

**Supplementary Information for “Thousand-Atom Ab Initio Calculations of
Excited States at Organic/Organic Interfaces: Toward First-Principles
Investigations of Charge Photogeneration”**

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Fragment-based excited-state theory

In this section, we present the details of the excited-state calculations. Following our earlier study,⁴ we briefly summarize the formulations of the fragment-based excited-state method. This method is based on the multi-layer formulation of fragment molecular orbital method (FMO)⁵⁻⁷ and configuration interaction single (CIS) theory.⁸ In this theory, an excited-state wave function of a total system is described from the diabatic states representing localized excitations or intermolecular charge-transfer (CT) states. The diabatic state is represented by a singly-substituted configuration state function (CSF), $|e_{Ia}h_{Ji}\rangle$, which denotes a state comprising an electron on an a th orbital of an I th molecule and a hole on an i th orbital of a J th molecule. Hereafter, subscripts i and j refer to the indices of occupied MOs, and a and b refer to the indices of virtual MOs. The fragment CSF for the intramolecular local excitation is described, $|LE_{Im}\rangle = \sum_{ia} b_{ia}^{Im} |e_{Ia}h_{Ji}\rangle$, where $|LE_{Im}\rangle$ indicates an m th excited state of an I th molecule, and $b_{ia}^{(Im)}$ is a corresponding singlet CIS amplitude. The fragment CSFs of the intermolecular CT states is given by $|CT\rangle = |e_{Ia}h_{Ji}\rangle$ ($I \neq J$). Using this notation, each term in Eq.(1) can be rewritten as follows:

$$\begin{aligned}
 |LE(C)\rangle &= |LE_I\rangle (I = C_{60}) \\
 |CT(C^-P^+)\rangle &= |e_{Ia}h_{Ji}\rangle \\
 (I = C_{60}, J = \text{PEN}, a = \text{LUMO}, \text{LUMO} + 1 \text{ or } \text{LUMO} + 2, i = \text{HOMO}) \\
 |LE(P)\rangle &= |LE_I\rangle (I = \text{PEN}) \\
 |CT(P^-P^+)\rangle &= |e_{Ia}h_{Ji}\rangle (I, J = \text{PEN}, a = \text{LUMO}, i = \text{HOMO}). \tag{S1}
 \end{aligned}$$

Hereafter, we drop the subscript m because the first excited states ($m=1$) are only considered as the LE states. The number of those fragment CSFs are shown in the Table S1.

We summarize the Hamiltonian matrix elements. Diagonal elements describe the excitation

TABLE S1: The number of fragment CSFs to describe the excited-state wavefunction in the face-on and edge-on configurations

	Face-on	Edge-on
LE(C)	20	15
LE(P)	24	36
CT(C ⁻ P ⁺)	1440	1620
CT(P ⁻ P ⁺)	552	1260

energies of the LE and CT states:⁸

$$E(LE_I) = \sum_{ijab} b_{ia} b_{jb} \left[\delta_{ij} \delta_{ab} (\epsilon_a - \epsilon_i) + 2(ia|jb) - (ij|ab) \right] \quad (ijab \in I) \quad (\text{S2})$$

$$E(e_{Ia} h_{Ji}) = \epsilon_a - \epsilon_i - (ii|aa) \quad (i \in J, a \in I), \quad (\text{S3})$$

where ϵ_i and ϵ_a are i th and a th orbital energies, and $(ia|jb)$ is an electron-electron interaction term and is defined by

$$(ia|jb) = \int \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\psi_i(\mathbf{r}_1) \psi_a(\mathbf{r}_1) \psi_j(\mathbf{r}_2) \psi_b(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (\text{S4})$$

Note that $(ii|aa)$ describes the Coulomb interaction between an electron in an a th orbital and an hole in an i th orbital.

