

Research & Reviews: Journal of Chemistry

Donor-Acceptor Conjugated Molecules: Charge Transfer, Mechanism and Significance

Naresh Kumar, Jagdeep Kumar and Prasanta Kumar Hota*

Department of Chemistry, School of Sciences, Hemwati Nandan Bahuguna Garhwal University, Srinagar Garhwal, Uttarakhand, India

REVIEW ARTICLE

Received date: 03/09/2015

Accepted date: 23/12/2015

Published date: 28/12/2015

*For Correspondence

Prasanta Kumar Hota, Department of Chemistry, School of Sciences, Hemwati Nandan Bahuguna Garhwal University, Srinagar Garhwal, Uttarakhand, India, Tel: 911346252229

E-mail: p.hota@hnbgu.ac.in

Keywords: Charge transfer, Fluorescence, Fluorescent probe, Donor-acceptor molecules.

ABSTRACT

Donor-acceptor molecules with charge transfer behavior have received a great deal of attention because of their critical role in industrial and biological applications. In this context, numerous studies on the donor-acceptor molecules were carried out in recent years. In this article, some of the mentioned aspects have been discussed in detail.

INTRODUCTION

Donor-acceptor based conjugated linear polyenes in the series of retinoids, carotenoids play important role in the structure and function of retinal-bound photoreceptor^[1-3]. Such molecules are sensitive to their local environment and thus widely used in other applications such as optoelectronic device^[4-7], diagnostic and optical imaging application etc.^[8-10]. Donor-acceptor based molecules with varied optical properties (*i.e.*, wavelength, light intensity, etc.) are used as a probe for monitoring biological events. In this regards, a great deal of attention has been given to understand the optical properties of donor-acceptor conjugated system^[11-14]. In general, upon absorption of photon, linear polyenes get excited to their locally planar excited (LE) state, which further undergoes carbon-carbon double bond twisting to yield the perpendicular species (phantom state, P*) from where the *cis*, *trans*-isomerization occurs^[11,13]. Alternatively, the molecule after excited to the planar LE state, a partial charge separation can occurs upon twisting around the bond linking to the electron donor and electron acceptor groups^[15-26]. A considerable energy gap between the P* and the charge transfer (CT) excited states of the molecule leads to drastic changes in its optical properties. Substituent can raise or lower the torsional energy barrier and thus the optical properties of conjugated molecules is altered. Thus, the optical properties of such polyenes are highly dependent upon the order of the singlet excited state and the involvement of charge transfer excited state specie. The nature of energy barrier to the excited state and the charge transfer specie are believed to play important role in the photoprocesses of linear polyenes and most likely in the natural photoreceptors such as retinal-bound photoreceptor, chlorophyll, etc. (**Figure 1**).

CHARGE TRANSFER IN DONOR-ACCEPTOR SYSTEM

Long year back, Lippert *et al.*^[27] had reported dual fluorescence in N,N-dimethyl aminobenzonitrile (DMABN) due to solvent-induced reversal of excited states L_a and L_b . Later on, dual emission in such molecule was explained interms of internal twisting of the dimethylamino group, orthogonal conformation of the dimethylamino group, rehybridisation intramolecular charge transfer (RICT), configurational change of the amino nitrogen from pyramidal to planar geometry^[28-30] etc. It is also shown that in such

molecules, the dipole moment of excited state increases from 10D to 20D with increasing solvent polarity. Recent studies on DMABN indicates the dependency of charge transfer excited state on the solvent polarity, viscosity and temperature of the medium [31].

