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Supporting Information: Charge transfer characteristics in rhodopsin mimics during photoexcitation

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List of Figures

List of Tables

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The definitions of hole and electron in the electronic excitation process are as follows

$$\rho^{\text{hole}}(\mathbf{r}) = \rho^{\text{hole}}_{(\text{loc})}(\mathbf{r}) + \rho^{\text{hole}}_{(\text{cross})}(\mathbf{r}) \tag{1}$$

$$\rho^{\text{hole}}_{(\text{loc})}(\mathbf{r}) = \sum_{i\rightarrow a} \left(w_i^a\right)^2 \varphi_i\varphi_i - \sum_{i\leftarrow a} \left(w_i'^a\right)^2 \varphi_i\varphi_i \tag{2}$$

$$\rho^{\text{hole}}_{(\text{cross})}(\mathbf{r}) = \sum_{i\rightarrow a}\sum_{j\neq i\rightarrow a} w_i^a w_j^a \varphi_i\varphi_j - \sum_{i\leftarrow a}\sum_{j\neq i\leftarrow a} w_i'^a w_j'^a \varphi_i\varphi_j \tag{3}$$

$$\rho^{\text{ele}}(\mathbf{r}) = \rho^{\text{ele}}_{(\text{loc})}(\mathbf{r}) + \rho^{\text{ele}}_{(\text{cross})}(\mathbf{r}) \tag{4}$$

$$\rho^{\text{ele}}_{(\text{loc})}(\mathbf{r}) = \sum_{i\rightarrow a} \left(w_i^a\right)^2 \varphi_a\varphi_a - \sum_{i\leftarrow a} \left(w_i'^a\right)^2 \varphi_a\varphi_a \tag{5}$$

$$\rho^{\text{ele}}_{(\text{cross})}(\mathbf{r}) = \sum_{i\rightarrow a}\sum_{i\rightarrow b\neq a} w_i^a w_i^b \varphi_a\varphi_b - \sum_{i\leftarrow a i\leftarrow b\neq a} \sum_{i}^{'a} w_i'^b \varphi_a\varphi_b \tag{6}$$

In the above equation, r represents the coordinate vector, φ is the orbital wave function, i or j is the index of occupied orbitals, and a or b is the index of virtual orbitals. Therefore, expressions such as $\sum i \rightarrow a$ denote cycling through each excited configuration, while $\sum i \leftarrow a$ denote cycling through each de-excited configuration. The distributions of the hole density ρ^{hole} and the electron density ρ^{ele} are divided into two parts: the local term and the cross term. The local term generally dominates and reflects the contribution of the configuration function itself, while the cross term cannot be ignored; otherwise, the quantification will be inaccurate. It reflects the influence of coupling between configuration functions on the distributions of holes and electrons. That is, the integrals of the hole and electron distributions over the entire space are both 1 (corresponding to one electron), and they are positive everywhere. Therefore, the distribution of "holes" defined in the above manner perfectly describes where the excited electron comes from, while the distribution of "electrons" perfectly describes where the excited electron goes.

In fact, if the excitation of an electron can be described by a single pair of orbital transitions i→a in other words, if the contribution of this configuration function is exactly 100%, then φ_i and φ_a can ideally be directly regarded as the hole and electron, respectively. However, the definition of holes and electrons given above corresponds to $|\varphi_i|^2$ and $|\varphi_a|^2$ respectively, which can be considered as the electron densities associated with orbitals i and a (assuming both orbitals are singly occupied). Therefore, the electrons and holes defined above lack phase information because the square modulus of the orbital wave functions is taken. Since the actual excited states of electrons are typically contributed by many configuration functions, and no single pair of orbital transitions can perfectly describe electron excitation, in order to fully describe the electron and hole in this situation, the specific definition of electrons and holes considers all orbital transitions. This approach can ideally, comprehensively, and adequately represent the characteristics of electron excitation.

