Supplementary Information

Switching Charge Transfer Characteristics of Quaterthiophene from p-type to n-type via Interactions with Carbon Nanotube

Ankita Joshi and C.N. Ramachandran*
Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee, Uttarakhand, India-247667
*e-mail: ramcnfcy@iitr.ac.in

Calculation of Charge Transport Parameters

The transfer integral for an electron (t_-) can be calculated from the energies of LUMO and LUMO+1,

$$t_- = \frac{E_{LUMO+1} - E_{LUMO}}{2} \quad (1)$$

and that for a hole (t_+) can be determined from the energies of HOMO and HOMO-1,

$$t_- = \frac{E_{HOMO} - E_{HOMO-1}}{2} \quad (2)$$

The reorganization energy for any charged species (hole/electron) is given by,

(E (charged species) - E^o) (charged species) + (E (neutral geometry obtained from the charged species) – E^o (neutral geometry)), where E is the energy of unoptimized and E^o is the energy of optimized species.

The rate of charge transfer (k) is calculated based on Marcus theory,

$$k = \frac{4\pi^2}{h} \frac{1}{\sqrt{4\pi k_B T}} t^2 e^{-\lambda / k_B T} \quad (3)$$

where, h is the Planck's constant, T is the room temperature (298 K) and k_B is the Boltzmann constant.

The diffusion coefficient D is given by

$$D = \frac{kL^2}{2} \quad (4)$$

where L is the nearest center-to-center distance

The Einstein relation for the mobility of charge carriers (μ) is given by,

$$\mu = \frac{eD}{k_B T} \tag{5}$$

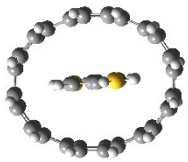
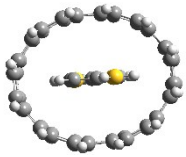
Functional	4T	4T@CNT	4T-CNT
B3LYP-GD3			
ωB97X-D			

Figure S1. Optimized geometries of **4T**, **4T@CNT** and **4T-CNT** obtained at B3LYP-GD3 and ωB97X-D levels.

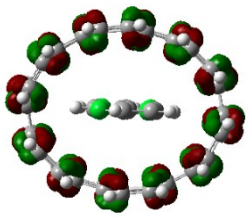
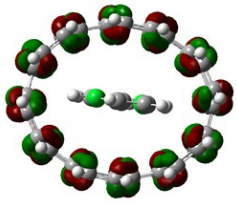
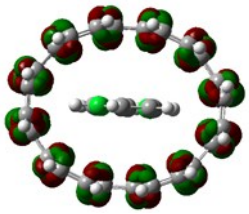
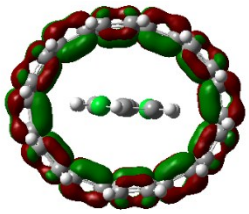
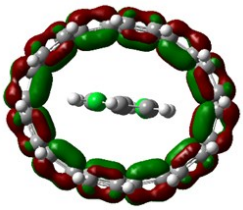
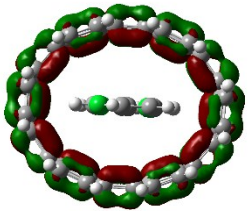
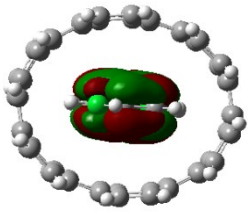
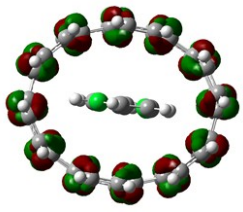
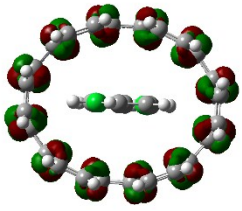
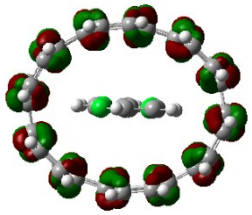
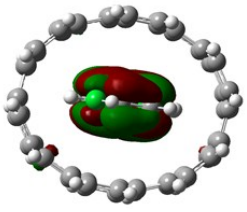
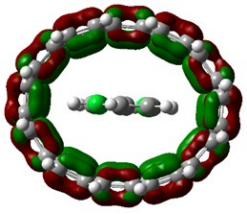
B97-D	B3LYP-GD3	ωB97X-D
		
E_{LUMO+1} = -2.93 eV	E_{LUMO+1} = -2.60 eV	E_{LUMO+1} = -1.42 eV
		
E_{LUMO} = -3.11 eV	E_{LUMO} = -2.79 eV	E_{LUMO} = -1.66 eV
		
E_{HOMO} = -3.76 eV	E_{HOMO} = -4.29 eV	E_{HOMO} = -5.64 eV
		
E_{HOMO-1} = -3.91 eV	E_{HOMO-1} = -4.44 eV	E_{HOMO-1} = -5.86 eV

Figure S2. Selected molecular orbitals and the corresponding energy for **4T@CNT** obtained at different levels.