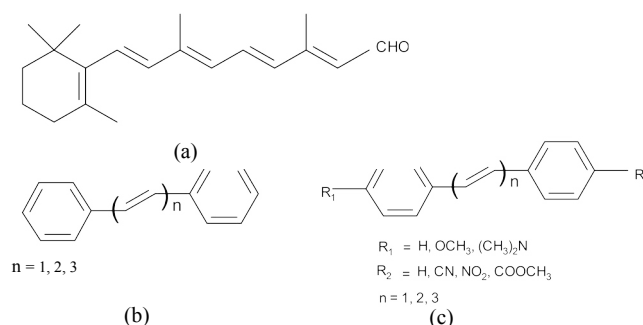
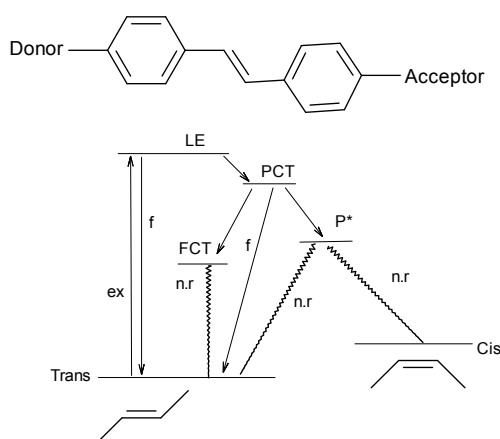


Figure 1. Structure of (a) all-trans Retinal, (b) Diphenyl polyenes, stilbene (n=1), diphenyl butadiene (n=2), diphenyl hexatriene (n=3), (c) Donor-acceptor substituted diphenyl polyenes.

Like DMABN, upon excitation to singlet excited state, the donor-acceptor diphenylpolyenes form intramolecular charge transfer excited state (ICT) [16-26]. The ICT state is highly dependent upon the solvent polarity and the substituent present on phenyl ring. In non-polar solvents, the excited state of DPP decays to the perpendicular (P*) state from where *trans-cis* isomerisation occurs. In polar solvents, due to twist over the single bond, a more stabilised charge transfer state forms, which relaxed directly to the ground state. Thus, the photo process is highly dependent on the charge transfer character of donor-acceptor system. Earlier, it has been shown that N,N-dimethylamino-*p*-cyano stilbene exhibits dual fluorescence due to the existence of planar locally excited (LE) state and intramolecular charge transfer (ICT) excited states. In such system, the ICT state is found to be the main fluorescent specie [16-20]. It is shown that for DCS, single excited state specie is found in non-polar solvents, whereas, it shows two excited state species in polar solvents. In such system a blue-shifted fluorescence maximum with enhanced quantum yield (Φ_f) is observed in ethanol-methanol matrix at 77 K. This is due to restriction of single bond rotation in solid state environment.

In order to understand the role of withdrawing group in CT state formation, the excited state properties of several other stilbene molecule including nitro substitution were studied [21-26]. In nitro substituted DPP, a highly polar charge transfer excited state form that induces large solvatochromic fluorescence behavior in DPP. In such systems, the Φ_f increases with increasing solvent polarity. In case of ethenyl indole, which has restricted single bond rotation around the phenyl and amino group, a highly fluorescent specie is found even in non-polar solvent and the fluorescence efficiency decreases in polar solvent. Interestingly, such ethenyl shows very low efficiency towards photoisomerization (P* excited state pathway). It is shown that Φ_f and photoisomerization quantum yield (Φ_{tc}) are highly dependent upon the solvent polarity. On increasing the solvent polarity, Φ_f increases, while Φ_{tc} decreases. Various photophysical studies show that these compounds contain three type of excited species, namely locally excited (LE), partially charge transfer excited (PCT) and fully charge transfer excited (FCT) states that are highly dependent on the magnitude of solvent polarity and the electronic nature of the substituent present on the phenyl ring (**Scheme 1**). Further, a blue-shifted emission maximum is found for DPP at 77 K and in solid state, which suggested that emission originates from charge transfer excited state.



Scheme 1. Photoprocesses in donor-acceptor substituted stilbene like molecules, locally excited state (LE), Partially charge transfer excited state (PCT), Fully charge transfer excited state (FCT), Phantom excited state (P*), excitation (ex), fluorescence (f), non-radiative (n.r) pathway.

