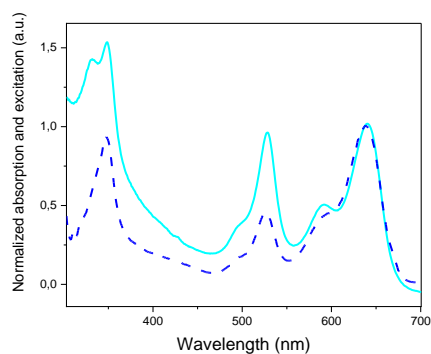
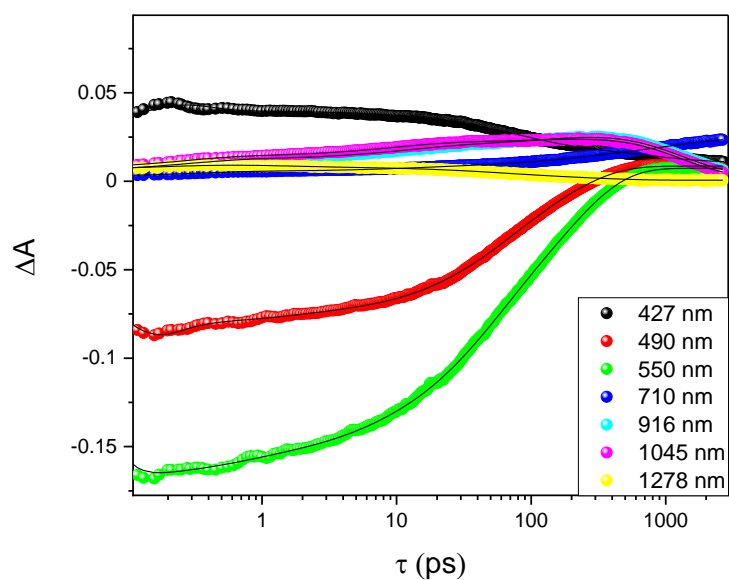


Supplementary Information



SI Fig. 1. Excitation spectrum (dashed blue, $\lambda_{em} = 670$ nm) overlapped with the absorption spectrum (cyan) of the BDP-C₆₀-DSBDP triad.

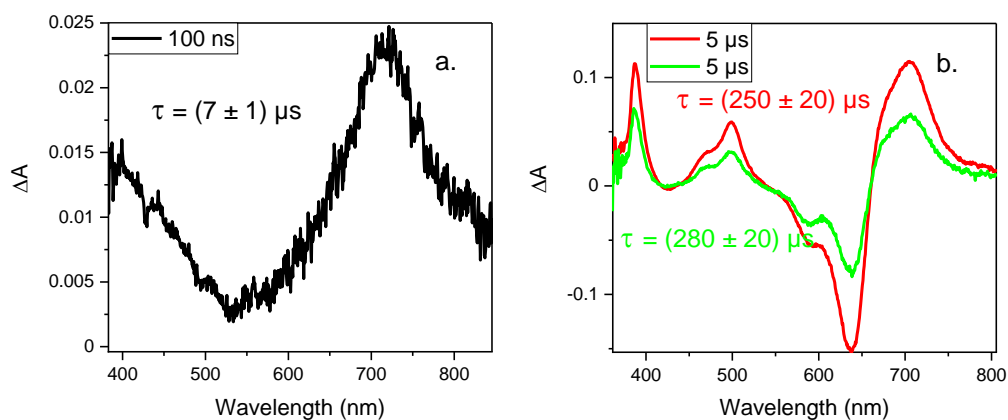


SI Fig. 2. Decay traces of transient absorptions of BDP-C₆₀ dyad at specific probe wavelengths in deaerated benzonitrile fitted with a four exponential model

