Supporting Information

Interplay between Intra- and Inter-Molecular Charge Transfer in the Optical Excitations of J-aggregates

Michele Guerrini,[1,2,3] Caterina Cocchi,[3*] Arrigo Calzolari,[2] Daniele Varsano,[2*] and Stefano Corni[2,4]

[1]*Dipartimento FIM, Università di Modena e Reggio Emilia, Italy*

[2]*CNR Nano Istituto Nanoscienze, Centro S3, Modena, Italy*

[3]*Department of Physics and IRIS Adlershof, Humboldt-Universität zu Berlin, Berlin, Germany*

[4]*Dipartimento di Scienze Chimiche, Università di Padova, Italy*

Corresponding Authors: caterina.cocchi@physik.hu-berlin.de, daniele.varsano@nano.cnr.it

Section 1 – Additional information about the electronic and optical properties of the isolated push-pull monomer

Table S1 - *HOMO-LUMO gap of the isolated push-pull monomer computed with different approximations for the exchange-correlation functionals as starting points for GW calculations (G_0W_0 and self-consistent on the eigenvalues only ev-GW). Calculations performed on relaxed geometry (cc-pVTZ basis set, force minimization threshold 10^{-4} Hartree /Bohr).*

Starting point	DFT	G_0W_0	ev-GW
HARTREE-FOCK	8.42 eV	7.10 eV	6.91 eV
CAM-B3LYP	5.57 eV	6.46 eV	6.59 eV
B3LYP	3.25 eV	5.89 eV	6.44 eV
PBE0	3.56 eV	5.98 eV	6.47 eV
PBE	2.05 eV	5.19 eV	6.40 eV

Table S2 *Comparison between the HOMO-LUMO gap of the monomer calculated from DFT with localized basis set using MOLGW and with plane-waves using the Quantum Espresso code. Calculations referred to the non-relaxed monomer geometry extracted from bulk J-aggregate.*

Code + convergence parameters	***DFT gap***
MOLGW *(cc-pVTZ, PBE, all electrons, 10^{-8} Ry energy convergence accuracy)*	1.70 eV
QUANTUM ESPRESSO *(plane waves cut-off 60 Ry, PBE, optimized norm-conserving pseudopotentials, 10^{-8} Ry energy convergence accuracy).* *Supercell type: orthorhombic (a=18 Å, b=18 Å, c=29 Å)* *Vacuum layer of 20 Å to avoid spurious interactions between the replicas.*	1.67 eV

Table S3 – *Energy and composition of the first five excited state of the push-pull monomer $C_{24}H_{19}F_4N$, including the excitation energy and the weight given by the square of the normalized BSE coefficients. Only weights contributing more than 10% are reported. Calculations are performed on the non-relaxed geometry using the MOLGW code and the PBE functional as starting point for ev-GW calculations.*

Excited state energy (eV)	**Occupied level**	**Unoccupied level**	**Weight $\left\|A_{cv}^{\lambda}\right\|^2$**	**Oscillator strength**
E^{M}= 3.39	HOMO	LUMO	0.83	3.50
E^{M2} = 4.12	HOMO	LUMO+3	0.73	0.08
E^{M3} = 4.39	HOMO-4 HOMO-1 HOMO HOMO	LUMO LUMO LUMO+1 LUMO+2	0.16 0.30 0.12 0.13	0.09
E^{M4} = 4.45	HOMO-4 HOMO-1 HOMO	LUMO LUMO LUMO+2	0.21 0.42 0.21	0.30
E^{M5} = 4.56	HOMO-2 HOMO-2	LUMO LUMO+1	0.63 0.13	0.04
E^{M6} = 4.62	HOMO-1 HOMO	LUMO LUMO+1	0.11 0.59	0.04

Table S4 – *Energy and composition of the first five excited state of the push-pull monomer $C_{24}H_{19}F_4N$, including the excitation energy and the weight given by the square of the normalized BSE coefficients. Only weights contributing more than 10% are reported. Calculations are performed on the relaxed geometry using the MOLGW code and the PBE functional as starting point for ev-GW calculations.*

