

Electronic Supplementary Information for “Intermolecular charge transfer enhances two-photon absorption in yellow fluorescent protein”

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1 Orbital transitions

1.1 DFT and CC2 ICT- α orbital transitions

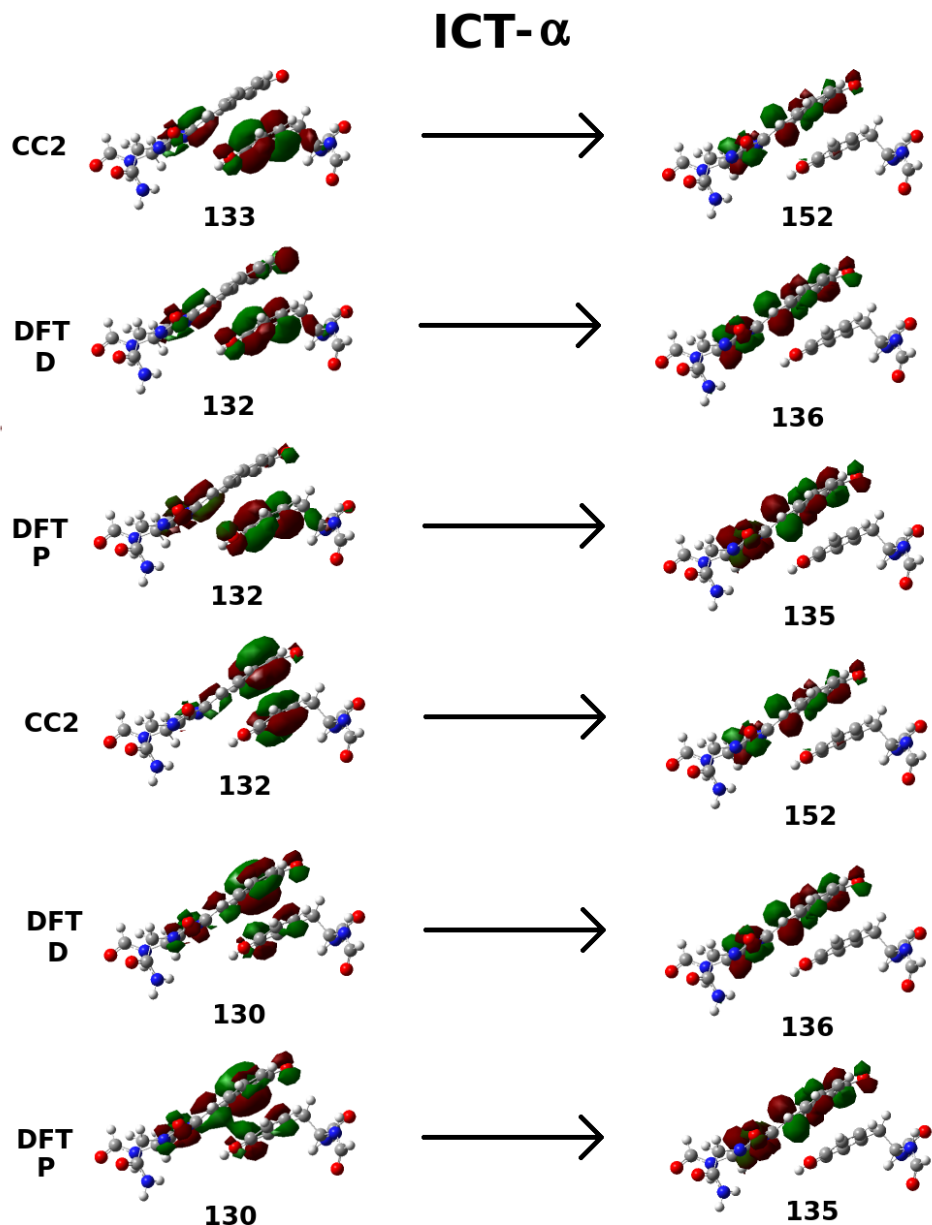


Figure S1: Comparison of Hartree-Fock (CC2) orbitals and Kohn-Sham orbitals (DFT) for the ICT- α transitions, in which electron density is transferred from Tyr203 to the chromophore. The CC2 calculations were done with the Dunning aug-cc-pVDZ basis, the DFT calculations with both Dunning's aug-cc-pVDZ (DFT D) and Pople's 6-31+G* (DFT P). In the spectra, two different ICT- α transitions can clearly be identified, with the involved orbitals showing remarkable similarity. Orbital numbers are shown underneath the orbitals; 134 and 135 are the HOMO and the LUMO, respectively.

