



Excitation Wavelength and Concentration Dependent Photophysical behaviour of Dipolar Molecular rotors in Solution: Role of Structural Modification

ARIVALAGAN SHABASHINI¹, ANAS FAZAL²,
SUMIT KUMAR PANJA^{2*} and GANESH CHANDRA NANDI^{1*}

¹Department of Chemistry, National Institute of Technology-Tiruchirappalli, Tamil Nadu, India.

²Tarsadia Institute of Chemical Science, Uka Tarsadia University, Maliba Campus, Gopal Vidyanagar, Bardoli, Mahuva Road, Surat, Gujrat, India.

Abstract

The present work demonstrates that the twisted intramolecular charge transfer (TICT) and Intramolecular charge transfer (ICT) process can be achieved by structural modification of a molecule. The DMMC (2-(4-(dimethylamino)benzylidene)malononitrile) and DMDC (2-(4-(dimethylamino)benzylidene)malononitrile) exhibit TICT and ICT state respectively via structural modification at the ground state. Solvent-dependent fluorescence enhancement of these molecules is monitored by comparing the relative intensity of locally excited (LE) and ICT emission band from excitation wavelength and concentration-dependent study. Both molecules display the ICT emission process at excited state depending upon excitation wavelength and concentration in solution. Interestingly, aggregation behaviour is also observed during excitation wavelength and concentration-dependent study in H₂O. Solvent and excitation wavelength-dependent quenching and enhancement of fluorescence properties are also observed. Dipolar state and molecular orientation may play an important role in excitation and concentration-dependent fluorescence process in solution.



Article History

Received: 06 March 2023

Accepted: 25 August 2023

Keywords

Aggregates;
Dipolar molecule;
Intramolecular Charge Transfer (ICT);
Twisted Intramolecular Charge Transfer (TICT).

Introduction

Photoinduced intramolecular charge transfer (ICT) is a fascinating fundamental research field and plays an important role to understand the process

of photosynthesis and vision.¹⁻³ Experimental and theoretical studies of photoinduced ICT processes have been investigated significantly due to their biological importance.⁴⁻⁶ The molecule with strong

CONTACT Sumit Kumar Panja ✉ sumitkpanja@gmail.com 📍 Department of Chemistry, National Institute of Technology-Tiruchirappalli, Tamil Nadu, India.



© 2023 The Author(s). Published by Oriental Scientific Publishing Company

This is an Open Access article licensed under a Creative Commons license: Attribution 4.0 International (CC-BY).

Doi: <https://dx.doi.org/10.13005/OJPS08.02.05>

ICT nature displays large Stokes' shifts with instantaneous quantum yield changes and promote the charge separation.⁷ The photoinduced ICT is used for probing heterogeneous solution structures in various environments and its fluorescence characteristics are strongly depend upon local polarity.⁸ Fluorescence behaviour of ICT molecule is applied in chemical sensors, molecular electronic devices, nonlinear optical materials and solar energy conversion. These are also used for characterizing various host systems, including biomolecular systems, pH, bulk and confined liquids.⁹⁻¹⁴ These applications stimulate the researchers to design and analyse the photophysical properties of ICT molecules in diverse environments.^{7,15-16}

Molecular rotors are ICT based fluorescent molecules, which show a twisting motion of donor group in the excited state while changing the external conditions like temperature, pressure, and solvent polarity.^{17,20} The twisted motion lead to a charge separation in the molecule and results in a red shift emission with narrow band gap.^{18,19} These chromophores are often known as TICT based molecules, which help to observed conformational

alterations in the excited states.²⁰ The twisted intramolecular charge transfer (TICT) hypothesis revealed that the molecule can show interesting intramolecular twisting motion around a single bond and interpreted the anomalous dual emission band of 4-(dimethylamino)benzointrile (DMABN).²¹ Due to the molecular rotation, dual emission bands are observed from locally excited (LE) and TICT states in organic solutions.²² TICT is strongly dependent on the solvent-fluorophore interaction like solvent polarity, hydrogen bonding interaction, and steric hindrance. In TICT state of quasi-planar fluorophore, the donor or acceptor moiety rotate towards a nearly perpendicular alignment upon photoexcitation. The rotation greatly enhances the ICT and the TICT state becomes stabilized in polar solvents due to strong solvent-solute interaction. The phenomena promote the formation of highly reactive charge separated non-emissive species.²³ Tuning the TICT state in organic fluorophores have found numerous applications in functional material field such as bulk viscosity measurement, fluorescent sensors of micro viscosity probe in living cells, probing dynamics of polymer formation and protein aggregation solvent free volume.²⁴⁻²⁷

