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Dicyanovinylcoumarin as a turn-on fluorescent sensor for cyanide ion

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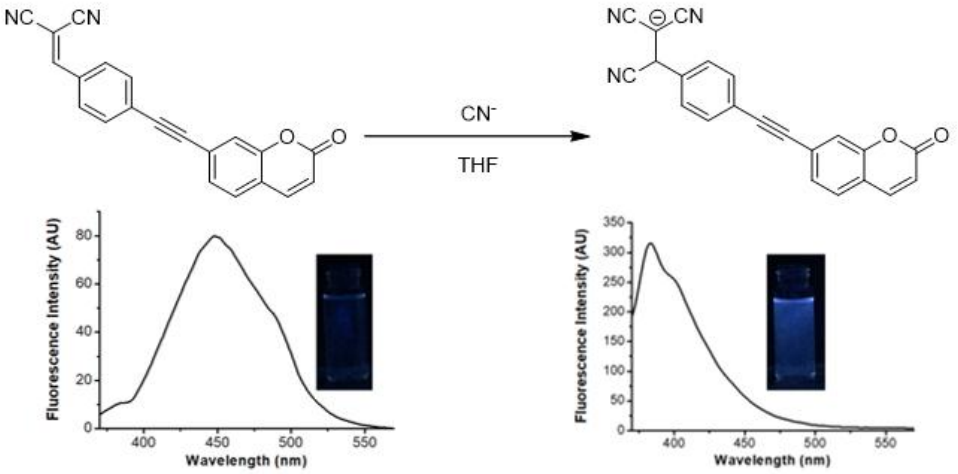
Graphical Abstract



Highlights

- Synthesis of dicyanovinylcoumarins (**4a**, **4b** and **4c**) by Knoevenagel condensation reaction.
- The dicyanovinylcoumarin (**4b**) shows turn-on fluorescence towards cyanide anion.
- The dicyanovinylcoumarin **4b** detection limit for CN^- was found to be 1.14×10^{-8} M.

Abstract: Dicyanovinylcoumarin chemosensors (**4a**, **4b** and **4c**) were designed and synthesized by the Knoevenagel condensation reaction. The electronic absorption and emission spectra of the dicyanovinylcoumarin isomers exhibited red shifted absorption and less emission as compared to their precursor's coumarin aldehydes. The sensing behavior of dicyanovinylcoumarin isomers were studied for different anions. In these dicyanovinylcoumarin isomers, the 7-substituted isomer shows high selectivity towards CN^- in the presence of other F^-, Cl^-, Br^-, I^-, ClO_4^-, HSO_4^- and NO_2^- ions. The effect of CN^- on the structure of dicyanovinylcoumarin isomer was studied by performing DFT calculations. The theoretical calculations show strong agreement with the experimental results. The detection limit for CN^- were found to be 1.14×10^{-8} M for 7-substitued dicyanovinylcoumarin isomer **4b**.

Keywords: Dicyanovinylcoumarin, fluorescence, sensor, Sonogashira cross–coupling reaction and cyanide ion.

1. Introduction

The design and development of new chemosensors for the detection of anions is an area of growing interest in supramolecular chemistry due to key roles of anions in chemical and biological events [1-4]. The cyanide anion is extremely toxic to living organisms and is used in various applications, such as gold mining, dyes and textiles, electroplating, synthetic fertilizers, pesticides, automobiles, metallurgy and pharmaceuticals [5-8]. Hence, several fluorescent chemosensors have been reported for the detection of cyanide anions during recent years [9-12]. Coumarins are a group of natural compounds found in a variety of plant sources, as well as widely studied functional materials [13]. Coumarin derivatives are widely used as laser dyes, and they are attractive fluorescent molecules due to their extended spectral range, strong fluorescence, large Stokes-shift, and high thermal and chemical stability [14-23]. Coumarin derivatives are widely used in various applications, including fluorescent probes, laser dyes, organic light emitting diodes, solar cells, nonlinear optical chromophores and

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biomedicines [24-30]. In recent years, chemosensors containing a dicyanovinyl group have attracted considerable attention due to their applications in biology and anion sensing [31-38]. Jalal Isaad *et al.*, reported water-soluble polymer containing coumarin-dicyanovinyl motif [39]. In water-soluble polymer containing coumarin-dicyanovinyl motif, dicyanovinyl group is attached at C-3 carbon of coumarin ring. Water-soluble polymer fluorescence emission maximum is at 581 nm. Upon addition of CN^- ion to the water-soluble polymer, its fluorescence was decreased and blue shifted to 500 nm.

Generally, non-substituted parent coumarin (2-oxo-2H-chromene) is not fluorescent, and optical properties of substituted coumarins depend highly on the type and position of the substituent on the coumarin ring [40]. Coumarin derivatives substituted at the 7-position with an electron donating group are highly fluorescent compared to 6 and 8-position substituted coumarins [41]. Coumarin derivatives substituted at the 7-position with an electron donating group (amino or hydroxyl groups) are highly fluorescent in the blue or green region [42]. In this context, herein, we report the design and synthesis of three dicyanovinylcoumarin isomers (**4a**, **4b** and **4c**) and their anion sensing ability.

2. Experimental

2.1. Materials

All the chemicals were purchased from commercial sources and used without further purification. ^1H NMR and ^{13}C NMR spectra were performed on 600 MHz and 150 MHz Bruker Ultra shield (Avance–III) Nano Bay spectrometer. All the spectra were recorded at 298K. ^1H NMR data are reported as follows: s: singlet, d: doublet, t: triplet, bs: broad singlet and coupling constants, *J*, are given in Hz. Chemical shifts in ^1H NMR and ^{13}C NMR spectra were reported in parts per million (ppm) with TMS (0 ppm) and $CDCl_3$ (77.00) as standards. Mass spectroscopy was performed on gas chromatography high resolution mass spectrometer, JMS-700 (JEOL, Japan), 6890 series (Agilent, USA) (EI-MS). TLC analysis was carried out using silica gel 60 F_{254} plates. UV–vis absorption spectra of all compounds were recorded in THF on a Jasco V-670 UV–visible Spectrophotometer. Emission spectra were taken in a PerkinElmer LS 55 fluorescence spectrometer. The excitation and emission slits were 2.5/2.5 nm for the emission measurements. All the measurements were done at 298K. For fluorescence titrations, the anion (F^-, Cl^-, Br^-, I^-, ClO_4^-, HSO_4^- , NO_2^- and CN^-) stock solutions were prepared in THF in the order of 10^{-3} M. The dicyanovinylcoumarins (**4a**, **4b**, **4c**) stock solution was prepared (C=1mM) in THF. Working solutions of dicyanovinylcoumarins (**4a**, **4b**, **4c**) and anions were freshly prepared from stock solutions. Column chromatography was performed on Merck silica gel (230-400 mesh). The anions were used in their tetrabutylammonium salts.

