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Substituent Dependence Charge Transfer and Photochemical Properties of Donor-Acceptor Substituted Ethenyl Thiophenes

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Abstract Donor-acceptor conjugated molecules with efficient light induced properties represent interesting material for electronic device application. In this context, we have calculated excited state dipole moment of three ethenyl thiophenes (1–3) bearing varied electron donoracceptor substituent in *p*-phenyl unit using Lippert-Mataga, Bakhshiev and Kawski method. It is found that 1 with strong electron-withdrawing nitro substituent, is exhibiting charge transfer and highly dipolar excited state as compared to 2 and 3. Photochemical studies of 1–3, indicate towards the charge transfer dependence *trans-cis* photoisomerization under direct irradiation condition. Compound 1 exhibits charge transfer and less efficient towards photoisomerization, whereas 2 and 3 undergo efficient photoisomerization.

Keywords Absorption · Fluorescence · Dipole moment · Photoisomerization · Charge transfer · Fluorescence quantum yield · Photoisomerization quantum yield

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Introduction

Light induced photoisomerization in linear polyene plays important role in several biological photoreceptors such as Rhodopsin in vision process [1, 2], Bacteriorhodopsin in proton pump mechanism [3, 4], etc. In order to understand the trans-cis or cis-trans photoisomerization in linear polyene, the photophysics and photochemistry of diphenylpolyenes have been extensively studied [5-12] as a model for linear polyene. In addition to that donor-acceptor substituted diphenylpolyene that exhibits charge transfer phenomena [13-18] and switchable photochemical properties [19, 20] are highly sensitive to their local environment and useful for other biological [21, 22] as well as organic electronics device applications [23, 24]. There are several mechanisms that have been proposed in order to understand the photoisomerization in biological photoreceptors. This includes volume conserving, one bond rotation (OBR) [25–27], hula twist (HT) [28–31], bicycle pedal (BP) [32, 33] pathway. In general, upon absorption of light, the donor-acceptor conjugated molecule is excited to its locally planar excited state (S_1 , LE, singlet excited state), which further undergoes twisting to yield the phantom excited state (P*) from where the *cis-trans* isomerization around the carbon-carbon double bond (>C = C<) occurs [6, 25, 27]. In case of heterocyclic based conjugated systems, the molecule follows the similar type of cis-trans photoisomeization pathway, but from its triplet excited state (T_1) due to the hetero atom [34-36]. On the other hand, charge transfer excited state in a molecules causes a considerable energy gap for P* state, whether it is singlet or triplet excited state and hence, molecule shows inefficient towards photoisomerization [17, 18]. The donor-acceptor substituent can raise or lower the energy barrier of the excited state properties of conjugated molecules. Thus, the nature of energy barrier to the excited state plays important role in altering the fluorescence and

photoisomerization properties of conjugated system. Though numerous studies on the diphenylpolyene and its substituted model compounds have been carried out extensively, little attention has been given to heterocyclic and aryl substituted model compounds [17, 18, 34-41]. Previous work on compound 3 [34-36] and on other heterocyclic conjugated molecules (e.g. pyridine, dithinylethene systems, etc) [37-39] suggest that these compounds undergo trans-cis photoisomerization predominantly from their triplet excited state. In this paper, we reports the charge transfer dependence *trans-cis* photoisomerization of three ethenyl thiphene (1–3) under direct irradiation condition. Calculation of excited state dipole moment using Lippert-Mataga, Bakhshiev and Kawski equations suggest that excited state of 1 is highly dipolar, exhibits charge transfer excited state and less efficient towards photoisomerization. On the other hand, excited state of 2 and 3 is non-polar as compared to 1 and undergo efficient photoisomerization. The ethenyl thiophenes (1-3), substituted with substituent (NO₂, Cl, H) in decreasing order of electron attracting capacity are shown in (Scheme 1). In such system, thiophene act as a weak electron donor and the substituted pphenyl as an electron acceptor group. Our results show that by replacing the nitro group with halogen or hydrogen atom, the photoisomerization efficiency of ethene is drastically increased.

Experimental

Material and Methods

The starting materials and reagents for the synthesis were procured from the local suppliers (M/s. Sisco Research Laboratory, E. Merck, Sigma-Aldrich, Himedia Chemicals). UV grade solvents were used for spectroscopic studies. Synthetic compounds were purified by column chromatography using 60–120 mesh silica gel. The compounds were



Scheme 1 Structure of molecules studied

characterized by UV-vis, IR, ¹H and ¹³C NMR, Mass spectroscopy. The absorption spectra were measured on a Perkin Elmer Lambda 25 and the fluorescence spectra were recorded on a Perkin Elmer LS-55 fluorescence spectrophotometer using a red PMT detector system. FTIR spectra in KBr discs were recorded on a Impact Nicolet-400 spectrophotometer. The ¹H–NMR spectra in CDCl₃ were recorded on a JEOL 500 MHz FTNMR instrument using TMS as an internal standard. GC-Mass spectra were recorded on a GCD 1800A Hewlett packard GC-mass spectrometer. Melting points were determined on a Lab India make melting point apparatus and are uncorrected.

