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Synthesis of of 5,10-dihydrobenzo[*a*]indolo[2,3-*c*]carbazoles via Scholl reaction of 1,2-bis(indol-2-yl)benzenes, promising molecules for optoelectronic applications

Drs. Mathias Daniels, Flip de Jong, Dr. Koen Kennes, Dr. Cristina Martin, Prof. Johan Hofkens, Prof. Mark Van der Auweraer, and Prof. Wim Dehaen**

Drs. Mathias Daniels, Prof. Wim Dehaen: Molecular Design and Synthesis, Department of Chemistry, KU Leuven, Leuven Chem&Tech Celestijnenlaan 200F, 3001 Leuven, Belgium
Dr. Koen Kennes, Dr. Cristina Martin, Prof. Johan Hofkens, Prof. Mark Van der Auweraer: Molecular Imaging and Photonics, Department of Chemistry, KU Leuven, Leuven Chem&Tech - Celestijnenlaan 200F, B-3001 Leuven, Belgium.
E-mail: cristina.martinalvarez@kuleuven.be , http://hofkensgroup.org ,
wim.dehaen@kuleuven.be, https://chem.kuleuven.be/en/research/mds/losa

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Abstract:

Only a few straightforward procedures for the preparation of indolo[2,3-*c*]carbazoles are known, despite promising features for material applications. Herein we present a convenient synthesis of 5,10-dihydrobenzo[*a*]indolo[2,3-*c*]carbazoles via oxidative cyclization of 1,2-bis(1H-indol-2-yl)benzenes prepared from readily accessible starting materials. Functionalization through electrophilic aromatic substitution reactions and palladium catalyzed cross-coupling reactions were investigated leading to the isolation of new functionalized 5,10-dihydrobenzo[*a*]indolo[2,3-*c*]carbazoles, whose steady state electronic spectroscopy has been examined.

1. Introduction

Indolocarbazoles are nitrogen-containing fused polyaromatic molecules with five possible isomers. For most of these isomers, interesting optoelectronic and biological properties have been described together with their synthetic methods or isolation.[1] Being an analogue of carbazole, with a large, planar, rigid, conjugated structure, they are characterized with similar interesting properties, such as thermal and chemical stability, but with a higher hole mobility, and stronger electron-donating character than carbazole.[2, 3] These properties make them interesting materials for transistors, photovoltaic cells and dye-sensitized solar cells.[3, 4] Another possibility is their implementation in organic light emitting diodes (OLED), where the indolocarbazole derivatives have been used either as host materials for different phosphorescent devices or as a dopant/host in thermally-activated delayed fluorescence (TDAF) OLEDs. [5, 6]

Several isomers have been reported in those applications, the most ubiquitous being the indolo[3,2-*b*]carbazole, on which we reported several synthetic methodologies.[7, 8] On the other hand,the indolo[2,3-*c*]carbazole isomers offer interesting possibilities for the use in organic light-emitting diodes and similar devices,[9] but were not yet fully explored.

Several synthetic procedures have been investigated but most of them are rather elaborate or complicated. Simple 5,8-dihydroindolo[2,3-*c*]carbazole **1a** (**Figure 1**) has been prepared using cyclization reactions in diphenyl ether,[10] palladium catalyzed cyclization in acetic acid[11] and the Cadogan reaction,[9] all requiring rather drastic reaction conditions. The methylated analog *N,N'*-dimethylindolo[2,3-*c*]carbazole 1b was prepared photochemically in two steps from *N,N'*-dimethyl-*N,N'*-diphenyl-1,4-phenylenediamine.[12]

Similarly, a few synthetic pathways toward benzo[*a*]indolo[2,3-*c*]carbazoles are known. Previously these compounds have been prepared using a gold(I)-catalyzed cascade cyclization and a thermal nitrene insertion.[13, 14] We considered that the preparation of these compounds could be simplified significantly by using more readily available starting materials like indole. In this contribution we present a novel synthetic approach for indolo[2,3-*c*]carbazole and demonstrate potential pathways for functionalization. The basic electronic spectroscopic properties of these derivatives are probed in toluene and acetonitrile.

