Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION FOR:

Photoinduced electron transfer in [10]CPP⊃C_{60} oligomers with stable and well-defined supramolecular structure

Anton J. Stasyuk,*[a,b]

a. Institut de Química Computacional i Catàlisi and Departament de Química, Universitat de Girona, C/ Maria Aurèlia Capmany 69, 17003 Girona, Spain.

Abstract

Recent synthesis of a new type of polymers containing conjugated cycloparaphenylene (CPP) macrocycles interconnected by a linear conjugated backbone opens up a fantastic potential of cyclic π-conjugated materials in organic photovoltaics. In this work, we report a theoretical study of ground and excited state properties of such polymer and investigate an effect of inclusion of fullerene molecules into polymer chains. MD simulations revealed that oligomers **([10]CPP_Fused⊃C_{60})$_{24}$** and **([10]CPP_Fused⊃C_{60})$_{32}$** with π-extended linker between CPPs tend to form stable, helix-like structures. We show that photoinduced electron transfer from the CPP-based polymer to **C_{60}** fullerene is favorable and occurs on nanosecond time scale. Fast hole- and excess-electron transfer rates was found to be significantly faster than corresponding charge recombination rates.

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Computational Methodology

Quantum-chemical calculations

Geometry optimizations were performed employing BLYP[1, 2] exchange−correlation functional with def2-SVP basis set[3, 4] and resolution of identity approximation (RI, alternatively termed density fitting)[5, 6] implemented in the ORCA 4.2.1 program.[7-9] The empirical D3 dispersion correction with Becke–Johnson damping[10,11] was employed. Vertical excitation energies were calculated using TDA formalism[12] with range-separated CAM-B3LYP[13] functional and def2-SVP basis set,[3, 4] using Gaussian 16 (rev. A03).[14] The same program was used for population analysis and calculation of Mulliken,[15,16] Lowdin,[17] Hirshfeld,[18] CM5,[19] and iterative Hirshfeld[20] charges. Interaction energy of the complexes was computed using BLYP functional coupled with def2-TZVP basis[3,4] (BLYP-D3(BJ)/def2-TZVP//BLYP-D3(BJ)/def2-SVP). Energy decomposition analysis (EDA) was performed using the Amsterdam Density Functional (ADF) program.[21] The excited states have been analyzed in terms of the natural transition orbitals (NTO) concept introduced by Luzanov *et al.*[22] and implemented within modern many-body codes by Head-Gordon *et al.*[23] Molecular structures and frontier molecular orbitals were visualized by Chemcraft 1.8 program.[24]

Energy decomposition analysis

The interaction energy in the gas phase was examined in the framework of the Kohn-Sham MO model using a quantitative energy decomposition analysis (EDA)[25-27] into electrostatic interactions, Pauli repulsive orbital interactions, and attractive orbital interactions, to which a term ΔE_{disp} is added to account for the dispersion correction:

$$\Delta E_{\text{int}} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{oi} + \Delta E_{disp} \quad (1)$$

The term ΔV_{elstat} corresponds to the classical electrostatic interactions between the unperturbed charge distributions of the prepared (i.e. deformed) fragments and is usually attractive. The Pauli repulsion, ΔE_{Pauli}, comprises the destabilizing interactions between occupied orbitals and is responsible for any steric repulsion. The orbital interactions, ΔE_{oi}, account for electron-pair bonding, charge transfer (*i.e.*, donor–acceptor interactions between occupied orbitals on one moiety and unoccupied orbitals on the other, including HOMO-LUMO interactions) and polarization (empty-occupied orbital mixing on one fragment due to the presence of another fragment). The term ΔE_{disp} accounts for the dispersion corrections.[28,29]

Analysis of excited states

The quantitative analysis of exciton delocalization and charge transfer in the donor-acceptor complexes was carried out in terms of the transition density.[30-32] The analysis was done in the Löwdin orthogonalized basis, which is more convenient. The matrix ${}^{\lambda}\mathbf{C}$ of orthogonalized MO coefficients is obtained from the coefficients **C** in the original basis ${}^{\lambda}\mathbf{C} = \mathbf{S}^{1/2}\,\mathbf{C}$, where **S** is the atomic orbital overlap matrix. The transition density matrix T^{0i} for an excited state Φ^{*} constructed as a superposition of singly excited configurations (where an occupied MO ψ_i is replaced a virtual MO ψ_a) is computed,

$$\mathrm{T}^{0\mathrm{i}}_{\alpha\beta} = \sum_{\mathrm{ia}} \mathrm{A}_{\mathrm{i}\rightarrow\mathrm{a}}\, {}^{\lambda}\mathrm{C}_{\alpha\mathrm{i}}\, {}^{\lambda}\mathrm{C}_{\beta\mathrm{a}} \quad (2)$$

where $A_{i\rightarrow a}$ is the expansion coefficient.

A key quantity $\Omega(D,A)$ is determined by:

$$\Omega(D,A) = \sum_{\alpha\in D,\,\beta\in A} \left(T_{\alpha\beta}^{0i}\right)^2 \quad (3)$$

The weights of local excitations on D and A are Ω(D,D) and Ω(A,A). The weight of electron transfer configurations D→A and A→D is represented by Ω(D,A) and Ω(A,D), respectively. The index Δq, which describes charge separation and charge transfer between D and A, is

$$\Delta q(CS) = \sum \Omega(D,A) - \Omega(A,D) \quad (4)$$

$$\Delta q(CT) = \sum \Omega(D,A) + \Omega(A,D) \quad (5)$$

Solvent Effects

The equilibrium solvation energy E_S^{eq} of a molecule (in the ground or excited state) in the medium with the dielectric constant ε was estimated using a COSMO-like polarizable continuum model[33-36] in the monopole approximation:

$$E_S^{eq}(Q,\varepsilon) = -\frac{1}{2} f(\varepsilon) Q^{+} D Q \quad (6)$$

where the *f*(ε) is the dielectric scaling factor, $f(\varepsilon) = \frac{\varepsilon - 1}{\varepsilon}$, **Q** -the vector of *n* atomic charges in the molecular system, **D** is the *n* x *n* symmetric matrix determined by the shape of the boundary surface between solute and solvent. $\mathbf{D=B^{+}A^{-1}B}$, where the *m* x *m* matrix **A** describes electrostatic interaction between *m* surface charges and the *m* x *n* **B** matrix describes the interaction of the surface charges with *n* atomic charges of the solute.[33,37] The GEPOL93 scheme[38] was used to construct the molecular boundary surface.

The charge on atom X in the excited state Φ_i, q_X^i, was calculated as:

$$q_X^i = q_X^0 + \Delta_X^i, \quad \Delta_X^i = \sum_{Y\neq X} \sum_{\alpha\in X,\,\beta\in Y} (T_{\alpha\beta}^{0i} T_{\alpha\beta}^{0i} - T_{\beta\alpha}^{0i} T_{\beta\alpha}^{0i}), \quad (7)$$

where q_X^0 is the atomic charge on A in the ground state and Δ_X^i is its change due to the redistribution of the electron density between the atoms X and the rest of atoms Y which is caused by the excitation $\psi_0 \rightarrow \psi_i$.

The non-equilibrium solvation energy for excited state ψ_i can be estimated as:[39]

$$E_S^{neq}(Q^0,\Delta,\varepsilon,n^2) = f(\varepsilon)\Delta^{+} D Q^0 - \frac{1}{2} f(n^2)\Delta^{+} D \Delta, \quad (8)$$

In Eq. (8), n^2 (the refraction index squared) is the optical dielectric constant of the medium and the vector Δ describes the change of atomic charges in the molecule by excitation in terms of atomic charges, see Eq. (7). By definition, the external (solvent) reorganization energy is the difference of the non-equilibrium (Eq. 8) and equilibrium (Eq. 6) solvation energies of the excited state.

Electron transfer rates

The rate of the nonadiabatic electron transfer (ET), k_{ET}, can be expressed in terms of the electronic coupling squared, V^2, and the Franck-Condon Weighted Density of states (FCWD):

$$k_{ET} = \frac{2\pi}{\hbar} V^2 \left(FCWD\right) \tag{9}$$

that accounts for the overlap of vibrational states of donor and acceptor and can be approximately estimated using the classical Marcus equation:[40]

$$\left(FCWD\right) = \left(4\pi\lambda kT\right)^{-1/2} \exp\left[-\left(\Delta G^0 + \lambda\right)^2 \Big/ 4\lambda kT\right] \tag{10}$$

where λ is the reorganization energy and ΔG^0 is the standard Gibbs energy change of the process. The fragment charge difference (FCD)[41,42] method was employed to calculate the electronic couplings in this work.