PHOTOCHEMISTRY OF DIPHENYL POLYENES (DPP)

Photoisomerisation of diphenylpolyenes has been extensively studied due to its similarity as a model compounds to retinal and carotenoids. Among diphenylpolyenes, isomerisation of *trans*-stilbene has been investigated in detail. Saltiel and his co-workers [11,13] have proposed a first mechanism of *trans-cis* photoisomerisation for stilbene by using one dimensional reaction

coordinate. In this model, the torsional angle about the C=C double bond plays important role in the photoisomerisation process and is highly dependent upon the solvent polarity and substituent present in the polyene. Later on, several other mechanism were proposed for substituted donor-acceptor stilbenes [32-35]. In presence of a weak donor and weak acceptor substituents, the singlet excited state (S_1) is weakly polar than phantom excited state and, hence, it stabilised less by the polar solvent. Thus, the rate of photoisomerisation increases ($S_1 \rightarrow {}^1P^*$) in polar solvents. On the other hand, in presence of a strong donor substituent, the singlet excited state is more polar as compared to the phantom excited state (P^*) and, hence, molecules predominantly participate in charge transfer phenomena. This leads to decrease in its photoisomerisation efficacy. In third category, stilbenes with strong donor-acceptor substituent, exhibits a highly polarised excited state and do not participates in photoisomerisation process. Thus, the photoisomerisation efficacy highly dependent upon the solvent and substituent present on it.

APPLICATION

The optical properties of π -conjugated donor-acceptor organic molecules are highly sensitive to their surrounding environment. Thus, many of these compounds are used in optoelectronic device application such as luminescent material, organic light-emitting diodes (OLEDs), nonlinear optics (NLO), dye-sensitized solar cell are few of them. For example, *p*-cyano substituted stilbenes are used in organic optoelectronics [4,6], diaryl ethenes are used in memories and switches [7], π -conjugated semiconducting polymers based on thiophene, isoindigo, stilbene find application in organic solar cells [36-39] and act as an efficient photo-chromic material [2], polymethine cyanine dyes are well known for their use in photography [40]. In addition, some of these compounds are used as a fluorescence probe for studying the protein, antibodies, peptides, nucleic acids, lipid, cell imaging, immunoassay, cell staining, cancer imaging as well as characterization of interface of proteins and organized assemblies [18,22,41-43]. Recently, ethenyl indoles are used for the detection of protein, bovine serum albumin [44]. Similarly, heterocyclic based conjugated systems act as a sensor for the detection of ions [44]. The absorption and fluorescence wavelength data are also used to explain the wavelength / colour regulation mechanism in biological photoreceptors. Retinal-bound photoreceptor is one of such example, in which, the colour regulation mechanism is explained in terms of charge transfer phenomena that involved in biological energy- and sensory-transductions [42] (Figures 2 and 3).

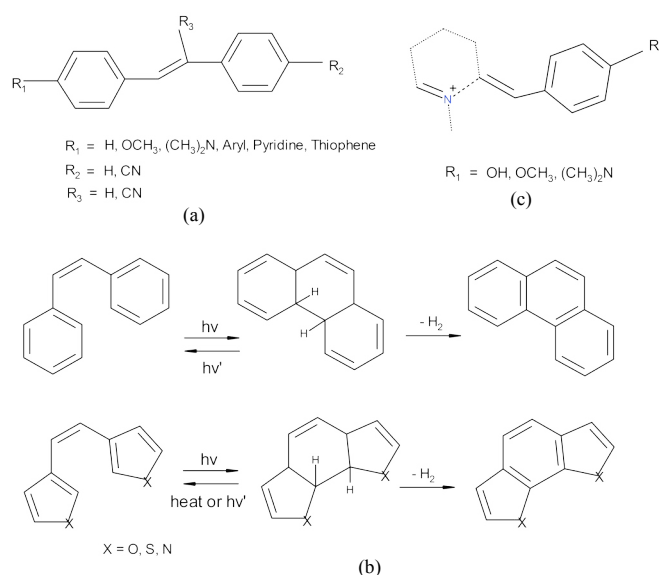


Figure 2. Structure of, (a) substituted stilbene framework that are used to build molecules for organic optoelectronics, (b) Reversible reaction of Stilbene and heterocyclic based conjugated molecules that act as photoswitches, (c) Cyanine dyes that are used in photography.

