λ_{abs} (nm)	ε (10^{-3} M^{-1} cm^{-1})	ΔS^a (cm^{-1})	λ_{em} (nm)	Φ_{fl}^b
3	440, 469	14.9	3050	472, 508	0.35
4	438, 466	11.8	3100	472, 505	0.20
5	433, 460	32.6	3000	468, 497	0.74
7	438, 475	25.6	3300	486, 512	0.52
8	447, 477	41.3	3250	490, 523	0.83
10	447, 476	36.8	3100	483, 519	0.36
11	457, 478	6.1	3300	500, 538	0.33
12	450, 477	16.6	2900	484, 518	0.15
13	447, 475	24.2	3000	487, 516	0.45
14	450, 476	32.7	2600	543	0.35
15	459, 486	29.1	3700	552	0.13
7-hydroxycoumarin[c]	325	4.1	5500	410	0.07
11-hydroxy-1-oxaperylene-2-one[d]	418	10.6	3000	466	0.19
3-hydroxycoumarino[3,4-*c*]coumarin[e]	374	16.9	4760	455	0.18
9-hydroxy-1-methylbenzo[*f*]coumarin[f]	361	12.3	6000	462	0.02

[a] Stokes shift. [b] Determined with fluorescein in NaOH (0.1 M) as a standard. [c] ref 26. [d] ref 11f. [e] ref 11c. [f] ref 27.

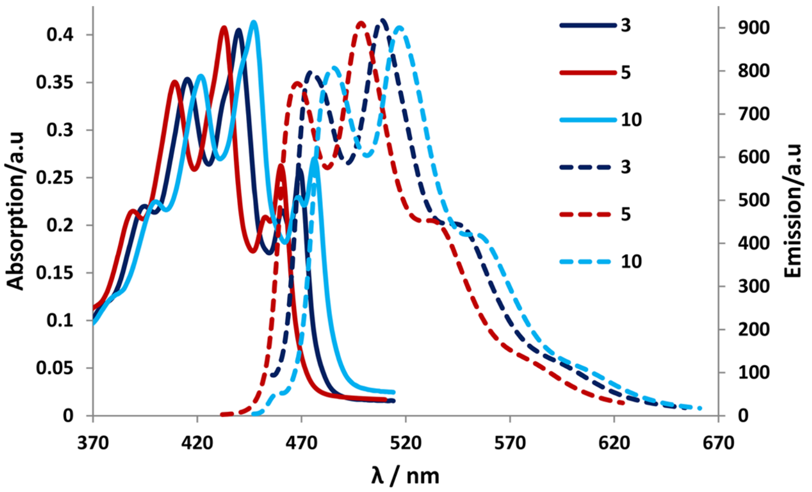

Figure 3. Absorption (solid lines) and emission (dashed lines) spectra for compounds **3**, **5** and **10** in 2-MeTHF. Optical measurements were performed at 25 °C, using dilute solutions (10^{-6} M, optical density <0.1) contained in standard 1 cm quartz cuvettes at room temperature. Emission spectra were obtained, for each compound, under excitation at λ = 430 nm. Fluorescence quantum yields were determined using fluorescein in NaOH (0.1 M) as a standard.

were 17 nm for **3** → **15** and 10 nm for **4** → **14** (Table 3). On the other hand, the emission was bathochromically shifted much more significantly (39 nm for **3** → **15** and 38 nm for **4** → **14**). This difference must originate from the change of geometry between the ground- and excited-states for compounds **14** and **15**. In the excited state, planarization of these two compounds must occur, which is reflected in the stronger conjugation between both moieties.

Intriguingly, all new π-expanded coumarins displayed solvatochromism. As an example, in bis-phenol **7** both absorption and emission maxima were shifted bathochromically when moving from nonpolar to polar solvents (Figure 5). Solvatochromism displayed by 1-oxapyren-2-ones can be explained by the charge-transfer character of the optical transition.[26,28,29] In nonpolar media (toluene, CH_2Cl_2), the absorption spectra showed only short-wavelength band around 430 nm. However, with an increase in the solvent polarity (MeOH, DMSO), a second absorption band appeared at 503 and 520 nm, respectively.

To gain a deeper understanding of the electronic and photophysical properties of synthesized naphtho[2,1,8-*def*]coumarins, we performed quantum-chemical simulations for 5-hydroxy-naphtho[2,1,8-*def*]chromen-2-one (**3**), its methoxylated analogue **5**, and 5,6-dihydroxy-naphtho[2,1,8-*def*]chromen-2-one (**7**) using DFT/TDDFT calculations at the PBE0/6-311++g(d,p) level of theory within a polarized continuum model using the integral equation formalism variant (IEFPCM).

To determine the lowest-energy conformer(s) in the series of hydroxyl-substituted naphtho[2,1,8-*def*]chromen-2-ones, we initially conducted a systematic conformational analysis in the gas phase. We have found that 5-hydroxy-naphtho[2,1,8-*def*]chromen-2-one (**3**) can exist in two conformations with different orientations of the hydroxyl group with respect to the carbonyl group, whereas compound **7** can be represented by three conformers (see Figure S2 of the SI). All subsequent calculations were conducted for the most stable conformers.

