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Rapid Communication

Novel fluorescence emissions from 3-styrylindoles

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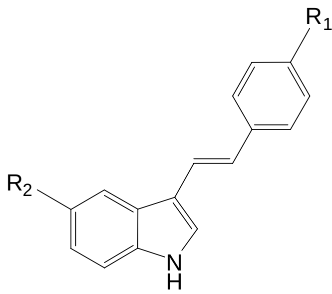
Fluorescence spectral properties of variously substituted 3-styrylindoles *viz.* 3-(2-phenylethenyl-*E*)-NH-indole **1**, 3-[2-(4-nitrophenyl)ethenyl-*E*]-NH-indole **2**, 5-methoxy-3-[2-(4-nitrophenyl)ethenyl-*E*]-NH-indole **3**,3-[2-(4-chlorophenyl)ethenyl-*E*]-NH-indole **4** and 5-methoxy-3-[2-(4-chlorophenyl)ethenyl-*E*]-NH-indole **5** in solution and solid-state are described.

Keywords: 3-Styrylindoles, fluorescence, solid state, charge transfer

Recently we have reported enhanced fluorescence emissions from solid 3-styrylindole bearing a cyano substituent on the ethylenic C,C double bond[1]. Origin of its fluorescence properties has been traced in the restricted molecular motions brought in by intra- and intermolecular hydrogen bond interactions in the solid state. Organic compounds in solution state can exhibit enhanced fluorescence emission but in the condensed state these are usually weakly fluorescent. Intermolecular hydrogen bonding, strong intermolecular π-π interactions between neighboring fluorophores, aggregation and formation of less emissive species like excimers are usually associated with diminished luminescence in the condensed state[2]. Host-guest doped emissive systems[3] and fluorescent salts and clathrates[4] have been designed to avoid concentration/aggregation-induced luminescence quenching. Introduction of bulky substituents in emissive systems is also known to be effective in preventing aggregations, leading to enhanced luminescence[2e,5]. However, aggregate/excimer formation does not always lead to diminished luminescence and enhanced fluorescence emissions due to aggregation and restricted intramolecular rotations are also known[5d,6].

In view of these findings[1] and several recent efforts[2-7] made towards molecular design of organic molecules capable of exhibiting strong luminescence in the solid state it was thought desirable to investigate solid state fluorescence emission behaviour of differently substituted 3-styrylindoles. Thus, herein are reported solid state fluorescence emission studies of 3-[2-(4-nitrophenyl)ethenyl-*E*]-NH-indole **2**,5-methoxy-3-[2-(4-nitrophenyl)ethenyl-*E*]-NH-indole **3**, 3-[2-(4-chlorophenyl)ethenyl-*E*]-NH-indole **4** and 5-methoxy-3-[2-(4-chlorophenyl)ethenyl-*E*]-NH-indole **5** (**Figure 1**). 3-(2-Phenylethenyl-*E*)-NH-indole **1**, whose solid state fluorescence properties have been reported elsewhere is included here for comparison purpose[1].

The absorption and fluorescence spectral data of **1**-**5** in various organic solvents and in the solid state are summarized in **Tables I** and **II**. **Figure 2** shows absorption spectra of solid **1**-**5**. The absorption maxima ($\lambda_{\text{ab max}}$) of *p*-NO_2 substituted 3-styrylindoles **2** and **3** get significantly red-shifted as the solvent polarity increases from *n*-hexane to acetonitrile. However, the red shift in $\lambda_{\text{ab max}}$ of **1**, **4** and **5** is relatively small for the same solvent polarity change. This is indicative of a small difference between the dipole moments of the ground state and the locally excited state of **1**, **4** and **5**. The large red shift in $\lambda_{\text{ab max}}$ of **2** and **3** can be attributed to the mesomeric effect exerted by the substituent groups, particularly the *p*-NO_2 group. As compared to the solution state absorption, the absorption spectra of **1**-**5** in the solid state are red-shifted and much broader. The *p*-NO_2 substituted compounds **2** and **3** show relatively larger red shift in their $\lambda_{\text{ab max}}$ in the solid state (126 and 119 nm respectively as compared to their $\lambda_{\text{ab max}}$ in *n*-hexane). Further, the solid state absorption spectra of these two compounds are characterized by much broader bands as compared to the other compounds.