1.2 DFT and CC2 ICT- β orbital transitions

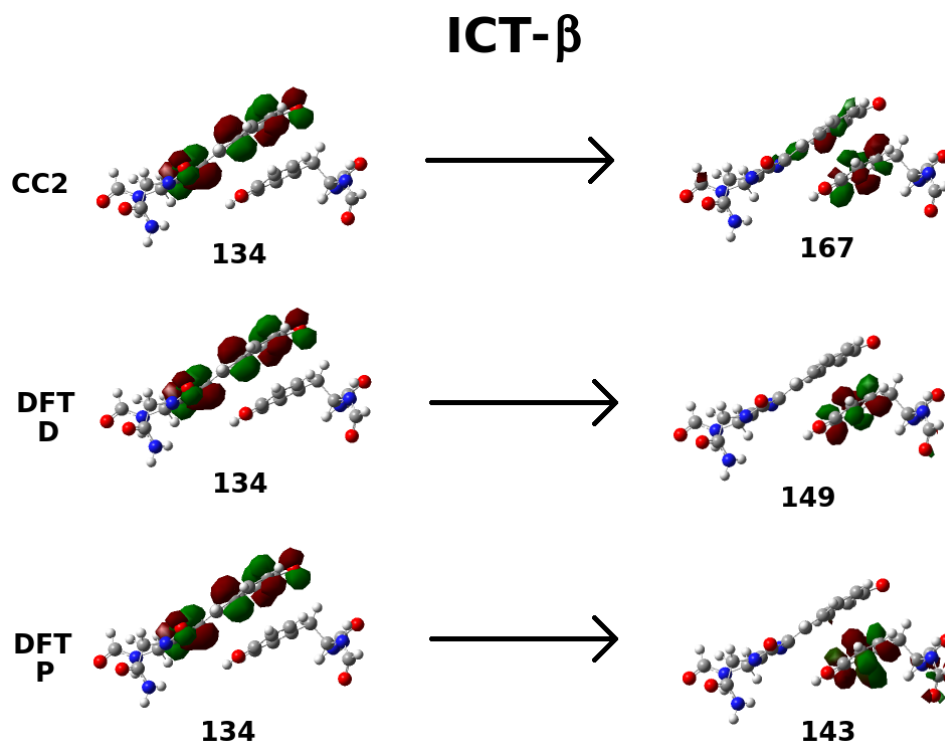


Figure S2: Comparison of Hartree-Fock (CC2) orbitals and Kohn-Sham orbitals (DFT) for the ICT- β transitions, in which electron density is transferred from Tyr203 to the chromophore. The CC2 calculations were done with the Dunning aug-cc-pVDZ basis, the DFT calculations with both Dunning's aug-cc-pVDZ (DFT D) and Pople's 6-31+G* (DFT P). Although the orbital number of the virtual orbital is not the same in DFT (143, 149) and CC2 (167), the involved orbitals are qualitatively very similar. Orbital numbers are shown underneath the orbitals; 134 and 135 are the HOMO and the LUMO, respectively.

