

**Supporting Information for
Variable Electronic Coupling in Phenylacetylene Dendrimers: The Role of Förster,
Dexter, and Charge-Transfer Interactions**

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Synthetic Procedures

General procedure for synthesis of 1-Ph, 2-Ph and 3-Ph: As described in Xu et al.,¹ a flask was charged with the reagents. The flask was evacuated and back-filled with nitrogen three times, sealed and stirred at 70°C for 24 hours or longer. The solution was removed from heat, washed 3x with ether, dried with anhydrous magnesium sulfate, and filtered. The solvent was then removed by rotary evaporation. Products were purified by silica gel column chromatography, eluting with n-hexanes, and multiple recrystallizations from 2:1 CH₂Cl₂/methanol solution. The purity of each product was verified by HPLC, using a mobile phase of 4:1 n-hexanes/CH₂Cl₂.

Preparation of 1-Ph: A heavy-walled flask was charged with 3,5-di-*tert*-butylphenylacetylene (0.52 g, 2.49 mmol), 1,3-diiodobenzene (0.90 g, 2.88 mmol), Pd(dba)₂ (43.8 mg, 0.0478 mmol), triphenylphosphine (67.8 mg, 0.258 mmol), copper(I) iodide (9.3 mg, 0.0496 mmol), and dry triethylamine (12 mL, 0.48 mmol). Product is a white crystalline solid, 0.460 g, yield 48%. EI *m/z* (relative intensity): 84.0 (5), 115.0 (3), 172.1 (5), 186.1 (25), 209.1 (2), 215.1, 241.1 (1), 275.2 (2), 301.1 (7), 316.1 (2), 359.3 (2), 373.0 (5), 387.3 (55), 402.3 (M⁺, 100), 426.3 (1), 489.2 (1).

Preparation of 2-Ph: A heavy-walled flask was charged with 3,5-di-*tert*-butylphenylacetylene (0.97 g, 4.53 mmol), 1,3-diiodobenzene (0.74 g, 2.24 mmol), Pd(dba)₂ (41.4 mg, 0.0452 mmol), triphenylphosphine (59.3 mg, 0.226 mmol), copper(I) iodide (8.1 mg, 0.0428 mmol), and dry triethylamine (23 mL, 0.908 mmol). Product is a white crystalline solid, 0.233 g, yield 20%. EI *m/z* (relative intensity): 222.1 (3), 236.2 (21), 252.0 (5), 315.1 (1), 359.2 (1), 415.3 (1), 473.1 (5), 487.4 (45), 502.4 (M⁺, 100).

Preparation of 3-Ph: A heavy-walled flask was charged with 3,5-di-*tert*-butylphenylacetylene (1.10 g, 5.14 mmol), 1,3,5-tribromobenzene (0.56 g, 1.78 mmol), Pd(dba)₂ (30.1 mg, 0.0331 mmol), triphenylphosphine (47.0 mg, 0.180 mmol), copper(I) iodide (6.4 mg, 0.0335 mmol), and dry triethylamine (25 mL, 0.99 mmol). Product is a white crystalline solid, 0.310 g, yield 26%. EI *m/z* (relative intensity): 77.1 (21), 103.1 (2), 131.0 (2), 168.1 (1), 183.1 (15), 198.2 (15), 233.1 (10), 262.1 (11), 277.1 (43), 290.2 (1), 328.2 (1), 342.3 (23), 357.3 (1), 383.2 (12), 426.4 (38), 446.2 (53), 517.4 (2), 532.4 (12), 582.3 (1), 685.0 (1), 699.6 (12), 714.6 (M⁺, 100). Mass spectrum taken prior to recrystallization.

Preparation of 1,3-bis(trimethylsilyl ethynyl)benzene (2-TMS): To a Schlenk tube containing Cl₂Pd(PPh₃)₂ (0.42 g, 0.6 mmol), CuI (0.06 g, 0.3 mmol), 1,3-diiodobenzene (4.95 g, 15.0 mmol) in NEt₃ (20 mL), was added trimethylsilyl acetylene (5.89 g, 60.0 mmol). The mixture was frozen and thawed for three times, then it was heated at 75 °C in an oil bath for 20 hours. The mixture was rinsed with ether and filtered, the solvent was then removed by rotary evaporation. Silica gel column chromatography (hexanes 100 %, R_f = 0.50) gave white solid 3.87 g, yield 96%. mp: 48–49 °C. ¹H NMR (CDCl₃) δ 7.59 (broad s, 1 H), 7.39 (broad d, J = 7.9 Hz, 2 H), 7.23 (broad t, J = 7.7 Hz, 1 H), 0.24 (s, 18 H) ppm; ¹³C NMR (CDCl₃) δ 135.4, 131.7, 128.2, 123.3, 104.0, 94.8, -0.1 ppm; EIMS *m/z* (relative intensity): 272 (4), 271 (9), 270 (M⁺, 35), 257 (11), 256 (26), 255 (100), 241 (2), 225 (5), 197 (2), 155 (1), 120 (4), 73 (5); HRMS: calculated 270.1260 for C₁₆H₂₂Si₂, obtained 270.1254.

Preparation of 1,3,5-tris(trimethylsilyl ethynyl)benzene (3-TMS): To a Schlenk tube containing Cl₂Pd(PPh₃)₂ (0.42 g, 0.6 mmol), CuI (0.03 g, 0.15 mmol), 1,3,5-tribromobenzene (3.15 g, 10.0 mmol) in NEt₃ (40 mL), was added trimethylsilyl acetylene (4.42 g, 45.0 mmol). The mixture was frozen and thawed for three times, then it was heated at 45 °C in an oil bath for 50 hours. The mixture was rinsed with ether and filtered, the solvent was then removed by rotary evaporation. Silica gel column chromatography (hexanes 100 %, R_f = 0.63) followed by recrystallization from hexanes gave white crystals 2.67 g, yield

73%. mp: 75-76 °C. ^1H NMR (CDCl_3) δ 7.49 (s, 3 H), 0.23 (s, 27 H) ppm; ^{13}C NMR (CDCl_3) δ 134.9, 123.6, 103.1, 95.5, -0.2 ppm; EIMS m/z (relative intensity): 368 (9), 367 (18), 366 (M^+ , 48), 353(19), 352 (38), 351 (100), 336 (3), 321 (4), 279 (6), 255 (3), 181 (9), 168 (10), 73 (10); HRMS: calculated 366.1655 for $\text{C}_{21}\text{H}_{30}\text{Si}_3$, obtained 366.1653.

