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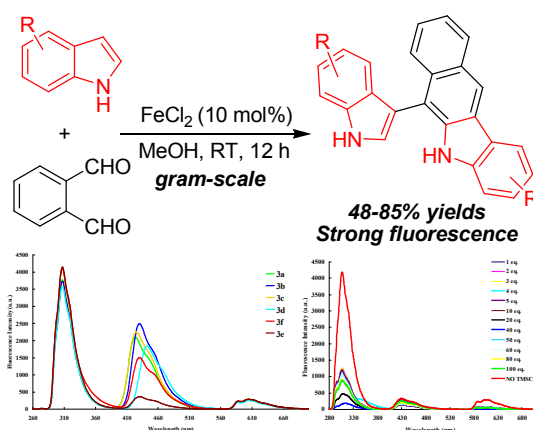
Graphic Abstract for *RSC Advances*

Fe-Catalyzed Cycloaddition of Indoles and *o*-Phthalaldehyde for the Synthesis of Benzo[*b*]carbazoles with TMSCl- or Acid-responsive Properties

Jin-Feng Zou,^a Hu Wang,^a Li Li,^{*a} Zheng Xu,^a Ke-Fang Yang^a, and Li-Wen Xu^{*a,b}

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The indolyl benzo[*b*]carbazoles that achieved by iron catalysis via sequential carbon-carbon bond-forming reaction could be worked as fluorescent sensors for TMSCl and acid.

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ARTICLE TYPE

Fe-Catalyzed Cycloaddition of Indoles and *o*-Phthalaldehyde for the Synthesis of Benzo[*b*]carbazoles with TMSCl- or Acid-responsive Properties

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The one-pot iron-catalyzed cycloaddition of indole and *o*-phthalaldehyde afforded indolyl benzo[*b*]carbazoles via sequential carbon-carbon bond-forming addition, cyclization involving intramolecular alkylation and aromatization forming a benzene ring. In addition, the fluorescence properties of such indolyl benzo[*b*]carbazoles were also investigated, in which it showed significant changes in fluorescent intensity upon addition of trimethylchlorosilane (TMSCl) or trifluoroacetic acid (TFA).

Carbazoles are important alkaloids displaying significant biological activities and physicochemical properties.¹ In the past years, the construction of carbazoles and its derivatives has been attracted considerable attention because of their applications in pharmacological chemistry and material science.² For examples, carbazole derivatives were widely used as building blocks for potential organic light-emitting diodes (OLED),³ electroluminescent materials.⁴ Very recently, they have been observed as potential anticancer agents,⁵ and especially in 2011, benzocarbazole analogues were discovered as highly selective and potent anaplastic lymphoma kinase (ALK) inhibitors.⁶

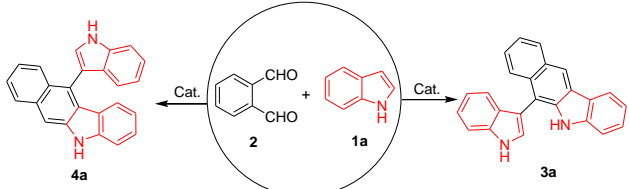
Consequently, syntheses of carbazoles and benzocarbazoles have been extensively studied in the past decades.⁷ Notably in this context, Ma group recently reported a route to construct carbazole alkaloids via the PtCl₂-catalyzed cyclization of 1-(indol-2-yl)-2,3-allenols.^{7m,n} In particular, a number of useful synthetic approaches are available now for catalytic synthesis of benzo[*b*]carbazoles.⁸ For instances, Tsuchimoto and Shirakawa^{2a} reported a concise synthesis of benzocarbazoles through indium-catalyzed annulation of 2-arylindoles with propargyl ethers. Sa á and coworkers^{8a} described an approach to carbazoles by means of intramolecular dehydro Diels-Alder reactions of ynamides, which allowed the synthesis of carbazoles and benz-annulated carbazoles in moderate to good yields. Snieckus et al.^{8b} found that a general anionic N-C carbamoyl migration of 2-arylindoles offered an alternative to benzocarbazoles in low to moderate yields. Very recently, Turner and Procter^{8c} developed a new

