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† Electronic Supplementary Information (ESI) to "Structural Determinants in the Bulk Heterojunction"

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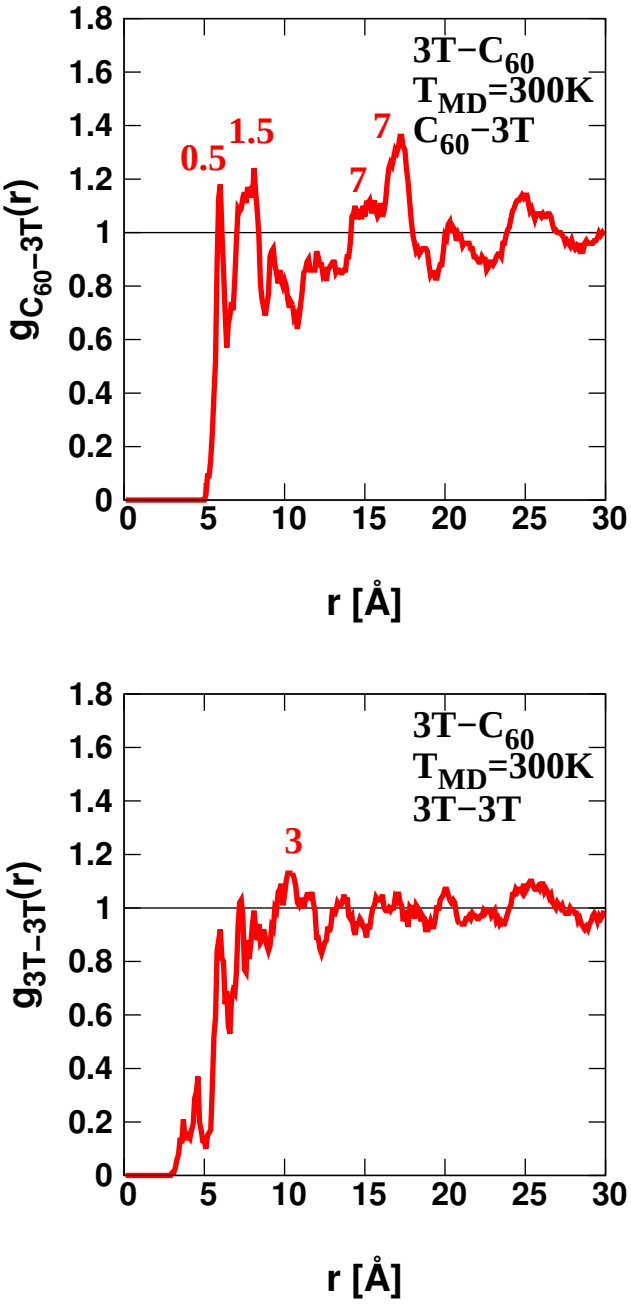


Fig. S1 Radial distribution functions, $g(r)$, for an ensemble of 216 crosslinked terthiophene-fullerene dyads (3T-C60) split into subgroups (A: C60 and D: 3T) considering geometric centres. Significant structural information is revealed for C60 where a central fullerene is surrounded by 6 other fullerenes separated by 9.75 Å (centre-centre distance, see Figure 1 in main text). Thiophene chains are arranged in various orientations around a central C60 with little structural regularity (upper panel). Likewise, little structural order is seen between individual thiophene chains (lower panel).

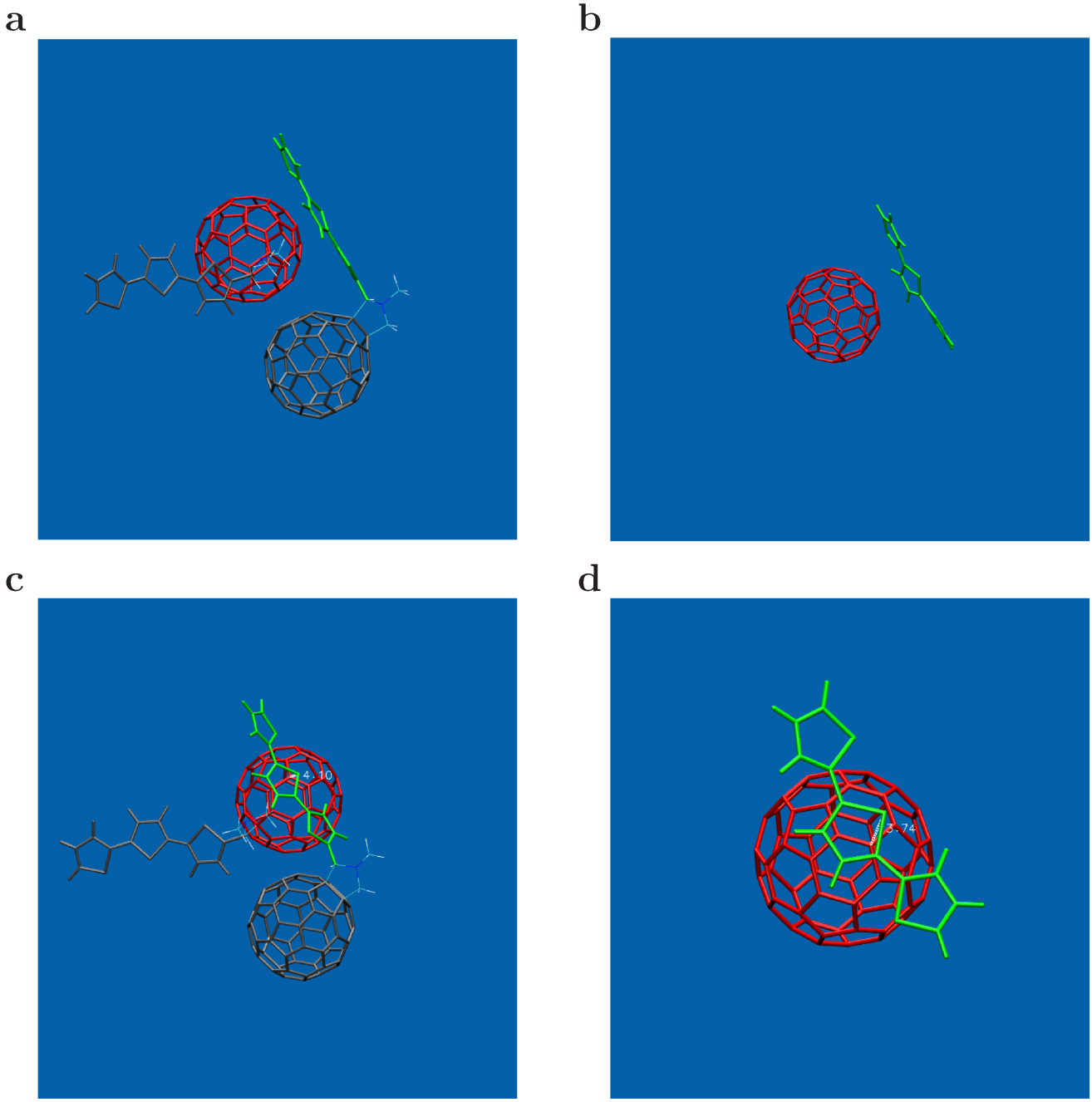
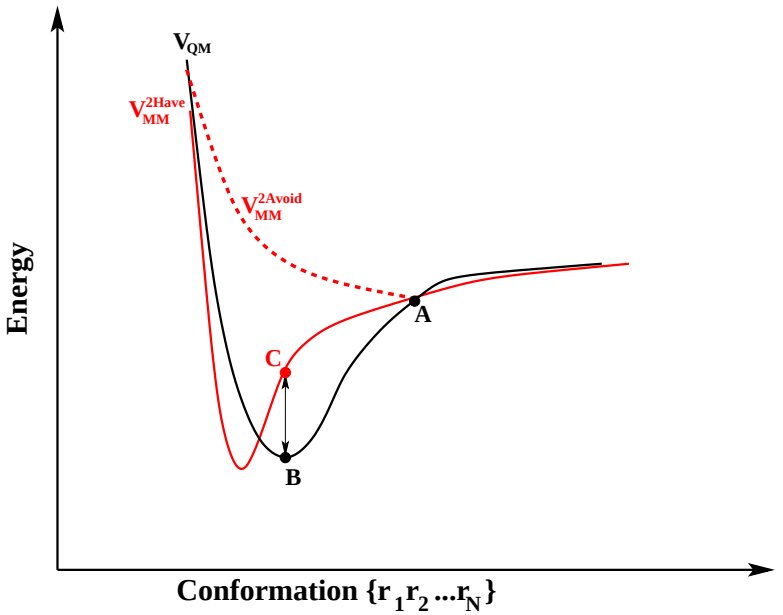


Fig. S2 Comparison of minimum structures in either reduced form (after removal of the linker and saturation of open valencies with H-atoms) or full integral form of entire 3T-C60 units on the example 3T-C60[162](case 2). **a)** Side view of minimized pair of 3T-C60 units in full integral form. Redundant parts that are removed are shown in grey or cyan/white/blue. **b)** Side view of minimized D/A pair in reduced form in identical orientation to the one used in Fig. 2 of the main text (upper right panel). **c)** Top view of minimized pair of fully integral 3T-C60 units. The plane of the 3T ring system is slightly more tilted when compared to the reduced form and the approximate distance to the C60-surface is slightly increased from 3.74 Å to 4.10 Å . **d)** Top view of minimized D/A pair in reduced form.



