Synthesis, spectroscopic characterization and DFT calculations of a new highly fluorescent heterocyclic system: imidazo[4,5-*a*]quinindoline

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Abstract
New N-alkyl-substituted heterocyclic system imidazo[4,5-*a*]quinindolines (imidazo[4,5-*f*]-indolo[2,3-*b*]quinolines) were synthesized by one pot reaction of 1-alkyl-5-nitro-1*H*-benzimidazole with 2-(1-alkyl-1*H*-3-indolyl)acetonitrile in basic media *via* the nucleophilic substitution of hydrogen and concomitant cyclisation in good yields. Physical spectral (UV-vis, IR, NMR and fluorescence) and analytical data have established the structures of synthesized compounds. The fluorescence properties of these new heterocyclic compounds were studied. The fluorescence of all compounds was very intense and fluorescence quantum yields were very high (> 0.70). Solvent effects on absorption and emission spectra of these dyes have also been studied; the absorption and emission bands in polar solvents undergo a red shift. Density function theory (DFT) calculations of one structure by using the B3LYP hybrid functional and the 6-311+G(d,p) basis set to provide the relevant frontier orbitals were also performed.

Keywords: Nucleophilic substitution of hydrogen; imidazo[4,5-*a*]quinindoline; fluorescence; emission and absorption spectra; DFT calculations

Introduction

Nitrogen fluorescent heterocyclic compounds are of special interest, because they exhibit unique electrical and optical properties such as emitters for electroluminescence devices,[1] molecular probes for biochemical research,[2] in traditional textile and polymer fields,[3] fluorescent whitening agents[4] and photo conducting materials.[5] Naturally occurring substituted imidazoles, as well as synthetic derivatives thereof, exhibit wide ranges of biological activities and optical applications such as fluorescence compounds, dyes, and TPA (Two-photon absorption) materials[6–8] making them attractive compounds for organic chemists. Also, many commercial fluorescent brighteners for application to synthetic fibers contain an imidazole moiety.[9]

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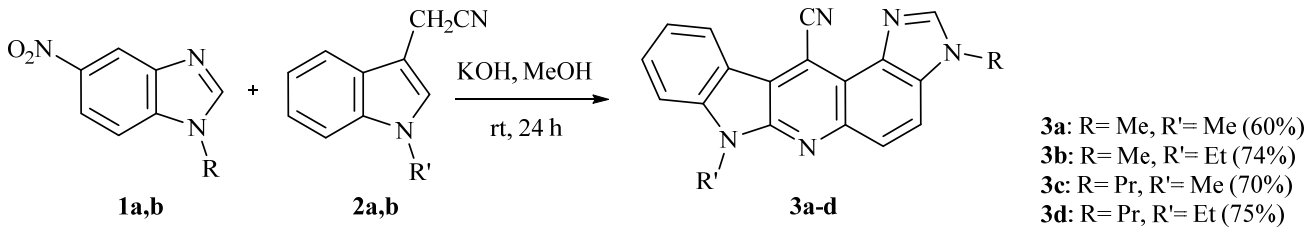
On the other hand, indoloquinoline alkaloids have recently received considerable attention due to their promising DNA intercalating[10] and antimalarial properties.[11-13] Particularly, indolo[2,3-*b*]quinolines (also called quinindolines), are a group of synthetic analogues of the natural alkaloid neocryptolepine. They share many biological properties with this compound, including the ability to interact with DNA as intercalators and to inhibit topoisomerase II reactivity. The quinindoline derivatives also revealed antimicrobial, antimuscarinic, antiviral, and cytotoxic potential.[14-16] A combination of the quinindoline moiety with the imidazole nucleus may enhance optical and biological properties.

Based on these aspects and in continuation with our research work on the efficient synthesis of new dyes and fluorescent nitrogen heterocyclic compounds,[17-23] we examined the transformation of 1-alkyl-5-nitro-1*H*-benzoimidazole with 2-(1-alkyl-1*H*-3-indolyl)acetonitrile to new fluorescent heterocyclic system imidazo[4,5-*a*]quinindoline *via* the nucleophilic substitution of hydrogen.[24,25] The fluorescence properties of these new heterocyclic compounds and DFT calculations of one structure by using the B3LYP hybrid functional and the 6-311+G(d,p) basis set have also been studied.

