HETEROCYCLES, Vol. 96, No. 8, 2018, pp. 1398 - 1409. © 2018 The Japan Institute of Heterocyclic Chemistry
Received, 12th May, 2018, Accepted, 28th June, 2018, Published online, 6th July, 2018
DOI: 10.3987/COM-18-13922

# 5,11-DIETHYL-6-FORMYLINDOLO[3,2-*b*]CARBAZOLE: CRYSTAL, INTERACTION WITH PROTEIN AND THEORETIAL STUDY

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**Abstract** – In this work, 5, 11-diethyl-6-formylindolo[3,2-*b*]carbazole (DEFICZ) was crystallized in a monoclinic crystal system with the space group of P121/n1. Its spectral properties and potential interaction with protein including BSA and HSA were also studied correspondingly. The crystal structure was theoretically investigated using the density functional tight-binding method. In order to address the regioselective associated with the synthesis of DEFICZ, the B3LYP density functional theory (DFT) calculation has been carried out to estimate the relative stability of different active intermediates. In addition, time-dependent density functional theory method was used to unveil the origin of the absorption spectra of DEFICZ as observed experimenta.

## INTRODUCTION

Indolo[3,2-*b*]carbazole (ICZ) and its derivatives, a kind of important nitrogen-containing aromatic heterocyclic compounds, have drawn much attention in the past two decades. They have several significant properties: (1) low HOMO and large band gap, (2) easy formation of a relatively stable caption, (3) a large conjugated planar system for strong intramolecular electron transfer capability,[1] (4) a rigid

conjugated structure for luminescent efficiency, (5) being fabricated easily to obtain a series of derivatives,[2] (6) good environmental and chemical stability. Therefore, many compounds related to ICZ have been applied to various fields such as organic-based electronic material[3] and device,[2c,4] medicine,[5] biology[6] and food.[7]

Considering these reasons, our research group have designed and synthesized various compounds derived from ICZ, which were frequently used as materials or intermediates in medicine, chemistry and biology. In this paper, we presented a combined experimental and theoretical study on 5,11-diethyl-6-formylindolo[3,2-*b*]carbazole (DEFICZ) synthesized from ICZ, with the main attention paid to the characterizations of crystal structure, spectra properties and potential interaction with protein.

## RESULTS AND DISCUSSION

**X-Ray Crystal Determination.** Crystal structure is one of the most basic properties of an interesting compound. The mode of the spatial arrangement of a compound could in part determine its geometrical characteristic, physical property, chemical property and so on. So, it is important to understand the intermolecular interactions, intermolecular packing state, and structure-activity relationship of material crystal structures.

In this paper, the crystal structure of DEFICZ was obtained and measured by X-ray analysis. The molecular structure and packing diagram are shown in **Figure 1**, respectively.

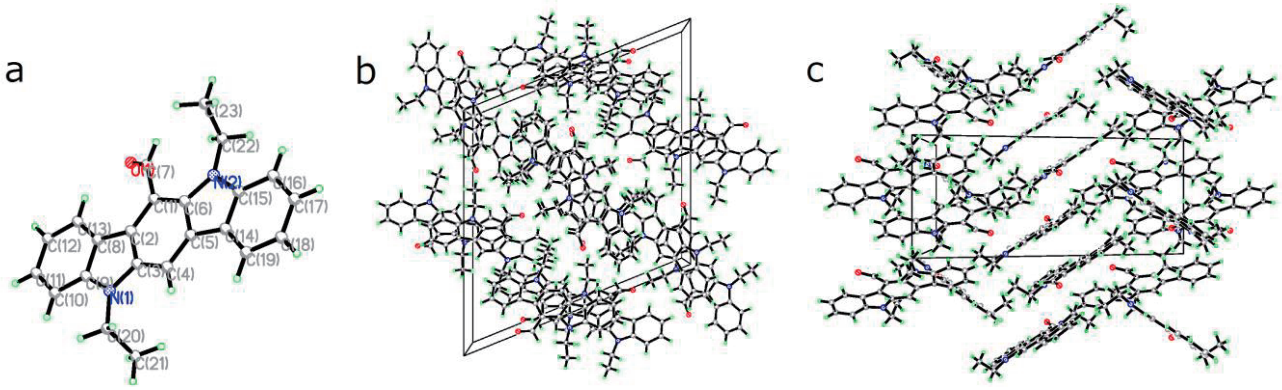



**Figure 1.** (a) X-Ray crystal structure, (b) A packing diagram along b axis and (c) c axis for DEFICZ

The torsion angles of C3-C4-C5-C14, C15-N2-C6-C5, C4-C5-C6-N2, C15-N2-C6-C1, C5-C14-C19-C18, C4-C5-C14-C19 and C19-C14-C15-N2 are -179.37, -0.57, 179.65, -179.13, 178.92, 178.46 and 179.90, which suggest that the five rings are almost in the same plane. The torsion angle of C2-C1-C7-O1 is -25.4, which indicates that the carbonyl group somewhat deviates from the same plane. The torsion angles of C9-N1-C20-C21, C3-N1-C20-C21, C15-N2-C22-C23 and C6-N2-C22-C23 are 101.45, -79.97, -89.27

