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## **Synthesis, Photophysical, Thermal Properties and X-Ray Studies of Novel Organic Dyes bearing Inden-1-ylidene and Fluorene**

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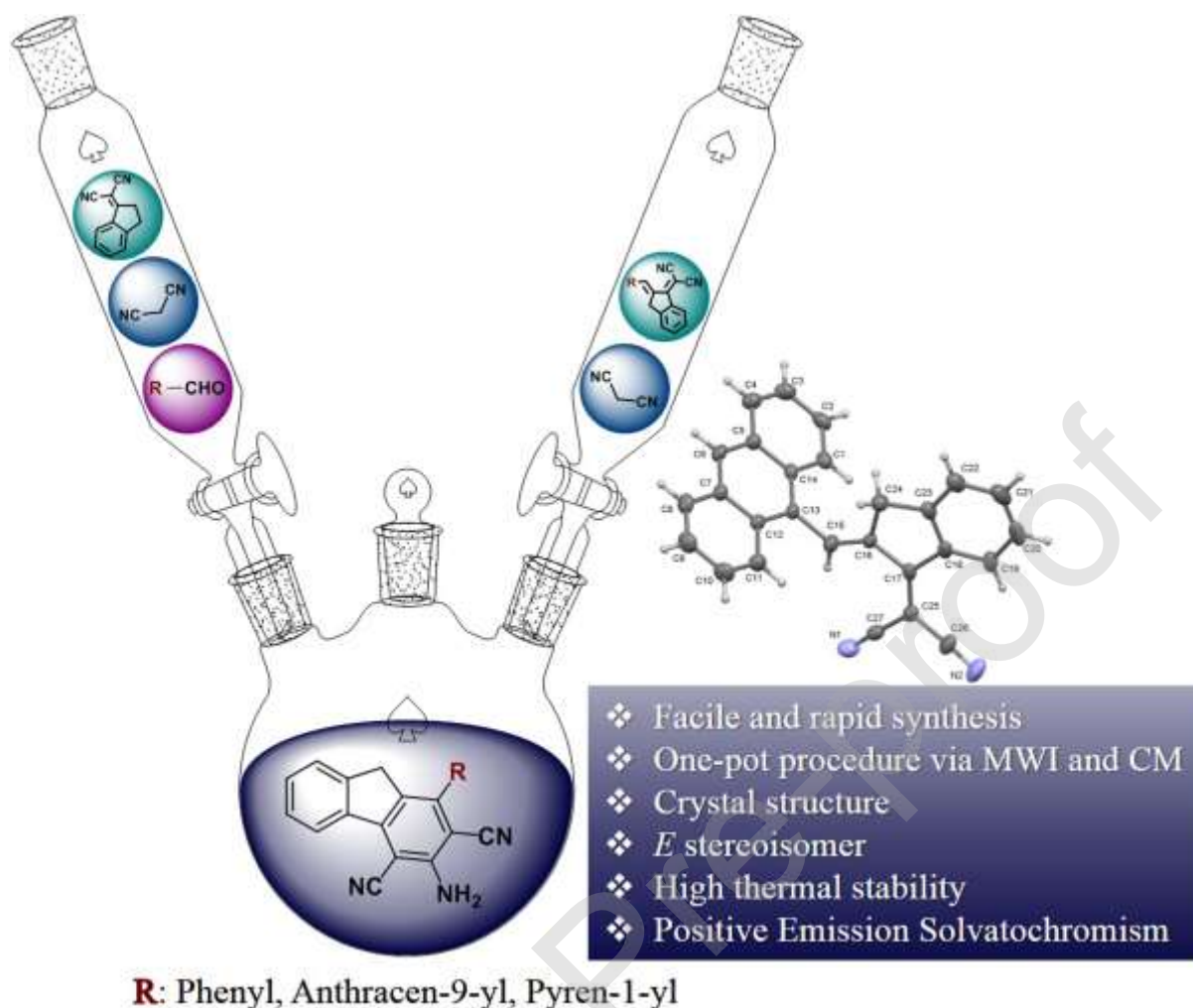
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## Graphical Abstract

**Highlights**

- A novel series of 3-Amino-1-phenyl/antranyl/pyrenyl-2,4-dicyanofluorene derivatives were synthesized.
- Fluorene-antracene and fluorene-pyrene hybrids system will be present firstly in this manuscript.
- Conventional and microwave irradiation methods were compared to obtain better methods and high yields.
- Di/three-components one-pot method was used to synthesis the compounds.
- Photophysical and thermal properties of the compounds were investigated.

**Abstract**

Organic conjugated compounds containing various substituents 3-amino-2,4-dicyano-1-aryl-9H-fluorene and 1-dicyanomethylene-2-aryl-indone derivatives were successfully obtained. Various routes and synthesis methods, such as one-pot, multi-step, and microwave irradiation (MWI), were explored for efficiency. Spectroscopic methods were used to characterize the synthesized compounds. Furthermore (*E*)-2-(2-(anthracen-9-ylmethylene)-2,3-dihydro-1H-inden-1-ylidene) malononitrile (**2b**) compound which exhibited a crystal structure was characterized via X-ray technique. The thermogravimetric analysis (TGA) was used to investigate the thermal stability. Finally, the photophysical properties of the synthesized compounds were also investigated using UV-vis and fluorescence.

**Keywords:** Fluorene derivatives, Microwave irradiation, Thermogravimetric analysis, UV-vis, Fluorescence

## 1. Introduction

In the last decades, organic conjugated molecules have drawn significant interest due to several prospective optoelectronic applications. Organic materials offer several prospective and different benefits compared to their inorganic equivalents, such as good flexibility, better transparency, and lighter weight. Optoelectronic devices based on organic materials can be built onto an adjustable substrate to generate flexible electronic tools [1–4]. Organic light-emitting diodes (OLEDs) [5,6] and organic photovoltaic (OPV) [7–9] have thus attracted considerable interest. OLEDs are highly promising flat panel technologies that can generate large-area displays and solid-state illumination systems. Furthermore, OPV devices are a promising alternative solution for acquiring clean, renewable energy.

The design of such organic molecules is driven by the aim of enhancing the performance of the devices via molecular structure adjustment. In this context, fluorene, pyrene, and anthracene fragments are particularly interesting.

Fluorene-based molecules have been extensively studied and found applications in electronic devices, medical fields, and optics [10–14]. The fluorene core is indeed an excellent  $\pi$ -conjugated core due to the planarization of the biphenyl unit [15–18]. The fluorene group is also electro-rich that can enhance the absorption properties and decrease the oxidation potential of materials. Additionally, the bulky fluorene fragment can restrain aggregation and excimer formation [19,20].

Moreover, pyrene and anthracene belong to the polycyclic aromatic hydrocarbons family, and are known to act as an electron donor and electron acceptor. Pyrene displays intense photoluminescence (PL) in solution [21,22]. Usually, in condensed media, pyrene and its derivatives have a tendency to produce excimers [23,24]. On the other hand, anthracene derivatives have attracted many researchers due to their exceptional PL and electroluminescence (EL) properties, wide-energy gap, and good thermal stability, making these derivatives appealing as blue-emitting materials in OLEDs [25–27].