Theoretical Methods

Unless otherwise specified, all calculations use the 6-31G basis set² and are calculated using the MOLPRO 2002.4 program.³ Ground state DFT optimizations are done using JAGUAR⁴ using the basis set 6-31G**. All coordinates are in Å unless otherwise specified. Transition dipole moments and energies are specified in atomic units. State averaged CASSCF calculations are described by SA- N -CASSCF(m/n), where N specifies the number of states present in the state averaging and m and n specify the number of electrons and orbitals in the active space.^{5,6} The particular CASSCF wavefunction is specified for each calculation. CASPT2 calculations are done using an internally contracted second order perturbation theory code within MOLPRO.^{7,8} The same active space is used for the CASPT2 as is used for the CASSCF calculation at a particular geometry. Level shifts are sometimes used for these calculations and the specific shift is mentioned for each molecule. The number of orbitals cored is mentioned for each calculation. Most calculations are performed in C_1 symmetry. Larger calculations are run in C_s symmetry and are noted individually. The coupling calculations on 2-Ph and P2-Ph are performed by taking linear combinations of the active orbitals to form orbitals which are localized on the two DPA units in the molecules. Following this rotation, a second CASSCF calculation is performed to find the Hamiltonian in the basis of the configurations using the localized orbitals. These matrix elements of the Hamiltonian are used to find the coupling. The coupling, T_{LR} , is computed based on the model presented by Harcourt, et al.⁹ The case of non-identical chromophores has previously been studied.¹⁰

Development of expressions for T_{LR}

Identical Chromophores

For the case of identical chromophores, we define the two localized wavefunctions to be:

$$\Psi_L = N \left(|A^*B\rangle + \lambda |A^+B^-\rangle + \mu |A^-B^+\rangle \right) \quad (\text{S1})$$

$$\Psi_R = N \left(|AB^*\rangle + \mu |A^+B^-\rangle + \lambda |A^-B^+\rangle \right) \quad (\text{S2})$$

and the normalization factor is

$$N = (1 + \lambda^2 + \mu^2)^{-1/2}. \quad (\text{S3})$$

Because of the non-orthogonal nature of these created wavefunctions, the overlap S_{LR} is not zero.

Therefore the expression for the coupling becomes

$$T_{LR} = H_{LR} - S_{LR} E_{RR} \quad (\text{S4})$$

and the energy E_{RR} is equal to E_{LL} because the chromophores are identical. The terms in this equation are

$$H_{LR} = N^2 (V_{cc} + 2\mu V_{ic} + 2\lambda V_{ic} + 2\lambda\mu E_i + (\lambda^2 + \mu^2)V_{ii}) \quad (\text{S5})$$

$$E_{RR} = N^2 (E_c + (\lambda^2 + \mu^2)E_i + 2\lambda V_{ic} + 2\mu V_{ic} + 2\lambda\mu V_{ii}) \quad (\text{S6})$$

$$S_{LR} = N^2 (2\lambda\mu). \quad (\text{S7})$$

The Hamiltonian in the basis of the four configurations of interests for identical chromophores is

$$H = \begin{pmatrix} E_c & V_{ic} & V'_{ic} & V_{cc} \\ V_{ic} & E_i & V_{ii} & V'_{ic} \\ V'_{ic} & V_{ii} & E_i & V_{ic} \\ V_{cc} & V'_{ic} & V_{ic} & E_c \end{pmatrix} \quad (S8)$$

The expression for T_{LR} in terms of these matrix elements is

$$T_{LR} = N^2 \left(V_{cc} + 2\mu V_{ic} (1 - 2N^2 \lambda^2) + 2\lambda V'_{ic} (1 - 2N^2 \mu^2) \right. \\ \left. + V_{ii} (\lambda^2 + \mu^2 - 4N^2 \lambda^2 \mu^2) + 2\lambda\mu N^2 (E_i - E_c) \right) \quad (S9)$$

In order to calculate the values for T_{LR} we must obtain values for λ and μ . The values can be determined by perturbation theory or more exactly by finding the eigenvectors of the Hamiltonian matrix that only includes the configurations for one of the localized wavefunctions. Therefore, for Ψ_L we find the eigenvectors of the following matrix in which the basis is $|A^*B\rangle$, $|A^+B^-\rangle$, and $|A^-B^+\rangle$.

$$H = \begin{pmatrix} E_c & V_{ic} & V'_{ic} \\ V_{ic} & E_i & V_{ii} \\ V'_{ic} & V_{ii} & E_i \end{pmatrix} \quad (S10)$$

The eigenvector corresponding to the mainly covalent state is of the form

$$\Psi_L = c_1 |A^*B\rangle + c_2 |A^+B^-\rangle + c_3 |A^-B^+\rangle \quad (S11)$$

and the coefficients λ and μ are determined by

$$\lambda = \frac{c_2}{c_1}; \quad \mu = \frac{c_3}{c_1}. \quad (S12)$$

When we compare the values of λ and μ found in Equation (S12) to those calculated with perturbation theory, we find that first order perturbation theory overestimates the values by more than 30%. Because of this, we choose not to use perturbation theory to calculate the values of λ and μ . Instead we use the values found from Equation (S12). Using these values in Equation (S9), the coupling becomes

$$T_{LR} = c_1^2 V_{cc} + 2c_1 c_3 V_{ic} (1 - 2c_2^2) + 2c_1 c_2 V'_{ic} (1 - 2c_3^2) \\ + 2c_1^2 c_2 c_3 (E_i - E_c) + V_{ii} (c_2^2 + c_3^2 - 4c_2^2 c_3^2) \quad (S13)$$

This form of the coupling equation is used to calculate the coupling for all cases of identical chromophores in this work.

Non-identical Chromophores

When the two chromophores are not identical, the form of the coupling terms become more complicated because we can no longer assume the same form of the Hamiltonian seen in Equation (S10). The form of the Hamiltonian becomes

$$H = \begin{pmatrix} E_{cl} & V_{ic1} & V'_{ic1} & V_{cc} \\ V_{ic1} & E_{i1} & V_{ii} & V'_{ic2} \\ V'_{ic1} & V_{ii} & E_{i2} & V_{ic2} \\ V_{cc} & V'_{ic2} & V_{ic2} & E_{c2} \end{pmatrix} \quad (S14)$$

where instead of six unique matrix elements seen in Equation (S8), there are now ten unique elements. Additionally, the equations for the localized wavefunctions are now

$$\Psi_L = N_1 (|A^*B\rangle + \lambda |A^+B^-\rangle + \mu |A^-B^+\rangle) \quad (S15)$$

$$\Psi_R = N_1 (|AB^*\rangle + \gamma |A^+B^-\rangle + \eta |A^-B^+\rangle) \quad (S16)$$

and the normalization constants are

$$N_1 = (1 + \lambda^2 + \mu^2)^{-1/2} \quad (\text{S17})$$

$$N_2 = (1 + \gamma^2 + \eta^2)^{-1/2} \quad (\text{S18})$$

The form of the coupling becomes

$$T_{LR} = H_{LR} - S_{LR} \left(\frac{E_{RR} + E_{LL}}{2} \right) \quad (\text{S19})$$

