Supporting information for:

Nitrogen-embedded molecular bowls as electron donors in photoinduced electron transfer reactions

A. J. Stasyuk,* a,b O. A. Stasyuk, a,b M. Solà* a and A. A. Voityuk* a

a. Institut de Química Computacional and Departament de Química, Universitat de Girona, C/ Maria Aurèlia Capmany 69, 17003 Girona, Spain
b. Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

Abstract

In recent years, the chemistry of curved $\pi$-conjugated molecules has experienced a sharp rise. The inclusion of a heteroatom in the carbon network significantly affects its semiconducting properties. In this work, we computationally study the photoinduced electron transfer in a series of C60 fullerene complexes with experimentally established nitrogen-doped molecular bowls. Our results demonstrate that introducing nitrogen into pentagonal rings of the bowl-shaped $\pi$-conjugated molecules and extending the $\pi$-conjugation can modulate their electron-transfer properties. Among the studied complexes, the hub-NCor$\supset$C60 complex exhibits the most desirable combination of ultrafast charge separation and slow charge recombination, suggesting its potential use in photovoltaics.
Table of Contents

1. Computational methodology  
   p. S3-S7

2. **Table S1.** HOMO/LUMO energies and HOMO-LUMO (HL) gap for studied bowls in equilibrium and complex geometries.  
   p. S8

3. **Table S2.** Charge separation between the fragments in electronic ground state for studied complexes.  
   p. S8-S9

4. **Table S3.** Parameters of selected bond critical points related to the non-covalent interactions of the fragments in studied complexes.  
   p. S9-S11

5. **Table S4.** Main contributions of the Kohn-Sham molecular orbitals to the corresponding occupied and vacant natural transition orbitals.  
   p. S11

6. **Table S5.** Excitation energies, main singly excited configuration (HOMO(H)-LUMO(L)) and its weight, oscillator strength, extent of charge transfer or localization of exciton computed for studied complexes in DCM.  
   p. S12

7. **Table S6.** Relative energies and solvation energies calculated for studied complexes in DCM.  
   p. S12-S13

8. **Table S7.** ET rates computed with different effective Huang-Rhys factors for **Cor** ⊃ **C₆₀**, **Sum** ⊃ **C₆₀** and **hub-NCor** ⊃ **C₆₀**, complexes.  
   p. S13

9. **Figure S1.** QTAIM molecular graphs for studied complexes.  
   p. S14

10. **Figure S2.** Plot of RDG vs. sign(λ²)×ρ for studied complexes.  
    p. S15

11. **Figure S3.** NCI isosurfaces of van der Waals interactions in studied complexes.  
    p. S16

12. **Figure S4-S11.** Natural transition orbitals for studied complexes  
    p. S17-S24

13. **Figure S12.** Dependence of the charge separation rate in the **Cor** ⊃ **C₆₀**, **Sum** ⊃ **C₆₀** and **hub-NCor** ⊃ **C₆₀** complexes on the effective frequency.  
    p. S25

14. Cartesian coordinates  
    p. S26-S31

15. References  
    p. S34-S35
Computational Methodology

Quantum-chemical calculations
Geometry optimization of the complexes was performed employing the DFT B3LYP exchange–correlation functional with Ahlrichs’ def2-SVP basis set. The empirical dispersion D3 correction was computed using the Becke–Johnson damping. Vertical excitation energies were calculated using TDA formalism with the range-separated functional from Handy and coworkers’ CAM-B3LYP and Ahlrichs’ def2-SVP basis set, as implemented in the Gaussian16 (rev. A03) program. The same program was used for population analysis and calculation of Mulliken, Lowdin, Hirshfeld, CMS, and iterative Hirshfeld charges. The formation energy of the complexes was computed using B3LYP functional coupled with def2-TZVP basis. Canonical energy decomposition analysis (EDA) was performed using the Amsterdam Density Functional (ADF) program. The excited states have been analyzed in terms of the natural transition orbitals (NTO) concept introduced by Luzanov et al. and implemented within modern many-body codes by Head-Gordon et al. Molecular structures and frontier molecular orbitals were visualized by Chemcraft 1.8.

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) into electrostatic interactions, Pauli repulsive orbital interactions, and attractive orbital interactions, to which a term $\Delta E_{\text{disp}}$ is added to account for the dispersion correction:

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{oi}} + \Delta E_{\text{disp}}$$

The term $\Delta E_{\text{elstat}}$ 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, $\Delta E_{\text{Pauli}}$, comprises the destabilizing interactions between occupied orbitals and is responsible for any steric repulsion. The orbital interactions, $\Delta E_{\text{oi}}$, 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 $\Delta E_{\text{disp}}$ accounts for the dispersion corrections.

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. The analysis was done in the Löwdin orthogonalized basis, which is more convenient. The matrix $^1C$ of orthogonalized MO coefficients is obtained from the coefficients $C$ in the original basis $^1C = S^{1/2}C$, where $S$ is the atomic orbital overlap matrix. The transition density matrix $T_{\Omega}$ for an excited state $\Phi^*$ constructed as a superposition of singly excited configurations (where an occupied MO $\psi_i$ is replaced a virtual MO $\psi_a$) is computed,
\[ T_{ab}^{0i} = \sum_{ia} A_{ia} \lambda C_{ai}^\lambda C_{\beta a} \]  

where \( A_{ia} \) is the expansion coefficient.

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

\[ \Omega(D, A) = \sum_{\alpha\in D, \beta\in A} (T_{ab}^{0i})^2 \]  

The weights of local excitations on \( D \) and \( A \) are \( \Omega(D,D) \) and \( \Omega(A,A) \). The weight of electron transfer configurations \( D\rightarrow A \) and \( A\rightarrow D \) is represented by \( \Omega(D,A) \) and \( \Omega(A,D) \), respectively. The index \( \Delta q \), which describes charge separation and charge transfer between \( D \) and \( A \), is

\[ \Delta q(CS) = \sum \Omega(D, A) - \Omega(A, D) \]  

\[ \Delta q(CT) = \sum \Omega(D, A) + \Omega(A, D) \]  

**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 \( \varepsilon \) was estimated using a COSMO-like polarizable continuum model\(^{30-33} \) in the monopole approximation:

\[ E_S^{eq}(Q, \varepsilon) = -\frac{1}{2} f(\varepsilon) Q^T D Q \]  

where the \( f(\varepsilon) \) 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 \( n \times n \) symmetric matrix determined by the shape of the boundary surface between solute and solvent. \( D = B^T A^{-1} B \), where the \( m \times m \) matrix \( A \) describes electrostatic interaction between \( m \) surface charges and the \( m \times n \) matrix describes the interaction of the surface charges with \( n \) atomic charges of the solute.\(^{30,34} \) The GEPOL93 scheme\(^{35} \) was used to construct the molecular boundary surface.

