January 2010

Solvent-Dependent Fluorescence Emission in Heterocyclic Compounds Having Isoquinoline Backbone

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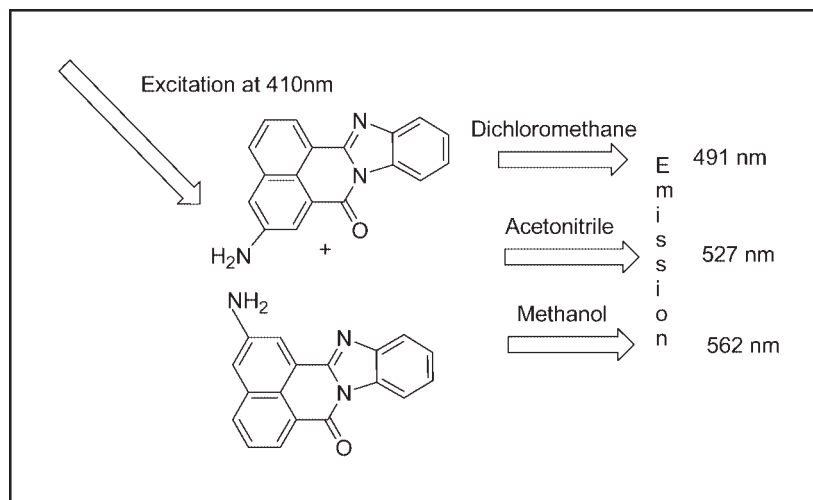Assam, India
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Additional Supporting Information may be found in the online version of this article.
Received July 20, 2009
DOI 10.1002/jhet.310
Published online 8 January 2010 in Wiley InterScience (www.interscience.wiley.com).

Few amino derivatives of benzo[de]benzo[4,5]imidazo[2,1-a]isoquinolin-7-one having amino groups at different positions of the rings are prepared and characterized. Solvent-dependent emission and changes in emission properties on protonation of amine group are observed.

J. Heterocyclic Chem., **47**, 199 (2010).

INTRODUCTION

The organic compounds having fluorophores that are sensitive to environment are of great importance [1–5] in chemistry and biology. The fluorescence emission spectra of some heterocyclic compounds such as benzo [de]benzo[4,5]imidazo[2,1-a]isoquinoline (Fig. 1) are sensitive to environment [6–8], and some of such heterocyclic compounds are used as organic photoconductive materials [9]. Therefore, the functionalization of such heterocyclic compounds is expected to form derivatives that may possess interesting optical properties [10]. Heterocyclic compounds having more numbers of delocalized aromatic rings in conjugation to each other would lead to better as well as novel optical properties [9]. With an interest to identify and characterize and also to understand optical properties of compounds bearing fluorophores that are sensitive to environment, we have synthesized few heterocyclic compounds as shown in Figure 1. We have studied fluorescence emission of these compounds and compared with some of their derivatives.

RESULTS AND DISCUSSION

Synthesis of the heterocycles. The compounds **2** and **4** were prepared by the reactions as depicted in Schemes 1 and 2. The condensation of 1,8-naphthalic anhydride with 4-nitro 1,2-diaminobenzene in acetic acid gave 11-nitro-benzo[de] benzo[4,5] imidazo[2,1-a] isoquinolin-7-one (**1**). Although this reaction is expected to give two isomeric products, we obtained a single isomeric product. This is due to the fact that such cyclization process passes through imide intermediates. It is recently shown that only one imide isomer is formed in this reaction before cyclization. This was shown by trapping the intermediate imide derivative in dimethylformamide (DMF) as a solvent. The formation of specific imide in this reaction, between the two possible isomers, may be attributed to the ease of attack of the less sterically crowded [11] amino group at *p*-position to the nitro group of 4-nitro 1,2-diaminobenzene. The reduction of the nitro group of the compound **1** resulted in the formation of the corresponding amine **2**. Acetic acid is found
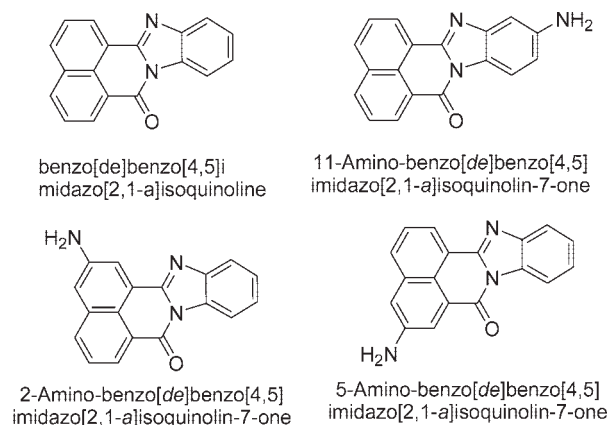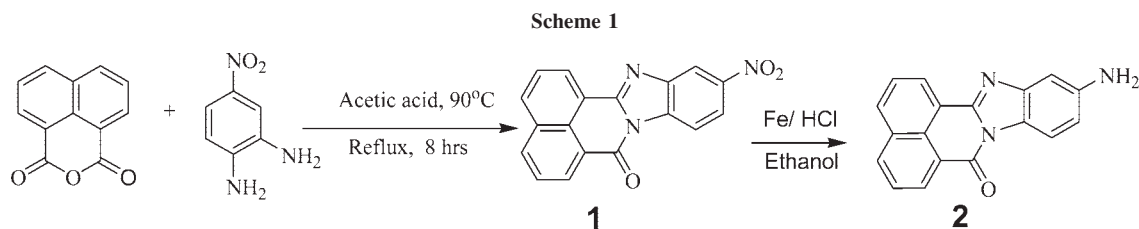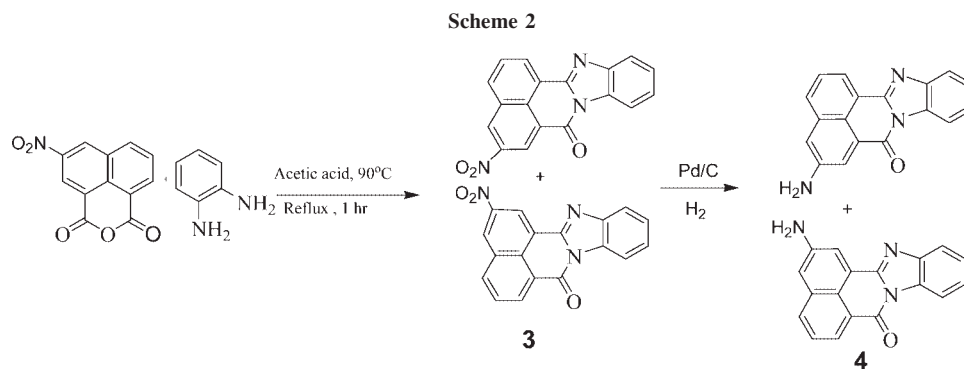
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benzo[de]benzo[4,5]i
midazo[2,1-a]isoquinoline