Excited state energy (eV)	Occupied level	Unoccupied level	Weight $\left\|A_{cv}^{\lambda}\right\|^2$	Oscillator strength
E^{M}= 3.85	HOMO	LUMO	0.76	3.36
E^{M2} = 4.43	HOMO	LUMO+3	0.64	0.02
E^{M3} = 4.52	HOMO-2 HOMO-2	LUMO LUMO+1	0.64 0.15	0.05
E^{M4} = 4.63	HOMO-5 HOMO-1 HOMO-1 HOMO	LUMO LUMO LUMO+2 LUMO+1	0.21 0.25 0.10 0.19	0.08
E^{M5} = 4.68	HOMO-5 HOMO-1	LUMO LUMO	0.20 0.46	0.20
E^{M6} = 5.00	HOMO HOMO	LUMO LUMO+1	0.10 0.49	0.08

Table S5 – *Energy and composition of the first five excited state of the push-pull monomer $C_{24}H_{19}F_4N$, including the excitation energy and the weight given by the square of the normalized BSE coefficients. Only weights contributing more than 10% are reported. Calculations are performed on the relaxed geometry using the MOLGW code and the CAM-B3LYP functional as starting point for ev-GW calculations.*

Excited state energy (eV)	Occupied level	Unoccupied level	Weight $\left\|A_{cv}^{\lambda}\right\|^2$	Oscillator strength
E^{M}= 3.73	HOMO	LUMO	0.768	2.44
E^{M2} = 4.50	HOMO HOMO	LUMO+2 LUMO+3	0.12 0.39	0.001
E^{M3} = 4.58	HOMO-5 HOMO-2 HOMO	LUMO LUMO LUMO+3	0.13 0.18 0.19	0.05
E^{M4} = 4.60	HOMO-2 HOMO-2	LUMO LUMO+1	0.39 0.12	0.01
E^{M5} = 4.70	HOMO-5 HOMO-1 HOMO	LUMO LUMO LUMO+1	0.11 0.44 0.15	0.05
E^{M5} = 5.16	HOMO-1 HOMO HOMO	LUMO LUMO LUMO+1	0.20 0.12 0.41	0.15

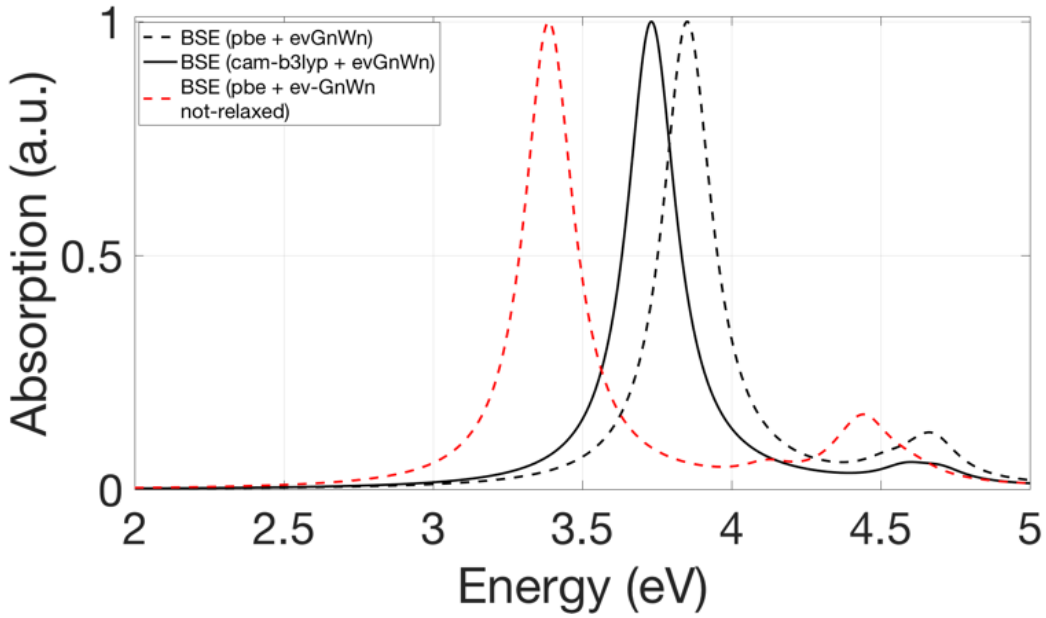

Figure S1 – BSE absorption spectra of the push-pull dye $C_{24}H_{19}F_4N$ obtained using two different xc-starting point functionals as starting point for ev-GW calculations: PBE (dashed line) and CAM-B3LYP (solid line). Calculations performed with the MOLGW cc-pVTZ basis in the Tamm-Dancoff approximation on the non-relaxed geometry in red and on the relaxed geometry in black.