The Marcus expression is derived for the high-temperature condition, $\hbar\omega_l \ll kT$, for all vibrational modes *l*. The semi-classical description of ET[43,44] includes the effect of the quantum vibrational modes in an effective way, the solvent (low frequency) modes are treated classically, while a single high-frequency intramolecular mode ω_i, $\hbar\omega_i \gg kT$, is described quantum mechanically. Because ET occurs normally from the lowest vibrational level of the initial state, the rate *k* can be expressed as a sum over all channels connecting the initial state with the vibrational quantum number n = 0 to manifold vibrational levels of the final state,

$$k = \sum_{n=0}^{\infty} k_{0\to n} \text{ , where } k_{0\to n} = \frac{2\pi}{\mathsf{h}} V_{0\to n}^2 \frac{1}{\sqrt{4\pi\lambda_s kT}} \exp\left[-\frac{\left(\Delta G + n\mathsf{h}\omega_i + \lambda_s\right)^2}{4\lambda_s kT}\right] \tag{11}$$

with

$$V_{0\to n}^2 = V^2 \frac{S^n}{n!} \exp\left(-S\right) \tag{12}$$

An effective value of the Huang-Rhys factor *S* is estimated from the internal reorganization energy λ_i,

$$S = \lambda_i / \mathsf{h}\omega_i$$

As seen, an additional parameter (as compared to the Marcus equation) enters the semi-classical expression - the frequency ω_i of a vibrational mode that effectively describes the nuclear intramolecular relaxation following the ET. Typically, in organic systems (including fullerene and nanotube derivatives) the main contribution to the internal reorganization energy is due to stretching of C=C bonds (the corresponding frequencies are found to be in the range 1400-1800 cm^{-1}). Thus, the effective frequency was set to 1600 cm^{-1}. We have demonstrated that varying the parameter ω_i within a reasonable range does not change significantly the computed ET rate (Table S4).

Reorganization energy

The reorganization energy is usually divided into two parts, $\lambda = \lambda_i + \lambda_s$, including internal and solvent terms. The solvent reorganization energy corresponds to the energy required to move solvent molecules from

the position they occupy in the initial state to the location they have in the CT state, but without charge transfer having occurred. The λ_s for a particular CT states was computed as a difference between the equilibrium (E^{eq}, see eq. 6) and non-equilibrium (E^{neq}, see eq. 8) solvation energies for states of interest. The internal reorganization energy λ_i corresponds to the energy of structural changes when donor/acceptor fragments going from initial-state geometries to final-state geometries.

$$\lambda_i = \lambda_i^1 + \lambda_i^2, \text{ where:}$$

$$\lambda_i^1(C_{60}^{\ *} \rightarrow C_{60}^{\ -}) = \frac{1}{2}\left[\left(\left(C_{60}^{\ *}\right)_- - \left(C_{60}^{\ *}\right)_*\right) + \left(\left(C_{60}^{\ -}\right)_* - \left(C_{60}^{\ -}\right)_-\right)\right] \quad (13)$$

$$\lambda_i^2(CPP^0 \rightarrow CPP^+) = \frac{1}{2}\left[\left(\left(CPP^0\right)_+ - \left(CPP^0\right)_0\right) + \left(\left(CPP^+\right)_0 - \left(CPP^+\right)_+\right)\right]$$

Interaction energies

The interaction energies were calculated directly from electronic energy of complex and electronic energies of subsystems. For **U1** and **U2** complexes, the interaction energy can be expressed as:

$$E_{\text{int}}^{Type1} = E_{([10]CPP\_Fused)_2 \supset C_{60}} - (E_{([10]CPP\_Fused)_2} + E_{C_{60}})$$

$$E_{\text{int}}^{Type2} = E_{([10]CPP\_Fused \supset C_{60})_2} - (E_{([10]CPP\_Fused)_2 \supset C_{60}^1} + E_{C_{60}^2})$$

$$E_{\text{int}}^{Type3} = E_{C_{60}^1 \cdots C_{60}^2} - (E_{C_{60}^1} + E_{C_{60}^2}) \quad (14)$$

$$E_{\text{int}}^{TOTAL} = E_{([10]CPP\_Fused \supset C_{60})_2} - (E_{([10]CPP\_Fused)_2} + E_{C_{60}^1} + E_{C_{60}^2})$$

Quantum Theory of Atoms in Molecules (QTAIM)

Topological analysis of the electron distribution was conducted using the "Quantum Theory of Atoms in Molecules" (QTAIM) approach proposed by Bader.[45,46] Electron density properties measured at the bond critical point (BCP, saddle point on electron density curvature corresponding to a minimum in the direction of the atomic interaction line and a maximum in two perpendicular directions) give information about the character of different chemical bonds.[47-49] The AIMALL suite of programs[50] was applied to evaluate the BCP properties and the associated bond descriptors – the electron density [$\rho(r)$] in BCPs, its Laplacian [$\nabla^2\rho(r)$], potential energy density [$V(r)$], kinetic energy density [$G(r)$], and total electron energy density [$H(r)$].

Non-covalent interactions (NCI)

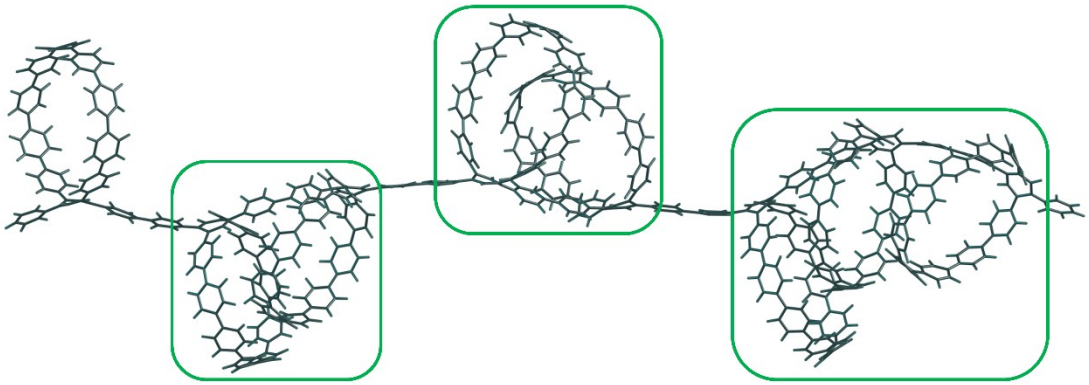
The NCI method[51-53] relies on two scalar fields to map local bonding properties: the electron density (ρ) and the reduced-density gradient (RDG, s), defined as:

$$s = \frac{1}{2(3\pi)^{1/3}} \frac{|\nabla\rho|}{\rho^{4/3}} \quad (15)$$

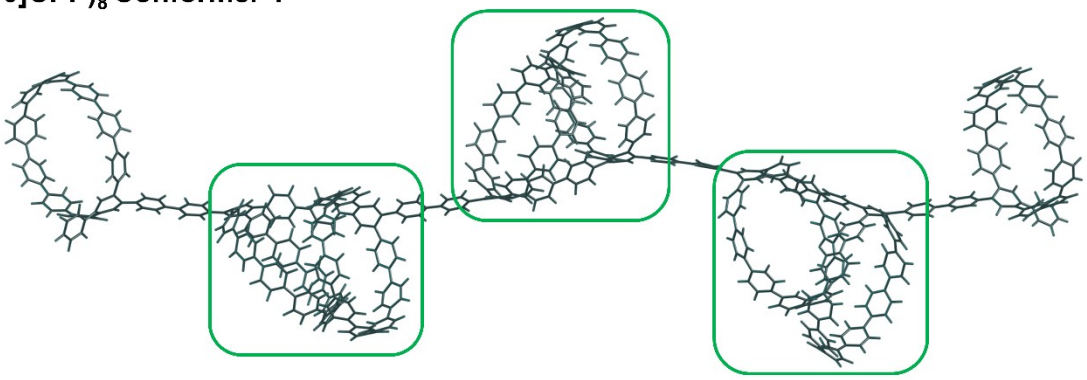
a quantity that is essential to the design of DFT functionals. The combination of *s* and *ρ* allows a rough partition of real space into bonding regions: high-*s* low-*ρ* corresponds to non-interacting density tails, low-*s* high-*ρ* to covalent bonds, and low-*s* low-*ρ* to non-covalent interactions. The NCI analysis was carried out at the CAM-B3LYP/def2-SVP level using Multiwfn program.[54]

Molecular Dynamics Simulation

Molecular Dynamics Simulation was performed using Tinker-HP 1.1 program suit.[55-58] Initial structures of studied oligomers were generated using optimized structural parameters for ([10]_CPP_Fused⊃C_{60})$_2$ complex. The minimized geometry was subjected to simulations. MD simulations were performed using classical Merck molecular force field (MMFF)[59-63] with a step size of 0.5 fs up to a total of 5 or 10 ns (depending on particular oligomer) at 300 K within NVT ensemble (Andersen termostat)[64,65] using dynamic module in Tinker-HP program. For small 8-unit oligomers, MD simulations were started from 5 different initial geometries, which differ by dihedral angle between monomer units. For the 24-unit oligomer, the simulations were carried out twice, starting from the same initial geometry. Root Mean Square Deviation (RMSD) was used to show how much molecular structure deviates from an initial geometry. All non-hydrogen atoms were taken into account in the RMSD calculation. The final representative structure was taken as the average structure of the last 1 ns (1000 frames). Data analysis and figure rendering were done using VMD software.[66]



([10]CPP)$_8$ Conformer 1



([10]CPP)$_8$ Conformer 2

Figure S1. Two comformations observed in MD simulation of fullerene-free **([10]CPP)$_8$** oligomer.

