Supplementary information for

Energy Decomposition Analysis for excited states: An Extension based on TDDFT

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Ground state EDA for the test set

The ground state EDA results for the different functional were taken from the exc-EDA calculation. Because of that there is only the decomposition of interaction energy.

Table S1. Ground state EDA result for fluorenone-methanol.

	PBE0		B3LYP		CAMY-B3LYP		LC-BLYP		LC-PBE	
$\Delta E_{inter}^{\mathrm{GS}}$	-29		-26		-32		-38		-33	
ΔE_{Pauli}^{GS}	36		41		35		29		32	
ΔE_{elstat}^{GS} [a]	-44	68%	-45	67%	-46	69%	-47	70%	-46	70%
$\Delta E_{orb}^{\mathrm{GS}}$ [a]	-21	32%	-22	33%	-21	31%	-20	30%	-20	30%

[a] Percentage values give the relative contributions to the attractive EDA terms ΔE_{elstat} and ΔE_{orb}. Energies in kJ mol^{-1}.

Table S2. Ground state EDA result for quinoline-water.

	PBE0		B3LYP		CAMY-B3LYP		LC-BLYP		LC-PBE	
$\Delta E_{inter}^{\mathrm{GS}}$	-32		-28		-34		-40		-37	
ΔE_{Pauli}^{GS}	50		56		50		44		46	
ΔE_{elstat}^{GS} [a]	-55	67%	-56	67%	-57	67%	-59	70%	-58	70%
$\Delta E_{orb}^{\mathrm{GS}}$ [a]	-27	33%	-27	33%	-27	33%	-25	30%	-25	30%

[a] Percentage values give the relative contributions to the attractive EDA terms ΔE_{elstat} and ΔE_{orb}. Energies in kJ mol^{-1}.

Table S3. Ground state EDA result for benzene-TCNE.

	PBE0		B3LYP		CAMY-B3LYP		LC-BLYP		LC-PBE	
$\Delta E_{inter}^{\mathrm{GS}}$	-16		-10		-16		-24		-21	
ΔE_{Pauli}^{GS}	8		15		9		3		5	
ΔE_{elstat}^{GS} [a]	-16	67%	-17	68%	-18	72%	-19	73%	-18	72%
$\Delta E_{orb}^{\mathrm{GS}}$ [a]	-8	33%	-8	32%	-7	28%	-7	27%	-7	28%

[a] Percentage values give the relative contributions to the attractive EDA terms ΔE_{elstat} and ΔE_{orb}. Energies in kJ mol^{-1}.

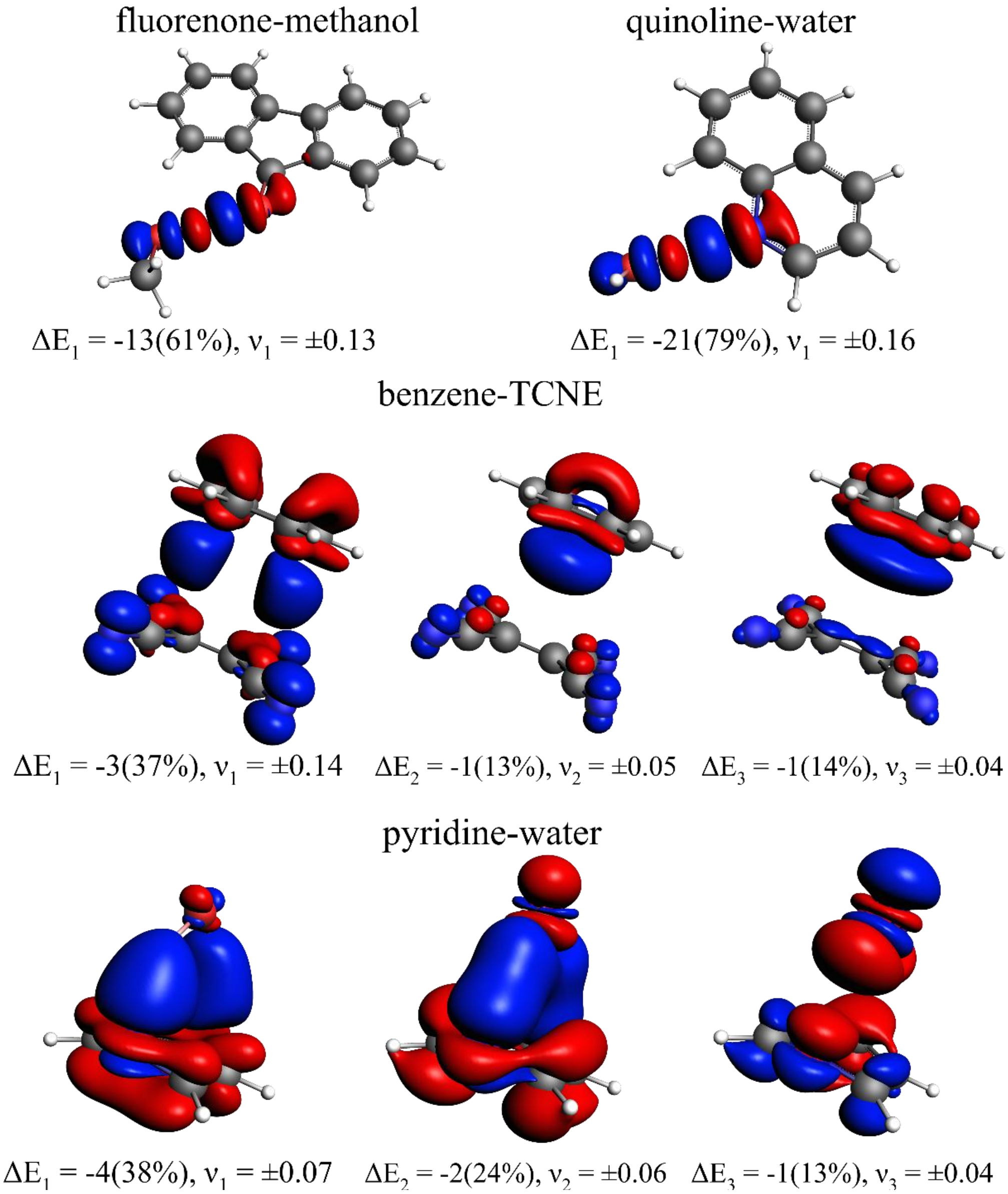
Table S4, Ground state EDA result for pyridine-water.

	PBE0		B3LYP		CAMY-B3LYP		LC-BLYP		LC-PBE	
$\Delta E_{inter}^{\mathrm{GS}}$	-8		-4		-9		-15		-13	
ΔE_{Pauli}^{GS}	16		21		15		10		11	
ΔE_{elstat}^{GS}[a]	-15	63%	-15	63%	-16	64%	-16	67%	-16	67%
$\Delta E_{orb}^{\mathrm{GS}}$[a]	-9	37%	-9	37%	-9	36%	-8	33%	-8	33%

[a] Percentage values give the relative contributions to the attractive EDA terms ΔE_{elstat} and ΔE_{orb}. Energies in kJ mol^{-1}.

