Supporting Information for: Solid-state effects on the optical excitation of push-pull molecular J-aggregates by first principles simulations

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S1. Response charge density and optical spectra

The complete analysis of the response charge density and of the optical spectra for the systems discussed in the main text is collected in Figure S1 and S2, respectively. Red-blue colors in Fig. S1 indicates the positive-negative sign of the response charge densities.

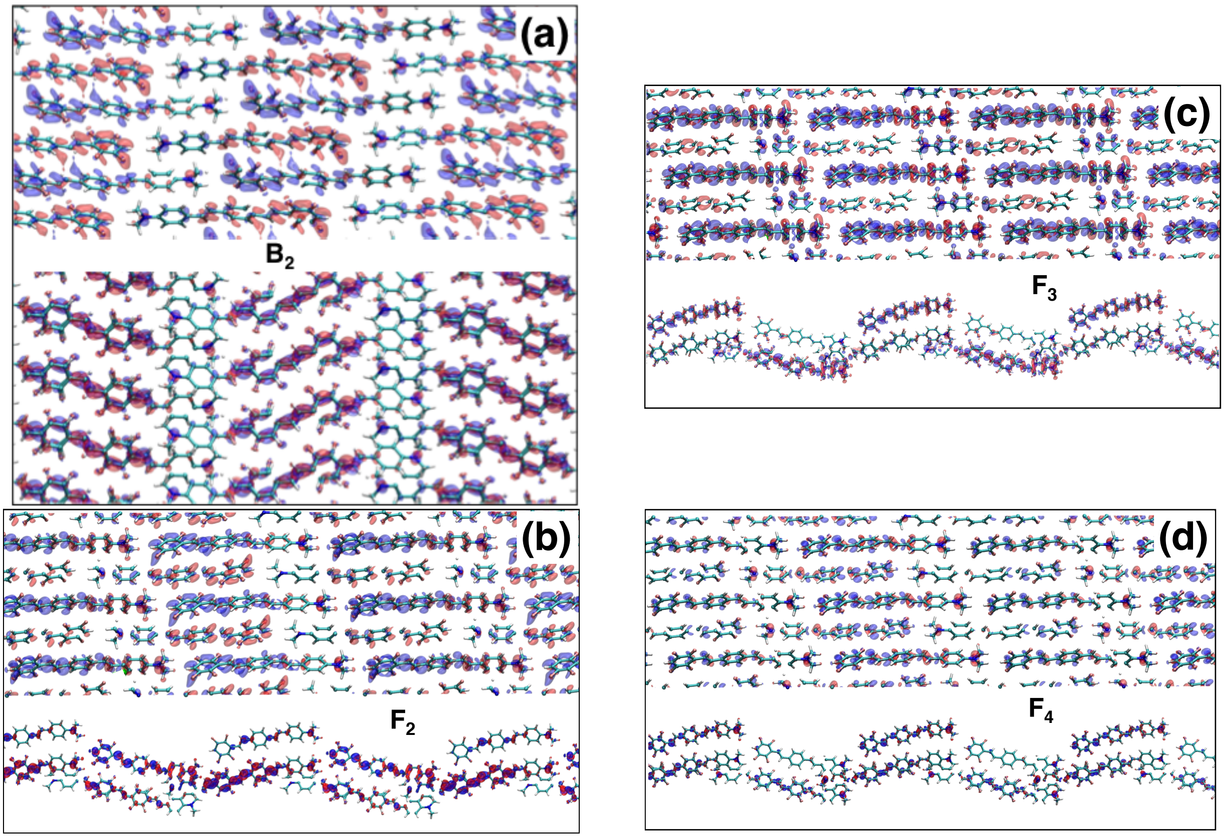


Figure S1 – (a) Imaginary part of induced charge density peak B2 of 3D bulk crystal. (b-d) Imaginary parts of induced charge densities of peaks F2-F4 of 2D film crystal. For each induced charge density we have plotted two different side-views, one along the plane where both 3D bulk and 2D film are extended and the other along the plane where the film is confined. All induced charge density isosurfaces are fixed at 0.1 Bohr $^{-3}$.