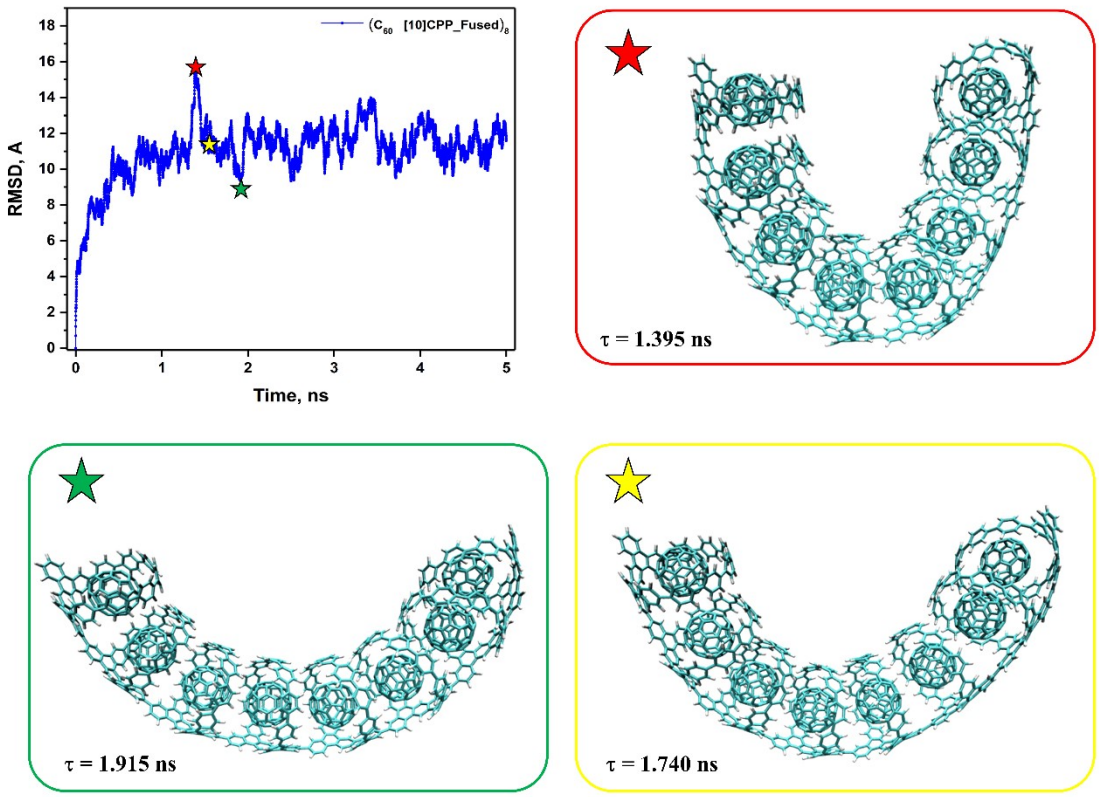


Figure S2. Frames with highest (red star), lowest (green star) and average (yellow star) RMSD values from MD trajectory of **([10]CPP_Fused⊃C_{60})$_8$**.

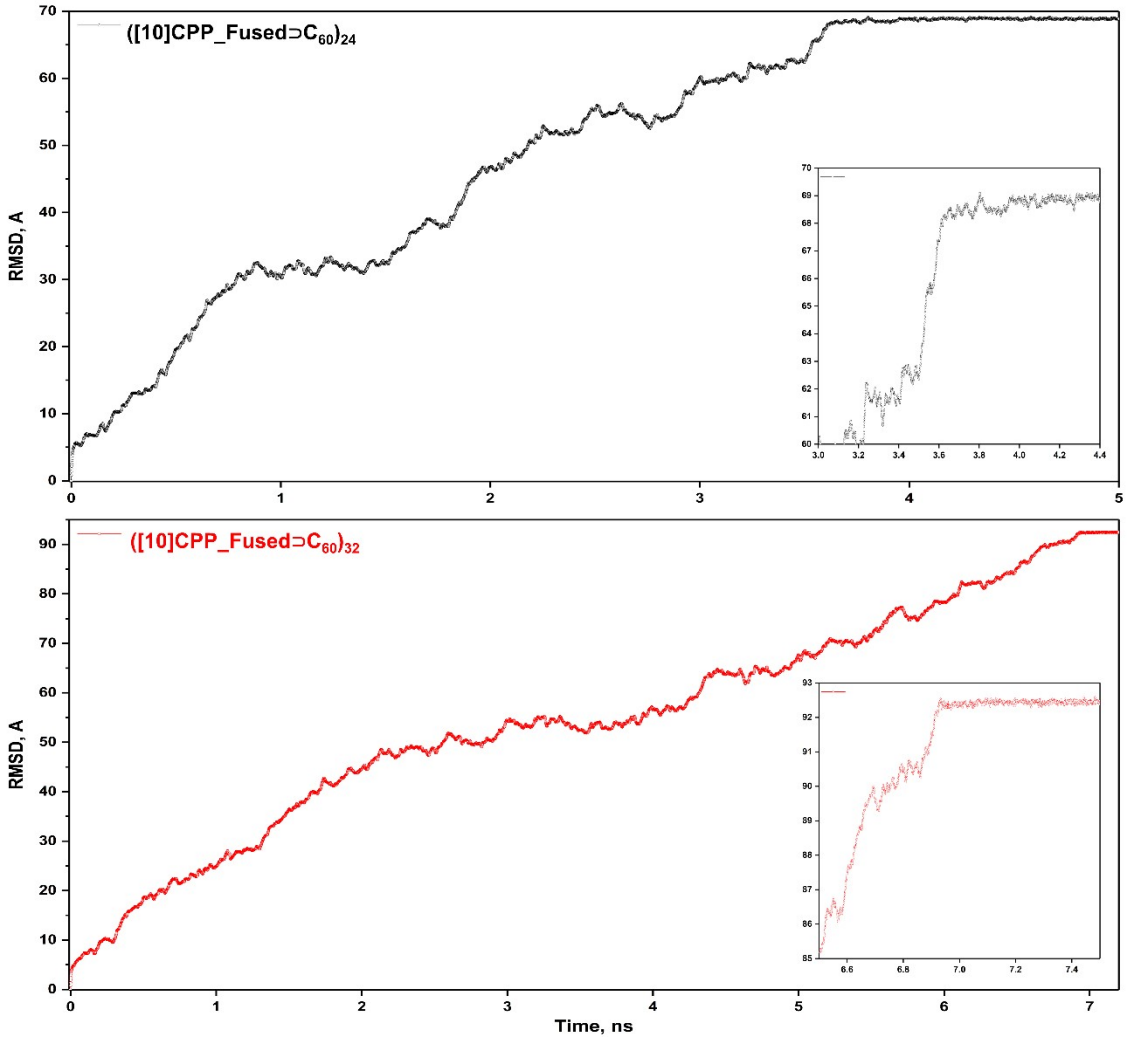


Figure S3. RMSD diagrams for MD simulation runs of **([10]CPP_Fused)$_{24}$** and **([10]CPP_Fused⊃C$_{60}$)$_{32}$** oligomers with zoomed regions of interest.