	R_1	R_2
1	H	H
2	NO_2	H
3	NO_2	OCH_3
4	Cl	H
5	Cl	OCH_3

Figure 1 — Structure of 3-styrylindoles **1**-**5**.

The fluorescence maximum ($\lambda_{f\ max}$) of **1-5** gets dramatically affected by the solvent polarity where a much red-shifted fluorescence is observed on increasing the solvent polarity from *n*-hexane to acetonitrile (**Table II**). Typical fluorescence emission spectra of compound **3** showing solvent polarity effect is presented in **Figure 3**. The solvatochromic fluorescence emission indicates that the dipole moment of the emissive state is significantly higher as compared to ground state, a phenomenon that has been observed in other such compounds as well and explained in terms of intramolecular charge transfer (ICT) that can occur in the locally excited state generating conformationally relaxed, more polar emissive excited states[8].

Table I — UV-Vis absorption data of **1-5** in organic solvents and solid state

Medium	3-Styrylindoles and their $\lambda_{ab\ max}$ (nm)				
	1	**2**	**3**	**4**	**5**
n-Hexane	322	389	396	330	334
1,4-Dioxane	328	406	413	334	339
THF	330	416	423	336	341
Acetonitrile	326	409	417	332	337
Methanol	327	414	419	332	337
Solid state	379	515	515	369	384

Table II — Fluorescence emission data of **1-5** in organic solvents and solid state

Medium	3-Styrylindoles and their $\lambda_{f\ max}$ (nm)				
	1	**2**	**3**	**4**	**5**
n-Hexane	382	516	508	376[a], 389	376, 393[a]
1,4-Dioxane	384, 404	526	558	391	398
THF	403	588	586	406	404
Acetonitrile	407	645	658	412	414
Methanol	408	-	-	406	407
Solid state	408, 422[a]	600	579	437[a], 460	421[a], 442

[a] Main band.

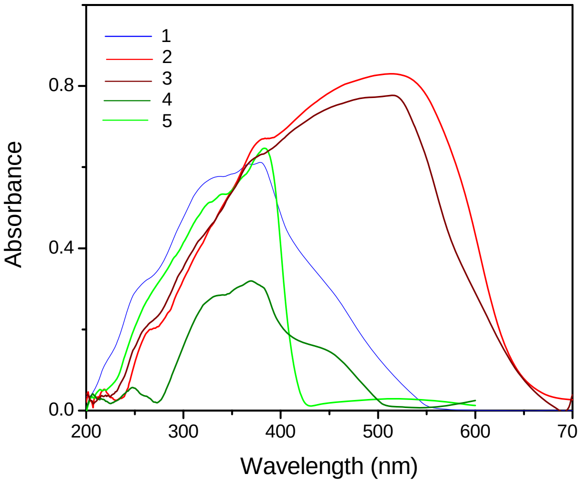


Figure 2 — UV-Vis absorption spectra of **1-5** in solid state.

The fluorescence band of **1-5** in solid state is significantly red-shifted as compared to those in the solution state in *n*-hexane (**Table II, Figure 4**). The positions of the solid state $\lambda_{f\ max}$ of **2-5** were observed at longer wavelengths than the parent 3-styrylindole **1**. While the fluorescence emission band in the solid state for **1**, **4** and **5** is structured, it is non-structured, single emission band in the case of **2** and **3**. Further, while the $\lambda_{f\ max}$ of **2** and **3** is significantly red-shifted in solid state relative to that in solution state in *n*-hexane, it is blue-shifted as compared to their emission in polar-aprotic acetonitrile.

