A new pyrrolyl-pyranone based AIEgen with solution solid dual emissive property

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The design and synthesis of organic molecules having aggregation induced emission (AIE) property has been a prime area of research in recent years. In this regard, we have synthesized new pyranone based AIEgens with interesting photophysical properties. The synthesized donor-acceptor based pyranones **3** and **4a-d** show multicolour emission in the range of 476-585 nm in solid state. The compound **3** also showed blue emission (485 nm) in DMSO solution and surprisingly exhibits orange emission (572 nm) with remarkable bathochromic shift in 99% water in DMSO due to AIE characteristics. The detailed study of AIE behaviour of **3** was carried out in increasing fraction of water (0-99%) in THF, the intensity of emission at 485 nm gradually increased upto 80% of water and then decreased at 90% water. Interestingly, the THF solution of **3** in 99% water showed remarkable bathochromic shift (~100 nm) of emission maximum from blue (λ_{max} 485 nm) to orange region (λ_{max} 585 nm) due to formation of nano-aggregates leading to restriction in intramolecular rotation (RIR). The time-correlated single photon counting (TCSPC) analysis of **3** in the water−THF (99:1) mixture showed an average lifetime of 4.8 ns for these nano-aggregates. The pyrrolyl-pyranone **3** having Solution-Solid Dual Emissive (SSDE) characteristics may be utilized in exploring its application in both biomedical and material research fields.

Keywords: AIEgen, luminogens, pyranones, solution-solid dual emissive (SSDE), restriction in rotation (RIR)

The discovery of Aggregation Induced Emission (AIE) phenomenon by Tang *et al*.[1] has led to the emergence of a new core area of research. The organic molecules which were sometimes considered inefficient due to their aggregation caused quenching (ACQ)[2] property found relevance in diverse areas with the advent of aggregation induced emission[3]. In the past few years, several archetypal luminogens with AIE properties have been developed[4]. These molecules exhibit AIE mainly due to the restriction of intramolecular motions (RIM) comprising of either restricted rotations (RIR) and/or restricted vibrations (RIV). Out of these, RIR have been extensively explored and several compounds such as silole (HPS), distyrylanthracene (DSA), tetraphenylethene (TPE), tetraphenyl-1,4-butadiene (TPBD), tetraphenylpyrazine (TPP), and conjugated polymers have been employed in biological and material applications[5,6].

However, limited examples of RIV-based molecules like 10,10′,11,11′-tetrahydro-5,5′-bidibenzo[*a,d*][7]-annulenylidene (THBA) and Bicyclooctatetraene (BCOT), coumarin derivative (CD7) and Λ-shaped pyridinium salt 2,8-(6*H*,12*H*-5,11-methanodibenzo-[*b,f*]diazocineylene)-di(*p*-ethenyl-N-methyl-pyridinium) ditosylate (DMDPS) showing AIE behaviour *via* restriction in intramolecular vibration have been reported[7] in the literature (Figure 1). Moreover, there are few compounds that show emission both in solution and solid state. Such solution-solid dual emissive (SSDE) compounds are very few and the concept of solution-solid dual emission (SSDE) is now gaining much attention[8]. In search of novel solution solid dual emissive (SSDE) fluorophore, very recently we screened a small chemical library of 108 fluorescent organic compounds comprising of donor-acceptor (D-A) based pyranones and their derived aromatic and hetero-aromatic scaffolds[9]. The photophysical studies in solution and solid state was conducted using UV-Vis and fluorescence spectro-photometry. Following the SSDE characteristics, 17
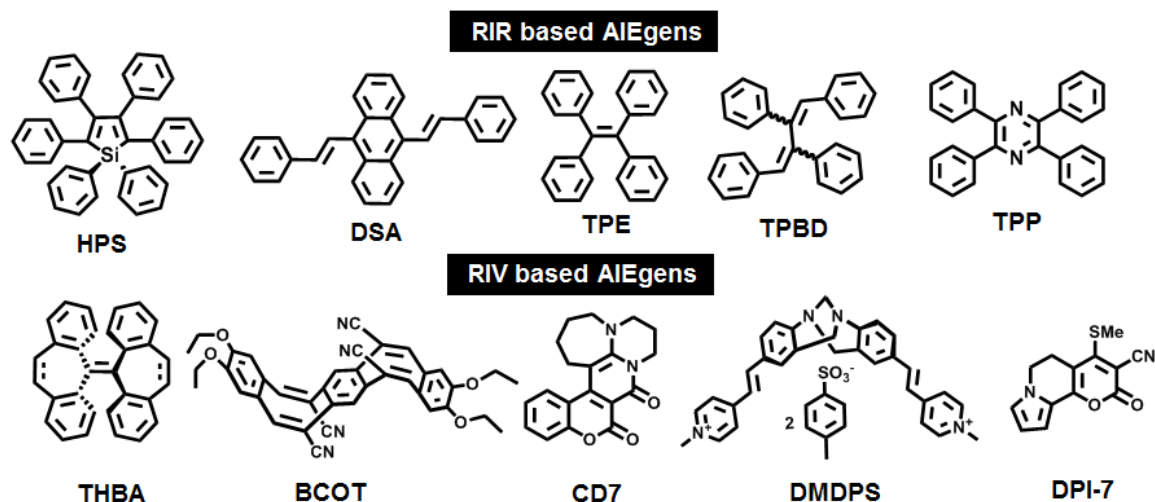
Figure 1 — Structure of some reported RIR and RIV based AIEgens along with the new lactone based Solution-Solid Dual Emissive (SSDE) AIEgens discovered