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2. Results and Discussion

Synthesis:1,2-Bis(indol-2-yl)benzenes **3a-d** were prepared through Negishi-coupling[15] of *N*-substituted indoles with 1,2-dibromobenzene (**Scheme 1**). Organozinc derivatives of indoles were prepared in situ by 2-lithiation of indoles **2a-d** with n-butyllithium and subsequent reaction with $ZnCl_2$. Lithiation of *N*-phenylsulfonyl indole proceeded quickly, even at low temperatures. For the lithiation of other indoles, longer reaction times at room temperature were required. Subsequent coupling with 1,2-dibromobenzene was catalyzed by $Pd(PPh_3)_4$ in 1,2-dimethoxyethane (DME) under reflux. Tetrahydrofuran (THF) can be used as an alternative for DME, but the isolated yield is significantly lower. The coupled compounds **3a-d** were obtained in moderate to high yield. The phenylsulfonyl protecting group was easily removed from **3d** with tetrabutylammonium fluoride in THF at reflux to yield compound **3e** in 67% yield (Scheme 1).

Oxidative cyclization of 1,2-bis(indol-2-yl)benzene (**Scheme 2**) was accomplished with iron(III) chloride in DCM, an effective and economical reagent for the Scholl reaction.[16] Reaction conditions were optimized for the phenyl substituted compound **3c**. When a DCM:nitromethane (10:1) solvent combination was used, complete conversion could be obtained with shorter reaction times, but the isolated yield decreased significantly. Similarly, shorter reaction times could be realized by an increase in reaction temperature from room temperature to 50°C (DCE) with only a minor decrease in isolated yield (**Table 1**). The desired products **4** could also be isolated after oxidative cyclization with DDQ (2,3-dichloro-5,6-dicyano-p-benzoquinone) in the presence of a Lewis acid ($BF_3.Et_2O$). When these reaction conditions were used, an increase in isolated yield was observed compared to the reaction with iron(III) chloride. Another advantage is the significantly shorter reaction time needed for the complete conversion of the starting material. Although all *N*-protecting groups are rather robust, a decreased stability of the alkylated indolocarbazoles was observed. Alkylated product **4b** showed increased solubility in most organic solvents, but was significantly more sensitive to light than **4c**.

The expected indolocarbazoles **4** could be isolated after most reactions. Only the cyclization of the phenylsulfonyl protected bis-indole **3d** with iron(III) chloride in the presence of nitromethane resulted in the formation of spiro-indole **5** in low yield (**Scheme 3**). Reaction with DDQ or under photocyclization conditions resulted in the almost complete recovery of starting material **3d**.