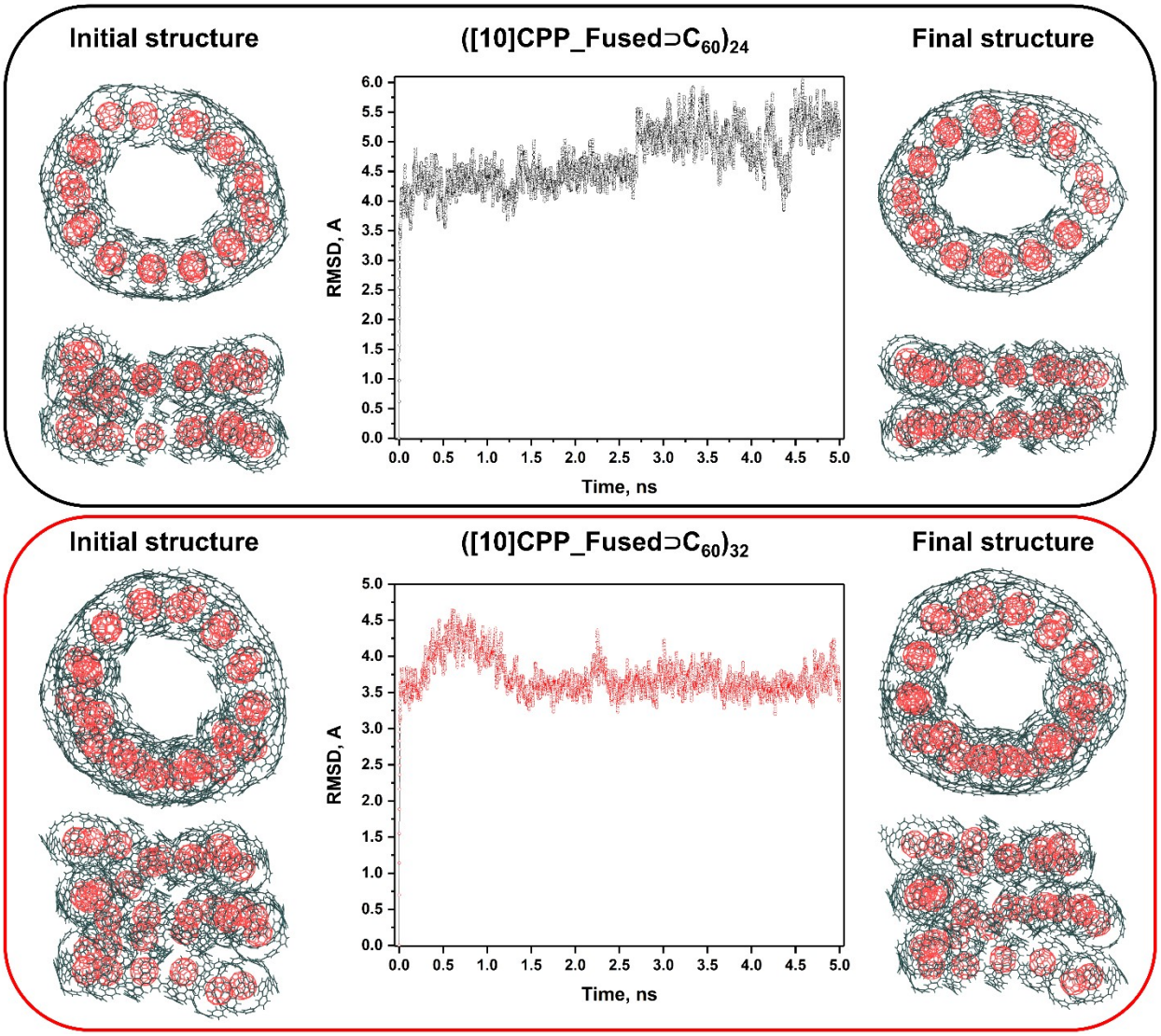


Figure S4. Initial and final representative structures of **([10]CPP_Fused)$_{24}$** and **[10]CPP_Fused⊃C$_{60}$)$_{32}$** oligomers of 5 ns of MD simulation runs at 500K.

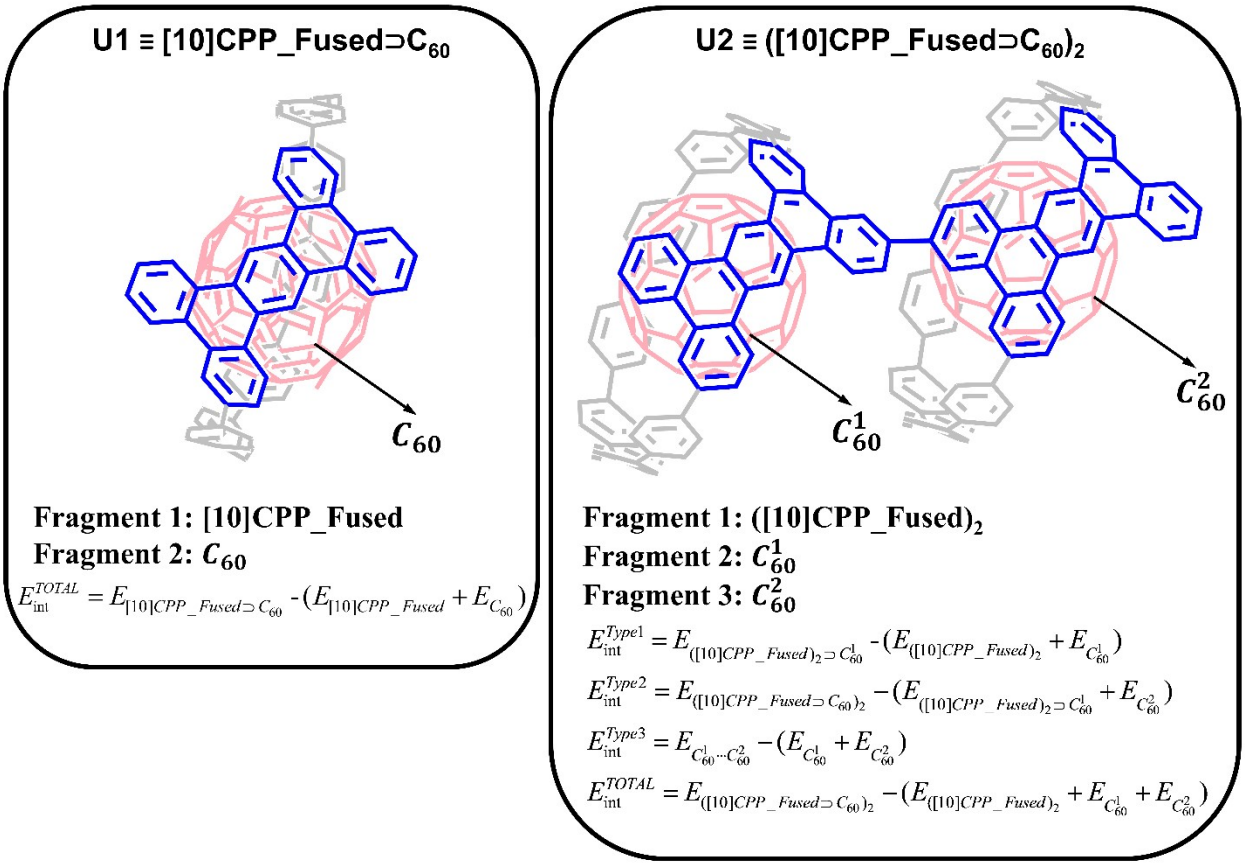


Figure S5. Structures of of **U1** and **U2** complexes and fragmentation scheme.

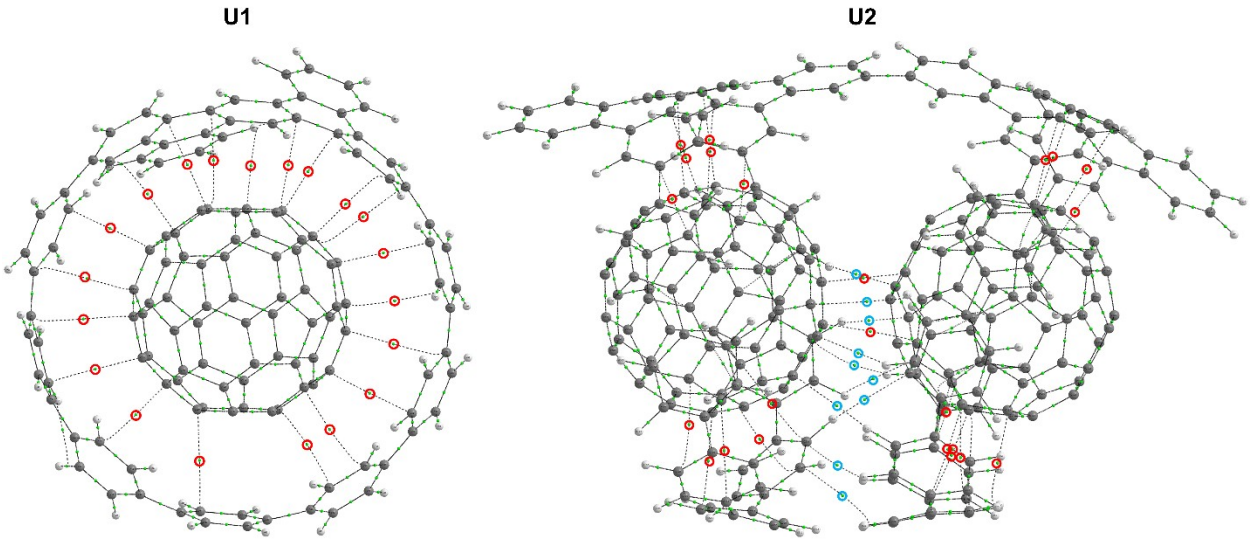


Figure S6. QTAIM molecular graph for **U1** and **U2** complexes. Lines connecting the nuclei are the bond paths. Small green dots correspond to BCPs. BCPs of interest are marked by red and blue circles. Red circles correspond to C···C contacts while the blue one to H···C contacts.