The charge on atom \( X \) in the excited state \( \Phi_i q_X^i \), was calculated as:

\[ q_X^i = q_X^0 + \Delta_X^i, \quad \Delta_X^i = \sum_{Y \neq X} \sum_{\alpha \in X, \beta \in Y} (T_{ab}^{0i} T_{ab}^{0i} - T_{ba}^{0i} T_{ba}^{0i}) \]  

where \( q_X^0 \) is the atomic charge on \( A \) in the ground state and \( \Delta_X^i \) 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 \( \psi_i \) can be estimated as\(^{36} \):

---

\[ S4 \]
In Eq. (8), \( n^2 \) (the refraction index squared) is the optical dielectric constant of the medium and the vector \( \Delta \) 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):

\[
k_{ET} = \frac{2\pi}{\hbar} V^2 \left( FCWD \right)
\]

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

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

where \( \lambda \) is the reorganization energy and \( \Delta G^0 \) is the standard Gibbs energy change of the process. The fragment charge difference (FCD) 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\(^\text{40,41} \) 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 \( \omega_i, \hbar \omega_i \gg kT \), 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,

\[
k = \sum_{n=0}^{\infty} k_{0\rightarrow n}, \text{ where } k_{0\rightarrow n} = \frac{2\pi}{\hbar} V^2_{0\rightarrow n} \frac{1}{\sqrt{4\pi \lambda kT}} \exp \left[ -\left( \Delta G + n\hbar \omega_i + \lambda \right)^2 / 4\lambda kT \right]
\]

with

\[
V^2_{0\rightarrow n} = \nu^2 \frac{S^n}{n!} \exp (-S)
\]

An effective value of the Huang-Rhys factor \( S \) is estimated from the internal reorganization energy \( \lambda_i \),

\[
S = \lambda_i / \hbar \omega_i
\]
As seen, an additional parameter (as compared to the Marcus equation) enters the semi-classical expression - the frequency $\omega_i$ 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 $\omega_i$ 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 the 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 $\lambda_s$ 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 $\lambda_i$ corresponds to the energy of structural changes when donor/acceptor fragments going from initial-state geometries to final-state geometries.

$$\lambda_i = \lambda_{i1} + \lambda_{i2},$$

where:

$$\lambda_{i1}(C_60^* \rightarrow C_60^-) = \frac{1}{2} \left[ \left( (C_60^*) - (C_60^-) \right) + \left( (C_60^-) - (C_60^*) \right) \right]$$

$$\lambda_{i2} (Bowl^0 \rightarrow Bowl^+) = \frac{1}{2} \left[ \left( (Bowl^0) - (Bowl^+ \circ) \right) + \left( (Bowl^+) - (Bowl^0) \right) \right]$$

Activation energy
The activation energies or the electron transfer reaction were computed based on traditional Marcus theory and can be expressed as:

$$\Delta G^* = (\lambda + \Delta G^0)^2 / 4 \lambda$$  \hfill (13)

Interaction energies
The interaction energies were calculated directly from the electronic energy of complex and electronic energies of subsystems. For Host ⊆ C$_60$, the interaction energy can be expressed as follows:

$$E_{int} = E_{Host \supset C_60} - (E_{Host} + E_{C_60})$$  \hfill (14)

Quantum Theory of Atoms in Molecules (QTAIM)
Topological analysis of the electron distributions was conducted using the “Quantum Theory of Atoms in Molecules” (QTAIM) approach proposed by Bader.42,43 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.44-46 The AIMALL suite of programs47 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\(^{48-50} \) relies on two scalar fields to map local bonding properties: the electron density \( \rho \) and the reduced-density gradient (RDG, \( s \)), defined as:

\[
s = \frac{1}{2(3\pi)^{1/3}} \frac{\left| \nabla \rho \right|}{\rho^{4/3}}
\]  

(15)

a quantity that is essential to the design of DFT functionals. The combination of \( s \) and \( \rho \) allows a rough partition of real space into bonding regions: high-\( s \) low-\( \rho \) corresponds to non-interacting density tails, low-\( s \) high-\( \rho \) to covalent bonds, and low-\( s \) low-\( \rho \) to non-covalent interactions. The NCI analysis was carried out at the CAM-B3LYP/Def2-SVP level using Multiwfn program.\(^{51} \)
### Table S1. HOMO/LUMO energies and HOMO-LUMO (HL) gap (in eV) for isolated bowls in equilibrium geometry and their complexes with fullerene computed at CAM-B3LYP-D3(BJ)/def2-SVP//B3LYP-D3(BJ)/def2-SVP level of theory.

| System | Energy | HOMO | LUMO | HL gap$^a$ |
|--------|--------|------|------|-----------|
| Bowl   |        |      |      |           |
| Cor    | -7.57  | -0.77| 6.80 |           |
| rim-NCor | -7.24  | -1.10| 6.13 |           |
| hub-NCor | -6.16  | -0.81| 5.34 |           |
| PP-bowl| -5.81  | -0.69| 5.12 |           |
| Hyd-bowl | -5.98  | -0.82| 5.16 |           |
| Cyc-bowl| -7.14  | -0.32| 6.82 |           |
| rim-3NSum| -7.82  | -0.69| 7.13 |           |
| Sum    | -6.98  | 0.12 | 7.10 |           |
| Bowl$\supseteq$C$_{60}$ | | | | |
| Cor$\supseteq$C$_{60}$ | -7.31 | -2.56 | 4.75 |
| rim-NCor$\supseteq$C$_{60}$ | -7.28 | -2.51 | 4.77 |
| hub-NCor$\supseteq$C$_{60}$ | -6.29 | -2.47 | 3.82 |
| PP-bowl$\supseteq$C$_{60}$ | -5.97 | -2.416| 3.56 |
| Hyd-bowl$\supseteq$C$_{60}$ | -6.14 | -2.50 | 3.65 |
| Cyc-bowl$\supseteq$C$_{60}$ | -7.13 | -2.54 | 4.59 |
| rim-3NSum$\supseteq$C$_{60}$ | -7.43 | -2.63 | 4.80 |
| Sum$\supseteq$C$_{60}$ | -7.04 | -2.61 | 4.43 |

$^a$ The HL= $E_{\text{LUMO}}-E_{\text{HOMO}}$

### Table S2. Charge separation (units are electrons) between the fragments in electronic ground state for Cor$\supseteq$C$_{60}$, rim-NCor$\supseteq$C$_{60}$, hub-NCor$\supseteq$C$_{60}$, PP-bowl$\supseteq$C$_{60}$, Hyd-bowl$\supseteq$C$_{60}$, Cyc-bowl$\supseteq$C$_{60}$, rim-3NSum$\supseteq$C$_{60}$, and Sum$\supseteq$C$_{60}$ complexes. $Q_{\text{Bowl}}$ - charge on host, and $Q_{\text{C}_{60}}$ - charge on fullerene moiety. Total charge of the complexes $Q_{\text{tot}} = 0$.

| System        | Mulliken  | Löwdin | Hirshfeld | CM5  | Hirshfeld-Iter |
|---------------|-----------|--------|-----------|------|----------------|
| $Cor\supseteq$C$_{60}$ |           |        |           |      |                |
| $Q_{\text{Bowl}}$ | 0.028     | 0.025  | -0.001    | 0.002| -0.070         |
| $Q_{\text{C}_{60}}$ | -0.028    | -0.025 | 0.001     | -0.002| 0.070          |
| $rim-NCor\supseteq$C$_{60}$ |           |        |           |      |                |
| $Q_{\text{Bowl}}$ | 0.026     | 0.026  | -0.002    | -0.001| -0.082         |
| $Q_{\text{C}_{60}}$ | -0.026    | -0.026 | 0.001     | 0.000 | 0.081          |
| $hub-NCor\supseteq$C$_{60}$ |           |        |           |      |                |
| $Q_{\text{Bowl}}$ | 0.025     | 0.035  | 0.004     | 0.005| -0.088         |
Table S3. Parameters (electron density [$\rho(r)$], 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 the non-covalent interactions between the fragments in Cor$\supset$C$_{60}$, rim-NCor$\supset$C$_{60}$, hub-NCor$\supset$C$_{60}$, PP-bowl$\supset$C$_{60}$, Hyd-bowl$\supset$C$_{60}$, Cyc-bowl$\supset$C$_{60}$, rim-3NSum$\supset$C$_{60}$, and Sum$\supset$C$_{60}$ complexes computed in the gas phase.