synthetic strategy to benzo[*b*]carbazoles that the induction and removal of a phase tag in combination with tag-assisted purification have been used to trigger cyclization events in the synthesis of benzo[*b*]carbazole end-capped oligothiophenes. On the other hand, intramolecular cyclodehydration has also attracted much attention for their application in the construction of benzo[*b*]carbazole-based building blocks. As a down-to-date example, Jana and coworkers^{8k} have demonstrated an iron(III)-catalyzed novel and efficient strategy for the synthesis of structurally diverse benzo[*b*]carbazoles, in which the intramolecular domino isomerization/cyclization/aromatic reaction substituted 2-[(indoline-3-ylidene)(methyl)]benzaldehyde derivatives could be easily made in the presence of FeCl₃. However, many of previous protocols have some limitations, such as the difficulty in the preparation of the starting substrates, lengthy synthetic sequences, harsh reaction conditions, and unsatisfied chemical yields calculated from commercial available materials. Accordingly, the development of new approaches for the construction of benzo[*b*]carbazoles derivatives is highly desirable. Herein, we now report a facile process to the synthesis of indolyl benzo[*b*]carbazoles using easily available compounds via intermolecular cycloaddition of indoles and *o*-phthalaldehyde. In addition, the novel indolyl benzo[*b*]carbazoles, readily prepared by the present one-pot approach, is disclosed to exhibited highly strong fluorescence intensity because of the existence of π -conjugated system on benzo[*b*]carbazoles.

Our initial investigation began with the coupling reaction of indole **1a** with *o*-phthalaldehyde **2**, in the presence of TsOH (4-methylbenzenesulfonic acid). Interestingly, when the reaction was carried out in various solvents at room temperature with 10 mol% of TsOH as catalyst, two different indolyl benzo[*b*]carbazoles **3a** and **4a** were obtained unexpectedly in varied ratios.⁹ Under the Brønsted acid catalysis, reaction of indole **1a** and *o*-phthalaldehyde led to the formation of mixture **3a** and **4a** (Entries 1-4, Table 1). Although the total yield was excellent in acetonitrile, there is no selectivity in the domino addition/cyclodehydration reaction. Dichloromethane and tetrahydrofuran resulted in the **4a**-selective product from the ratio

of 45/55 to 18/82 (**3a/4a**), while methanol facilitated the formation of **3a** in good selectivity (**3a/4a** = 87/13, entry 1 of Table 1). These preliminary results in this reaction prompted us to investigate the effect of various Brønsted acid or Lewis acid catalysts, in which it was expected to determine a highly efficient catalyst system for the synthesis of atropisomeric benzo[*b*]carbazoles **3a** or **4a**. To test the above idea, we then attempted to carry out the screening experiment. As shown in Table 1, representative and commercially available Brønsted acid or Lewis acid catalysts gave different results in term of yield and chemoselectivity. Except THF, almost all catalysts evaluated in this work resulted in the formation of major product **4a** and minor **3a** in non-protic solvents (such as CH₃CN and DCM). For examples, catalytic amount of I₂ gave the mixture of **3a/4a** in 67% yield (Entry 5, **3a/4a** = 37/63), and other Lewis acid or Brønsted acid catalysts including FeCl₂, Al(OTf)₃, Bi(OTf)₃, TfOH, and TMSOTf gave similar selectivities (up to 27/73 of **3a/4a**, entries 7, 13, 15, 18 and 20 respectively). Fortunately, it was found that FeCl₂ was good catalyst for the coupling reaction of indole **1a** and *o*-phthalaldehyde **2** in methanol. High yield and good selectivity was achieved under mild reaction conditions (80% yield and 91/9 of **3a/4a**).