In addition to defining electrons and holes, further analysis involves deriving quantities related to electron-hole pairs. The S factor defines the overlap degree of electron-hole pairs:

$$S_{\text{m}} \text{ index } = \int S_{\text{m}}(\mathbf{r})d\mathbf{r} \equiv \int \min\left[\rho^{\text{hole}}(\mathbf{r}), \rho^{\text{ele}}(\mathbf{r})\right] d\mathbf{r} \tag{7}$$

$$S_{\text{r}} \text{ index } = \int S_{\text{r}}(\mathbf{r})d\mathbf{r} \equiv \int \sqrt{\rho^{\text{hole}}(\mathbf{r})\rho^{\text{ele}}(\mathbf{r})}d\mathbf{r} \tag{8}$$

he D index measures the distance between the center of mass of the hole and the electron:

$$D_{\text{x}} = |X_{\text{ele}} - X_{\text{hole}}| \tag{9}$$

$$D_{\text{y}} = |Y_{\text{ele}} - Y_{\text{hole}}| \tag{10}$$

$$D_{\text{z}} = |Z_{\text{ele}} - Z_{\text{hole}}| \tag{11}$$

$$D \text{ index } = \sqrt{(D_{\text{x}})^2 + (D_{\text{y}})^2 + (D_{\text{z}})^2} \tag{12}$$

Hole and electron are defined by σ, whose x, y, z components are equivalent to the root mean square deviation (RMSD) of the distribution of holes or electrons in the x, y, z directions, reflecting the breadth of distribution or the degree of dispersion. The following are the x, y, z components of σ for the hole:

$$\begin{aligned}
&\sigma_{\text{hole },x}=\sqrt{\int\left(x-X_{\text{hole }}\right)^{2} \rho^{\text{hole }}(\mathbf{r}) d \mathbf{r}} \\
&\sigma_{\text{hole },y}=\sqrt{\int\left(y-Y_{\text{hole }}\right)^{2} \rho^{\text{hole }}(\mathbf{r}) d \mathbf{r}} \\
&\sigma_{\text{hole },z}=\sqrt{\int\left(z-Z_{\text{hole }}\right)^{2} \rho^{\text{hole }}(\mathbf{r}) d \mathbf{r}} \\
&\sigma=\sqrt{\sigma_{\text{hole },x}^{2}+\sigma_{\text{hole },y}^{2}+\sigma_{\text{hole },z}^{2}}
\end{aligned} \tag{13}$$

The σ index is the square root of the sum of the squares of the three components, which measures the overall spread of the distribution of the hole or electron.

Below is a sequential introduction to the uses of these quantities:

$\Delta\sigma_{\lambda}$: Measures the difference in the spatial spread of the distribution of electrons and holes in the λ direction.

$\Delta\sigma$ index: Reflects the overall difference in the spatial spread of the distribution of electrons and holes.

H_{λ}: Measures the average extent of stretching of holes and electrons in the λ direction.

H_{CT}: Measures the average extent of stretching of holes and electrons in the CT (charge transfer) direction. The bold H in the formula represents the vector composed of H_x, H_y, and H_z together, and the bold $\mathbf{u}_{\text{CT}}$ is the unit vector in the CT direction, which can be directly obtained using the centroid positions of the electron and hole.

H index: Reflects the overall average spread of the distribution of electrons and holes.

t index: Measures the degree of separation between the hole and electron.

$$\begin{aligned}
&\Delta \sigma_{\lambda}=\sigma_{\text{ele}, \lambda}-\sigma_{\text{hole}, \lambda} \quad \lambda=\{x, y, z\} \\
&\Delta \sigma \text{ index }=\left|\sigma_{\text{ele}}\right|-\left|\sigma_{\text{hole}}\right| \\
&H_{\lambda}=\left(\sigma_{\text{ele}, \lambda}+\sigma_{\text{hole}, \lambda}\right) / 2 \quad \lambda=\{x, y, z\} \\
&H_{\text{CT}}=\left|\mathbf{H} \cdot \mathbf{u}_{\text{CT}}\right| \\
&H=\left(\left|\sigma_{\text{ele}}\right|+\left|\sigma_{\text{hole}}\right|\right) / 2 \\
&t=D-H_{\text{CT}}
\end{aligned} \tag{14}$$