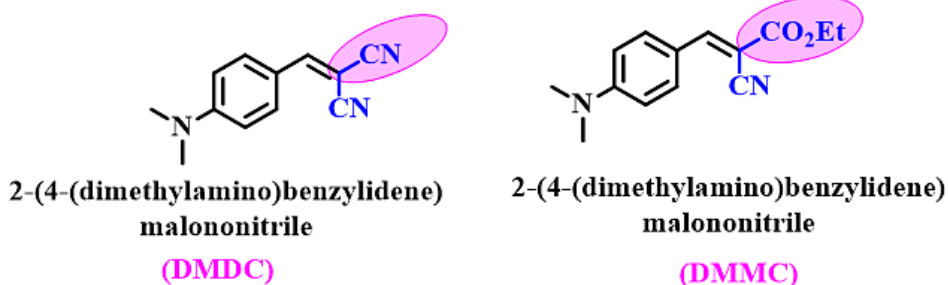


Chart 1: Structural Formula and Abbreviation for Investigated System

Donor-acceptor (D-A) organic compounds are the subject of many interests regarding ICT processes in solution. The photophysical study of D-A systems has drawn considerable attention in applied research fields.^{28,29} The phenomenon of charge transfer processes has been established through theoretical and spectroscopic studies.³⁰⁻³² We are interested to investigated the ground and excited state properties of cyano substituted aromatic compounds (Chart 1) depending upon excitation wavelength

and concentration in solution. These compounds show interesting photophysical properties due to the presence of cyanide groups. These properties can be significantly explored in laser matrix for obtaining lesser band-width.

Experimental Section

Chemicals and Synthesis

All the chemicals (analytical grade) were procured from reputed company and used as received.

Procedure for Synthesis of DMDC and DMMC

A mixture of 4-(Dimethylamino)benzaldehyde (1.0 mmol), manolonitrile derivative (1.01 mmol) and catalyst MP(DNP) (N-methylpiperidine-dinitrophenol MP(DNP): 0.05 mmol) in ethanol containing round bottom flask. The reaction mixture was stirred at room temperature for 2 h. The reaction was monitored using TLC. After completion of the reaction, the solid product was obtained and collected by filtration. During filtration, the solid ppt was washed with water and aqueous ethanol several time. The pure product was obtained and collected from recrystallization from ethanol.³³

Characterization of DMMC

State: Solid; Colour: Yellow; MP.: 122 °C; FTIR (KBr, cm^{-1}): 2945; 3059, 3036, 2938, 2220, 1600, 1542, 1550, 1490; ^1H NMR (500 MHz, CDCl_3): δ (ppm) 8.07 (s, 1H), 7.93 (d, $J = 9.0$ Hz, 2H), 6.69 (d, $J = 9.5$ Hz, 2H), 4.34 (q, $J = 7.5$ Hz, 2H), 3.10 (s, 6H), 1.37 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 164.3, 154.6, 153.6, 134.0, 119.5, 117.7, 111.6, 94.2, 62.1, 40.1, 14.3.

Characterization of DMDC

State: Solid; Colour: Yellow; MP.: 180 °C; FTIR (KBr, cm^{-1}): 3050, 3030, 2939, 2225, 1545, 1555, 1499; ^1H -NMR (300MHz, CDCl_3): δ (ppm) 7.80 (d, $J = 9.0$

Hz, 2H), 7.45 (s, 1H), 6.69 (d, $J = 8.4$ Hz, 2H), 3.16 (s, 6H); ^{13}C -NMR (75MHz, CDCl_3): δ (ppm) 158, 133.7, 131.9, 111.5, 110.9, 40.0.

Instrumentation

UV-Vis and Fluorescence Measurement

The steady state absorption spectra were recorded on Hitachi UV-vis U-3501 spectrophotometer. The fluorescence spectra were recorded on a Perkin-Elmer LS55 fluorescence spectrophotometer equipped with a 10 mm quartz cell and a thermostat bath.

Results and Discussion

UV-Visible Studies in Different Solvents

Initially the UV-Vis spectra of DMMC and DMDC is carried out in different solvents. The normalized spectra of DMMC and DMDC is shown in Figure 1 and 2 respectively. Presence one strong electron donor (NMe_2) and two electron acceptor (CN and CO_2Et) group led to the formation of ICT band in DMMC (Figure 1). The spectral shift is found to be ~ 28 nm from cyclohexane (405 nm) to DMSO (433 nm). The $\pi \rightarrow \pi^*$ electron transition for core benzene ring of the D-A system is found to be very strong compared to weak ground state ICT of DMMC molecule and appeared at 326 nm in cyclohexane and 354 nm in H_2O respectively.