11-Amino-benzo[de]benzo[4,5]
imidazo[2,1-a]isoquinolin-7-one

2-Amino-benzo[de]benzo[4,5]
imidazo[2,1-a]isoquinolin-7-one

5-Amino-benzo[de]benzo[4,5]
imidazo[2,1-a]isoquinolin-7-one

Figure 1. Structure of the heterocycles.

to be appropriate solvent for the synthesis of **2**. Recently, we have discussed about the role of solvent in the formation of similar heterocycles [11] and also mentioned about the usefulness of acetic acid in the synthesis of such heterocycles. Similarly, the condensation reaction of 3-nitro-1,8-naphthalic anhydride with 1,2-diaminobenzene gave a mixture of isomeric products, namely 2-nitro-benzo[de]benzo[4,5]imidazo[2,1-a]one-methane and 5-nitro-benzo[de]benzo[4,5]imidazo[2,1-a]isoquinolin-7-one (**3**). We could not separate the two isomers by conventional chromatographic techniques such as preparative thin layer (TLC) or column chromatography. The ¹H-NMR chemical shift and the integration values of the mixture of isomers suggest formation of almost an equimolar mixture of the two isomers. In an earlier report, it was suggested that similar reaction under microwave irradiation in the presence of alumina resulted only one isomer [12], but in our case we have failed to obtain pure isomer through the reaction condition described herein, and the isomeric product separation of **3** was not successful. However, the condensation reaction of 3-nitro-1,8-naphthalic anhydride with 1,2-diaminobenzene under solvothermal condition in acetic acid at 150°C in an autoclave gave only one isomer. The ¹H-NMR spectra of this isomer obtained from this reaction is given as Supporting Information. It has eight peaks in aromatic region and tallies the structure of 2-nitro-benzo[de]benzo[4,5]imidazo[2,1-a]one   methane. The assignment of the ¹H-NMR of this compound is on

the assumption that the simulated ¹H-NMR of other isomer namely 5-nitro-benzo[de]benzo[4,5]imidazo[2,1-a]isoquinolin-7-one shows proton signals at relatively high chemical shift than the 2-nitro-benzo[de]benzo[4,5]imidazo[2,1-a]one methane. As the optical properties of these two isomers and derivatives are indistinguishable, we proceeded to take the mixture of isomers for optical study described in the Experimental section. The reduction of the nitro groups of these isomers (**3**) was carried out by hydrogen gas with a catalytic amount of palladized carbon to prepare two isomeric amine derivatives **4** (Scheme 2). In the case of **1**, we have obtained only one isomer because of the presence of nitro-group on diamino benzene ring, which could differentiate the two amino groups on the ring in terms of reactivity. The nitro group on the compound **1** was reduced to amino group, and the amino group was further functionalized to various derivatives **5–8** as illustrated in Scheme 3. Methyl and acyl derivatives (**9–12**) of compound **4** were also synthesized by similar procedure (Scheme 4).

Optical properties. The compounds **2** and **4** show solvatochromic properties, and the absorption features of **2** and **4** differ in different solvents, which are listed in Table 1. The compounds **2** and **4** are derived from a planar aromatic ring system, which is derived from 1,8-naphthalic anhydride [6]. The imides derived from naphthalic anhydride are useful as fluorescence probes, and their applications are decided by the presence of tether connecting two similar or dissimilar molecules [12]. The compounds **2** and **4** have reasonable fluorescence emission properties on excitation at appropriate wavelengths. The UV–visible absorption spectra as well as fluorescence emission spectra of several derivatives of 11-amino benzo[de]benzo[4,5]imidazo[2,1-a]isoquinolin-7-one (**2**) are recorded and listed in Table 2. Among the nitro and amino group (compounds **1** and **2**), the later shifts the fluorescence emission towards higher wavelength. In the case of substituted amines, it is observed that the substituent attached on nitrogen also leads to emission to higher wavelength. Among the N-substituent compounds **5–8**, the highest shift is observed in N-benzoylated derivative (**7**). It is attributed to the fact that benzoate group participates in delocalization of electrons with the aromatic ring of the heterocycle. The fluorescence emission of **2** in dichloromethane solution is