The terms in this equation are given by

$$H_{LR} = N_1 N_2 \left((V_{cc} + \mu V_{ic2} + \lambda V'_{ic2} + \gamma V_{ic1} + \eta V'_{ic1} + \lambda \gamma E_{i1} + \mu \eta E_{i2} + (\lambda \eta + \mu \gamma) V_{ii}) \right) \quad (\text{S20})$$

$$E_{LL} = N_1^2 \left(E_{c1} + \lambda^2 E_{i1} + \mu^2 E_{i2} + 2\lambda V_{ic1} + 2\mu V'_{ic1} + 2\lambda \mu V_{ii} \right) \quad (\text{S21})$$

$$E_{RR} = N_2^2 \left(E_{c2} + \gamma^2 E_{i1} + \eta^2 E_{i2} + 2\eta V_{ic2} + 2\gamma V'_{ic2} + 2\gamma \eta V_{ii} \right) \quad (\text{S22})$$

$$S_{LR} = N_1 N_2 (\lambda \mu + \gamma \eta). \quad (\text{S23})$$

The expression for T_{LR} can be written as

$$\begin{aligned} T_{LR} = & N_1 N_2 \left\{ V_{cc} + V_{ic2} (\mu - N_2^2 \lambda \mu \eta - N_2^2 \gamma \eta^2) + V'_{ic2} (\lambda - N_2^2 \lambda \mu \gamma - N_2^2 \gamma^2 \eta) \right. \\ & + V_{ic1} (\gamma - N_1^2 \lambda^2 \mu - N_1^2 \lambda \gamma \eta) + V'_{ic1} (\eta - N_1^2 \lambda \mu^2 - N_1^2 \mu \gamma \eta) \\ & + V_{ii} (\lambda \eta + \mu \gamma - N_1^2 \lambda^2 \mu^2 - N_2^2 \gamma^2 \eta^2 - \lambda \mu \gamma (N_1^2 + N_2^2)) \\ & + E_{i1} \left(\gamma \lambda - \frac{N_1^2 \lambda^3 \mu + N_1^2 \lambda^2 \gamma \eta + N_2^2 \lambda \mu \gamma^2 + N_2^2 \gamma^3 \eta}{2} \right) \\ & + E_{i2} \left(\mu \eta - \frac{N_1^2 \lambda \mu^3 + N_1^2 \mu^2 \gamma \eta + N_2^2 \lambda \mu \eta^2 + N_2^2 \gamma \eta^3}{2} \right) \\ & \left. - \frac{1}{2} N_1^2 E_{c1} (\lambda \mu + \gamma \eta) - \frac{1}{2} N_2^2 E_{c2} (\lambda \mu + \gamma \eta) \right\} \end{aligned} \quad (\text{S24})$$

In order to determine the coefficients λ , μ , γ and η , the two small Hamiltonian matrices corresponding to each of the localized wavefunctions Ψ_R and Ψ_L are formed, as shown below.

$$H_1 = \begin{pmatrix} E_{c1} & V_{ic1} & V'_{ic1} \\ V_{ic1} & E_{i1} & V_{ii} \\ V'_{ic1} & V_{ii} & E_{i2} \end{pmatrix} \quad H_2 = \begin{pmatrix} E_{i1} & V_{ii} & V'_{ic2} \\ V_{ii} & E_{i2} & V_{ic2} \\ V'_{ic2} & V_{ic2} & E_{c2} \end{pmatrix} \quad (\text{S25})$$

The eigenvectors of these matrices corresponding to the mainly covalent state, shown below,

$$\Psi_L = c_1 |A^*B\rangle + c_2 |A^+B^-\rangle + c_3 |A^-B^+\rangle \quad (\text{S26})$$

$$\Psi_R = d_1 |AB^*\rangle + d_2 |A^+B^-\rangle + d_3 |A^-B^+\rangle \quad (\text{S27})$$

are used to determine the coefficients

$$\lambda = \frac{c_2}{c_1}; \quad \mu = \frac{c_3}{c_1}; \quad \gamma = \frac{d_2}{d_1}; \quad \eta = \frac{d_3}{d_1}. \quad (\text{S28})$$

By inserting these values, along with the matrix elements of the Hamiltonian seen in Equation (S14), into the relationship for the coupling, Equation (S24), the value of the coupling for a system with non-identical chromophore can be calculated. In the limit of identical chromophores ($\lambda=\eta$, $\mu=\gamma$), Equation (S24) reduces to Equation (S9). The coupling relation seen in Equation (S24) is used to find the coupling for all non-identical chromophores in this work.

References

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Table I
 Cartesian coordinates of **1-Ph S₀** minimum at B3LYP/6-31G**, optimized using Jaguar with C₁ symmetry.

C	-4.8349911	-0.0001850	0.0000000
C	-4.1328869	1.2033854	0.0000000
C	-2.7412050	1.2018935	0.0000000
C	-2.0350419	0.00666392	0.0000000
C	-2.7421684	-1.2087250	0.0000000
C	-4.1329968	-1.2092552	0.0000000
C	-0.5991214	0.0067512	0.0000000
C	0.5991792	0.0068446	0.0000000
C	2.0351172	0.0069565	0.0000000
C	2.7414106	1.2021605	0.0000000
C	2.7419478	-1.2085701	0.0000000
C	4.1327526	-1.2094275	0.0000000
C	4.8348727	-0.0005198	0.0000000
C	4.1331325	1.2032330	0.0000000
H	-5.9079688	0.0007961	0.0000000
H	-4.6626915	2.1363227	0.0000000
H	-2.2034329	2.1297736	0.0000000
H	-2.1983699	-2.1328208	0.0000000
H	-4.6653818	-2.1409159	0.0000000
H	2.2038498	2.1301549	0.0000000
H	4.6632931	2.1359674	0.0000000
H	5.9078559	0.0003161	0.0000000
H	4.6649721	-2.1411828	0.0000000
H	2.1978598	-2.1324901	0.0000000

Table IICartesian coordinates of 2-Ph S₀ minimum at B3LYP/6-31G**, optimized using Jaguar with C₁ symmetry.