1.3 Rydberg transitions

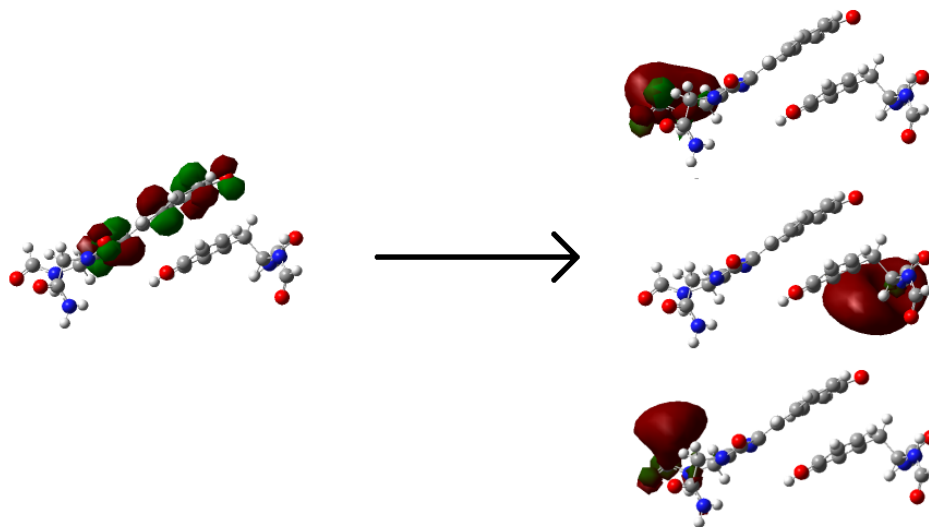


Figure S3: Kohn–Sham orbitals for some of the Rydberg transitions found in the CAM-B3LYP/6-31+G* calculations. In almost all CAM-B3LYP and RI-CC2 Rydberg transitions, electron density is transferred from the HOMO — which is delocalized over the conjugate system of the chromophore (left) — to Rydberg states on the chromophore or on Tyr203 (right). The Rydberg transitions can therefore be both *intramolecular* and *intermolecular*. Note that the Rydberg transitions are an artefact of not including the surrounding protein in the model system.

2 Coordinates

2.1 Coordinates of the Chromophore-Tyr203 stack at 3.4 Å

C	23.913	26.557	33.411
C	37.819	26.128	36.742
C	36.539	27.059	34.872
C	37.353	27.393	33.634
C	35.531	28.235	34.825
C	34.416	27.695	35.689
C	34.315	28.022	37.041
C	33.321	27.136	35.033
C	33.228	27.562	37.773
C	32.239	26.663	35.752
C	32.241	26.823	37.129
C	26.488	26.579	33.281
C	27.276	27.047	34.499
C	27.919	27.568	36.627
C	28.892	27.981	35.653
C	25.607	26.817	36.458
C	25.261	25.431	37.009
C	29.917	28.808	36.095
C	30.963	29.540	35.519
C	31.278	29.626	34.128
C	31.822	30.241	36.427
C	32.416	30.253	33.699
C	32.953	30.881	36.012
C	33.353	30.848	34.632
O	23.038	25.817	33.890
O	37.571	24.950	36.426
O	38.306	28.171	33.654
O	31.269	26.279	37.907
O	27.832	27.814	37.849
O	24.337	25.383	37.794
O	34.493	31.299	34.270
N	25.916	24.315	36.674
N	37.445	27.164	35.989
N	36.879	26.778	32.567
N	25.161	26.069	33.560
N	28.449	27.614	34.372
N	26.926	26.915	35.853
H	23.659	27.509	32.920
H	25.663	23.396	37.005
H	26.648	24.372	35.969
H	38.370	26.395	37.657
H	37.711	28.111	36.260
H	36.047	26.081	34.785
H	35.939	29.173	35.184
H	35.148	28.437	33.824
H	35.097	28.603	37.522
H	33.331	27.033	33.952
H	33.088	27.813	38.815
H	31.413	26.195	35.232
H	30.596	25.793	37.376
H	37.205	26.886	31.618
H	36.098	26.142	32.704
H	25.118	25.128	33.930
H	27.052	25.769	32.809
H	26.417	27.346	32.516
H	25.459	27.525	37.279
H	24.823	27.140	35.782
H	29.876	28.887	37.181
H	30.619	29.168	33.400
H	31.561	30.230	37.483
H	32.645	30.280	32.639
H	33.616	31.374	36.718

3 Absorption properties for the stack at 3.4 Å

3.1 CAM-B3LYP/6-31+G*

Table SI: Results from the CAM-B3LYP/6-31+G* DFT calculation on the chromophore–Tyr203 stack at a distance of 3.4 Å. Shown are the number of the electronic excitation (#), the energy of the excitation (E) both in eV and nm, the wavelength after the 51 red shift as discussed in the article (E*), the OPA oscillator strength (f) in atomic units and the TPA cross section (o) in Göppert–Mayer.

#	E [eV]	E [nm]	E* [nm]	f [a.u.]	o [GM]
1	2.959	419	470	0.879	17
2	3.585	346	397	0.017	13
3	3.697	335	386	0.000	0
4	3.971	312	363	0.004	55
5	4.123	301	352	0.007	134
6	4.204	295	346	0.014	301
7	4.240	292	343	0.002	30
8	4.352	285	336	0.073	2
9	4.425	280	331	0.037	320
10	4.447	279	330	0.009	80
11	4.557	272	323	0.001	2
12	4.581	271	322	0.001	2
13	4.662	266	317	0.002	276
14	4.737	262	313	0.014	90
15	4.792	259	310	0.018	43
16	4.861	255	306	0.008	48
17	4.899	253	304	0.042	129
18	4.975	249	300	0.051	48
19	5.015	247	298	0.001	68
20	5.047	246	297	0.023	142

3.2 CAM-B3LYP/aug-cc-pVDZ

Table SII: Results from the CAM-B3LYP/aug-cc-pVDZ DFT calculation on the chromophore-Tyr203 stack at a distance of 3.4 Å. Shown are the number of the electronic excitation (#), the energy of the excitation (E) both in eV and nm, the wavelength after the 46 red shift as discussed in the article (E*), the OPA oscillator strength (f) in atomic units and the TPA cross section (o) in Göppert-Mayer.