Ground-state EDA-NOCV results

To gain insight into the impact of excitation on the bonding in test systems, the orbital interaction was examined further using the EDA-NOCV at the B3LYP/TZP level. The resulting most important NOCV deformation densities are presented in Figure S1 for all test systems.



fluorenone-methanol

$\Delta E_1 = -13(61\%)$, $\nu_1 = \pm 0.13$

quinoline-water

$\Delta E_1 = -21(79\%)$, $\nu_1 = \pm 0.16$

benzene-TCNE

$\Delta E_1 = -3(37\%)$, $\nu_1 = \pm 0.14$ $\Delta E_2 = -1(13\%)$, $\nu_2 = \pm 0.05$ $\Delta E_3 = -1(14\%)$, $\nu_3 = \pm 0.04$

pyridine-water

$\Delta E_1 = -4(38\%)$, $\nu_1 = \pm 0.07$ $\Delta E_2 = -2(24\%)$, $\nu_2 = \pm 0.06$ $\Delta E_3 = -1(13\%)$, $\nu_3 = \pm 0.04$

Figure S1. The most important NOCV deformation densities for the test system fluorenone-methanol (iso value = 0.0008), quinoline-water (iso value = 0.0008), benzene-TCNE (iso value = 0.0001) and pyridine-water (iso value = 0.0001). All energy contributions ΔE_i in kJ/mol and eigenvalues ν_i in e are given. Contribution to the total orbital interaction ΔE_{orb} are given in brackets.

Comparison of exc-EDA, GKS-EDA and ALMO-EDA

The electrostatic contribution of ALMO-EDA and GKS-EDA taken from their method paper correspond to quasi-electrostatic contribution of the exc-EDA. The Pauli contribution of ALMO-EDA and exc-EDA was also considered equal, which in turn corresponds to the exchange-repulsion contribution of GKS-EDA. For the orbital contribution of exc-EDA, the sum of CT and polarization of ALMO-EDA was considered, whereas only the polarization contribution of GKS-EDA was considered. In addition, for GKS-EDA there is a correlation term which corresponds to the difference of the correlation part of the density functional between fragments and system which does not have some correspondence in other EDA methods. Table S5 shows the comparison between the different methods for the fluorenone-methanol bond.

Table S5. EDA results of exc-EDA (with and without TDA), ALMO-EDA and GKS-EDA for the fluorenone-methanol bond.

	Exc-u-EDA	Exc-r-EDA	Exc-u-EDA (TDA)	Exc-r-EDA (TDA)	ALMO-EDA	GKS-EDA
ω_{int}	-12	-12	-12	-12	-13	-11
ω_{Pauli}	13	13	13	13	2	2
ω_{elstat}	-15	-17	-16	-16	-10	-16
ω_{orb}	-9	-8	-9	-9	-4	0
ω_{corr}						2
ΔE^*_{int}	-38	-38	-38	-38	-23	-32
ΔE^*_{Pauli}	54	54	54	54	44	52
ΔE^*_{elstat}	-60	-62	-61	-61	-54	-63
ΔE^*_{orb}	-31	-30	-31	-31	-22	-16
ΔE^*_{corr}						-5

[a] Energies in kJ mol^{-1}.

The outcomes of the different approaches to investigate the interaction between quinoline and water in the excited state are illustrated in Figure S2 and Table S6.

Table S6. EDA results of exc-EDA (with and without TDA), ALMO-EDA and GKS-EDA for the quinoline-water bond.

	Exc-u-EDA	Exc-r-EDA	Exc-u-EDA (TDA)	Exc-r-EDA (TDA)	ALMO-EDA	GKS-EDA
ω_{int}	-9	-9	26	26	5	-11
ω_{Pauli}	11	139	-17	149	9	1
ω_{elstat}	-5	-134	81	-113	43	-7
ω_{orb}	-16	-14	-39	-10	-30	-14
ω_{corr}						10
ΔE^*_{int}	-37	-37	-2	-2	-22	-37
ΔE^*_{Pauli}	67	194	39	204	57	61
ΔE^*_{elstat}	-61	-191	25	-169	-11	-62
ΔE^*_{orb}	-44	-41	-66	-37	-56	-35
ΔE^*_{corr}						-1

[a] Energies in kJ mol^{-1}.

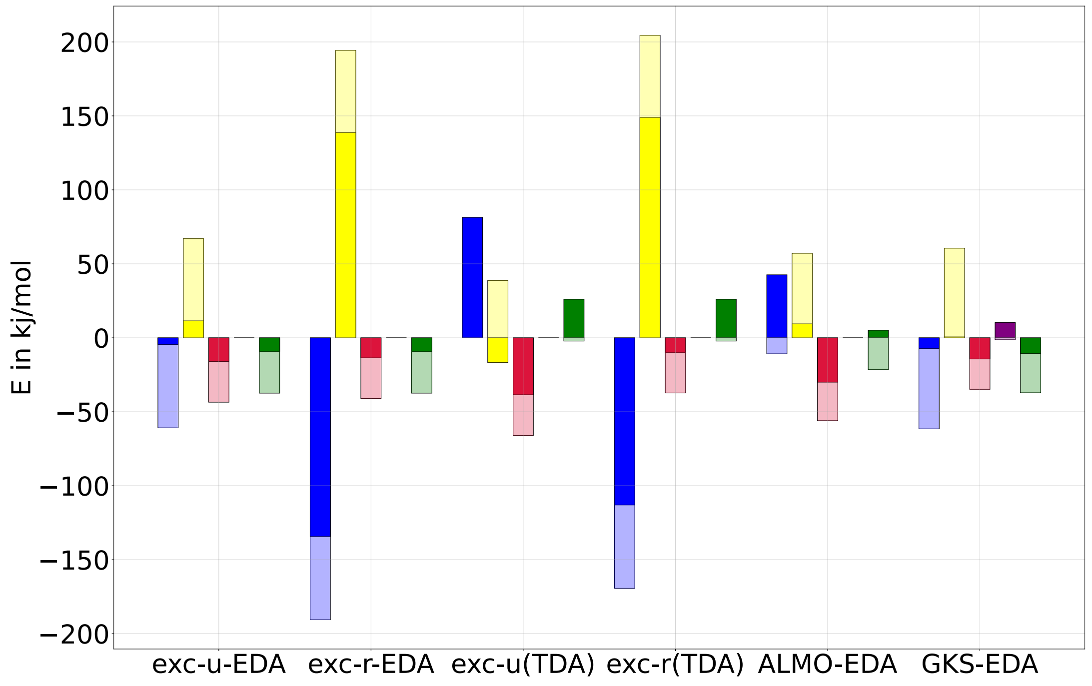


Figure S2. Comparing the exc-EDA (with and without TDA), ALMO-EDA and GKS-EDA for the first singlet excitation of benzene TCNE. Thereby is the electrostatic (blue), Pauli repulsion (yellow), orbital term (red) and interaction (green). Additionally, the correlation contribution (purple) is presented for GKS-EDA. The more intense colored bar represents the change in the respective contribution resulting from excitation, while the total (including the paler portion) bars indicate the value of the contribution for the excited state.

The outcomes of the different approaches to investigate the interaction between benzene and TCNE in the excited state are illustrated in Figure S3 and table S7.