Absorption and Fluorescence Studies

For all absorption and fluorescence studies, 0.5×10^{-5} M solution of compounds were prepared in different solvents, which have less than 0.5% of acetonitrile. Fluorescence spectra were recorded by exciting the sample at their absorption maximum ($\lambda_{abs\ max}$). Fluorescence quantum yields (Φ_f) of compounds were determined using quinine sulfate in 0.1 N H₂SO₄ ($\Phi_f = 0.51$) [42] and rhodamine B in ethanol ($\Phi_f = 0.69$) [43] as standard and using eq. 1.

$$\Phi = \Phi_{std} x \left(n^2_{std} / n^2 \right) x \left(Abs_{std} / Abs \right) x \left(A / A_{std} \right)$$
(1)

where n, n_{std} : refractive index of the solvent; Abs, Abs_{std}: absorbance; Φ , Φ_{std} : fluorescence quantum yield; A, A^{std}: area of the fluorescence spectrum; of the compound and the reference standard respectively.

Calculation of Dipole Moment

The change of excited state dipole moment is calculated using Lippert-Mataga eq. 2 [44, 45]. The ground and excited state dipole moment are calculated using Bakhshiev's eq. 3a [46] and Kawski's eq. 3b [47]. The above two equations is based on the quantum-mechanical second order perturbation theory and the Onsager's model, which are obtained based on the absorption and fluorescence spectral shift of the molecules. As per Onsager's reaction field theory the molecule is a point dipole residing in the center of a spherical cavity.

$$v_a - v_f = MF_1(\varepsilon, n) + constant = \left[2\left(\mu_e - \mu_g\right)^2 / hca^3\right]F_1(\varepsilon, n) + constant$$
(2a)

$$\begin{split} 0.5 \left(\nu_{a}+\nu_{f}\right) &= -M^{'} \left[0.5 F_{1}(\epsilon,n)+g(n)\right]+\text{constant} \\ &= -\left[2 \left(\mu^{2}{}_{e}{}-\mu^{2}{}_{g}\right) \Big/hca^{3}\right] \left[0.5 F_{1}(\epsilon,n)+g(n)\right]+\text{constant} \end{split} \label{eq:constant} \end{split}$$

$$\begin{split} F_1(\epsilon,n) &= \left[\{(\epsilon\text{-}1)/(2\epsilon+1)\} - \{(n^2-1)/(2n^2+1)\} \right] \; / \; \left[\{1\text{-}(2\alpha/a^3)\} \{(\epsilon\text{-}1)/(2\epsilon+1)\} \right] \; \{1\text{-}(2\alpha/a^3)\} (n^2-1)/(2n^2+1)\}; \\ g(n) &= \; \{(n^2-1)/(2n^2+1)\} \; \left[\{1\text{-}(\alpha/a^3)\} \; \{(n^2-1)/(2n^2)\} \; / \; \{1\text{-}(2\alpha/a^3)\} \{(n^2-1)/(2n^2+1)\} \right]. \end{split}$$

 v_a is absorption maximum wave number, v_f fluorescence maximum wave number $v_a - v_f$ is the Stokes' shift, $v_a + v_f$ is sum of the absorption and fluorescence maximum wave number, μ_e and μ_g are the excited state and ground state dipole moments respectively, $\mu_e - \mu_g = \Delta \mu$ is the change in dipole moment, h is the Planck constant (6.62 × 10⁻³⁴ joule sec), c is the velocity of light in vacuum (3 × 10⁸ m/s), ε is the relative permittivity (i.e. dielectric constant) and n is the refractive index of the solvent (**supporting information, Table S1**) [48, 49],

 α is mean static isotropic polarizability of the solute, F1, F2 are the reaction field factors, a is Onsager's cavity radius of the solute.

