Ultrafast nonradiative decay of electronically excited states of malachite green: *ab initio* calculations

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Supporting Information

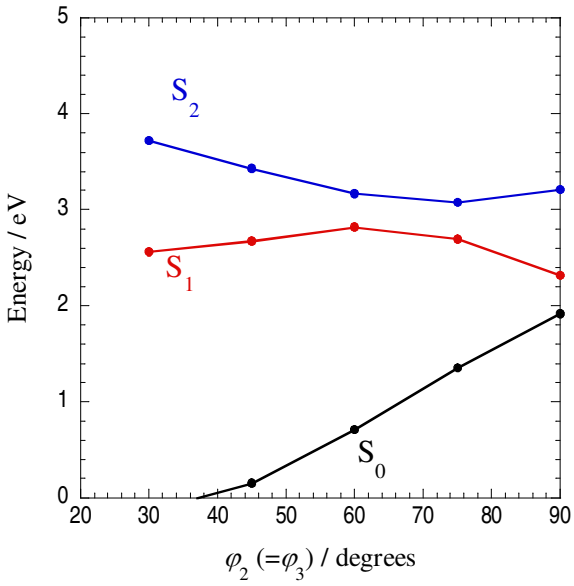

Figure S1. Potential energy profiles for fixed torsional angles of substituted phenyl rings $\varphi_2 = \varphi_3$, obtained by SA-CASSCF calculations. All other internal coordinates are optimized in the S_1 state at the SA-CASSCF level. Energies are relative to that at the equilibrium structure in the ground state.

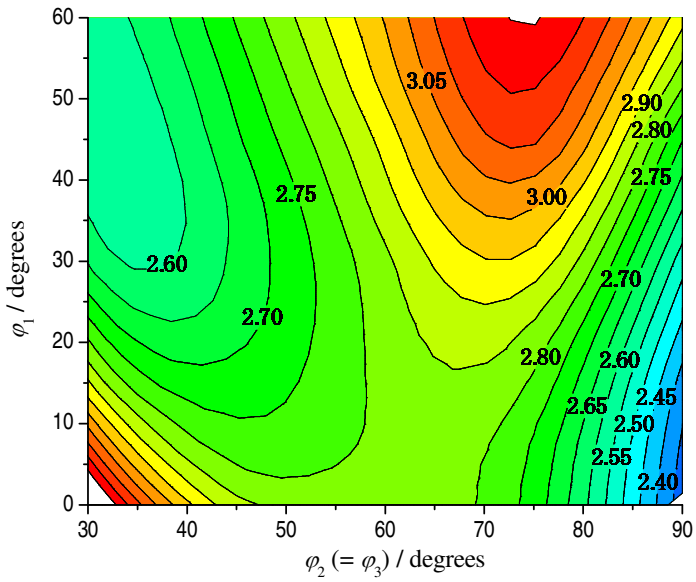

Figure S2. Contour plots of two-dimensional potential energy surface in the S_1 state for fixed torsinal angles, φ_1 and $\varphi_2 = \varphi_3$, obtained by SA-CASSCF calculations, where all other internal coordinates are optimized. Energies are relative to that at the equilibrium structure in the ground state.

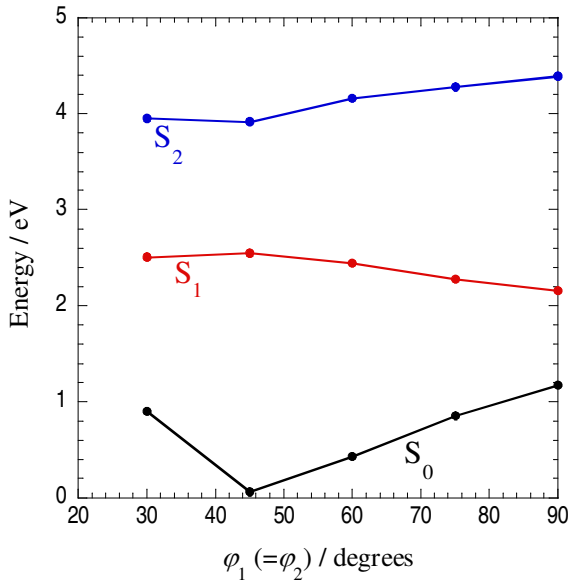

Figure S3. Potential energy profiles for fixed torsional angles of unsubstituted and one of substituted phenyl rings $\varphi_1 = \varphi_2$, obtained by SA-CASSCF calculations. Energies are relative to that at the equilibrium structure in the ground state. All other internal coordinates are optimized in the S_1 state at the SA-CASSCF level.