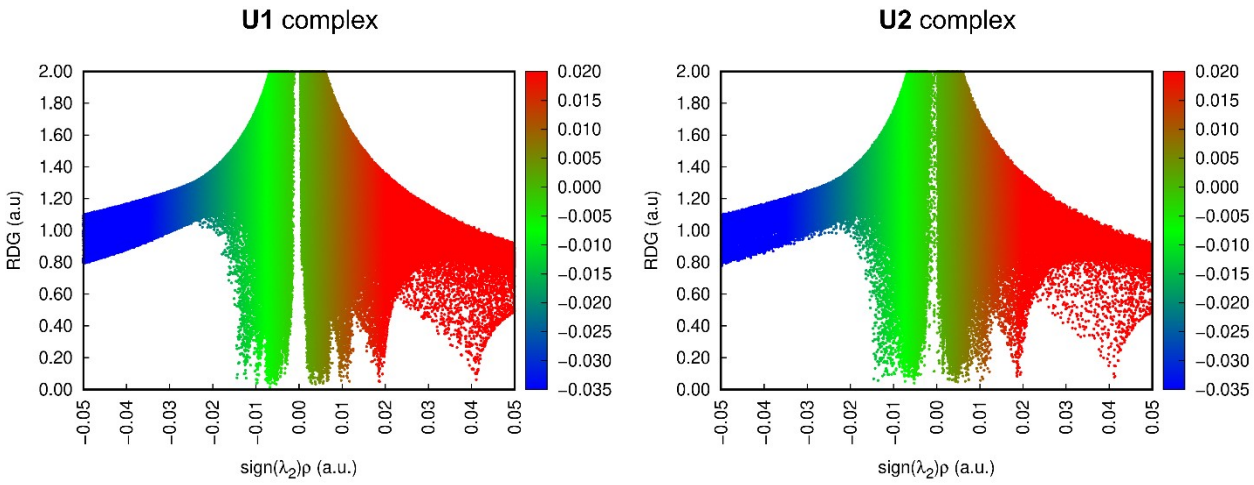


Figure S7. Plot of RDG *vs.* sign(λ2)×ρ for **U1** and **U2** complexes.

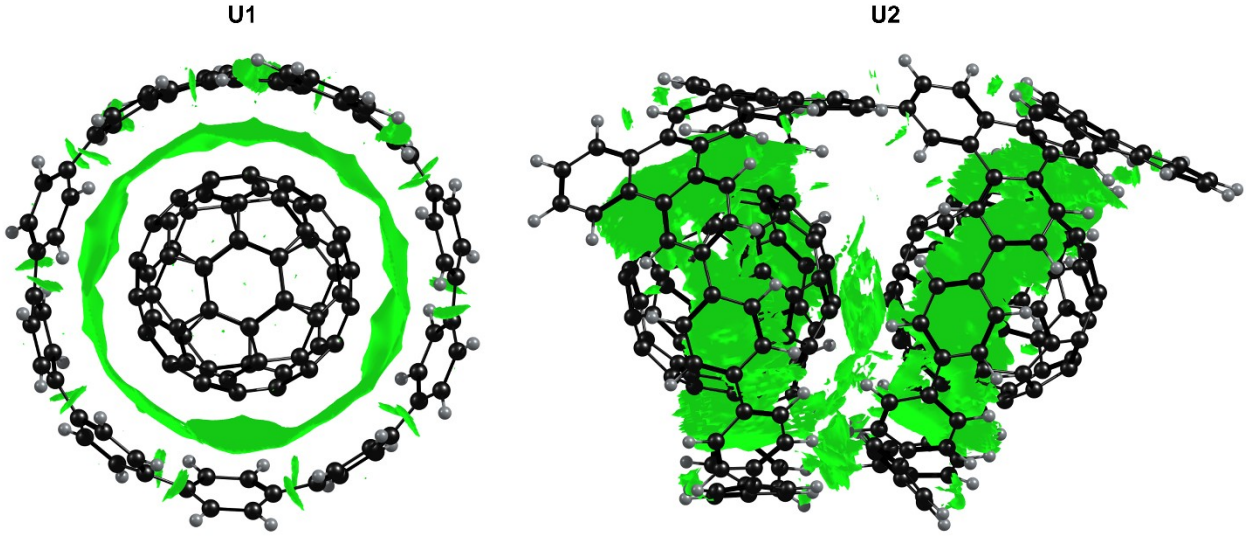


Figure S8. NCI isosurfaces of van der Waals interactions for **U1** and **U2** complexes. Isosurfaces were generated for RDG = 0.65 a.u.

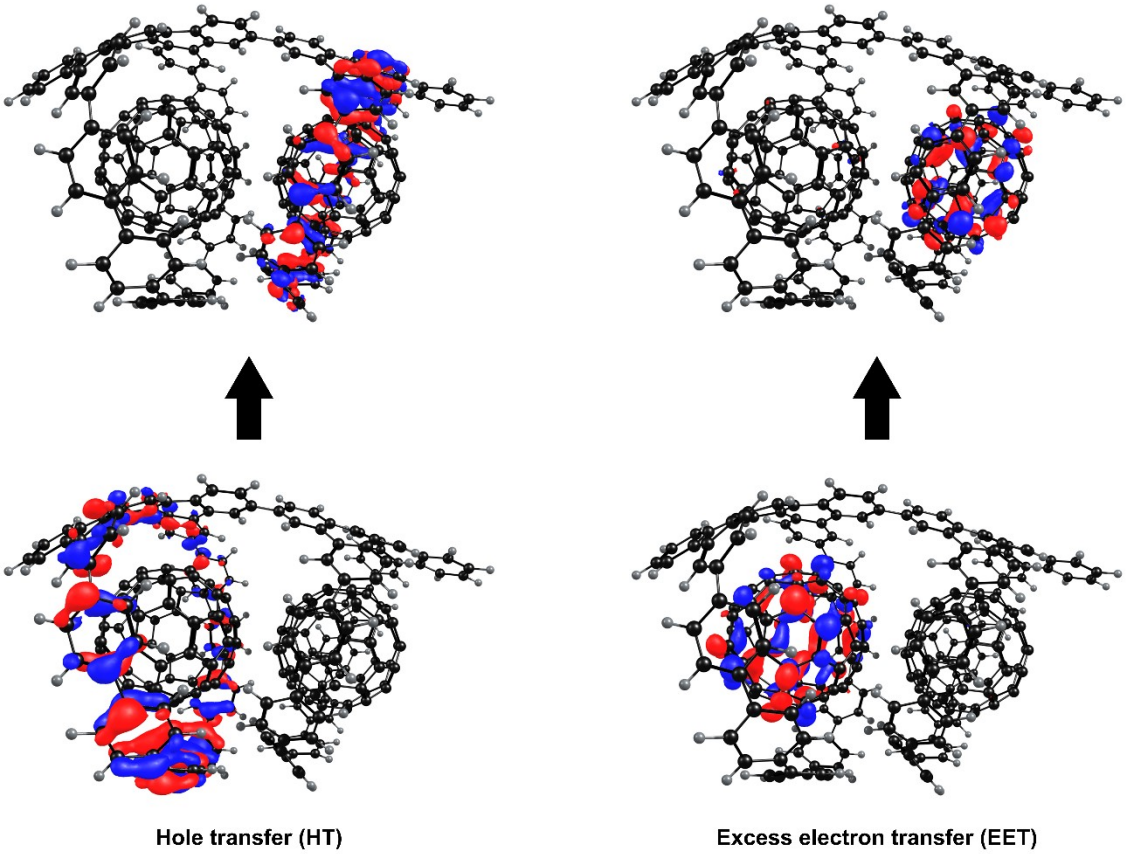


Figure S9. Molecular orbitals representing different states for simulation of hole transfer and excess electron transfer.