The hole delocalization index (HDI) and the electron delocalization index (EDI) are defined as follows:

$$\begin{aligned}
&HDI=100 \times \sqrt{\int\left[\rho^{\text{hole }}(\mathbf{r})\right]^{2} \mathrm{~d} \mathbf{r}} \\
&EDI=100 \times \sqrt{\int\left[\rho^{\text{ele }}(\mathbf{r})\right]^{2} \mathrm{~d} \mathbf{r}}
\end{aligned} \tag{15}$$

In the three-dimensional case, g, g^{IGM}, and δg are defined as follows. the $\mathbf{r}$ is the position vector, i runs over all atoms, the | | symbol denotes the magnitude of the vetor inside, ∇ is the vector differential operator, and ρ_i represents the electron density of the i-th atom.

$$\begin{aligned}
\delta g(\mathbf{r}) &= g^{\text{IGM}}(\mathbf{r})-g(\mathbf{r}) \\
g(\mathbf{r}) &= \left|\sum_{i} \nabla \rho_{i}(\mathbf{r})\right| \\
g^{\text{IGM}}(\mathbf{r}) &= \sum_{i}\left|\nabla \rho_{i}(\mathbf{r})\right|
\end{aligned} \tag{16}$$

δg represents the interaction between all atoms in the current system. The terms δg^{inter} and δg^{intra} are defined as the interactions between specific fragments (interfragment) and within a fragment (intrafragment), respectively. The following illustrates this, where A iterates through the defined fragments.

$$\begin{aligned}
\delta g^{\text{inter}}(\mathbf{r}) &= g^{\text{IGM inter}}(\mathbf{r}) - g^{\text{inter}}(\mathbf{r}) \\
g^{\text{inter}}(\mathbf{r}) &= \left| \sum_{A} \sum_{i \in A} \nabla \rho_i(\mathbf{r}) \right| \\
g^{\text{IGM, inter}}(\mathbf{r}) &= \sum_{A} \left| \sum_{i \in A} \nabla \rho_i(\mathbf{r}) \right| \\
\delta g^{\text{intra}}(\mathbf{r}) &= \delta g(\mathbf{r}) - \delta g^{\text{inter}}(\mathbf{r})
\end{aligned} \tag{17}$$