| Bond critical points | Interaction | $\rho(r)$, au | $\nabla^2 \rho(r)$, au | $V(r)$, au | $G(r)$, au | $H(r)$, au |
|---------------------|-------------|---------------|---------------------|-----------|-----------|-----------|
| Cor$\cdots$C$_{60}$ | $\pi\cdots\pi$ C$\cdots$C | 7.54E-03 | 2.31E-02 | -3.76E-03 | 4.77E-03 | 1.01E-03 |
|                      |             | 7.59E-03 | 2.37E-02 | -3.85E-03 | 4.89E-03 | 1.04E-03 |
|                      |             | 8.11E-03 | 2.43E-02 | -4.07E-03 | 5.07E-03 | 9.99E-04 |
|                      |             | 7.70E-03 | 2.29E-02 | -3.75E-03 | 4.74E-03 | 9.91E-04 |
|                      |             | 8.11E-03 | 2.34E-02 | -3.96E-03 | 4.90E-03 | 9.40E-04 |
|                      |             | 7.13E-03 | 2.08E-02 | -3.35E-03 | 4.28E-03 | 9.25E-04 |
|                      |             | 7.84E-03 | 2.13E-02 | -3.59E-03 | 4.46E-03 | 8.65E-04 |
| rim-NCor$\cdots$C$_{60}$ | $\pi\cdots\pi$ C$\cdots$C | 9.35E-03 | 2.80E-02 | -4.37E-03 | 5.68E-03 | 1.31E-03 |
|                      |             | 7.39E-03 | 2.12E-02 | -3.74E-03 | 4.52E-03 | 7.85E-04 |
|                      |             | 9.40E-03 | 2.88E-02 | -4.41E-03 | 5.80E-03 | 1.39E-03 |
|                      |             | 7.84E-03 | 2.25E-02 | -3.52E-03 | 4.57E-03 | 1.05E-03 |
|                      |             | 9.34E-03 | 2.82E-02 | -4.45E-03 | 5.75E-03 | 1.30E-03 |
|                      |             | 8.66E-03 | 2.62E-02 | -4.08E-03 | 5.31E-03 | 1.23E-03 |
| Combination                  | rim-3NSum $\supset C_{60}$ | Hyd-bowl $\supset C_{60}$ | PP-bowl $\supset C_{60}$ | hub-NCor $\supset C_{60}$ |
|-----------------------------|-----------------------------|-----------------------------|---------------------------|-----------------------------|
| Cyc-bowl $\supset C_{60}$   |                             |                             |                           |                             |
|                             | $\pi\cdots\pi$              |                             |                           |                             |
|                             | C$\cdots$C                  |                             |                           |                             |
| 9.26E-03                    | 2.20E-02                    | -2.32E-03                   | 4.18E-03                  | 7.32E-04                    |
|                             | 6.18E-03                    | 1.64E-02                    | -2.65E-03                 | 3.38E-03                    |
|                             |                             |                             |                           |                             |
| Hyd-bowl $\supset C_{60}$   |                             |                             |                           |                             |
|                             | $\pi\cdots\pi$              |                             |                           |                             |
|                             | C$\cdots$C                  |                             |                           |                             |
| 6.15E-03                    | 1.57E-02                    | -2.60E-03                   | 3.27E-03                  | 6.66E-04                    |
|                             | 8.10E-03                    | 2.36E-02                    | -3.73E-03                 | 4.81E-03                    |
|                             | 9.20E-03                    | 2.71E-02                    | -4.30E-03                 | 5.54E-03                    |
|                             | 7.58E-03                    | 2.20E-02                    | -3.50E-03                 | 4.50E-03                    |
|                             | 9.46E-03                    | 2.80E-02                    | -4.39E-03                 | 5.70E-03                    |
|                             | 8.52E-03                    | 2.39E-02                    | -3.93E-03                 | 4.96E-03                    |
|                             | 7.43E-03                    | 2.06E-02                    | -3.22E-03                 | 4.18E-03                    |
|                             | 6.18E-03                    | 1.64E-02                    | -2.65E-03                 | 3.38E-03                    |
|                             |                             |                             |                           |                             |
| PP-bowl $\supset C_{60}$    |                             |                             |                           |                             |
|                             | $\pi\cdots\pi$              |                             |                           |                             |
|                             | C$\cdots$C                  |                             |                           |                             |
| 9.06E-03                    | 2.73E-02                    | -4.31E-03                   | 5.57E-03                  | 1.26E-03                    |
|                             | 1.12E-02                    | 3.37E-02                    | -5.49E-03                 | 6.96E-03                    |
|                             | 6.55E-03                    | 1.85E-02                    | -2.92E-03                 | 3.77E-03                    |
|                             | 8.46E-03                    | 2.63E-02                    | -4.31E-03                 | 5.44E-03                    |
|                             | 7.51E-03                    | 2.16E-02                    | -3.38E-03                 | 4.39E-03                    |
|                             | 8.72E-03                    | 2.55E-02                    | -4.02E-03                 | 5.20E-03                    |
|                             | 8.65E-03                    | 2.65E-02                    | -4.24E-03                 | 5.44E-03                    |
|                             | 4.77E-03                    | 1.23E-02                    | -2.10E-03                 | 2.59E-03                    |
|                             |                             |                             |                           |                             |
| hub-NCor $\supset C_{60}$   |                             |                             |                           |                             |
|                             | $\pi\cdots\pi$              |                             |                           |                             |
|                             | C$\cdots$C                  |                             |                           |                             |
| 5.90E-03                    | 1.54E-02                    | -2.53E-03                   | 3.18E-03                  | 6.58E-04                    |
| 7.31E-03                    | 2.09E-02                    | -3.35E-03                   | 4.28E-03                  | 9.37E-04                    |
| 8.22E-03                    | 2.40E-02                    | -3.85E-03                   | 4.93E-03                  | 1.08E-03                    |
| 7.79E-03                    | 2.30E-02                    | -3.61E-03                   | 4.68E-03                  | 1.06E-03                    |
| 7.24E-03                    | 2.01E-02                    | -3.18E-03                   | 4.10E-03                  | 9.19E-04                    |
| 6.87E-03                    | 1.98E-02                    | -3.46E-03                   | 4.21E-03                  | 7.47E-04                    |
| 9.29E-03                    | 2.83E-02                    | -4.41E-03                   | 5.74E-03                  | 1.33E-03                    |
| 7.71E-03                    | 2.27E-02                    | -3.62E-03                   | 4.65E-03                  | 1.03E-03                    |
| 9.27E-03                    | 2.81E-02                    | -4.31E-03                   | 5.67E-03                  | 1.36E-03                    |
| 6.59E-03                    | 1.76E-02                    | -2.83E-03                   | 3.61E-03                  | 7.82E-04                    |
| 6.71E-03                    | 1.83E-02                    | -2.93E-03                   | 3.76E-03                  | 8.26E-04                    |
Table S4. Main contributions of the Kohn-Sham molecular orbitals to the corresponding occupied (Occ) and vacant (Vac) natural transition orbitals.