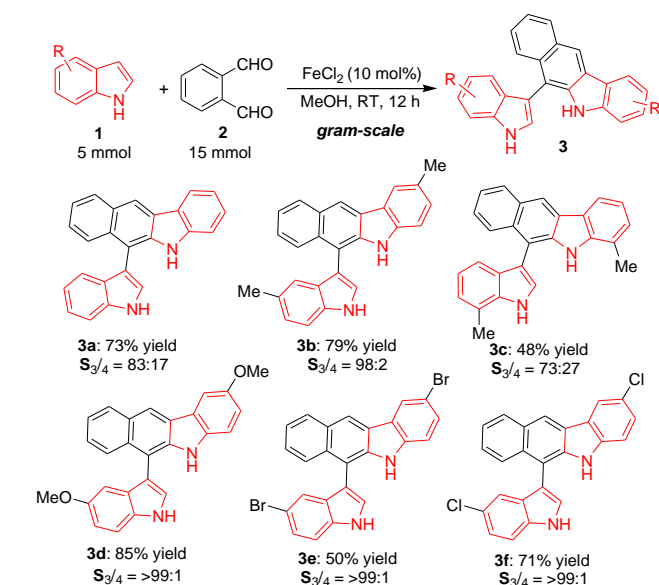
Table 1. Optimization of Lewis acid-catalyzed cycloaddition of indole (**1a**) and *o*-phthalaldehyde (**2**)^a



Run	Cat.	Solvent	Temperature (°C)	Time (h)	3a/4a (S3/4) ^b	Yield (%) ^c
1	TsOH	MeOH	RT	24	87/13	80
2	TsOH	CH ₃ CN	RT	24	50/50	88
3	TsOH	THF	RT	24	45/55	54
4	TsOH	DCM	RT	24	18/82	67
5	I ₂	CH ₃ CN	RT	24	37/63	78
6	FeCl ₂	MeOH	RT	48	91/9	80
7	FeCl ₂	DCM	RT	48	27/73	59
8	FeCl ₂	CH ₃ CN	RT	48	34/66	88
9	FeCl ₂	THF	RT	48	52/48	43
10	FeCl ₂	H ₂ O	RT	48	ND ^d	17
11	InCl ₃	THF	RT	48	ND ^d	<10
12	Al(OTf) ₃	THF	RT	24	52/48	46
13	Al(OTf) ₃	CH ₃ CN	RT	24	32/68	70
14	Bi(OTf) ₃	THF	RT	24	52/48	49
15	Bi(OTf) ₃	CH ₃ CN	RT	24	34/66	91
16	Bi(OTf) ₃	CH ₃ OH	RT	24	83/17	83
17	Bi(OTf) ₃	EtOH	RT	24	83/17	83
18	TfOH	CH ₃ CN	RT	24	32/68	93
19	TfOH	THF	RT	24	50/50	50
20	TMSOTf	CH ₃ CN	RT	24	33/67	86
21	Mg(OTf) ₂	THF	RT	24	ND	<10
22	FeCl ₃	MeOH	RT	24	86/14	90
23	FeCl ₃	THF	RT	24	54/46	60

^a Reaction conditions: **1a** (0.5 mmol), **2a** (3.5 mmol), Brønsted acid or Lewis acid catalyst (10 mol%). ^b The ratio of **3** to **4** (also simplified as S_{3/4}) was determined by ¹H-NMR. ^c Isolated yields. ^d Not determined.