Case 1. when the molecule has spherical cavity radius "a" with zero polarizability ($\alpha = 0$), then

$$\begin{split} \nu_{a} &- \nu_{f} = \left\{ \left[2 \left(\mu_{e} - \mu_{g} \right)^{2} / hca^{3} \right] F_{1}(\epsilon, n) \right\} + \text{constant} \\ &= m_{1} F_{1}(\epsilon, n) + \text{constant} \end{split} \tag{2c}$$

and $F_1(\varepsilon,n) = [\{(\varepsilon-1)/(2\varepsilon + 1)\} - \{(n^2-1)/(2n^2 + 1)\}]$, which is Lippert Mataga equation with slope m_1

Case 2. In case of polarized molecule ($\alpha \neq 0$, but $2\alpha/a^3 = 1$). In such case, in addition to non-specific interaction, specific interaction like hydrogen bonding or electron-pair donor and electron-pair acceptor interaction is taking place among solute and solvent molecules. In this case, eq. 2 become eq. 3a (Bakhshiev) and eq. 3b (Kawski) with the field factor $F_2(\varepsilon,n)$ and $F_3(\varepsilon,n)$ and slopes, m_2 and m_3 respectively.

$$\begin{split} \nu_{a} \neg \nu_{f} &= \Big\{ \Big[2 \big(\mu_{e} \neg \mu_{g} \big)^{2} \Big/ hca^{3} \Big] F_{2}(\epsilon, \eta) \Big\} + constant \\ &= m_{2} F_{2}(\epsilon, n) + constant \end{split} \label{eq:powerstress}$$

where, slope $m_2 = 2(\mu_e - \mu_g)^2 / hca^3$ for $F_2(\varepsilon, n) = [(\varepsilon-1)/(\varepsilon+2) - (n^2-1)/(n^2+2)](2n^2+1)/(n^2+2)$

$$\label{eq:constant} \begin{split} (\nu_a+\nu_f)/2 = -\big\{\big[2\big(\mu_e^2-\mu_g^2\big)/hca^3\big]\,F_3(\epsilon,n)\big\} + \text{constant} = -m_3\,F_3(\epsilon,n) + \text{constant} \end{split} \tag{3b}$$

where, slope $m_3 = 2(\mu_e^2 - \mu_g^2)/hca^3$. for $F_3(\epsilon,n) = (2n^2 + 1)/\{2(n^2 + 2)\}[(\epsilon-1)/(\epsilon + 2) - (n^2-1)/(n^2 + 2)] + 3(n^4-1)/\{2(n^2 + 2)^2\}$. where, $m_2 = [2(\mu_e - \mu_g)^2/hca^3]$, $m_3 = [2(\mu_e^2 - \mu_g^2)/hca^3]$. and $(m_2 + m_3)/(m_3 - m_2) = \mu_e/\mu_g$, when $m_3 > m_2$ and both the ground and excited state dipole are in same direction.

"*a*" the Onsagar cavity radius (radius of molecule) can be calculated using eq. 4 and eq. 5.

$$a = (3M/4\pi\delta N)^{1/3},$$
 (4)

where, M = Molecular weight of molecule, N = Avogadro number = 6.023×10^{23}

$$\delta = \text{Molecular density of molecule}$$
(5)

The molecular volume of the molecule is obtained from the online software available at http://www.molinspiration.com/cgi-bin/properties.

Photoisomerization Studies

For photoisomerisation study, 10 mg of sample in 5 mL solution was irradiated in a pyrex glass tube using 10% copper sulfate solution as a chemical filter for five hour using a merry-go-round photoreactor (Perfit, India) fitted with a 125 watt medium pressure mercury vapor lamp. After irradiation, the excess of solvent was evaporated and the photoproduct was analyzed by GC-mass and ¹H NMR spectroscopy. Photoisomerisation quantum yield ($\Phi_{t\rightarrow c}$) is determined using potassium ferrioxalate chemical actinometer method [50].

Synthesis of Compounds 1–3

Compound 1-3 were synthesized using thiophene-2 aldehyde and corresponding substituted phenyl acetic acid [e.g. p-nitro phenyl acetic acid (for 1), p-chloro phenyl acetic acid (for 2) and phenyl acetic acid (for 3)] in pyridine and piperidine mixture as described elsewhere [17]. For this purpose, 2-formyl thiophene (0.93 mL, 0.01 mol), freshly distilled pyridine (10 mL), piperidine (0.6 mL) and corresponding substituted phenyl acetic acid (0.02 mol) were refluxed at 110 °C for eight hours. The reaction mixture was cooled to room temperature and poured in ice-cold water containing 100 mL of 2 N hydrochloric acid to remove excess of pyridine from the reaction mixture. The crude product was extracted in dichloromethane and purified by column chromatography using 2-5% of ethyl acetate in petroleum ether as the eluting solvent. Compounds were characterized using ¹H NMR, ¹³C NMR, GC-Mass and FTIR. All the ethenes show satisfactory physico-chemical data (Table 1).