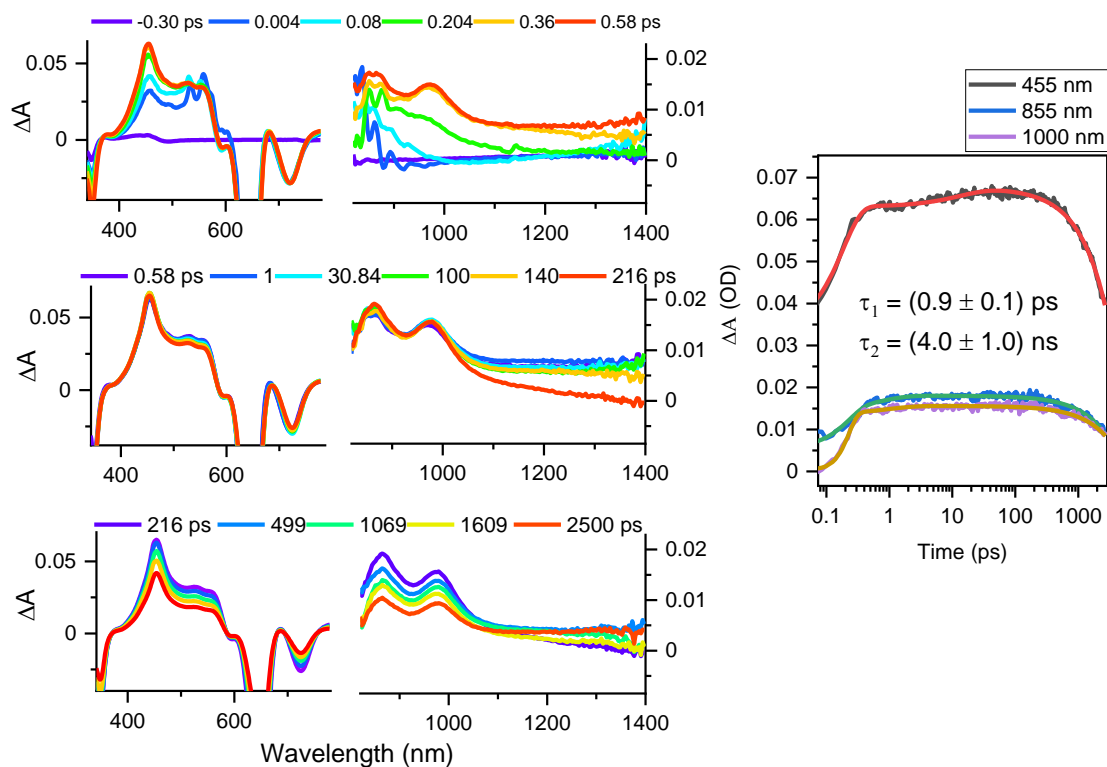
Wavelength (nm) (transient species)	τ_1 (ps) [#]	τ_2 (ps)	τ_3 (ps)	τ_4 (ps)
427 (¹ BDP* & ¹ C ₆₀ *)	0.1 (r) [#]	2.8 (d) \pm 0.3 ^b	69 (d) \pm 4 ^c	591 (d) \pm 62 ^d
490 (GSB)	0.09 (r) [#]	2.0 (d) \pm 0.1 ^b	54 (d) \pm 7 ^c	185 (d) \pm 13 ^d
550 (GSB)	0.6 (r) [#]	4 (d) \pm 2 ^b	37 (d) \pm 3 ^c	184 (d) \pm 5.3 ^d
710 (³ C ₆₀ *)	0.3 (r) [#]	11 (r) \pm 1 ^{b,c}	165 (r) \pm 16 ^d	1093 (r) \pm 91 ^e

916 ($^1C_{60}^*/C_{60}^-$)	0.7 (r) ^{a#}	12 (r) \pm 1 ^{b,c}	233 (r) \pm 12 ^d	1207 (d) \pm 73 ^e
1045 ($C_{60}^-/^1C_{60}^*$)	0.2 (r) ^{a#}	8 (r) \pm 1 ^{b,c}	340 (r) \pm 33 ^d	1000 (d) \pm 95 ^e
1278 ($^1BDP^*$)	0.1 (r) [#]	1.3 (d) \pm 0.5 ^b	43 (d) \pm 6 ^c	243 (d) \pm 28 ^d