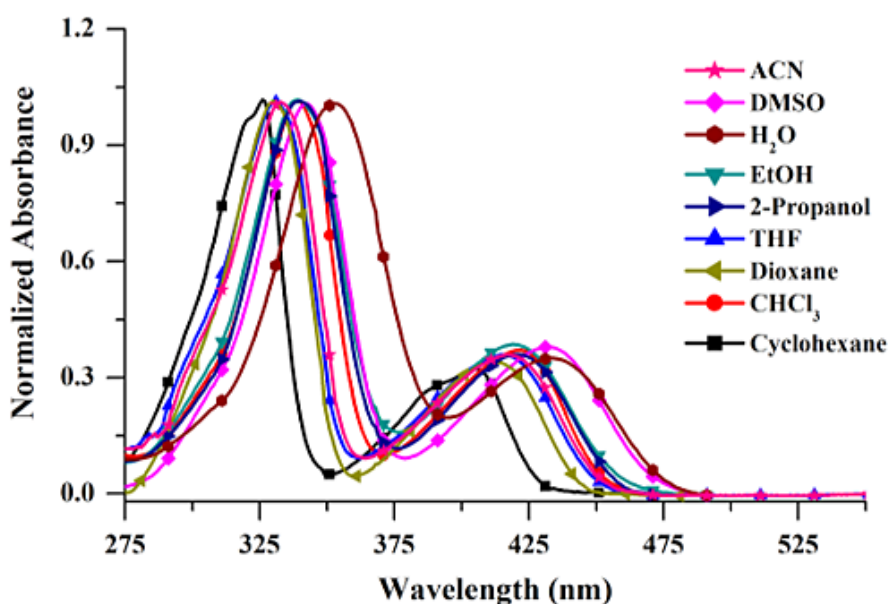


Fig. 1: Normalized UV-Vis spectra of DMMC in solvents (Conc: $1.2 \times 10^{-5}\text{M}$)

Further, strong ICT band is observed in DMDC due to presence of one strong electron donor (-NMe₂) and two electron acceptor (-CN) groups. The relatively strong ICT band of DMDC is shown in Figure 2 and spectral shift is found to be 26 nm from cyclohexane

(414 nm) to DMSO (440 nm). The $\pi \rightarrow \pi^*$ electron transition for core of the donor-acceptor system is found to be very weak compared to strong ICT band and appeared at 340 nm.

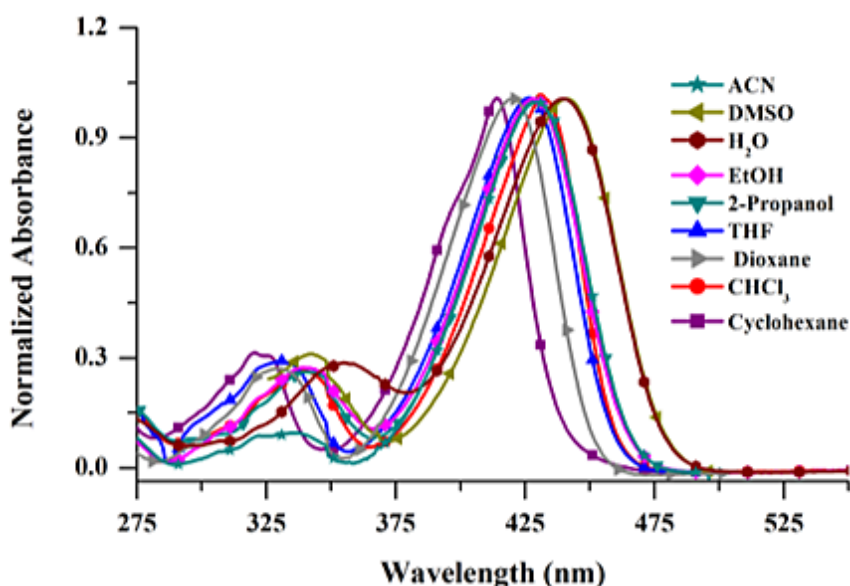


Fig. 2: Normalized UV-Vis spectra of DMDC in solvents (Conc: $1.2 \times 10^{-5} \text{M}$)

The strong $\pi \rightarrow \pi^*$ electron transition of DMDC is due to high electron rich character of benzene ring (Figure 1) and the weak $\pi \rightarrow \pi^*$ electron transition of DMDC is due to quinoid character of the benzene ring (Figure 2).

Fluorescence Studies in Different Solvents at Different Excitation Wavelength

The fluorescent (FL) spectra of DMDC and DMDC are measured in different solvent and shown in figure 3 and 4 respectively at different excitation wavelength. The FL spectra of DMDC in different solvents revealed that an emission band is observed for solvents (Figure 3a-3b) except H₂O (at 330 nm and 420 nm excitation wavelength). The emission band is strong and observed at lower energy (445 nm-500 nm) for DMSO (493 nm), ACN (487 nm), CHCl₃ (473 nm), and hexane (448 nm) (figure 3a-3b) at 330 nm and 420 nm excitation wavelength. In case of H₂O, a strong emission is observed at 542 nm in both excitation wavelength (Figure 3a-3b at 330 nm and 420 nm excitation wavelength).

Interestingly, solvent polarity affects the emission spectra significantly. From nonpolar solvent to polar solvents, emission band is shifted from 449 nm (Hexane) to 493 nm (DMSO) (fig. 3a-3b) except emission band in H₂O. In H₂O, a single emission band is observed at 542 nm (at 420 nm excitation) due to the presence of aggregates. The emission band is observed at 360 nm due to emission from higher excited energy state (S_2) at 330 nm excitation (Fig 3b).

