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ARTICLE TYPE

Substituent dependent tunable fluorescence in thieno[3,2-*c*]pyrans

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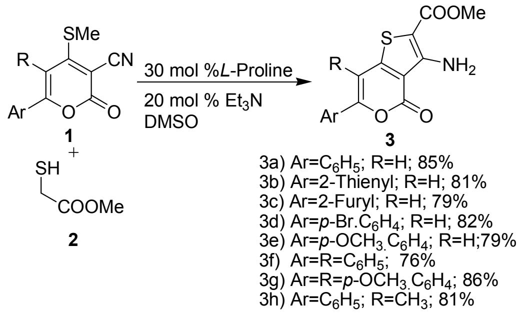
A series of thieno[3,2-*c*]pyrans were designed and synthesized by *L*-proline catalyzed reaction of 6-aryl/5,6-diaryl-4-methylthio-2*H*-pyrane-2-one-3-carbonitriles or 4-(methylthio)-2-oxo-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitrile and methylthioglycolate in good yields. These thieno[3,2-*c*]pyrans exhibits substituent dependent fluorescence. The 6-aryl-thieno[3,2-*c*]pyrans 3a–3e exhibit high fluorescence quantum yields (95 %) with large stokes shifts, whereas the 6,7-di-substituted-thieno[3,2-*c*]pyrans 3f, 3g and 3h show poor fluorescence in solution and exhibit an aggregation-induced emission (AIE). Interestingly fused 6,7-di-substituted-thieno[3,2-*c*]pyran is highly fluorescent in the solution state, which reveals restricted intramolecular rotation is the cause for AIE in the 3f, 3g and 3h.

Organic light-emitting materials are of wide interest due to their applications in organic field effect transistors (OFETs), organic light-emitting diodes (OLEDs), and organic Photovoltaics (OPVs) and bioimaging.[1] Design and synthesis of efficient light emitters in solution as well as in solid state has gained momentum.[2] Conventional fluorophores are poorly emissive in solid state due to the aggregation caused quenching (ACQ). To overcome ACQ Tang et al. introduced the concept of aggreagation induced emission (AIE).[3] Thiophene, fused thiophenes (thienothiophene, dithienothiophene) have been explored in OFETs, and OPV's.[4,5] The thieno[3,2-*c*]pyran is thiophene and pyranone fused ring system. Thieno[3,2-*c*]pyransare known for antileishmanial and antifungal activities.[6,7] Few reports on synthesis of pyranothiophene are available and their photophysical properties are unexplored. In this communication, we wish to report substituent dependent variation in photonic properties of various functionalized thieno[3,2-*c*]pyrans. They could be synthesized by reaction of 6-aryl/5,6-diaryl-4-(methylthio)-2-oxo-2*H*-pyran-3-carbonitriles and methyl thioglycolate using organocatalytic approach.

The required precursors were synthesized by reaction of ethyl 2-cyano-3,3-dimethylthioacrylate and various acetophenones or deoxy-benzoin/anisoin in presence of potassium hydroxide in DMSO.[8]

Synthesis of functionalized 6-aryl/5,6-diaryl-thieno[3,2-*c*]pyrans **3a–3h** were carried out by the 6-aryl/5,6-diaryl-4-(methylthio)-2-oxo-2*H*-pyran-3-carbonitriles and methyl thioglycolate in presence of *L*- proline (30 mol %) and Et_3N (20 mol %) in DMSO at 90 °C (Table 1). For further derivatisation4-(methylthio)-2-oxo-5,6-dihydro-2*H*-benzo[*h*]-chromene-3-carbonitrile **4** was used as precursor, which react with methyl thioglycolate under similar conditions and afforded methyl 1-amino-11-oxo-5,11-dihydro-4*H*-benzo[*h*]thieno[3,2-*c*]chromene-2-carboxylate in good yield (Scheme 1)

Table 1. *L*-proline/Et_3N catalyzed synthesis of thieno[3,2-*c*]pyrans[a,b]



3a) Ar=C_6H_5; R=H; 85%
3b) Ar=2-Thienyl; R=H; 81%
3c) Ar=2-Furyl; R=H; 79%
3d) Ar=*p*-Br.C_6H_4; R=H; 82%
3e) Ar=*p*-OCH_3.C_6H_4; R=H;79%
3f) Ar=R=C_6H_5; 76%
3g) Ar=R=*p*-OCH_3.C_6H_4; 86%
3h) Ar=C_6H_5; R=CH_3; 81%

