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Planar, Fluorescent Push–Pull System That Comprises Benzofuran and Iminocoumarin Moieties

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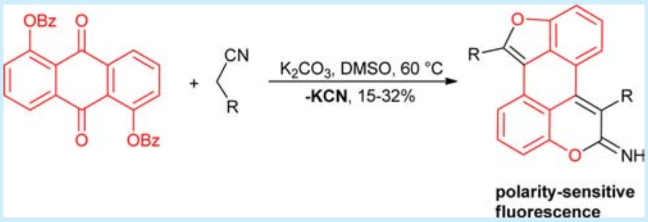
S Supporting Information

ABSTRACT: Previously unknown, vertically linked heterocycles comprised of benzofuran and iminocoumarin moieties have been synthesized directly from 1,5-dibenzoyloxyanthraquinone and arylacetonitriles via double Knoevenagel condensation followed by formal HCN elimination. The structural assembly of fully conjugated, electron-rich benzofuran and electron-deficient iminocoumarin is responsible for the strongly polarized nature of these heterocycles which translates into their polarity-sensitive fluorescence.

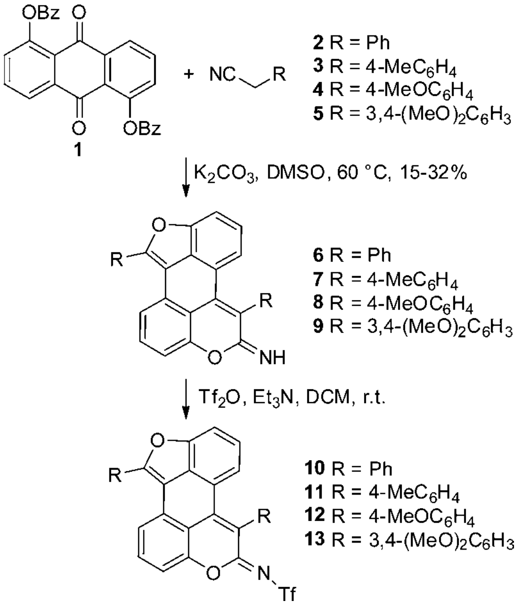


Vertically expanded polycyclic aromatic hydrocarbons such as rylene[1] are more difficult to synthesize than linear acenes.[2] The same holds true for vertically expanded heterocyclic systems involving either six-membered rings or five- and six-membered rings.[3,4] The majority of such compounds possess either C_2 or D_2 symmetry, since the preparation of their unsymmetrical, dipolar analogs is more complex. While numerous dipolar functional dyes have been reported, they usually contain carbon–carbon double bonds (which inevitably leads to *Z*/*E* isomers) or carbon–carbon triple bonds (which allow for full overlap between orbitals associated with all moieties in one conformation only).[5] Fully rigid derivatives of polycyclic aromatic hydrocarbons possessing electron-donating and electron-accepting substituents have also been studied.[6] Herein, we would like to present a serendipitously discovered synthesis of the first, highly polarized planar aromatic system, where electron-rich and electron-deficient poles are imparted by the very nature of heterocyclic rings rather than by substituents.

Taking inspiration from the work of Klimenko and co-workers[7] we recently discovered that the reaction of 1,5-dibenzoyloxyanthraquinone (**1**) with esters of arylacetic acids leads to head-to-tail bis-coumarins possessing C_2 symmetry.[8] At the same time, Liu and co-workers presented an analogous synthesis of bis-quinolin-2-ones starting from 1,5-diaminoanthraquinone.[9] In our approach, while studying the reaction of various CH-acids with 1,5-dibenzoyloxyanthraquinone we came upon arylacetonitriles.

Condensation of salicylaldehydes or 2-hydroxyacetophenones with arylacetonitriles typically leads to iminocoumarins.[10] Owing to advantageous optical properties,[11] iminocoumarins have been investigated as fluorescent probes most prominently by Ahn and Fery-Fourges.[11c,d,12,13] The reaction of phenylacetonitrile (**2**) with derivative **1** under basic conditions unexpectedly led to a new heterocycle **6** in 32% yield, containing the heretofore unknown system comprising benzofuran and iminocoumarin linked at positions 1 and 5 respectively (Scheme 1). Detailed elucidation of the structure based on 2D NMR can be found in the Supporting Information (SI). Neither expected bis-iminocoumarin nor other products could be isolated from this reaction. Mass spectrometry analysis

