P-doped graphene- C_{60} nanocomposite: A donor -acceptor complex with P-C dative bond

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Scheme S1 The surfaces studied: a) $C_{240}H_{38}$ and b) $C_{54}H_{18}$ (CC). The circle indicates the dopant

position.



Fig. S1 The isosurface map of electrostatic potential (isosurface of 0.001) of a) graphene (CC), b) N-doped (N-CC) and c) P-doped graphene (P-CC) surfaces. Scale is in kcal/mol.



Fig. S2 The isosurface maps of electron localization function of a) P-CC and b) N-CC surfaces with isovalue of 0.8.



Fig. S3 The isosurface maps of electron localization function of a) P-Gr and b) N-Gr surfaces with isovalue of 0.7.



Fig. S4 The spin density distributions on the a) N-doped, b) P-doped surface. The iso-surface value is 0.01 au.

Table S1 Fukui indices for electrophilic attack of different surfaces.

	f_k
N-CC	0.043
P-CC	0.076
P-CC _{DV}	0.066



Fig. S5 Electron affinities (EA, in eV), and LUMO energies (eV) for the acceptor molecules.

	ΔE_{Def} (acceptor)	ΔE_{Def} (surface)	ΔE_{Def}
C ₆₀ P-CC	12.7	5.7	18.4
CarbonconeP-CC	13.9	7.0	20.9
CorannuleneP-CC	14.8	4.7	19.5
C ₆₀ N-CC	0.0	1.0	1.0
CarbonconeN-CC	0.7	3.0	3.7
CorannuleneN-CC	1.7	1.4	3.1
C ₆₀ CC	-0.2	1.3	1.1
CarbonconeCC	0.7	4.2	4.9
CorannuleneCC	1.5	1.4	2.9

Table S2 Total and fragment deformation energies calculated at the PBE0-D3BJ/6-31G* level of theory. All values are in kcal/mol.



Fig. S6 Three-dimensional NCI surfaces of a) C_{60} ...P-CC, b) Carboncone...P-CC, and c) Corannulene...P-CC. The surfaces are coloured according to a blue-green-red scale with an isosurface value of 0.50 a.u. The green indicates attractive interactions and the red marks a strong nonbonded overlap.

Table S3 The interaction energies and Bader charge transfer for the complexes calculated from periodic calculations. The dispersion energies are given in round brackets.

	ΔΕ	Bader charge transfer
C ₆₀ graphene	-20.2 (-23.1)	-0.028
C ₆₀ Graphitic P-doped graphene	-11.6 (-23.2)	-0.270
C ₆₀ Graphitic N-doped graphene	-19.7 (-22.5)	-0.250

Fig. S7 The results of natural bond order (NBO) analysis for various dative bond complexes.

Table S4 The NBO charges on P atom and three C atoms attached with it in the surface. The NBO charges of isolated P-CC are given in parenthesis.

	C ₆₀ P-CC	CarbonconeP-CC	CorannuleneP-CC
C1	-0.468 (-0.320)	-0.460 (-0.320)	-0.467 (-0.320)
C2	-0.434 (-0.325)	-0.435 (-0.325)	-0.430 (-0.325)
C3	-0.462 (-0.325)	-0.470 (-0.325)	-0.463 (-0.325)
Р	1.817 (1.098)	1.815 (1.098)	1.816 (1.098)

Fig. S8 The charge density differences of a) C_{60} ...P-Gr, b) C_{60} ...N-Gr, and c) C_{60} ...Gr complexes. Cyan indicates a loss of electrons whereas yellow indicates accumulation of electrons. Isosurface levels are set to 0.001 e/Å³.

Table S5 Data for the P-C bond, obtained from the topological analysis of electron localization function (ELF) of various dative bond complexes.

	N (e)	C V(C,P)(e)	P V(C,P)(e)	%P
C ₆₀ P-CC	1.836	1.158	0.678	36.9
CarbonconeP-CC	1.827	1.099	0.728	39.9
CorannuleneP-CC	1.805	1.069	0.736	40.8

Scheme S2 The studied P-doped surfaces a) with 2 dopants at 1,2 (black–blue circles) and 1,3 (black-red circles) positions and b) with 3 dopants at same ring (black–red-green circles) and different rings (black-blue-green circles). The circle indicates the dopant position.