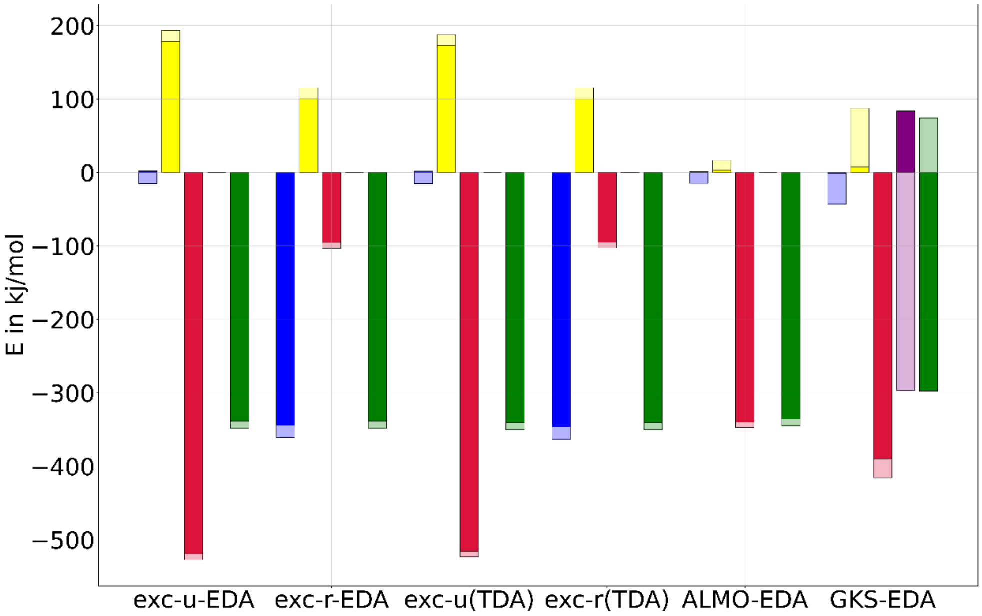


Figure S3. Comparing the exc-EDA (with and without TDA), ALMO-EDA and GKS-EDA for the first singlet excitation of benzene TCNE. Thereby is the electrostatic (blue), Pauli repulsion (yellow), orbital term (red) and interaction (green). Additionally, the correlation contribution (purple) is presented for GKS-EDA. The more intense colored bar represents the change in the respective contribution resulting from excitation, while the total (including the paler portion) bars indicate the value of the contribution for the excited state.

A comparison of the methods for the other test systems shows (especially for quinoline water) that the methods are divided into two groups (with and without TDA). The methods with TDA are ALMO-EDA and exc-EDA with TDA. The exc-u-EDA and ALMO-EDA show comparable results, with the exc-u-EDA showing slightly higher results. The Pauli contribution is particularly pronounced in exc-u-EDA compared to ALMO-EDA. However, the binding character is similar in both methods. In contrast, the exc-r-EDA results differ. The other groups consist of GKS-EDA and methods without TDA. The results are also similar for exc-u-EDA and GKS-EDA, whereas there are deviations from exc-r-EDA. The reason for this becomes clear when looking at the charge transfer excitation of the benzene-TCNE bond. In ALMO-EDA and GKS-EDA, the charge transfer is considered in the orbital term in a similar way to exc-u-EDA, whereby ALMO-EDA explicitly combines these terms. In contrast, exc-r-EDA splits the CT over all EDA contributions. This is why the exc-r-EDA results differ from the other methods.

Table S7. EDA results of exc-EDA (with and without TDA), ALMO-EDA and GKS-EDA for the benzene-TCNE bond.

	Exc-u-EDA	Exc-r-EDA	Exc-u-EDA (TDA)	Exc-r-EDA (TDA)	ALMO-EDA	GKS-EDA
ω_{int}	-12	-12	-12	-12	-13	-11
ω_{Pauli}	179	101	173	101	3	7
ω_{elstat}	2	-344	2	-347	1	-1
ω_{orb}	-519	-95	-516	-95	-340	-390
ω_{corr}						84
ΔE^{*}_{int}	-348	-348	-350	-350	-345	-297
ΔE^{*}_{Pauli}	194	116	188	115	17	88
ΔE^{*}_{elstat}	-15	-361	-15	-363	-15	-43
ΔE^{*}_{orb}	-527	-103	-523	-103	-347	-415
ΔE^{*}_{corr}						-74

[a] Energies in kJ mol^{-1}.

Pentacen oligomers

Values are given averaged over the monomers

Table S8. EDA results of new EDA method for pentacene oligomers in kJ/mol. The EDA contribution is displayed, as it undergoes alteration because of the excitation within the model. The outcomes obtained for the exc-u-EDA and exc-r-EDA. Thereby, the results are averaged over different excited monomers

Unrelaxed	Dimer	Tetramer	Tetramer 2	Pentamer	Hexamer	Heptamer
ω_{int}	-6	-9	-8	-11	-11	-12
ω_{Pauli}	36	82	69	73	80	90
ω_{elstat}	-1	-2	-1	-2	-1	-2
ω_{orb}	-41	-89	-76	-81	-89	-101
ΔE^{*}_{int}	-153	-320	-287	-295	-364	-410
$\Delta E_{int}(disp)$	-52	-117	-107	-109	-135	-154
ΔE^{*}_{Pauli}	38	95	85	89	95	108
ΔE^{*}_{elstat}	-56	-126	-114	-114	-144	-163
ΔE^{*}_{orb}	-84	-172	-151	-161	-180	-201

Relaxed	Dimer	Tetramer	Tetramer 2	Pentamer	Hexamer	Heptamer
ω_{int}	-6	-9	-8	-11	-11	-12
ω_{Pauli}	21	36	26	30	18	28
ω_{elstat}	-8	-13	-10	-14	-15	-18
ω_{orb}	-18	-31	-24	-26	-15	-22
ΔE^{*}_{int}	-153	-320	-287	-295	-364	-410
$\Delta E_{int}(disp)$	-52	-117	-107	-109	-135	-154
ΔE^{*}_{Pauli}	23	49	42	47	33	46
ΔE^{*}_{elstat}	-64	-137	-123	-127	-157	-179
ΔE^{*}_{orb}	-61	-114	-100	-106	-105	-123

[a] Energies in kJ mol^{-1}.

Dimer

Table S9. EDA results of new EDA method for pentacene dimer in kJ/mol. The EDA contribution is displayed, as it undergoes alteration because of the excitation within the model. The outcomes obtained for the exc-u-EDA and exc-r-EDA. Thereby, the numeration of excited monomer corresponds to numeration of figure 5 from main paper

Unrelaxed	Frag 1	Frag 2
ω_{int}	-7	-5
ω_{Pauli}	13	59
ω_{elstat}	0	-1
ω_{orb}	-19	-62
ΔE^{*}_{int}	-154	-152
$\Delta E_{int}(disp)$	-52	-52
ΔE^{*}_{Pauli}	15	61
ΔE^{*}_{elstat}	-56	-57
ΔE^{*}_{orb}	-62	-105

Relaxed	Frag 1	Frag 2
ω_{int}	-7	-5
ω_{Pauli}	21	21
ω_{elstat}	-10	-7
ω_{orb}	-18	-18
ΔE^{*}_{int}	-154	-152
$\Delta E_{int}(disp)$	-52	-52
ΔE^{*}_{Pauli}	23	23
ΔE^{*}_{elstat}	-65	-63
ΔE^{*}_{orb}	-61	-61

[a] Energies in kJ mol^{-1}.