Scheme 1



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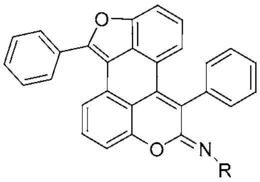
of the crude reaction mixture did reveal the presence of neither head-to-tail bis-iminocoumarin nor head-to-tail bis-benzofuran. The difference in the course of this reaction versus previously studied condensation of esters of arylacetic acids[8] plausibly originates from the more energetically favored elimination of a weak acid (HCN) under strongly basic conditions, compared to elimination of carbon(II) oxide. The elimination of the cyanide anion requires Knoevenagel type addition of a carbonyl group to the corresponding R_2CCN anion (see mechanistic Scheme S1 in SI). First such an addition is easier due to the activating presence of the carbonyl group, enhancing the acidity of the CH-acid. The second addition however is unfavorable because now the acidity of the corresponding CH-acid is decreased by the electron-donating influence of benzofuran.

Under the same conditions, the series of π-expanded iminocoumarins **7**−**9** were subsequently obtained from ketone **1** and substituted arylacetonitriles **3**−**5** in yields of 15−26% (Scheme 1). The presence of the iminocoumarin moiety inclined us to transform these dyes into the *N*-triflyl derivatives **10**−**13** under standard conditions (Scheme 1). In parallel, model compound **6** was transformed into other *N*-derivatives **14** and **15** via reaction with 4-MeC$_6$H$_4$COCl or *p*-TsCl (Figure 1).



14 R = 4-MeC$_6$H$_4$CO
15 R = 4-MeC$_6$H$_4$SO$_2$

Figure 1. Structures of compounds **14** and **15**.

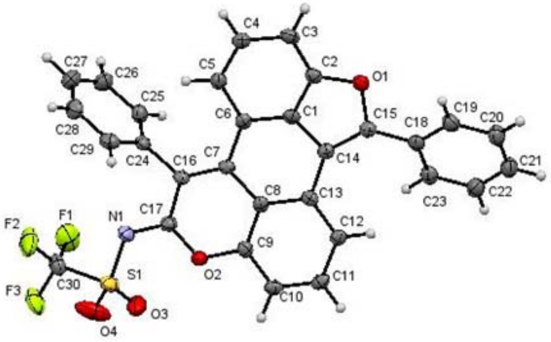


Figure 2. X-ray structure of compound **10**.

The structure was eventually confirmed by a single-crystal X-ray diffraction study (Figure 2), which also demonstrated that compound **10** was almost but not entirely flat.[14] According to our expectations, the angle that the benzofuran substituent forms is only 32° while for imino-coumarin it is 76° (Figure 2). Subsequently, DFT calculations have been performed for all new compounds **6**−**15** (SI, Figure 3). They confirmed that in all cases, although the main chromophore was almost planar, the dihedral angle between the chromophore and substituent was different for each aryl group.

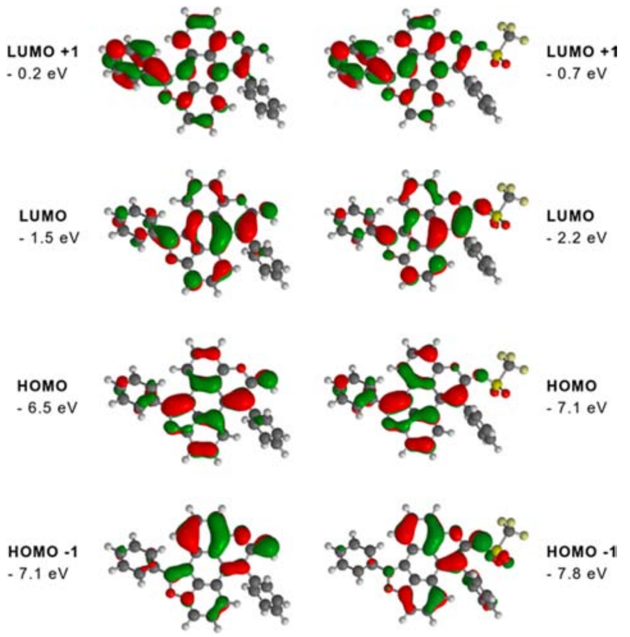


Figure 3. Energy diagrams of compounds **6** (left) and **10** (right) calculated at M06-2X/6-31(d) level of theory.