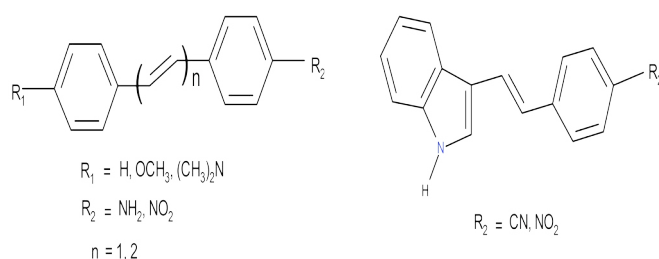


Figure 3. Donor-Acceptor substituted diphenyl polyenes and ethenyl indoles that act as a fluorescent probe for studying membrane, lipid, organized assembly and protein detection.

FUTURE PERSPECTIVES

From the above discussion, it is clear that donor-acceptor conjugated linear polyenes play important role in several areas of chemistry, biology, medicinal and industrial applications. Donor-acceptor conjugated molecules with varied optical properties are

used as a probe for tracking the biological events. These molecules are better fluorescent and can be easily synthesized. Thus, there is a constant demand for development of novel molecules based on conjugated systems with greater efficiency that find application in above discussed area.

ACKNOWLEDGEMENTS

PKH gratefully acknowledges UGC, New Delhi for providing UGC-FRPS start-up grants. The authors are also thankful to the reviewers for their valuable comments and suggestions.

