The novel sensitive and selective chemosensors for determination multiple analytes

Deniz ÇAKMAZ, Arda ÖZARSLAN, Burcu AYDINER, Ahmet Burak EROĞLU, Nurgül SEFEROĞLU, Hülya ŞENÖZ, Zeynel SEFEROĞLU

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	Journal Pre-proof
1	The novel sensitive and selective chemosensors for determination multiple
2	analytes
3	
4	Deniz ÇAKMAZ <sup>a</sup> , Arda ÖZARSLAN <sup>a,b</sup> , Burcu AYDINER <sup>a,*</sup> , Ahmet Burak EROĞLU <sup>c</sup> ,
5	Nurgül SEFEROĞLU <sup>c</sup> , Hülya ŞENÖZ <sup>b*</sup> , Zeynel SEFEROĞLU <sup>a</sup>
6	<sup>a</sup> Department of Chemistry, Faculty of Science, Gazi University, Ankara 06560, Turkey
7	<sup>b</sup> Department of Chemistry, Faculty of Science, Hacettepe University, Ankara 06800, Turkey
8	<sup>c</sup> Department of Advanced Technology, Gazi University, Ankara 06560, Turkey
9	
10	Abstract
11	Novel chemosensors that are azo dyes bearing coumarin with indole and thiophene
12	recognition moieties were synthesized. Sensor properties of the dyes were investigated within
13	multiple basic environments that include various pH ranges, anions, and organic amines.
14	Recognition of the basic media by the chemosensors that have acidic NH and NH <sub>2</sub> groups,
15	occurs via the deprotonation process which was supported with reversibility study and ${}^{1}\mathrm{H}$
16	NMR experiments. The density functional theory calculations have employed to support the
17	experimental results. Chemosensors 6a and 6b showed remarkable detection ability in a pH
18	range of 7–11 and they have been also successfully utilized in the determination of $CN^{-}$ in
19	semi-aqueous media.
20	
21	Keywords: Colorimetric chemosensors, Azo dyes, pH sensors, Anions, Organic bases, DFT.
22	*Corresponding authors:

23 \**E-mail addresses*: <u>baydiner@gazi.edu.tr</u> (B. Aydıner), <u>senoz@hacettepe.edu.tr</u> (H. Şenöz)

# 2 1. Introduction

Luminescent chemosensors for detection of ions are highly valuable in many research fields 3 due to various neutral and ionic species find widespread use in physiology, medical 4 diagnostics, catalysis, and environmental chemistry [1-3]. A colorimetric chemosensor 5 transforms the action of binding to a specific analyte into a readable signal as a change in 6 7 color and absorption [4]. More importantly, chemosensors have enabled the study of molecular interactions in a range of different media and interfaces. These fast and easily 8 observable responses make the sensors more significant as a research area to improve. When 9 the designs of the colorimetric sensors are examined, it is seen that they consist of two main 10 parts, generally, the receptor part and signaling unit (chromophore) that they are covalently 11 linked by  $\pi$ -bridges like vinyl, imine, azo, or aromatic rings [5-7]. Interaction of the guest-12 host system is investigated under three main mechanisms as binding site, displacement and 13 chemodosimeter [8, 9]. Binding site mechanism is usually caused by hydrogen-bond 14 15 interactions and basic analytes are easily detectable with this approach [10]. Moreover, this interaction can be reversible and sensors can be reusable. 16

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The anions are one of the most studied analytes due to their many important parts in 18 biological systems, the environment and industrial applications [3, 11]. Especially, fluoride 19 20 and cyanide are frequently studied anions due to their presence in biological systems and environmental waste [9, 12]. Cyanide is a highly toxic anion that is waste in many industrial 21 processes. Therefore, the detection of this anion is very important for environmental concern, 22 23 especially in aqueous media [13]. Fluoride anion plays a vital role in physiological processes and associated with nerve gases, the analysis of drinking water, and the refinement of uranium 24 used in nuclear weapons manufacture [14,15]. The usual method for this anions selectivity is 25

deprotonation process between a molecule that had an acidic proton (OH, NH) and anions [16]. Optical chemosensors containing a chromophoric group have been known as powerful tools for signalling fluoride and cyanide ions [17-20]. Other widespread pollutants in nature are organic amines. Because of their extensive use in pharmaceutical industries and dye manufacturing, it is necessary to develop new and effective sensors for these amines [21-28]. Recent studies show that generally developed sensors are sensitive to only one media [29]. Multifunctional chemosensors acting for multi-analyte sensing through different binding sites, can provide excellent advantages of low-cost, real-time detection in real-world chemical and biological samples. In our previous studies, we investigated a similar coumarin-thiophene core that has receptor parts as Schiff base with hydroxyl groups, or amide group for their anions selectivity, and indole bearing allylidenemalononitrile group for detection of cyanide and nonlinear optic (NLO) properties of dyes [30-32]. In this study, we designed new chemosensors bearing 7-diethylaminocoumarin-thiophene and 3-allylidenemalononitrileindole groups which conjugated by the azo bridge (Fig. 1). Dimethine group is an important part of many functional dyes such as polymethine and cyanine dyes [33-36]. Azo dyes are one of the most studied dye classes due to their wide range of color, and easily synthesized and good dyeing performance [37, 38]. Moreover, functionalized azo dyes are used in optical systems like NLO, dye-sensitized solar cells, etc. and sensor systems such as detection of anions and cations [39-41]. Although dimethine and azo groups containing dyes were studied

by many researchers, there are not many compounds bearing both of these functional groups.
Our synthesized dyes showed that they can be a useful tool to determinate different basic
environmental changes such as cyanide in partial aqueous media, pH changes, and few
aliphatic amines.

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2 Fig. 1. Design of the chemosensors.

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# 4 **2. Experimental**

# 5 2.1. Materials and instrumentation

All chemicals used were commercially available and no further purification was carried out. 6 Thin-layer chromatography (TLC) was used to monitor the reaction with pre-coated silica gel 7 60 F254 plates. NMR spectra were measured on Bruker Avance 300 (<sup>1</sup>H NMR: 300 MHz, <sup>13</sup>C 8 NMR: 75 MHz) and Bruker Avance 400 (<sup>1</sup>H NMR: 400 MHz, <sup>13</sup>C NMR: 100 MHz) 9 spectrometers at 20 °C (293 K). Chemical shifts ( $\delta$ ) are given in parts per million (ppm) using 10 the residue solvent peaks as a reference relative to TMS. Coupling constants (J) are given in 11 hertz (Hz). Signals are abbreviated as follows: singlet. s; doublet. d; doublet-doublet. dd; 12 triplet. t; quartet. q; multiplet. m. High-resolution mass spectra (HR-MS) were recorded at the 13 Gazi University Faculty of Pharmacy using electron ionization (EI) mass spectrometry 14 Waters-LCT-Premier-XE-LTOF (TOF-MS) instruments in m/z (rel. %) and Bilkent 15 16 University National Nanotechnology Research Center using Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS. The microwave syntheses were carried out in a Milestone 17 Start microwave reaction system. The melting points were measured using Electrothermal 18 IA9200 apparatus. Absorption spectra were recorded on a Shimadzu 1800 spectrophotometer; 19 fluorescence spectra were recorded on a Hitachi F-7000 fluorescence spectrophotometer. 20

- 1 2.2. Synthesis
- 2 Synthesis of 3-acetyl-7-(diethylamino)-2H-chromen-2-one (1)
- 3 **1** was synthesized according to the literature procedure [42].
- 4 Yield: 89 %; mp: 152-153 °C (lit: 151-152 °C), <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, δ ppm) 8.49
- 5 (s, 1H), 7.67 (d, J=9.5 Hz, 1H), 6.80 (dd,  $J_1 = 2.4$  Hz,  $J_2 = 2.0$  Hz, 1H), 6.58 (d, J = 2.3 Hz,
- 6 1H), 3.50 (q, *J* = 7.0 Hz 4H), 2.50 (s, 3H), 1.14 (t, *J* = 7.0 Hz, 6H).
- 7
- 8 Synthesis of 2-(1-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)ethylidene)malononitrile (2)
- 9 **2** was synthesized according to the literature procedure [42].
- 10 Yield: 75 %; mp: 145-146 °C (lit: 145-146 °C), <sup>1</sup>H NMR (300 MHz, DMSO- $d_{6}$ ,  $\delta$  ppm) 8.33
- 11 (s, 1H), 7.56 (d, J = 9.0 Hz, 1H), 6.83 (dd,  $J_1 = 2.3$  Hz,  $J_2 = 2.3$  Hz, 1H), 6.63 (d, J = 2.1 Hz
- 12 1H), 3.50 (q, J = 6.95 Hz, 4H), 2.55 (s, 3H), 1.15 (t, J = 7.0 Hz, 6H).
- 13 Synthesis of 2-amino-4-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)thiophene-3-carbonitrile
  14 (3):
- 15 **3** was synthesized according to the literature procedure [42].
- 16 Yield: 92 %; mp: 211-212 °C (lit: 211-213 °C), <sup>1</sup>H NMR (300 MHz, DMSO- $d_{6}$ ,  $\delta$  ppm) 7.98
- 17 (s, 1H), 7.48 (d, J = 8.9 Hz, 1H), 7.20 (s, 2H), 6.73 (dd,  $J_1 = 2.4$  Hz,  $J_2 = 2.4$  Hz, 1H), 6.66 (s,
- 18 1H), 6.56 (d, J = 2.2 Hz, 1H), 3.45 (q, J = 7.69 Hz, 4H), 1.10 (t, J = 7.58 Hz, 6H).