2-(4-Nitrophenylethenyl-E)-Thiophene

Yield 31%; M.p. 172–173 °C; UV-vis (MeOH): λ_{max} nm (ε , 1 mol⁻¹ cm⁻¹) 372 (21,500); IR (KBr): ν_{max} (cm⁻¹) 3100 (C-Hst), 1620 (vinyl C = Cst), 1588, 1421 (Ar C = Cst), 1505 (Ar-NO₂, N = O Asym-st), 1340 (Ar-NO₂, N = O Sym-st); ¹H NMR (CDCl₃, 500 Hz): δ 6.94 (1H, d, J = 16.2 Hz, -C = CH-Ar), 7.03–7.06 (1H, m, $-C_4$ -H), 7.17 (1H, d, J = 3.3 Hz, $-C_3$ -H), 7.30 (1H, d, J = 5.1 Hz, $-C_5$ -H), 7.39 (1H, d, J = 16.2 Hz, -CH = C-Ar), 7.57 (2H, d, J = 8.7 Hz, -Ar), 8.20 (2H, d, J = 8.7 Hz, $-ArNO_2$); ¹³C NMR (CDCl₃, 500 MHz): δ 124.22, 125.67, 126.24, 126.63, 128.00, 128.17, 141.75, 143.60, 146.68; TOF MS ES⁺ (for C₁₂H₉NO₂S): calculated 231.1 (M⁺), found 231.06.

	Solvents	$\lambda_{abs\ max}\ (nm)$	$\lambda_{f\;max}\;(nm)$	$\lambda_{ex max} (nm)$	Stokes' Shift V_a - V_f (cm ⁻¹)	$V_a + V_f (cm^{-1})$	$\Phi_{\rm f}$
1	<i>n</i> -Hexane	365	405(m), 425	370	2706	52,088	0.014
	1,4- Dioxan	370	416, 495(m)	372	6825	47,229	0.020
	THF	373	516	375	7430	46,188	0.110
	MeOH	372	614	379	10,595	43,167	0.020
	AcCN	372	574	380	9460	44,302	0.220
	DMF	380	561	390	8490	44,140	0.140
2	<i>n</i> -Hexane	327	380	323	4265	56,896	0.003
	1,4- Dioxan	330	382	325	4125	56,481	0.002
	THF	330	384	327	4261	56,344	0.001
	MeOH	327	384	323	4539	56,622	0.001
	AcCN	327	401	333	5643	55,518	0.003
	DMF	331	388	335	4438	55,984	0.001
3	<i>n</i> -Hexane	322	372	319	4174	57,936	0.039
	1,4- Dioxan	325	377,402(m),426	329	5894	55,644	0.030
	THF	325	378	324	4314	57,224	0.012
	MeOH	321	385	330	5178	57,126	0.009
	AcCN	323	401,424(m)	333	7375	54,543	0.029
	DMF	326	385	331	4700	56,648	0.017

 Table 1
 UV-Vis absorption and fluorescence data for compound 1–3

2-(4-Chlorophenylethenyl-E)-Thiophene

Yield 22%; M.p. 130–131 °C; UV-vis (MeOH): λ_{max} nm (ε , 1 mol⁻¹ cm⁻¹) 327 (30,400); IR (KBr): ν_{max} (cm⁻¹) 3080 (C-Hst), 1620 (vinyl C = Cst), 1589, 1513, 1486, 1426 (Ar, C = C), 700 (C-Cl st) cm⁻¹, ¹H NMR (CDCl₃, 500 Hz): δ 6.86 (1H, d, J = 15.8 Hz, -C = CH-Ar), 6.99–7.01 (1H, m, $-C_4$ -H), 7.07 (1H, d, J = 3.4 Hz, $-C_3$ -H), 7.19 (1H, d, J = 15.8 Hz, -CH = C-Ar), 7.30 (2H, d, J = 8.25 Hz, -Ar), 7.38 (2H, d, J = 8.9 Hz, -Ar-Cl), 7.20 (1H, d, J = 5.5 Hz, $-C_5$ -H); ¹³C NMR (CDCl₃, 500 Hz): δ 122.33, 124.65, 126.44, 126.89, 127.39, 127.64, 128.84, 133.06, 135.44, 142.46; TOF MS ES⁺ (for C₁₂H₉SCl): calculated mass 220.12 (M⁺), found 220.07.

2-(Phenylethenyl-E)-Thiophene

Yield 20%; M.p. 107–108 °C; UV-vis (MeOH): λ_{max} nm (ϵ , 1 mol⁻¹ cm⁻¹) 321 (21,000); IR (KBr): ν_{max} (cm⁻¹) 3027 (C-Hst), 1594 (vinyl C = Cst), 1490, 1427 (Ar, C = C) cm⁻¹; ¹H NMR (CDCl₃, 500 Hz): δ 6.96 (1H, d, J = 15.8 Hz, -C = CH-Ar), 7.03–7.05 (1H, m, -C₄-H), 7.11 (1H, d, J = 3.4 Hz, -C₅-H), 7.23 (1H, d, J = 4.8 Hz, -C₃-H), 7.27 (1H, d, J = 15.8 Hz, -CH = C-Ar), 7.27–7.30 (1H, m, -Ar-H), 7.38 (2H, t, J = 8.2 Hz, -Ar), 7.50 (2H, d, J = 7.5 Hz, -Ar); ¹³C NMR (CDCl₃, 500 MHz): δ 121.73, 124.31, 126.09, 126.25, 127.56, 128.27, 128.66, 136.91, 142.84; TOF MS ES⁺ (for C₁₂H₁₀S): calculated mass 186.17 (M⁺), found 186.08.

