Supporting Information

Structural, optoelectronic and charge transport properties of the complexes of indigo encapsulated in carbon nanotubes

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Details of the charge transport calculations

To calculate various charge transport parameters of the studied complexes, we have used the equations[1, 2] (1-5):

The transfer integral for an electron, t_- can be written in terms of energies of LUMO+1 (E_{L+1}) and LUMO (E_L),

$$t_- = \frac{E_{L+1} - E_L}{2} \qquad (1)$$

In case of transfer integral for hole, t_+ can be approximated from the energies of HOMO (E_H) and HOMO-1 (E_{H-1}),

$$t_+ = \frac{E_H - E_{H-1}}{2} \qquad (2)$$

Reorganization energy (λ) 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 single-point energy and E^o is the optimized energy.

According to Marcus theory, the rate of charge transfer is given by,

$$k_{CT} = \frac{4\pi^2}{h} \frac{1}{\sqrt{4\pi\lambda k_B T}} t^2 e^{\frac{-\lambda}{k_B T}} \qquad (3)$$

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

Diffusion Coefficient, D is calculated using the Smoluchowski equation,

$$D = \frac{L^2 k_{CT}}{2} \qquad (4)$$

where, L denotes the centre-to-centre equilibrium distances.

The Einstein relation between mobility (μ) and diffusion constant (D) is given by,

$$\mu = \frac{eD}{k_B T} \qquad (5)$$

References

1. H. Liu, S. Kang and J. Y. Lee, J. Phys. Chem. B, 2011, 115, 5113-5120.
2. A. Joshi and C. N. Ramachandran, Phys. Chem. Chem. Phys., 2016, 18, 14040-14045.

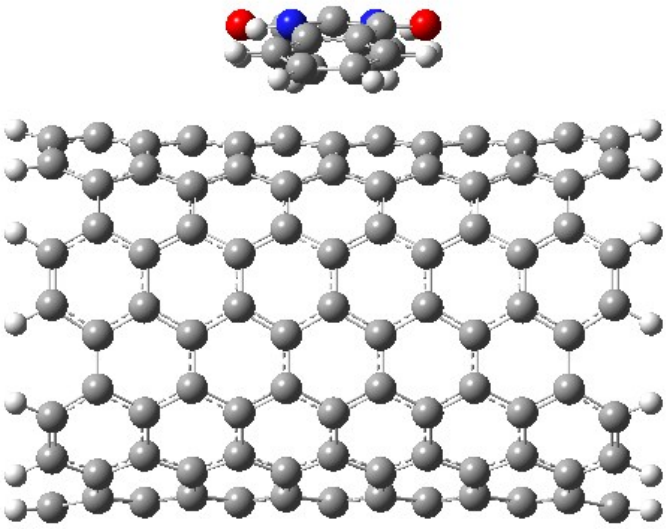


Figure S1. Optimized geometry of the exohedral complex of indigo with (7,7)CNT with the lowest vibrational mode of -114 cm^{-1} obtained at B97D/6-31g** level of theory.

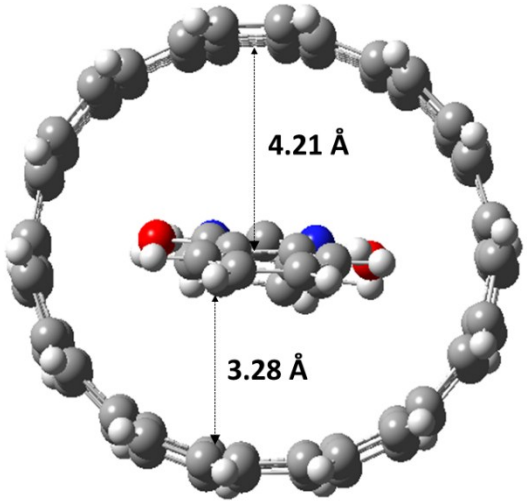


Figure S2. Optimized geometry of the complex indigo@(7,7)CNT obtained at B3LYP-GD3/6-31g** level of theory