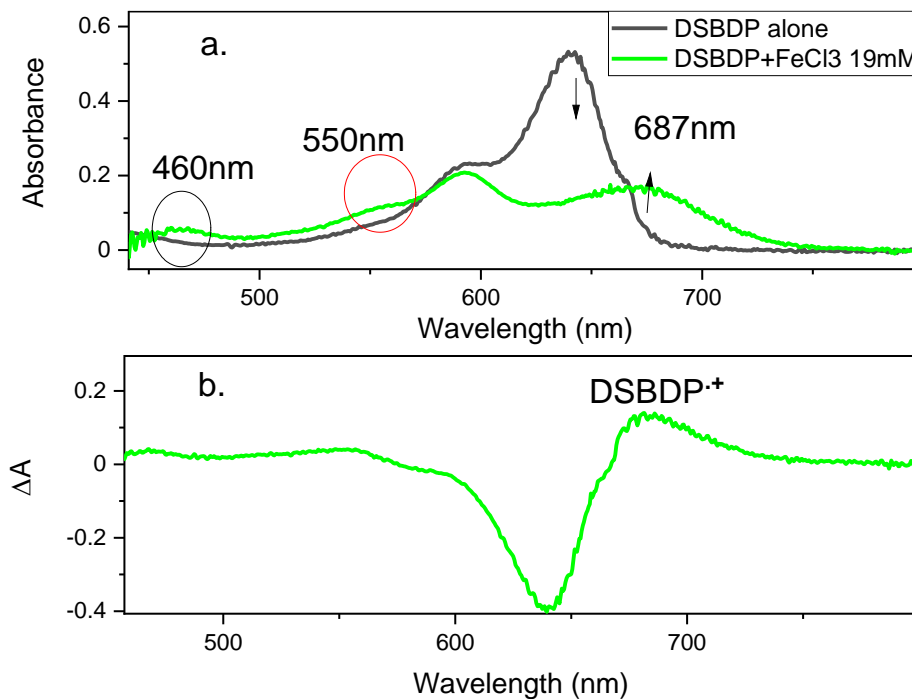
SI Table 1. Time constants obtained by fitting femtosecond transient absorption kinetics at specific wavelengths s in BDP- C_{60} dyad, $\lambda_{exc} = 525$ nm. (r): rising time, (d): decay time; ^aultrafast electron transfer from $^1BDP^*$ to C_{60} from Franck-Condon zone ^bvibrational cooling of C_{60}^- from Franck Condon region, ^cenergy transfer from $^1BDP^*$ to C_{60} , ^dsecond energy transfer from $^1BDP^*$ to C_{60} , ^eformation of triplet excited state $^3C_{60}$ by ISC. [#]Note: Time constant of <1 ps could not be retrieved with a precision due to strong signal from benzonitrile.



SI Fig. 3. Nanosecond transient absorption spectra of a. BDP- C_{60} dyad ($\lambda_{exc} = 525$ nm) and b. DSBDP- C_{60} dyad (red curve; $\lambda_{exc} = 635$ nm) and the triad (green curve; $\lambda_{exc} = 525$ nm) in deaerated benzonitrile at specified delay times.