(a). All the reactions were carried out by using **1** (0.5 mmol), **2** (0.6 mmol) and L-proline (30 mol %)+ Et_3N (20 mol %) in 4.0 mL of DMSO at 90 °C; (b) all the reactions were performed twice and average yields are reported

The electronic absorption, and fluorescence spectra of the thieno[3,2-*c*]pyrans **3a–3h** and **5** in dichloromethane solutionare shown in FigureS2, and their photophysical data are listed in Table 2. The thieno[3,2-*c*]pyrans **3a–3h** and **5** absorbs in 300-450 nm region. Time-dependent DFT calculation was performed to understand the absorption properties of thieno[3,2-*c*]pyrans. The contributions of the molecular orbitals involved in the UV−vis transitions were determined on the basis of their oscillator strengths (*f*). The TD-DFT calculation shows that, the lower-energy bands (350–450 nm) in the absorption spectra show a

Scheme 1. Synthesis of methyl 1-amino-11-oxo-5,11-dihydro-4H-benzo[*h*]thieno[3,2-*c*]chromene-2-carboxylate 5

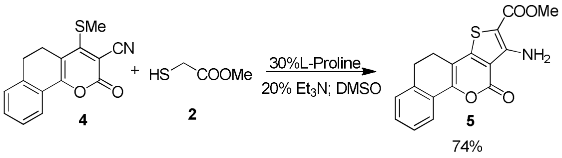


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Table 2. Photophysical and thermal properties of the thieno[3,2-*c*]pyrans **3a-3h** and **5**.

Compound	λ_{max}[nm] (ε[Lmol^{-1}cm^{-1}])^{a}	$\lambda_{em.}$(nm)^{a}	Stokes Shift(cm^{-1})	Φ_f^{b}(%)	Optical band gap (eV)	Theoretical band gap (eV)^{c}	T_d (°C)
3a	326 (16026) 390 (21745)	478	4721	88.89	2.83	3.40	267
3b	340 (17994) 354 (18766) 405 (31021)	498	4611	73.63	2.71	3.24	246
3c	334 (18160) 350 (20519) 400 (30256)	477	4036	95.95	2.78	3.32	245
3d	330 (17562) 395 (22146)	485	4698	72.50	2.75	3.29	-
3e	346 (14759) 396 (25609)	476	4244	54.88	2.80	3.40	232
3f	328 (12620) 384 (19581)	-	-	-	2.88	3.48	273
3g	276 (18147) 390 (27507)	-	-	-	2.84	3.46	289
3h	322 (16740) 375 (22099)	464	5299	7.98	2.95	3.56	258
5	337 (13243) 353 (16378) 399 (28432)	476	4054	95.76	2.80	3.38	271

^{a}Measured in dichlomethane.^{b}The fluorescence quantum yields were calculated by using 9, 10-diphenylanthracence as a standard in ethanol solution (λ_{ex} 370 nm). ^{c}Theoretical values at B3LYP/6-31G(d) level.

preferential contribution from HOMO→LUMO and HOMO−1→LUMO transitions (Table S4).

The photophysical properties of the thieno[3,2-*c*]pyrans can be tuned by varying the substituents. The replacement of phenyl unit with thiophene results in 15 nm red shift in the absorption spectra. The heterocyclic substituent thiophene and furan on pyranothiophene show high extinction coefficient and the trend in ε follows the order **3b** >**3c** >**5**>**3e** >**3d** >**3g** >**3a** >**3f** > **3h**. The fluorescence spectra of thieno[3,2-*c*]pyrans in dichloromethane show emission from 464 nm to 500 nm. The 6-aryl-thieno[3,2-*c*]pyrans (**3a**–**3e**) show high fluorescence quantum yields up to 95 %, with large Stokes shifts ~4720 cm^{-1}. The sensitivity of 6-aryl-thieno[3,2-*c*]pyrans towards solvent polarity were investigated. The absorption spectra show solvent independent nature, whereas emission was found to be solvent dependent. The bathochromic shift in the fluorescence spectra with solvent polarity suggests the polar nature of the excited state. The solvent dependence was confirmed by the Lippert-Mataga plot, which shows a linear correlation of the Stokes shift with solvent polarity (Figure S4 and S6).[9]

