Aggregates of quadrupolar dyes for two-photon absorption: the role of intermolecular interactions

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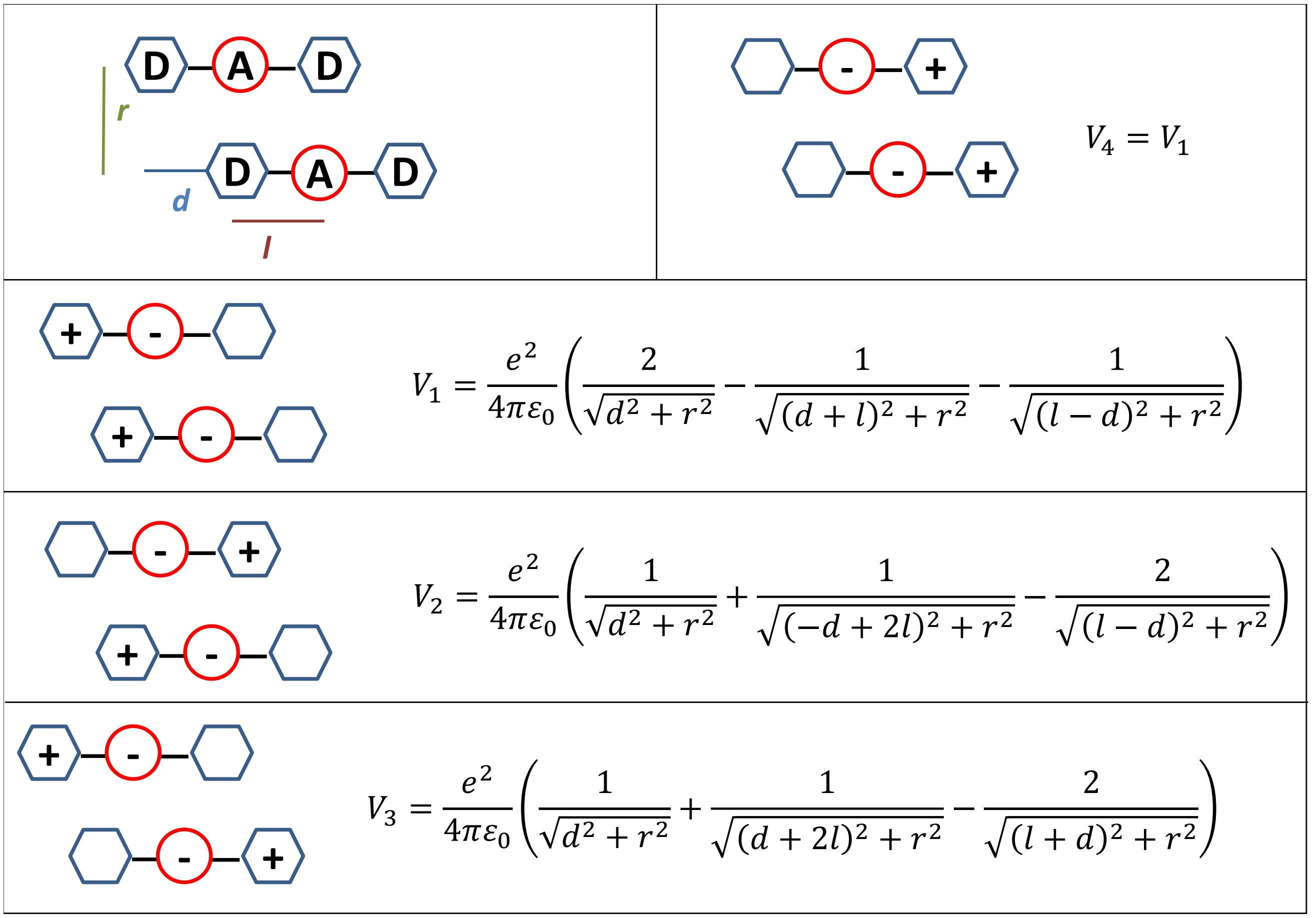
Supporting Information



$$V_4 = V_1$$

$$V_1 = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{2}{\sqrt{d^2+r^2}} - \frac{1}{\sqrt{(d+l)^2+r^2}} - \frac{1}{\sqrt{(l-d)^2+r^2}}\right)$$

$$V_2 = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{\sqrt{d^2+r^2}} + \frac{1}{\sqrt{(-d+2l)^2+r^2}} - \frac{2}{\sqrt{(l-d)^2+r^2}}\right)$$

$$V_3 = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{\sqrt{d^2+r^2}} + \frac{1}{\sqrt{(d+2l)^2+r^2}} - \frac{2}{\sqrt{(l+d)^2+r^2}}\right)$$

Figure S1. Point-charge interactions in the dimer arranged in a “faced” geometry. Geometrical parameters are defined in the top-left panel.

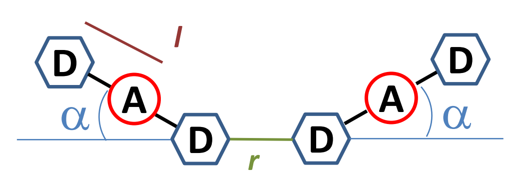
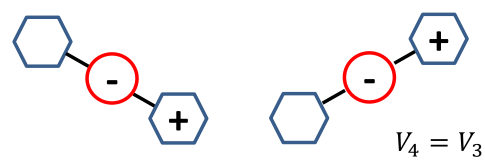
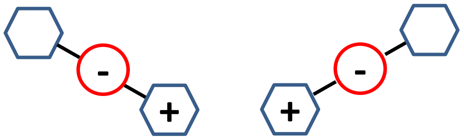
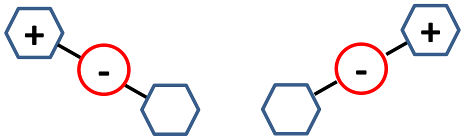
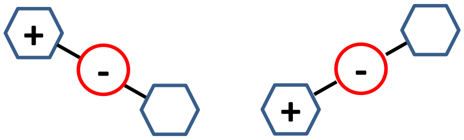
	 $V_4 = V_3$
	$V_1 = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r} + \frac{1}{r + 2l\,cos(\alpha)} - \frac{2}{\sqrt{[l\,sin(\alpha)]^2 + [d + l\,cos(\alpha)]^2}}\right)$
	$V_2 = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r + 2l\,cos(\alpha)} + \frac{1}{r + 4l\,cos(\alpha)} - \frac{2}{\sqrt{[l\,sin(\alpha)]^2 + [d + 3l\,cos(\alpha)]}}\right)$
	$V_3 = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r + 2l\,cos(\alpha)} + \frac{1}{\sqrt{[2l\,sin(\alpha)]^2 + [r + 2l\,cos(\alpha)]^2}} - \frac{1}{\sqrt{[l\,sin(\alpha)]^2 + [r + l\,cos(\alpha)]^2}} - \frac{1}{\sqrt{[l\,sin(\alpha)]^2 + [r + 3l\,cos(\alpha)]^2}}\right)$

Figure S2. Point-charge interactions in the dimer arranged in a "fan" geometry. Geometrical parameters are defined in the top-left panel.