- 20 Synthesis of 2-(1-(4-aminophenyl)ethylidene)malononitrile (4)
- **4** was synthesized according to the literature procedure [43].
- 22 Yield: 80 %; mp: 185-186 °C (lit: 185 °C), <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  <sup>1</sup>H NMR (300 23 MHz, DMSO- $d_{6}$ ,  $\delta$  ppm) 7.58 (d, J = 8.8 Hz, 2H), 6.62 (d, J = 8.8 Hz, 2H), 6.43 (s, 2H), 2.51 24 (s, 3H).
- 25
- 26 Synthesis of (E)-2-(1-(4-aminophenyl)-3-(1H-indol-3-yl)allylidene)malononitrile (5a)
- **5a** was synthesized according to the literature procedure [44].
- 28 Yield: 60 %; mp: 248-249 °C (lit: 247-249 °C), <sup>1</sup>H NMR (300 MHz, DMSO- $d_{6}$ ,  $\delta$  ppm) 8.10
- 29 (s, 1H), 7.90 (dd, 1H), 7.60 (dd, 1H), 7.36 (m, 7H), 6.71 (d, *J* = 8.6 Hz, 2H), 6.10 (s, 2H).

 $2 \quad Synthesis \quad of \quad (E)-2-(1-(4-aminophenyl)-3-(1-methyl-1H-indol-3-yl)allylidene) malononitrile \\$ 

- 3 (*5b*)
- **5b** was synthesized according to the literature procedure [44].
- 5 Yield: 50 %; mp: 254-255 °C (lit: 254-256 °C), <sup>1</sup>H NMR (300 MHz, DMSO- $d_{6}$ ,  $\delta$  ppm) 8.10
- 6 (s, 1H), 7.85 (dd, 1H), 7.60 (dd, 1H), 7.36 (m, 6H), 6.71 (d, *J* = 8.6 Hz, 2H), 6.10 (s, 2H).
- 7

# 8 General Synthesis of The Dyes (6a-6b).

3 (1.0 mmol) was dissolved in hydrochloric acid (1.0 mL of conc. HCl in 2.0 mL of water) 9 10 and the solution cooled to (-5)-0 °C. Sodium nitrite solution (c = 0.5 M in water) was slowly added to the mixture. After 1 hour of stirring, urea (a small amount) was added to remove 11 12 excess nitrous acid and used immediately for the coupling reaction. 5a / 5b (1.0 mmol) was dissolved in acetic acid/propionic acid (6 mL, 4:2, v/v) and cooled to (-5)-0 °C and the 13 diazonium salt solution was slowly added to the mixture of 3 while stirring. After 1 hour, 14 conc. sodium carbonate solution was added to the mixture till pH 5-6. The mixture was stirred 15 for an additional 1 hour at (-5)-0 °C. After 1 hour, water was added to the mixture and the 16 precipitate was filtered, washed with cold water, dried and recrystallized with ethanol to 17 obtain pure compounds. 18

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20 Synthesis of 2-((2E)-1-(4-((5-amino-4-cyano-3-(7-(diethylamino)-2-oxo-2H-chromen-321 yl)thiophen-2-yl)diazenyl)phenyl)-3-(1H-indol-3-yl)allylidene)malononitrile (6a):

Yield: 78 %, mp: 249-250 °C, FT-IR (KBr, cm<sup>-1</sup>): 3412, 3292, 3178, 2971, 2212, 1709, 22 1677.87, 1636, 1615, 1586, 1570, 1525, 1494, 1467, 1418, 1350, 1316, 1258. <sup>1</sup>H NMR (400 23 MHz, DMSO- $d_6$ ,  $\delta$  ppm) 12.28 (s, 1H), 8.76 (s, 2H), 8.21 (s, 1H), 8.11 (s, 1H), 7.83 (d, J = 5.524 25 Hz, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.58 (t, J = 10.1 Hz, 3H), 7.52 (d, J = 5.0 Hz, 1H), 7.45 (d, J = 15.3 Hz, 1H), 7.30 (d, J = 2.9 Hz, 2H), 7.24 (d, J = 15.2 Hz, 1H), 6.77 (d, J = 8.6 Hz, 1H), 26 6.62 (s, 1H), 3.46 (d, J = 6.0 Hz, 4H), 1.13 (t, J = 6.1 Hz, 6H). <sup>13</sup>C NMR (100 MHz, DMSO-27 *d*<sub>6</sub> δ ppm) 171.4, 167.7, 158.9, 156.6, 153.3, 151.5, 146.8, 145.0, 143.4, 138.1, 138.0, 137.2, 28 133.5, 130.5, 130.5, 124.4, 123.7, 122.4, 121.8, 119.9, 117.6, 115.1, 114.6, 114.5, 114.1, 29 113.3, 110.7, 109.7, 107.6, 96.3, 88.6, 73.4, 44.3, 12.4. HRMS m/z calculated for 30 31 C<sub>38</sub>H<sub>28</sub>N<sub>8</sub>O<sub>2</sub>SNa: 683.1948, found 683.2005 (M-Na)<sup>+</sup>.

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- 4 Red solid; Yield: 45 %; mp: 329-330 °C; FT-IR (KBr, v<sub>maks</sub>, cm<sup>-1</sup>): 3291, 3178, 2972, 2213,
- 5 1679, 1248. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ ppm) 8.76 (s, 2H), 8.21 (s, 1H), 8.12 (s, 1H),
  6 7.81 (d, *J* = 6.6 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 2H), 7.64 7.52 (m, *J* = 15.4, 8.1 Hz, 4H), 7.42
- 7 (d, J = 15.3 Hz, 1H), 7.35 (s, 2H), 7.18 (d, J = 15.2 Hz, 1H), 6.77 (d, J = 8.6 Hz, 1H), 6.62 (s,
  8 1H), 3.82 (s, 3H), 3.47 (d, J = 6.6 Hz, 4H), 1.14 (t, J = 6.5 Hz, 6H). <sup>13</sup>C NMR (100 MHz,
  9 DMSO-*d*<sub>6</sub>, δ ppm) 171.1, 167.6, 158.8, 156.5, 153.2, 151.4, 146.7, 144.1, 138.4, 138, 133.4,
  10 130.4, 125, 123.6, 122.6, 121.7, 119.8, 117.4, 115.1, 114.5, 113.0, 111.7, 110.6, 109.5, 107.5,
- 11 96.3, 88.5, 73.2, 44.2, 33.4, 12.3. HRMS m/z calculated for  $C_{39}H_{31}N_8O_2S$ : 675.2291, found 12 675.2307 (M-H)<sup>+</sup>.
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# 14 2.4. Photophysical properties of the dyes

The dyes (10 µM for absorption and fluorescence emission), were studied in five solvents
with different polarities (THF, DCM, DMSO, Diox, and ACN).

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18 2.5. Anion Selectivity Study

The UV-vis and fluorometric spectra were recorded in order to study the selectivity of various anions as their tetrabutylammonium (TBA) salts (TBAX where X=F<sup>-</sup>,  $\Gamma$ , Cl<sup>-</sup>, Br<sup>-</sup>, AcO<sup>-</sup>, CN<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> and HSO<sub>4</sub><sup>-</sup>) towards the compound **6a-b**. The dyes **6a** and **6b** were titrated with studied anions by UV-Vis absorption spectra in DMSO/water 9/1 (v/v) and the 8/2 (v/v) binary mixture, respectively.

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26 2.6. <sup>1</sup>H NMR titration study

27 Spectra were recorded first on the dye **6a** (10 mM), followed by the addition of aliquots of a

solution of anions as TBA salts,  $F^-$  and  $CN^-$ , (1 M) in DMSO- $d_6$ .

# 2 2.7. Computational methods

The ground state geometries of the compounds and their complexes were obtained by performing the density functional theory (DFT) calculations in the Gaussian 09 program package [45]. The confirmation of the convergence to minima on the potential energy surface was made from the vibrational analysis for each compound. The absorption spectra were obtained within time-dependent DFT (TD-DFT) calculations using the PCM model [46,47]. The natural charges were estimated from Natural Bond Orbital calculations in DMSO. All calculations were carried out using B3LYP functional with 6-31g(d,p) basis set [48-50].

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# 11 **3. Results and discussion**

# 12 *3.1. Design and synthesis of the sensors*

13 The chemosensors (6a and 6b) which are the coumarin-thiophene-indole conjugated by diazo and methylene bridges were synthesized. In this molecule design, we aimed to investigate the 14 effect of the multiple heterocyclic (coumarin, thiophene, and indole) and chromophore groups 15 (methylene and diazo) in the same system. 7-diethylaminocoumarin derivatives are good 16 fluorescent dyes that have tunable properties from the blue to near-infrared (NIR) region by 17 changing the electron acceptor at usually 3-position of the coumarin [29,30]. The synthesis 18 route of the dyes (6a-b) is depicted in Scheme 1. Coumarin-thiophene intermediate (3) was 19 synthesized by the method that our group previously was improved by three-step reactions 20 with good yield (92 %) [42]. Indole/N-methylindole and phenyl conjugated by 21 allylidenemalononitrile moiety (5a and 5b) were synthesized by Knoevenagel condensation 22 reaction with moderate yield (60 % and 50 %, respectively). The chemosensors were 23 synthesized by the reaction between coumarin intermediated (3) and compound 5a/5b that 24

were prepared as a diazonium salt. The chemosensors were obtained with good to moderate
 yields as 78 % (6a) and 45 % (6b).