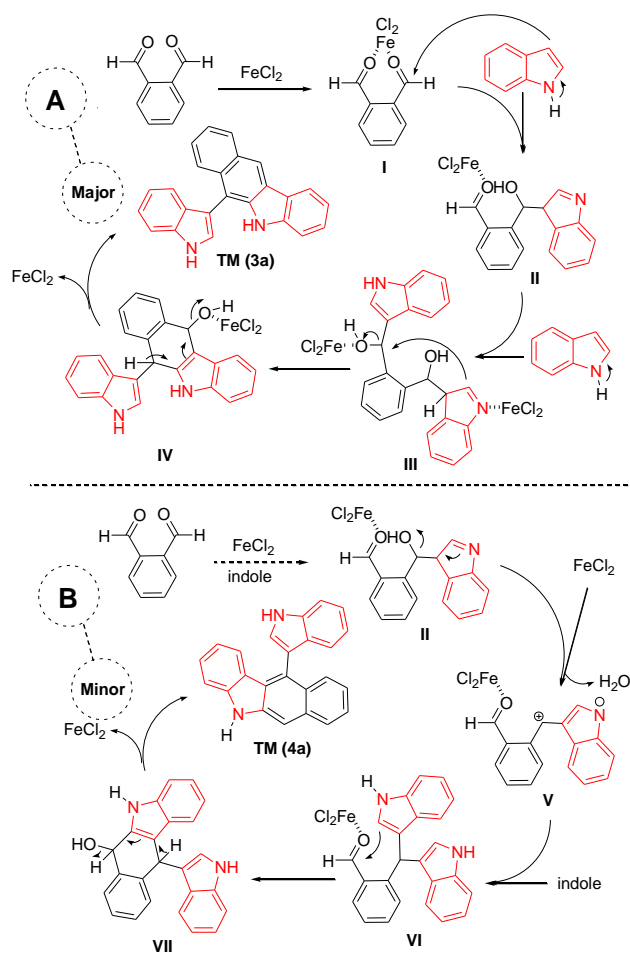
Subsequent studies (Entries 7-23) further supported the privileged role of FeCl₂ in this reaction because a great deal of investigation using various catalysts revealed the difficulty in the improvement of chemoselectivity for product **3a**. Our another goal was the highly selective synthesis of isomer **4a** of the interesting benzo[*b*]carbazole, but all attempts to prepare benzo[*b*]carbazole **4a** with higher chemoselectivity (>90/10 of **4a/3a**) met with failure. Notably, the pure benzo[*b*]carbazole **3** could be obtained by recrystallization, thus it provides a novel backbone for the development of fluorescent molecules. Thus, FeCl₂ (10 mol%) in MeOH at room temperature have been defined as the optimized reactions for scope study of the synthesis of benzo[*b*]carbazole **3**. With the optimal reaction conditions in hand, we then turned to the investigation of the various indoles in this reactions. As shown in Scheme 1, the substituted indoles was also proved to be effective substrates under the optimal reaction conditions, and moderate to good yields were observed for the gram-scale synthesis of the corresponding indolyl benzo[*b*]carbazoles. But no reaction occurred for 3-substituted indoles, implying the key nucleophilic effect on the reactivity of 3-position on indoles. When 5-methylindole was employed, the corresponding product **3b** was obtained in 79% yield. The reaction yield decreased dramatically when the methyl group was located at C-7 position in the indole ring (**3c**, 48% yield). Slightly higher yields could be achieved when 5-methoxyindole was employed in this reaction (**3d**, 85% yield). Interestingly, when the C-5 position of the indole ring was occupied by a halo group, the desired products were also obtained in good yields. Therefore, this method provides a simple and facile approach for the straightforward synthesis of indolyl benzo[*b*]carbazoles with good selectivities (Scheme 1).



Scheme 1. Synthesis of indolyl benzo[*b*]carbazoles by Fe-catalyzed coupling of indoles and *o*-phthalaldehyde.

Based on these results and previous reports on iron catalysis,¹⁰ a plausible mechanism for this intermolecular cycloaddition of indoles and *o*-phthalaldehyde toward divergent indolyl benzo[*b*]carbazoles is proposed in Scheme 2. Initially, Lewis acidic FeCl₂ would activate *o*-phthalaldehyde to give possible intermediate **I**, followed by addition of indole to intermediate **I**,

giving an adduct **II**. And subsequently, another molecule of indole was subjected to attack the activated intermediate **II** containing aldehyde moiety, which led to the formation of diol **III**. Then, Lewis acid-catalyzed intramolecular alkylation of **III** would furnish a cyclization to give intermediate **IV**. As the catalytic dehydration of compound **IV** in the presence of Lewis acid was easily occurred, the oxidative aromatization of **IV** may occur smoothly with the aid of FeCl_2 to give the product **3** (Path **A** of Scheme 2). As a different pathway, the formation of minor product **4** maybe arise from the key alkylation of intermediate **V** with indole in the presence of Lewis acidic FeCl_2 . Thus the formation of key intermediate **VI** would lead to intramolecular and desymmetric addition of indole motif to aldehyde group, which was followed by dehydration/ aromatization to generate the desired compound **4** (Path **B** of Scheme 2).



