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Synthesis, characterization and laser flash photolysis studies of some naphthothiophenes bearing electron donor and acceptor functional groups

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Abstract

Photoinduced electron transfer processes have been investigated in a rigid naphthothiophene moiety which contains both electron donor (methoxy group, OCH_3) and acceptor (dicyanovinyl or methoxycarbonyl group) functional groups at its two different ends. Both steady state absorption and fluorescence measurements coupled with the estimation of electronic coupling matrix elements, H_{DA}, show the possibilities of occurrence of charge separation reactions within the donor and acceptor functional groups. Transient absorption measurements by laser flash photolysis technique using different delays in microsecond time domain demonstrate the presence of ion-pair in the triplet state and the stabilization of the radical ions within β-cyclodextrin (βCD) cavity against destructive charge recombination process. It appears that βCD microenvironment serves as the suitable medium to achieve one of the key requirements (enhancement of the survival duration of charge-separated species by retarding the charge recombination) for developing artificial photosynthetic device.

Keywords: Charge recombination; Charge-separated species; Laser flash photolysis; Naphthothiophenes; Charge transfer complex

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1. Introduction

To restrict the center-to-center (or edge-to-edge) distances between electron donors and acceptors without resorting to covalent attachments of the molecules, the photoinduced electron transfer (PET) studies could be conducted in rigid media. However, covalently linked donor–acceptor molecules have been extensively studied by several authors [1–8] in order to alleviate some uncertainties that may arise from electron transfer (ET) experiments in rigid matrices. Though in most of the bichromophoric or multichromophoric systems, the donor and acceptor moieties are connected by flexible spacers, lately attention has been paid mostly to study PET within linked donor–acceptor compounds where rigid polynorbornane bridges [9–11] and steroid structure [12] were used as linkers. Using of the rigid spacers is helpful to estimate the distance (center-to-center or edge-to-edge), which is fixed, between the redox centers within which charge separation or forward electron transfer reactions would occur. Nevertheless, due to the difficulties encountered in synthesizing, the number of donor–acceptor molecules in which the donor–acceptor distance and orientation are well defined by the molecular structure remains very small. So far, studies have been made on the synthesized donor–acceptor (DA) systems where the redox centers are mostly the organic molecules connected by the flexible polymethylene spacers or with semi-rigid/rigid spacers. In the present investigation electrochemical, steady state/time-resolved spectroscopic and laser flash photolysis measurements were made on the novel synthesized DA systems where the electron donor and acceptor functional groups are attached at the two different ends of a rigid structured naphthothiophene moiety (Fig. 1). In the two

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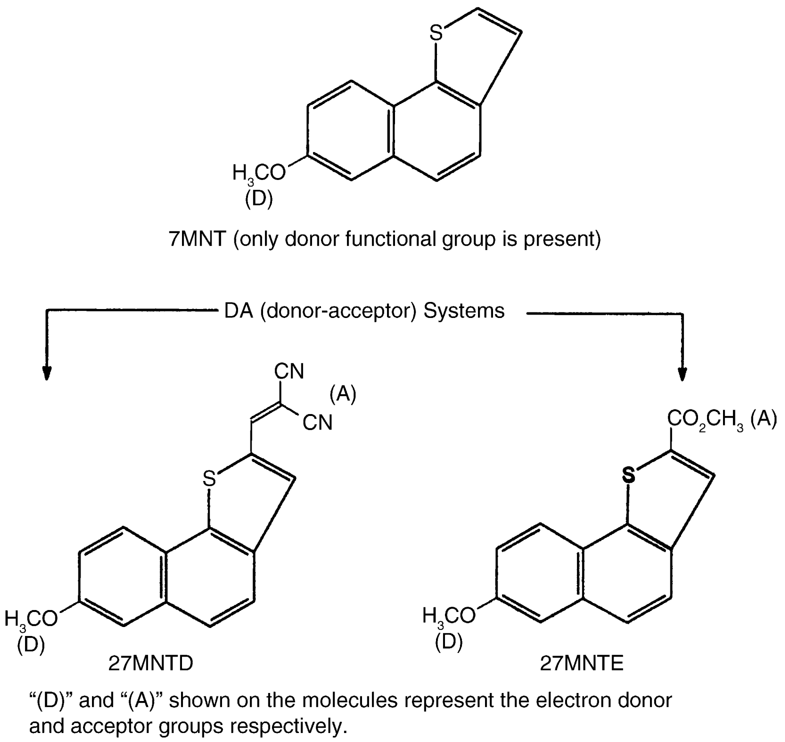


Fig. 1. Molecular structures of 7MNT, 27MNTD and 27MNTE.

novel synthesized DA systems, 2-(7-methoxynaphtho[1,2-*b*]thiophene-2-ylmethyelene) malononitrile (27MNTD) and 7-methoxynaphtho[1,2-*b*]thiophene-2-carbaxylic acid methyl ester (27MNTE), though the similar donor functional group (methoxy group, OCH_3) has been attached but the different acceptor functionalities (dicyanovinyl in case of 27MNTD and methoxycarbonyl for 27MNTE, Fig. 1) are present at the opposite end of the site of the molecules containing the donor group. The photophysical properties of these two DA systems have been compared with the another synthesized compound 7-methoxynaphtho[1,2-*b*]thiophene (7MNT), which appears to be the donor part of the above two DA systems as it contains only the donor functional group OCH_3 (Fig. 1). Due to the rigidity of the naphthothiophene moiety the distance between the donor and acceptor groups employed and their orientations are well defined. Our primary aim is to investigate the characteristics of undergoing charge separation reactions and to enhance the longevity of the resulting charge-separated species by reducing the energy wasting charge recombination process within the rigid structured DA systems. The present study may form the basis for building artificial photosynthetic device.

2. Experimental

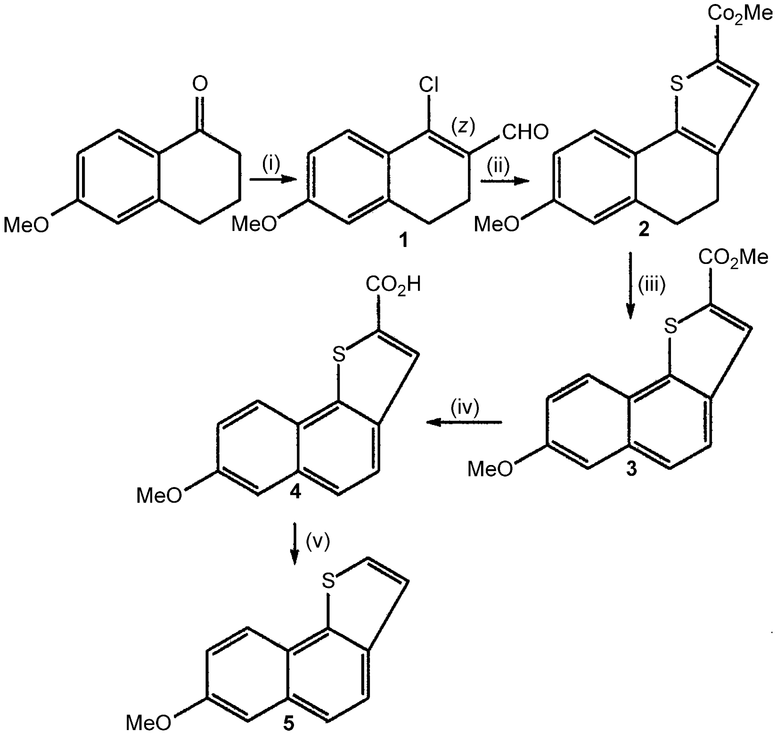
2.1. Materials

The details of synthesis of 7MNT, 27MNTD and 27MNTE (Fig. 1) and their characterizations are presented below. The steps involved in the synthesis are shown in Schemes 1 and 2.