Type	<ΔE> [kcal/mol]	StndDev [kcal/mol]
bond	+58.3	±9.6
angle	-30.7	±5.8
dihed	-11.7	±4.0
vdW	-1.5	±13.5
eel	+0.4	±1.3
vdw14	-25.4	±2.6
eel14	-0.7	±3.4
ene	-11.3	

Fig. S3 BHJ structures reported in Table 1 and Figure 2 of the main text were extracted from the potential energy surface of the MM-description (point A) and ground state energy calculations as well as structural minimizations were based on QM methods (black curve), hence the reported energy gap was due to the difference between points A and B in the schematic plot shown above. It is unrealistic to anticipate perfect agreement between MM- and QM-surfaces of potential energy (hence the differently shaped red and black curves), but for the conclusions drawn here it is important to show that geometry optimizations based on the MM-description would still have gone into the same direction, hence from point A to point C on the red line (otherwise we had not observed an intrinsic property of the BHJ but merely been talking about limitations of the force field). In other words, it is essential to demonstrate that the applied force field has not "trapped" individual D/A complexes in point A following a hypothetical potential as indicated by the dashed red line above. The resulting offset to the QM-based minimum structure (arrow between points B and C) is qualitatively acceptable as long as the energy difference $\Delta E = V_{MM}^{2Have}(C) - V_{MM}^{2Have}(A)$ remains of significant size and negative sign. Such a situation is confirmed here as demonstrated by the average ΔE over all 13 structures with partial contributions summarized in the table above.

Table S1 Transition dipole moments in a.u. for the selected D/A pair 3T-C60[156] in bulk conformation (above the bar values) and in relaxed conformation (below the bar values).

	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+4	LUMO+5	LUMO+6	LUMO+7	LUMO+8
LUMO	$^{0.666}/_{0.087}$									
LUMO+1	$^{0.201}/_{0.073}$	$^{0.729}/_{0.039}$								
LUMO+2	$^{0.244}/_{0.763}$	$^{0.151}/_{0.060}$	$^{0.468}/_{0.012}$							
LUMO+3	$^{0.096}/_{0.338}$	$^{3.027}/_{0.557}$	$^{2.626}/_{3.476}$	$^{2.414}/_{3.422}$						
LUMO+4	$^{0.214}/_{0.035}$	$^{3.210}/_{3.435}$	$^{1.868}/_{3.423}$	$^{2.724}/_{0.858}$	$^{0.702}/_{0.036}$					
LUMO+5	$^{0.277}/_{0.334}$	$^{1.045}/_{3.480}$	$^{3.440}/_{0.656}$	$^{2.846}/_{3.447}$	$^{0.225}/_{0.057}$	$^{0.717}/_{0.011}$				
LUMO+6	$^{3.348}/_{3.290}$	$^{0.259}/_{0.184}$	$^{0.252}/_{0.131}$	$^{0.175}/_{0.339}$	$^{0.472}/_{0.333}$	$^{0.311}/_{0.137}$	$^{0.883}/_{0.743}$			
LUMO+7	$^{0.154}/_{0.032}$	$^{1.534}/_{0.043}$	$^{0.779}/_{0.049}$	$^{1.263}/_{0.067}$	$^{0.713}/_{0.002}$	$^{1.807}/_{0.011}$	$^{1.091}/_{0.008}$	$^{0.172}/_{0.149}$		
LUMO+8	$^{0.211}/_{0.083}$	$^{0.498}/_{0.107}$	$^{0.627}/_{0.141}$	$^{0.273}/_{0.115}$	$^{0.227}/_{0.011}$	$^{0.486}/_{0.018}$	$^{0.174}/_{0.026}$	$^{0.894}/_{0.223}$	$^{1.177}/_{0.263}$	
LUMO+9	$^{0.267}/_{0.095}$	$^{0.293}/_{0.162}$	$^{0.400}/_{0.104}$	$^{0.653}/_{0.107}$	$^{0.403}/_{0.016}$	$^{0.616}/_{0.015}$	$^{0.336}/_{0.022}$	$^{1.044}/_{0.246}$	$^{1.041}/_{0.142}$	$^{5.265}/_{0.116}$

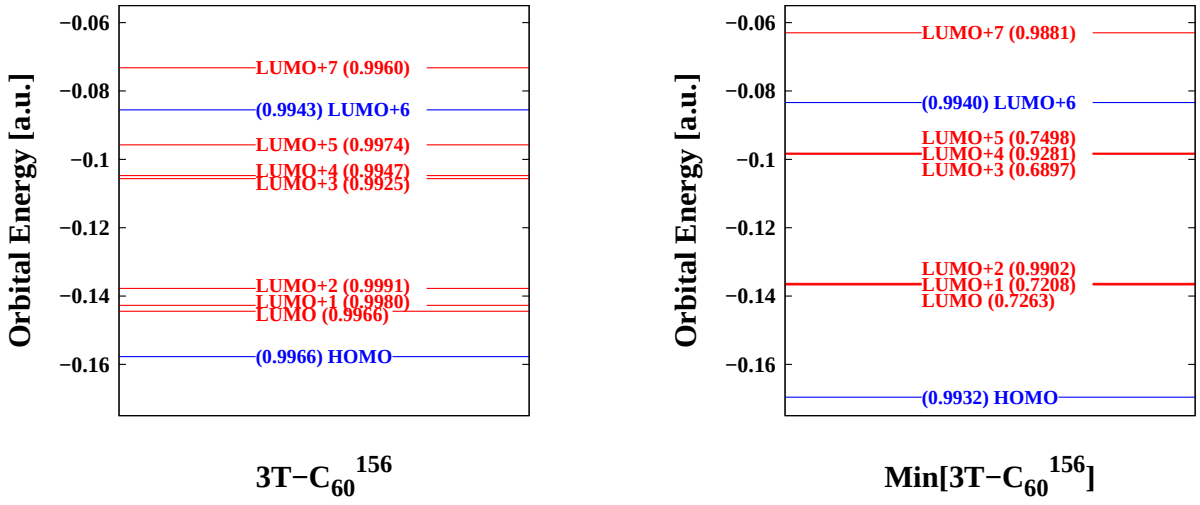


Fig. S4 Comparison of key orbitals involved in photo-excitation and primary electron transfer emphasizing differences/similarities between bulk conformation (left panel) and relaxed form (right panel) — sample 3T-C60[156]. Orbitals predominantly located on D are indicated in blue while those concentrated on A are given in red. A measure of similarity is also included in parentheses (1.0 indicating perfect agreement) where the resemblance is quantified between a particular orbital of the assembled D/A pair and its corresponding D- or A-orbital of the isolated donor- or acceptor-systems considered stand-alone. The bulk (i) distributes vacant energy levels more evenly (ii) makes accessible LUMO+7 for direct excitation into an acceptor orbital (also see Table S1) (iii) decouples electronic degrees of freedom (compare similarity coefficients);

Table S2 Transition dipole moments in a.u. for the selected D/A pair 3T-C60[162](case 1) in bulk conformation (above the bar values) and in relaxed conformation (below the bar values).

	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+4	LUMO+5	LUMO+6	LUMO+7	LUMO+8
LUMO	$^{0.669}/_{0.273}$									
LUMO+1	$^{1.662}/_{0.032}$	$^{0.548}/_{0.006}$								
LUMO+2	$^{0.545}/_{0.061}$	$^{0.525}/_{0.028}$	$^{0.197}/_{0.020}$							
LUMO+3	$^{0.324}/_{0.099}$	$^{3.290}/_{3.482}$	$^{2.918}/_{0.513}$	$^{1.265}/_{3.440}$						
LUMO+4	$^{0.641}/_{0.024}$	$^{0.820}/_{0.613}$	$^{2.896}/_{3.477}$	$^{3.573}/_{3.430}$	$^{0.635}/_{0.011}$					
LUMO+5	$^{0.260}/_{0.045}$	$^{3.344}/_{3.435}$	$^{0.635}/_{3.444}$	$^{3.086}/_{0.739}$	$^{0.715}/_{0.035}$	$^{0.615}/_{0.020}$				
LUMO+6	$^{2.166}/_{3.369}$	$^{0.544}/_{0.116}$	$^{1.804}/_{0.020}$	$^{0.970}/_{0.079}$	$^{1.263}/_{0.272}$	$^{1.760}/_{0.061}$	$^{0.578}/_{0.024}$			
LUMO+7	$^{2.315}/_{0.016}$	$^{0.169}/_{0.139}$	$^{0.856}/_{0.185}$	$^{0.750}/_{0.122}$	$^{0.827}/_{0.042}$	$^{1.080}/_{0.023}$	$^{0.520}/_{0.020}$	$^{7.863}/_{0.114}$		
LUMO+8	$^{0.053}/_{0.037}$	$^{0.777}/_{0.077}$	$^{0.580}/_{0.051}$	$^{0.216}/_{0.101}$	$^{0.586}/_{0.017}$	$^{0.360}/_{0.004}$	$^{0.295}/_{0.014}$	$^{1.096}/_{0.482}$	$^{0.568}/_{0.113}$	
LUMO+9	$^{0.131}/_{0.003}$	$^{1.212}/_{0.015}$	$^{1.568}/_{0.019}$	$^{1.086}/_{0.027}$	$^{0.771}/_{0.011}$	$^{0.489}/_{0.006}$	$^{0.763}/_{0.001}$	$^{0.179}/_{0.032}$	$^{0.231}/_{0.275}$	$^{2.486}/_{0.091}$