Results and discussion

Synthesis and Structures of the new compounds 3a-d

The treatment of 1-alkyl-5-nitro-1*H*-benzoimidazoles **1a,b** with 2-(1-alkyl-1H-3-indolyl)acetonitriles **2a,b** led to the formation of the new 3-alkyl-7-alkyl-3,7-dihydroimidazo[4,5-*a*]quinindoline-12-carbonitriles **3a-d** in basic MeOH solution *via* the nucleophilic substitution of hydrogen,[24,25] which proceeded at room temperature with subsequent cyclisation and in good yields (Scheme 1). One of the noteworthy points in this reaction was the simple work-up procedure performed by filtration of the precipitated product after the mixture was concentrated at reduced pressure. Washing the precipitated product with suitable solvents (water and then acetone) gives practically pure compounds **3a-d**.



Scheme 1. Synthesis of new compounds **3a-d**

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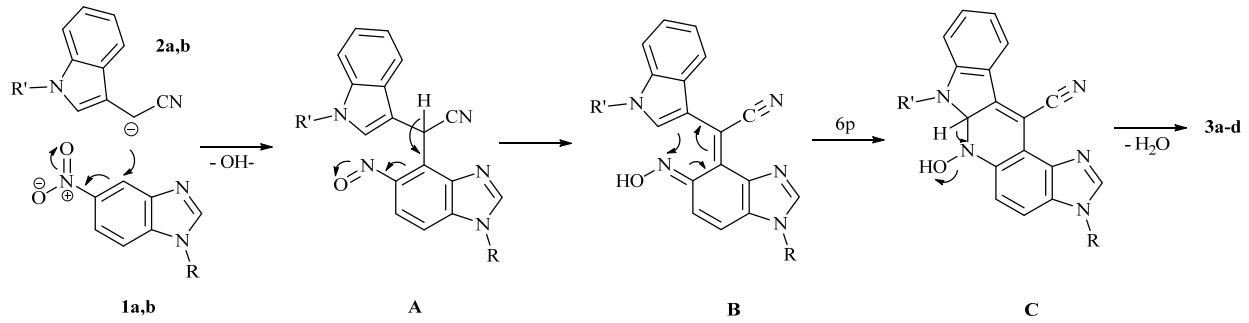
In the following mechanism[17-23] the ring closure proceeds *via* an electrocyclic pathway, wherein intermediate B is converted into C followed by loss of one H_2O molecule, whereupon compounds **3a-d** are obtained (Scheme 2).



Scheme 2. Proposed reaction mechanism for the formation of compounds **3a-d**

The structures of the pentacyclic products **3a-d** were confirmed by NMR techniques, IR spectroscopy, mass spectral and microanalytical data. The spectral details of all these are given in the Experimental section. For example, there are two triplet of doublet signals at δ = 7.43 and 7.73 ppm and two doublet signals (δ = 7.55 and 8.95 ppm) can be attributed to A ring, two doublet peaks at δ = 7.87 and 8.11 ppm assignable to two protons of D aromatic ring and a singlet peak at δ = 8.21 ppm correspond to E ring in the ^{1}H NMR spectrum of compound **3d** in the expanded aromatic region (Figure 1). Also, there are 22 different carbon atoms in the ^{13}C NMR spectrum of compound **3d.** Moreover, the FT-IR spectrum of **3d** in KBr showed an absorption band at 2223 cm^{-1} corresponding to the cyano group. All this evidence plus molecular ion peak at *m/z* 353 (M^+) and microanalytical data strongly support the pentacyclic structure of compound **3d**.

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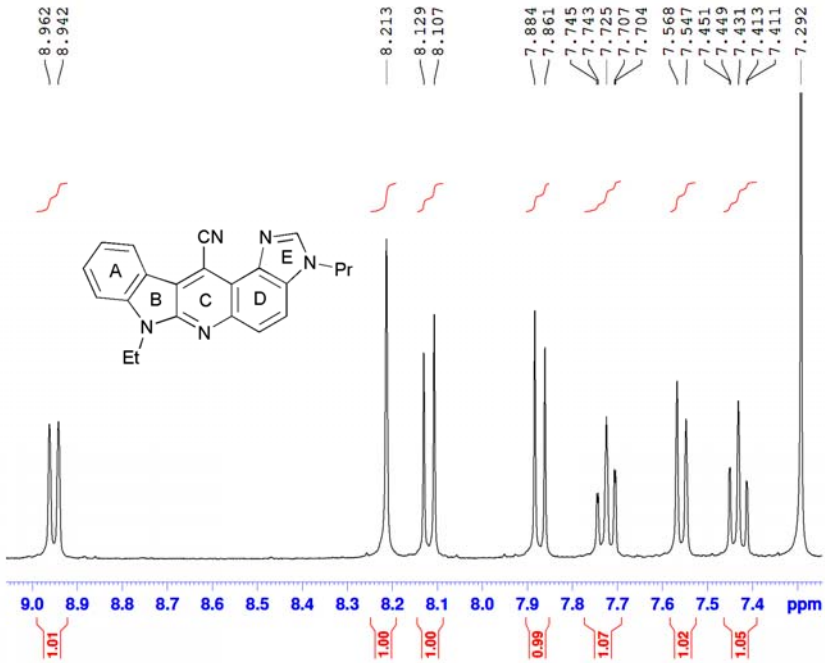