2.2. Synthesis

General synthetic procedure for **3a/3b/3c:** 6-Bromocoumarin (0.5 g, 2.23 mmol), (4–ethynyl)benzaldehyde (0.29 g, 2.23mmol) were dissolved in THF-triethylamine (1:1, v/v, 120 mL) and the mixture was deaerated for 10 min with nitrogen bubbling and then $Pd(PPh_3)_2Cl_2$ (31 mg, 2mol%), PPh_3 (23 mg, 4 mol%)and CuI (8 mg, 2mol%) were added. The solution was deaerated for an additional 5 min; after that, reaction was left under nitrogen at 60 °C for 12h. After completion of the reaction, the reaction mixture was cooled at room temperature and the solvent was evaporated. The crude product was dissolved in CH_2Cl_2 and purified by a column chromatography on a silica gel using (chloroform) as an eluent.

Synthesis of **3a**. Yield, 61 % (0.37 g), ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.04 (s, 1H, -CHO), 7.89 (d, *J* =8.25, 2H, aromatic), 7.70-7.68 (m, 5H, aromatic), 7.35 (d, *J* =9.17, 1H, aromatic), 6.48 (d, *J* =9.55, 1H, aromatic).^{13}C (150 MHz, $CDCl_3$) δ 192.67, 159.58, 153.76, 143.58, 135.70, 134.89, 132.15, 131.81, 129.82, 127.88, 119.28, 117.80, 117.35, 117.30, 91.58, 88.79. MS (*m/z*) 275 (M+H).

General synthetic procedure for dicyanovinylcoumarins **4a/4b/4c**. **3a** (0.2 g, 0.73 mmol) and malononitrile (0.057 g, 0.875 mmol) were dissolved in 20 mL of ethanol with two drops of piperidine. The reaction mixture refluxed for 4 h, and the solvent was removed under reduced pressure. The crude product was dissolved in CH_2Cl_2 and purified by column chromatography on a silica gel using (chloroform) as an eluent.

Synthesis of **4a**. Yield 68 % (0.16 g), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.56 (s, 1H, - C=CH), 8.08 (d, *J* =9.35 Hz, 1H, aromatic), 8.02-7.99 (m, 3H, aromatic), 7.82-7.80 (m, 3H, aromatic), 7.48 (d, *J* =8.5 Hz, 1H, aromatic), 6.59 (d, *J* =10.2 Hz, 1H, aromatic). ^{13}C (150 MHz, $CDCl_3$) δ 160.194, 159.55, 153.84, 143.57, 134.93, 132.32, 131.88, 131.34, 130.89, 127.60, 119.30, 117.67, 117.37, 117.35, 114.29, 113.27, 92.42, 88.87, 82.16. HRMS (*m/z*): [M^+] calculated for $C_{21}H_{10}N_2O_2$: 322.0742; Found: 322.0746.

Synthesis of **3b**. Yield 63 % (0.387 g), ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.05(s, 1H, -CHO), 7.91-7.89 (m, 2H, aromatic), 7.73-7.69 (m, 3H, aromatic), 7.50-7.43 (m, 3H, aromatic), 6.46 (d, *J* =9.34, 1H, aromatic).^{13}C (150 MHz, $CDCl_3$) δ 191.33, 160.22, 153.77, 142.65, 135.87, 132.32, 129.62, 128.53, 127.87, 127.75, 126.06, 119.77, 119.17, 117.32, 91.64, 91.61. HRMS (*m/z*): [M$^+$] calculated for $C_{18}H_{10}O_3$: 274.0630; Found: 274.0629.

Synthesis of **4b**. Yield 76 % (0.18 g), ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94-7.89(m, 2H, aromatic), 7.77 (s, 1H, C=CH), 7.73-7.69 (m, 3H, aromatic), 7.52-7.44 (m, 3H, aromatic), 6.54 (d, *J* =9.6, 1H, aromatic).^{13}C (150 MHz, $CDCl_3$) δ 160.12, 158.36, 153.76, 142.60, 132.67, 130.77, 130.66, 128.83, 127.93, 127.80, 125.69, 119.86, 119.39, 117.50, 113.53, 112.44, 93.04, 91.31, 83.39. HRMS (*m/z*): [M+H] calculated for $C_{21}H_{11}N_2O_2$: 323.0821; Found: 322.0825.

Synthesis of **3c**. Yield 69 % (0.42 g), ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.06(s, 1H, -CHO), 8.22 (d, *J* =9.60, 1H, aromatic), 7.93 (d, *J* =8.59,2H, aromatic), 7.75 (d, *J* =8.08,2H, aromatic), 7.56-7.50 (m, 2H, aromatic), 7.37-7.35(m, 1H, aromatic), 6.54 (d, *J* =9.60, 1H, aromatic).^{13}C (150 MHz, $CDCl_3$) δ 192.74, 159.55, 153.82, 141.68, 136.05, 132.50, 132.12, 129.77, 128.47, 127.34, 120.41, 119.55, 117.92, 117.73, 94.53, 88.35. MS (*m/z*) 275 (M+H).

Synthesis of **4c**. Yield 85 % (0.2 g), ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.586(s, 1H, =CH), 8.381 (d, *J* =9.60, 1H, aromatic), 8.03 (d, *J* =8.4,2H, aromatic, phenyl), 7.94 (d, *J* =8.4,2H, aromatic, phenyl), 7.708-7.646 (m, 2H, aromatic), 7.52 (d, *J* =7.6, 1H, aromatic), 6.62 (d, *J* =10, 1H, aromatic).^{13}C (150 MHz, $CDCl_3$) δ 160.202, 159.540, 153.837, 141.691, 132.657, 132.146, 131.778, 130.787, 128.52, 127.01, 120.292, 119.614, 118.062, 117.787, 114.263, 113.263, 94.559, 89.127, 82.566. MS (*m/z*) 322 (M+H).