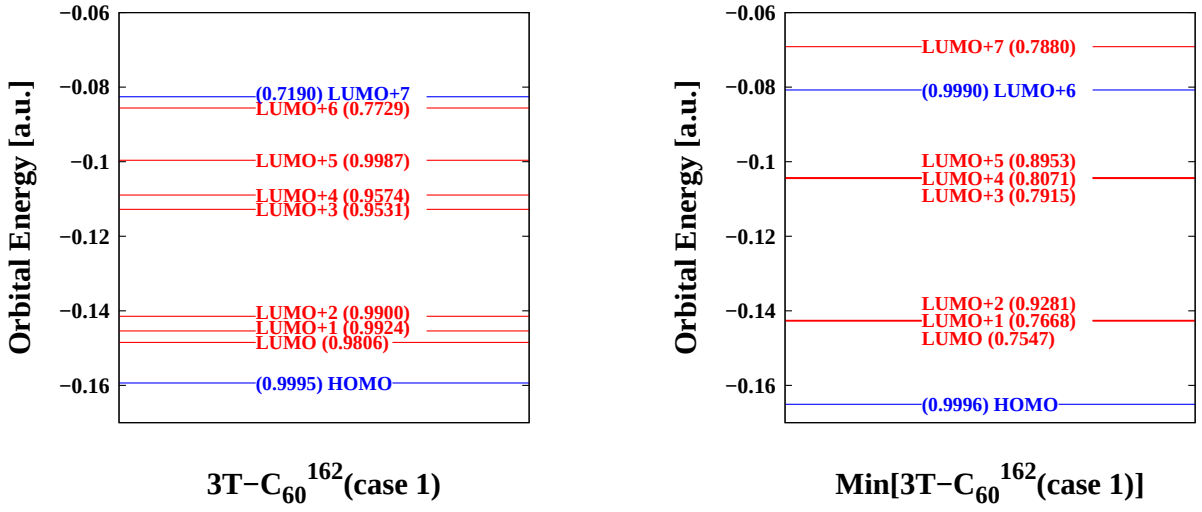


Fig. S5 Comparison of key orbitals involved in photo-excitation and primary electron transfer emphasizing differences/similarities between bulk conformation (left panel) and relaxed form (right panel) — sample 3T-C60[162](case 1). Orbitals predominantly located on D are indicated in blue while those concentrated on A are given in red. A measure of similarity is also included in parentheses (1.0 indicating perfect agreement) where the resemblance is quantified between a particular orbital of the assembled D/A pair and its corresponding D- or A-orbital of the isolated donor- or acceptor-systems considered stand-alone. The bulk (i) distributes vacant energy levels more evenly (ii) makes accessible LUMO+7 for direct excitation into an acceptor orbital (also see Table S2) (iii) decouples electronic degrees of freedom (compare similarity coefficients);

Table S3 Transition dipole moments in a.u. for the selected D/A pair 3T-C60[162](case 2) in bulk conformation (above the bar values) and in relaxed conformation (below the bar values).

	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+4	LUMO+5	LUMO+6	LUMO+7	LUMO+8
LUMO	$^{1.034}/_{0.095}$									
LUMO+1	$^{0.867}/_{0.153}$	$^{2.619}/_{0.884}$								
LUMO+2	$^{0.891}/_{0.473}$	$^{0.444}/_{0.511}$	$^{2.246}/_{0.376}$							
LUMO+3	$^{0.935}/_{0.109}$	$^{5.441}/_{0.590}$	$^{4.885}/_{1.570}$	$^{1.357}/_{1.317}$						
LUMO+4	$^{1.19}/_{0.078}$	$^{0.773}/_{1.252}$	$^{3.267}/_{1.210}$	$^{8.696}/_{0.815}$	$^{0.359}/_{0.275}$					
LUMO+5	$^{0.409}/_{0.314}$	$^{0.967}/_{1.391}$	$^{2.322}/_{0.722}$	$^{6.786}/_{1.231}$	$^{0.290}/_{0.354}$	$^{1.328}/_{0.309}$				
LUMO+6	$^{2.538}/_{2.533}$	$^{0.559}/_{0.177}$	$^{0.738}/_{0.185}$	$^{0.911}/_{0.113}$	$^{0.681}/_{0.700}$	$^{2.299}/_{0.185}$	$^{2.055}/_{0.378}$			
LUMO+7	$^{0.377}/_{0.171}$	$^{1.922}/_{0.684}$	$^{0.803}/_{0.262}$	$^{2.220}/_{0.960}$	$^{1.455}/_{0.816}$	$^{5.774}/_{1.040}$	$^{3.031}/_{0.672}$	$^{2.434}/_{0.179}$		
LUMO+8	$^{1.550}/_{0.191}$	$^{0.243}/_{0.808}$	$^{1.705}/_{0.520}$	$^{0.331}/_{0.867}$	$^{0.755}/_{0.843}$	$^{0.586}/_{1.037}$	$^{0.372}/_{0.873}$	$^{1.664}/_{0.341}$	$^{1.708}/_{0.223}$	
LUMO+9	$^{0.854}/_{0.150}$	$^{1.104}/_{0.488}$	$^{1.779}/_{0.820}$	$^{1.148}/_{0.136}$	$^{0.701}/_{0.348}$	$^{0.358}/_{0.976}$	$^{1.012}/_{0.406}$	$^{0.852}/_{0.194}$	$^{1.120}/_{0.718}$	$^{2.921}/_{0.907}$

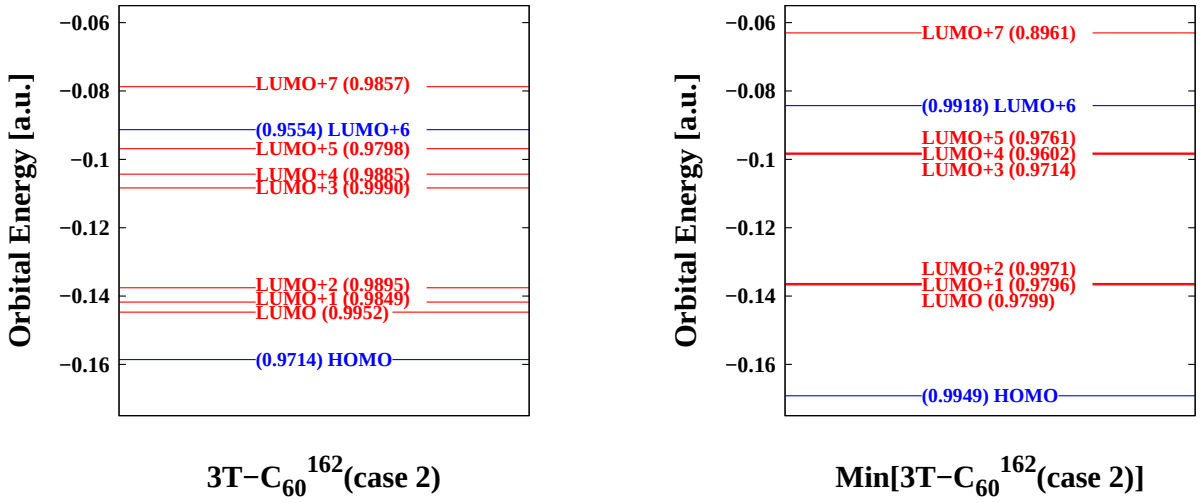


Fig. S6 Comparison of key orbitals involved in photo-excitation and primary electron transfer emphasizing differences/similarities between bulk conformation (left panel) and relaxed form (right panel) — sample 3T-C60[162](case 2). Orbitals predominantly located on D are indicated in blue while those concentrated on A are given in red. A measure of similarity is also included in parentheses (1.0 indicating perfect agreement) where the resemblance is quantified between a particular orbital of the assembled D/A pair and its corresponding D- or A-orbital of the isolated donor- or acceptor-systems considered stand-alone. The bulk (i) distributes vacant energy levels more evenly (ii) makes accessible LUMO+7 for direct excitation into an acceptor orbital (also see Table S3) (iii) decouples electronic degrees of freedom (compare similarity coefficients);

Table S4 Transition dipole moments in a.u. for the selected D/A pair 3T-C60[167] in bulk conformation (above the bar values) and in relaxed conformation (below the bar values).