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- 5 **Scheme 1**. Synthetic pathway of the dyes.
- 6

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# 7 3.2. Photophysical properties

Absorption and emission spectra of the dyes were investigated in solvents with different 8 9 polarities at room temperature. The absorption coefficients ( $\epsilon$ ) were calculated according to the Beer-Lambert Law and found 56800-68000  $M^{-1}$ .cm<sup>-1</sup> for **6a** and 45800-59800  $M^{-1}$ .cm<sup>-1</sup> for 10 **6b**. As can be seen from Table 1, absorption and emission maxima of the dyes were showed 11 correlation with the increase in solvent polarity except acetonitrile (Figs. 2 and 3). Absorption 12 maxima of **6a** and **6b** were found between 437-467 nm and 452-473 nm, respectively, and 13 14 emission maxima ranging from 477-552 for both dyes. Changing indole NH hydrogen with methyl group shifted absorption maxima to the bathochromic region about 6-15 nm. A 15 similar result obtained previous study that (4-aminophenyl)-16 was at our 17 allylidenemalononitrile-3-indole molecules with NH and N-methyl parts was investigated and

found that adding the methyl group to indole nitrogen changed the absorption maxima to slightly to bathochromic region due to methyl group have more electron donor properties compared to free NH [43]. Stokes shifts were calculated from the difference between wavenumber of absorption and emission maxima and found between 2079 and 3343 cm<sup>-1</sup> for **6a** and 1061 and 3252 cm<sup>-1</sup> for **6b**.

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 $\lambda_{fl}(nm)^{b}$  $\lambda_{abs}(nm)^{a}$ Stokes Shiff (cm<sup>-1</sup>)  $\varepsilon (M^{-1}.cm^{-1})^{\circ}$ Dyes **Solvents** 68004 DiOX 437 479 2006 THF 448 494 2079 60916 2965 68904 DMF 461 534 6a DMSO 467 552 65395 3343 494 ACN 443 2330 56800 DiOX 452 477 1160 59870 THF 458 513 2341 45898 6b DMF 468 552 3252 48991 DMSO 473 498 59125 1061 458 ACN 530 2966 47413

 $\frac{a}{b} = \frac{a}{c} \frac{b}{c} \frac$ 

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11 6a that has an NH group exhibited yellow color under daylight except for DMSO that was 12 brown and was emitted from blue to green under UV-light (Fig. 2-inset). 6b that has the 13 methyl group at the nitrogen of indole exhibited orange color under daylight and also showed 14 very low orange emission under UV light (Fig. 3-inset).

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**Table 1.** Photophysical properties of the **6a-b** ( $c = 10 \,\mu\text{M}$ ) in different solvents.





Fig. 2. The normalized absorption (a) and normalized emission (b) spectra of **6a** ( $c = 10 \mu$ M) in different polarity solvents. Insets: Photographs of **6a** ( $c = 25 \mu$ M) in different polarity solvents under ambient light (a) and UV light (b).



**Fig. 3.** The normalized absorption (a) and normalized emission (b) spectra of **6b** ( $c = 10 \mu$ M) in different polarity solvents. Insets: Photographs of **6b** ( $c = 25 \mu$ M) in different polarity solvents under ambient light (a) and UV light (b).

11 3.3. Spectrophotometric and spectrofluorometric titrations of the dyes with various anions

The sensing ability of the dyes were investigated by using spectrophotometric titration methods and the dyes were titrated F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, AcO<sup>-</sup>, CN<sup>-</sup>, OH<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> with tetrabutylammonium (TBA) salts as the counter cation. Fig. 4 shows that change in absorption spectra of **6a** and **6b** (10  $\mu$ M) measured in DMSO with respective anions as a n-Bu<sub>4</sub>N<sup>+</sup> salt (20 equiv.). The absorption spectra of these two dyes in DMSO showed a strong band centered around 470 nm. After the addition of various anions to the dyes, only F<sup>-</sup>, AcO<sup>-</sup>, CN<sup>-</sup>, OH<sup>-</sup>, and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> were showed a significant change. Upon addition of these anions to **6a**,

the absorption band of the dye decreased and showed two bands at 440 and 475 nm. 1 2 Moreover, the new two bands formed with one of them at 527 nm and the other one as broadband at 610-620 nm (Table 2). 6b showed different shifts at absorption spectra after 3 addition the same anions, band at 472 nm gave only bathochromic shifts to 660-670 nm. 6a 4 has two acidic parts, one of them is indole NH attaching allylidenemalononitrile at 3-position 5 of the indole ring, the second one is amino group attaching thiophene moiety while **6b** has an 6 only amino group as acidic part. These results show that the band formed at a longer 7 wavelength (660-670 nm) is caused by deprotonation of the amino group, while the other new 8 band at 527 nm was formed after the deprotonation of indole NH (Scheme 2). 9

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**Fig. 4.** UV-vis titration spectra titration spectra of **6a** (a) and **6b** (b) ( $c = 10 \ \mu\text{M}$  in DMSO) with different anion 20 equiv. in DMSO. Insets: Photographs of **6a** and **6b** ( $c = 25 \ \mu\text{M}$  in DMSO) after addition of 20 equiv. of various anions ( $c = 1.0 \ \text{M}$  in DMSO) under ambient light.

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To understand the sensing mechanism between the dyes and anions, titration study were 4 conducted with <sup>1</sup>H NMR method (Fig. 5). Upon addition of 2 equiv. of F<sup>-</sup>, CN<sup>-</sup>, AcO<sup>-</sup> to **6a**, 5 NH and NH<sub>2</sub> signals at 12.39 and 8.77 ppm were disappeared and a slight upper field shift of 6 the signals were observed due to the incensement of electron density in the conjugated 7 system. After addition of F<sup>-</sup>, CN<sup>-</sup>, AcO<sup>-</sup>, Ha signal at 8.12 ppm, 3-position of indole, shifted to 8 7.79, 7.68, and 7.88 ppm while Hb signal at 8.22 ppm, 4-position of coumarin, was shifted to 9 8.06, 8.03, and 8.09, respectively. The most significant change was observed after the 10 addition of cyanide. 11





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The colorimetric sensitivity of the dyes (6a-b) was investigated in DMSO with studies anions. 5 6 As depicted in Fig. 5, upon the addition of F<sup>-</sup>, CN<sup>-</sup>, and OH<sup>-</sup>, significant color changes were 7 observed in the solution of 6a in DMSO from orange to purple, and light brown with AcO while distinctive color changes were observed solution of **6a** in ACN from orange to purple 8 9 with F<sup>-</sup>, CN<sup>-</sup>, and OH<sup>-</sup>, and green with AcO<sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> (Fig. 6). Furthermore, **6a** showed fluorescence quenching when interacted with F<sup>-</sup>, CN<sup>-</sup>, and OH<sup>-</sup> in ACN while 6a did not have 10 significant emission under UV-light in DMSO. Meanwhile, 6b was given less selective color 11 changes from orange to green upon the addition of F<sup>-</sup>, AcO<sup>-</sup>, CN<sup>-</sup>, OH<sup>-</sup>, and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> in both 12 DMSO and ACN (Fig. 5 and Fig. S38). 13

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(a)	ļ	Ļ								Ļ			
6a	F	- 1	Cŀ	Br	ŀ	AcO-	CN-	H <sub>2</sub> PO <sub>4</sub>	HSO <sub>4</sub> -	NO <sub>3</sub> -	ClO <sub>4</sub>	OH-	
				2									
(b)													
ų	6a .	F	Cl-	Br	I-	AcO-	CN-	H <sub>2</sub> PO <sub>4</sub> -	HSO4 <sup>-</sup>	NO <sub>3</sub> -	ClO <sub>4</sub> -	OH-	

**Fig. 6.** Photographs of **6a** ( $c = 25 \mu$ M in ACN) after addition of 20 equiv. of studied anions under ambient light (a) and under UV light (b).



**Table 2.** The shift values of absorption maxima upon addition anions in DMSO for **6a-6b**.

Dyes	Anions	$\lambda_{abs} max (nm)$ (after addition of 20 equiv. of anions)
	F	438, 527, 608
	AcO	472, 527, 621
$6a \\ (\lambda_{\rm b} \max = 466 \text{nm})$	CN	440, 480, 527, 608
aus	H <sub>2</sub> PO <sub>4</sub>	467, 659
	OH	441, 475, 527, 610
	F	463, 660
	AcO	460, 670
$6b$ ( $\lambda_{-1}$ -max = 472 nm)	CN	458, 670
abs	H <sub>2</sub> PO <sub>4</sub>	463, 671
	OH	465, 660



# *3.4. Reversibility*

9 The reversibility of chemosensors is a very important feature for the applications in the real
10 environment. The determination of the reversibility of dyes was investigated by absorption
11 spectroscopy and colorimetric changes. Upon addition of 20 equiv. of anions (only F<sup>-</sup>, AcO<sup>-</sup>,
12 CN<sup>-</sup>, OH<sup>-</sup>, and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>) to the solution of **6a** and **6b**, absorption maxima of the dyes were

shifted to bathochromic region. After 20 equiv. of trifluoroacetic acid (TFA) was added to the 1 2 mixture, absorption maxima of dyes were shifted hypsochromicly to original maxima of the dyes (Fig.7 and Fig. S39-S46). Moreover, colorimetric changes of the dyes 6a and 6b were 3 restored from purple and green to orange, respectively. This reversibility of dyes was also 4 indicated that only the deprotonation mechanism occurred although there was a possibility of 5 cyanide that can behave as nucleophile as well as base and could give addition reaction to 6 7 methylene bridges.