3. Results and Discussion

3.1. Synthesis

The synthetic route of dicyanovinylcoumarins (**4a, 4b** and **4c**) are shown in Scheme 1 and the structures are outlined in Chart 1. Bromophenols were reacted with malic acid in the presence of sulfuric acid to give bromo coumarins (**2a**, **2b** and **2c**) [43-45]. Coumarin aldehydes (**3a**, **3b** and **3c**) were synthesized by the Pd–catalyzed Sonogashira cross–coupling reaction of bromocoumarins (**2a**, **2b** and **2c**) with 4–ethynylbenzaldehyde respectively [46]. Coumarin aldehydes were characterized by ^{1}H, ^{13}C NMR (Figure S1-S12) spectra, and High-resolution mass spectrometry (HRMS) techniques. Coumarin aldehydes **3b** was synthesized by the Sonogashira cross–coupling reaction of 7-bromocoumarin (**2b)** with 4–ethynylbenzaldehyde using the catalyst $Pd(PPh_3)2$, CuI, PPh_3 in tetrahydrofuran (THF) solvent, triethylamine as base at 60 °C for 12h, which resulted **3b** in 63% yield. In the proton NMR spectrum of **3b**, an aldehyde proton show a singlet signal at 10.05 ppm and coumarin characteristic C-3 proton show a doublet signal at 6.46 ppm indicates the formation **3b**. Further conformation was obtained from the mass spectroscopy. In the mass spectrum, the molecular ion peak observed at 274 [M+] confirms the formation of **3b**. Dicyanovinylcoumarins (**4a**, **4b** and **4c**) were synthesized from its precursor aldehydes (**3a**, **3b** and **3c**) reacting with malononitrile in EtOH solvent [47]. Dicyanovinylcoumarins were characterized by ^{1}H, ^{13}C NMR spectra (Figure S1-S12), and High-resolution mass spectrometry (HRMS) techniques. In the proton NMR spectrum of **4b**, disappearance of an aldehyde proton at 10.05 ppm and the appearance of a new singlet signal at 7.77 ppm confirms the formation of **4b**. Further conformation was obtained from ^{13}C NMR and mass spectroscopy. In the mass spectrum, the molecular ion peak observed at 322 [M+] confirms the formation of **4b**.

3.2. Photophysical properties

The electronic absorption and emission spectra of the dicyanovinylcoumarins (**4a**, **4b**, **4c**) and its precursors the coumarinaldehydes (**3a**, **3b** and **3c**) were recorded in THF at room temperature (Figure 1-3 and Table 1). The coumarinaldehyde **3b** absorbs at 345 nm with a shoulder at 360 nm attributed to the π–π* electronic transition, whereas **3a** and **3c** absorbs at 315 nm and 322 nm attributed to the π–π* electronic transition. The coumarinaldehyde **3b** show red shifted absorption compared to coumarinaldehydes **3a** and **3c**. The dicyanovinylcoumarin **4b** absorbs at 365 nm attributed to the π–π* electronic transition with a shoulder at 385 nm may be attributed to the charge transfer. The dicyanovinylcoumarins **4a** and **4c** absorbs at 360 and 356 nm attributed to the π–π* electronic transition respectively. The dicyanovinylcoumarin **4b** show red shifted absorption compared to dicyanovinylcoumarins **4a** and **4c**. The dicyanovinylcoumarins **4a**, **4b** and **4c** exhibited weak florescence and an emission maximum are located at 482, 447 and 436 nm respectively.

3.3. Anion binding studies

The anion sensing ability of the dicyanovinylcoumarins **4a, 4b** and **4c** were investigated by the fluorescence emission spectra, using various anions (F^-, Cl^-, Br^-, I^-, NO_2^-, HSO_4^-, ClO_4^- and CN^-) in THF solvent. The anions were used in their tetrabutylammonium salts. Among the dicyanovinylcoumarins (**4a, 4b** and **4c**), a dicyanovinyl group substituted at the 7-position of coumarin i.e., **4b** shows turn-on fluorescence behavior in the presence of (F^-) and cyanide (CN^-) ions, and no significant change in the presence of Cl^-, Br^-, I^-, NO_2^-, HSO_4^-, and ClO_4^- anions (Figures 4). However, dicyanovinyl group substituted at the 6 and 8-position of coumarin, **4a** and **4c,** are not showing significant changes in the presence of anions (Figure 5). This may be due to that the substituent at positions 6, 7 or 8 is a strong electron withdrawing group. After gradual addition of the CN^- ions to the solution of **4b** in THF, the emission intensity of **4b** at 450 nm gradually decreased and a new emission maximum observed at 386 nm (Figure 4b). After addition of CN^- ion, one isosbestic point was observed at 443 nm. The addition of CN^- ion caused blue shift in emission maximum at 386 nm and fluorescence increased (Figure 4b). The increase in the fluorescence intensity of **4b** with the added CN^- ion follows a linear relationship between 2.30×10^{-7} M to 2.26×10^{-6} M ($R^2=0.994$). The detection limit of dicyanovinylcoumarin **4b** for CN^- ion was up to 11.4 nM, which is far lower than the maximum level for cyanide in drinking water according to WHO guidelines [44].

The dicyanovinylcoumarin **4a** show a weak turn-off fluorescence behavior in the presence of F^- and CN^- anions (Figure 5a). After addition of F^- and CN^- anions to the dicyanovinylcoumarin **4a**, its emission maximum was blue shifted to 434 nm and 422 nm respectively. However, no significant changes were observed in the presence of Cl^-, Br^-, I^-, NO_2^-, HSO_4^-, and ClO_4^- anions (Figures 5a). The dicyanovinylcoumarin **4c** show weak turn-on fluorescence behavior in the presence of F^- and CN^- anions. Whereas, no significant changes observed in the presence of Cl^-, Br^-, I^-, NO_2^-, HSO_4^-, and ClO_4^- anions (Figures 5b). After addition of F^- and CN^- anions to the dicyanovinylcoumarin **4c**, its emission maximum was blue shifted to 398 nm and 398 nm respectively. The sensing ability of the dicyanovinylcoumarins towards CN^- anion is in the order of **4b**>**4c**>**4a**.

3.4. Sensing mechanism and ^{1}H-NMR study

To gain further insight into the cyanide binding, ^{1}H-NMR spectrum was recorded after the addition of cyanide ion to the **4b**. The comparison of ^{1}H–NMR spectra of **4b** before and after addition of cyanide ion is shown in Figure 6, and it can be observed that the addition of cyanide ion to the **4b** results in a upfield shift of the Ha proton form 7.77 ppm to 4.38 ppm. The ^{1}H–NMR results clearly confirm that the Michael addition of CN^- on the C=C double bond yields a new C-C single bond between CN^- and the α-carbon of the dicyanovinyl group. Michael addition of CN^- caused the break of intramolecular charge transfer in the **4b** and resulted in “turn-on” fluorescence behavior.

3.5. Theoretical Study

To understand the structure and electronic properties of dicyanovinylcoumarins **4a**, **4b** and **4c**, time-dependent density functional theory (TD–DFT) calculations were performed using Gaussian 09 program. The TD–DFT calculations were performed by using Gaussian 09 program 6–31G** for C, N, and H at B3LYP level for the dicyanovinylcoumarins **4a**, **4b** and **4c** [48-52]. The frontier molecular orbitals of the **4a**, **4b**, **4c** and **4b-CN** are shown in figure S13 and S14. In **4a**, HOMO and LUMO are located on the coumarin ring and dicyanovinyl group. In **4b**, HOMO is primarily located on the coumarin ring and LUMO is majorly located on the dicyanovinyl group. In **4b**, slight charge transfer occurs from the coumarin ring oxygen atom to dicyanovinyl group. In **4b-CN**, frontier molecular orbitals HOMO and LUMO are majorly localized on coumarin ring and it indicates that the breaking of conjugation and intramolecular charge transfer between coumarin ring and dicyanovinyl group. In **4c**, HOMO and LUMO are located on the coumarin ring and dicyanovinyl group. The theoretical band gap values of **3a**-**3c** and **4a**-**4c** calculated at B3LYP level are 3.50, 3.22, 3.61, 3.16, 3.09 and 3.24 eV respectively (Table 1). The optical band gap values of of **3a**-**3c** and **4a**-**4c** are 3.36, 3.31, 3.39, 2.94, 2.91 and 2.98 eV respectively. The optical band gap values agree with theoretical band gap values.