Figure 1. Expanded view (aromatic region) of the proton NMR spectrum of compound **3d.**

Fluorescent activity

The compounds **3a-d** were spectrally characterized by using an UV-Vis spectrophotometer and a fluorescence spectrophotometer. The wavelength range of both spectrophotometers is 200 nm-1000 nm. The fluorescence absorption and emission spectra of **3a-d** were recorded at concentrations of 1×10^{-6} and 3×10^{-7} mol L^{-1} in dichloromethane (DCM), respectively. Numerical data are presented in Table 1; Figures 2 and 3 show the visible absorption and emission spectra of compounds **3a-d**.

Table 1. Photophysical data for absorption (abs) and fluorescence (flu) of **3a-d**

Dye	**3a**	**3b**	**3c**	**3d**
λ_{abs} (nm)[a]	371	373	373	375
$\varepsilon \times 10^{-4}$ [(mol L^{-1})$^{-1}$ cm^{-1}][b]	92	95	84	81
λ_{ex} (nm)[c]	400	400	400	400
λ_{flu} (nm)[d]	484	476	476	473
Φ_F[e]	0.71	0.77	0.80	0.85

[a] Wavelengths of maximum absorbance; [b] Extinction coefficient; [c] Wavelengths of fluorescence excitation; [d] Wavelengths of fluorescence emission; [e] Fluorescence quantum yield.

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Values of extinction coefficient (ε) were calculated as the slope of the plot of absorbance *vs* concentration. The fluorescence excitation (λ_{ex}) wavelength at 400 nm (λ_{ex} /nm) was used for all compounds **3a-d.** The fluorescence quantum yields (Φ_F) of compounds **3a-d** were determined *via* comparison methods, using fluorescein as a standard sample in 0.1 M NaOH and MeOH solution.[26] The used value of the fluorescein emission quantum yield is 0.79. The absorbance and fluorescence spectral properties (Table 1) of compounds **3a-d** are similar to each other and the fluorescence quantum yield in compound **3d** (R=Pr, R'=Et) was the highest.

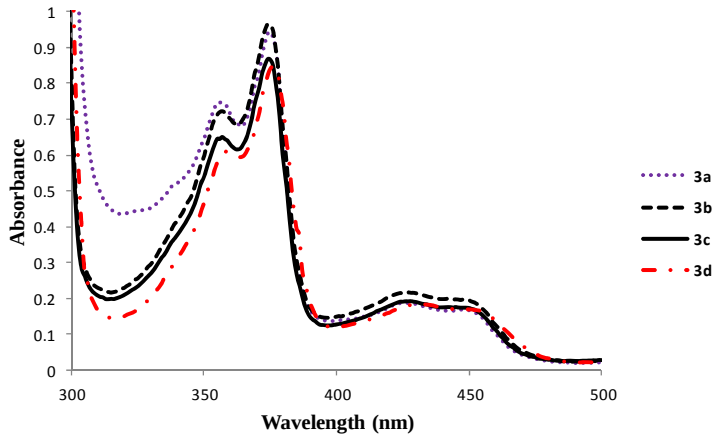

Figure 2. Visible absorption spectra of compounds **3a-d** in DCM solution (1×10^{-6} mol L^{-1}).

The fluorescence intensity in these compounds can be explained by an efficient intramolecular charge transfer (ICT) states from the donor site (endocyclic N) to the acceptor moiety (CN group).[17-22] In Scheme 3 neutral and some charge-separated mesomeric structures of **3a-d** are presented. As seen in this scheme, there are two nitrogen donors which can explain the shoulder on the right side of the peaks in emission spectra of compounds **3a-d** (Figure 3).

The fluorescence quantum yield (Φ_F) of the new compound **3d** is comparable with some of the fluorescent heterocyclic compounds which we have previously synthesized. A comparison of Φ_F and λ_{flu} between **3d** and some of these is shown in Table 2.