Determination of η and τ parameters

The model parameters η and τ are determined from experimental spectral data. In particular, when the maxima of the 1PA and 2PA spectra are available, η and τ can be easily estimated as follows[1] (here τ = $\sqrt{2}t$):

$$\hbar\omega_{gc} = \sqrt{2}\tau\sqrt{\frac{1-\rho}{\rho}}$$

$$\hbar\omega_{ge} = \sqrt{2}\tau\sqrt{\frac{1-\rho}{\rho}}$$

where ρ is the quadrupolar character: $\rho = 0.5\left(1 - \eta/\sqrt{\eta^2 + 2\tau^2}\right)$. $\hbar\omega_{gc}$ and $\hbar\omega_{ge}$ are derived from the experiment (for curcumins $\hbar\omega_{gc} = 2.54$ eV and $\hbar\omega_{ge} = 3.22$ eV). From the relations reported above, for **1** we obtain η = 0.94 eV and τ = 0.93 eV (corresponding to ρ = 0.21).

When molecular vibrations are introduced into the model (it is not the case in this paper), the parameters have to be slightly modified accordingly[2].

When the 2PA maximum is not available, the guess of the parameters is more arbitrary, but other spectral properties (such as solvatochromic data and band-shapes) are exploited to best fix the parameters.

Dimer structures of molecule 1

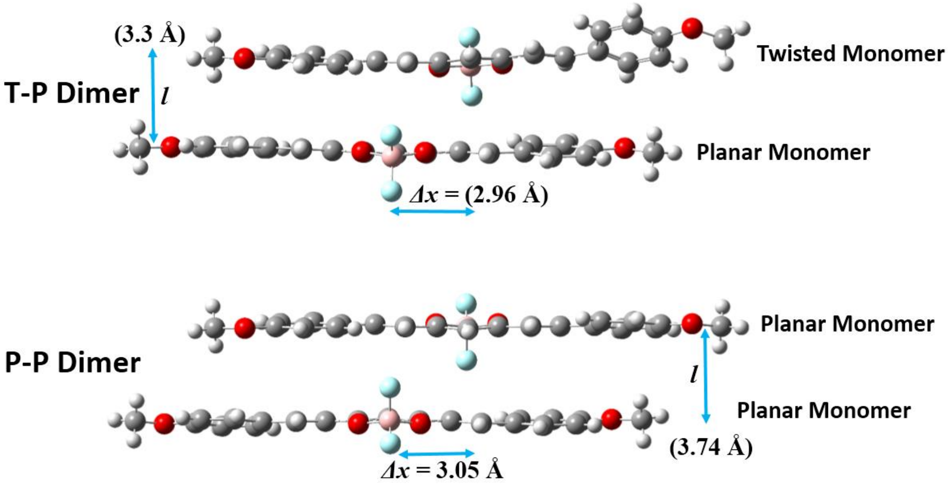


Figure S3. Two different structures for the molecular entity can be identified from X-ray data of crystals of **1** [A. D'Aléo, A. Felouat, V. Heresanu, A. Ranguis, D. Chaudanson, A. Karapetyan, M. Giorgi and F. Fages, J. Mater. Chem. C, 2014, 2, 5208–5215]: a twisted structure (T) and a planar (P) structure. In the crystal, a tetrameric structure of the kind T-P-P-T can be singled out. Accordingly, two different dimers will be considered, the T-P and the P-P dimers, as shown in the figure.

TDDFT results for curcumin monomer

Table S1. TDDFT results for curcumin monomer (crystallographic geometry, gas phase).

System	Transitions	1PA Energy (eV) and Wavelength (nm)	Oscillator Strength	Nature of transitions (Contributions >15%)	2PA Energy (eV)	σ_2 (GM)
Gas phase Non-Planar	*s0→s1 (c)*	3.35 eV 372 nm	2.0422	*h→l* (90%)	3.33	21.5
	s0→s2 (e)	4.10 eV 302 nm	0.1053	*h-1→l* (90%)	4.10	1950
	s0→s3	4.63 eV 268 nm	0.0233	*h-2→l* (81%)	4.62	42
	s0→s4	4.80 eV 258 nm	0.0009	*h-4→l* (44%)	4.80	39.4
	s0→s5	4.86 eV 255 nm	0.0007	*h-3→l* (42%)	4.86	17.3
	s0→s6	5.06 eV 245 nm	0.0039	*h-7→l* (91%)	5.06	4.11
	s0→s7	5.22 eV 238 nm	0.0191	*h→l+1* (79%)	5.22	3920
Gas phase Planar	*s0→s1 (c)*	3.28 eV 378 nm	2.11	*h→l* (90%)	3.28	17
	s0→s2 (e)	4.10 eV 304 nm	0.084	*h-1→l* (90%)	4.08	2030
	s0→s3	4.59 eV 270 nm	0.0404	*h-2→l* (82%)	4.59	30.5
	s0→s4	4.80 eV 258 nm	0.0005	*h-4→l* (23%) *h-3→l* (19%) *h-1→l+2* (16%)	4.80	82.5
	s0→s5	4.81 eV 258 nm	0.0021	*h-4→l* (21%) *h-3→l* (22%) *h-1→l+3* (15%)	4.81	21.9
	s0→s6	5.06 eV 245 nm	0.0010	*h-7→l* (89%)	5.06	22.4
	s0→s7	5.12 eV 242 nm	0.0102	*h→l+1* (79%)	5.06	4270

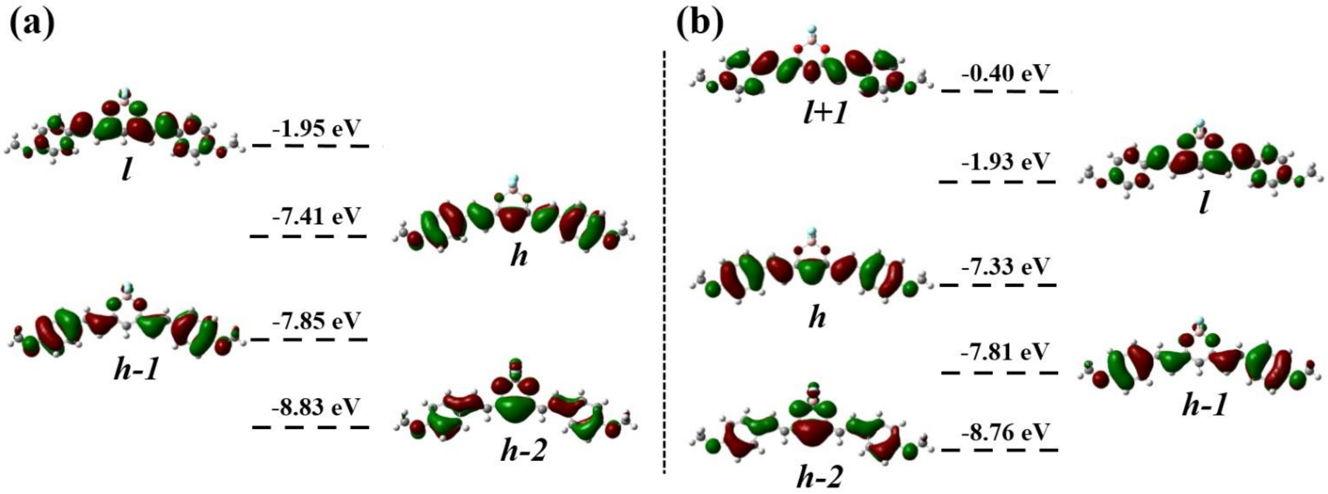


Figure S4. Frontier Molecular Orbital plots for (a) the twisted and (b) the planar monomers (crystallographic geometry, gas phase).