Functionalization *via* different electrophilic aromatic substitution reactions was investigated on dibutyl-benzo[*a*]indolo[2,3-*c*]carbazole **4b** and diphenyl-benzo[*a*]indolo[2,3-*c*]carbazole **4c** (**Scheme 4**). Acylation with acetyl chloride in the presence of aluminum(III) chloride of **4c** at room temperature yields both mono- (**7**), di- (**8**) and tri- (**9**) substituted products. These products **7-9** can be easily separated and by adjusting the amount of reagent according to the desired product, a reasonable yield can be obtained (Table 2). Another advantage of this reaction is that the introduction of one or multiple acyl groups significantly increases the solubility. No product could be isolated after acylation of **4b** under similar conditions, and even at 0°C, decomposition of the starting material and/or product was unavoidable. After bromination of dibutyl compound **4b** in dichloromethane (DCM) with NBS, the dibrominated compound **6** can be obtained in a 83% yield. The reaction time can be decreased from several days to 5 hours by using 2.2 equivalents of NBS and only a small reduction in isolated yield (73%) was observed. The monobrominated product could not be obtained, as the bromination with less than 2 equivalents of NBS resulted in an inseparable mixture of starting material, mono- and dibrominated products. In the bromination reaction of diphenyl compound **4c** with NBS, no complete conversion can be obtained at room temperature even after long reaction time and excess of NBS. Reaction at higher temperatures results in the formation of a very complicated mixture. When NBS was exchanged for bromine, complete conversion can be obtained, but the product formed was impossible to characterize or use due to poor solubility. Formylation of **4c** with DMF and $POCl_3$ under classical Vilsmeier conditions at room temperature resulted in the complete recovery of starting material. Even at high temperatures and with significant excess of reagents, formylation of compound **4b** was not possible, only decomposition of starting material was observed. However, Rieche formylation with tin(IV)chloride and dichloromethyl-methylether in DCM at 0°C resulted in the formation of the di-formylated compound **10**, which could be isolated in a 67% yield. Comparable conditions were tested for the formylation of **4b**, but no product can be isolated. Brominated compound **6** can be used in various metal catalyzed reactions. As an example the Suzuki cross-coupling with 4-cyanophenylboronic acid **11** to form compound **12** in 42% yield and the Heck reaction with methyl acrylate **13** to form compound **14** in 45% yield are shown in **Scheme 4**. Following similar strategies, rapid access to more functionalized analogs is possible (**Scheme 4**).

To sum up, we developed a straightforward and efficient method for the synthesis of benzo[*a*]indolo[2,3-*c*]carbazoles from *N*-substituted indoles employing a palladium catalyzed Negishi-coupling with 1,2-dibromobenzene followed by a Scholl reaction with 2,3-dichloro-5,6-dicyano-p-benzoquinone and boron trifluoride etherate. Different functionalized analogs were prepared through electrophilic aromatic substitution reactions. The reactivity of 2,13-dibromo benzo[*a*]indolo[2,3-*c*]carbazole in the palladium catalyzed Suzuki and Heck cross coupling reactions was investigated.