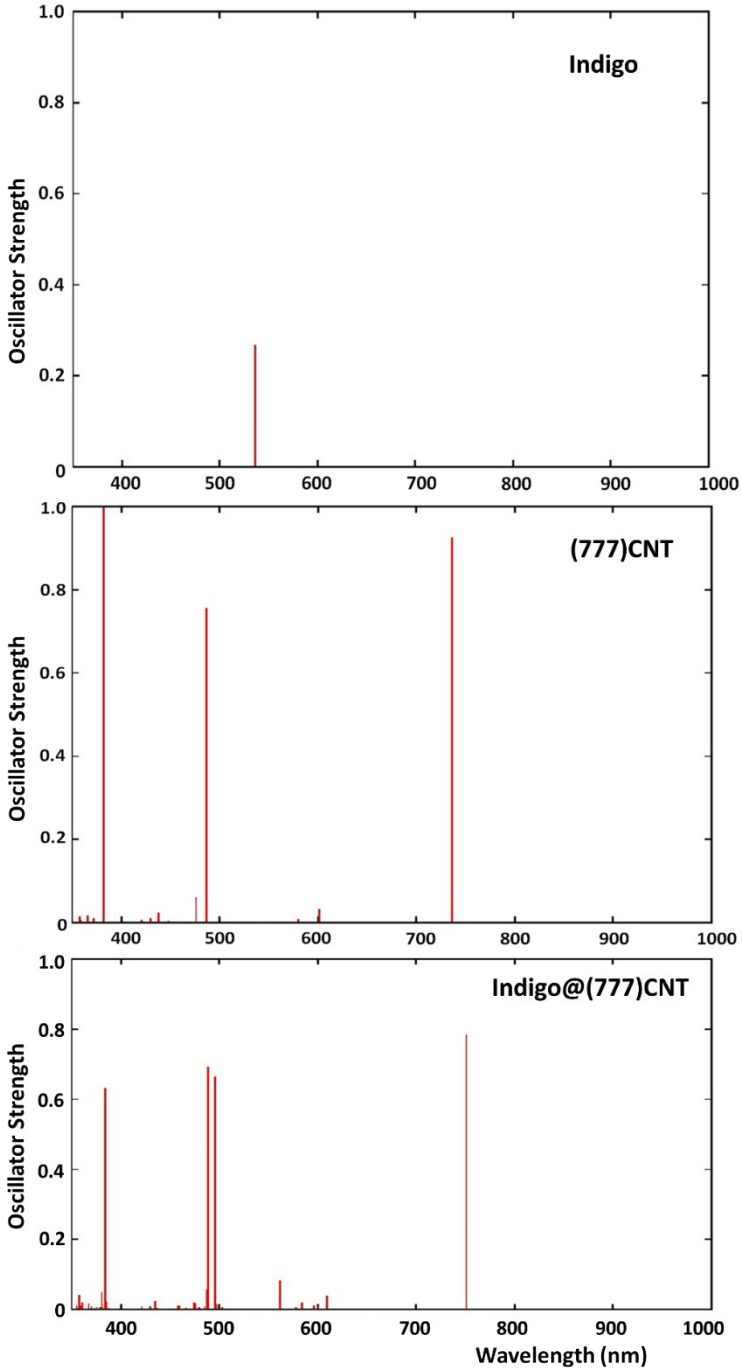


Figure S3. The optical absorption spectra of indigo, (7,7)CNT and the complex indigo@(7,7)CNT obtained at B3LYP-GD3/6-31g** level