Numerous studies have tackled the advantages of combining pyrene or anthracene and fluorene groups into one chromophore [14, 28–31]. In this contribution, we designed two series of 1-dicyanomethylene-2-aryl-indones **2** and 3-amino-2,4-dicyano-1-aryl-9*H*-fluorene **3** (Chart 1) obtained by di/three-component one-pot method. Phenyl, anthracen-9-yl, and pyren-1-yl groups were used as aromatic fragments to enhance the PL properties. The photophysical of these compounds were studied in various media.

## 2. Experimental part

### 2.1. Materials and instrumentation

The chemicals used in the synthesis of all compounds were obtained from Aldrich Chemical Company (USA) and were used without further purification. Compound 1 was obtained according to reported procedure [32]. All solvents used were of analytical grade. All reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) using Merck silica gel (60 F<sub>254</sub>) plates (0.25 mm) and visualized with Ultraviolet light. FT-IR (ATR) spectra were recorded on Jasco FTIR 6800Q spectrometer (Sanko Tekstil İşletmeleri Sanayi ve Ticaret A. S. Isko Sb, Bursa, Turkey). <sup>1</sup>H NMR and <sup>13</sup>C spectra were recorded on Bruker ASCEND 600 (<sup>1</sup>H: 600 MHz, <sup>13</sup>C: 151 MHz) spectrometer (Sanko Tekstil İşletmeleri Sanayi ve Ticaret A. S. Isko Sb, Bursa, Turkey) and Bruker Avance 300 (<sup>1</sup>H NMR: 300 MHz) spectrometer (Gazi University Department of Chemistry, Turkey) in DMSO-*d*<sub>6</sub> and CDCl<sub>3</sub>. Chemical shifts are expressed in  $\delta$  units (ppm) with tetramethylsilane (TMS) as the internal reference. Coupling constants (*J*) are given in hertz (Hz). Signals are abbreviated as follows: singlet, s; doublet, d; doublet-doublet, dd; triplet, t; multiplet, m. All melting points are uncorrected and in degrees Celsius (°C) (Electrothermal 9200 melting point apparatus). High-resolution mass spectra (HRMS) were recorded at Gazi University, Faculty of Pharmacy, Turkey using electron ionization (EI) mass spectrometry Waters-LCT-Premier-XE-LTOF (TOF-MS) instruments in *m/z* (rel. %). The microwave syntheses were carried out in Milestone Start microwave reaction system. Thermal analysis was performed with Shimadzu DTG-60H system, up to 600 °C (10 °C min<sup>-1</sup>) under dynamic nitrogen atmosphere (15 mL min<sup>-1</sup>). Absorption and Photoluminescence spectra were recorded on a Spex Fluoromax-3 Jobin-Yvon Horiba

spectrophotometer (at IUT Lannion, University of Rennes 1, France). Compounds were excited at their absorption maxima (band of lowest energy) to record the emission spectra. Fluorescence quantum yields ( $\pm 10\%$ ) were determined relative to 9,10-bis(phenylethynyl)anthracene in cyclohexane ( $\Phi_F = 1.00$ ) according to known procedure [33].

## 2.2. X-ray Diffraction Analysis

For the crystal structure determination, a single-crystal of the compound 2a was used for the data collection on a four-circle Rigaku R-AXIS RAPID-S diffractometer (equipped with a two-dimensional area IP detector). Graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and oscillation scans technique with  $\Delta w = 5^\circ$  for one image were used for data collection. The lattice parameters were determined by the least-squares methods based on all reflections with  $F_2 > 2\sigma(F_2)$ . Integration of the intensities, correction for Lorentz and polarization effects, and cell refinement were performed using CrystalClear (Rigaku/MSI Inc., 2005) software. The structure was solved by direct methods using SHELXS-97, and non-hydrogen atoms were refined using anisotropic displacement parameters by a full-matrix least-squares procedure using the program SHELXL-97. H atoms were positioned geometrically and refined using a riding model. The final difference Fourier maps showed no peaks of chemical significance. Crystal data for **2a**: C<sub>16</sub>H<sub>20</sub>O<sub>8</sub>Br<sub>2</sub>, crystal system, space group: monoclinic, P2<sub>1</sub>/n; (no:14); unit cell dimensions:  $a = 9.4760(2)$ ,  $b = 15.7020(4)$ ,  $c = 12.9350(3) \text{ \AA}$ ,  $\alpha = 90$ ,  $\beta = 91.61(2)$ ,  $\gamma = 90^\circ$ ; volume;  $1923.87(8) \text{ \AA}^3$ ,  $Z=4$ ; calculated density:  $1.272 \text{ g/cm}^3$ ; absorption coefficient:  $0.075 \text{ mm}^{-1}$ ;  $F(000)$ : 768;  $\theta$ -range for data collection  $2.9\text{--}25.2^\circ$ ; refinement method: full-matrix least-squares on  $F_2$ ; data/parameters: 3100/263; goodness-of-fit on  $F_2$ : 0.98; final R-indices [ $I > 2\sigma(I)$ ]:  $R_1 = 0.075$ ,  $wR_2 = 0.162$ ; largest diff. peak and hole: 0.170 and  $-0.190 \text{ e \AA}^{-3}$ .

CCDC-2026782 number contains the supplementary crystallographic data for this structure (**2a**). These data are provided free of charge via the joint CCDC/FIZ Karlsruhe deposition service, [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

### *2.3. Syntheses procedures for the preparation of dyes and characterization*

**Method A** - Microwave irradiation procedure.

Compound **1** (1.00 mmol) and appropriate aldehyde (1.00 mmol) were dissolved in 10 mL ethanol. A few drops of piperidine as a catalyst was added. The mixture was heated under MWI (300 W) for 5 min. The reaction mixture was then cooled to room temperature, and the precipitated solid was filtered and washed with ethanol.

**Method B** - Conventional procedure.

Compound **1** (1.00 mmol) and appropriate aldehyde (1.00 mmol) were dissolved in cyclohexane (10 ml). A few drops of piperidine were added under stirring. After adding piperidine, and the reaction mixture becomes reddish. After refluxing for 3 – 4 h, The reaction mixture was then cooled to room temperature, and the precipitated solid was filtered and recrystallized from ethanol.

**Method C** - Microwave irradiation procedure.



Corresponding compound **2** (1.00 mmol) and malononitrile (1.50 mmol) were dissolved in acetonitrile (10 mL). Pyrrolidine (1.20 mmol) as a catalyst was slowly added. The mixture was heated under MWI (300 W) to 78 °C for 5 min. The reaction mixture was then cooled to room temperature and the precipitated solid was filtered and washed with ethanol.

**Method D** - Conventional procedure.

The corresponding compound **2** (1.00 mmol) and malononitrile (1.50 mmol) were dissolved in acetonitrile (10 ml). Pyrrolidine (1.20 mmol) as a catalyst was slowly added. The solution was stirred for 45 min at room temperature. The precipitated solid was filtered and washed with ethanol.

**Method E** – Microwave irradiation one-pot procedure.

Compound **1** (1.00 mmol), appropriate aldehyde (1.50 mmol) and malononitrile (1.50 mmol) were dissolved in (15 mL) acetonitrile. Pyrrolidine (1.20 mmol) as a catalyst was slowly added. The mixture was heated under MWI (300 W) to 78 °C for 5 min. Then the reaction mixture was cooled to room temperature and the precipitated solid was filtered and washed with ethanol.