The FL spectra DMDC displays almost similar fluorescence behaviour in solution under identical condition. Emission spectra is observed at range of 350-500 nm depending upon the nature of solvents (Figure 4a-4b, ESI-Table S4) except H₂O (at 330 nm and 420 nm excitation wavelength). The strong emission bands are appeared at lower energy (465-490 nm) for DMSO (495 nm), ACN (490 nm), CHCl₃ (477 nm), and hexane (454 nm) (figure 4a-4b) at 330 nm and 420 nm excitation wavelength respectively. In case of H₂O, a strong

emission band is observed at 488 and 547 nm in both excitation wavelength (Figure 4a-4b at 330 nm and 420 nm excitation wavelength). The overlapped two emission bands are observed at 488 nm and 555 nm with different intensity (at 420 nm and 320 nm excitation, after deconvolution). At 420 nm excitation, the intensity of in 547 nm emission band is slightly lower compare to higher energy (488 nm) emission band in H₂O (Figure 4). Interestingly, the solvent polarity influences the emission spectra significantly. Form nonpolar solvent to polar solvents, emission

band is shifted from 454 nm (Hexane) to 495 nm (DMSO) (fig. 4a-4b) except emission band in H₂O. In H₂O, two emission band is observed at 488 nm and 547 nm (at 420 nm and 310 nm excitation) due to the formation of aggregates. The intensity of these two emission band in H₂O is altered depending upon excitation wavelength (Fig4a-4b). The emission band at 345 nm is observed due to emission from higher excited energy state (S₂) at 310 nm excitation (Fig 3b).

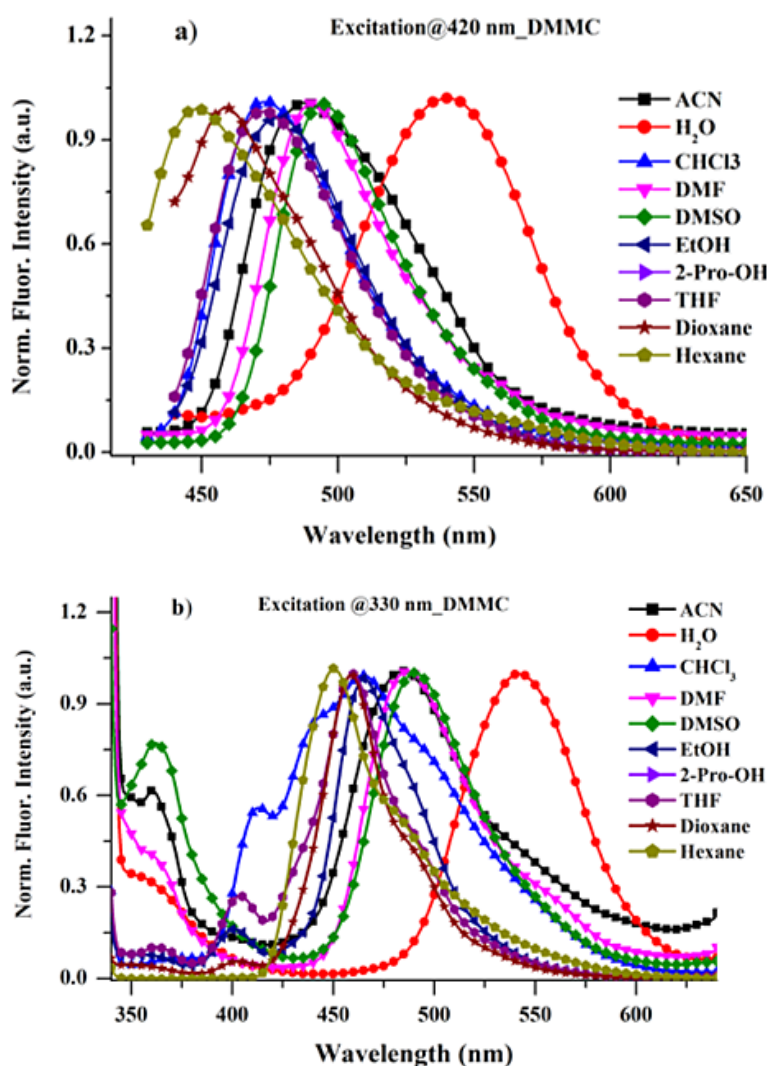


Fig. 3: Fluorescence Spectra of DMMC in different solvents (@420 nm (a) and @330 nm (b)) (Conc: 1.2×10^{-5} M)