DFT and TDDFT approaches have proven to be very efficient and versatile tools for investigation both ground and excited state properties of various organic and inorganic compounds.[30−32] Despite this, it has been shown that describing π−π* transitions for hydroxyl-coumarins is still

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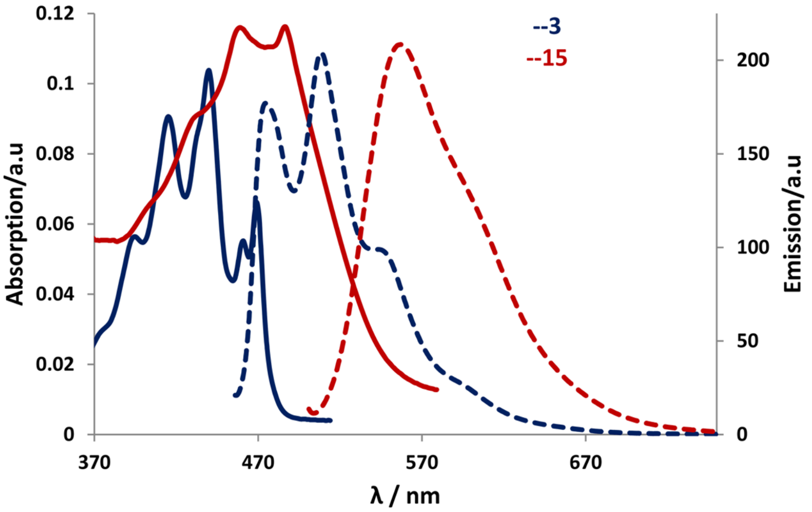

Figure 4. Absorption (solid lines) and emission (dashed lines) spectra for compounds **3** and **15** in 2-MeTHF. Optical measurements were performed at 25 °C, using dilute solutions (10^{-6} M, optical density <0.1) contained in standard 1 cm quartz cuvettes at room temperature. Emission spectra were obtained, for each compound, under excitation at λ = 430 nm. Fluorescence quantum yields were determined using fluorescein in NaOH (0.1 M) as a standard.

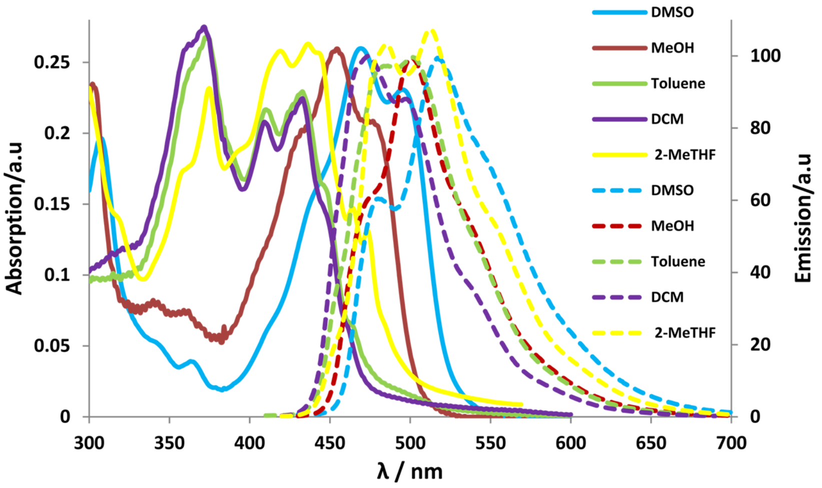

Figure 5. Absorption (solid lines) and emission (dashed lines) of dye **7** in various solvents. Optical measurements were performed at 25 °C, using dilute solutions (10^{-6} M, optical density <0.1) contained in standard 1 cm quartz cuvettes at room temperature. Emission spectra were obtained, for each compound, under excitation at λ = 430 nm.

quite a challenge. For a series of hydroxyl-substituted coumarins, Adamo and Jacquemin demonstrated that PBE0 functional provides the smallest error with an average absolute deviation for reproducing the experimental UV/vis $\pi-\pi^*$ absorption wavelength among the most popular hybrid functionals.[33]

Since naphtho[2,1,8-*def*]chromen-2-one substantially differs from ordinary coumarin core, we performed a benchmark study for 5-hydroxy-naphtho[2,1,8-*def*]chromen-2-one (**3**) using three hybrid functionals (B3LYP, PBE0 and M06) in several implicit solvents simulated by using the IEFPCM formalism. Both $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_0$ were taken into account (see Table S1 of the SI). All tested functionals demonstrated relatively poor reproducibility of the $S_0 \rightarrow S_1$ transition values. It should be noted that the aforementioned functionals substantially underestimated the UV/vis absorption wavelength. The B3LYP functional demonstrated the best performance (mean absolute error (MAE) is 51 nm), followed by M06 and PBE0 with MAEs of 59 and 63 nm, respectively. At the same time, B3LYP exhibited the largest MAE value (19 nm) for $S_1 \rightarrow S_0$ transitions among the tested functionals, while PBE0 provided the smallest one—only 3 nm. Taking the above results into account, we have chosen PBE0 functional for all subsequent calculations. Table 4 demonstrates key results of these calculations.

