The Lowest Triplet of Tetracyanoquinodimethane via UV/vis Absorption Spectroscopy with Br-containing Solvents

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Supporting Information

S1. Experimental details

In order to search for the lowest (the first) triplet of the isolated molecule of TCNQ, the UV\vis spectra of this compound (98 % purity, Aldrich) were recorded in 10 mm and 100 mm cuvettes in various solvents (including B-containing ones), with the Shimadzu UV-2401 (900 – 190 nm, Japan). The following solvents were used: Br-propane (99.96 %, abcr), 1,2-di-Br-ethane (98 %, Fluca, Sigma-Aldrich), hexane (95 %, Sigma-Aldrich), tetrahydrofuran (99.9 %, Sigma-Aldrich), CCl_4 (98 %, Sigma-Aldrich), ethanol (99.8 %, Sigma-Aldrich), and isopropanol (98 %, FG Sigma-Aldrich). All compounds were not rectified additionally. In one case, the Shimadzu UV-3600 (3600 – 190 nm, Japan) was used for recording of the UV/vis spectrum of TCNQ in a 100 mm cuvette in Br-propane. As a result, it was found that no spectral bands (apart from several narrow vibrational peaks mainly due to the solvent) appear in the range between 3600 nm (0.35 eV) and 900 nm (1.38 eV), i.e., between the lower limits of the two instruments. This allowed to search for the triplet band in the energy region of E > 1.38 eV with the Shimadzu UV-2401 throughout all of the work. For recording of spectra, the slit width was 1 nm, the recording speed was 210 nm/min, and the spectral resolution 0.1 nm.

The overall spectrum of TCNQ, which shows its general absorbance in the range 900 – 190 nm (1.38 – 6.5 eV), including singlet (S) transitions of the neutral $TCNQ^o$ molecule and doublet (D) transitions of the $TCNQ^-$ negative ions, which were observed in the polar solutions, were recorded in all of the solvents listed above. A 10 mm cuvette was used with the appropriate concentration of TCNQ that allowed for recording of spectra without any “off-scale” readings in the energy region studied. Two typical spectra, recorded in hexane and in ethanol, are shown in the text of the paper. The rest spectra, recorded in CCl_4, 1,2-B2-ethane, Br-propane, tetrahydrofuran, and isopropanol in a 10 mm cuvette are shown in Figure S1 of the Supporting Information (A, B, C, D, and E, respectively).

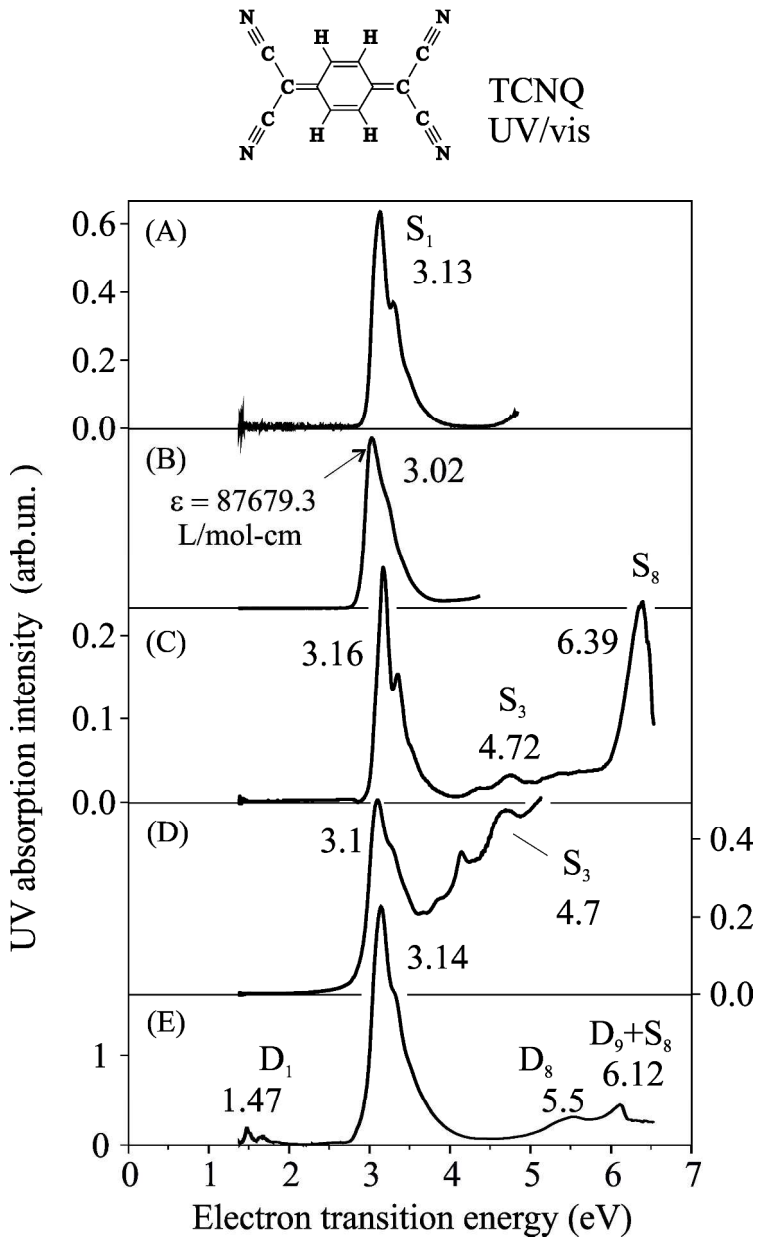

Figure S1. UV/vis absorption spectra of TCNQ recorded in CCl_4 (A), 1,2-di-Br-ethane (B), Br-propane (C), tetrahydrofuran (D), and isopropanol (E) in a 10 mm cuvette. Part of the spectrum at ~ 4.5 – 6.5 eV in (A), (B), (D) and (E) is suppressed by intensive absorption of the solvent.

TCNQ is poorly soluble almost in all of the solvents listed above. It is easily soluble only in tetrahydrofuran (as it is well-known). Besides, we revealed that TCNQ is fully soluble in 1,2-di-Br-ethane after mixing by electromagnet mixer within two hours. The latter allowed determination of TCNQ concentration in 1,2-di-Br-ethane, and, as a consequence — determination of the molar absorptivity (ε) of the triplet band (3.12 L/mol-cm) that is shown in Figure 3 (A) of the paper, and of the first singlet band (87679.3 L/mol-cm) that is shown in Figure S1 (B) of the Supporting Information. Concentration in hexane, CCl_4, Br-propane, and isopropanol we could not find. This hindered

determination the value of ε in these solvents. In tetrahydrofuran, where TCNQ is quite soluble, the ε value could not be determined because the portion of TCNQ molecules, which transform themselves into ions in this solution, is unknown. Thus, in all spectra excluding obtained in 1,2-di-Br-ethane only relative measure of absorption strength is given on the ordinate axis.

The solutions under study (excluding that in tetrahydrofuran) were prepared mainly by adding to the solvent a large amount of TCNQ to obtain the saturated solution, which was then mixed manually and filtered. In some cases, the electromagnet mixer was applied for different periods of time, from 0.5 hours to 48 hours. However, we did not find any influence of the long mixing on the spectra in the case of poorly soluble TCNQ in the given solvent. Only one case may be interesting; that of the spectrum recorded in a 100 mm cuvette in Br-propane. In this case, the additional mixing was applied for 48 hours and resulted in an increase in the observable spectral bands almost a factor of 10. These are the bands at 1.47 eV from the $TCNQ^-$ negative ion, and at 1.85 eV, which we assign to the first triplet of TCNQ. The difference between the manual and electromagnet mixing of the solution of TCNQ in Br-propane is shown in Figure S2.

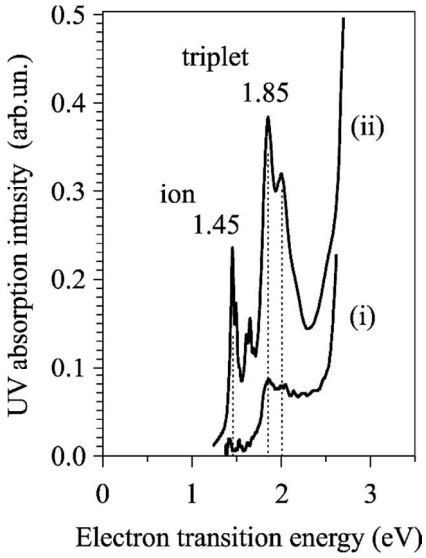

Figure S2. Fragment of UV/vis absorption spectrum of TCNQ in Br-propane in 100 mm cuvette; (i) solution prepared with manual mixing for several minutes; (ii) solution mixed for 48 hours by electromagnet mixer.