Table S2. TDDFT results for curcumin monomer (optimized geometry, gas phase and DCM solvent).

System	Transitions	1PA Energy (eV) and Wavelength (nm)	Oscillator Strength	Nature of transitions (Contributions >15%)	2PA energy (eV)	σ_2 (GM)
Monomer in gas phase	*s0→s1 (c)*	3.17 eV 391 nm	2.1456	*h*→*l* (67%)	3.17	15.3
	s0→s2 (e)	3.98 eV 312 nm	0.0740	*h-1*→*l* (67%)	3.98	2170
	s0→s3	4.56 eV 272 nm	0.0337	*h-2*→*l* (64%)	4.56	28.8
	s0→s4	4.72 eV 263 nm	0.0007	*h-3*→*l* (41%) *h*→*l+4* (33%)	4.71	220
	s0→s5	4.73 eV 262 nm	0.0033	*h-4*→*l* (44%) *h*→*l+2* (34%)	4.72	195
	s0→s6	4.92 eV 252 nm	0.0018	*h-7*→*l* (56%)	4.92	789
	s0→s7	4.96 eV 250 nm	0.0034	*h*→*l+1* (54%)	4.96	4620
Monomer in DCM	*s0→s1 (c)*	2.84 eV 437 nm	2.3359	*h*→*l* (67%)	2.83	31.2
	s0→s2 (e)	3.70 eV 335 nm	0.0935	*h-1*→*l* (66%)	3.69	4930
	s0→s3	4.54 eV 273 nm	0.0179	*h-2*→*l* (59%)	4.54	79.4
	s0→s4	4.60 eV 269 nm	0.0013	*h-3*→*l* (52%)	4.60	326
	s0→s5	4.61 eV 269 nm	0.0005	*h-4*→*l* (53%)	4.61	90.4
	s0→s6	4.81 eV 258 nm	0.0075	*h*→*l+1* (64%)	4.81	26300

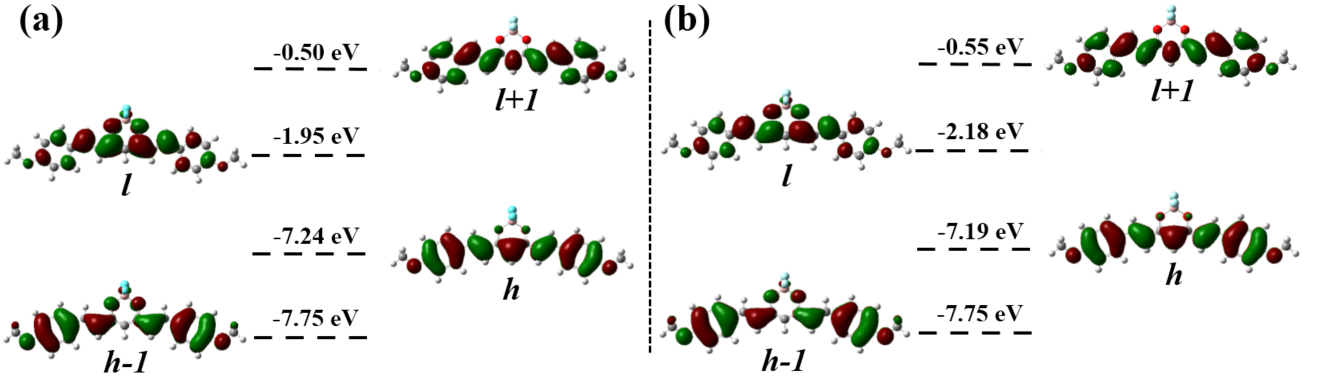


Figure S5. Frontier Molecular Orbital plots for curcumin monomer for optimized geometry in gas phase (a) and DCM solvent (b).

TDDFT Results for curcumin dimers

P-P curcumin dimer

Table S3. TDDFT results for P-P curcumin dimer at distance 4.74 Å.

Transitions	1PA Energy (eV)	Oscillator Strength	Nature of transitions (Contributions >15%)
S0→S1 (C_1)	3.13 eV	0.0000	*H-1→L+1* (38%) c_a-c_b, CT *H→L* (51%) c_a-c_b, CT
S0→S2 (C_2)	3.36 eV	3.9797	*H-1→L* (42%) c_a+c_b, CT *H→L+1* (46%) c_a+c_b, CT
S0→S3	3.89 eV	0.0062	*H-1→L* (42%) c_a+c_b, CT *H→L+1* (33%) c_a+c_b, CT
S0→S4	3.90 eV	0.0015	*H-1→L+1* (46%) c_a-c_b, CT *H→L* (31%) c_a-c_b, CT
S0→S5 (E_1)	4.01 eV	0.1308	*H-3→L+1* (38%) e_a-e_b, CT *H-2→L* (45%) e_a-e_b, CT
S0→S6 (E_2)	4.12 eV	0.0000	*H-3→L* (44%) $e_{a+}e_b$, CT *H-2→L+1* (46%) $e_{a+}e_b$, CT

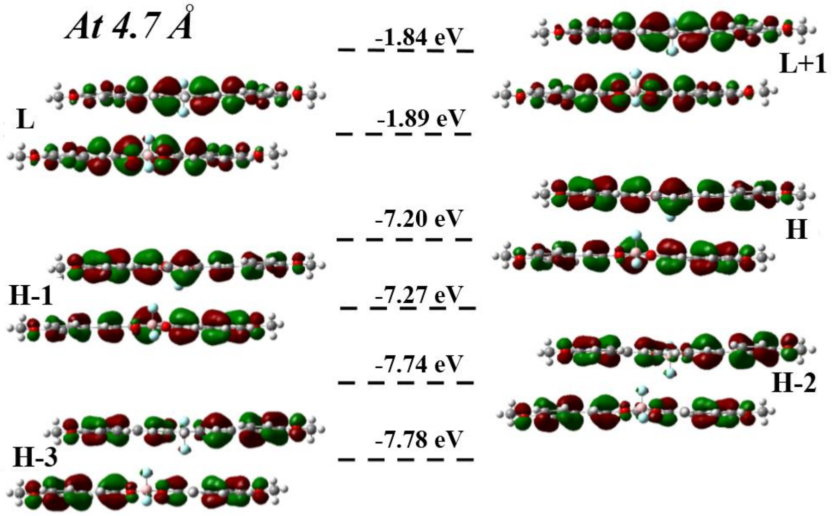


Figure S6. Frontier Molecular Orbital diagrams, TDDFT results for P-P curcumin dimer at distance 4.7 Å.

Table S4. TDDFT results for P-P curcumin dimer at distance 5.74 Å.