Section 2 –Additional information about the electronic and optical properties of the J-aggregate

Table S6 - *DFT and GW gaps for the J-aggregate. G_0W_0 is perturbative GW; ev-G_nW_0 is eigenvalues-only self-consistent GW where in each cycle one updates the energy eigenvalues only in the Green's function G while maintaining the screening W_0 as in the G_0W_0 first step; ev-G_nW_n updates at each cycle the energy eigenvalues in both the Green's function G and the screening W*

DFT (PBE)	G_0W_0	ev-G_nW_0	ev-G_nW_n
1.47 eV	3.21 eV	3.37 eV	3.37 eV

Table S7 - *Energy and composition of the J and J_{CT} excitations of the J-aggregate, including the excitation energy, the **k**-point at which the transition take place expressed in reciprocal crystal units (rcu), and the weight given by the square of the normalized BSE coefficients. Only weights larger than 2% are reported.*

Excited state energy (eV)	**Occupied band**	**Unoccupied band**	**k-point (rcu)**	$\epsilon_{ck}^{QP} - \epsilon_{vk}^{QP}$ **(eV)**	**Weight** $10 \times \left\|A_{cvk}^{\lambda}\right\|^2$
E^{J1}= 2.786	VBM	CBm	(-0.4, 0, 0)	3.21	0.75
	VBM	CBm	(0.4, 0, 0)	3.21	0.72
	VBM	CBm	(0.4, 0, -0.5)	3.22	0.66
	VBM	CBm	(-0.4, 0, 0.5)	3.22	0.64
	VBM-1	CBm+1	(-0.4, 0, 0.5)	3.23	0.64
	VBM-1	CBm+1	(0.4, 0, -0.5)	3.23	0.58
	VBM-1	CBm+1	(-0.4, 0, 0)	3.24	0.54
	VBM-1	CBm+1	(0.4, 0, 0)	3.24	0.53
E^{J3}= 2.813	VBM-2	CBm+1	(-0.4, 0, 0)	3.33	0.24
	VBM-2	CBm+1	(-0.4, 0, 0.5)	3.34	0.24
	VBM-2	CBm+1	(0.4, 0, 0)	3.33	0.23
	VBM-3	CBm	(-0.4, 0, 0)	3.35	0.22
	VBM-3	CBm	(0.4, 0, -0.5)	3.34	0.22
	VBM-3	CBm	(-0.4, 0, 0.5)	3.34	0.22
	VBM-2	CBm+1	(0.4, 0, -0.5)	3.34	0.21
	VBM-3	CBm	(0.4, 0, 0)	3.35	0.21
E^{J5}= 2.903	VBM	CBm	(-0.4, 0, 0)	3.21	0.66
	VBM	CBm	(-0.2, 0, 0)	3.27	0.53
	VBM	CBm	(-0.2, 0, 0.5)	3.28	0.49
	VBM	CBm	(-0.4, 0, 0.5)	3.22	0.45
	VBM	CBm	(0.4, 0.333, -0.5)	3.31	0.38
	VBM-1	CBm+1	(0.4, -0.333, -0.5)	3.32	0.38
	VBM-1	CBm+1	(-0.4, 0, 0.5)	3.23	0.37
	VBM	CBm	(0.4, 0.333, 0)	3.31	0.33
	VBM-1	CBm+1	(0.4, -0.333, 0)	3.32	0.32
	VBM-1	CBm+1	(-0.2, 0, 0.5)	3.30	0.26
	VBM-1	CBm+1	(-0.2, 0, 0)	3.32	0.24
	VBM-1	CBm+1	(-0.4, 0, 0)	3.24	0.21

	VBM	CBm	(0.4, -0.333, 0)	3.31	0.21
	VBM-1	CBm+1	(-0.4, 0.333, 0.5)	3.32	0.21
	VBM-1	CBm+1	(0.4, 0.333, 0)	3.32	0.21
	VBM	CBm	(-0.4, -0.33, 0.5)	3.31	0.21
E^{J18}= 3.03	VBM	CBm+1	(0.4, 0, 0)	3.22	0.76
	VBM	CBm+1	(-0.4, 0, 0)	3.22	0.68
	VBM	CBm+1	(-0.2, 0, 0.5)	3.29	0.64
	VBM	CBm+1	(0.2, 0, -0.5)	3.29	0.63
	VBM-1	CBm	(0, 0, 0)	3.37	0.33
	VBM-1	CBm	(0.4, 0, -0.5)	3.23	0.22
	VBM-2	CBm	(-0.2, 0, 0)	3.34	0.21
	VBM	CBm+1	(0, 0, -0.5)	3.37	0.20