compounds were identified as potential hits, which showed good dual emission behaviour. Among them, two luminogens exhibited a drastic change in shifting of fluorescence from solution to solid state (~80-120 nm) whereas the remaining SSDEs showed only marginal shift in fluorescence maxima. The new compound with SSDE behaviour 4-(methylthio)-2-oxo-5,6-dihydro-2*H*-pyrano[3,2-*g*]indolizine-3-carbonitrile (DPI-7) showed RIV based AIE behaviour (Figure 1)[9]. This dual behaviour of fluorophores is of great importance in abridging the gap among interdisciplinary areas of scientific domain like bio-imaging, chemical sensing, and optoelectronic devices. Therefore, the design and development of new dual emissive AIEgen-based fluorescent probes are highly desirable. Herein, we report the synthesis and photophysical property of *N*-methyl-pyrrole substituted pyranones with interesting photophysical properties.
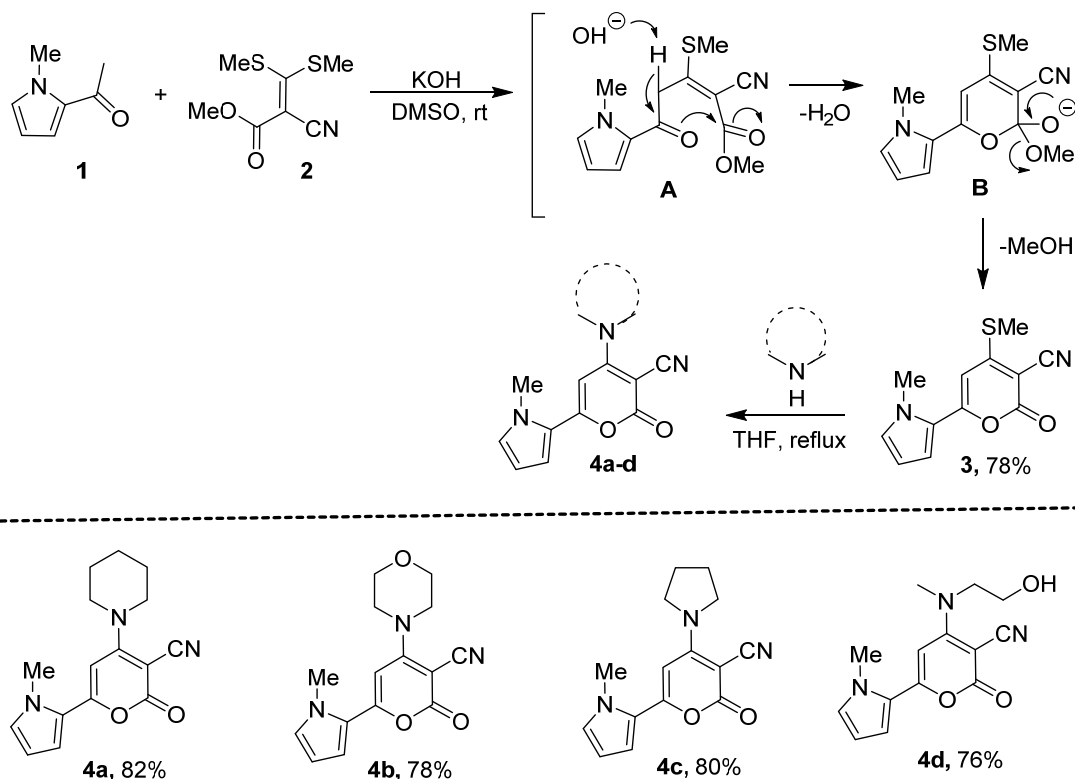
Results and Discussion

Synthesis of 6-(1-methyl-1*H*-pyrrol-2-yl)-4-(methylthio)-2-oxo-2*H*-pyran-3-carbonitrile, 3 and 4-(amino)-6-(1-methyl-1*H*-pyrrol-2-yl)-2-oxo-2*H*-pyran-3-carbonitrile, 4a-d