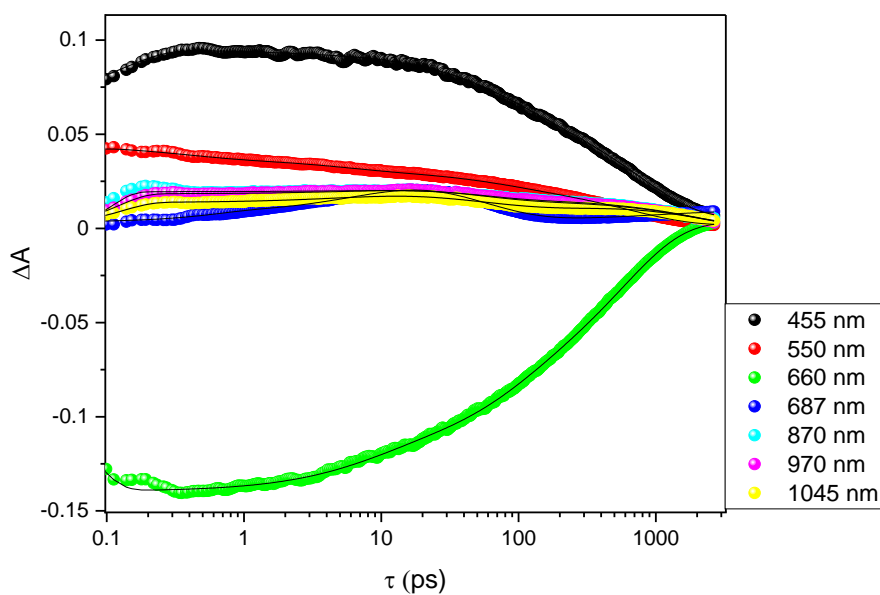
SI Fig. 4. Femtosecond transient absorption spectra of DSBDP at specified delay times: a) -0.3 to 0.58 ps; b) 0.58 to 216 ps; and c) 216 to 2500 ps and the fitted kinetic traces at chosen probe wavelengths in deaerated benzonitrile. $\lambda_{\text{exc}} = 640 \text{ nm}$.



SI Fig. 5. Chemical oxidation of DSBDP- C_{60} dyad using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. a. Absorbance of DSBDP- C_{60} dyad before and after adding the oxidant and b. the difference absorption spectrum of DSBDP^+ showing the positive band largely absorbing at 687 nm.

Wavelength (nm) (transient species)	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	τ_4 (ps)
455 $^1\text{DSBDP}^*$	4.8 ± 0.2 (d) ^a	80 ± 2 (d) ^b	736 ± 23 (d) ^c	
550 $^1\text{DSBDP}^*$	6.5 ± 0.4 (d) ^a	72 ± 7 (d) ^b	670 ± 52 (d) ^c	
660 GSB	9 ± 1 (d) ^a	95 ± 14 (d) ^b	612 ± 30 (d) ^c	
687 $\text{DSBDP} \cdot + ^3\text{C}_{60}^* / ^3\text{DSBDP}^*$	8 ± 2 (r) ^a	54 ± 4 (d) ^d	1096 ± 54 (r) ^e	
870 $^1\text{DSBDP}^*$, $^1\text{C}_{60}^*$ & $\text{C}_{60}^{\cdot-}$	14 ± 3 (r) ^a	38 ± 3 (d) ^{b, d}	2220 ± 67 (d) ^e	
970 $^1\text{DSBDP}^*$, $^1\text{C}_{60}^*$ & $\text{C}_{60}^{\cdot-}$	12 ± 3 (r) ^a	46 ± 5 (d) ^{b, d}	2700 ± 150 (d) ^e	
1045 $^1\text{C}_{60}^*$, $^3\text{C}_{60}^*$ & $\text{C}_{60}^{\cdot-}$	9 ± 2 (r) ^a ($\text{C}_{60}^{\cdot-}$ rise) ; CS	48 ± 8 (d) ^d (CR)	749 ± 53 (r) ^c	2600 ± 250 (d) ^e

