



Synthesis and Characterization of Novel Carbazole Based Dyes

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In this work, 9*H*-carbazole acted as precursor to synthesize a new organic dye, which involved the alkylation of carbazole with butyl bromide in the presence of phase transfer catalyst tetrabutylammonium bromide (TBAB) to give **BC** (9-butyl-9*H*-carbazole) followed by the formylation with hexamethylenetetramine (HMTA) in the presence of trifluoroacetic acid (TFA) and tetrahydrofuran (THF). Formyl groups at 3- and 3,6-positions afforded **CC** (9-butyl-9*H*-carbazole-3-carbaldehyde) and **CD** (9-butyl-9*H*-carbazole-3,6-dicarbaldehyde), respectively. The formylation reaction with HMTA suffered with low yield, therefore another methodology was adopted for the formylation of **BC** with POCl₃ in the presence of dry DMF to afford **CC** and **CD**. Then condensation reaction was carried out **CC** and **CD** with cyanoacetic acid in the presence of ammonium acetate as catalyst. This reaction resulted in formation of **CA** (3-(9-butyl-9*H*-carbazol-3-yl)-2-cyanoacrylic acid) and **DA** (3,6-(9-butyl-9*H*-carbazol-3-yl)-2,2'-cyanoacrylic acid). All the synthesized compounds were characterized by FTIR, GC-MS, MS and UV-visible methods. The UV-Visible absorption spectra of **CA** was observed at 239 nm while the absorption region is from 190 nm to 340 nm and **DA** shows the absorption peak at 338 nm while the absorption region is from 290 to 440 nm. The energy band gaps for **CA** and **DA** were found to be 5.2 eV and 3.6 eV, respectively.

Keywords: Carbazole, Tetrabutylammonium bromide, Hexamethylenetetramine, Cyanoacetic acid, Ammonium acetate.

INTRODUCTION

Carbazoles represent a significant class of heterocyclic aromatic compounds, exhibiting favourable characteristics for the transport of electrons and charges across the molecular framework [1,2]. The compound exhibits a structural configuration derived from indole, characterized by the fusion of an additional benzene ring onto the five-membered ring at the 2,3 position of indole. Moreover, the carbazole structural motif is widely found in a significant array of naturally occurring alkaloids derived from both plant and bacterial sources [3-5].

As a low-cost starting material, 9*H*-carbazole can be easily functionalized at 3-, 6- or 9-position to covalently bond onto other molecules. The nitrogen atom can be easily substituted with extensive variety of functional groups [6]. Carbazole based dyes have been studied extensively in several applications which

include n-type DSSCs [7]. Metal free organic dyes are an attractive alternative because they offer high absorption, various structures, low material cost and ease of purification [8]. In recent years, significant hard work have been devoted to enhance cell efficiencies. In this respect, many efficient sensitizers with donor- π -acceptor frameworks have been developed [9]. Several dyes based on carbazole are either donor or π -linker have been synthesized and established as sensitizers in DSSCs [10].

Organic solar cells and certainly OLEDs [11] due to their high thermal stability, emission efficiencies, easy chemical functionalization, film-forming proficiency and their potential hole-transporting mobility related to the electron donating ability of the carbazole unit [12,13]. Due to their powerful adherence to the semiconductor surface, the carboxylic acids are often utilized anchors for most sensitizers [14]. When the number of anchoring groups in a molecule is increased and

the absorption shifts towards the bathochromic range [15]. The effect of the cyano group on the dye's anchoring component only when it adsorbs *via* CN does cyano group boost adsorption stability [16,17]. Thus, in this work, we designed two new carbazole compounds carrying 9*H*-carbazole as donor scaffold, and butyl bromide, hexamethylenetetramine (HTMA) and cyanoacetic acid as effective acceptor/anchoring groups. The new carbazole based dyes have been synthesized as per **Scheme-I**, following the synthetic strategies like *N*-alkylation, Duff formylation, Vilsmeier Haack-reaction, *etc.* The compounds were finally characterized by FTIR, NMR, Mass, UV-Vis absorption and fluorescent emission spectroscopy.