Our research group is actively involved in exploring the chemistry of 2*H*-pyran-2-ones for developing new fluorescent molecules with a variety of emission characteristics by swapping of donor, acceptor and chromophoric functionalities[10,11]. In order to synthesize 6-(1-methyl-1*H*-pyrrol-2-yl)-4-(methylthio)-2-oxo-2*H*-pyran-3-carbonitrile 3, 1-(1-methyl-1*H*-pyrrol-2-yl)ethanone 1 was reacted with α-oxo-

ketene-S,S-acetal 2 in the presence of base potassium hydroxide at RT in good yield. Further, the easily replaceable thiomethyl group of 3 was further substituted with different secondary amines to furnish 4-(amino)-6-(1-methyl-1*H*-pyrrol-2-yl)-2-oxo-2*H*-pyran-3-carbonitriles **4a-d** in excellent yields (Scheme I).

The plausible reaction mechanism operates by Michael addition of an enolate of **1** to ketene dithioacetal **2** to form an intermediate (**A**). This intermediate in presence of a base undergoes intramolecular cyclization which on elimination of methanol afforded 6-(1-methyl-1*H*-pyrrol-2-yl)-4-(methylthio)-2-oxo-2*H*-pyran-3-carbonitrile 3. All the synthesized compounds **3**, **4a-d** were characterized by spectroscopic analysis. IR spectrum of compound **3** showed peaks at 2206 and 1700 cm^{-1} due to a cyano and cyclic ester group respectively. The ^{1}H NMR spectrum of compound **3** showed a singlet at δ 2.75 for 3H (thiomethyl protons). A singlet at δ 3.90 for 3H was assigned to protons of N-methyl group of pyrrole ring. The multiplet at δ 6.26-6.28, a singlet at δ 6.78 and a multiplet at δ 7.22-7.28 were assigned to 1H, 1H and 2H respectively for the aromatic protons of pyranone and pyrrole ring. The ^{13}C NMR of **3** was in agreement with the proposed structure. Mass spectrum (ESI) of **3** at *m/z* 247 [M+H]$^+$ together with HRMS confirmed the structure as 6-(1-methyl-1*H*-pyrrol-2-yl)-4-(methylthio)-2-oxo-2*H*-pyran-3-carbonitrile **3**. The other derivatives **4a-d** were also characterized similarly using ^{1}H and ^{13}C NMR, IR and HRMS techniques (Experiment Section).

Scheme I — Synthesis of 6-(1-methyl-1*H*-pyrrol-2-yl)-4-(methylthio)-2-oxo-2*H*-pyran-3-carbonitrile **3** and 4-(amin-1-yl)-6-(1-methyl-1*H*-pyrrol-2-yl)-2-oxo-2*H*-pyran-3-carbonitrile **4a-d**

Photophysical properties of synthesized compounds 3, 4a-d

The photophysical properties of compounds **3** and **4a-d** were conducted in DMSO. Figure 2 represents the normalized absorbance and normalized fluorescence spectra of the compounds (10^{-6} M) in dimethyl sulphoxide (DMSO) solution. The absorption maxima ($\lambda_{max,abs}$), emission maxima in solution ($\lambda_{max,em}$) and solid state are summarized in Table I. The absorption spectrum of **3** exhibited two bands with maxima at 324 nm and 424 nm in DMSO. All these compounds showed blue to bluish-green emission characteristics with the emission maxima in the range of 438-486 nm as shown in Table I. The compounds **3** and **4a-d** showed bright solid state fluorescence with multicolour emission ranging from cyan to orange (476-585 nm) as shown in Figure 2.

TDDFT study of the synthesized fluorescent compounds, 3 and 4a-d

To study the electronic behaviour of the compounds **3**, **4a-d** time-dependent density functional theory (TDDFT) calculations were performed using a

Table I — Photophysical data of **3** and **4a-d**

Entry	Solution (DMSO)		Solid
	$\lambda_{max,abs}$ (nm)	$\lambda_{max,em}$ (nm)	$\lambda_{max,em}$ (nm)
3	324,424	486	585
4a	362	444	492
4b	368	443	504
4c	356	438	476
4d	361	440	493

