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4,7-Diaryl indole-based fluorescent chemosensor for iodide ions

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ABSTRACT

Simple and selective indole based fluorescent sensors for iodide anions are reported. A series of 4,7-diaryl indole derivatives (**DAIs**) are designed and synthesized using Suzuki coupling. These **DAIs** shows significant changes in UV–vis and fluorescent intensity only with addition of iodides and not with other anions. The ability of these **DAIs** to function as selective iodide chemosensor is reported.

1. Introduction

The design and synthesis of systems that are capable of sensing various biologically and chemically important anions are currently of major interest because they play a fundamental role in chemical, biological, and environmental processes.[1] The search for a chemosensor for recognition and sensing of specific anionic analytes through naked eye, electrochemical and optical responses are emerging research areas of considerable importance.[2] On account of simplicity, high sensitivity, and response time, fluorescence is becoming of increasing importance for trace chemical detection. The practical detection of anions has continued to be a more challenging issue than the detection of cations, which has been developed for almost 40 years.[3]

The iodide ion is one of the most significant, since it plays an important role in biological activities, such as thyroid function and neurological activity. In many systems the iodide content of milk and urine is often required for metabolic, nutritional, and epidemiological studies of thyroid disorder.[4] In addition; elemental iodine has been frequently used in many areas of chemistry for synthesizing valuable molecules, such as drugs, dyes, and molecular electronics. There are few reports on the fluorescent recognition of iodide using small molecules and conjugated polymers.[5] In most cases, hydrogen bonding between the N–H of the molecule and anions was used for the recognition, without the involvement of hydrogen bonds, quaternized ammonium hosts,[6] azamacrocycles,[7] and phosphonium hosts[8] are known to form anion complexes. A cyclic peptide has been reported for anion sensing, which includes iodides, bromides, chlorides, and fluorides, but there is no selectivity.[9] Adenine,[10] bis-imidazolinium,[11] trifluoroacetyl aminophthalimide based derivatives,[12] benzimidazole based tripodal receptor,[13] pyrenyl-appended triazole-based calix[4]arene,[14] silver nanoparticles,[15] *N*-fused tetraphenylporphyrin,[16] and macrocyclic binuclear copper(II) complex[17] have been reported as selective iodide sensors. Herein we report the synthesis of new indole sensors containing heterocyclic moieties and their selective sensing of iodide ions. The electronic nature of the substituents was used to tune the selectivity and the photophysical properties of the chemosensors. The present receptors are designed based on; N–H bonds in the receptor aligned in parallel, which can effectively make a complex with iodide ions.

2. Results and discussion

2.1. Synthesis of 4,7-diaryl indoles A–G

Compound **2** was obtained from 1,4-dibromobenzene, with concd HNO_3/H_2SO_4 and compound **3** was synthesized using the procedure reported in the literature.[18] The target **DAIs** were then synthesized by Suzuki coupling of 4,7-dibromo indole **3** with the

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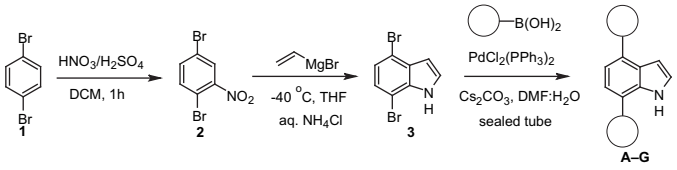
corresponding boronic acid (Scheme 1). All the target receptors were soluble in common organic solvents, such as CH_2Cl_2, $CHCl_3$, MeOH, and THF (Fig. 1).



Scheme 1. Synthesis of 4,7-diaryl indole derivatives **A**–**G**.

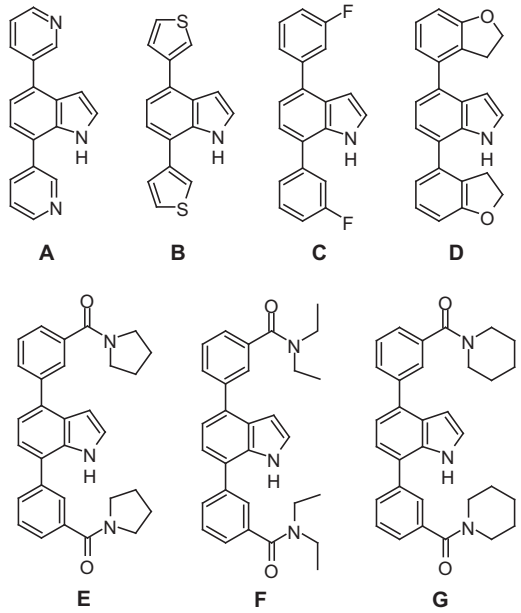


Fig. 1. Structure of synthesized 4,7-diaryl indoles.