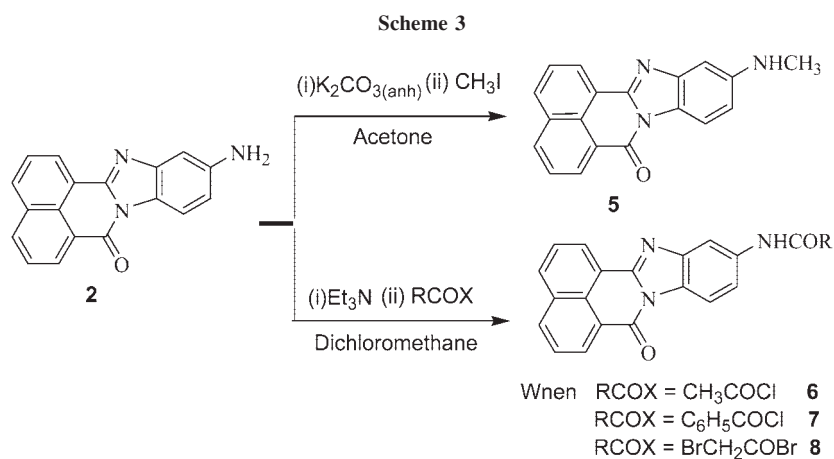**Scheme 1**

Scheme 2

3

4

observed at 508 nm upon excitation at 410 nm. The compound **2** is found to be fluorescence inactive in methanol. Accordingly, the fluorescence emission of the **2** observed from dichloromethane solution also gets quenched on addition of methanol (Fig. 2). The fluorescence emission spectra of various derivatives of 11-amino-benzo[de]benzo[4,5]imidazo[2,1-a]isoquinolin-7-one (**2**) and mixture of 2-amino-benzo[de]benzo[4,5]-imidazo[2,1-a]isoquinolin-7-one and 5-amino-benzo[de]-benzo[4,5]imidazo[2,1-a]isoquinolin-7-one (**4**) were also recorded, and the emission wavelengths and quantum yields are listed in Table 2. Although the compound **4** is a mixture of two isomers, in none of the cases, we could obtain any distinguishable fluorescence emission features of the two isomers. The wavelength shifts and intensity changes in various derivatives of **2** and **4** predominantly occur from the electronic effect caused to the overall electronic environment by the presence of the substituents. It is important to note that the emission spectra of naphthalimide fluorophores having amine groups are proton responsive [13], and such compounds have relevance in recognition of anions [14].
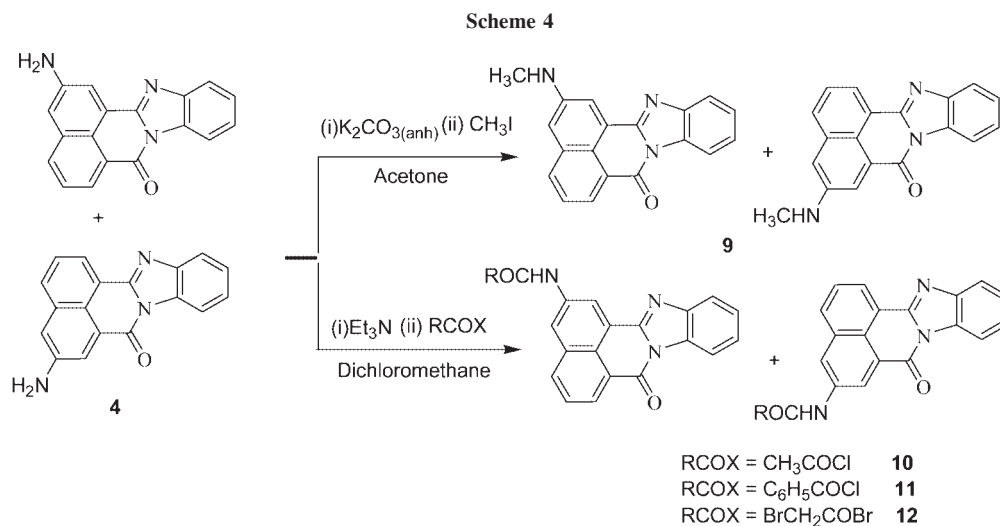
In the case of compound **2**, the protonation causes shift in the fluorescence emission to a lower wavelength from the parent compound. For example, the parent compound **2** in dichloromethane on excitation at 410 nm

emits at 514 nm, and the shifts to 508 and 498 nm, respectively, on addition of 1 and 2 equiv of hydrochloric acid (HCl).

The emission spectra of **4** are highly solvent dependent. A solution of **4** on excitation at 410 nm in dichloromethane, acetonitrile, and methanol shows fluorescence emission at 491 ($\Phi = 0.458$), 527, and 562 nm, respectively [Fig. 3(a)]. Such large characteristic shifts in emission spectra make it possible to distinguish these three solvents. From Table 1, it is clear that the compound **4** shows very small solvatochromicity in visible spectra, whereas it shows a large shift in emission spectra on change of solvents. This suggests that a polar excited state capable of forming exciplex with different solvents is involved in the fluorescence emission.