C	0.0000000	0.0000000	0.0000000
C	1.3926100	0.0000000	0.0000000
C	2.1047500	1.2165700	0.0000000
C	1.3837200	2.4282800	0.0000000
C	-0.0086600	2.4187100	0.0000000
C	-0.7054100	1.2068200	0.0000000
C	3.5307400	1.2247600	0.0000000
C	4.7469000	1.2388700	0.0000000
C	6.1726800	1.2720900	0.0000000
C	6.9232000	0.0779200	0.0000000
C	8.3159700	0.1269400	0.0000000
C	8.9841900	1.3498300	0.0000000
C	8.2529000	2.5558900	0.0000000
C	6.8485000	2.5043000	0.0000000
C	8.9215400	3.8153500	0.0000000
C	9.4796100	4.8960800	0.0000000
C	10.1246600	6.1677100	0.0000000
C	11.5312500	6.2609600	0.0000000
C	12.1535200	7.5067800	0.0000000
C	11.3892500	8.6772400	0.0000000
C	9.9936700	8.5955800	0.0000000
C	9.3628800	7.3542600	0.0000000
H	6.4036000	-0.8745800	0.0000000
H	8.8862800	-0.7972700	0.0000000
H	10.0685200	1.3875900	0.0000000
H	6.2790900	3.4269900	0.0000000
H	12.1210300	5.3498700	0.0000000
H	13.2381400	7.5652800	0.0000000
H	11.8781300	9.6471100	0.0000000
H	9.3953000	9.5021100	0.0000000
H	8.2797100	7.2859900	0.0000000
H	1.9440400	-0.9348000	0.0000000
H	-0.5370200	-0.9441600	0.0000000
H	-1.7915100	1.2029500	0.0000000
H	-0.5522100	3.3591300	0.0000000
H	1.9287700	3.3668000	0.0000000

Table IIICartesian coordinates of 3-Ph S₀ minimum at B3LYP/6-31G**, optimized using Jaguar with C_s symmetry.

C	1.1798892	7.5928326	0.0000000
C	1.1864489	6.2004144	0.0000000
C	-0.0270801	5.4830039	0.0000000
C	-1.2424584	6.1973925	0.0000000
C	-1.2393834	7.5899113	0.0000000
C	-0.0305808	8.2921534	0.0000000
C	-0.0245839	4.0576288	0.0000000
C	-0.0210667	2.8419711	0.0000000
C	-0.0139861	1.4164167	0.0000000
C	-1.2241287	0.7002588	0.0000000
C	-1.2227010	-0.7054286	0.0000000
C	0.0025131	-1.3951728	0.0000000
C	1.2195496	-0.6913129	0.0000000
C	1.2043239	0.7146012	0.0000000
C	2.4582111	-1.3975847	0.0000000
C	3.5139962	-2.0006275	0.0000000
C	4.7515432	-2.7085891	0.0000000
C	5.9762545	-2.0104843	0.0000000
C	7.1823081	-2.7066251	0.0000000
C	7.1894164	-4.1045489	0.0000000
C	5.9800391	-4.8059965	0.0000000
C	4.7691972	-4.1183023	0.0000000
C	-2.4516579	-1.4277926	0.0000000
C	-3.4980306	-2.0474295	0.0000000
C	-4.7244028	-2.7747754	0.0000000
C	-5.9597070	-2.0952529	0.0000000
C	-7.1549046	-2.8096398	0.0000000
C	-7.1407549	-4.2075472	0.0000000
C	-5.9211134	-4.8906260	0.0000000
C	-4.7207296	-4.1847567	0.0000000
H	-2.1662562	1.2363837	0.0000000
H	0.0081010	-2.4791808	0.0000000
H	2.1398267	1.2621511	0.0000000
H	5.9654060	-0.9251835	0.0000000
H	8.1195024	-2.1575948	0.0000000
H	8.1319685	-4.6442558	0.0000000
H	5.9808171	-5.8921938	0.0000000
H	3.8276594	-4.6581942	0.0000000
H	2.1235576	5.6529224	0.0000000
H	2.1214075	8.1344269	0.0000000
H	-0.0319131	9.3782968	0.0000000
H	-2.1821975	8.1292384	0.0000000
H	-2.1782329	5.6475924	0.0000000
H	-5.9653239	-1.0098976	0.0000000
H	-8.1002212	-2.2747787	0.0000000
H	-8.0749903	-4.7614647	0.0000000
H	-5.9054154	-5.9766939	0.0000000
H	-3.7710758	-4.7102917	0.0000000

Table IV Optimized geometries of 2-Ph using C_{2v} symmetry and the 6-31G basis set

Cartesian coordinates of the ground state minimum geometry at SA-1-CASSCF(4/4)

C	0.0000000	0.0000000	0.8217651
C	0.0000000	0.0000000	3.5929848
C	0.0000000	1.2106467	1.5102201
C	0.0000000	-1.2106467	1.5102201
C	0.0000000	1.2021010	2.9051129
C	0.0000000	-1.2021010	2.9051129
C	0.0000000	2.4551789	0.7882670
C	0.0000000	-2.4551789	0.7882670
C	0.0000000	3.4984511	0.1830649
C	0.0000000	-3.4984511	0.1830649
C	0.0000000	4.7432664	-0.5390524
C	0.0000000	-4.7432664	-0.5390524
C	0.0000000	4.7511006	-1.9342922
C	0.0000000	-4.7511006	-1.9342922
C	0.0000000	5.9584846	0.1465382
C	0.0000000	-5.9584846	0.1465382
C	0.0000000	7.1555877	-0.5508185
C	0.0000000	-7.1555877	-0.5508185
C	0.0000000	5.9506361	-2.6274912
C	0.0000000	-5.9506361	-2.6274912
C	0.0000000	7.1553893	-1.9386273
C	0.0000000	-7.1553893	-1.9386273
H	0.0000000	0.0000000	-0.2496138
H	0.0000000	0.0000000	4.6655080
H	0.0000000	2.1319871	3.4384046
H	0.0000000	-2.1319871	3.4384046
H	0.0000000	3.8197713	-2.4656854
H	0.0000000	-3.8197713	-2.4656854
H	0.0000000	5.9577275	1.2188150
H	0.0000000	-5.9577275	1.2188150
H	0.0000000	8.0839515	-0.0130877
H	0.0000000	-8.0839515	-0.0130877
H	0.0000000	5.9444467	-3.7003199
H	0.0000000	-5.9444467	-3.7003199
H	0.0000000	8.0833785	-2.4770644
H	0.0000000	-8.0833785	-2.4770644

Cartesian coordinates of the emitting geometry (S_2) at SA-5-CASSCF(4/4).

