Synthesis and Characterization of a Class of Donor-Acceptor Conjugated Molecules: Experiments and Theoretical Calculations

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A class of conjugated molecules containing donor (thiophene) and acceptor (malononitrile) is synthesized by Knoevenagel condensation reaction between 2-(2,6-dimethyl-4*H*-pyran-4-ylidene) malononitrile and thiophene carbaldehyde containing two and three thiophene units. The resulting molecules are characterized by ¹H and ¹³C NMR. We have performed UV-vis absorption, fluorescence, and cyclic voltammetry measurements on these materials. The spectroscopic and electrochemical measurements proved beyond doubt that these materials possess low excitation gap and are suitable for being an active material in various electronic devices. We have also performed electronic structure calculations using density functional theory (DFT) and INDO/SCI methods to characterize the ground and excited states of this class of molecules. These donor-acceptor molecules show a strong charge transfer character that increases with the increase in the number of thiophene rings coupled to the malononitrile acceptor moiety. We have also calculated the π -coherence length, Stoke's shift, and effect of solvents on excited states for this class of molecules. Our theoretical values agree well with experimental results.

I. Introduction

From the past two decades, considerable efforts have been directed toward the improvement of organic electronic materials. Low band gap organic materials are best suited for application in organic electronics. Lowering of the excitation gap can be achieved by choosing the appropriate donor and acceptor groups in the donor–acceptor–donor (D-A-D) conjugated molecules. Nowadays, these materials have become attractive because of their tunable electronic properties, low cost of synthesis, ease of processability, and flexible device structures. Many kinds of organic dyes such as thiophenes, carbazoles, squarines, benzothiadiazoles, and diphenyl-dithienyl-thienopyrazines are used as a donor or an acceptor group. A detailed understanding of the underlying electronic structure of these materials as well as a study of their response to external fields is required to exploit them systematically for technological applications.

One of the important classes of molecules that satisfies the above criterion comprises a donor group (D) and an acceptor group (A) separated by a conjugated backbone (D- π -A). The π -electron density in these chromophores is highly polarized because of the presence of both an electron-donating (donor) and an electron-withdrawing (acceptor) group, thus creating a dipole moment in the ground state. This is why: this class of molecules is aptly named dipolar systems. Because such charge imbalance is a characteristic feature of this class of compounds, large nonlinear optical responses,¹ high polaronic mobilities,² and low singlet gaps are demonstrated by the devices containing such chromophores as active material. We can also slightly modify these dipolar systems to create quadrupolar (D-A-D, A-D-A)³ or more generally multipolar systems.⁴ Similar to their dipolar counterpart, they exhibit large charge displacement, strong nonlinear optical responses,⁴ and low-energy intramo-



Figure 1. Schematic representation of the oligo-thiophene (D-A-D) molecules, where n indicates the number of thiophene units present in it. In this article, n is varied between 4 and 14.

lecular charge transfer states.⁴ In addition to these useful electronic properties, the D-A-D systems usually possess high lattice energies.⁵ This leads to the generation of highly ordered crystalline films having enhanced device performance.⁶ In this article, we report a novel synthesis and characterization of a class of D-A-D systems (Figure 1) with thiophene as a donor and malononitrile derivative as an acceptor.

This article is organized as follows. In section II, we present the synthesis and characterization of the D-A-D systems shown in Figure 1; we name these molecules as oligo-thiophenes and are characterized by the number of thiophene units present in conjugation with the malononitrile acceptor. In section III, we present the absorption and fluorescence spectra of these systems in various solvents. Furthermore, in this section, we present the cyclic voltammetry (CV) measurements to characterize various energy levels of the synthesized oligo-thiophene molecules. In section IV, we turn our attention to the theoretical calculations of ground and excited-state geometries of these systems and characterize the excited states by calculating various properties. We do not restrict our theoretical calculations only to the synthesized small oligo-thiophenes but also calculated the effective conjugation length in this system, which is shown to be larger than that in the usual polymeric systems. We summarize our results in the final section.