4. Conclusions

Dicyanovinylcoumarins **4a**, **4b** and **4c** were synthesized by the Knoevenagel condensation reaction and characterized by NMR and mass spectra. The dicyanovinylcoumarin **4b** shows “turn-on” fluorescence behavior upon addition of fluoride and cyanide ions. The sensing ability of the dicyanovinylcoumarins towards CN^- is in the order of **4b**>**4c**>**4a**. The dicyanovinylcoumarin **4b** detection limit for CN^- was found to be 1.14×10^{-8} M.

5. Acknowledgements

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References

1. M. Wenzel, J. R. Hiscock, P. A. Gale, Anion receptor chemistry: highlights from 2010, Chem. Soc. Rev. 41 (2012) 15–23.
2. R. M. Duke, E. B. Veale, F. M. Pfeffer, P. E. Kruger, T. Gunnlaugsson, Colorimetric and fluorescent anion sensors: an overview of recent developments in the use of 1,8-naphthalimide-based chemosensors, Chem. Soc. Rev. 39 (2010) 3936–3953.
3. Z. Xu, X. Chen, H. N. Kim, J. Yoon, Sensors for the optical detection of cyanide ion, Chem. Soc. Rev. 39 (2010) 127-137.
4. S. K. Kim, J. L. Sessler, Ion pair receptors, Chem. Soc. Rev. 39 (2010) 3784–3809.
5. P. B. Nunn, J. R. A. Lyddiard, K. P. W. C. Perera, Brain glutathione as a target for aetiological factors in neurolathyrism and konzo, Food Chem. Toxicol. 49 (2011) 662–667.
6. J. L. Cadens, S. A. Montero, C. Leal, M. Lemus, E. Portilla–de Buen, B. A. Alvarado, E. R. De Alvarez–Buylla, Nitric oxide in the hypothalamus-pituitary axis mediates increases in brain glucose retention induced by carotid chemoreceptor stimulation with cyanide in rats, Nitric Oxide. 22 (2010) 296–303.
7. W. E. Ghann, O. Aras, T. Fleiter, M. C. Daniel, Syntheses and Characterization of Lisinopril-Coated Gold Nanoparticles as Highly Stable Targeted CT Contrast Agents in Cardiovascular Diseases, Langmuir. 28 (2012) 10398–10408.
8. V. S. Bebarta, R. Pitotti, J. Laire, P. Dixon, A. Bush, D. A. Tanen, Utility of sodium thiosulfate in acute cyanide toxicity, Ann. Emerg. Med. 61 (2013) 125–126.
9. H-L. Zhang, T-B. Wei, W-T. Li, W-J. Qu, Y-L. Leng, J-H Zhang, Q. Lin, Y-M. Zhang, H. Yao, Phenazine-based colorimetric and fluorescent sensor for the selective detection of cyanides based on supramolecular self-assembly in aqueous solution, Spectrochim. Acta. A. Molecular and Biomolecular Spectroscopy 175 (2017) 117–124.
10. W. Zhang, K. Xu, L. Yue, Z. Shao, Y. Feng, M. Fang, Two-dimensional carbazole-based derivatives as versatile chemosensors for colorimetric detection of cyanide and two-photon fluorescence imaging of viscosity in vitro, Dyes Pigm. 137 (2017) 560-568.
11. K. Prakash, P. R. Sahoo, S. Kumar, A fast, highly selective and sensitive anion probe stemmed from anthracene-oxazine conjugation with CN induced FRET, Dyes Pigm.143 (2017) 393-400.

12. R. Balasaravanan, V. Sadhasivam, G. Sivaraman, A. Siva, Triphenylamino α-Cyanovinyl-and cyanoaryl-based fluorophores: solvatochromism, aggregation-induced emission and electrochemical properties, Asian J. Org. Chem. 5 (2016) 399-410.
13. R. D. H. Murray, J. Mendez, S. A. Brown, The natural coumarins: occurrence, chemistry, and biochemistry, John Wiley & Sons, New York, 1982.
14. N. Kitamura, T. Fukagawa, S. Kohtani, S-I. Kitoh, K-K. Kunimoto, R. Nakagaki, Synthesis, absorption and fluorescence properties and crystal structures of 7-aminocoumarin derivatives, J. Photochem. Photobiol. A 188 (2007) 378-386.
15. K. Hara, K. Sayama, Y. Ohga, A. Shinpo, S. Sugab, H. Arakawa, A coumarin-derivative dye sensitized nanocrystalline TiO_2 solar cell having a high solar-energy conversion efficiency up to 5.6%, Chem. Commun. 2001 (2001) 569-570.
16. S. L. Gilat, A. Adronov, J. M. J. Frechet, Light Harvesting and Energy Transfer in Novel Convergently Constructed Dendrimers, Angew. Chem. Int. Ed. 38 (1999)1422-1427.
17. N. Prachumrak, S. Potjanasopa, R. Rattanawan, S. Namuangruk, S. Jungsuttiwong, T. Keawin, T. Sudyoadsuk, V. Promarak, Coumarin-cored carbazole dendrimers as solution-processed non-doped green emitters for electroluminescent devices, Tetrahedron. 70 (2014) 6249-6257.
18. G. JonesII, W. R. Jackson, C. Y. Choi, W. R. Bergmark, Solvent effects on emission yield and lifetime for coumarin laser dyes. Requirements for a rotatory decay mechanism, J. Phys. Chem. 89 (1985) 294-300.
19. T. Yu, P. Zhang, Y. Zhao, H. Zhang, J. Meng, D. Yu, Synthesis and photoluminescent properties of two novel tripodal compounds containing coumarin moieties, Spectrochim. Acta. A. 73 (2009)168-173.
20. J. Gordo, J. Avo, A. J. Parola, J. C. Lima, A. Pereira, P.S. Branco, Convenient synthesis of 3-vinyl and 3-styryl coumarins, Org. Lett. 13 (2011) 5112-5115.
21. R. M. Christie, C. H. Lui, Studies of fluorescent dyes: part 2. An investigation of the synthesis and electronic spectral properties of substituted 3-(20 -benzimidazolyl)coumarins, Dyes Pigm. 47 (2000) 79-89.
22. T. V. Soumya, P. Thasnim, D. Bahulayan, Step-economic and cost-effective synthesis of coumarin based blue emitting fluorescent dyes, Tetrahedron Lett. 55 (2014) 4643-4647.