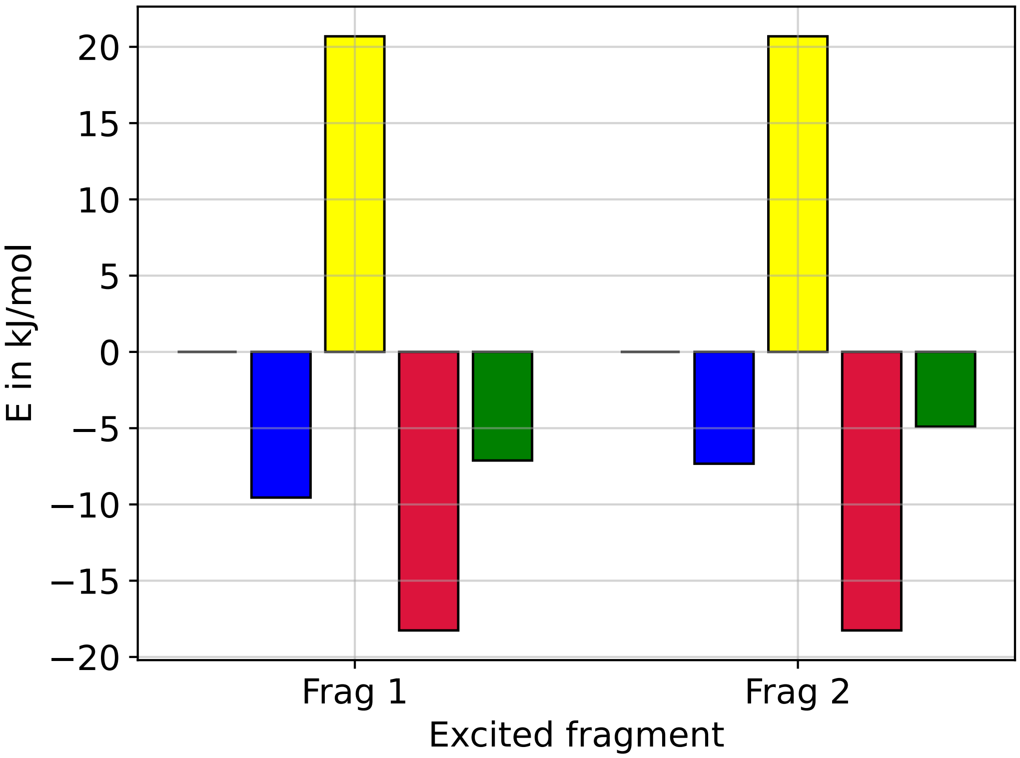


Figure S4. Exc-u-EDA for the first singlet excitation of pentacene dimer, whereby different monomers are excited. Thereby is the electrostatic (blue), Pauli repulsion (yellow), orbital term (red) and interaction (green).

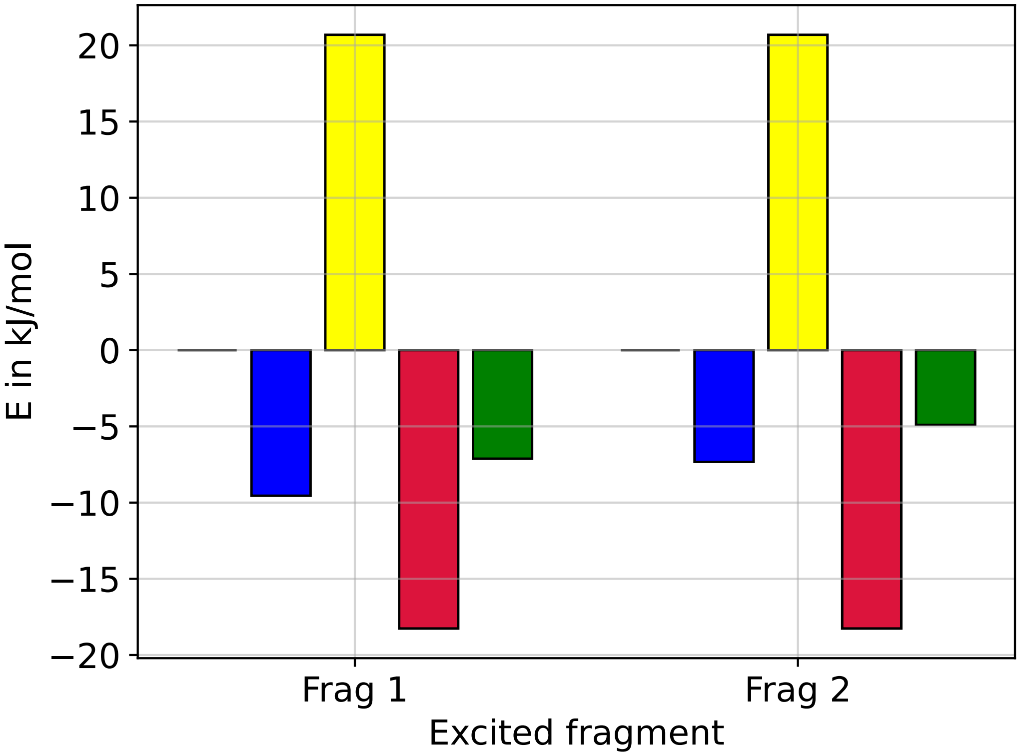


Figure S5. Exc-r-EDA for the first singlet excitation of pentacene dimer, whereby different monomers are excited. Thereby is the electrostatic (blue), Pauli repulsion (yellow), orbital term (red) and interaction (green).

Tetramer

Table S10. EDA results of new EDA method for pentacene tetramer in kJ/mol. The EDA contribution is displayed, as it undergoes alteration because of the excitation within the model. The outcomes obtained for the exc-u-EDA and exc-r-EDA. Thereby, the numeration of excited monomer corresponds to numeration of figure 5 from main paper

Unrelaxed	Frag 1	Frag 2	Frag 3	Frag 4
ω_{int}	-9	-9	-9	-9
ω_{Pauli}	70	93	93	70
ω_{elstat}	-2	-2	-2	-2
ω_{orb}	-77	-100	-100	-77
ΔE^{*}_{int}	-283	-356	-356	-283
$\Delta E_{int}(disp)$	-104	-131	-131	-104
ΔE^{*}_{Pauli}	82	108	108	82
ΔE^{*}_{elstat}	-110	-141	-142	-110
ΔE^{*}_{orb}	-151	-192	-192	-152

Relaxed	Frag 1	Frag 2	Frag 3	Frag 4
ω_{int}	-9	-9	-9	-9
ω_{Pauli}	37	34	34	37
ω_{elstat}	-12	-15	-15	-12
ω_{orb}	-34	-27	-27	-34
ΔE^{*}_{int}	-283	-356	-356	-283
$\Delta E_{int}(disp)$	-104	-131	-131	-104
ΔE^{*}_{Pauli}	48	49	49	48
ΔE^{*}_{elstat}	-119	-155	-155	-119
ΔE^{*}_{orb}	-108	-119	-120	-108

[a] Energies in kJ mol^{-1}.