2.2. Photophysical study of 4,7-diaryl indoles A–G

The optical properties of **A**–**G** were measured using UV–vis and fluorescence in THF solution (10^{-4} M solution) and the results were summarized in Table 1. Fig. 2 shows that all the absorption maximum (λ_{max}) of these **DAIs** fall in the range of 315–328 nm. The λ_{max} of **A**–**G** were observed at 321, 315, 320, 321, 320, 319, and 328 nm, respectively. Since there is no significant difference in the conjugation length, there are no significant changes in the λ_{max} with changes in the alkyl group. The fluorescence spectra of the **DAIs** were recorded with the excitation wavelength corresponding to

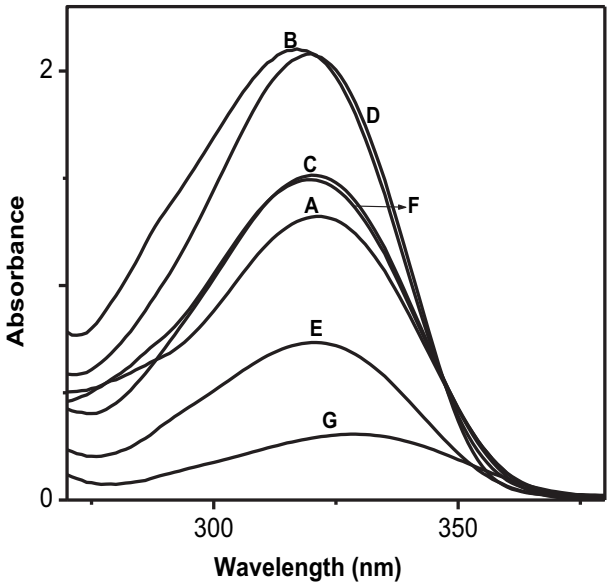


Fig. 2. Absorption spectra of **A**–**D** was 4.67×10^{-4} and **E**–**G** were 2.67×10^{-4} M, respectively.

their maximum absorption wavelength. Heterocycles incorporated compounds (**A** and **B**) are comparatively blue shifted. Fig. 3 shows all the λ_{em} of **A**–**G** are 396, 397, 409, 405, 398, 406, and 438 nm, respectively. In the emission spectra of **C**, **D**, and **F** in dilute solution, there was a shoulder peak observed (Fig. 3).

2.3. Spectrophotometric and spectrofluorimetric sensing study with anions

The variation of indole through the introduction of UV active aryl groups at 4, 7 position is expected to improve the photophysical properties for the chemosensing studies. Considering the biological, environmental analytical relevance of anions, such as F^-, Cl^-, Br^- and I^-, the interaction of **DAIs** with these anions was evaluated through UV–vis and fluorescence sensing in THF, through the sequential addition of increasing anion equivalents. The sensing abilities of synthesized **DAI** compounds were tested with the anions fluoride, chloride, bromide, and iodide. During iodide ion titration with compound **G**, the absorbance at 328 nm was shifted to 298 nm (Fig. 4). In this series maximum shift was observed for compound **G** (−30 nm) followed by compound **A** (−23 nm) and the results were summarized in Table 2. The changes in the absorption spectra upon the complexations are due to the direct interaction between the **DAIs** N–H and anions.

To further evaluate the selectivity of **DAIs** toward various anions, the fluorescence spectra of **DAIs** were taken in the presence of TBA salts. There are many examples where other halides predominantly

Table 1
Physical properties of 4,7-diaryl indoles **A**–**G**

Compounds	Absorption λ_{max}	Emission λ_{em}	λ_{onset}	Band gap[a] (eV)	ϵ_{max}	Decomposition temp °C	DSC °C
A	321	396	361	3.43	2.86×10^3	288	189
B	315	397	355	3.49	4.34×10^3	229	129
C	320	409	359	3.45	3.26×10^3	192	—[b]
D	321	405	356	3.48	4.56×10^3	300	210
E	320	398	361	3.43	2.69×10^3	241	195
F	319	406	360	3.44	5.76×10^3	265	224
G	328	438	370	3.35	1.12×10^3	260	195

[a] Calculated from onset wavelength.
[b] Not measured.