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Figure 2. Synthetic scheme for the preparation of thiophene carbaldehydes with varying number of thiophene units. The thiophene carbaldehydes thus synthesized are used as precursors for preparation of oligo-thiophene dyes.



Figure 3. Synthetic scheme for the preparation of oligo-thiophene molecules. For 4-oligo-thiophene molecule, *n* is equal to 4, whereas for 6-oligo-thiophene, it is 6.

II. Experimental Details

First, we focus on the preparation of thiophene carbaldehydes (compounds 4 and 6 in Figures 2 and 3), which are used as precursor for the synthesis of oligo-thiophenes. The alkyl thiophene derivatives are added to cooled DMF solution containing POCl₃, which is previously stirred for about 30-45 min. The mixture thus formed is heated at 70-75 °C for 6 h. The solution is brought to room temperature, which is followed by neutralization by sodium hydroxide (NaOH) and extraction by ethylacetate. Organic layer is washed by brine solution and dried over anhydrous sodium sulfate. The solution of thiophene carbaldehyde thus prepared is concentrated in vacuum and purified by column chromatography. A brief outline of the synthetic procedure is summarized in Figure 2. The details of the preparation, characterization, and yields of intermediate steps are presented in the Supporting Information.

Now, we turn our attention to the synthesis of thiophene oligomers shown in Figure 1 by Knoevenagel condensation between 2-(2,6-dimethyl-4*H*-pyran-4-ylidene) malononitrile (compound 7 in Figure 3) and respective thiophene carbaldehydes (compounds 4 and 6 in Figures 2 and 3). Both the reactants along with piperidine are mixed in a round-bottomed flask fitted with a reflux condenser. The whole reaction mixture is kept under an inert argon atmosphere. The reaction mixture is refluxed for about 24 h and then filtered, which is followed by washing in acetonitrile and drying in vacuum. The schematic for this reaction is presented in Figure 3. Further experimental details are also presented in the Supporting Information. In this article, we report the preparation and characterization of two oligo-thiophene molecules with four and six thiophene units.

III. Spectroscopic and Electrochemical Analysis

Here we turn our attention to the photophysical properties of the prepared oligo-thiophenes. Both UV-visible absorption and fluorescence spectra presented in Figure 4a,b are recorded using toluene as solvent and the oligo-thiophene concentration is maintained at $\sim 1 \times 10^{-6}$ M. The UV–visible spectra of these oligomers were obtained with Perkin-Elmer (Lambda 35) spectrometer. All measurements were undertaken at room temperature.

The general features of the absorption spectra consist of a broadband in the visible range and a less intense band in form of a shoulder near the UV region. On the contrary, the fluorescence spectra consist of a single broad peak that is redshifted compared with absorption maxima. The absence of multiband structure in the fluorescence spectra can be attributed to the fact that fluorescence mainly occurs from the lowest singlet excited state⁷ in accordance with Kasha's rule. It is evident from the above spectra that both the absorption and fluorescence maxima get red shifted as we increase the number of thiophene units in conjugation with the malononitrile acceptor. Such a red shift is generally associated with the increase in the conjugation length⁸ and subsequent increase in the donating capability of the thiophene units.⁹ We also recorded UV-visible absorption as well as fluorescence spectra of both dyes in various solvents other than toluene.

Although the absorption spectra roughly remain the same in all of these solvents, the fluorescence maximum shows a nominal red shift as we increase the solvent polarity. The related photophysical data are presented in Table 1, and the corresponding absorption and fluorescence spectra are presented in the Supporting Information. The energy gaps estimated from the absorption band edges are also presented in the same Table.

It is evident from Table 1 that the photoluminescence of these oligo-thiophene dyes is not highly solvent sensitive.⁵ A nominal bathochromic shift (\sim 40 nm) of the emission maxima is observed with increasing solvent polarity, which saturates in highly polar solvents like DMF. Such saturation effect is highly prominent in 6-oligo-thiophene dye.