Thus, the solvent polarity effects on the photophysical behaviour of **2** and **3** are much larger as compared to the other 3-styrylindoles studied. It is possible that these compounds in acetonitrile fluoresce from their conformationally relaxed intramolecular charge transfer (CRICT) state, wherein the conformational relaxation can occur through twisting around either the single bond connecting the nitro group to the phenyl ring or the single bond connecting the C,C double bond and the *p*-nitrophenyl moiety. Polar solvents like acetonitrile stabilize the dipolar CRICT state from which highly red-shifted emission occurs. However, in the condensed solid state condition, the conformational relaxation *via* single bond rotation becomes improbable. Therefore, formation of CRICT state in the solid state is inhibited and, hence, the solid state emission of *p*-NO_2 substituted 3-styrylindoles **2** and **3** is blue-shifted as compared to their emission in acetonitrile.

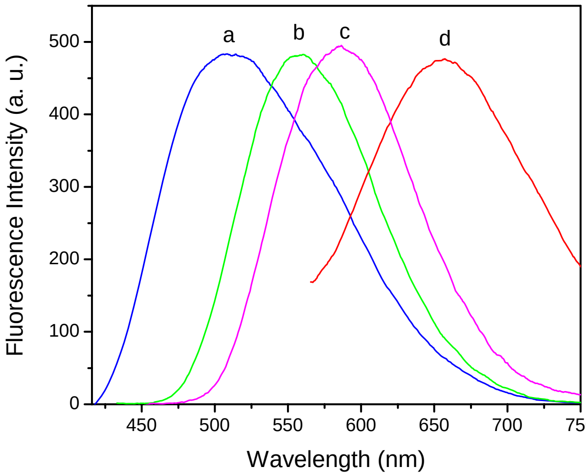


Figure 3 — Normalized fluorescence emission spectra of **3**. a) *n*-hexane. b) 1,4-dioxane. c) THF. d) acetonitrile.

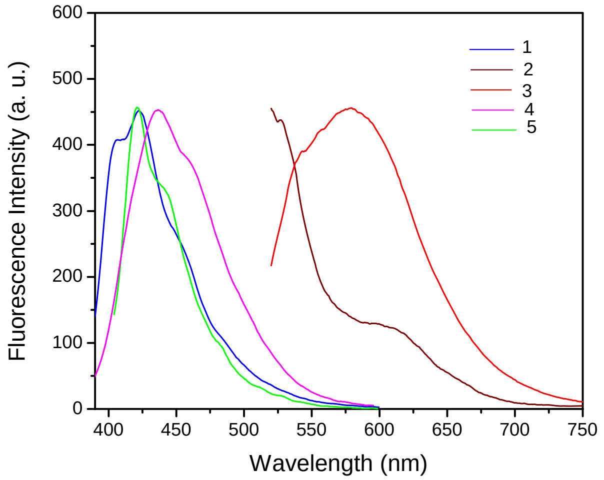


Figure 4 — Normalized fluorescence emission spectra of **1**-**5** in solid state.

Table III — Fluorescence quantum yield of **1**-**5** in organic solvents and solid state

Media	3-Styrylindoles and their Φ_f (± 0.002)				
	1	**2**	**3**	**4**	**5**
n-Hexane	0.0016	0.044	0.0080	0.0029	0.0024
1,4-Dioxane	0.0028	0.980	0.8828	0.0038	0.0038
THF	0.0013	0.628	0.4325	0.0041	0.0024
Acetonitrile	0.0010	0.004	0.0017	0.0019	0.0031
Methanol	0.0012	-	-	0.0015	0.0027
Solid state	0.039	< 0.001	0.009	0.089	0.021

Except for *p*-NO_2 substituted compounds **2** and **3**, which show high Φ_f in solvents like 1,4-dioxane and THF (**Table III**), the Φ_f of the other 3-styrylindoles in solution is in general low. In solid state, however, enhancement of Φ_f was observed for **1**, **4** and **5**, with **4** showing the maximum Φ_f enhancement. The Φ_f of **2** and **3** in the solid state is, however, found to be very small. The red-shifted fluorescence emission and the enhancement in Φ_f in the solid state can be attributed to planarisation and restricted motion of the molecules in the solid state.

The solid state fluorescence emission spectra of **1, 4** and **5** are structured, similar to those in the solution state in *n*-hexane. Additionally, these compounds show relatively smaller Stokes' shifts (2291-4217 cm^{-1}) in the solid state. These observations suggest that the solid state fluorescence emissions of **1, 4** and **5** do not originate from excimer species, but from monomeric species.

