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

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### REVIEW ARTICLE

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#### 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.

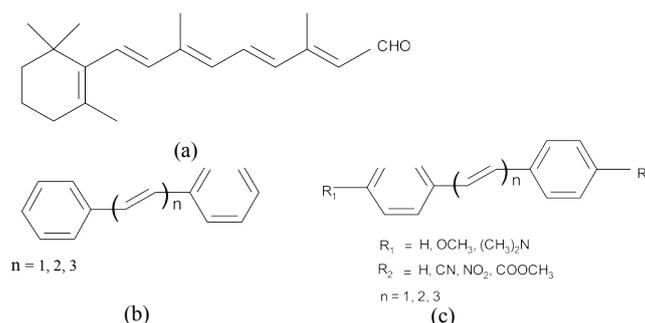
### INTRODUCTION

Donor-acceptor based conjugated linear polyenes in the series of retinoids, carotenoids play important role in the structure and function of retinal-bound photoreceptor<sup>[1-3]</sup>. Such molecules are sensitive to their local environment and thus widely used in other applications such as optoelectronic device<sup>[4-7]</sup>, diagnostic and optical imaging application etc.<sup>[8-10]</sup>. 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<sup>[11-14]</sup>. 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<sup>[11,13]</sup>. 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<sup>[15-26]</sup>. 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.*<sup>[27]</sup> 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<sup>[28-30]</sup> etc. It is also shown that in such

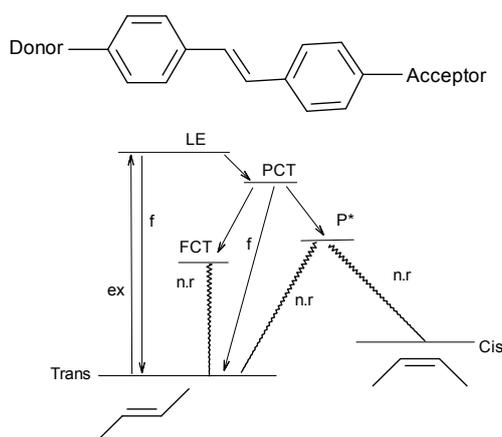
molecules, the dipole moment of excited state increases from 10D to 20D with increasing solvent polarity. Recent studies on DMABN indicates the dependency of charge transfer excited state on the solvent polarity, viscosity and temperature of the medium [31].



**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 ( $\Phi_f$ ) 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  $\Phi_f$  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  $\Phi_f$  and photoisomerization quantum yield ( $\Phi_{tc}$ ) are highly dependent upon the solvent polarity. On increasing the solvent polarity,  $\Phi_f$  increases, while  $\Phi_{tc}$  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.

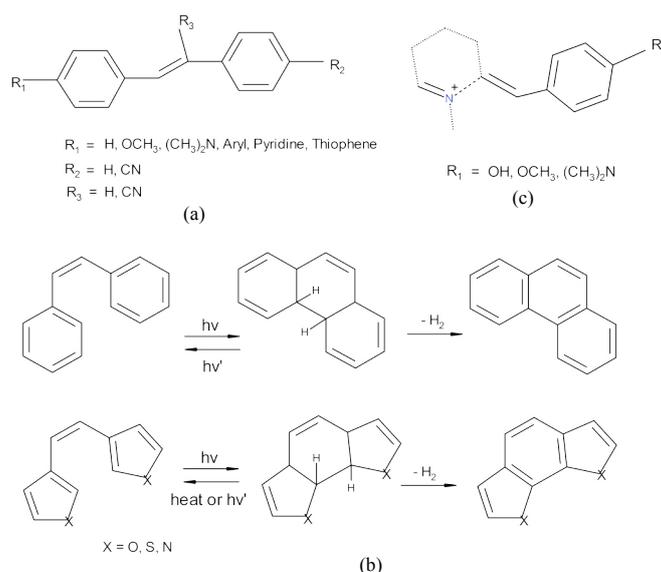
## PHOTOCHEMISTRY OF DIPHENYL POLYENES (DPP)

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

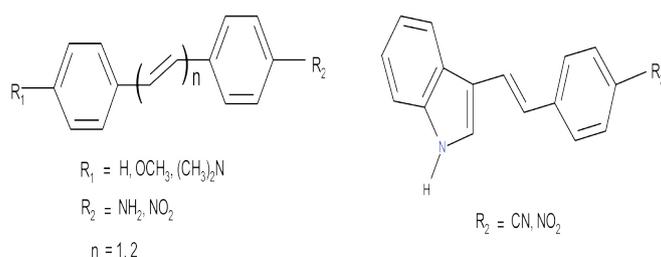
coordinate. In this model, the torsional angle about the C=C double bond plays important role in the photoisomerisation process and is highly dependent upon the solvent polarity and substituent present in the polyene. Later on, several other mechanism were proposed for substituted donor-acceptor stilbenes [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  $\pi$ -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],  $\pi$ -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.

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