8



Fig. 7. UV-vis spectra of 6a (a) and 6b (b) ( $c = 10 \ \mu M$ ) after addition of CN<sup>-</sup> and its 10 reversibility control using TFA acid (c = 1.0 M in DMSO) in DMSO. Insert: Photographs of 11 **6a** and **6b** ( $c=25 \mu$ M in DMSO) upon the addition of 20 equiv. of CN<sup>-</sup> and TFA under ambient 12 light. 13

14

#### 3.5. Anion interaction in the partial aqueous medium for selectivity 15

To demonstrate the potential application of the chemosensors, the titration studies also were 16 done in the partial aqueous medium. Absorption spectra of the dyes 6a-6b in different 17 mixtures of water and DMSO were taken after the addition of 50 equiv. of TBACN (Fig. S47-18 55) and the best ratio of DMSO:water was decided as 9:1 (v/v) and 8:2 (v/v), respectively. 19 20 Titration experiments were carried out by stepwise addition of CN<sup>-</sup>, F<sup>-</sup>, OH<sup>-</sup>, AcO<sup>-</sup>, and  $H_2PO_4^-$  to the dyes and can be seen from Fig. 8. The results showed only CN<sup>-</sup> responded 21 towards **6a** and **6b** in the binary aqueous medium. Similar to titration studies in DMSO, upon 22

addition of cyanide to **6a**, absorption maxima at 463 nm was shifted to the bathochromic 1 2 region at 526 nm and two weak bands at 415 and 640 nm were formed. Even though F, OH, AcO<sup>-</sup>, and  $H_2PO_4^-$  interacted with the dyes in DMSO, they did not show any change in the 3 binary mixture. These results can explain that the hydrogen bonding affinity of anions 4 changed as the same titration experiment is carried out in an aqueous medium. A factor 5 contributing to this selectivity of cyanide is the high hydration enthalpy( $\Delta H_{hvd}$ ) of F<sup>-</sup> (-504 6 kJ/mol), OH<sup>-</sup> (- 403 kJ/mol), AcO<sup>-</sup> (-375 kJ/mol) and  $H_2PO_4^-$  (-260 kJ/mol). Compared the 7 other anions, cyanide has low hydration energy (-67 kJ/mol ) [51-55]. Moreover, reversibility 8 test of dyes in aqueous media were done to established that deprotonation is still main 9 interaction mechanism. Upon addition of 20 equiv. of cyanide to the dyes, bathochromic 10 shifts were observed. Then, 20 equiv. of TFA was added to the mixture, and hypochromic 11 shifts were occurred and absorption maxima shifted to original maxima of the dyes (Fig S56). 12

13



14



After established that **6a** and **6b** are showed selectivity to cyanide in aqueous solution by using distilled water, it was decided to investigate the performance of the dyes in tap water as

the real sample. In this investigation, KCN was used instead of TBACN and absorption titration experiments were carried out. The results showed that similar to distilled water experiments, new absorption bands were appeared at 527 and 618 nm for **6a** and 634 nm for **6b** (Fig. 9). Moreover, distinctive colorimetric changes for **6a** and **6b** were observed from orange to red-brown and green, respectively (Fig. 9-inset).





**Fig. 9.** UV-Vis titration spectra of **6a** (a) and **6b** (b) ( $c = 10 \ \mu\text{M}$  in DM $\Box$ O) with 20 equiv. of KCN in DM $\Box$ O:Tap water mixture 9:1 (v/v) and 8:2 (v/v), respectively. Insert: Photographs of **6a** and **6b** ( $c = 25 \ \mu\text{M}$  in DMSO:Tap water) after the addition of 20 equiv. of CN<sup>-</sup> under ambient light in DMSO:Tap water mixture.

12

7

## 13 3.6. pH-dependent study

In order to understand the effect of the basic environment to the dyes, the chemosensors were 14 also studied in mixtures of DMSO and buffer solution. The pH-dependent spectral 15 characteristics of the dyes (10 µM) were evaluated in a Britton Robinson buffer solution that 16 pH values ranged between 7.0-11.0, with DMSO as a co-solvent (Fig. 10). Absorption spectra 17 of **6a** showed that only at pH 11.0, a new band began to form at 515 nm. But photographs of 18 19 **6a** showed a significant color changed when the pH of media change from 8.0 to 8.5, the absorption color of the dye changed from orange to purple (Fig. 10a-inset). pH-dependent 20 study of **6b** gave more sensitive response at absorption spectra compared to **6a** when pH 21

- media changed to 8.5 from 8.0, a new band at 630 nm and absorbance of the band increased at
  higher pH (Fig. 10b). Colorimetric changes were similar to 6a, absorbance color was changed
- 3 to green from orange when pH increased from 8.0 to 8.5.
- 4





**Fig. 10.** UV-vis spectra of **6a** (a) and **6b** (b) ( $c = 10 \mu$ M) different pH values in DMSO:Buffer 7 7:3 (v/v). Inset: Photographs of **6a** (a) and **6b** (b) ( $c = 25 \mu$ M in DMSO:Buffer 7:3) different 9 pH value.

10 3.7. Sensitivity Study of Organic Amines

Amines are widespread pollutants in nature and detection of them has become of large interest 11 since they used extensively in pharmaceutical industries and dye manufacturing [22]. 12 Therefore, we also studied various amines for their detection. Seven different amines were 13 investigated and only three of them which are secondary aliphatic amines were interacted with 14 6a and 6b (Fig. 11 and S57-62). As depicted in Fig. 11, upon addition of various amines to 15 **6a**, piperidine, pyrrolidine, and diethylamine gave response as a new band at 653-658 nm and 16 shoulder at 519 nm. Furthermore, colorimetric changes were observed with naked eye-17 detection that the orange color of the chemosensor was changed to green under ambient-light. 18 19 Interestingly, these three amines when were added to **6b** gave a new band at 658-675 nm with

low absorbance but there were not any significant changes observed at the absorption color of 1 2 the dye (Fig. 11b). Basicity is the primary factor in determining interaction with the chemosensors but also other factors are interfering with the interaction as steric and 3 conformational effects, resonance, and induction. Piperidine (11.12), pyrrolidine (11.31) and 4 diethylamine (10.84) have high  $pK_a$  values that they are more basic properties than 5 diphenylamine (0.79) and triphenylamine (not considered as a base). Interestingly,  $pK_a$  of 6 trimethylamine is 10.75 that is close value to interacted three amines. But no changes 7 observed when trimethylamine was added to the dyes due to steric hindrance. Also, pyridine 8 that is an aromatic amine with low  $pK_a(5.23)$  did not give any spectral change. 9

10



**Fig. 11.** UV-vis titration of **6a** (a) and **6b** (b) ( $c = 10 \mu$ M in DMSO) with 200 equiv. of different organic bases in DMSO. Inset: Photographs of the dyes **6a** (a) and **6b** (b) ( $c = 2.5 \mu$ M in DMSO) after addition of 200 equiv. of studies amine bases (c = 1.0 M in DMSO) under ambient light.

16

11

# 17 *3.8. LOD of the dyes towards sensing of cyanide and aromatic amines*

18 The limit of detection (LOD) of  $CN^{-}$  in DMSO and aqueous media were calculated on the

- 19 basis of the equations; LOD= $3\delta/S$ , where  $\delta$  is the standard deviation of the response and S is
- 20 the slope of the absorption calibration curve of  $CN^{-}$  and the results are represented in Figs.

S63-68 of the Supporting Information. 6a showed the detection of cyanide with LODs of 7.9 1 2 µM in DMSO, 19 µM in DMSO/water (9:1, v/v) mixture, and 0.40 mM in DMSO/tap water (9:1, v/v) mixture. Meanwhile, **6b** showed the detection of cyanide with LODs of 2.2  $\mu$ M in 3 DMSO, 5.6 µM in DMSO/water (9:1, v/v) mixture, and 26 µM in DMSO/tap water (9:1, v/v) 4 mixture. Consequently, **6b** is more sensitive for cyanide in tap water media comparing to **6a**. 5 Moreover, the same calculations were done for the dyes with titration of piperidine, 6 pyrrolidine, and diethylamine in DMSO and calculated as 0.09 mM, 0.57 mM, and 0.2 mM 7 for **6a**, and 0.50 mM, 1.2 mM, and 1.8 mM for **6b**, respectively (Fig. S69-74.) 8

9

# 10 *3.9. Theoretical Results*

The structures of **6a**, **6b** and their anionic structures formed by interactions with F<sup>-</sup>, CN<sup>-</sup>, OH<sup>-</sup>, 11 AcO<sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> anions within the framework of density functional theory (DFT) 12 calculations at B3LYP/631g(d,p) level in the gas phase. The optimized structures and 13 geometry parameters are illustrated in Fig. 12, Fig. S75 and Table S3, with the atomic 14 numbering in Fig. S76. The optimized structures clearly showed that the indole -NH and 15 NH...H (in the -NH<sub>2</sub> group attaching thiophene moiety) bond distances increase after the 16 interaction **6a** with  $F^-$ ,  $CN^-$ ,  $OH^-$  and  $AcO^-$  via di-deprotonation process, for  $H_2PO_4^-$ 17 18 interactions, the anion deprotonated the indole -NH exactly and interacted with -NH<sub>2</sub> group 19 (Fig. 12, Table S3).



Fig. 12. The optimized structures of 6a and their complexes 6a+F,  $6a+CN^-$ ,  $6a+OH^-$ ,  $6a+AcO^-$ ,  $6a+H_2PO^{4-}$  and change in the negative charges on selected atoms.