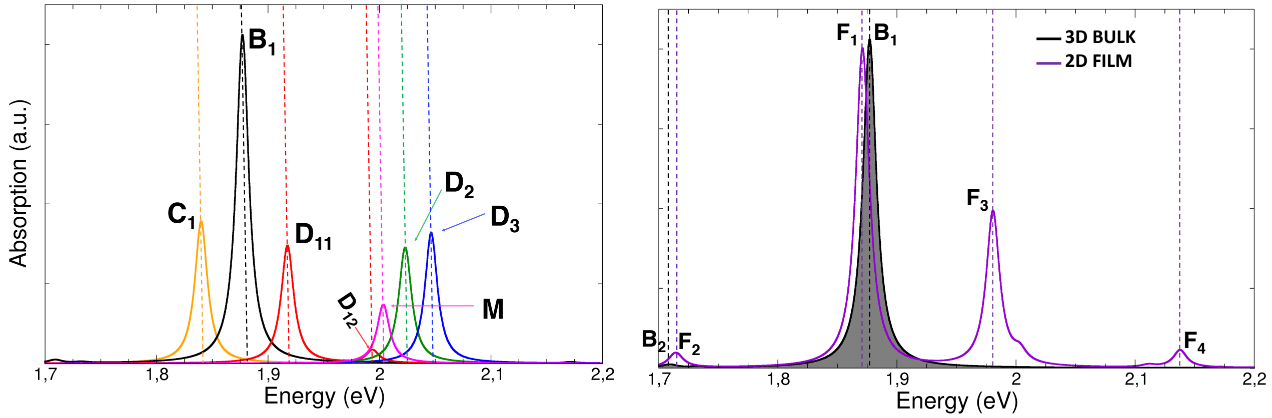


Figure S2 – Absorption optical spectra of 3D bulk (black), 2D film (violet), 1D chain (ochre), dimers (red, blue, green) and monomer (magenta) extracted from the 3D bulk crystal.

TABLE S.1

	Peak energy (eV)		Oscillator strength		Homo – Lumo gap (eV)
Monomer	M 2		1.537		1.667
Dimer 1	D_{11} 1.918	D_{12} 1.994	3.153	0.331	1.442
Dimer 2	D_2 2.023		2.981		1.693
Dimer 3	D_3 2.047		3.282		1.635
1D chain	C_1 1.841	C_2 1.968	3.95	0.0725	1.636
2D film	F_1 1.87	F_2 1.71	7.821	0.24	1.5
	F_3 1.98	F_4 2.138	3.912	0.27	
3D bulk	B_1 1.887	B_2 1.71	7.96	0.08	1.567

TABLE S.2

	Peak energy	Transitions (occ →vir)	Tran. amplitude
Monomer	2 eV (M)	H → L (1.66 eV)	0.96
		H-1 → L (2.607 eV)	-0.19
		H → L + 1 (2.637 eV)	0.21
Dimer 1	1.918 eV (D_{11})	H-2 → L (2.394 eV)	-0.15
		H-1 → L (1.605 eV)	-0.84
		H → L+1 (1.642 eV)	-0.48
		H-1 → L+2 (2.598 eV)	-0.18
	1.994 eV (D_{12})	H-3 → L (2.577 eV)	-0.123
		H-2 → L+1 (2.594 eV)	-0.181
		H-1 → L (1.605 eV)	-0.464
		H-1 → L+2 (2.598 eV)	-0.122
		H → L+1 (1.642 eV)	0.828
		H → L+3 (2.623 eV)	-0.2
Dimer 2	2.023 eV (D_2)	H-1 → L (1.694 eV)	0.84
		H-1 → L+1 (1.698 eV)	0.34
		H → L+1 (1.697 eV)	-0.26
		H-2 → L (2.615 eV)	-0.17
		H-1 → L+2 (2.654 eV)	-0.17
		H → L (1.693 eV)	-0.14