Transitions	1PA Energy (eV)	Oscillator Strength	Nature of transitions (Contributions >15%)
S0→S1 (C_1*)*	3.17	0.0001	*H-1→L+1* (41%) c_a-c_b, CT *H→L* (43%) c_a-c_b, CT
S0→S2 (C_2*)*	3.35	4.0191	*H-1→L* (44%) c_a+c_b, CT *H→L+1* (45%) c_a+c_b, CT
S0→S3 (E_1*)*	4.04	0.1431	*H-3→L+1* (39%) e_a-e_b, CT *H-2→L* (42%) e_a-e_b, CT
S0→S4	4.11	0.0001	*H-1→L* (23%) c_a+c_b, CT *H→L* (36%) c_a-c_b, CT *H→L+1* (18%)
S0→S5 (E_2*)*	4.11	0.0000	*H-3→L* (40%) $e_{a+}e_b$, CT *H-2→L+1* (42%) $e_{a+}e_b$, CT
S0→S6	4.12	0.0001	*H-1→L+1* (39%) c_a-c_b, CT *H→L+1* (23%) c_a+c_b, CT *H-1→L* (18%)

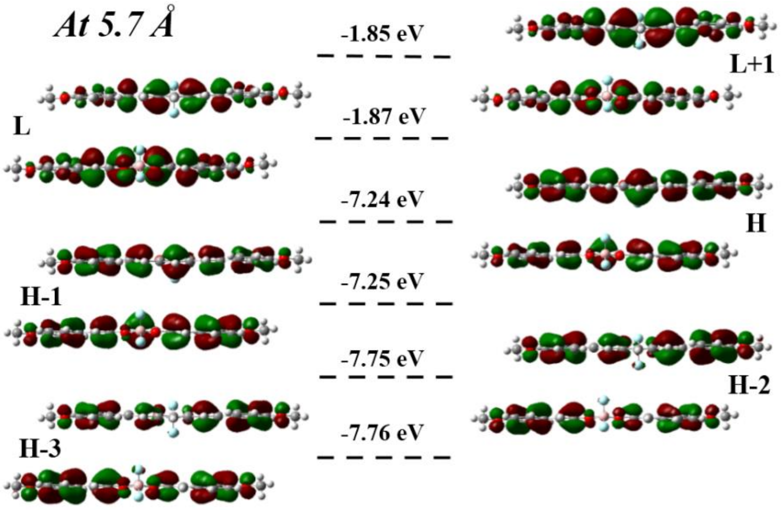


Figure S7. Frontier Molecular Orbital diagrams, TDDFT results for P-P curcumin dimer at distance 5.7 Å.

Table S5. TDDFT results for P-P curcumin dimer at distance 7.74 Å.

Transitions	1PA Energy (eV)	Oscillator Strength	Nature of transitions (Contributions > 15%)
S0→S1 (C_1)	3.21	0.0002	*H-1→L* (46%) c_a *H→L+1* (44%) c_b
S0→S2 (C_2)	3.33	4.0717	*H-1→L* (44%) c_a *H→L+1* (46%) c_b
S0→S3 (E_1)	4.06	0.1537	*H-3→L* (46%) e_a *H-2→L+1* (43%) e_b
S0→S4 (E_2)	4.10	0.0000	*H-3→L* (43%) e_a *H-2→L+1* (47%) e_b
S0→S5	4.39	0.0000	*H→L* (98%) CT
S0→S6	4.40	0.0000	*H-1→L+1* (98%) CT

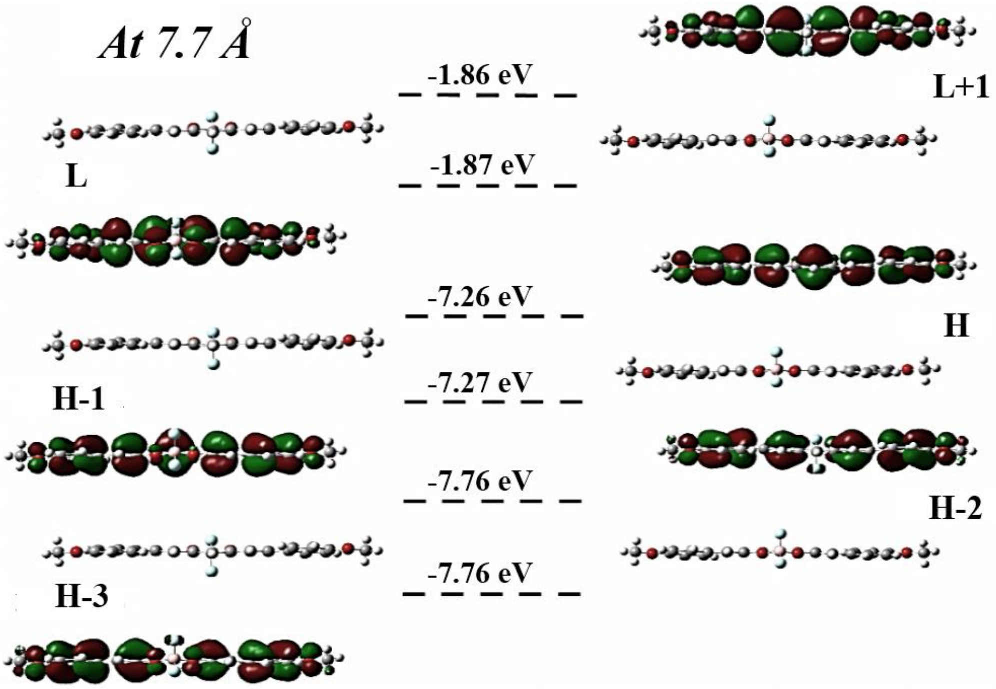


Figure S8. Frontier Molecular Orbital diagrams, TDDFT results for P-P curcumin dimer at distance 7.74 Å.

T-P curcumin dimer

Table S6. TDDFT results for T-P curcumin dimer at distance 3.3 Å.

Transitions	1PA Energy (eV)	Oscillator Strength	Nature of transitions (Contributions >15%)	2PA Energy (eV)	σ_2 (GM)
$S0\rightarrow S1$ (C_1)	2.91	0.0113	$H\rightarrow L$ (81%) c_a-c_b, CT	2.91	23.5
$S0\rightarrow S2$ (C_2)	3.39	3.6025	$H\rightarrow L+1$ (62%) c_a+c_b, CT	3.39	0.813
$S0\rightarrow S3$	3.56	0.2806	$H\text{-}1\rightarrow L$ (66%) c_a+c_b, CT	3.56	3.20
$S0\rightarrow S4$	3.78	0.0114	$H\text{-}1\rightarrow L+1$ (73%) c_a-c_b, CT	3.78	9.84
$S0\rightarrow S5$ (E_1)	3.91	0.0950	$H\text{-}2\rightarrow L$ (57%) e_a-e_b, CT	3.91	10.1
$S0\rightarrow S6$ (E_2)	4.12	0.0071	$H\text{-}3\rightarrow L$ (49%) e_a+e_b, CT $H\text{-}2\rightarrow L+1$ (38%) e_a+e_b, CT	4.12	2530