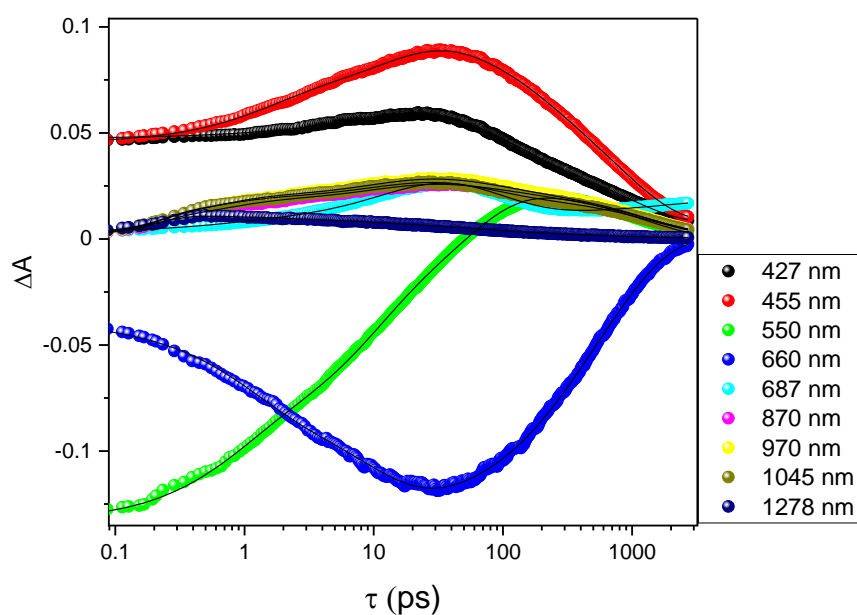
SI Table 2. Time constants obtained by fitting femtosecond transient absorption kinetics at specific probe wavelengths in the DSBDP- C_{60} dyad, $\lambda_{\text{exc}} = 640$ nm. (r): rising time, (d): decay time; ^{a,d} photoinduced charge transfer and charge recombination of DSBDP and C_{60}^* ^benergy transfer from $^1\text{DSBDP}^*$ to C_{60} , ^c second energy transfer from $^1\text{DSBDP}^*$ to C_{60} , ^e ISC process of $^1\text{C}_{60}^*$.



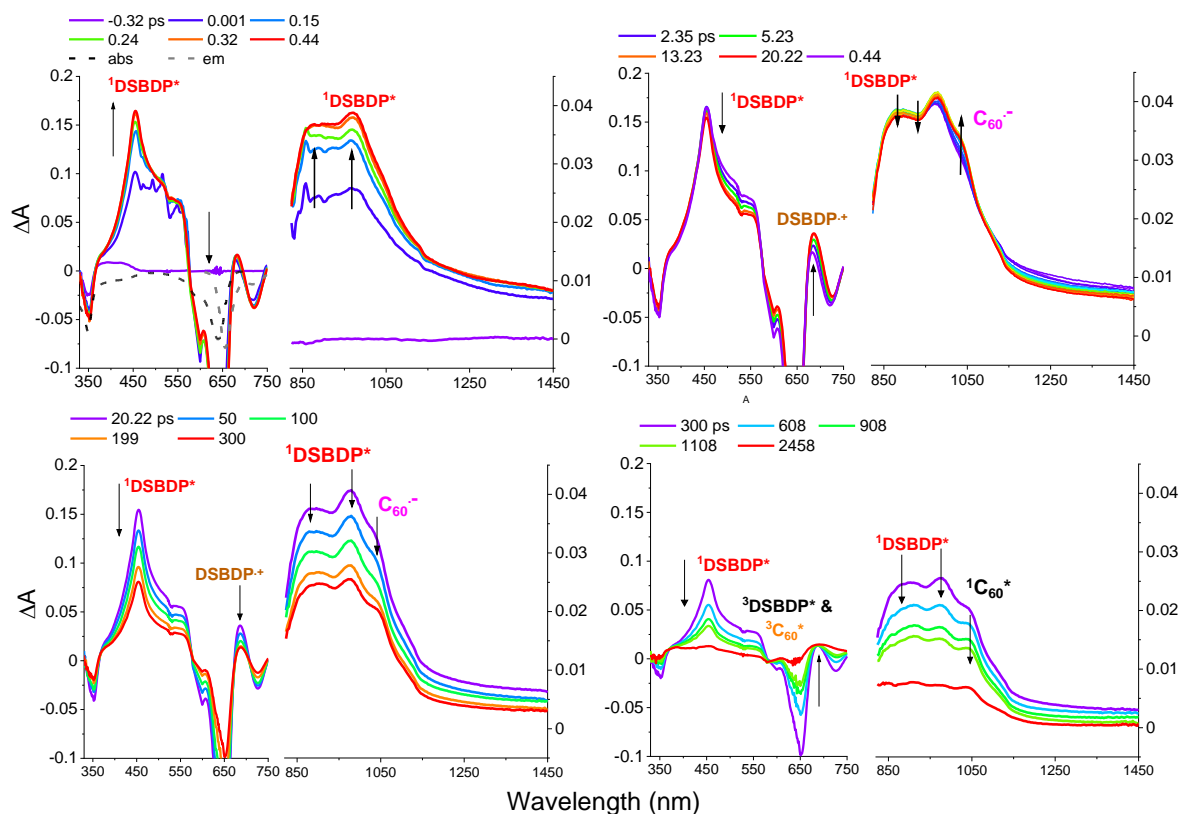
SI Fig. 6. Time traces of transient absorptions of the DSBDP- C_{60} dyad at specific probe wavelengths in deaerated benzonitrile fitted with a three exponential model except for 1045 nm which fits with a four exponential model, $\lambda_{\text{exc}} = 640$ nm