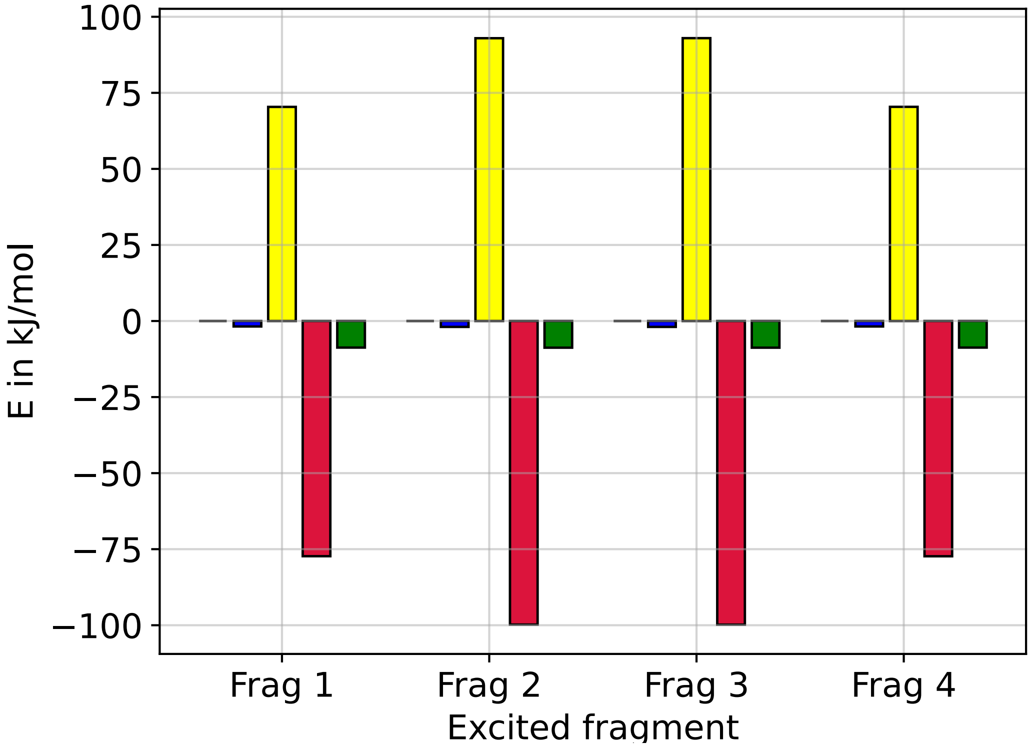


Figure S6. Exc-u-EDA for the first singlet excitation of pentacene tetramer, whereby different monomers are excited. Thereby is the electrostatic (blue), Pauli repulsion (yellow), orbital term (red) and interaction (green).

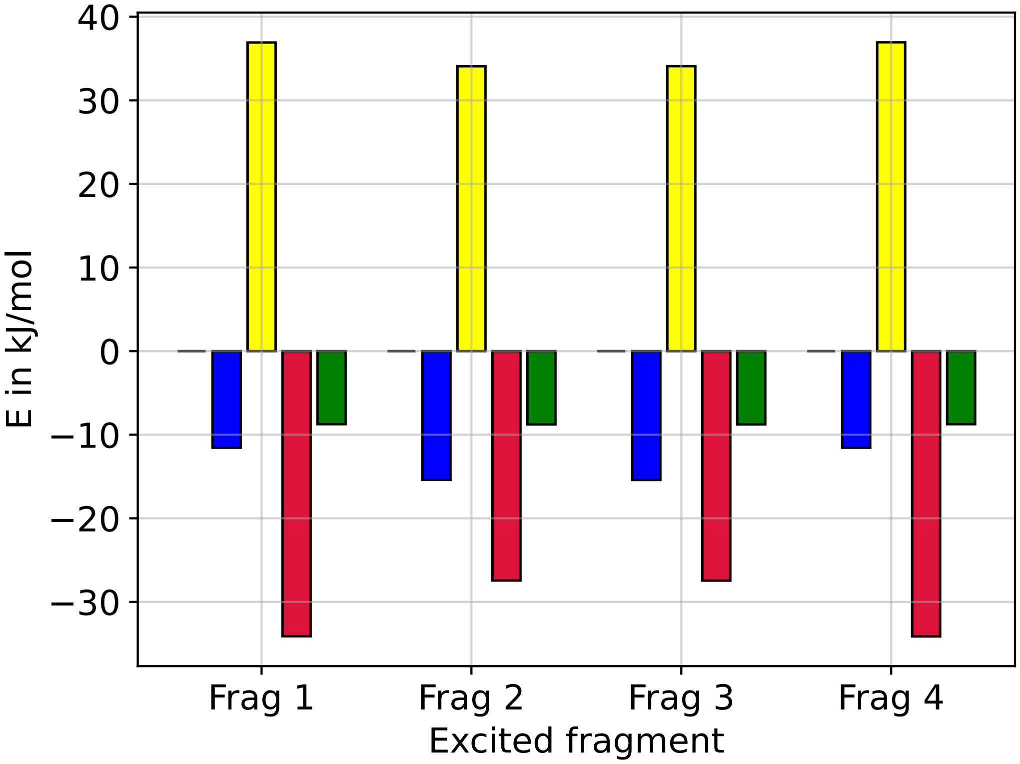


Figure S7. Exc-r-EDA for the first singlet excitation of pentacene tetramer, whereby different monomers are excited. Thereby is the electrostatic (blue), Pauli repulsion (yellow), orbital term (red) and interaction (green).

Tetramer 2

Table S11. EDA results of new EDA method for pentacene tetramer 2 in kJ/mol. The EDA contribution is displayed, as it undergoes alteration because of the excitation within the model. The outcomes obtained for the exc-u-EDA and exc-r-EDA. Thereby, the numeration of excited monomer corresponds to numeration of figure 5 from main paper

Unrelaxed	Frag 1	Frag 2	Frag 3	Frag 4
ω_{int}	-8	-8	-8	-8
ω_{Pauli}	77	91	84	25
ω_{elstat}	-1	-2	-2	-1
ω_{orb}	-83	-97	-90	-32
ΔE^{*}_{int}	-225	-348	-352	-224
$\Delta E_{int}(disp)$	-82	-132	-132	-82
ΔE^{*}_{Pauli}	87	117	105	30
ΔE^{*}_{elstat}	-88	-142	-143	-82
ΔE^{*}_{orb}	-143	-191	-182	-90

Relaxed	Frag 1	Frag 2	Frag 3	Frag 4
ω_{int}	-8	-8	-8	-8
ω_{Pauli}	13	24	34	35
ω_{elstat}	-9	-5	-15	-12
ω_{orb}	-11	-26	-27	-31
ΔE^{*}_{int}	-225	-348	-352	-224
$\Delta E_{int}(disp)$	-82	-132	-132	-82
ΔE^{*}_{Pauli}	24	50	55	41
ΔE^{*}_{elstat}	-96	-145	-156	-93
ΔE^{*}_{orb}	-71	-121	-119	-89

[a] Energies in kJ mol^{-1}.