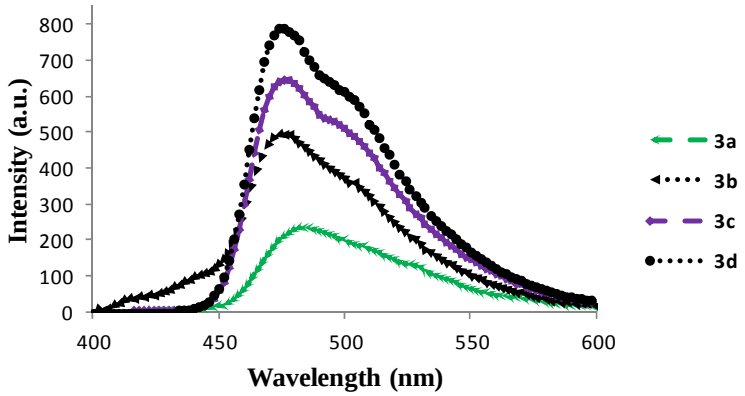

Figure 3. Emission spectra of compounds **3a-d** in DCM solution (3×10^{-7} mol L^{-1}).

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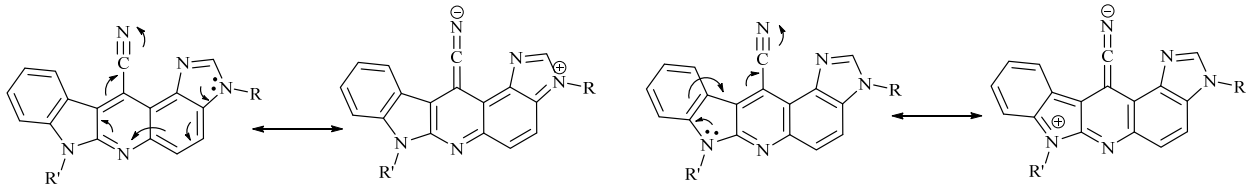
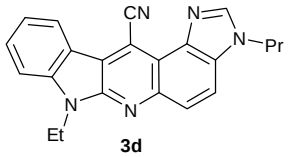
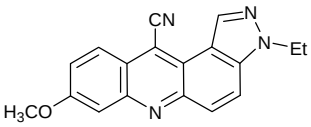
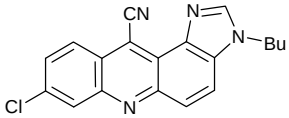
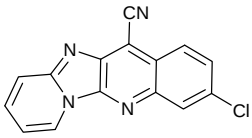
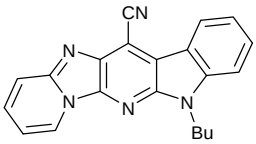
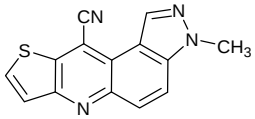


Scheme 3. Neutral and some charge-separated mesomeric structures of **3a-d.**

Table 2. Comparison of the Φ_F and λ_{flu} of **3d** and some recently synthesized fluorescent heterocyclic compounds

Compound	Φ_F	λ_{flu} (nm)	Compound	Φ_F	λ_{flu} (nm)
 **3d**	0.85	473		0.59 [19]	454
	0.92 [18]	488		0.90 [17]	485
	0.66 [21]	490		0.65 [22]	435

Solvatochromic properties of compound **3c** were studied in some solvents (Figs. 4 and 5). As it is depicted in these figures, the fluorescence absorption and particularly emission spectra of **3c** in polar solvents undergo a red shift. Increasing solvent polarity stabilizes the ICT excited-state molecule relative to the ground-state molecule with the observed red shift of the absorption and emission maximums as the experimentally observed result (Table 3). For example, λ_{flu} shifts from 465 to 495 nm is observed as the solvent is changed from toluene to methanol.

Table 3. Spectroscopic data for **3c** at 298K in dependence of the solvent

Solvent	λ_{abs} (nm)	λ_{flu} (nm)
Toluene	372	465
Ethyl acetate	374	471
DMF	377	480
Acetonitrile	376	477
Methanol	380	495