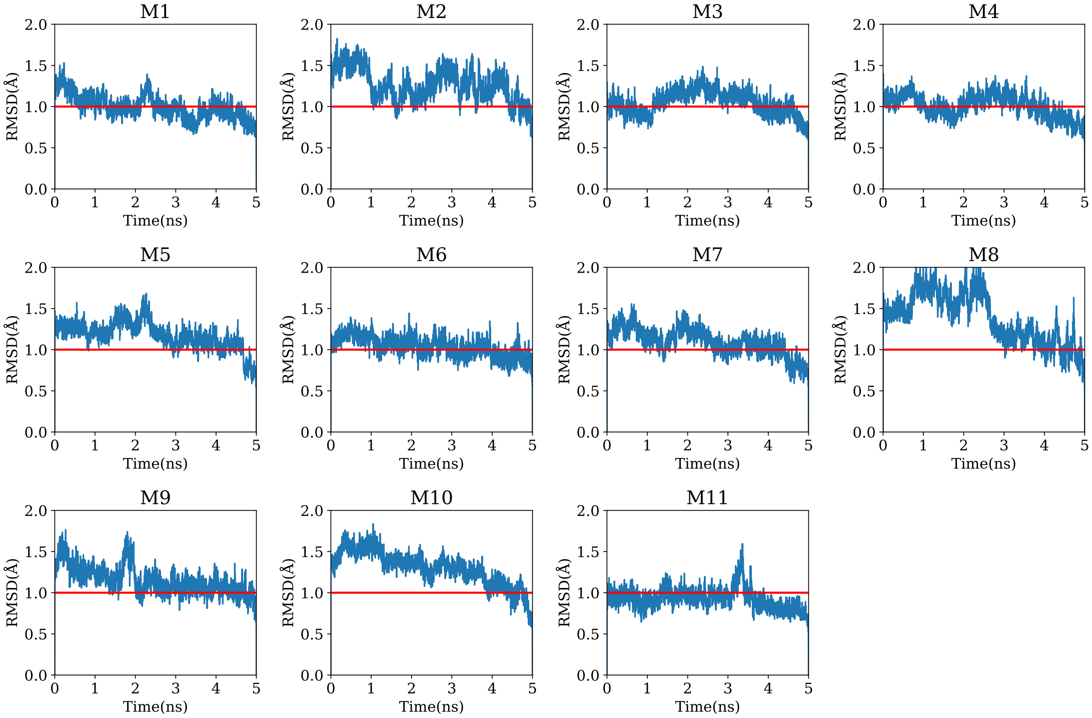


Fig. S1 The heavy-atom RMSD of a rhodopsin mimic throughout a 5 ns MD simulation.

Table S1 Charge transfer parameters of rhodopsin mimic M3-M8, M10, and M11

PDB	Sr	D	H	HDI	EDI	t
M3	0.57465	5.64	3.947	7.2	8.47	2.802
M4	0.54435	6.393	3.903	7.53	8.83	3.814
M5	0.55935	5.305	3.853	6.84	9.00	2.756
M6	0.57848	6.216	3.963	7.62	8.76	3.599
M7	0.57772	6.221	3.962	7.61	8.76	3.604
M8	0.48786	7.161	3.741	7.72	9.28	4.853
M10	0.49276	7.1	3.715	8.17	8.87	4.525
M11	0.59633	5.571	3.997	7.2	8.49	3.068

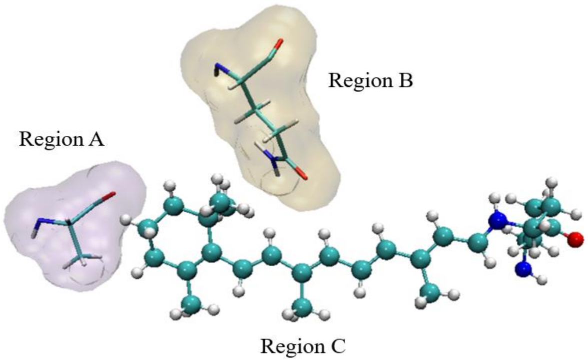


Fig. S2 Spatial relative position of interaction between chromophore and mutation site. Region A represents the amino acid at position 32, Region B represents the amino acid at position 39, and Region C represents the chromophore.