**Method F** - Conventional one-pot procedure.

Compound **1** (1.00 mmol), appropriate aldehyde (1.50 mmol) and malononitrile (1.50 mmol) were dissolved in acetonitrile. Pyrrolidine (1.20 mmol) as a catalyst was slowly added. The solution was stirred for 45 min at room temperature. The precipitated solid was filtered and washed with ethanol.

**(E)-2-(2-benzylidene-2,3-dihydro-1H-inden-1-ylidene)malononitrile (2a):** Obtained according to **Method B**, Yield: 97 % (260 mg), yellow solid m.p.: 180 - 182 °C (lit. m.p.: 175 - 177 °C) [20] FT-IR (Attenuated total reflectance (ATR),  $\text{cm}^{-1}$ ): 3061 (C-H Aromatic), 2940 (C H Aliphatic), 2328 (C=N), 1616 (C=C),  $^1\text{H}$  NMR (600 MHz, DMSO- $d_6$ ,  $\delta$  ppm) 8.40 (d,  $J = 8.1$  Hz, 1H), 8.20 (s, 1H), 7.74 – 7.70 (m, 3H), 7.67 (d,  $J = 7.6$  Hz, 1H), 7.60 – 7.53 (m, 3H), 7.53 – 7.49 (m, 1H), 4.15 (s, 2H),  $^{13}\text{C}$  NMR (151 MHz, DMSO- $d_6$ ,  $\delta$  ppm) 167.5, 148.4, 137.5, 136.3, 134.9, 134.7, 130.7, 130.4, 129.2, 128.2, 126.1, 124.8, 115.4, 115.0, 36.8. HRMS  $m/z$  calculated for  $\text{C}_{19}\text{H}_{13}\text{N}_2$ : 269.1079, found 269.1071 (M+H) $^+$ .

**(E)-2-(2-(anthracen-9-ylmethylene)-2,3-dihydro-1H-inden-1-ylidene)malononitrile (2b):** Obtained according to **Method B**, Yield: 43 % (158 mg), Orange solid, m.p.: 253 - 254 °C, FT-IR (ATR,  $\text{cm}^{-1}$ ): 3043 (C-H Aromatic), 2962 (C-H Aliphatic), 2327 (C=N), 1603 (C=C),  $^1\text{H}$  NMR (600 MHz, DMSO- $d_6$ ,  $\delta$  ppm) 8.95 (d,  $J = 0.8$  Hz, 1H), 8.76 (s, 1H), 8.45 (d,  $J = 8.2$  Hz, 1H), 8.28 – 8.10 (m, 4H), 7.64 (dd,  $J = 11.5, 4.1$  Hz, 1H), 7.62 – 7.55 (m, 5H), 7.41 (d,  $J = 7.6$  Hz, 1H), 3.34 (s, 2H),  $^{13}\text{C}$  NMR (151 MHz, DMSO- $d_6$ ,  $\delta$  ppm) 165.5, 147.7, 142.5, 136.3, 134.9, 133.8, 130.9, 129.0, 128.8, 128.6, 128.4, 128.2, 127.0, 126.1, 125.8, 125.4, 124.9, 114.9, 108.9, 70.1, 36.1, HRMS  $m/z$  calculated for  $\text{C}_{27}\text{H}_{17}\text{N}_2$ : 369.1392, found 369.1388 (M+H) $^+$ .

**(E)-2-(2-(pyren-1-ylmethylene)-2,3-dihydro-1H-inden-1-ylidene)malononitrile****(2c):**

Obtained according to **Method B**, Yield: 52 % (204 mg), purple solid, m.p.: 280 - 281 °C, FT-IR (ATR, cm<sup>-1</sup>): 3038 (C-H Aromatic), 2961 (C-H Aliphatic), 2327 (C=N), 1601 (C=C), <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>, δ ppm) 9.24 (s, 1H), 8.60 (d, *J* = 9.5 Hz, 1H), 8.52 (d, *J* = 8.2 Hz, 1H), 8.47 (d, *J* = 8.8 Hz, 1H), 8.44 (d, *J* = 8.5 Hz, 1H), 8.43 – 8.37 (m, 3H), 8.33 (d, *J* = 9.3 Hz, 1H), 8.29 (d, *J* = 8.2 Hz, 1H), 8.16 (t, *J* = 7.6 Hz, 1H), 7.72 (t, *J* = 7.2 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 3.86 (s, 2H). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, δ ppm) δ 9.34 (s, 1H), 8.66 (d, *J* = 7.6 Hz, 1H), 8.39 (d, *J* = 9.0 Hz, 1H), 8.29 – 8.21 (m, 5H), 8.18 (d, *J* = 8.7 Hz, 1H), 8.11 (d, *J* = 8.6 Hz, 1H), 8.07 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 7.1 Hz, 1H), 4.05 (s, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>, δ ppm) 147.8, 138.7, 136.9, 135.4, 135.4, 134.7, 134.6, 134.5, 132.8, 131.3, 131.0, 130.5, 129.9, 129.3, 129.3, 128.4, 127.6, 127.4, 126.9, 126.7, 126.5, 126.4, 126.4, 125.5, 124.9, 124.7, 123.3, 118.7, 37.4. HRMS *m/z* calculated for C<sub>29</sub>H<sub>17</sub>N<sub>2</sub>: 393.1392, found 393.1384 (M+H)<sup>+</sup>.

**3-amino-2,4-dicyano-1-phenyl-9H-fluorene (3a):** Obtained according to **Method F**, the compound was purified by column chromatograph. Yield: 41 % (126 mg), grass solid m.p.: 299 - 300 °C (lit. m.p.: 303 - 305 °C) [34], FT-IR (ATR, cm<sup>-1</sup>): 3472 (N-H), 3376 (N-H), 3055 (C-H Aromatic), 2986 (C-H Aliphatic), 2328 (C=N), 1628(C=C), <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>, δ ppm) 8.37 – 8.31 (m, 1H), 7.62 (dt, *J* = 6.4, 2.3 Hz, 1H), 7.59 – 7.56 (m, 4H), 7.56 – 7.52 (m, 2H), 7.50 (td, *J* = 7.3, 1.4 Hz, 1H), 6.72 (s, 2H), 3.68 (s, 2H), <sup>13</sup>C NMR (151 MHz, DMSO-d<sub>6</sub>, δ ppm) 153.5, 146.7, 146.5, 146.3, 137.6, 136.4, 130.4, 129.8, 129.1, 128.7, 128.6, 127.4, 125.6, 121.9, 116.3, 115.9, 94.4, 87.2, 35.3, HRMS *m/z* calculated for C<sub>21</sub>H<sub>14</sub>N<sub>3</sub>: 308.1188, found 308.1175 (M-H)<sup>+</sup>.