1

The change in the natural charges on some atoms for 6a+F<sup>-</sup>, 6a+CN<sup>-</sup>, 6a+OH<sup>-</sup>, 6a+AcO<sup>-</sup> and 5  $6a+H_2PO_4$  with respect to 6a in DMSO after the interactions with related anions were also 6 shown in Fig. 12 and Table S4. The natural charges on given atoms increase after interactions 7 and as expected, these changing will reflect absorption spectra. To see the effects of these 8 9 expectations, the absorption spectra were calculated within TD-DFT calculations in DMSO. The absorption maxima, oscillator strengths and corresponding transitions with their 10 contributions were listed in Table S5. The absorption maxima of **6a** was observed at 497 nm 11 with f = 0.516 and the major contributions of H-1 $\rightarrow$ L and H-2 $\rightarrow$ L transitions. For **6a+F**, 12 6a+CN<sup>-</sup>, 6a+OH<sup>-</sup> and 6a+AcO<sup>-</sup>, the absorption maxima shifted to 435-438 nm and there was 13 a new peak at 578-584 nm. For  $6a+H_2PO_4$ , the shifted in absorption maxima at 492 nm was 14 negligible and only the occurring new peak at 565 nm was seen, which can be attributed to the 15 fact that the dihydrogen phosphate ion deprotonated indole -NH proton and interacted with -16

NH<sub>2</sub> proton weakly. The calculated results were in good agreement with experimental ones
 (Table 2).

In case of **6b**, the deprotonation process was possible between  $-NH_2$  proton and anions (**Fig. S75**) the increased negative charges on amine nitrogen (N43) after the deprotonation of  $-NH_2$ proton are distributed to both of the nitrogen of cyano (C46  $\equiv$  N47) and azo bridge through thiophene and dicyano group through phenyl (Fig. S76 and Table S6). The absorption maxima seen at 472 nm for **6b**, shifted to a lower wavelength at about 464-468 nm and a new peak at the higher wavelength at about 595-653 nm for **6b+F'**, **6b+CN'**, **6b+OH'**, **6b+AcO'** and **6a+H\_2PO\_4'** (Table S5), which were consistent with experimental results.

10

# 11 4. Conclusions

Multifunctional colorimetric chemosensors were designed and synthesized within mild 12 conditions and moderate to good yields. The dyes are sensitive to F, AcO, CN, OH, and 13 H<sub>2</sub>PO<sub>4</sub><sup>-</sup> in DMSO compared to other studies anions while both of the dyes are selective to 14 only CN<sup>-</sup> in partial aqueous solution. Furthemore, the change of pH from 8.0 to 8.5 can be 15 easily determined by the dyes with colorimetrically. Moreover, 6a can be sense 16 colorimetrically some of the organic amines that are piperidine, pyrrolidine, and diethylamine. 17 The proposed sensing mechanisms as deprotonation of amino groups were supported by the 18 theoretical calculations, which were compatible with experimental results. The results showed 19 that the dyes can be used as novel colorimetric chemosensors as multimedia basic sensors. 20

21

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- 3

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Fig. 11. UV-vis titration of 6a (a) and 6b (b) ( $c = 10 \mu M$  in DMSO) with 200 equiv. of 1 different organic bases in DMSO. Inset: Photographs of the dyes 6a (a) and 6b (b) (c = 2.52  $\mu$ M in DMSO) after addition of 200 equiv. of studies amine bases (c = 1.0 M in DMSO) under 3 ambient light. 4 Fig. 12. The optimized structures of 6a and their complexes  $6a+F^{-}$ ,  $6a+CN^{-}$ ,  $6a+OH^{-}$ , 5  $6a + AcO^{-}$ ,  $6a + H_2PO^{4-}$  and change in the negative charges on selected atoms. 6 7 **Scheme Captions** 8 9 Scheme 1. Synthetic pathway of the dyes. Scheme 2. The possible anion sensing mechanism of 6a. 10 11 **Table Captions** 12 **Table 1.** Photophysical properties of the **6a-b** ( $c = 10 \mu M$ ) in different solvents. 13 Table 2. The shift values of absorption maxima upon addition anions in DMSO for 6a-6b. 14 15

$\mathbf{P} = \mathbf{C} \mathbf{L} \mathbf{L} \mathbf{L} \mathbf{L} \mathbf{L} \mathbf{L} \mathbf{L} L$							
Dyes	Solvents	$\lambda_{abs}(\mathbf{nm})$	۲ <sub>fl</sub> (nm)	Stokes Shiff (cm)	$\varepsilon$ (M .cm )		
	DiOX	437	479	2006	68004		
	THF	448	494	2079	60916		
6a	DMF	461	534	2965	68904		
	DMSO	467	552	3343	65395		
	ACN	443	494	2330	56800		
	DiOX	452	477	1160	59870		
	THF	458	513	2341	45898		
6b	DMF	468	552	3252	48991		
	DMSO	473	498	1061	59125		
	ACN	458	530	2966	47413		

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<sup>a</sup>Long wavelength absorption maximum, in nm; c = 10  $\mu$ M. <sup>b</sup> Fluorescence maximum, in nm; c = 10  $\mu$ M. <sup>c</sup>  $\epsilon$  = molar absorption coefficient (cm<sup>-1</sup>M<sup>-1</sup>). m,

Table 2. 7	The shift values of absorption maxima upon addition anions in DMSO for <b>6a-6b</b> .

Dyes	Anions	<b>20 Equiv.</b> $\lambda_{abs}$ max (nm)
	F	438, 527, 608
	AcO	472, 527, 621
$6a \\ (\lambda_{abc} max = 466nm)$	CN	440, 480, 527, 608
aus	H <sub>2</sub> PO <sub>4</sub>	467, 659
	OH	441, 475, 527, 610
	F	463, 660
	AcO	460, 670
$6b \\ (\lambda_{ab} max = 472 \text{ nm})$	CN	458, 670
aus	H <sub>2</sub> PO <sub>4</sub>	463, 671
	OH	465, 660



Fig. 1. Design of the chemosensors.



Fig. 2. The normalized absorption (a) and normalized emission (b) spectra of **6a** ( $c = 10 \mu$ M) in different polarity solvents. Insets: Photographs of **6a** ( $c = 25 \mu$ M) in different polarity solvents under ambient light (a) and UV light (b).



**Fig. 3.** The normalized absorption (a) and normalized emission (b) spectra of **6b** ( $c = 10 \ \mu$ M) in different polarity solvents. Insets: Photographs of **6b** ( $c = 25 \ \mu$ M) in different polarity solvents under ambient light (a) and UV light (b).


**Fig. 4.** UV-vis titration spectra titration spectra of **6a** (a) and **6b** (b) ( $c = 10 \ \mu\text{M}$  in DMSO) with different anion 20 equiv. in DMSO. Insets: Photographs of **6a** and **6b** ( $c = 25 \ \mu\text{M}$  in DMSO) upon addition of 20 equiv of various anions ( $c = 1.0 \ \text{M}$  in DMSO) under ambient light.



**Fig. 5.** <sup>1</sup>H-NMR spectral change of **6a** (10 mM) in the absence (a) and presence of 2 equiv of TBACN (b), TBAF (c) and TBAAcO (d) in DMSO- $d_6$ .

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**Fig. 6.** Photographs of **6a** ( $c = 25 \mu$ M in ACN) upon addition of 20 equiv. studied anions under ambient light (a) and under UV light (b).



**Fig. 7.** UV-vis spectra of **6a** (a) and **6b** (b) ( $c = 10 \ \mu$ M) upon addition of CN and its reversibility control using trifluoroacetic acid ( $c = 1.0 \ M$  in DMSO) in DMSO. Insert: Photographs of **6a** and **6b** ( $c = 25 \ \mu$ M in DMSO) upon the addition of 20 equiv. CN and TFA under ambient light.



**Fig. 8.** UV-vis titration spectra of **6a** (a) and **6b** (b) ( $c = 10 \mu$ M) with different 20 equiv. of TBA salts in DMSO:water 9:1 (v/v) and 8:2 (v/v), respectively. Insert: Photographs of **6a** and





**Fig. 9.** UV-Vis titration spectra of **6a** (a) and **6b** (b) ( $c = 10 \ \mu\text{M}$  in DMSO) with 20 equiv. of KCN in DMSO: Tap water mixture 9:1 (v/v) and 8:2 (v/v), respectively. Insert: Photographs of **6a** and **6b** ( $c = 25 \ \mu\text{M}$  in DMSO: Tap water) after the addition of 20 equiv. of CN<sup>-</sup> under ambient light in DMSO: Tap water mixture.



**Fig. 10.** UV-vis spectra of **6a** (a) and **6b** (b) ( $c = 10 \mu$ M) different pH values in DMSO:Buffer 7:3 (v/v). Inset: Photographs of **6a** (a) and **6b** (b) ( $c = 25 \mu$ M in DMSO:Buffer 7:3) different pH value.



**Fig. 11.** UV-vis titration of **6a** (a) and **6b** (b) ( $c = 10 \ \mu\text{M}$  in DMSO) with 200 equiv. of different organic bases in DMSO. Inset: Photographs of the dyes **6a** (a) and **6b** (b) ( $c = 2.5 \ \mu\text{M}$  in DMSO) after addition of 200 equiv. of studies amine bases ( $c = 1.0 \ \text{M}$  in DMSO) under ambient light.



Fig. 12. The optimized structures of 6a and their complexes  $6a+F^{-}$ ,  $6a+CN^{-}$ ,  $6a+OH^{-}$ ,  $6a+AcO^{-}$ ,  $6a+H_2PO^{4-}$  and change in the negative charges on selected atoms.





Scheme 2. The possible anion sensing mechanism of 6a.