Photophysics: Figures 2 and 3 show the normalized steady-state absorption and emission spectra of benzo[*a*]indolo[2,3-*c*]carbazole derivates in toluene and acetonitrile, respectively (**Table 3**). In order to be able to compare the influence of the different substituents, the results were divided in two families: in the first family the *N*-position of the benzo[*a*]indolo[2,3-*c*]carbazole is substituted by an alkyl chain (**4b**, **6** and **14**), while in the second class the same position is substituted by a phenyl group in (**4c, 7, 8, 9** and **10**). As it can be seen in Figures **2A-C and Figure 3A-C**, compounds **4b**, **4c** and **6** show several transitions with a resolved vibrational fine structure resembling those of other indolocarbazoles[17] both in toluene and acetonitrile. The $S_0 \rightarrow S_1$ transition is at about 1500 cm^{-1} higher energy than those of 5,11-dihydroindolo[3,2-*b*]carbazoles (**Table 3**). This indicates that the transitions are localized in the indolocarbozole moiety, as has previously been reported for dihydrobenzindolocarbazoles.[8, 13, 18]_ENREF_22 For compounds **7**, **8** and **10,** the individual vibronic bands become broader and less outspoken while they are merged in a structureless band for compounds **9** and **14** suggesting a progressive increase of the charge transfer character or increased coupling with low energy, possibly torsional, vibrations of the $S_0 \rightarrow S_1$ transition. One should note also that for compound **9** the $S_0 \rightarrow S_1$ transition is shifted over 2000 cm^{-1} to longer wavelengths compared to the other compounds (**Table 3**). This indicates that for the latter compound the acetophenone substituent on the nitrogen is part of the conjugated system involved in the $S_0 \rightarrow S_1$ transition. For all compounds except **4b** (**Table 3**) a minor blue shift of the absorption maximum occurs between toluene and acetonitrile. This can be attributed to a decreased polarisability of acetonitrile[19] and indicates furthermore that none of the molecules have an appreciable dipole moment in the ground state. For compounds **4b**, **4c**, **6**, **8** and **10** the emission spectra in toluene (**Figure 2B-D**) are a mirror image of the $S_0 \rightarrow S_1$ transition of the absorption spectra. They combine a small Stokes shift with vibrational fine structure in toluene suggesting a transition mainly localized on the dihydrobenzindolocarbazole moiety. The similarity between **4b** on one hand and **4c** or **6** on the other hand indicates that the *N*-phenyl groups are not involved in the conjugation in these compounds. For **7**, **8** and **10** both the Stokes shift and FWHM of the emission spectra are about 50% larger than for **4b**, **4c** and **6**. This can be associated with a coupling with torsional vibrations of the carbonyl moieties and an increased coplanarity of these moieties in the excited state. Furthermore one can not exclude that the excited state has some charge transfer character. Both factors indicate that the carbonyl substituents participate in the LUMO. For compounds **9** and **14** the emission spectrum is a structureless band with increased Stokes shift (from 600 à 900 cm^{-1} to 3260 cm^{-1}) especially for compound **14**. This suggests a stronger interaction with the carbonyl moieties and/or a larger excited state dipole moment. In acetonitrile the emission spectra of compounds **4b**, **4c** and **6** (**Figure 3B-D**) resemble those in toluene and have a similar Stokes shift and FWHM. This indicates that for these compounds also the excited state has no appreciable dipole moment or charge transfer character. However the spectra of compounds **7**, **8** and **10** become structureless and broader and are characterized by a much larger Stokes shift (**Table 3**). This indicates that for the latter compounds the dipole moment of the relaxed excited state is much larger than that of the ground state in acetonitrile suggesting an outspoken charge transfer character of the relaxed excited state in polar solvents as has been observed previously for similar charge transfer molecules.[6, 20] The emission spectra of compounds **9** and **14** become broader and undergo a red shift (less pronounced for compound **9**) compared to analogous spectra in toluene. These features indicate that the introduction of electron withdrawing groups and especially the acrylate moieties favor the charge transfer process from indolocarbazole moiety to electron accepting group. The increase of the Stokes shift is more than two times smaller for **9** compared to **7**, **8**, **10** and **14**, indicating an excited state dipole moment that is at least 30% smaller:[21] _ENREF_41 This is probably due to a decreased electron donating character of one of the nitrogens in **9** due to the acetophenone substituent. It is furthermore worth noting that the quantum yield of molecule **6** (3.3±0.3%) is low despite the fact that the bromine atom is not strong enough to induce a noticeable charge transfer character (Table 3). However, since Br is a heavy atom, an increased rate of intersystem crossing and hence,[22] a lower quantum yield of fluorescence can be expected.

3. Conclusions

We presented a straightforward and efficient method for the synthesis of benzo[*a*]indolo[2,3-*c*]carbazoles from N-substituted indoles employing a palladium catalyzed Negishi-coupling with 1,2-dibromobenzene followed by a Scholl reaction with 2,3-dichloro-

5,6-dicyano-p-benzoquinone and boron trifluoride etherate. Different functionalized analogs were prepared through electrophilic aromatic substitution reactions. The reactivity of 2,13-dibromo benzo[*a*]indolo[2,3-*c*]carbazole in the palladium catalyzed Suzuki and Heck cross coupling reactions was investigated. The basic electronic spectroscopy has been examined in two solvents with different polarity, which revealed a large charge transfer character for the compounds with electron-withdrawing substituents. A peculiar result was obtained for the compound possessing a COCH3 substituent on one of the N-phenyls, where a decrease of the electron donating propeties of the carbazole moiety induced a significant red shift of the absorption spectrum. In a follow-up study the spectroscopy and photophysics of this promising building block and its possible application in OLEDs will be systematically investigated.