The electrochemical behavior of the oligomers was investigated by CV.¹⁰ CV measurements are performed on a Solartron SI1287 potentiostat. The electrochemical analyzer consists of



Figure 4. (a) UV-visible absorption and (b) fluorescence spectra of oligo-thiophene dyes ($\sim 1 \times 10^{-6}$ M). All spectra are recorded with Perkin Elmer spectrometers at room temperature in toluene.

 TABLE 1: Absorption and Fluorescence Maxima in Different Solvents^a

system	solvent	dielectric constants of solvents	$absorption \\ maxima \lambda_{ab} \\ (nm)$	fluorescence maxima λ_{em} (nm)	energy gap (eV)
4 oligo- thiophene	toluene THF	2.4 7.5	476	572 609	2.23
6 oligo- thiophene	DMF toluene THF DMF	38.0 2.4 7.5 38.0	490	637 601 640 649	2.13

 $^{\it a}$ Energy gaps of 4 and 6 oligo-thiophenes estimated from absorption edges are also presented here.

three electrode cells with Pt disk as working electrode, Pt wire as counter electrode, and Ag/AgCl (saturated KCl) as reference electrode. The scan rate is fixed at 50 mV/s. Anhydrous tetrabutylammonium perchlorate (Bu₄NClO₄) in nitrogen-saturated DMF solvent is used as supporting electrolyte. Oligo-thiophene dye (1×10^{-5} M) is mixed with the supporting electrolyte, and both cathodic and anodic sweeps are performed to obtain the redox potentials.

The voltammograms obtained from CV measurements are presented in Figure 5. As evident from these voltammograms, these oligo-thiophenes do not show good reversible behavior. On anodic sweep, the oxidation peaks are found to be 1.22 and 1.20 V for 4-oligo-thiophene and 6-oligo-thiophene, respectively. The corresponding rereduction peaks are observed at 0.91 and 1.01 V. In contrast, the cathodic sweep shows reduction peaks at -1.10 and -0.96 V for 4-oligo-thiophene and 6-oligothiophene, respectively. The corresponding reoxidation peaks are observed at -0.83 and -0.66 V. The reduction peak around -0.40 V and its corresponding reoxidation peak at -0.30 V is attributed to the solution containing only secondary electrolyte (Bu₄NClO₄) as solute and DMF as solvent. This is confirmed from the voltammogram of the 0.10 M solution of the secondary electrolyte in DMF in the absence of oligo-thiophene dye. From these potentials of oxidation and reduction processes we can estimate the HOMO and LUMO energies and their corresponding HOMO-LUMO gaps. For calculating the HOMO and LUMO energy levels of oligo-thiophenes, we have considered the potentials corresponding to the peak position of the current in the oxidation and reduction processes.¹⁰ The HOMO and LUMO energy levels for 4-oligo-thiophenes are -5.87 and -3.55 eV, and those of 6-oligo-thiophene are at -5.85 and -3.69 eV. The HOMO-LUMO gaps calculated from these values are 2.32 and 2.16 eV for 4-oligo-thiophene and 6-oligo-



Figure 5. Cyclic voltammograms of oligo-thiophene dyes (4-oligo-thiophene and 6-oligo-thiophene) with platinum disk as working electrode in the presence of Bu_4NClO_4 (0.10 M) as supporting electrolyte in DMF with Ag/AgCl (saturated KCl) as reference electrode. The scan rate is fixed at 50 mV/s. Cyclic voltammogram of only 0.10 M Bu_4NClO_4 in DMF without the oligo-thiophene dye is also shown. All measurements are performed in ambient temperature.

thiophene, respectively. The HOMO-LUMO gaps thus calculated compare well with those obtained from spectroscopic measurements. We will see in the next section that although the HOMO and LUMO energies differ significantly from the gas-phase calculated values, the HOMO-LUMO gaps obtained from both CV and spectroscopic measurements compare well with theoretical values.