**3-amino-2,4-dicyano-1-(anthracen-9-yl)-9H-fluorene (3b):** Obtained according to **Method F**, the compound was purified by column chromatography. Yield: 32 % (130 mg), grass solid m.p.: 367 - 368 °C, FT-IR (ATR,  $\text{cm}^{-1}$ ): 3470 (N-H), 3362 (N-H), 3048 (C-H Aromatic), 2929 (C-H Aliphatic), 2328 (C=N), 1632 (C=C),  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm)  $\delta$  8.64 (s, 1H), 8.55 (d,  $J = 7.8$  Hz, 1H), 8.12 (d,  $J = 8.4$  Hz, 2H), 7.53 (d,  $J = 1.4$  Hz, 1H), 7.50 (d,  $J = 8.3$  Hz, 4H), 7.46 (d,  $J = 0.5$  Hz, 2H), 7.44 – 7.37 (m, 3H), 7.32 (d,  $J = 7.7$  Hz, 1H), 5.35 (s, 2H), 3.27 (s, 2H),  $^{13}\text{C}$  NMR (151 MHz,  $\text{DMSO}-d_6$ ,  $\delta$  ppm) 153.7, 147.1, 145.8, 143.7, 137.8, 132.1, 130.9, 129.9, 129.9, 128.8, 128.5, 128.4, 127.6, 127.2, 125.8, 125.7, 124.7, 122.1, 115.9, 115.8, 96.5, 88.3, 34.8, HRMS  $m/z$  calculated for  $\text{C}_{29}\text{H}_{18}\text{N}_3$ : 408.1501, found 408.1494 (M-H) $^+$ .

**3-amino-2,4-dicyano-1-(pyren-1-yl)-9H-fluorene (3c):** Obtained according to **Method F**, the compound was purified by column chromatograph. Yield: 30 % (129 mg), dark green solid m.p.: 327 - 328 °C, FT-IR (ATR,  $\text{cm}^{-1}$ ): 3493 (N-H), 3392 (N-H), 3040 (C-H Aromatic), 2896 (C-H Aliphatic), 2211 (C=N), 1614 (C=C),  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO}-d_6$ ,  $\delta$  ppm) 8.48 (d,  $J = 7.8$  Hz, 1H), 8.42 (t,  $J = 8.4$  Hz, 2H), 8.35 (d,  $J = 7.7$  Hz, 1H), 8.32 (dd,  $J = 8.1, 4.7$  Hz, 2H), 8.21 – 8.17 (m, 1H), 8.14 (ddd,  $J = 14.1, 7.6, 1.0$  Hz, 2H), 7.75 (d,  $J = 9.2$  Hz, 1H), 7.56 (tt,  $J = 6.9, 3.3$  Hz, 1H), 7.53 – 7.45 (m, 2H), 6.89 (s, 2H),  $^{13}\text{C}$  NMR (151 MHz,  $\text{DMSO}-d_6$ ,  $\delta$  ppm) 153.5, 146.8, 146.1, 145.6, 137.8, 131.8, 131.3, 131.3, 130.8, 130.3, 129.8, 128.7, 128.2, 127.6, 127.5, 127.3, 126.7, 126.6, 125.9, 125.7, 125.0, 124.0 123.9, 123.8, 122.1, 120.0, 116.1, 101.1, 95.9, 87.8, 35.2. HRMS  $m/z$  calculated for  $\text{C}_{31}\text{H}_{18}\text{N}_3$ : 432.1501 found 432.1489 (M-H) $^+$ .

### 3. Results and discussion

#### 3.1. Synthesis

Many methods were reported in the literature for the synthesis of fluorene core [35–39]. In these methods, the fluorene-1-yl fragment is only substituted by small groups. Although such compounds can be obtained with good yields, the synthesis of fluorene-1-yl with bulky substituent is more challenging. Targeted fluorenes **3** were obtained from 1-dicyanomethyleneindane and appropriate aldehydes in two steps using a previously published method (Scheme 1) [35]. In this strategy, 2-arylidene-1-dicyanomethyleneindone derivatives **2** were isolated and converted to the corresponding fluorene **3** in the presence of malononitrile and pyrrolidine as catalyst. Alternatively the fluorene **3** can be obtained via a one-pot synthetic procedure (Scheme 1) [35]. Therefore, two different synthetic ways can be compared. Moreover, conventional and microwave irradiation (MWI) were used and compared in each cases and the results are presented in Table 1.

As shown in Table 1, the one pot method permit to obtain the fluorine derivatives **3** whatever the nature of the aldehyde. A decrease of the yield is however observed with anthracen-9-yl and pyren-1-yl bulky substituents and MWI does not improve the yield. On the other hand, the sequential synthesis of fluorene **3** can be only achieved for **3a** with a phenyl substituent, dicyanomethyleneindones **2b** and **2c** cannot be converted to fluorene **3b** and **3c** respectively. All compounds have been characterized by  $^1\text{H}$  and  $^{13}\text{C}$  nmr, IR spectrometry as was as HRMS.

### 3.2. X-ray crystallography analysis

The structure of {2-[(anthracen-9-yl)methylidene]-2,3-dihydro-1*H*-inden-1-ylidene}propanedinitrile (**2b**) was characterized by single crystal X-ray diffraction analysis. The suitable crystal for X-ray analysis was obtained by recrystallization of solid with toluene as solvent. The plot shown in Figure 1 confirms the proposed molecular structure, in particular the *E* stereoisomery of the exocyclic double bond. Compound **2b** crystallized as red prisms and was solved in the monoclinic space group P21/n with four molecules in the unit cell. The structure has cyano and anthracenyl groups linked with the C=C double bonds (C17=C25, 1.360 Å, and C15=C16, 1.319 Å) to the indan core. The average C≡N bond length is 1.143 (3) Å, and the average C–C single bond length is 1.435 (4) Å in the malononitrile group. The anthracene and indan rings are almost planar. Dihedral angle between these planes is 77.2 degrees. Deviation from the planarity of the molecule is due to significant steric effects and intermolecular interactions. The crystal packing shows (**Fig. 1** - Bottom) that molecules are connected by slight C-H⋯N [D⋯A = 3.28-3.54 Å] interactions. The π-π stacking interactions between the delocalized π-electrons of the anthracenyl and indanyl groups are relatively weak. The distance between the ring centroids is in the range of 3.69–5.43 Å.

### 3.3. Thermal stability

The thermal stabilities of the compounds were analysed using TGA. It was found that fluorene derivatives **3** were thermally more stable than their 1-dicyanomethyleneindane analogues **2** (Table 2) and phenyl derivatives **2a** and **3a** are the less stable in each series. The fact that the compounds do not lose weight up to 100-150 °C indicates the absence of water or organic

solvent in the environment. Significantly, **3b** and **3c** compound decomposed at temperatures above 330 °C and lose 24% and 29% of their mass (Figure 2), respectively, indicating that the compounds have the potential to be used in thermally stable and advanced optical fields.