Wavelength (nm) (transient species)	τ_1 (ps) [#]	τ_2 (ps)	τ_3 (ps)	τ_4 (ps)
427 (¹ BDP*/ ¹ DSBDP*)	0.6 (r) [#]	10 ± 1 (r) ^a	93 ± 8 (d) ^d	913 ± 70 (d) ^f
455 (¹ DSBDP*)	0.3 (r) [#]	13 ± 1 (r) ^a	152 ± 10 (d) ^c	841 ± 57 (d) ^f
550 (BDP GSB/ ¹ DSBDP*)	0.8 (d) [#]	9 ± 1 (d) ^a	50 ± 2 (d) ^d	1304 ± 100 (d) ^f
660 (DSBDP GSB)	0.9 (r) [#]	9 ± 1 (r) ^a	164 ± 22 (d) ^c	725 ± 44 (d) ^f
687 (DSBDP ⁺ / ³ C ₆₀ */ ³ DSBDP*)	0.6 (r) [#]	14 ± 1 (r) ^b	88 ± 3 (d) ^e	1328 ± 124 (r) ^g
870 (¹ DSBDP*/C ₆₀ ⁻ / ¹ C ₆₀ *)	0.4 (r) [#]	11 ± 1 (r) ^a	163 ± 12 (d) ^c	1286 ± 82 (d) ^g
970 (¹ DSBDP*/C ₆₀ ⁻ / ¹ C ₆₀ *)	0.4 (r) [#]	12 ± 1 (r) ^a	146 ± 9 (d) ^c	1300 ± 82 (d) ^g
1045 (C ₆₀ ⁻ / ¹ C ₆₀ *)	0.3 (r) [#]	13 ± 1 (r) ^b	72 ± 5 (d) ^e	1491 ± 102 (d) ^g
1278 (¹ BDP*/ ¹ DSBDP*)	0.6 (r) [#]	7 ± 1 (d) ^a	60 ± 7 (d) ^d	540 ± 79 (d) ^f