and 95.20, respectively, showing that two ethyl groups on the nitrogen are roughly perpendicular to the conjugate planar framework. From **Figure 1**, we also can see that ICZ, the precursor skeleton of DEFICZ, is almost in the same plane, which is similar to that of pentacene. The planar structure is advantageous to the charge carriers' transmission. We also see that the molecular structure is tightly packed along the B axis. Two molecules parallel to each other along C axis and four molecules appear as a parallelogram structure. It is of a surface to surface stacking structure.

**Spectroscopic Characterization.** The absorption spectra of DEFICZ (6 μmol/L) in different solvents showed that three broad absorption bands appear at around 320, 379 and 461 nm in all cases, among which the last one is relatively weak. The wavelengths and absorption intensities were rather close in different solvents, showing that it was stable in different solvents with a wide application prospect.

Spectra of DEFICZ samples (6 μmol/L) in different pH solutions (10 mmol/L of $Na_2HPO_4$-citric acid buffer) were showed in **Figure 2**.

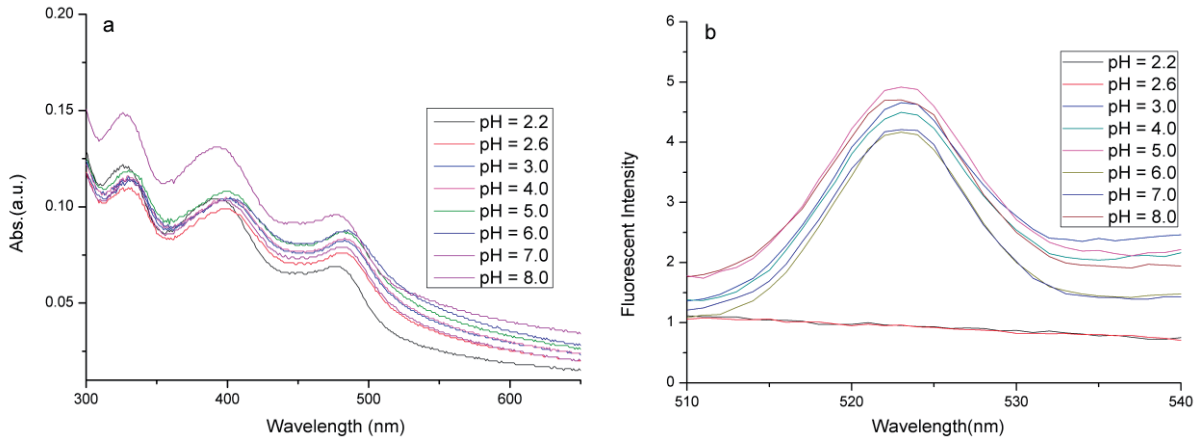



**Figure 2.** (a) Absorption and (b) fluorescence spectra ($E_{ex}$=330 nm) in different pH

As pH increased, the absorption bands shifted to the red region while the intensity increased a little. The fluorescent intensity also increased a little but the fluorescent wavelength hardly changed. It is said that DEFICZ has a good stability in the pH range of 2.2-8.0, which means it may have a wider application in biological, pharmic and environmental fields.

**Photostability.** Herein we tested the absorption spectra (**Figure 3**) when the compound solution was illuminated under iodine-tungsten lamp (500 W) with 50.0 g/L $NaNO_2$ aqueous solution as the cold trap.