### 3.4. Photophysical properties

The UV/Vis and PL spectra were measured in CH<sub>2</sub>Cl<sub>2</sub> at room temperature and the data are reported in Table 3. The normalized spectra are displayed in Figures 3 and S26. The analyses were carried out using low concentration of chromophores (0.5-1.5 × 10<sup>-5</sup> M). Except **3a**, all compound exhibit various absorption band in UV or blue region of the spectrum. The less energetic absorption band for dicyanomethyleneindanes **2** is significantly more red-shifted than for fluorene analogues **3**. Dicyanomethyleneindanes **2** are not emissive but fluorenes exhibit purple (**3a**) or blue (**3b** and **3c**) emission with moderate quantum yield (QY). It should be noted that the QY is significantly higher for the pyren-1-yl derivative **3c** ( $\Phi_F = 0.32$ ) than for the anthracen-9-yl chromophore **3b** ( $\Phi_F = 0.09$ ). According to  $\lambda_{\text{onset}}$  values, the HOMO-LUMO gap were estimated to 0.318, 0.334 and 0.338 eV for compounds **3a**, **3b** and **3c**. In solid state, only compound **3a** significant emission with maxima at 465 and 530 (Figure S27)

The emission properties of compounds **3** have been measured in a series of solvents of increasing polarity (Table 4, Figures 4, S28 and S29). A positive emission solvatochromic is globally observed which is characteristic of compounds presenting intramolecular charge

transfer [40–42]. As expected, the solvatochromic range is more extended for anthracen-9-yl and pyren-1-yl derivatives **3b** and **3c** due to more extended  $\pi$ -conjugated structure. The Stokes shifts have been plotted versus the solvent polarity function for compounds **3a-c**. (Lippert Mataga plot, Figure S30) [43-45]. The slope of the regression lines provide estimation of the increase in dipole moment in the fluorescence state compared to the ground state of ca. 19.1, 22.3 and 21.6 D for **3a**, **3b** and **3c** respectively [46].

In order to study the effect of aggregation on the PL properties of compounds **3**, their emission spectra were recorded in THF-water mixtures of different ratio, the spectra are displayed in Figures 5, 6 and S29. None of the chromophores exhibits aggregation induced emission (AIE) but the behavior of compound **3a** is different to what is observed for compounds **3b** and **3c**. For compound **3a**, the addition of water (up to 80%) leads to an increase of emission intensity with a slight red-shift of emission maximum (from 428 to 436 nm) attributed to an increase of the polarity of the media. For higher ratio of water, the intensity of this emission band significantly decreases and a second emission band of low intensity centered at 535 nm appears that may be attributed to the formation of J-aggregates. This leads to turquoise emission for 10:90 THF/water ratio where both bands have similar intensity and green emission for 3:97 THF/water ratio where the first band is almost fully quenched. The behavior of compound **3b** and **3c** is different. In pure THF, compound **3b** exhibits an emission maxima at 447 nm. Between 50% and 70% of water a new emission band moving from 499 to 512 nm leading to green emission is observed (Figure 6). For higher ratio of water, the emission is fully quenched. Compound **3c** exhibits similar behavior (Figure S31).

#### 4. Conclusions



Two series of chromophores based on 3-amino-2,4-dicyano-1-aryl-9*H*-fluorene and 1-dicyanomethylene-2-aryl-indone scaffold were successfully synthesized. The one-pot synthetic route using conventional heating revealed to be the most efficient strategy to obtain fluorene derivatives. X-ray structure of 1-dicyanomethylene-2-anthracen-9-yl-indone **2b** confirms the *E* stereoisomery of the double bond. All fluorene derivatives **3** are thermally stable up to 300°C and exhibit moderate emission properties in solution with emission solvatochromism, characteristic of push-pull derivatives, especially for anthracen-yl and pyren-1-yl derivatives **3b** and **3c**. Fluorenes **3** exhibit aggregation quenched emission behaviour but for compound **3a**, the emission intensity is slightly enhanced when water is added to a THF solution in the 50:50 to 70:30 water/THF ratio.

#### **Declaration of interests .**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### **CRedit authorship contribution statement**

**Mohamed Yahya:** Investigation. **Deniz Çakmaz:** Investigation. **Nurgül Seferoğlu:** Software, Writing - Review & Editing. **Sylvain Achelle:** Methodology, Writing - original draft - Review

& Editing. **Estelle Legall:** Methodology. **Ertan Şahin:** Methodology, Writing - original draft  
- Review & Editing. **Zeynel Seferoğlu:** Supervision, Writing - Review & Editing

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## CAPTIONS

## Scheme Captions

**Chart 1.** Structure of studied compounds.

**Scheme 1.** Synthetic routes for compounds 2a-c and 3a-c.

## Figure Captions

**Figure 1.** (Top) Molecular structure of 2b (asymmetric unit). Thermal ellipsoids are drawn at the 40% probability level. (Bottom) Stacking motif with the unit cell viewed down along the c-axis. Dashed lines indicate C-H...N interactions.

**Figure 2.** TGA curves of chromophores 2 and 3 under nitrogen atmosphere in the temperature range of 50-600 °C at a heating rate of 10 °C min<sup>-1</sup>.

**Figure 3.** Normalized absorption (dashed lines) and emission (solid lines) spectra of compounds 3 in CH<sub>2</sub>Cl<sub>2</sub>. Insert: photographs of CH<sub>2</sub>Cl<sub>2</sub> solution taken in the dark upon irradiation with hand-held UV lamp ( $\lambda_{em} = 366$  nm).

**Figure 4.** Normalized emission spectra of compound 3b in various solvent ( $\lambda_{ext} = 369$  nm)

**Figure 5.** Emission spectra of compound 3a in THF/water mixture ( $c = 1.5 \times 10^{-5}$  M,  $\lambda_{ext} = 379$  nm) Insert: photographs of solution with 100:0 10:90 3:97 THF/water ratio taken in the dark upon irradiation with hand-held UV lamp ( $\lambda_{em} = 366$  nm).

**Figure 6.** Emission spectra of compound **3b** in THF/water mixture ( $c = 1.5 \cdot 10^{-5}$  M,  $\lambda_{\text{ext}} = 360$  nm) Insert: photographs of solution with 100:0 50:50 10:90 THF/water ratio taken in the dark upon irradiation with hand-held UV lamp ( $\lambda_{\text{em}} = 366$  nm).