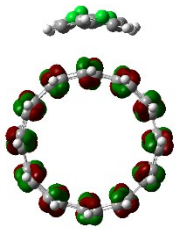
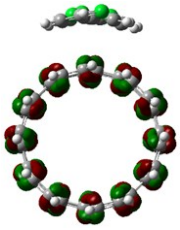
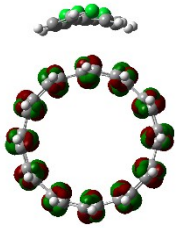
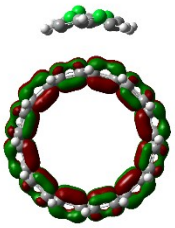
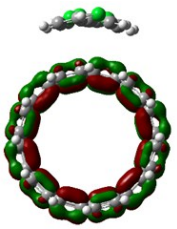
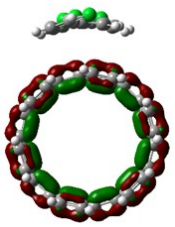
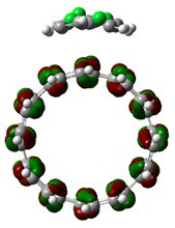
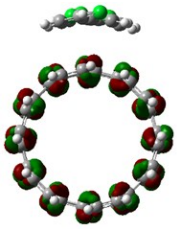
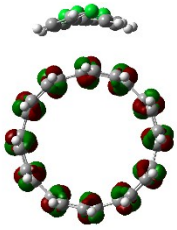
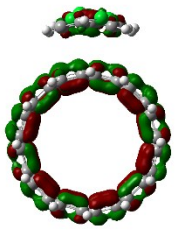
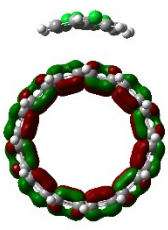
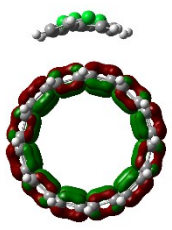
B97-D	**B3LYP-GD3**	**ωB97X-D**
		
E_{LUMO+1} = -2.90 eV	E_{LUMO+1} = -2.56 eV	E_{LUMO+1} = -1.40 eV
		
E_{LUMO} = -3.09 eV	E_{LUMO} = -2.78 eV	E_{LUMO} = -1.65 eV
		
E_{HOMO} = -3.89 eV	E_{HOMO} = -4.26 eV	E_{HOMO} = -5.61 eV
		
E_{HOMO-1} = -4.08 eV	E_{HOMO-1} = -4.47 eV	E_{HOMO-1} = -5.84 eV

Figure S3. Selected molecular orbitals and the corresponding energy for **4T-CNT** obtained at different levels.

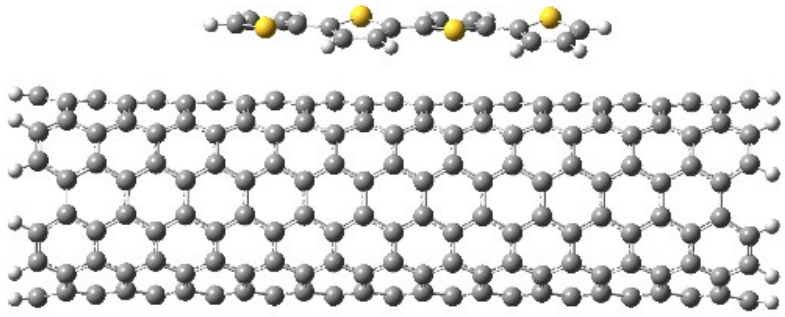


Figure S4. Optimized geometry of the exohedral complex of **long CNT** with **4T** obtained at B3LYP-GD3 level.