Dimer 3	2.047 eV (D_3)	H-1 → L (1.703 eV) H → L+1 (1.754 eV) H-3 → L (2.706 eV) H-2 → L+1 (2.57 eV) H-1 → L+2 (2.698 eV) H → L+3 (2.646 eV)	0.59 -0.76 -0.17 -0.128 0.13 0.13

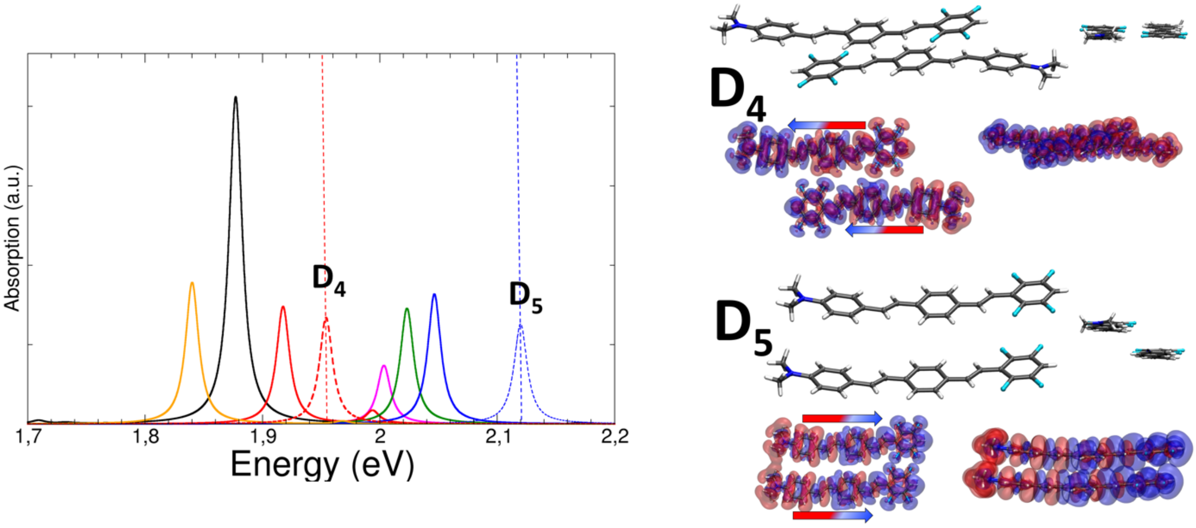


Figure S3 – (Left) Absorption optical spectra of other two dimer configurations extracted from the bulk crystal. The new spectra have been plotted in dashed lines. (Right) Spatial arrangements of new dimers with the associated induced charge densities associated to the absorption peaks D4 and D5. The values of the isosurface plots have been fixed to 0.05 Bohr $^{-3}$.

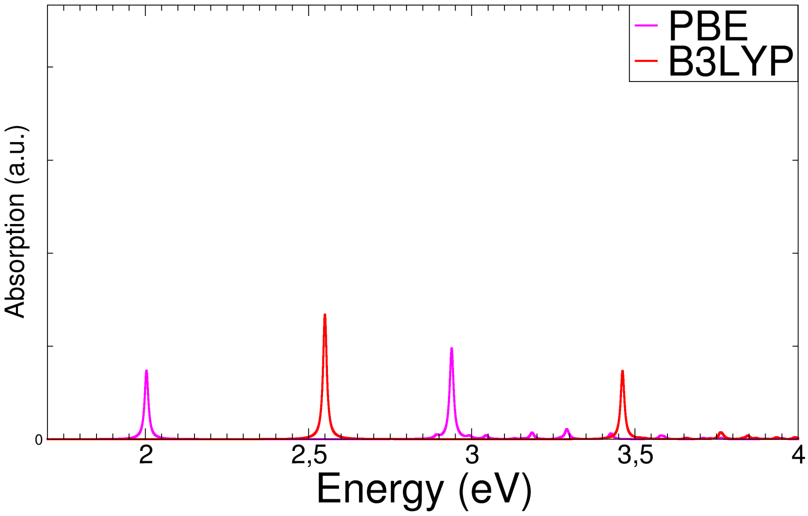


Figure S4 – Comparison of absorption optical spectra of single push-pull monomer using two different xf-functionals: PBE and B3LYP. The hybrid functional gives a blue-shift with respect to the semi-local PBE of ~0.55 eV for the first two principal peaks

S2. Structural and crystal characterizations

We report here the unit cells of 3D bulk, 2D film and 1D chain, dimers and monomer extracted from the bulk crystal.