Gaussian 09 package[12]. The geometries were optimized at DFT/B3LYP level using a 6-31G(d,p) basis set. TDDFT calculations were performed using a B3LYP/6-311++G(d,p) method. Figure 3 showed the theoretically computed molecular orbitals in the ground states for **3**, **4a-d**. The energies of the HOMO and LUMO levels, HOMO-LUMO gap, main orbital transition, and oscillator strength *f* are listed in Table II. The charge density distribution for **3** in HOMO was spread over the pyrrole, and the pyranone backbone while the LUMO has more charge distribution over the sulphur of thio-methyl and nitrile acceptor group. Thereby, the electronic transition at higher wavelength (HOMO to LUMO, oscillator
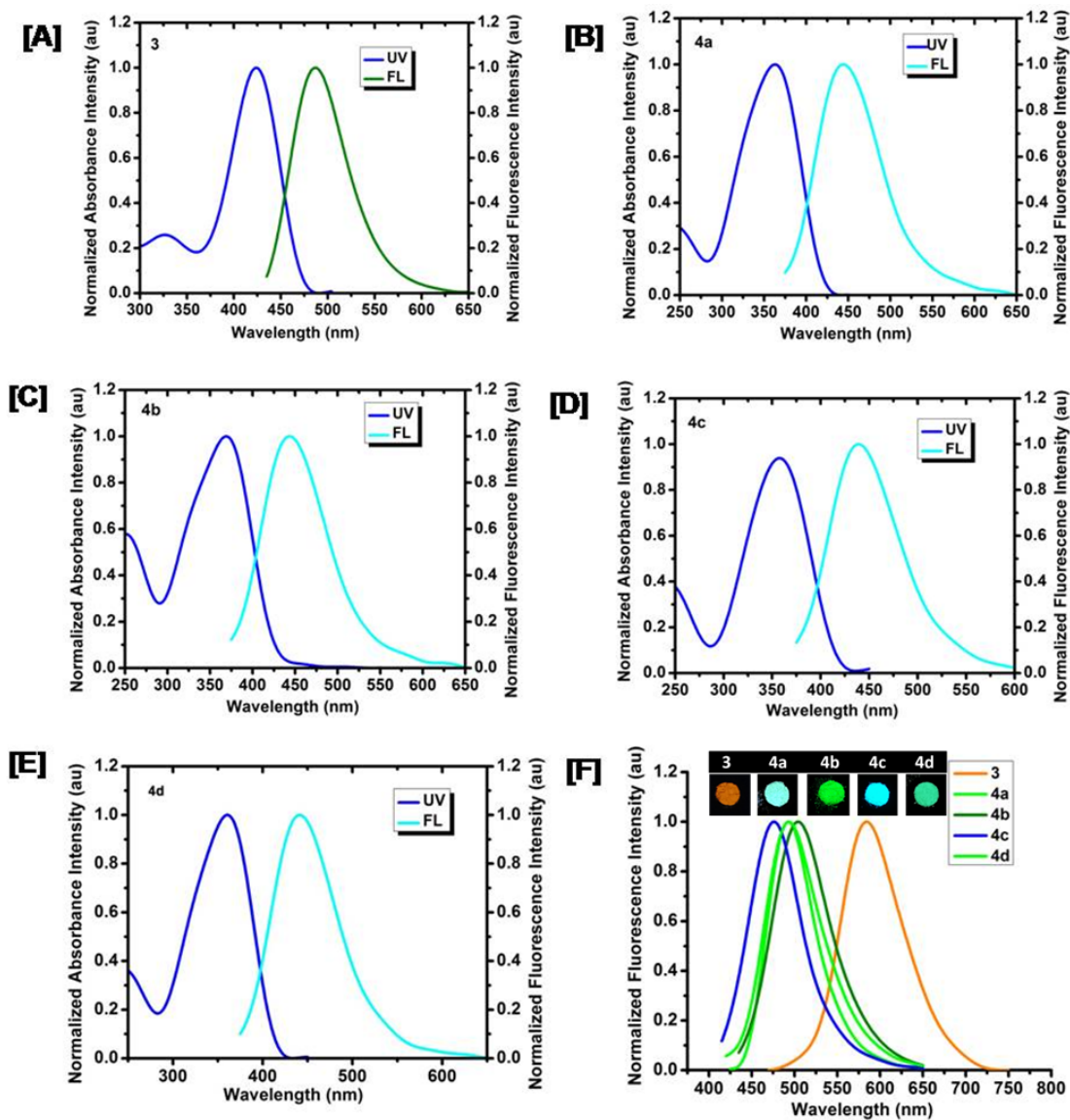
Figure 2 — [A]-[E]; Fluorescence spectra of **3** and **4a-d** in solution (~10^{-6} M in DMSO) and [F] solid state fluorescence spectra of **3** and **4a-d**
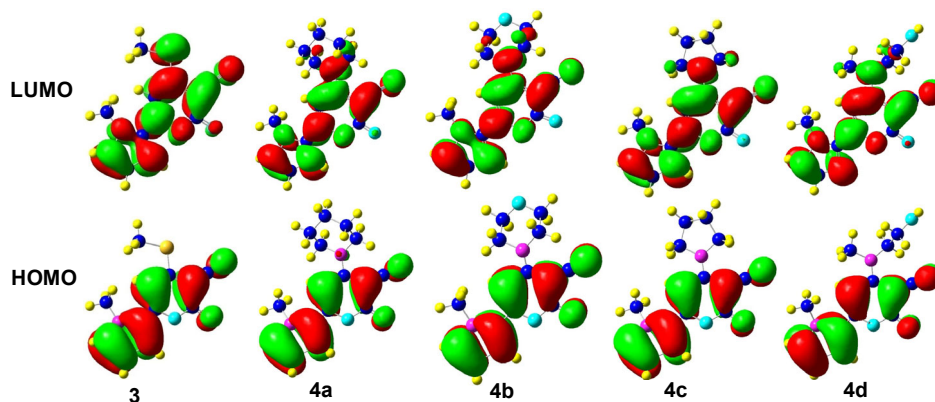