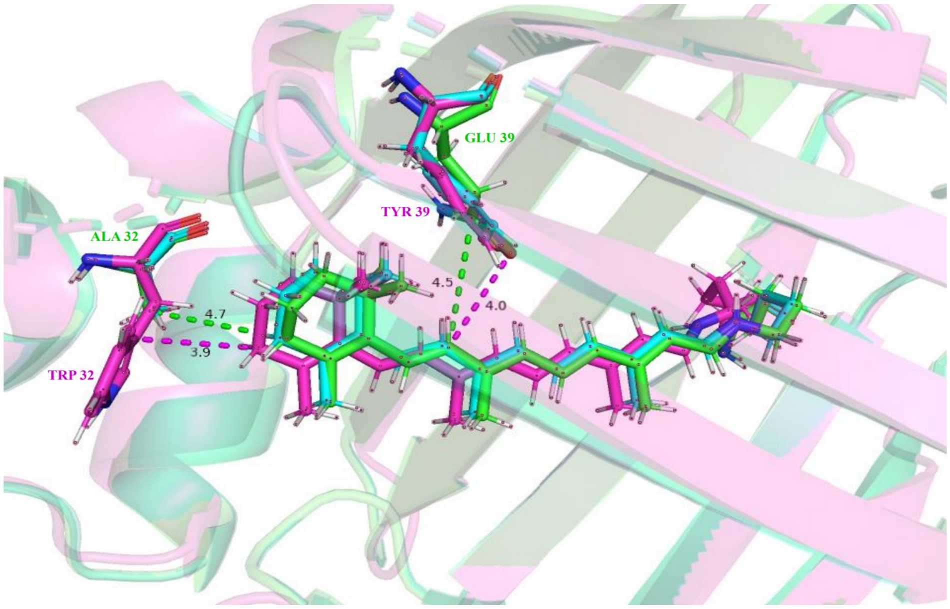
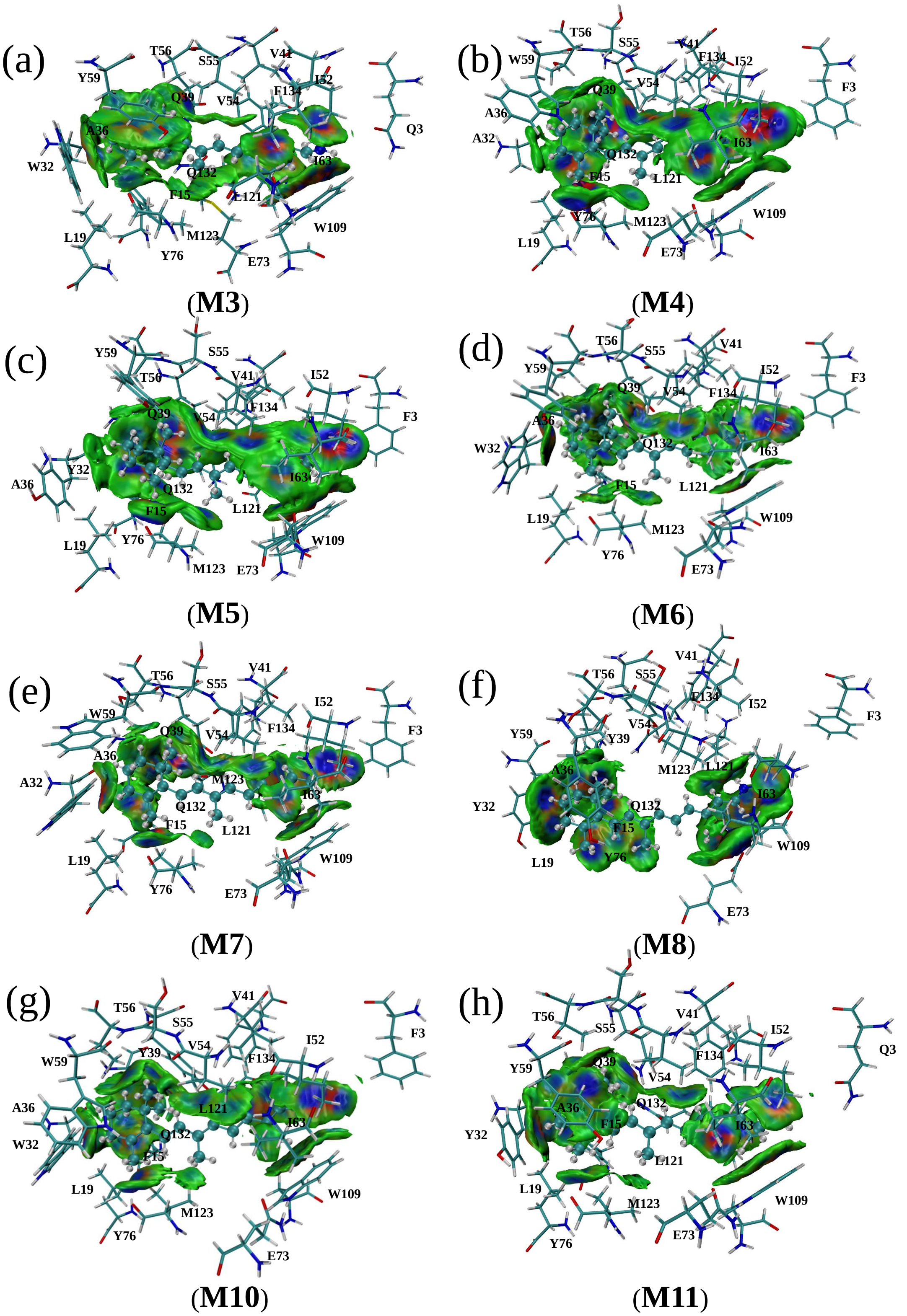