The solvatochromism demonstrated by compounds **3**, **5** and **7** attracted our attention. Compound **5** exhibited the smallest dependence of the absorption maximum on the medium polarity. For **3**, the absorption maxima shift was slightly larger, ~11 nm, while for **7** the shift of the absorption band shift reached several tens of nanometers. In both molecules, the $S_0 \rightarrow S_1$ transition has a $\pi-\pi^*$ character and essentially corresponds to a HOMO−LUMO transition. Figure 6 shows that both HOMO and LUMO orbitals are distributed over the whole molecule with a significant contribution from π orbitals of the central core, and their shape for compounds **3** and **5** were similar. Analysis of electronic configurations of the HOMO−LUMO for all compounds, describing the transition

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Table 4. Calculated Photophysical Properties for Compounds **3**, **5** and **7**[a]

solv.	λ_{abs}	f	μ_0	λ_{fl}	f	μ_{FC}	μ_1	$\Delta\mu_1$	$\Delta\mu_2$	$\Delta\nu$	Q_{CT}^{FC}	Q_{CT}^{1EC}
Compound **3**												
TOL	406.0	0.3476	7.78	467.6	0.3202	6.25	6.59	1.53	1.19	3245	0.36	0.28
DCM	402.9	0.3505	9.05	478.0	0.4574	7.63	7.97	1.42	1.08	3900	0.42	0.29
MeOH	400.6	0.3355	9.50	482.3	0.5104	8.11	8.46	1.39	1.04	4229	0.42	0.31
ACN	400.9	0.3390	9.52	482.5	0.5123	8.13	8.46	1.39	1.06	4218	0.42	0.32
Compound **5**[b]												
TOL	402.3	0.3430	8.34	460.7	0.3199	7.09	7.43	1.25	0.91	3151	0.19	0.16
DCM	399.5	0.3445	9.60	471.3	0.4570	8.47	8.82	1.13	0.78	3813	0.23	0.20
MeOH	397.2	0.3292	10.05	475.6	0.5106	8.94	9.28	1.11	0.77	4150	0.24	0.23
ACN	397.5	0.3327	10.06	475.8	0.5125	8.95	9.29	1.11	0.77	4140	0.24	0.23
Compound **7**												
TOL	401.6	0.3904	7.58	468.0	0.3306	6.45	6.49	1.13	1.09	3533	0.22	0.18
DCM	399.2	0.4014	8.93	476.0	0.4875	8.13	8.11	0.80	0.82	4142	0.30	0.25
MeOH	397.0	0.3866	9.42	479.5	0.5482	8.72	8.68	0.70	0.74	4334	0.32	0.28
ACN	397.3	0.3907	9.44	479.6	0.5504	8.74	8.70	0.70	0.74	4319	0.32	0.28

[a] Absorption (λ_{abs}) and emission (λ_{fl}) maximum, in nm, and oscillator strength (f) corresponding to the indicated transitions, dipole moments for ground (μ_0), Frank–Condon (μ_{FC}) and excited states (μ_1), in Debye, Stokes shift (ΔS) values, in cm^{-1}, difference between the electric dipole moments in the S_0 state and S_1^{FC} and S_0 state and S_1 excited state ($\Delta\mu_1 = |\mu_{FC} - \mu_0|$ and $\Delta\mu_2 = |\mu_1 - \mu_0|$, in Debye) in various solvents. The amount of electron charge transferred (Q_{CT}, in electron charge units, e) between the initial state and state of interest (FC state and 1st excited state) is also reported. [b] *n*-Hexyl group was replaced with CH_3 to simplify the calculations.

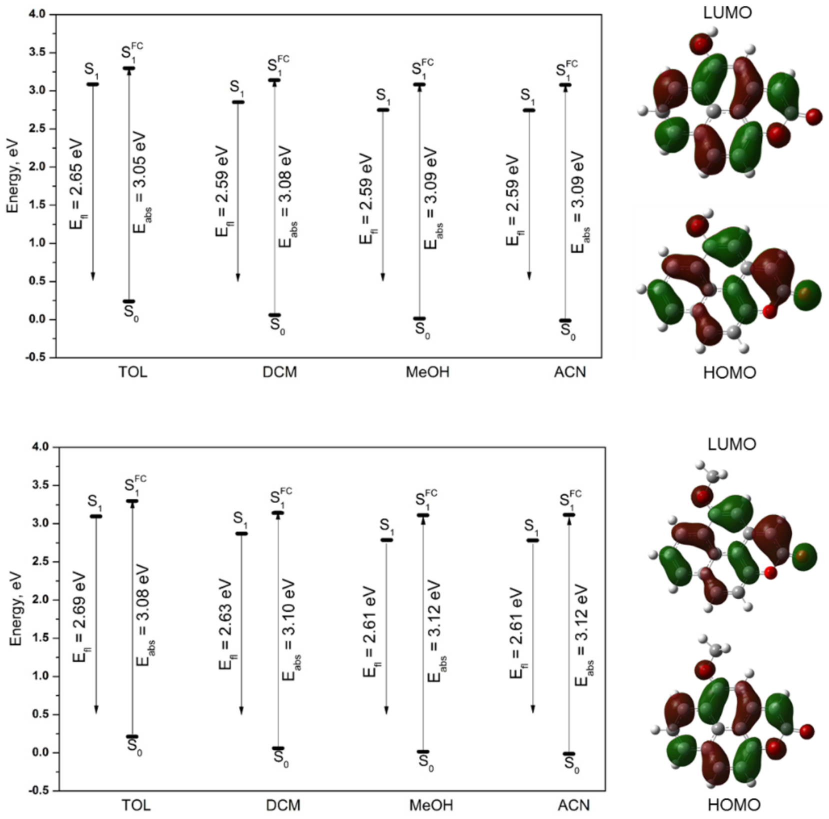

Figure 6. Energy diagram calculated for coumarins **3** and **5** at the PBE0/6-311++G(d,p) level together with the electron distribution of the Kohn–Sham molecular orbitals involved during transition $S_0 \rightarrow S_1$.

between the S_0 and S_1 states, revealed a very minor dependence of absorption maximum on the polarity of the solvent.