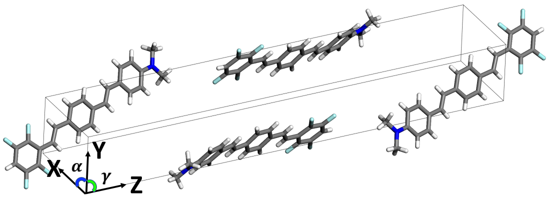
3D bulk

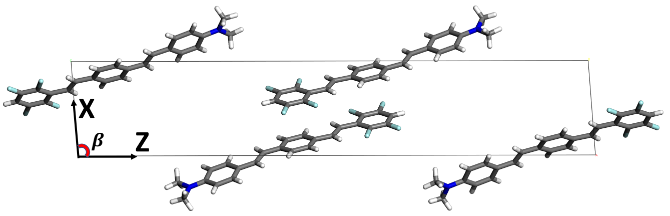
Primitive cell parameters:

- Lattice type : *monoclinic*
- Crystal lengths (Å) : X = 7,59 Y = 5,87 Z = 41,51
- Angles (degrees) : α (XY) = 90,00° β (ZX) = 94,30° γ (YZ) = 90,00°

Computational parameters:

- Number of atoms = 192
- Number of electrons = 592
- Kinetic energy cut-off = 50 Ry
- Charge density cut-off = 500 Ry
- Exchange-correlation = PBE





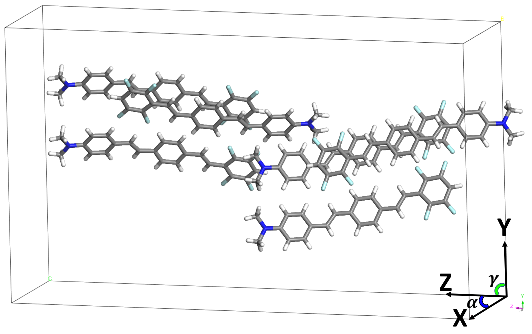
2D film

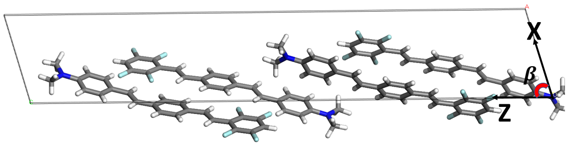
Primitive cell parameters:

- Lattice type : *monoclinic*
- Crystal lengths (Å) : X = 7,59 Y = 26,64 Z = 43,12
- Angles (degrees) : α (XY) = 90,00° β (ZX) = 73,74° γ (YZ) = 90,00°

Computational parameters:

- Number of atoms= 288
- Number of electrons= 888
- Kinetic energy cut-off = 50 Ry
- Charge density cut-off = 500 Ry
- Exchange-correlation = PBE





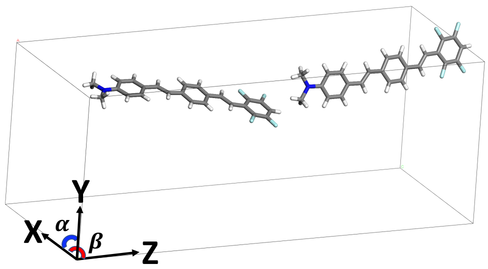
1D chain

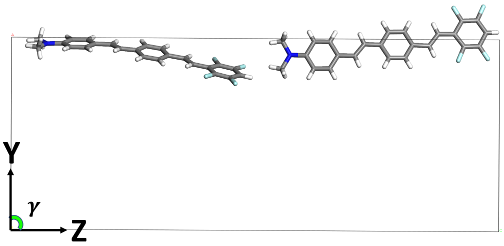
Primitive cell parameters:

- Lattice type : *orthorombic*
- Crystal lengths (Å) : X = 16,90 Y = 16,90 Z = 43,12
- Angles (degrees) : α (XY) = 90,00° β (ZX) = 90,00° γ (YZ) = 90,00°

Computational parameters:

- Number of atoms= 96
- Number of electrons= 296
- Kinetic energy cut-off = 50 Ry
- Charge density cut-off = 500 Ry
- Exchange-correlation = PBE





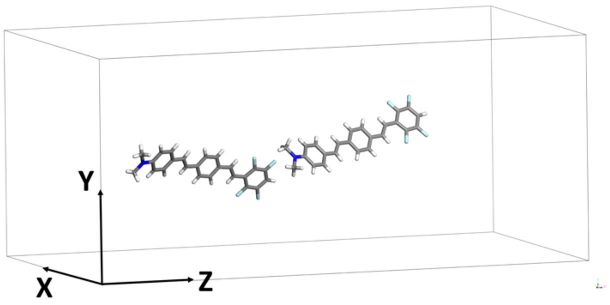
Dimer 1

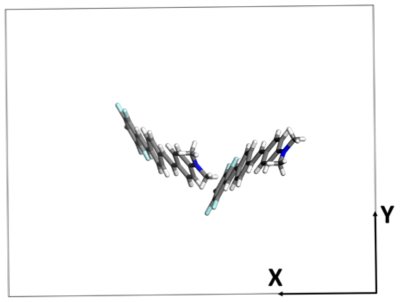
Primitive cell parameters:

- Lattice type : *orthorombic*
- Crystal lengths (Å) : X = 31,75 Y = 24,77 Z = 56,22
- Angles (degrees) : α (XY) = 90,00° β (ZX) = 90,00° γ (YZ) = 90,00°

Computational parameters:

- Number of atoms= 96
- Number of electrons= 296
- Kinetic energy cut-off = 50 Ry
- Charge density cut-off = 500 Ry
- Exchange-correlation = PBE





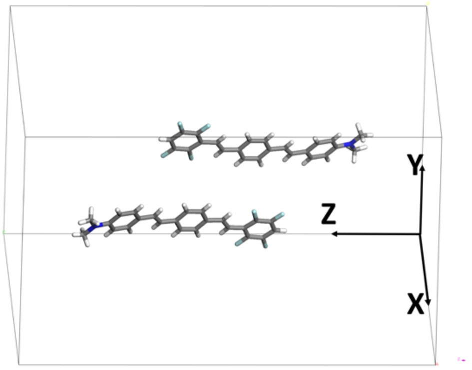
Dimer 2

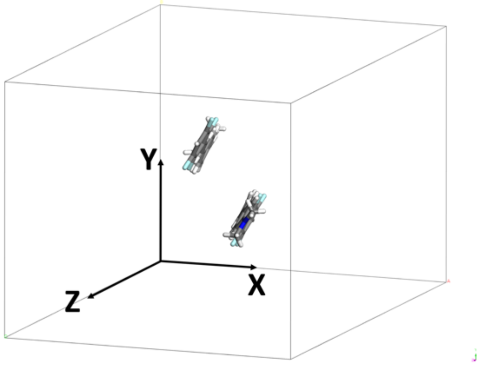
Primitive cell parameters:

- Lattice type : *orthorombic*
- Crystal lengths (Å) : X = 26,02 Y = 22,33 Z = 36,75
- Angles (degrees) : α (XY) = 90,00° β (ZX) = 90,00° γ (YZ) = 90,00°

Computational parameters:

- Number of atoms= 96
- Number of electrons= 296
- Kinetic energy cut-off = 50 Ry
- Charge density cut-off = 500 Ry
- Exchange-correlation = PBE