	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+4	LUMO+5	LUMO+6	LUMO+7	LUMO+8
LUMO	0.605/0.055									
LUMO+1	0.069/0.253	0.511/0.015								
LUMO+2	0.675/0.083	0.415/0.039	0.176/0.020							
LUMO+3	0.181/0.073	3.159/3.403	2.289/0.960	2.383/3.429						
LUMO+4	0.073/0.079	2.128/1.061	2.980/3.419	2.640/3.378	1.216/0.007					
LUMO+5	0.160/0.053	2.765/3.414	2.592/3.408	2.805/0.979	0.444/0.043	0.482/0.025				
LUMO+6	2.934/3.353	0.156/0.039	0.622/0.126	0.598/0.093	0.596/0.206	0.452/0.122	0.248/0.078			
LUMO+7	1.088/0.038	0.357/0.124	1.317/0.103	1.652/0.109	1.581/0.041	1.061/0.020	0.556/0.022	4.741/0.099		
LUMO+8	0.101/0.134	0.415/0.055	0.714/0.103	0.47/0.106	0.198/0.016	0.433/0.006	0.328/0.013	0.173/0.764	0.975/0.167	
LUMO+9	0.077/0.061	0.656/0.085	0.366/0.039	0.551/0.066	0.390/0.024	0.337/0.007	0.352/0.004	0.540/0.296	1.113/0.270	1.098/0.149

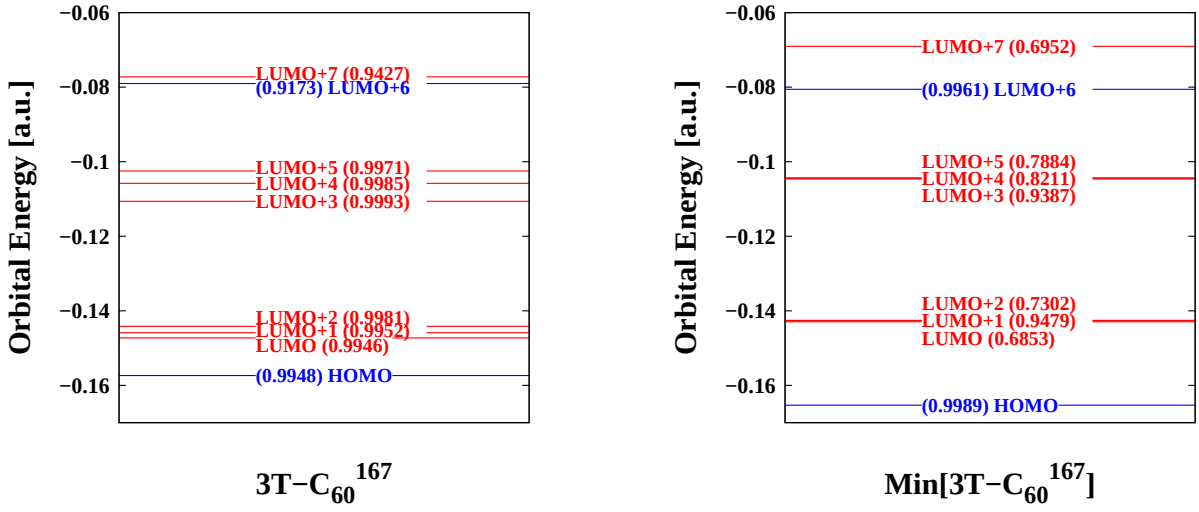


Fig. S7 Comparison of key orbitals involved in photo-excitation and primary electron transfer emphasizing differences/similarities between bulk conformation (left panel) and relaxed form (right panel) — sample 3T-C60[167]. Orbitals predominantly located on D are indicated in blue while those concentrated on A are given in red. A measure of similarity is also included in parentheses (1.0 indicating perfect agreement) where the resemblance is quantified between a particular orbital of the assembled D/A pair and its corresponding D- or A-orbital of the isolated donor- or acceptor-systems considered stand-alone. The bulk (i) distributes vacant energy levels more evenly (ii) makes accessible LUMO+7 for direct excitation into an acceptor orbital (also see Table S4) (iii) decouples electronic degrees of freedom (compare similarity coefficients);

Table S5 Transition dipole moments in a.u. for the selected D/A pair 3T-C60[168] in bulk conformation (above the bar values) and in relaxed conformation (below the bar values).

	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+4	LUMO+5	LUMO+6	LUMO+7	LUMO+8
LUMO	0.475/0.117									
LUMO+1	0.234/0.346	0.411/0.039								
LUMO+2	0.397/0.645	0.262/0.051	0.251/0.023							
LUMO+3	0.163/0.311	3.288/0.769	3.015/3.390	0.972/3.466						
LUMO+4	0.032/0.221	3.152/3.476	1.391/3.483	3.017/0.125	0.802/0.044					
LUMO+5	0.146/0.324	1.625/3.397	3.149/0.773	3.201/3.500	0.555/0.056	0.348/0.028				
LUMO+6	3.320/3.330	0.181/0.209	0.212/0.262	0.493/0.159	0.254/0.607	0.368/0.586	0.176/0.574			
LUMO+7	0.607/0.040	0.709/0.048	1.378/0.066	1.274/0.057	1.253/0.005	1.749/0.007	0.470/0.015	2.777/0.145		
LUMO+8	0.078/0.118	0.444/0.091	0.500/0.148	0.513/0.090	0.199/0.008	0.124/0.022	0.223/0.023	0.944/0.360	0.608/0.275	
LUMO+9	0.071/0.072	1.178/0.156	1.062/0.082	0.725/0.110	0.404/0.018	0.311/0.005	0.100/0.016	0.661/0.103	1.816/0.166	2.075/0.190

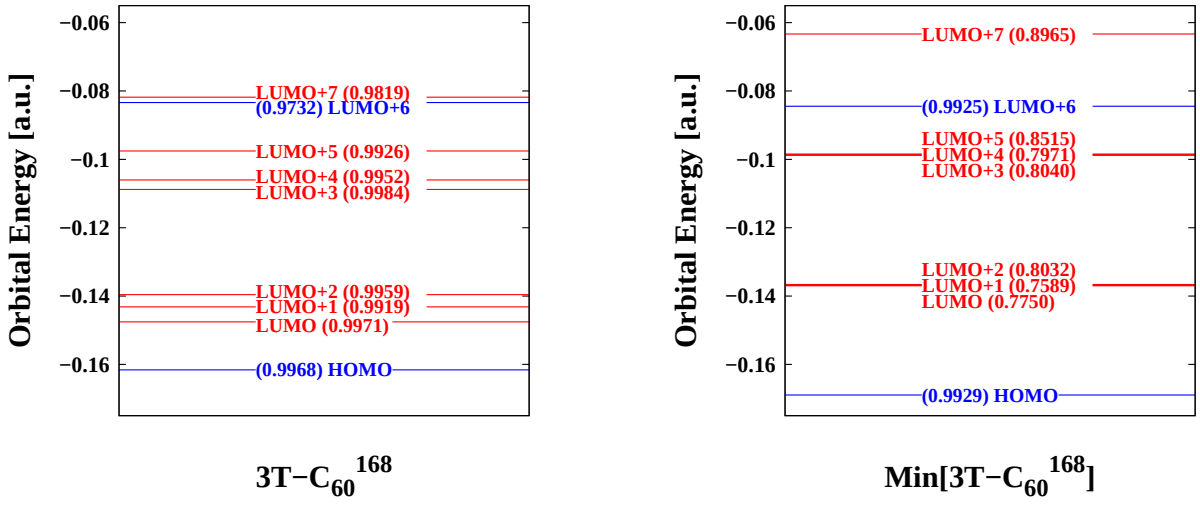


Fig. S8 Comparison of key orbitals involved in photo-excitation and primary electron transfer emphasizing differences/similarities between bulk conformation (left panel) and relaxed form (right panel) — sample 3T-C60[168]. Orbitals predominantly located on D are indicated in blue while those concentrated on A are given in red. A measure of similarity is also included in parentheses (1.0 indicating perfect agreement) where the resemblance is quantified between a particular orbital of the assembled D/A pair and its corresponding D- or A-orbital of the isolated donor- or acceptor-systems considered stand-alone. The bulk (i) distributes vacant energy levels more evenly (ii) makes accessible LUMO+7 for direct excitation into an acceptor orbital (also see Table S5) (iii) decouples electronic degrees of freedom (compare similarity coefficients);

Table S6 Transition dipole moments in a.u. for the selected D/A pair 3T-C60[171](case 2) in bulk conformation (above the bar values) and in relaxed conformation (below the bar values).