S2. Computational details

Quantum-chemical calculations of TCNQ were carried out using a cluster supercomputer at the Ufa Institute of Chemistry of the RAS using the Gaussian 09 [1] software package and the B3LYP hybrid exchange-correlation functional [2, 3] and 6-31G basis set. [4, 5] For visualization of the calculations, Chemcraft 1.7 was used. [6] Structures of the neutral $TCNQ^o$ molecule and the $TCNQ^-$

negative ion were optimized. Single-point calculations, based on the optimized structures, were performed at the time-dependent (TD) B3LYP/6-31G level [7, 8] to obtain information on the

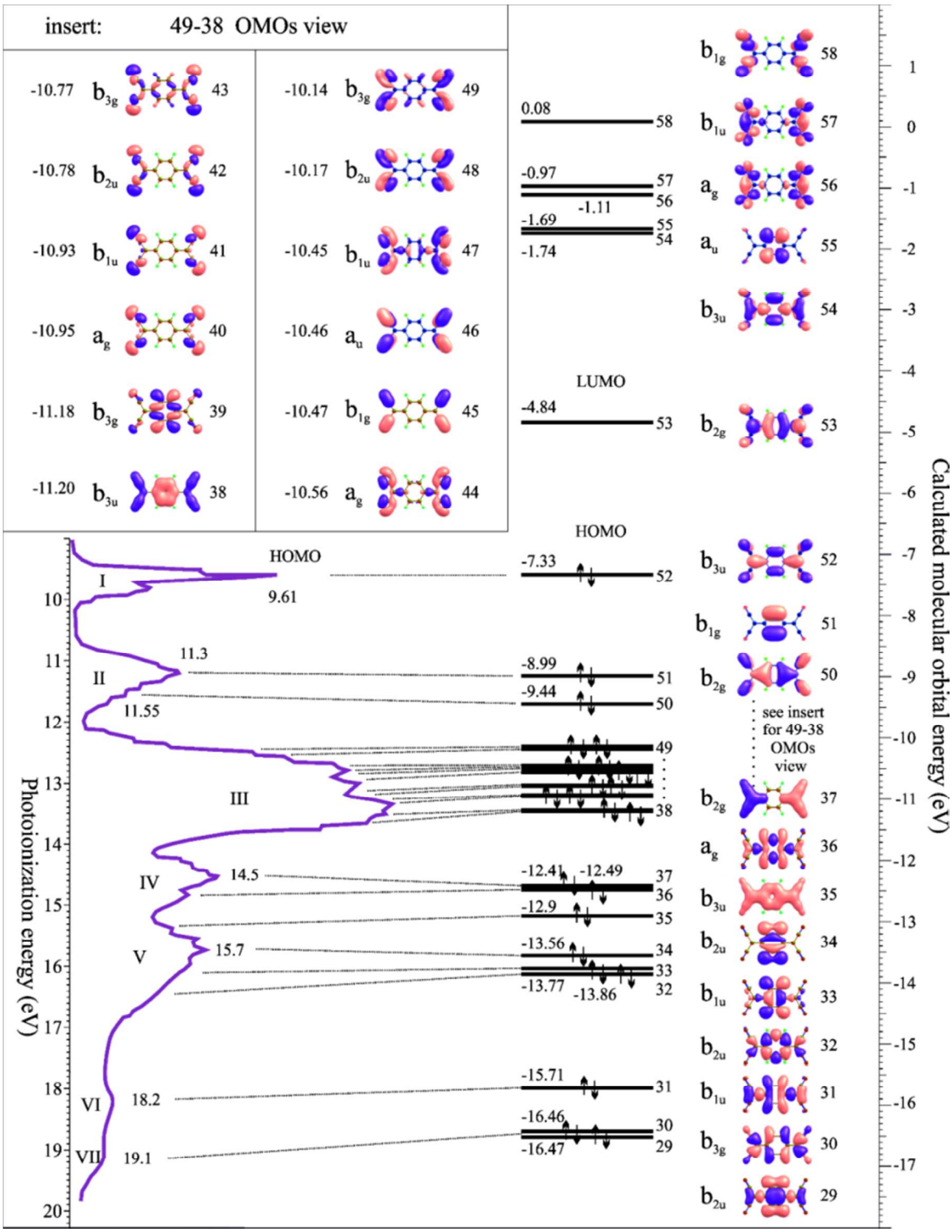

Figure S3. Photoelectron spectrum of TCNQ from Ref. [11], and B3LYP/6-31G calculation of the $TCNQ^{o}$ molecule (present paper).

electronically excited states of both the TCNQ^{o} molecule and the TCNQ^{-} ion. The choice of this calculation method was made following a series of calculations, including other DFT methods, MP2

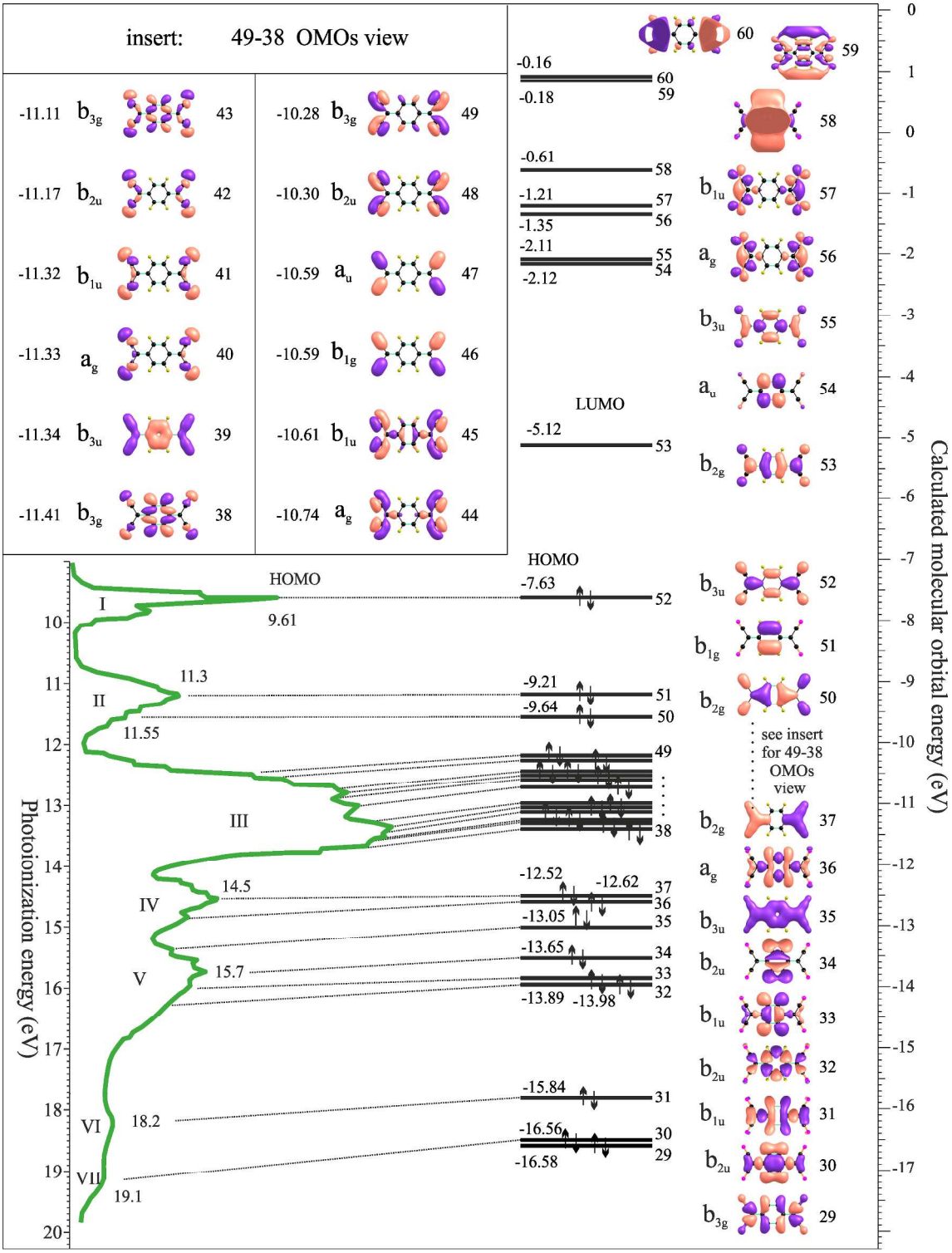

Figure S4. Photoelectron spectrum of TCNQ from Ref. [11], and B3LYP/6-31+G** calculation of the TCNQ^{o} molecule (present paper).

and HF, as well as various basis sets with polarization and diffuse s and p functions. The B3LYP/6-31G approach with a little basis set was chosen in the end because it, on the one hand, gives good reproducibility of the absolute values of the energies of the electronic transitions from the experimental UV/vis spectra of TCNQ, and on the other, it does not produce diffuse empty orbitals that have no physical significance, which appear when more complete basis sets are applied. [9, 10] This can be seen from Figures S3 and S4, where calculated molecular orbitals of TCNQ are shown, which were obtained by means of B3LYP/6-31G and B3LYP/6-31+G** approaches, along with the data from the photoelectron spectrum (PES) recorded in the work [11].