| Supramolecular host-guest systems Bowl ⊂ C_{60} | Cor | rim-NCor | hub-NCor | PP-bowl | Hyd-bowl | Cyc-bowl | rim-NSum | Sum |
|---------------------------------|-----|---------|---------|---------|---------|---------|---------|-----|
| **LE1 (Fullerene C_{60})** |     |         |         |         |         |         |         |     |
| Occ                             |     |         |         |         |         |         |         |     |
| H(0.75)                        | H(0.75) | H-1(0.54) | H-2(0.89) | H-3(0.76) | H-1(0.97) | H-1(0.65) | H(0.88) | H(0.49) |
| H(0.37)                        | H(0.37) | H-2(0.62) | H-3(0.34) | H-4(0.58) | H-2(0.16) | H-2(0.51) | H(0.36) | H-4(0.64) |
| Vac                             |     |         |         |         |         |         |         |     |
| L(0.58)                        | L(0.58) | L+1(0.58) | L+1(0.66) | L(0.66)  | L(0.58)  | L(0.58)  | L+1(0.81) | L+2(0.29) | L+1(0.95) | L+2(0.28) |
| L+1(0.81)                      | L+1(0.81) | L+2(0.71) | L+1(0.66) | L+1(0.55) | L+1(0.81) | L+2(0.29) | L+2(0.28) |     |
| **LE2 (Bowl)** |     |         |         |         |         |         |         |     |
| Occ                             |     |         |         |         |         |         |         |     |
| H-6(0.85)                      | H-6(0.85) | H-1(0.37) | H-2(0.37) | H-1(0.14) | H(0.98) | H-1(0.15) | H(0.997) | H(0.89) | H-1(0.17) | H(0.94) | H-1(0.26) |
| H-7(0.38)                      | H-7(0.38) | H-3(0.74) | H-5(0.74) | H(0.98) | H-1(0.15) | H(0.997) | H(0.43) | H(0.89) | H-1(0.17) | H(0.94) | H-1(0.26) |
| Vac                             |     |         |         |         |         |         |         |     |
| L+6(0.72)                      | L+6(0.72) | L+3(0.86) | L+6(0.49) | L+6(0.84) | L+6(0.29) | L+3(0.20) | L+5(0.19) | L+6(0.97) | L+6(0.70) | L+6(0.34) |
| L+7(0.58)                      | L+7(0.58) | L+6(0.37) | L+7(0.37) | L+7(0.92) | L+7(0.97) | L+7(0.97) | L+6(0.95) | L+7(0.17) |     |
| **CT (Bowl → Fullerene C_{60})** |     |         |         |         |         |         |         |     |
| Occ                             |     |         |         |         |         |         |         |     |
| H-5(0.25)                      | H-5(0.25) | H-3(0.34) | H-6(0.95) | H-5(0.86) | H(0.96) | H(0.999) | H(0.996) | H(0.64) | H-5(0.57) | H-5(0.81) | H(0.38) | H-1(0.85) |
| H-6(0.95)                      | H-6(0.95) | H-3(0.34) | H-6(0.86) | H-2(0.19) | H(0.96) | H(0.999) | H(0.996) | H(0.64) | H-5(0.57) | H-5(0.81) | H(0.38) | H-1(0.85) |
| Vac                             |     |         |         |         |         |         |         |     |
| L(0.93)                        | L(0.93) | L+2(0.97) | L+5(0.22) | L(0.20)  | L(0.53)  | L+1(0.21) | L+2(0.94) | L+2(0.95) | L+2(0.59) | L+2(0.31) |
| L+2(0.30)                      | L+2(0.30) | L+1(0.95) | L+5(0.22) | L+1(0.95) | L+2(0.94) | L+2(0.94) | L+2(0.59) | L+2(0.31) |     |
Table S5. Excitation energies (E_x, eV), main singly excited configuration (HOMO(H)-LUMO(L)) and its weight (W), oscillator strength (f), extent of charge transfer (CT, e) or localization of exciton (X) computed for Cor⊃C_{60}, rim-NCor⊃C_{60}, hub-NCor⊃C_{60}, PP-bowl⊃C_{60}, Hyd-bowl⊃C_{60}, Cyc-bowl⊃C_{60}, rim-3NSum⊃C_{60}, and Sum⊃C_{60} complexes in DCM.

| Supramolecular host-guest systems | Cor | rim-NCor | hub-NCor | PP-bowl | Hyd-bowl | Cyc-bowl | rim-NSum | Sum |
|----------------------------------|-----|----------|----------|---------|----------|----------|----------|-----|
| Ex (Fullerene C_{60})            |     |          |          |         |          |          |          |     |
| LE1                              |     |          |          |         |          |          |          |     |
| Ex                               | 2.555 | 2.567 | 2.563 | 2.565 | 2.553 | 2.550 | 2.568 | 2.556 |
| Trans. (W)                       | H-L | H-L+2 | H-2-L+2 | H-3-L+2 | H-1-L | H-2-L | H-L | H-1-L |
| f                                | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| X                                | 0.976 | 0.977 | 0.923 | 0.958 | 0.967 | 0.973 | 0.980 | 0.953 |
| Ex (Bowl)                        | 3.994 | 3.849 | 3.282 | 3.020 | 3.329 | 4.147[a] | 4.181 | 4.143 |
| Trans. (W)                       | H-6-L+6 | H-5-L+3 | H-L+6 | H-L+7 | H-L+7 | H-5-L+6 | H-5-L+7 | H-6-L+7 |
| f                                | <0.001 | 0.029 | 0.187 | 0.003 | 0.001 | 0.030 | 0.025 | 0.038 |
| X                                | 0.799 | 0.796 | 0.924 | 0.920 | 0.955 | 0.508 | 0.831 | 0.633 |
| Most absorptive transition       |     |          |          |         |          |          |          |     |
| Ex (Fullerene C_{60})            |     |          |          |         |          |          |          |     |
| CT (Bowl → Fullerene C_{60})     |     |          |          |         |          |          |          |     |
| Ex                               | 4.390 | 4.381 | 4.392 | 4.410 | 4.409 | 4.370 | 4.396 | 4.394 |
| Trans. (W)                       | H-L+5 | H-1-L+5 | H-1-L+6 | H-1-L+4 | H-1-L+5 | H-4-L+3 | H-2-L+3 | H-2-L+3 |
| f                                | 0.806 | 0.489 | 0.671 | 0.688 | 0.823 | 0.863 | 0.847 | 0.748 |
| Localization                    | C_{60} | C_{60} | C_{60} | C_{60} | C_{60} | C_{60} | C_{60} | C_{60} |
| X                                | 0.946 | 0.842 | 0.819 | 0.847 | 0.899 | 0.956 | 0.950 | 0.953 |

[a] LE2 state is partially delocalized over C_{60} unit

Table S6. 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 (Δµ= µ_i-µ_0, D), and DCM solvation energies (E_{solv}, eV) calculated for Cor⊃C_{60}, rim-NCor⊃C_{60}, hub-NCor⊃C_{60}, PP-bowl⊃C_{60}, Hyd-bowl⊃C_{60}, Cyc-bowl⊃C_{60}, rim-3NSum⊃C_{60}, and Sum⊃C_{60} complexes.

| Supramolecular host-guest systems | Cor | rim-NCor | hub-NCor | PP-bowl | Hyd-bowl | Cyc-bowl | rim-NSum | Sum |
|----------------------------------|-----|----------|----------|---------|----------|----------|----------|-----|
| Ground state (GS)                |     |          |          |         |          |          |          |     |
| E_x                              | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| µ_0                              | 0.40 | 1.86 | 1.16 | 0.23 | 0.21 | 0.89 | 0.74 | 0.99 |
| E_{solv}                         | -0.161 | -0.225 | -0.220 | -0.276 | -0.180 | -0.156 | -0.261 | -0.155 |
Table S7. Computed semi-classical rates ($k_X$ in s$^{-1}$) and characteristic times ($\tau$ in ns/ps) for the charge separation processes in Cor$\supset$C$_{60}$, Sum$\supset$C$_{60}$ and hub-NCor$\supset$C$_{60}$, complexes in DCM solution using different effective Huang-Rhys ($S_{eff}$) factors.