Figure 3 — Computed molecular orbital energy diagrams and isodensity surface plots of **3, 4a-d** as obtained from TDDFT calculations

Table II — Computed values of vertical excitations, oscillator strength (f), assignment, HOMO, LUMO and energy bandgap of **3** and **4a-d**

| Entry	λ_{max} (nm)	f	Assignment	HOMO (eV)	LUMO (eV)	E_g (eV)
3	392	0.7610	HOMO →LUMO (98.8%)	−6.2368	−2.7495	3.487
4a	359	0.7189	HOMO →LUMO (97.5%)	−6.1129	−2.2565	3.806
4b	345	0.7244	HOMO→LUMO (96.4%)	−6.0221	−2.0581	3.964
4c	354	0.7066	HOMO →LUMO (97.5%)	−6.0996	−2.1827	3.916
4d	359	0.7341	HOMO →LUMO (97.8%)	−6.129	−2.280	3.849
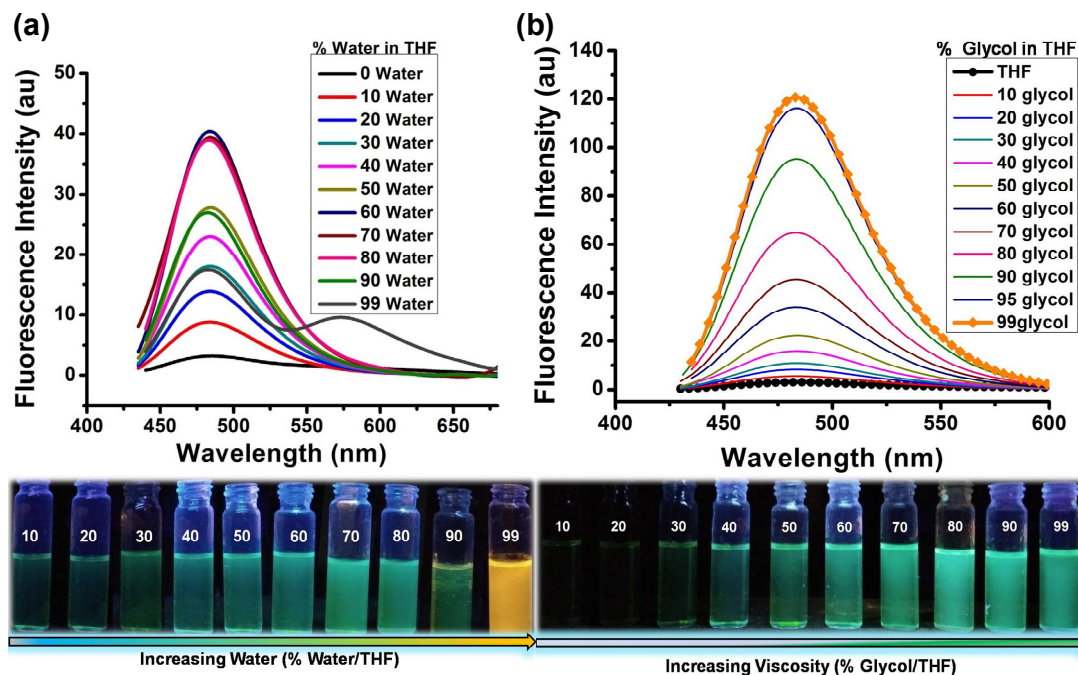
Figure 5 — Variation in the fluorescence intensity of **3** with gradually (a) increasing water fraction (0-99% v/v) in THF (10^{-6} M); (b) increasing viscosity using ethylene glycol (0-99% v/v) in THF

strength f = 0.7610) corresponded to an intramolecular charge-transfer (ICT) band. In case of **4a-d**, in HOMO the charge density was localised over the pyrrole, and the pyranone backbone which gets shifted towards the corresponding amine donors in LUMO (Figure 3).