Off-diagonal elements among the LE states are given by the excitonic Coulomb coupling.^{4,9}

$$\langle LE_I | H | LE_J \rangle = V_{IJ}^{Ex}. \quad (\text{S5})$$

Those between the LE and CT states are calculated by the CIS amplitude and the electron (t^e) or hole (t^h) transfer integrals.^{10,11}

$$\langle LE_I | H | e_{Ib} h_{Lj} \rangle = - \sum_i b_{ib}^{(Im)} t_{ij}^h \quad (\text{S6})$$

$$\langle LE_I | H | e_{Jb} h_{Ij} \rangle = \sum_i b_{ib}^{(Im)} t_{ij}^e \quad (\text{S7})$$

$$\langle e_{Ia} h_{Ji} | H | e_{Ib} h_{Jj} \rangle = \delta_{JL} \delta_{ij} t_{ab}^e - \delta_{IK} \delta_{ab} t_{ij}^h \quad (\text{S8})$$

Here, the orbital energies and transfer integrals were obtained as the diagonal and off-diagonal elements of the Fock represented in the basis fragment MOs. The Fock matrix were calculated using the FMO-linear combination of molecular orbital (LCMO) method.^{10,11} The adiabatic excited states of the total system was obtained by diagonalizing the Hamiltonian matrix elements represented in the diabatic basis.

The FMO excited-state calculations were performed using the locally-modified version of the ABINIT-MP program.^{12,13} In the FMO calculations, each molecule was assigned as single independent fragment. Here, the number of parameters for the excited-state calculations are $(n_{LE}, n_{occ}, n_{vir})=(1, 0, 3)$ for a C_{60} molecule and $(1, 1, 1)$ for a PEN molecule.⁴ Same number of occupied and virtual orbitals were used to constructing the FMO-LCMO Fock matrix. The dimer-es and dimer-2e approximation were employed with threshold values of 2.0 and 0.0, respectively.^{4,12} Environmental electrostatic potentials in monomer and dimer self-consistent field calculations were approximated by using the Mulliken point-charge approximation.¹²

Corrections for electron correlation

Here, we present the energy corrections for the diagonal elements calculated at the FMO-CIS/6-31G** level. The diagonal elements of LE and CT states were corrected according to

$$E(LE_I) = E(CIS-LE_I) + \Delta E_{LE}, \quad (S9)$$

$$E(CT_{IaJi}) = E(CIS-CT_{IaJi}) + \Delta\epsilon_a + \Delta\epsilon_i. \quad (S10)$$

Here, ΔE_{LE} is the excitation energy difference between CIS and time-dependent density functional theory (TDDFT), and $\Delta\epsilon_a$ and $\Delta\epsilon_i$ are orbital energy differences between the Hartree-Fock and the Kohn-Sham (KS) theories

The correction term of the excitation energy was obtained using TDDFT with Tamm-Dancoff approximation (TDA).¹⁴ The TDA is more appropriate than the conventional TDDFT, because it corresponds to the CIS theory using KS orbitals. The long-range corrected ω B97XD functional¹⁵ was used for the reference KS/TDA calculations. In this study, we used $\omega=0.18$ for the range separation parameter, which was determined for C_{60} and pentacene molecules.¹⁶ The energy difference

between HF/CIS and KS/TDA were computed for the isolated molecule of pentacene or C₆₀; each molecular structure was optimized at the B3LYP/6-31G** level. The single-molecule calculations were performed using the Gaussian09 software.¹⁷ The correction terms of the excitation energy, HOMO and LUMO energies are presented in Table S2.

We note that above correction scheme is inconsistent for LE and CT energies. The excitation energies can be decomposed into one-electron term of orbital difference and two-electron term of electron-electron interactions. The ΔE_{LE} includes both the one-electron and two-electron terms. By contrast, the CT energies were corrected by the one-electron term, which is not consistent with the correction for the LE states. However, we argue that the two-electron correction term in the CT energy would be negligible. First, with the long-range correction, the exchange potential becomes pure HF exchange for larger electron-electron separation, which is the case for the interfragment CT state. Second, the electron correlation is short-range interaction, and the interfragment electron correlation does not play significant role in the CT energies. Therefore, we expect that the present correction does not play crucial artifacts in the results.