EXPERIMENTAL

Carbazole and bromo butane were purchased from Alfa-Aesar while hexamethylenetetramine (HMTA), trifluoroacetic acid (TFA) and tetrahydrofuran (THF) was procured from Daejung, China Benzene. Tetra *n*-butylammonium bromide (TBAB) and DMF solvent were purchased Sigma-Aldrich Chemicals, USA. The IR spectra were recorded using Perkin-Elmer Spectrum IR version 10.6.2 in the range 4000–450 cm^{-1} . The GC analysis was conducted on GC-2010 plus Shimadzu triple quadrupole-8040 with EI source, USA, MS technology Isb (PC1). The overall GC column temperature was 330 °C, however a temperature of 280 °C was selected to prevent the GC column from burning. The mass spectra were acquired on a Thermo Fisher Scientific LTQ Orbitrap XL. The PG UV-160A spectrophotometer was used to record the UV-visible spectra.

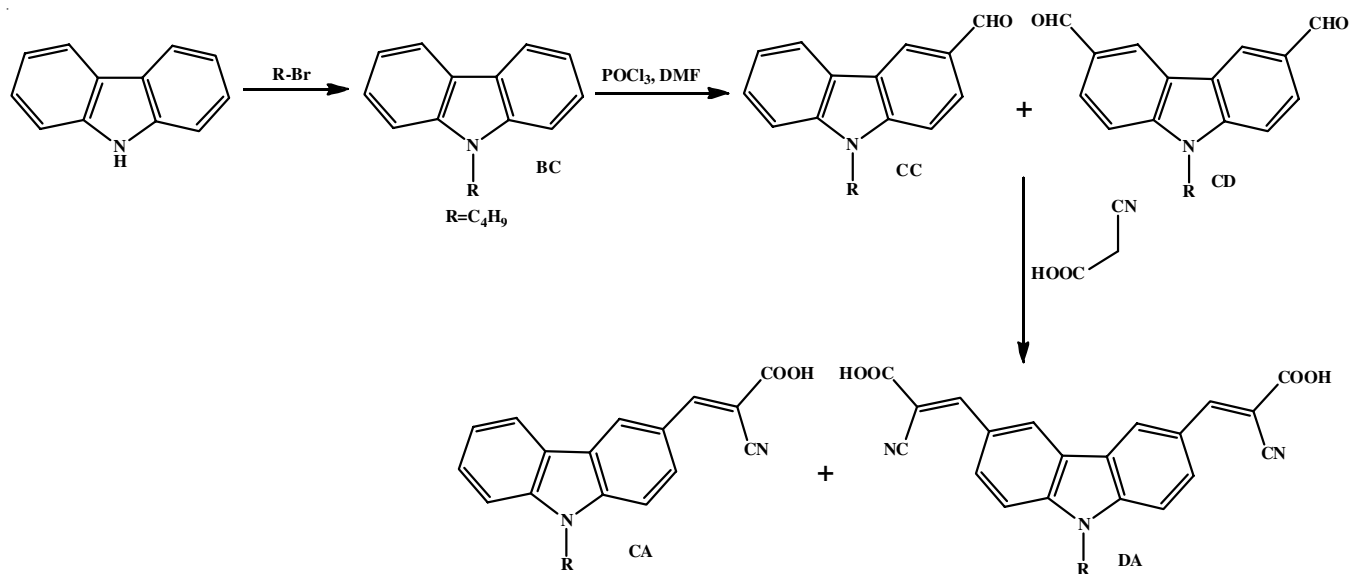
Synthesis of 9-butyl-9*H*-carbazole (BC): Carbazole (2 mmol, 0.33 g) was dissolved in benzene (10 mL) while stirring for 1 h followed by the addition of tetrabutylammonium bromide (TBAB) (0.1 g) as a catalyst in reaction mixture and then 50% NaOH as base and butyl bromide (2 mmol, 0.38 g) as an alkylating agent. The reaction mixture was allowed to reflux in 250 mL round bottom flask for 14 h at 80–90 °C. The reaction progress was monitored by TLC using solvent system pet. ether: EtOAc (9:1). After completion, the reaction mixture was diluted

with ethyl acetate in separating funnel and washed for at least three times with distilled water. The aqueous layer was disposed off whereas organic layer was dried over anhydrous MgSO_4 , filtered and finally solvent was evaporated under vacuum by using rotary evaporator. The residual organic component, designated as **BC**, placed in the fume hood, yields a white precipitate.