We have proposed that solvatochromism observed for studied compounds, for example bis-phenol **7**, is connected with pronounced charge transfer CT character in these dyes. At the same time structured character of bands demonstrated at Figure 5 is not really typical for strong CT states. To get more insight into strength of CT for studied compounds we have investigated charges in ground, S_1^{FC} and S_1 at the same level of theory, using partial atomic charges estimated according to the Merz–Singh–Kollman scheme.

Table 4 shows that all studied compounds demonstrated notable CT considering Q_{CT}. Expectedly, compound **5** demonstrated weaker CT than **3**. At the same time derivative **7** holds an intermediate position by strength of charge transfer between **3** and **5**. It has to be mentioned that according to

PBE0, the CT character decreases significantly from FC geometry to the first exited state. Most clearly it seen for compound **3**—in case of DCM solvent reduction reaches half times. Intriguingly, all studied π-expanded coumarins exhibit pronounce CT and at the same time relatively small (about 1D) difference between the electric dipole moments in the S_0 state and S_1^{FC} and S_0 state and S_1 excited state.

Thus, the enhanced solvatochromism of compounds **3** and **7** with respect to **5** may be caused by specific solvation. Indeed, the correlation between absorption shift value and the number of free hydroxyl groups is evident. At the same time, quantum-chemical calculations that take into account only the expected nonspecific solvation do not reproduce the experimental observations.

■ CONCLUSIONS

In conclusion, tandem process consisting of Pechmann coumarin synthesis followed by intramolecular Friedel−Crafts reaction of benzo[*f*]coumarins proved to be a viable strategy for assembling naphtho[2,1,8-*def*]coumarins (1-oxapyren-2-ones). We found that the reaction conditions affected the product formation and that sulfonation can occur at higher temperature. The presented strategy seems to be versatile and other derivatives of 2-naphthol can be employed, leading to 1-oxapyren-2-ones possessing useful functional groups. The presence of electron-donating OH group makes it possible to further functionalize naphtho[2,1,8-*def*]coumarins and to perform intermolecular oxidative aromatic coupling. Despite the fact that DFT/TDDFT calculations with applied PCM equilibrium solvation are not able to provide perfect agreement with experimental data they do, however, at semiquantitative level allows explain solvatochromism of studied 1-oxapyren-2-ones by the charge-transfer character of the optical transition. The comparison of the absorption and emission spectra of naphtho[2,1,8-*def*]coumarins with known π-expanded coumarins revealed that, in general, naphtho[2,1,8-*def*]coumarins have more advantageous properties. With respect to other chromophores of similar size, the emission of the described compounds is significantly red-shifted, while fluorescence quantum yields are higher.

■ EXPERIMENTAL SECTION

General Remarks. All reagents and solvents were purchased from commercial sources and were used as received unless otherwise noted. DMF was dried over magnesium sulfate and then distilled and stored under argon. The reaction progress was monitored by thin layer chromatography (TLC) with silica gel 60 F254 (Merck) with detection by UV-lamp. Product purifications were done by column chromatography with Kieselgel 60. Occasionally, dry column vacuum chromatography (DCVC) was performed for purification of products using silica gel Type D 5F. All melting points for crystalline products were measured with an automated melting point apparatus and are given without correction. The mass spectra were obtained via electron ionization (EI-MS) or electrospray ionization (ESI-MS). For HRMS measurements both quadruple and TOF mass analyzer types were used.

*Methyl 2-(3-oxo-3H-benzo[f]chromen-1-yl)acetate (**2**).* 2-Naphthol (**1**, 3.6 g, 25 mmol) was added to the concentrated sulfuric acid (30 mL) at room temperature. After 5 min, the reaction mixture was cooled to 0 °C and dimethyl 1,3-acetonedicarboxylate (3.62 mL, 25 mmol) was added dropwise over 10 min. After stirring for 24 h at room temperature, the resulting dark brown mixture was cooled, then poured into ice−water. Subsequently, the precipitate was collected and thoroughly washed with water. Recrystallization from EtOH (twice) gave 2.75 g (41%) as an off-white powder. R_f = 0.6 (EtOAc:hexanes = 1:1); mp 191- 193 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 8.29 (d, J = 8.5 Hz, 1H, Ar), 8.21 (d, J = 9 Hz, 1H, Ar), 8.07 (d, J = 7.5 Hz, 1H, Ar), 7.67 (t, J = 15.5 Hz, 1H, Ar), 7.60−7.56 (m, 2H, Ar), 6.62 (s, 1H, Ar), 4.49 (s, 2H), 3.60 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 169.8, 159.0, 154.1, 150.1, 134.0, 130.8, 129.7, 129.0, 128.1, 125.5, 123.9, 118.2, 117.5, 113.3, 52.2, 42.1; HRMS (ESI) m/z ($[M + Na]^+$) $C_{16}H_{12}O_4Na$ calculated 291.0633; found 291.0635.