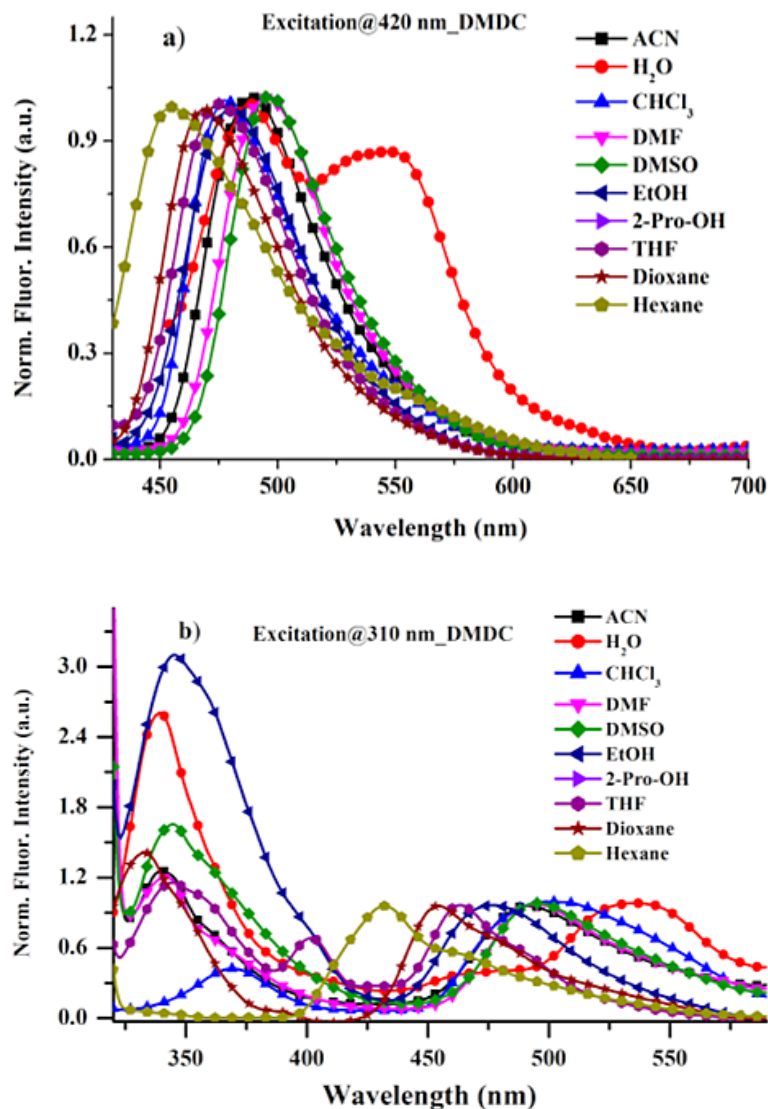


Fig. 4: Fluorescence Spectra of DMDC in different solvents (@420 nm (a) and @310 nm (b)) (Conc: 1.2×10^{-5} M)

Concentration dependent Fluorescence Spectra

Further, the concentration dependent and excitation wavelength dependent fluorescence spectra of DMMC and DMDC are measured in different solvents (Fig. 5a-5b and 6a-6b and ESI-Fig. 1-36). Concentration effect on fluorescence spectra of DMMC is observed at different excitation (at 420 nm and 330 nm excitation). At 420 nm excitation, fluorescence quenching is observed in all solvents except H₂O (Fig. 5 and ESI-Fig.1-9). There is no change of fluorescence spectral pattern at 420

nm excitation for DMMC in solution (ESI Fig.1-9). However, change of spectral pattern is observed at 330 nm excitation in solution (ESI-Fig. 10-18). Interestingly, concentration dependent fluorescence quenching is not observed with the variation of concentration in polar solvents (ESI-Fig.10-14), but observed in non-polar solvents at 330 nm excitation (ESI-Fig. 15-18). Hence, FL spectra DMMC exhibits different emission behaviour depending upon concentration and excitation wavelength in solution.