TABLE S2: Excitation energy (eV) of first excited state ($E(LE)$), and HOMO and LUMO energies calculated at ω B97XD/TDA and HF/CIS levels with 6-31G** basis set.

	ω B97/TDA	HF/CIS	Δ
C ₆₀			
E(LE)	2.575	2.895	-0.320
HOMO	-5.992	-5.870	-0.121
LUMO	-1.056	0.590	-1.647
Pentacene			
E(LE)	2.518	3.059	-0.542
HOMO	-7.519	-7.583	0.065
LUMO	-2.004	-0.429	-1.575

Wave function analyses

In the manuscript, the excited states were characterized by different wave function properties defined below. Inverse participation ratios (IPRs) denote the number of molecules where the electron or hole wave function is delocalized. To extract the IPRs from an adiabatic state, we first calculated the electron or hole population on an I th molecule as follows:

$$p_I^e = \sum_k |\langle k | \Psi \rangle|^2 \quad (\text{S11})$$

$$p_I^h = \sum_k |\langle k | \Psi \rangle|^2 \quad (\text{S12})$$

Here, $\langle k |$ denotes some diabatic state (LE or CT). Each summation runs over basis functions (LE or CT) whose electron or hole wave function belong to the I th molecule. The IPRs of electron and hole wave functions were calculated from electron and hole populations, respectively.

$$IPRe = \frac{1}{\sum_I (p_I^e)^2}, \quad (\text{S13})$$

$$IPRh = \frac{1}{\sum_I (p_I^h)^2}, \quad (\text{S14})$$

where the summation runs over the total number of molecules in the quantum-mechanical regions (44 in the face-on configuration and 51 in the edge-on configuration).

The electron-hole separation was calculated from the center-of-mass distance between electron and hole wave functions. With \mathbf{r}_e or \mathbf{r}_h being the electron or hole position operator, the center-of-mass of electron or hole wave function (\mathbf{R}_e or \mathbf{R}_h) is

$$\mathbf{R}_e = \langle \Psi | \mathbf{r}_e | \Psi \rangle, \quad (\text{S15})$$

$$\mathbf{R}_h = \langle \Psi | \mathbf{r}_h | \Psi \rangle. \quad (\text{S16})$$

The electron-hole separation was defined as $R_{eh} = |\mathbf{R}_e - \mathbf{R}_h|$. The extent of the delocalization was quantified as the variance of electron-hole separation (σ_{eh}^2) as follows:

$$S_{eh}^2 = \langle \Psi | (\mathbf{r}_e - \mathbf{r}_h) - R_{eh})^2 | \Psi \rangle \quad (\text{S17})$$

The quantities above were computed from the non-relaxed density matrix of CIS excited states.;[?] this analysis is essentially the same as the detachment-attachment analysis proposed by Head-Gordon et al.¹⁸ To calculate the quantities above, for each diabatic state, the atomic charges describing electron and hole densities were first computed as the Mulliken atomic charges of virtual-virtual and occupied-occupied blocks of the non-relaxed density matrix, respectively. The electron or hole atomic charges for an excited state adiabatic state can be described as the linear combination of those for diabatic states. Eqs. S13-S17 were computed from the electron or hole Mulliken charges and nuclear coordinates.

Finally, the oscillator strength (OS) of an adiabatic excited state was calculated according to

$$OS = \frac{2}{3} E |\langle G|\mu|\Psi_A\rangle|^2. \quad (\text{S18})$$

The absorption spectra were computed from the OSs.

