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ELECTRONIC AND FT-IR SPECTRAL INVESTIGATIONS OF THE CHARGE-TRANSFER INTERACTIONS BETWEEN THREE SYMMETRICALLY SUBSTITUTED TRIAZINE-STILBENE DERIVATIVES WITH SOME π-ACCEPTORS. PART THREE : TCNQ

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ABSTRACT

Fluorescent brighteners (FBs) are primarily applied to textiles to enhance their whiteness and brightness and they also significantly increase the UV-blocking properties of the medium to which they are applied. In order to improve the chemical and physical properties of fluorescent brighteners, the charge-transfer (CT) complexes of three triazine-stilbene derivatives (**TS**) with 7,7',8,8'-tetracyanoquinodimethane (TCNQ) were synthesized and spectroscopically investigated. The obtained complexes with the general formula [(**TS**)(acceptor)$_2$] with a 2 : 1 acceptor: donor molar ratio. Elemental analysis (CHN), electronic spectra, photometric titration and mid infrared spectra were used to predict the position of the CT interaction between the donating and accepting sites.

Key words: Fluorescent brighteners, Triazine-stibene derivatives, Charge-transfer, TCNQ.

INTRODUCTION

Charge-transfer (CT) complexation is of great importance in chemical reactions, including addition, substitution, condensation[1], biochemical and bioelectrochemical energy-transfer processes[2], biological systems[3], and drug–receptor binding mechanisms. For example, drug action, enzyme catalysis, ion transfers through lipophilic membranes[4], and certain π-acceptors have been successfully utilized in the pharmaceutical analysis of some drugs in pure form or in pharmaceutical preparations[5-7]. Furthermore, CT complexation is also of great importance in many applications and fields, such as in non-linear optical

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materials, electrically conductive materials, second-order non-linear optical activity, microemulsions, surface chemistry, photocatalysts, dendrimers, solar energy storage, organic semiconductors, and the investigation of redox processes[8-13]. CT complexes that use organic species are intensively studied because of their special type of interaction, which is accompanied by the transfer of an electron from the donor to the acceptor[14]. In addition, the protonation of the donor from acidic acceptors is a route for the formation of ion-pair adducts[15].

The aim of this paper is directed to investigate the CT complexes of three triazine-stilbene derivatives; namely sodium(E)-6,6′-(ethene-1,2-diyl)bis(3-(4-(dimethyl-amino)-6-(2-hydroxyethyl -amino)-1,3,5-triazin-2-ylamino) benzenesulfonate (**TS1**), sodium (E)-6,6′-(ethene-1,2-diyl) bis(3-(4-(2-hydroxyethyl-amino)-6-morpholino-1,3,5-triazin-2-yl-amino) benzenesulfonate (**TS2**) and sodium (E)-6,6′-(ethene-1,2-diyl) bis(3-(4-(diethyl-amino)-6-(2-hydroxyethylamino)-1,3,5-triazin-2-yl-amino) benzene-sulfonate (**TS3**) as the donors with 7,7',8,8'-tetracyanoquinodimethane (TCNQ) as π-acceptor spectrophotometrically. These complexes are readily prepared from the reaction of the donors with TCNQ in methanol media. The synthesized CT complexes were structurally characterized to interpret the behavior of interactions using IR, UV-Vis techniques and elemental analyses (CHN). Benesi-Hildebrand and its modification methods were applied for the determination of the spectroscopic physical data such as formation constant (K_{CT}), molar extinction coefficient (ε_{CT}), standard free energy ($\Delta G°$), oscillator strength (f) and transition dipole moment (μ).