*2.1.1. Synthesis of 7MNT (**5**), 27MNTD (**8**) and 27MNTE (**3**)*

*2.1.1.1. 1-Chloro-6-methoxy-3,4-dihydronaphthalene-2-carbaldehyde (**1**).* Phosphoryl chloride (14 mL, 150 mmol) was added dropwise under stirring and cooling (−10 to −5 °C) to dry DMF (40 mL) over 30 min. 6-Methoxy tetralone (17.6 g, 100 mmol) was added dropwise to the reaction mixture at the same temperature, which was stirred for 30 min at 0 °C and at 80 °C for 90 min. After cooling it was poured into ice cold solution of sodium acetate (25%, w/v) (100 mL). Compound extracted with ether (3× 100 mL), washed with water and dried (Na_2SO_4). A red colored, air sensitive solid material was obtained which was sufficiently pure for the next step.

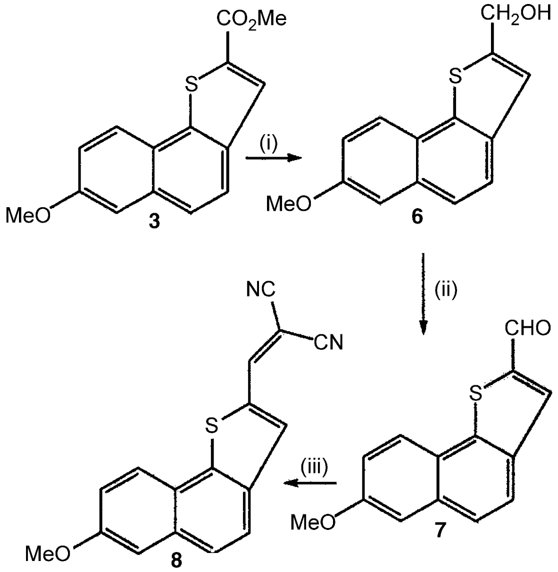
*2.1.1.2. 7-Methoxy-4,5-dihydronaphtho[1,2-b]thiophene-2-carboxylic acid methyl ester (**2**).* Methylthioglycolate (3.18 g, 30 mmol) was added dropwise to a well stirred solution of sodium methoxide prepared from Na (0.7 g, 30 mmol) and dry methanol (50 mL), in methanol at −10 to −5 °C. After 30 min the chloroaldehyde (**1**) (4.45 g, 20 mmol) in dry methanol (20 mL) was added dropwise over 30 min to the reaction mixture at the same temperature. After allowing the reaction mixture to attain room temperature and stirring for further 8 h at that temperature in an inert atmosphere, it was poured into ice water. After extraction with $CHCl_3$ (3× 50 mL) the organic layer was washed with water (3× 50 mL) and dried (Na_2SO_4). Removal of solvent left a solid which was crystallized from dichloromethane, white crystalline solid, mp 84 °C, yield 4.72 g, 86%; IR, ν_{max}



Reagents: (i) $POCL_3$/DMF; (ii) $HSCH_2CO_2Me$/NaOMe/MeOH; (iii) DDQ/1,4-dioxane; (iv) KOH/aqueous methanol; (v) Cu-bronze/quinoline.

Scheme 1.

(KBr) 1701 cm^{-1} (CO_2Me); NMR, δ_H (300 MHz, $CDCl_3$), 7.57 (1H, s), 7.37–7.34 (1H, m), 6.78–6.69 (2H, m), 3.87 (3H, s, CO_2Me), 3.83 (3H, s, OMe), 2.95–2.90 (2H, m, CH_2), 2.86–2.77 (2H, m, CH_2); δ_C (75 MHz, $CDCl_3$) 160.1, 143.9, 137.8, 134.3, 128.9, 125.3, 124.2, 114.5, 113.7, 112.6, 111.9, 55.8, 52.8, 52.4, 29.7, 24.0. Anal. Calcd for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14. Found: C, 65.78; H, 5.21.



Reagents: (i) LAH/THE; (ii) Oxalyl chloride/DMSO/triethylamine/ dichloromethane; (iii) Malononitrile/triethylamine/ethanol

Scheme 2.

*2.1.1.3. 7-Methoxynaphtho[1,2-b]thiophene-2-carboxylic acid methyl ester (**3**) (27MNTE).* To a warm solution of DDQ (4.76 g, 21 mmol) in dry 1,4-dioxan (150 mL), 7-methoxy-4,5-dihydronaphtho[1,2-*b*]thiophene-2-carboxylic acid methyl ester (**2**) was added. The resulting dark brown solution was heated under reflux for 90 min after which the stirring was discontinued, the mixture cooled and filtered. Evaporation of the filtrate under reduced pressure left a brown solid, which was crystallized from ether–petroleum ether mixture to leave a white crystalline solid, mp 98 °C, yield 4.38 g, 80%; IR, ν_{max} (KBr) 1712.7 cm^{-1} (CO_2Me); NMR, δ_H (300 MHz, $CDCl_3$) 8.11–8.02 (2H, m), 7.77 (1H, d, $J = 8.7$ Hz), 7.65 (1H, d, $J = 8.7$ Hz), 7.26–7.22 (2H, m), 3.96 (3H, s, CO_2Me), 3.95 (3H, s, OMe); δ_C (75 MHz, $CDCl_3$) 163.6, 159.0, 141.9, 135.5, 133.8, 132.0, 131.1, 125.8, 125.8, 123.9, 123.6, 119.1, 108.3, 55.8, 52.8. Anal. Calcd for $C_{15}H_{12}O_3S$: C, 66.16; H, 4.44. Found: C, 66.23; H, 4.33.

*2.1.1.4. 7-Methoxynaphtho[1,2-b]thiophene-2-carboxylic acid (**4**).* 7-Methoxynaphtho[1,2-*b*]thiophen-2-carboxylic acid methyl ester (**3**) (2.72 g, 10 mmol) was hydrolyzed with KOH (2.8 g, 50 mmol) in aqueous methanol (1:1) for 8 h. Reaction mixture was cooled and acidified in cold condition.