A comparison between Figure S3 and Figure S4 shows that more complete 6-31+G** basis gives 58 and 60 empty orbitals, which absent when the little 6-31G one is used. As a result, the excess electron transition also appears related with 58 orbital in the calculated electron spectra of the molecule. Even more excess transitions appear in the spectrum of the ion calculated with 6-31+G** basis set. One can see these effects in the extended Tables S1 and S2, where both TD B3LYP/6-31 and TD B3LYP/6-31+G** calculations of the electronic spectra are presented for the neutral and for the negatively charged TCNQ. The additional transitions are marked in Tables S1 and S2 by red.

Table S1. Electronically excited S_1 – S_8 singlet transitions of the $TCNQ^o$ molecule from UV/vis spectra recorded in hexane (^{exp}E), and from a TD B3LYP/6-31G and TD B3LYP/6-31+G** calculations; (^{calc}E; oscillator strengths f > 0; sym – symmetry of the singlet state; red – additional transition related to an empty orbital that has no physical significance.

N^o	sym	TD B3LYP/6-31G			TD B3LYP/6-31+G**			^{exp}E (eV)
		f	OMO-UMO [a]	^{calc}E (eV)	f	OMO-UMO [a]	^{calc}E (eV)	
S_1	$^1B_{1U}$	1.0742	52 → 53	3.02	1.0539	52 → 53	2.91	3.17
S_2	$^1B_{3U}$	0.0006	47 → 53	4.72	0.0002	45 → 53	4.49	~ 4.34
S_3	$^1B_{2U}$	0.0707	46 → 53	5.08	0.084	47 → 53	4.83	~ 4.55
S_4	$^1B_{3U}$	0.0117	41 → 53	5.42	0.0042	41 → 53	5.50	~ 4.80
S_5	$^1B_{1U}$	0.0073	38 → 53	5.70	0.0088	39 → 53	5.51	~ 4.97
S_6	$^1B_{2U}$	0.0097	51 → 54	6.42	(S_6) 0.0141 0.0111	51 → 54 52 → 58	6.22 6.28	5.61
S_7	$^1B_{2U}$	0.0967	52 → 58	6.81	0.08	52 → 59	6.68	6.20
S_8	$^1B_{1U}$	0.4059	51 → 55	6.98	0.4362	51 → 55	6.70	6.32

[a] Numeral of valent empty MOs from TD B3LYP/6-31G and TD B3LYP/6-31+G** calculations are different for S_2, S_3, S_5 and S_7 because of some changes occurred in the MOs sequences in different calculations.

Table S2. Electronically excited doublet transitions of the $TCNQ^-$ negative ion from UV/vis spectra recorded in ethanol and isopropanol (^{exp}E), and from TD B3LYP/6-31G and TD B3LYP/6-31+G** calculations; (^{calc}E; oscillator strengths f > 0.01; sym –symmetry of the doublet state; red – additional transitions related to empty orbitals of the ion that has no physical significance.

N°	N° of doublet	Sym	B3LYP/6-31G			B3LYP/6-31+G**			^{exp}E (eV)
			f	OMO-UMO	^{calc}E (eV)	f	OMO-UMO	^{calc}E (eV)	
1	D_1	$^2B_{3U}$	0.3065	52β → 53β	1.78	0.3156	52β → 53β	1.75	1.47
2	D_2	$^2B_{3U}$	0.5739	53α → 55α	3.60	0.5617	53α → 55α	3.48	3.59
3	D_3	$^2B_{3U}$	0.0812	51β → 54β	4.51	0.0493	51β → 54β	4.39	~ 4.41
4	D_4	$^2B_{1U}$	0.0818	47β → 53β	5.28	0.1094	47β → 53β	5.20	~ 4.75
5	D_{new-1}	-	-	-	-	0.0358	53α → 65α	5.40	-
6	D_5	^2A_U	0.0300	53α → 59α	5.79	0.0361	53α → 64α	5.8	~ 4.90
7	D_6	^2A_U	0.0369	52β → 58β	6.03	0.0265	49β → 58β	6.01	~ 5.11
8	D_{new-1}	-	-	-	-	0.0417	50β → 54β	6.10	-
9	D_7	^2A_U	0.1077	52α → 58α	6.61	0.0613	52β → 69β	6.32	~ 5.30
10	D_{new-3}	-	-	-	-	0.0432	53α → 74α	6.38	-
11	D_8	$^2B_{3U}$	0.1805	35β → 53β	6.65	0.3059	35β → 53β	6.45	5.53
12	D_{new-4}	-	-	-	-	0.0798	52α → 63α	6.58	-
13	D_{new-5}	-	-	-	-	0.0520	50β → 55β	6.69	-
14	D_9	$^2B_{3U}$	0.1950	51α → 54α	6.88	0.3014	50α → 54α	6.93	6.09

It should be remarked that the B3LYP calculations does not reproduce the absolute values of the energies of the occupied molecular orbital (OMO). This disagreement is a well-known feature of DFT methods. In the case of B3LYP/6-31G, it results in a shift of the calculated OMOs upwards by ~ 2 eV in comparison with PES. [12] However, this defect does not hinder the solid assignment of the photoionization bands because the shifting occurs for all orbitals as a whole.

As it is mentioned in the paper, the most calculations give a rather low value of the energy of the vertical E (T_1) of TCNQ: < 1 eV from the time dependent method (TD) and ≈ 1 eV, when it is estimated as the difference (ΔE_{total}) between the total energies of the molecule in the ground state and in the triplet state computed in the optimized molecular ground-state geometry. Only TD and CIS(D) with MP2 gives another results (Table S3).

Table S3 shows that TD, CIS(D) and ΔE_{total}, used with different functionals and basis sets do not give uniform E(T_1). What's more TDHF calculations give entirely unsuited negative E(T_1). At the same time, the evaluation of E(T_1) via ΔE_{total} gives ~ 1 eV in the most cases, although one result obtained via ΔE_{total} entirely drops out here too. This is ΔE_{total} = 5.21 eV obtained with MP2/6-31G. There is only one suitable calculated value of E(T_1). It was obtained with CIS(D). This method gives E(T_1) = 1.57 eV that

is rather close to the experimental 1.96 eV. On the other hand, $E(T_1)$ = ~ 1 eV obtained via ΔE_{total} is the most reproducible in various calculation. Therefore, namely the 1 eV number is mentioned in the paper that needs to be checked with the Shimadzu UV-3600.

Table S3. Energies (eV) of the first vertical triplet $E(T_1)$ and the first excited singlet $E(S_1)$ of $TCNQ^o$ molecule from various calculations and UV/vis experiment; TD – time dependent calculation method; CIS(D) – *ab initio* calculation method of excited states including correlation energy; ΔE_{total} – the difference between total energy of molecule in its ground state (in optimized ground state geometry) and total energy of molecule in its triplet state (obtained in the same molecular ground-state geometry). All calculations (except N° 7) were performed in the optimized molecular ground-state geometry obtained by the same method, which is indicated in the column "Calculation method". All calculations presented in row N° 7 were carried out in MP2-optimized ground state geometries of $TCNQ^o$ molecule.