4. Experimental Section

Spectroscopy measurements: UV-visible steady-state absorption and emission spectra were recorded using a Lambda-950 spectrometer and Edinburgh FLS980 fluorometer. The fluorescence spectra were corrected for the wavelength dependence of the detector channel. The fluorescence quantum yields were determined using an integrating sphere.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Tables, Schemes and Figures:

Table 1: Oxidative cyclization

R	Oxidant	Solvent	Temperature	Reaction time	Yield (%)
Ph	$FeCl_3$[a]	DCM	rt	9days	91
Ph	$FeCl_3$[b]	DCM:CH_3NO_2	0°C to rt	2days	72
Ph	$FeCl_3$[b]	DCM:CH_3NO_2	rt	3days	50
Ph	$FeCl_3$[a]	DCE	50°C	14h	79
Ph	$FeCl_3$[b]	DCE:CH_3NO_2	50°C	14h	42
Ph	DDQ/BF_3•Et_2O[c]	DCM	0°C to rt	1h	96
H	DDQ/BF_3•Et_2O[c]	DCM	0°C to rt	1h	67
CH_3	DDQ/BF_3•Et_2O[c]	DCM	0°C to rt	1h	90
C_4H_9	DDQ/BF_3•Et_2O[c]	DCM	0°C to rt	1h	100

a. Reaction conditions: Iron trichloride (2.2eq) was added to **3** (0.01M solution in DCM or DCE) at the indicated temperature.

b. Reaction conditions: Iron trichloride (2.2eq, 0.22M solution in nitromethane) was added dropwise to **3** (0.01M solution in DCM or DCE) at the indicated temperature.

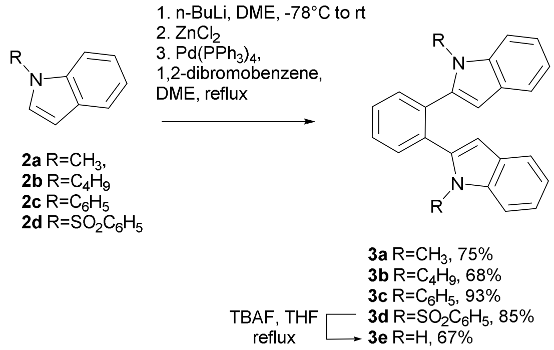
c. DDQ (1.5eq) was added to a mixture of **3** (0.01M solution in DCM) and boron trifluoride etherate (10eq) at 0°C.

Table 2: Acylation of **4c**

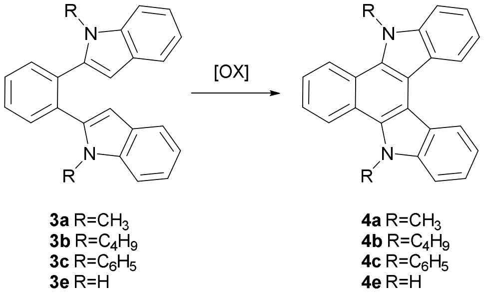
Amount of reagent	Yield
1 eq	**4c** (27%), **7** (50%), **8** (13%)
2.2 eq	**7** (trace), **8** (73%)
5 eq	**8** (19%), **9** (43%)

Table 3. Steady-state absorption and fluorescence emission maxima, Stokes shift, full width at half maximum of the emission spectrum and fluorescence quantum yield of the investigated compounds.

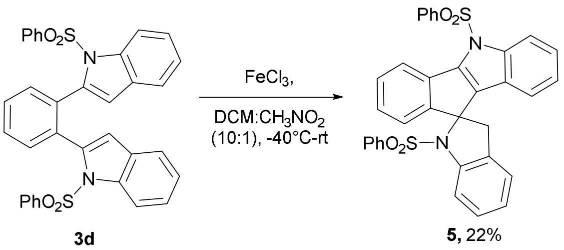
	Molecule	**λ_{abs} / nm**	**λ_{em} / nm**	**(ν_{abs} - ν_{em}) / cm^{-1}**	**FWHM$_{em}$ / cm^{-1}**	**ϕ**
toluene	**4b**	412	423	630±50	2360±50	0.35±0.04
	4c	400	410	610±50	2200±50	0.40±0.04
	6	418	429	610±50	2760±50	0.03±0.01
	7	399	414	910±50	3220±50	0.28±0.03
	8	397	412	920±50	3110±50	0.28±0.03
	9	434	471	1810±50	3180±50	0.27±0.03
	10	393	408	930±50	4080±50	0.21±0.02
	14	412	476	3260±50	4090±50	0.16±0.02
acetonitrile	**4b**	413	420	400±50	2560±50	-
	4c	398	410	740±50	2380±50	-
	6	413	428	850±50	2580±50	-
	7	396	523	6130±50	4590±50	-
	8	395	498	5240±50	4690±50	-
	9	426	510	3870±50	3650±50	-
	10	392	523	6390±50	4520±50	-
	14	407	595	7760±50	4380±50	-



