COMMUNICATION

Luminescent bichromophoric spiroindolones – synthesis and electronic properties†

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Novel bichromophoric spirocyclic indolones have been synthesized by an insertion–coupling–isomerization–Diels–Alder domino reaction. The emission colors are strongly affected by the substituents: *N*-Boc leads to intense blue fluorescence, *N*-dansyl causes turquoise emission, whereas a 1-anthryl substituent on the butadiene results in yellow luminescence. The latter behavior is rationalized by TDDFT computations as a result of significant geometrical changes.

Functional π-systems such as chromophores, fluorophores, and electrophores have received particular attention as functional molecular materials.[1] Applications in organic light emitting diodes (OLEDs),[2] dye sensitized solar cells (DSSCs),[3] organic field effect transistors (OFETs),[4] as cation selective sensors,[5] and in medical diagnosis and therapy have become increasingly important. Among numerous classes of chromophore scaffolds we have particularly focussed on indolone based frameworks (highlighted in Fig. 1) as part of solid-state luminescent push–pull chromophores,[6] protochromic pyranoindole fluorophores,[7] and conformationally rigidified, highly fluorescent butadienes in a spirocyclic corset (Fig. 1).[8]
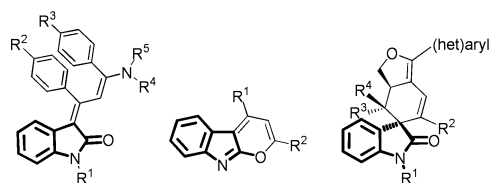
Fig. 1 Push–pull solid-state luminophores, protochromic pyranoindole fluorophores, and highly fluorescent butadienes fixed in spirocyclic indolones.

All three series of luminophores are accessed by a related synthetic strategy based upon an insertion–coupling domino reaction giving prop-3-ynylidene indolones as common intermediates.

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† Electronic supplementary information (ESI) available: Experimental details, NMR, absorption and emission spectra of compounds **4a–m**, and TDDFT computational data of the model chromophore. See DOI: 10.1039/c1ob05703k
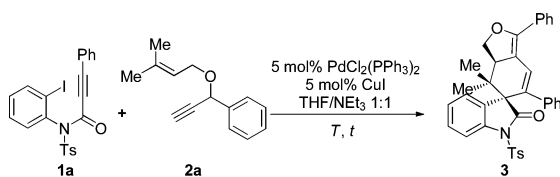
Subsequent Michael addition in a one-pot fashion gives push–pull chromophores, whereas the terminal cycloisomerization of the prop-3-ynylidene indolone intermediate furnishes pyranoindoles, or *in situ* propargyl–allene isomerization and final intramolecular Diels–Alder reaction generates spirocyclic indolones. In particular, the latter class of indolone based luminophores is highly interesting with respect to their unique photophysical properties, because the bright fluorescence and the high quantum yield of the central 1,4-diphenyl butadiene chromophore, embedded in the rigid spirocyclic framework, is quite unusual.[8] As a consequence of the conformational rigidification, nonradiative deactivation pathways such as internal conversion or *cis–trans*-isomerization, typical for *E,Z*- and *Z,Z*-1,4-diphenyl buta-1,3-dienes,[9] are completely suppressed. Dependent on the electronic nature of the (hetero)aryl substituents at the positions 1 and 4 of the butadiene moiety the emission color of the spirocyclic chromophores can be tuned in the range from blue to orange with high quantum yields Φ_f.

With this particular diaryl butadiene luminophore in a confined and defined steric environment in hand, we became intrigued in addressing intramolecular luminophore–luminophore interactions by introduction of a second strongly emissive substituent, either as a conjugated, yet torsionally twisted part of the butadiene luminophore or as a remote nonconjugated, yet strongly emissive second luminophore. Here we communicate the synthesis, electronic spectra and selected DFT computations of spirocyclic indolone bichromophores bearing an anthryl substituent in position 1 of the butadiene moiety and/or a dansyl luminophore ligated to the indolone nitrogen atom.

In recent years we have established and developed diversity-oriented syntheses of chromophores[10] based on transition-metal catalysis as an entry to consecutive multi-component[11] and domino[8,12] reactions for accessing hetero- and carbocyclic frameworks. For tackling the synthesis of chromophore substituted spirocyclic indolones we first had to reiterate and optimize the domino sequence starting from alkynyl *ortho*-iodo anilides **1** and aryl propargyl allyl ethers **2**, in particular, because simple transposition of the previously published synthetic protocol[8] to dansyl (5-(*d*imethyl*a*mino)-*n*aphthalene-1-*s*ulfon*yl*) or Boc-protected alkynyl *ortho*-iodo anilides **1** turned out to be very temperature sensitive, particularly in the terminal isomerization–Diels–Alder step. For an optimization study a model reaction with alkynyl *ortho*-iodo anilide **1a** and 1-phenylpropargyl prenyl ether (**2a**) as substrates and PdCl₂(PPh₃)₂ and CuI as a catalyst system was chosen (Scheme 1).