### **Research Highlights**

- Two novel colorimetric chemosensors based coumarin-indole that conjugated by the azo and dimethine bridge were synthesized for basic media detection.
- The reaction between the dyes and cyanide caused an apparent color change and can be seen with the naked eye.
- The dyes can be used as a chemosensor for selective cyanide detection in partial aqueous media.
- The dyes are affected by the change in pH of media and can detect that colorimetrically.

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# - Supporting Information -

## The novel sensitive and selective chemosensors for determination multiple

#### analytes

Deniz ÇAKMAZ<sup>a</sup>, Arda ÖZARSLAN<sup>a,b</sup>, Burcu AYDINER<sup>a,\*</sup>, Ahmet Burak EROĞLU<sup>c</sup>,

Nurgül SEFEROĞLU<sup>c</sup>, Hülya ŞENÖZ<sup>b\*</sup>, Zeynel SEFEROĞLU<sup>a</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, Gazi University, Ankara 06560, Turkey

<sup>b</sup> Department of Chemistry, Faculty of Science, Hacettepe University, Ankara 06800, Turkey

<sup>c</sup> Department of Advanced Technology, Gazi University, Ankara 06560, Turkey

\*Corresponding authors:

\*E-mail addresses: <u>baydiner@gazi.edu.tr</u> (B. Aydıner), <u>senoz@hacettepe.edu.tr</u> (H. Şenöz)

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Fig. S2. <sup>1</sup>H NMR spectrum of **2** in DMSO- $d_6$ .



Fig. S4. <sup>1</sup>H NMR spectrum of **4** in DMSO- $d_6$ .



Fig. S6. <sup>1</sup>H NMR spectrum of **5b** in DMSO- $d_6$ .



Fig. S8. <sup>1</sup>H NMR spectrum of **6a** in DMSO- $d_6$ .



Fig. S9. <sup>13</sup>C NMR spectrum of **6a** in DMSO- $d_6$ .



Fig. S10. HR-MS spectrum of 6a.



Fig. S12. <sup>1</sup>H NMR spectrum of **6b** in DMSO- $d_6$ .



Fig. S14. HR-MS spectrum of 6b.







Fig. S16. UV-Vis titration spectra of 6a ( $c = 10 \mu M$  in DMSO) with TBAAcO in DMSO.







Fig. S18. UV-Vis titration spectra of **6a** ( $c = 10 \mu$ M in DMSO) with TBAH<sub>2</sub>PO<sub>4</sub> in DMSO.



Fig. S19. UV-Vis titration spectra of **6a** ( $c = 10 \mu$ M in DMSO) with TBAOH in DMSO.



Fig. S20. UV-Vis titration spectra of **6b** ( $c = 10 \mu$ M in DMSO) with TBAF in DMSO.



Fig. S21. UV-Vis titration spectra of **6b** ( $c = 10 \mu$ M in DMSO) with TBAAcO in DMSO.



Fig. S22. UV-Vis titration spectra of **6b** ( $c = 10 \mu$ M in DMSO) with TBACN in DMSO.



Fig. S23. UV-Vis titration spectra of **6b** ( $c = 10 \mu$ M in DMSO) with TBAH<sub>2</sub>PO<sub>4</sub> in DMSO.



Fig. S24. UV-Vis titration spectra of **6b** ( $c = 10 \mu$ M in DMSO) with TBAOH in DMSO.



Fig. S25. UV-vis titration spectra (left) and fluorescence titration spectra (right) of **6a** (c = 10  $\mu$ M in ACN (%1 DMSO)) with TBAF in ACN (%1 DMSO).



Fig. S26. UV-vis titration spectra (left) and fluorescence titration spectra (right) of **6a** ( $c = 10 \mu$ M in ACN (%1 DMSO)) with TBAAcO in ACN (%1 DMSO).



Fig. S27. UV-vis titration spectra (left) and fluorescence titration spectra (right) of **6a** ( $c = 10 \mu$ M in ACN (%1 DMSO)) with TBACN in ACN (%1 DMSO).



Fig. S28. UV-vis titration spectra (left) and fluorescence titration spectra (right) of **6a** (c = 10  $\mu$ M in ACN (%1 DMSO)) with TBAH<sub>2</sub>PO<sub>4</sub> in ACN (%1 DMSO).



Fig. S29. UV-vis titration spectra (left) and fluorescence titration spectra (right) of **6a** ( $c = 10 \mu$ M in ACN (%1 DMSO)) with TBAOH in ACN (%1 DMSO).



Fig. S30. UV-vis titration spectra (left) and fluorescence titration spectra (right) of **6a** ( $c = 10 \mu$ M in ACN (%1 DMSO)) with different 20 equiv. TBA salts in ACN (%1 DMSO).

ACN ( $\lambda_{abs}$ max = 443)	1 eq. $\lambda_{abs}$ max (nm)	20 eq. $\lambda_{abs}$ max (nm)			
F	440, 631	420, 520, 590 431, 518, 637			
AcO	440, 634				
CN	443	424, 520, 593 433, 521, 634			
H <sub>2</sub> PO <sub>4</sub>	440, 635				
OH	431, 520, 632	420, 520, 581			

Table S1. The shift values of absorption maxima upon addition anions in ACN for compound **6a**.



Fig. S31. Photographs of **6a** ( $c = 25 \mu$ M in ACN (%1 DMSO)) ) upon addition of 4 equiv. studied anions under ambient light (top) and under UV light (bottom) in ACN (%1 DMSO).



Fig. S32. UV-vis titration spectra (left) and fluorescence titration spectra (right) of **6b** ( $c = 10 \mu$ M in ACN (%1 DMSO)) with TBAF in ACN (%1 DMSO).



Fig. S33. UV-vis titration spectra (left) and fluorescence titration spectra (right) of **6b** ( $c = 10 \mu$ M in ACN (%1 DMSO)) with TBAAcO in ACN (%1 DMSO).



Fig. S34. UV-vis titration spectra (left) and fluorescence titration spectra (right) of **6b** (c = 10  $\mu$ M in ACN (%1 DMSO)) with TBACN in ACN (%1 DMSO).



Fig. S35. UV-vis titration spectra (left) and fluorescence titration spectra (right) of **6b** ( $c = 10 \mu$ M in ACN (%1 DMSO)) with TBAH<sub>2</sub>PO<sub>4</sub> in ACN (%1 DMSO).



Fig. S36. UV-vis titration spectra (left) and fluorescence titration spectra (right) of **6b** ( $c = 10 \mu$ M in ACN (%1 DMSO)) with TBAOH in ACN (%1 DMSO).



Fig. S37. UV-vis titration spectra (left) and fluorescence titration spectra (right) of **6b** ( $c = 10 \mu$ M in ACN (%1 DMSO)) with different 20 equiv. TBA salts in ACN (%1 DMSO).

Table S2. The shift values of absorption maxima upon addition anions in ACN for compound **6b**.

ACN ( $\lambda_{abs}$ max = 458)	1 eq. λ <sub>abs</sub> max (nm)	20 eq. λ <sub>abs</sub> max (nm)
F	415, 455	439, 640
AcO	415, 455	441, 641
CN	415, 456	439, 639
H <sub>2</sub> PO <sub>4</sub>	415, 457	445, 643
OH	415, 456	439, 439



Fig. S38. Photographs of **6b** ( $c = 25 \mu$ M in ACN) upon addition of 20 equiv. studied anions under ambient light (top) and under UV light (bottom).



Fig. S39. UV-vis spectra of **6a** ( $c = 10 \ \mu$ M) upon addition of F<sup>-</sup> and its reversibility control using trifluoroacetic acid ( $c = 1.0 \ M$  in DMSO) in DMSO. Insert: photographs of **6a** ( $c = 25 \ \mu$ M in DMSO) upon addition of 20 equiv. F<sup>-</sup> and its reversibility control using 20 equiv. trifluoroacetic acid under ambient light.



Fig. S40. UV-vis spectra of **6a** ( $c = 10 \,\mu\text{M}$ ) upon addition of AcO<sup>-</sup> and its reversibility control using trifluoroacetic acid ( $c = 1.0 \,\text{M}$  in DMSO) in DMSO. Insert: photographs of **6a** ( $c = 25 \,\mu\text{M}$  in DMSO) upon addition of 20 equiv. AcO<sup>-</sup> and its reversibility control using 20 equiv. trifluoroacetic acid under ambient light.



Fig. S41. UV-vis spectra of **6a** ( $c = 10 \ \mu$ M) upon addition of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and its reversibility control using trifluoroacetic acid ( $c = 1.0 \ M$  in DMSO) in DMSO. Insert: photographs of **6a** ( $c = 25 \ \mu$ M in DMSO) upon addition of 20 equiv. H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and its reversibility control using 20 equiv. trifluoroacetic acid under ambient light.



Fig. S42. UV-vis spectra of **6a** ( $c = 10 \ \mu\text{M}$ ) upon addition of CN<sup>-</sup> and its reversibility control using trifluoroacetic acid ( $c = 1.0 \ \text{M}$  in DMSO) in DMSO. Insert: photographs of **6a** ( $c = 25 \ \mu\text{M}$  in DMSO) upon addition of 20 equiv. CN<sup>-</sup> and its reversibility control using 20 equiv. trifluoroacetic acid under ambient light.



Fig. S43. UV-vis spectra of **6b** ( $c = 10 \ \mu$ M) upon addition of F<sup>-</sup> and its reversibility control using trifluoroacetic acid ( $c = 1.0 \ M$  in DMSO) in DMSO. Insert: photographs of **6b** ( $c = 25 \ \mu$ M in DMSO) upon addition of 20 equiv. F<sup>-</sup> and its reversibility control using 20 equiv. trifluoroacetic acid under ambient light.