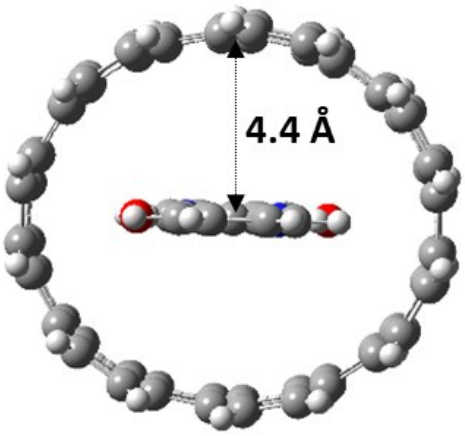


Figure S4. Optimized geometries of the complex indigo@(7,7)CNT obtained at ωB97X-D/6-31g** level

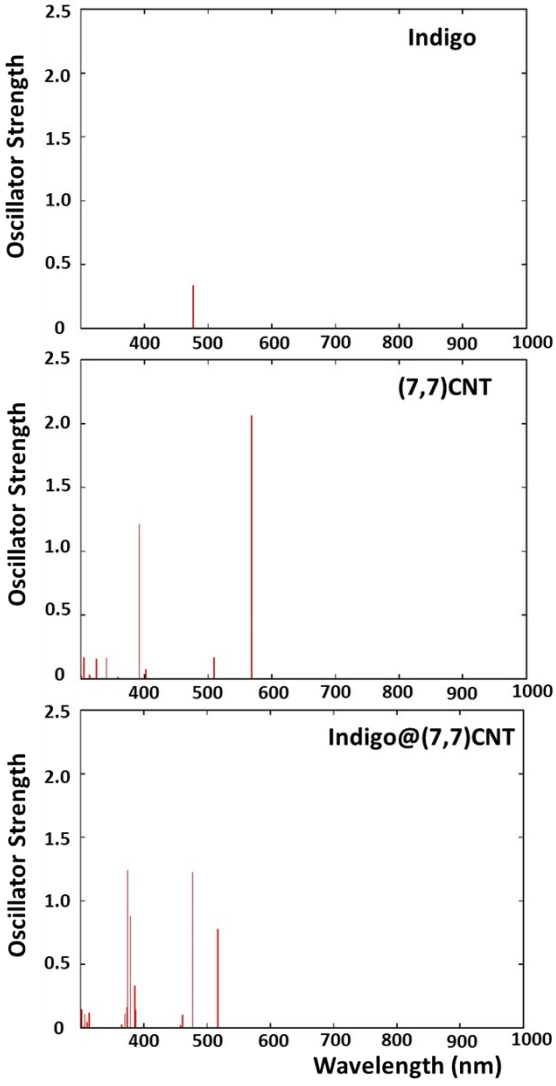


Figure S5. The optical absorption spectra of indigo, (7,7)CNT and the complex indigo@(7,7)CNT obtained at ωB97X-D/6-31g** level

Table S1. Contribution of various interaction energy components (dispersion, electrostatic and induction) for the complexes indigo@(*n,n*)-CNT, *n*=6-8. All the values are in kcal/mol

Complex	**Dispersion**	**Electrostatic**	**Induction**
Indigo@(6,6)CNT	-137.29	-92.51	-17.33
Indigo@(7,7)CNT	-71.70	-24.70	-7.82
Indigo@(8,8)CNT	-59.24	-21.14	-6.22

Table S2. Calculated values of hole and electron reorganization energy (λ_+ and λ_-) for free indigo, CNTs and their complexes at B97D/6-31g(d,p) level

System	**λ_+ (eV)**	**λ_- (eV)**
Indigo	0.197	0.272
(6,6)CNT	0.051	0.038
(7,7)CNT	0.028	0.033
(8,8)CNT	0.029	0.027
Indigo@(6,6)CNT	0.047	0.040
Indigo@(7,7)CNT	0.038	0.033
Indigo@(8,8)CNT	0.032	0.029