Synthesis of 9-butyl-9*H*-carbazole-3-carbaldehyde (CC) and 9-butyl-9*H*-carbazole-3,6-dicarbaldehyde (CD): Method was adopted to proceed the formylation of carbazole *via* duff reaction in the presence of trifluoroacetic acid (TFA). In duff reaction, the solution mixture consist of **BC** (1 mmol, 0.223 g), HMTA (4 mmol, 0.56 g) in 5 mL THF solvent and TFA added dropwise (4 mmol, 0.4 mL) was heated on reflux at 90 °C for 9 h. However, some residual reactant in the final product was observed as revealed by TLC. In order to use up the rest of the compound **BC**, 0.5 mL TFA and 0.38 g HMTA was added and stirred the mixture for another 4 h.

Since Duff reaction suffered from low yield. This was also synthesized by Vilsmeier-Haack formylation [18] by using POCl_3 and DMF. In this method, first DMF (20 mmol, 1.46 g, 1.5 mL) was added in round bottom flask which was stirred and cooled at -5 °C. Then, POCl_3 (15 mmol, 2.29 g, 1.4 mL) was added dropwise while stirring for 15 min in ice bath. After the formation of white precipitate, compound **BC** (1.11 g, 5 mmol) solution in 3mL of DMF was added. Then reaction mixture was heated at 100 °C for 8 h to obtain reddish brown solid (**Scheme-I**).

Synthesis of 3-(9-butyl-9*H*-carbazol-3-yl)-2-cyanoacrylic acid (CA) and 3,6-(9-butyl-9*H*-carbazol-3-yl)-2,2'-cyanoacrylic acid (DA): Compounds **CC** or **CD** (1 mmol, 0.279 g), cyano acetic acid (1.9 mmol, 0.16 g) and ammonium acetate (1.9 mmol, 0.14 g) were added in 20 mL acetic acid and then the mixture was heated for 16 h at 110 °C. The reaction was monitored by TLC. The product was extracted with CHCl_3 and the organic layer was dried by using MgSO_4 . The organic layer was filtered, evaporated using vacuum evaporator and finally the product was obtained as yellow paste (**Scheme-I**).



Scheme-I: The targeted molecules

RESULTS AND DISCUSSION

The 9*H*-carbazole was used as the precursor to obtain the desired novel carbazole based dyes. The methodology involved the synthesis of 9-butyl-9*H*-carbazole **BC** followed by the formylation *via* Duff formylation reaction using TFA and THF and Vilsmeier Haack-reaction. The formylated carbazole underwent condensation reaction with cyanoacetic acid to get the target dye. The IR spectrum of compound **BC** (Fig. 1), the *sp*³ C-H antisymmetric stretch appeared at 2958 cm⁻¹ indicating the presence of CH₃ moiety of butyl chain. The peak was observed at 2871 cm⁻¹ which is attributed the symmetric stretch of C-H. Similarly, the aromatic C=C stretch was observed at 1483 and 1452 cm⁻¹, whereas the C-N stretching absorption occurred at 1325 cm⁻¹. The peaks at 1379 cm⁻¹ and 1325 cm⁻¹ show the -CH₃ and -CH₂ anti-symmetric deformation, respectively. The C-H out of plan distorting benzene ring intertwined with five membered heterocyclic rings have been found to be within the range of 749-724 cm⁻¹ of FTIR, a characteristic of four adjoining benzenoid hydrogen atoms. The gas chromatogram (Fig. 2) shows only peak one, which indicated the pure product

9-butylcarbazole. The molecular ion peak of **BC** appeared at *m/z* 223 and base peak of molecule is 180 which was obtained by removing propyl fragment *m/z* value of 152 is obtained when CH₂=N fragment is lost (Fig. 3).