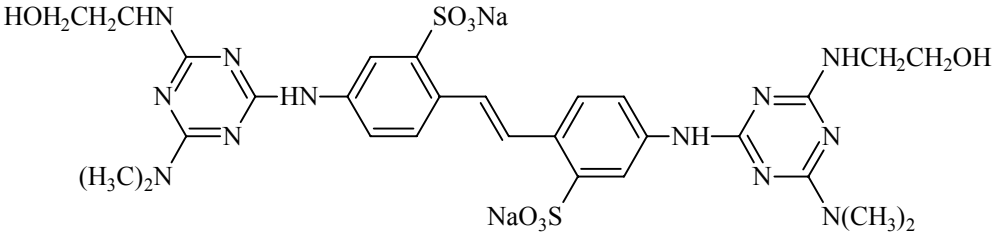
EXPERIMENTAL

Materials and analysis

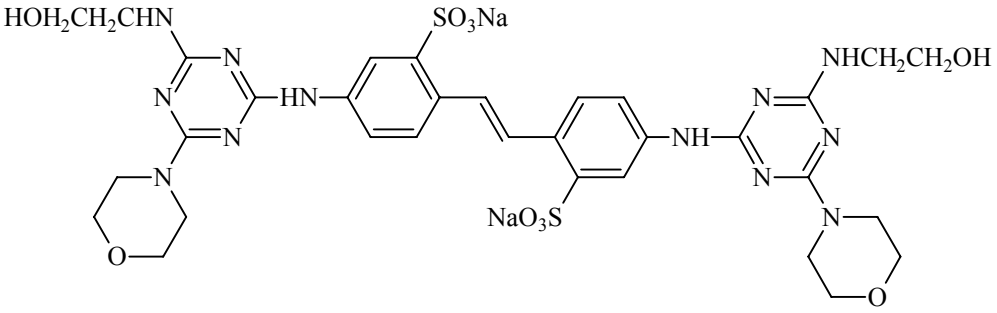
All chemicals, which were purchased from commercial sources (Sigma-Aldrich and Merck), were of analytical grade. The solvents were used without further purification. The three 4,4′-bis-(1,3,5-triazinylamino)stilbene-2,2′-disulfonate donors (**TS1**, **TS2** and **TS3**; Formula I) were obtained by synthesis according to the literature methods[16]. The elemental analyses of the carbon, hydrogen and nitrogen content were performed using a Perkin-Elmer CHN 2400 (USA). The electronic absorption spectra of the donors, the acceptor and the synthesized complexes were recorded in methanol over a wavelength range of 200-800 nm using a Perkin-Elmer Lambda 25 UV/Vis double-beam spectrophotometer. The instrument was fitted with a quartz cell that had a path length of 1.0 cm. The infrared (IR) spectra using KBr discs within the range of 4000-400 cm^{-1} for the complexes were recorded on a Shimadzu FT-IR spectrophotometer with 30 scans at 2 cm^{-1} resolution.

Synthesis

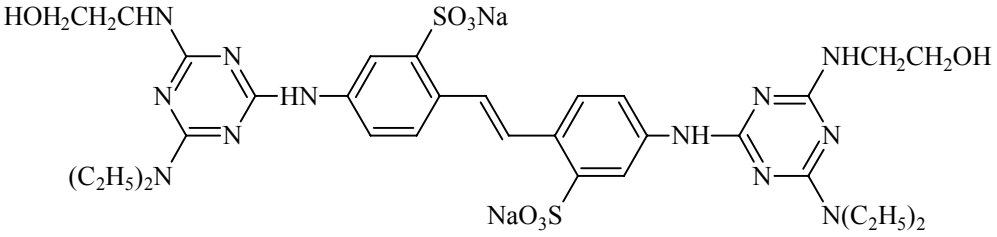
The charge-transfer complexes of the **TS1**, **TS2** and **TS3** donor with the TCNQ acceptor were prepared by mixing 1 mmol of each donor in pure–grade methanol (20 mL) with 1 mmol of TCNQ acceptor in methanol (20 mL). The mixtures were stirred for approximately 30 min and allowed to evaporate slowly at room temperature resulting in the precipitation of the solid complexes. The resultant complexes were filtered and washed well with methanol. Then, the synthesized complexes were collected and dried under vacuum over anhydrous calcium chloride for 24 h.