Addition of methanol to dichloromethane solution of **4** changes its fluorescence emission; initially, the emission occurring due to excitation at 410 nm decreases, but the emission shifts to a higher wavelength and on gradual addition of methanol it once again increases and reaches the emission wavelength that corresponds to the observed emission wavelength from a methanolic solution of **4** [Fig. 3(b)]. Similarly, the addition of methanol to an acetonitrile solution of **4** shifts the fluorescence emission to higher wavelength [Fig. 3(c)]. The compound **4** also shows proton responsive fluorescence

Scheme 3

Wnen   RCOX = CH_3COCl **6**
RCOX = C_6H_5COCl **7**
RCOX = $BrCH_2COBr$ **8**

Scheme 4

RCOX = CH₃COCl   **10**
RCOX = C₆H₅COCl   **11**
RCOX = BrCH₂COBr   **12**

emission, which is dependent on the hydrogen ion concentrations. For example, treatment of a solution of **4** with HCl (1 equiv) causes a change of fluorescence emission from 491 to 501 nm, and on addition of 2 equiv of the acid, the emission occurs at 510 nm [Fig. 3(d)]. These results suggest that the protonation effects the delocalization of electrons of the amino group, which in turn contributes to the changes in the emission spectra of these compounds. The solvato-emissive properties can be attributed to the stabilization of polar exited state by polar solvent, whereas the proton responsive nature is attributed to the hydrogen bonding by protic solvent and protonation by mineral acid. Similar properties are seen in receptors of carboxylic acids [15].

CONCLUSIONS

A large shift in fluorescence emission wavelength is observed on introduction of amino group at different positions of benzo[de]benzo[4,5]imidazo[2,1-a]isoquinolin-7-one. Different organic solvents such as dichloromethane, acetonitrile, and methanol can be distinguished

from the emission wavelengths of the **4** in these solvents. Depending on the position of an amino group on the rings and protonation of the amino groups at different positions, the fluorescence emissions shifts to higher or lower wavelength.

EXPERIMENTAL

UV–visible spectra were recorded on Perkin Elmer Lamda 25 UV–visible spectrometer, and the fluorescence spectra were recorded on Perkin Elmer LS-55 fluorescence spectrometer.

Table 2
The visible spectra and fluorescence emission (λ_{ex} = 410 nm) of derivatives of **2** and **4**.

	Dichloromethane			
	λ_{max} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Φ
R = NO₂ (**1**)	390	19,772	463	0.134
R = NH₂ (**2**)	430	12,727	508	0.252
R = NHCH₃ (**5**)	395	6818	515	0.060
R = NHCOCH₃ (**6**)	397	6136	545	0.350
R = NHCOC₆H₅ (**7**)	401	8409	546	0.452
R=NHCOCH₂Br (**8**)	393	10,909	518	0.343
R=NH₂ (**4**)	427	11,212	491	0.288
R=NHCH₃ (**9**)	375	18,909	538	0.156
R=NHCOCH₃ (**10**)	401	10,303	493	0.290
R=NHCOC₆H₅ (**11**)	401	19,181	493	0.324
R=NHCOCH₂Br (**12**)	395	10,393	495	0.215

Table 1
Effect of solvent on the visible spectra of **2** and **4**.

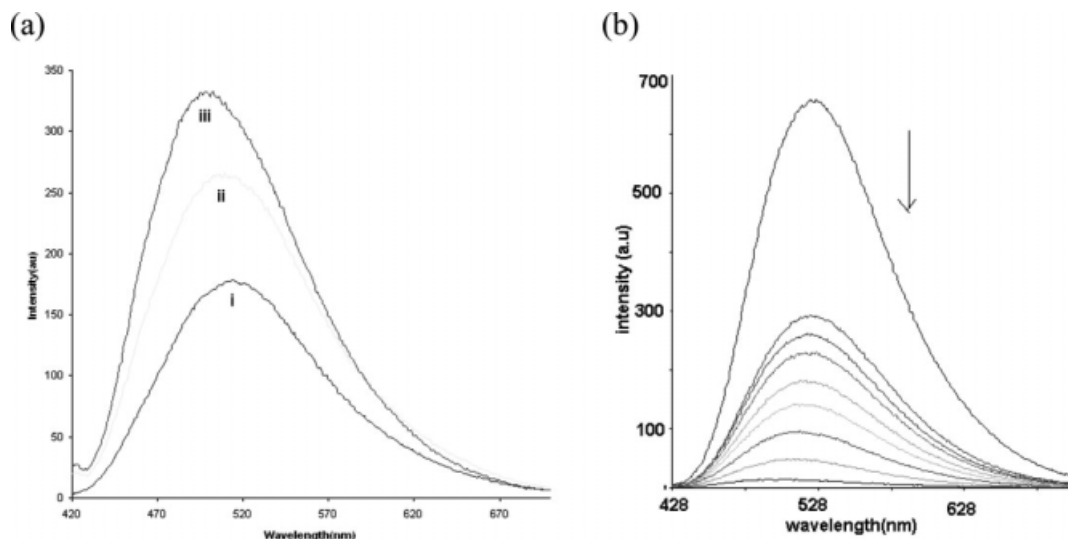|	Solvent	λ_{max} (nm)	ε (M^{-1} cm^{-1})
R = NH₂, R₁, R₂ = H (**2**)	Dichloromethane	430	12,727
R = NH₂, R₁, R₂ = H (**2**)	Methanol	437	10,227
R = NH₂, R₁, R₂ = H (**2**)	Acetonitrile	444	9545
R = H, R₁, R₂ = H/NH₂ (**4**)	Dichloromethane	427	11,212
R = H, R₁, R₂ = H/NH₂ (**4**)	Acetonitrile	432	10,000
R = H, R₁, R₂ = H/NH₂ (**4**)	Methanol	438	9696

Figure 2. (a) Fluorescence emission ($\lambda_{ex} = 410$ nm) spectra of (i) **2** in dichloromethane: (ii) on addition of 1 mol equiv of HCl and (iii) on addition of 2 mol equiv of HCl (in each cases 3 mL of $1.1 \times 10^{-5}M$ solution). (b) Effect of the addition of methanol (100 μL aliquots) to a solution of **2** in dichloromethane.