Results and Discussion

Absorption and Fluorescence Studies

The absorption and fluorescence data of compounds 1-3in different solvents are summarized in Table 1. The absorption and fluorescence spectra of 1-3 are shown in Fig. 1 and supporting information, Fig. S1-S2. The absorption coefficient of ethenes 1-3 in methanol lies in between $21,000-30,400 \ 1 \ mol^{-1} \ cm^{-1}$, which suggest, the π - π * nature of electronic transition in ethenyl thiophene. In nitro substituted ethene, 1, the absorption maximum ($\lambda_{abs max}$) is moderately red shifted by 15 nm from *n*-hexane to dimethylformamide. On the other hand, the $\lambda_{abs\ max}$ of ethene 2 and 3 is not much sensitive to solvent polarity and a red shift of only 4 nm is observed. It is shown that the in hexane, λ_{abs} max enhances from 322 nm (in case of 3: phenyl substitution) to 365 nm (in case of 1: p-nitro phenyl substitution). In contrast to $\lambda_{abs max}$, the fluorescence maximum $(\lambda_{f\mbox{ max}})$ is significantly red shifted on increasing the solvent polarity from hexane to acetonitrile by 169 nm, 21 nm and 52 nm for 1-3 respectively. The excited state of 1 is stabilized further in protic solvent, methanol and exhibits a $\lambda_{f max}$ of 614 nm. The deviations in $\lambda_{f max}$ in protic polar solvent, methanol is due to net stabilization of the excited state due to specific solute-solvent interactions [51]. This suggest that the excited state of 1 is highly dipolar in nature and



Fig. 1 a Absorption and (b) fluorescence spectra of compound 1 in solvents of varying polarity

interacts strongly with polar solvent. In the present ethenyl thiophenes, the thiophene group behaves like a weak electron donor group and the substituted phenyl as an electron acceptor group. The red-shifted $\lambda_{f max}$ is attributed to the increased in conjugation and electron delocalization from electron donor-to-the electron acceptor group. Compound 1 exhibits highest red shift in $\lambda_{\rm f}$ $_{max}$ as compared to 2 and 3. This is because of the presence of strong electron acceptor -NO₂ group $(\sigma_p + 0.81, \text{ for } 1)$ [52] at the *p*- position of phenyl ring in 1, that induces a moderate and a strong electron delocalization in the ground and excited state respectively. The presence of weak acceptor group -Cl (σ_p + 0.24, in case of 2) and -H (σ_p 0.0 in case of 3), however, do not facilitate the electron delocalization as compared to 1.

In order to understand nature of excited state and the effect of solvent polarity, the Stokes' shift (v_a-v_f) vs solvent polarity parameter $E_T(30)$ [48, 53] (Fig. 2) and



Fig. 2 A plot of Dimroth empirical solvent parameter Stokes' shift vs $E_T(30)$ of 1–3 in n-hexane, 1,4-dioxane, THF, MeOH, AcCN and DMF