TS1



TS2



TS3

Formula I: Chemical structure of triazine-stilbene derivatives; TS1, TS2 and TS3

RESULTS AND DISCUSSION

Elemental analysis

Elemental analyses (C, H, and N) of the CT complexes were performed, and the obtained results are as follows:

(i) [(**TS1**)(TCNQ)$_2$]: $C_{52}H_{42}N_{20}O_8Na_2S_2$; Mol. wt. = 1184.38; Calc.: %C, 52.68; %H, 3.54; %N, 23.64, Found: %C, 52.61; %H, 3.49; %N, 23.60.

(ii) [(**TS2**)(TCNQ)$_2$]: $C_{56}H_{46}N_{20}O_{10}Na_2S_2$; Mol. wt. = 1268.62; Calc.: %C, 52.97; %H, 3.62; %N, 22.07, Found: %C, 53.05; %H, 3.59; %N, 21.94.

(iii) [(**TS3**)(TCNQ)$_2$]: $C_{56}H_{50}N_{20}O_8Na_2S_2$; Mol. wt. = 1240.38; Calc.: %C, 54.17; %H, 4.03; %N, 22.57, Found: %C, 54.22; %H, 3.99; %N, 22.60.

The resulting values are in good agreement with the calculated values, and the suggested values are in agreement with the molar ratios determined from the spectrophotometric titration curves. The stoichiometry of the complexes with the TCNQ acceptor was found to have a 1 : 2 ratio. Based on the obtained data, the synthesized complexes were formulated as [(**TS1**)(TCNQ)$_2$], [(**TS2**)(TCNQ)$_2$] and [(**TS3**)(TCNQ)$_2$]. All the complexes all the complexes have a green color and are insoluble in cold and hot water, but easily soluble in DMSO and DMF.

Absorption spectral characteristics

Fig. 1 shows the electronic absorption spectra of the synthesized complexes. This figure revealed the presence of the absorption bands that correspond to the CT interactions. These bands are observed at 465, 615 and 460 nm for the [(**TS1**)(TCNQ)$_2$], [(**TS2**)(TCNQ)$_2$] and [(**TS3**)(TCNQ)$_2$] complexes, respectively. The stoichiometry of the synthesized CT complexes was obtained from the determination of the conventional spectrophotometric molar ratio according to previously published protocols[17]. Representative spectrophotometric titration plots based on these characterized absorption bands are shown in Fig. 2. Based on this figure, the complex formation occurred with a ratio (**TS**: acceptor) of 1 : 2.

The Benesi-Hildebrand and its modification methods were applied for the determination of the spectroscopic physical data such as formation constant (K_{CT}), molar extinction coefficient (ε_{CT}), energy of the complex (E_{CT}), standard free energy ($\Delta G°$), oscillator strength (f) and transition dipole moment (μ) for the synthesized complexes as

described elsewhere[18-23]. The calculated values of these spectroscopic data for the complexes are presented in Table 1. The three complexes exhibit high values for the K_{CT}. These high K_{CT} values reflect the high stabilities of the synthesized complexes due to the strong donation of the triazine-stilbene derivatives. The [(**TS2**)$(TCNQ)_2$] complex exhibited higher value for both K_{CT} and $\Delta G°$. The ε values of the complexes decrease in the following order: [(**TS3**)$(TCNQ)_2$] > [(**TS1**)$(TCNQ)_2$] > [(**TS2**)$(TCNQ)_2$].

Table 1: Spectroscopic data of the synthesized complexes (25°C)

Complex	λ_{max} (nm)	K ($Lmol^{-1}$)	ε_{max} ($Lmol^{-1}cm^{-1}$)	E_{CT} (eV)	f	μ	ΔG° (KJ mol^{-1})
[(**TS1**)$(TCNQ)_2$]	465	11.17×10^8	11.43×10^4	2.67	1.23	11.04	40.215
[(**TS2**)$(TCNQ)_2$]	615	105.2×10^8	84.24	2.02	0.09	3.45	45.773
[(**TS3**)$(TCNQ)_2$]	460	9.49×10^8	12.28×10^4	2.70	1.33	11.39	39.812

It is well known that ε values reflect the molecular planarity and enlargement of π-conjugation. **TS3** and **TS1** complexes have higher ε values than that of **TS2** complex which indicates that complexes of **TS3** and **TS1** have much more planar and rigid π-conjugation system than that of **TS2** complex[24].