The NMR spectra were recorded on a 400 MHz Varian FT-NMR instrument with TMS as an internal standard. Mass spectra were recorded in a Water LC-MS. The melting points of the compounds were determined in a Buchi B-540 melting point apparatus. All the optical measurements were carried out by dissolving calculated amount of the compounds in spectroscopic grade solvents. The fluorescence titrations were carried out in quartz cuvette by adding different aliquots of titrant/s by micropipette to a parent solution (3 mL).

Determination of fluorescence quantum yield. Fluorescence quantum yields were determined by calibrating with perylene ($\Phi = 0.94$) by fluorescence excitation at 410 nm as standard. The fluorescence quantum yield was calculated by using the following formula [16]:

$$\frac{(\text{Quantum yield})_{sample}}{(\text{Quantum yield})_{standard}} = \frac{\text{Absorption of standard} \left(\text{Area under the graph of emission spectra}\right)_{Sample}}{\text{Absorption of sample} \left(\text{Area under the graph of emissio spectra}\right)_{Standard}}.$$

For calculation of the quantum yield of the other samples, the identical procedures were used.

Synthesis and characterization of various compounds.

Compound 1. A mixture of 1,8-naphthalic anhydride (0.99 g, 5 mmol) and 4-nitro 1,2 diaminobenzene (0.77 g, 5 mmol) was refluxed in acetic acid (10 mL) for 4 h. The reaction mixture was cooled and water (20 mL) was added to the reaction mixture and stirred for 20 min. The precipitate was filtered and washed several times with water to remove acetic acid. The product was air dried to obtain 11-nitro-benzo[de]benzo[4,5]imidazo[2,1-a]isoquinolin-7-one in 77% yield. Elemental Anal. Calcd. for $C_{19}H_9N_3O_3$; C, 68.57; H, 2.88; Found C, 68.60, H, 2.86. ^{1}H-NMR (400 MHz, CDCl$_3$): 9.17 (d, 1H, $J = 2.4$), 8.75 (m, 4H), 8.51 (dm, 1H, $J = 7.2$), 8.19 (s, 1H), 7.87 (m, 2H). IR (KBr, cm^{-1}): 1699 (s), 1517 (s), 1335 (s). ESI-MS: 316.1757 (M + H$^+$) m.p. 415°C.

Compound 2. To a solution of 11-nitro-benzo[de]benzo[4,5]imidazo[2,1-a]isoquinolin-7-one (0.32 g, 1 mmol) in ethanol/water (2:1, 20 mL), iron powder (35 mmol) and aqueous HCl (10%, 5 mL) were added. The mixture was kept at 90°C for 2 h. The reaction mixture was brought to room temperature and then water (10 mL) was added to the reaction

mixture and filtered. The solid product obtained was washed with water and the product was purified by preparative TLC. Yield: 55%. Elemental Anal Calcd. for $C_{18}H_{11}N_3O$; C, 75.78; H, 3.89; Found C, 75.80, H, 3.90. ^{1}H-NMR (400 MHz, CDCl$_3$) 8.76 (m, 2H), 8.26 (d, 1H, $J = 8.4$ Hz), 8.1 (d, 1H, $J = 8$ Hz), 7.9 (d,1H, $J = 2.4$ Hz), 7.8 (m, 2H), 7.66 (d, 1H, $J = 8.4$ Hz), 6.85 (d, 1H, $J = 8.4$ Hz), 5.0 (s, 2H).^{13}C-NMR (CDCl$_3$): 158.9, 145.8, 137.4, 134.3, 134.2, 131.6, 130.8, 129.7, 129.5, 129.3, 127.4, 125.9, 125.7, 123.1, 120.2, 120.1, 118.5, 115.3. IR (KBr, cm^{-1}): 3232 (w), 3363 (s), 1589 (m), 1621 (s), 1697 (s). ESI-MS = 286.1864 (M + H$^+$). m.p. 406°C.