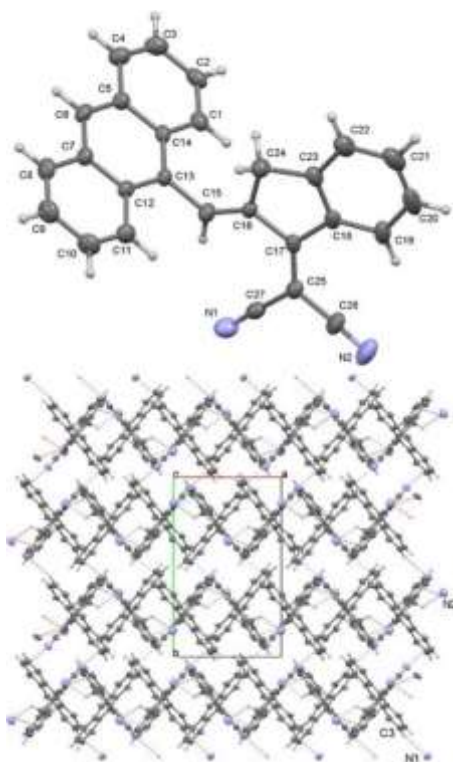
### Table Captions

**Table 1.** Yields of compounds according to the methods used.

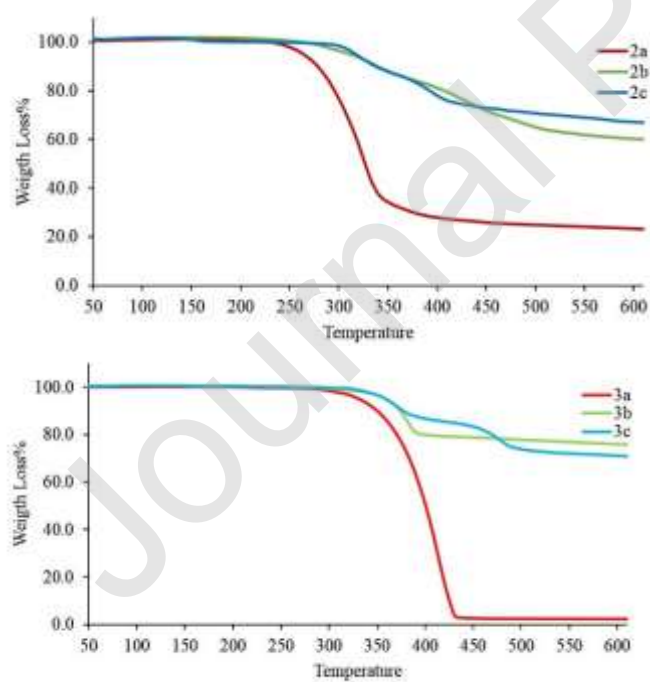
**Table 2.** Thermal decomposition values (weight loss of 5%) of compounds **2** and **3**.

**Table 3.** UV-Vis and photoluminescence (PL) data of compounds **2** and **3** in  $\text{CH}_2\text{Cl}_2$

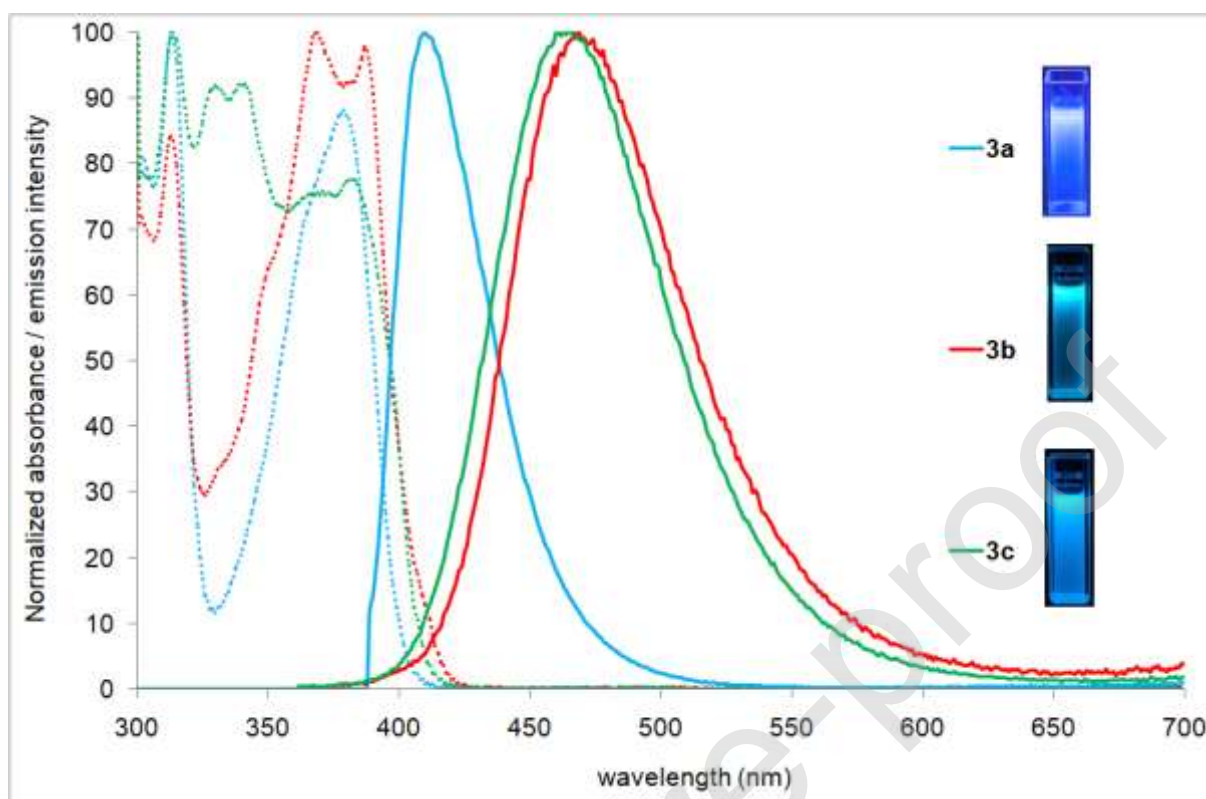
**Table 4.** Emission solvatochromism of compounds **3** in various solvents.



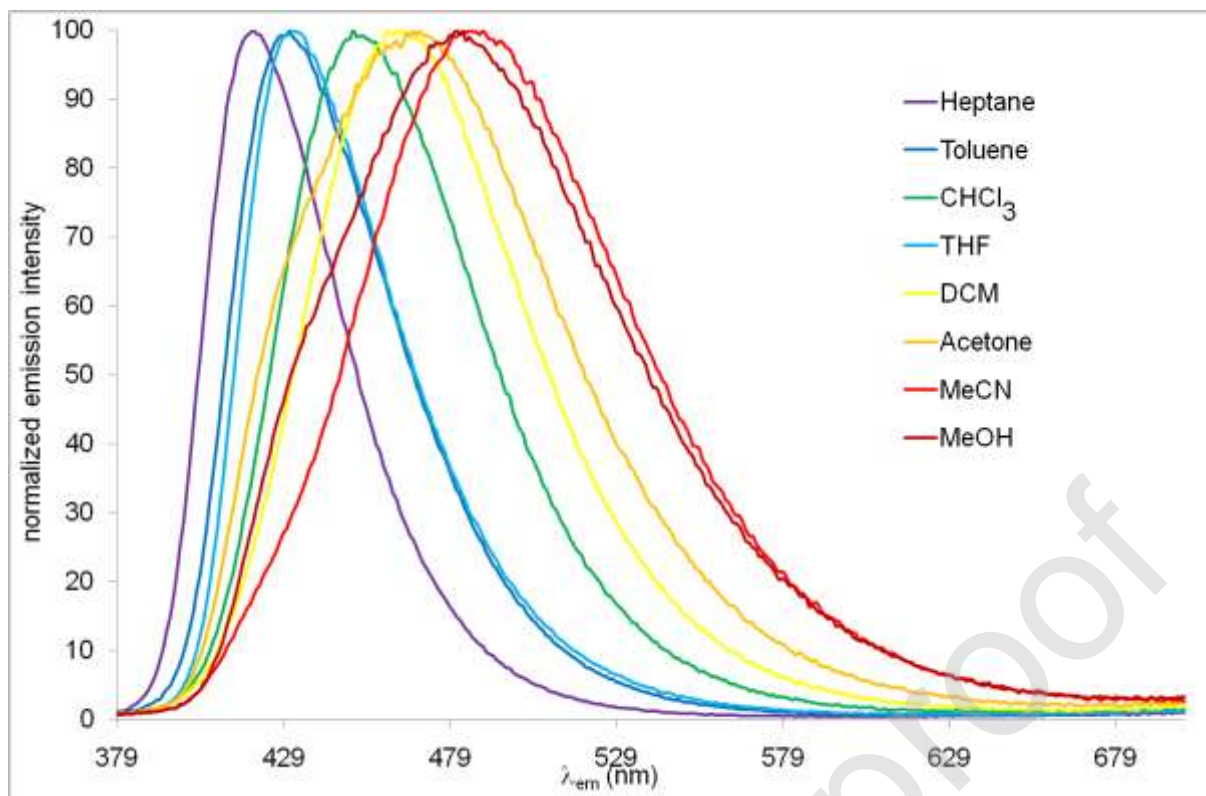
**Fig.1.** (Top) Molecular structure of **2b** (asymmetric unit). Thermal ellipsoids are drawn at the 40% probability level. (Bottom) Stacking motif with the unit cell viewed down along the *c*-axis. Dashed lines indicate C-H...N interactions.