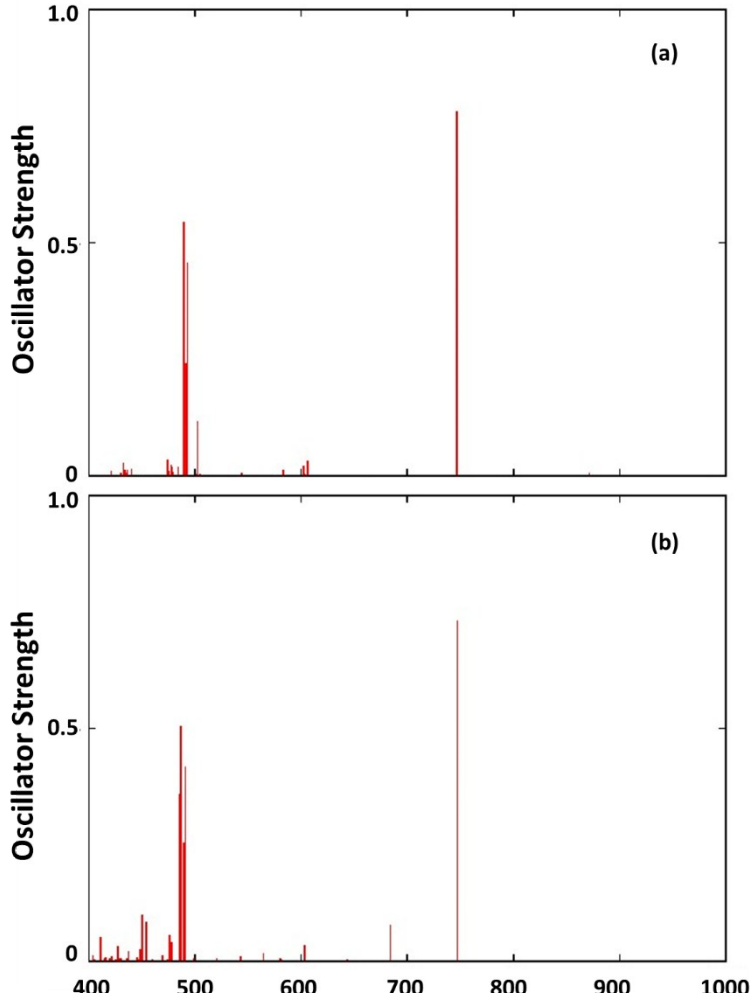


Figure S5. Simulated absorption spectra of (a) 4T@(7,7)CNT and (b) 4T-(7,7)CNT at B3LYP-GD3/6-31G(d,p) level.

Table S1. Calculated values of ionization energy (IE), electron affinity (EA), energy gap between HOMO and LUMO (ΔE_{H-L}) for **4T**, **CNT** and their complexes at different levels. All values are in eV.

Complex	**Functional**	**VIE**	**AIE**	**VEA**	**AEA**	**ΔE_{H-L}**
4T	B97-D	6.01	5.89	-0.72	-0.82	1.87
	B3LYP-GD3	6.33	6.13	-0.59	-0.77	3.15 (*3.13*[a])
	ωB97X-D	6.86	6.49	-0.21	-0.56	6.93
(6,6)CNT[b]	B97-D	4.93	4.90	-2.15	-2.17	0.80
	B3LYP-GD3	5.06	5.03	-2.06	-2.09	1.47
	ωB97X-D	5.50	5.43	-1.83	-1.90	3.97
4T@CNT	B97-D	—[c]	—[c]	-2.13	-2.15	0.64
	B3LYP-GD3	5.03	5.01	-2.04	-2.07	1.50
	ωB97X-D	5.48	5.43	-1.81	-1.87	3.98
4T-CNT	B97-D	4.86	4.83	-2.13	-2.15	0.80
	B3LYP-GD3	5.01	4.97	-2.04	-2.07	1.45
	ωB97X-D	5.45	5.37	-1.81	-1.88	3.96

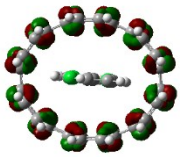
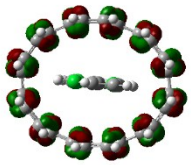
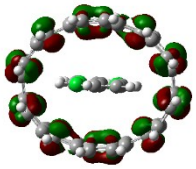
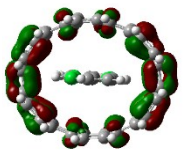
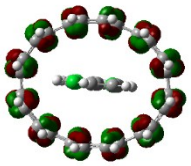
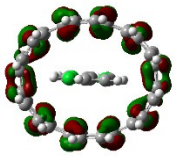
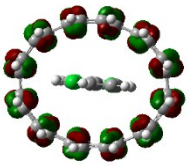
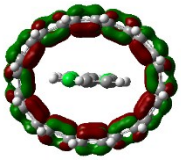
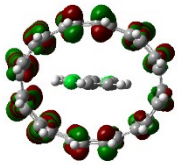
[a]Ref. [48]
[b]Ref. [42-44]
[c]Converegence criteria not met.

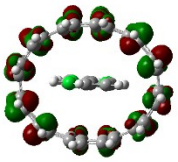
Table S2. Calculated values of maximum absorption wavelength (λ_{max}), oscillator strength (f) and light-harvesting efficiency (LHE) for **4T** at different levels.

Functional	λ_{max} (nm)	f	LHE (%)
B97-D	490	1.14	93
B3LYP-GD3	423 (*436*)[a]	1.19	94
ωB97X-D	344	1.20	94

[a]Ref. [59]

Table S3. The absorption wavelength, oscillator strength, orbital contribution and molecular orbitals involved in the transition of the complex **4T@CNT** obtained at B3LYP-GD3/6-31G(d,p) level.