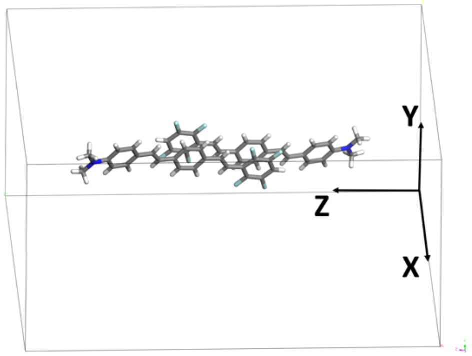
Dimer 3

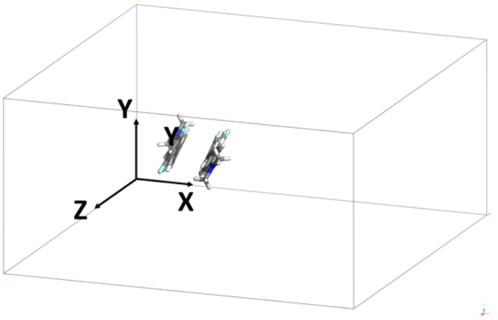
Primitive cell parameters:

- Lattice type : *orthorombic*
- Crystal lengths (Å) : X = 36,75 Y = 17,83 Z = 36,75
- Angles (degrees) : α (XY) = 90,00° β (ZX) = 90,00° γ (YZ) = 90,00°

Computational parameters:

- Number of atoms= 96
- Number of electrons= 296
- Kinetic energy cut-off = 50 Ry
- Charge density cut-off = 500 Ry
- Exchange-correlation = PBE





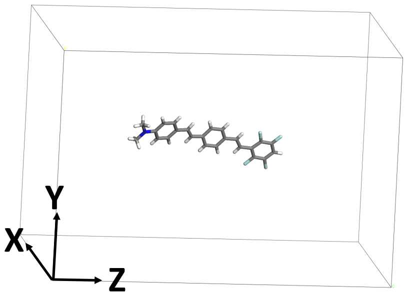
Monomer

Primitive cell parameters:

- Lattice type : *orthorombic*
- Crystal lengths (Å) : X = 27,52 Y = 27,52 Z = 40,18
- Angles (degrees) : α (XY) = 90,00° β (ZX) = 90,00° γ (YZ) = 90,00°

Computational parameters:

- Number of atoms= 48
- Number of electrons= 148
- Kinetic energy cut-off = 50 Ry
- Charge density cut-off = 500 Ry
- Exchange-correlation = PBE



S3. Evaluation of the response charge density

In this section we will explain the post-processing procedure we have used in order to get the induced charge densities for each peak. Firstly, we have performed three independent excitations with three (orthogonal) electric field linear polarizations of frequency ω

$$E^{i}_{ext,P}(\omega) = E_0(\omega)\delta^{i}{}_{P} \qquad (1)$$

where index *P=x,y,z* fixes direction of external electric field polarization, index *i* refers to electric field *i*-th component and δ^i_j is delta Kronecker symbol. Since we are in dipolar regime, we have assumed uniform electric field. Using linear response theory in space-frequency domain, for each specific polarization direction *P*, one gets a different induced charge density, namely

$$n_P(\vec{r},\omega) = \int \varphi_{ext,P}(\vec{r}\,',\omega)\chi(\vec{r},\vec{r}\,',\omega)d^3r' = -\int r_i' E^{i}_{ext,P}(\omega)\chi(\vec{r},\vec{r}\,',\omega)d^3r' = -E_0(\omega)\int r_P'\chi(\vec{r},\vec{r}\,',\omega)d^3r' \qquad (2)$$

where repeated indices are implicitly summed and χ is the polarizability causal response function. Since we want to plot a unique induced charge density, we decided to evaluate the one which gives the maximum absorption for a certain peak or, in other words, the one whose transition dipole moment is oriented along the direction of the external field. In order to do that, we have applied a simple post-processing procedure by linearly combining the three induced charge densities obtained in (2). From the knowledge of the induced charge density (2) one can evaluate the induced dipole moment for a certain field polarization *P* in the following way

$$d_{i,P}(\omega) = \int n_P(\vec{r},\omega) r_i d^3r = -\int r_i r'_{i'}\chi(\vec{r},\vec{r}\,',\omega)E^{i'}_{ext,P}(\omega)d^3r'd^3r = \alpha_{ii'}(\omega)E^{i'}_{ext,P}(\omega) \qquad (3)$$