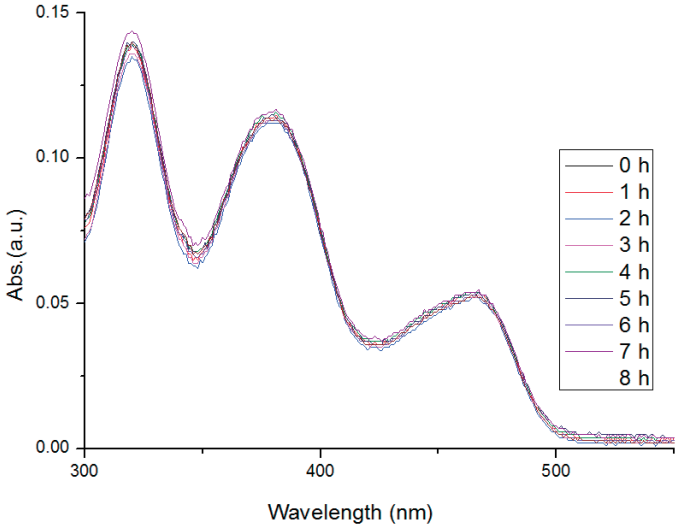



**Figure 3.** Absorption spectra for illumination times

As shown in **Figure 3**, with the irradiation time prolonged, the absorption intensities hardly changed even after continuous illumination for 8 h, which demonstrate that DEFICZ is of as good photostability as other carbazole derivatives.[8]

**Interaction with BSA and HAS.** Bovine serum albumin (BSA) and Human Serum Albumin (HSA) were used to study the interaction between the albumen and DEFICZ. BSA/HSA stock solution was prepared to be 4 mg/mL solution in Tris-HCl (10 mmol/L, pH = 7.4). The test samples were prepared by adding BSA/HSA stock solutions into the DEFICZ stock solution to give the concentration of 6 μmol/L with BSA/HSA concentrations of 0, 0.1, 0.4, 0.6 and 0.8 mg/mL, respectively, then the corresponding spectra were measured (**Figure 4**).

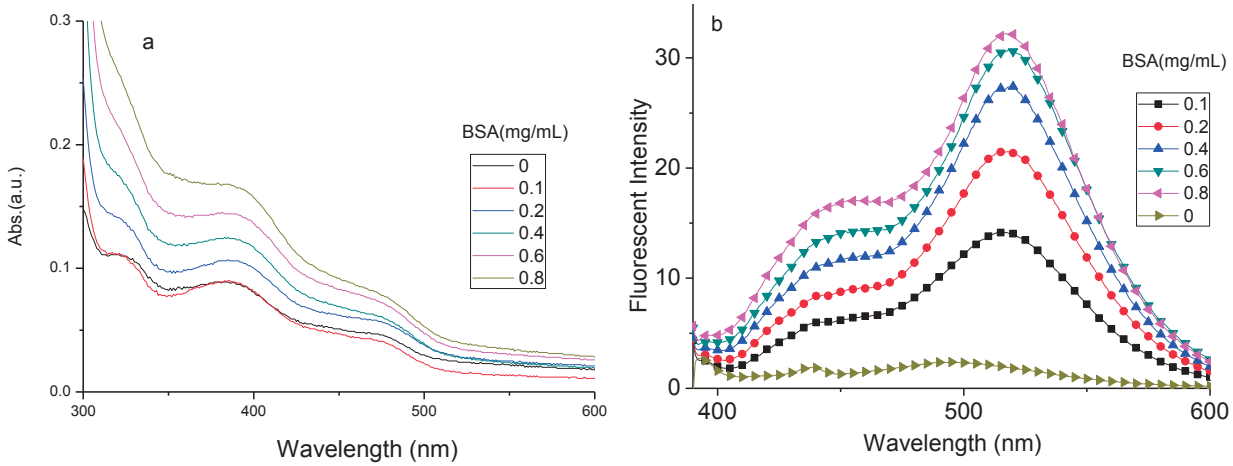



**Figure 4.** (a) Absorption and (b) fluorescence spectra interacted with BSA

With the addition of BSA, the absorption intensities increased a little at all of the absorption bands except that at about 320 nm. With the addition of BSA, the absorption at 320 nm decreased and almost disappeared over 0.4 mg/mL. The fluorescence wavelength somewhat shifted to the red region, but the fluorescent intensity increased evidently. It increased up to 14 times when 0.8 mg/mL of BSA was added. It indicated an interaction between DEFICZ and BSA. In addition, a new band appeared at about 450 nm in the present of BSA, and the fluorescent intensity increased with the addition of BSA. An energy transfer may occur between DEFICZ and BSA.

When HSA was added into DEFICZ solution, the absorption and fluorescence spectra also changed (**Figure 5**). With the addition of HSA, the absorption intensities increased a little with the wavelength changed little. With the addition of HSA, the absorption intensities increased a little at all of the absorption bands except that at about 320 nm. The absorption at 320 nm decreased and almost disappeared over 0.4 mg/mL. While the fluorescent intensities increased evidently, and even up to 14 times when 0.6 mg/mL of HSA was added. It indicated an interaction between the compound and HSA. In addition, a new band appeared at about 450 nm in the present of HSA, and the fluorescent intensity increased with the addition of HSA.