Aggregation induced emission behaviour of compounds 3, 4a-d

In order to check the aggregation induced emission (AIE) behavior of the fluorescent compounds **3** and **4a-d**, we carried out the fluorescence study initially in DMSO/Water fraction (v/v). In DMSO, the compound **3** showed good fluorescence but the other compounds **4a-d** either showed weak fluorescence (**4a,b**) or no fluorescence (**4c,d**). Interestingly, the compound **3** emitted strongly in orange region in 99% water fraction in DMSO (Figure 4).

In order to confirm the AIE behaviour of **3**, the fluorescence study was conducted in varying fraction of water in THF (Figure 5a). The fluorescence
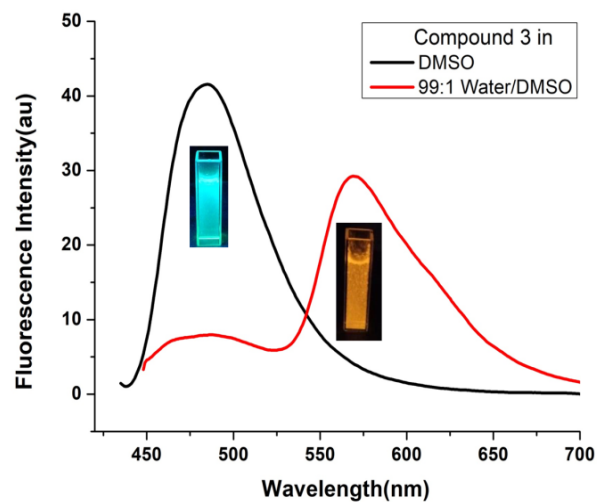
Figure 4 — Fluorescence spectra of **3** in pure DMSO (10^{-5} M) and 99% water in DMSO (v/v)

emission increased systematically upto 80 percent but surprisingly the wavelength shifted bathochromically in orange region at 99 percent water in THF fraction. This may be attributed to the formation of nano-aggregates in highly aqueous medium. Further the effect of solvent viscosity on the emission characteristics of compound **3** revealed that the restriction of intramolecular motion in highly viscous solvent like ethylene glycol promoted the radiative emission with enhanced fluorescence intensity as compared to other less viscous solvents (Figure 5b). The study showed no change in the wavelength of absorption spectrum but the emission intensity of the fluorescence spectrum showed a remarkable enhancement. These results clearly suggested that as the viscosity of the solution was changed by increasing the relative volume of ethylene glycol (upto 99%), dramatic enhancement in the fluorescence intensity was observed. This behaviour can be attributed to the RIR (Restriction in Intramolecular Motions) mechanism of AIEgens. It is observed that in systems with low viscosity (low content of ethylene glycol), the intramolecular rotations are prominent with non-radiative relaxation in the fluorophores leading to weak emissions. As viscosity of the system is increased, inhibition of these non-radiative motions promotes the emissive pathways resulting in increased emission intensities.

To measure the average fluorescence lifetime of **3**, time-correlated single photon counting (TCSPC) analysis was performed taking ludox as a prompt. The fluorescence lifetime decay of **3** in the water−THF (99:1) mixture is shown in Figure 6. The fluorescence decay profile of **3** nicely fitted with tri-exponential
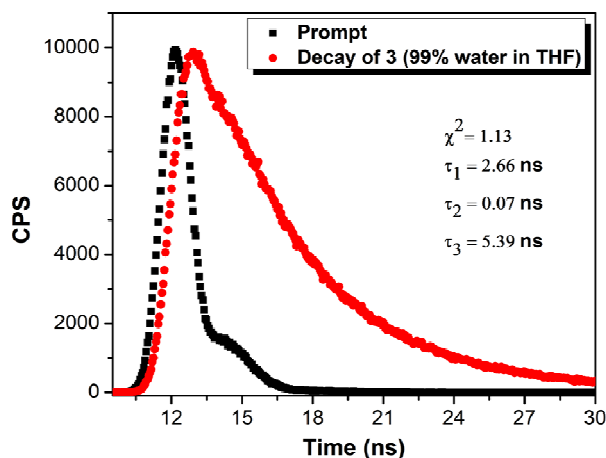

$\chi^2 = 1.13$
$\tau_1 = 2.66$ ns
$\tau_2 = 0.07$ ns
$\tau_3 = 5.39$ ns

Figure 6 — Time-resolved luminescence decay of **3** in 99% water in THF (λ_{ex} = 390 nm and λ_{em} = 585 nm)

function having an average lifetime of 4.8 ns due to the formation of nano-aggregates in THF-water mixture.