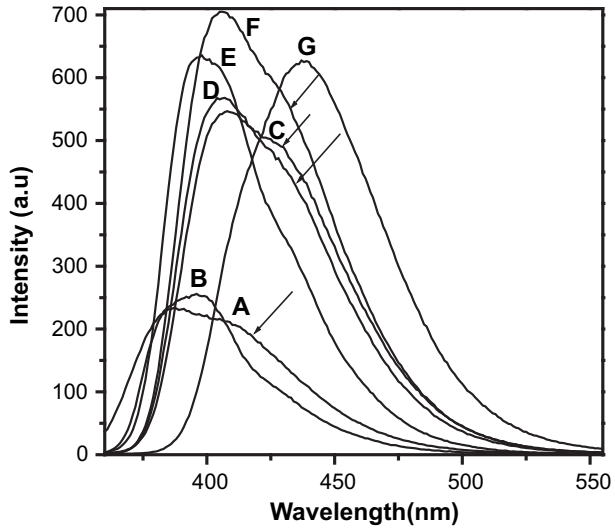


Fig. 3. Emission spectra of **A**–**G** in THF, The concentration of **A**–**D** was 2.67×10^{-4} and E–G were 1.3×10^{-4} M, respectively.

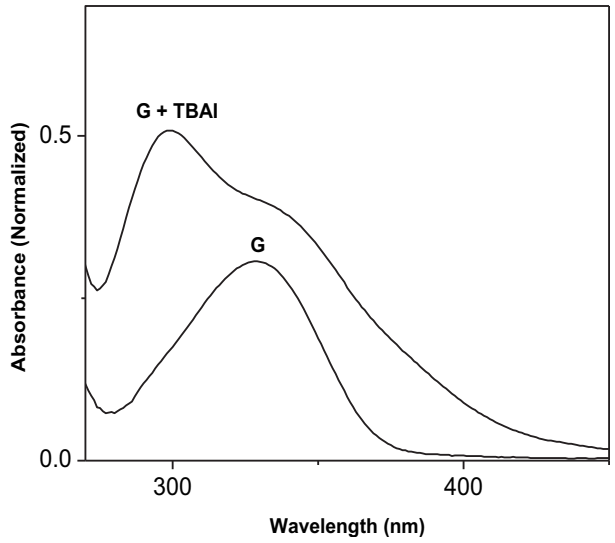


Fig. 4. Absorption spectrum of **G**, **G**+iodides. Concentration of **G** is 2.67×10^{-4} M.

absorption (see Figures in Supplementary data). However, addition of the iodide ion results in a blue shift in the absorption spectrum (Fig. 5) and decrease in fluorescence intensity.

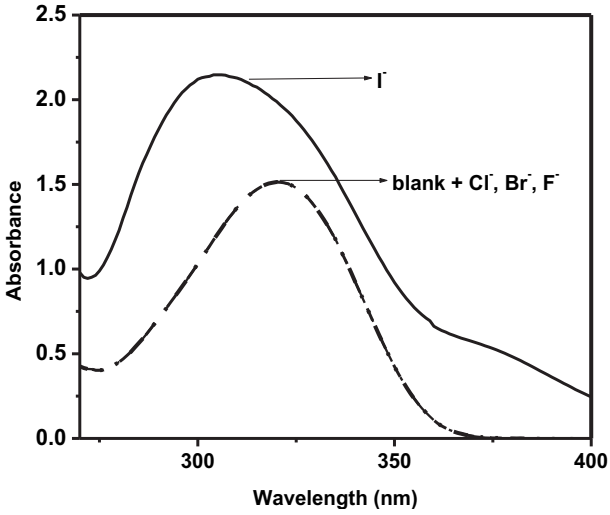


Fig. 5. The effect of various ions (80 μM) on the UV–vis spectra of **F** is 2.6×10^{-4} M.