C	0.0000000	0.7368090	0.0000000
C	0.0000000	3.5592593	0.0000000
C	1.2188046	1.4283989	0.0000000
C	-1.2188046	1.4283989	0.0000000
C	1.2058806	2.8774402	0.0000000
C	-1.2058806	2.8774402	0.0000000
C	2.4445332	0.7494022	0.0000000
C	-2.4445332	0.7494022	0.0000000
C	3.5047297	0.1621026	0.0000000
C	-3.5047297	0.1621026	0.0000000
C	4.7434645	-0.5240990	0.0000000
C	-4.7434645	-0.5240990	0.0000000
C	4.7843964	-1.9278834	0.0000000
C	-4.7843964	-1.9278834	0.0000000
C	5.9550663	0.1858281	0.0000000
C	-5.9550663	0.1858281	0.0000000
C	7.1614710	-0.4886483	0.0000000
C	-7.1614710	-0.4886483	0.0000000
C	5.9957708	-2.5924342	0.0000000
C	-5.9957708	-2.5924342	0.0000000
C	7.1891621	-1.8784606	0.0000000
C	-7.1891621	-1.8784606	0.0000000
H	0.0000000	-0.3345039	0.0000000
H	0.0000000	4.6317318	0.0000000
H	2.1379234	3.4043745	0.0000000
H	-2.1379234	3.4043745	0.0000000
H	3.8640011	-2.4777648	0.0000000
H	-3.8640011	-2.4777648	0.0000000
H	5.9331062	1.2577591	0.0000000
H	-5.9331062	1.2577591	0.0000000
H	8.0798239	0.0659685	0.0000000
H	-8.0798239	0.0659685	0.0000000
H	6.0129203	-3.6651269	0.0000000
H	-6.0129203	-3.6651269	0.0000000
H	8.1274405	-2.3983121	0.0000000
H	-8.1274405	-2.3983121	0.0000000

Table V Optimized geometries of P2-Ph using C_s symmetry and the 6-31G basis set

Cartesian coordinates of the ground state minimum optimized with SA-1-CASSCF(4/4).

C	1.4066538	0.0000001	0.0000000
C	-1.3980303	0.0000001	0.0000000
C	0.6937726	1.2031083	0.0000000
C	0.6937726	-1.2031081	0.0000000
C	-0.6862509	-1.2031785	0.0000000
C	-0.6862509	1.2031786	0.0000000
C	2.8379839	0.0000001	0.0000000
C	-2.8320848	0.0000001	0.0000000
C	4.0360238	0.0000001	0.0000000
C	-4.0393543	0.0000001	0.0000000
C	5.4741399	0.0000000	0.0000000
C	-5.4775248	0.0000000	0.0000000
C	6.1804107	1.2017784	0.0000000
C	6.1804106	-1.2017784	0.0000000
C	-6.1845357	-1.2031158	0.0000000
C	-6.1845358	1.2031158	0.0000000
C	7.5664434	1.1998351	0.0000000
C	7.5664433	-1.1998352	0.0000000
C	-7.5698624	-1.2006087	0.0000000
C	-7.5698625	1.2006086	0.0000000
C	8.2623363	-0.0000001	0.0000000
C	-8.2660120	-0.0000001	0.0000000
H	1.2302303	2.1310618	0.0000000
H	1.2302303	-2.1310617	0.0000000
H	-1.2225391	-2.1312983	0.0000000
H	-1.2225391	2.1312985	0.0000000
H	5.6415213	2.1288212	0.0000000
H	5.6415212	-2.1288212	0.0000000
H	-5.6456589	-2.1301333	0.0000000
H	-5.6456591	2.1301333	0.0000000
H	8.0992438	2.1310595	0.0000000
H	8.0992436	-2.1310597	0.0000000
H	-8.1030473	-2.1315471	0.0000000
H	-8.1030475	2.1315469	0.0000000
H	9.3352899	-0.0000001	0.0000000
H	-9.3388758	-0.0000001	0.0000000

Cartesian coordinates of the emitting geometry (S_1) at SA-4-CASSCF(4/4).

C	1.4001150	0.0000000	0.0000000
C	-1.4337103	0.0000000	0.0000000
C	0.6711168	1.2229614	0.0000000
C	0.6711168	-1.2229614	0.0000000
C	-0.6888289	-1.2311025	0.0000000
C	-0.6888289	1.2311025	0.0000000
C	2.8061140	0.0000000	0.0000000
C	-2.8060147	0.0000000	0.0000000
C	4.0209194	0.0000000	0.0000000
C	-4.0382477	0.0000000	0.0000000
C	5.4459244	0.0000000	0.0000000
C	-5.4206980	0.0000000	0.0000000
C	6.1594147	1.2055308	0.0000000
C	6.1594147	-1.2055308	0.0000000
C	-6.1548618	-1.2214951	0.0000000
C	-6.1548618	1.2214950	0.0000000
C	7.5427721	1.2012958	0.0000000
C	7.5427721	-1.2012958	0.0000000
C	-7.5290073	-1.2085253	0.0000000
C	-7.5290073	1.2085252	0.0000000
C	8.2407231	0.0000000	0.0000000
C	-8.2303567	0.0000000	0.0000000
H	1.2161825	2.1460941	0.0000000
H	1.2161825	-2.1460940	0.0000000
H	-1.2278057	-2.1578558	0.0000000
H	-1.2278057	2.1578558	0.0000000
H	5.6209457	2.1327638	0.0000000
H	5.6209457	-2.1327638	0.0000000
H	-5.6163147	-2.1482590	0.0000000
H	-5.6163147	2.1482590	0.0000000
H	8.0764198	2.1321228	0.0000000
H	8.0764198	-2.1321228	0.0000000
H	-8.0679277	-2.1361196	0.0000000
H	-8.0679277	2.1361196	0.0000000
H	9.3135084	0.0000000	0.0000000
H	-9.3024879	0.0000000	0.0000000

Table VI Optimized Geometries of 1-H compounds
 Cartesian coordinates of 1-H ground state minimum at SA-3-CASSCF(4/4)/6-31G with no symmetry constraints.

C	-2.2312437	0.0083525	0.0005846
C	-1.5296389	1.2164214	0.0002259
C	-0.1355226	1.2131887	0.0000483
C	0.5662522	-0.0045530	0.0000790
C	-0.1483844	-1.2039475	0.0000739
C	-1.5277325	-1.2002897	0.0006221
C	2.0076431	-0.0113684	-0.0005561
C	3.2008164	-0.0169371	-0.0009564
H	4.2536994	-0.0216635	-0.0011401
H	-3.3038542	0.0074323	0.0009676
H	0.3883590	-2.1324646	-0.0010497
H	-2.0632530	-2.1298959	0.0005769
H	-2.0616421	2.1480345	0.0001454
H	0.4106876	2.1358034	-0.0002903

Cartesian coordinates of 1-H emitting geometry (S_2) at SA-3-CASSCF(4/4)/6-31G with no symmetry constraints.