Experimental Section

6-(1-Methyl-1*H*-pyrrol-2-yl)-4-(methylthio)-2-oxo-2*H*-pyran-3-carbonitrile, 3

A mixture of methyl 2-cyano-3,3-bis(methylthio)-acrylate **2** (203 mg, 1 mmol, 1 equiv), 1-(1-methyl-1*H*-pyrrol-2-yl)ethanone **1** (123 mg, 1.0 mmol, 1equiv) and KOH (68 mg, 1.2 mmol, 1.2 equiv) in dry DMSO (5 mL) was stirred at RT for 8 h. Progress of reaction was monitored by TLC and on completion, reaction mixture was poured into crushed ice with stirring and finally neutralized with 10% HCl. The precipitate obtained was filtered and purified over a silica gel column using 1-2% methanol in chloroform as the eluent to furnish 192 mg (78%) of product as orange solid. R_f = 0.54 (methanol/chloroform, 1:99, v/v). m.p. 242-43°C (methanol/chloroform); IR (KBr): 2206 (CN), 1700 cm^{-1} (CO); ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.75 (s, 3H), 3.90 (s, 3H), 6.27 (dd, 1H, J = 4Hz, 2.6 Hz), 6.78 (s, 1H), 7.23 (dd, 1H, J = 4.1 Hz, 1.6 Hz) 7.25-7.28 (m, 1H); ^{13}C NMR (400 MHz, DMSO-d_6): δ 170.8, 157.7, 157.4, 133.8, 123.7, 119.1, 115.3, 110.5, 97.3, 84.7, 37.9, 14.7; HRMS (ESI): Calcd for C$_{12}$H$_{11}$N$_2$O$_2$S: *m/z* 247.0541 [M+H]$^+$. Found: 247.0532.

6-(1-Methyl-1*H*-pyrrol-2-yl)-2-oxo-4-(piperidin-1-yl)-2*H*-pyran-3-carbonitrile, 4a

A mixture of 6-(1-methyl-1*H*-pyrrol-2-yl)-4-(methylthio)-2-oxo-2*H*-pyran-3-carbonitrile **3** (246 mg, 1 mmol, 1equiv.) was refluxed with piperidine (101 µL, 1.2 mmol, 1.2 equiv) in tetrahydrofuran for 4 h. The progress of reaction was monitored by TLC and on completion, reaction mixture was poured into crushed ice with stirring and finally neutralized with 10% HCl. The precipitate obtained was filtered and purified over a silica gel column using 1-2% methanol in chloroform as the eluent to furnish 232 mg (82%) of product as green solid. R_f = 0.58 (methanol/chloroform, 2/98, v/v). m.p.148-50°C (methanol/chloroform); IR (KBr): 2196 (CN), 1694 cm^{-1} (CO); ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.70-1.85 (m, 6H), 3.70-3.79 (m, 4H), 3.89 (s, 3H), 6.14 (s, 1H), 6.16 (dd, 1H, J = 4 Hz, 2.6 Hz), 6.70 (dd, 1H, J = 4 Hz, 1.7 Hz), 6.78-6.79 (m, 1H); ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 23.8, 26.2, 37.5, 50.7, 70.8, 92.8, 109.2, 115.0, 117.6, 124.1, 129.8, 156.1, 161.1, 162.2; HRMS (ESI): Calcd for C$_{16}$H$_{18}$N$_3$O$_2$: *m/z* 284.1399 [M+H]$^+$. Found: 284.1399.

6-(1-Methyl-1*H*-pyrrol-2-yl)-4-morpholino-2-oxo-2*H*-pyran-3-carbonitrile, 4b

A mixture of 6-(1-methyl-1*H*-pyrrol-2-yl)-4-(methylthio)-2-oxo-2*H*-pyran-3-carbonitrile **3** (246 mg, 1 mmol, 1equiv.) was refluxed with morpholine (104 μL, 1.2 mmol, 1.2 equiv) in tetrahydrofuran for 5 h. The extent of reaction was monitored by TLC and on completion, reaction mixture was poured into crushed ice with stirring and finally neutralized with 10% HCl. The precipitate obtained was filtered and purified over a silica gel column using 1-2% methanol in chloroform as the eluent to furnish 223 mg (78%) of **4b** as green solid. R_f = 0.50 (methanol/chloroform, 2/98, v/v). m.p.214-15°C (methanol/chloroform). IR (KBr): 2201 (CN), 1692 cm^{-1} (CO); ^{1}H NMR (400 MHz, CDCl$_3$): δ 3.80-3.86 (m, 8H), 3.90 (s, 3H), 6.12 (s, 1H), 6.18 (dd, 1H, *J* = 4 Hz, 2.6 Hz), 6.73 (dd, 1H, *J* = 4 Hz, 1.7 Hz), 6.80-6.82 (m, 1H); ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 37.6, 49.4, 66.4, 71.7, 92.0, 109.5, 115.6, 117.3, 123.8, 130.5, 156.8, 161.7, 161.9; HRMS (ESI): Calcd for C$_{15}$H$_{16}$N$_3$O$_3$: *m/z* 286.1192 [M+H]$^+$. Found: 286.1191.