The quenching effects of the **DAIs** fluorescence in the presence of TBAI salts have been investigated in detail. In Fig. 6 is shown the fluorescence quenching of compound **F** with iodide ion at the wavelength of maximum emission at 406 nm. The addition of iodide salt into the **DAIs** solution quenched the fluorescence intensities of **A**–**G** (see Supplementary data for spectrofluorimetric titration of **A**–**G** with iodide). The changes in the emission of **F** at 406 nm upon titration with different anion solutions in THF are shown in Fig. 7. The addition of iodide anion resulted in decrease in the fluorescence intensity. The solid lines represent the generated fit-curve from the data sets (Fig. 7). Fig. 8 shows the fluorescence spectra of receptor **B** in the presence of various anions. The association constants K_a of **A**–**G** for iodide were calculated on the basis of Benesi–Hildebrand plot[20] and were found to be 2.9×10^3 M^{-1}, 4.3×10^3 M^{-1}, 3.5×10^3 M^{-1}, 2.7×10^4 M^{-1}, and 2.14×10^3 M^{-1}, respectively. The stoichiometry of the complex formed was determined by Job's plot,[21] and turned out to be 1:1 stoichiometry (Fig. 9). This indicated that sensor had reached a saturation level as it binds to its anion guest. The nature of other anions, such as tetrabutylammonium halides (F^-, Cl^-, Br^-) does not influence the fluorescence change. The observed $\Delta\lambda_{max}$ and $\Delta\lambda_{em}$ are given in Table 2. In general the fluorescence quenching is explained through different mechanisms, like ground state complexation,[22] charge-

Table 2
Absorption and emission responses of **A**–**G** upon addition of iodides

A–**G**	λ_{max} I^- free (nm)	λ_{max} with I^- (nm)	$\Delta\lambda_{max}$	λ_{em} I^- free (nm)	λ_{em} with I^- (nm)	$\Delta\lambda_{em}$ (nm)	*K*sv upon addition of (TBA)I 10^5
A	322	299	−23	387	420	+33	2.73
B	319	306	−13	375	390	+15	3.86
C	318	299	−19	388	421	+33	2.81
D	317	306	−11	377	413	+36	2.72
E	320	298	−22	386	416	+30	5.97
F	319	312	−07	385	420	+35	6.28
G	328	298	−30	417	445	+28	3.66

bind with the receptor ions due to the size matching between the receptor and anion.[19] The sensing properties of **A**–**G** were investigated using the corresponding tetrabutylammonium salts in tetrahydrofuran solution. Interestingly, these **DAIs** detect only iodide among other common anions, such as fluorides, chlorides, and bromides. In the case of the addition of fluoride, chloride, and bromide ions into the **DAIs** solution, no significant changes in

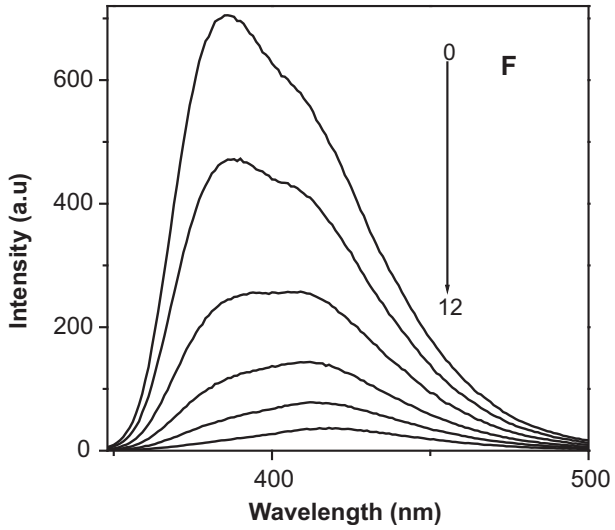


Fig. 6. Change in the emission spectra of F with different concentrations of TBAI in THF solution; (1) 0 μM, (2) 2 μM, (3) 4 μM, (4) 6 μM, (5) 8 μM, (6) 10 μM, (7) 12 μM.

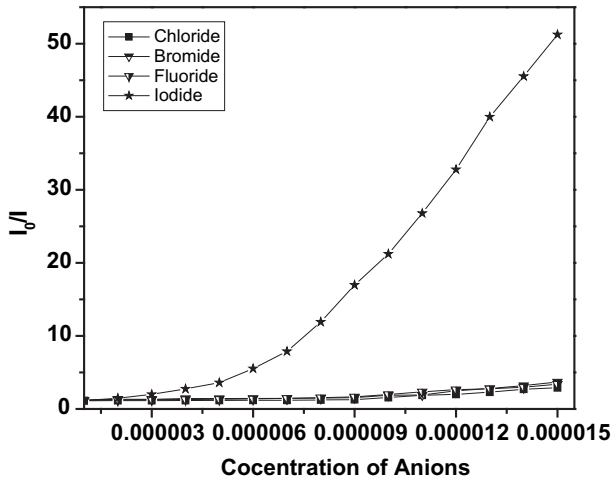


Fig. 7. Relative change in the emission of **F** upon titration with different anions (0μ–13 μM) solutions in THF.