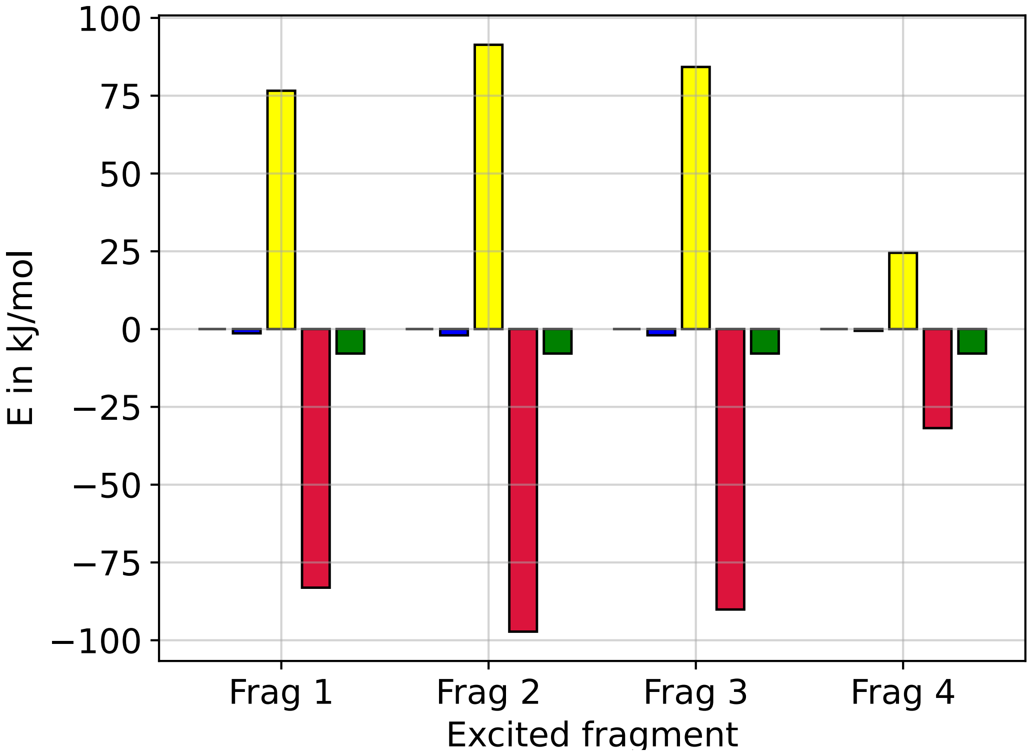


Figure S8. Exc-u-EDA for the first singlet excitation of pentacene tetramer 2, whereby different monomers are excited. Thereby is the electrostatic (blue), Pauli repulsion (yellow), orbital term (red) and interaction (green).

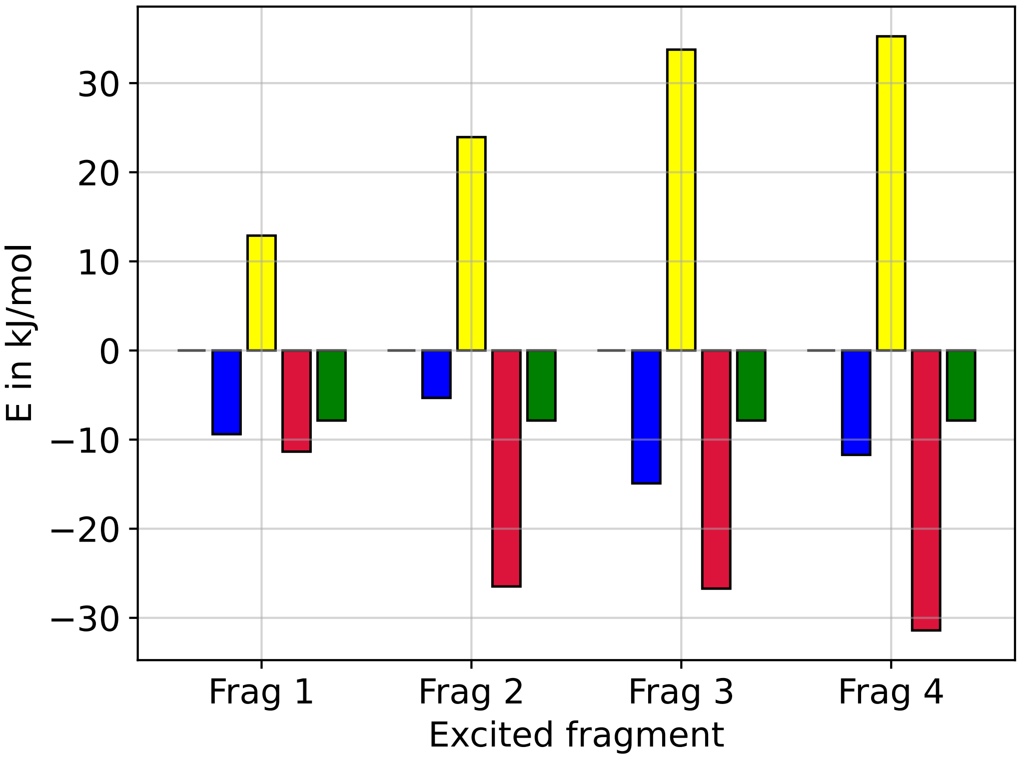


Figure S9. Exc-r-EDA for the first singlet excitation of pentacene tetramer 2, whereby different monomers are excited. Thereby is the electrostatic (blue), Pauli repulsion (yellow), orbital term (red) and interaction (green).

Pentamer

Table S12. EDA results of new EDA method for pentacene pentamers in kJ/mol. The EDA contribution is displayed, as it undergoes alteration because of the excitation within the model. The outcomes obtained for the exc-u-EDA and exc-r-EDA. Thereby, the numeration of excited monomer corresponds to numeration of figure 5 from main paper

Unrelaxed	Frag 1	Frag 2	Frag 3	Frag 4	Frag 5
ω_{int}	-11	-11	-11	-11	-11
ω_{Pauli}	25	77	158	77	25
ω_{elstat}	-1	-1	-4	-1	-1
ω_{orb}	-35	-86	-164	-86	-35
ΔE^*_{int}	-236	-230	-543	-230	-236
$\Delta E_{int}(disp)$	-85	-84	-206	-84	-85
ΔE^*_{Pauli}	29	88	213	88	29
ΔE^*_{elstat}	-85	-87	-226	-87	-85
ΔE^*_{orb}	-95	-145	-324	-145	-95

Relaxed	Frag 1	Frag 2	Frag 3	Frag 4	Frag 5
ω_{int}	-11	-11	-11	-11	-11
ω_{Pauli}	28	10	74	10	28
ω_{elstat}	-6	-10	-41	-10	-6
ω_{orb}	-32	-11	-43	-11	-32
ΔE^*_{int}	-236	-230	-543	-230	-236
$\Delta E_{int}(disp)$	-85	-84	-206	-84	-85
ΔE^*_{Pauli}	32	21	129	21	32
ΔE^*_{elstat}	-90	-96	-263	-96	-90
ΔE^*_{orb}	-92	-70	-203	-70	-92

[a] Energies in kJ mol^{-1}.