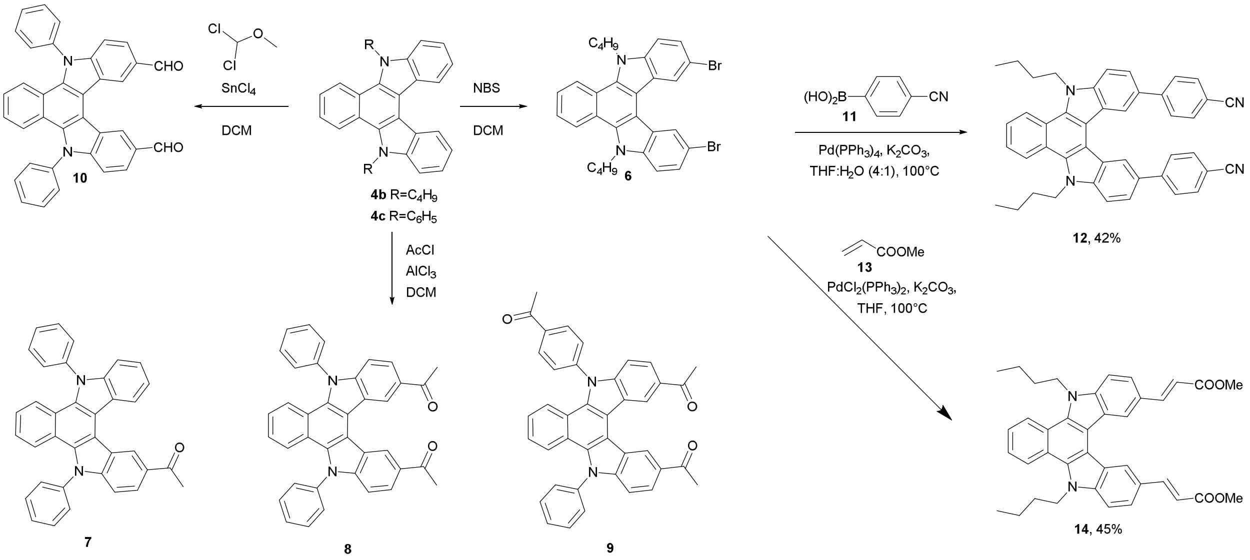
Scheme 1: Negishi coupling of indoles with 1,2-dibromobenzene



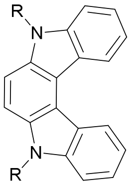
Scheme 2: Oxidative cyclization



Scheme 3: Formation of spiro-indole **5**



Scheme 4: Electrophilic aromatic substitution of benzo[*a*]indolo[2,3-*c*]carbazole **4b,c** and palladium catalyzed reactions of dye **6**



1a R=H
1b R=CH_3

Figure 1. Skeleton of indolo[2,3-*c*]carbazole.