#	E [eV]	E [nm]	E* [nm]	f [a.u.]	o [GM]
1	2.922	424	470	0.855	5
2	3.350	370	416	0.023	3
3	3.680	337	383	0.000	0
4	3.785	328	374	0.000	1
5	3.868	321	367	0.000	1
6	3.907	317	363	0.004	22
7	4.077	304	350	0.007	44
8	4.085	304	350	0.016	52
9	4.147	299	345	0.010	27
10	4.312	288	334	0.008	11
11	4.331	286	332	0.014	1
12	4.388	283	329	0.072	78
13	4.489	276	322	0.005	22
14	4.525	274	320	0.005	1
15	4.533	274	320	0.001	3
16	4.563	272	318	0.021	13
17	4.645	267	313	0.006	6
18	4.717	263	309	0.021	24
19	4.740	262	308	0.013	43
20	4.780	259	305	0.004	12

3.3 RI-CC2/aug-cc-pVDZ

Table SIII: Results from the RI-CC2/aug-cc-pVDZ calculation on the chromophore–Tyr203 stack at a distance of 3.4 Å. Shown are the number of the electronic excitation (#), the energy of the excitation (E) both in eV and nm, the OPA oscillator strength (f) in atomic units and the TPA cross section (o) in Göppert–Mayer.

#	E [eV]	E [nm]	f [a.u.]	o [GM]
1	2.636	470	0.816	33
2	2.814	441	0.171	14
3	2.937	422	0.000	0
4	3.243	382	0.000	6
5	3.329	372	0.001	12
6	3.497	355	0.004	21
7	3.592	345	0.002	58
8	3.653	339	0.001	16
9	3.672	338	0.008	434
10	3.782	328	0.009	174
11	3.805	326	0.001	3
12	3.864	321	0.013	628
13	3.894	318	0.006	24
14	3.969	312	0.003	26
15	4.013	309	0.002	38
16	4.081	304	0.000	9
17	4.081	304	0.002	6
18	4.111	302	0.018	190
19	4.160	298	0.032	15
20	4.187	296	0.002	486
21	4.200	295	0.030	8
22	4.218	294	0.004	17
23	4.256	291	0.003	480
24	4.308	288	0.003	1
25	4.345	285	0.002	667
26	4.371	284	0.003	684
27	4.383	283	0.002	3
28	4.402	282	0.036	7
29	4.447	279	0.010	385
30	4.457	278	0.003	66
31	4.479	277	0.001	219
32	4.534	273	0.001	1
33	4.544	273	0.018	502
34	4.553	272	0.010	45
35	4.616	269	0.024	728

4 Excitations for the stack at different distances

4.1 DFT lowest excitation energies

Table SIV: Calculated CAM-B3LYP/6-31+G* lowest excitation for the chromophore–Tyr203 stack at different distances (d in Å) between the centres of the phenol rings. Shown are also the number of the electronic excitation ($\#$), the energy of the excitation (E) both in eV and nm and the TPA cross section (σ) in Göppert–Mayer.

d [Å]	$\#$	E [eV]	E [nm]	σ [GM]
3.3	1	2.925	424	16.8
3.4	1	2.959	419	16.7
3.5	1	2.984	415	16.7
3.6	1	3.003	413	16.9
3.7	1	3.017	411	17.1
4.1	1	3.048	407	4.52
5.1	1	3.071	404	4.94
7.1	1	3.082	402	5.22

4.2 CC2 lowest excitation energies

Table SV: Calculated RI-CC2/aug-cc-pVDZ lowest excitation for the chromophore–Tyr203 stack at different distances (d in Å) between the centres of the phenol rings. Shown are also the number of the electronic excitation ($\#$), the energy of the excitation (E) both in eV and nm and the TPA cross section (σ) in Göppert–Mayer.

d [Å]	$\#$	E [eV]	E [nm]	σ [GM]
3.3	1	2.608	475	30
3.4	1	2.636	470	33
3.5	1	2.656	467	35
3.6	1	2.671	464	37
3.7	1	2.681	462	39