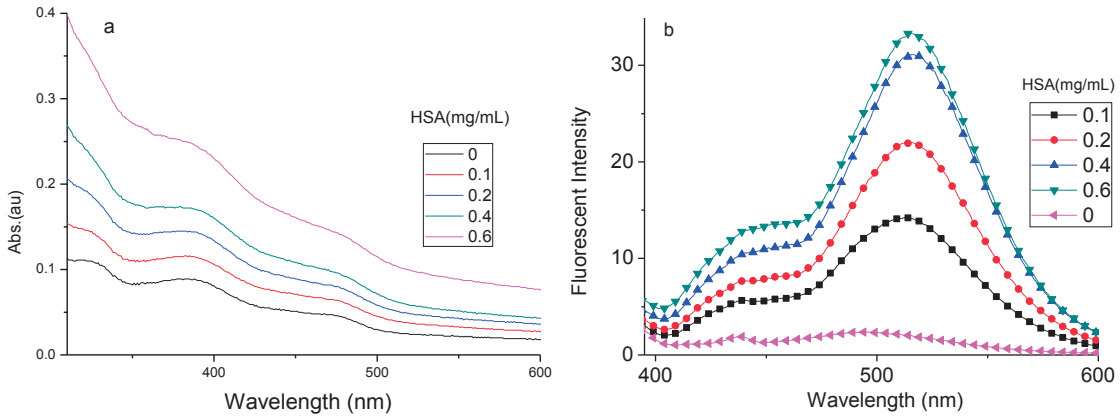



**Figure 5.** (a) Absorption and (b) Fluorescence spectra interaction with HSA

**Theoretical Study.** In order to understand the reactivity and regioselectivity of the formylation step in the overall synthetic route, the molecular geometry of 5,11-diethylindolo[3,2-*b*]carbazole was first optimized at the B3LYP-SCRF/6-31+G* level of theory. The located structural parameters of the most stable conformer indicated the trans-orientation of the two ethyl groups (**Figure 6**). It can be easily realized that this reactant has five possible reaction sites associated with the attack of electrophile. The active electrophile involved in this hydroformylation should be $ClCH=N^{+}(Me)_2$, which could react with 5,11-diethylindolo[3,2-*b*]carbazole to produce the hydroformylation products via the electrophilic aromatic substitution mechanism. Therefore, the regioselectivity of electrophilic substitution should be

dictated by the relative stability of the corresponding σ-complex cationic intermediates, the common intermediates in the electrophilic aromatic substitution.