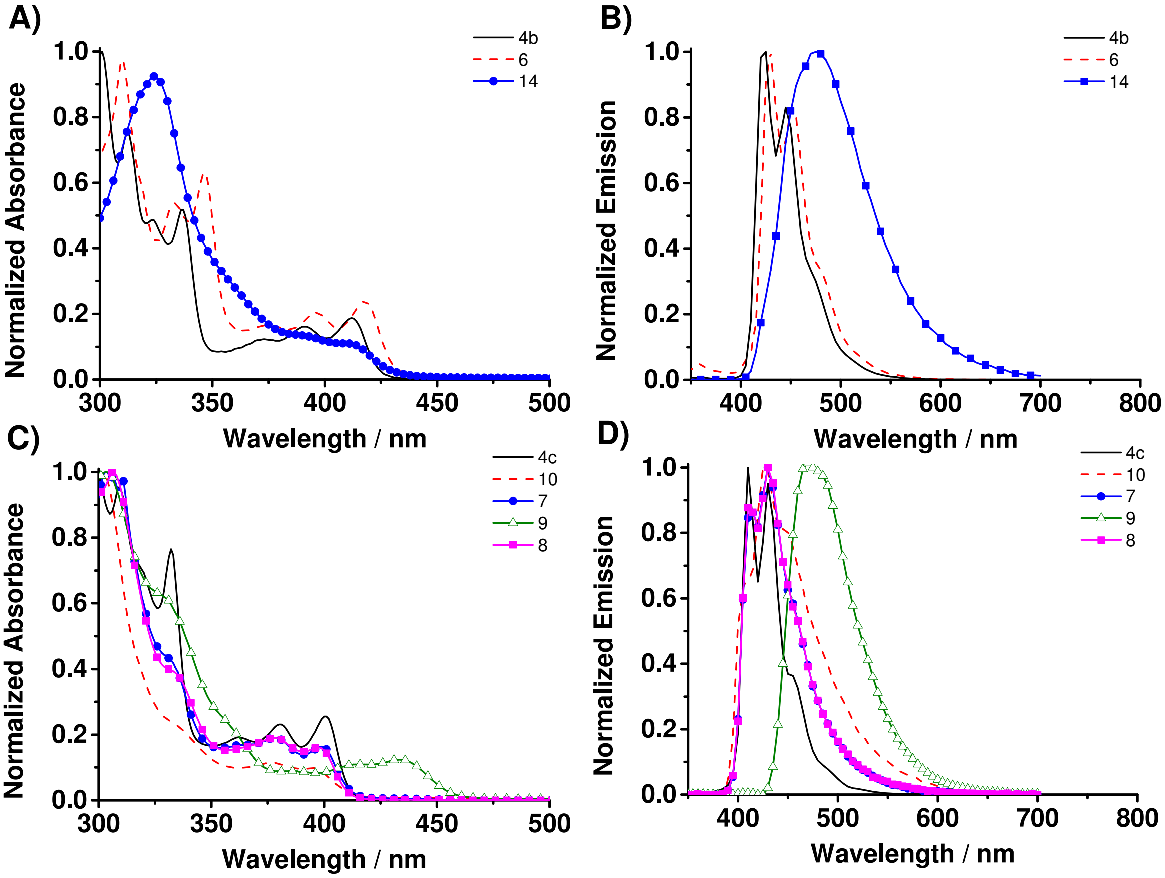


Figure 2. Normalized UV-visible absorption (A and C) and emission (B and D) of indolocarbazole molecules in toluene solution (~10^{-5} M). For emission, the excitation wavelength was 335 nm.