The poor quantum yields of the thieno[3,2-*c*]pyrans **3f**–**3h** suggest the possibility of molecular rotation within the molecule.[3d,10] The excited state energy of these molecules were dissipated by the molecular rotation, which results in weak-fluorescent nature of these thieno[3,2-*c*]pyrans (**3f**–**3h**) in the solution state. The aggregation induced emission study was performed by making the small aggregates, using THF-water mixtures, with the increasing percentage of water in THF (Figure 1). The fluorescence intensity of **3f** in THF was increased by 200 folds in the aggregate suspension (98% aqueous mixture). In the solid state (aggregates) the molecular rotation was ceased and the fluorescence was restored.[3d] Similar study was performed on **3g** and **3h**. The **3g** exhibits aggregation induced emission with 20 fold increase in fluorescence intensity. In **3h** fluorescence intensity was increased upto 40 % of water fraction and get almost constant upto 90 % of water fraction and after that fluorescence intensity was decreased by increase in water fraction (98 %). To confirm the AIE in 6,7-disubstitued thieno[3,2-*c*]pyrans, we synthesized fused 6,7-disubstitued thieno[3,2-*c*]pyran **5**. The high fluorescence quantum yield (95%) in the solution was observed for *5* which confirms the RIR (Restricted intramolecular rotation) is the main cuase for low fluorescence quantum yields in the 6,7-disubstitued thieno[3,2-*c*]pyrans.

The thermal stability is one of key requirement for various practical applications. The thieno[3,2-*c*]pyrans **3a**–**3h** and **5** shows thermal decomposition (T_d) temperature corresponding to 5% weight loss in nitrogen atmosphere in the range of 230–290 °C (Figure S1). The 6,7-di-substituted-thieno[3,2-*c*]pyrans (**3f**–**3h**, and **5**) shows higher thermal stability compared to 6-aryl-thieno[3,2-*c*]pyrans (**3a**–**3e**).

In order to understand the geometrical and electronic structure of the thieno[3,2-*c*]pyrans, computational calculation was performed using density functional theory (DFT) at the B3LYP/6-31G(d) level using the Gaussian 09 program.[11] The energy minimized structures of the thieno[3,2-*c*]pyrans **3a**–**3e** and **5** show planar structure whereas the 6,7-disubstituted thieno[3,2-*c*]pyrans **3f**–**3h**

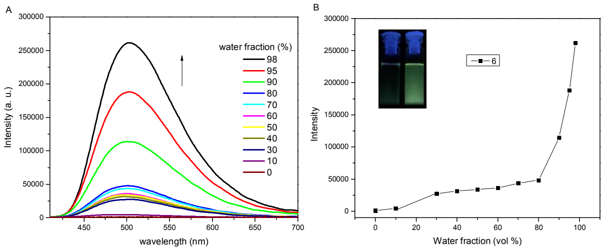

Figure 1(A) Fluoroscence spectra of **3f** in THF–water mixtures with different water fractions. (B) Plot of PL peak intensity at 502 nm vs. water fraction of the aqueous mixture. Luminogen concentration: 20 µm; excitation wavelength: 370 nm. Inset: solution of **3f** in THF (fw = 0%) and its suspension in a THF–water mixture with fw = 98%; photographs taken under UV illumination.

are non-planar (Figure S7). The DFT calculated HOMO-LUMO gap values shows good agreement with optical band gap values calculated from the absorption spectra.

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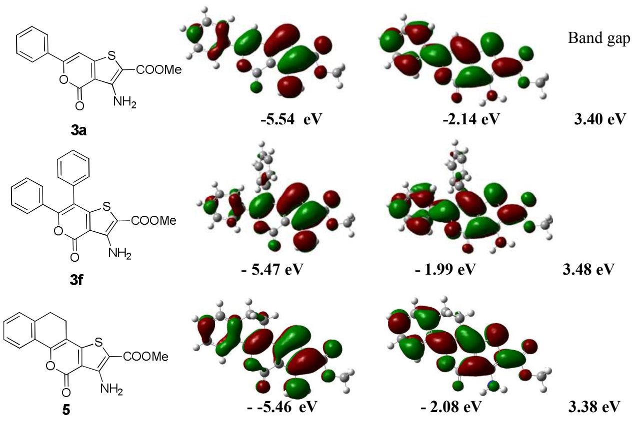

