

Supplementary information to

## Model Potential Study of Non-Valence Correlation-Bound Anions of (C<sub>60</sub>)<sub>n</sub> Clusters: the Role of Electric Field-Induced Charge Transfer

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### 1. The extended Mayer-Åstrand model allowing for intermolecular charge transfer

For a molecular dimer such as (C<sub>60</sub>)<sub>2</sub>, the constrained charge-flow equation in the Mayer-Åstrand model, which does not permit intermolecular charge transfer, is

$$f = E_{tot} + \lambda_1 \left( \sum_{i=1}^{N_1} q_{1,i} - Q_{1,tot} \right) + \lambda_2 \left( \sum_{i=1}^{N_2} q_{2,i} - Q_{2,tot} \right) \quad (S1)$$

where  $\lambda_1$  and  $\lambda_2$  are Lagrange multipliers and  $Q_{1,tot}$  and  $Q_{2,tot}$  are the total charges of the isolated molecules 1 and 2, respectively. The total polarization energy,  $E_{tot}$  is given by eqn (2) in the manuscript. In extending the model to allow for intermolecular charge transfer we use the expression:

$$f = E_{tot} + \lambda_1 \left( \sum_{i=1}^{N_1} q_{1,i} - Q_{1,tot} \right) + \lambda_2 \left( \sum_{i=1}^{N_2} q_{2,i} - Q_{2,tot} \right) + \eta(\lambda_1 - \lambda_2)^2 \quad (S2)$$

where  $\eta$  is represented by exponential depending on the internuclear separation as described below. By applying  $df/\mathbf{q}_1 = 0$ ,  $df/\mathbf{q}_2 = 0$ ,  $df/\mathbf{p}_1 = 0$ ,  $df/\mathbf{p}_2 = 0$ ,  $df/d\lambda_1 = 0$ , and  $df/d\lambda_2 = 0$ , the following set of

equations is obtained:

$$\begin{pmatrix} \mathbf{T}_{11}^{qq} & \mathbf{T}_{12}^{qq} & -\mathbf{T}_{11}^{pq} & -\mathbf{T}_{21}^{pq} & 1 & 0 \\ \mathbf{T}_{21}^{qq} & \mathbf{T}_{22}^{qq} & -\mathbf{T}_{12}^{pq} & -\mathbf{T}_{22}^{pq} & 0 & 1 \\ -\mathbf{T}_{11}^{pq} & -\mathbf{T}_{12}^{pq} & -\mathbf{T}_{11}^{pp} & -\mathbf{T}_{12}^{pp} & 0 & 0 \\ -\mathbf{T}_{21}^{pq} & -\mathbf{T}_{22}^{pq} & -\mathbf{T}_{21}^{pp} & -\mathbf{T}_{22}^{pp} & 0 & 0 \\ 1 & 0 & 0 & 0 & 2\eta & -2\eta \\ 0 & 1 & 0 & 0 & -2\eta & 2\eta \end{pmatrix} \begin{pmatrix} \mathbf{q}_1 \\ \mathbf{q}_2 \\ \mathbf{p}_1 \\ \mathbf{p}_2 \\ \lambda_1 \\ \lambda_2 \end{pmatrix} = \begin{pmatrix} -\mathbf{V}_1 \\ -\mathbf{V}_2 \\ \mathbf{E}_1 \\ \mathbf{E}_2 \\ Q_{1,tot} \\ Q_{2,tot} \end{pmatrix} \quad (\text{S3})$$