For the formylation of **BC** under reaction conditions were applied. First of all, Duff formylation reaction of 9-butyl-9*H*-carbazole (**BC**) was carried out with HMTA and TFA which afforded di-**CD** and mono-formylated **CC**. Since Duff reaction suffered with low yield. Then the formylation of **BC** was also synthesized by Vilsmeier-Haack reaction by using POCl₃ and DMF. In FTIR spectra of compound **CC** and **CD** (Fig. 4), the characteristic peak of C=O stretching appeared at 1697 cm⁻¹ and the -C-H alkane stretching peak was observed at 2922 cm⁻¹. Similarly, the peak at 2854 cm⁻¹ indicates the -CH stretch of aldehyde and the aromatic C=C stretch was observed at 1596 and 1464 cm⁻¹. The absorption stretching peak of aromatic -CN was observed at 1378 cm⁻¹, whereas the peak appeared at 781cm⁻¹ indicating the out of plane deformation aromatic -CH.

The molecular ion peak of **CC** appeared at *m/z* 251 and base peak of molecule appeared at *m/z* 208 due to the removal of propyl fragment. The peak at *m/z* 180 is obtained when

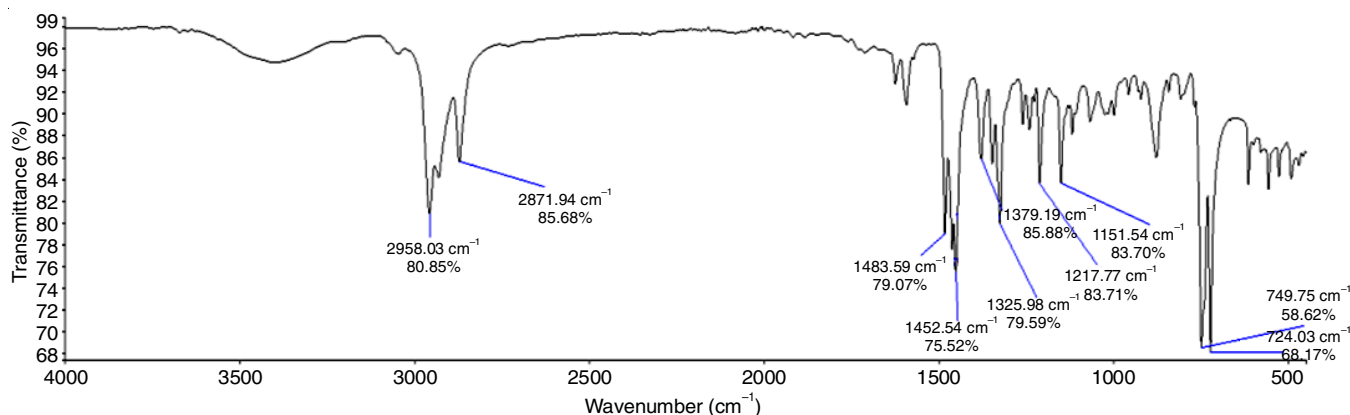


Fig. 1. FT-IR spectrum of 9-butylcarbazole