The separated solid, insoluble in most of the solvents, was filtered and dried. Crystallized from acetone, mp 222–225 °C. Yield 2.37 g, 92%; IR, $\nu_{\max}$ (KBr) 1674 cm^{-1} (C=O), 2951 cm^{-1} (COOH); NMR, δ_H (300 MHz, Acetone-d$_6$) 8.19 (1H, s), 8.13 (1H, d, $J = 8.9$ Hz), 7.93 (1H, d, $J = 8.7$ Hz), 7.81 (1 H, d, $J = 8.7$), 7.48 (1H, d, $J = 2.4$ Hz), 7.33 (1H, dd, $J = 2.4$, 8.9 Hz), 3.96 (3H, s, O*Me*); δ_C (75 MHz, Acetone-d$_6$) 205.7, 159.2, 148.0, 135.8, 134.0, 132.0, 126.0, 125.5, 124.2, 123.6, 123.6, 119.2, 108.5, 55.3. Anal. Calcd for $C_{14}H_{10}O_3S$: C, 65.10; H, 3.90. Found: C, 65.23; H, 3.84.

*2.1.1.5. 7-Methoxynaphtho[1,2-b]thiophene (**5**) (7MNT).* Activated copper-bronze (0.23 g, 4 mmol), 7-methoxynaphtho[1,2-*b*]thiophene-2-carboxylic acid (**4**) (0.258 g, 1 mmol) and quinoline (10 mL) were mechanically stirred at 200 °C for 60 min with a continuous flow of N_2 to expel the CO_2 formed. After cooling the reaction mixture was diluted with ether (50 mL) and filtered. The filtrate was washed with (1:1) aqueous HCl (3× 20 mL) to remove quinoline followed by washing with brine and dried (Na_2SO_4). Removal of solvent left a gray solid which was crystallized from ether-petroleum ether, mp 78 °C. Yield 0.19 g, 88%; NMR, δ_H (300 MHz, $CDCl_3$) 8.07 (1H, d, $J = 8.7$ Hz), 7.81 (1H, d, $J = 8.6$ Hz), 7.66 (1H, d, $J = 8.6$ Hz), 7.43 (2H, s), 7.26–7.22 (2H, m), 3.95 (3H, s, O*Me*); δ_C (75 MHz, $CDCl_3$), 157.9, 138.0, 136.3, 132.5, 125.5, 125.4, 124.9, 124.5, 124.2, 122.9, 118.7, 108.2, 55.8. Anal. Calcd for $C_{13}H_{10}O_3S$: C, 72.87; H, 4.70. Found: C, 72.98; H, 4.58.

*2.1.1.6. (7-Methoxynaphtho[1,2-b]thiophene-2-yl)methanol (**6**).* 7-Methoxynaphtho[1,2-*b*]thiophene-2-carboxylic acid methyl ester (**3**) (2.72 g, 10 mmol) dissolved in minimum quantity of dry THF was added dropwise from a pressure equalizing dropping funnel to a stirred suspension of LAH (0.45 g, 12 mmol) in dry THF (5 mL) at room temperature and stirring was continued for 30 min, followed by heating under reflux for 2 h. After cooling, saturated aqueous Na_2SO_4 solution was slowly added dropwise until a solid Na_2SO_4 was precipitated. The organic layer was separated by decantation, the aqueous part was washed with diethyl ether and the combined organic layer was washed with brine and dried (Na_2SO_4). Removal of solvent left a solid material which was purified by crystallization from ethyl acetate–petroleum ether to afford white crystalline solid, mp 84–86 °C, yield 2.24 g, 92%; IR, $\nu_{\max}$ (KBr) 3377 cm^{-1} (OH); NMR, δ_H (300 MHz, $CDCl_3$) 7.94 (1H, d, $J = 8.5$ Hz), 7.66 (1H, d, $J = 8.7$ Hz), 7.60 (1H, d, $J = 8.5$ Hz), 7.25–7.17 (3H, m), 4.91 (2H, s, CH_2OH), 3.91 (3H, s, O*Me*); δ_C (75 MHz, $CDCl_3$) 157.9, 142.8, 138.1, 136.0, 132.4, 125.4, 124.9, 124.4, 123.3, 122.8, 118.9, 108.1, 61.1, 55.8. Anal. Calcd for $C_{14}H_{12}O_2S$: C, 68.83; H, 4.95. Found: C, 68.73; H, 5.12.

*2.1.1.7. 7-Methoxynaphtho[1,2-b]thiophene-2- carboxaldehyde (**7**).* Oxalyl chloride (1 mL, 12 mmol) dissolved in dry dichloromethane (10 mL) was cooled to −78 °C under argon. Dry DMSO (1.8 mL, 25 mmol) in dry dichloromethane was added to it dropwise and stirred at −78 °C for 15 min. (7-Methoxynaphtho[1,2-*b*]thiophene-2-yl)methanol (**6**) (2.4 g, 10 mmol) in dry dichloromethane was then added to the reaction mixture and stirred for 45 min. Triethylamine (5.5 mL, 40 mmol) was then added to the reaction mixture which was allowed to come to room temperature and stirred for further 90 min. The reaction mixture was washed repeatedly with water to remove DMSO and dried (Na_2SO_4). Removal of solvent afforded a solid material which was crystallized from ethyl acetate petroleum ether, mp 118 °C. Yield 2.0 g, 83%; IR, $\nu_{\max}$ (KBr) 1660.6 cm^{-1} (CHO); NMR, δ_H (300 MHz, $CDCl_3$) 10.06 (1H, s, C*H*O), 8.07 (2H, d, $J = 8.4$ Hz), 7.79 (1H, d, $J = 8.7$ Hz), 7.66 (1H, d, $J = 8.7$ Hz), 7.26–7.23 (2H, m), 3.95 (3H, s, O*Me*); δ_C (75 MHz, $CDCl_3$) 184.4, 159.6, 141.4, 135.6, 135.4, 134.3, 126.3, 126.2, 126.2, 123.8, 123.7, 119.3, 108.5, 55.9. Anal. Calcd for $C_{14}H_{10}O_2S$: C, 69.40; H, 4.16. Found: C, 69.53; H, 4.23.

*2.1.1.8. 2-(7-Methoxynaphtho[1,2-b]thiophene-2-ylmethelene)malononitrile (**8**) (27MNTD).* 7-Methoxynaphtho[1,2-*b*]thiophene-2-carboxaldehyde (**7**) (0.19 g, 0.8 mmol) and malononitrile (0.068 g, 1 mmol) dissolved in minimum quantity of ethanol were stirred with 2–5 drops of triethyl amine at room temperature for 60 min. The precipitated solid was filtered and the residue was crystallized from alcohol. A dark yellow crystalline solid was obtained, mp 203–205 °C, yield 0.21 g, 93%; IR, $\nu_{\max}$ (KBr) 2116 cm^{-1} (CN), 1618 cm^{-1} (C=C); NMR, δ_H (300 MHz, $CDCl_3$) 8.04 (1H, d, $J = 8.5$ Hz), 7.95 (1H, s), 7.87 (1H, s), 7.72 (1H, d, $J = 8.8$ Hz), 7.63 (1H, d, $J = 8.8$ Hz), 7.24–7.19 (2H, m), 3.90 (3H, s, O*Me*); δ_C (75 MHz, $CDCl_3$) 160.3, 151.8, 137.6, 135.1, 134.8, 133.0, 127.1, 126.6, 123.2, 119.6, 114.5, 108.9, 55.9. Anal. Calcd for $C_{17}H_{10}N_2OS$: C, 70.33; H, 3.47; N, 9.65. Found: C, 70.38; H, 3.56; N, 9.73.