IV. Theoretical Investigation

Here we focus on quantum theoretical investigation of oligothiophene dyes, which include calculations of ground and excitedstate geometries and properties such as oscillator strengths and permanent dipole moments. We do not restrict ourselves only to the oligo-thiophenes synthesized by us but perform calculations on larger oligo-thiophene molecules to generalize the experimental results presented in previous sections. Our theoretical calculations are not only restricted to the gas phase but also incorporate the effects of different solvents on excited states of these oligo-thiophenes.

The theoretical investigations are carried out by employing the Gaussian 03 package¹¹ and Zerner's intermediate neglect of differential overlap (ZINDO) program.¹² First, we illustrate

TABLE 2: Molecular Orbital Energies of Various Oligo-Thiophene Molecules

no. of thiophene units	HOMO-2 (eV)	HOMO-1 (eV)	HOMO (eV)	LUMO (eV)	LUMO+1 (eV)	LUMO+2 (eV)	GAPS (eV)
4	-6.0073	-5.4726	-5.4002	-2.7662	-2.4549	-1.4182	2.6340
6	-5.7645	-5.2611	-5.2598	-2.8152	-2.5422	-1.7471	2.4446
8	-5.6312	-5.1357	-5.1177	-2.8456	-2.5961	-1.9588	2.2721
10	-5.5327	-5.0364	-5.0198	-2.8661	-2.6307	-2.1020	2.1537
12	-5.4492	-4.9879	-4.9493	-2.8859	-2.6598	-2.2111	2.0633
14	-5.3553	-5.0177	-4.8987	-2.8974	-2.6748	-2.2560	2.0013

the computational details of the gas-phase quantum theoretical calculations. Optimized ground-state geometries of oligothiophene dyes in the ground state are obtained using density functional theory (DFT) method. In these calculations, we include the hybrid functional, which incorporates both Hartree-Fock and DFT exchange correlations. This hybrid functional, usually described in literature as the B3LYP functional, is an improvement over the LDA exchange correlation.¹³ Furthermore, to perform this geometry optimization, we use split valence basis set along with polarizable functions for heavier atoms (6-31g*). For smaller oligomers, we also optimize the geometry by adding diffuse functions (6-31+g*) to the previously mentioned basis set. In the Supporting Information, we present selected structural parameters of 6-oligo-thiophene dye obtained by optimizing the geometry using both B3LYP/6-31g* and B3LYP/6-31+g* methods.

The optimized geometries obtained from both these methods are quite similar; bond lengths and bond angles obtained differ only in the third decimal place and the dihedral angles differ by $4-6^{\circ}$ (Table 1, Supporting Information). We have computed the excited-state energies and other properties in both geometries by the ZINDO single configuration interaction (SCI) method keeping 33 highest occupied molecular orbitals (HOMOs) and 33 LUMOs. The results obtained for the two geometries compare quite well with each other (Table 2, Supporting Information). We therefore conclude that the density functional method with 6-31g* as basis set and B3LYP as hybrid potential, followed by ZINDO SCI, is sufficient to obtain consistent prediction of properties such as excitation energies, oscillator strengths from ground state, and dipole moments of low-lying states for this class of D-A-D systems. These sets of methods have also been applied by other workers with reasonable success to obtain various excited-state properties for dipolar and multipolar14 molecules.

Now we focus our attention on the calculation of excitation energies, oscillator strengths, and dipole moments of ground and excited states for various oligo-thiophenes, the largest of which contains 14 thiophene units. First, we optimize the ground-state geometry of all oligo-thiophenes by B3LYP/6-31g* method. The density functional calculation provides us with MO energies that are listed in Table 2. It is evident from Table 2 that the two of the HOMOs are nearly degenerate, whereas the LUMO consists of a pair of closely spaced energy levels. The energy difference between LUMO and LUMO+1 decreases with the increase in the number of thiophene units. This difference can be attributed to the slight difference in orientation of the thiophene units in either arm of the D-A-D systems. The nature of HOMO and LUMO can be well understood from the electron density distribution, which is presented in Figure 6a,b. The HOMO-1 and HOMO correspond to charge density being localized on one arm or the other whereas LUMO and LUMO+1 are akin to resonance structures.