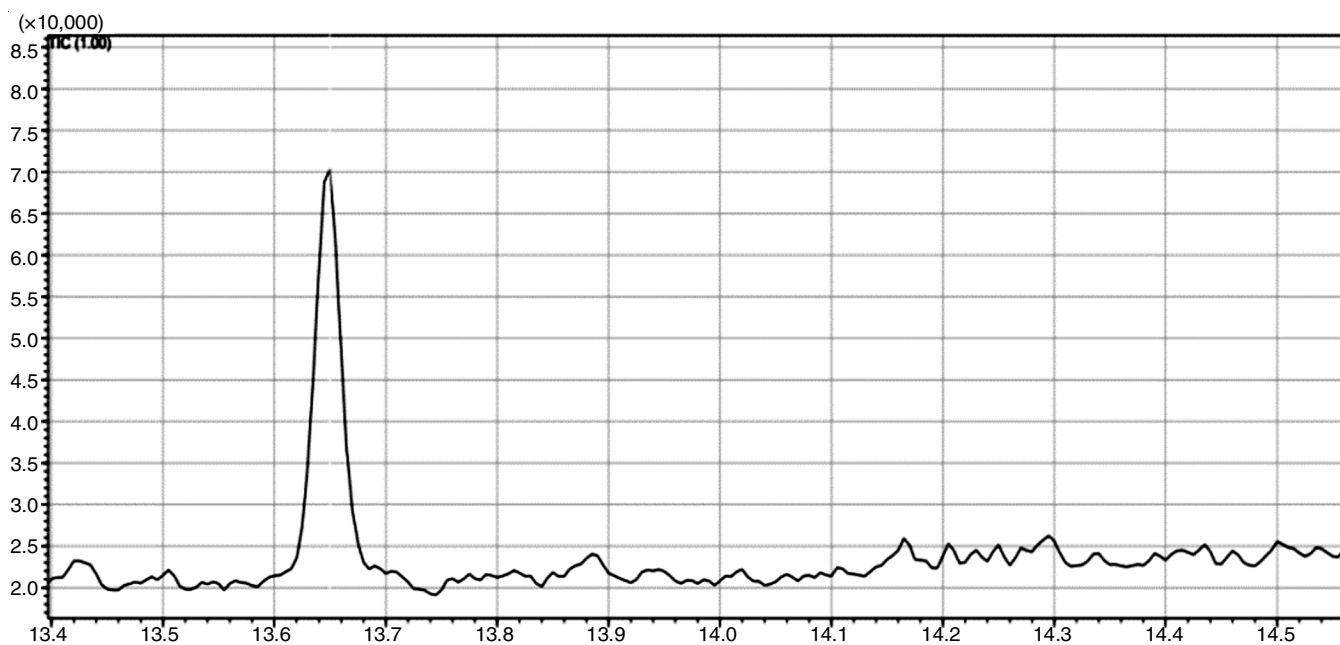


Fig. 2. Shape of gas chromatography peak in close view

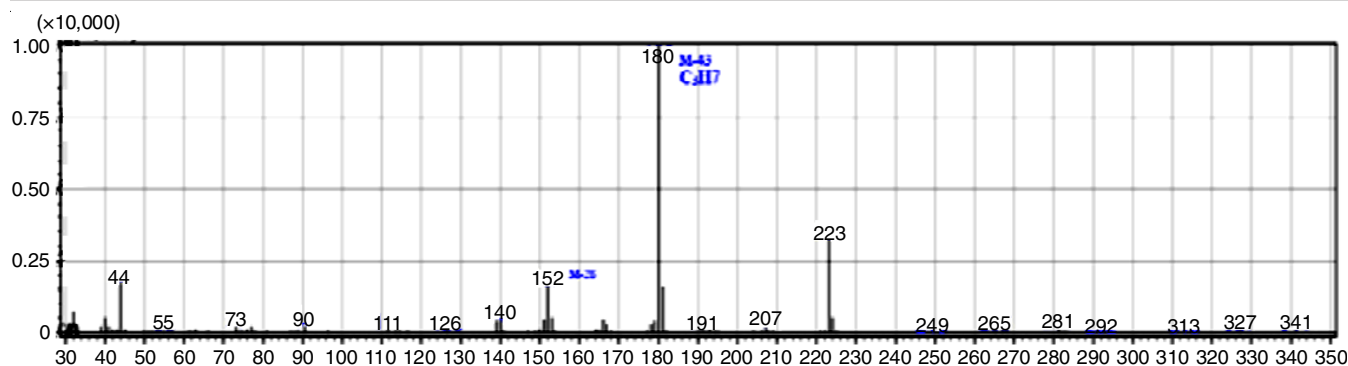


Fig. 3. Mass spectrum of 9-butylcarbazole

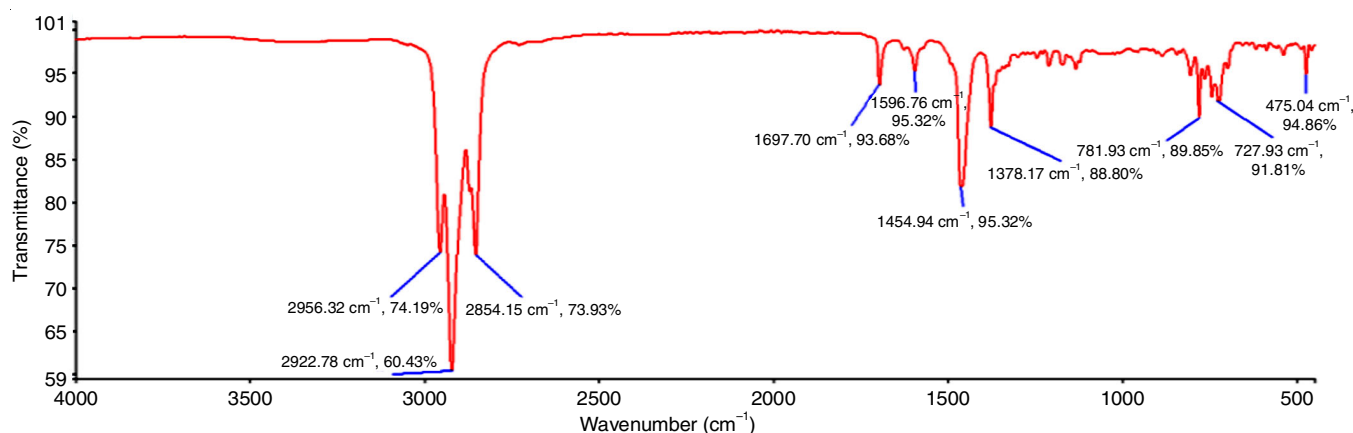


Fig. 4. FTIR spectra of CC and CD

$\text{CH}_2=\text{N}$ fragment is lost, while the peaks at m/z 152 and m/z 151 are observed when $-\text{C}=\text{O}$ and (CHO) fragments are lost, respectively. Molecular weight of **CD** compound is 279 g/mol, therefore molecular ion peak the m/z appeared at m/z 279 and base peak appeared at m/z 236.

CA and DA compounds: For both **CA** and **DA** indicating the characteristic peak of $-\text{C}=\text{O}$ stretching appeared at 1709 cm^{-1} (Fig. 5). The $-\text{C}-\text{H}$ alkane stretching peak was observed at 2958 cm^{-1} , while the aromatic $\text{C}=\text{C}$ stretch was observed at 1527 cm^{-1} and 1458 cm^{-1} . The absorption stretching peak of $-\text{C}=\text{N}$ was observed at 2214 cm^{-1} . The peak appeared at 781 cm^{-1} indicating the out of plane deformation aromatic $-\text{CH}$ and the peaks at 1408 cm^{-1} to 1330 cm^{-1} are due to the $sp^3\text{ C}-\text{H}$ bending.