	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+4	LUMO+5	LUMO+6	LUMO+7	LUMO+8
LUMO	$^{0.338}/_{0.130}$									
LUMO+1	$^{0.019}/_{0.725}$	$^{0.056}/_{0.047}$								
LUMO+2	$^{0.535}/_{0.077}$	$^{0.537}/_{0.047}$	$^{0.330}/_{0.009}$							
LUMO+3	$^{0.173}/_{0.257}$	$^{2.736}/_{0.398}$	$^{3.498}/_{3.469}$	$^{1.508}/_{3.453}$						
LUMO+4	$^{0.140}/_{0.349}$	$^{2.080}/_{3.457}$	$^{2.132}/_{3.494}$	$^{3.427}/_{0.407}$	$^{0.576}/_{0.044}$					
LUMO+5	$^{0.104}/_{0.063}$	$^{2.875}/_{3.481}$	$^{2.216}/_{0.249}$	$^{2.832}/_{3.482}$	$^{0.446}/_{0.047}$	$^{0.760}/_{0.008}$				
LUMO+6	$^{1.961}/_{3.332}$	$^{1.184}/_{0.170}$	$^{1.271}/_{0.236}$	$^{0.433}/_{0.144}$	$^{1.451}/_{0.411}$	$^{0.889}/_{0.634}$	$^{0.695}/_{0.025}$			
LUMO+7	$^{2.632}/_{0.055}$	$^{0.855}/_{0.065}$	$^{0.917}/_{0.061}$	$^{0.368}/_{0.084}$	$^{1.140}/_{0.005}$	$^{0.637}/_{0.013}$	$^{0.578}/_{0.013}$	$^{7.316}/_{0.356}$		
LUMO+8	$^{0.049}/_{0.084}$	$^{0.056}/_{0.103}$	$^{0.257}/_{0.081}$	$^{0.297}/_{0.089}$	$^{0.222}/_{0.017}$	$^{0.289}/_{0.008}$	$^{0.122}/_{0.021}$	$^{0.251}/_{0.065}$	$^{0.187}/_{0.216}$	
LUMO+9	$^{0.110}/_{0.038}$	$^{0.549}/_{0.130}$	$^{0.391}/_{0.117}$	$^{0.377}/_{0.097}$	$^{0.720}/_{0.015}$	$^{0.556}/_{0.013}$	$^{0.255}/_{0.018}$	$^{1.298}/_{0.044}$	$^{0.813}/_{0.196}$	$^{0.597}/_{0.109}$

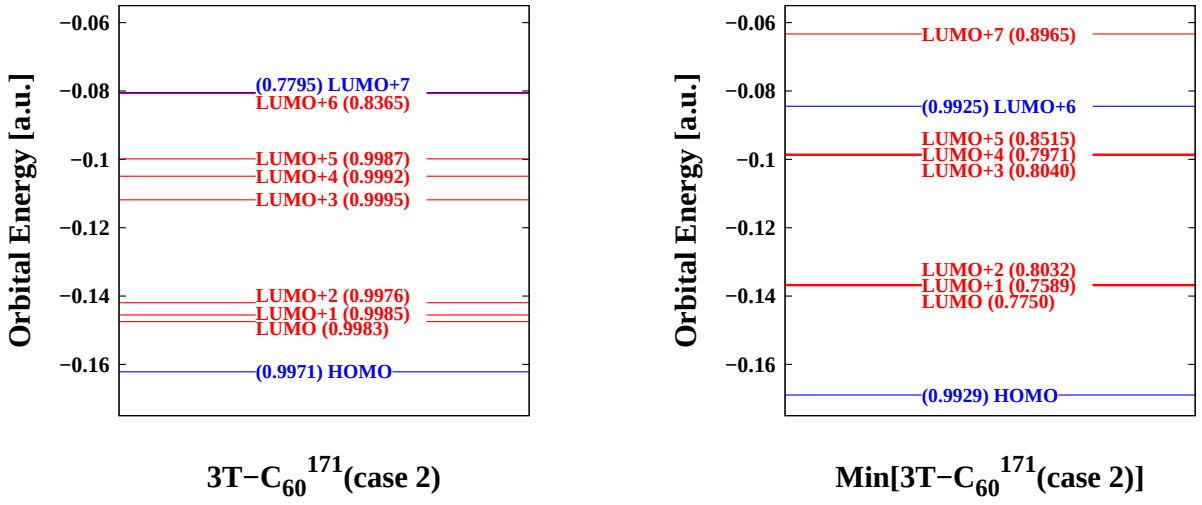


Fig. S9 Comparison of key orbitals involved in photo-excitation and primary electron transfer emphasizing differences/similarities between bulk conformation (left panel) and relaxed form (right panel) — sample 3T-C60[171](case 2). Orbitals predominantly located on D are indicated in blue while those concentrated on A are given in red. A measure of similarity is also included in parentheses (1.0 indicating perfect agreement) where the resemblance is quantified between a particular orbital of the assembled D/A pair and its corresponding D- or A-orbital of the isolated donor- or acceptor-systems considered stand-alone. The bulk (i) distributes vacant energy levels more evenly (ii) makes accessible LUMO+6 for direct excitation into an acceptor orbital (also see Table S6) (iii) decouples electronic degrees of freedom (compare similarity coefficients);

Table S7 Transition dipole moments in a.u. for the selected D/A pair 3T-C60[199](case 1) in bulk conformation (above the bar values) and in relaxed conformation (below the bar values).

	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+4	LUMO+5	LUMO+6	LUMO+7	LUMO+8
LUMO	$^{0.879}/_{0.062}$									
LUMO+1	$^{0.068}/_{0.053}$	$^{0.347}/_{0.014}$								
LUMO+2	$^{0.031}/_{0.067}$	$^{0.310}/_{0.021}$	$^{0.362}/_{0.007}$							
LUMO+3	$^{0.139}/_{0.045}$	$^{3.190}/_{3.481}$	$^{3.021}/_{0.818}$	$^{1.552}/_{3.396}$						
LUMO+4	$^{0.251}/_{0.081}$	$^{3.166}/_{1.846}$	$^{1.346}/_{3.481}$	$^{3.288}/_{2.948}$	$^{0.662}/_{0.010}$					
LUMO+5	$^{0.205}/_{0.118}$	$^{0.643}/_{2.965}$	$^{3.324}/_{3.390}$	$^{3.264}/_{1.985}$	$^{0.245}/_{0.029}$	$^{0.283}/_{0.012}$				
LUMO+6	$^{3.069}/_{3.345}$	$^{0.281}/_{0.171}$	$^{0.227}/_{0.109}$	$^{0.110}/_{0.206}$	$^{0.135}/_{0.159}$	$^{0.502}/_{0.284}$	$^{0.765}/_{0.446}$			
LUMO+7	$^{0.131}/_{0.020}$	$^{1.321}/_{0.066}$	$^{1.153}/_{0.086}$	$^{0.918}/_{0.097}$	$^{1.545}/_{0.032}$	$^{0.736}/_{0.003}$	$^{0.801}/_{0.016}$	$^{1.208}/_{0.115}$		
LUMO+8	$^{0.114}/_{0.149}$	$^{0.381}/_{0.059}$	$^{0.759}/_{0.031}$	$^{0.311}/_{0.035}$	$^{0.795}/_{0.026}$	$^{0.374}/_{0.022}$	$^{0.354}/_{0.026}$	$^{0.363}/_{0.542}$	$^{1.178}/_{0.054}$	
LUMO+9	$^{0.068}/_{0.077}$	$^{0.371}/_{0.067}$	$^{0.217}/_{0.063}$	$^{0.348}/_{0.029}$	$^{0.421}/_{0.015}$	$^{0.283}/_{0.012}$	$^{0.403}/_{0.010}$	$^{0.271}/_{0.314}$	$^{0.876}/_{0.040}$	$^{0.659}/_{0.131}$