As seen from Figure 6b, the electron density in the LUMO level is primarily localized on the acceptor (malononitrile) unit. This clearly indicates to an intramolecular charge transfer phenomenon that plays a dominant role in the low-energy photophysics of these D-A-D systems. In Figure 7, we show schematically the dominant electron configurations in the ground and first two excited states.

Now, we turn our attention to the calculation of excited-state properties by ZINDO SCI method. We choose to work with SCI method because the low-lying excited states obtained so compare reasonably well with experiments because SCI incorporates electron correlation effects in the excited states to the same extent as in ground state. Moreover, this method has the advantage of being size-consistent, whereas the other restricted CI methods are not.¹⁵

We present the excitation gaps, oscillator strengths from the ground state, and permanent dipole moments in the ground and low-lying excited states of different thiophene oligomers in Table 3. The first and the second excited states are found to be nearly degenerate.

The first excited state is dominated by the HOMO to LUMO excitations (Figure 7), whereas the excitations involving HOMO and LUMO+1 dominate the second excited state. The energy difference between the first and the second excited state is slightly higher than that obtained from the DFT calculations because SCI incorporates to some extent the effects of electron correlations in the excited states.

The gap is 2.60 eV in the oligomer with 4 thiophene units, which reduces to 2.18 eV in the oligomer with 14 thiophene units. However, the gap in the largest oligomer shown here (14-oligo-thiophene) is very nearly the same as that in the oligomer with 12 thiophene units. In Figure 8, we plot different excited state energies as a function of the inverse of number of thiophene units (*N*). This clearly indicates that the effective coherence length for π -conjugation in these systems saturates for 14-oligo-thiophene molecule. This coherence length is much longer compared with polythiophenes without the acceptor moiety, which only spans about six oligomer units.¹⁶ We present the oscillator strengths of the low-lying excited states for these oligo-thiophenes. It is noted that for all oligomers, the lowest excited state is transitionally coupled to the ground state.

This theoretical fact matches well with our experimental findings. As shown from Table 3, the oscillator strength of the lowest excited state for 6-oligo-thiophene is higher compared with that of the 4-oligo-thiophene molecule. On the contrary, the oscillator strength of the second excited state for both the oligo-thiophenes is roughly same. The slight difference between the calculated and the observed absorption spectrum, in the 375 nm region, can be attributed to Franck—Condon factors and the solvent effects. As presented in Figure 9, the oscillator strengths per thiophene unit of low-lying excited states show convergence behavior similar to that of excited-state energies.

Now we turn our attention to the estimation of permanent dipole moments in ground and low-lying excited states of these oligo-thiophenes. Although the absolute values of dipole moments are quite large in the ground and excited states, the difference between them varies from 1.4 to 2.8 D. The variation of the dipole moments in ground and low-lying excited states



Figure 6. (a) Electron density plots of three HOMOs for 14-oligo-thiophene molecule. The carbon atoms are marked in gray, sulfur in yellow, nitrogen in blue, oxygen in red, and hydrogen in white. The positive and negative lobes of electron density are marked in brown and green, respectively. (b) Electron density plots of three LUMOs for 14-oligo-thiophene molecule. Color coding is same as in part a.



Figure 7. Energy level diagram depicting the contributions of various excitations to ground and the degenerate first and second excited states. Proper linear combination of the microstates shown in the Figure need to be constructed to obtain the corresponding singlets.