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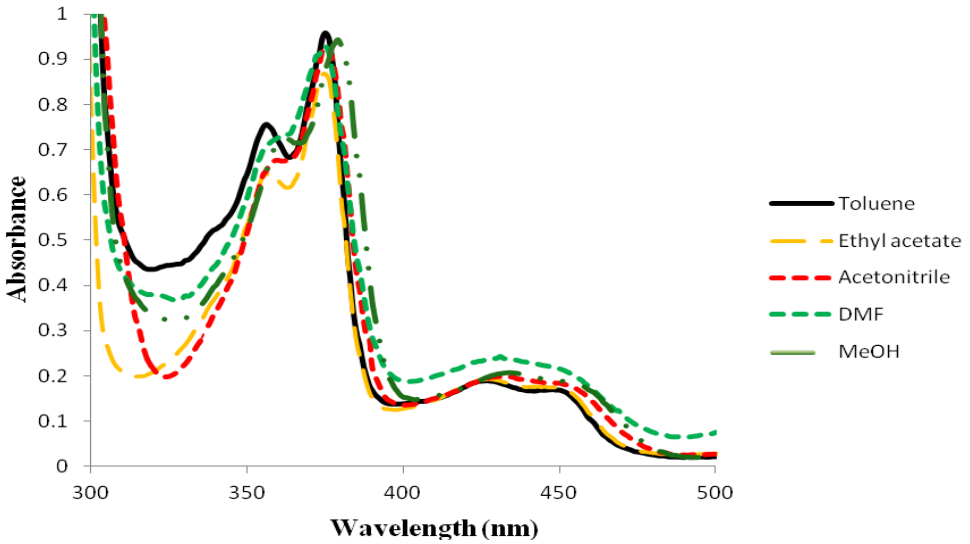

Figure 4. Visible absorption spectra of compound **3c** in different solvents (1×10^{-6} mol L^{-1}).

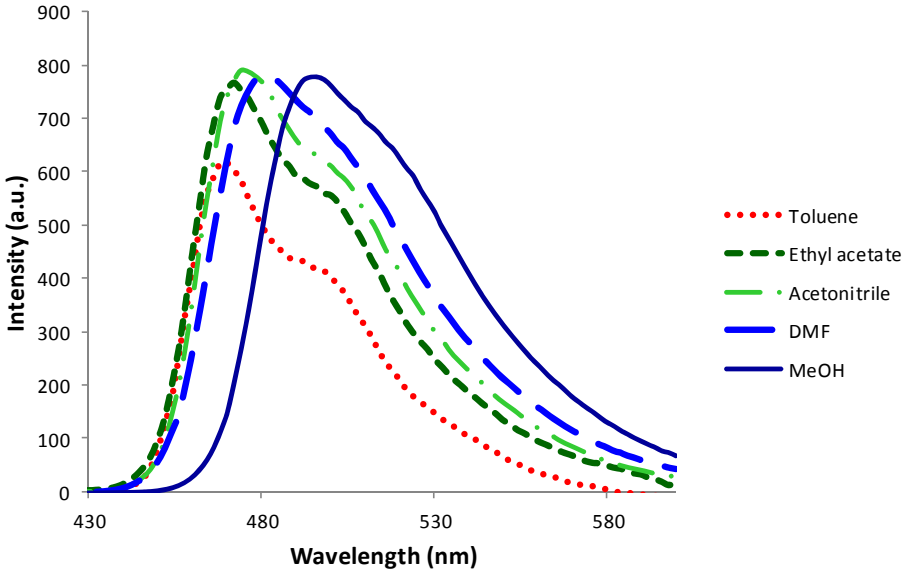

Figure 5. Emission spectra of compound **3c** in some solvents (5×10^{-7} mol L^{-1}).

DFT calculations

The optimized geometry of compound **3a** is shown in Figure 6. In the optimized geometry of the **3a**, all of these rings and cyano group are essentially planar and the C=C bond lengths (1.38-1.44 Ångstrom) of the aromatic rings are in the expected range (Table S1; see Supplementary data).[27]

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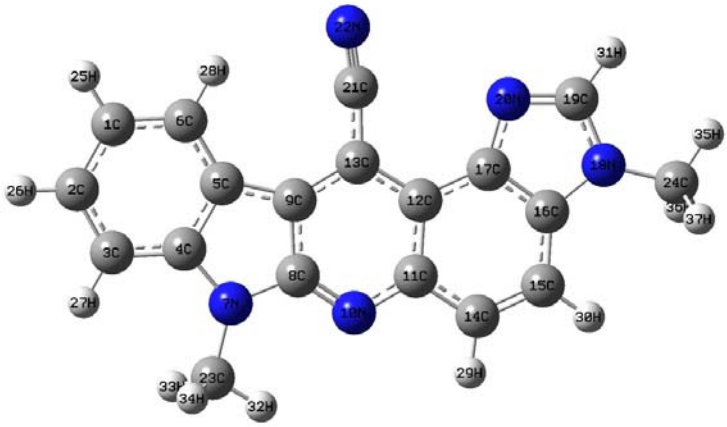

Figure 6. Optimized geometry of the compound **3a.**

As seen in Table 4, the DFT calculated chemical shifts (δ) of the compound **3a** are well in agreement with the experimental values, confirming validity of the optimized geometry as a proper structure for **3a**.