N^o	Calculation method	TD eV		CIS (D) eV		$E(T_1) = \Delta E_{total}$ eV	Experiment UV/vis eV	
		$E(T_1)$	$E(S_1)$	$E(T_1)$	$E(S_1)$		$E(T_1)$	$E(S_1)$
1	B3LYP/6-31G	0.49 [a]	3.02 [a]	-	-	1.04	1.96 [d]	3.17 [e]
2	B3LYP/6-31G*	0.58 [b]	3.01 [b]	-	-	1.07		
3	B3LYP/cc-pVDZ	0.60 [b]	3.00 [b]	-	-	1.07		
4	B3LYP/6-31+G**	0.60 [c]	2.95 [c]	-	-	1.07		
5	MP2/6-31G	0.69 [a]	3.66 [a]	-	-	5.21		
6	HF/6-31G	-3.04 [a]	3.84 [a]	-	-	0.53		
7	HF/6-31G (with MP2-optimized geometry)	-3.20 [a]	3.38 [a]	1.57 [c]	3.83 [c]	0.42		
8	HF/6-31G*	-2.82 [c]	3.97 [c]	-	-	1.00		
9	HF/cc-pVDZ	-2.77 [c]	3.95 [c]	-	-	0.99		

[a] N states = 100, singlets and triplets: 50-50; [b] N states = 30, singlets and triplets: 50-50;
[c] N states = 50, singlets and triplets: 50-50; [d] in 1,2-di-Br-ethane; [e] in hexane.

One can see that there is full chaos in the calculated values of $E(T_1)$, which leads to a conclusion that only experiment provides obviously the most reliable means to find this hard-to-reach value of $E(T_1)$. This allows taking the experimental value of 1.96 eV of the lowest triplet of the isolated TCNQ molecule as the main basis. As to the calculated $E(S_1)$ and $E(D_1)$, B3LYP/6/31G gives the best energy of these states. This provides grounds to use B3LYP/6/31G for assignment of the UV/vis singlet and doublet spectra obtained here. Two examples of this assignment are shown in Figures S5 and S6, where the electronic configurations of the electronically excited singlet states of the neutral $TCNQ^o$ molecule and of the electronically excited doublet states of $TCNQ^-$ ion are presented.

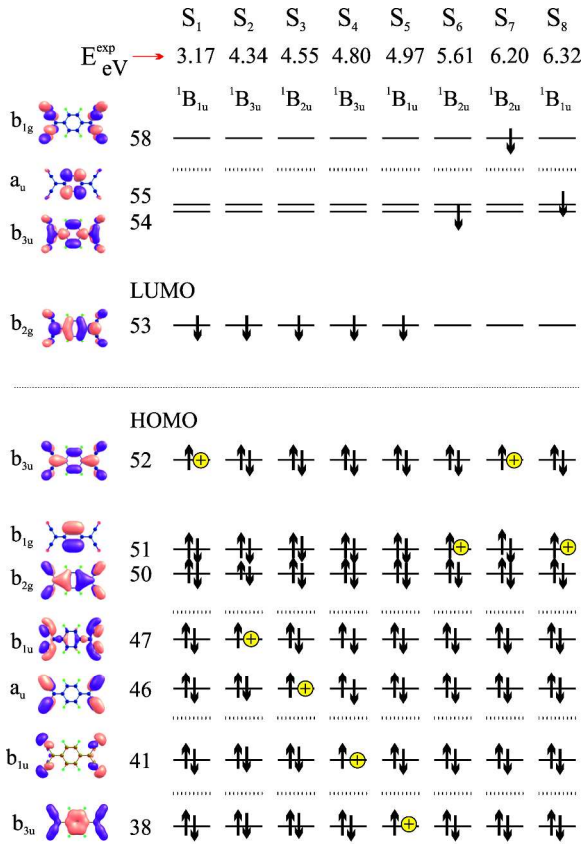

Figure S5. Electronic configurations of S_1 - S_8 singlets of $TCNQ^o$ molecule from TD B3LYP/6-31G calculation. Experimental energies of S_1 - S_8 are taken from UV/vis absorption spectra of TCNQ recorded in hexane.

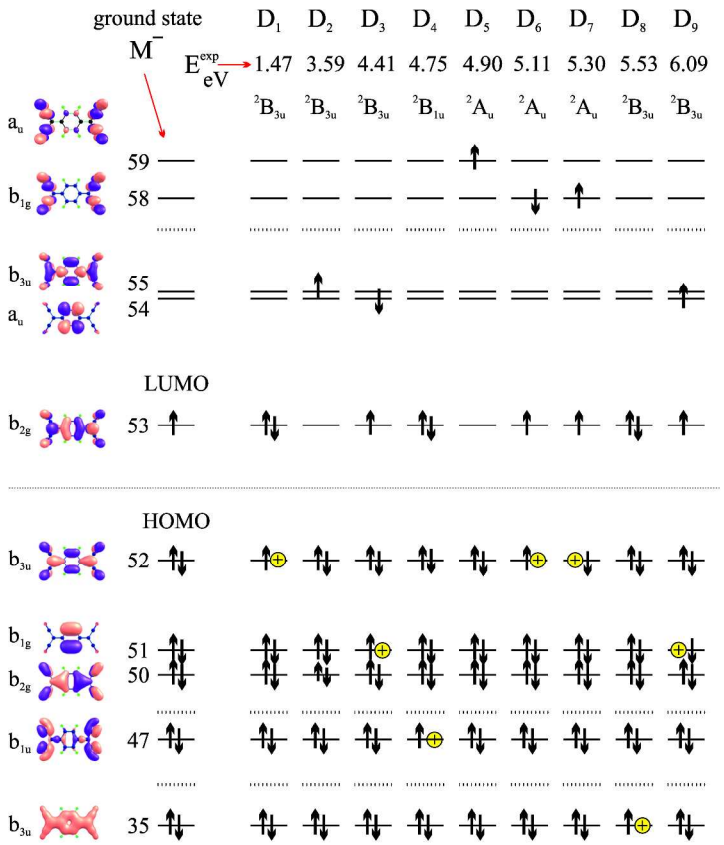

Figure S6. D_1 - D_9 doublet states of $TCNQ^-$ ion from TD B3LYP/6-31G calculation. Experimental energies of D_1, D_2, D_8, and D_9 — from UV/vis spectrum recorded in ethanol in a 10 mm cuvette; of D_3 - D_7 — from spectrum recorded in isopropanol in a 100 mm cuvette.

S3. Cartesian coordinates of computed (B3LYP/6-31G) TCNQ structures

S3a. Cartesian coordinates of isolated TCNQ (molecule and ion)

$TCNQ^o$ molecule				TCNQ negative ion			
E_{total} = - 678.382850415 a.u.				E_{total} = - 678.506820079 a.u.			
Atom	x	y	z	Atom	x	y	z
7	-2.223620	4.173092	0.000000	7	0.000000	4.201142	-2.230704
6	1.239868	0.680074	0.000000	6	0.000000	0.689285	1.216613
6	1.239896	-0.680023	0.000000	6	0.000000	-0.689285	1.216613
6	0.000000	-1.431254	0.000000	6	0.000000	-1.438209	0.000000
6	-1.239868	-0.680074	0.000000	6	0.000000	-0.689285	-1.216613

6	-1.239896	0.680023	0.000000	6	0.000000	0.689285	-1.216613
6	0.000000	1.431254	0.000000	6	0.000000	1.438209	0.000000
6	0.000000	2.825352	0.000000	6	0.000000	2.873849	0.000000
6	0.000000	-2.825352	0.000000	6	0.000000	-2.873849	0.000000
6	-1.213798	3.571337	0.000000	6	0.000000	3.607439	-1.208806
6	1.213836	3.571239	0.000000	6	0.000000	3.607438	1.208807
6	1.213798	-3.571337	0.000000	6	0.000000	-3.607438	1.208807
6	-1.213836	-3.571239	0.000000	6	0.000000	-3.607439	-1.208806
7	2.223741	4.172856	0.000000	7	0.000000	4.201142	2.230705
7	-2.223741	-4.172856	0.000000	7	0.000000	-4.201142	-2.230704
7	2.223620	-4.173092	0.000000	7	0.000000	-4.201142	2.230705
1	2.177904	1.223412	0.000000	1	0.000000	1.224680	2.160641
1	2.177942	-1.223339	0.000000	1	0.000000	-1.224680	2.160641
1	-2.177904	-1.223412	0.000000	1	0.000000	-1.224680	-2.160642
1	-2.177942	1.223339	0.000000	1	0.000000	1.224680	-2.160642

S3b. Cartesian coordinates of cycled dimer of TCNQ (neutral and ion)