Compound 3. A mixture of 3-nitro-1,8-naphthalic anhydride (1.22 g, 5 mmol) and 1,2 diaminobenzene (0.54 g, 5 mmol) was refluxed in acetic acid (20 mL) at 90°C for 4 h. The reaction mixture was cooled and then water (20 mL) was added to the reaction mixture and stirred for 20 min. The precipitate was filtered and washed several times with water to remove acetic acid, and the product was air dried to obtain a mixture of 2-nitro-benzo[de]benzo[4,5]imidazo[2,1-a]onemethane and 5-nitro-benzo[de]benzo[4,5]imidazo [2,1-a]isoquinolin-7-one in
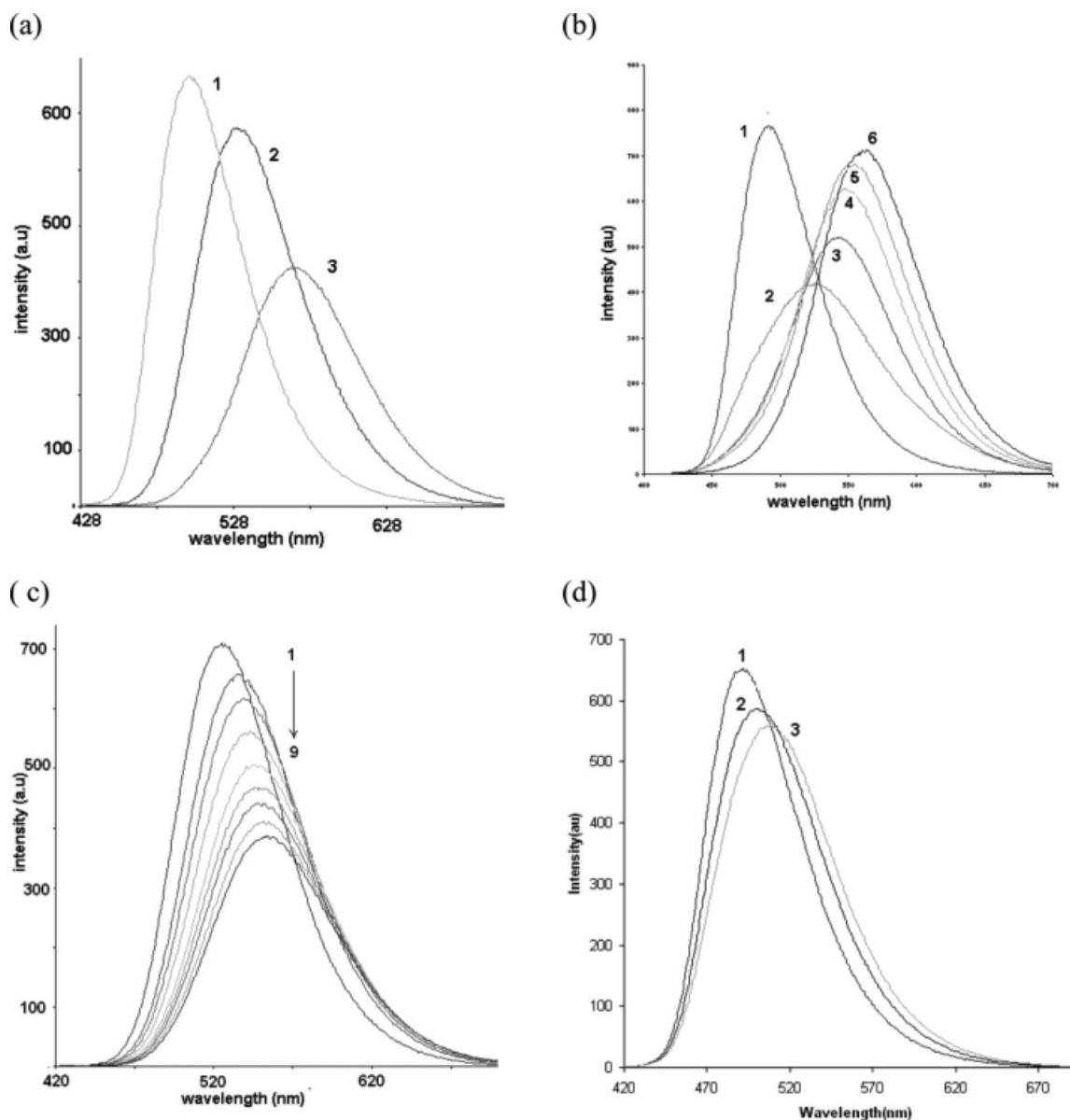
Figure 3. The fluorescence emission of (λ_{ex} = 410 nm): (a) **4** in (i) dichloromethane, (ii) acetonitrile, and (iii) methanol (in each cases 3 mL of $1.1 \times 10^{-5}M$ solution **4**); (b) **4** on addition of different aliquots of methanol (50 µL each from 2–6) to a dichloromethane solution of **4**; (c) **4** on addition of different aliquots of methanol (50 µL each from 2–6) to an acetonitrile solution of **4**; (d) **4** (1) in dichloromethane and on addition of (2) 1 equiv of HCl or (3) 2 equiv of HCl.

86% yield. ^{1}H-NMR (400 MHz, CDCl$_3$): 9.55 (d, J = 4 Hz, 1H) 9.48 (d, J = 4 Hz, 1H), 9.18 (d, J = 4 Hz, 1H), 9.0 (d, J = 4 Hz, 1H), 8.98 (d, 1H, J = 8 Hz), 8.95 (d, 1H, J = 8 Hz), 8.54 (m, 2H), 8.48 (d, 1H, J = 8 Hz), 8.35 (d, J = 8 Hz, 1H), 7.99 (t, J = 8 Hz, 2H), 7.91–7.94 (m, 2H), 7.50–7.53 (m, 4H). IR (KBr, cm^{-1}): 3444 (m), 3067 (m), 1696 (s), 1596 (m), 1531 (m), 1443 (w), 1343 (s), 1234 (m), 1152 (w), 1039 (w), 751 (m), 557 (w). ESI-MS: 316.1814 (M + H$^+$). m.p. 410°C.

Compound 4. To a solution of mixture of 2-nitro-benzo[de]-benzo[4,5]imidazo[2,1-a]onemethane and 5-nitro-benzo[de]-benzo[4,5]imidazo [2,1-a]isoquinolin-7-one (1.58 g, 5 mmol) in tetrahydrofuran (20 mL), palladized carbon (10%, 0.1 g) was added. The mixture was stirred under hydrogen atmosphere (50 psi) for 24 h, filtered, and the solvent was removed from filtrate under reduced pressure to get the desired product. The yield after purification was 85%. ^{1}H-NMR (400 MHz, CDCl$_3$): 8.48–8.56 (m, 4H), 8.25 (d, J = 3 Hz, 1H), 8.18 (d, 1H, J = 3 Hz), 7.96 (d, J = 8 Hz, 1H), 7.83–7.85 (m, 2H), 7.62–7.67 (m, 2H), 7.43–7.48 (m, 4H), 7.35 (d, J = 3 Hz, 1H) 4.2 (broad s, 2H). ^{13}C-NMR (CDCl$_3$): 158.1, 145.4, 134.2,

133.3, 130.0, 128.2, 127.8, 127.4, 125.9, 125.6, 125.4, 123.9, 122.4, 120.1, 118.0, 116.1, 115.7, 112.5. IR (KBr, cm^{-1}): 3448 (w), 3362 (s), 2924 (m), 2851 (m), 1690 (s), 1627 (s), 1550 (w), 1448 (w), 1352 (s), 1330 (s), 1166 (w), 1050 (w), 872 (w), 764 (w). ESI-MS: 286.1957 (M + H$^+$). m.p. 405°C.