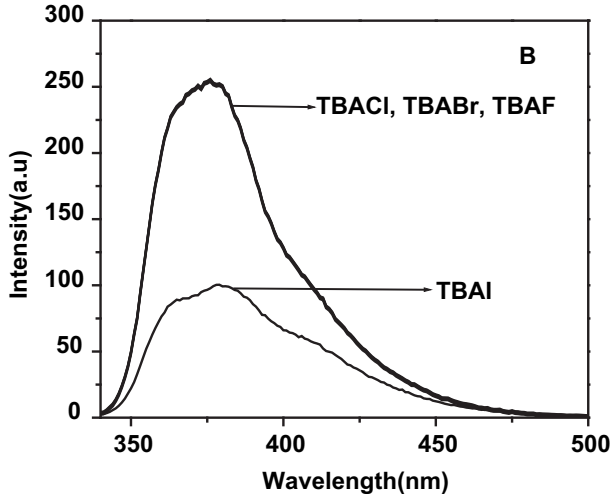


Fig. 8. Change in the emission spectra of **B** at different Anions. After addition of TBA salts at 20 μM.

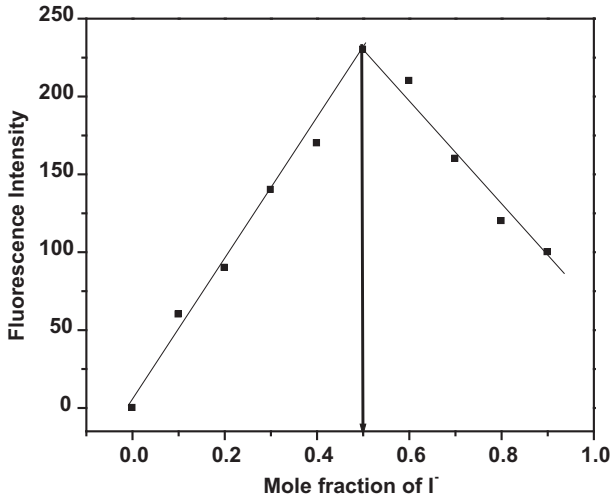


Fig. 9. Fluorescence Job's plot of F with TBAI in THF measured at 406 nm.

transfer phenomena,[23] electronic energy transefer,[24] fluorescence resonance energy transfer,[25] and heavy atom effect.[26] In this case, the charge–transfer complex via a heavy atom effect is proposed. The heavy atom interaction between the excited state of the **DAI** and the anions leads to an enhancement of the spin–orbital coupling.[27] There are two types of quenching, one is the static quenching through formation of a complex and another is the dynamic quenching due to random collisions between the emitter and the quencher. In both quenching mechanisms, the electron/energy transfer is involved from the emitter to the each can be quantitatively described by the Stern–Volmer studies.[27]

Dynamic quenching involves the deactivation of **DAIs** exciton through collisions with quencher molecules or ions in solution. The rate of quenching can be determined by using the slope of the Stern–Volmer plot and lifetime measurements. Conversely, the static quenching results from complexation of the analyte to the receptor sites, are creating a new absorption, relaxation or energy transfer processes that favor non-radiative decay or through a new excitation/emission behavior. Using Stern–Volmer plots, the equilibrium constant for static quenching (*K*sv) could be calculated and considered as the binding constants for the quencher–acceptor system.[28] The fluorescence intensities are decreasing with increase in time and become constant.

The Stern–Volmer equation states that $(I_0/I)=1+\mathrm{Ksv}[\mathrm{quencher}]$, Where I_0 is the intensity of the fluorescence from the **DAIs** in the absence of quencher and I is the intensity of the **DAIs** in the presence of the quencher. *K*sv is the Stern–Volmer constant, which provides the quantitative measure of the quenching. At low concentration of quenchers (TBAI), the quenching efficiency was more efficient and I_0/I versus the concentration of the quencher gives a linear plot,[29] indicating a static quenching due to complex formation between **A**–**G** and quencher was observed. Among the **A**–**G**, the highest *K*sv values were obtained for *F* (6.28×10^5), which may be due to the formation of diazonium salt (see Supplementary data). The Stern–Volmer constant *K*sv for all **DAIs** are summarized in Table 2. Fig. 10 shows the comparative fluorimetric response of **A**–**G** in the presence of fluoride, chloride, bromide, and iodide ions.

