Supporting Information

Controlling the Photo-stability of Pyrrole with Optical Nano Cavities

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Figure S1: Molecular orbitals of pyrrole considered in cas(8,7) active space used for the CASSCF calculations. The orbitals involved in the electronic transition of $\pi\sigma^*$ state are highlighted with red colored boxes.



Figure S2: Surface (a) and contour (b) plots of diabatic Couplings between ground and $\pi\sigma^*$ states of pyrrole along DIP and DOP coordinates computed at CASSCF(8,7)/aug-cc-pVDZ level of theory.



Figure S3: Suface (a) and contour (b) plots for the Y-component of transition dipole moments between ground and $\pi\sigma^*$ states of pyrrole along DIP and DOP coordinates in diabatic basis computed at CASSCF(8,7)/aug-cc-pVDZ level of theory.



Figure S4: Surface (a) and contour (b) plots for the Y-component of permanent dipole moments for the ground state of pyrrole along DIP and DOP coordinates in diabatic basis computed at CASSCF(8,7)/aug-cc-pVDZ level of theory.



Figure S5: Surface (a) and contour (b) plots for the Y-component of permanent dipole moments for the $\pi\sigma^*$ states of pyrrole along DIP and DOP coordinates in diabatic basis computed at CASSCF(8,7)/aug-cc-pVDZ level of theory.



Figure S6: Bonding and dissociative regions in the span of DIP and DOP coordinates. Red and cyan curves indicate radial dividing surface and intersection regions, respectively.



Figure S7: Time evolution of the survival probabilities upon excitation to the $\pi\sigma^*$ state of pyrrole under the influence of different cavity field strengths (ε_c) with cavity frequency (ω_c), 0.28 eV (a), 0.54 eV (b), 1.36 eV (c) and 3.54 eV (d). The cavity field interacts with the x-component of the molecular dipole moments.



Figure S8: Time evolution of the survival probabilities upon excitation to the $\pi\sigma^*$ state of pyrrole under the influence of different cavity field strengths (ε_c) with cavity frequency (ω_c), 0.28 eV (a), 0.54 eV (b), 1.36 eV (c) and 3.54 eV (d). The cavity field interacts with the z-component of the molecular dipole moments.



Figure S9: Expectation value of the spread in the DIP coordinate, $\langle q_1^2 \rangle$, in the excited state, obtained by using the time-dependent wave functions for cavity frequencies (a) $\omega_c = 0.28 \text{ eV}$, (b) $\omega_c = 0.54 \text{ eV}$, (c) $\omega_c = 1.56 \text{ eV}$ and (d) $\omega_c = 3.54 \text{ eV}$.



Figure S10: Expectation value of the spread in the DOP coordinate, $\langle q_2^2 \rangle$, in the excited state, obtained by using the time-dependent wave functions for cavity frequencies (a) $\omega_c = 0.28 \text{ eV}$, (b) $\omega_c = 0.54 \text{ eV}$, (c) $\omega_c = 1.56 \text{ eV}$ and (d) $\omega_c = 3.54 \text{ eV}$



Figure S11: Time evolution of the survival probabilities upon excitation to the $\pi\sigma^*$ state of pyrrole under the influence of the cavity field strength, $\varepsilon_c = 3.92$ GV/m with different resonance frequencies, ω_c . Full Hamiltonian represents the Hamiltonian in Eq. 8 of the main article, whereas \hat{H}_{red1} and \hat{H}_{red2} refer to the reduced Hamiltonians. DSE term, $\langle \mu^2 \rangle_{ij}$ is excluded in the former reduced Hamiltonian and, both DSE and g_{ii} terms are excluded in the latter.



Figure S12: Time evolution of the survival probabilities upon excitation to the $\pi\sigma^*$ state of pyrrole under the influence of the cavity field strength, $\varepsilon_c = 1.96$ GV/m with different resonance frequencies, ω_c . Full Hamiltonian represents the Hamiltonian in Eq. 8 of the main article, whereas \hat{H}_{red1} and \hat{H}_{red2} refer to the reduced Hamiltonians. DSE term, $\langle \mu^2 \rangle_{ij}$ is excluded in the former reduced Hamiltonian and, both DSE and g_{ii} terms are excluded in the latter.



Figure S13: Time evolution of the survival probabilities upon excitation to the $\pi\sigma^*$ state of pyrrole under the influence of the cavity field strength, $\varepsilon_c = 0.78$ GV/m with different resonance frequencies, ω_c . Full Hamiltonian represents the Hamiltonian in Eq. 8 of the main article, whereas \hat{H}_{red1} and \hat{H}_{red2} refer to the reduced Hamiltonians. DSE term, $\langle \mu^2 \rangle_{ij}$ is excluded in the former reduced Hamiltonian and, both DSE and g_{ii} terms are excluded in the latter.