Compounds 5–8. The 11-amino-benzo[de]benzo[4,5]imidazo[2,1-a]isoquinolin-7-one (**2**) was converted to corresponding *N*-methyl (**5**), *N*-acetyl (**6**), *N*-benzoyl (**7**), and *N*-bromoacetyl derivatives (**8**) by reactions with suitable reagents as follows:

Compound 5. A mixture of compound **1** (0.1 g, 0.35 mmol) and anhydrous potassium carbonate was refluxed in dry acetone with methyl iodide (0.08 g, 0.53 mmol) for 24 h. The reaction mixture was evaporated, water (15 mL) and dichloromethane (15 mL) were added, the organic layer was separated, and the product was extracted from the dichloromethane by evaporation. The compound was further purified by TLC. Yield: 25 %. ^{1}H-NMR (400 MHz, DMSO-d_6): 8.65 (d, 1H, J = 7.2 Hz), 8.16 (d, 1H, J = 8.4 Hz), 7.98 (d, 1H, J = 8.4 Hz), 7.82 (d, 1H, J = 2.8 Hz), 7.7 (m, 4H), 6.86 (dd, 1H, J = 2.8 Hz), 3.0 (s, 3H). IR (KBr, cm^{-1}): 3390 (s), 2924 (s), 2853 (m), 1693 (s), 1621 (s), 1502 (s), 1318 (m). ESI-MS: 300.1132 (M + H$^+$). m.p. 386°C.

Compounds 6–8. The compound **2** (0.06 g, 0.2 mmol) was mixed with RCOX (for **6, 7** R = CH$_3$, Ph and X = Cl, respectively, whereas for **8** R = BrCH$_2$CO- and X = Br) and triethylamine (0.4 mL) in dry dichloromethane (10 mL). The mixture was stirred overnight at room temperature. On adding 40 mL water to the reaction mixture, the solid products in pure form were obtained from dichloromethane in quantitative yield.

Compound 6. ^{1}H-NMR (400 MHz, DMSO-d_6): 10.26 (s,1H), 8.9 (s,1H), 8.72 (d, 2H, J = 8 Hz), 8.54 (d, 1H, J = 8.4 Hz), 8.38 (d, 1H, J = 8.4 Hz), 7.94 (m, 2H), 7.8 (d, 1H, J = 8.8 Hz), 7.64 (d, 1H, J = 8.4 Hz), 2.1 (s, 3H). ^{13}C-NMR (100 MHz, DMSO-d_6): 168.4, 159.8, 149.9, 143.7, 139.2, 137.2, 135.5, 132.1, 131.7, 131.1, 127.4, 127.1, 126.7, 122.5, 119.92, 117.5, 116.9, 115.0, 109.6, 105.9, 24.1. IR (KBr, cm^{-1}): 3302 (s), 2923 (s), 2852 (m), 1702 (s), 1662 (s), 1597 (m). ESI-MS: 328.1220 (M + H$^+$). m.p. 395°C.

Compound 7. ^{1}H-NMR (400 MHz, DMSO-d_6) 10.57 (s, 1H), 8.7 (d, 1H, J = 3.6 Hz), 8.52 (d, 1H, J = 7.6 Hz), 8.36 (d, 1H, J = 7.2 Hz), 8.15 (d,1H, J = 4.8 Hz), 8.04 (d,1H, J = 4.8 Hz), 7.94 (d, 2H, J = 4.8 Hz), 7.9 (s, 1H), 7.83 (d, 1H, J = 7.2 Hz), 7.63 (d, 2H, J = 4.8 Hz), 7.57 (s, 1H), 7.51 (d, 2H, J = 4.8 Hz). ^{13}C-NMR (100 MHz, DMSO-d_6): 165.5, 160.0, 148.63, 139.5, 136.7, 135.3, 135.0, 131.7, 131.4, 131.0, 129.3, 128.4, 127.8, 127.3, 127.0, 126.1, 122.5, 120.0, 119.2, 118.7, 115.0, 111.1, 107.2. IR (KBr, cm^{-1}): 3301 (m), 3071 (m), 1703 (s), 1601 (m), 1699 (s). ESI-MS: 390.1217 (M + H$^+$). m.p. 385°C.

Compound 8. ^{1}H-NMR (400 MHz, DMSO-d_6): 10.72 (s, 1H), 8.90 (s, 1H), 8.70 (d, 2H, J = 8.4 Hz), 8.53 (d, 1H, J = 8.4 Hz), 8.37 (d, 1H, J = 8.4 Hz), 7.9 (m, 2H), 7.8 (m, 1H), 7.65 (d, 1H, J = 8.4 Hz), 4.1 (s, 2H). ^{13}C-NMR (100 MHz, DMSO-d_6): 170.9, 160.0, 148.5, 136.5, 136.1, 135.5, 132.4, 131.8, 131.3, 127.4, 127.1, 126.2, 122.5, 119.8, 119.47, 119.2, 118.3, 117.6, 106.5, 62.0. IR (KBr, cm^{-1}): 3253 (s), 2959 (s), 1698 (m), 1654 (s), 1737 (s), 1591 (m), 1233 (m). ESI-MS: 405.9840 and 407.9832 (M + H$^+$). m.p. 378°C.