Hexamer

Table S13. EDA results of new EDA method for pentacene hexamer in kJ/mol. The EDA contribution is displayed, as it undergoes alteration because of the excitation within the model. The outcomes obtained for the exc-u-EDA and exc-r-EDA. Thereby, the numeration of excited monomer corresponds to numeration of figure 5 from main paper

Unrelaxed	Frag 1	Frag 2	Frag 3	Frag 4	Frag 5	Frag 6
ω_{int}	-11	-11	-11	-11	-11	-11
ω_{Pauli}	30	81	141	75	71	82
ω_{elstat}	0	-2	-3	-1	-1	-1
ω_{orb}	-40	-91	-148	-85	-81	-91
ΔE^{*}_{int}	-244	-363	-601	-360	-246	-368
$\Delta E_{int}(disp)$	-87	-135	-230	-134	-89	-136
ΔE^{*}_{Pauli}	36	100	169	89	80	94
ΔE^{*}_{elstat}	-94	-147	-240	-139	-97	-146
ΔE^{*}_{orb}	-99	-181	-301	-176	-141	-181

Relaxed	Frag 1	Frag 2	Frag 3	Frag 4	Frag 5	Frag 6
ω_{int}	-11	-11	-11	-11	-11	-11
ω_{Pauli}	14	14	35	18	8	21
ω_{elstat}	-11	-18	-24	-10	-9	-15
ω_{orb}	-14	-6	-22	-19	-10	-16
ΔE^{*}_{int}	-244	-363	-601	-360	-246	-368
$\Delta E_{int}(disp)$	-87	-135	-230	-134	-89	-136
ΔE^{*}_{Pauli}	21	32	63	32	17	34
ΔE^{*}_{elstat}	-105	-163	-260	-148	-105	-160
ΔE^{*}_{orb}	-73	-96	-175	-110	-70	-106

[a] Energies in kJ mol^{-1}.

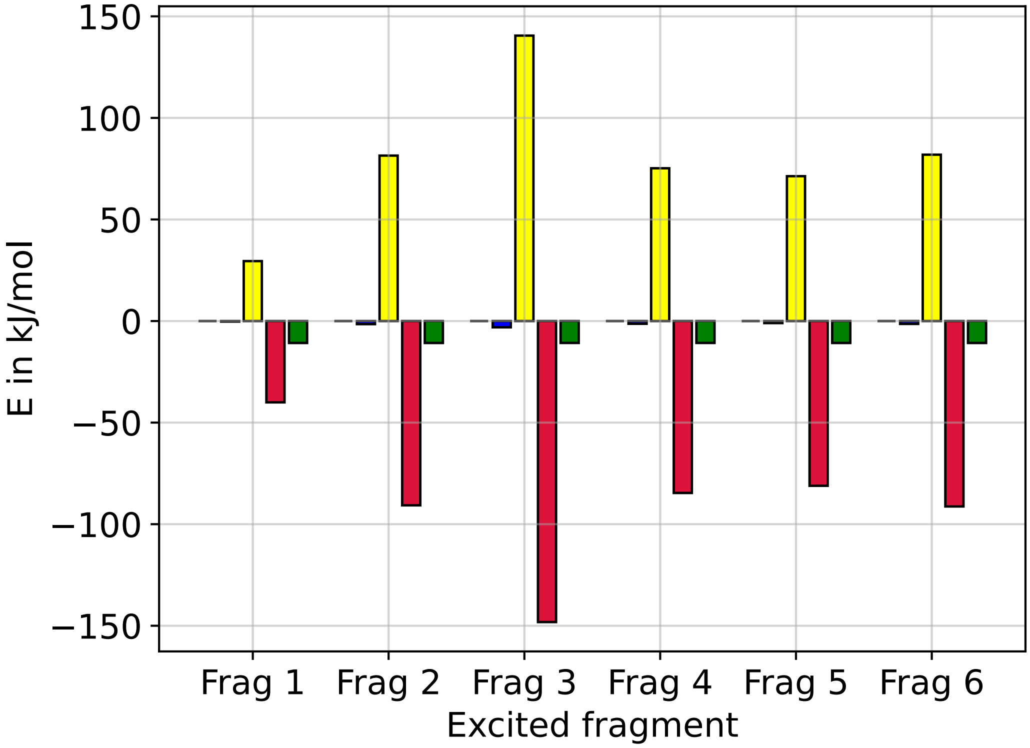


Figure S10. Exc-u-EDA for the first singlet excitation of pentacene hexamer, whereby different monomers are excited. Thereby is the electrostatic (blue), Pauli repulsion (yellow), orbital term (red) and interaction (green).

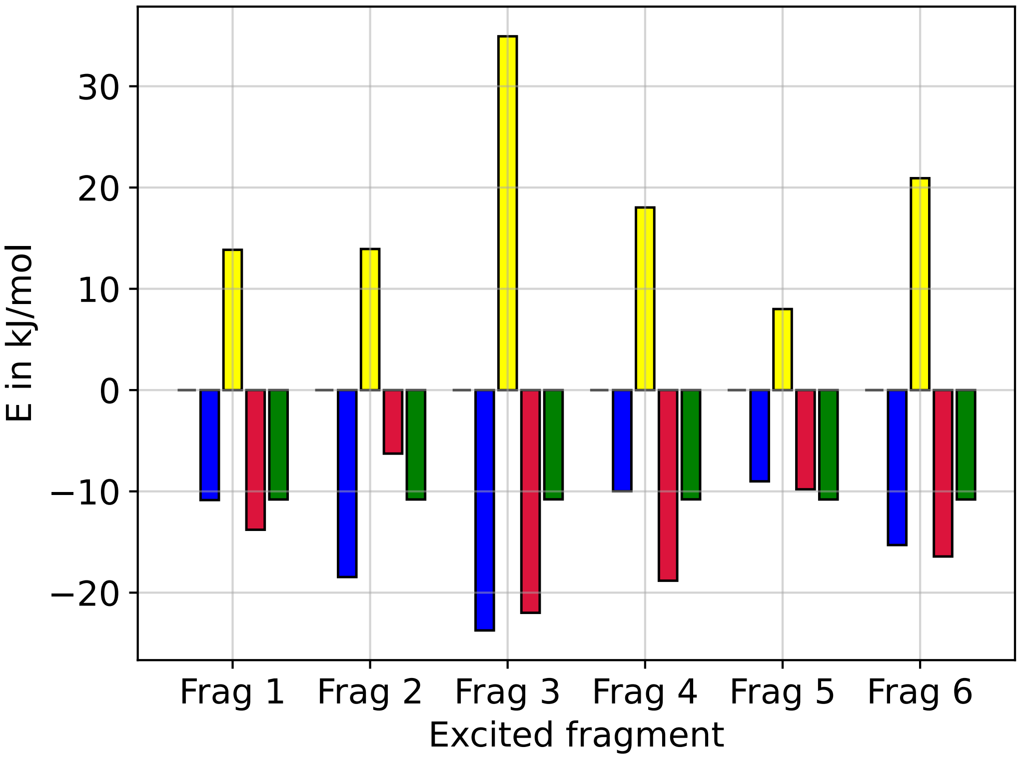


Figure S11. Exc-r-EDA for the first singlet excitation of pentacene hexamer , whereby different monomers are excited. Thereby is the electrostatic (blue), Pauli repulsion (yellow), orbital term (red) and interaction (green).