Fig. 6 shows the UV-visible absorption spectra of **CA** and **DA**. The absorption peak of **CA** can be seen at 239 nm while the absorption region is from 190 nm to 340 nm and **DA** shows

the absorption peak at 338 nm while the absorption region is from 290 nm to 440 nm . The energy band gaps for the synthesized dyes **CA** and **DA** are 5.2 eV and 3.6 eV , respectively as calculated by equation below:

$$E = (1240/\lambda_{\text{max}})\text{ eV so } \lambda_{\text{max}} = 239\text{ nm,}$$

$$E = 1240/239 = 5.2\text{ eV for CA compound}$$

$$E = (1240/\lambda_{\text{max}})\text{ eV so } \lambda_{\text{max}} = 338\text{ nm,}$$

$$E = 1240/338 = 3.6\text{ eV for DA compound}$$

Conclusion

In present work, synthesis of two new carbazole based dyes *viz.* 3-(9-butyl-9H-carbazol-3-yl)-2-cyanoacrylic acid (**CA**) and 3,6-(9-butyl-9H-carbazol-3-yl)-2,2'-cyanoacrylic acid (**DA**) was carried out successfully multistep reactions. The *N*-alkylation of carbazole was carried out in the presence of TBAB as a phase transfer catalyst and butyl bromide as an alkylating