Table S6 Thermodynamic characteristics (in kcal/mol, T = 298 K) for the formation of various dative bonds between P2-CC and C₆₀.

C ₆₀ P2-CC	spin	ΔΕ	ΔG	ΔH	-TΔS
1,2_up-up	Singlet	-9.7	4.1	-8.8	12.9
1,2_up-down		-15.0	-3.1	-13.8	10.7

1,3_up-up		-10.4	4.8	-8.6	13.4
1,3_up-down		-8.9	6.9	-7.3	14.2
1,2_up-up	Triplet	4.1	16.1	4.0	12.1
1,2_up-down		13.8	25.6	14.0	11.7
1,3_up-up		-17.7	-3.4	-16.3	12.9
1,3_up-down		-17.1	-1.7	-15.7	14.1

Table S7 Thermodynamic characteristics (in kcal/mol, T = 298 K) for the formation of various dative bonds between P3-CC and C₆₀.

C ₆₀ P3-CC	spin	P positions	ΔE	ΔG	ΔH	-TΔS
up-up-up	doublet	same ring	-15.2	-2.7	-12.9	10.2
up-up-down		same ring	-16.0	-3.0	-13.9	10.9
up-up-up		different ring	-18.4	-4.5	-17.1	12.6
up-up-down		different ring	-19.2	-5.0	-17.2	12.1
up-up-up	quartet	same ring	-12.5	-0.9	-11.1	10.2
up-up-down		same ring	-8.1	4.5	-6.8	11.3
up-up-up		different ring	-20.1	-6.7	-18.8	12.1
up-up-down		different ring	-6.3	7.5	-5.4	12.8

Scheme S3 The studied P-doped surface with four-coordination in a divacancy defect (P-CC_{DV}).

Table S8 Thermodynamic characteristics (in kcal/mol, T = 298 K) for the formation of dative bond complex between P-CC_{DV} and C₆₀. The dispersion energies are given in round brackets.

C ₆₀ P-CC _{DV}	spin	ΔΕ	ΔG	ΔH	-ΤΔS	ΔE_{INTR}
	doublet	-24.3 (-27.5)	-8.3	-22.2	14.0	-45.7

Table S9 Thermodynamic characteristics (in kcal/mol, T = 298 K) for the formation of various dative bond between graphene surface and acceptor molecules. The dispersion energies are given in round brackets.

	ΔΕ	ΔG	ΔH	-TΔS	ΔE_{INTR}
C ₆₀ CC	-21.3 (-23.8)	-9.9	-19.7	9.8	-22.4
CarbonconeCC	-40.1 (-49.8)	-25.5	-38.9	13.4	-45.1
CorannuleneCC	-24.0	-12.1	-22.8	10.7	-27.0
	(-29.8)				

Table S10 Thermodynamic characteristics (in kcal/mol, T = 298 K) for the formation of various dative bond between N-doped surface and acceptor molecules. The dispersion energies are given in round brackets.

	ΔΕ	ΔG	ΔH	-TΔS	ΔE_{INTR}
C ₆₀ N-CC	-22.1 (-23.6)	-10.9	-20.6	9.7	-23.0
CarbonconeN-CC	-40.7 (-48.4)	-25.9	-39.5	13.6	-44.4
CorannuleneN-CC	-25.3 (-30.0)	-12.6	-24.1	11.5	-28.4

Fig. S9 The variation of the a) $N...C(C_{60})$ (black) and b) C-P (red) dative-bond lengths of the $C_{60}...N/P$ -CC complexes in the trajectory simulated at 300K.

Fig. S10 The variation of the a) P-C(C₆₀) (red) dative bond and b) P...C(C₆₀) (blue) bond lengths of the C₆₀...P-CC complex in the trajectory simulated at 300K.

Fig. S11 The variation of the bond length between the center of mass of C_{60} and P atom of the C_{60} ...P-Gr complex in the trajectory simulated at 300K.