| $h\omega_{eff}$ | $\Delta G^0$, eV | $|V|$, eV | $\lambda_s$ | $\lambda_i$ | $S_{eff}$ | $k_X$, s$^{-1}$ | $\tau$ |
|----------------|-----------------|------------|------------|------------|-----------|---------------|--------|
| 1200           | 0.652           | 9.35$\cdot$10$^{-3}$ | 0.413      | 0.170      | 1.143     | 5.67$\cdot$10$^0$ | n/a    |
| 1400           | 0.034           | 1.96$\cdot$10$^{-3}$ | 0.410      | 0.166      | 1.116     | 9.46$\cdot$10$^8$ | 1.06 ns |
| 1600           | -0.598          | 1.98$\cdot$10$^{-3}$ | 0.246      | 0.165      | 1.109     | 4.31$\cdot$10$^{11}$ | 0.23 ps |
Figure S1. QTAIM molecular graph for Cor$\supseteq\text{C}_60$, rim-NCor$\supseteq\text{C}_60$, hub-NCor$\supseteq\text{C}_60$, PP-bowl$\supseteq\text{C}_60$, Hyd-bowl$\supseteq\text{C}_60$, Cyc-bowl$\supseteq\text{C}_60$, rim-3NSum$\supseteq\text{C}_60$, and Sum$\supseteq\text{C}_60$ 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, blue to H···C, and purple to N···C contacts.
Figure S2. Plot of RDG vs. $\text{sign} (\lambda_2) \times \rho$ for $\text{Cor} \supset C_{60}$, $\text{rim-NCor} \supset C_{60}$, $\text{hub-NCor} \supset C_{60}$, $\text{PP-bowl} \supset C_{60}$, $\text{Hyd-bowl} \supset C_{60}$, $\text{Cyc-bowl} \supset C_{60}$, $\text{rim-3NSum} \supset C_{60}$, and $\text{Sum} \supset C_{60}$ complexes.
Figure S3. NCI isosurfaces of van der Waals interactions ($-0.015 < \text{sign}(\lambda_2)x_p < 0.010$ a.u.) for $\text{Cor} \supset \text{C}_60$, $\text{rim-NCor} \supset \text{C}_60$, $\text{hub-NCor} \supset \text{C}_60$, $\text{PP-bowl} \supset \text{C}_60$, $\text{Hyd-bowl} \supset \text{C}_60$, $\text{Cyc-bowl} \supset \text{C}_60$, $\text{rim-3NSum} \supset \text{C}_60$, and $\text{Sum} \supset \text{C}_60$ complexes. Isosurfaces were generated for RDG = 0.65 a.u.
Figure S4. Natural transition molecular orbitals representing the LE$_1$, LE$_2$ and CT states in Cor$\supseteq$C$_{60}$ complex.
Figure S5. Natural transition molecular orbitals representing the LE₁, LE₂ and CT states in \textit{rim-NCor} ⊃ C_{60} complex.
Figure S6. Natural transition molecular orbitals representing the LE\textsubscript{1}, LE\textsubscript{2} and CT states in hub-NCor$\supset$C\textsubscript{60} complex.
Figure S7. Natural transition molecular orbitals representing the LE$_1$, LE$_2$ and CT states in PP-bowl$\supseteq$C$_{60}$ complex.
Figure S8. Natural transition molecular orbitals representing the LE₁, LE₂ and CT states in \textit{Hyd-bowl}⊃\textit{C₆₀} complex.
Figure S9. Natural transition molecular orbitals representing the LE$_1$, LE$_2$ and CT states in Cyc-bowl$\supset$C$_{60}$ complex.
Figure S10. Natural transition molecular orbitals representing the LE₁, LE₂ and CT states in *rim-3NSum* ≻ C₆₀ complex.
Figure S11. Natural transition molecular orbitals representing the LE$_1$, LE$_2$ and CT states in $\text{Sum}\supset C_{60}$ complex.
Figure S12. Dependence of the charge separation rate for the Cor$\supseteq$C$_{60}$, Sum$\supseteq$C$_{60}$ and hub-NCor$\supseteq$C$_{60}$ complexes on the effective frequency computed using Marcus-Levich-Jortner approach.
## Cartesian coordinates

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| 6    | 0.934401000 | 1.329324000 | -3.10306000 |
| 6    | 0.948428000 | -0.100654000 | -3.38466600 |
| 6    | 0.002510000 | -0.938604000 | -2.78515000 |
| 6    | -0.994690000 | -0.382560000 | -1.88208900 |
| 6    | -1.007847000 | 0.987465000 | -1.61357800 |
| 6    | -0.025122000 | 1.861821000 | -2.23639600 |
| 6    | 2.315749000 | 1.786029000 | -3.02707900 |
| 6    | 3.183784000 | 0.640053000 | -3.26259400 |
| 6    | 2.338611000 | -0.526260000 | -3.48237200 |
| 6    | 2.725568000 | -1.772919000 | -2.98036100 |
| 6    | 0.404891000 | -2.238642000 | -2.25437500 |
| 6    | -1.209130000 | -1.353732000 | -0.80452600 |
| 6    | -1.426838000 | -0.880884000 | 0.603019000 |
| 6    | -1.443915000 | 0.545330000 | 0.775762000 |
| 6    | -1.238931000 | 1.461488000 | -0.25675600 |
| 6    | -0.396341000 | 2.629651000 | -0.037610000 |
| 6    | 0.354852000 | 2.876806000 | -1.260930000 |
| 6    | 1.680625000 | 3.146910000 | -1.189897000 |
| 6    | 2.681150000 | 2.758612000 | -2.091245000 |
| 6    | 4.381106000 | 0.512011000 | -2.551249000 |
| 6    | 4.761530000 | 1.525377000 | -1.576015000 |
| 6    | 3.927650000 | 2.624355000 | -1.350352000 |
| 6    | 3.977745000 | 3.098072000 | 0.007360000 |
| 6    | 2.308867000 | 3.524770000 | 0.107165000 |
| 6    | 1.586749000 | 3.288073000 | 1.280610000 |
| 6    | 0.204676000 | 2.834736000 | 1.208156000 |
| 6    | -0.010666000 | 1.877386000 | 2.287174000 |
| 6    | -0.815217000 | 0.756349000 | 2.072990000 |
| 6    | -0.346419000 | -2.484691000 | -1.040041000 |
| 6    | 1.649114000 | -1.818062000 | 3.071437000 |
| 6    | 1.283263000 | -2.790160000 | 2.137180000 |
| 6    | 2.283619000 | -3.344690000 | 1.235129000 |
| 6    | 3.609041000 | -2.905700000 | 1.305775000 |
| 6    | 3.989946000 | -1.892812000 | 2.280862000 |
| 6    | 3.015296000 | 0.070019000 | 3.427963000 |
| 6    | 1.662520000 | 0.496109000 | 3.529879000 |
| 6    | 0.781791000 | -0.617405000 | 3.310960000 |
| 6    | -0.412979000 | -0.542446000 | 2.596360000 |
| 6    | -0.790837000 | -1.554490000 | 1.619180000 |
| 6    | 0.035728000 | -2.658223000 | 1.397227000 |
| 6    | 1.654415000 | -3.557040000 | -0.062019000 |
| 6    | 2.376173000 | -3.319255000 | -1.236151000 |
| 6    | 3.757036000 | -2.862092000 | -1.162121000 |
| 6    | 4.360447000 | -2.659473000 | 0.082680000 |
| 6    | 5.207313000 | -1.493994000 | 0.301375000 |
| 6    | 4.976302000 | -1.019726000 | 1.659896000 |