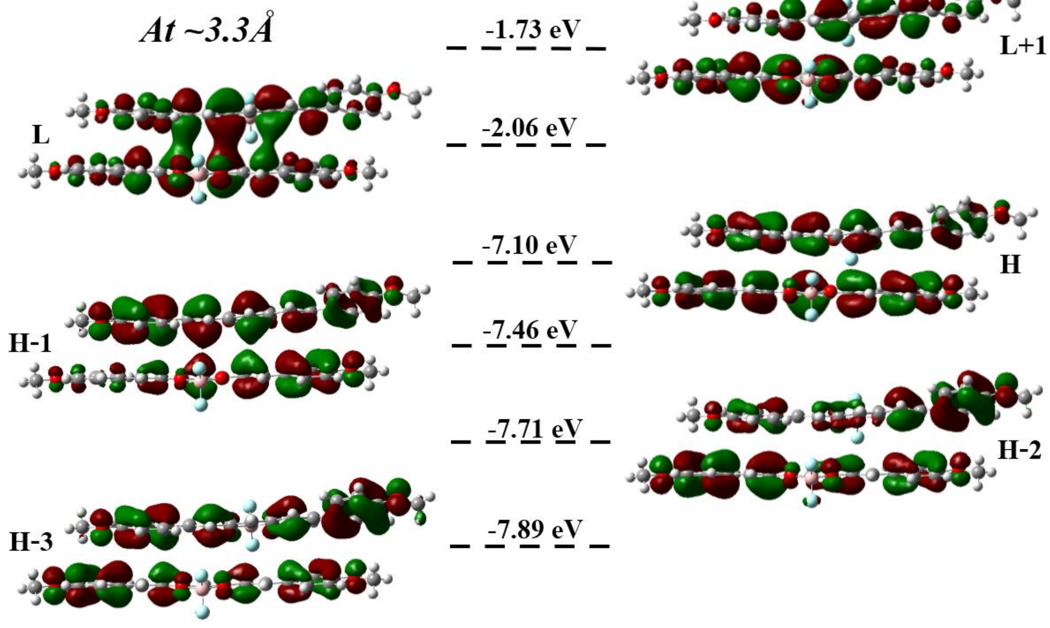


Figure S9. Frontier Molecular Orbital diagrams, TDDFT results for T-P curcumin dimer at distance 3.3 Å.

Table S7. TDDFT results for T-P curcumin dimer at distance 4.3 Å.

Transitions	1PA Energy (eV)	Oscillator Strength	Nature of transitions (Contributions >15%)
S0→S1 (C_1)	3.15	0.0554	*H-1→L (17%)* c_a *H→L (30%) CT* *H→L+1 (29%)* c_b
S0→S2 (C_2)	3.40	3.8751	*H-1→L (49%)* c_a *H→L+1 (38%)* c_b
S0→S3	3.83	0.0031	*H→L (62%) CT* *H→L+1 (19%)* c_b
S0→S4	3.99	0.0397	*H-1→L+1 (53%) CT*
S0→S5 (E_1)	4.04	0.1073	*H-3→L+1 (21%)* *H-2→L (19%) CT* *H-2→L+1 (18%)* e_b *H-1→L+1 (19%) CT*
S0→S6 (E_2)	4.13	0.0091	*H-3→ L (49%)* e_a *H-2→L+1 (38%)* e_b

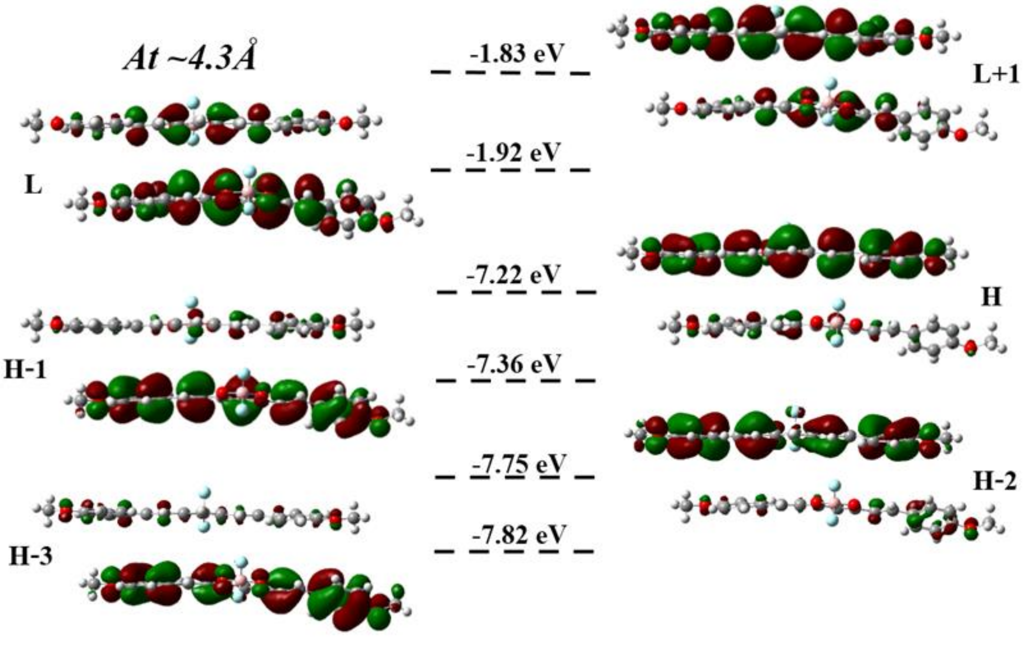


Figure S10. Frontier Molecular Orbital diagrams, TDDFT results for T-P curcumin dimer at distance 4.3 Å.

Table S8. TDDFT results for T-P curcumin dimer at distance 5.3 Å.

Transitions	1PA Energy (eV)	Oscillator Strength	Nature of transitions (Contributions > 15%)
S0→S1(C_1)	3.20	0.1023	*H-1→L (30%)* c_a *H→L+1 (56%)* c_b
S0→S2 (C_2)	3.39	3.8651	*H-1→L (58%)* c_a *H→L+1 (32%)* c_b
S0→S3	4.04	0.0107	*H→L (86%) CT*
S0→S4 (E_1)	4.05	0.1431	*H-3→L (29%)* e_a *H-2→L+1 (51%)* e_b
S0→S5 (E_2)	4.13	0.0122	*H-3→L (57%)* e_a *H-2→L+1 (33%)* e_b
S0→S6	4.22	0.0001	*H-1→L+1 (91%) CT*

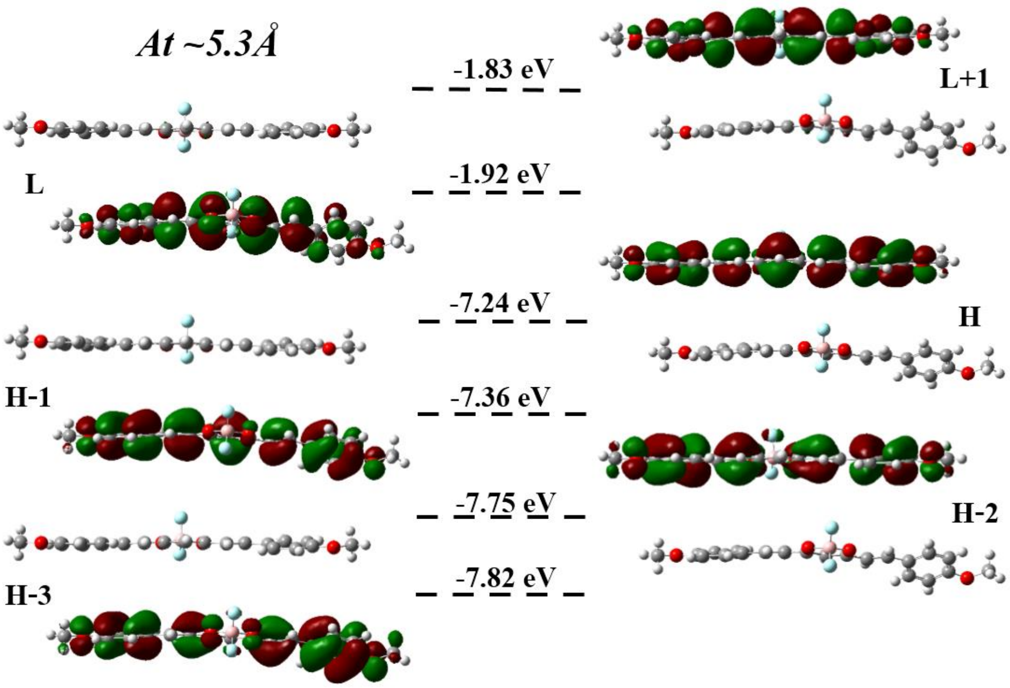


Figure S11. Frontier Molecular Orbital diagrams, TDDFT results for T-P curcumin dimer at distance 5.3 Å.