Neutral cycled dimer of TCNQ				Negative ion of cycled dimer of TCNQ			
E_{total} = - 1356.77747166 a.u.				E_{total} = - 1356.91653867 a.u.			
Atom	x	y	z	Atom	x	y	z
6	3.251080	-1.653675	0.000126	6	-3.252114	1.659483	-0.000127
6	3.048874	-0.217687	-0.001974	6	-3.055880	0.233373	-0.001411
6	4.108386	0.635933	-0.002105	6	-4.124097	-0.625245	-0.001321
6	5.472673	0.146982	-0.000162	6	-5.479300	-0.144400	0.000050
6	5.671867	-1.289899	0.001940	6	-5.671416	1.281912	0.001381
6	4.615732	-2.145811	0.002079	6	-4.607852	2.143006	0.001295
6	2.172836	-2.537712	0.000288	6	-2.160322	2.558769	-0.000232
6	6.556239	1.022592	-0.000294	6	-6.582307	-1.029734	0.000115
6	0.824660	-2.076541	-0.001638	6	-0.816716	2.105820	-0.001638
6	2.360569	-3.950358	0.002402	6	-2.362216	3.964565	0.001161
6	6.376313	2.436321	-0.002354	6	-6.409536	-2.438434	-0.001090
6	7.900334	0.548198	0.001623	6	-7.917396	-0.546903	0.001615
1	3.935398	1.706075	-0.003669	1	-3.945098	-1.694843	-0.002296

1	2.042506	0.187780	-0.003403	1	-2.051775	-0.178429	-0.002413
1	4.783657	-3.216710	0.003661	1	-4.780592	3.213711	0.002306
1	6.684978	-1.675534	0.003401	1	-6.683107	1.672734	0.002452
7	-0.285209	-1.694181	-0.003333	7	0.297461	1.726019	-0.002841
7	2.530847	-5.113690	0.004122	7	-2.554137	5.127574	0.002333
7	6.216940	3.601004	-0.004066	7	-6.260126	-3.607558	-0.002108
7	9.003477	0.141834	0.003198	7	-9.019217	-0.127531	0.002866
6	-3.251239	1.653901	0.000175	6	3.252048	-1.659393	-0.000131
6	-4.615957	2.145842	0.002067	6	4.607756	-2.143001	0.001330
6	-5.671959	1.289758	0.001925	6	5.671378	-1.281979	0.001441
6	-5.472549	-0.147096	-0.000131	6	5.479359	0.144342	0.000103
6	-4.108188	-0.635841	-0.002005	6	4.124187	0.625274	-0.001312
6	-3.048817	0.217941	-0.001858	6	3.055909	-0.233272	-0.001428
6	-2.173079	2.538041	0.000317	6	2.160211	-2.558625	-0.000261
6	-6.555982	-1.022868	-0.000282	6	6.582422	1.029607	0.000188
6	-2.360921	3.950666	0.002361	6	2.362042	-3.964432	0.001132
6	-0.824888	2.076902	-0.001580	6	0.816618	-2.105636	-0.001698
6	-7.900148	-0.548673	0.001581	6	7.917480	0.546689	0.001634
6	-6.375843	-2.436568	-0.002336	6	6.409742	2.438317	-0.001121
1	-6.685129	1.675240	0.003346	1	6.683044	-1.672870	0.002543
1	-4.784045	3.216716	0.003600	1	4.780426	-3.213716	0.002352
1	-2.042353	-0.187293	-0.003227	1	2.051840	0.178619	-0.002462
1	-3.935041	-1.705953	-0.003530	1	3.945260	1.694885	-0.002299
7	-2.531330	5.113979	0.004110	7	2.553909	-5.127450	0.002302
7	0.284935	1.694415	-0.003254	7	-0.297565	-1.725850	-0.002920
7	-9.003351	-0.142475	0.003123	7	9.019273	0.127243	0.002843
7	-6.216297	-3.601229	-0.004069	7	6.260403	3.607450	-0.002223

S3c. Cartesian coordinates of stacked dimer of TCNQ (neutral and ion)

Neutral stacked dimer of TCNQ				Negative ion of stacked dimer of TCNQ			
E_{total} = - 1356.76195816 a.u.				E_{total} = - 1356.90531067 a.u.			
Atom	x	y	z	Atom	x	y	z
6	0.680130	2.546946	1.239625	6	0.684518	2.508462	1.227687

6	-0.680130	2.546946	1.239625	6	-0.684518	2.508462	1.227687
6	-1.432037	2.553752	0.000000	6	-1.434680	2.528190	0.000000
6	-0.680130	2.546946	-1.239625	6	-0.684518	2.508462	-1.227687
6	0.680130	2.546946	-1.239625	6	0.684518	2.508462	-1.227687
6	1.432037	2.553752	0.000000	6	1.434680	2.528190	0.000000
6	-2.825883	2.567046	0.000000	6	-2.846906	2.585877	0.000000
6	2.825883	2.567046	0.000000	6	2.846906	2.585877	0.000000
6	3.571527	2.577225	-1.214383	6	3.584979	2.637614	-1.211485
6	3.571527	2.577225	1.214383	6	3.584979	2.637614	1.211485
6	-3.571527	2.577225	1.214383	6	-3.584979	2.637614	1.211485
6	-3.571527	2.577225	-1.214383	6	-3.584979	2.637614	-1.211485
7	4.169300	2.587960	-2.226585	7	4.177600	2.695917	-2.228514
7	4.169300	2.587960	2.226585	7	4.177600	2.695917	2.228514
7	-4.169300	2.587960	-2.226585	7	-4.177600	2.695917	-2.228514
7	-4.169300	2.587960	2.226585	7	-4.177600	2.695917	2.228514
1	1.223033	2.545517	2.178029	1	1.224407	2.502412	2.168200
1	-1.223033	2.545517	2.178029	1	-1.224407	2.502412	2.168200
1	-1.223033	2.545517	-2.178029	1	-1.224407	2.502412	-2.168200
1	1.223033	2.5455170	-2.178029	1	1.224407	2.502412	-2.168200
6	0.680130	-2.546946	1.239625	6	0.684518	-2.508462	1.227687
6	-0.680130	-2.546946	1.239625	6	-0.684518	-2.508462	1.227687
6	-1.432037	-2.553752	0.000000	6	-1.434680	-2.528190	0.000000
6	-0.680130	-2.546946	-1.239625	6	-0.684518	-2.508462	-1.227687
6	0.680130	-2.546946	-1.239625	6	0.684518	-2.508462	-1.227687
6	1.432037	-2.553752	0.000000	6	1.434680	-2.528190	0.000000
6	-2.825883	-2.567046	0.000000	6	-2.846906	-2.585877	0.000000
6	2.825883	-2.567046	0.000000	6	2.846906	-2.585877	0.000000
6	3.571527	-2.577225	-1.214383	6	3.584979	-2.637614	-1.211485
6	3.571527	-2.577225	1.214383	6	3.584979	-2.637614	1.211485
6	-3.571527	-2.577225	1.214383	6	-3.584979	-2.637614	1.211485
6	-3.571527	-2.577225	-1.214383	6	-3.584979	-2.637614	-1.211485
7	4.169300	-2.587960	-2.226585	7	4.177600	-2.695917	-2.228514
7	4.169300	-2.587960	2.226585	7	4.177600	-2.695917	2.228514

7	-4.169300	-2.587960	-2.226585	7	-4.177600	-2.695917	-2.228514
7	-4.169300	-2.587960	2.226585	7	-4.177600	-2.695917	2.228514
1	1.223033	-2.545517	2.178029	1	1.224407	-2.502412	2.168200
1	-1.223033	-2.545517	2.178029	1	-1.224407	-2.502412	2.168200
1	-1.223033	-2.545517	-2.178029	1	-1.224407	-2.502412	-2.168200
1	1.223033	-2.545517	-2.178029	1	1.224407	-2.502412	-2.168200

S3d. Cartesian coordinates of dimer-'butterfly' of TCNQ (neutral and ion)