Interestingly, there is significant enhancement of Φ_f in the solid state of chloro-substituted compounds **4** and **5**. Recently, the roles of Cl.....N and Cl.....π interactions have been highlighted in crystal engineering and supramolecular chemistry[9]. It would be interesting to examine whether such interactions play any role in the solid state fluorescence emission from chloro-substituted 3-styrylindoles.

Thus, this work has revealed several novel and interesting fluorescence emission features of 3-styrylindoles, including large red shift in $\lambda_{f\ max}$ in polar solvents, a blue-shifted $\lambda_{f\ max}$ for solid state **2** and **3** as compared to their emission in polar-aprotic acetonitrile, very high Φ_f for **2** and **3** in dioxane and THF but very low Φ_f in other solvents and in solid state, enhanced Φ_f for all the compounds in the solid state, particularly for the chloro-substituted compounds. The work provides new directions for molecular design of organic fluorophores capable of strong and modulative fluorescence emissions in the solid state.

Experimental Section

Quinine sulfate, rhodamin B and *p*-chlorophenylacetic acid were purchased from M/s. Sigma-Aldrich Chemical Company (USA). All other chemicals, reagents and solvents were obtained from M/s. SRL Pvt. Ltd. Mumbai and M/s. Spectrochem, Mumbai (India). All AR grade solvents were dried and freshly distilled prior to use. The UV grade solvents were used for spectral studies.

Melting points were determined on a Veego melting point apparatus. FTIR spectra in KBr discs were measured on Perkin-Elmer Spectrum One FTIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on Varian VXR 400 MHz spectrometer using tetramethylsilane (TMS) as internal standard and $CDCl_3$ as solvent. Mass spectra were obtained on Micromass Q-TOF spectrometer. CHN analyses were performed on Thermo Qquest CE instruments 1112 Series CHNS analyser.

The absorption spectra were measured on JASCO V-570 UV-Vis spectrophotometer, and for the measurement of the absorption spectrum of the solid state samples, the diffuse reflectance spectra were recorded on the same instrument equipped with an integrating sphere accessory (JASCO ISN-470). The solid samples were placed between quartz plates (200 mm^2). The fluorescence spectra were recorded on Perkin-Elmer LS-55 Luminescence spectrometer by exciting the samples at their $\lambda_{ab\ max}$. Both, samples and standard were excited at the same excitation wavelength and the optical density (OD) of standard and the OD of the sample was adjusted to be nearly equal. Fluorescence emission spectra of the compounds in the solid state were recorded by using the front face accessory. The solid samples were placed between quartz plates (200 mm^2) on the sample holder.

The Φ_f relative to quinine sulfate in 0.05 mol L^{-1} H_2SO_4 (Φ_f = 0.51) (Ref. 10) and rhodamin B (for compounds **2**) in ethanol (Φ_f = 0.69) (Ref. 11) were measured at RT by following the procedure described earlier[8,12]. The Φ_f in the solid state was estimated relative to anthracene whose absolute Φ_f is reported[13] to be 0.47. In our case, we have determined relative Φ_f of our compounds by comparing the integrated area under the corrected fluorescence spectrum of the compounds with the integrated area under the corrected fluorescence spectrum of anthracene. The fluorescence spectra of both sample and standard are measured under identical conditions. For all electronic spectroscopic studies (absorption, fluorescence excitation and emission) 1.0×10^{-5} mol L^{-1} solutions of the compounds **1**-**5** were used.

3-(2-Phenylethenyl-*E*)-NH-indole **1**, 3-[2-(4-nitrophenyl)ethenyl-*E*]-NH-indole **2** and 5-methoxy-3-[2-(4-nitrophenyl)ethenyl-*E*]-NH-indole **3** were prepared as described elsewhere[8]. 3-[2-(4-chlorophenyl)ethenyl-*E*]-NH-indole **4** and 5-methoxy-3-[2-(4-chlorophenyl)-ethenyl-*E*]-NH-indole **5** were prepared by condensation of either indole-3-carboxaldehyde or 5-metoxy-indole-3-carboxaldehyde with *p*-chlorophenylacetic acid in presence of piperidine in pyridine at 90°C.