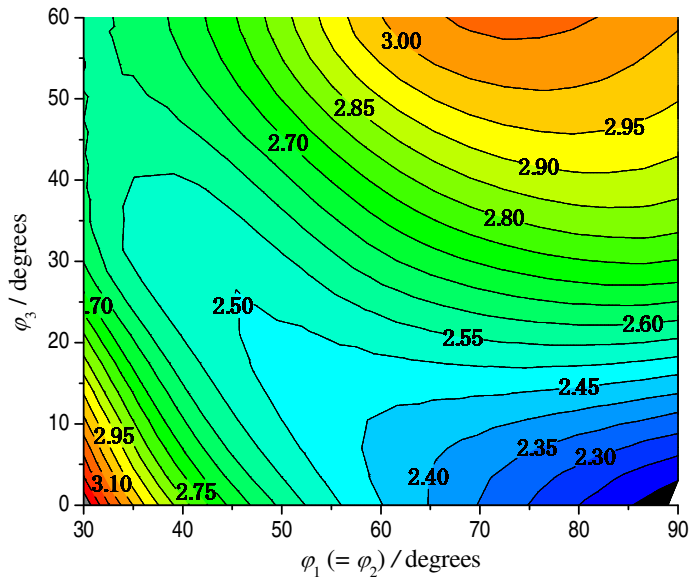

Figure S4. Contour plots of two-dimensional potential energy surface in the S_1 state for fixed torsional angles, $\varphi_1 = \varphi_2$ and φ_3, obtained by SA-CASSCF calculations, where all other internal coordinates are optimized. Energies are relative to that at the equilibrium structure in the ground state.

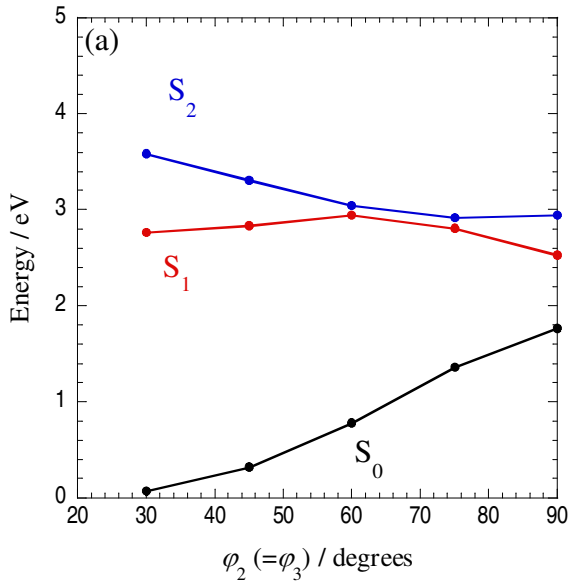

Figure S5. Potential energy profiles for fixed torsional angles of substituted phenyl rings $\varphi_2 = \varphi_3$, obtained by SA-CASSCF calculations. All other internal coordinates are optimized in the S_2 state at the SA-CASSCF level. Energies are relative to that at the equilibrium structure in the ground state.