Fig. S3 The minimum distance of the heavy atom on the M1(Cyan), M2(green), M9(purple) between the chromophore and the mutation site.

Table S2 Interaction between the chromophore and mutated amino acids. A represents the amino acid at position 32, B represents the amino acid at position 39, and C represents the chromophore, the spatial position of A, B, and C is shown in Figure S1.

	delta A-C	delta B-C
M1	0.293369	-2.527595
M2	0.117771	-0.871877
M9	0.342297	-0.370241



(**M3**) (**M4**) (**M5**) (**M6**) (**M7**) (**M8**) (**M10**) (**M11**)

Fig. S4 A schematic diagram of the interactions between the chromophore and amino acids within the 4Å of rhodopsin mimic M3-M8, M10, and M11

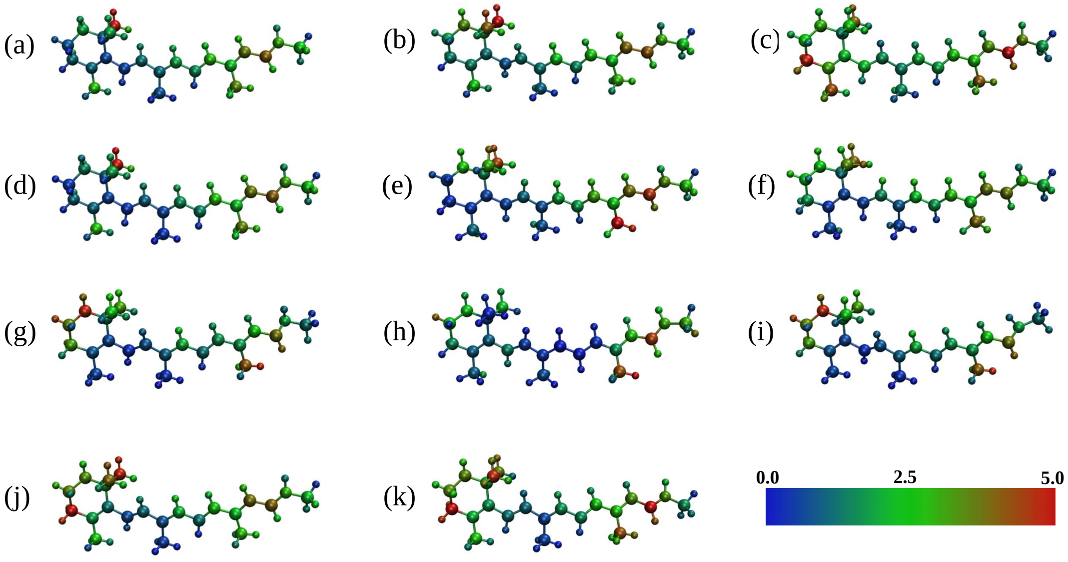


Fig. S5 The molecular structure diagram, where the chromophore atoms are color-coded by their δg for interaction analysis, with the color of the atoms corresponding to the strength of the interactions.