4.3 DFT ICT- α transitions

Table SVI: Calculated CAM-B3LYP/6-31+G* excitations for which the ICT- α transition has the largest orbital contribution. Shown are the distances between the centres of the phenol rings of the chromophore and Tyr203 (d in Å), the number of the electronic excitation (#), the energy of the excitation (E) both in eV and nm and the TPA cross section (o) in Göppert–Mayer.

d [Å]	#	E [eV]	E [nm]	o [GM]
3.3	3	3.689	336	0.017
3.4	9	4.425	280	320
	17	4.899	253	129
	20	5.047	246	142
3.5	10	4.494	276	217
3.6	10	4.557	272	132
3.7	12	4.643	267	129
4.1	14	4.763	260	27.8

4.4 CC2 ICT- α transitions

Table SVII: Calculated RI-CC2/aug-cc-pVDZ excitations for which the ICT- α transition has the largest orbital contribution. Shown are the distances between the centres of the phenol rings of the chromophore and Tyr203 (d in Å), the number of the electronic excitation (#), the energy of the excitation (E) both in eV and nm and the TPA cross section (o) in Göppert–Mayer.

d [Å]	#	E [eV]	E [nm]	o [GM]
3.3	19	4.122	301	122
3.4	20	4.187	296	486
	31	4.479	277	219
3.5	21	4.235	295	360
	22	4.249	292	125
	34	4.477	271	129
3.6	23	4.286	289	103

4.5 DFT ICT- β transitions

Table SVIII: Calculated CAM-B3LYP/6-31+G* excitations for which the ICT- β transition has the largest orbital contribution. Shown are the distances between the centres of the phenol rings of the chromophore and Tyr203 (d in Å), the number of the electronic excitation ($\#$), the energy of the excitation (E) both in eV and nm and the TPA cross section (σ) in Göppert-Mayer.

d [Å]	$\#$	E [eV]	E [nm]	σ [GM]
3.3	4	3.916	317	47.5
	13	4.640	267	268
3.4	4	3.971	312	54.5
	13	4.662	266	276
3.5	4	4.014	309	61.1
	13	4.679	265	258
3.6	4	4.047	306	64.8
	13	4.690	264	219
3.7	14	4.755	261	67.7
	16	4.858	255	65.9

4.6 CC2 ICT- β transitions

Table SIX: Calculated RI-CC2/aug-cc-pVDZ excitations for which the ICT- β transition has the largest orbital contribution. Shown are the distances between the centres of the phenol rings of the chromophore and Tyr203 (d in Å), the number of the electronic excitation ($\#$), the energy of the excitation (E) both in eV and nm and the TPA cross section (σ) in Göppert-Mayer. At distances of 3.5 and 3.6 Å, the ICT- β transition contributes to several electronic excitations without being the largest orbital contribution to any of them.

d [Å]	$\#$	E [eV]	E [nm]	σ [GM]
3.3	8	3.639	341	275
3.4	9	3.672	338	434
3.7	13	3.912	317	256

5 Quality of CC2 calculations

5.1 Details of CC2 quality for calculations at different distances

Table SX: Orbital occupation numbers of the natural highest occupied molecular orbital (ON HOMO) and D1 diagnostics for the RI-CC2/aug-cc-pVDZ calculations of the chromophore–Tyr203 stack at difference distances (d in Å).