Fig. S44. UV-vis spectra of **6b** ( $c = 10 \,\mu\text{M}$ ) upon addition of AcO<sup>-</sup> and its reversibility control using trifluoroacetic acid ( $c = 1.0 \,\text{M}$  in DMSO) in DMSO. Insert: photographs of **6b** ( $c = 25 \,\mu\text{M}$  in DMSO) upon addition of 20 equiv. AcO<sup>-</sup> and its reversibility control using 20 equiv. trifluoroacetic acid under ambient light.



Fig. S45. UV-vis spectra of **6b** ( $c = 10 \ \mu$ M) upon addition of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and its reversibility control using trifluoroacetic acid ( $c = 1.0 \ M$  in DMSO) in DMSO. Insert: photographs of **6b** ( $c = 25 \ \mu$ M in DMSO) upon addition of 20 equiv. H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and its reversibility control using 20 equiv. trifluoroacetic acid under ambient light.



Fig. S46. UV-vis spectra of **6b** ( $c = 10 \ \mu$ M) upon addition of OH<sup>-</sup> and its reversibility control using trifluoroacetic acid ( $c = 1.0 \ M$  in DMSO) in DMSO. Insert: photographs of **6b** ( $c = 25 \ \mu$ M in DMSO) upon addition of 20 equiv. OH<sup>-</sup> and its reversibility control using 20 equiv. trifluoroacetic acid under ambient light.



Fig. S47. UV-vis spectra of **6a** ( $c = 10 \,\mu\text{M}$ ) in different rate DMSO:H<sub>2</sub>O mixture.

6a	%10	%20	%30	%40	%50	%60	%70	%80	%90

Fig. S48. Photographs of **6a** ( $c = 10 \ \mu M$ ) in different rate DMSO:H<sub>2</sub>O mixture under ambient light.



Fig. S49. UV-vis titration spectras of **6a** ( $c = 10 \ \mu$ M) with TBACN in different rate DMSO:H<sub>2</sub>O mixture.



Fig. S50. UV-Vis titration spectra of **6a** ( $c = 10 \ \mu\text{M}$  in DMSO) with TBACN in 9:1 DMSO: H<sub>2</sub>O mixture.

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Fig. S51. UV-Vis titration spectra of **6a** ( $c = 10 \mu$ M in DMSO) with TBAOH in 9:1 DMSO: H<sub>2</sub>O mixture.

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Fig. S52. UV-vis spectra of **6b** ( $c = 10 \,\mu\text{M}$ ) in different rate DMSO:H<sub>2</sub>O mixture.



Fig. S53. Photographs of **6b** ( $c = 10 \ \mu M$ ) in different rate DMSO:H<sub>2</sub>O mixture under ambient light.



Fig. S54. UV-vis titration spectras of **6b** ( $c = 10 \ \mu$ M) with TBACN in different rate DMSO:H<sub>2</sub>O mixture.



Fig. S55. UV-Vis titration spectra of **6b** ( $c = 10 \ \mu\text{M}$  in DMSO) with TBACN in 9:1 DMSO: H<sub>2</sub>O mixture.



Fig. S56. UV-vis spectra of 6a (a) and 6b (b) ( $c = 10 \ \mu$ M) upon addition of CN- and its reversibility control using TFA ( $c = 1.0 \ M$  in DMSO) in DMSO:water 9:1 (v/v) and 8:2 (v/v), respectively. Insert: Photographs of 6a and 6b ( $c = 25 \ \mu$ M in DMSO) upon the addition of 20 equiv. of CN- and TFA under ambient light.



Fig. S57. UV-vis titration of **6a** ( $c = 10 \mu$ M in DMSO) with piperidine in DMSO.


Fig. S58. UV-vis titration of **6a** ( $c = 10 \mu M$  in DMSO) with pyrrolidine in DMSO.



Fig. S59. UV-vis titration of **6a** ( $c = 10 \mu$ M in DMSO) with diethylamine in DMSO.



Fig. S60. UV-vis titration of **6b** ( $c = 10 \mu$ M in DMSO) with piperidine in DMSO.



Fig. S61. UV-vis titration of **6b** ( $c = 10 \mu$ M in DMSO) with piperidine in DMSO.



Fig. S62. UV-vis titration of **6b** (c = 10  $\mu$ M in DMSO) with pyrrolidine in DMSO.



Fig. S63. The absorbance calibration curve of  $CN^{-}$  for **6a** in DMSO.



Fig. S64. The absorbance calibration curve of CN<sup>-</sup> for **6a** in DMSO/water (9:1, v/v) mixture.



Fig. S65. The absorbance calibration curve of  $CN^{-}$  for **6a** in DMSO/tap water (9:1, v/v) mixture.







Fig. S66. The absorbance calibration curve of CN<sup>-</sup> for **6b** in DMSO/water (8:2, v/v) mixture.



Fig. S68. The absorbance calibration curve of  $CN^{-}$  for **6b** in DMSO/tap water (8:2, v/v) mixture.



Fig. S69. The absorbance calibration curve of piperidine for **6a** in DMSO.



Fig. S70. The absorbance calibration curve of pyrrolidine for **6a** in DMSO.



Fig. S71. The absorbance calibration curve of diethylamino for **6a** in DMSO.



Fig. S67. The absorbance calibration curve of piperidine for **6b** in DMSO.



Fig. S68. The absorbance calibration curve of pyrrolidine for **6b** in DMSO.



Fig. S69. The absorbance calibration curve of diethylamino for **6b** in DMSO.

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Fig. S70. The optimized structures of **6b** and their complexes **6b+F**<sup>-</sup>, **6b+CN**<sup>-</sup>, **6b+OH**<sup>-</sup>, **6b+AcO**<sup>-</sup>, **6b+H2PO4**<sup>-</sup> and change in the negative charges on selected atoms.

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Fig. S71. Atomic numbering for optimized geometry of **6a**.

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Bond lengths (Å)	6a	6a+F	6a+CN <sup>-</sup>	6a+OH <sup>-</sup>	6a+AcO <sup>-</sup>	6a+H <sub>2</sub> PO <sub>4</sub>	6b	6b+F <sup>-</sup>	6b+CN <sup>-</sup>	6b+OH <sup>-</sup>	6b+AcO <sup>-</sup>	6b+H <sub>2</sub> PO <sub>4</sub>
N37-H32	1.008	1.583	1.831	1.864	1.513	1.072	-	-	-	-	-	-
N42-H44	1.007	1.586	1.849	1.887	1.554	1.053	1.007	1.611	1.910	1.911	1.627	1.069
F-H32	-	0.981	-	-	-	-	-	-	-	-	-	-
F-H44	-	0.976	-	-	-	-	- 6	0.969	-	-	-	-
C-H32	-	-	1.119	-	-	-	-	-	-	-	-	-
C-H44	-	-	1.114	-	-	-	-	-	1.104	-	-	-
C-H32	-	-	-	-	-	-	20	-	-	-	-	-
C-H44	-	-	-	-	-	-	-	-	-	-	-	-
O-H32	-	-	-	0.9891	1.071	1.549	-	-	-	-	-	-
O-H44	-	-	-	0.985	1.049	1.664	-	-	-	0.982	1.028	1.587
C16-N18	1.166	1.169	1.169	1.169	1.168	1.167	1.165	1.167	1.167	1.167	1.167	1.166
C15-C16	1.429	1.422	1.422	1.422	1.422	1.425	1.428	1.426	1.426	1.426	1.427	1.427
C15-C17	1.430	1.424	1.423	1.423	1.423	1.426	1.429	1.428	1.428	1.427	1.428	1.429
C17-N19	1.166	1.169	1.169	1.169	1.168	1.167	1.165	1.167	1.167	1.168	1.167	1.167
C4-C2	1.441	1.417	1.417	1.415	1.418	1.426	1.439	1.454	1.454	1.455	1.454	1.449
C2-C1	1.365	1.389	1.388	1.390	1.387	1.377	1.364	1.356	1.358	1.358	1.358	1.360
C1-C23	1.435	1.405	1.405	1.403	1.406	1.417	1.433	1.441	1.441	1.442	1.441	1.438
C4-C5	1.486	1.485	1.484	1.485	1.484	1.484	1.485	1.461	1.462	1.460	1.462	1.472
C12-N21	1.408	1.399	1.398	1.398	1.398	1.403	1.405	1.377	1.377	1.375	1.377	1.389
N21-N22	1.277	1.297	1.297	1.298	1.296	1.288	1.279	1.314	1.314	1.317	1.314	1.299
N22-C38	1.348	1.333	1.330	1.330	1.331	1.337	1.346	1.319	1.317	1.317	1.318	1.329
C39-N43	1.352	1.297	1.295	1.291	1.296	1.314	1.350	1.291	1.289	1.287	1.289	1.308
C40-C46	1.419	1.414	1.413	1.413	1.414	1.417	1.420	1.416	1.416	1.416	1.417	1.418
C46-N47	1.166	1.169	1.169	1.169	1.168	1.166	1.166	1.168	1.168	1.168	1.167	1.166
C42-C48	1.468	1.475	1.475	1.475	1.475	1.473	1.467	1.473	1.474	1.474	1.474	1.472
<i>Bond angles</i> (°)												
C15-C4-C2	119.81	119.85	119.78	119.91	119.84	119.60	119.56	117.24	117.31	117.17	117.33	118.21
C2-C1-C23	127.49	127.95	127.94	128.11	128.03	127.36	127.36	127.34	127.37	127.36	127.26	127.45

Table S3. The selected geometrical parameters of **6a**, **6b** and their complexes formed via interactions with  $F^-$ ,  $CN^-$ ,  $OH^-$ ,  $AcO^-$  and  $H_2PO_4^-$  anions.