## CorC<sub>60</sub>

Gas-phase. B3LYP-D3(BJ)/def2-SVP

## rim-NCorC<sub>60</sub>

Gas-phase. B3LYP-D3(BJ)/def2-SVP
|   |   |   |   |
|---|---|---|---|
| 6 | 4.962599000 | 0.352073000 | 1.929379000 |
| 6 | 3.962059000 | 0.907828000 | 2.830695000 |
| 6 | 1.238529000 | 1.742320000 | 3.026844000 |
| 6 | 2.224925000 | 2.614515000 | 2.405046000 |
| 6 | 3.558572000 | 2.205565000 | 2.308841000 |
| 6 | 4.310232000 | 2.452655000 | 1.085696000 |
| 6 | 5.178799000 | 1.307936000 | 0.851332000 |
| 6 | 5.400685000 | 0.852979000 | -0.452456000 |
| 6 | 5.415183000 | -0.576421000 | -0.733069000 |
| 6 | 4.785468000 | -0.786941000 | -2.030589000 |
| 6 | 3.972810000 | -1.905375000 | -2.239573000 |
| 6 | 0.264331000 | -3.132612000 | 0.037849000 |
| 6 | 1.738704000 | -2.645689000 | -2.360331000 |
| 6 | 3.029535000 | -1.359844000 | 3.146382000 |
| 6 | -4.779752000 | -0.686940000 | 0.932634000 |
| 6 | -4.793919000 | -1.109196000 | -0.425527000 |
| 6 | -4.787502000 | 0.052702000 | -1.245337000 |
| 6 | -4.772540000 | 1.193060000 | -0.395538000 |
| 6 | -4.766525000 | 0.736513000 | 0.950729000 |
| 6 | -4.238912000 | -1.457206000 | 1.953414000 |
| 6 | -4.272059000 | -2.326605000 | -0.842667000 |
| 6 | -4.267931000 | 0.065533000 | -2.532059000 |
| 6 | -4.230936000 | 2.412010000 | -0.781743000 |
| 6 | -4.214674000 | 1.471801000 | 1.991873000 |
| 6 | -3.840064000 | 2.825507000 | 1.636918000 |
| 6 | -3.847409000 | 3.271738000 | 0.319058000 |
| 6 | -3.891463000 | 2.497716000 | -2.188436000 |
| 6 | -3.905749000 | 1.381743000 | -3.017680000 |
| 6 | -3.925710000 | -2.379489000 | -2.248714000 |
| 6 | -3.921368000 | -1.242138000 | -0.304976900 |
| 6 | -3.906247000 | -3.222676000 | 0.234888000 |
| 6 | -3.889586000 | -2.809070000 | 1.562933000 |
| 6 | -3.865990000 | -0.706548000 | 3.135946000 |
| 6 | -3.856625000 | 0.684596000 | 3.154838000 |
| 1 | -3.438596000 | 3.489103000 | 2.047656000 |
| 1 | -3.448955000 | 4.267364000 | 0.104176000 |
| 1 | -3.509646000 | 3.439608000 | -2.592827000 |
| 1 | -3.528788000 | 1.490140000 | -0.403882700 |
| 1 | -3.552981000 | -3.315458000 | -2.674687000 |
| 1 | -3.541939000 | -1.330430000 | -0.071859000 |
| 1 | -3.527908000 | -4.220523000 | -0.004923000 |
| 1 | -3.501044000 | -3.499078000 | 2.316759000 |
| 1 | -3.480691000 | -1.240281000 | 4.009196000 |
| 1 | -3.463382000 | 1.189500000 | 4.041492000 |
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| 6    | -3.480975000 | -2.03411000 | 2.570163000 |
| 6    | -3.823472000 | -2.387025000 | 1.194720000 |
| 6    | -3.345115000 | -3.463980000 | 0.370759000 |
| 6    | -2.819445000 | -3.271208000 | 3.187093000 |
| 6    | -2.698646000 | -4.503788000 | 1.065874000 |
| 6    | -3.632604000 | -0.838840000 | 3.159330000 |
| 6    | -3.159917000 | -0.481248000 | 4.432948000 |
| 6    | -3.353343000 | 1.897232000 | 3.920041000 |
| 6    | -4.059748000 | 0.245303000 | 2.335625000 |
| 6    | -3.836243000 | 1.623945000 | 2.628969000 |
| 6    | -4.448622000 | -1.325741000 | 0.534608000 |
| 6    | -4.558847000 | -0.064475000 | 1.090904000 |
| 6    | -4.626933000 | 0.860028000 | 0.065998000 |
| 6    | -4.476275000 | -1.196086000 | -0.847016000 |
| 6    | -4.584979000 | 0.177064000 | -1.140397000 |
| 6    | -3.333114000 | -3.312398000 | -1.124080000 |
| 6    | -3.826297000 | -2.101898000 | -1.699487000 |
| 6    | -3.453864000 | -1.617680000 | -3.000684000 |
| 6    | -2.771886000 | -2.536651000 | -3.809941000 |
| 6    | -3.228976000 | 2.693832000 | 4.538322000 |
| 6    | -3.019658000 | 0.456979000 | -4.450222000 |
| 6    | -3.570379000 | -0.151878000 | -3.313230000 |
| 6    | -3.789083000 | 2.160384000 | -2.280437000 |
| 6    | -4.051458000 | 0.751346000 | -2.304961000 |
| 6    | -3.485559000 | 4.231793000 | -0.081146000 |
| 6    | -3.898772000 | 2.900334000 | -0.991751000 |
| 6    | -4.212034000 | 2.185002000 | 0.215470000 |
| 6    | -3.459884000 | 3.961016000 | 1.640960000 |
| 6    | -3.897833000 | 2.636523000 | 1.533763000 |
| 6    | -2.659207000 | -4.182004000 | -1.991569000 |
| 6    | -2.428538000 | -3.806797000 | -3.318182000 |
| 6    | -2.898220000 | 1.855036000 | -4.256123000 |
| 6    | -3.307014000 | 4.746865000 | 0.486805000 |
| 6    | -3.057646000 | 0.861586000 | 4.810963000 |
| 6    | -2.478942000 | -4.414153000 | 2.444884000 |
| 6    | -2.509682000 | -3.210529000 | 4.232011000 |
| 6    | -2.310470000 | -5.369709000 | 0.526880000 |
| 6    | -2.821994000 | -1.255251000 | 5.123212000 |
| 6    | -3.159512000 | 2.927632000 | 2.242210800 |
| 6    | -2.447115000 | -2.258341000 | -4.814383000 |
| 6    | -2.996732000 | 3.758183000 | -3.534888000 |
| 6    | -2.628951000 | -0.148232000 | -5.270058000 |
| 6    | -3.244542000 | 4.863465000 | -1.659803000 |
| 6    | -3.184771000 | 4.385649000 | 2.607880000 |
| 6    | -2.257138000 | -5.131839000 | -1.634471000 |
| 6    | -1.892348000 | -4.496143000 | -3.974694000 |
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| 6    | -3.739281000 | -0.028091000 | 2.907804000 |
| 6    | -3.846426000 | -3.498931000 | 1.593734000 |
| 1    | -3.580146000 | -4.531151000 | 1.356294000 |
| 6    | -4.229390000 | -2.597297000 | 0.584716000 |
| 6    | -4.568794000 | -1.291479000 | 1.024094000 |
| 6    | -4.347387000 | -0.735036000 | 2.299103000 |
| 6    | -3.939304000 | -1.671395000 | 3.257301000 |
| 1    | -3.712440000 | -1.347591000 | 4.275239000 |
| 7    | -4.893496000 | -0.548474000 | -0.089064000 |
| 6    | -4.205335000 | -2.536220000 | -0.889061000 |
| 6    | -3.763706000 | -3.346060000 | -1.950932000 |
| 6    | -4.536688000 | -1.199140000 | -1.232526000 |
| 6    | -3.611709000 | -2.767120000 | -3.216688000 |
| 1    | -3.482457000 | -4.388620000 | -1.786863000 |
| 6    | -4.288021000 | -0.540531000 | -2.453092000 |
| 6    | -3.831885000 | -1.391147000 | -3.467169000 |
| 6    | -3.577449000 | -0.985147000 | -4.448418000 |
| 6    | -4.273597000 | 0.760543000  | 2.356617000 |
| 6    | -4.454289000 | 1.437616000  | 1.133323000 |
| 6    | -3.765231000 | 1.571077000  | 3.379432000 |
| 6    | -4.010855000 | 2.742080000  | 0.796422000 |
| 7    | -4.847187000 | 0.817142000  | -0.024527000 |
| 6    | -3.438460000 | 2.925227000  | 3.135469000 |
| 6    | -3.551523000 | 1.143948000  | 4.361622000 |
| 6    | -3.523558000 | 3.516310000  | 1.866791000 |
| 6    | -4.449027000 | 1.532336000  | -1.249166000 |
| 6    | -3.159170000 | 4.531109000  | 1.708987000 |
| 6    | -0.008380000 | 2.804126000  | -0.677987000 |
| 6    | -4.249799000 | 0.957497000  | -2.396248000 |
| 6    | -3.521809000 | 3.668588000  | -1.678069000 |
| 6    | -3.745950000 | 1.854325000  | -3.345688000 |
| 6    | -3.431650000 | 3.187898000  | -2.990469000 |
| 1    | -3.161476000 | 4.668457000  | -1.433387000 |
| 1    | -3.524708000 | 1.511118000  | -4.358553000 |
| 6    | -2.798184000 | 2.046759000  | -0.701668000 |
| 6    | -0.882491000 | 2.282885000  | -2.249202000 |
| 6    | -0.199042000 | 3.097451000  | -1.253417000 |
| 6    | -0.815107000 | 3.362216000  | -0.026189000 |
| 6    | -2.154222000 | 1.767400000  | -1.978979000 |
| 6    | -1.527097000 | -0.395083000 | -2.997444000 |
| 6    | -0.202263000 | 0.140919000  | -3.278903000 |
| 6    | 0.113304000  | 1.452646000  | -2.912592000 |
| 6    | -2.482546000 | 0.402006000  | -2.360340000 |
| 6    | -3.182933000 | -1.507150000 | -0.955123000 |
| 6    | -2.186464000 | -2.337217000 | -1.617724000 |
| 6    | -1.375543000 | -1.792909000 | -2.618298000 |
| 6    | -3.323873000 | -0.165034000 | -1.319210000 |
| 6    | -3.567480000 | 0.484610000  | 1.054632000 |
| 6    | -3.415887000 | -0.915707000 | 1.433952000 |
| 6    | -3.228560000 | -1.891602000 | 0.449819000 |
| 6    | -3.523557000 | 0.851401000  | -0.294001000 |