In a typical procedure, indole-3-carboxaldehyde (0.668 g, 4.6 mmol) and *p*-chlorophenylacetic acid (2 g, 11.7 mmol) were taken in 17 mL dried and distilled pyridine in a 100 mL, two necked, round-bottomed flask. A few drops (0.5 mL) of piperidine were added and the reaction mixture was stirred continuously at 90°C for 20 hr. The reaction mixture was allowed to cool to RT and then it was poured into a beaker containing crushed ice. The contents of the beaker were treated with dilute hydrochloric acid (1.0 mol L^{-1}). This resulted in the formation of a yellowish solid, which on being subjected to column chromatography (silca gel, 5% EtOAc in petroleum ether) gave 3-[2-(4-chlorophenyl)ethenyl-*E*]-NH-indole **4**: Yield: 16%; m.p. 214-15°C [Lit[14] 214-15°C]; HPLC: R$_t$ = 11.56 min (EtOAc-*n*-hexane 8:100) (flow rate 2 mL/min, detector wavelength 334 nm); UV-Vis (MeOH): λ_{max} = 334 nm (ε, 27160 L mol^{-1} cm^{-1}); IR (KBr): 3388 (-NH str), 2922 (C-H str), 1634 cm^{-1} (C=C str); ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.21 (1H, s, br, -NH), 7.98 (1H, d, *J* = 7.02 Hz, -C$_4$-H), 7.44 (2H, d, *J* = 8.8 Hz, -ArCl), 7.31 (2H, d, *J* = 8.8 Hz, -ArCl), 7.29 (1H, d, *J* = 16.4 Hz, -CH=C*H*-ArCl), 7.08 (1H, d, 16.4 Hz, -C*H*=CH-ArCl), 7,23-7.28 (4H, m, indole); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 137.2, 137.0, 132.1, 128.9 (2C), 127.0 (2C), 125.6, 124.4, 124.1, 122.9, 122.5, 120.7, 120.3, 115.5, 111.6. Anal. Calcd for $C_{16}H_{12}ClN$: C, 75.74; H, 4.77; N, 5.52. Found: C, 75.45; H, 4.35; N, 6.05%. MS: *m/z* (%) 254 (MH$^+$, 70.7).

For the preparation of compound **5**, a procedure similar to the one described above for compound **4** was used. 5-Methoxy-3-[2-(4-chlorophenyl)ethenyl-*E*]-NH-indole **5**: Yield: 43%; m.p. 140-42°C; HPLC: R$_t$ = 14.38 min (EtOAc-*n*- hexane 8:100) (flow rate 1 mL/min, detector wavelength 337 nm); UV-Vis (MeOH): λ_{max} = 337 nm (ε, 27590 L mol^{-1} cm^{-1}); IR (KBr): 3373 (-NH str), 2935 (C-H str), 1633 cm^{-1} (C=C str); ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.11 (1H, s, br, -NH), 7.43 (2H, d, *J* = 8.8 Hz, Ar-Cl), 7.39 (1H, d, *J* = 2.4 Hz, C$_4$-H), 7.35 (1H, d, *J* = 2.8 Hz, C$_2$-H), 7.31 (2H, d, *J* = 8.8 Hz, Ar-Cl), 7.29 (1H, d, *J* = 8.8 Hz, C$_7$-H), 7.26 (1H, d, *J* = 16.6 Hz, -CH=CH-Ar-Cl), 6.99 (1H, d, *J* = 16.6 Hz, -CH=CH-Ar-Cl), 6.92 (1H, dd, *J* = 8.8 Hz, *J* = 2.4, C$_6$-H), 3.91 (3H, s, -OCH$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 155.0, 137.2, 132.2, 132.1, 128.8, 127.0, 126.2, 124.7, 123.9, 122.5, 115.3, 112.7, 112.2, 102.6, 56.2. Anal. Calcd for $C_{17}H_{14}ClNO$: C, 71.96; H, 4.97; N, 4.94. Found: C, 71.51; H, 5.11; N, 5.28%. MS: *m/z* (%) 284 (MH$^+$, 100).

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