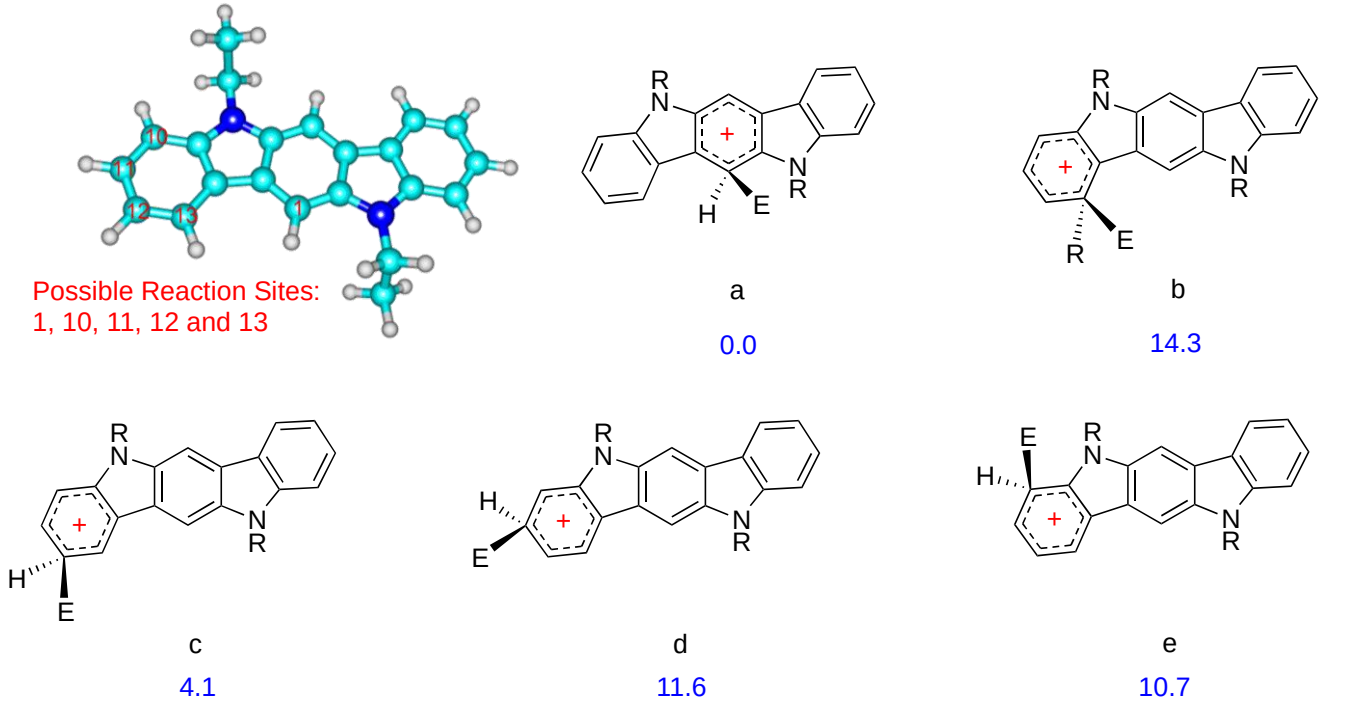



**Figure 6.** Molecular geometry of reactant and relative energies (in kcal/mol) of possible isomoeric σ-complex intermediates, calculated at the B3LYP-SCRF/6-31+G* level of theory. The electrophile fragment $ClCH=N^{+}(Me)_2$ is simplified in each structure as E for clarity.

Figure 6 shows five regio-isomeric σ-complex cationic intermediates and their relative energies, which indicate that **species (a)** is the most stable and thus probable intermediate along the reaction coordinates, demonstrating that $ClCH=N^{+}(Me)_2$ tends to react at the C1 site in comparison to the remaining sites and hence the corresponding 5,11-diethyl-6-formylindolo[3,2-*b*]carbazole is the main product. These results indicate that the C1 site should be the most active site due to the stabilization effect of the corresponding carbonium.

In order to explain the spectral absorption properties of DEFICZ observed experimentally, we have carried out TDDFT/B3LYP/6-31+G* calculations on the molecular structure of DEFICZ (**Figure 7**). We found that are several absorption bands corresponding to different orbital-to-orbital transitions. DFT calculation results indicate that the electron transition of HOMO → LUMO+1can occur at about 319 nm with the calculated f value of 0.1395, which should correspond to the first peak shown in **Figure 2a**. Computationally, the electron transition of HOMO−1 → LUMO could occur at about 383 nm with the calculated f value of 0.3174, which might be assigned to be the second peak shown in **Figure 2a**. Despite the first peak having a smaller f value than the second peak, **Figure 2** demonstrates that they have close intensities. The electron transition of HOMO → LUMO is predicted to occur at 447 nm using DFT

calculations, which has the f value of 0.0711 and should correspond to the third peak shown in **Figure 2a**. Our calculation results appear to be consistent with the experimental findings, because the third peak is the weakest one. All of the remaining electron transitions have a negligible transition probability. In addition, the HOMO distributions also suggest the attack on C1 to be favorable, because HOMO has a large lobe on C1.