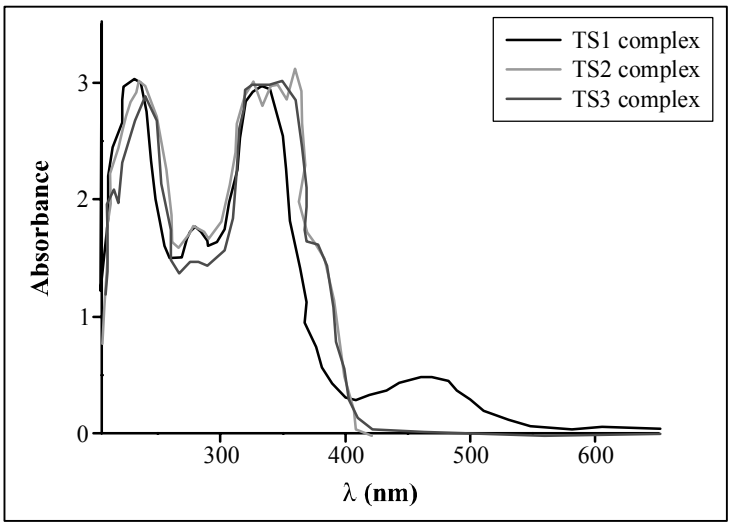
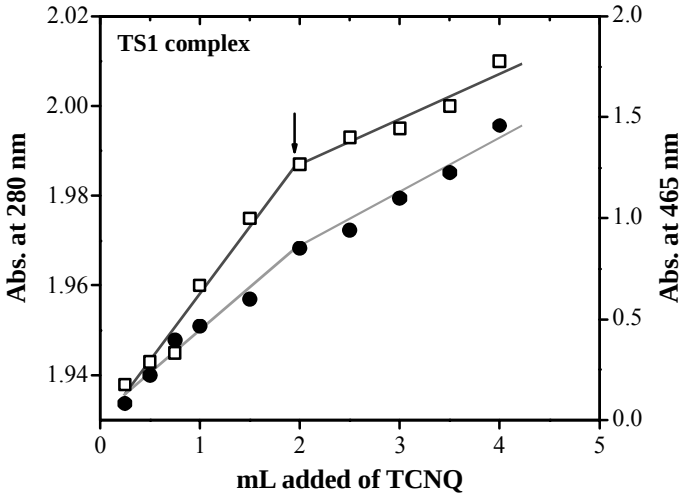


Fig. 1: Electronic absorption spectra of TS1/TCNQ, TS2/TCNQ and TS3/TCNQ complexes

IR spectral characteristics

The IR absorption spectra of the synthesized CT complexes were recorded in the frequency range 4000-400 cm^{-1} using a KBr disc, and their peak assignments for the important characteristic IR spectral bands are provided in Table 2. A comparison of the relevant IR spectral bands of the free donors and TCNQ acceptor with the corresponding bands in the IR spectra of the isolated solid CT complexes clearly indicated that the characteristic bands of the donors exhibit small shifts in frequency and changes in their band intensities. This result could be attributed to the expected changes in symmetry and electronic configurations upon the formation of the CT complexes. In the IR spectra of the complexes, the characteristic band of the free TCNQ acceptor (ν(C≡N); 2220 cm^{-1}) exhibited a significant decrease in intensity and shifted to a lower wavenumber value at 2193 cm^{-1} for **TS1** complex, at 2188 cm^{-1} for **TS2** complex, and at 2189 cm^{-1} for **TS3** complex. These shifts clearly indicates that the –C≡N group in the acceptor participated in the complexation process. Because TCNQ lacks acidic centers, the molecular complexes can be concluded to form through $\pi \rightarrow \pi^*$ and/or $n \rightarrow \pi^*$ charge migration from the HOMO of the donor to the LUMO of the acceptor. The $\pi \rightarrow \pi^*$ CT complex is formed via the benzene ring (electron-rich group) of the donors and the TCNQ reagent (electron acceptor). The cyano group (–C≡N) is an electron-withdrawing group that exists in TCNQ in a conjugated bonding system. The 4CN groups in TCNQ withdraw electrons from the aromatic ring, and such a process will make the aromatic ring an electron-accepting region. This behavior will decrease the CN bond order and therefore lower its vibrational wavenumber value upon complexation[25-27]. The proposed structures of these CT complexes are shown in Formulas II-IV.