Charge-transfer couplings

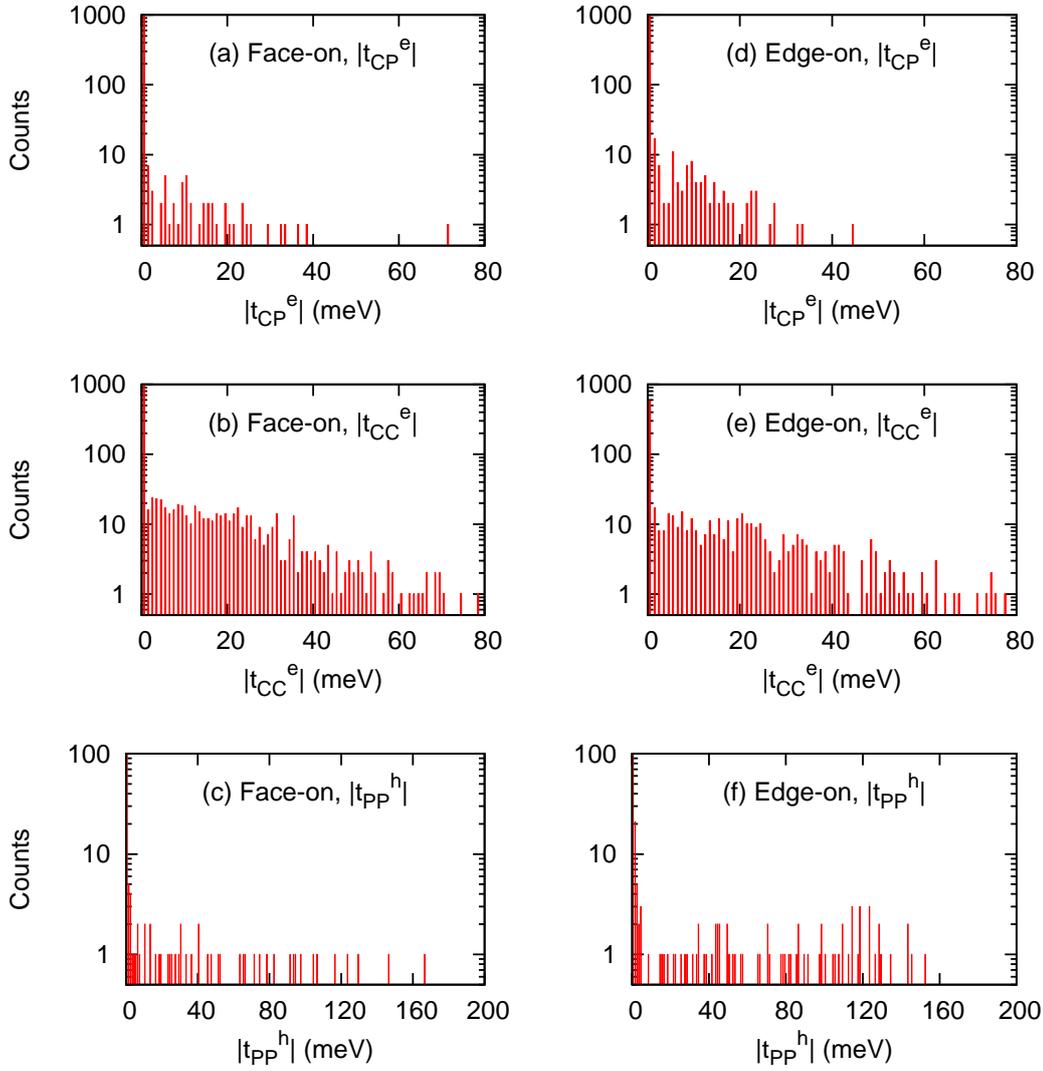


FIG. S1: The electron and hole transfer integrals (TIs) in the face-on and edge-on configurations: (a)(d) C_{60} -pentacene (PEN) electron TIs (t_{CP}^e), (b)(e) C_{60} - C_{60} electron TIs (t_{CC}^e), and (c)(f) PEN-PEN hole TIs (t_{PP}^h).