**Hyd-bowl C60**

Gas-phase. B3LYP-D3(BJ)/def2-SVP

**Cyc-bowl C60**

Gas-phase. B3LYP-D3(BJ)/def2-SVP
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| 1    | -0.589393000 | -1.492355000 | -1.478279000 |
| 6    | 0.831552000  | -1.282973000 | -1.531711000 |
| 6    | 1.337385000  | 0.010463000  | -1.571647000 |
| 6    | 0.443075000  | 1.134789000  | -1.632509000 |
| 6    | -0.930777000 | 0.929402000  | -1.577158000 |
| 6    | -1.456545000 | -0.407101000 | -1.531776000 |
| 6    | 0.999474000  | 2.217406000  | -0.928464000 |
| 6    | 0.230229000  | 3.139972000  | -0.364232000 |
| 6    | -1.124235000 | 2.958107000  | -0.355414000 |
| 6    | -1.762936000 | 1.819381000  | -0.872836000 |
| 6    | -2.624137000 | -0.430729000 | -0.750643000 |
| 6    | -3.002700000 | -1.532246000 | -0.115083000 |
| 6    | -2.173937000 | -2.617791000 | -0.113074000 |
| 6    | -0.900777000 | -2.627397000 | -0.707044000 |
| 6    | 1.480123000  | -2.247972000 | -0.741100000 |
| 6    | 2.650960000  | -1.994879000 | -0.168445000 |
| 6    | 3.166329000  | -0.731469000 | -0.247234000 |
| 6    | 2.512643000  | 0.342964000  | -0.872209000 |
| 6    | -3.047170000 | 1.041747000  | -0.492232000 |
| 6    | 2.485581000  | 1.873582000  | -0.638251000 |
| 6    | 0.436256000  | -3.345616000 | -0.395160000 |
| 6    | -3.914610000 | 1.329717000  | -1.115558000 |
| 6    | -3.336914000 | 1.192630000  | 0.558051000  |
| 6    | 2.768368000  | 2.154354000  | 0.385148000  |
| 6    | 3.163318000  | 2.413040000  | -1.322770000 |
| 6    | 0.582511000  | -4.245646000 | -1.018704000 |
| 6    | 0.516260000  | -3.662278000 | 0.654027000  |
| 6    | 4.075366000  | -0.568133000 | 0.342594000  |
| 6    | -1.685160000 | 3.701348000  | 0.221492000  |
| 6    | -2.510791000 | -3.451091000 | 0.513035000  |
| 6    | -1.025734000 | 1.570487000  | 2.469740000  |
| 6    | -0.940618000 | 0.166510000  | 2.093780000  |
| 6    | -1.857397000 | -0.748952000 | 2.614698000  |
| 6    | -2.903490000 | -0.302654000 | 3.522912000  |
| 6    | -2.986323000 | 1.046536000  | 3.881032000  |
| 6    | -2.029385000 | 2.003765000  | 3.340668000  |
| 6    | 0.329969000  | 2.083726000  | 2.603397000  |
| 6    | 1.253307000  | 0.997692000  | 2.311753000  |
| 6    | 0.469202000  | -0.188019000 | 1.991991000  |
| 6    | 0.904471000  | -1.442200000 | 2.425421000  |
| 6    | -1.405066000 | -2.059056000 | 3.056740000  |
| 6    | -3.095949000 | -1.336656000 | 4.531700000  |
| 6    | -3.363470000 | -0.980554000 | 5.856970000  |

*S32*
|   |   |   |   |
|---|---|---|---|
| 6 | -3.448707000 | 0.425621000 | 6.229896000 |
| 6 | -3.264499000 | 1.418745000 | 5.261933000 |
| 6 | -2.476345000 | 2.603990000 | 5.574320000 |
| 6 | -1.715121000 | 2.967398000 | 4.387179000 |
| 6 | -0.412063000 | 3.458348000 | 4.516177000 |
| 6 | 0.631430000 | 3.009724000 | 3.603637000 |
| 6 | 2.444760000 | 0.878094000 | 3.033593000 |
| 6 | 2.759905000 | 1.842168000 | 4.080141000 |
| 6 | 1.869550000 | 2.884215000 | 4.359900000 |
| 6 | 1.591619000 | 3.255767000 | 5.740142000 |
| 6 | 0.181631000 | 3.610439000 | 5.836931000 |
| 6 | -0.549822000 | 3.263349000 | 6.976496000 |
| 6 | -1.906121000 | 2.750096000 | 6.842614000 |
| 6 | -2.096858000 | 1.715624000 | 7.849369000 |
| 6 | -2.852451000 | 0.577759000 | 7.550719000 |
| 6 | -2.168742000 | -2.423404000 | 4.242314000 |
| 6 | -0.283320000 | -1.939683000 | 8.430176000 |
| 6 | -0.585180000 | -2.863779000 | 7.425790000 |
| 6 | 0.457832000 | -3.311688000 | 6.516265000 |
| 6 | 1.760127000 | -2.819468000 | 6.640812000 |
| 6 | 2.073989000 | -1.856446000 | 7.685886000 |
| 6 | 0.986766000 | -0.021223000 | 8.937142000 |
| 6 | -0.423163000 | 0.333038000 | 9.033916000 |
| 6 | -1.209009000 | -0.853261000 | 8.721598000 |
| 6 | -2.397941000 | -0.733137000 | 7.994697000 |
| 6 | -2.712873000 | -1.696306000 | 6.947781000 |
| 6 | -1.823570000 | -2.738605000 | 6.668945000 |
| 6 | -0.135935000 | -3.464718000 | 5.191791000 |
| 6 | 0.596158000 | -3.117012000 | 4.053045000 |
| 6 | 1.953531000 | -2.604010000 | 4.185040000 |
| 6 | 2.522739000 | -2.457785000 | 5.453348000 |
| 6 | 3.310374000 | -1.272626000 | 5.766080000 |
| 6 | 3.030661000 | -0.900243000 | 7.146346000 |
| 6 | 2.947800000 | -0.448698000 | 7.504514000 |
| 6 | 1.904782000 | 0.896892000 | 8.417941000 |
| 6 | -0.858288000 | 1.590457000 | 8.606051000 |
| 6 | 0.098178000 | 2.546831000 | 8.066497000 |
| 6 | 1.450910000 | 2.206766000 | 7.973437000 |
| 6 | 2.213472000 | 2.568444000 | 6.786955000 |
| 6 | 3.140014000 | 1.482154000 | 6.496138000 |
| 6 | 3.409087000 | 1.125873000 | 5.170680000 |
| 6 | 3.495631000 | -0.280427000 | 4.793724000 |
| 6 | 2.901038000 | -0.433562000 | 3.475220000 |
| 6 | 2.143961000 | -1.570335000 | 3.177180000 |
| 6 | -1.545823000 | -3.110035000 | 5.288370000 |
| 6 | -0.052222000 | -2.398176000 | 2.964760000 |
| 6 | 1.073301000 | -1.426311000 | 8.563953000 |
References:

1. A. D. Becke, Phys. Rev. A 1988, 38, 3098-3100.
2. C. Lee, W. Yang and R. G. Parr, Phys. Rev. B 1988, 37, 785-789.
3. S.H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 1980, 58, 1200-1211.
4. F. Weigend and R. Ahlrichs, Phys. Chem. Chem. Phys. 2005, 7, 3297-3305.
5. F. Weigend, Phys. Chem. Chem. Phys. 2006, 8, 1057-1065.
6. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys. 2010, 132, 154104.
7. S. Grimme, S. Ehrlich and L. Goerigk, J. Comput. Chem. 2011, 32, 1456-1465.
8. S. Hirata and M. Head-Gordon, Chem. Phys. Lett. 1999, 314, 291-299.
9. T. Yanai, D. P. Tew and N. C. Handy, Chem. Phys. Lett. 2004, 393, 51-57.
10. Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparrini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
11. R. S. Mulliken, J. Chem. Phys. 1955, 23, 1833-1840.
12. R. S. Mulliken, J. Chem. Phys. 1955, 23, 1841-1846.
13. P. O. Löwdin, J. Chem. Phys. 1950, 18, 365-375.
14. F. L. Hirshfeld, Theor. Chim. Acta 1977, 44, 129-138.
15. A. V. Marenich, S. V. Jerome, C. J. Cramer, D.G. Truhlar, J. Chem. Theory Comput. 2012, 8, 527-541.
16. P. Bultinck, C. V. Alsenoy, P. W. Ayers, R. Carbó-Dorca, J. Chem. Phys., 2007, 126, 144111.
17. K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs; Theor. Chem. Acc. 1997, 97, 119.
18. ADF 2018, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, E.J. Baerends, T. Ziegler, A.J. Atkins, J. Autschbach, O. Baseggio, D. Bashford, A. Bèrces, F.M. Bickelhaupt, C. Bo, P.M. Boerrigter, L. Cavallo, C. Daul, D.P. Chong, D.V. Chulhai, L. Deng, R.M. Dickson, J.M. Dieterich, D.E. Ellis, M. van Faassen, L. Fan, T.H. Fischer, A. Förster, C. Fonseca Guerra, M. Franchini, A. Ghyseels, A. Giammona, S.J.A. van Gisbergen, A. Goez, A.W. Götz, J.A. Groeneveld, O.V. Gritsenko, M. Grüning, S. Gusarov, F.E. Harris, P. van den Hoek, Z. Hu, C.R. Jacob, H. Jacobsen, L. Jensen, L. Joubert, J.W. Kaminski, G. van Kessel, C. König, F. Kootstra, A. Kovalenko, M.V. Krykunov, E. van Lenthe, D.A. McCormack, A. Michalak, M. Mitoraj, S.M. Morton, J. Neugebauer, V.P. Nicu, L. Noodleman, V.P. Otinga, S. Patchkovskii, M. Pavanello, C.A. Peeples, P.H.T. Philipsen, D. Post, C.C. Pye, H. Ramanantoanina, P. Ramos, W. Ravenek, J.I. Rodríguez, P. Ros, R. Rüger, P.R.T. Schipper, D. Schlüns, H. van Schoot, G. Schreckenbach, J.S. Seldenthuis, M. Seth, J.G. Snijders, M. Solà, M. Stener, M. Swart, D. Swerhorne, V. Tognetti, G. te Velde, P. Vernooij, L. Versluis, L. Visscher, O. Visser, F. Wang, T.A. Wesolowski, E.M. van Wezenbeek, G. Wiesenekker, S.K. Wolff, T.K. Woo, A.L. Yakovlev
19. A. V. Luzanov, A. A. Sukhorukov, and V. E. Umanskii, *Theor. Exp. Chem.* 1976, **10**, 354–361.
20. M. Head-Gordon, A. M. Grana, D. Maurice and C. A. White, *J. Phys. Chem.* 1995, **99**, 14261–14270.
21. G. A. Zhurko, Chemcraft 1.80 (build 523b) - graphical program for visualization of quantum chemistry computations. (https://chemcraftprog.com).
22. T. Ziegler and A. Rauk, *Theor. Chim. Acta* 1977, **46**, 1-10.
23. T. Ziegler and A. Rauk, *Inorg. Chem.* 1979, **18**, 1558-1565.
24. T. Ziegler and A. Rauk, *Inorg. Chem.* 1979, **18**, 1755-1759.
25. S. Grimme, *J. Comput. Chem.* 2004, **25**, 1463-1473.
26. S. Grimme, *J. Comput. Chem.* 2006, **27**, 1787-1799.
27. F. Plasser and H. Lischka, *J. Chem. Theory Comput.* 2012, **8**, 2777-2789.
28. F. Plasser, S. A. Bäppler, M. Wormit and A. Dreu, *J. Chem. Phys.* 2014, **141**, 024107.
29. A. V. Luzanov and O. A. Zhikol, *Int. J. Quantum Chem.* 2010, **110**, 902-924.
30. A. Klamt, G. Schüürmann, *J. Chem. Soc. Perkin Trans.* 1993, **2**, 799–805.
31. J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.* 2005, **105**, 2999-3093.
32. A.A. Voityuk and S.F. Vyboishchikov, *Phys. Chem. Chem. Phys.* 2019, **21**, 18706-18713.
33. S.F. Vyboishchikov and A.A. Voityuk, *Phys. Chem. Chem. Phys.* 2020, **22**, 14591-14598.
34. A. Klamt, G. Schüürmann, *J. Chem. Soc. Perkin Trans.* 1993, **2**, 799–805.
35. J. L. Pascual-Ahuir, E. Silla, and I. Tuñón, *J. Comp. Chem.* 1994, **15**, 1127–1138.
36. A. Klamt, *J. Phys. Chem.* 1996, **100**, 3349-3353.
37. R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta, Rev. Bioenerg.* 1985, **811**, 265-322.
38. A. A. Voityuk and N. Rösch, *J. Chem. Phys.* 2002, **117**, 5607-5616.
39. A. A. Voityuk, *Phys. Chem. Chem. Phys.* 2012, **14**, 13789-13793.
40. J. Ulstrup, J. Jortner, *J. Chem. Phys.* 1975, **63**, 4358-4368.
41. J. Jortner, *J. Chem. Phys.* 1976, **64**, 4860-4867.
42. R. F. W. Bader, *Chem. Rev.* 1991, **91**, 893–928.
43. R. F. W. Bader, *Atoms in Molecules: A Quantum Theory; International Series of Monographs on Chemistry 22; Oxford University Press: Oxford, U.K.*, **1990**.
44. C. F. Matta, N. Castillo and R. J. Boyd, *J. Phys. Chem. B* 2006, **110**, 563–578.
45. C. R. Wick and T. Clark, *J. Mol. Model.* 2018, **24**, 142.
46. P. S. V. Kumar, V. Raghavendra and V Subramanian, *J. Chem. Sci.* 2016, **128**, 1527–1536.
47. Keith, T. A. AlMAll, version 14.06.21; TK Gristmill Software: Overland Park, KS, **2014**.
48. E. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. Cohen and W. Yang, *J. Am. Chem. Soc.* 2010, **132**, 6498–6506.
49. J. Contreras-García, E. Johnson, S. Keinan, R. Chaudret, J. Piquemal, D. Beratan and W. Yang, *J. Chem. Theory Comput.* 2011, **7**, 625–632.
50. J. Contreras-García, W. Yang and E. Johnson, *J. Phys. Chem. A*, 2011, **115**, 12983–12990.
51. T. Lu and F. Chen, *J. Comput. Chem.* 2012, **33**, 580-592.