2.2. Other chemicals used and preparation of solutions

β-Cyclodextrin (βCD) (Aldrich), methanol (MeOH) (E. Merck, Germany) of spectroscopic grade were used as received. Water was deionized using a Millipore Milli-Q system. The solutions were prepared by dissolving the appropriate amount of βCD in water. Because of the low solubility in water, the compounds studied were dissolved in MeOH and added to the water solution of CDs, this is a well-known procedure implemented in earlier cases [13,14]. The final methanol concentration in a mixture was <2% (v/v).

2.3. Spectroscopic apparatus

At the ambient temperature (296 K) steady state electronic absorption and fluorescence emission spectra of dilute solutions (10^{-4} to 10^{-6} mol dm^{-3}) of the samples were recorded using 1 cm path length rectangular quartz cells by means of an absorption spectrophotometer (Shimadzu UV-VIS 2101PC) and F-4500 fluorescence spectrophotometer (Hitachi), respectively. Fluorescence lifetimes were measured by using a time-correlated single photon counting (TCSPC) fluorimeter. The experimental setup for picosecond TCSPC is as follows. Briefly, a picosecond diode laser at 408 nm (IBH, UK, NanoLED-07, s/n0391) was used as a light source. The fluorescence signal was detected in magic angle (54.7°) polarization using Hamamatsu MCP PMT (3809U). The typical system response for this laser system is ~75 ps. The decays were analyzed using IBH DAS-6 decay analysis software.

2.4. Laser flash photolysis

Transient absorption spectra were measured using nanosecond flash photolysis setup (Applied Photophysics) containing a Nd:YAG laser (DCR-11, Spectra Physics). The samples were excited by 355 nm laser light (FWHM = 8 ns). Triplet spectra were monitored through absorption light from a pulsed Xe lamp (250 W). The photomultiplier (IP28) output was fed into a combiscope (Fluke PM3394B, 200 MHz) and the data were analyzed using Fluke View Combiscope software.

2.5. Electrochemical measurements

The redox potentials of the synthesized compounds containing electron donor and acceptor functional groups were determined in ACN solvent by cyclic voltammetric method using the PAR model 370-4 electrochemistry system with a three electrode configuration including SCE as a standard. Tetraethylammonium perchlorate (TEAP) was used as the supporting electrolyte [2]. The oxidized species of 7MNT has been prepared by constant current charger (model DB 300 DB Electronics, India).

3. Results and discussion

3.1. Electrochemical measurements

Fig. 2 reproduces the cyclic voltammogram of 27MNTD in ACN. The observed reversible patterns indicate the stability of the radical ions. The half-wave oxidation potential, estimated from the cyclic voltammogram of 27MNTD, is found to be +0.43 V. Scanning the cathode region up to −1.4 V show redox waves related to the reduction of the acceptor group. The reduction potential was determined to be −0.94 V. This value should correspond to the half-wave reduction potential of the acceptor part due to substitution of the dicyanovinyl group (Fig. 1). The observed oxidation potential value, on the other hand, should be responsible due to the presence of the donor part containing methoxy functional group.

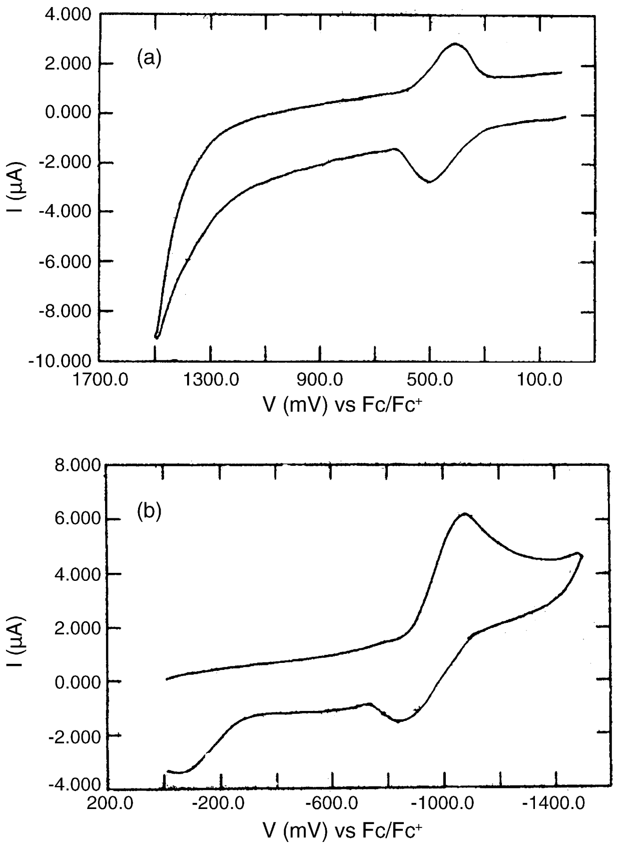


Fig. 2. Cyclic voltammogram of 27MNTD in ACN.

In the other DA system 27MNTE, the donor group (OCH_3) is the same as in 27MNTD but the acceptor group is different (methoxycarbonyl group, Fig. 1). In the cyclic voltammogram of 27MNTE, the half-wave oxidation potential value (+0.47 V) looks very similar to that of the other DA system 27MNTD. This observation is in accord to our expectation as similar donor group (OCH_3) is present in both the molecules. However, due to the presence of the different acceptor group in 27MNTE, the reduction potential value is found to be somewhat different (~−1.11 V).

Thus, the results obtained from the electrochemical measurements by cyclic voltammetry suggest that from the thermodynamical point of view there is a possibility of occurrence of charge separation or forward electron transfer reactions within 27MNTD and 27MNTE molecules where electron donor and acceptor groups are attached at the two different ends of the rigid aromatic framework (naphthothiophene moiety).

As the voltammogram of the DA system exhibits redox waves, of reversible nature, related to the both oxidation and reduction of the donor and acceptor groups, respectively, the following inference could be drawn.

Methoxy group being a well-known electron donor group undergoes mesomeric interaction with the electron acceptor functions by delocalization of its lone pair of electrons through the aromatic system.