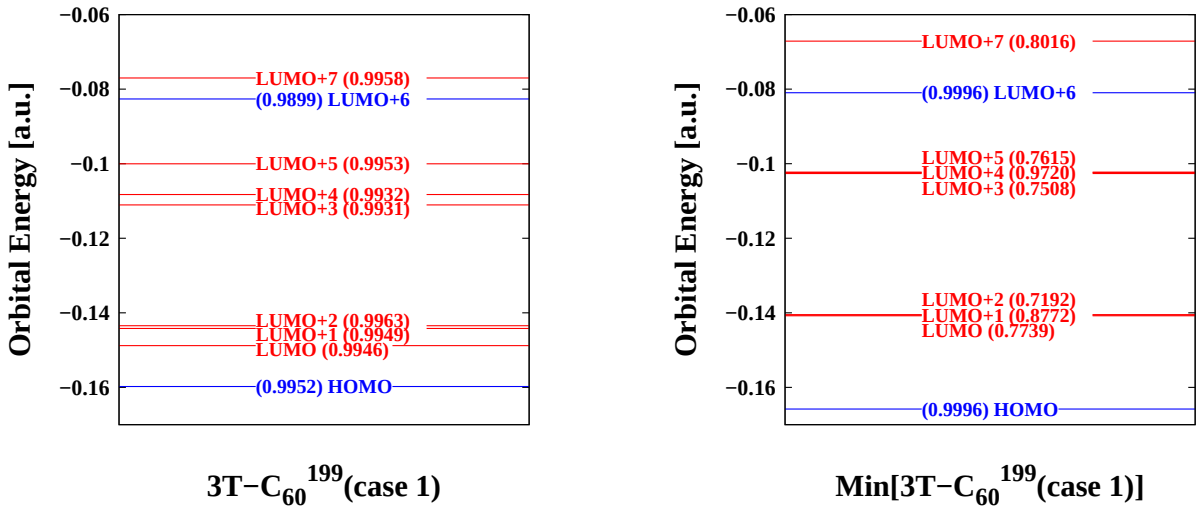


Fig. S10 Comparison of key orbitals involved in photo-excitation and primary electron transfer emphasizing differences/similarities between bulk conformation (left panel) and relaxed form (right panel) — sample 3T-C60[199](case 1). Orbitals predominantly located on D are indicated in blue while those concentrated on A are given in red. A measure of similarity is also included in parentheses (1.0 indicating perfect agreement) where the resemblance is quantified between a particular orbital of the assembled D/A pair and its corresponding D- or A-orbital of the isolated donor- or acceptor-systems considered stand-alone. The bulk (i) distributes vacant energy levels more evenly (ii) makes accessible LUMO+7 for direct excitation into an acceptor orbital (also see Table S7) (iii) decouples electronic degrees of freedom (compare similarity coefficients);

Table S8 Transition dipole moments in a.u. for the selected D/A pair 3T-C60[199](case 2) in bulk conformation (above the bar values) and in relaxed conformation (below the bar values).

	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+4	LUMO+5	LUMO+6	LUMO+7	LUMO+8
LUMO	0.190/0.099									
LUMO+1	0.020/0.030	0.351/0.044								
LUMO+2	0.130/0.492	0.319/0.054	0.304/0.008							
LUMO+3	0.057/0.313	3.202/1.022	3.270/3.325	0.739/3.461						
LUMO+4	0.097/0.063	3.141/3.479	0.730/3.450	3.503/0.478	0.674/0.044					
LUMO+5	0.048/0.208	0.710/3.328	3.264/1.120	3.319/3.461	0.230/0.051	0.275/0.010				
LUMO+6	3.262/3.283	0.109/0.031	0.201/0.168	0.084/0.331	0.271/0.719	0.246/0.070	0.345/0.286			
LUMO+7	0.254/0.028	1.316/0.058	1.228/0.042	0.758/0.057	1.431/0.007	0.808/0.009	0.761/0.014	0.923/0.146		
LUMO+8	0.383/0.114	0.367/0.148	0.406/0.152	0.108/0.102	0.550/0.023	0.367/0.017	0.264/0.014	2.038/0.266	1.387/0.255	
LUMO+9	0.098/0.093	0.341/0.125	0.737/0.097	0.355/0.126	0.763/0.014	0.348/0.012	0.378/0.016	0.396/0.030	1.466/0.210	1.452/0.138

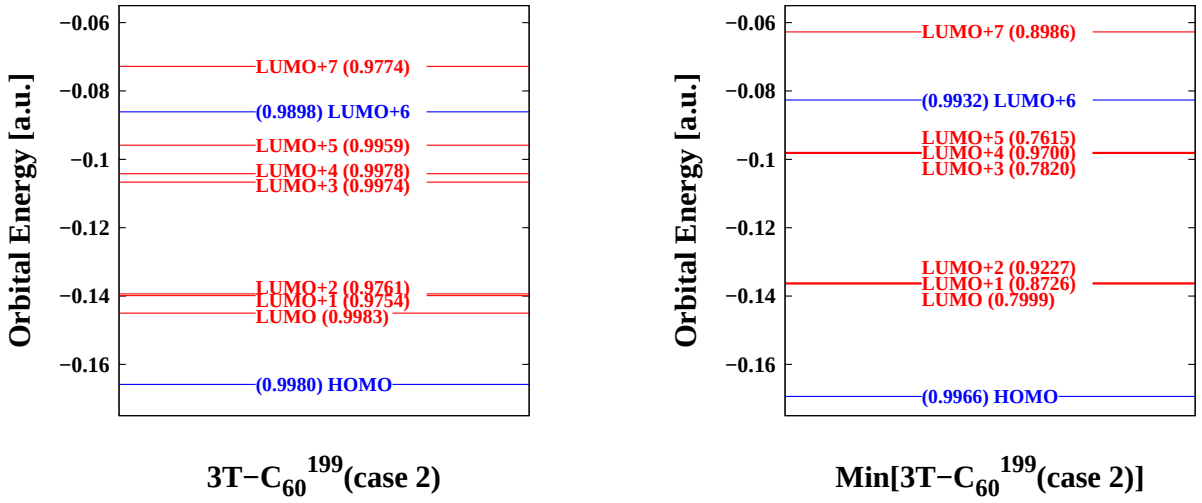


Fig. S11 Comparison of key orbitals involved in photo-excitation and primary electron transfer emphasizing differences/similarities between bulk conformation (left panel) and relaxed form (right panel) — sample 3T-C60[199](case 2). Orbitals predominantly located on D are indicated in blue while those concentrated on A are given in red. A measure of similarity is also included in parentheses (1.0 indicating perfect agreement) where the resemblance is quantified between a particular orbital of the assembled D/A pair and its corresponding D- or A-orbital of the isolated donor- or acceptor-systems considered stand-alone. The bulk (i) distributes vacant energy levels more evenly (ii) makes accessible LUMO+7 for direct excitation into an acceptor orbital (also see Table S8) (iii) decouples electronic degrees of freedom (compare similarity coefficients);

Table S9 Transition dipole moments in a.u. for the selected D/A pair 3T-C60[56](case 1) in bulk conformation (above the bar values) and in relaxed conformation (below the bar values).

	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+4	LUMO+5	LUMO+6	LUMO+7	LUMO+8
LUMO	0.164/0.057									
LUMO+1	0.247/0.028	0.649/0.009								
LUMO+2	0.010/0.006	0.527/0.033	0.308/0.022							
LUMO+3	0.046/0.014	3.271/3.418	2.222/1.059	2.499/3.379						
LUMO+4	0.073/0.028	2.825/1.549	2.856/3.467	2.479/3.133	0.482/0.012					
LUMO+5	0.045/0.015	2.271/3.199	3.064/3.328	2.506/1.703	0.146/0.038	0.459/0.022				
LUMO+6	3.163/3.310	0.060/0.015	0.116/0.038	0.096/0.030	0.084/0.023	0.202/0.085	0.068/0.014			
LUMO+7	0.136/0.004	0.952/0.102	1.009/0.159	1.711/0.083	0.874/0.025	0.924/0.013	1.750/0.014	0.704/0.087		
LUMO+8	0.082/0.025	0.226/0.091	0.330/0.027	0.490/0.116	0.663/0.032	0.423/0.012	0.409/0.016	0.251/0.146	0.503/0.158	
LUMO+9	0.994/0.042	0.015/0.022	0.039/0.037	0.028/0.040	0.077/0.009	0.070/0.003	0.029/0.005	3.071/0.282	0.254/0.247	1.224/0.101

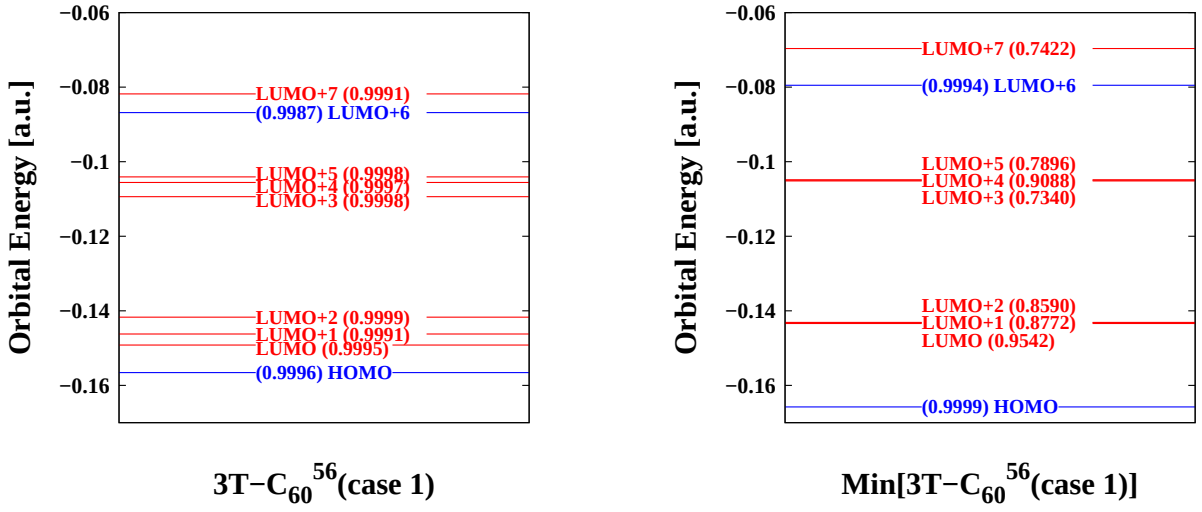


Fig. S12 Comparison of key orbitals involved in photo-excitation and primary electron transfer emphasizing differences/similarities between bulk conformation (left panel) and relaxed form (right panel) — sample 3T-C60[56](case 1). Orbitals predominantly located on D are indicated in blue while those concentrated on A are given in red. A measure of similarity is also included in parentheses (1.0 indicating perfect agreement) where the resemblance is quantified between a particular orbital of the assembled D/A pair and its corresponding D- or A-orbital of the isolated donor- or acceptor-systems considered stand-alone. The bulk (i) distributes vacant energy levels more evenly (ii) makes accessible LUMO+7 for direct excitation into an acceptor orbital (also see Table S9) (iii) decouples electronic degrees of freedom (compare similarity coefficients);