23. X. Zhuang, W. Liu, J. Wu, H. Zhang, P. Wang, A novel fluoride ion colorimetric chemosensor based on coumarin, Spectrochim. Acta. A. 79 (2011) 1352– 1355.
24. Y. X. Song, Z. Chen, H. Q. Li, Advances in Coumarin-Derived Fluorescent Chemosensors for Metal Ions, Curr. Org. Chem. 16 (2012) 2690–2707.
25. Y. Shiraishi, S. Sumiya, T. Hirai, Highly sensitive cyanide anion detection with a coumarin-spiropyran conjugate as a fluorescent receptor, Chem. Commun. 47 (2011) 4953-4955.
26. X. Lv, J. Liu, Y. Liu, Y. Zhao, Y-Q Sun, P. Wang, W. Guo, Ratiometric fluorescence detection of cyanide based on a hybrid coumarin-hemicyanine dye: the large emission shift and the high selectivity, Chem. Commun. 47 (2011) 12843-12845.
27. T. S. Reddy, A. R. Reddy, Synthesis and fluorescence study of 6,7-diaminocoumarin and its imidazolo derivatives, Dyes Pigm. 96 (2013) 525-534.
28. M. T. Lee, C. K. Yen, W. P. Yang, H. H. Chen, C. H. Liao, C. H. Tsai, Efficient green coumarin dopants for organic light-emitting devices, Org. Lett. 6 (2004) 1241-1244.
29. K. D. Seo, H. M. Song, M. J. Lee, M. Pastore, C. Anselmi, F. D. Angelis, M. K. Nazeeruddin, M. Gräetzel, H. K. Kim, Coumarin dyes containing low-band-gap chromophores for dye-sensitised solar cells. Dyes Pigm. 90 (2011) 304-310.
30. F. Borges, F. Roleira, N. Milhazes, L. Santana, E. Uriarte, Simple coumarins and analogues in medicinal chemistry: occurrence, synthesis and biological activity, Curr. Med. Chem. 12 (2005) 887-916.
31. J. W. Jeong, S. Angupillai, I. J. Kim, J. Jeong, H-S. Kim, H-S. So, Y-A Son, Michael addition-based colorimetric and fluorescence chemodosimeters for the nanomolar-level tracking of cyanide ions in aqueous-organic media. Sens. Actuators B. 237 (2016) 341–349.
32. J. S.J. Hong, S.H. Yoo, J.S. Kim, J. Kim, C.H.L. Yoon, β-Vinyl substituted calix[4] pyrrole as a selective ratiometric sensor for cyanide anion, Chem. Commun. 2 (2009) 189-191.
33. P. Jayasudha, R. Manivannan, K.P. Elango, Simple colorimetric chemodosimeters for selective sensing of cyanide ion in aqueous solution via termination of ICT transition by Michael addition, Sens. Actuators B. 221(2015) 1441–1448.
34. G. J. Kim, H. J. Kim, Coumarinyl aldehyde as a Michael acceptor type of colorimetric and fluorescent probe for cyanide in water, Tetrahedron Lett. 51(2010) 2914–2916.

35. Y. R. Zhu, H. Li, G. T. Yan, B. B. Shi, Y. M. Zhang, Q. Lin, H. Yao, T. B. Wei, A simple Michael acceptor type quinoline derivative for highly selective sequential recognition of CN^- and Cu^{2+}in aqueous solution, RSC Adv. 5 (2015) 49953–49957.
36. L. Yang, X. Li, J. Yang, Q. Yi, J. Hua, Colorimetric and ratiometric near-infrared fluorescent cyanide chemodosimeter based on phenazine derivatives, ACS Appl. Mater. Interfaces 5 (2013) 1317–1326.
37. Y.D. Lin, Y.S. Pen, W. Su, K.L. Liau, Y.S. Wen, C.H. Tu, C.H. Sun, T.J. Chow, Reaction-based colorimetric and ratiometric fluorescence sensor for detection of cyanide in aqueous media, Chem. Asian J. 7 (2012) 2864–2871.
38. R. Manivannan, A. Satheshkumar, K. P. Elango, Highly selective colorimetric/fluorometric chemodosimeters for cyanide ions in aqueous solution based on Michael addition to C-atom possessing different polar substituents, Tetrahedron Lett. 55 (2014) 6281–6285.
39. J. Isaad, F. Malek, A. E. Achari, Water soluble and fluorescent copolymers as highly sensitive and selective fluorescent chemosensors for the detection of cyanide anions in biological media, RSC Adv. 3 (2013) 22168-22175.
40. H. Ammar, S. Abid, S. Fery-Forgues, Synthesis and spectroscopic study of new biscoumarin dyes based on 7-(4-methylcoumarinyl) diesters, Dyes Pigm. 78 (2008) 1-7.
41. W. Retig, A. Kloc, Intramolecular fluorescence quenching in aminocoumarines. Identification of an excited state with full charge separation, Can. J. Chem. 63 (1985) 1649-1653.
42. N. Prachumrak, S. Potjanasopa, R. Rattanawan, S. Namuangruk, S. Jungsuttiwong, T. Keawin, T. Sudyoadsuk, V. Promarak, Coumarin-cored carbazole dendrimers as solution-processed non-doped green emitters for electroluminescent devices, Tetrahedron 70 (2014) 6249-6257.
43. B. H. Jhun, K. Ohkubo, S. Fukuzumi, Y. You, Synthetic control over intra- and intermolecular charge transfer can turn on the fluorescence emission of non-emissive coumarin, J. Mater. Chem. C. 4 (2016) 4556-4567.
44. F. Belluti, R. Perozzo, L. Lauciello, F. Colizzi, D. Kostrewa, A. Bisi, S. Gobbi, A. Rampa, M. L. Bolognesi, M. Recanatin, R. Brun, L. Scapozza, A. Cavalli, Design, synthesis, and biological and crystallographic evaluation of novel inhibitors of

plasmodium falciparum enoyl-ACP-reductase (PfFabI), J. Med. Chem. 56 (2013) 7516-7526.