Table S9. TDDFT results for T-P curcumin dimer at distance 6.3 Å.

Transitions	1PA Energy (eV)	Oscillator Strength	Nature of transitions (Contributions > 15%)
S0→S1 (C_1)	3.22	0.1606	*H-1→L (28%)* c_a *H→L+1 (62%)* c_b
S0→S2 (C_2)	3.38	3.8305	*H-1→L (62%)* c_a *H→L+1 (28%)* c_b
S0→S3 (E_1)	4.07	0.1543	*H-3→L (25%)* e_a *H-2→L+1 (63%)* e_b
S0→S4 (E_2)	4.12	0.0181	*H-3→L (64%)* e_a *H-2→L+1 (26%)* e_b
S0→S5	4.21	0.0000	*H→L (97%) CT*
S0→S6	4.38	0.0000	*H-1→L+1 (95%) CT*

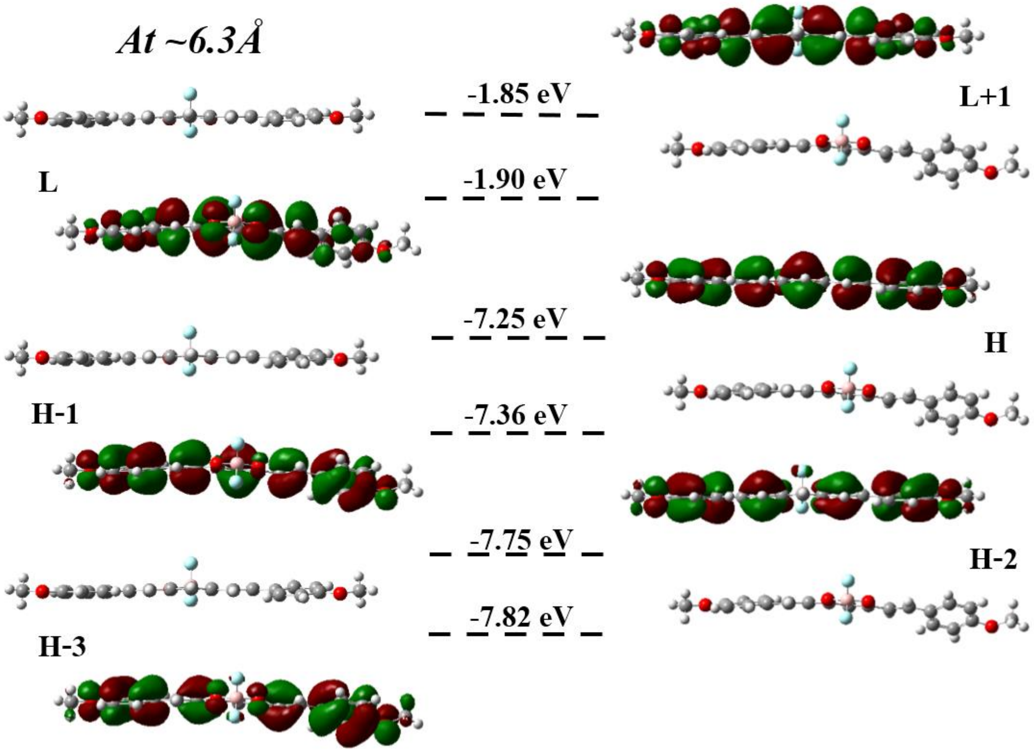


Figure S12. Frontier Molecular Orbital diagrams, TDDFT results for T-P curcumin dimer at distance 6.3 Å.

Table S10. TDDFT results for T-P curcumin dimer at distance 7.3 Å.

Transitions	1PA Energy (eV)	Oscillator Strength	Nature of transitions (Contributions >15%)
S0→S1 (C_1)	3.24	0.2352	*H-1→L (25%)* c_a *H→L+1 (66%)* c_b
S0→S2 (C_2)	3.37	3.7767	*H-1→L (65%)* c_a *H→L+1 (25%)* c_b
S0→S3 (E_1)	4.07	0.1501	*H-3→L (19%)* e_a *H-2→L+1 (70%)* e_b
S0→S4 (E_2)	4.12	0.0266	*H-3→L (71%)* e_a *H-2→L+1 (19%)* e_b
S0→S5	4.33	0.0000	*H→L (98%) CT*
S0→S6	4.50	0.0000	*H-1→L+1 (96%) CT*

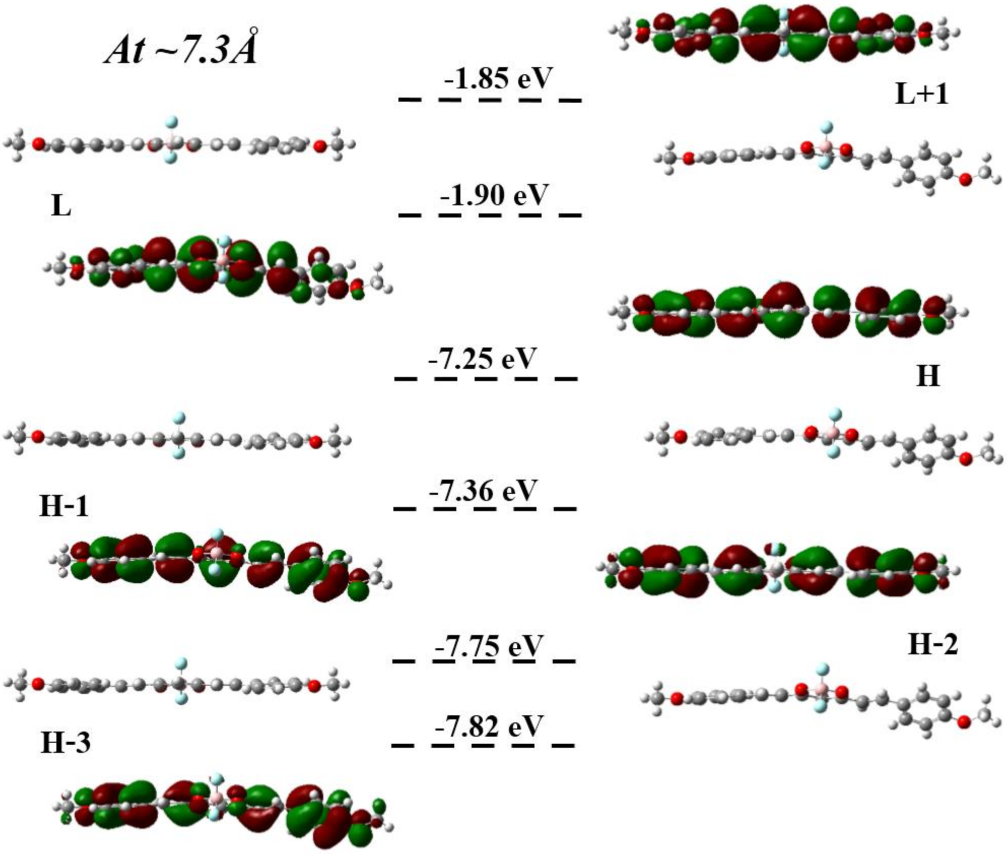


Figure S13. Frontier Molecular Orbital diagrams, TDDFT results for T-P curcumin dimer at distance 7.3 Å.