*5-Hydroxy-2H-naphtho[2,1,8-def]chromen-2-one (**3**). Method A*: A suspension of **2** (1.34 g, 5 mmol) in concentrated sulfuric acid (15 mL) was stirred at 50 °C for 16 h. The resulting mixture was poured into ice−water. The precipitate was washed with water and chromatography was performed (SiO_2, hexanes:EtOAc = 1:5) to obtain the desired product **3** as a yellow powder in 59% yield. *Method B*: 2-Naphthol (**1**, 720 mg, 5 mmol) was added to the concentrated sulfuric acid (10 mL) at room temperature. After 5 min, the reaction mixture was cooled to 0 °C and dimethyl 1,3-acetonedicarboxylate (725 μL, 5 mmol) was added dropwise over 10 min. After stirring for 8 h at 50 °C, the resulting dark brown mixture was cooled, poured into ice−water. Subsequently, the precipitate was collected and thoroughly washed with water. Recrystallization from EtOH (twice) gave 469 mg (39%) as yellow powder. R_f = 0.7 (CH_2Cl_2−MeOH = 97:3); mp 200−201 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.7 (s, 1H, OH), 8.36−8.27 (m, 3H, Ar), 7.84 (t, J = 15.5 Hz, 1H, Ar), 7.73 (d, J = 9 Hz, 1H, Ar), 6.57 (s, 1H, Ar)), 6.27 (s, 1H, Ar); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 161.0, 159.3, 153.6, 147.1, 133.1, 130.3, 128.0, 125.9, 125.1, 124.6, 124.0, 117.1, 108.6, 100.3, 100.2; HRMS (ESI) m/z ($[M + H]^+$) $C_{15}H_9O_3$ calculated 237.0552; found 237.0553. UV−vis (2-Methyltetrahydrofuran) λ_{max}, nm ($\varepsilon \times 10^{-3}$) 469, λ_{em} max, 508 nm; Φ_{fl} = 0.35.

*5-Hydroxy-2-oxo-2H-naphtho[2,1,8-def]chromene-4-sulfonic acid (**4**).* A suspension of **2** (1.34 g, 5 mmol) in concentrated sulfuric acid (10 mL) was heated at 130 °C for 1 h. The resulting mixture was cooled and poured into ice−water. The precipitate was washed with water and chromatography was performed (SiO_2, CH_2Cl_2−MeOH = 95:5) to obtain the desired product **4** as a yellow solid in 51% yield (809 mg). R_f = 0.6 (CH_2Cl_2−MeOH = 90:10); mp 274−277 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 13.67 (s, 1H, OH), 8.41−8.34 (m, 3H, Ar), 7.89 (t, J = 15.5 Hz, 1H, Ar), 7.78 (d, J = 9 Hz, 1H, Ar), 6.98 (s, 1H, Ar); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 160.8, 156.0, 153.3, 142.4, 132.8, 131.2, 127.9, 126.2, 125.5, 124.2, 123.8, 117.6, 114.0, 108.4, 102.9; HRMS (ESI) m/z ($[M-H]^-$) $C_{15}H_7O_6S$ calculated 314.9963; found 314.9964. UV−vis (2-Methyltetrahydrofuran) λ_{max}, nm ($\varepsilon \times 10^{-3}$) 466, λ_{em} max, 505 nm; Φ_{fl} = 0.20.

*5-(Hexyloxy)-2H-naphtho[2,1,8-def]chromen-2-one (**5**).* A mixture of **3** (236 mg, 1 mmol), 1-iodohexane (0.22 mL, 1.5 mmol) and K_2CO_3 (207 mg, 1.5 mmol) in dry DMF (5 mL) was heated at 100 °C for 1 h. The resulting solution was poured into a water, extracted with EtOAc (3 times), and the organic phase was separated and dried over $MgSO_4$. The filtrate was evaporated under reduced pressure with Celite and chromatography (DCVC) was performed (SiO_2, hexanes:EtOAc = 10:1) to obtain the desired product **5** as a yellow solid in 74% yield (229 mg). R_f = 0.7 (hexanes:EtOAc = 5:1); mp 155−157 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 8.39 (d, J = 9 Hz, 1H, Ar), 8.30−8.25 (m, 2H, Ar), 7.85 (t, J = 15.5 Hz, 1H, Ar), 7.75 (d, J = 9 Hz, 1H, Ar), 6.79 (s, 1H, Ar), 6.37 (s, 1H, Ar), 4.29 (t, J = 12.5 Hz, 2H), 1.93−1.87 (m, 2H), 1.56−1.51 (m, 2H), 1.41−1.24 (m, 4H), 0.91 (t, J = 14 Hz, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 165.3, 161.0, 159.1, 153.8, 146.9, 133.2, 130.3, 128.2, 126.1, 124.8, 124.3, 123.6, 117.2, 102.1, 98.8, 68.6, 30.8, 28.2, 25.1, 21.9, 13.8 ; HRMS (ESI) m/z ($[M + H]^+$) $C_{21}H_{20}O_3$ calculated 321.1491; found 321.1490. UV−vis (2-Methyltetrahydrofuran) λ_{max}, nm ($\varepsilon \times 10^{-3}$) 460, λ_{em} max, 497 nm; Φ_{fl} = 0.74.