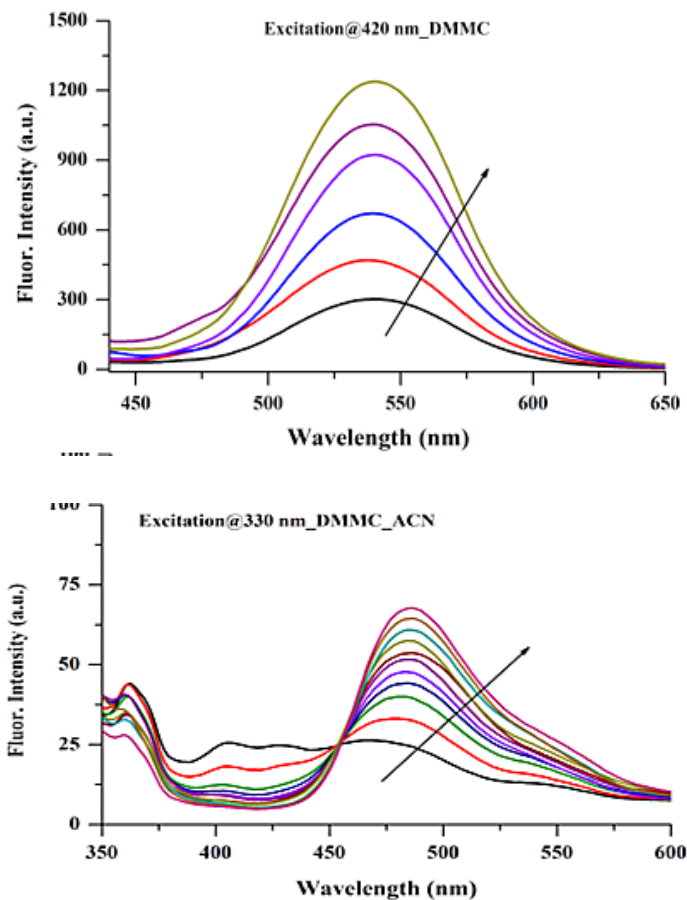


Fig. 5: Concentration dependent Fluorescence Spectra of DMMC in H₂O (@330 nm (left) and in ACN@420 nm(right))

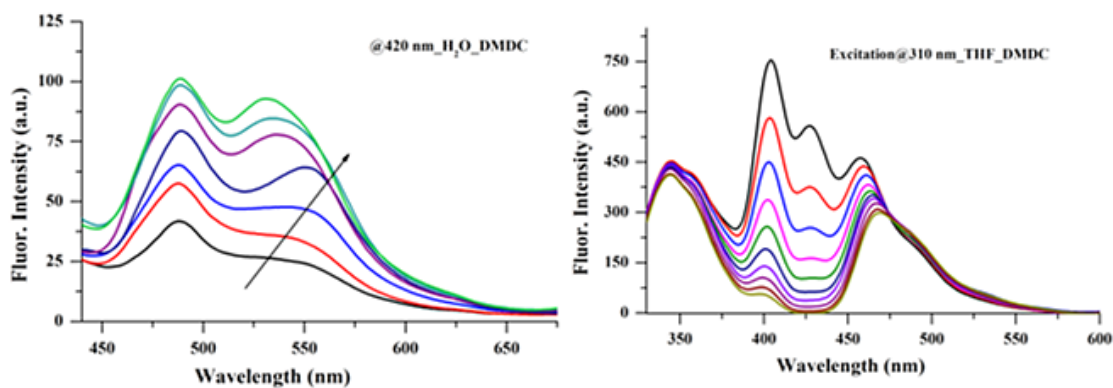


Fig. 6: Concentration dependent Fluorescence Spectra of DMDC in H₂O (@310 nm (left) and THF @310 nm(right))

Concentration effect on fluorescence spectra of DMDC is also investigated at different excitation

(at 420 nm and 310 nm excitation). Excitation at 420 nm resulted in fluorescence quenching in all solvents

except H₂O (Fig. 6a and ESI-Fig.19-36). There is no change of fluorescence spectral pattern at 420 nm excitation for DMDC in solution (ESI Fig.18-27). However, in H₂O, two emission bands are observed and altered depending upon concentration (fig 5a). At 310 nm excitation, fluorescence intensity increases with concentration in polar solvents, whereas solvent dependent fluorescence quenching or enhancement are observed for DMMC at 310 nm excitation. The change of spectral pattern is witnessed at 310 nm excitation in nonpolar solvents (ESI-Fig. 23-27). Remarkably, the fluorescence intensity increases with the variation of concentration in polar solvents (ESI-Fig.18-23), but decreases in non-polar solvents at 330 nm excitation (ESI-Fig. 24-27). From the detailed analysis of FL spectra DMDC, it shows different emission behaviour depending upon concentration and excitation wavelength in solution.

Conclusion

In conclusion, we have demonstrated the TICT and ICT process of dipolar molecule (DMMC and DMDC) in solution at ground state. Excitation wavelength and concentration dependent emission behavior of dipolar molecule (DMMC and DMDC) have been investigated in solution. DMMC shows TICT process but DMDC shows ICT process at ground state in solution. Both molecule show the ICT emission process at excited state depending upon excitation wavelength and concentration. During concentration dependent study, concentration dependent quenching is observed in all solvents except H₂O at

420 nm excitation for DMDC and DMMC in solution. Concentration dependent quenching is not observed in polar solvent but observed in nonpolar solvent at 330 nm excitation for DMDC and DMMC in solution. Further, interesting factor is DMMC shows single emission band is observed at 542 nm due to the presence of aggregates. But in case of DMDC in H₂O, two emission band is observed at 488 nm and 547 nm due to the presence of ICT emission and aggregates. Interestingly, solvent polarity effects the emission spectra significantly. From nonpolar solvent to polar solvents, emission band is shifted from ~449 nm (Hexane) to ~ 493 nm (DMSO) except emission band in H₂O. These different ground and excited state of DMMC and DMDC are obtained due to slight modification of structural and dipolar state.

Acknowledgment

GCN and AS are grateful to DST-SERB (Early Career Research Award; ECR/2018/001462) and NIT-Trichy (MHRD) for research grants and fellowship. SKP acknowledges Tarsadia Institute of Chemical Science, Uka Tarsadia University, Surat-394350, Gujrat, India for providing the infrastructure and instrument facilities.