Table S10 Transition dipole moments in a.u. for the selected D/A pair 3T-C60[56](case 2) in bulk conformation (above the bar values) and in relaxed conformation (below the bar values).

	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+4	LUMO+5	LUMO+6	LUMO+7	LUMO+8
LUMO	$^{0.829}/_{0.046}$									
LUMO+1	$^{0.362}/_{0.125}$	$^{0.686}/_{0.035}$								
LUMO+2	$^{0.475}/_{0.423}$	$^{0.526}/_{0.046}$	$^{0.288}/_{0.016}$							
LUMO+3	$^{0.298}/_{0.268}$	$^{3.362}/_{0.875}$	$^{2.200}/_{3.448}$	$^{2.428}/_{3.385}$						
LUMO+4	$^{0.562}/_{0.305}$	$^{2.157}/_{3.365}$	$^{3.077}/_{3.131}$	$^{2.878}/_{1.760}$	$^{0.428}/_{0.050}$					
LUMO+5	$^{1.132}/_{0.184}$	$^{2.821}/_{3.479}$	$^{2.684}/_{1.589}$	$^{2.271}/_{3.120}$	$^{0.219}/_{0.050}$	$^{0.530}/_{0.034}$				
LUMO+6	$^{3.082}/_{3.352}$	$^{0.509}/_{0.254}$	$^{0.876}/_{0.222}$	$^{0.452}/_{0.236}$	$^{0.421}/_{0.526}$	$^{2.246}/_{0.832}$	$^{3.344}/_{0.489}$			
LUMO+7	$^{0.229}/_{0.085}$	$^{0.931}/_{0.060}$	$^{1.085}/_{0.074}$	$^{1.718}/_{0.081}$	$^{0.894}/_{0.012}$	$^{1.072}/_{0.018}$	$^{1.261}/_{0.019}$	$^{1.655}/_{0.112}$		
LUMO+8	$^{0.196}/_{0.075}$	$^{0.217}/_{0.148}$	$^{0.321}/_{0.080}$	$^{0.520}/_{0.103}$	$^{0.754}/_{0.013}$	$^{0.467}/_{0.011}$	$^{0.387}/_{0.012}$	$^{0.526}/_{0.032}$	$^{0.415}/_{0.147}$	
LUMO+9	$^{0.202}/_{0.034}$	$^{0.900}/_{0.064}$	$^{0.785}/_{0.146}$	$^{0.967}/_{0.100}$	$^{0.412}/_{0.011}$	$^{0.163}/_{0.008}$	$^{0.420}/_{0.014}$	$^{0.350}/_{0.155}$	$^{0.582}/_{0.306}$	$^{1.411}/_{0.176}$

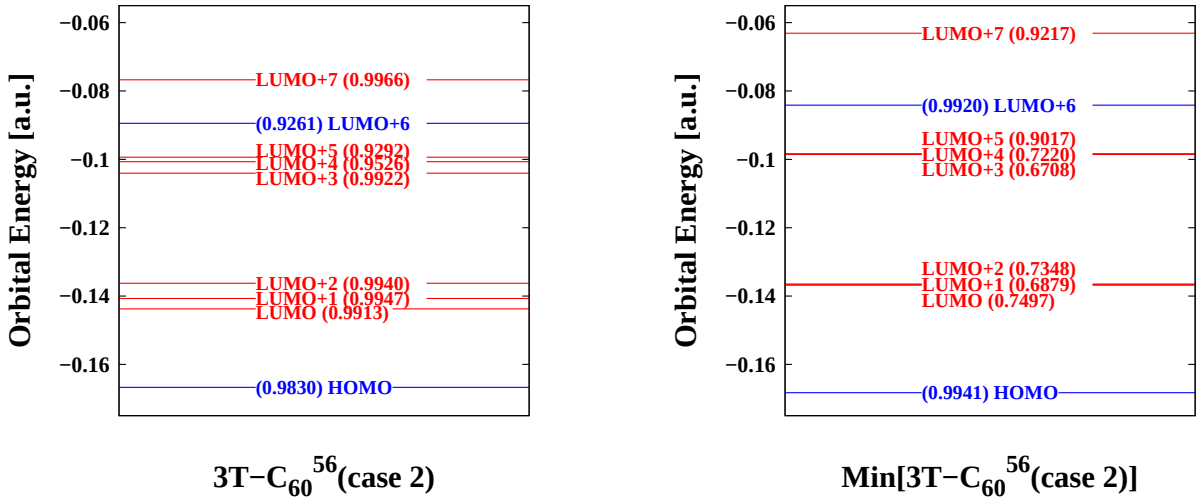


Fig. S13 Comparison of key orbitals involved in photo-excitation and primary electron transfer emphasizing differences/similarities between bulk conformation (left panel) and relaxed form (right panel) — sample 3T-C60[56](case 2). Orbitals predominantly located on D are indicated in blue while those concentrated on A are given in red. A measure of similarity is also included in parentheses (1.0 indicating perfect agreement) where the resemblance is quantified between a particular orbital of the assembled D/A pair and its corresponding D- or A-orbital of the isolated donor- or acceptor-systems considered stand-alone. The bulk (i) distributes vacant energy levels more evenly (ii) makes accessible LUMO+7 for direct excitation into an acceptor orbital (also see Table S10) (iii) decouples electronic degrees of freedom (compare similarity coefficients);

Table S11 Transition dipole moments in a.u. for the selected D/A pair 3T-C60[76] in bulk conformation (above the bar values) and in relaxed conformation (below the bar values).

	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+4	LUMO+5	LUMO+6	LUMO+7	LUMO+8
LUMO	$^{0.350}/_{0.109}$									
LUMO+1	$^{0.370}/_{0.035}$	$^{0.275}/_{0.041}$								
LUMO+2	$^{0.045}/_{0.386}$	$^{0.342}/_{0.041}$	$^{0.499}/_{0.009}$							
LUMO+3	$^{0.216}/_{0.120}$	$^{3.045}/_{0.717}$	$^{2.916}/_{3.473}$	$^{1.910}/_{3.402}$						
LUMO+4	$^{0.318}/_{0.207}$	$^{2.110}/_{3.439}$	$^{2.948}/_{1.894}$	$^{2.857}/_{2.978}$	$^{0.691}/_{0.034}$					
LUMO+5	$^{0.144}/_{0.125}$	$^{3.151}/_{3.439}$	$^{1.585}/_{2.932}$	$^{3.124}/_{1.963}$	$^{0.290}/_{0.036}$	$^{0.663}/_{0.011}$				
LUMO+6	$^{3.284}/_{3.327}$	$^{0.161}/_{0.228}$	$^{0.527}/_{0.042}$	$^{0.190}/_{0.061}$	$^{0.354}/_{0.059}$	$^{0.254}/_{0.708}$	$^{0.215}/_{0.040}$			
LUMO+7	$^{0.298}/_{0.080}$	$^{0.621}/_{0.067}$	$^{1.558}/_{0.086}$	$^{1.363}/_{0.101}$	$^{1.822}/_{0.007}$	$^{1.135}/_{0.018}$	$^{0.673}/_{0.007}$	$^{1.514}/_{0.128}$		
LUMO+8	$^{0.112}/_{0.035}$	$^{0.293}/_{0.078}$	$^{0.366}/_{0.056}$	$^{0.326}/_{0.074}$	$^{0.254}/_{0.007}$	$^{0.210}/_{0.010}$	$^{0.403}/_{0.005}$	$^{0.612}/_{0.182}$	$^{1.010}/_{0.216}$	
LUMO+9	$^{0.340}/_{0.093}$	$^{0.461}/_{0.100}$	$^{0.381}/_{0.104}$	$^{0.281}/_{0.102}$	$^{0.238}/_{0.009}$	$^{0.274}/_{0.029}$	$^{0.155}/_{0.024}$	$^{1.665}/_{0.264}$	$^{0.740}/_{0.105}$	$^{1.969}/_{0.273}$