Lippert-Mataga plot, (v_a-v_f) vs. solvent polarity parameter, $F_1(\varepsilon,n)$ (eq. 2c) (Fig. 3a) are plotted. On increasing the $E_T(30)$ value, the Stokes' shift values are increased linearly with good correlation factor (in case of ethene, 1). Compound, 2 and 3, however, deviate from linearity in solvents, 1,4-dioxan and acetonitrile. In order to get a good correlation factor, these two solvents were excluded from our calculation. The slope (m) of the plot is markedly larger for 1 [m = 295.8, R = 0.91] in comparison to 2 [m = 12.41, R = 0.91] and 3 [m = 42.91,R = 0.98]. From Lippert-Mataga plot, (v_a-v_f) vs. F₁(ε ,n), the following correlation are obtained (1: $m_1 = 23,751$, R = 0.98; **2**: $m_1 = 954.4$, R = 0.84; **3**: $m_1 = 1187$, R = 0.73;). The calculated change of dipole moments are shown in Table 2. A large change in the excited state dipole moment is observed for 1 (21.33 D) as compared to 2 (3.71 D) and 3 (4.47 D). The solvatochromic shift of 1-3 are also analyzed using the modified Lippert-Mataga equation as described in literature using eq. 3a and 3b. This is because, in addition to non-specific solute-solvent interaction, there is also involvement of specific solute-solvent interaction due to polarizability of the molecules (e.g. hydrogen bonding and electron pair donor-electron pair acceptor interaction), which is not considered in Lippert-Mataga eq. [54]. (Fig. S3, supporting information, plot of emission wave number vs. Kamlet Taft solvent polarizability parameter, π^*) [55]. The plots of [(v_a-v_f) vs. $F_2(\varepsilon,n)$] and [half of $(v_a + v_f)$ vs. $F_3(\varepsilon,n)$] are shown in Fig. 3b and c respectively. Compound 1-3 show reasonable correlation-(1: $m_2 = 8111$, R = 0.96, $m_3 = -9635, R = 0.97; 2: m_2 = 269.3, R = 0.85,$ $m_3 = -767.4, R = 0.79; 3: m_2 = 921, R = 0.81,$ $m_3 = -1269$, R = 0.93). From the slope of the plots, the ground and excited state dipole moment of 1-3 are calculated (Table 2). The change in excited state dipole



Fig. 3 (a) Lippert-Mataga plots, Stokes' shift vs $F1(\varepsilon,n)$ and (b) Stokes' shift vs $F2(\varepsilon,n)$, (c) $(V_a + V_f)/2$ vs $F3(\varepsilon,n)$ of 1–3 in n-hexane, 1,4-dioxane, THF, MeOH, AcCN and DMF

moment thus obtained for 1-3 using eq. 3 are: 1: 12.40 D, 2: 2.22 D and 3: 3.93 D. In both the cases, 1 exhibits large excited state dipole moment as compared to 2 and 3. The ground state dipole moment for 1-3 is very small (1: 1.16 D, 2: 2.04 D and 3: 0.74 D). Thus, the solvatochromic shift in these molecules is due to change in the dipole moment in their excited state. A large change in the excited state dipole moment

(21.33 Debye, Lippert-Mataga), suggest the formation of charge transfer (CT) excited state in 1. On the other hand, the excited state ethenyl thiophenes 2 and 3, bearing a weak acceptor group -Cl (σ_p + 0.24, for 2), -H $(\sigma_p 0, \text{ for } 3)$ are less polar (2.79–4.47 Debye). This suggest a partial charge transfer can occur for 2 and 3 in the excited state and hence, the fluorescence spectrum is moderately sensitive to solvent polarity. The formation of highly dipolar excited state in 1 could be due to twist over the single bond attached to the nitro group and phenyl ring as suggested in other donoracceptor substituted styryl systems [13-18, 41]. The change of dipole moment obtained through eq. 3 is lower than the change of dipole moment obtained through Lippert-Mataga eq. 2. This is due to polarized nature of the excited state of ethenyl 1-3 (as shown in Fgure S3). and hence involvement of specific interaction in addition to non-specific solute-solvent interaction.

Photoisomerisation Studies

On direct irradiation, compounds 1-3 undergo trans-cis isomerization. The analysis of the photomixture shows the presence of two components as confirmed by GC-Mass. One GC peak correspond to trans-isomer and the other GC peak correspond to cis-isomer (Supporting information, Figs. S4-S6). For 1-3, along with the starting reactant (trans-1, R_f: 17.57 min m/z 231.06; trans-2, Rt:14.59 min, m/z 220.07; trans-3, Rt:15.04 min, m/z 186.08), a new GC peak corresponding to cis-isomer is formed (cis-1, Rt of 15.20 min, cis-2, Rt of 11.87 min and cis-3, Rt of 12.73 min). The cis isomer of the respective compound matched with the molecular ion peak (e.g. m/z 231.06 for 1, m/z 220.07 for 2 and m/z 186.08 for 3). The *cis*-isomer is also confirmed by ¹H NMR through their coupling constant of olefin proton (Table 3, Fig. 4, supporting information, Fig. S7-S8). The generation of two new doublet peaks near δ 6.5 to 6.8 (each of 1H, $J \sim 12.4$ Hz), which are corresponding to the olefin proton of cis-isomer. In case of trans-isomer, the olefin proton doublet peaks appear near 6.9 to 7.3 (each of 1H, J \sim 16 Hz). The percentage of *cis* and *trans* isomer is calculated from the peak height of olefin doublet peaks (ratio of both *cis* and *trans* isomers) in ¹H NMR spectrum (Table 4). In relatively non-polar hexane, 1, 2 and 3 undergo trans to cis photoisomerisation with 35.9%, 77.3% and 56.3% of cis isomer respectively. In polar solvent, methanol, only 16.3% of cis isomer is observed for 1, whereas 64.2% and 41.2% of cis is observed for cis-2 and cis-3 respectively. This indicates that trans-cis photoisomerization in 2 and 3 is very similar in both non-polar and polar solvents. On the other hand, for 1,