Both the HOMO and LUMO are partially localized on the phenyl ring attached to the benzofuran moiety while they are not present on the phenyl ring attached to iminocoumarin (Figure 3). The calculated E_{HOMO} was in the range −6.5 to −7.1 eV while E_{LUMO} was −1.2 to −2.3 eV which resulted in $\Delta E_{\mathrm{HOMO-LUMO}}$ = 4.4−5.0 eV.

Table 1. Photophysical Properties (in CHCl$_3$) Determined for Compounds 6−15 and Their Analogs[a]

compd	λ_{abs}, nm	λ_{em}, nm (Φ_{fl})[b,c]	τ (ns)[b]	k_{f} (10^8 s^{-1})[d]	k_{nr} (10^8 s^{-1})
6	397	488 (0.04)	2.6	0.1	3.7
7	400	495 (0.10)	3.1	0.3	2.9
8	408	505 (0.35)	1.5	2.3	4.3
9	410	510 (0.41)	1.9	2.1	3.1
10	460	558 (0.92)	5.6	1.6	0.2
11	470	577 (0.93)	5.4	1.7	0.1
12	480	612 (0.96)	5.1	1.9	0.1
13	485	613 (0.10)	4.4	0.2	2.0
14	385	535 (0.17)	2.1	0.8	3.9
15	445	560 (0.64)	3.4	1.9	1.0
BGIC[e]	357	522 (0.26)	–	–	–
DPD[f]	385	527 (0.16)	1.1	1.5	7.6

[a] Concentrations of compounds were in the range 5−10 μM. [b] The λ_{ex} = 400 nm. [c] Measured using integrating sphere. [d] ±0.1. [e] Reference 13a. [f] Reference 8.

The photophysical properties were examined for compounds **6**−**15** and compared to those determined for other π-expanded coumarins,[15] structurally simpler iminocoumarins,[11−13] and head-to-tail bis-coumarins[8] (Table 1, Figures 4−5). The analysis of the absorption spectra taken for compounds **6**−**9** showed that the introduction of electron-donating aryl substituents into a new system had negligible influence on both the absorption and emission properties (**6** → **9**, bathochromic shift ≤20 nm). On the other hand the introduction of the strongly electron-withdrawing CF$_3$SO$_2$ group further increased the push−pull character of parent dyes leading to a uniformly large bathochromic shift of absorption (~70 nm) and an even larger shift in fluorescence

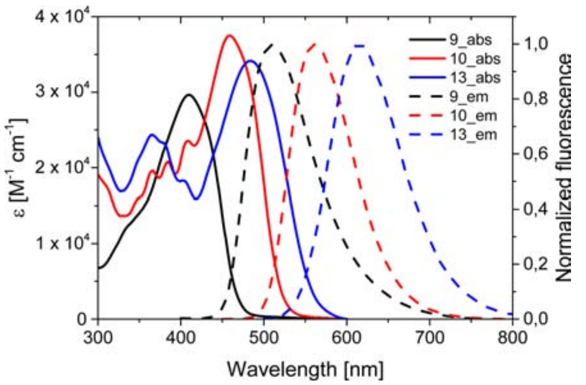


Figure 4. Electronic absorption (solid) and steady-state fluorescence (dashed) spectra of compounds **9**, **10**, and **13** in $CHCl_3$ at room temperature.

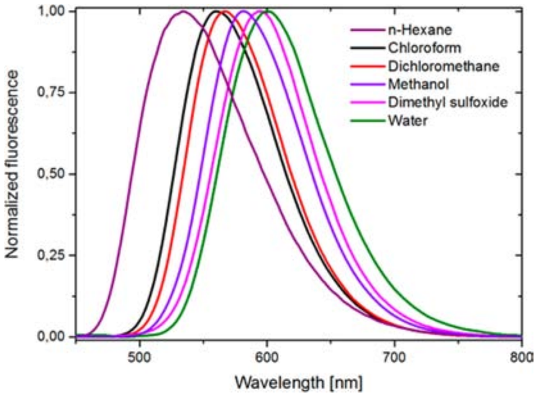


Figure 5. Normalized fluorescence spectra of compound **10** in various solvents.