REFERENCES

1. Rando R R. The biochemistry of the visual cycle. *Chem Rev* 2001; 101: 1881- 1896.
2. Dugave C, Demange L. *Cis-Trans* isomerisation of organic molecules and biomolecules: Implications and applications. *Chem Rev* 2003; 103: 2475-2532.
3. Singh AK, Hota PK. Development of bacteriorhodopsin analogues and studies of charge separated excited states in the photoprocesses of linear polyenes. *Photochem Photobiol* 2007; 83: 50-62.
4. An BK, Gierschner J, Park SY. π -Conjugated cyanostilbene derivatives: A unique self-assembly motif for molecular nanostructures with enhanced emission and transport. *Acc Chem Res* 2012; 45: 544-554.
5. Chung JW, Yoon SJ, Lim SJ, An BK, Park SY. Dual-Mode Switching in Highly Fluorescent Organogels: Binary Logic Gates with Optical/Thermal Inputs. *Angew Chem Int Ed* 2009; 48: 7030–7034.
6. Kim JH, Chung JW, Jung Y, Yoon SJ, An BK, et al. High Performance n-Type Organic Transistors Based on Distyrylthiophene Derivative. *J Mater Chem* 2010; 20: 10103–10106.
7. Irie M. Diarylethenes for Memories and Switches. *Chem Rev* 2000; 100: 1685-1716.
8. Lukyanov KA, Chudakov DM, Lukyanov S, Verkhusha V. Innovation: photoactivatable fluorescent protein. *Nat Rev Mol Cell Biol* 2005; 6: 885–891.
9. Liu L, Shao M, Dong X, Yu X, Liu Z, et al. Homogeneous immunoassay based on two-photon excitation fluorescence resonance energy transfer. *Anal Chem* 2008; 80: 7735-7741.
10. Kobayashi H, Ogawa M, Alford R, Choyke PL, Urano Y. New strategies for fluorescent probe design in medical diagnostic imaging. *Chem Rev* 2010; 110: 2620-2640.
11. Saltiel J, Sun YP. *Cis-trans* isomerisation of C=C double bonds. In *Photochromism: Molecules and systems*. Durr H, Bouas-Laurent H (ed) Elsevier, New York.
12. Waldeck DH. Photoisomerisation dynamics of stilbenes. *Chem Rev* 1991; 91: 415-436.
13. Saltiel J, Sears DF, Jr, Ko DH, Park DM. *Cis-trans*-isomerisation of alkenes. In *CRC Handbook of organic photochemistry & photobiology*. Horspool WHM, Song PS (ed) CRC press, Boca Raton, New York.
14. Liu RSH, Hammond GS. Photochemical reactivity of polyenes: from dienes to rhodopsin, from microseconds to femtoseconds. *Photochem Photobiol Sci* 2003; 2: 835-844.
15. Viel A, Krawczyk RP, Manthe U, Domcke W. The sudden-polarisation effect and its role in the ultrafast photochemistry of ethene. *Angew Chem Int Ed* 2003; 42: 3434-3436.
16. Rettig W, Majenz W. Competing adiabatic photoreaction channels in stilbene derivatives. *Chem Phys Lett* 1989; 154: 335-341.
17. Abraham E, Oberle J, Jonusauskas G, Lapouyade R, Rulliere C. Photophysics of 4-dimethylamino-4'-cyanostilbene and model compounds: dual excited states revealed by sub-picosecond transient absorption and Kerr ellipsometry. *Chem Phys* 1997; 214: 409-423.
18. Singh AK, Kanvah S. Photophysical studies of substituted 1,2-diarylethenes: Twisted intramolecular charge transfer fluorescence in dimethoxy cyano-substituted 1,2-diarylethene. *J Chem Soc Perkin Trans* 2001; 2: 395-401.
19. Pines D, Pines E, Rettig W. Dual fluorescence and excited state structural relaxations in donor-acceptor stilbenes. *J Phys Chem A* 2003; 107: 236-242.
20. Gezawy HE, Rettig W, Lapouyade R. Model studies of spectral and photophysical characteristics of donor-acceptor-polyenes: dimethylamino-cyano-diphenylbutadiene. *Chem Phys Lett* 2005; 401: 140-148.
21. Letard JF, Lapouyade R, Rettig W. Structure-photophysics correlations in a series of 4-(Dialkylamino) stilbenes: Intramolecular charge transfer in the excited state as related to the twist around the single bonds. *J Am Chem Soc* 1993; 115: 2441-2447.
22. Singh AK, Manjula D, Kanvah S. α,ω -Diphenylpolyenes capable of exhibiting twisted intramolecular charge transfer fluorescence: A fluorescence and fluorescence probe study of nitro- and nitrocyano-substituted 1,4- diphenylbutadienes. *J Phys Chem A* 2000; 104: 464-471.