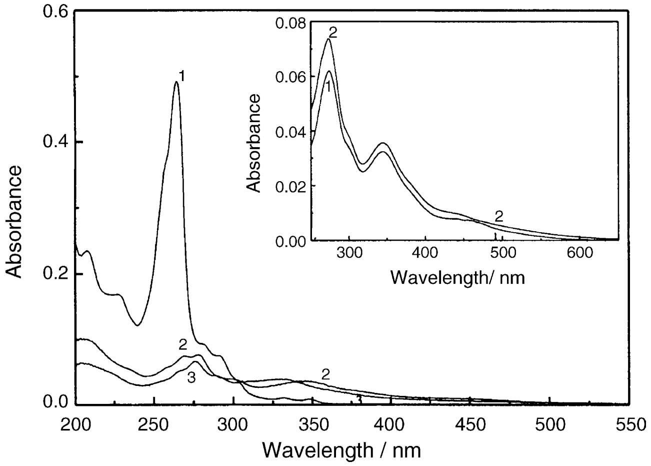


Fig. 3. Steady state electronic absorption spectra of (curve 1) 7MNT, (curve 2) 27MNTD and (curve 3) 27MNTE in aqueous medium. (Inset) Steady state electronic absorption spectra of 27MNTD (Conc. ~3.5 $\times 10^{-5}$ mol dm^{-3}) in aqueous medium (curve 1) without and (curve 2) with the presence of βCD (Conc. ~3.2 $\times 10^{-4}$ mol dm^{-3}).

3.2. Steady state absorption measurements

Fig. 3 shows the UV absorption spectra of the molecule 7MNT which contains only the donor functional group OCH_3 being attached with rigid naphthothiophene moiety (Fig. 1) and the donor–acceptor (DA) systems 27MNTD and 27MNTE in aqueous solution. Only the absorption spectra of the DA systems exhibit a low energy tail having a weak but finite absorption and extending down to 550 nm. These low energy bands (Fig. 3) possess the typical features of charge transfer (CT) transition such as a broad and structureless shape. These CT bands appeared in the absorption spectra of DA systems in aqueous medium indicate the presence of appreciable interaction in the ground state between the donor and the acceptor sites, present within the DA systems 27MNTD and 27MNTE.

With the addition of βCD the entire absorption spectra including the long-wavelength band, assigned as CT, undergoes a small hyperchromic effect without any noticeable spectral shift (inset of Fig. 3). On the basis of this spectral change it appears that both 27MNTD and 27MNTE form inclusion complexes with βCD.

3.3. Charge-transfer spectra

In the present DA systems, the electron donor and acceptor groups are separated by a rigid aromatic framework of naphthothiophene (Fig. 1). In 7MNT, only the donor group OCH_3 is attached with this rigid framework which consists of extended π-systems (Fig. 1). Attachment of the donor function to the aromatic frame and subsequent delocalization of the lone pair of electrons of the former makes the molecule electron-rich. Examination of the different canonical structures will demonstrate that several sites in the molecule have high concentration of negative charge.

Now, when the functional acceptor groups would be incorporated in the other side of the 7MNT moiety i.e., in the case of 27MNTD and 27MNTE where dicyanovinyl and methoxycarbonyl are present as acceptor functional groups, overlapping between acceptor functionalities and the electron-rich site (which corresponds 7MNT moiety) in the molecules are not unexpected. It is logical to presume that this overlapping causes the formation of ground state CT. From the UV absorption spectral measurements, the formation of ground state CT has been confirmed (see above).

From the charge transfer band in these systems the electronic coupling matrix element (H_{DA}) for electron transfer can be estimated by using the Hush relation [15],

$$H_{DA}(\mathrm{cm}^{-1}) = \left(\frac{2.06 \times 10^{-2}}{R}\right)(\epsilon^{CT}_{max}\bar{\nu}^{CT}_{max}\Delta\bar{\nu}^{CT}_{1/2})^{1/2} \qquad (1)$$

where R, separation between the center of 7MNT nucleus and the acceptor group, is in Å, ϵ^{CT}_{max} is the molar absorptivity at the absorbance maximum of the CT absorption band in M^{-1} cm^{-1} and $\Delta\bar{\nu}^{CT}_{1/2}$ is the full width of the band at the half maximum in cm^{-1}. It is to be pointed out here that the value of R was chosen as ~3 Å to estimate H_{DA}. As steady state experiments clearly demonstrate the formation of charge transfer complex it is obvious that the minimum distance between the center of the donor part (7MNT moiety) and the acceptor functionalities (groups) which overlaps with the former one in space should be around 3 Å. This sort contact distance enables a close interaction between the donor part 7MNT and the electron acceptor group (dicyanovinyl group in case of 27MNTD and methoxycarbonyl for 27MNTE) to facilitate the formation of charge transfer complex [16]. The values of the electronic coupling matrix element are given in Table 1. The large values of H_{DA} indicate strong cou-

Table 1
Electronic interaction energies in different donor–acceptor systems

System	ϵ^{CT}_{max} (M^{-1} cm^{-1})	$\bar{\nu}^{CT}_{max}$ (cm^{-1})	$\Delta\bar{\nu}^{CT}_{1/2}$ (cm^{-1})	H_{DA}[a] (eV)
27MNTD + water	1023	29248	4454	0.31
27MNTD + water + βCD	937	29199	4233	0.29
27MNTE + water	2757	31417	7385	0.67
27MNTE + water + βCD	3567	30690	4347	0.59

[a] Values were estimated using $R \sim 3$ Å (see text).

pling between the 7MNT nucleus (electron-rich) and acceptor groups due to their close proximity [17]. The value of H_{DA} for 27MNTE is observed to be larger (nearly doubled) than that for 27MNTD (Table 1) in both aqueous and aqueous βCD media. In 27MNTE molecule the acceptor group being connected with the 7MNT nucleus by a single bond (Fig. 1) undergoes free rotation and this would result in formations of various canonical structures through the weak as well as strong coupling between the ester group and the aromatic core. However, the observed large value of H_{DA} seemingly indicates the predominance of the structures formed mostly from the latter coupling. In case of 27MNTD, the rotation of dicyanovinyl group seems to be significantly hindered due to its attachment with 7MNT by a rigid double bond. Moreover, the magnitude of the electronic coupling matrix element, H_{DA}, remains unchanged (Table 1) when the molecule in aqueous medium is incorporated into βCD cavity. This is in accord to our expectation. As the molecules are structurally rigid and the lengths of the molecules are very close to that of βCD (~7.9 Å), the conformational geometry (overlapping of the acceptor functionalities with the donor part) remains more or less unchanged even after inclusion within βCD cavity.