Figure 2: HOMO and LUMO Frontier Molecular Orbitals of Thieno[3,2-*c*]pyrans **3a**, **3f**, and **5** at the B3LYP/6-31G(d) level

The HOMO, and LUMO frontier molecular orbital (FMO) distribution of thieno[3,2-*c*]pyrans **3a, 3f** and **5** are shown in Figure 2. The HOMOs and LUMOs are distributed on the whole molecule. The careful observation reveals that the thiophene ring fused with pyranone shows more contribution in the HOMO, whereas pyranone ring and the substituents on it contribute more to the LUMO orbital. The HOMO and LUMO orbitals show similar distribution in 6-aryl-thieno[3,2-*c*]pyran-4-one **3a** and 6,7-di-substituted-thieno[3,2-*c*]pyrans **3f**, and very small contribution from second phenyl ring was observed for pyranothiophene 3f. The trend in the HOMO-LUMO gap of thieno[3,2-c]pyrans follows the order 6,7-di-substituted-thieno[3,2-c]pyrans (**3f–3h**) > 6-aryl-thieno[3,2-c]pyran-4-one (3a–3e) > fused 6,7 diarylated thieno[3,2-*c*]pyran (5). This is due to more planar and conjugated structure in fused 6,7 diarylated thieno[3,2-c]pyrans **5** compared to 6-aryl-thieno[3,2-*c*]pyran-4-one **3a**–**3e** and 6,7 diarylated thieno[3,2-*c*]pyrans**3f–3h**.

Conclusions

In conclusion, we have demonstrated a simple, efficient and organocatalytic approach for synthesis of thermally stable thieno[3,2-*c*]pyrans by reaction of 6-aryl/6,7-diaryl-4-methylthio-2*H*-pyran-2-one-3-carbonitriles and methylthioglycolate using L-proline in good yields. Photophysical studies of the **3a–3e** and **5** exhibit high fluorescence quantum yields up to 95% with large stokes shift. Presence of additional aryl ring at position 7 of thieno[3,2-*c*]pyrans shows change in photophysical properties and their studies in different THF–water mixtures shows that they exhibit AIE. The fused 6,7-di-substituted-thieno[3,2-*c*]pyran confirms the RIR is responsible for AIE in 6,7-di-substituted-thieno[3,2-*c*]pyrans. These functionalized thieno[3,2-*c*]pyrans are highly fluorescent and can be used as a fluorescent probes in bioimaging.

Experimental Section

General remarks: Commercially available reagents and solvents were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on 400MHz NMR spectrometer respectively. $CDCl_3$ and DMSO-d$_6$ were used as solvent for NMR. Chemical shift is reported in ppm considering ($CDCl_3$) δ 7.24 ppm for ^{1}H NMR and δ 77.00 ppm for ^{13}C NMR as an internal standard. Signal patterns are indicated as s, singlet; d, doublet; dd, double doublet; t, triplet; m, multiplet; br s, broad singlet. Coupling constants (*J*) are given in hertz (Hz). Infrared (IR) spectra were recorded on AX-1 spectrophotometer and reported as wave number (cm^{-1}). UV-Visible absorption spectra of all compounds were recorded on a Carry-100 Bio UV-Visible Spectrophotometer. HRMS was recorded on Brucker-Daltonics, Micro-TOF-Q II mass spectrometer.

General procedure for the synthesis of 3-amino-2-carbmethoxy-6-aryl-4*H*-thieno[3,2-*c*]pyran-2-one: A mixture of 4-(methylthio)-2-oxo-6-aryl-2*H*-pyran-3-carbonitriles (0.5 mmol) and methyl thioglycolate (0.75 mmol) in 4.0 mL DMSO in presence of triethylamine (20 mole %) and *L*-proline (30 mole %) was stirred for 8-9 h at 90 °C. Completion of reaction was monitored by TLC. The reaction mixture was poured onto crushed ice with vigorous stirring. Obtained precipitate was filtered, dried and purified by column chromatography by using 1:1 hexane:dichloromethane as an eluent.