Neutral dimer-'butterfly' of TCNQ				Negative ion of dimer-'butterfly' of TCNQ			
E_{total} = - 1356.71044143 a.u.				E_{total} = - 1356.81624883 a.u.			
Atom	x	y	z	Atom	x	y	z
6	-0.796917	0.797009	1.249959	6	0.783498	0.823340	1.239132
6	-0.796917	-0.797009	1.249959	6	-0.783498	0.823340	1.239132
6	-1.381079	-1.381058	0.000000	6	-1.377318	1.391610	0.000000
6	-0.796917	-0.797009	-1.249959	6	-0.783498	0.823340	-1.239132
6	-0.796917	0.797009	-1.249959	6	0.783498	0.823340	-1.239132
6	-1.381079	1.381058	0.000000	6	1.377318	1.391610	0.000000
6	-2.346349	-2.346275	0.000000	6	-2.510754	2.190702	0.000000
6	-2.346349	2.346275	0.000000	6	2.510754	2.190702	0.000000
6	-2.878664	2.878264	-1.220175	6	3.115660	2.633504	-1.214177
6	-2.878664	2.878264	1.220175	6	3.115660	2.633504	1.214177
6	-2.878664	-2.878264	1.220175	6	-3.115660	2.633504	1.214177
6	-2.878664	-2.878264	-1.220175	6	-3.115660	2.633504	-1.214177
7	-3.303237	3.302600	-2.228698	7	3.598054	2.998557	-2.224070
7	-3.303237	3.302600	2.228698	7	3.598054	2.998557	2.224070
7	-3.303237	-3.302600	-2.228698	7	-3.598054	2.998557	-2.224070
7	-3.303237	-3.302600	2.228698	7	-3.598054	2.998557	2.224070
1	-1.224564	1.224743	2.156148	1	1.221533	1.233010	2.149602
1	-1.224564	-1.224743	2.156148	1	-1.221533	1.233010	2.149602
1	-1.224564	-1.224743	-2.156148	1	-1.221533	1.233010	-2.149602
1	-1.224564	1.224743	-2.156148	1	1.221533	1.233010	-2.149602
6	0.796917	0.797009	1.249959	6	0.783498	-0.823340	1.239132
6	0.796917	-0.797009	1.249959	6	-0.783498	-0.823340	1.239132

6	1.381079	-1.381058	0.000000	6	-1.377318	-1.391610	0.000000
6	0.796917	-0.797009	-1.249959	6	-0.783498	-0.823340	-1.239132
6	0.796917	0.797009	-1.249959	6	0.783498	-0.823340	-1.239132
6	1.381079	1.381058	0.000000	6	1.377318	-1.391610	0.000000
6	2.346349	-2.346275	0.000000	6	-2.510754	-2.190702	0.000000
6	2.346349	2.346275	0.000000	6	2.510754	-2.190702	0.000000
6	2.878664	2.878264	-1.220175	6	3.115660	-2.633504	-1.214177
6	2.878664	2.878264	1.220175	6	3.115660	-2.633504	1.214177
6	2.878664	-2.878264	1.220175	6	-3.115660	-2.633504	1.214177
6	2.878664	-2.878264	-1.220175	6	-3.115660	-2.633504	-1.214177
7	3.303237	3.302600	-2.228698	7	3.598054	-2.998557	-2.224070
7	3.303237	3.302600	2.228698	7	3.598054	-2.998557	2.224070
7	3.303237	-3.302600	-2.228698	7	-3.598054	-2.998557	-2.224070
7	3.303237	-3.302600	2.228698	7	-3.598054	-2.998557	2.224070
1	1.224564	1.224743	2.156148	1	1.221533	-1.233010	2.149602
1	1.224564	-1.224743	2.156148	1	-1.221533	-1.233010	2.149602
1	1.224564	-1.224743	-2.156148	1	-1.221533	-1.233010	-2.149602
1	1.224564	1.224743	-2.156148	1	1.221533	-1.233010	-2.149602

S4. Vibrational frequencies of computed (B3LYP/6-31G) TCNQ structures

S4a. Vibrational frequencies of isolated TCNQ (molecule and ion)

TCNQ^o neutral molecule			TCNQ negative ion		
N^o	Frequency cm^{-1}	IR intensity	N^o	Frequency cm^{-1}	IR intensity
1	48.9103	9.2647	1	42.1624	0
2	49.5267	0.0028	2	57.2078	10.6479
3	85.5001	4.989	3	83.3636	3.1882
4	116.1859	0	4	97.3085	0
5	119.0339	0	5	121.2775	0
6	136.8417	0	6	134.5257	0
7	141.1377	8.7814	7	144.7029	11.7406
8	148.9436	0	8	154.3328	0

9	219.1989	11.9608	9	231.1022	11.8015
10	289.8877	0.0097	10	288.9379	0.0442
11	307.0683	0	11	342.6745	0
12	340.0494	0	12	344.2896	0
13	380.8165	0	13	386.8611	0
14	401.0745	0	14	427.0973	0
15	439.0437	0	15	458.3561	0
16	471.4339	0	16	462.2415	0
17	485.1954	16.7625	17	499.2699	21.724
18	514.5334	0.0352	18	524.5172	0.1191
19	539.1179	0	19	546.462	0
20	565.8583	3.6982	20	557.419	10.6354
21	617.3543	0	21	629.8531	0
22	618.3737	0.2781	22	632.0795	0
23	644.0894	0	23	632.438	0.0424
24	656.1567	0	24	660.8782	0
25	709.9215	6.6518	25	665.8831	0.0104
26	735.384	0	26	751.035	0
27	813.1732	0	27	783.3643	0
28	838.5335	0	28	850.5153	0
29	905.0509	64.5972	29	883.0948	69.8708
30	982.2323	0	30	1003.547	0
31	1002.2551	0.7757	31	1005.5523	0
32	1027.0543	0.0123	32	1014.459	0
33	1040.9455	0	33	1026.7971	7.2221
34	1050.3328	0	34	1041.0897	2.2981
35	1146.4521	13.8523	35	1155.639	0.2579
36	1217.404	0	36	1238.6582	0
37	1249.887	4.1131	37	1252.848	4.048
38	1265.0391	0	38	1253.5843	0
39	1374.7404	0	39	1369.7224	8.2768
40	1402.2425	8.6267	40	1386.4732	0

41	1453.3155	1.7759	41	1390.6306	49.745
42	1494.8498	0	42	1400.7087	0
43	1497.9497	0	43	1524.3289	0.7366
44	1595.7099	59.3046	44	1544.9091	0
45	1605.9668	14.2108	45	1556.9485	62.0032
46	1682.2514	0	46	1663.1456	0
47	2276.0971	1.3691	47	2207.3306	0
48	2276.1558	0	48	2207.6291	288.2093
49	2289.9543	0	49	2239.9498	743.6229
50	2292.0151	85.4919	50	2246.8414	0
51	3223.1858	0	51	3198.9327	0.4254
52	3223.2394	1.7598	52	3199.5272	0
53	3238.616	0.7709	53	3216.7829	20.7824
54	3240.8293	0	54	3219.8832	0

S4b. Vibrational frequencies of cycled dimer of TCNQ (neutral and ion)

Neutral cycled dimer of TCNQ			Negative ion of cycled dimer of TCNQ		
N°	**Frequency cm^{-1}**	**IR intensity**	**N°**	**Frequency cm^{-1}**	**IR intensity**
1	7.6434	0.0651	1	5.3719	0.0025
2	10.493	0.0424	2	7.5413	0.1853
3	19.2652	0	3	16.8647	0
4	22.5479	0.4204	4	20.5113	1.7874
5	34.5667	0	5	33.4839	0
6	48.5007	0.0001	6	47.616	2.3634
7	49.6688	6.7082	7	51.9299	0
8	55.9975	0	8	54.5705	0
9	58.7834	10.2007	9	59.8514	0.0459
10	63.4736	0.0005	10	60.2273	15.7773
11	90.2093	17.2212	11	88.0981	1.3647
12	90.5975	0.0004	12	88.3801	0

13	119.9647	0	13	112.1751	0
14	122.13	2.6374	14	119.5297	0.1827
15	124.1493	0	15	122.8351	1.1879
16	126.2015	0.0405	16	124.0739	0
17	136.9422	0.702	17	135.4274	0.1659
18	141.2385	0	18	139.5107	0
19	145.1861	10.0167	19	145.7963	22.2959
20	149.5172	0	20	150.0733	0
21	151.9797	0	21	152.8025	0
22	154.2155	0.0058	22	157.5564	0.0016
23	220.9705	23.6811	23	227.2503	23.6292
24	222.9413	0.0001	24	229.9363	0
25	291.1411	0	25	290.6508	0
26	293.2993	1.1107	26	292.6309	1.2377
27	307.4238	0	27	327.0392	0.0082
28	308.7585	0	28	330.0875	0.0002
29	340.4688	0.0002	29	333.5823	356.7493
30	340.8589	2.4509	30	341.7109	0
31	379.3911	0	31	382.2527	0
32	379.5496	0.349	32	382.5036	0.4809
33	401.655	0	33	416.7918	0
34	402.9986	0.0364	34	418.5992	0.0735
35	441.7596	0.0193	35	449.9278	0.0001
36	442.3443	0	36	450.8652	0
37	473.1858	0.1705	37	465.2324	0.0209
38	474.2391	0	38	466.5388	0
39	492.6831	0.0002	39	499.6785	0
40	494.0207	29.6171	40	501.5064	34.5461
41	514.0897	0	41	518.8434	0
42	515.6235	0.6761	42	520.0293	0.9289
43	538.626	0	43	542.1637	0
44	540.2418	0.787	44	543.5576	0.4984