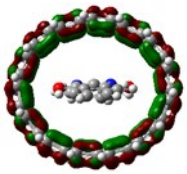
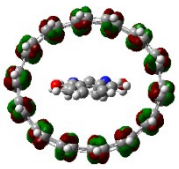
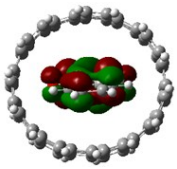
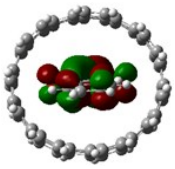
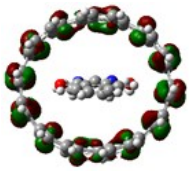
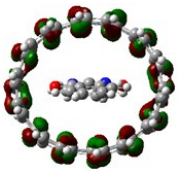
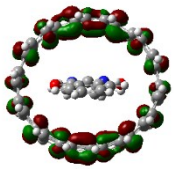
Table S3. Computed values of ionization energy (IE), electron affinity (EA), energy of HOMO and LUMO orbitals (E_{HOMO}, E_{LUMO}) and their energy gap (ΔE_{H-L}) for indigo, (7,7)CNT and their complex obtained at B97D/6-31g(d,p), B3LYP-GD3/6-31G(d,p) and ωB97X-D/6-31g(d,p) levels. All energy values are in eV

System	VIE	AIE	VEA	AEA	E_{HOMO}	E_{LUMO}	ΔE_{H-L}
B97D/6-31g(d,p)							
Indigo	6.58	6.52	-1.25	-1.38	-4.58	-3.28	1.30
(7,7)CNT	4.90	4.88	-2.20	-2.21	-4.00	-3.11	0.89
Indigo@(7,7)CNT	4.89	4.86	-2.18	-2.20	-3.97	-3.10	0.87
B3LYP-GD3/6-31g(d,p)							
Indigo	6.77	6.68	-1.25	-1.42	-5.27	-2.77	2.51
(7,7)CNT	5.07	5.04	-2.09	-2.12	-4.35	-2.80	1.55
Indigo@(7,7)CNT	5.04	5.01	-2.08	-2.10	-4.33	-2.79	1.54
ωB97X-D/6-31g(d,p)							
Indigo	6.98	6.81	-1.24	-1.43	7.10	1.09	6.01
(7,7)CNT	5.02	4.38	-2.34	-2.99	-5.16	-2.19	2.97
Indigo@(7,7)CNT	5.51	5.49	-1.80	-1.86	-5.65	-1.67	3.98

Table S4. Calculated values of the transfer integral (t), internal reorganization energy (λ), rate constant (k) and carrier mobility (μ) for the most stable complex indigo@(7,7)CNT at different distances (d) obtained at B97D/6-31G(d,p) and B3LYP-GD3/6-31G(d,p) levels

Method	**d (Å)**	**λ_+ (eV)**	**t^+ (eV)**	**k^+ (s^{-1})**	**μ^+ [cm^2/(Vs)]**	**λ_- (eV)**	**t^- (eV)**	**k^- (s^{-1})**	**μ^- [cm^2/(Vs)]**
B97D	4.67	0.038	0.055	18.002×10^{13}	7.644	0.033	0.056	21.022×10^{13}	8.918
	2.97				3.092				3.067
B3LYP-GD3	4.21	0.059	0.061	2.299×10^{13}	0.895	0.053	0.061	4.070×10^{13}	1.401
	3.28				0.544				0.851
ωB97X-D	4.40	0.131	0.060	1.080×10^{12}	0.041	0.122	0.076	2.619×10^{12}	0.098

Table S5. The absorption wavelength (λ), oscillator strength (f), corresponding electronic transitions, percentage contribution and molecular orbitals involved for the complex indigo@(7,7)CNT obtained at B3LYP-GD3/6-31g** level

λ (nm)	**f**	**Transition**	**% Contribution**	**Molecular orbitals involved in the transition**	
751	0.78	H-1 → L	48		
		H → L+1	49		
562	0.08	H-2 → L+2	77		
495	0.66	H-6 → L	32		
		H→ L+6	26		
488	0.69	H-7 → L	32		
		H →L+7	28		