Scheme 2. A proposed mechanism (path **A** or **B**) for iron-catalyzed synthesis of benzo[*b*]carbazole **3a** or **4a** from indole and *o*-phthalaldehyde

With the successful synthesis of the indolyl benzo[*b*]carbazoles **3**, we wondered whether such conjugated heterocycles might exhibit special photophysical properties and could be used as a fluorescent probe for Lewis acid or Brønsted acid because of NH-group on indole ring. In the past years, the fluorescence-based detection technique is the most powerful method in the field of sensors, information displays, chirality chemistry, and catalysis.¹¹ Especially, various fluorescent sensors provide simple and

efficient method for detection of a wide range of chemical species in many diverse areas including host-guest chemistry, pharmaceutical and biological science, industry, and the environment science.¹² However, to the best of our knowledge, no such fluorescent probe for silicon-based Lewis acids has yet been reported. In addition, there are no reports on the application of indolyl benzo[*b*]carbazoles as fluorescent probe in analytic chemistry.

With regard to fluorescence properties, it was found that their fluorescent spectra excited at three different wavelengths (307 nm, 425-445 nm, and 604 nm). And all the indolyl benzo[*b*]carbazoles shows a strongly intense emission with maximum wavelength of 307 nm that may be attributed to the possibility of photoinduced electron transfer (PET) process involving nitrogen lone pairs of the indole moiety of indolyl benzo[*b*]carbazoles (Figure 1). Similarly, the benzo[*b*]carbazole moiety of compounds **3a-e** was crucial to the 425-445 nm excitation. And notably, the indolyl benzo[*b*]carbazole **3e** containing bromide group exhibited strong fluorescence in emission intensity at 307 nm but give quite weak intensity between 425-445 nm. These results suggest that these indolyl benzo[*b*]carbazoles are effective building backbones for the π -electron systems with well-extended π -conjugation.