Funding

No

Conflict of Interest

No

References

1. Rappoport D, Furche F. Photoinduced Intramolecular Charge Transfer in 4-(Dimethyl) aminobenzonitrile - A Theoretical Perspective. *J Am Chem Soc* 2004;126:1277–84. <https://doi.org/10.1021/ja037806u>.
2. Rettig W. Charge Separation in Excited States of Decoupled Systems—TICT Compounds and Implications Regarding the Development of New Laser Dyes and the Primary Process of Vision and Photosynthesis. *Angew Chemie Int Ed English* 1986;25:971–88. <https://doi.org/10.1002/anie.198609711>.
3. Zigmantas D, Hiller RG, Yartsev A, Sundström V, Polívka T. Dynamics of excited states of the carotenoid peridinin in polar solvents: Dependence on excitation wavelength, viscosity, and temperature. *J Phys Chem B* 2003;107:5339–48. <https://doi.org/10.1021/jp0272318>.
4. Siders P, Cave RJ, Marcus RA. A model for orientation effects in electron-transfer reactions. *J Chem Phys* 1984;81:5613–24. <https://doi.org/10.1063/1.447665>.
5. Guchhait B, Pradhan T, Biswas R. Effects of acid concentration on intramolecular charge transfer reaction of 4-(azetidiny) benzonitrile

- in solution. *J Chem Sci* 2014;126:55–63. <https://doi.org/10.1007/s12039-013-0558-8>.
6. Eads DD, Dimer BG, Fleming GR. A subpicosecond, subnanosecond and steady-state study of diffusion-influenced fluorescence quenching. *J Chem Phys* 1990;93:1136–48. <https://doi.org/10.1063/1.459177>.
 7. Lee S, Jen M, Jang T, Lee G, Pang Y. Twisted intramolecular charge transfer of nitroaromatic push–pull chromophores. *Sci Rep* 2022;12:1–11. <https://doi.org/10.1038/s41598-022-10565-6>.
 8. Pradhan T, Ghoshal P, Biswas R. Excited state intramolecular charge transfer reaction in binary mixtures of water and tertiary butanol (TBA): Alcohol mole fraction dependence. *J Phys Chem A* 2008;112:915–24. <https://doi.org/10.1021/jp0770460>.
 9. Grabowski ZR, Rotkiewicz K, Rettig W. Structural Changes Accompanying Intramolecular Electron Transfer: Focus on Twisted Intramolecular Charge-Transfer States and Structures. *Chem Rev* 2003;103:3899–4031. <https://doi.org/10.1021/cr940745l>.
 10. He C, He Q, He Y, Li Y, Bai F, Yang C, *et al.* Organic solar cells based on the spin-coated blend films of TPA-th-TPA and PCBM. *Sol Energy Mater Sol Cells* 2006;90:1815–27. <https://doi.org/10.1016/j.solmat.2005.11.004>.
 11. Santhosh K, Samanta A. Modulation of the excited state intramolecular electron transfer reaction and dual fluorescence of crystal violet lactone in room temperature ionic liquids. *J Phys Chem B* 2010;114:9195–200. <https://doi.org/10.1021/jp1039805>.
 12. Datta A, Mandal D, Pal SK, Bhattacharyya K. Intramolecular charge transfer processes in confined systems. Nile red in reverse micelles. *J Phys Chem B* 1997;101:10221–5. <https://doi.org/10.1021/jp971576m>.
 13. Biswas R, Rohman N, Pradhan T, Buchner R. Intramolecular charge transfer reaction, polarity, and dielectric relaxation in AOT/water/heptane reverse micelles: Pool size dependence. *J Phys Chem B* 2008;112:9379–88. <https://doi.org/10.1021/jp8023149>.
 14. Pradhan T, Gazi HAR, Guchhait B, Biswas R. Excited state intramolecular charge transfer reaction in non-aqueous reverse micelles: Effects of solvent confinement and electrolyte concentration#. *J Chem Sci* 2012;124:355–73. <https://doi.org/10.1007/s12039-011-0149-5>.
 15. Kovalenko SA, Farztdinov VM, Schanz R, Hennig H, Ernsting NP. Femtosecond relaxation of photoexcited p-nitroaniline in water: solvation internal conversion and cooling. *Conf Quantum Electron Laser Sci - Tech Dig Ser* 2000:195.
 16. Singh C, Modak B, Mondal JA, Palit DK. Ultrafast twisting dynamics in the excited state of auramine. *J Phys Chem A* 2011;115:8183–96. <https://doi.org/10.1021/jp2020287>.
 17. Lee S.-C., Heo J, Woo HC, Lee JA, Seo YH, Lee CL, Kim S, Kwon OP. Fluorescent Molecular Rotors for Viscosity Sensors. *Chemistry A European Journal* 2018; 24:13706-13718. <https://doi.org/10.1002/chem.201801389>
 18. Li S, Shi N, Zhang M, Chen Z, Xia D, Zheng Q, *et al.* A novel benzotriazole derivate with Twisted intramolecular charge transfer and Aggregation Induced emission features for proton determination. *Spectrochim Acta - Part A Mol Biomol Spectrosc* 2022;269:120780. <https://doi.org/10.1016/j.saa.2021.120780>.
 19. Mei J, Hong Y, Lam JWY, Qin A, Tang Y, Tang BZ. Aggregation-induced emission: The whole is more brilliant than the parts. *Adv Mater* 2014;26:5429–79. <https://doi.org/10.1002/adma.201401356>.
 20. Haidekker MA, Nipper M, Mustafic A, Lichlyter D, Dakanali M, Theodorakis EA. Dyes with Segmental Mobility: *Molecular Rotors*. 2010. https://doi.org/10.1007/978-3-642-04702-2_8.
 21. Rotkiewicz K, Grellmann KH, Grabowski ZR. Reinterpretation of the anomalous fluorescence of p-n,n-dimethylamino-benzonitrile. *Chem Phys Lett* 1973;19:315–8. [https://doi.org/10.1016/0009-2614\(73\)80367-7](https://doi.org/10.1016/0009-2614(73)80367-7).
 22. Li J, Yang C, Peng X, Chen Y, Qi Q, Luo X, *et al.* Stimuli-responsive solid-state emission from: O-carborane-tetraphenylethene dyads induced by twisted intramolecular charge transfer in the crystalline state. *J Mater Chem C* 2017;6:19–28. <https://doi.org/10.1039/>