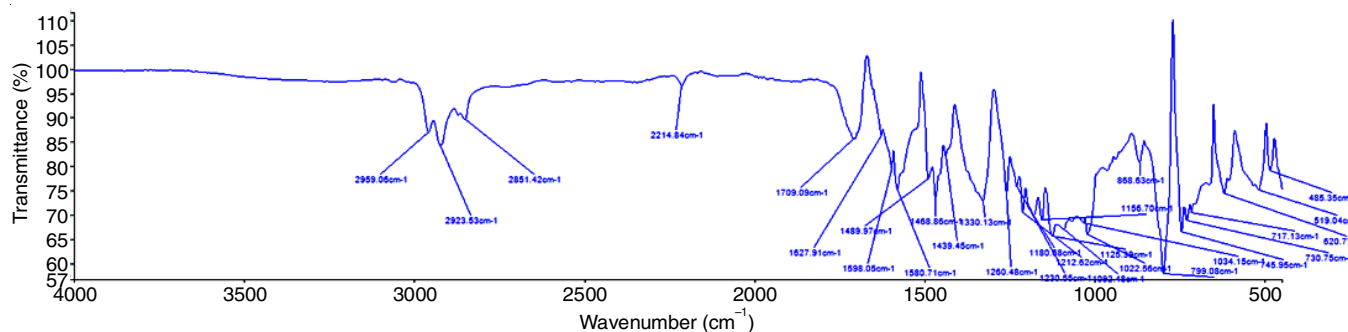


Fig. 5. FT-IR spectra of both CA and DA compounds

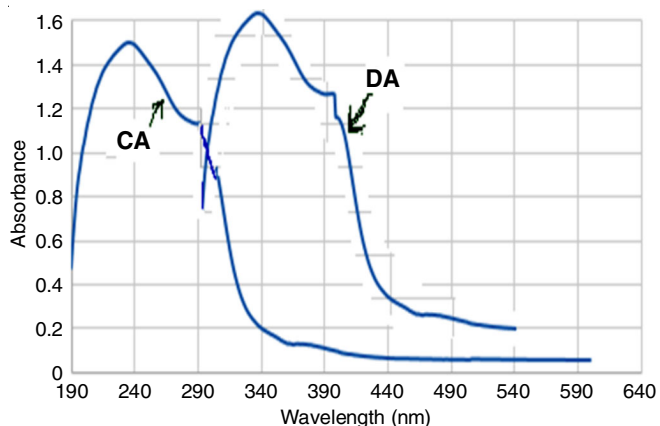


Fig. 6. UV spectra of CA and DA dye compounds

agent followed by the formylation reaction *via* Duff reaction and Vilsmeier-Hack reaction. The different reaction conditions were applied for formylation reaction. The HMTA and 70% acetic acid were used to formylate butyl carbazole, but the results were unsatisfactory, therefore, 9-butyl-9*H*-carbazole-3-carbaldehyde (CC) and 9-butyl-9*H*-carbazole-3,6-dicarbaldehyde (CD) products were obtained *via* Vilsmeier-Hack reaction. Finally, the condensation of CC and CD with cyanoacetic acid in the presence of ammonium acetate as mild base catalyst lead to the formation of new carbazoles CA and DA. The products CA and DA were separated via column chromatography using varying ratios of polar and non-polar solvents, resulting in the earlier elution of CA compared to DA. Purity of all the synthesized compounds were checked by TLC. The characterization of all the synthesized compounds were successfully performed by FT-IR, UV-visible, GC-MS and MS techniques. The dye molecules CA and DA showed the energy band gaps values of 5.2 eV and 3.6 eV, respectively, which can be consider suitable sensitizers for use in the dye-sensitized solar cells (DSSCs).