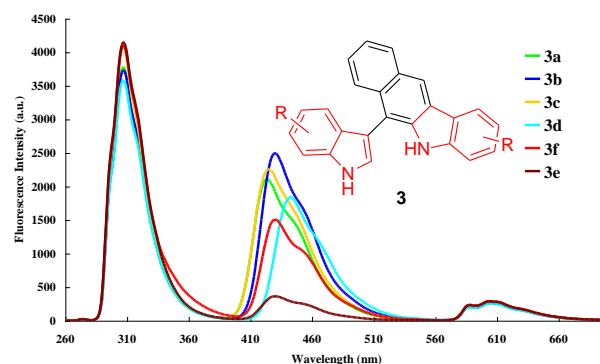


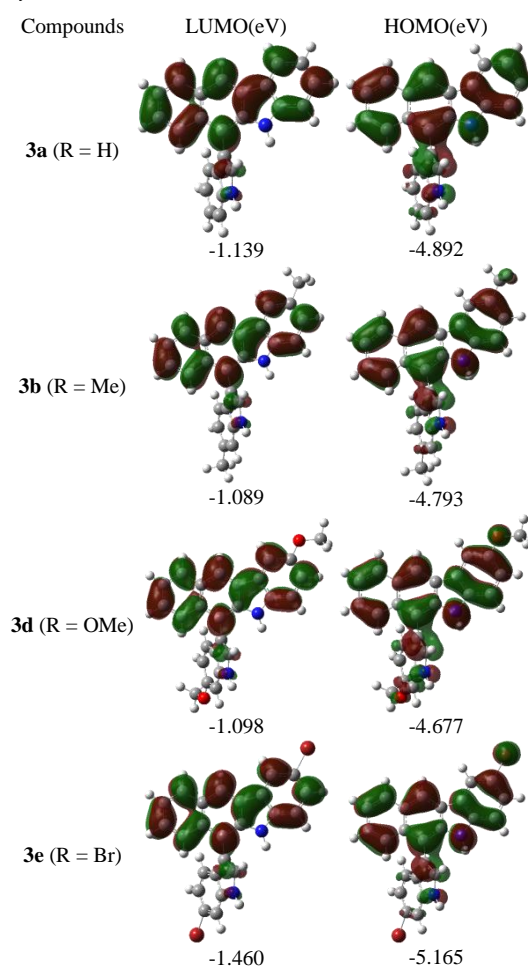
Figure 1. Fluorescence emission spectra of indolyl benzo[*b*]carbazoles **3a-f** (5×10^{-6} M) in CH_3CN .

To elucidate the electronic structure of indolyl benzo[*b*]carbazoles **3**, density functional theory (DFT) calculations at the B3LYP/6-31G(d,p) level were performed for representative compounds **3a**, **3b**, **3d**, and **3e**. As shown in Table 2, the HOMO of compounds **3a-e** is delocalized in the benzo[*b*]carbazole core with the contribution of π -conjugated skeleton. Despite the substitution of electron-donor groups on this skeleton, the HOMO level of bromo-substituted benzo[*b*]carbazole **3e** is 0.27-0.49 eV lower than that of **3a**, **3b**, or **3d**, indicative of the electron-withdrawing effect or halide p - π conjugation of the substitution. Similarly, the characteristics of the LUMOs for **3a-e** are almost the same and are also mainly localized on the benzo[*b*]carbazole core. As a result, **3e** would be used as a representative indolyl benzo[*b*]carbazole in the next FL analysis.

Considering the FL emission peak at 307 nm, we expected that the interaction of metal-free Lewis acid or Brønsted acid (guests) with the indolyl benzo[*b*]carbazoles would result in significant changes to their excited state properties because of Lewis basic

NH-group on the backbone of indole (Figure 2). To evaluate the effects of organic Lewis acid or Brønsted acid on the photophysical properties of indolyl benzo[*b*]carbazole **3e**, their fluorescent spectra were measured using trimethylchlorosilane (TMSCl) or trifluoroacetic acid (TFA) titration. In this process, addition of TFA resulted in the decreasing emission intensity of the band at 307 and 430 nm. Upon addition of TFA to indolyl benzo[*b*]carbazole **3e**, the lowest emission peak was observed at 307 nm or 430 nm when 40 eq. of TFA was used. Such changes suggest that the acid-base interaction involving nitrogen lone pairs of indolyl benzo[*b*]carbazoles is responsible for the FL changes observed with excess TFA. Interestingly, addition of larger amount of TFA in this solution of **3e** (>40 eq.) turns on fluorescence slightly (Figure S2 of ESI), which could be ascribed to the anion- π or cation- π interaction between TFA and aromatic rings of protonated indolyl benzo[*b*]carbazole **3e**.

Table 2. Frontier orbital energy (in eV) calculated at B3LYP/6-31G(d,p) level of theory¹³



The benzo[*b*]carbazole **3e** also exhibited a FL change when the addition of TMSCl. Similarly, the fluorescence emission intensity of **3e** decreased as the concentration of TMSCl increased as shown in Figure 3. Thus the indolyl benzo[*b*]carbazole exhibited a high sensitivity toward organic Lewis acid or Brønsted acid, quenching 94% of its fluorescence intensity with 40 equiv of TMSCl or TFA. The FL system was further extended to estimate