(70−100 nm) (Table 1, Figure 4). A similar effect has been observed for dyes **14** and **15** possessing weaker electron-withdrawing groups on the nitrogen atom. Fluorescence quantum yields determined for dyes **6**−**9** were low or moderate (Φ_{fl} = 0.04−0.41), and the Stokes shifts (4500−5000 cm^{-1}) were lower than those for corresponding head-to-tail bis-coumarins.[8]

This difference can be explained by the following rationale. Both X-ray diffraction study and DFT calculations (the difference in dihedral angles between both aryl substituents can be observed while analyzing HOMO−LUMO localization within the molecules) have proven that out of two aryl groups present, the one directly linked with the five-membered ring significantly influences the electron density of the benzofuran moiety while the second one only moderately alters the charge distribution for iminocoumarin. The resulting stronger push−pull character of dye **9** vs **6** gives rise to the bathochromic shift of both absorption and luminescence (Table 1). This effect becomes stronger when comparing compounds **10** and **13**. Consequently, the geometry difference between the ground and the excited state are smaller than that for the corresponding head-to-tail bis-coumarins.

The drastic change in fluorescence quantum yield between dyes **6**−**9** and their *N*-substituted analogs **10**−**13** (Φ_{fl} > 90%, with the notable exception of compound **13**) can be associated with the effect of radiationless deactivation triggered by intermolecular proton transfer originating from NH group (Table 1).

When compared with a well-known iminocoumarin derivative such as 3-cyano-8-methoxybenzo[*g*]iminocoumarin (BGIC)[13a] or 3,9-dioxa-perylene-2,8-diones (DPD),[8] compounds **10**−**13** exhibit bathochromically shifted absorption and emission maxima as well as higher fluorescence quantum yields (Table 1). Similar effects can be observed when analyzing decay times (τ), quantum yields (Φ_{fl}), and associated rates of radiative (k_f) and nonradiative (k_{nr}) processes. Moderately short decay times for the compounds **6**, **7**, **13**, and **14** and low Φ_{fl} confirm that for those compounds the nonradiative processes dominate during relaxation to the ground state.

The compounds **8**, **9** exhibit moderate quantum yields with rather low decay times, while compounds **10**−**12** exhibit comparably longer decay times (∼5 ns) and high quantum yields (∼0.95) that can be associated with a highly effective radiative decay path from the excited state. For the compound **13** a drastic decrease in Φ_{fl} is observed and a slight decrease in the decay time, presumably due to intramolecular charge transfer (ICT).

We also found that even though the absorption of **10** was virtually unaffected by differences in solvent polarity, this compound displayed strong polarity-dependent fluorescence (Figure 5). With an increase in solvent polarity, the steady-state fluorescence spectrum narrows and exhibits a significant shift toward the red. This is attributed to a highly polarized ICT excited state, which is a typical phenomenon observed for D−π−A compounds. From cyclohexane to MeOH, the emission maxima (λ_{em}) of **10** shifted from 525 to 600 nm, and the color of the emission changed from green to orange. Simultaneously, the full width half-maximum (fwhm) changes from 3500 cm^{-1} (105 nm) for cyclohexane to 2500 cm^{-1} (85 nm) for MeOH. This effect can be associated with a more effective dye reorientation in polar solvent than in nonpolar. When collected in a mixture of DMSO and water (1:1000) the fwhm stays virtually unaffected (2500 cm^{-1}) even though a spectrum broadening to 95 nm is observed on the wavelength scale. The Stokes shift of the compound **10** was largely dependent on the solvent polarity, and the Lippert−Mataga analysis showed very good correlation (for details see SI).

This phenomenon could be explained by ICT,[16] which occurs in all synthesized derivatives of furo[4′,3′,2′:4,5]-naphtho[1,2,3-*de*]chromen-7-imine due to the electronic interactions between electron-deficient iminocoumarin and electron-rich benzofuran. Analogous, positive solvatochromism has been observed before for *N*-(4-methylbenzoyl)-3-cyano-7-diethylaminoiminocoumarin.[11c]

In conclusion, the replacement of esters of arylacetic acids with arylacetonitriles in a base-catalyzed condensation with diacyloxyanthraquinone triggered the new reaction pathway. Double Knoevenagel condensation was followed by elimination of KCN leading to heterocycles containing heretofore an unknown furo[4′,3′,2′:4,5]naphtho[1,2,3-*de*]chromen-7-imine skeleton. These compounds, comprising benzofuran and iminocoumarin units, were intrinsically dipolar (strong intramolecular charge transfer). Their push−pull character led to strong light absorption and polarity-sensitive fluorescence. Substitution of NH with NTf led to the formation of green-yellow-orange emitters with close to unity fluorescence quantum yields.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02042.

All experimental details, copies of ^{1}H NMR and ^{13}C NMR spectra for compounds **6−15**, X-ray diffraction data for compound **10**, detailed elucidation of the structure of compound **6** based on 2D NMR, mechanistic proposal, and Cartesian coordinates (PDF)
Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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