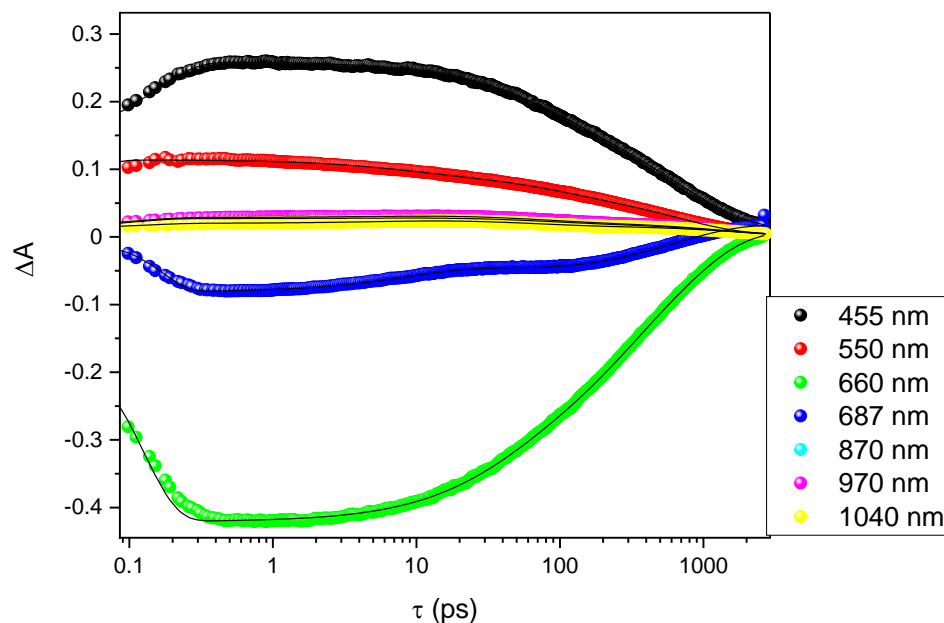
SI Table 3. Time constants obtained by fitting femtosecond transient absorption kinetics at specific probe wavelengths in the BDP-C₆₀-DSBDP triad, $\lambda_{exc} = 525$ nm. (r): rising time, (d): decay time; ^a energy transfer from ¹BDP* to DSBDP, ^{b,e} photoinduced charge transfer and charge recombination of DSBDP and C₆₀, ^c energy transfer from ¹DSBDP* to C₆₀, ^d energy transfer from ¹BDP* to C₆₀, ^f second energy transfer from ¹DSBDP* to C₆₀, ^g decay of ¹C₆₀* and formation of triplet excited states (³C₆₀* and ³DSBDP*). [#] Note: time constant of <1 ps could not be retrieved with precision due to strong signal from benzonitrile.



SI Fig. 7. Decay traces of transient absorptions of BDP-C₆₀-DSBDP dyad at specific wavelengths in deaerated benzonitrile fitted with a four-exponential model, $\lambda_{exc} = 525$ nm