45	565.0102	12.4902	45	561.5399	8.9695
46	565.0734	0.0598	46	561.8123	0.0001
47	617.9169	0	47	626.6638	20.2816
48	617.9388	0.2956	48	626.8378	0.0001
49	621.9494	0.5217	49	628.2171	6.3747
50	622.1459	0.0012	50	628.4828	0.0008
51	642.8075	3.3979	51	642.3698	0
52	642.9222	0.0003	52	642.6261	0.0038
53	655.4547	0.0072	53	651.147	5.6739
54	655.4556	0.0053	54	651.5297	0
55	711.6699	9.5991	55	688.4521	1.6933
56	711.9547	0.0001	56	688.989	0.0001
57	735.8199	3.4215	57	740.1369	456.1955
58	736.853	0	58	746.0811	0
59	813.9331	0.0001	59	797.7399	0.0115
60	813.9457	0.1437	60	797.7985	0
61	851.9036	0.0003	61	856.1395	0.0007
62	852.0135	4.693	62	856.1672	10.7136
63	917.4086	0.0009	63	907.8578	0.0001
64	918.161	125.7135	64	908.5156	125.6088
65	980.9304	0	65	991.3608	284.4357
66	982.0539	3.0184	66	992.7884	0
67	997.351	0	67	1012.5507	7.9286
68	998.0437	18.4489	68	1012.7749	0.0002
69	1026.8976	1.0085	69	1024.5452	0
70	1027.3426	0	70	1024.5489	0.0485
71	1044.9782	0.0019	71	1032.4997	2.1092
72	1044.98	0.0415	72	1032.6397	0
73	1080.9742	0.0005	73	1066.7236	0.0004
74	1081.3373	2.0306	74	1066.8854	2.327
75	1147.2252	40.4243	75	1153.7147	3.2719
76	1147.4017	0.0016	76	1153.7492	0

77	1214.474	0.4733	77	1225.8328	7.1614
78	1214.9568	0	78	1226.2897	0
79	1249.6569	0.0007	79	1238.8419	3689.6594
80	1249.7503	5.0261	80	1250.4246	0
81	1267.6303	0.0004	81	1251.1937	99.8801
82	1268.7484	24.2069	82	1261.4177	0
83	1371.5997	0.0001	83	1379.5751	92.3724
84	1371.7361	6.511	84	1379.7199	0.005
85	1401.1587	0.003	85	1386.1618	6.1331
86	1401.2446	31.4611	86	1386.2366	0.0001
87	1454.9454	18.9397	87	1415.6071	5089.726
88	1455.274	0.0008	88	1429.4302	275.6503
89	1494.0314	0.1264	89	1429.5003	0.0014
90	1494.2555	0	90	1448.0303	0
91	1500.3999	0.0048	91	1517.1887	0.2105
92	1500.4489	7.401	92	1517.391	0
93	1594.4491	0.0006	93	1559.0909	3.4432
94	1594.9258	157.3293	94	1559.1181	0.0155
95	1605.192	0.059	95	1567.2398	0.0008
96	1605.2983	62.9616	96	1567.6888	160.1177
97	1681.7861	0	97	1652.8036	3000.7478
98	1682.28	2.2665	98	1668.2856	0
99	2275.6269	1.932	99	2238.9726	150.0213
100	2275.63	0.0362	100	2238.997	0.2309
101	2276.6422	15.0409	101	2242.5747	59.1784
102	2276.7565	0.0091	102	2242.8242	0.0097
103	2290.3177	36.6111	103	2255.4477	3497.4504
104	2290.3224	1.0774	104	2265.0308	0.0018
105	2293.8172	243.1044	105	2265.6806	542.8419
106	2293.9363	0.2321	106	2270.4384	0.0001
107	3221.0673	0.0036	107	3210.8495	1.108
108	3221.6575	206.579	108	3210.8726	0.0014

109	3223.0648	0.1495	109	3214.6337	64.1904
110	3223.0713	0.5611	110	3215.2184	0.0077
111	3235.802	0.2856	111	3227.5562	39.3092
112	3235.9643	39.6653	112	3227.64	0.0851
113	3240.013	7.1766	113	3229.8801	34.8792
114	3240.0462	0.0204	114	3229.9634	0.031

S4c. Vibrational frequencies of stacked dimer of TCNQ (neutral and ion)

Neutral stacked dimer of TCNQ			Negative ion of stacked dimer of TCNQ		
N^o	Frequency cm^{-1}	IR intensity	N^o	Frequency cm^{-1}	IR intensity
1	-7.8525	0	1	-12.8473	0
2	2.4156	0	2	-12.7221	0.2791
3	5.5858	0	3	2.3432	0
4	16.2227	0.0099	4	7.6721	0
5	16.5025	0	5	10.0541	0
6	21.3623	0.001	6	17.1351	0.0191
7	48.0274	18.0741	7	46.978	0
8	48.8254	0	8	49.8534	0
9	51.917	0	9	52.8348	7.6252
10	53.1162	0	10	53.9341	0
11	84.7754	0	11	83.7228	0
12	86.0137	8.931	12	84.7252	7.1986
13	116.4672	0	13	107.9249	0
14	118.3808	0.0105	14	110.0629	0.0067
15	119.3036	0.107	15	119.6624	0.6299
16	119.4141	0	16	121.0919	0
17	136.4088	0	17	135.7132	0
18	136.847	0	18	136.0516	0
19	140.6451	0	19	142.9387	0
20	141.5731	14.811	20	143.8596	18.5232

21	148.1615	0	21	152.8188	0
22	150.8405	0.7442	22	153.0267	0.3942
23	218.5859	23.9879	23	225.8369	0
24	220.1134	0	24	226.4566	12.7383
25	289.4228	0	25	289.8557	0.0036
26	289.4852	0.0186	26	289.894	0
27	306.7661	0	27	325.4562	0.0516
28	307.4832	0.1084	28	327.2271	0
29	340.1343	0	29	335.5282	160.374
30	340.5864	0	30	342.8913	0
31	380.6206	0	31	383.9387	0
32	380.6476	0	32	384.0073	0
33	401.0423	0	33	416.5587	0
34	401.6453	0	34	416.5934	0
35	438.4788	0	35	448.3974	0.0007
36	438.709	0.0001	36	448.8012	0
37	471.4566	0	37	463.807	0
38	471.7426	0	38	464.1802	0
39	484.6605	34.8904	39	491.1807	5.0106
40	485.5378	0	40	492.1222	0
41	514.713	0	41	520.2312	0
42	514.8001	0.0666	42	520.2837	0.0107
43	539.2037	0	43	543.5358	0
44	539.3597	0	44	543.621	0
45	566.0745	0	45	563.3631	0
46	566.2889	4.9652	46	563.5933	9.4848
47	616.1131	0.0003	47	624.1126	13.4578
48	616.1264	0	48	624.4598	0
49	617.0986	0	49	625.0707	0
50	617.1152	0.4615	50	625.082	0.1889
51	644.1467	0	51	642.745	0.0116
52	644.25	0	52	643.0569	0

53	656.2684	0	53	652.6637	0
54	656.4746	0.0026	54	652.7037	0
55	709.9823	14.7933	55	685.813	0
56	710.547	0	56	686.3701	5.0264
57	734.9816	0.0042	57	740.6724	191.9761
58	735.191	0	58	744.9321	0
59	812.2859	0	59	795.7908	0.4026
60	812.4884	0.4889	60	796.3622	0
61	838.6692	0	61	841.3433	0
62	841.1322	0.8117	62	843.7173	0.5569
63	904.1173	137.6854	63	890.4925	12.9866
64	906.2113	0	64	893.5942	0
65	981.7875	0.0398	65	992.6384	88.1982
66	982.1342	0	66	993.9575	0
67	1002.008	0	67	1017.6603	2.9704
68	1002.0782	1.0183	68	1017.7959	0
69	1026.7382	0	69	1021.9193	0
70	1026.8573	0.0966	70	1022.4318	0
71	1041.7535	0	71	1030.2023	0
72	1042.4825	0	72	1030.4184	1.7013
73	1050.615	0	73	1032.2327	0
74	1051.5601	0.3026	74	1032.8281	0.3404
75	1145.5673	0	75	1151.658	0
76	1145.9816	23.7858	76	1151.9105	5.7832
77	1216.475	0	77	1227.5384	0
78	1216.7788	0	78	1227.5499	0
79	1249.2623	0	79	1240.2533	1742.8596
80	1249.6624	7.4238	80	1250.2455	0
81	1264.6953	0.0002	81	1250.3616	0.0293
82	1265.2059	0	82	1259.2555	0
83	1374.3647	0	83	1381.9808	0
84	1374.4014	0	84	1382.0342	0