*5,6-Dihydroxy-2H-naphtho[2,1,8-def]chromen-2-one (**7**).* Naphthalene-2,7-diol (**6**, 800 mg, 5 mmol) was added to the concentrated sulfuric acid (15 mL) at room temperature. After 5 min, the reaction mixture was cooled to 0 °C and dimethyl 1,3-acetonedicarboxylate (0.725 mL, 5 mmol) was added dropwise over 10 min. After stirring for 24 h at room temperature, the resulting dark brown mixture was cooled and poured into ice−water. The precipitate was washed with water and recrystallized from EtOH (twice) to give **7** as an orange solid in 62% yield (782 mg). R_f = 0.7 (CH_2Cl_2−MeOH = 90:10); mp

195−197 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 7.95 (d, *J* = 9 Hz, 1H, Ar), 7.89 (d, *J* = 9 Hz, 1H, Ar), 7.13 (d, *J* = 8.5 Hz, 1H, Ar), 6.91 (d, *J* = 9 Hz, 1H, Ar), 5.78 (s, 1H, Ar)), 5.24 (s, 1H, Ar); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 173.6, 170.2, 161.7, 154.8, 150.1, 132.7, 11.6, 127.0, 119.9, 119.3, 110.6, 109.0, 108.7, 95.8, 86.0; HRMS (ESI) *m*/*z* ([M + Na]$^+$) $C_{15}H_8O_4Na$ calculated 275.0319; found 275.0320. UV−vis (2-Methyltetrahydrofuran) λ_{max}, nm ($\varepsilon \times 10^{-3}$) 475, λ_{em} max, 512 nm; Φ_{fl} = 0.52.

5,6-Bis(hexyloxy)-2H-naphtho[2,1,8-def]chromen-2-one (**8**). A mixture of **7** (252 mg, 1 mmol), 1-iodohexane (0.435 mL, 3 mmol) and K_2CO_3 (414 mg, 3 mmol) in dry DMF (5 mL) was heated at 100 °C for 8 h. The resulting solution was poured into a water, extracted with EtOAc (3 times), and the organic phase was separated and dried over (MgSO$_4$). The filtrate was evaporated under reduced pressure with Celite and chromatography (DCVC) was performed (SiO$_2$, hexanes:EtOAc = 20:1) to obtain the desired product **8** as a yellow solid in 53% yield (224 mg). R_f = 0.7 (hexanes:EtOAc = 10:1); mp 131−133 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 8.31 (d, *J* = 9 Hz, 2H, Ar), 7.66 (d, *J* = 9 Hz, 1H, Ar), 7.58 (d, *J* = 8.5 Hz, 1H, Ar), 6.68 (s, 1H, Ar), 6.10 (s, 1H, Ar), 4.28 (t, *J* = 13 Hz, 2H), 4.21 (t, *J* = 13 Hz, 2H), 1.88−1.83 (m, 4H), 1.52 (m, 4H), 1.36−1.35 (m, 8H), 0.91 (t, *J* = 11.5 Hz, 6H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 162.9, 162.7, 158.9, 155.5, 147.8, 132.9, 132.6, 127.5, 123.2, 115.1, 113.8, 111.6, 109.7, 98.5, 31.68, 31.66, 29.5, 29.1, 25.9, 25.8, 22.68, 22.67, 14.05, 14.04; HRMS (ESI) *m*/*z* ([M + Na]$^+$) $C_{27}H_{32}O_4Na$ calculated 443.2198; found 443.2191. UV−vis (2-Methyltetrahydrofuran) λ_{max}, nm ($\varepsilon \times 10^{-3}$) 477, λ_{em} max, 523 nm; Φ_{fl} = 0.83.

5,7-Dihydroxy-2H-naphtho[2,1,8-def]chromen-2-one (**10**). Naphthalene-2,6-diol (**9**, 320 mg, 2 mmol) was added to the concentrated sulfuric acid (5 mL) at room temperature. After 5 min, the reaction mixture was cooled to 0 °C and dimethyl 1,3-acetonedicarboxylate (0.290 mL, 2 mmol) was added dropwise over 5 min. After stirring for 24 h at 50 °C, the resulting dark brown mixture was cooled, and poured into ice−water. The precipitate was washed with water and recrystallized from MeOH (twice) to give **10** as an orange solid in 9% yield (46 mg). R_f = 0.7 (CH_2Cl_2−MeOH = 90:10); mp 163−165 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 10.17 (s, 1H, OH), 8.18 (d, *J* = 9 Hz, 1H, Ar), 7.82 (d, *J* = 2.5 Hz, 1H, Ar), 7.64 (d, *J* = 9 Hz, 1H, Ar),6.56 (d, *J* = 2.5 Hz, 1H, Ar)), 6.56 (s, 1H, Ar), 6.25 (s, 1H, Ar) ; ^{13}C NMR (DMSO-d_6, 125 MHz) δ 157.4, 150.3, 137.7, 133.13, 133.12, 133.10, 131.2, 128.1, 126.2, 125.2, 124.9, 122.7, 117.3, 109.1, 105; HRMS (ESI) *m*/*z* ([M + Na]$^+$) $C_{15}H_8O_4Na$ calculated 275.0320; found 275.0318. UV−vis (2-Methyltetrahydrofuran) λ_{max}, nm ($\varepsilon \times 10^{-3}$) 476, λ_{em} max, 519 nm; Φ_{fl} = 0.36.

3,4-Dichloro-5-hydroxy-2H-naphtho[2,1,8-def]chromen-2-one (**11**). Compound **3** (59 mg, 0.25 mmol) was dissolved in warm 1,2-dichlorobenzene (10 mL). After cooling to room temperature, the mixture was purged with argon and anhydrous iron(III) chloride (405 mg, 2.5 mmol, 10 equiv) was added in one portion. The reaction mixture was heated at 150 °C for 30 min and the resulting solution was poured into water. The precipitate was washed with water and recrystallized from MeOH (twice) to give **11** as orange solid in 93% yield (71 mg). R_f = 0.65 (CH_2Cl_2−MeOH = 95:5); ^{1}H NMR (DMSO-d_6, 500 MHz) 8.42 (d, *J* = 7.5 Hz, 1H, Ar), 8.36 (d, *J* = 9 Hz, 1H, Ar), 8.32 (d, *J* = 8 Hz, 1H, Ar),7.86 (t, *J* = 15.5 Hz, 1H, Ar) 7.72 (d, *J* = 8.5 Hz, 1H, Ar); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 168.2, 161.6, 152.2, 144.4, 131.5, 131.2, 129.2, 127.9, 125.5, 125.1, 124.7, 117.0, 108.6, 102.5, 83.6; HRMS (ESI) *m*/*z* ([M + Na]$^+$) $C_{15}H_6O_3NaCl_2$ calculated 326.9592; found 326.9586. UV−vis (2-Methyltetrahydrofuran) λ_{max}, nm ($\varepsilon \times 10^{-3}$) 478, λ_{em} max, 538 nm; Φ_{fl} = 0.33.