3. Conclusion

In summary, we have developed a new indole based **DAIs** series **A**–**G** and studied the absorption and fluorescence sensing properties toward ions (tetrabutylammonium salts) have been

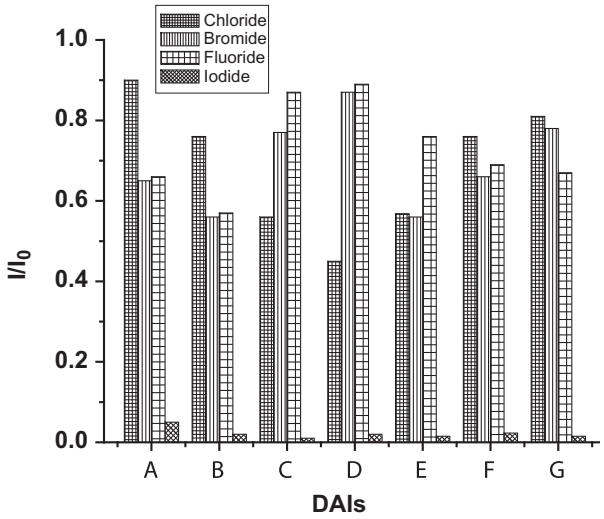


Fig. 10. Relative fluorimetric responses I/I_0 of **A**–**G** in the presence of TBA salts in THF.

investigated. Selectivity and sensitivity for the iodide ion was well observed for all systems. The molecular interactions between **DAIs** and anions are really important because the knowledge base in the field of chemosensors and fluorescence 'turn on' sensors still needs to be improved before going for applications.

4. Experimental section

4.1. General

All reagents were purchased from Aldrich, Fluka and/or Merck and were used without further purification unless otherwise stated. All reactions were carried out with dry, freshly distilled solvents under anhydrous conditions or in an inert atmosphere. Tetrahydrofuran was purified by distillation from sodium in the presence of benzophenone under nitrogen atmosphere. 1,4-Dibromo-2-nitrobenzene and 4,7-dibromo indole were prepared using literature methods.[18] All boronic acid were purchased from Aldrich. The NMR spectra were collected on a Bruker ACF 300 spectrometer with MeOD, DMSO-d_6, $CDCl_3$ solvent and tetramethylsilane as internal standard. Elemental analyses were done in VarioMicro analyzer. UV–vis spectra were recorded on a PG Instrument Ltd spectrophotometer. Fluorescence measurements were carried out on an RF-5301PC Shimadzu spectrofluorophotometer.

4.2. General procedure for the preparation of 4,7-di-aryl-3-yl-1*H*-indoles A–G

4,7-Dibromoindole (**3**, 100 mg, 0.364 mmol) and 3-pyridine boronic acid (134 mg, 1.097 mmol) were dissolved in DMF and water (3:3 mL). After the addition of Cs_2CO_3 (293 mg, 0.912 mmol), the reaction mixture was degassed then bis(triphenylphosphine) palladium(II) chloride (38 mg, 0.0547 mmol) was added and the mixture stirred vigorously for 16 h at 120 °C in sealed tube. The mixture was then cooled to room temperature and poured into water and extracted with ethylacetate (2×25 mL). The organic layer was separated, washed with brine (20 mL), dried (Na_2SO_4), and the solvent evaporated in vacuo. Purification of the crude product by flash chromatography (20% ethyl acetate/hexane) gave the *title compound* **A**.