85	1401.068	0	85	1387.2637	15.8316
86	1401.3117	18.0617	86	1387.7033	0
87	1453.4251	0	87	1414.5658	3010.2005
88	1453.5455	1.0996	88	1428.5727	0
89	1494.6789	0	89	1428.8353	28.5002
90	1494.9621	0	90	1450.791	0
91	1497.9689	0.0001	91	1517.9948	0
92	1498.2059	0	92	1518.1046	0
93	1596.1026	0	93	1562.1063	0
94	1596.6882	72.4741	94	1562.1283	8.5871
95	1605.5261	0	95	1568.7482	0
96	1605.6842	25.0357	96	1568.8216	111.5114
97	1681.6104	0.0136	97	1650.6177	1715.7298
98	1681.9075	0	98	1671.8455	0
99	2275.466	0	99	2241.8292	0
100	2275.5371	0	100	2241.8544	0
101	2275.573	0.4064	101	2242.2613	0
102	2275.6339	0	102	2242.3764	144.6594
103	2289.1747	0.0004	103	2255.6899	1598.2972
104	2289.2734	0	104	2265.4339	0
105	2291.2661	0	105	2266.6956	522.0543
106	2291.7717	101.5143	106	2268.7533	0
107	3222.1322	0	107	3212.8707	0
108	3222.1871	0	108	3212.9475	0.2108
109	3222.2055	0	109	3213.1987	0
110	3222.2519	3.9022	110	3213.3038	0
111	3237.4689	0	111	3229.3321	0
112	3237.7004	0.6054	112	3229.6178	10.7976
113	3239.7077	0.0522	113	3231.697	54.7547
114	3239.8736	0	114	3232.1859	0

S4d. Vibrational frequencies of bonded dimer-‘butterfly’ of TCNQ (neutral and ion)

Neutral dimer-‘butterfly’ of TCNQ			Negative ion of dimer-‘butterfly’ of TCNQ		
N^o	Frequency cm^{-1}	IR intensity	N^o	Frequency cm^{-1}	IR intensity
1	29.1841	0	1	33.9822	0
2	34.5116	3.154	2	35.3934	7.6775
3	34.5149	3.1555	3	36.9973	2.5557
4	53.0453	0	4	50.7723	0
5	59.3276	0	5	56.0602	0
6	59.328	0	6	56.4039	0
7	59.4612	0	7	56.562	0.0141
8	65.3162	0	8	64.402	0
9	82.6826	8.8301	9	82.7323	7.3147
10	109.0047	0	10	104.0209	0
11	116.2916	0	11	119.2435	0
12	117.5529	0	12	119.883	0
13	124.5715	0	13	126.0809	0
14	124.5844	0	14	128.3858	0
15	132.8067	16.4843	15	131.3717	11.0697
16	132.8123	16.4929	16	138.4972	20.5149
17	186.5477	0	17	186.6779	0
18	214.2409	0	18	221.3865	0
19	215.6458	12.0049	19	221.646	4.0034
20	215.6504	11.9969	20	222.232	13.4583
21	252.4162	0	21	252.4855	0
22	280.2219	0.0008	22	280.9819	0.0078
23	314.1332	0	23	318.901	0
24	319.6907	0	24	329.1888	0
25	338.8797	0	25	332.4127	0
26	338.895	0	26	347.7817	0
27	403.4826	0	27	376.9502	793.967
28	413.1468	2.0329	28	381.2039	21.7767

29	413.1507	2.0403	29	422.9207	0
30	425.6066	0	30	433.7182	0
31	425.6145	0	31	439.3535	0
32	432.2994	0	32	443.0988	0
33	441.2221	0	33	449.9909	0.0168
34	494.8116	0	34	484.732	0
35	494.8382	0	35	498.4705	0
36	504.254	0.4198	36	506.346	0
37	513.7023	0	37	509.9453	0
38	536.9342	0	38	537.3579	0
39	536.9455	0	39	537.3954	0
40	571.0845	0	40	571.522	0
41	603.6087	0	41	578.3113	191.6507
42	608.4329	1.1677	42	582.7479	309.8727
43	608.4489	1.1536	43	601.3582	0
44	608.9476	0	44	619.5246	18.7729
45	610.0263	0	45	619.6498	0
46	611.6949	1.8114	46	619.9225	0
47	611.7197	1.8329	47	620.5882	0.1033
48	670.3487	0	48	646.6345	0
49	676.9458	0	49	669.0643	379.2044
50	737.1272	0.9045	50	681.9968	0
51	737.1341	0.8983	51	694.8279	130.2312
52	738.7813	0	52	709.3396	0
53	768.8915	0	53	728.2966	0
54	801.4847	0.0011	54	744.8624	0.0188
55	801.7324	0.0015	55	751.2325	0.632
56	854.4913	0	56	766.2731	0
57	860.2506	0	57	803.0558	61.6965
58	875.9104	0	58	804.4334	0
59	879.9739	0	59	810.267	0
60	880.4067	0	60	863.3075	0

61	905.5741	0	61	908.5973	9.8749
62	927.8104	4.7722	62	910.0181	0
63	927.8244	4.7482	63	916.4389	36.8735
64	930.2423	0	64	928.6897	0
65	934.2408	1.8428	65	958.7163	0.6091
66	973.7245	0	66	980.728	174.0931
67	1031.5166	13.0585	67	987.3525	0
68	1031.7754	13.0225	68	1054.1494	0
69	1069.1137	0	69	1080.577	2.2375
70	1087.724	0	70	1083.2602	0
71	1149.3472	0	71	1101.5418	0
72	1149.5128	0	72	1115.6562	0.9858
73	1154.9491	0.0001	73	1144.5849	0
74	1164.9251	0	74	1196.1722	0
75	1184.2678	0	75	1199.7902	0
76	1193.0629	30.5638	76	1206.2024	0
77	1206.7173	0	77	1208.8036	10.9494
78	1206.7654	0	78	1214.8749	2.3396
79	1238.8161	2.3323	79	1216.6338	0
80	1256.1395	26.3509	80	1249.7767	1.7488
81	1256.2588	26.338	81	1253.1482	14.7882
82	1286.4449	0	82	1262.4832	0
83	1287.1758	0	83	1264.0009	0
84	1315.9208	0	84	1301.8766	0
85	1334.7716	0	85	1323.3566	0
86	1334.8249	0	86	1330.14	119.4542
87	1353.7773	0	87	1337.4616	0
88	1353.8015	0	88	1353.4954	0
89	1359.6028	0	89	1363.9008	0
90	1362.6458	0.1743	90	1368.868	79.9638
91	1362.7144	0.1762	91	1370.8611	0
92	1378.7255	37.623	92	1374.5986	20.3132

93	1404.0426	0	93	1393.3955	0
94	1406.6079	0	94	1410.3158	0
95	1647.2259	0	95	1527.9589	3276.8889
96	1651.6081	62.4756	96	1543.9315	0
97	1651.6105	62.4158	97	1568.9531	1056.4577
98	1653.2961	0	98	1589.4695	0
99	2300.7527	0	99	2259.2404	0
100	2300.7995	0	100	2259.4414	0
101	2300.7996	0	101	2259.7312	0
102	2300.8666	1.5014	102	2260.0914	201.5033
103	2308.249	0	103	2260.8158	0
104	2308.5096	24.6733	104	2263.9118	1744.9111
105	2308.5097	24.6691	105	2268.3206	853.5471
106	2308.7978	0	106	2284.6278	0
107	3150.0945	0	107	3137.0959	0
108	3151.0176	0	108	3138.2656	0
109	3156.0613	0.0384	109	3143.8588	8.8005
110	3156.0719	0.0377	110	3144.2443	0
111	3156.362	0	111	3144.9679	22.1011
112	3156.3723	0	112	3145.7222	0
113	3165.4726	5.1417	113	3155.5243	25.5805
114	3166.1711	0	114	3156.3957	0

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