3.4. Steady state and time-resolved fluorescence measurements

The steady state fluorescence spectrum of 7MNT in aqueous medium shows remarkable difference from the corresponding spectra of 27MNTD and 27MNTE (Fig. 4a and b). To prevent any nonlinearity of the fluorescence intensity, the isosbestic point of the absorption spectra (~312 nm, Fig. 3) of the 7MNT and 27MNTD (or 27MNTE) was chosen as the excitation wavelength [18]. On excitation of 27MNTD at the isosbestic point it was surprisingly observed that the fluorescence band which observed clearly for 7MNT, between 340 and 550 nm, was almost quenched, and a long wavelength broad band of large intensity peaking at about 475 nm appeared in aqueous medium (Fig. 4a). Moreover on direct excitation of the CT absorption band of 27MNTD, situated at 350 nm, fluorescence band of considerable intensity at the same energy position 475 nm was found in aqueous medium. Almost similar type of observation was found in case of 27MNTE in aqueous medium, only difference being that the long-wavelength fluorescence band of considerable intensity appeared at about 440 nm (Fig. 4b).

From the above observations, it reveals that longer wavelength band (475 nm for 27MNTD and 440 nm for 27MNTE) should be the CT emission band whose formation is largely facilitated in intramolecular system comprising the donor and acceptor groups [2].

On direct excitation of CT absorption band (350 nm for 27MNTD and 330 nm for 27MNTE) in aqueous solution with addition of very small amount of βCD (~10^{-4} mol dm^{-3}, Fig. 4c), a considerable blue shift (~10 nm for 27MNTD and ~15 nm for 27MNTE) in emission maxima accompanied by

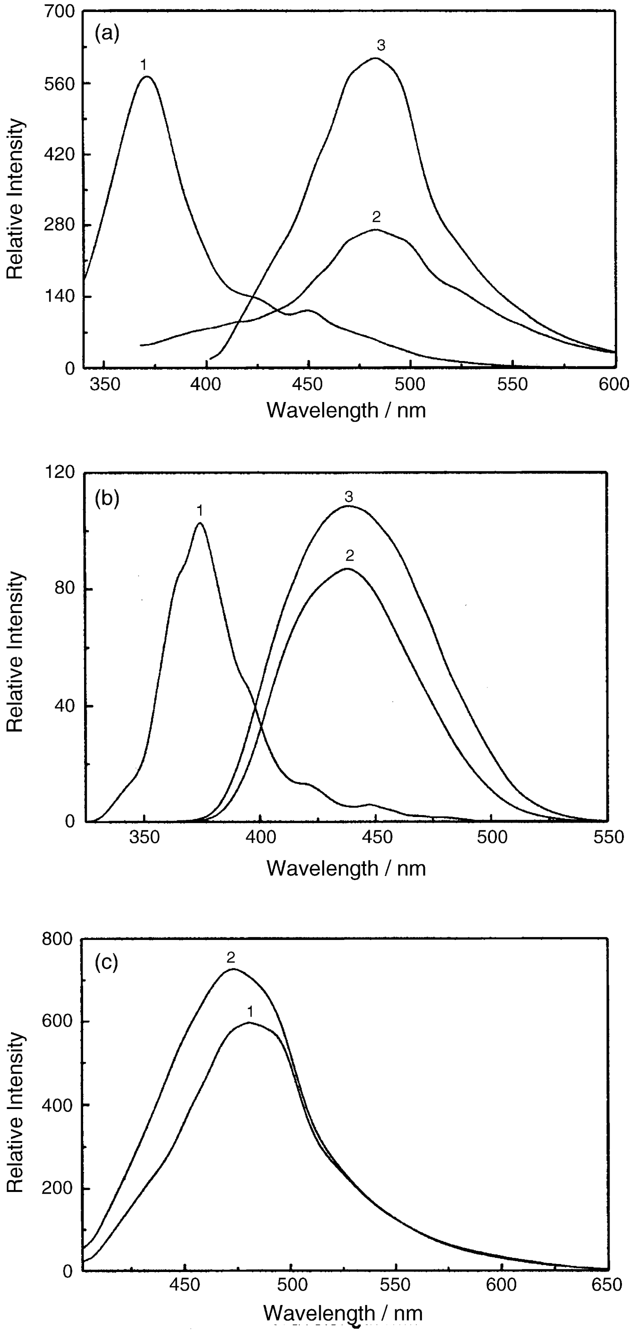


Fig. 4. (a) Fluorescence emission spectra of 7MNT (Conc. ~6.6 × 10^{-5} mol dm^{-3}) with excitation wavelength ~312 nm (curve 1), 27MNTD (Conc. ~3.5 × 10^{-5} mol dm^{-3}) with excitation wavelength ~312 nm (curve 2) and ~350 nm (curve 3) in aqueous medium. (b) Fluorescence emission spectra of 7MNT (Conc. ~5.6 × 10^{-5} mol dm^{-3}) with excitation wavelength ~307 nm (curve 1), 27MNTE (Conc. ~1.4 × 10^{-5} mol dm^{-3}) with excitation wavelength ~307 nm (curve 2) and ~330 nm (curve 3) in aqueous medium. (c) Fluorescence emission spectra of 27MNTD (Conc. ~3.5 × 10^{-5} mol dm^{-3}) without (curve 1) and with βCD (Conc. ~3.2 × 10^{-4} mol dm^{-3}) (curve 2) in aqueous medium with excitation of CT band (λ_{ex} = 350 nm).

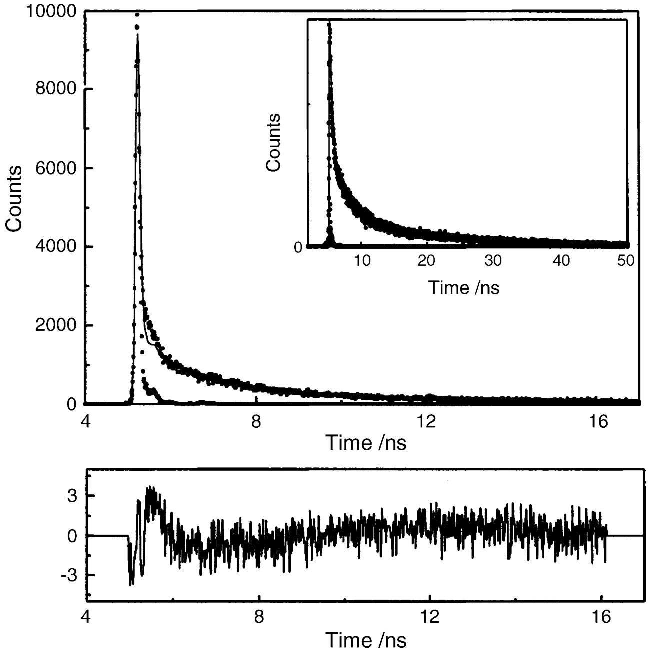


Fig. 5. Fluorescence decay curve of 27MNTD associated with laser profile in aqueous medium at 296 K after 408 nm laser irradiation (emission wavelength ∼ 475 nm). The curve shows the bi-exponential fit and residuals ($\chi^2 \sim 1.3$). (Inset) Fluorescence decay curve of 27MNTD associated with laser profile in aqueous medium with βCD at 296 K. The emission wavelength ∼450 nm ($\chi^2 \sim 1.3$).

increment of emission intensity was apparent. This could be taken as an evidence for the formation of inclusion complexes in the case of these DA systems [13]. When 27MNTD or 27MNTE is included within the βCD cavity, water is expelled and the hydrophobic interior of the βCD molecule offers a non-polar environment to the donor–acceptor (DA) system. When the environment is changed from polar to non-polar, fluorescence band (here CT emission band) undergoes a blue shift in accordance with the normal characteristics of a CT band.