$$\alpha_{ii'}(\omega) = -\int r_i r'_{i'}\chi(\vec{r},\vec{r}\,',\omega)d^3r d^3r' \qquad (4)$$

where (4) is the so called dynamic polarizability tensor. Since the induced dipole (3) is a functional of the induced charge density, its magnitude and orientation depend on the external field polarization also. By diagonalizing (4), one can get the special directions along which the induced dipole has the same orientation of the external applied field. These special directions are the eigenvectors of the polarizability tensor and are an intrinsic property of the system. The spectral decomposition of the polarizability tensor (4) is

$$\alpha_{ij}(\omega) = -\sum_{\alpha} d^{\alpha}_i d^{*\alpha}_j \left[\frac{1}{\omega-\omega_\alpha+i\eta} - \frac{1}{\omega+\omega_\alpha+i\eta}\right] \qquad (5)$$

where indices α, β refer to many-body excited states, ω_α is the excitation energy from ground state to excited state α and d^α_i is i-th component of the transition dipole moment from ground state to excited state α. We can give a more compact representation of expression (5) by using a matrix notation

$$\boldsymbol{\alpha}(\omega) = W\Lambda W^{-1} = \sum_{\alpha} \boldsymbol{w}^{\alpha}\boldsymbol{w}^{\dagger\alpha}\lambda_{\alpha}(\omega) \qquad (6)$$

$$w_i^\alpha = \frac{\int \langle \alpha | \hat{\Psi}^\dagger(\vec{r}) \hat{r}_i \hat{\Psi}(\vec{r}) | 0 \rangle}{\sqrt{\sum_{i=x,y,z} \left| \langle \alpha | \hat{\Psi}^\dagger(\vec{r}) \hat{r}_i \hat{\Psi}(\vec{r}) | 0 \rangle \right|^2}} = \frac{d_i^\alpha}{\left\| \boldsymbol{d}^\alpha \right\|} \tag{7}$$

$$\lambda_\alpha(\omega) = \left\| \boldsymbol{d}^\alpha \right\|^2 \left[\frac{1}{\omega - \omega_\alpha + i\eta} - \frac{1}{\omega + \omega_\alpha + i\eta} \right] \tag{8}$$

where W matrix contains column by column the normalized eigenvectors $\mathbf{w}^\alpha$ with components (7), which gives the normalized direction of the transition dipole moment associate to peak α, while diagonal matrix Λ contains the associated eigenvalue λ_α that is frequency dependent. If one assumes that the excitation energies are well separated, when in proximity of a certain peak of energy ω_α there is a dominant pole in (5) and the response is dominated by the imaginary part of the polarizability tensor evaluated at the energy $\omega = \omega_\alpha$. Each peak has associated a normalized eigenvector (8) whose components are the weights we can use to combine our induced charge densities in (2) in order to get the one which gives the maximum absorption at the selected peak at frequency ω_α. At the end we obtain our final density as

$$n(\vec{r}, \omega = \omega_\alpha) = w_x^\alpha n_x(\vec{r}, \omega) + w_y^\alpha n_y(\vec{r}, \omega) + w_z^\alpha n_z(\vec{r}, \omega) \Big|_{\omega = \omega_\alpha} \tag{9}$$

TABLE S.3

Peak (α)	weights w_i^α
M	(0.335, -0.187, 0.923)
D_{11} D_{12}	(0.341, -0.06, 0.938) (0.319, 0.293, 0.887)
D_2	(0.344, 0.173, 0.923)
D_3	(0.386, 0.186, 0.904)
C_1 C_2	(-0.011, 0.037, 0.999) (0, 0.035, 0.999)
B_1 B_2	(0.276, 0, 0.961) (0.278, 0, 0.954)
F_1 F_2 F_3 F_4	(0.255, 0.967, 0.014) (0.34, 0.929, -0.003) (0.259, 0.965, -0.03) (0.313, 0.946, -0.042)