- c7tc03780e.
23. Wang C, Qiao Q, Chi W, Chen J, Liu W, Tan D, *et al.* Quantitative Design of Bright Fluorophores and AIEgens by the Accurate Prediction of Twisted Intramolecular Charge Transfer (TICT). *Angew Chemie* 2020;132:10246–58. <https://doi.org/10.1002/ange.201916357>.
 24. Wang C, Chi W, Qiao Q, Tan D, Xu Z, Liu X. Twisted intramolecular charge transfer (TICT) and twists beyond TICT: From mechanisms to rational designs of bright and sensitive fluorophores. *Chem Soc Rev* 2021;50:12656–78. <https://doi.org/10.1039/d1cs00239b>.
 25. Betzig E. Single Molecules, Cells, and Super-Resolution Optics (Nobel Lecture). *Angew Chemie - Int Ed* 2015;54:8034–53. <https://doi.org/10.1002/anie.201501003>.
 26. Wysocki LM, Lavis LD. Advances in the chemistry of small molecule fluorescent probes. *Curr Opin Chem Biol* 2011;15:752–9. <https://doi.org/10.1016/j.cbpa.2011.10.013>.
 27. Huang B, Babcock H, Zhuang X. Breaking the diffraction barrier: *Super-resolution imaging of cells*. *Cell* 2010;143:1047–58. <https://doi.org/10.1016/j.cell.2010.12.002>.
 28. Sharma A, Thomas KRJ, Kesavan KK, Siddiqui I, Ram Nagar M, Jou JH. Effect of Cyano on the Functional Properties of Phenanthroimidazole-Substituted Carbazole Derivatives. *ACS Appl Electron Mater* 2021;3:3876–88. <https://doi.org/10.1021/acsaelm.1c00482>.
 29. Zhou L, Xu D, Gao H, Han A, Yang Y, Zhang C, *et al.* Effects of cyano groups on the properties of thiazole-based β -ketoiminate boron complexes: Aggregation-induced emission and mechanofluorochromism. *RSC Adv* 2016;6:69560–8. <https://doi.org/10.1039/c6ra14595g>.
 30. Deibe C, Strobe T, Dyakonov V. Role of the charge transfer state in organic donor-acceptor solar cells. *Adv Mater* 2010;22:4097–111. <https://doi.org/10.1002/adma.201000376>.
 31. Hou Y, Zhang X, Chen K, Liu D, Wang Z, Liu Q, *et al.* Charge separation, charge recombination, long-lived charge transfer state formation and intersystem crossing in organic electron donor/acceptor dyads. *J Mater Chem C* 2019;7:12048–74. <https://doi.org/10.1039/c9tc04285g>.
 32. Hussain M, El-Zohry AM, Hou Y, Toffoletti A, Zhao J, Barbon A, *et al.* Spin-Orbit Charge-Transfer Intersystem Crossing of Compact Naphthalenediimide-Carbazole Electron-Donor-Acceptor Triads. *J Phys Chem B* 2021;125:10813–31. <https://doi.org/10.1021/acs.jpcc.1c06498>.
 33. Panja SK, Dwivedi N, Saha S. First report of the application of simple molecular complexes as organo-catalysts for Knoevenagel condensation. *RSC Adv* 2015;5:65526–31. <https://doi.org/10.1039/c5ra09036a>.