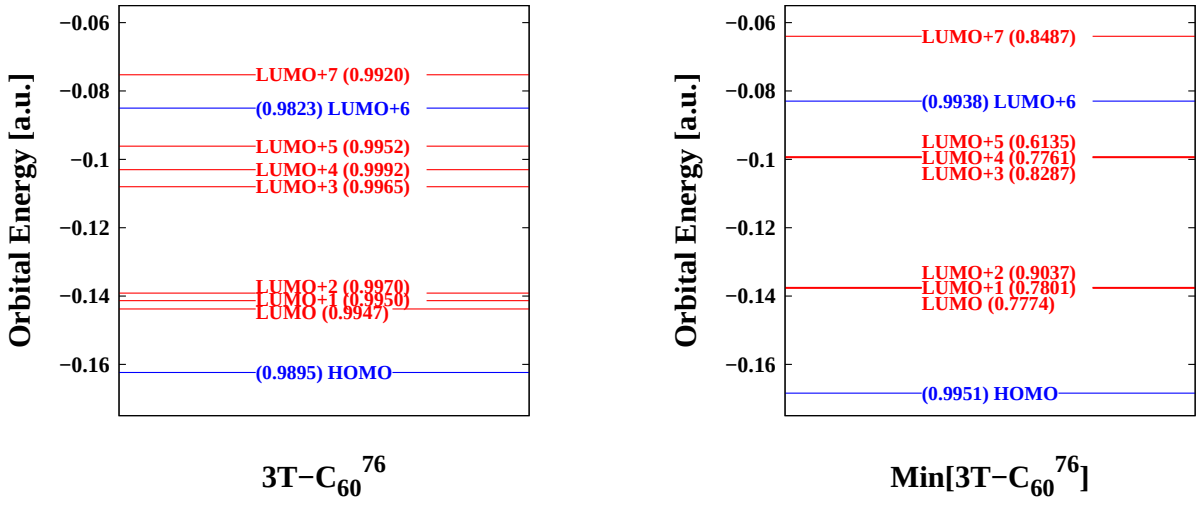


Fig. S14 Comparison of key orbitals involved in photo-excitation and primary electron transfer emphasizing differences/similarities between bulk conformation (left panel) and relaxed form (right panel) — sample 3T-C60[76]. Orbitals predominantly located on D are indicated in blue while those concentrated on A are given in red. A measure of similarity is also included in parentheses (1.0 indicating perfect agreement) where the resemblance is quantified between a particular orbital of the assembled D/A pair and its corresponding D- or A-orbital of the isolated donor- or acceptor-systems considered stand-alone. The bulk (i) distributes vacant energy levels more evenly (ii) makes accessible LUMO+7 for direct excitation into an acceptor orbital (also see Table S11) (iii) decouples electronic degrees of freedom (compare similarity coefficients);

Table S12 Transition dipole moments in a.u. for the selected D/A pair 3T-C60[98] in bulk conformation (above the bar values) and in relaxed conformation (below the bar values).

	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+4	LUMO+5	LUMO+6	LUMO+7	LUMO+8
LUMO	0.287/0.049									
LUMO+1	0.014/0.238	0.289/0.025								
LUMO+2	0.100/0.314	0.477/0.032	0.520/0.026							
LUMO+3	0.049/0.062	3.118/3.429	2.995/2.050	1.679/2.881						
LUMO+4	0.040/0.136	3.246/0.694	1.393/3.419	2.806/3.474	0.778/0.004					
LUMO+5	0.036/0.074	1.741/3.471	3.221/2.896	2.971/1.947	0.436/0.043	0.959/0.024				
LUMO+6	3.196/3.369	0.044/0.029	0.015/0.065	0.050/0.133	0.031/0.123	0.100/0.297	0.121/0.044			
LUMO+7	0.020/0.019	0.507/0.168	1.311/0.107	1.527/0.091	1.187/0.031	1.351/0.022	0.902/0.007	0.324/0.265		
LUMO+8	0.034/0.024	0.638/0.050	0.574/0.094	0.766/0.100	0.237/0.013	0.462/0.019	0.360/0.009	0.078/0.245	0.745/0.175	
LUMO+9	0.017/0.031	0.476/0.054	1.006/0.044	1.109/0.076	0.502/0.016	0.784/0.012	0.155/0.009	0.072/0.251	0.729/0.276	3.108/0.163

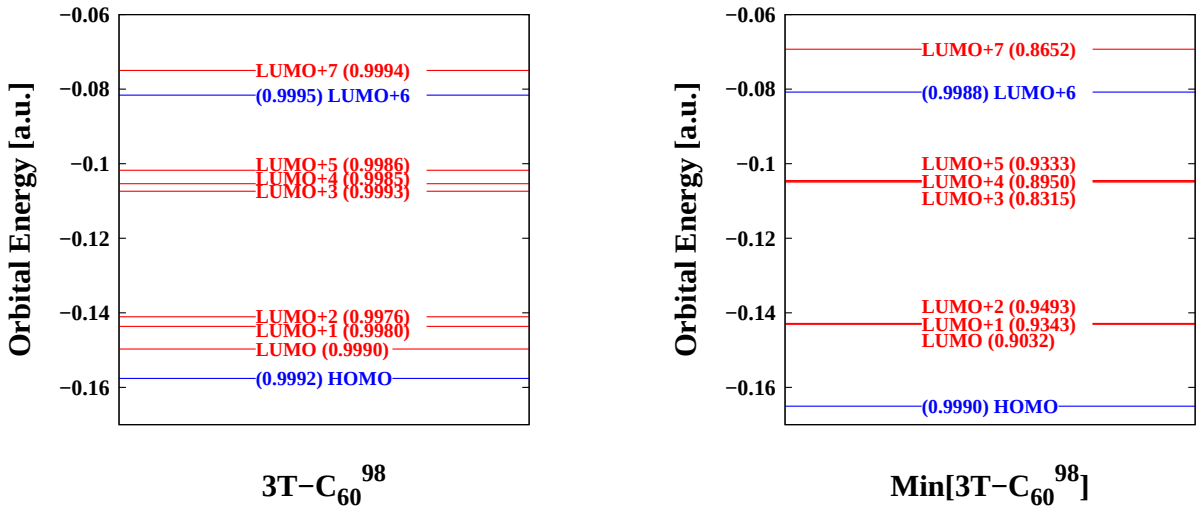


Fig. S15 Comparison of key orbitals involved in photo-excitation and primary electron transfer emphasizing differences/similarities between bulk conformation (left panel) and relaxed form (right panel) — sample 3T-C60[98]. Orbitals predominantly located on D are indicated in blue while those concentrated on A are given in red. A measure of similarity is also included in parentheses (1.0 indicating perfect agreement) where the resemblance is quantified between a particular orbital of the assembled D/A pair and its corresponding D- or A-orbital of the isolated donor- or acceptor-systems considered stand-alone. The bulk (i) distributes vacant energy levels more evenly (ii) makes accessible LUMO+7 for direct excitation into an acceptor orbital (also see Table S12) (iii) decouples electronic degrees of freedom (compare similarity coefficients);

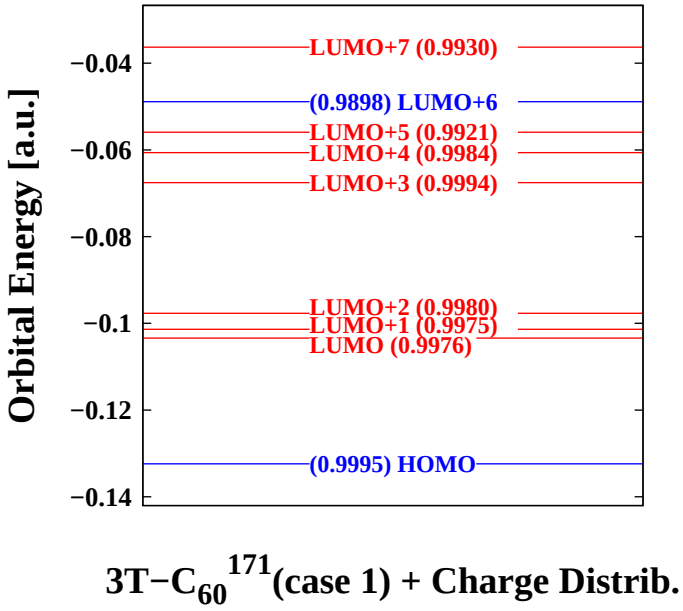


Fig. S16 Key orbitals involved in photo-excitation and primary electron transfer of the bulk conformation 3T-C60[171](case 1) including adjacent 3T-C60 units (see Movie 1, ESI†) via atomic point charges (background charge distribution). Changes with respect to the isolated D/A system (Figure 3 of the main text) are minor, hence the simplification to single isolated D/A systems appears to be justified.