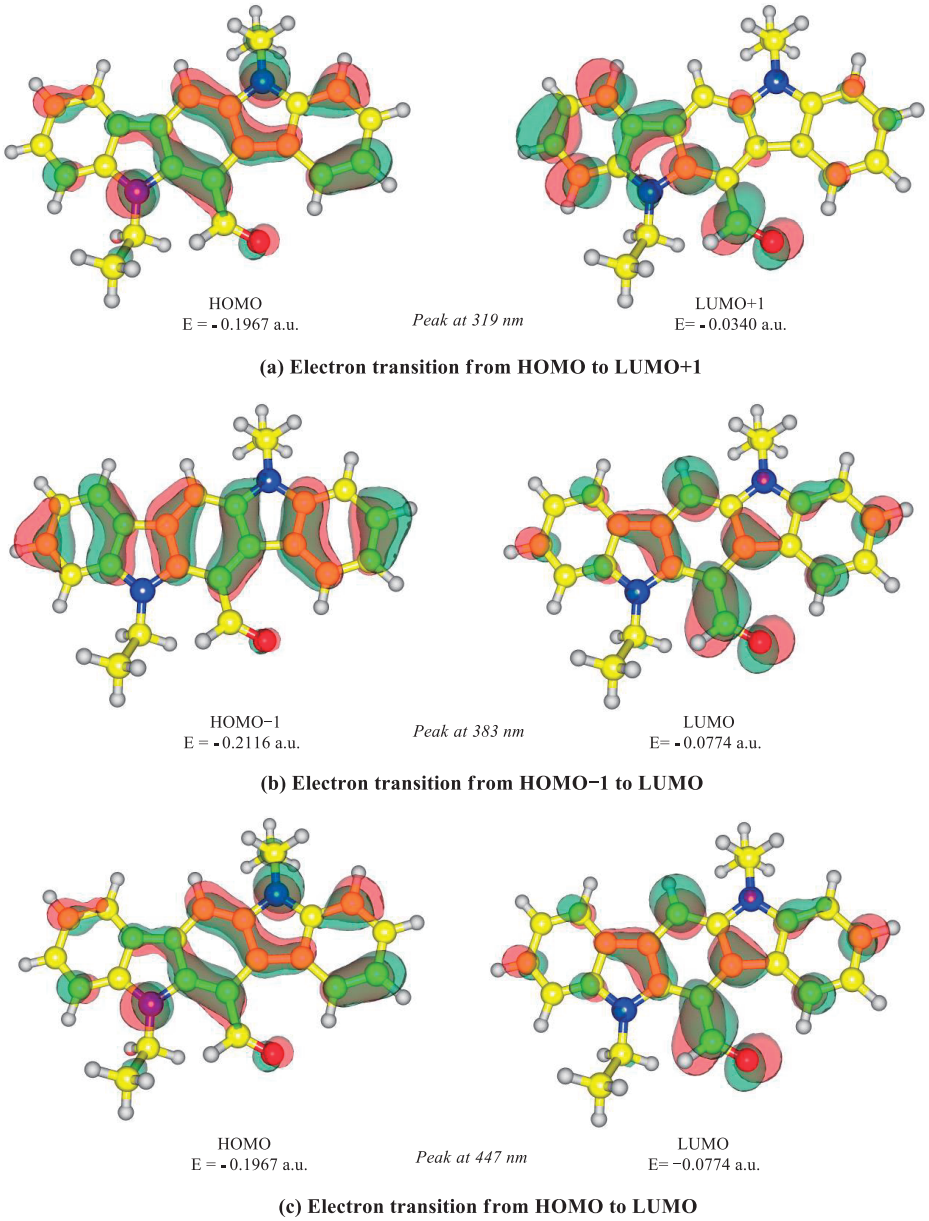



**Figure 7.** Main electron transitions of DEFICZ, determined using TDDFT method

## CONCLUSIONS

In summary, a series of experimental and theoretical studies on 5,11-diethyl-6-formylindolo[3,2-*b*]-carbazole (DEFICZ) have been performed. The crystal belongs to a monoclinic crystal system. The ICZ skeleton is a near planar geometry and the molecular structure is tightly packed along the B axis. The

orbital energy and band gap of the crystal suggest that it may serve a semiconductor. The spectra studies indicate that it has a good pH stability and photostability. The observations in its interaction with BSA and HSA suggest that it is a potential compound serving as a fluorescent biomarker of protein in biological, pharmic and environmental field, and will give a clue to design fluorescent materials, dyes and pigments structures with excellent properties on indolo[3,2-*b*] carbazole moiety. Further DFT and TDDFT calculations confirm experimental results and provide additional insights.

## EXPERIMENTAL

All commercial reagents were used without further purification. Mass spectral analyses were obtained using an electrospray ionization (ESI) mass spectrometer.$^{1}$H NMR spectra were obtained on a Bruker AVANCE III 400 MHz spectrometer. IR absorption spectra were measured on a Thermo Nicolet 380 spectrophotometer using KBr films. The fluorescence spectra and UV-Vis absorption spectra were measured on a HITACHIF-7000 Fluorescence spectrophotometer rand Perkin Eimer Lambda 35UV-vis spectrometer, respectively.