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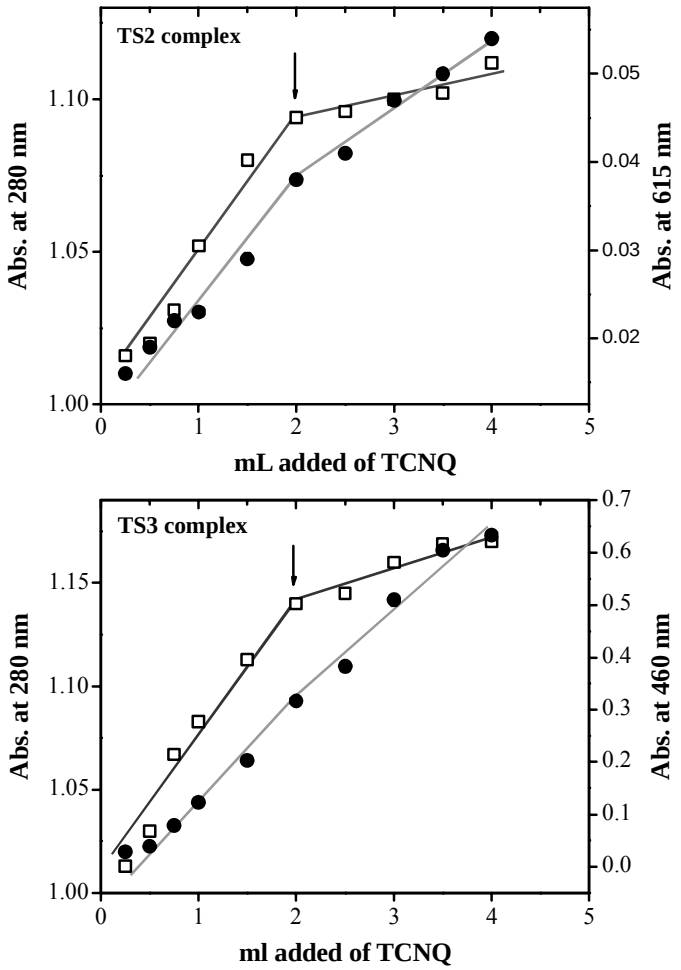


Fig. 2: Spectrophotometric titration curves for TS1/TCNQ, TS2/TCNQ and TS3/TCNQ system

Table 2: Infrared frequencies[(a)] (cm^{-1}) and tentative assignments for TS1, TS2 and TS3 complexes with TCNQ acceptor