Heptamer

Table S14. EDA results of new EDA method for pentacene heptamer in kJ/mol. The EDA contribution is displayed, as it undergoes alteration because of the excitation within the model. The outcomes obtained for the exc-u-EDA and exc-r-EDA. Thereby, the numeration of excited monomer corresponds to numeration of figure 5 from main paper

Unrelaxed	Frag 1	Frag 2	Frag 3	Frag 4	Frag 5	Frag 6	Frag 7
ω_{int}	-12	-12	-12	-12	-12	-12	-12
ω_{Pauli}	82	82	75	152	75	82	82
ω_{elstat}	-1	-2	-1	-3	-1	-2	-1
ω_{orb}	-93	-92	-86	-162	-86	-92	-93
ΔE^{*}_{int}	-371	-367	-362	-671	-362	-367	-371
$\Delta E_{int}(disp)$	-137	-137	-135	-263	-135	-137	-137
ΔE^{*}_{Pauli}	94	100	89	190	89	100	94
ΔE^{*}_{elstat}	-146	-147	-139	-275	-139	-147	-146
ΔE^{*}_{orb}	-182	-183	-177	-323	-177	-183	-182

Relaxed	Frag 1	Frag 2	Frag 3	Frag 4	Frag 5	Frag 6	Frag 7
ω_{int}	-12	-12	-12	-12	-12	-12	-12
ω_{Pauli}	26	18	12	81	12	18	26
ω_{elstat}	-13	-9	-6	-70	-6	-9	-13
ω_{orb}	-26	-21	-19	-23	-19	-21	-26
ΔE^{*}_{int}	-371	-367	-362	-671	-362	-367	-371
$\Delta E_{int}(disp)$	-137	-137	-135	-263	-135	-137	-137
ΔE^{*}_{Pauli}	39	36	26	119	26	36	39
ΔE^{*}_{elstat}	-157	-155	-144	-342	-144	-155	-157
ΔE^{*}_{orb}	-115	-111	-110	-185	-110	-111	-115

[a] Energies in kJ mol^{-1}.

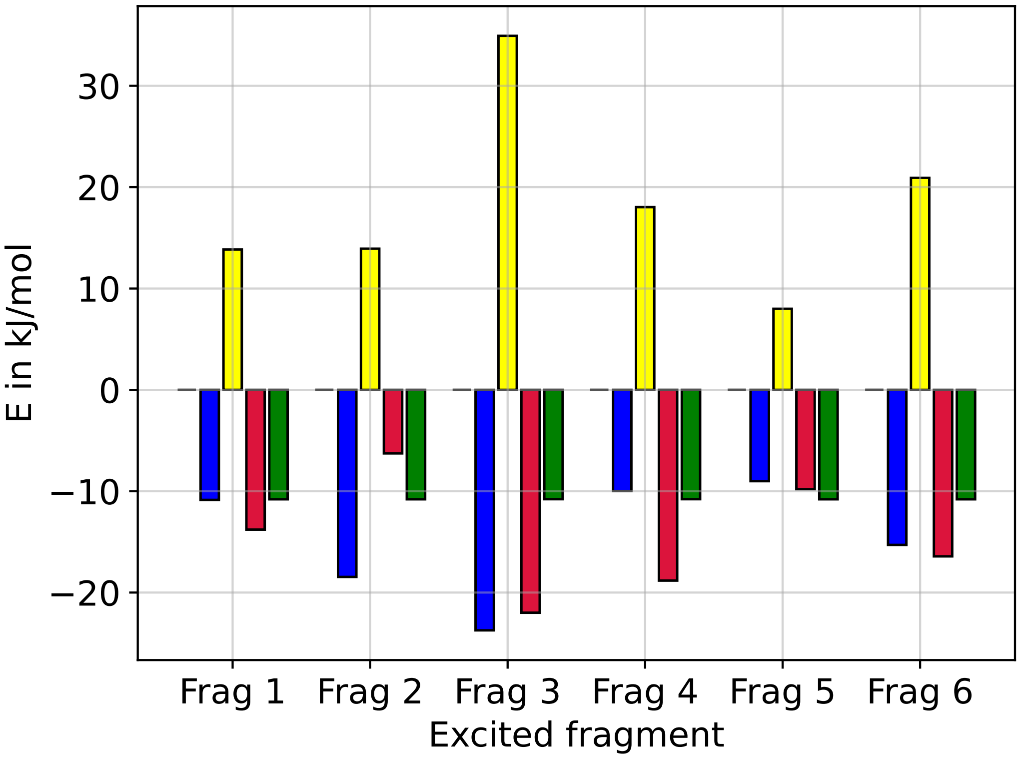


Figure S12. Exc-u-EDA for the first singlet excitation of pentacene heptamer, whereby different monomers are excited. Thereby is the electrostatic (blue), Pauli repulsion (yellow), orbital term (red) and interaction (green).

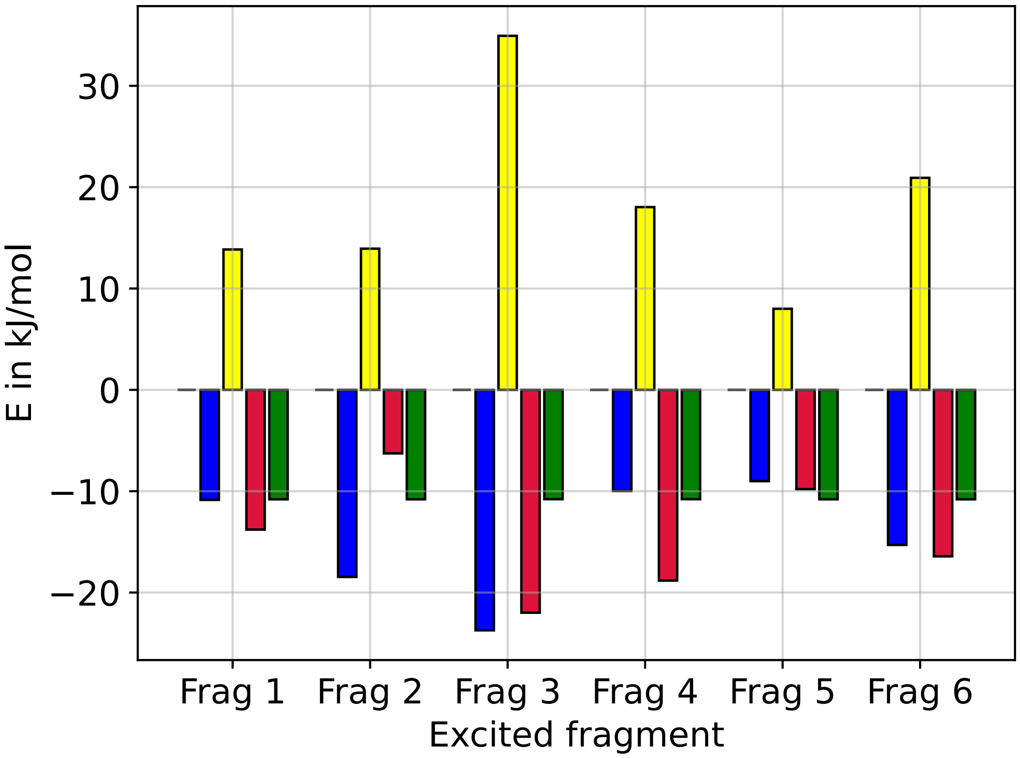


Figure S13. Exc-r-EDA for the first singlet excitation of pentacene heptamer, whereby different monomers are excited. Thereby is the electrostatic (blue), Pauli repulsion (yellow), orbital term (red) and interaction (green).