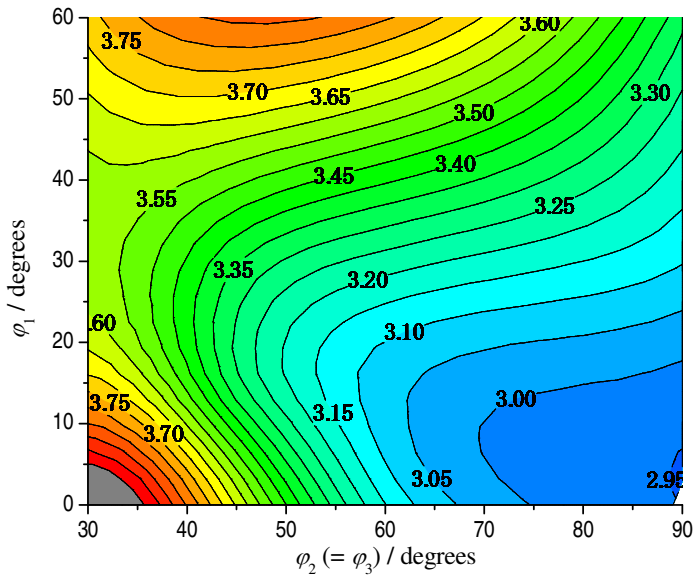

Figure S6. Contour plots of two-dimensional potential energy surface in the S_2 state for fixed torsional angles, φ_1 and $\varphi_2 = \varphi_3$, obtained by SA-CASSCF calculations, where all other internal coordinates are optimized. Energies are relative to that at the equilibrium structure in the ground state. The cross mark represents the position of the equilibrium structure in the electronic ground state.

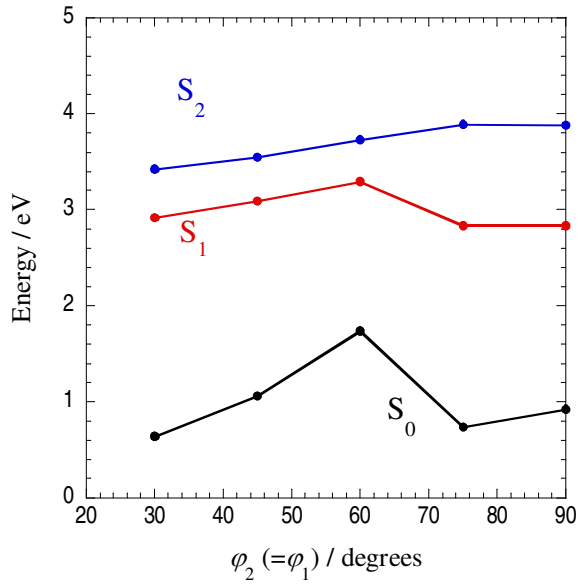

Figure S7. CASSCF potential energy profiles for fixed torsional angles of unsubstituted and one of substituted phenyl rings $\varphi_1 = \varphi_2$. All other internal coordinates are optimized in the S_2 state at the SA-CASSCF level. Energies are relative to that at the equilibrium structure in the ground state.

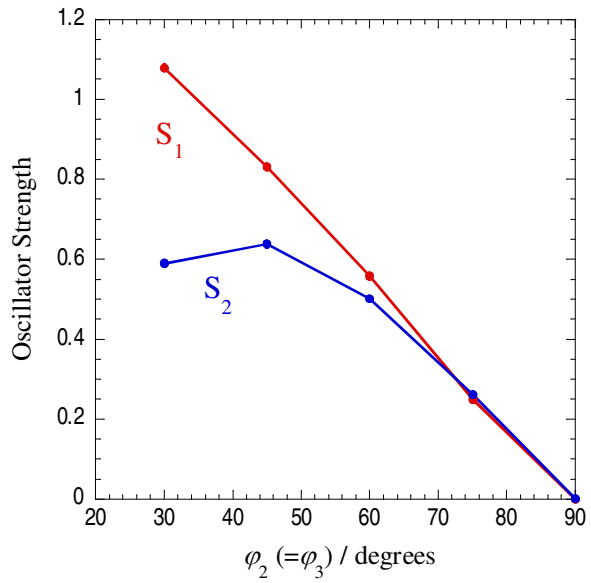

Figure S8. Oscillator strength for transitions from the S_1 and S_2 states to the S_0 state calculated by the SA-CASSCF method along the geometries given in Figure 5(a) and Figure 10(a).