Fig. S12 The snapshots of the C₆₀...P-Gr complex taken at a) t= 0.322 ps, b) t= 6.583 ps, and c) t= 8.960 ps in the trajectory simulated at 300K.

Fig. S13 The variation of the bond length between the center of mass of C_{60} and N atom of the C_{60} ...N-Gr complex in the trajectory simulated at 300K.

					Average
					NICS
CC	NICS(0)	-4.8658	-4.8605	-13.9507	-7.892
	NICS(1)	-8.8890	-9.3695	-16.7364	-11.665
C ₆₀ CC	NICS(0)	-4.4555	-4.3788	-14.2833	-7.706
	NICS(1)	-9.3218	-9.1195	-19.1416	-12.528
N-CC	NICS(0)	15.2576	15.2592	36.5676	22.361
	NICS(1)	9.9535	10.0290	26.4491	15.477
C ₆₀ N-CC	NICS(0)	13.2594	11.4349	27.9252	17.540
	NICS(1)	8.4676	6.4652	19.2721	11.402
P-CC	NICS(0)	4.3853	4.3872	3.6825	4.152
	NICS(1)	0.5967	0.5578	0.0664	0.407
C ₆₀ P-CC	NICS(0)	-2.3787	-2.2385	-7.5152	-4.044
	NICS(1)	-3.5743	-3.1631	-6.8193	-4.519

Table S11 NICS values (in ppm) at the ring centers (NICS(0)) and points 1 Å above (NICS(1)) for the surfaces and C_{60} -complexes.

	Excitation energy (eV)	Wavelength (nm)	Oscillator strength (<i>f</i>)
CC	3.618	342.7	1.578
C ₆₀ CC	3.596	344.8	0.730
	3.590	345.4	1.132
	3.570	347.3	0.446
N-CC	3.955	313.5	0.231
	3.604	344.0	0.207
	3.456	358.8	0.193
	3.068	404.1	0.265
	3.041	407.7	0.254
C ₆₀ N-CC	2.020	613.9	0.051
P-CC	3.820	324.6	0.397
	3.734	332.0	0.493
	3.476	356.7	0.377
C ₆₀ P-CC	2.632	471.1	0.053
	2.333	531.3	0.061
	2.224	557.6	0.040
	2.199	563.7	0.047
	1.224	1013.4	0.098

Table S12 The transition coefficients and associated eigenvalues of the dominated excitation in various systems.

Fig. S14 The difference in total electron density (isovalue 0.001) computed for ground and excited states of a) C_{60} ...N-CC and b) C_{60} ...CC with significant oscillator strengths (*f*). Blue regions represent increase and red regions represent decrease in electron density due to the excitation.

Fig. S15 The difference in total electron density (isovalue 0.001) computed for ground and excited states of C_{60} ...P-CC with significant oscillator strengths (*f*). Blue regions represent increase and red regions represent decrease in electron density due to the excitation.

Computational details

All the surfaces, acceptor molecules and complexes have been fully optimized using the dispersioncorrected-DFT method, employing the PBE0-D3^{1,2} functional and 6-31G* basis set. In the DFT study of cluster models, we have modelled pristine graphene surface with circumcoronene (CC) having 54 C atoms ($C_{54}H_{18}$). The large surface having 240 C ($C_{240}H_{38}$), allows the acceptor C_{60} molecule to freely move on it. The model molecules of finite polyaromatic hydrocarbon are capped with hydrogen atoms at their edges. For two-dopants, 2 P atoms are introduced in the surface at 1,2 and 1,3 positions respectively (Scheme S2, ESI). As the P atoms prefer to occupy at nearest-neighbour positions in the surface, so other configurations are not considered in the study. These two P atoms can stay in the same (up-up) or opposite (up-down) sides and with singlet or triplet spin states. So, all together 8 surfaces are considered for the complexation with C_{60} . In the same way with three P–dopants, we have considered two possible spins, doublet and quartet state for the complex formation. All the surfaces are fully optimized at PBE0-D3BJ/6-31G* level of theory.