Visualization of the lowest ICT states

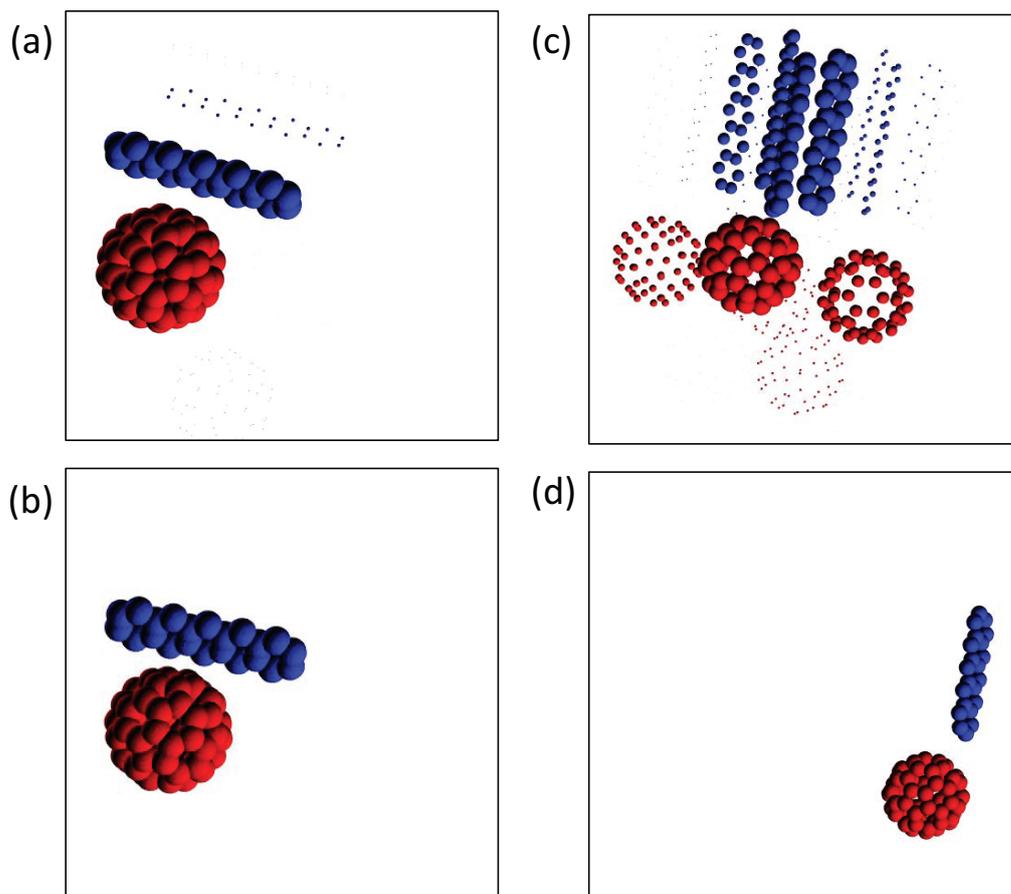


FIG. S2: Visualization of the lowest ICT states shown in Table 1. The lowest (a) adiabatic and (b) diabatic ICT states in the edge-on configuration; the lowest (c) adiabatic and (d) diabatic ICT states in the face-on configuration. In (a)-(d), the red and blue color represent electron and hole wave functions, respectively. The atoms were visualized according to the electron or hole population on the molecule.