	Radius of molecule (A°)	m ₁	m ₂	m ₃	$\Delta \mu^{a}$ (Debye)	μ _g (Debye)	μ _e (Debye)	$\mu_{e}\!/\mu_{g}$	Δμ ^b (Debye)
1	4.27	23751	8111	-9635	21.33	1.16	13.57	11.64	12.40
2	4.20	754	269	-1281	3.71	2.04	4.26	2.08	2.22
3	4.09	1187	921	-1269	4.47	0.74	4.68	6.29	3.93

 Table 2
 Change of excited state dipole moments, ground and excited state dipole moments of 1–3 calculated using Lippert-Mataga eq. 1 and eqs. 2 and 3

a: calculated using Lippert-Mataga plot, eq. 1; b: calculated using eqs. 2 and 3;

 m_1 , m_2 and m_3 are the slope of the plots: Stokes's shift vs $F_1(\epsilon, n)$ (Fig. 3a), Stokes's shift vs $F_2(\epsilon, n)$ (Fig. 3b), and $(V_a + V_f)/2$ vs $F_3(\epsilon, n)$ (Fig. 3c), respectively. $\Delta \mu = \mu_e - \mu_g$

the *trans-cis* isomerization decreases from hexane to methanol. A high photoisomerisation quantum yield $(\Phi_{t\rightarrow c})$ is found for 2 and 3 as compared to 1 (Table 4) $(\Phi_{t\rightarrow c}1:$ 0.15 in hexane, 0.09 in methanol; 2: 0.48 in hexane, 0.44 in methanol; 3: 0.41 in hexane, 0.31 in methanol). Compound 1 exhibits highly dipolar charge transfer excited. Thus, the excited state is stabilized more upon increasing the solvent polarity. This leads to a large energy barrier to the P* state and exhibit inefficient photoisomerization. On the other hand, 2 and 3 predominately follow the photoisomerization pathway in both nonpolar and polar solvents.

Fluorescence Quantum Yield

The fluorescence efficiency of ethenyl thiophenes is highly dependent upon the nature of substituent. Compound 1 exhibits high fluorescence quantum yield (Φ_f) in medium polar and polar aprotic solvents (Φ_f : 0.11–0.22). On the other hand, 2 and 3 exhibit very low Φ_f [2: 0.001–0.003 and 3: 0.02–0.04] in all the solvents. The decrease in fluorescence efficiency suggests a different type of non-radiative decay pathway. From the previous work, it is suggested that compound 3 predominantly follows the triplet pathway and hence non-fluorescent in organic solvents [34-36]. There are several other non-radiative pathway that compete with fluorescence of styryl based conjugated systems. This includes internal conversion [56], intersystem crossing in presence of heavy atom [34-36, 57, 58], solvent relaxation [59], intra molecular charge transfer (CT) through single bond twist [13-18], etc. The CT excited state is destabilized in non-polar solvent, hence, it relaxes to the ground state through radiative pathway. However, in polar solvent, it predominantly follows the non-radiative pathway due to solvent-solute interactions as suggested in other molecules [60-62]. The trans-cis isomerization is another alternative that cause for the low Φ_{f} . In the present case, due to CT excited state, 1 exhibits little higher $\Phi_{\rm f}$ in non-polar solvent, whereas become non-fluorescent in polar solvent. Compound 2 and 3 show efficient trans-cis photoisomerization in both non-polar and polar solvents and non-fluorescent in both solvent. In the present case, the CT state formation competes with the P* state, which results in low photoisomerization quantum yield. On the other hand, by putting a less electron withdrawing group at phenyl ring (e.g. Cl, H in case of 2 and 3), the photoisomerization increases drastically due to low energy barrier to P* state.

 Table 3
 Comparison of ¹H NMR peaks of compounds 1–3 before and after the irradiation