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. M. Bashir, A. Bano, A.S. Ijaz and B.A. Chaudhary, *Molecules*, **20**, 13496 (2015); <https://doi.org/10.3390/molecules200813496>
2. F.-F. Zhang, C.-H. Zhou and J.-P. Yan, *Chinese J. Org. Chem.*, **30**, 783 (2010).
3. H. Greger, *Phytochem. Rev.*, **16**, 1095 (2017); <https://doi.org/10.1007/s11101-017-9521-5>
4. M. Kobayashi and T. Kuzuyama, *Biomolecules*, **10**, 1147 (2020); <https://doi.org/10.3390/biom10081147>
5. M.S. Shaikh, R. Karpoornath, N. Thapliyal, R.A. Rane, M.B. Palkar, A.M. Faya, H.M. Patel, W.S. Alwan, K. Jain and G.A. Hampannavar, *Anti-Cancer Agents Med. Chem.*, **15**, 1049 (2015); <https://doi.org/10.2174/1871520615666150113105405>
6. H. Wang, Z. Zhang, J. Yu, X. Liu, S. Qu, S. Guang and W. Tang, *J. Mater. Chem. A*, **7**, 31903 (2019); <https://doi.org/10.1039/C9TA08573D>
7. A. Venkateswararao, K.R. Justin Thomas, C.-P. Lee, C.-T. Li and K.-C. Ho, *ACS Appl. Mater. Interfaces*, **6**, 2528 (2014); <https://doi.org/10.1021/am404948w>
8. W. Lee, N. Cho, J. Kwon, J. Ko and J.-I. Hong, *Chem. Asian J.*, **7**, 343 (2012); <https://doi.org/10.1002/asia.201100661>
9. Y. Wang, B. Chen, W. Wu, X. Li, W. Zhu, H. Tian and Y. Xie, *Angew. Chem.*, **126**, 10955 (2014); <https://doi.org/10.1002/ange.201406190>
10. N. Blouin, A. Michaud and M. Leclerc, *Adv. Mater.*, **19**, 2295 (2007); <https://doi.org/10.1002/adma.200602496>
11. M. Reig, J. Puigdollers and D. Velasco, *J. Mater. Chem. C*, **3**, 506 (2015); <https://doi.org/10.1039/C4TC01692K>
12. S. Chen, B. Sun, W. Hong, Z. Yan, H. Aziz, Y. Meng, J. Hollinger, D.S. Seferos and Y. Li, *J. Mater. Chem. C*, **2**, 1683 (2014); <https://doi.org/10.1039/c3tc31753f>
13. N. Grimblat, A.M. Sarotti, T.S. Kaufman and S.O. Simonetti, *Org. Biomol. Chem.*, **14**, 10496 (2016); <https://doi.org/10.1039/C6OB01887D>
14. T. Suresh, R.K. Chitumall, N.T. Hai, J. Jang, T.J. Lee and J.H. Kim, *RSC Adv.*, **6**, 26559 (2016); <https://doi.org/10.1039/C6RA00636A>
15. T. Swetha and S.P. Singh, *Oxford Open Mater. Sci.*, **3**, itac018 (2023); <https://doi.org/10.1093/oxfmat/itac018>
16. W.-C. Chen, S. Nachimuthu and J.-C. Jiang, *Sci. Rep.*, **7**, 4979 (2017); <https://doi.org/10.1038/s41598-017-05408-8>
17. L. Zhang and J.M. Cole, *ACS Appl. Mater. Interfaces*, **7**, 3427 (2015); <https://doi.org/10.1021/am507334m>
18. Y.-J. Xue, M.-Y. Li, X.-J. Jin, C.-J. Zheng and H.-R. Piao, *J. Enzym. Inhib. Med. Chem.*, **36**, 295 (2021); <https://doi.org/10.1080/14756366.2020.1850713>