CT-state manifold in the face-on configurations

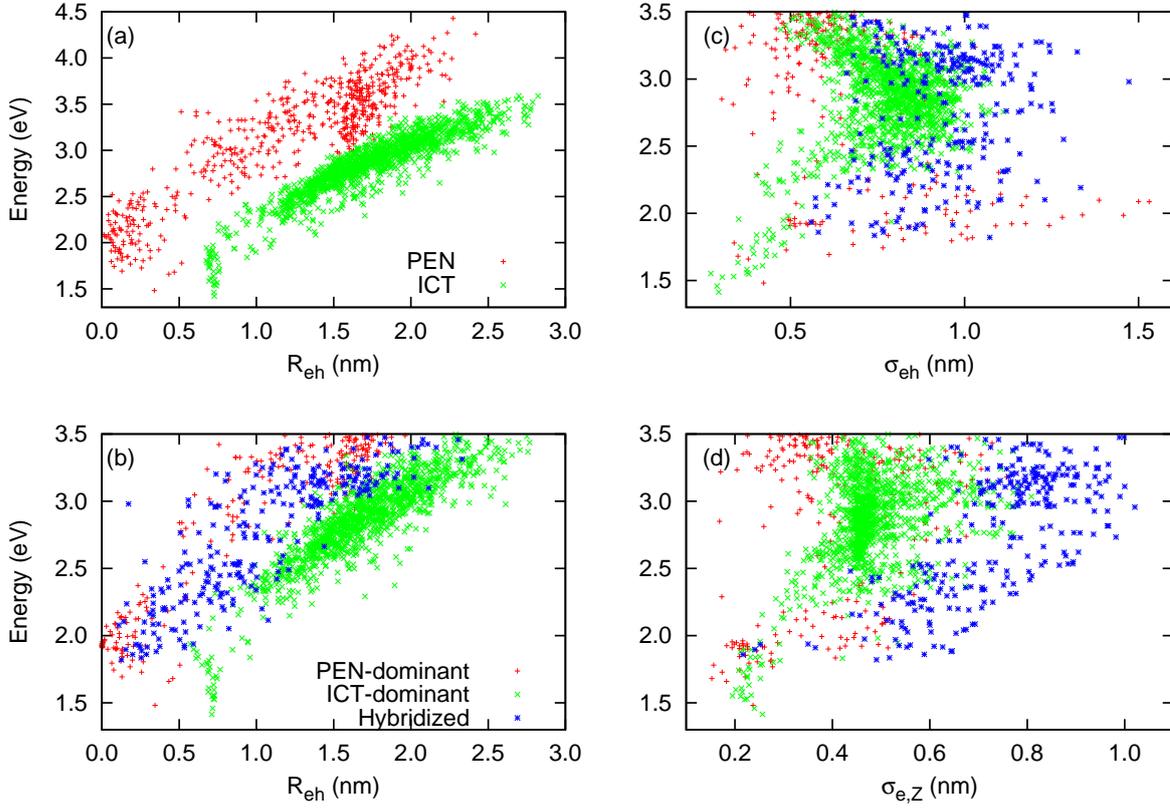


FIG. S3: (a) Excitation energy versus electron-hole separation (R_{eh}) for pure PEN states and pure ICT states of the face-on configuration. Excitation energy versus (b) R_{eh} , (c) electron-hole delocalization (σ_{eh}), and (d) electron delocalization along Z direction ($\sigma_{e,z}$) for adiabatic excited states of the face-on configuration. In (b)–(d), the PEN-dominant, ICT-dominant, and hybridized state are plotted respectively in red, green, and blue.