Compound	¹ H NMR peaks correspond to <i>trans</i> isomer	Extra ¹ H NMR peaks in photomixture that correspond to <i>cis</i> isomer
1	$\begin{split} \delta \ 6.94 \ (1\text{H}, \text{d}, \text{J} = 16.2 \text{ Hz}, -\text{C} = \text{CH-Ar}), \ 7.03 - 7.06 \\ (1\text{H}, \text{m}, -\text{C}_4 - \text{H}), \ 7.17 \ (1\text{H}, \text{d}, \text{J} = 3.3 \text{ Hz}, -\text{C}_3 - \text{H}), \ 7.30 \\ (1\text{H}, \text{d}, \text{J} = 5.1 \text{ Hz}, -\text{C}_5 - \text{H}), \ 7.39 \ (1\text{H}, \text{d}, \text{J} = 16.2 \text{ Hz}, -\text{CH} = \text{C-Ar}) \end{split}$	δ 6.54 (1H, d, J = 12.4 Hz, -C = CH-Ar), 6.83 (1H, d, J = 12.4 Hz, -CH = C-Ar), 6.91–6.92 (1H, m, -C ₄ -H), 6.99 (1H, d, J = 4.15 Hz, -C ₃ -H), 7.18 (1H, d, J = 4.15 Hz, -C ₅ -H)
2	δ 6.86 (1H, d, J = 15.8 Hz, -C = CH-Ar), 6.99–7.01 (1H, m, -C ₄ -H), 7.07 (1H, d, J = 3.4 Hz, -C ₃ -H), 7.19 (1H, d, J = 15.8 Hz, -CH = C-Ar), 7.20 (1H, d, J = 5.5 Hz, -C ₅ -H),	$ \begin{split} &\delta \ 6.48(1H, d, J = 11.6 \ Hz, -C = CH-Ar), \ 6.69 \\ &(1H, d, J = 12.3 \ Hz, -CH = C-Ar), \ 6.88-6.90 \\ &(1H, m, -C_4-H), \ 6.95(1H, d, J = 3.4 \ Hz, -C_3-H), \ 7.11 \\ &(1H, d, J = 4.8 \ Hz, -C_5-H) \end{split} $
3	$ \begin{split} &\delta~6.96~(1\mathrm{H},~\mathrm{d},~\mathrm{J}=15.8~\mathrm{Hz},~\mathrm{-C}=\mathrm{CH}\mathrm{-Ar}),~7.03\mathrm{-}7.05\\ &(1\mathrm{H},~\mathrm{m},~\mathrm{-C_4}\mathrm{-H}),~7.11~(1\mathrm{H},~\mathrm{d},~\mathrm{J}=3.4~\mathrm{Hz},~\mathrm{-C_5}\mathrm{-H}),~7.23\\ &(1\mathrm{H},~\mathrm{d},~\mathrm{J}=4.8~\mathrm{Hz},~\mathrm{-C_3}\mathrm{-H}),~7.27~(1\mathrm{H},~\mathrm{d},~\mathrm{J}=15.8~\mathrm{Hz},~\mathrm{-CH}=\mathrm{C}\mathrm{-Ar}), \end{split} $	$ \begin{split} &\delta~6.57~(1\mathrm{H},\mathrm{d},\mathrm{J}=12.4~\mathrm{Hz},-\mathrm{C}=\mathrm{CH}\text{-}\mathrm{Ar}),6.70\\ &(1\mathrm{H},\mathrm{d},\mathrm{J}=12.4~\mathrm{Hz},-\mathrm{CH}=\mathrm{C}\text{-}\mathrm{Ar}),6.87\text{-}6.89\\ &(1\mathrm{H},\mathrm{m},-\mathrm{C}_4\text{-}\mathrm{H}),6.96~(1\mathrm{H},\mathrm{d},\mathrm{J}=3.4~\mathrm{Hz},-\mathrm{C}_5\text{-}\mathrm{H}),7.19\\ &(1\mathrm{H},\mathrm{d},\mathrm{J}=5.5~\mathrm{Hz},-\mathrm{C}_3\text{-}\mathrm{H}) \end{split} $

Fig. 4 ¹H NMR spectrum of **1** in CDCl₃. (**a**) after irradiation and (**b**) before irradiation in methanol



Table 4Photoisomerization data for compound 1–3

	Solvent	photostationary	$\Phi_{t \to c}$	
		Trans (E)	Cis(Z)	
1	Hexane	64.1	35.9	0.15
	Methanol	83.7	16.3	0.09
2	Hexane	22.7	77.3	0.48
	Methanol	35.8	64.2	0.44
3	Hexane	43.7	56.3	0.41
	Methanol	58.8	41.2	0.31

Conclusion

In summary, it is shown that the excited state of ethenyl thiophene is highly sensitive to the solvent and the substituent present on it. It has been shown that ethene with a strong electron acceptor group exhibits solvent dependent red shifted fluorescence due to charge transfer excited state. This leads to an inefficient *trans-cis* photoisomerization. On the other hand, the absorption and fluorescence properties of ethenes bearing weak electron acceptor groups are moderately sensitive to solvent polarity. Such molecule has non- polar excited state, low energy barrier to P* excited state and hence, follows predominantly *trans-cis* photoisomerization. This studies will provide useful information in understanding the photochemistry of conjugated molecules and linear polyene bound biological photoreceptors. It also provide a new direction in designing and developing novel materials for biological and organic electronic applications.

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