3-Amino-4-oxo-6-phenyl-4*H*-thieno[3,2-*c*]pyran-2-carboxylic acid methyl ester (**3a**): Yield: 85 % (128 mg) R_f = 0.32 (50% hexane in dichloromethane); yellow colored floppy solid; mp: 204-206 °C; IR (KBr): 3457, 3351, 1707, 1675, 1573 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.88 (s, 3H, OCH_3), 6.74 (br s, 2H, NH_2), 6.98 (s, 1H, CH), 7.44 (m, 3H, ArH), 7.84(m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 51.4, 98.51, 112.0, 125.6, 128.9, 130.9, 153.0,157.6, 158.4, 164.2; HRMS (ESI): calculated for $C_{15}H_{11}NO_4S$, 324.0301 (M+ Na$^+$); found for *m/z*, 324.0301.

3-Amino-4-oxo-6-thiophen-2-yl-4*H*-thieno[3,2-*c*]pyran-2-carboxylic acid methyl ester (**3b**): Yield:81 % (124 mg); R_f = 0.35 (50% hexane in dichloromethane); yellow solid; mp: 212-214 °C, IR (KBr): 3468, 3340, 1725, 1676, 1582 cm^{-1}; ^{1}H NMR(400 MHz, $CDCl_3$): δ 3.84 (s, 3H, OCH_3), 6.73 (br s, 2H, NH_2), 6.84 (s, 1H, CH), 7.12 (t, *J* = 4.76 Hz, 1H, ArH), 7.46 (d, *J* = 5.13 Hz, 1H, ArH), 7.60 (d, *J* = 2.93 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 51.4, 97.5, 111.5, 127.6, 128.4, 129.1, 134.6, 152.9, 153.3, 157.8, 164.2; HRMS (ESI): calculated for $C_{13}H_9NO_4S_2$, 329.9865 (M+ Na$^+$);found for *m/z* 329.9865.

3-Amino-6-furan-2-yl-4-oxo-4*H*-thieno[3,2-*c*]pyran-2-

carboxylic acid methyl ester (3c): Yield: 79 % (115 mg); R_f = 0.27 (50% hexane in dichloromethane); yellow solid; mp: 204-206 °C, IR (KBr): 3475, 3347, 1725, 1677, 1604 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82 (s, 3H, OCH_3), 6.54 (m, 1H, ArH), 6.73 (br s, 2H, NH_2), 6.93 (s, 1H, CH), 7.02 (d, *J* = 3.2 Hz, 1H, ArH), 7.52 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 51.4, 96.8, 111.5, 112.2, 112.6, 145.0, 146.0, 149.5, 152.7, 157.7, 164.2; HRMS (ESI): calculated for $C_{13}H_9NO_5S$, 314.0094 (M+ Na$^+$); found for *m/z* 314.0094.

3-Amino-6-(4-bromo-phenyl)-4-oxo-4*H*-thieno[3,2-*c*]pyran-2-carboxylic acid methyl ester (3d): Yield: 82 % (155 mg); R_f = 0.25 (50% hexane in dichloromethane); yellow solid; mp: 230-232 °C; IR (KBr): 3478, 3362 1708, 1675, 1604 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.85 (s, 3H, OCH_3), 6.73 (br s, 2H, NH_2), 7.00 (s, 1H, CH), 7.59 (d, *J* = 9.16Hz, 2H, ArH), 7.69 (d, *J* = 9.16Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 51.5, 98.7, 112.2, 125.5, 127.0, 129.8, 132.3, 152.6, 156.5, 158.1, 164.2; HRMS (ESI) calculated for $C_{15}H_{10}$ $BrNO_4S$, 379.9587 (M+ H$^+$); found for *m/z* 379.9585.

3-Amino-6-(4-methoxy-phenyl)-4-oxo-4*H*-thieno[3,2-*c*]pyran-2-carboxylic acid methyl ester (3e): Yield: 79 % (130 mg); R_f = 0.19 (50% hexane in dichloromethane); yellow solid; mp: 203-205 °C; IR (KBr): 3481, 3366, 1733, 1685, 1677, 1583 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 6.72 (br s, 2H, NH_2), 6.87 (s, 1H, CH), 6.94 (d, *J* = 9.16 Hz, 2H, ArH), 7.77 (d, *J* = 9.16 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 51.3, 55.4, 96.9,111.3, 114.4, 123.3, 127.4, 153.5, 157.7, 158.5, 161.8, 164.3; HRMS(ESI): calculated for $C_{16}H_{13}NO_5S$, 332.0587 (M+H$^+$); found for *m/z* 332.0578.