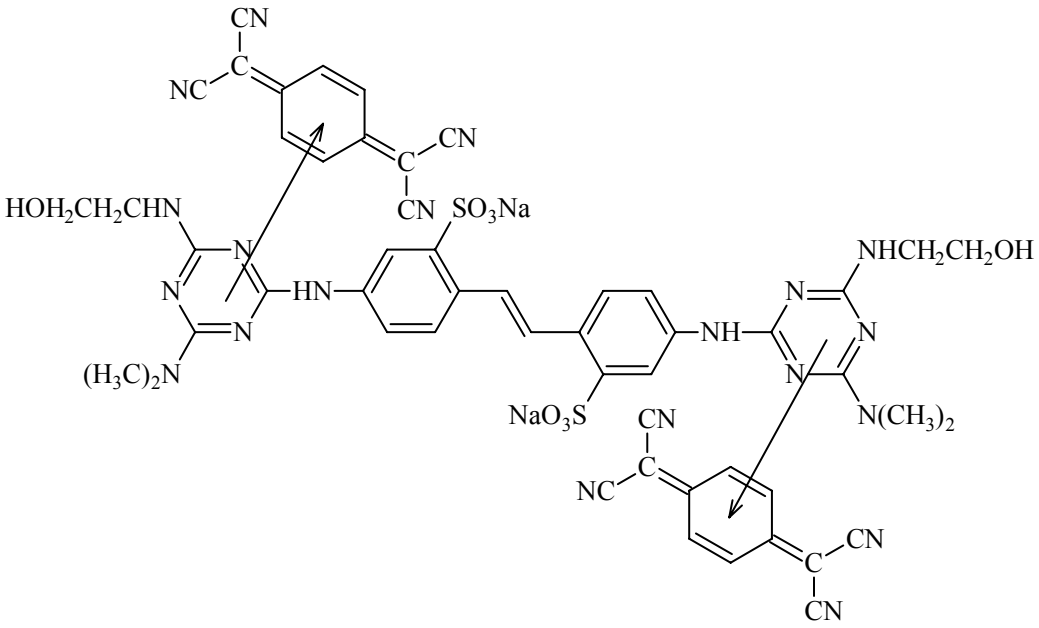
Donors			Acceptor	Complexes			Assignments[(b)]
TS1	TS2	TS3	TCNQ	TS1-TCNQ	TS2-TCNQ	TS3-TCNQ	
3423	3374	3420	3137 3050	3421	3419	3407	ν (O-H) ν(N-H) ν(C-H); aromatic

Cont…

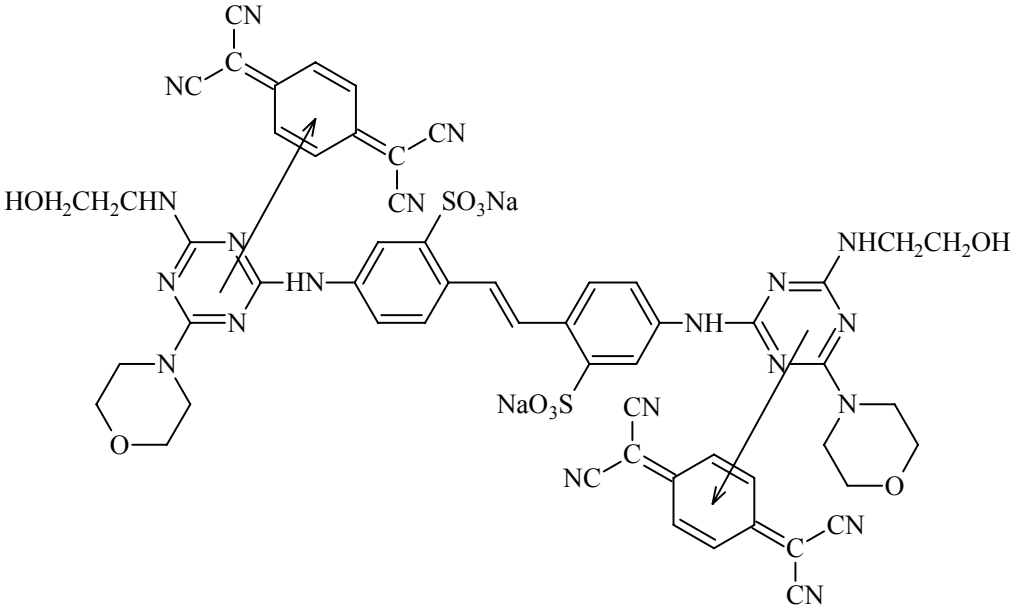
Donors			Acceptor	Complexes			Assignments[(b)]
TS1	**TS2**	**TS3**	**TCNQ**	**TS1-TCNQ**	**TS2-TCNQ**	**TS3-TCNQ**	
2927	2928	2972	2969	2929	2925	2972	ν(C-H) + ν_{as}(C-H)
2877	2861	2931	2851		2862	2931	
		2872					
-	-	-	2220	2193	2187	2189	ν(C≡N)
1620	1616	1614	-	1703	1656	1620	ν(C=O)
				1618	1625		
1575	1567	1570	-	1596	1592	1594	δ_{def}(N-H)
							Ring breathing bands
1529	1541	1516	1540	1523	1539	1536	ν(C=C)
1490	1492	1488		1405	1486	1490	δ(C-H) deformation
1402	1442	1412			1418	1414	
	1416						
1286	1357	1358	1352	1339	1360	1361	ν(C-C) + ν(C-O) + ν_{as}(C-N)
1187	1303	1308	1285	1225	1283	1310	
1078	1276	1225	1205	1184	1220	1227	
1021	1226	1180	1117	1080	1182	1178	
	1180	1080	1044	1023	1182	1117	
	1108	1024			1109	1082	
	1078				1077	1024	
	1021				1021		
993	888	983	997	993	896	898	δ_{rock}; NH
903	832	894	962	909	868	807	δ(CH) in-plane bending
829	805	829	860	805	806	780	
801	699	806	808	772	774	697	
717		782			716	670	
		695					
625	626	625	473	672	624	626	δ(C-N) out-of-plane bending
540	543	544		628	544	549	skeletal vibration
				547			CNC deformation