C	-2.2131854	-0.0152073	0.0004774
C	-1.5171640	1.2395922	-0.0001979
C	-0.1566810	1.2679384	-0.0001013
C	0.5944731	-0.0003798	-0.0000506
C	-0.1452443	-1.2459900	-0.0001057
C	-1.5182230	-1.2390930	-0.0002031
C	1.9664613	-0.0019756	0.0000467
C	3.1901178	-0.0033989	0.0001335
H	4.2517941	-0.0046338	0.0002089
H	-3.2851716	-0.0157888	0.0003886
H	0.4046461	-2.1661224	-0.0006153
H	-2.0647217	-2.1608033	0.0003273
H	-2.0837414	2.1499820	-0.0002362
H	0.3873086	2.1796584	-0.0000608

Table VII Optimized Geometries of **2-H** compounds

Cartesian coordinates of **2-H** ground state minimum at SA-4-CASSCF(4/4)/6-31G with no symmetry constraints.

C	-0.0023295	0.0191614	-0.0020634
C	1.3829339	0.0182713	-0.0002126
C	2.0890235	1.2100947	0.0024060
C	1.4071370	2.4349710	0.0032146
C	0.0036302	2.4403518	0.0016597
C	-0.7078637	1.2306049	-0.0009019
C	2.1356839	3.6767416	0.0044403
C	2.7399302	4.7052680	0.0053662
C	-2.1475620	1.2372016	-0.0020572
C	-3.3404376	1.2412237	-0.0030267
H	-0.5457110	-0.9047479	-0.0041288
H	1.9136405	-0.9136852	-0.0009113
H	3.1608718	1.2059906	0.0037960
H	-0.5263872	3.3711209	0.0022937
H	3.2728230	5.6135161	0.0062361
H	-4.3934696	1.2448498	-0.0038905

Cartesian coordinates of **2-H** emitting geometry (S_2) at SA-4-CASSCF(4/4)/6-31G with no symmetry constraints.

C	-0.7202850	1.1007884	0.5127266
C	0.0415274	0.0133488	-0.1303493
C	1.4070012	-0.0837988	0.0598052
C	2.0764850	0.8286133	0.8533466
C	1.3352988	1.9194752	1.5141367
C	-0.0418457	2.0164938	1.3162311
C	2.0424990	2.8234589	2.3213967
C	2.6947761	3.5737960	3.0057720
C	-2.1042068	1.1763114	0.2934750
C	-3.2913242	1.2001699	0.0768328
H	-0.4861935	-0.6896720	-0.7413631
H	1.9535873	-0.8751710	-0.4140220
H	3.1343223	0.7633998	1.0042568
H	-0.5875779	2.8068896	1.7914898
H	3.2553325	4.2330624	3.6057264
H	-4.3277814	1.2303632	-0.1066024

Table VIII Optimized Geometries of **3-H** compounds

Cartesian coordinates of **3-H** ground state minimum at SA-7-CASSCF(6/6)/6-31G with no symmetry constraints.

C	1.0971387	0.0017784	0.0000000
C	2.2899885	0.0073269	0.0000000
C	3.7333084	0.0145885	0.0000000
C	4.4454890	-1.1961470	0.0000000
C	5.8501380	-1.1932785	0.0000000
C	6.5425748	0.0288566	0.0000000
C	5.8377865	1.2439081	0.0000000
C	4.4331547	1.2324827	0.0000000
C	6.5530864	2.4974712	0.0000000
C	7.1443990	3.5334627	0.0000000
C	6.5782377	-2.4395128	0.0000000
C	7.1808262	-3.4689862	0.0000000
H	0.0440393	-0.0027855	0.0000000
H	7.6665264	4.4480236	0.0000000
H	3.9146709	-2.1264017	0.0000000
H	7.6136077	0.0342726	0.0000000
H	3.8929207	2.1573001	0.0000000
H	7.7125872	-4.3779796	0.0000000

Cartesian coordinates of **3-H** emitting geometry (**S₄**) at SA-7-CASSCF(6/6)/6-31G with no symmetry constraints.

C	1.0615602	-0.0160998	0.0000000
C	2.2581573	0.0349766	0.0000000
C	3.6782430	0.0672519	0.0000000
C	4.4253684	-1.2305436	0.0000000
C	5.9226638	-1.2133218	0.0000000
C	6.6077809	0.0035625	0.0000000
C	5.8715048	1.3042565	0.0000000
C	4.3772479	1.2761979	0.0000000
C	6.5613092	2.5127972	0.0000000
C	7.1606455	3.5579535	0.0000000
C	6.6176816	-2.4521926	0.0000000
C	7.1844697	-3.5072641	0.0000000
H	0.0093272	-0.0575732	0.0000000
H	7.6836814	4.4720147	0.0000000
H	3.8960441	-2.1583707	0.0000000
H	7.6779603	0.0256867	0.0000000
H	3.8517595	2.2087581	0.0000000
H	7.6850754	-4.4337099	0.0000000

Calculations done on 1-Ph, 2-Ph, and 3-Ph.

Calculations are done at ground state geometries, optimized using B3LYP/6-31G**. (See Tables I-III.)
CASSCF calculations are done using C_s symmetry. All the 1s orbitals are cored.

1-Ph	SA-4-CASSCF(8/8)		
State	E (hartree)	ΔE (eV)	TDM (a.u.)
S ₀	-535.82905343		
S ₁	-535.60834114	6.01	0.15
S ₂	-535.60785981	6.02	0.06
S ₃	-535.57794386	6.83	3.26

2-Ph	SA-4-CASSCF(4/4)		
State	E (hartree)	ΔE (eV)	TDM (a.u.)
S ₀	-840.89895604		
S ₁	-840.69948327	5.43	0.04
S ₂	-840.65635696	6.60	2.09
S ₃	-840.63556866	7.17	3.66

2-Ph	SA-6-CASSCF(12/12)		
State	E (hartree)	ΔE (eV)	TDM (a.u.)
S ₀	-840.99190687		
S ₁	-840.79425487	5.38	0.14
S ₂	-840.77270130	5.96	0.13
S ₃	-840.77267594	5.97	0.09
S ₄	-840.74475733	6.73	2.44
S ₅	-840.74298686	6.77	4.03

3-Ph	SA-7-CASSCF(6/6)		
State	E (hartree)	ΔE (eV)	TDM (a.u.)
S ₀	-1144.43817198		
S ₁	-1144.28494753	4.17	0.00
S ₂	-1144.18655664	6.85	0.32
S ₃	-1144.18647892	6.85	0.32
S ₄	-1144.18258588	6.95	0.00
S ₅	-1144.15553302	7.69	2.94
S ₆	-1144.15550052	7.69	2.94

Calculations done on 1-H

Calculations done on geometries listed in Table VI. All calculations use C_1 symmetry except for CASSCF(8/8) in which C_s symmetry is used. All calculations use 6-31G basis set unless otherwise mentioned. No orbitals are cored in the SA-3-CASSCF(4/4) calculations. The CASPT2 values are found from coring 8 orbitals (the 1s only) with a level shift of 0.1 hartree. Eight orbitals are cored in the CASSCF(8/8) calculations.