Using the excitation at CT absorption band maximum and monitoring at $\lambda_{em} \sim 475$ nm the fluorescence decay curve of 27MNTD in aqueous solution was measured (Fig. 5). The decay of bi-exponential nature was observed which on analyzing yields a very fast decay of less than 40 ps along with a relatively slower decay (2.4 ns for 27MNTD and 1.1 ns for 27MNTE). Since fast component seems to be spurious as it is less than the time resolution of the instrument, we may consider only the longer one as the lifetime of the excited CT complex [19].

Table 2
Values for fluorescence lifetimes (τ) of DA systems in different media (λ_{ex} = 408 nm)

System	λ_{fluo} (nm)	τ (ns) (±5%)	χ^2
27MNTD + water	475	2.4	1.3
27MNTD + water + βCD	450	6.5	1.3
27MNTE + water	430	1.1	1.2
27MNTE + water + βCD	420	1.2	1.1

In the case of both the DA systems further increase in the magnitudes of the CT emission lifetimes in aqueous medium was observed with addition of βCD, the effect being more pronounced in the case of 27MNTD (inset of Fig. 5) (Table 2). So from the observations, specially for 27MNTD molecule, it seemingly indicates that the encapsulation of the DA systems in βCD cavity in aqueous medium imposes some constraints on it, which oppose the energy wasting charge recombination process and the charge-separated species sustain for relatively longer period within the cavity before undergoing destructive charge recombination. In presence of βCD, the enhanced fluorescence lifetimes of 27MNTD indicate that in non-polar environment of the interior of the cavity CT complex becomes more stable before undergoing destruction through charge recombination mechanism though the degree of overlapping

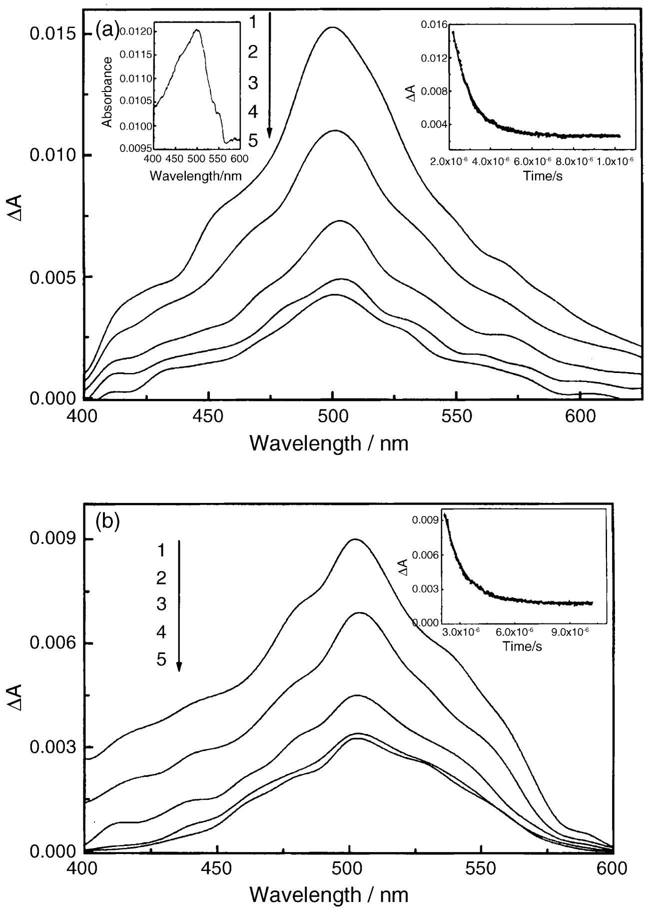


Fig. 6. (a) Transient absorption spectra of 27MNTD (excitation wavelength ∼355 nm) at the ambient temperature at delay times: (1) 2.3 μs; (2) 2.5 μs; (3) 3.0 μs; (4) 3.5 μs; (5) 4.0 μs measured in aqueous medium without βCD. (Left inset) Steady state electronic absorption spectra of radical cation of 7MNT in aqueous medium without βCD at 296 K. (Right inset) The time profile of the absorbance (ΔA) of the cationic band of 27MNTD (∼500 nm) in aqueous medium without βCD at 296 K. (b) Transient absorption spectra of 27MNTD (excitation wavelength ∼ 355 nm) at the ambient temperature at delay times: (1) 2.3 μs; (2) 2.5 μs; (3) 3.0 μs; (4) 3.5 μs; (5) 4.0 μs measured in aqueous medium with βCD. (Inset) The time profile of the absorbance (ΔA) of the cationic band of 27MNTD (∼500 nm) in aqueous medium with βCD at 296 K.

between the acceptor groups and the electron-rich 7MNT moiety remains nearly the same. However to look better insight the mechanism transient absorption measurements were made by laser flash photolysis technique (vide infra).