Compounds 9–12. The compounds **9**, **10**, **11**, and **12** were synthesized from compound **4** by identical procedure that is described for **5**, **6**, **7**, and **8**, respectively.

Compound 9. Yield: 28%. ^{1}H-NMR (400 MHz, CDCl$_3$): 8.53 (m,4H), 8.43 (d, 1H, J = 6.4 Hz), 8.39 (d, 1H, J = 2.8 Hz), 8.32 (d, 1H, J = 2.8 Hz), 8.00 (d, 1H, J = 8.0 Hz), 7.85 (m, 4H), 7.62 (m, 2H), 7.45 (m, 4H), 7.21 (d, 1H, J = 2.4 Hz), 7.10 (d, 1H, J = 2.4 Hz), 3.07 (d, 6H, J = 6.8 Hz). IR (KBr, cm^{-1}): 3445 (s), 2924 (m), 2852 (w), 2357 (w), 1622 (s), 1430 (m), 1327 (s), 1231 (m), 1159 (w), 927 (w), 842 (w), 763 (m). ESI-MS: 300.1147 (M + H$^+$). m.p. 367°C.

Compound 10. Yield: 82%. ^{1}H-NMR (400 MHz, CDCl$_3$): 9.92 (s,1H), 9.85 (s,1H), 8.43 (s,1H), 8.28 (d, 2H, J = 4.0 Hz), 8.26 (s,1H), 8.15 (d, 1H, J = 4.0 Hz), 8.08 (d, 1H, J = 7.2 Hz), 8.00 (t, 2H, J = 5.6 Hz), 7.73 (d, 1H, J = 8.4 Hz), 7.60 (d, 1H, J = 7.2 Hz), 7.34 (m, 2H), 7.28 (t, 2H, J = 8.0 Hz), 6.98 (dd, 4H, J = 3.6 Hz), 2.08 (s, 4H). ^{13}C-NMR (100 MHz, DMSO-d_6): 169.1, 160.0, 148.6, 143.2, 138.3, 134.7, 132.4, 131.3, 129.2, 127.2, 125.4, 125.0, 122.8, 122.2, 120.2, 119.7, 119.5, 118.4, 115.1, 45.3. IR (KBr, cm^{-1}): 3433 (s), 2983 (m), 2738 (w), 2678 (w), 1657 (s), 1558 (m), 1347 (m), 1262 (m), 1161 (w), 1035 (m), 878 (w), 767 (m). ESI-MS: 328.1239 (M + H$^+$). m.p. 356°C.

Compound 11. Yield: 84%. ^{1}H-NMR (400 MHz, CDCl$_3$): 10.24 (s, 1H), 10.18 (s, 1H), 8.72 (s, 1H), 8.58 (s, 1H), 8.22 (d, 1H, J = 7.2 Hz), 8.10 (dd, 2H, J = 3.6 Hz), 7.87 (d, 1H, J = 8.4 Hz), 7.70 (t, 4H, J = 8.0 Hz), 7.59 (d, 4H, J = 6.4 Hz), 7.40 (dd, 2H, J = 6.0 Hz), 7.31 (t, 2H, J = 7.6 Hz), 7.15 (m, 5H), 7.04 (m,5H). ^{13}C-NMR (100 MHz, DMSO-d_6): 168.2, 166.6, 163.1, 143.5, 138.3, 135.8, 134.6, 133.6, 132.6, 131.5, 131.1, 130.8, 129.91, 129.8, 129.2, 128.4, 128.3, 125.6, 120.0, 115.0. IR (KBr, cm^{-1}): 3394 (s), 3054 (w), 2923 (w), 1788 (m), 1705 (s), 1657 (m), 1543 (s), 1351 (m), 1243 (s), 1174 (m), 1040 (m), 877 (w), 750 (w), 705 (m). ESI-MS: 390.1074 (M + H$^+$). m.p. 362°C

Compound 12. Yield: 80%. ^{1}H-NMR (400 MHz, CDCl$_3$): 10.44 (s, 1H), 10.38 (s, 1H), 8.46 (s, 1H), 8.37 (s, 1H), 8.31 (s, 2H), 8.22 (d, 1H, J = 7.6 Hz), 8.16 (d, 1H, J = 7.2 Hz), 8.03 (t, 1H, J = 6.8 Hz), 7.79 (d, 1H, J = 8.4 Hz), 7.66 (d, 1H, J = 8.0 Hz), 7.35 (m, 3H), 7.14 (m, 2H), 7.05 (dd, 4H, J = 3.2 Hz), 3.64 (s, 4H). ^{13}C-NMR (100 MHz, DMSO-d_6): 172.4, 160.5, 149.4, 143.8, 138.2, 135.6, 133.1, 132.0, 130.2, 128.1, 126.2, 125.8, 123.8, 123.0, 120.8, 120.2, 119.9, 115.9, 62.7. IR (KBr, cm^{-1}): 3437 (s), 3274 (s), 1697 (s), 1673 (s), 1599 (m), 1552 (m), 1492 (w), 1431 (m), 1347 (m), 1050 (w), 868 (w), 766 (m), 677 (w). ESI-MS: 405.9780 and 407.9749 (M + H$^+$). m.p. 360°C.

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