6-(1-Methyl-1*H*-pyrrol-2-yl)-2-oxo-4-(pyrrolidin-1-yl)-2*H*-pyran-3-carbonitrile, 4c

A mixture of 6-(1-methyl-1*H*-pyrrol-2-yl)-4-(methylthio)-2-oxo-2*H*-pyran-3-carbonitrile **3** (246 mg, 1 mmol, 1equiv.) was refluxed with pyrrolidine (92 μL, 1.3 mmol, 1.2 equiv) in tetrahydrofuran for 4 h. The progress of reaction was monitored by TLC and on completion, reaction mixture was poured into crushed ice with stirring and finally neutralized with 10% HCl. The precipitate obtained was filtered and purified over a silica gel column using 1-2% methanol in chloroform as the eluent to furnish 216 mg (80%) of **4c** as green solid. R_f = 0.56 (methanol/chloroform, 2/98, v/v). m.p.238-40°C (methanol/chloroform). IR (KBr): 2195 (CN), 1685 cm^{-1} (CO); ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.98-2.06 (m, 4H), 3.55-3.64 (m, 2H), 3.89 (s, 3H), 3.96-4.12 (m, 2H), 6.03 (s, 1H), 6.16 (dd, 1H, *J* = 4 Hz, 2.6 Hz), 6.68 (dd, 1H, *J* = 4 Hz, 1.7 Hz), 6.76-6.79 (m, 1H);^{13}C NMR (100.6 MHz, CDCl$_3$): δ 26.6, 37.5, 50.5, 69.0, 92.4, 109.1, 115.0, 118.4, 124.0, 129.8, 155.6, 157.6, 162.1; HRMS (ESI): Calcd for C$_{15}$H$_{16}$N$_3$O$_2$: *m/z* 270.1243 [M+H]$^+$. Found: 270.1236.

4-((2-Hydroxyethyl)(methyl)amino)-6-(1-methyl-1*H*-pyrrol-2-yl)-2-oxo-2*H*-pyran-3-carbonitrile, 4d

A mixture of 6-(1-methyl-1*H*-pyrrol-2-yl)-4-(methylthio)-2-oxo-2*H*-pyran-3-carbonitrile **3** (246 mg, 1 mmol, 1 equiv.) was refluxed with 2-(methylamino)ethanol (97 μL, 1.3 mmol, 1.2 equiv) in tetrahydrofuran for 4 h. The progress of reaction was monitored by TLC and on completion, reaction mixture was poured into crushed ice with stirring and finally neutralized with 10% HCl. The precipitate obtained was filtered and purified over a silica gel column using 1-2% methanol in chloroform as the eluent to furnish 208 mg (76%) of **4d** as green solid. R_f = 0.50 (methanol/chloroform, 2/98, v/v). m.p.218-19°C (methanol/chloroform). IR (KBr): 2202 (CN), 1700 cm^{-1} (CO); ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.41 (s, 3H), 3.64-3.81 (m, 4H), 3.83 (s, 3H), 4.99 (t, 1H), 6.15-6.19 (dd, 1H, *J* = 4 Hz, 2.6 Hz), 6.52 (s, 1H), 6.88 (dd, 1H, *J* = 4 Hz, 1.8 Hz), 7.08-7.11 (m,1H); ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 37.2, 56.2, 59.4, 68.3, 93.6, 109.1, 115.6, 118.9, 124.3, 130.7, 154.2, 160.6, 162.3; HRMS (ESI): Calcd for C$_{14}$H$_{16}$N$_3$O$_3$: *m/z* 274.1192 [M + H]$^+$. Found: 274.1190.

Conclusion

In conclusion, we have synthesized N-methylpyrrole substituted 2*H*-pyranones using the chemistry of ketene-S,S-acetals under mild basic conditions. The photophysical properties of all the pyranones were investigated using UV-Vis and fluorescence techniques, which revealed that the compound 6-(1-methyl-1*H*-pyrrol-2-yl)-4-(methylthio)-2-oxo-2*H*-pyran-3-carbonitrile **3** showed interesting Solution Solid Dual Emissive (SSDE) AIEgen behaviour *via* the restriction of intramolecular rotation (RIR). Such SSDE luminogens are rare in the literature. Owing to unique dual emissive nature of the new AIEgen **3**, it can be utilized for both bioimaging and optoelectronic application. Further studies in these directions are in progress.

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