45. G. Bratulescu, A quick and advantageous synthesis of 2H-1-benzopyran-2-ones unsubstituted on the pyranic neucleus, Synthesis. 18 (2008) 2871-2873.
46. T. S. Reddy, R. Maragani, R. Misra, Triarylborane substituted naphthalimide as fluoride and cyanide ion sensor, Dalton Trans. 45 (2016) 2549–2553.
47. M. Reda, El-Shishtawy, A. M. Fatimah, Al-Zahrani, Z. M. Al-amshany, A. M. Asiri, Synthesis of a new fluorescent cyanide chemosensor based on phenothiazine derivative, Sens. Actuators B. 240 (2017) 288–296.
48. W-W. Zhang, Y-G. Yu, Z-D. Lu, W-L. Mao, Y-Z. Li, Q-J. Meng, Ferrocene−Phenothiazine Conjugated Molecules: Synthesis, Structural Characterization, Electronic Properties, and DFT-TDDFT Computational Study, Organometallics.26 (2007) 865–873.
49. M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. Defrees, J. A. Pople, Self- consistent molecular orbital methods. XXIII. A polarization- type basis set for second- row elements, J. Chem. Phys. 77 (1982) 3654–3665.
50. F. Ding, S. Chen and H. Wang, Computational Study of Ferrocene-Based Molecular Frameworks with 2,5-Diethynylpyridine as a Chemical Bridge, Materials. 3 (2010) 2668–2683.
51. A. D. Becke, Density- functional thermochemistry. III. The role of exact exchange J. Chem. Phys. 98 (1993) 5648–5652.
52. C. T. Lee, W. T. Yang and R. G. Parr, Development of the colle-salvetti correlation-energy formula into a functional of the electron density, Phys. Rev. B. 37 (1988) 785–789.

Figure Legends

Figure 1. Normalized absorption (solid lines) and fluorescence spectra (dotted lines) of **3a** (λ_{ex} =328 nm) and **4a** (λ_{ex} =360 nm) in THF solvent at 25 °C.

Figure 2. Normalized absorption (solid lines) and fluorescence spectra (dotted lines) of **3b** (λ_{ex} =360 nm) and **4b** (λ_{ex} =365 nm) in THF solvent at 25 °C.

Figure 3. Normalized absorption (solid lines) and fluorescence spectra (dotted lines) of **3c** (λ_{ex} =340 nm) and **4c** (λ_{ex} =356 nm) in THF solvent at 25 °C.

Figure 4. a) Effect of various anions on fluorescence emission spectra of **4b** in THF (λ_{ex} =365 nm) and b) fluorescence titration spectra of **4b** (7.76×10^{-6} M) with TBACN in THF solvent at 25 °C.

Figure 5. Effect of various anions on fluorescence emission spectra of a) **4a** (7.76×10^{-6} M) (λ_{ex} =360 nm) and b) **4c** (λ_{ex} =356 nm) (7.76×10^{-6} M) in THF solvent at 25 °C.

Figure 6. ^{1}H–NMR spectra of dicyanovinylcoumarin **4b** (top) and **4b** with TBACN (bottom) in $CDCl_3$.

Chart 1. Structure of dicyanovinylcoumarins **4a**, **4b** and **4c**.

Scheme 1. Synthesis of dicyanovinylcoumarins (**4a**, **4b** and **4c**).

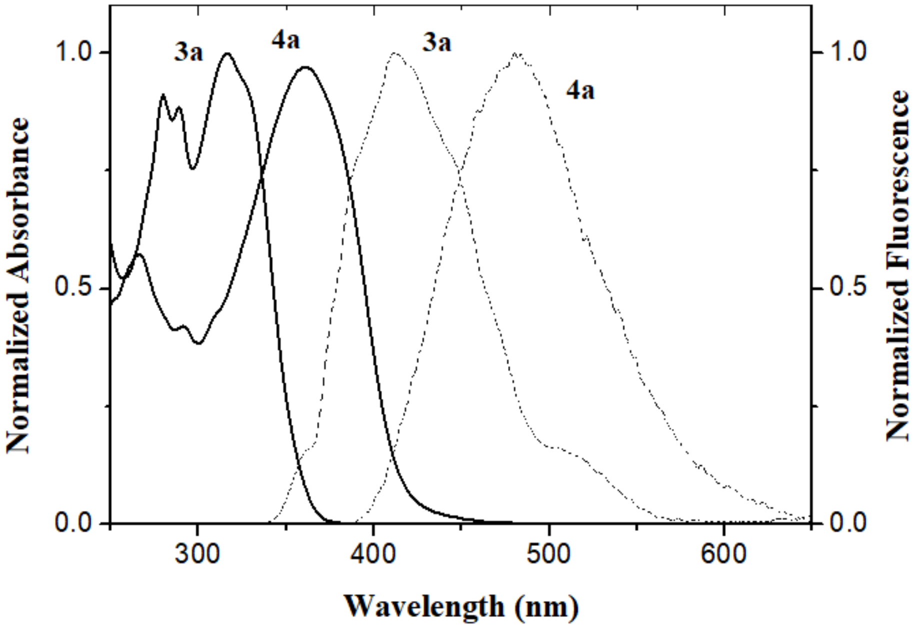


Figure 1. Normalized absorption (solid lines) and fluorescence spectra (dotted lines) of **3a** (λ_{ex} =328 nm) and **4a** (λ_{ex} =360 nm) in THF solvent at 25 °C.

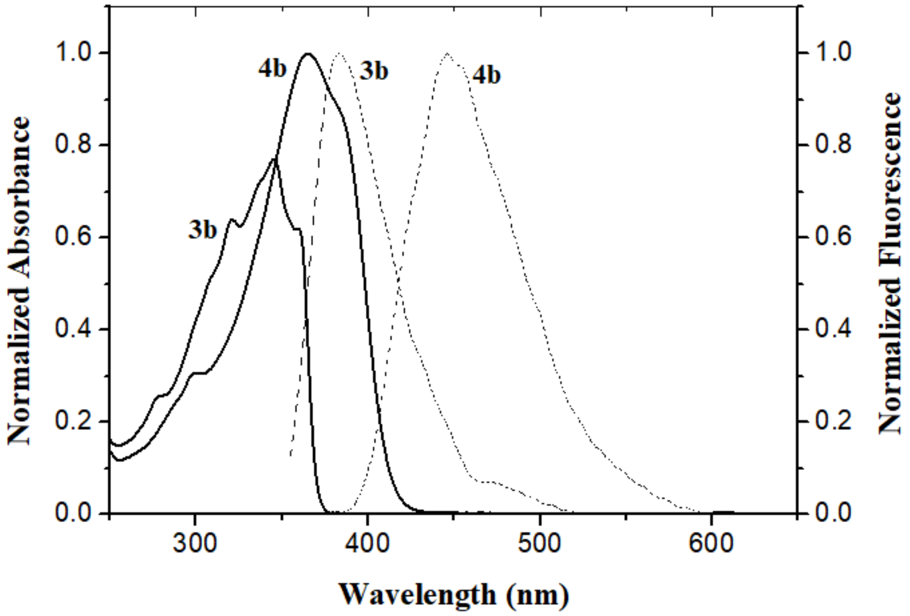


Figure 2. Normalized absorption (solid lines) and fluorescence spectra (dotted lines) of **3b** (λ_{ex} =360 nm) and **4b** (λ_{ex} =365 nm) in THF solvent at 25 °C.