Table S1. Electronic coupling for hole transfer in a series of randomly selected *syn* and *anti* conformers of **([10]CPP)$_8$**

Syn		*Anti*	
Structure	**V_{ij}**	**Structure**	**V_{ij}**
Syn1	$2.67\cdot10^{-2}$	Anti1	$9.74\cdot10^{-3}$
Syn2	$2.84\cdot10^{-2}$	Anti2	$2.14\cdot10^{-2}$
Syn3	$4.34\cdot10^{-2}$	Anti3	$8.19\cdot10^{-3}$
Syn4	$2.39\cdot10^{-2}$	Anti4	$1.65\cdot10^{-2}$
Syn5	$2.41\cdot10^{-2}$	Anti5	$1.96\cdot10^{-2}$
Syn6	$3.16\cdot10^{-2}$	Anti6	$2.09\cdot10^{-2}$
Syn7	$2.26\cdot10^{-2}$	Anti7	$1.34\cdot10^{-2}$
Syn8	$2.99\cdot10^{-2}$	Anti8	$1.19\cdot10^{-2}$
Syn9	$2.68\cdot10^{-2}$	Anti9	$8.75\cdot10^{-3}$
Syn10	$5.67\cdot10^{-2}$	Anti10	$2.25\cdot10^{-2}$
Average V_{ij} =$3.14\cdot10^{-2}$		Average V_{ij} =$1.53\cdot10^{-2}$	

Table S2. Interaction energies computed for **U1** and **U2** complexes using different partitioning schemes.

Complexes	
Fragment	E_{BOND}/E_{int}, kcal/mol
U1 complex	
[10]CPP_Fused⊃C_{60}	-29477.49
[10]CPP_Fused	-17809.60
C60	-11576.94
$E_{\text{int}}^{TOTAL} = E_{\text{int}}^{[10]CPP\_Fused\supset C_{60}} - (E_{[10]CPP\_Fused} + E_{C_{60}})$	-60.95
U2 complex	
([10]CPP_Fused⊃ C_{60})$_2$	-58760.02
([10]CPP_Fused)2⊃ C_{60}^1	-47108.52
([10]CPP_Fused)2⊃ C_{60}^2	-47104.78
C_{60}^1+ C_{60}^2	-23161.08
([10]CPP_Fused)$_2$	-35460.45
C_{60}^1	-11576.91
C_{60}^2	-11576.81
Type 1: $E_{\text{int}}^{([10]CPP\_Fused)_2\cdots C_{60}^1}$	-71.16
Type 1: $E_{\text{int}}^{([10]CPP\_Fused)_2\cdots C_{60}^2}$	-67.52
Type 2: $E_{\text{int}}^{([10]CPP\_Fused)_2\supset C_{60}^1\cdots C_{60}^2}$	-74.69
Type 2: $E_{\text{int}}^{([10]CPP\_Fused)_2\supset C_{60}^2\cdots C_{60}^1}$	-78.33
Type 3: $E_{\text{int}}^{C_{60}^1\cdots C_{60}^2}$	-7.36
$E_{\text{int}}^{TOTAL} = E_{\text{int}}^{([10]CPP\_Fused\supset C_{60})_2} - (E_{([10]CPP\_Fused)_2} + E_{C_{60}^1} + E_{C_{60}^2})$	-145.85

Table S3. Charge separation (in electrons) between the fragments in electronic ground state for **U1** and **U2** complexes. $Q_{[10]CPP\_Fused}$ / $Q_{([10]CPP\_Fused\supset C_{60})_2}$ - charge on host, and $Q_{C_{60}}$ - charge on fullerene moiety. Total charge of the complexes $Q_{Tot} = 0$.

	Mulliken	**Löwdin**	**Hirshfeld**	**CM5**
	U1 complex			
$Q_{[10]CPP\_Fused}$	0.023	0.016	-0.077	-0.068
$Q_{C_{60}}$	-0.023	-0.016	0.078	0.068
	U2 complex			
$Q_{([10]CPP\_Fused\supset C_{60})_2}$	0.033	0.007	0.101	0.133
$Q_{C_{60}^1}$	-0.016	-0.001	-0.033	-0.050
$Q_{C_{60}^2}$	-0.017	-0.006	-0.067	-0.083

Table S4. Parameters (electron density [*ρ(r)*], its Laplacian [$\nabla^2\rho(r)$], potential energy density [*V(r)*], kinetic energy density [*G(r)*], and total electron energy density [*H(r)*] for selected bond critical points related to non-covalent interactions in **U1** and **U2** complexes computed in the gas phase.

Bond critical points between fragments	Interaction	*ρ(r)*, au	$\nabla^2\rho(r)$, au	*V(r)*, au	*G(r)*, au	*H(r)*, au
		U1 complex				
[10]CPP_Fused···C$_{60}$		6.17E-03	1.66E-02	-2.54E-03	3.34E-03	8.04E-04
		5.06E-03	1.35E-02	-2.18E-03	2.78E-03	6.05E-04
		5.29E-03	1.43E-02	-2.29E-03	2.93E-03	6.39E-04
		7.29E-03	2.08E-02	-3.06E-03	4.13E-03	1.07E-03
		5.61E-03	1.45E-02	-2.38E-03	3.01E-03	6.28E-04
		5.79E-03	1.54E-02	-2.43E-03	3.15E-03	7.16E-04
		6.69E-03	1.95E-02	-2.91E-03	3.89E-03	9.85E-04
		6.86E-03	2.00E-02	-3.02E-03	4.02E-03	9.94E-04
		7.77E-03	2.25E-02	-3.32E-03	4.48E-03	1.16E-03
	π···π	6.73E-03	1.90E-02	-2.95E-03	3.86E-03	9.02E-04
	C···C	6.68E-03	1.99E-02	-2.99E-03	3.98E-03	9.94E-04
		7.21E-03	2.00E-02	-2.93E-03	3.97E-03	1.04E-03
		6.52E-03	1.79E-02	-2.70E-03	3.58E-03	8.84E-04
		5.22E-03	1.40E-02	-2.24E-03	2.87E-03	6.27E-04
		5.66E-03	1.57E-02	-2.44E-03	3.18E-03	7.47E-04
		7.02E-03	1.94E-02	-2.88E-03	3.87E-03	9.90E-04
		7.47E-03	2.08E-02	-3.04E-03	4.12E-03	1.08E-03
		5.62E-03	1.50E-02	-2.30E-03	3.02E-03	7.28E-04
		6.00E-03	1.57E-02	-2.41E-03	3.17E-03	7.61E-04
		6.35E-03	1.68E-02	-2.50E-03	3.35E-03	8.45E-04
		U2 complex				