the TMSCl in the presence of triethylamine (See Figures S4 and S5 of ESI). The fluorescence titration of indolyl benzo[*b*]carbazole **3e** with TMSCl/Et₃N (Figure S5) or the mixture of indolyl benzo[*b*]carbazole **3e** and TMSCl (40 eq.) with Et₃N (Figure S4) was carried out respectively. Interestingly, upon the addition of TMSCl and Et₃N (1:1), the fluorescence emission intensity was almost identical to that obtained in the presence of TMSCl. Notably, the fluorescence response of the mixture of indolyl benzo[*b*]carbazole **3e** with TMSCl (1/40) toward Et₃N was concentration-dependent, and remarkable fluorescence turn-on was observed in the presence of low or high concentration of Et₃N, whereas 40 equiv Et₃N did not cause any interference in the estimation of the quenching **3e** with TMSCl (See Figure S4 of ESI). This also indicates that the strange FL properties or 40-fold-effect in this work can be employed to support that highly complex and multiple parameters could have an impact on the outcomes of intermolecular interaction between indolyl benzo[*b*]carbazole and metal-free Lewis acid or Brønsted acid.

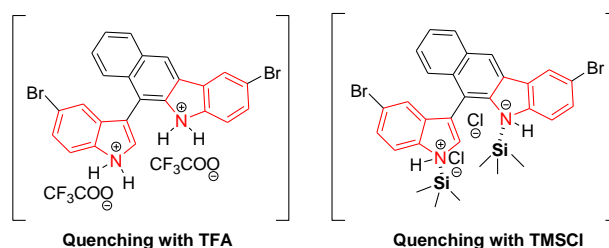


Figure 2. Working hypothesis for the turning off fluorescence emission of indolyl benzo[*b*]carbazole **3e** with trimethylchlorosilane (TMSCl) or trifluoroacetic acid (TFA).

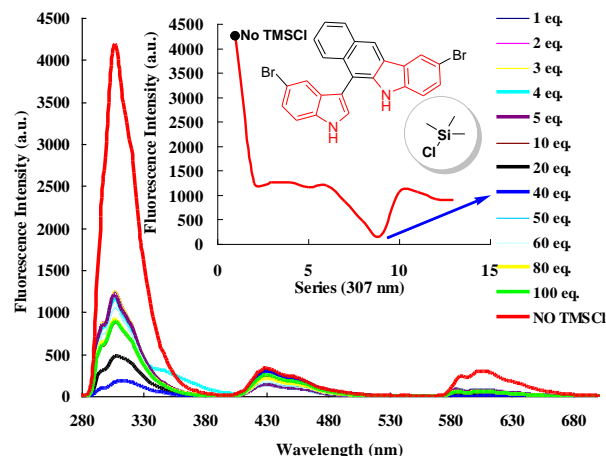


Figure 3 Changes observed in the fluorescence emission spectrum of **3e** (5×10^{-6} M) upon addition of TMSCl (1 ~ 100 eq.) in CH₃CN.

In summary, we have developed a iron-catalyzed one-pot cycloaddition for the synthesis of indolyl benzo[*b*]carbazoles from indole and *o*-phthalaldehyde. The coupling/cyclization approach is environmentally benign and proceeds via sequential carbon-carbon bond-forming addition, cyclization involving intramolecular alkylation and aromatization forming a benzene ring. The possible mechanism of divergent processes was also provided on the basis of experimental results. In addition, preliminary results on the fluorescence properties of such indolyl

benzo[*b*]carbazoles were also investigated. It showed an extremely high selectivity for TFA or TMSCl with quenching 94% of its fluorescence intensity. Although the exact reason for abnormal intramolecular interaction between indolyl benzo[*b*]carbazole and 40 equiv TMSCl (or TFA) was unclear at present, the sensing protocol can be applicable for the quantification of TMSCl or TFA in consumer products. Nevertheless, this type of benzo[*b*]carbazoles constituents a rare example of fluorescent sensor containing indole moiety, which would contribute usefully to the development of fluorescent sensors or dyes. Furthermore, this chemistry will be of great interest to chemists in diverse areas for further application in this area. Further investigations on the chemistry of indolyl benzo[*b*]carbazole are currently underway in our laboratory.

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Notes and references

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