Supporting Information

Nonlinear plexciton: exciton coupled with plasmon in two-photon absorption

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1. More details on the FDTD simulations.

FDTD simulations were performed using the FDTD Solution software. Absorption cross-section of the single Au @Ag nanorod and nanorod coupled with Ag film was simulated using a total-field scattered-field (TFST) source in a 1 μ m³ box surrounded by perfectly matched layer (PML) boundary condition. Non-uniform mesh was used. The Au nanorod and Au@Ag nanorod were divided into 1 nm and 2 nm meshes. The thickness of Ag film was 40 nm. The gap between nanorod and Ag film was 1.5 nm. The mesh in gap was set as (2nm, 2nm, 0.15nm). The configuration to study the angle dependence of polarization and incidence are plane wave, Au@Ag nanorod, dielectric layer (1.5 nm thick), Ag film (40 nm thick), ITO substrate (40 nm thick), SiO₂ substrate from top to bottom. Place a x-y plane electric field (E) monitor in the dielectric layer. The refractive index of surrounding was set as 1.

2. Reason for the redshift of the absorption peak for the longer chain.

The redshift in OPA spectrum for the longer D-A structure can be attributed to the S_1 redshift for the donor, see Fig. S1.



Figure S1. The thiophene-length dependent S1 excited energy, where the inset is the chemical structure of PT. (*J. Phys. Chem. C, 2021, 125(38): 21301-21309.*)

3. TPA spectrum of $IC_{60}BA$ at the wavelength from 400 nm to 1900 nm.



Figure S2. TPA spectrum of $IC_{60}BA$ at the wavelength from 400 nm to 1900 nm, in which the TPA cross-section of S_1 is relatively weak.

4. TPA spectrum of PT:IC₆₀BA (n=9) D-A structure.



Figure S3. TPA spectra of $PT:IC_{60}BA$ (n=9) D-A structure, where the inserts is CT with different transition channels, and the red and green represent electrons and holes, respectively.

5. More details about TDM and CDD.

Atom indexes are ordered regularly during Gaussian calculations. Both TDM and CDD mapping data are derived from Multiwfn program. The TDM between ground state and an excited state can be calculated as

$$P^{tran}_{\mu\nu} = \sum_{i}^{occ} \sum_{a}^{\nu ir} w^{a}_{i} C_{\mu i} C_{\nu a}$$

where $C_{\mu i}$ denotes the expansion coefficient of basis function μ in MO *i*. The offdiagonal elements of TDM essentially represent the coupling between various basis functions during electron excitation. Assume there are only two basis functions and meantime the excitation can be perfectly represented as $i \rightarrow a$ MO transition, then the TDM could be explicitly written as below form

$$P^{tran} = \begin{bmatrix} 1,2 & 2,2\\ 1,1 & 2,1 \end{bmatrix} = \begin{bmatrix} C_{1i}C_{2a} & C_{2i}C_{2a}\\ C_{1i}C_{1a} & C_{2i}C_{1a} \end{bmatrix}$$

If magnitude of off-diagonal element $P_{1,2}^{tran}$ is large, it implies that basis functions 1 and 2 significantly participate in occupied orbital i and virtual orbital a, respectively. More generally, it is meaning that basis functions 1 and 2 have large contribution to hole and electron, respectively, in this case the two basis functions are strongly coupled during

the excitation. The diagonal terms are also meaningful, if element $P_{\mu\mu}^{tran}$ has large

magnitude, it implies that basis function μ must simultaneously have large contribution to both hole and electron. To put it simply, strong electron-hole coherence on the diagonal is called local excitation, while the one on the off-diagonal is called charge transfer.

Use CDD to represent hole and electron distributions when there is no single dominant MO pair transition, which is similar to the more common natural transition orbital (NTO) analysis. It can be shown that density distribution of hole and electron can be perfectly defined as

$$\rho^{hole}(r) = \rho^{hole}_{(loc)}(r) + \rho^{hole}_{(cross)}(r) = \sum_{i \to a} (\omega_i^a)^2 \varphi_i(r) \varphi_i(r) + \sum_{i \to aj} \sum_{\neq i \to a} \omega_i^a \varphi_i(r) \varphi_i(r) + \sum_{i \to aj} \sum_{\neq i \to a} \omega_i^a \omega_j^a \varphi_i(r) \varphi_j(r)$$

where φ denotes MO wavefunction. "loc" and "cross" stand for the contribution of local term and cross term to the hole and electron distribution, respectively. Due to the orthonormality of MOs and the fact that the sum of square of all configuration coefficients are 1, it is clear that

$$\int \rho^{hole}(r)dr = 1 \qquad \int \rho^{ele}(r)dr = 1$$

The CDD between excited state and ground state can be evaluated as $\Delta \rho(r) = \rho^{ele}(r) - \rho^{hole}(r)$

We use VMD software to plot CDD maps and the isovalue is set to 0.003, green and red correspond to increase and decrease of the excited state density with respect to the ground state density, respectively.

6. Absorption spectra of bare Ag film and nanorod coupled Ag film.



Figure S4. Absorption spectra of Ag film and nanorod coupled with Ag film, and the subtraction between them.

7. Another configuration for increasing the incident angle is shown in Fig. S4, while keeping the polarization angle and rotating the incident light around the longitudinal

axis of nanorod.



Figure S5. Plasmonic-enhanced electric field with different incident angles.