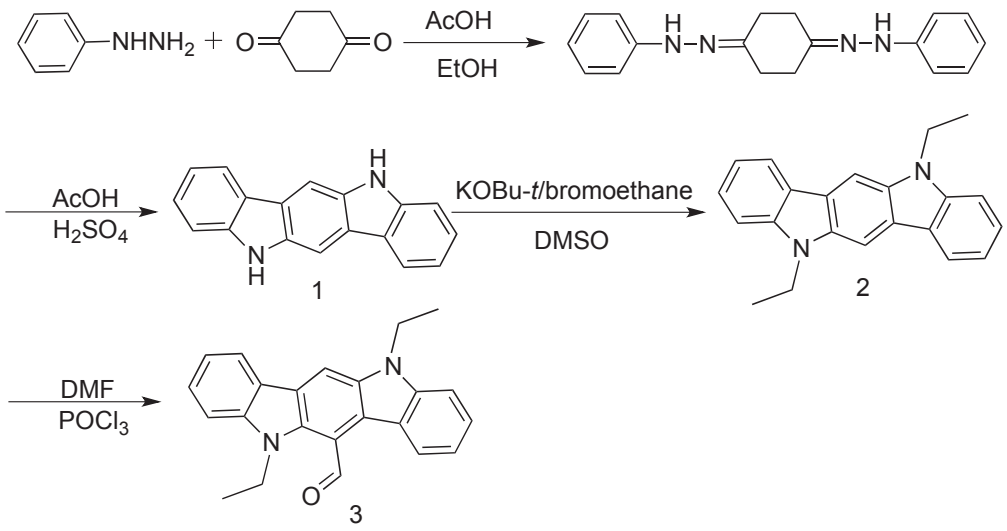
X-Ray single-crystal diffraction was determined from a Bucker Smart -1000 CCD diffractometer. The datum was collected with $MoK_{\alpha}$ radiation of 0.71073 Å with $1.18 \leq \theta \leq 27.86°$. A total of 34153 reflections were collected with 8142 independent ones ($R_{int} = 0.0398$) and 6712 with $I > 2\sigma(I)$ reflections were observed for analysis. The approximate dimensions were $0.22 \times 0.20 \times 0.16$ mm$^3$. The structure was solved by direct method using SHELXS-97 and SHELXL-97[9] and refined by full-matrix least- squares procedure on $F^2$. The crystal parameters data were summarized in **Table 1**.

**Table 1.** Crystal structure data for the target compound

| | |
|---|---|
| Empirical formula | $C_{23}H_{20}N_2O$ |
| Formula weight | 340.41 |
| Temperature | 113(2) K |
| Wavelength | 0.71073 A |
| Crystal system | Monoclinic |
| Space group | P2(1)/n |
| a (Å) | 20.847(4) |
| b (Å) | 8.4679(17) |
| c (Å) | 20.872(4) |
| α (°) | 90.00 |
| β (°) | 111.93(3) |

| | |
|---|---|
| γ (°) | 90.00 |
| μ ($mm^{-1}$) | 0.08 |
| Volume ($Å^3$) | 3417.9(12) |
| Z | 8 |
| Crystal size (mm) | 0.22 x 0.20 x 0.16 |
| θ range for data collection (°) | 1.18 - 27.86 |

**Synthesis.** DEFICZ was synthesized via four steps. Firstly, 1,4-cyclohexanedione and phenylhydrazine were used as raw materials to form cyclohexane-1,4-dione bis(phenylhydrazone), and then ICZ by Fischer indolization. At last, DEFICZ was synthesized by alkylation and formylation reaction, respectively. The route was shown in Scheme 1.




**Scheme 1.** Synthetic route of 5,11-diethyl-6-formylindolo[3,2-*b*]carbazole (DEFICZ)

**Synthesis of cyclohexane-1,4-dione bisphenylhydrazone.** 5.60 g (0.05 mol) of cyclohexanedione in absolute EtOH was added into a round-bottom flask. Then phenylhydrazine (13.50 g, 0.125 mol) and AcOH (0.25 mL, 0.0043 mol) were also added. The mixture was stirred by magnetic stirring apparatus at room temperature until precipitate appeared. Then it was heated up to 50 °C and stirred for another 2 h. After the reaction ended, the precipitate was filtrated, collected and then washed three times with cool EtOH, and finally it was dried to afford yellow solid (10.01 g, yield = 67%) .

**Synthesis of ICZ (Compound 1).** Compound **1** was synthesized according to this reference.[10] 40 mL of AcOH and 8 mL of concentrated $H_2SO_4$ were added into a round-bottom flask in an ice bath. Cyclohexane-1,4-dione bis(phenylhydrazone) (8.80 g, 30 mmol) was added dropwise. After that, the

temperature was warmed up to 30 ºC and stayed for 20 min and the colour changed to reddish orange. When the temperature was heated to 50 ºC, the reaction released heat and the temperature continued to rise, and when the temperature reached up to 107 ºC the colour changed to grass green. The heat source was removed to cool the reaction to room temperature and kept overnight. 50 mL of EtOH was added for another 1 h stirring. The precipitate was filtrated, washed by cooled $H_2O$ and EtOH, and then dried to afford merdoie solid (2.50 g, yield = 32%).