d [Å]	ON HOMO	D1
3.3	1.867	0.132
3.4	1.866	0.130
3.5	1.867	0.129
3.6	1.868	0.128
3.7	1.868	0.127

6 Additional figures

6.1 TPA spectrum of the chromophore

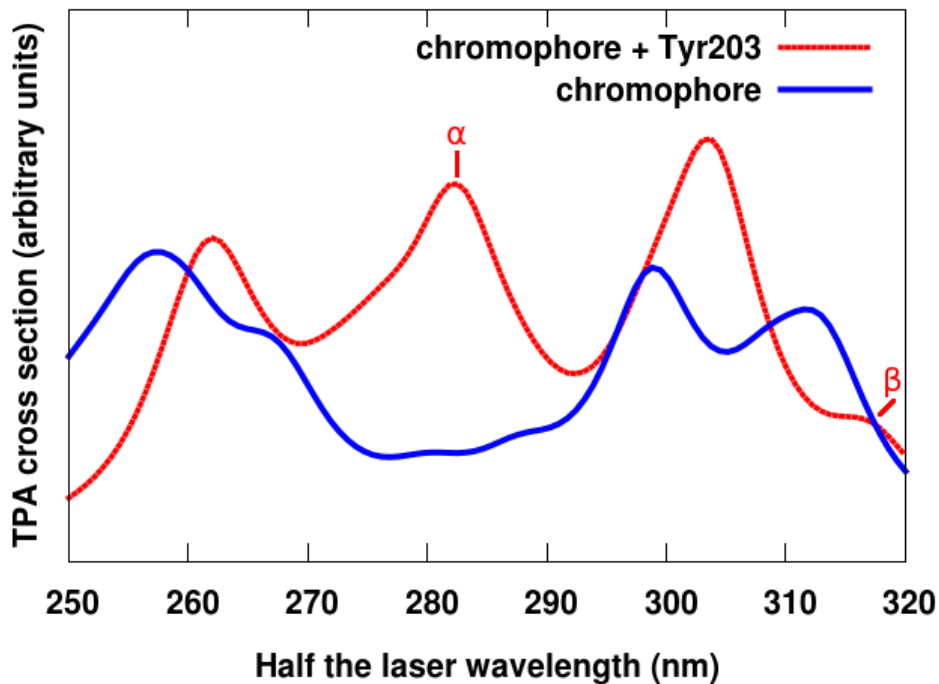


Figure S4: Comparison of the TPA spectra of the anionic YFP chromophore with and without Tyr203, both calculated with CAM-B3LYP/aug-cc-pVDZ. The TPA cross sections have been plotted with a Lorentzian broadening factor of 5 nm for the lowest 20 electronic excitations. The wavelengths have not been shifted as in Figure 2 in the main article. The main intermolecular charge-transfer transitions in the π -stacking system are labeled α and β (see Figures 3 and 4 in the main article).

6.2 Additional distances of the stack

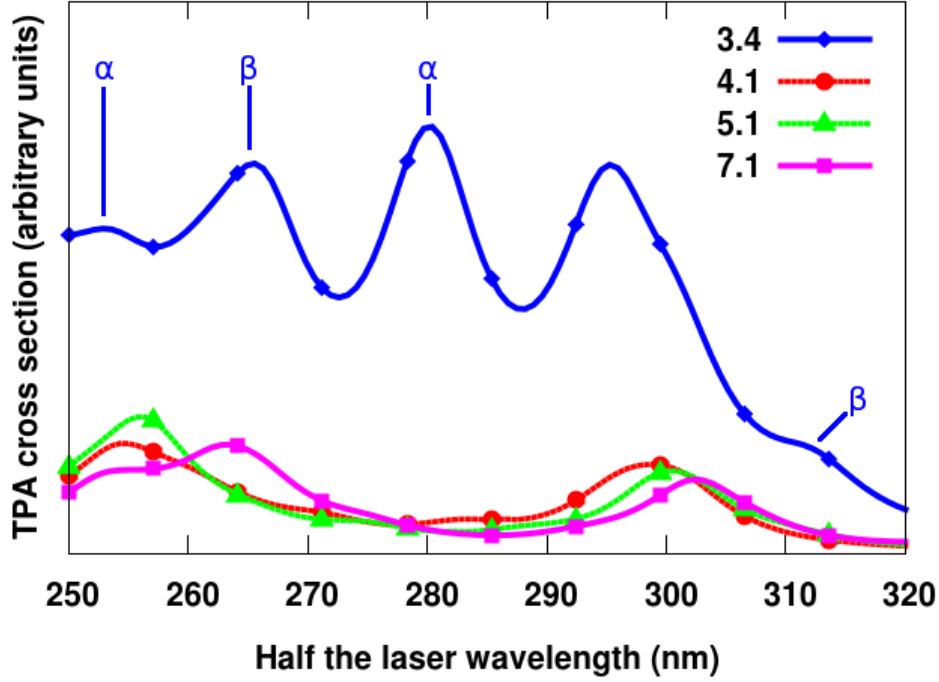


Figure S5: Calculated CAM-B3LYP/6-31+G* TPA spectra of the chromophore and Tyr203 from yellow fluorescent protein at various intermolecular distances. The different lines refer to a different distance (in Å) between the centre of the phenol rings of the chromophore and Tyr203. The TPA cross sections have been plotted with a Lorentzian broadening factor of 5 nm for the lowest 20 electronic excitations. The wavelengths have not been shifted as in Figure 2 in the main article. The main intermolecular charge-transfer transitions are labeled α and β (see Figures 3 and 4 in the main article).