Ground State, State Averaged Minimum					
State	SA-3-CASSCF(4/4)			SA-3-CASSCF(4/4)*PT2	
	E (hartree)	ΔE (eV)	TDM (a.u.)	E (hartree)	ΔE (eV)
S_0	-306.30809865			-306.97380663	
S_1	-306.08576556	6.05	0.13	-306.78773403	5.06
S_2	-306.02202379	7.78	1.97	-306.74740208	6.16
SA-3-CASSCF(4/4)/6-31G**					
State	SA-3-CASSCF(4/4)/6-31G**			SA-3-CASSCF(4/4)*PT2/6-31G**	
	E (hartree)	ΔE (eV)	TDM (a.u.)	E (hartree)	ΔE (eV)
S_0	-306.42169543			-307.42257431	
S_1	-306.20223942	5.97	0.13	-307.24306410	4.88
S_2	-306.14256669	7.60	1.94	-307.21300793	5.70
SA-5-CASSCF(8/8) C_s symmetry					
State	SA-5-CASSCF(8/8) C_s symmetry				
	E (hartree)	ΔE (eV)	TDM (a.u.)		
S_0	-306.37035357				
S_1	-306.19477754	4.78	0.06		
S_2	-306.09986328	7.36	0.49		
S_3	-306.07933334	7.92	1.58		
S_4	-306.07294595	8.09	0.07		
Excited State, State Averaged Minimum					
State	SA-3-CASSCF(4/4)			SA-3-CASSCF(4/4)*PT2	
	E (hartree)	ΔE (eV)	TDM (a.u.)	E (hartree)	ΔE (eV)
S_0	-306.29489723			-306.97009055	
S_1	-306.08667020	5.67	0.13	-306.79388870	4.79
S_2	-306.03551130	7.06	2.20	-306.76666780	5.54
SA-3-CASSCF(4/4)/6-31G**					
State	SA-3-CASSCF(4/4)/6-31G**			SA-3-CASSCF(4/4)*PT2/6-31G**	
	E (hartree)	ΔE (eV)	TDM (a.u.)	E (hartree)	ΔE (eV)
S_0	-306.40676347			-307.41648483	
S_1	-306.20122437	5.59	0.13	-307.24630668	4.63
S_2	-306.15229926	6.92	2.21	-307.22890725	5.10
SA-5-CASSCF(8/8) C_s symmetry					
State	SA-5-CASSCF(8/8) C_s symmetry				
	E (hartree)	ΔE (eV)	TDM (a.u.)		
S_0	-306.36020996				
S_1	-306.19367083	4.53	0.07		
S_2	-306.12767281	6.33	0.44		
S_3	-306.09125683	7.32	1.86		
S_4	-306.07276796	7.82	0.74		

Calculations done on 2-H

Calculations done on geometries listed in Table VII. All calculations use C_1 symmetry and the 6-31G basis set unless otherwise mentioned. No orbitals are cored in the SA-4-CASSCF(4/4) calculations. The CASPT2 values are found from coring 10 orbitals (the 1s only) with no level shift. Ten orbitals are cored in the CASSCF(10/10) calculations.

Ground State, State Averaged Minimum					
State	SA-4-CASSCF(4/4)			SA-4-CASSCF(4/4)*PT2	
	E (hartree)	ΔE (eV)	TDM (a.u.)	E (hartree)	ΔE (eV)
S_0	-381.95007102			-382.80325989	
S_1	-381.73925227	5.74	0.00	-382.62988525	4.72
S_2	-381.67470648	7.49	1.53	-382.58730026	5.88
S_3	-381.64236692	8.37	2.79	-382.58359051	5.98
SA-4-CASSCF(4/4)/6-31G**, C_s					
State	SA-4-CASSCF(4/4)/6-31G**, C_s			SA-4-CASSCF(4/4)*PT2/6-31G**, C_s	
	E (hartree)	ΔE (eV)	TDM (a.u.)	E (hartree)	ΔE (eV)
S_0	-382.08964248			-383.34183240	
S_1	-381.88179049	5.67	0.00	-383.17707507	4.48
S_2	-381.82155385	7.29	1.48	-383.14279690	5.42
S_3	-381.78722706	8.23	2.78	-383.14067408	5.47
SA-7-CASSCF(10/10) C_s symmetry					
State	SA-7-CASSCF(10/10) C_s symmetry				
	E (hartree)	ΔE (eV)	TDM (a.u.)		
S_0	-382.04323568				
S_1	-381.87453580	4.59	0.04		
S_2	-381.78329272	7.07	0.48		
S_3	-381.76847934	7.48	0.60		
S_4	-381.75943527	7.72	1.01		
S_5	-381.74202690	8.20	2.50		
S_6	-381.73622305	8.35	0.05		
Excited State, State Averaged Minimum					
State	SA-4-CASSCF(4/4)			SA-4-CASSCF(4/4)*PT2	
	E (hartree)	ΔE (eV)	TDM (a.u.)	E (hartree)	ΔE (eV)
S_0	-381.93908171			-382.80018250	
S_1	-381.74362900	5.32	0.00	-382.63420169	4.52
S_2	-381.68488191	6.92	1.75	-382.60536564	5.30
S_3	-381.64016366	8.13	2.91	-382.58726246	5.79
SA-7-CASSCF(10/10) C_s symmetry					
State	SA-7-CASSCF(10/10) C_s symmetry				
	E (hartree)	ΔE (eV)	TDM (a.u.)		
S_0	-382.03536774				
S_1	-381.87622517	4.33	0.05		
S_2	-381.80487740	6.27	0.35		
S_3	-381.77874143	6.98	1.00		
S_4	-381.76347998	7.40	0.98		
S_5	-381.74792085	7.82	2.05		
S_6	-381.74661808	7.86	0.49		

Calculations done on 3-H

Calculations done on geometries listed in Table VIII. All calculations use C_s symmetry. No orbitals are cored in the SA-7-CASSCF(6/6) calculations. The CASPT2 values are found from coring 12 orbitals (1s only) with a level shift of 0.3 hartree. Twelve orbitals are cored in the CASSCF(12/12) calculations.