The fully optimized structures of complex and fully optimized isolated monomers have been used to calculate the total interaction energies as

$$\Delta E = E_{complex} - E^{i}_{monomer\,1} - E^{i}_{monomer\,2} \tag{1}$$

The intrinsic interaction energy (ΔE_{INTR}), is calculated as a difference in energy between the optimized complex and the sum of the energies of subsystems with geometries obtained from the optimized complex geometry.

$$\Delta E_{INTR} = E_{complex} - E_{monomer\,1} - E_{monomer\,2} \tag{2}$$

The deformation energies (ΔE_{Def}) are termed as energy necessary to distort the isolated optimized monomers into their complex geometries and it's calculated as a difference of energies of monomers with the isolated-optimal and complex-optimal geometries. The respective deformation energy is positive.

$$\Delta E_{Def} = \left(E_{monomer \, 1} - E^{i}_{monomer \, 1} \right) + \left(E_{monomer \, 2} - E^{i}_{monomer \, 2} \right) \tag{3}$$

The total interaction energy is thus defined as

$$\Delta E = \Delta E_{INTR} + \Delta E_{Def} \tag{4}$$

Wiberg Bond indexes (WBI) have been calculated from NBO calculations using the complex geometries optimized at PBE0-D3BJ/6-31G* level.

Molecular dynamics trajectories were simulated by ORCA 4.2.1 code³ and visualized by VMD 1.9.2 visualization software.⁴ All the simulations calculated at the PBE0-D3BJ/6-31G* level of theory. The simulation time was performed up to 10 ps. In the simulation, the step size was set to 1 fs, Berendsen thermostat⁵ with time constant of 20 fs was employed to control the temperatures.

The NBO calculations have been performed using NBO 3.1 program⁶ as implemented in Gaussian 09.⁷ Electron localisation function (ELF) isosurfaces and Non-covalent index (NCI) analyses were carried out using the Multiwfn 3.6 software⁸ and plotted using the VMD 1.9.2 visualization software, based on Multiwfn-generated Gaussian cube files. The solvent effects were considered via the COSMO solvation model,⁹ with *o*-dichlorobenzene solvent medium. The nucleus-independent chemical shift (NICS) calculations were performed using the PBE0-D3 optimized geometries with gauge-invariant atomic orbitals (GIAO).^{10,11} The local nucleophilicity index calculations, using Fukui functions^{12,13} were performed for the isolated surfaces. These functions give atom-specific information on the propensity to undergo electrophilic or nucleophilic attack.¹⁴

Periodic calculations are performed using the VASP (Vienna Ab initio Simulation Package) implementation of DFT in the projected augmented plane-wave scheme.^{15,16} The plane-wave cutoff energy is set to 500 eV. The Monkhorst-Pack scheme using a $4 \times 4 \times 1$ *k*-point mesh is used to generate the *k*-point sampling grids. The computational slab included 6×6 graphene unit cells intercalated by a wide vacuum layer. The "Accurate" precision level is utilized in all cases. The positions of all atoms are fully optimized with an electronic energy convergence threshold of 10^{-6} eV. The 10 ps molecular dynamics was performed in the canonical ensemble (NVT) using a 1fs

time step with Nose-Hoover thermostat^{17,18} at 300 K. Bader charge transfers were calculated using the Bader analysis program¹⁹.

For time dependent (TD)-DFT calculations, the complex geometries are optimized at the ω B97XD/6-31G* level. The hybrid meta-GGA functional ω B97XD has a 100% fraction of HF exchange at long-range in addition to about 22% at short-range and also contains empirical dispersion terms.²⁰ In contrast to PBE0, long-range-corrected functional, ω B97XD properly describe the ground and excited state properties of complex molecules.²¹ The importance of long-range corrected functionals for charged systems and for describing CT states is mentioned previously.^{22,23} The lowest 40 vertical excitation energies have been calculated by time-dependent density functional theory (TDDFT) on the optimized geometries. The differences in total electron density computed for ground and excited states²⁴ were generated using the Multiwfn 3.6 software based on wfn files generated from Gaussian calculations.

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