23. Singh AK, Hota PK. Photoreactivity of donor-acceptor ethenes. *Indian J Chem* 2003; 42B: 2048-2053.
24. Singh AK, Hota PK. Fluorescence and photoisomerization studies of *p*-nitrophenyl substituted indolic ethenes. *J Phys Org Chem* 2006; 19: 43-52.
25. Sonoda Y, Shimoi Y, Goto M, Tohnai N, Kanesato M. Fluorescence properties of (*E,E,E*)-1,6-Di(*n*-naphthyl)-1,3,5-hexatriene (*n*=1,2): Effect of internal rotation. *J Phys Chem A* 2013; 117: 566-578.
26. Lin CK, Wang YF, Cheng YC, Yang JS. Multisite constrained model of *trans*-4-(*N,N*-Dimethylamino)-4-nitrostilbene for structural elucidation of radiative and nonradiative excited state. *J Phys Chem A* 2013; 117: 3158-3164.
27. Lippert E, Luder W, Moll F, Nagele W, Boos H, et al. Umwandlung von Elektronenanregungsenergie. *Angew Chem* 1961; 73: 695-706.
28. Al-Hassan KA, Azumi T, Rettig W. The role of the angle of pre twist of some molecules forming twisted intramolecular charge transfer (TICT) state in polymer matrices. *Chem Phys Lett* 1993; 206: 25-29.
29. Il'ichev YV, Kuhnle W, Zachariasse KA. Intramolecular charge transfer in dual fluorescent 4-(dialkylamino)benzonitriles. Reaction efficiency enhancement by increasing the size of the amino and benzonitrile subunits by alkyl substituents. *J Phys Chem A* 1998; 102: 5670-5680.
30. 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: 3899-4032.
31. Park M, Kim CH, Joo T. Multifaceted ultrafast intramolecular charge transfer dynamics of 4-(Dimethylamino)benzonitrile (DMABN). *J Phys Chem A* 2013; 117: 370-377.
32. Papper V, Pines D, Likhtenshtein G, Pines E. Photophysical characterisation of *trans*-4,4'-disubstituted stilbenes. *J Photochem Photobiol A Chem* 1997; 111: 87-96.
33. Papper V, Likhtenshtein GI. Substituted stilbenes: A new view on well-known systems. New applications in chemistry and biophysics. *J Photochem Photobiol A Chem* 2001; 140: 39-52.
34. Yang JS, Chiou SY, Liao KL. Fluorescence enhancement of *trans*-4-aminostilbene by *N*-phenyl substitutions: "The amino conjugation effect." *J Am Chem Soc* 2002; 124: 2518-2527.
35. Carlotti B, Kikas I, Skoric I, Spalletti A, Elisei F. Photophysics of push-pull distyryl furans, thiophenes and pyridines by fast and ultrafast techniques. *Chem Phys Chem* 2013; 14: 970-981.
36. Paek S, Lee JK, Ko J. Synthesis and photovoltaic characteristics of push-pull organic semiconductors containing an electron-rich dithienosilole bridge for solution-processed small-molecule organic solar cells. *Solar Energy Materials & Solar Cells* 2014; 120: 209-217.
37. Wang T, Chen Y, Bao X, Du Z, Guo J, et al. A new isoindigo-based molecule with ideal energy levels for solution-processable organic solar cells. *Dyes and Pigments* 2013, 98: 11-16.
38. Sharma GD, Mikroyannidis JA, Sharma SS, Justin Thomas KR. Bulk heterojunction organic photovoltaic devices based on small molecules featuring pyrrole and carbazole and 2-(4-nitrophenyl) acrylonitrile acceptor segments as donor and fullerene derivatives as acceptor. *Dyes and Pigments* 2012; 94: 320-329.
39. Mikroyannidis JA, Tsagkournos DV, Sharma SS, Vijay YK, Sharma GD. Conjugated small molecules with broad absorption containing pyridine and pyran units: Synthesis and application for bulk heterojunction solar cells. *Organic Electronics* 2010; 11: 2045-2054.
40. Mishra A, Behera RK, Behera PK, Mishra BK, Behera GB. Cyanines during the 1990s: A Review *Chem Rev* 2000; 100: 1973-2011.
41. Singh AK, Hota PK. Ethenyl indoles as neutral hydrophobic fluorescence probes. *J Phys Org Chem* 2007; 20: 624-629.
42. Algi F. Novel donor-acceptor type thiophene pyridine conjugates: synthesis and ion recognition features. *Tetrahedron* 2013; 69: 3523-3529.
43. Hota PK, Singh AK. Donor-acceptor conjugated polyenes: A study of excited state intramolecular charge transfer, photoisomerisation and fluorescence probe properties. *J Fluoresc.* 2014; 4: 1-8.
44. Palakollu V, Kanvah S. Diphenylpolyene-cholesterol conjugates as fluorescent probes formicroheterogeneous media. *J Photochem Photobiol A Chem* 2014; 281: 18- 26.