Intraunit_1 interactions [10]CPP_Fused···C_{60}	π···π C···C	5.48E-03	1.45E-02	-2.23E-03	2.93E-03	6.95E-04
		5.21E-03	1.46E-02	-2.15E-03	2.90E-03	7.47E-04
		6.58E-03	1.88E-02	-2.85E-03	3.77E-03	9.24E-04
		6.98E-03	2.00E-02	-3.01E-03	4.01E-03	9.98E-04
		8.38E-03	2.53E-02	-3.74E-03	5.03E-03	1.29E-03
		8.11E-03	2.38E-02	-3.63E-03	4.78E-03	1.16E-03
		7.34E-03	2.06E-02	-3.04E-03	4.09E-03	1.06E-03
		5.08E-03	1.28E-02	-2.05E-03	2.62E-03	5.72E-04
		5.88E-03	1.62E-02	-2.52E-03	3.28E-03	7.68E-04
		7.81E-03	2.32E-02	-3.49E-03	4.65E-03	1.16E-03
		6.49E-03	1.85E-02	-2.80E-03	3.71E-03	9.14E-04
		5.31E-03	1.43E-02	-2.26E-03	2.92E-03	6.52E-04
		5.09E-03	1.30E-02	-2.08E-03	2.67E-03	5.85E-04
		5.38E-03	1.32E-02	-2.06E-03	2.68E-03	6.19E-04
		5.06E-03	1.30E-02	-2.07E-03	2.66E-03	5.89E-04
		4.99E-03	1.30E-02	-2.09E-03	2.67E-03	5.79E-04
		9.00E-03	2.65E-02	-3.84E-03	5.23E-03	1.39E-03
Intraunit_2 interactions [10]CPP_Fused···C_{60}	π···π C···C	4.71E-03	1.21E-02	-2.02E-03	2.51E-03	4.99E-04
		8.83E-03	2.58E-02	-3.76E-03	5.11E-03	1.34E-03
		6.01E-03	1.66E-02	-2.54E-03	3.34E-03	8.03E-04
		6.32E-03	1.76E-02	-2.67E-03	3.54E-03	8.70E-04
		9.48E-03	2.82E-02	-4.08E-03	5.56E-03	1.49E-03
		8.46E-03	2.51E-02	-3.67E-03	4.98E-03	1.30E-03
		7.44E-03	2.26E-02	-3.35E-03	4.49E-03	1.14E-03
		7.53E-03	2.27E-02	-3.37E-03	4.53E-03	1.16E-03
		7.23E-03	2.03E-02	-3.02E-03	4.05E-03	1.03E-03
		6.58E-03	1.75E-02	-2.62E-03	3.50E-03	8.81E-04
		6.54E-03	1.79E-02	-2.68E-03	3.58E-03	9.04E-04
		5.35E-03	1.43E-02	-2.27E-03	2.93E-03	6.54E-04
		4.83E-03	1.32E-02	-2.11E-03	2.70E-03	5.92E-04
		4.96E-03	1.40E-02	-2.17E-03	2.84E-03	6.67E-04
		5.40E-03	1.45E-02	-2.28E-03	2.95E-03	6.75E-04
		6.42E-03	1.86E-02	-2.67E-03	3.65E-03	9.87E-04
		4.81E-03	1.35E-02	-2.11E-03	2.73E-03	6.28E-04
Interunit interactions	π···π C···C	1.19E-02	3.76E-02	-5.67E-03	7.54E-03	1.87E-03
		7.57E-03	2.29E-02	-3.23E-03	4.48E-03	1.25E-03
		7.57E-03	2.29E-02	-3.23E-03	4.48E-03	1.25E-03
	CH···π H···C	3.53E-03	1.10E-02	-1.40E-03	2.08E-03	6.71E-04
		1.08E-02	3.05E-02	-5.74E-03	6.68E-03	9.39E-04
		4.85E-03	1.40E-02	-2.07E-03	2.79E-03	7.18E-04
		1.07E-02	3.01E-02	-5.72E-03	6.63E-03	9.05E-04
		9.44E-03	2.83E-02	-4.72E-03	5.90E-03	1.17E-03
		6.95E-03	2.14E-02	-3.16E-03	4.25E-03	1.10E-03
		5.14E-03	1.49E-02	-2.23E-03	2.98E-03	7.50E-04
		4.67E-03	1.31E-02	-1.97E-03	2.62E-03	6.53E-04
		4.39E-03	1.35E-02	-1.70E-03	2.54E-03	8.44E-04

Table S5. Excitation energies (E_x, eV) and dipole moments in ground state (μ_0, D), change in dipole moments between ground state and state of interest ($\Delta\mu = \mu_i - \mu_0$, D) and solvation energies (E_{solv}, eV) in DCM calculated for **U1** and **U2** complexes.

	Supramolecular host-guest systems	
	U1 complex	**U2** complex
	Ground state (GS)	
E_x	0.000	0.000
μ_0	0.441	0.846
E_{solv}	-0.492	-0.895
	LE^{Guest} (Fullerene **C_{60}**)	
E_x	2.503	2.474
$\Delta\mu$	0.22	0.89
E_{solv}	-0.500	-0.894
	LE_2 (Host [10]CPP_Fused)	
E_x	3.335	3.232
$\Delta\mu$	0.15	0.94
E_{solv}	-0.487	-0.887
	Most absorptive transition (Localized on [10]CPP_Fused)	
E_x	3.805	3.834
$\Delta\mu$	0.69	1.14
E_{solv}	-0.489	-0.893
	CT1 Intraunit ([10]CPP_Fused $\rightarrow$ Fullerene C_{60})	
E_x	2.449	2.429
$\Delta\mu$	4.61	5.86
E_{solv}	-0.784	-1.133
	CT2 Interunit ([10]CPP_Fused $\rightarrow$ Fullerene C_{60})	
E_x	n/a	2.578
$\Delta\mu$		32.65
E_{solv}		-1.429

Table S6. Computed semi-classical rates (k_x in s^{-1}) and characteristic times (τ in ns) for the charge separation processes in U1 and U2, complexes in DCM solution using different effective Huang-Rhys factors.

$h\omega_{eff}$	ΔG^0, eV	|V|, eV	λ_s	λ_i	S_{eff}	k_X, s^{-1}	τ, ns
	U1 comples (LE_1 (C_{60})→ CT1)						
1200	-0.054	$1.92\cdot10^{-4}$	0.200	0.161	1.344	$7.83\cdot10^{8}$	1.28
1400					1.152	$7.78\cdot10^{8}$	1.29
1600					1.008	$7.75\cdot10^{8}$	1.29
1800					0.896	$7.73\cdot10^{8}$	1.29
2000					0.807	$7.73\cdot10^{8}$	1.29
	U2 comples (LE_1 (C_{60})→ CT1)						
1200	-0.045	$5.39\cdot10^{-4}$	0.198	0.150	1.331	$6.23\cdot10^{9}$	0.16
1400					1.141	$6.19\cdot10^{9}$	0.16
1600					0.998	$6.18\cdot10^{9}$	0.16
1800					0.887	$6.17\cdot10^{9}$	0.16
2000					0.799	$6.17\cdot10^{9}$	0.16
	U2 comples (LE_1 (C_{60})→ CT2)						
1200	0.104	$2.44\cdot10^{-3}$	0.210	0.288	1.411	$1.04\cdot10^{9}$	0.96
1400					1.210	$1.04\cdot10^{9}$	0.96
1600					1.059	$1.04\cdot10^{9}$	0.96
1800					0.941	$1.04\cdot10^{9}$	0.96
2000					0.847	$1.04\cdot10^{9}$	0.96

Cartesian coordinates (in Å)

Cartesian coordinates for **U1** and **U2** complexes.

[10]CPP_Fused⊃C_{60} (U1 complex)

Gas-phase. BLYP-D3(BJ)/def2-SVP

Atom	X	Y	Z
6	4.667369000	-5.437610000	1.249891000
6	5.639122000	-4.432595000	1.185453000
6	5.855972000	-3.697878000	-0.008949000
6	5.178811000	-4.141080000	-1.173683000
6	4.211247000	-5.148377000	-1.110568000
6	3.869721000	-5.759352000	0.121706000
1	4.485207000	-5.947286000	2.206200000
1	6.202272000	-4.173645000	2.092696000
1	5.312139000	-3.599229000	-2.118639000
1	3.615266000	-5.364113000	-2.006845000
6	6.515199000	-2.368867000	-0.013565000
6	6.427718000	-1.543437000	1.135547000
6	6.991889000	-1.768524000	-1.208058000
6	6.624735000	-0.161038000	1.050624000
1	6.058883000	-1.963718000	2.080039000
6	7.184463000	-0.385382000	-1.294606000
1	7.156501000	-2.388652000	-2.100030000
6	6.914332000	0.461619000	-0.188911000
1	6.403682000	0.458383000	1.929865000
1	7.494122000	0.055421000	-2.252495000
6	2.573613000	-6.469977000	0.243363000
6	1.951267000	-7.100568000	-0.865131000
6	1.796962000	-6.304105000	1.416974000
6	0.579901000	-7.378064000	-0.861577000
1	2.542155000	-7.324416000	-1.764133000
6	0.426475000	-6.581727000	1.420300000
1	2.238079000	-5.816841000	2.296027000
1	0.118487000	-7.814250000	-1.758489000
1	-0.163806000	-6.305212000	2.302869000
6	6.644976000	1.911235000	-0.350780000
6	6.010609000	2.363031000	-1.535325000
6	6.735480000	2.825476000	0.729606000
6	5.344129000	3.591279000	-1.574067000
1	5.915271000	1.683274000	-2.391714000
6	6.072049000	4.057516000	0.689228000
1	7.287413000	2.540902000	1.636422000
6	5.284563000	4.427861000	-0.431130000
1	4.744179000	3.837998000	-2.459500000
1	6.116109000	4.719991000	1.564892000
6	4.220554000	5.457659000	-0.345618000
6	3.539141000	5.646558000	0.882394000
6	3.661326000	6.066011000	-1.499017000
6	2.276913000	6.246704000	0.923799000
1	3.935311000	5.189225000	1.798358000
6	2.398292000	6.667422000	-1.457485000
1	4.199598000	6.013774000	-2.455559000

([10]CPP_Fused⊃C_{60})$_2$ (U2 complex)