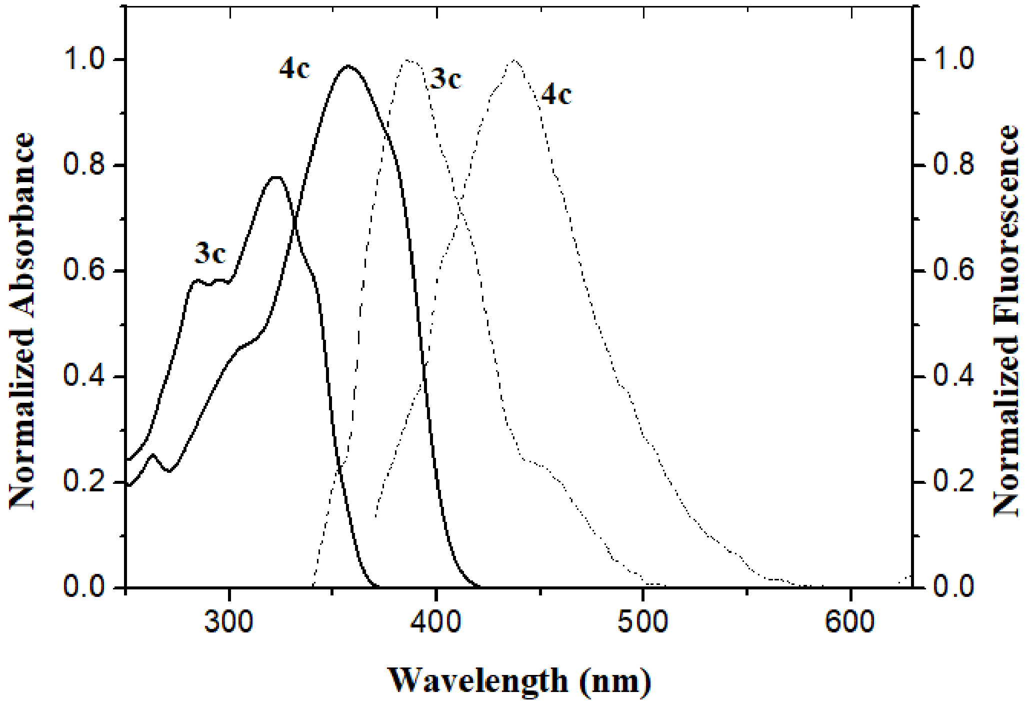
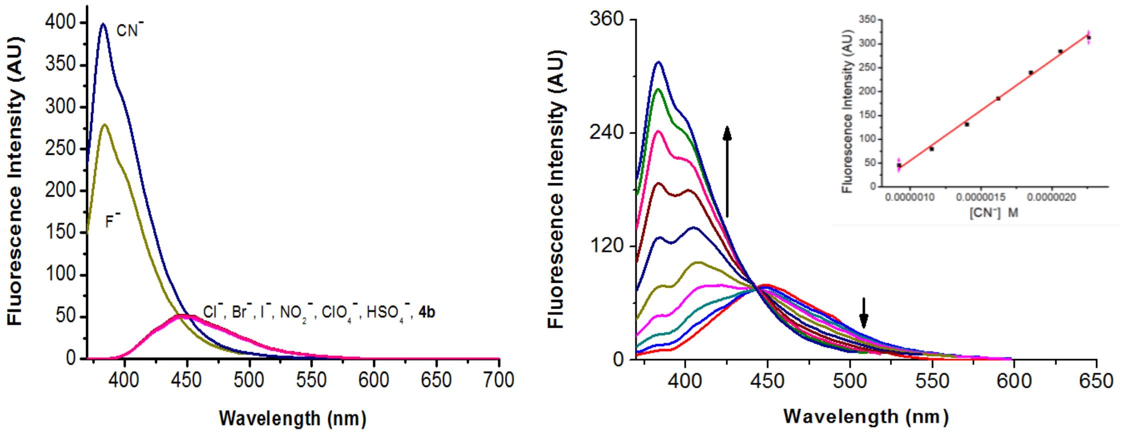
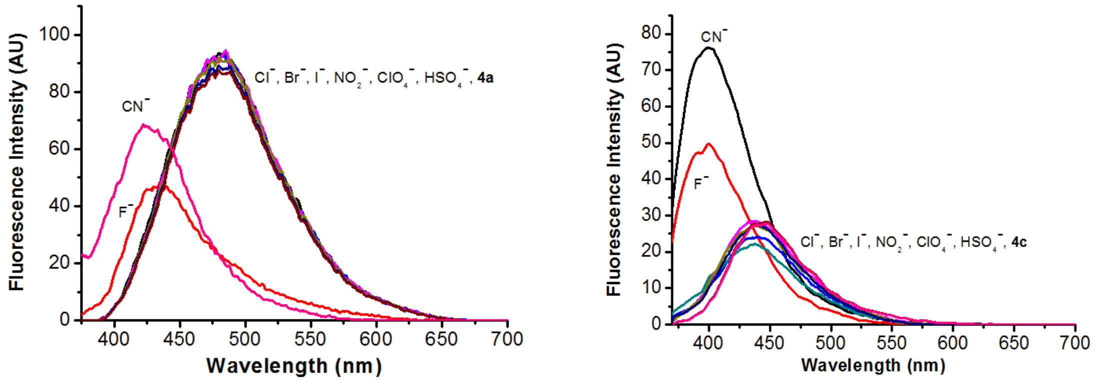


Figure 3. Normalized absorption (solid lines) and fluorescence spectra (dotted lines) of **3c** (λ_{ex} =340 nm) and **4c** (λ_{ex} =356 nm) in THF solvent at 25 °C.



a **b**

Figure 4. a) Effect of various anions on fluorescence emission spectra of **4b** in THF (λ_{ex} =365 nm) and b) fluorescence titration spectra of **4b** (7.76 x 10^{-6} M) with TBACN in THF solvent at 25 °C.



a **b**

Figure 5. Effect of various anions on fluorescence emission spectra of a) **4a** (7.76 x 10^{-6} M) (λ_{ex} =360 nm) and b) **4c** (λ_{ex} =356 nm) (7.76 x 10^{-6} M) in THF solvent at 25 °C.