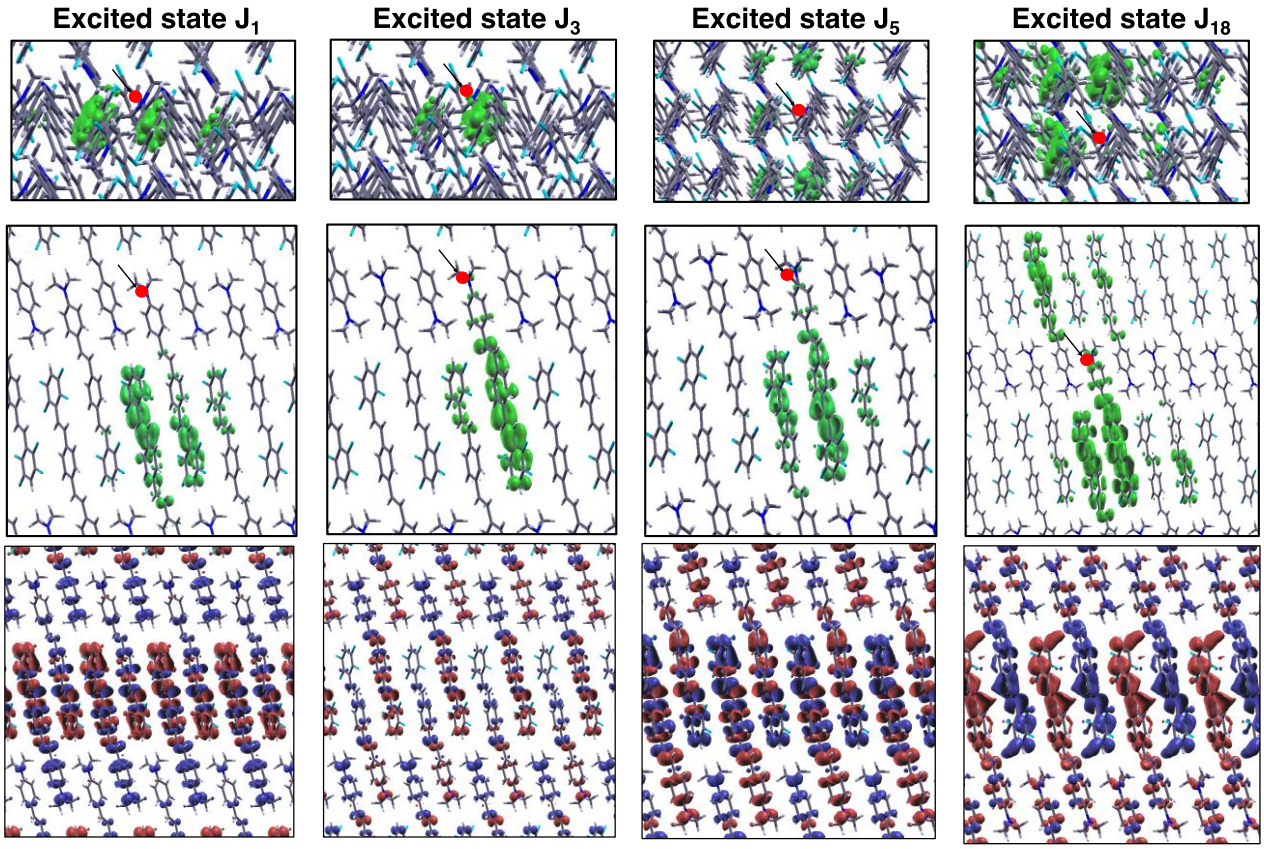

Figure S2 – Exciton probability densities with fixed hole position marked by the red dot (upper panels) and transition densities (lower panels) of the four excited states of J-aggregate, reported in Table S7. Isosurfaces fixed at 10% of the maximum value.