Gas-phase. BLYP-D3(BJ)/def2-SVP

Atom	X	Y	Z
6	3.683506623	4.446001660	-4.220438223
6	3.922706623	5.109026660	-3.011951223
6	3.099510623	4.883438660	-1.877656223
6	1.921019623	4.121726660	-2.077658223
6	1.676416623	3.464831660	-3.286293223
6	2.606382623	3.532238660	-4.355385223
1	10.659494623	-6.565269340	-2.659486223
1	4.377184623	4.595063660	-5.059632223
1	4.797556623	5.768348660	-2.930099223
1	1.245385623	3.928234660	-1.237768223
1	0.819490623	2.781486660	-3.345196223
6	3.551957623	5.183815660	-0.497462223
6	4.939082623	5.245803660	-0.203857223
6	2.661907623	5.161362660	0.607141777
6	5.413450623	5.117306660	1.104853777
1	5.667830623	5.287506660	-1.023560223
6	3.138484623	5.017065660	1.914339777
1	1.576113623	5.172216660	0.442534777
6	4.527135623	4.899535660	2.190369777
1	6.498186623	5.099613660	1.273202777
1	2.405745623	4.891547660	2.719166777
6	2.591725623	2.481741660	-5.402067223
6	1.409569623	1.783735660	-5.762049223
6	3.820704623	1.956499660	-5.874907223
6	1.472596623	0.537080660	-6.393169223
1	0.429080623	2.197798660	-5.488659223
6	3.882885623	0.705306660	-6.497728223
1	4.760127623	2.465079660	-5.623373223
1	0.536588623	0.003592660	-6.607150223
1	4.870255623	0.276414660	-6.711153223
6	4.990325623	4.293458660	3.463175777
6	4.158077623	4.211950660	4.608146777
6	6.177826623	3.517944660	3.485661777
6	4.366280623	3.245860660	5.597649777
1	3.284701623	4.865283660	4.691631777
6	6.397303623	2.562460660	4.480355777
1	6.876019623	3.555435660	2.641141777
6	5.438549623	2.322888660	5.499562777
1	3.640496623	3.165449660	6.417319777
1	7.261536623	1.896540660	4.375010777
6	5.435334623	1.021232660	6.210172777
6	6.592349623	0.203558660	6.260859777
6	4.211466623	0.432097660	6.626796777
6	6.499805623	-1.166442340	6.517822777
1	7.573672623	0.628851660	6.012852777
6	4.123672623	-0.937239340	6.905686777

6	1.636239000	6.689161000	-0.260676000	1	3.290867623	1.030412660	6.636863777
1	1.723396000	6.242787000	1.871472000	6	5.248041623	-1.789975340	6.761701777
1	1.969379000	7.077850000	-2.382103000	1	7.405427623	-1.778950340	6.422548777
6	0.165658000	6.883644000	-0.261764000	1	3.144278623	-1.361066340	7.162356777
6	-0.589549000	6.467605000	-1.387528000	6	5.113615623	-3.256340340	6.583353777
6	-0.552210000	7.221050000	0.914483000	6	3.901805623	-3.808259340	6.095962777
6	-1.963907000	6.231516000	-1.289010000	6	6.239585623	-4.121127340	6.619707777
1	-0.073060000	6.192677000	-2.315853000	6	3.877859623	-5.059948340	5.472052777
6	-1.927079000	6.980513000	1.015369000	1	2.989751623	-3.198050340	6.073613777
1	-0.013348000	7.624829000	1.782771000	6	6.214232623	-5.371566340	5.995680777
6	-2.647631000	6.398024000	-0.058476000	1	7.173684623	-3.781347340	7.086943777
1	-2.485594000	5.777314000	-2.141480000	6	5.060879623	-5.826536340	5.303158777
1	-2.443617000	7.196993000	1.960957000	1	2.944565623	-5.377655340	4.992395777
6	-3.950262000	5.718392000	0.137696000	1	7.130072623	-5.977301340	5.992589777
6	-4.200879000	5.045965000	1.359716000	6	5.140254623	-6.873608340	4.252945777
6	-4.847158000	5.472182000	-0.932470000	6	6.390230623	-7.224418340	3.673980777
6	-5.162877000	4.036101000	1.442466000	6	3.981038623	-7.387069340	3.617486777
1	-3.535418000	5.211997000	2.216804000	6	6.470122623	-7.910144340	2.458070777
6	-5.816995000	4.467336000	-0.844451000	1	7.322808623	-6.877682340	4.136446777
1	-4.741330000	6.035729000	-1.869974000	6	4.059345623	-8.050481340	2.389332777
6	-5.928388000	3.650671000	0.311587000	1	2.989048623	-7.196704340	4.046675777
1	-5.217032000	3.450444000	2.367799000	6	5.302501623	-8.263101340	1.736487777
1	-6.452465000	4.270979000	-1.718072000	1	7.460853623	-8.107677340	2.026891777
6	-6.568062000	2.310264000	0.267730000	1	3.124717623	-8.319910340	1.881148777
6	-6.782132000	1.659675000	-0.981300000	6	5.327881623	-8.574441340	0.285034777
6	-6.736481000	1.533074000	1.429632000	6	4.192078623	-9.123521340	-0.378679223
6	-6.942376000	0.279784000	-1.047938000	6	6.371223623	-8.086038340	-0.525287223
1	-6.709735000	2.225207000	-1.918211000	6	4.016220623	-8.933553340	-1.745152223
6	-6.902382000	0.128933000	1.388648000	1	3.411747623	-9.636089340	0.199310777
1	-6.635267000	2.014887000	2.407524000	6	6.230284623	-7.915422340	-1.925290223
6	-6.891667000	-0.531282000	0.117483000	1	7.262599623	-7.673495340	-0.042467223
1	-7.015373000	-0.187697000	-2.037200000	6	4.962397623	-8.203711340	-2.517939223
6	-6.604566000	-1.968095000	0.055181000	1	3.094038623	-9.296726340	-2.217138223
6	-6.399436000	-2.699050000	1.275379000	6	4.593941623	-7.518628340	-3.760679223
6	-6.274419000	-2.597436000	-1.162643000	6	5.579230623	-6.775353340	-4.493960223
6	-5.743557000	-3.942388000	1.209934000	6	3.233417623	-7.308130340	-4.062491223
6	-5.597657000	-3.829785000	-1.226938000	6	5.139714623	-5.859198340	-5.471562223
1	-6.409102000	-2.040257000	-2.093605000	6	2.792728623	-6.313357340	-4.954552223
6	-5.263754000	-4.493801000	0.002597000	1	2.485684623	-7.806499340	-3.440197223
1	-5.475492000	-4.429430000	2.151964000	6	3.775651623	-5.554358340	-5.678184223
6	-4.238852000	-5.543323000	0.003094000	1	5.888726623	-5.222420340	-5.951673223
6	-3.504453000	-5.798732000	-1.198485000	6	3.374549623	-4.314494340	-6.354646223
6	-3.784683000	-6.160563000	1.202303000	6	2.075645623	-3.771854340	-6.091681223
6	-2.239265000	-6.424968000	-1.098284000	6	4.293904623	-3.506999340	-7.080954223
6	-2.551265000	-6.801884000	1.270356000	6	1.859065623	-2.394763340	-6.326829223
1	-4.383083000	-6.076448000	2.118043000	6	4.037968623	-2.163170340	-7.342835223
6	-1.699451000	-6.847357000	0.130271000	1	5.254929623	-3.932862340	-7.397321223
1	-1.596404000	-6.442930000	-1.984549000	6	2.843379623	-1.548743340	-6.867485223
1	-2.207281000	-7.214091000	2.228595000	1	0.937234623	-1.944385340	-5.947948223
6	-0.232356000	-7.034896000	0.249517000	1	4.795722623	-1.563401340	-7.864467223
6	-5.075597000	-4.342416000	-2.501811000	6	2.718824623	-0.080927340	-6.681822223
6	-4.006814000	-5.294399000	-2.485314000	6	1.382988623	-5.905577340	-4.974017223
6	-5.557387000	-3.876023000	-3.753713000	6	1.037122623	-4.610190340	-5.472219223

6	-3.455095000	-5.723984000	-3.721573000	6	0.358616623	-6.705195340	-4.399711223
6	-4.997748000	-4.310556000	-4.957943000	6	-0.295939377	-4.152076340	-5.318220223
6	-3.934400000	-5.239883000	-4.941591000	6	-0.939047377	-6.225906340	-4.240801223
1	-6.397965000	-3.170812000	-3.780006000	6	-1.284132377	-4.917643340	-4.677690223
1	-2.651116000	-6.470683000	-3.723792000	1	0.589265623	-7.725494340	-4.068365223
1	-5.394429000	-3.939121000	-5.913660000	1	-0.567127377	-3.150421340	-5.671091223
1	-3.493347000	-5.594084000	-5.884285000	1	-1.708368377	-6.867458340	-3.789518223
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