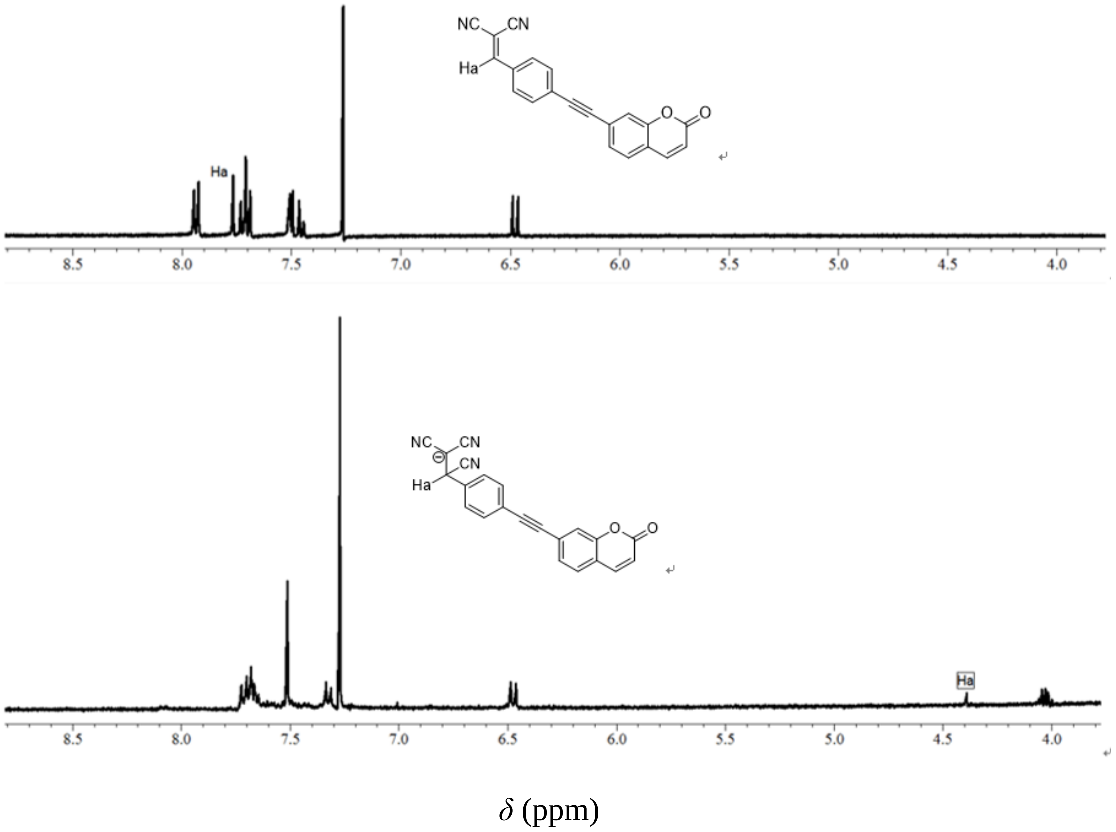
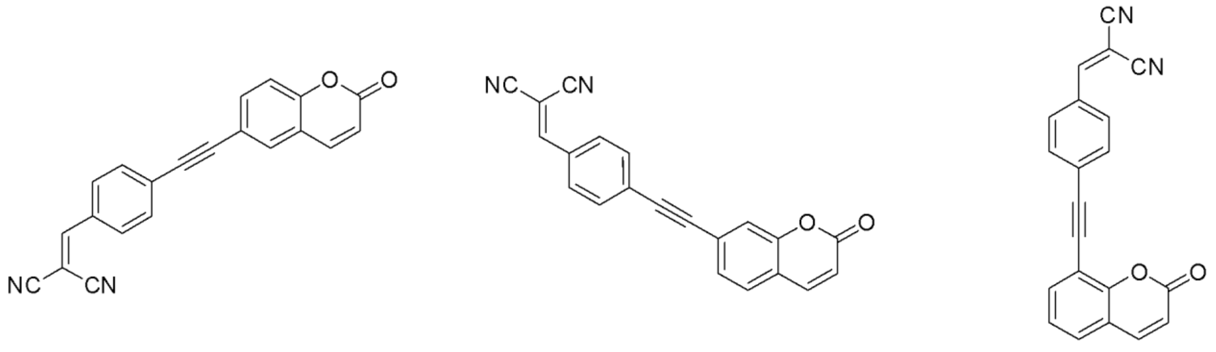
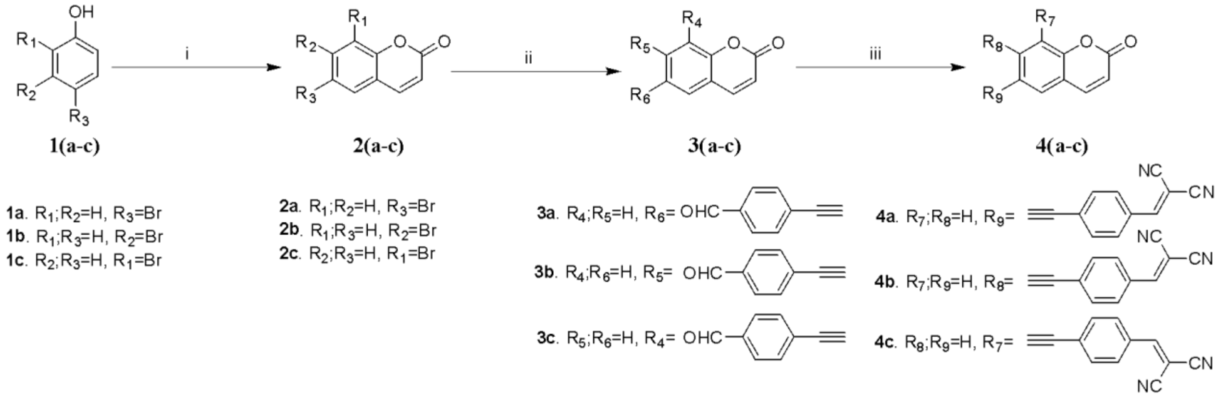


Figure 6. ^{1}H–NMR spectra of dicyanovinylcoumarin **4b** (top) and **4b** with TBACN (bottom) in $CDCl_3$.



4a **4b** **4c**

Chart 1. Structure of dicyanovinylcoumarins **4a**, **4b** and **4c**.



i) Malic acid, H_2SO_4, 120°C, 6h; ii) 4-Ethynylbenzaldehyde, $Pd(PPh_3)_2Cl_2$, CuI, THF, N_2 atm, 8 h, Reflux; iii) Malononitrile, Ethanol, Piperidine, reflux, 4h.

Scheme 1. Synthesis of dicyanovinylcoumarins (**4a**, **4b** and **4c**).

Table 1. Photophysical properties of **3a**–**3c** and **4a**–**4c**.

Compounds number	**λ_{max}(nm)**	**λ_{em}(nm)**	**Stokes-shift $\Delta\nu$ (cm^{-1})**	**Optical band gap (eV)**	**Theoretical band gap (eV)**		
					HOMO (eV)	**LUMO (eV)**	**E_g (eV)**
3a	315, 328	411	6077	3.36	6.22	2.72	3.50
3b	345, 360	383	1667	3.31	6.09	2.87	3.22
3c	321, 340	386	3504	3.39	6.24	2.62	3.61
4a	360	482	7023	2.94	6.32	3.16	3.16
4b	365	447	5025	2.91	6.20	3.10	3.09
4c	356	436	5154	2.98	6.32	3.07	3.24