4-Bromo-5-hydroxy-2H-naphtho[2,1,8-def]chromen-2-one (**12**). A solution of **3** (708 mg, 3.0 mmol) and $CuBr_2$ (1.33 g, 6 mmol, 2.0 equiv) in dry acetonitrile (15 mL) was stirred at room temperature for 1 h. After completion of the reaction, as indicated by TLC, the reaction mixture was concentrated, quenched with water and ethyl acetate (50 mL), and passed through a bed of Celite. The organic layer was washed with brine and dried over MgSO$_4$. The filtrate was evaporated under reduced pressure with Celite and chromatography (DCVC) was performed (SiO$_2$, CH_2Cl_2−MeOH = 98:2) to obtain the desired product **12** as a yellow solid in 91% yield (859 mg). R_f = 0.7 (CH_2Cl_2−MeOH: = 98:2); ^{1}H NMR (DMSO-d_6, 500 MHz) δ 12.16 (s, 1H, OH), 8.37−8.30 (m, 3H, Ar), 7.85 (t, *J* = 15.5 Hz, 1H, Ar), 7.70 (d, *J* = 9 Hz, 1H, Ar), 6.73 (s, 1H, Ar); ^{13}C NMR (DMSO-d6, 125 MHz) δ 161.6, 157.0, 152.1, 144.9, 133.4, 131.2, 128.1, 126.2, 124.8, 124.2, 123.9, 117.0, 108.3, 100.2, 96.5; HRMS (ESI) *m*/*z* ([M + Na]$^+$) $C_{15}H_7O_3NaBr$ calculated 336.9476; found 336.9474. UV−vis (2-Methyltetrahydrofuran) λ_{max}, nm ($\varepsilon \times 10^{-3}$) 477, λ_{em} max, 518 nm; Φ_{fl} = 0.15.

4-Bromo-5-methoxy-2H-naphtho[2,1,8-def]chromen-2-one (**13**). A mixture of **12** (315 mg, 1 mmol), iodomethane (186 μL, 2 mmol) and K_2CO_3 (276 mg, 2 mmol) in dry DMF (5 mL) was stirred at room temperature for 8 h. The resulting solution was poured into a water, extracted with EtOAc (3 times), and the organic phase was separated, dried over (MgSO$_4$). The filtrate was evaporated under reduced pressure with Celite and chromatography (DCVC) was performed (SiO$_2$, hexanes:EtOAc = 2:1) to obtain the desired product **13** as a yellow solid in 79% yield (261 mg). R_f = 0.6 (hexanes:EtOAc = 1:1); ^{1}H NMR (CDCl$_3$, 500 MHz) δ 8.25 (d, *J* = 7.5 Hz, 1H, Ar), 8.05 (t, *J* = 16.5 Hz, 2H, Ar), 7.73 (t, *J* = 15.5 Hz, 1H, Ar), 7.46 (d, *J* = 9 Hz, 1H, Ar), 6.50 (s, 1H, Ar)), 4.10 (s, 3H, −OCH$_3$); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 161.9, 158.1, 152.1, 144.6, 132.7, 130.6, 128.3, 126.1, 124.6, 124.5, 124.2, 117.0, 109.0, 100.2, 98.0, 56.2; HRMS (ESI) *m*/*z* ([M + Na]$^+$) $C_{16}H_9O_3NaBr$ calculated 350.9633; found 350.9632. UV−vis (2-Methyltetrahydrofuran) λ_{max}, nm ($\varepsilon \times 10^{-3}$) 475, λ_{em} max, 516 nm; Φ_{fl} = 0.45.

5,5′-Dimethoxy-2H,2′H-[4,4′-binaphtho[2,1,8-def]chromene]-2,2′-dione (**14**). A mixture of **13** (164.0 mg, 0.50 mmol), Pd(dppf)Cl_2 (18 mg, 0.025 mmol), and K_3PO_4 (318 mg, 1.50 mmol) in DMF (30 mL) was degassed with nitrogen for 15 min at room temperature. Bis(pinacolato)diboron (69 mg, 0.275 mmol) in DMF (20 mL) that was degassed with nitrogen was added to the mixture dropwise with stirring. The mixture was stirred at 100 °C for 20 h, and then the volatile solvents were removed under reduced pressure. The residue was purified by column chromatography (SiO$_2$) using CH_2Cl_2−MeOH (98:2) as an eluent to afford the pure product as an orange solid (114 mg, 69%). ^{1}H NMR (DMSO-d_6, 500 MHz) δ 8.50 (d, *J* = 9.5 Hz, 2H, Ar), 8.40 (d, *J* = 8 Hz, 2H, Ar), 8.27 (d, *J* = 7 Hz, 2H, Ar), 7.91−7.88 (m, 4H, Ar), 6.39 (s, 2H, Ar)), 3.85 (s, 6H, −OCH$_3$); ^{13}C NMR (DMSO-d_6, 125 MHz) δ;160.3, 159.7, 153.3, 144.7, 133.3, 130.7, 128.2, 126.1, 124.5, 124.4, 123.9, 117.4, 108.9, 108.1, 97.4, 56.4; HRMS (ESI) *m*/*z* ([M + Na]$^+$) $C_{32}H_{18}O_6Na$ calculated 521.1001; found 521.1002. UV−vis (2-Methyltetrahydrofuran) λ_{max}, nm ($\varepsilon \times 10^{-3}$) 476, λ_{em} max, 543 nm; Φ_{fl} = 0.35.