Table S11. TDDFT results for T-P curcumin dimer at distance 8.3 Å.

Transitions	1PA Energy (eV)	Oscillator Strength	Nature of transitions (Contributions > 15%)
S0→S1 (C_1)	3.25	0.3276	*H-1→L (21%)* c_a *H→L+1 (69%)* c_b
S0→S2 (C_2)	3.36	3.7032	*H-1→L (69%)* c_a *H→L+1 (21%)* c_b
S0→S3 (E_1)	4.08	0.1422	*H-3→L (13%)* e_a *H-2→L+1 (76%)* e_b
S0→S4 (E_2)	4.11	0.0374	*H-3→L (76%)* e_a *H-2→L+1 (13%)* e_b
S0→S5	4.43	0.0000	*H→L (98%) CT*
S0→S6	4.59	0.0417	*H-4→L+1 (82%)*

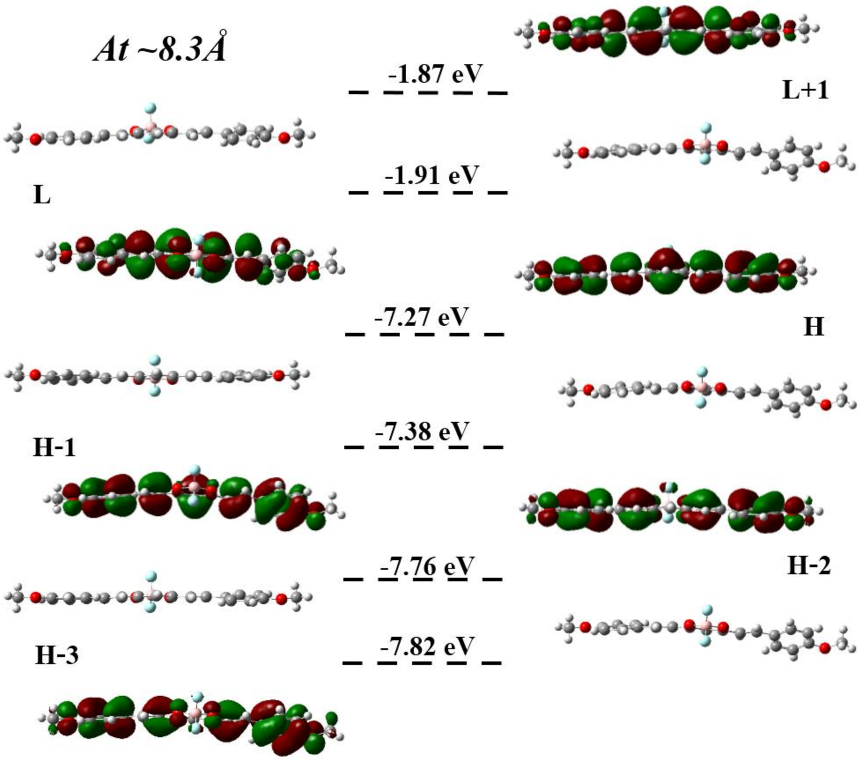


Figure S14. Frontier Molecular Orbital diagrams, TDDFT results for T-P curcumin dimer at distance 8.3 Å.

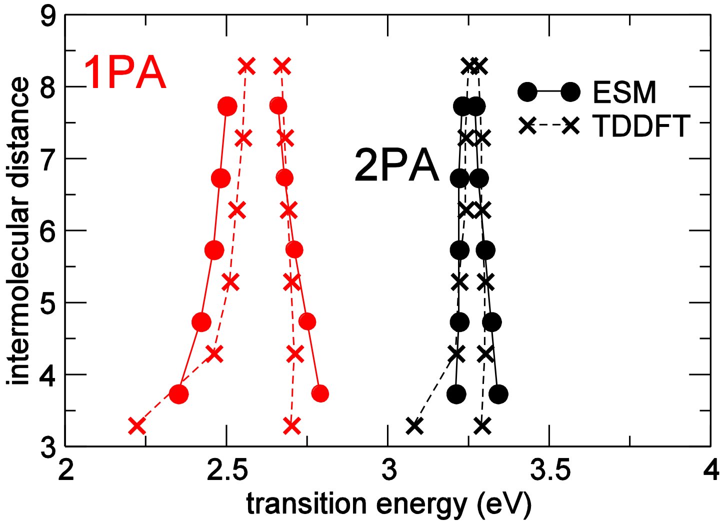


Figure S15. 1PA (red) and 2PA (black) transition energies calculated for the T-P curcumin dimer at variable intermolecular distance. ESM results (circles) are compared with TDDFT results (crosses). To favor the comparison, TDDFT energies are rigidly downshifted by 0.83 eV for 2PA and by 0.69 eV for 1PA.