Table 4. Experimental and DFT calculated ^{1}H NMR chemical shifts of compound **3a**

Atom number	Chemical shift		Atom number	Chemical shift	
	Calc.	Exp.		Calc.	Exp.
H28	9.34	8.96	H27	7.44	7.46
H29	8.11	8.09	H32	5.20	4.27
H30	7.83	7.89	H35	3.84	4.05
H31	7.82	8.22	H36	3.84	4.05
H26	7.73	7.71	H37	3.84	4.05
H25	7.52	7.57	H33, H34	3.36	4.27

The energy difference between the HOMO and LUMO frontier orbitals is one of the important characteristics of molecules, which has a determining role in such cases as electric properties, electronic spectra and photochemical reactions. The HOMO and LUMO maps of **3a** are shown in Fig. 7. It shows that the frontier molecular orbitals of **3a** are mainly composed of *p* atomic orbital, so electronic transition corresponds to above electronic spectra are due to π-π* electronic transitions. Energy separation between the HOMO and LUMO is 3.45 eV (359.4 nm). As seen; the HOMO and LUMO are totally delocalized because of the unsaturated nature of the system.

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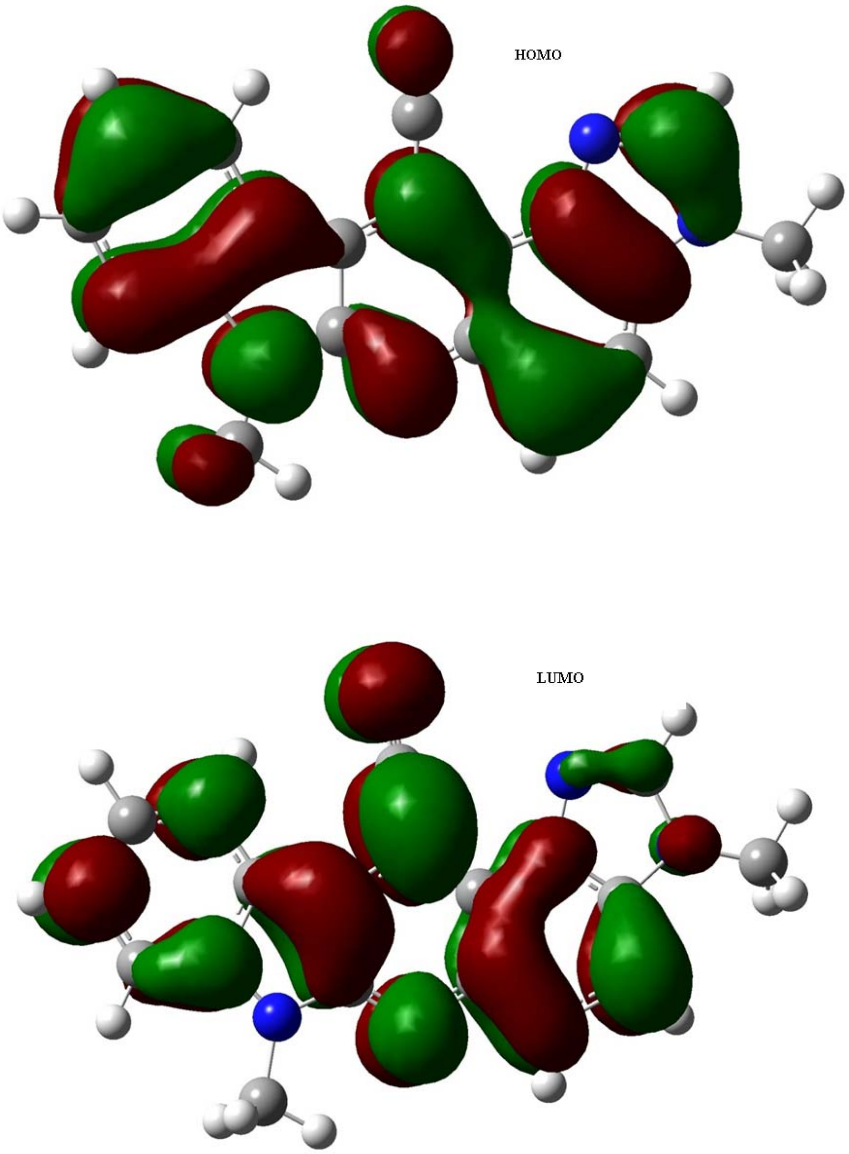

Figure 7. The HOMO and LUMO frontier orbitals of the compound **3a.**

Conclusions

We have successfully synthesized and characterized a new substituted heterocyclic system imidazo[4,5-*a*]quinindoline by one-pot reaction of 1-alkyl-5-nitro-1*H*-benzoimidazole with 2-(1-alkyl-1*H*-3-indolyl)acetonitrile in basic media. Considerable photophysical data of these dyes clearly show that they have very strong fluorescence intensities. DFT calculations to gain a deeper insight into the charge transfer properties were also performed. Because of the use of fluorescence for imaging in the biological and material science fields, further synthetic and

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fluorescence studies are necessary on similar substrates to expand this field of knowledge and establish sound conclusions. This work is in progress.