TABLE 3: Vertical Singlet Excitation Energies, Oscillator Strengths, and Permanent Dipole Moments of Various Oligo-Thiophene Molecules Calculated by ZINDO SCI Method^a

	Į	gaps (eV) (oscillator strength)				magnitude of permanent dipole moment (debye units)			
no. of thiophene units	1	2	3	4	G	1	2	3	4
4	2.60 (1.60)	2.76 (1.20)	3.63 (0.25)	3.79 (0.21)	12.79	15.51	13.62	11.65	15.62
6	2.38 (2.07)	2.56 (1.24)	3.36 (0.16)	3.41 (0.22)	17.01	19.69	18.32	16.64	19.73
8	2.30 (2.68)	2.45 (1.11)	3.14 (0.16)	3.19 (0.34)	13.37	15.42	14.43	14.86	14.34
10	2.24 (3.13)	2.37 (1.22)	2.95 (0.16)	3.01 (0.18)	15.63	17.39	16.60	17.33	16.28
12	2.20 (3.66)	2.31 (1.17)	2.81 (0.23)	2.87 (0.15)	12.80	14.32	13.62	14.43	13.30
14	2.18 (3.88)	2.30 (1.21)	2.71 (0.27)	2.85 (0.10)	13.01	14.42	13.87	14.51	13.87

^a Oscillator strengths are from the ground state (G) to the low-lying excited states labeled 1 through 4.



Figure 8. Convergence of low-lying excited state energies as an inverse function of number of thiophene units (*N*).

is presented in Figure 10. The permanent dipole moments show convergence at 14 thiophene units for all states. Before converging to the limiting value (at 14-oligo-thiophene), the dipole moments in all the states show an oscillatory behavior, which can be attributed to different orientation of thiophene units from one oligomer to the other by about 3 to 4°. The small difference in dipole moments between ground and first excited state for this class of compounds results in nominal solvatochromic shifts, as observed experimentally.

Until now, we have calculated vertical excited-state energies and properties in the gaseous phase. Here we focus on the



Figure 9. Convergence behavior of oscillator strengths per thiophene unit connecting low-lying excited sates and ground state with the number of thiophene units.

calculations of Stoke's shift¹⁷ and predicting the fluorescence spectra for oligo-thiophenes in the presence of solvents of various dielectric constants.¹⁸ For this purpose, we focus only on the molecules synthesized in our laboratory. To calculate the Stoke's shift, we obtain the optimized geometry of the first excited state by the following procedure. First, we obtain the first excited state under the Born–Oppenheimer approximation by SCI method. In this geometry, we calculate the matrix of force constants (Hessian matrix) along with the displacement vector. These force constants specify the curvature of the surface



Figure 10. Variation of the magnitude of permanent dipole moments ($|\mu|$) in ground and low-lying excited states of oligo-thiophene molecules with different number of thiophene units.

TABLE 4: Singlet Excitation Energies, Oscillator Strengths and Permanent Dipole Moments of Thiophene Oligomers Containing Four and Six Thiophene Units in Optimized Excited State Geometries Obtained As Described in the Text^a

	gaps (eV) (oscillator strength)			magnitude of permanent dipole moment (debye units)				e units)	
systems	1	2	3	4	G	1	2	3	4
4-oligo-thiophene 6-oligo-thiophene	2.33 (1.45) 2.15 (1.76)	3.12 (1.38) 3.00 (1.50)	3.61 (0.15) 3.31 (0.14)	3.84 (0.005) 3.70 (0.26)	13.03 17.06	15.01 19.60	14.34 18.68	11.99 17.96	9.04 17.71

^a Oscillator strengths are from the ground state (G) to the low-lying excited states (labeled 1 through 4).

at that electronic state and provides information useful for determining the displacement at the next step. In the displaced geometry, we again do a Hartree–Fock Gaussian (HFG) calculation, followed by an SCI calculation. The whole procedure is repeated until convergence is achieved for the excited state geometry. We perform the frequency calculation on the optimized geometry obtained from the previous self-consistent calculation to ensure that the geometry obtained from the SCI calculation is at the global minimum of the first electronic excited state. The absence of any imaginary frequencies prove beyond doubt that the geometry obtained from this selfconsistent SCI calculation is at the global minimum of the prescribed electronic state.