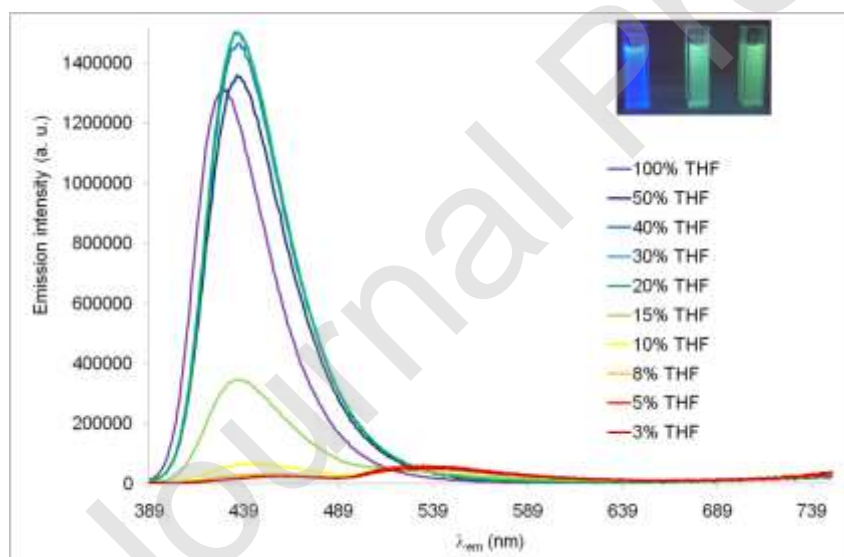
**Fig.2.** TGA curves of chromophores **2** and **3** under nitrogen atmosphere in the temperature range of 50-600 °C at a heating rate of 10 °C min<sup>-1</sup>.



**Fig.3.** Normalized absorption (dashed lines) and emission (solid lines) spectra of compounds **3** in CH<sub>2</sub>Cl<sub>2</sub>. Insert: photographs of DCM solution taken in the dark upon irradiation with hand-held UV lamp ( $\lambda_{em} = 366$  nm).