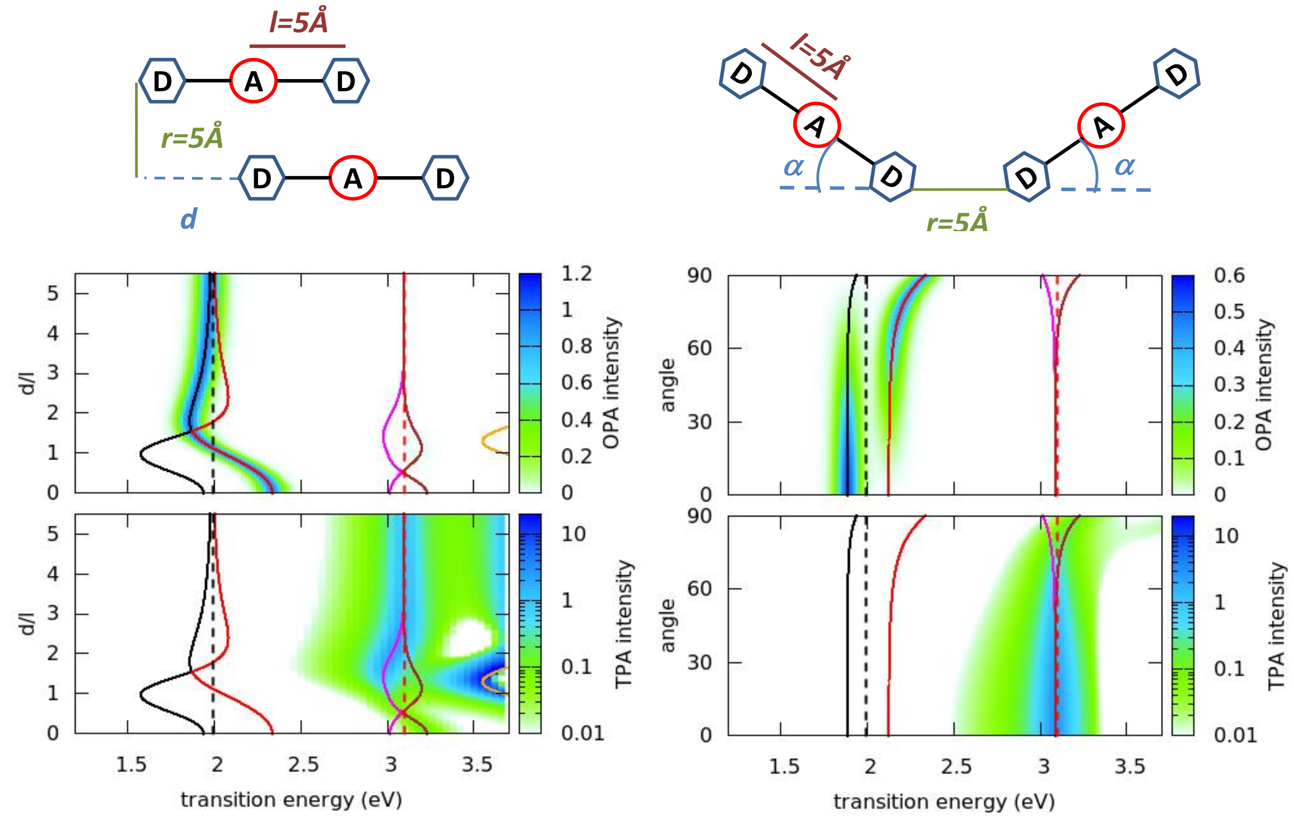


Figure S16. Top panels: geometry of dimers and definition of relevant parameters. Middle panels: the color maps show one-photon absorption intensity of the dimer of dye **2** (intensity per chromophore, normalized to the intensity of the monomer). Continuous lines report the transition energy of the first (black), second (red), third (magenta), etc. excited states. Dashed lines report the transition energy of the first (black) and second (red) excited state of the monomer. Bottom panels: the color maps show two-photon absorption intensity of the dimer (intensity per chromophore, normalized to the intensity of the monomer).

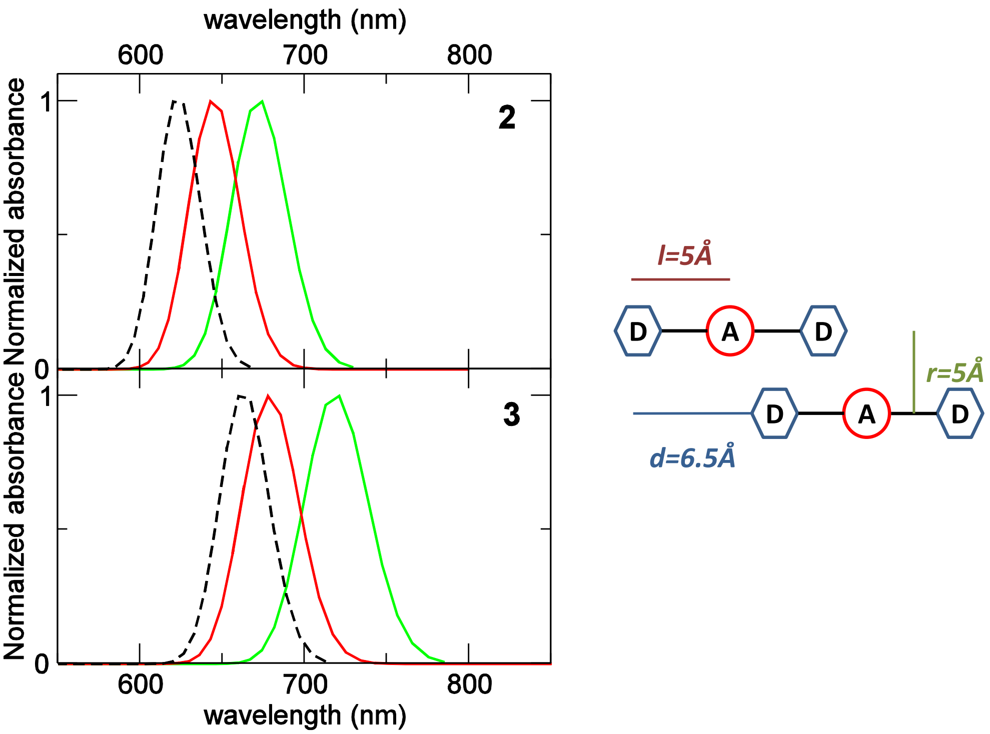


Figure S17. Absorption spectra of dye **2** (top) and **3** (bottom): dashed lines refer to the monomer; continuous lines refer to dimers (intensity per molecule) in the geometrical arrangement shown on the right. Red lines refer to the ESM results, green lines show results obtained in the mean-field approximation.

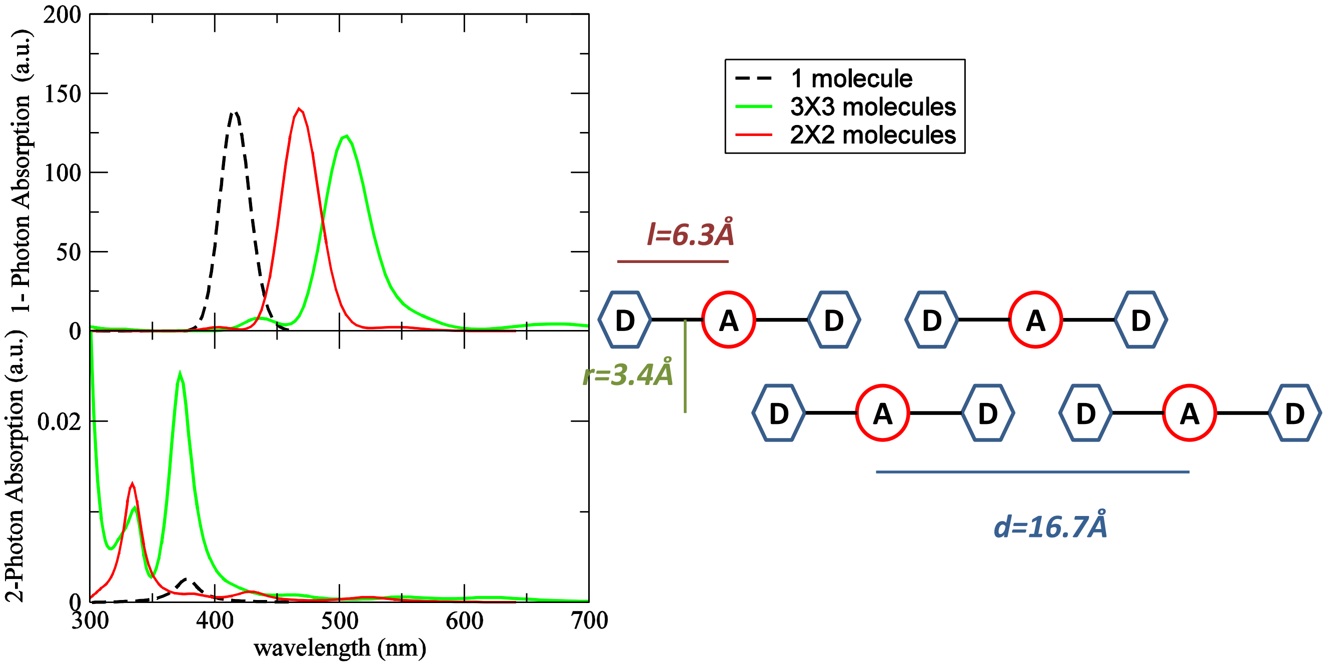


Figure S18. ESM calculation (top: 1PA, bottom: 2PA) for an aggregate in a brickwork arrangement. ESM parameters: η = 1.34 eV, τ = 0.67 eV. Dashed line: monomer; Red lines: aggregate formed by 4 (2×2) molecules; Green lines: aggregate formed by 9 (3×3) molecules.

References

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