*4.2.1. 4,7-Di-pyridin-3-yl-1H-indole (**A**).* Yield (45 mg, 45%) as a pale yellow crystalline solid; [found: C, 79.51; H, 4.80; N, 15.61. $C_{18}H_{13}N_3$ requires C, 79.68; H, 4.83; N, 15.49%]; *m*/*z* 271.0 (M); δ_H (400 MHz, MeOD) 6.69 (1H, d, *J* 3.2 Hz, indole C*H*), 7.29 (2H, t, *J* 7.5 Hz, indole C*H*), 7.41 (2H, d, *J* 3.2 Hz, pyridine C*H*), 7.58–7.59 (2H, m, indole C*H*), 8.15–8.19 (2H, m, pyridine C*H*), 8.58 (2H, dd, *J* 3.6, 8.3 Hz, pyridine C*H*) 8.86 (1H, d, *J* 7.6 Hz, pyridine C*H*), 8.90 (1H, s, indole N*H*); δ_C (100 MHz, MeOD) 100.3, 119.6, 121.9, 122.0, 123.9, 124.2, 125.2, 126.5, 127.0, 129.8, 130.2, 135.6, 136.7, 136.9, 137.5, 147.0, 147.5, 148.2.

*4.2.2. 4,7-Di-thiophen-3-yl-1H-indole (**B**).* Yield (83 mg, 81%) as a brown solid; [found: C, 68.37; H, 3.90; N, 4.81; S, 22.72. $C_{16}H_{11}NS_2$ requires C, 68.29; H, 3.94; N, 4.98; S, 22.79%]; *m*/*z* 281.3 (M); δ_H (400 MHz, DMSO-d_6) 6.78 (1H, s, indole C*H*), 7.29 (2H, q, *J* 7.6 Hz, indole C*H*), 7.42 (1H, s, thiophene C*H*), 7.55 (2H, t, *J* 4.6 Hz, indole C*H*), 7.68 (1H, d, *J* 3.6 Hz, thiophene C*H*), 7.74 (1H, d, *J* 3.6 Hz, thiophene C*H*), 7.83 (2H, dd, *J* 1.4, 11.6 Hz, thiophene C*H*), 11.10 (1H, s, indole N*H*); δ_C (100 MHz, DMSO-d_6) 101.2, 118.7, 119.3, 121.0, 121.6, 121.9, 122.1, 126.2, 126.5, 126.9, 127.0, 127.6, 127.8, 133.2, 138.9, 141.4.

*4.2.3. 4,7-Bis-(3-fluoro-phenyl)-1H-indole (**C**).* Yield (46 mg, 41%) as a yellow solid; [found: C, 78.59; H, 4.25; N, 4.48. $C_{20}H_{13}F_2N$ requires C, 78.68; H, 4.29; N, 4.59%]; *m*/*z* 305.0 (M); δ_H (400 MHz, $CDCl_3$) 6.82 (1H, d, *J* 2.2 Hz, indole C*H*), 6.83–7.09 (2H, m, Ph C*H*), 7.30 (4H, q, *J* 7.6 Hz, Ind and Ph C*H*), 7.38–7.43 (5H, m, Ind and Ph C*H*), 8.56 (1H, s, indole N*H*); δ_C (100 MHz, $CDCl_3$) 102.6, 113.9, 114.6, 115.7, 120.3, 122.3, 123.9, 124.0, 124.4, 125.1, 126.5, 129.9, 130.7, 130.9, 132.9, 133.9, 141.2, 143.2, 161.8, 164.6.

*4.2.4. 4,7-Bis-(2,3-dihydro-benzofuran-4-yl)-1H-indole (**D**).* Yield (71 mg, 55%) as a brown solid; [found: C, 81.50; H, 5.51; N, 3.99. $C_{24}H_{19}NO_2$ requires C, 81.56; H, 5.42; N, 3.96%]; *m*/*z* 353.1 (M); δ_H (400 MHz, DMSO-d_6) 3.28–3.35 (4H, m, CH_2), 4.59 (4H, q, *J* 8.4 Hz, OCH_2), 5.75 (1H, s, indole C*H*), 6.59 (2H, q, *J* 1.8 Hz, indole C*H*), 6.89 (2H, q, *J* 8.2 Hz, Ph C*H*), 7.05–7.07 (3H, m, Ind and Ph C*H*), 7.52 (2H, d, *J* 3.5 Hz, Ph C*H*), 10.99 (1H, s, indole N*H*); δ_C (100 MHz, DMSO-d_6) 29.2, 29.3, 71.0, 71.1, 100.9, 108.9, 109.2, 118.8, 121.2, 124.2, 124.9, 125.0, 126.1, 126.3, 127.7, 127.8, 127.9, 129.7, 130.9, 132.0, 133.3, 133.5, 158.9, 159.1.