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Scheme 1 Optimization of the insertion–coupling–isomerization–Diels–Alder domino reaction.

Table 1 Temperature dependence of the insertion–coupling–isomerization–Diels–Alder domino reaction

Entry	T [°C]	Mode of heating	Time [h]	Yield of 3[a]
1	110	thermal	16	48
2	120	thermal	16	59
3	**130**	**thermal**	**16**	**78**
4	130	thermal	16[b]	50
5	130	thermal	72	44
6	150	thermal	16	68
7	130	microwave	0.25	35
8	130	microwave	0.5	33

[a] 5 mol% $PdCl_2(PPh_3)_2$ and 5 mol% CuI; $c(1a) = c(2a) = 0.125$ mM; dry THF/NEt$_3$ 1 : 1; all yields were determined by HPLC. [b] Rapid heating in the preheated reactor.

All experiments were performed in dry THF and dry triethylamine in screw-capped reaction tubes, heated in a special heating block. The yields were determined by HPLC analysis (Table 1).
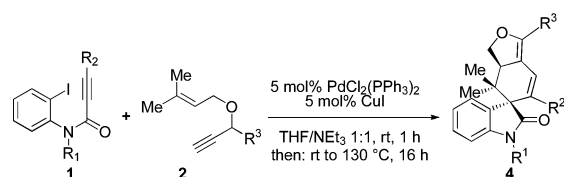
The optimization study revealed that best yields were obtained when the reaction mixture was stirred first for one hour at room temperature to assure the completion of the initial insertion–Sonogashira sequence. Then, conductive heating at exactly 130 °C for 16 h led to complete conversion and a maximal product yield (entry 3). It could also be shown that slow heating to the final reaction temperature resulted in significantly higher yields than rapid heating in the preheated reactor block (entry 4). Furthermore, dielectric heating in a microwave cavity led to an accelerated reaction, yet lower yields were obtained and prolonged irradiation was not favorable (entries 7 and 8).

According to this optimized protocol by reaction of *N*-Boc phenylethynyl *ortho*-iodo anilide **1b** and 1-aryl propargyl prenyl ethers **2a–c** the new *N*-Boc substituted spiroindolones **4a–c** were obtained in moderate yields as pale yellow solids (Scheme 2, Table 2).

Scheme 2 Synthesis of novel spirocyclic indolones.

Likewise, three novel bichromophoric spirocyclic indolones **4d–f** have been synthesized using *N*-dansyl substituted amides **1c–e** and 1-(*p*-chlorophenyl) propargyl prenyl ether (**2b**) under the same reaction conditions. In comparison to the *N*-tosyl derivatives the synthesis of the dansyl substituted compounds resulted in lower yields. Finally, the 1-(9-anthracenyl) propargyl prenyl ether (**2d**) and alkynyl *ortho*-iodo anilides **1** were successfully transformed into the anthryl substituted spirocyclic indolones **4g–k** in moderate yields. The latter bichromophores were obtained as bright yellow solids.

The deprotection of the Boc group of the spirocyclic indolone **4a** and **4h** is quantitatively achieved upon reaction with two equivalents of anhydrous zinc bromide in dry dichloromethane for two hours at room temperature[13] giving rise to the isolation of the free amides **4l** and **4m** (Scheme 3). The structures of all new spirocyclic chromophores were unambiguously supported by extensive ^{1}H and ^{13}C NMR and IR spectroscopy, mass spectrometry and combustion analysis.
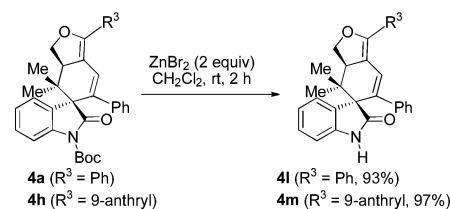
Scheme 3 Zn^{2+}-mediated deprotection of the Boc group of compounds **4a** and **4h**.

The photophysical properties of all luminophores **4** were determined by UV/vis and fluorescence spectroscopy (Table 3).