Experimental Section

Materials

Methanol, *N*,*N*-dimethylformamide (DMF), dichloromethane (DCM), toluene, ethyl acetate, acetonitrile, methyl iodide, ethyl bromide, n-propyl bromide, dimethylamine, formaldehyde, potassium cyanide, 5-nitro-1*H*-benzimidazole and indole were purchased from Merck. Potassium hydroxide was purchased from Sigma–Aldrich. All solvents were dried according to standard procedures. Compounds **1a,b**[28] and **2a,b**[29,30] were synthesized as in the cited references.

Equipment

Absorption and fluorescence spectra were recorded on Varian Cary 50-Bio UV-visible spectrophotometer and Varian Cary Eclipse spectrofluorophotometer. UV–vis and fluorescence scans were recorded from 200 to 1000 nm. Melting points were measured on an Electrothermal type-9100 melting-point apparatus. The IR (as KBr discs) spectra were obtained on a Tensor 27 spectrometer and only noteworthy absorptions are listed. The ^{13}C NMR (100 MHz) and the ^{1}H NMR (400 MHz) spectra were recorded at on a Bruker Avance DRX-400 FT spectrometer in $CDCl_3$. Chemical shifts are reported in ppm downfield from TMS as internal standard; coupling constant *J* is given in Hz. The mass spectra were recorded on a Varian Mat, CH-7 at 70 eV. Elemental analysis was performed on a Thermo Finnigan Flash EA microanalyzer. All measurements were carried out at room temperature.

Computational methods

DFT calculations were performed with the Gaussian 98 software package[31] by using the B3LYP hybrid functional[32] and the 6-311+G(d,p) basis set. Firstly, geometry of the compound **3a** was fully optimized in the chloroform solution. The optimized geometry was confirmed to have no imaginary frequency. Then, its optimized geometry was used for frequency calculations.

Here, one of self-consistent reaction field methods, the sophisticated Polarized Continuum Model (PCM)[33] has been used for investigation of the solvent effects. The PCM calculations have been performed in the chloroform solution and the zero-point corrections were considered to obtain energies.

The ^{1}H NMR chemical shifts of the **3a** were predicted with respect to tetramethylsilane (TMS). Here, the GIAO method was used for prediction of DFT nuclear shielding.[34]

General procedure for the synthesis of 3a-d from 1a,b and 2a,b

1-Alkyl-5-nitro-1*H*-benzimidazole **1a,b** (10 mmol) and 2-(1-alkyl-1*H*-3-indolyl)acetonitrile **2a,b** (12 mmol) were added with stirring to a solution of KOH (13 g, 238 mmol) in methanol (50 mL).

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The mixture was stirred at rt for 24 h. After concentration at reduced pressure, the precipitate was collected by filtration, washed with water, following with acetone, and then air dried to give practically pure **3a-d**.

3,7-Dimethyl-3,7-dihydroimidazo[4,5-*a*]quinindoline-12-carbonitrile (**3a**): compound **3a** was obtained as shiny yellow needles (EtOH), yield 60%, mp 360-362 °C; ^{1}H NMR ($CDCl_3$) δ 4.05 (s, 3H), 4.27 (s, 3H), 7.46 (td, J_1 8.0 Hz, J_2 0.8 Hz, 1H), 7.57 (d, *J* 8.4 Hz, 1H), 7.71 (td, J_1 8.0 Hz, J_2 1.2 Hz, 1H), 7.89 (d, *J* 9.2 Hz, 1H), 8.09 (d, *J* 9.2 Hz, 1H), 8.22 (s, 1H), 8.96 (d, *J* 8.0 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$): δ 31.1, 35.0, 104.2, 108.9, 113.2, 115.9, 117.7, 118.2, 119.1, 120.2, 124.87, 124.92, 129.6, 129.9, 137.8, 141.7, 142.2, 144.3, 149.6 ppm; IR (KBr disk): ν 2223 cm^{-1} (CN). MS (m/z) 311 (M^+). Anal. Calcd for $C_{19}H_{13}N_5$ (311.3): C, 73.30; H, 4.21; N, 22.49. Found: C, 73.09; H, 4.17; N, 22.19.

