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

Michele Guerrini\textsuperscript{1,2}, Arrigo Calzolari\textsuperscript{2} and Stefano Corni\textsuperscript{*2,3}

\textsuperscript{1}Dipartimento FIM, Università di Modena e Reggio Emilia, Italy
\textsuperscript{2}CNR Nano Istituto Nanoscienze, Centro S3, I-41125 Modena, Italy
\textsuperscript{3}Dipartimento di Scienze Chimiche, Università di Padova, Italy

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\textsuperscript{-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**    |                  |                    |                     |
|                | D11 1.918        | D12 1.994          | 3.153 0.331         | 1.442               |
| **Dimer 2**    |                  |                    |                     |
|                | D2 2.023         |                    | 2.981 1.693         |                     |
| **Dimer 3**    |                  |                    |                     |
|                | D3 2.047         |                    | 3.282 1.635         |                     |
| **1D chain**   |                  |                    |                     |
|                | C1 1.841         | C2 1.968           | 3.95 0.0725         | 1.636               |
| **2D film**    |                  |                    |                     |
|                | F1 1.87          | F2 1.71            | 7.821 0.24          | 1.5                 |
|                | F3 1.98          | F4 2.138           | 3.912 0.27          |                     |
| **3D bulk**    |                  |                    |                     |
|                | B1 1.887         | B2 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 (D11)   | 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           |
| **Dimer 2**    | 1.994 eV (D12)   | 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 (D2)    | 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 (D₃)  
|---|---|---|---|
| H-1 → L  (1.703 eV) | 0.59 |
| H → L+1 (1.754 eV) | -0.76 |
| H-3 → L (2.706 eV) | -0.17 |
| H-2 → L+1 (2.57 eV) | -0.128 |
| H-1 → L+2 (2.698 eV) | 0.13 |
| H → L+3 (2.646 eV) | 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 semi-local 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):  \(\alpha\) (XY) = 90.00°  \(\beta\) (ZX) = 94.30°  \(\gamma\) (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):  \(\alpha\) (XY) = 90.00°  \(\beta\) (ZX) = 73.74°  \(\gamma\) (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): \(\alpha (XY) = 90.00^\circ\) \(\beta (ZX) = 90.00^\circ\) \(\gamma (YZ) = 90.00^\circ\)

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): \(\alpha (XY) = 90.00^\circ\) \(\beta (ZX) = 90.00^\circ\) \(\gamma (YZ) = 90.00^\circ\)

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): \( X = 26.02 \quad Y = 22.33 \quad Z = 36.75 \)
- Angles (degrees): \( \alpha (XY) = 90.00^\circ \quad \beta (ZX) = 90.00^\circ \quad \gamma (YZ) = 90.00^\circ \)

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): \( X = 36.75 \quad Y = 17.83 \quad Z = 36.75 \)
- Angles (degrees): \( \alpha (XY) = 90.00^\circ \quad \beta (ZX) = 90.00^\circ \quad \gamma (YZ) = 90.00^\circ \)

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): \( \alpha (XY) = 90.00^\circ \), \( \beta (ZX) = 90.00^\circ \), \( \gamma (YZ) = 90.00^\circ \)

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 $\omega$

$$
E_{\text{ext},p}^i(\omega) = E_0(\omega)\delta_p^i
$$

where index $p=x,y,z$ fixes direction of external electric field polarization, index $i$ refers to electric field $i$-th component and $\delta_p^i$ 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

$$
n_p(r,\omega) = \int_{\text{ext},p} \chi(r',\omega) E_{\text{ext},p}^i(\omega) \chi(r,\omega) d^3r' = -\int r' E_{\text{ext},p}^i(\omega) \chi(r,\omega) d^3r' = -E_0(\omega) \int r' \chi(r',\omega) d^3r'
$$

where repeated indices are implicitly summed and $\chi$ 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

$$
d_{i,p}(\omega) = \int n_p(r,\omega) r^i d^3r = -\int r^i E_{\text{ext},p}^i(\omega) d^3r' = \alpha_{i,i}(\omega) E_{\text{ext},p}^i(\omega)
$$

$$
\alpha_{i,i}(\omega) = -\int r^i E_{\text{ext},p}^i(\omega) d^3r' = \alpha_{ii}(\omega)
$$

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

$$
\alpha_q(\omega) = -\sum_{\alpha} d_{i}^{\alpha} d_{j}^{\alpha*} \left[ \frac{1}{\omega - \omega_{\alpha} + i\eta} - \frac{1}{\omega + \omega_{\alpha} + i\eta} \right]
$$

where indices $\alpha, \beta$ refer to many-body excited states, $\omega_{\alpha}$ is the excitation energy from ground state to excited state $\alpha$ and $d_{i}^{\alpha}$ is $i$-th component of the transition dipole moment from ground state to excited state $\alpha$. We can give a more compact representation of expression (5) by using a matrix notation

$$
\alpha(\omega) = \mathbf{W} \Lambda \mathbf{W}^{-1} = \sum_{\alpha} \mathbf{w}^{\alpha} \mathbf{w}^{t\alpha} \lambda_{\alpha}(\omega)
$$
where $W$ matrix contains column by column the normalized eigenvectors $w^\alpha$ with components (7), which gives the normalized direction of the transition dipole moment associate to peak $\alpha$, while diagonal matrix $\Lambda$ contains the associated eigenvalue $\lambda_\alpha$ that is frequency dependent. If one assumes that the excitation energies are well separated, when in proximity of a certain peak of energy $\omega_\alpha$ 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 $\omega_\alpha$. At the end we obtain our final density as

$$n(\mathbf{r},\omega = \omega_\alpha) = w^\alpha_x n_x(\mathbf{r},\omega) + w^\alpha_y n_y(\mathbf{r},\omega) + w^\alpha_z n_z(\mathbf{r},\omega)|_{\omega = \omega_\alpha}$$

(9)

| Peak ($\alpha$) | weights $w^\alpha_i$ |
|-----------------|-----------------------|
| M               | (0.335, -0.187, 0.923) |
| D$_{11}$        | (0.341, -0.06, 0.938)  |
| D$_{12}$        | (0.319, 0.293, 0.887)  |
| D$_2$           | (0.344, 0.173, 0.923)  |
| D$_3$           | (0.386, 0.186, 0.904)  |
| C$_1$           | (-0.011, 0.037, 0.999) |
| C$_2$           | (0, 0.035, 0.999)      |
| B$_1$           | (0.276, 0, 0.961)      |
| B$_2$           | (0.278, 0, 0.954)      |
| F$_1$           | (0.255, 0.967, 0.014)  |
| F$_2$           | (0.34, 0.929, -0.003)  |
| F$_3$           | (0.259, 0.965, -0.03)  |
| F$_4$           | (0.313, 0.946, -0.042) |