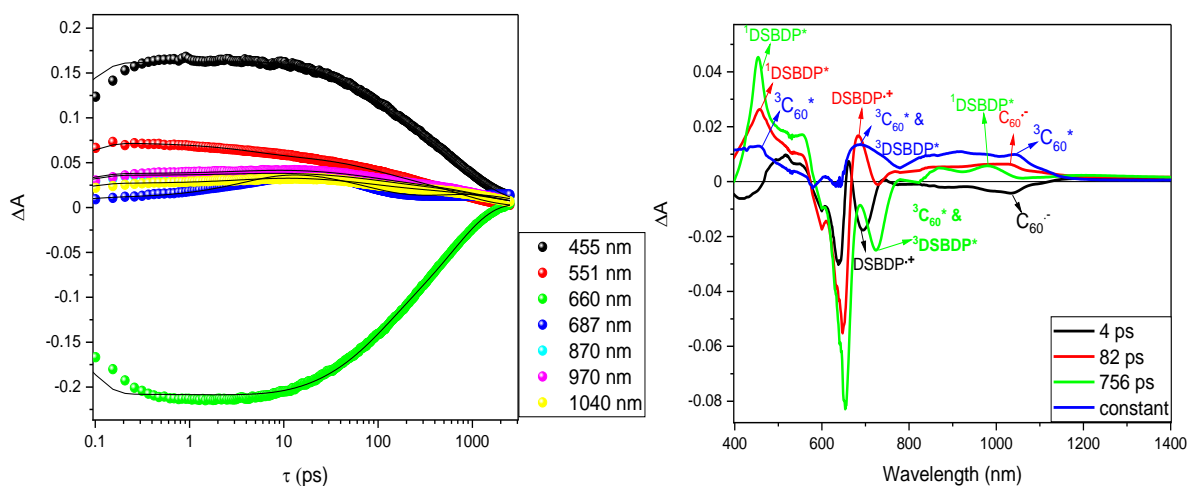
SI Fig. 8. Femtosecond transient absorption spectra of BDP- C_{60} -DSBDP at specified delay times: a. -0.32 to 0.44 ps; b. 0.44 to 20 ps; c. 20 to 300 ps and d. 300 to 2460 ps in solvent benzonitrile. $\lambda_{exc} = 580$ nm. The dashed grey and black curves in panel (a) represent the respective steady-state absorption (SS abs) and emission (SS em) spectrum of pristine DSB DP



SI Fig. 9. Decay traces of transient absorptions of BDP- C_{60} -DSBDP triad at specific wavelengths in deaerated benzonitrile fitted with a three-exponential model, $\lambda_{exc} = 580$ nm

Wavelength (nm) (transient species)	$\tau 1$ (ps)	$\tau 2$ (ps)	$\tau 3$ (ps)
455 $^1\text{DSBDP}^*$	11 ± 1 (d) ^a	84 ± 5 (d) ^b	731 ± 22 (d) ^c
551 $^1\text{DSBDP}^*$	6.8 ± 0.6 (d) ^a	75 ± 7 (d) ^b	667 ± 28 (d) ^c
660 GSB	14 ± 3 (d) ^a	87 ± 17 (d) ^b	595 ± 26 (d) ^c
687 $\text{DSBDP}^+, ^3\text{C}_{60}^*/^3\text{DSBDP}^*$	7.4 ± 0.3 (r) ^a	67 ± 3 (d) ^d	1365 ± 67 (r) ^c
870 $^1\text{DSBDP}^*, ^1\text{C}_{60}^* \& \text{C}_{60}^-$	8 ± 2 (r) ^a	72 ± 6 (d) ^{b, d}	1354 ± 87 (d) ^e
978 $^1\text{DSBDP}^*, ^1\text{C}_{60}^* \& \text{C}_{60}^-$	7.6 ± 0.8 (r) ^a	71 ± 5 (d) ^{b, d}	1392 ± 87 (d) ^e
1040 $^1\text{C}_{60}^*, ^3\text{C}_{60}^* \& \text{C}_{60}^-$	7.7 ± 0.6 (r) ^a (C_{60}^- rise) ; CS	63 ± 4 (d) ^d (CR)	2311 ± 271 (d) ^e

SI Table 4. Time constants obtained by fitting femtosecond transient absorption kinetics at specific probe wavelengths in BDP- C_{60} -DSBDP triad, $\lambda_{\text{exc}} = 580$ nm. (r): rising time, (d): decay time; ^{a,d} photoinduced charge transfer and recombination from $^1\text{DSBDP}^*$ to C_{60} , ^b photoinduced energy transfer from $^1\text{DSBDP}^*$ and C_{60} , ^c second energy transfer from $^1\text{DSBDP}^*$ to C_{60} , ^e ISC process of $^1\text{C}_{60}^*$.



SI Fig. 10. Global fit of kinetic traces using a four exponential model and b. decay associated difference spectra (DADS) obtained by global fit of femtosecond transient spectra of the BDP- C_{60} -DSBDP triad ($\lambda_{\text{exc}} = 580$ nm).