(a): s, strong; w, weak; m, medium; sh, shoulder; v, very; vs, very strong; br, broad

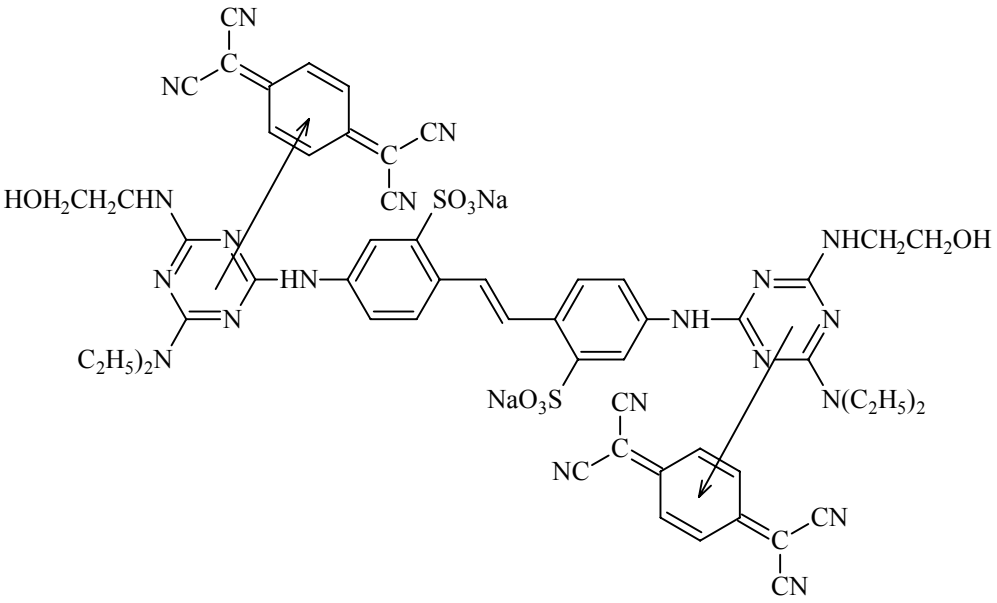
(b): ν, stretching; ν_s, symmetrical stretching; ν_{as}, asymmetrical stretching; δ, bending



Formula II: Suggested structural formula of [(TS1)(TCNQ)$_2$] complex



Formula III: Suggested structural formula of [(TS2)(TCNQ)$_2$] complex



Formula IV: Suggested structural formula of [(TS3)(TCNQ)$_2$] complex

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