**Synthesis of 5,11-diethylindolo[3,2-*b*]carbazole (Compound 2).** A mixture of 50 mL DMSO, ICZ (3.01 g, 11.7 mmol), potassium *tert*-butoxide (3.28 g, 0.02925 mol) and bromoethane (6.37 g, 0.0585 mol) was stirred for 2.5 h in a 150 mL flask under Ar at room temperature. Then potassium *tert*-butoxide (3.28 g, 0.02925 mol) and bromoethane (6.37 g, 0.0585 mol) were added to stir for another 1 h. During the process, TLC was used to monitor the progress until the reaction was ended and cooled to room temperature. 100 mL of distilled water was added and extracted by EtOAc (3 × 80 mL). The organic phase was combined together and washed by saturated brines, dried with anhydrous $MgSO_4$, and filtered. The filtrate was distilled under reduced pressure. The residue was chromatographed to give yellow solid 1.80 g, yield = 85%; mp 277-279 ºC. $^1$H NMR (300MHz, $CDCl_3$) data: δ ppm: 1.38~1.42 (6H, m), 4.46 (2H, m), 4.60 (2H, m), 7.26 (2H, m), 7.44 (2H, t, $J$ = 7.5 Hz), 7.53 (2H, t, $J$ = 7.1 Hz), 8.15 (1H, d, $J$ = 7.5 Hz), 8.21 (2H, s), 8.63 (1H, d, $J$ = 8.1 Hz). ESI-MS (*m/z*): 312 [$M^+$].

**Synthesis of 5, 11-diethyl-6-formylindolo[3,2-*b*]carbazole (DEFICZ) (Compound 3).** In a 100 mL flask, a mixture of $POCl_3$ (0.395 mL, 4.325 mmol), DMF (0.4 mL, 4.325 mmol), compound **2** (1.13 g, 3.62 mmol) and $CH_2Cl_2$ (20 mL) was stirred under $N_2$ and kept reflux overnight. The mixture was poured slowly into ice-water mixture after cooled to room temperature and extracted by $CH_2Cl_2$ (3 × 30 mL). The organic phase was combined together, washed by $H_2O$ and dried by anhydrous $MgSO_4$. The filtrate was distilled and the residue was purified by column chromatography. Compound **3** was given as yellow solid. Yield: 48%; purity: 99.3% (HPLC); mp 181~182 ºC; $^1$H NMR (300 MHz, $CDCl_3$) δ ppm: 1.42~1.50 (6H, m), 4.43~4.50 (2H, m), 4.57~4.64 (2H, m), 7.22~7.31 (2H, m), 7.42~7.47 (2H, t, $J$ = 7.5 Hz), 7.50~7.55 (2H, t, $J$ = 7.1 Hz), 8.16 (1H, d, $J$ = 7.5 Hz), 8.21 (1H, s), 8.63 (1H, d, $J$ = 8.1 Hz), 11.28 (1H, s, CHO); ESI-MS (*m/z*): 340.10 [$M^+$]. IR (KBr, $cm^{-1}$): CH (Ar, =C-H) 3045.199, $_{as}$CH (-$CH_2$-) 2975.771, O=CH 2873.557, 2798.344, C=O, $_{as}$C=C 1467.636, CH (Ar, =C-H) 856.282, 740.568.

**Single crystal.** We gathered the solution of DEFICZ in the process of column chromatography. Yellow prism single crystal of target compound was obtained after a few days in EtOAc and petroleum ether of 1:50. The solution was transferred to a beaker with plastic wrap and the crystal was obtained after volatilizating a part of solvent. DEFICZ (1.36 mg) was dissolved in DMSO (4 mL) to give the stock solution (1 mmol/L).

**Computational Details.** In this paper, the geometry structure and energy of the crystal was calculated by

density functional tight-binding (DFTB) method and with a complement of an empirical London dispersion energy term (DFTB-D) method. Before calculated, the structure was first optimized by the conjugate gradient algorithm. The charge convergence criterion and force converge criterion were set to $10^{-5}$ electrons and $10^{-4}$ a.u., respectively. All the calculations were carried out by the DFTB+ 1.2 program.[11]

The molecular structure of the target compound (DEFICZ) was theoretically studied using density functional theory (DFT) under the Gaussian 09 program package. The geometrical optimizations and energetic determinations of DEFICZ and the corresponding cationic intermediates were performed on the ground state energy surfaces using the B3LYP[12] density functional method in conjunction with the 6-31+G*[13] basis set for all elements. In the study of absorption spectra, the time-dependent density functional theory (TDDFT) was employed to locate the possible vertical transitions occurring in DEFICZ upon radiation, which was also based on the combination of the B3LYP method and 6-31+G* basis set.

## SUPPORTING INFORMATION

CCDC no. 930901 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033. Sheldrick GM. SHELXL97 and SHELXS97, program for refined crystal structure. University of Göttingen, Germany 1997.

## ACKNOWLEDGMENTS

The present study was financially supported by the National Natural Science Foundation of China (grant no. 21502137, 51578360, 11604238), the key technologies R & D program of Tianjin (15ZCZDSF00150), and Key Laboratory of Targeting Therapy and Diagnosis for Critical Diseases, Henan Province (Grant No. NMZL2018101).

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