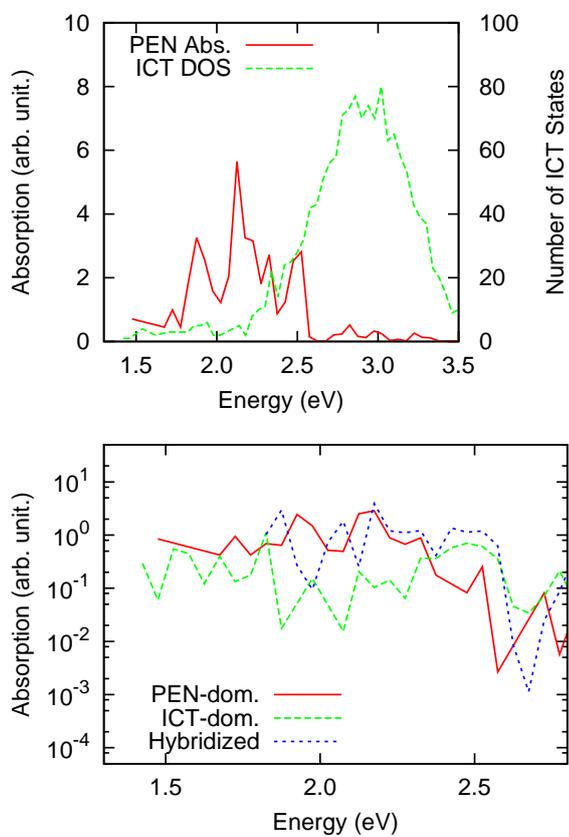


FIG. S4: (a) The absorption spectrum of pure PEN states (red) and the density of pure ICT states (green). (b) The absorption spectra of PEN-dominant (red), ICT-dominant (green), and hybridized states (blue) in the face-on configuration.

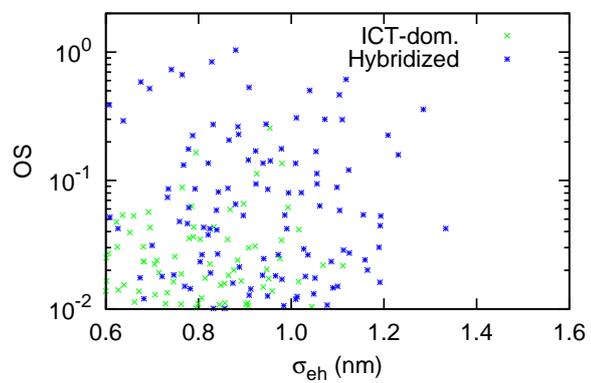


FIG. S5: Oscillator strength (OS) versus electron-hole delocalization (σ_{gh}) for ICT-dominant (green) and hybridized (blue) states in the face-on configuration.

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- ⁴ T. Fujita and Y. Mochizuki, *J. Phys. Chem. A*, 2018, **122**, 3886–3898.
- ⁵ K. Kitaura, E. Ikeo, T. Asada, T. Nakano and M. Uebayasi, *Chem. Phys. Lett.*, 1999, **313**, 701 – 706.
- ⁶ D. G. Fedorov, T. Ishida and K. Kitaura, *The Journal of Physical Chemistry A*, 2005, **109**, 2638–2646.
- ⁷ Y. Mochizuki, S. Koikegami, S. Amari, K. Segawa, K. Kitaura and T. Nakano, *Chem. Phys. Lett.*, 2005, **406**, 283–288.
- ⁸ J. B. Foresman, M. Head-Gordon, J. A. Pople and M. J. Frisch, *J. Phys. Chem.*, 1992, **96**, 135–149.
- ⁹ K. J. Fujimoto, *J. Chem. Phys.*, 2012, **137**, 034101.
- ¹⁰ S. Tsuneyuki, T. Kobori, K. Akagi, K. Sodeyama, K. Terakura and H. Fukuyama, *Chem. Phys. Lett.*, 2009, **476**, 104–108.
- ¹¹ H. Kitoh-Nishioka and K. Ando, *J. Chem. Phys.*, 2016, **145**, 114103.
- ¹² T. Nakano, T. Kaminuma, T. Sato, Y. Akiyama, M. Uebayasi and K. Kitaura, *Chem. Phys. Lett.*, 2002, **351**, 475–480.
- ¹³ S. Tanaka, Y. Mochizuki, Y. Komeiji, Y. Okiyama and K. Fukuzawa, *Phys. Chem. Chem. Phys.*, 2014, **16**, 10310–10344.
- ¹⁴ S. Hirata and M. Head-Gordon, *Chem. Phys. Lett.*, 1999, **314**, 291 – 299.
- ¹⁵ J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615–6620.
- ¹⁶ Z. Zheng, J.-L. Brédas and V. Coropceanu, *J. Phys. Chem. Lett.*, 2016, **7**, 2616–2621.
- ¹⁷ M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09 Revision E.01*, Gaussian Inc. Wallingford CT 2009.

¹⁸ M. Head-Gordon, A. M. Grana, D. Maurice and C. A. White, *J. Phys. Chem.*, 1995, **99**, 14261–14270.