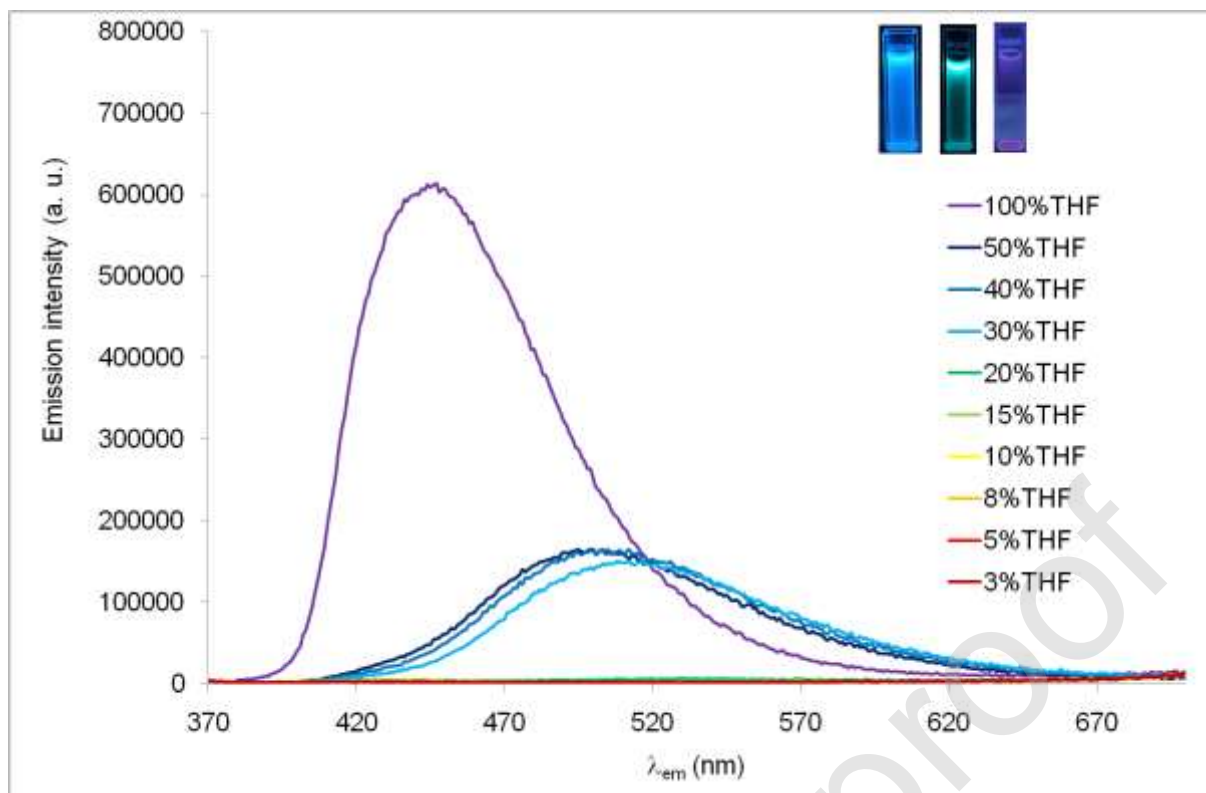


**Fig.4.** Normalized emission spectra of compound **3b** in various solvent ( $\lambda_{ext} = 369$  nm)



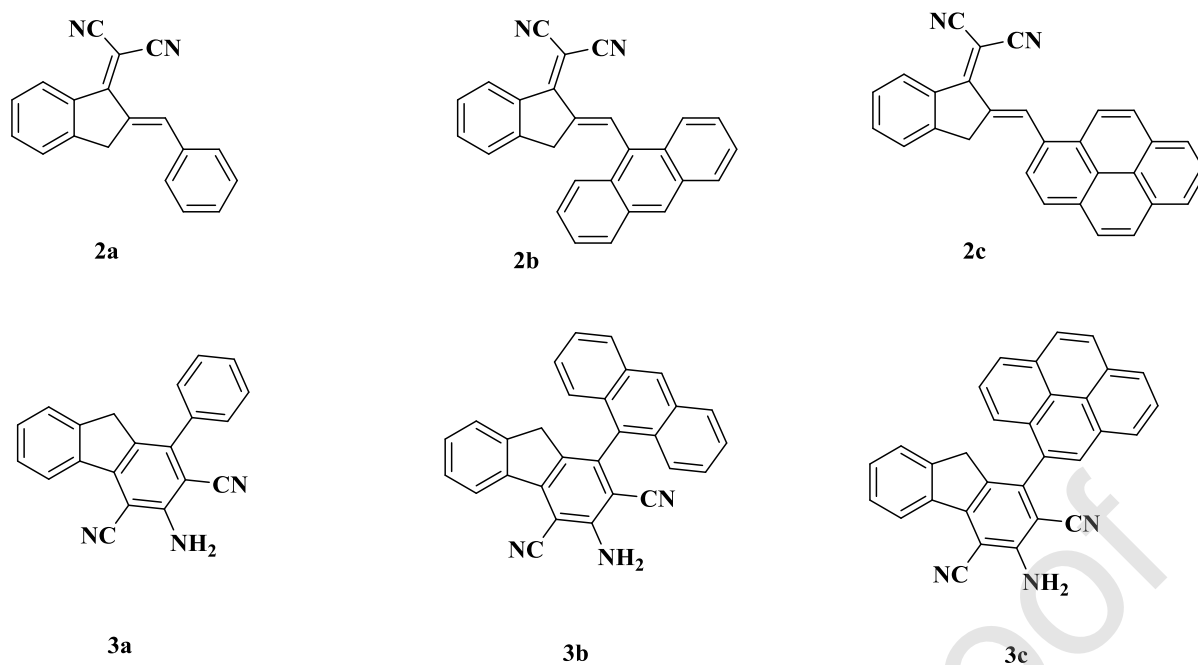
**Fig.5.** Emission spectra of compound **3a** in THF/water mixture ( $c = 1.5 \cdot 10^{-5}$  M,  $\lambda_{ext} = 379$  nm)

Insert: photographs of solution with 100:0 10:90 3:97 THF/water ratio taken in the dark upon irradiation with hand-held UV lamp ( $\lambda_{em} = 366$  nm).

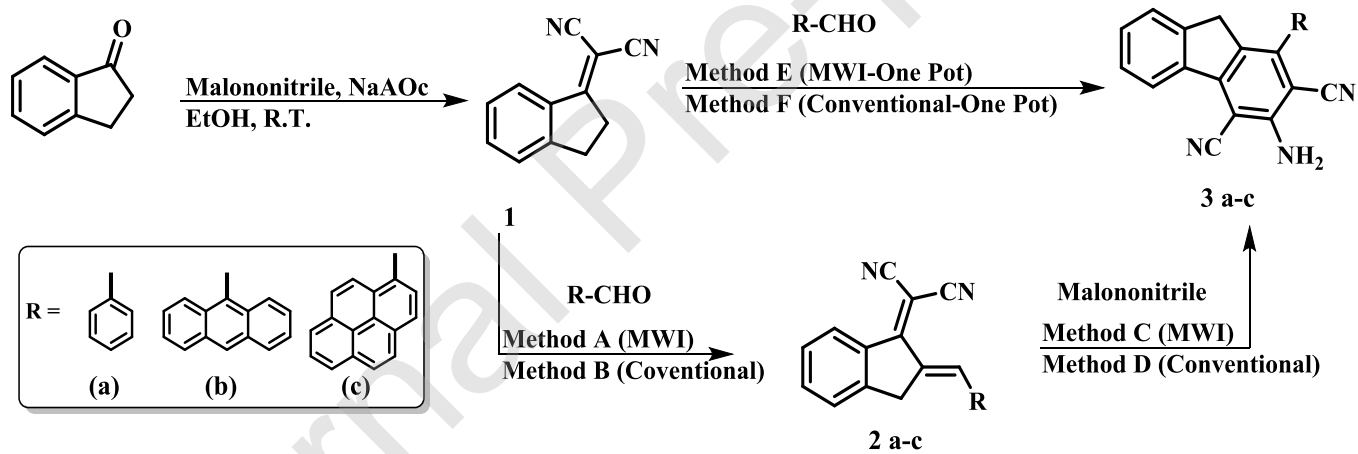


**Fig.6.** Emission spectra of compound **3b** in THF/water mixture ( $c = 1.5 \cdot 10^{-5}$  M,  $\lambda_{ext} = 360$  nm)

Insert: photographs of solution with 100:0 50:50 10:90 THF/water ratio taken in the dark upon irradiation with hand-held UV lamp ( $\lambda_{em} = 366$  nm).



**Chart 1.** Structure of studied compounds.



**Scheme 1.** Synthetic routes for compounds **2a-c** and **3a-c**



**Table 1.** Yields of compounds according to the methods used.

Entry	Compound	R	Method	Yield, %
1	<b>2a</b>	phenyl	A	- <sup>a</sup>
			B	97
2	<b>2b</b>	anthracen-9-yl	A	43
			B	43
3	<b>2c</b>	pyren-1-yl	A	52
			B	43
			C	14
4	<b>3a</b>	phenyl	D	14
			E	31
			F	41
			C	- <sup>a</sup>
			C	- <sup>a</sup>
5	<b>3b</b>	anthracen-9-yl	D	- <sup>a</sup>
			E	23
			F	32
			C	- <sup>a</sup>
			C	- <sup>a</sup>
6	<b>3c</b>	pyren-1-yl	D	- <sup>a</sup>
			E	30
			F	30

<sup>a</sup>compound could not be obtained.

**Table 2.** Thermal decomposition values (weight loss of 5%) of compounds **2** and **3**.

Compound	Temperature °C
<b>2a</b>	246
<b>2b</b>	282
<b>2c</b>	299
<b>3a</b>	300
<b>3b</b>	327
<b>3c</b>	334

**Table 3.** UV-Vis and photoluminescence (PL) data of compounds **2** and **3** in dichloromethane (DCM)

Compound	$\lambda_{\text{abs}}$ (nm)	$\epsilon$ (mM <sup>-1</sup> cm <sup>-1</sup> )	$\lambda_{\text{em}}$ (nm)	$\Phi_F$	Stokes shift (cm <sup>-1</sup> )
<b>2a</b>	362/390	26.9/22.0	- <sup>a</sup>	- <sup>a</sup>	- <sup>a</sup>
<b>2b</b>	365/475	23.7/5.3	- <sup>a</sup>	- <sup>a</sup>	- <sup>a</sup>

<b>2c</b>	343/487	42.9/22.1	_a	_a	_a
<b>3a</b>	379	10.5	410	0.32	1995
<b>3b</b>	313/369/387	19.2/22.8/22.3	467	0.09	4426
<b>3c</b>	314/330/341/382	31.2/28.7/28.7/24.2	463	0.32	4580

<sup>a</sup>no emission detected

**Table 4.** Emission solvatochromism of compounds **3** in various solvents.

<b>Compds</b>	<i>n</i> - heptane	Toluene	THF	CHCl <sub>3</sub>	DCM	Acetone	MeCN	MeOH
	30.9 <sup>[a]</sup>	33.9 <sup>[a]</sup>	37.4 <sup>[a]</sup>	39.1 <sup>[a]</sup>	40.7 <sup>[a]</sup>	42.2 <sup>[a]</sup>	45.6 <sup>[a]</sup>	55.4 <sup>[a]</sup>
<b>3a</b>	402	416	428	417	410	427	423	433
<b>3b</b>	420	443	447	460	467	481	493	496
<b>3c</b>	420	431	432	450	463	468	485	481

<sup>[a]</sup> E<sub>T</sub>(30), Dimoth-Reichardt polarity parameter in kcal mol<sup>-1</sup>. [47]