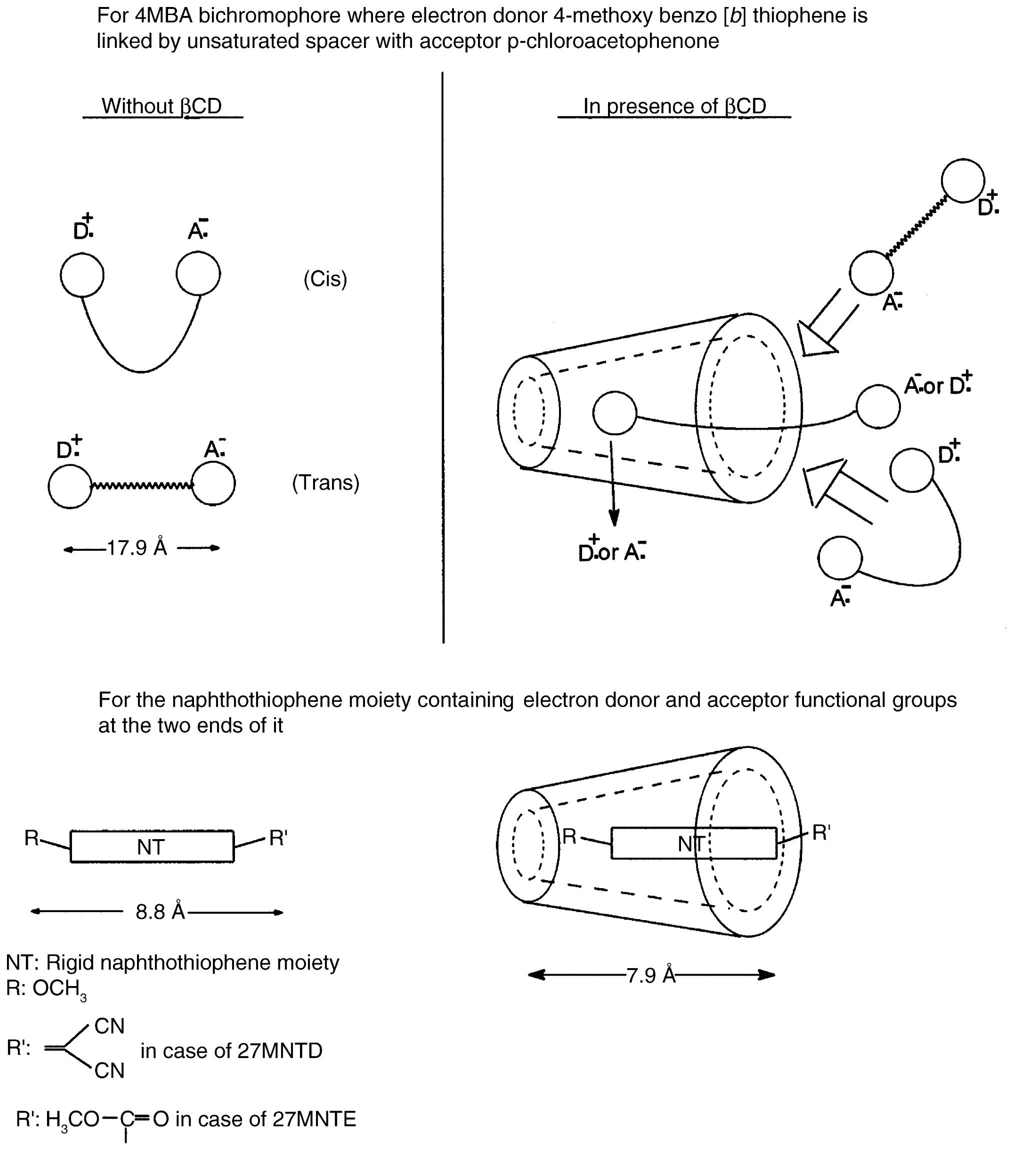
3.5. Transient absorption measurements

The transient absorption spectra of 7MNT, 27MNTD and 27MNTE in aqueous medium, without and with βCD, have been measured by direct excitation of the ground state CT complex situated at 355 nm region, using the third harmonic of Nd:YAG laser. A broad transient band of single lifetime peaking nearly at 500 nm was observed for 27MNTD (also for 27MNTE) in aqueous medium, in absence as well as in presence of βCD (Fig. 6a and b). This band was absent in case of 7MNT (donor part of both 27MNTD and 27MNTE) in aqueous medium.

Table 3
The values of the rates associated with the charge recombination (k_{CR}) and formation of loose-structured charge-separated species (k_{CST}) in different media for the present DA systems, values of yield, ϕ_R, of loose-structured charge-separated species and ion-pair lifetime, τ_{ip}, at the ambient temperature

System	ϕ_R	k_{CST} (s^{-1})	k_{CR} (s^{-1})	τ_{ip} (μs)
27MNTD + water	0.03	2.90×10^4	9.11×10^5	1.06
27MNTD + water + βCD	0.04	2.93×10^4	6.85×10^5	1.40
27MNTE + water	0.03	4.10×10^4	1.29×10^6	0.75
27MNTE + water + βCD	0.08	6.94×10^4	7.48×10^5	1.22

The naphthothiophene cation radical, produced by electrochemical oxidation of 7MNT, exhibits electronic absorption band at 500 nm (left inset of Fig. 6a). This observation confirms that 500 nm band observed in the transient spectra of D–A systems should be responsible due to



Scheme 3.

naphthothiophene cation radical. By monitoring directly the appearance and decay of the characteristic band at 500 nm for naphthothiophene cation radical of 27MNTD (and also 27MNTE) without and with βCD (inset of Fig. 6a and b), the first order rates associated with charge recombination (k_{CR}), formation of loose-structured species (k_{CST}), the yield ϕ_R and ion-pair lifetime τ_{ip} were determined (Table 3) using Eqs. (2) and (3) [13,20,21]:

$$\tau_{ip} = (k_{CR} + k_{CST})^{-1} \quad (2)$$

$$\phi_R = k_{CST}\tau_{ip} \quad (3)$$

In this study, the important finding is the enhancement of lifetime of the radical cation i.e., ion-pair lifetime (τ_{ip}) and ϕ_R values in presence of βCD. Increase of τ_{ip} value demonstrates that the radicals are protected within βCD cavity for relatively long periods before recombination starts.

From the observed k_{CR} values (Table 3) it is apparent that the charge recombination process within the present donor–acceptor systems (27MNTD and 27MNTE) when introduced in βCD cavity becomes slower than the rate observed in only aqueous medium. So, from the above observations coupled with the findings of the higher yield (ϕ_R) of the loose-structured charge-separated species in presence of βCD it could be concluded that the loose-structured charge-separated species are stabilized against the destructive charge recombination process in presence of βCD.

As in both the DA systems the base molecule, with which the electron-donating and accepting groups are attached, is rigid, it is reasonable to think that the core molecule should remain unaffected on inclusion within βCD cavity. The small changes observed in the rate parameters in βCD environment appears to be due to the change in environment from highly polar aqueous medium to non-polar interior of βCD.

In our earlier paper [13] we reported that in the case of the relatively flexible bichromophore molecule 4MBA the values of ϕ_R, τ_{ip}, k_{CR} changed significantly when it is encapsulated within βCD. In our present studies, both 27MNTD and 27MNTE systems have single rigid structural conformation unlike 4MBA and could be incorporated as a whole into the βCD cavity without deforming much of its stable conformation as their lengths are very similar to the length of βCD (Scheme 3). So, the geometrical constraints imposed by the cyclodextrin cavity on the photogenerated intermediates should not be too large. Nevertheless, even for rigid structured donor–acceptor systems, the βCD microenvironment seems to be the good medium to achieve one of the key requirements for artificial photosynthesis namely the enhancement of the longevity of charge-separated species by reducing the energy wasting charge recombination process as it was found, though relatively larger extent, in the case of 4MBA [13].

4. Conclusions

In this paper have been discussed the methods of synthesis and characterizations of the three novel naphthothiophene derivatives which contain, except one, both electron donor and acceptor functional groups being attached at the two different ends of the rigid framework of naphthothiophene moiety. UV absorption studies and steady state fluorescence measurements reveal the formation of charge transfer (CT) complex both in ground and excited electronic state S_1 in aqueous medium as well as in presence of βCD. The kinetic analysis on the transient cationic band shows the enhancement of the longevity of the charge-separated species when the molecules are incorporated within βCD. βCD appears to be the suitable medium to achieve one of the key requirements for designing artificial photosynthetic devices both with the rigid and flexible DA systems.

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