Ground State, State Averaged Minimum					
	SA-7-CASSCF(6/6)			SA-7-CASSCF(6/6)*PT2	
State	E (hartree)	ΔE (eV)	TDM (a.u.)	E (hartree)	ΔE (eV)
S ₀	-457.63157150			-458.61589573	
S ₁	-457.47035118	4.39	0.00	-458.45034848	4.50
S ₂	-457.36312643	7.30	0.17	-458.36511050	6.82
S ₃	-457.36312547	7.30	0.17	-458.36510917	6.82
S ₄	-457.35314302	7.58	0.00	-458.38883880	6.18
S ₅	-457.31711199	8.56	2.50	-458.38706603	6.23
S ₆	-457.31710704	8.56	2.50	-458.38705901	6.23
SA-7-CASSCF(12/12)					
State	E (hartree)	ΔE (eV)	TDM (a.u.)		
S ₀	-457.71650142				
S ₁	-457.55565626	4.38	0.00		
S ₂	-457.46378319	6.88	0.48		
S ₃	-457.46378013	6.88	0.48		
S ₄	-457.43931963	7.54	0.00		
S ₅	-457.42432950	7.95	2.35		
S ₆	-457.42432256	7.95	2.35		
Excited State, State Averaged Minimum					
	SA-7-CASSCF(6/6)			SA-7-CASSCF(6/6)*PT2	
State	E (hartree)	ΔE (eV)	TDM (a.u.)	E (hartree)	ΔE (eV)
S ₀	-457.60408496			-458.60033285	
S ₁	-457.46468304	3.79	0.01	-458.45499770	3.95
S ₂	-457.39014000	5.82	0.13	-458.38932301	5.74
S ₃	-457.35344044	6.82	0.14	-458.36243959	6.47
S ₄	-457.34469846	7.06	1.14	-458.40403219	5.34
S ₅	-457.30912993	8.03	2.43	-458.39312850	5.64
S ₆	-457.29793400	8.33	2.34	-458.37551101	6.12
SA-7-CASSCF(12/12)					
State	E (hartree)	ΔE (eV)	TDM (a.u.)		
S ₀	-457.69089090				
S ₁	-457.55261487	4.58	0.02		
S ₂	-457.49116503	5.43	0.27		
S ₃	-457.45279474	6.48	0.33		
S ₄	-457.43937383	6.84	1.22		
S ₅	-457.42310982	7.29	1.16		
S ₆	-457.41669445	7.46	2.03		

Calculations done on 2-Ph and P2-Ph

Calculations done on geometries listed in Tables IV and V. All calculations use C_s symmetry. The carbon 1s orbitals are cored in the calculations.

2-Ph			
	Absorbing geometry SA-5-CASSCF(4/4)		
State	E (hartree)	ΔE (eV)	TDM (a.u.)
S ₀	-840.89949145		
S ₁	-840.68657808	5.79	0.13
S ₂	-840.65415792	6.68	2.01
S ₃	-840.63798750	7.12	3.85
S ₄	-840.59414825	8.31	1.17
Emitting geometry SA-5-CASSCF(4/4)			
State	E (hartree)	ΔE (eV)	TDM (a.u.)
S ₀	-840.89162744		
S ₁	-840.69463738	5.36	0.15
S ₂	-840.66212935	6.24	2.24
S ₃	-840.64808057	6.63	4.15
S ₄	-840.59859248	7.97	0.77
Absorbing geometry SA-6-CASSCF(12/12)			
State	E (hartree)	ΔE (eV)	TDM (a.u.)
S ₀	-840.99529845		
S ₁	-840.78884524	5.62	0.12
S ₂	-840.76990754	6.13	0.16
S ₃	-840.76990059	6.13	0.07
S ₄	-840.74022320	6.94	2.33
S ₅	-840.73702291	7.03	3.94
Emitting geometry SA-6-CASSCF(12/12)			
State	E (hartree)	ΔE (eV)	TDM (a.u.)
S ₀	-840.98921843		
S ₁	-840.80055671	5.13	0.09
S ₂	-840.76811156	6.02	0.17
S ₃	-840.76806768	6.02	0.02
S ₄	-840.75134251	6.47	2.40
S ₅	-840.74560429	6.63	4.19
P2-Ph			
	Absorbing geometry SA-4-CASSCF(4/4)		
State	E (hartree)	ΔE (eV)	TDM (a.u.)
S ₀	-840.88929216		
S ₁	-840.69110102	5.39	4.96
S ₂	-840.63770700	6.85	0.00
S ₃	-840.62640026	7.15	0.00
Emitting geometry SA-4-CASSCF(4/4)			
State	E (hartree)	ΔE (eV)	TDM (a.u.)
S ₀	-840.87824772		
S ₁	-840.70425511	4.73	5.33
S ₂	-840.66330719	5.85	0.16
S ₃	-840.63052381	6.74	0.08

Elements of the Hamiltonian matrix in the basis of the constructed covalent and ionic configurations: $|A^*B\rangle$, $|AB^*\rangle$, $|A^+B\rangle$, and $|A^-B^+\rangle$. All energies are in hartree and all calculations are performed in C_s symmetry.

2-Ph Absorbing geometry using rotated orbitals from SA-6-CASSCF(12/12) calculation

	$ A^*B\rangle$	$ A^+B\rangle$	$ A^-B^+\rangle$	$ AB^*\rangle$
$\langle A^*B $	-1.8240988	0.0133021	0.0113739	0.0042090
$\langle A^+B $	0.0133021	-1.7736758	0.0130582	0.0113739
$\langle A^-B^+ $	0.0113739	0.0130582	-1.7736758	0.0133021
$\langle AB^* $	0.0042090	0.0113739	0.0133021	-1.8240988

2-Ph Emitting geometry using rotated orbitals from SA-6-CASSCF(12/12) calculation

	$ A^*B\rangle$	$ A^+B\rangle$	$ A^-B^+\rangle$	$ AB^*\rangle$
$\langle A^*B $	-1.8037965	0.0151326	0.0141326	0.0044582
$\langle A^+B $	0.0151326	-1.7534711	0.0133676	0.0141326
$\langle A^-B^+ $	0.0141326	0.0133676	-1.7534711	0.0151326
$\langle AB^* $	0.0044582	0.0141326	0.0151326	-1.8037965

P2-Ph Absorbing geometry using rotated orbitals from SA-4-CASSCF(4/4) calculation

	$ A^*B\rangle$	$ A^+B\rangle$	$ A^-B^+\rangle$	$ AB^*\rangle$
$\langle A^*B $	-1.8022643	-0.0345669	0.0287659	0.0155801
$\langle A^+B $	-0.0345669	-1.7389695	-0.0169664	0.0287659
$\langle A^-B^+ $	0.0287659	-0.0169664	-1.7389695	-0.0345669
$\langle AB^* $	0.0155801	0.0287659	-0.0345669	-1.8022643

P2-Ph Emitting geometry using rotated orbitals from SA-4-CASSCF(4/4) calculation

	$ A^*B\rangle$	$ A^+B\rangle$	$ A^-B^+\rangle$	$ AB^*\rangle$
$\langle A^*B $	-1.7818523	-0.0400289	0.0378268	0.0170246
$\langle A^+B $	-0.0400289	-1.7293053	-0.0203930	0.0311956
$\langle A^-B^+ $	0.0378268	-0.0203930	-1.7304168	-0.0396563
$\langle AB^* $	0.0170246	0.0311956	-0.0396563	-1.7864111

Localized Orbitals for P2-Ph