5,5′-Dihydroxy-2H,2′H-[4,4′-binaphtho[2,1,8-def]chromene]-2,2′-dione (**15**). *Method A*: A mixture of **14** (48 mg, 0.096 mmol), sodium chloride (63 mg, 1.07 mmol), and aluminum chloride (333 mg; 2.5 mmol) was placed in the flask under a continuous argon stream. The reaction mixture was heated at 160 °C for 8 h and cooled to room temperature. Afterward, water was added, the orange crystals were washed with water and recrystallized from EtOH (twice) to give **15** (42 mg, 93% yield) as an orange solid. *Method B*: A mixture of **12** (157.0 mg, 0.50 mmol), Pd(dppf)Cl_2 (18 mg, 0.025 mmol), and K_3PO_4 (318 mg, 1.50 mmol) in DMF (30 mL) was degassed with nitrogen for 15 min at room temperature. Bis(pinacolato)diboron (69 mg, 0.275 mmol) in DMF (20 mL) that was degassed with nitrogen was added to the mixture dropwise with stirring. The mixture was stirred at 100 °C for 20 h, and then the volatile solvents were removed under reduced pressure. The residue was purified by column chromatography (SiO$_2$) using CH_2Cl_2−MeOH (98:2) as an eluent to afford the pure product as an orange solid (27 mg, 21%). *Method C*: To a mixture of **3** (59 mg, 0.25 mol, 5 mol %), FeCl$_3$ (2 mg, 0.0125 mmol) in DCE (1 mL), di-*t*-butylperoxide (92 μL, 0.50 mmol, 2 equiv) was added dropwise at room temperature and stirred for 16 h at 70 °C. After complete consumption of substrate **3** (indicated by TLC), the volatiles were removed under reduced pressure and the crude residue was purified by column chromatography (SiO$_2$, CH_2Cl_2−MeOH, 95:2) to afford compound **15** (43 mg, 73% yield) as an orange solid. R_f = 0.6 (silica gel CH_2Cl_2−MeOH = 95:5) ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.54 (s, 2H, −OH), 8.51 (d, *J* = 8 Hz, 2H, Ar), 8.41

(d, $J = 7$ Hz, 2H, Ar), 8.34 (d, $J = 7$ Hz, 2H, Ar), 7.92−7.89 (m, 4H, Ar), 6.34 (s, 2H, Ar); 160.0, 159.6, 153.3, 145.3, 133.5, 130.9, 128.2, 126.2, 125.7, 124.6, 124.5, 117.2, 108.6, 105.5, 99.5; HRMS (ESI) m/z ($[M + Na]^+$) $C_{30}H_{14}O_6Na$ calculated 493.0688; found 493.0687. UV−vis (2-Methyltetrahydrofuran) λ_{max}, nm ($\varepsilon \times 10^{-3}$) 486, λ_{em} max, 552 nm; $\Phi_{fl} = 0.13$.

Optical Measurements. For the measurements of absorption and emission spectra, a typical UV/vis spectrophotometer and a spectrofluorimeter were used. All solvents were spectrophotometric grade and were used without further purification. Quartz cells (10 mm) were used for the measurements of absorption and emission spectra. As a standard, fluorescein in NaOH (0.1 M) was used to determine fluorescence quantum yields.

Computational Details. Geometry optimizations were performed to explore minimum energy structures for ground state S0 and first excited state S1 using density functional theory (DFT) and time-dependent DFT (TDDFT) with the PBE1PBE[33] (hereafter also termed PBE0, its usual name in the literature) hybrid functional for the ground and first excited singlet states, respectively. Here, the S1 state has the $^1(\pi\pi^*)$-excited electronic configuration. Pople's 6-311++G(d,p) triple-ξ quality basis set[34] with polarization and diffused functions was employed in both cases. Normal mode vibrational frequencies were also calculated in each case to confirm the presence of the local minimum, at the same level of theory. To simulate the effect of solvent, the geometries were optimized using a self-consistent reaction field (SCRF) approach coupled with integral equation formalism of the polarizable continuum model (IEFPCM).[35−38] Transferred charge (Q_{CT}) were defined from the GS, FC and first ES densities according to the procedure described in ref 39 and an its adapted version for partial atomic charges (determined according to the Merz−Singh−Kollman scheme), rather than densities.[40] All calculations were carried out using Gaussian 09.[41]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02094.

Crystal data (CIF)

^{1}H NMR and ^{13}C NMR spectra for compounds **2**−**5**, **7**, **8** and **10**−**15**, detailed analysis of the structure of compounds **7** on the basis of 2D NMR, X-ray crystallographic data as well as details of molecular calculations (PDF)

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Notes

The authors declare no competing financial interest.

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