*4.2.5. (3-{7-[3-(Pyrrolidine-1-carbonyl)-phenyl]-1H-indol-4-yl}-phenyl)-pyrrolidin-1-yl-methanone (**E**).* Yield (68 mg, 40%) as a yellow solid; [found: C, 77.81; H, 6.22; N, 9.13. $C_{30}H_{29}N_3O_2$ requires C, 77.73; H, 6.31; N, 9.06%]; *m*/*z* 464.1 (M); δ_H (400 MHz, $CDCl_3$) 1.90 (4H, m, pyrolidine CH_2), 1.92 (4H, m, pyrolidine CH_2), 3.53 (4H, q, *J* 7.1 Hz, pyrolidine CH_2), 3.69 (4H, d, *J* 3.4 Hz, pyrolidine CH_2), 6.71 (1H, s, indole C*H*), 6.78 (3H, t, *J* 1.2 Hz, indole C*H*), 7.27–7.31 (4H, m, Ph C*H*), 7.50–7.53 (1H, m, indole C*H*), 7.71–7.73 (1H, m, Ph), 7.88 (2H, s, Ph C*H*), 9.13 (1H, s, indole N*H*); δ_C (100 MHz, $CDCl_3$) 23.4. 25.3, 28.7, 29.9, 30.9, 45.7, 48.7, 64.8, 101.0, 119.1, 121.1, 123.3, 124.6, 124.7, 124.9, 125.1, 125.7, 125.8, 126.2, 127.5, 127.8, 128.1, 128.6, 129.1, 132.1, 132.9, 136.7, 140.1, 168.6, 168.8.

*4.2.6. 4,7-Bis-(3-N,N-diethylbenz- amide)-1H-indole (**F**).* Yield (85 mg, 50%) as a brown solid; [found: C, 77.13; H, 7.03; N, 8.91. $C_{30}H_{33}N_3O_2$ requires C, 77.06; H, 7.11; N, 8.99%]; *m*/*z* 467.1 (M); δ_H (400 MHz, DMSO-d_6) 1.64–1.67 (12H, m, CH_2Me), 3.36–3.42 (4H, m, CH_2Me), 3.61 (4H, s, NCH_2), 6.65 (1H, s, indole C*H*), 6.67 (2H, q, *J* 1.7 Hz, Ph C*H*), 7.25 (1H, t, *J* 7.6 Hz, indole C*H*), 7.42–7.51 (4H, m, Ind and Ph C*H*), 7.74 (4H, q, *J* 8.3 Hz, Ph C*H*), 11.26 (1H, s, indole N*H*); δ_C NMR (100 MHz, DMSO-d_6) 12.9, 14.2, 21.0, 29.2, 39.4, 43.4, 53.4, 60.4, 120.2, 122.1, 124.3, 124.9, 125.4, 126.0, 126.6, 127.8, 128.4, 128.9, 129.2, 129.5, 132.1, 133.3, 133.9, 137.6, 137.9, 139.4, 140.7, 141.3, 171.1, 171.3.

*4.2.7. (3-{7-[3-(Piperidine-1-carbonyl)-phenyl]-1H-indol-4-yl}-phenyl)-piperidin-1-yl-methanone (**G**).* Yield (82 mg, 46%) as a white solid; [found: C, 78.24; H, 6.72; N, 8.63. $C_{32}H_{33}N_3O_2$ requires C, 78.18;

H, 6.77; N, 8.55%]; *m*/*z* 491.3 (M); δ_H (400 MHz, $CDCl_3$) 1.22 (6H, s, piperidine CH_2), 1.24 (6H, t, *J* 3.8 Hz, piperidine CH_2), 3.34–3.41 (4H, m, piperidine N[CH_2]$_2$), 3.59–3.64 (4H, m, piperidine N[CH_2]$_2$), 6.75 (1H, s, indole C*H*), 7.30 (3H, q, *J* 3.0 Hz, indole C*H*), 7.41–7.46 (4H, m, Ph C*H*), 7.72 (4H, d, *J* 1.8 Hz, Ph C*H*), 9.13 (1H, s, indole N*H*); δ_C (100 MHz, $CDCl_3$) 24.6, 25.3, 26.5, 30.8, 36.2, 39.5, 39.7, 40.2, 42.0, 48.2, 101.2, 119.9, 122.2, 124.8, 126.9, 127.5, 127.6, 127.7, 127.9, 128.6, 128.7, 132.4, 133.9, 135.4, 135.8, 136.7, 139.8, 142.0, 169.1, 169.2.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2011.04.039.

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