Wavelength (nm)	Oscillator strength	Orbital contribution (%)	Molecular orbitals involved	
738	0.76	48	 HOMO-2	 LUMO
		47	 HOMO	 LUMO+1
473	0.27	22	 HOMO-7	 LUMO
		20	 HOMO-5	 LUMO+1
468	0.05	67	 HOMO-8	 LUMO+1
		35		

463	0.05		HOMO-2	LUMO+9
		42	HOMO-2	 LUMO+10

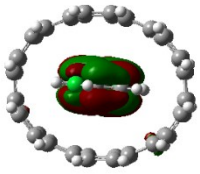
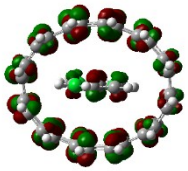
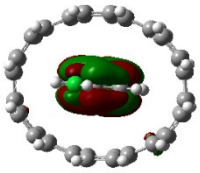
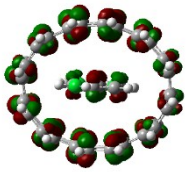
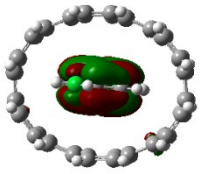
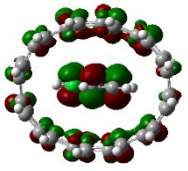
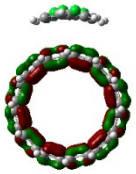
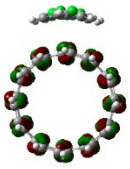
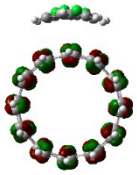
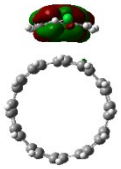
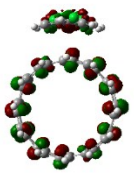
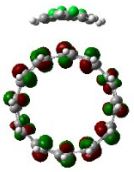
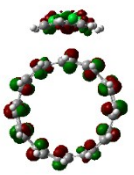
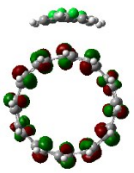
458	0.19	25	 HOMO-1	 LUMO+14
453	0.16	46	 HOMO-1	 LUMO+14
445	0.10	54	 HOMO-1	 LUMO+15

Table S4. The absorption wavelength, oscillator strength, orbital contribution and molecular orbitals involved in the transition of the complex **4T-CNT** obtained at B3LYP-GD3/6-31G(d,p) level.

Wavelength (nm)	**Oscillator strength**	**Orbital contribution (%)**	**Molecular orbitals involved**	
731	0.68	44	 HOMO-1	 LUMO
		42	 HOMO	 LUMO+1
685	0.17	87	 HOMO-2	 LUMO
464	0.24	61	 HOMO-2	 LUMO+3
462	0.26	50	 HOMO-2	 LUMO+4
460	0.32	26	 HOMO-2	 LUMO+3
459	0.31	34	 HOMO-2	 LUMO+4

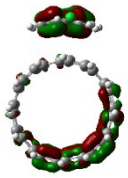
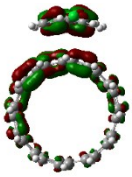
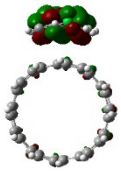
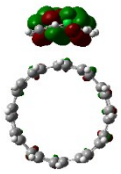
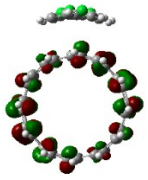
448	0.07	30	 HOMO-10	LUMO
		19	 HOMO-9	LUMO
446	0.14	35	HOMO-2	 LUMO+5
445	0.09	24	HOMO-2	 LUMO+5
		52	HOMO	 LUMO+12
439	0.05	19	HOMO-1	 LUMO+14

Table S5. Calculated values of transfer integral (t), internal reorganization energy (λ), rate constant (k) and carrier mobility (μ) for the complexes at different distance between centres of **4T** and **CNT** ($d_{c\text{-}c}$) obtained at B3LYP-GD3/6-31G(d,p) level.

Complex	**$d_{c\text{-}c}$ (Å)**	**λ^+ (meV)**	**λ^- (meV)**	**t^+ (meV)**	**t^- (meV)**	**k^+ (s^{-1})**	**k^- (s^{-1})**	**μ^+ ($cm^2\ V^{-1}s^{-1}$)**	**μ^- ($cm^2\ V^{-1}s^{-1}$)**
4T@(7,7)CNT	4.29	59	52	60	67	0.24×10^{14}	0.51×10^{14}	0.86	1.83
4T-(7,7)CNT	3.31	63	58	57	63	0.20×10^{14}	0.29×10^{14}	0.42	0.62