where  $\mathbf{T}^{qq}$ ,  $\mathbf{T}^{pq}$ , and  $\mathbf{T}^{pp}$  are charge-charge, charge-dipole and dipole-dipole interaction matrices, respectively. The matrix on the left-hand side is of Eq. S3 referred to as the molecular tensor matrix.  $\mathbf{q}_j$  and  $\mathbf{p}_j$  are vectors that contain, respectively, the  $q_{j,i}$  and the components of  $p_{j,i}$ , for molecule  $j$ .  $\mathbf{V}_j$  is a vector of length  $N_j$  that contains the  $V_{j,i}$ , and  $\mathbf{E}_j$  is a vector of length  $3N_j$  that contains the components of the external field  $\mathbf{E}_{ext}$ . The inverse of the molecular tensor matrix become the molecular polarizability matrix,  $\alpha^{mol}$ , which has charge-charge, charge-dipole, dipole-dipole components:

$$\alpha^{mol} = \begin{pmatrix} \alpha_{qq}^{mol} & \alpha_{qp}^{mol} & \dots \\ \alpha_{pq}^{mol} & \alpha_{pp}^{mol} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \quad (\text{S4})$$

The molecular polarizability tensor,  $\alpha$  is computed as

$$\alpha = \sum_{j=1}^N \sum_{i=1}^N \left( \alpha_{q_i q_j}^{mol} \mathbf{R}_j \otimes \mathbf{R}_i - 2\alpha_{q_i p_j}^{mol} \otimes \mathbf{R}_i + \alpha_{p_i p_j}^{mol} \right) \quad (\text{S5})$$

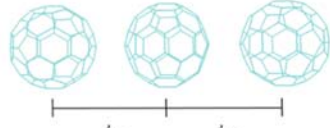
where  $N$  is the total number of atoms and  $\mathbf{R}_i$  is the vector defining atomic site  $i$ . The first, second, and third terms on the right-hand of eqn (S5) indicate charge flow, charge-dipole coupling, and induced dipole contributions to the molecular polarizability, respectively.

## 2. Charge transfer parameter and applying the extended Mayer-Åstrand model to the $(\text{C}_{60})_n$ cluster

The quantity  $2\eta$  is represented by exponential  $Ae^{-B \cdot R}$ , where  $A$  and  $B$  are determined by fitting the distance dependence of the intermolecular charge transfer of the  $\text{C}_{60}$  dimer from B3LYP calculations resulting from an external field of 0.001 a.u. in the  $z$  direction. Fig. 2 in the manuscript shows that the extended Mayer-Åstrand model closely reproduces the charge transfer from the B3LYP calculations over a wide range of  $R$  values. The charge transfer model described above is readily extended to clusters with more than two fullerene molecules.

Fig. S1 shows the molecular tensor matrices for  $(C_{60})_3$ .