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C15-C4-C5	119.49	118.62	118.66	118.59	118.67	118.85	119.70	122.07	121.99	122.14	122.01	121.22
C12-N21-N22	114.68	113.42	113.44	113.48	113.56	113.53	114.58	113.79	113.81	113.81	113.92	114.17
N21-N22-C38	116.23	117.03	117.09	117.01	116.90	116.87	115.62	115.73	115.86	115.73	115.67	115.64
Dihedral angles (°)												
C15-C4-C2-C1	-169.55	-169.41	-169.25	-169.32	-169.26	-169.20	-168.87	-159.25	-159.42	-158.79	-159.56	-163.47
C4-C2-C1-C23	178.99	179.661	179.58	-179.89	179.83	179.10	178.89	178.22	178.02	178.06	177.98	178.44
C2-C1-C23-C25	-179.13	-178.68	-178.39	-178.62	-178.62	-178.31	-179.15	173.19	173.57	173.37	172.57	175.33
C15-C4-C5-C6	-123.28	-129.46	-129.58	-129.62	-129.57	-128.35	-126.24	-140.25	-139.79	-140.63	-139.68	-134.89
C12-N21-N22-C38	178.76	-179.50	-179.30	-179.47	-179.34	-178.94	178.74	178.66	178.84	178.92	178.69	177.89
N21-N22-C38-C42	177.99	176.52	176.68	176.51	176.45	175.93	178.07	177.93	178.3	178.10	178.74	178.65

170.43 175.93 178.07 177.93

	6a	6a+F <sup>-</sup>	6a+CN <sup>-</sup>	6a+OH <sup>-</sup>	6a+AcO <sup>-</sup>	6a+H2PO4 <sup>-</sup>
Atom				Q		
C2	-0.285	-0.315	-0.316	-0.318	-0.314	-0.299
C5	-0.085	-0.096	-0.097	-0.097	-0.096	-0.088
C8	-0.224	-0.244	-0.246	-0.247	-0.244	-0.232
C10	-0.237	-0.259	-0.261	-0.262	-0.258	-0.246
C15	-0.313	-0.366	-0.368	-0.372	-0.364	-0.336
N18	-0.372	-0.419	-0.421	-0.425	-0.417	-0.392
N19	-0.371	-0.416	-0.418	-0.421	-0.414	-0.390
N21	-0.272	-0.332	-0.338	-0.340	-0.331	-0.294
N22	-0.211	-0.242	-0.244	-0.246	-0.240	-0.222
C23	-0.163	-0.185	-0.186	-0.186	-0.184	-0.173
C27	-0.220	-0.234	-0.234	-0.235	-0.234	-0.229
C30	-0.255	-0.267	-0.268	-0.269	-0.267	-0.259
C33	-0.242	-0.263	-0.264	-0.265	-0.263	-0.253
N37	-0.534	-0.581	-0.569	-0.569	-0.569	-0.536
C40	-0.273	-0.299	-0.299	-0.300	-0.297	-0.284
N43	-0.791	-0.806	-0.797	-0.792	-0.797	-0.784
N47	-0.381	-0.412	-0.414	-0.415	-0.410	-0.389
Atom				ΔQ		
C2		0.030	0.031	0.032	0.029	0.014
C5		0.010	0.012	0.012	0.010	0.003
C8		0.021	0.022	0.023	0.020	0.008
C10		0.022	0.023	0.024	0.021	0.008
C15		0.053	0.055	0.059	0.051	0.022
N18		0.047	0.049	0.052	0.045	0.020
N19		0.045	0.047	0.050	0.043	0.019
N21		0.060	0.066	0.068	0.059	0.022
N22		0.031	0.033	0.035	0.029	0.010
C23		0.022	0.024	0.024	0.022	0.011
C27		0.014	0.014	0.015	0.014	0.008
C30		0.012	0.013	0.014	0.012	0.004
C33		0.020	0.021	0.022	0.021	0.011
N37		0.047	0.036	0.035	0.035	0.002
C40		0.026	0.026	0.027	0.024	0.011
N43		0.015	0.006	0.001	0.006	0.007
N47		0.032	0.033	0.035	0.029	0.008

Table S4. The natural charges (Q) on selected atoms for **6a** ile **6a**+**F**, **6a**+**CN**, **6a**+**OH**, **6a**+**AcO**, **6a**+**H2PO4** and their relative values ( $\Delta Q$ ) with respect to **6a**.

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	$\lambda^{cal.}_{max}$	Transitions	W		$\lambda^{cal.}_{max}$	Transitions	W
6a	497	H-2→L	35	6b	482	H-4→L	9
	(0.516)	H-1→L	58		(0.6023)	H-2→L	71
		$H \rightarrow L+1$	4			H-1→L	5
						H-1 $\rightarrow$ L+1	3
						$H \rightarrow L+1$	8
6a+F <sup>-</sup>	435	H-1→L	2	6b+F <sup>-</sup>	468	H-3→L	4
	(0.7393)	H-1→L+1	88		(0.3232)	H-2→L	93
		$H \rightarrow L+2$	7				
	580	H→L	95		644	H→L	96
	(1.0339)				(1.0275)		
6a+CN <sup>-</sup>	437	H-4→L	2	6b+CN <sup>-</sup>	464	H-3→L	4
	(0.6976)	H-1→L	2		(0.3485)	H-2→L	92
		H-1→L+1	86				
		$H \rightarrow L+2$	6				
	584	H→L	95		649	H→L	96
	(1.0517)				(1.0231)		
6a+OH <sup>-</sup>	438	H-4→L	6	6b+OH <sup>-</sup>	465	H-3→L	6
	(0.6163)	H-2 →L	3		(0.3310)	H-2→L	89
		H-1 $\rightarrow$ L+1	83				
		H→L+2	4				
	585	H→L	95		653	H→L	96
	(1.0321)	H→L+2	2		(1.0417)		
6a+AoC <sup>-</sup>	435	$H-1 \rightarrow L$	2	6b+AoC <sup>-</sup>	467	H-2→L	95
	(0.7574)	H-1→L+1	88		(0.3315)		
		$H \rightarrow L+2$	7				
	578	H→L	95		641	H→L	96
	(1.0650)				(1.0412)		
6a+H2PO4 <sup>-</sup>	492	H-4→L	3	6b+H2PO4 <sup>-</sup>	468	H-2→L	94
	(0.4178)	H-2→L	79		(0.2226)		
		H-1→L	5		. ,		
		$H \rightarrow L+1$	6				
	565	H→L	95		595	H-1→L	2
	(0.7402)				(0.8012)	H→L	95

Table S5. The calculated absorption maxima ( $\lambda^{cal.}_{max}$ ), oscillator strengths (f), transitions and contributions (w) for **6a**, **6b** and their complexes. f values were given in parentheses.

	6b	6b+F <sup>-</sup>	6b+CN <sup>-</sup>	6b+OH <sup>-</sup>	6b+AcO <sup>-</sup>	6b+H2PO4 <sup>-</sup>
Atom				Q		
C1	-0.125	-0.138	-0.138	-0.139	-0.137	-0.131
C5	-0.084	-0.117	-0.119	-0.120	-0.117	-0.099
C8	-0.223	-0.249	-0.251	-0.252	-0.249	-0.234
C10	-0.237	-0.266	-0.267	-0.268	-0.265	-0.249
C15	-0.316	-0.331	-0.331	-0.333	-0.330	-0.321
N18	-0.375	-0.387	-0.387	-0.389	-0.386	-0.379
N19	-0.373	-0.389	-0.389	-0.390	-0.388	-0.379
N21	-0.271	-0.354	-0.358	-0.361	-0.354	-0.311
N22	-0.211	-0.249	-0.251	-0.253	-0.247	-0.224
N46	-0.381	-0.399	-0.400	-0.401	-0.398	-0.386
Atom				$\Delta \mathbf{Q}$		
C1		0.013	0.013	0.014	0.012	0.005
C5		0.033	0.035	0.036	0.033	0.015
C8		0.026	0.028	0.029	0.026	0.011
C10		0.028	0.029	0.031	0.028	0.012
C15		0.015	0.015	0.017	0.014	0.005
N18		0.012	0.013	0.014	0.011	0.004
N19		0.0148	0.015	0.017	0.014	0.005
N21		0.082	0.087	0.089	0.083	0.040
N22		0.038	0.039	0.042	0.036	0.013
N46		0.018	0.020	0.019	0.017	0.005
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**Table S6.** The natural charges (Q) on selected atoms for **6b** ile **6b+F**, **6b+CN**, **6b+OH**, **6b+AcO**, **6b+H2PO4** and their relative values ( $\Delta$ Q) with respect to **6b**.

## **1 CRediT author statement**

Deniz ÇAKMAZ: Visualization, Investigation. Arda ÖZARSLAN.: Visualization,
Investigation. Burcu AYDINER: Investigation, Validation, Writing- Original draft
preparation. Ahmet Burak EROĞLU: Formal analysis. Nurgül SEFEROĞLU:
Supervision, Validation, Writing- Reviewing and Editing. Hülya ŞENÖZ: Supervision,
Writing- Reviewing and Editing. Zeynel SEFEROĞLU: Supervision, Conceptualization,
Methodology.

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LIGHT Supervision,

## **Declaration of interests**

 $\boxtimes$  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.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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