7-Ethyl-3-methyl-3,7-dihydroimidazo[4,5-*a*]quinindoline-12-carbonitrile (**3b**): compound **3b** was obtained as shiny yellow needles (EtOH), yield 74%, mp 342-345 °C; ^{1}H NMR ($CDCl_3$) δ 1.51 (t, *J* 7.2 Hz, 3H), 4.28 (s, 3H), 4.33 (q, *J* 7.2 Hz, 2H), 7.45 (td, J_1 8.0 Hz, J_2 0.8 Hz, 1H), 7.56 (d, *J* 8.4 Hz, 1H), 7.72 (td, J_1 8.0 Hz, J_2 1.2 Hz, 1H), 7.88 (d, *J* 9.2 Hz, 1H), 8.10 (d, *J* 9.2 Hz, 1H), 8.21 (s, 1H), 8.96 (d, *J* 8.0 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$): δ 13.8, 31.1, 36.3, 104.1, 109.1, 113.1, 116.0, 117.7, 118.8, 119.1, 120.1, 124.1, 124.9, 129.6, 129.9, 137.9, 141.4, 142.4, 144.1, 149.6 ppm; IR (KBr disk): ν 2223 cm^{-1} (CN). MS (m/z) 325 (M^+). Anal. Calcd for $C_{20}H_{15}N_5$ (325.4): C, 73.83; H, 4.65; N, 21.52. Found: C, 73.60; H, 4.61; N, 21.39.

7-Methyl-3-propyl-3,7-dihydroimidazo[4,5-*a*]quinindoline-12-carbonitrile (**3c**): compound **3c** was obtained as shiny yellow needles (EtOH), yield 70%, mp 303-305 °C; ^{1}H NMR ($CDCl_3$) δ 1.03 (t, *J* 7.2 Hz, 3H), 1.98-2.08 (m, 2H), 4.09 (s, 3H), 4.35 (q, *J* 7.2 Hz, 2H), 7.44 (td, J_1 8.0 Hz, J_2 0.8 Hz, 1H), 7.53 (d, *J* 8.4 Hz, 1H), 7.73 (td, J_1 8.0 Hz, J_2 1.2 Hz, 1H), 7.87 (d, *J* 9.2 Hz, 1H), 8.12 (d, *J* 9.2 Hz, 1H), 8.23 (s, 1H), 8.92 (d, *J* 8.0 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$): δ 11.3, 23.6, 35.1, 47.1, 104.2, 109.0, 113.7, 115.8, 117.8, 118.7, 119.2, 120.23, 124.1, 124.9, 129.6, 129.9, 138.0, 141.6, 142.4, 144.1, 149.6 ppm; IR (KBr disk): ν 2225 cm^{-1} (CN). MS (m/z) 339 (M^+). Anal. Calcd for $C_{21}H_{17}N_5$ (339.4): C, 74.32; H, 5.05; N, 20.63. Found: C, 74.02; H, 4.99; N, 20.34.

7-Ethyl-3-propyl-3,7-dihydroimidazo[4,5-*a*]quinindoline-12-carbonitrile (**3d**): compound **3d** was obtained as shiny yellow needles (EtOH), yield 75%, mp 305-306 °C; ^{1}H NMR ($CDCl_3$) δ 1.05 (t, *J* 7.2 Hz, 3H), 1.57 (t, *J* 7.2 Hz, 3H), 2.00-2.09 (m, *J* 7.2 Hz, 2H), 4.35 (t, *J* 7.2 Hz, 2H), 4.69 (q, *J* 7.2 Hz, 2H), 7.43 (td, J_1 8.0 Hz, J_2 0.8 Hz, 1H), 7.55 (d, *J* 8.4 Hz, 1H), 7.72 (td, J_1 8.0 Hz, J_2 1.2 Hz, 1H), 7.87 (d, *J* 9.2 Hz, 1H), 8.11 (d, *J* 9.2 Hz, 1H), 8.21 (s, 1H), 8.95 (d, *J* 8.0 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$): δ 11.4, 13.8, 23.8, 36.4, 47.1, 104.1, 109.0, 113.7, 115.9, 117.8, 118.7, 119.4, 120.5, 124.0, 124.4, 129.5, 129.8, 138.1, 141.6, 142.4, 144.1, 149.7 ppm; IR (KBr disk): ν 2225 cm^{-1} (CN). MS (m/z) 353 (M^+). Anal. Calcd for $C_{22}H_{19}N_5$ (353.4): C, 74.77; H, 5.42; N, 19.82. Found: C, 75.01; H, 5.47; N, 19.61.

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