The 1,4-diaryl butadiene chromophore embedded in the spirocycles with *N*-Boc substitution (entries 1–3) displays relatively sharp absorption maxima around 350 nm and around 360 nm if the *N*-substituent is a dansyl moiety (entries 4–6). The molar extinction coefficients of the longest wavelength absorption

Table 2 Synthesis of novel spirocyclic indolones **4**

Entry	Arylethynyl *ortho*-iodo anilide **1**	Propargyl prenyl ether **2**	Spirocyclic indolone **4** (yield)[a]
1	R$_1$ = Boc, R$_2$ = Ph (**1b**)	R$_3$ = C$_6$H$_5$ (**2a**)	**4a** (44%)
2	**1b**	R$_3$ = *p*-ClC$_6$H$_4$ (**2b**)	**4b** (21%)
3	**1b**	R$_3$ = *p*-MeOC$_6$H$_4$ (**2c**)	**4c** (23%)
4	R$_1$ = dansyl, R$_2$ = Ph (**1c**)	**2b**	**4d** (24%)
5	R$_1$ = dansyl, R$_2$ = *p*-ClC$_6$H$_4$ (**1d**)	**2b**	**4e** (37%)
6	R$_1$ = dansyl, R$_2$ = *p*-MeOC$_6$H$_4$ (**1e**)	**2b**	**4f** (24%)
7	**1a**	R$_3$ = 9-anthryl (**2d**)	**4g** (50%)
8	**1b**	**2d**	**4h** (21%)
9	**1c**	**2d**	**4i** (13%)
10	**1d**	**2d**	**4j** (50%)
11	**1e**	**2d**	**4k** (29%)

[a] Isolated yields after chromatography and recrystallization.

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Table 3 Selected absorption and emission data of the new spirocyclic indolones **4** (recorded in CH_2Cl_2 at 298 K)

| Entry	No.	$\lambda_{abs,max}$ [nm] (ε) [L cm^{-1} mol^{-1}]	$\lambda_{em,max}$ [nm] (Φ_f)	Stokes shift $\Delta\tilde{v}$ [cm^{-1}][a]
1	**4a**	347 (19 100)	470, 510 (0.30)[b]	7500
2	**4b**	348 (18 800)	469, 512 (0.25)[b]	7100
3	**4c**	350 (18 900)	480, 508 (0.39)[b]	7700
4	**4d**	353 (18 800)	487, 512 (0.04)[b]	7800
5	**4e**	356 (15 200)	486, 510 (0.06)[b]	7500
6	**4f**	358 (24 900)	478, 511 (0.02)[b]	7050
7	**4g**	321 (17 200)	528, 557 (0.02)[c]	6800
		368 (10 600)		
		387 (10 500)		
8	**4h**	320 (19 300)	532, 555 (0.02)[c]	7050
		367 (10 100)		
		387 (10 600)		
9	**4i**	326 (10 800)	523, 561 (0.02)[c]	6800
		366 (7700)		
		385 (6800)		
10	**4j**	330 (22 000)	523, 564 (0.02)[c]	6800
		367 (16 700)		
		386 (14 700)		
11	**4k**	327 (22 800)	531, 558 (0.01)[c]	7200
		366 (15 700)		
		384 (13 500)		
12	**4l**	347 (19 100)	473, 511 (0.30)[b]	8100
13	**4m**	318 (18 500)	524, 565 (0.01)[c]	6800
		367 (9500)		
		386 (9200)		

[a] Stokes shift $\Delta\tilde{v} = \tilde{v}_{max,abs} - \tilde{v}_{max,em}$. [b] Determined with quinine sulfate as a standard (0.1 M H_2SO_4) $\Phi_f = 0.54$.[14] [c] Determined with coumarin 153 as a standard in ethanol $\Phi_f = 0.38$.[15]

maxima of the dyes **4a–4f** range from 15 200 to 24 900 L cm^{-1} mol^{-1}. In the fluorescence spectra of these compounds two maxima can be identified, the intense maximum around 510 nm and a short wavelength shoulder around 470 nm. In case of *N*-dansyl substitution (entries 4–6) the shoulder is less distinctive than in case of *N*-Boc substitution (entries 1–3) resulting in a turquoise fluorescence of the former compared to the blue luminescence of the Boc derivatives.

The Stokes shifts $\Delta\tilde{v}$ of dyes **4a–f** lie between 7000 and 7800 cm^{-1}, *i.e.* more or less in the same area as reported for the first generation spirocycles.[8b] The quantum yields, Φ_f, obtained for the *N*-Boc substituted chromophores **4a–c** are an order of magnitude larger than those obtained for the *N*-dansyl derivatives **4d–f**. Apparently, the interaction of the 1,4-diarylbutadiene and the dansyl chromophore in the excited state is accompanied by a deactivation of both luminophores.