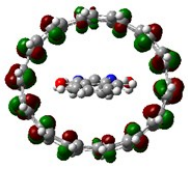
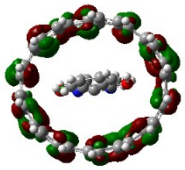
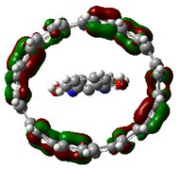
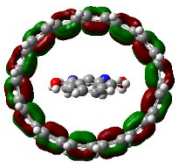
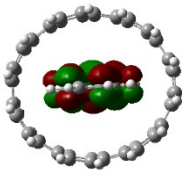
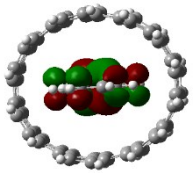
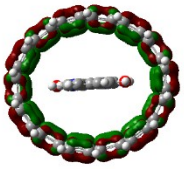
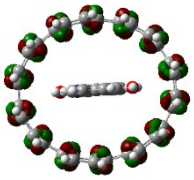
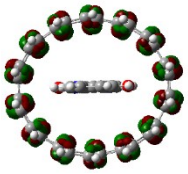
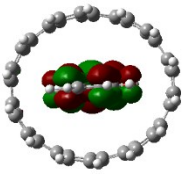
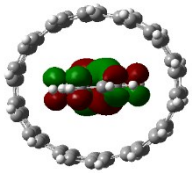
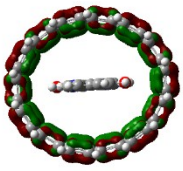
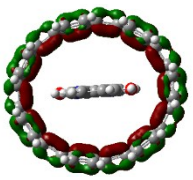
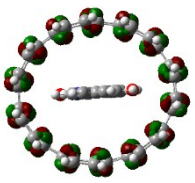
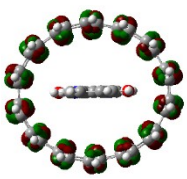
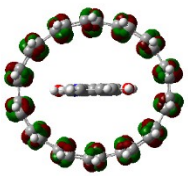
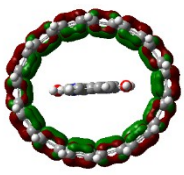
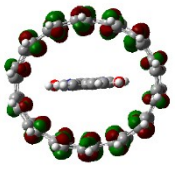
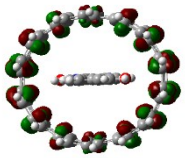
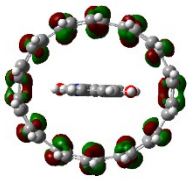
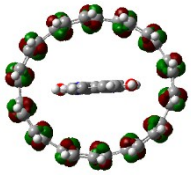
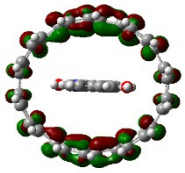
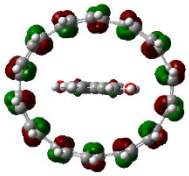
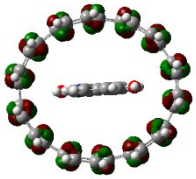
487	0.05	H-2 → L+4	89		
384	0.05	H-17 → L+1	29		
383	0.11	H-16 →L+2	25		
		H-15 → L+2	30		
380	0.05	H-2 → L+8	80		

Table S6. The absorption wavelength (λ), oscillator strength (f), corresponding electronic transitions, percentage contribution and molecular orbitals involved for the complex indigo@(7,7)CNT obtained at ωB97X-D/6-31g** level

λ (nm)	f	Transition	% Contribution	Molecular orbitals involved in the transition	
517	0.77	H-4 → L+2	37		
		H-1 → L	27		
		H → L+1	29		
477	1.22	H-4 → L+2	50		
		H-1 → L	20		
		H → L+1	21		
461	0.10	H-2 → L+1	25		
		H-1 → L+3	38		

387	0.14	H-1 → L+3	29		
386	0.33	H-1 → L+4	24		
374	1.24	H-7 → L	22		
		H → L+7	25		
374	0.16	H-5 → L	37		
		H → L+5	29		
370	0.11	H-2 → L+1	33		