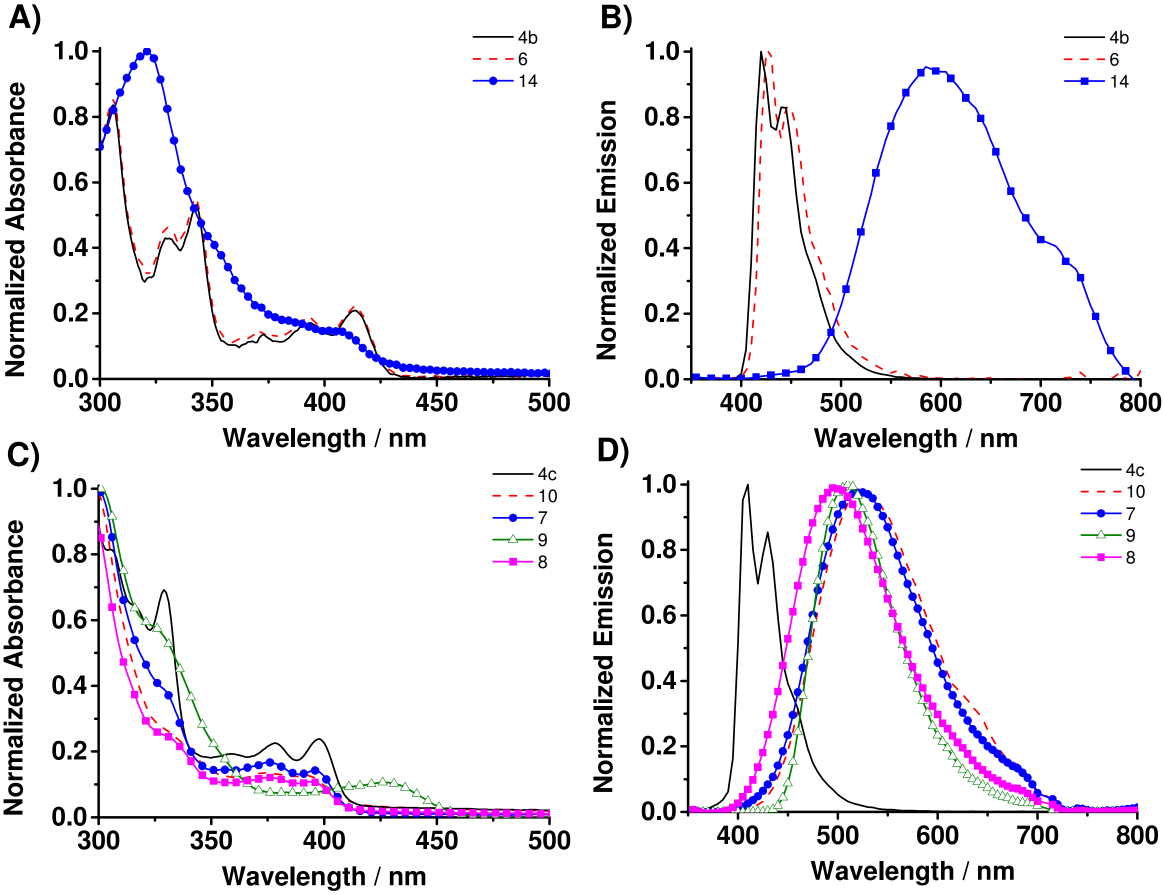
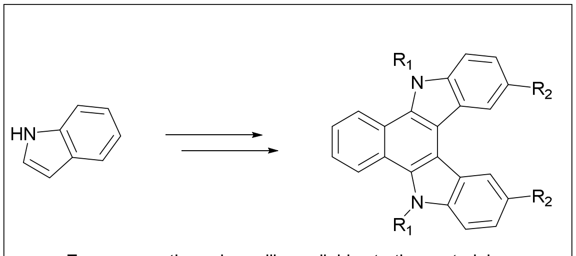


Figure 3. Normalized UV-visible absorption (A and C) and emission (B and D) of indolocarbazole molecules in acetonitrile solution (~10^{-5} M). For emission, the excitation wavelength was 335 nm.

The table of contents entry should be 50–60 words long,

The promising properties of indolocarbazoles for optoelectronic applications inspire to find new derivates of those emitters. In this contribution, new synthetic methods via oxidative cyclization were established to obtain 5,10-dihydrobenzo[*a*]indolo[2,3-*c*]carbazole. Several strategies for functionalization were explored, including palladium-catalyzed cross-coupling reactions. Steady-state electronic spectroscopy revealed interesting properties for optoelectronic applications.



Easy access through readily available starting materials

Keywords:, Indolo[2,3-*c*]carbazoles, Scholl reaction, fluorescence, indole, fused-systems, photophysics, UV-Vis spectroscopy