Most interestingly, anthracenyl substituted spirocycles **4g–k** reveal a significantly deviating absorption and emission behavior compared to the first representatives of the series. In the UV/vis spectra three discrete maxima and a shoulder can be assigned to the characteristic absorption bands of the butadiene and the anthracene chromophores. The longest wavelength maximum of anthracene is typically located around 385 nm and the corresponding molar extinction coefficients range from 6800 to 14 700 L cm^{-1} mol^{-1}. The broad maximum at around 325 nm stems from the butadiene moiety with extinction coefficients up to 22 800 L cm^{-1} mol^{-1}. In contrast to the absorption spectra the emission spectra of the anthryl substituted compounds **4g–k** are very similar to those of the aryl substituted dyes **4a–f** (Fig. 2).

However, instead of the expected typical anthracene and butadiene emission fingerprints, only a relatively sharp emission
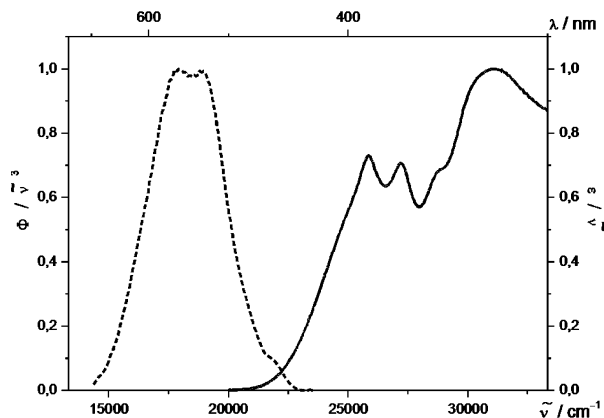
Fig. 2 Absorption (—) and emission (---) spectra of **4g** (recorded in CH_2Cl_2 at 298 K and at $c(\mathbf{4g}) = 10^{-3}$ M (absorption) and $c(\mathbf{4g}) = 10^{-6}$ M (emission)).

band with two discrete maxima is observed. In addition, and in comparison to the luminescence spectra of the dyes **4a–f**, the emission maxima are considerably shifted bathochromically by 50 nm and appear between 525 and 560 nm, resulting in an intense yellow fluorescence. The calculated Stokes shifts $\Delta\tilde{v}$ lie between 6800 and 7200 cm^{-1}. The quantum yields Φ_f of dyes **4g–k** are surprisingly low and do not exceed 0.02. Interestingly, the photophysical data of the chromophores **4l** and **4m** containing a free amide functionality are essentially identical with their Boc analogues **4a** and **4h**.

For a deeper understanding of the large Stokes shifts and the anthracenyl effect TDDFT calculations[16] of the ground state S_0 and of the relaxed first excited state S_1 were realized with a

spiroindolone model system containing an *N*-methyl substituent and embedded 1,4-diphenylbutadiene chromophore. According to the calculations, in the electronic ground state S_0 both terminal phenyl rings are significantly twisted out of coplanarity with the butadiene plane. The phenyl ring in position 1 is twisted by 28.0° and the 4-substituent is rotated by 48.0°. In contrast the computed relaxed S_1 geometry reveals an extensive coplanarization of both phenyl rings with corresponding torsional angles of 14.1° and 28.5°, respectively (Fig. 3).
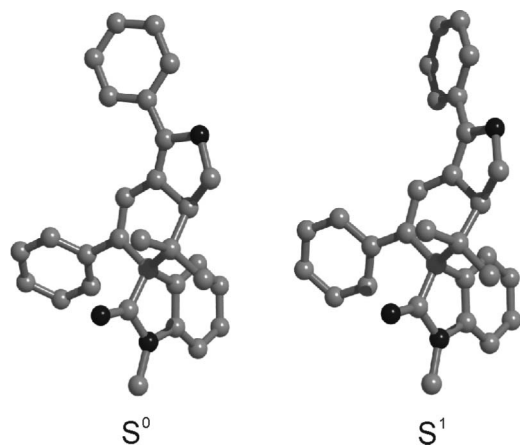

Fig. 3 TDDFT-optimized structures of the S_0 (left) and S_1 (right) state.

On the basis of these results, the absorption spectra of the anthryl substituted dyes can be qualitatively rationalized. In the S_0 state the anthryl substituent is significantly twisted out of the butadiene plane and thus both chromophores are essentially electronically decoupled. The anthracenyl absorption fingerprints clearly appear in the spectra. Excitation and relaxation to the S_1 state coplanarizes the anthryl group with the butadiene chromophore, resulting in a considerable expansion of the π-conjugation and hence, in a significant bathochromic shift of the emission maxima.

In conclusion we synthesized novel bichromophoric spirocyclic indolones. Whereas the simple *N*-Boc derivatives show intense blue fluorescence, *N*-dansyl substitution results in a turquoise emission. 1-Anthryl substitution on the butadiene causes significantly different absorption and emission properties due to large geometrical changes upon excitation. Studies addressing bichromophoric spiroindolones with enhanced excited state communication and interactions are currently underway.

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