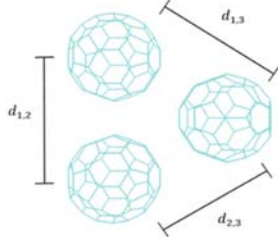
**(a) Linear  $C_{60}$  trimer**



$d_{1,2}$  : Center to center distance  
between molecule 1 and 2

$$\begin{pmatrix} \mathbf{T}_{11}^{qq} & \mathbf{T}_{12}^{qq} & \mathbf{T}_{13}^{qq} & -\mathbf{T}_{11}^{pq} & -\mathbf{T}_{12}^{pq} & -\mathbf{T}_{13}^{pq} & 1 & 0 & 0 \\ \mathbf{T}_{21}^{qq} & \mathbf{T}_{22}^{qq} & \mathbf{T}_{23}^{qq} & -\mathbf{T}_{21}^{pq} & -\mathbf{T}_{22}^{pq} & -\mathbf{T}_{23}^{pq} & 0 & 1 & 0 \\ \mathbf{T}_{31}^{qq} & \mathbf{T}_{32}^{qq} & \mathbf{T}_{33}^{qq} & -\mathbf{T}_{31}^{pq} & -\mathbf{T}_{32}^{pq} & -\mathbf{T}_{33}^{pq} & 0 & 0 & 1 \\ -\mathbf{T}_{11}^{pq} & -\mathbf{T}_{12}^{pq} & -\mathbf{T}_{13}^{pq} & -\mathbf{T}_{11}^{pp} & -\mathbf{T}_{12}^{pp} & -\mathbf{T}_{13}^{pp} & 0 & 0 & 0 \\ -\mathbf{T}_{21}^{pq} & -\mathbf{T}_{22}^{pq} & -\mathbf{T}_{23}^{pq} & -\mathbf{T}_{21}^{pp} & -\mathbf{T}_{22}^{pp} & -\mathbf{T}_{23}^{pp} & 0 & 0 & 0 \\ -\mathbf{T}_{31}^{pq} & -\mathbf{T}_{32}^{pq} & -\mathbf{T}_{33}^{pq} & -\mathbf{T}_{31}^{pp} & -\mathbf{T}_{32}^{pp} & -\mathbf{T}_{33}^{pp} & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 2\eta(d_{1,2}) & -2\eta(d_{1,2}) & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & -2\eta(d_{1,2}) & 2\eta(d_{1,2}) + 2\eta(d_{2,3}) & -2\eta(d_{2,3}) \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & -2\eta(d_{2,3}) & 2\eta(d_{2,3}) \end{pmatrix}$$

**(b) Triangular  $C_{60}$  trimer**



$$\begin{pmatrix} \mathbf{T}_{11}^{qq} & \mathbf{T}_{12}^{qq} & \mathbf{T}_{13}^{qq} & -\mathbf{T}_{11}^{pq} & -\mathbf{T}_{12}^{pq} & -\mathbf{T}_{13}^{pq} & 1 & 0 & 0 \\ \mathbf{T}_{21}^{qq} & \mathbf{T}_{22}^{qq} & \mathbf{T}_{23}^{qq} & -\mathbf{T}_{21}^{pq} & -\mathbf{T}_{22}^{pq} & -\mathbf{T}_{23}^{pq} & 0 & 1 & 0 \\ \mathbf{T}_{31}^{qq} & \mathbf{T}_{32}^{qq} & \mathbf{T}_{33}^{qq} & -\mathbf{T}_{31}^{pq} & -\mathbf{T}_{32}^{pq} & -\mathbf{T}_{33}^{pq} & 0 & 0 & 1 \\ -\mathbf{T}_{11}^{pq} & -\mathbf{T}_{12}^{pq} & -\mathbf{T}_{13}^{pq} & -\mathbf{T}_{11}^{pp} & -\mathbf{T}_{12}^{pp} & -\mathbf{T}_{13}^{pp} & 0 & 0 & 0 \\ -\mathbf{T}_{21}^{pq} & -\mathbf{T}_{22}^{pq} & -\mathbf{T}_{23}^{pq} & -\mathbf{T}_{21}^{pp} & -\mathbf{T}_{22}^{pp} & -\mathbf{T}_{23}^{pp} & 0 & 0 & 0 \\ -\mathbf{T}_{31}^{pq} & -\mathbf{T}_{32}^{pq} & -\mathbf{T}_{33}^{pq} & -\mathbf{T}_{31}^{pp} & -\mathbf{T}_{32}^{pp} & -\mathbf{T}_{33}^{pp} & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 2\eta(d_{1,2}) + 2\eta(d_{1,3}) & -2\eta(d_{1,2}) & -2\eta(d_{1,3}) \\ 0 & 1 & 0 & 0 & 0 & 0 & -2\eta(d_{1,2}) & 2\eta(d_{1,2}) + 2\eta(d_{2,3}) & -2\eta(d_{2,3}) \\ 0 & 0 & 1 & 0 & 0 & 0 & -2\eta(d_{1,3}) & -2\eta(d_{2,3}) & 2\eta(d_{1,3}) + 2\eta(d_{2,3}) \end{pmatrix}$$

**Fig. S1** Molecular tensor matrices with  $\eta$  terms that damp the intermolecular charge transfer for linear and triangular  $C_{60}$  trimers.