Here we present the results obtained from the ZINDO SCI calculation performed on the optimized excited-state geometry. Comparing the energy gaps from Table 4 with those from Table 3, we find that the Stoke's shifts in both these oligo-thiophenes are about \sim 0.25 to 0.27 eV. Besides, the near degeneracy of first and second excited states is lifted, and the oscillator strength decreases for the first excited state, whereas it increases for the second excited state.

Now we focus our attention to the effect of solvent polarity on the energies of the excited states. To compare our theoretical results with the observed fluorescence spectra, we should incorporate the effect of solvents on the theoretically calculated excitation spectra. For this reason, we perform the self-consistent reaction field calculation along with SCI method (SCRF-SCI)¹⁹ to take into account the effect of solvents on the excitation energies. In this method, the solvent is considered to be a continuum of uniform dielectric constant represented by the reaction field. The solute molecules are made to occupy a fixed cavity of radius a_0 within the solvent field. The radius a_0 is

TABLE 5: Comparison of Fluorescence Wavelength
Obtained from SCRF-SCI Calculation with Experimental
Results for Four and Six Oligo-Thiophene Molecules

systems	solvents	calculated wavelength (nm)	experimental wavelength (nm)
4-oligo-thiophene	Toluene	551	572
	THF	580	609
	DMF	607	637
6-oligo-thiophene	toluene	602	601
	THF	648	640
	DMF	680	649

fixed by calculating the greatest internuclear distance and by adding the van der Waals radii of the atoms involved. The gaps thus obtained for both four and six oligo-thiophene molecules are presented in Table 5.

Our theoretical fluorescence wavelengths match reasonably well with that of experimental values for solvents of low polarity, but the SCRF calculation gives a poorer estimate for highly polar solvents, as seen in case of 6-oligo-thiophene molecule. The experimentally observed red shift in the fluorescence spectra of 6-oligo-thiophene molecule is not significant as we increase the solvent polarity from 7.5 (THF) to 38.0 (DMF). Such a saturation effect is not well reproduced in the SCRF-SCI results tabulated in Table 5. Failure of the SCRF model for high-polarity solvent can be attributed to various factors like structural deformation of solute molecules, polarization of neighboring solvent molecules, nonuniform dielectric constant, and nonspherical cavity of the solute molecules within the solvent dielectric.

V. Summary

A class of new conjugated molecules containing donor (thiophene chain) and acceptor (malononitrile) moiety have been successfully synthesized. Their molecular structures are confirmed by ¹H NMR and ¹³C NMR. By increasing the number of thiophene units in the synthesized molecules, the excitation energy gap shifts toward the red region and finally saturates around 2.0 eV. From theoretical studies, we also observe a strong intramolecular charge transfer phenomenon between the thiophene donor and malononitrile acceptor in this class of D-A-D systems. The charge transfer character increases with the increase in the thiophene units and finally saturates in the oligomer with 14 thiophene units in conjugation with malononitrile. The saturation of gaps and other properties like permanent dipole moments and the oscillator strengths are arrived at from our theoretical calculations using DFT and ZINDO SCI. We have also calculated the Stoke's shift and the effect of solvents on the excited-state energies. Our theoretical results are in reasonable agreement with experiments.

Acknowledgment. We thank the Department of Science and Technology for supporting this work through the project SR/ S2/CMP-24/2003. We sincerely thank Snehangshu Patra for helping us in performing the CV measurements. We also thank Prof. N. Munichandraiah for useful discussions and comments regarding the CV measurements.

Supporting Information Available: Experimental procedures including the synthesis and NMR analysis, absorption and fluorescence spectra of 4-oligomer and 6-oligomer, and structural elucidation and geometry optimization of 6-oligo-thiophene molecule. This material is available free of charge via the Internet at http://pubs.acs.org.

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JP909635G