3-Amino-4-oxo-6,7-diphenyl-4*H*-thieno[3,2-*c*]pyran-2-carboxylic acid methyl ester (3f): Yield: 76 % (143 mg); R_f = 0.28 (50% hexane in dichloromethane); yellow solid; mp: 236-238 °C; IR(KBr):3467, 3345, 1726, 1678 cm^{-1}; ^{1}H NMR(400 MHz, $CDCl_3$): δ 3.80 (s, 3H, OCH_3), 6.76 (br s, 2H, NH_2), 7.20-7.40 (m, 10H , ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 51.4, 112.1, 115.4, 128.1 ,128.9, 129.2, 129.3, 129.7, 129.8, 131.5, 133.3, 153.9, 157.1, 158.4, 164.3; HRMS (ESI) calculated for $C_{21}H_{15}NO_4S$, 378.0795 (M+H$^+$) found for *m/z* 378.0786.

3-Amino-6,7-bis-(4-methoxy-phenyl)-4-oxo-4*H*-thieno[3,2-*c*]pyran-2-carboxylic acid methyl ester (3g): Yield: 86% (187 mg); R_f = 0.22 (50% hexane in dichloromethane); yellow solid; mp: 185-187 °C; IR (KBr): 3476, 3359, 1666, 1602 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.76 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 3.82.(s, 3H, OCH_3), 6.71 (br s, 2H, NH_2), 6.73 (s, 2H, ArH), 6.91 (d, *J*=8.79 Hz, 2H, ArH) ,7.19 (d, *J*=8.79 Hz ,2H, ArH), 7.30(d, *J*= 6.59 Hz , 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 51.3, 55.2, 111.6, 113.5, 113.9, 114.8, 123.9, 125.7, 130.8, 130.9, 153.9, 158.1, 158.5, 159.8, 160.6, 164.4: HRMS (ESI) calculated for $C_{23}H_{19}NO_6S$,438.1006 (M+H$^+$); found for *m/z* 438.1003.

3-Amino-7-methyl-4-oxo-6-phenyl-4*H*-thieno[3,2-*c*]pyran-2-carboxylic acid methyl ester(3h): Yield: 89% (140 mg); R_f = 0.31(50% hexane in dichloromethane); yellow solid; mp: 213-215 °C; IR (KBr): 3488, 3368, 1718, 1670, 1578, 1295 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$):δ 2.24 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 6.74 (br s, 2H, NH_2), 7.46 (m, ArH, 3H), 7.58 (m, ArH, 2H)) ^{13}C NMR (100 MHz, $CDCl_3$):δ 14.3, 51.5, 108.9, 112.1, 128.4, 128.5, 129.0, 130.0, 131.8, 154.6, 156.9, 158.7, 164.3; HRMS (ESI):calculated for $C_{16}H_{13}NO_4S$, 316.0638 (M+H$^+$); found for *m/z* 316.0638.

17-Amino-12-oxo-6,12-dihydro-7*H*-11-oxa-15-thiacyclopenta[*a*]phenanthrene-16-carboxylic acid methyl ester(3i): Yield: 89%(145 mg); .R_f = 0.32 (50% hexane – dichloromethane); yellow solid; mp: 232-234 °C IR (KBr) 3463, 3341, 1708, 1589, 1294 cm^{-1}, ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.78 (m, 2H, CH_2), 3.02 (t, *J*=7.32 Hz ,2H, CH_2),3.83 (s, 3H, OCH_3) 6.76 (br s, 2H, NH_2),7.32 (m, 3H, ArH), 7.85 (m, 1H, ArH), ^{13}C NMR (100 MHz, $CDCl_3$):δ= 22.5, 26.9, 51.4, 109.1, 123.6, 127.3, 127.4 127.9, 130.2, 136.8, 151.4, 154.5, 158.4, 164.3; HRMS (ESI)calculated for $C_{17}H_{13}NO_4S$, 328.0638 (M+H$^+$); found for *m/z* 328.0638.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [This material includes characterization data and ^{1}H and ^{13}C NMR spectra for all the reported compounds. It also includes detail about thermogravimetric analysis, solvent effect, AIE study and theoratical studies of all the synthesized compounds]. See DOI: 10.1039/b000000x/

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Graphical Abstract

Substituent dependent tunable fluorescence in thieno[3,2-*c*]pyrans

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