Supplementary Information:

Charge transfer dynamics in singlet fission organic molecule and organometal perovskite bilayer structure

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The TA decay traces were fitted using a convolution from the autocorrelation trace with a four-exponential differential equation (eq S3). The obtained negative A_0 represents the existence of a rise component τ_0.

$$\frac{d(\Delta A)}{dt} = -A_0 e^{-t/\tau_0} - A_1 e^{-t/\tau_1} - A_2 e^{-t/\tau_2} - A_3 e^{-t/\tau_3} \quad \text{(S1)}$$

Table S1. 800 nm excitation TA kinetics fitting parameters.

Sample	λ_{probe} (nm)	τ_0, ps (rise)	A_0	τ_1, ps	A_1	τ_2, ps	A_2	τ_3, ps	A_3
$MAPbI_3$	750	0.47 ±0.03	-44%	27 ±9	15%	200 ±42	46%	1900 ±450	39%
TIPS-pentacene/ $MAPbI_3$	750	0.56 ±0.03	-70%	17 ±4	14%	200 ±25	45%	1500 ±230	41%

Table S2. 650 nm excitation TA kinetics fitting parameters.

Sample	λ_{probe} (nm)	τ_0, ps (rise)	A_0	τ_1, ps	A_1	τ_2, ps	A_2	τ_3, ps	A_3
$MAPbI_3$	735 nm	0.8 ±0.1	-19.1%	27 ±3	60.2%	150 ±50	31%	1200 ±520	11.6%
TIPS-pentacene	530nm	0.69 ±0.04	-34.7%	44 ±8	33.1%	220 ±79	36.4%	1400 ±390	30.6%
	900 nm	--	--	6 ±1	13%	81 ±7	44.9%	950 ±80	42.1%
TIPS-pentacene /$MAPbI_3$	735nm	1.49 ±0.04	-38.5%	37 ±2	56.4%	200 ±43	29.1%	1400 ±390	14.5%
	530nm	0.41 ±0.03	-32.1%	18 ±2	31%	150 ±18	41.7%	1400 ±220	27.4%
	900 nm	--	--	1.5 ±0.1	32.1%	31±3	32.1%	570 ±40	35.8%

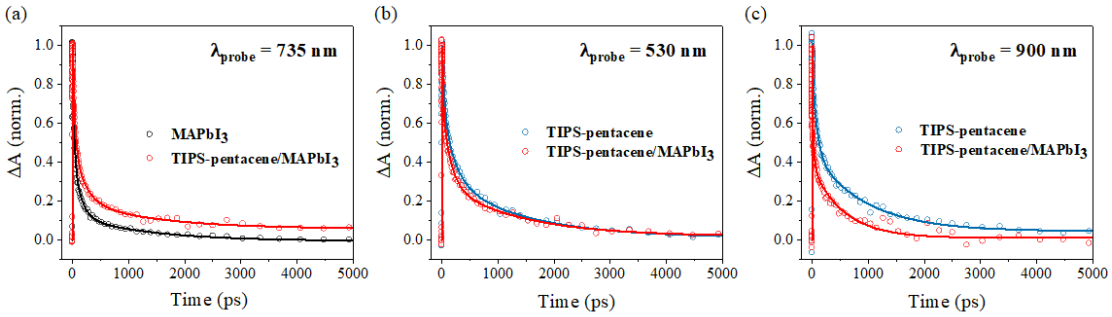
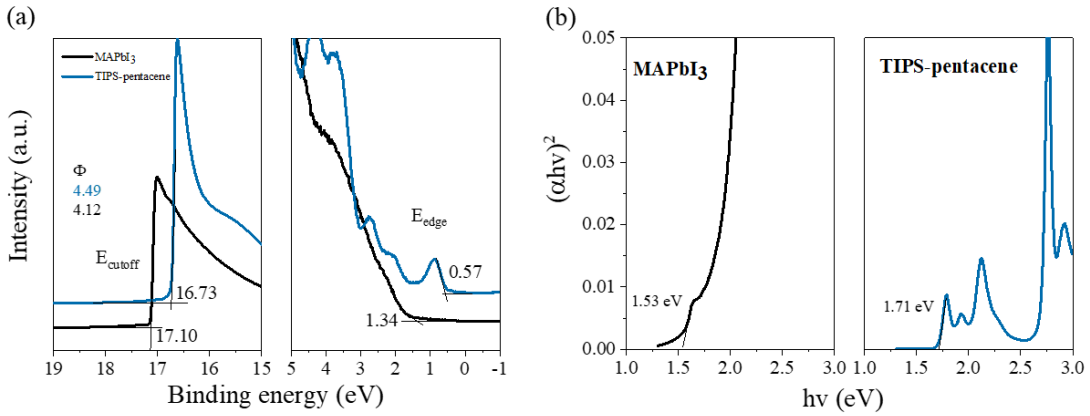


Figure S1. (a)-(c) Normalized transient kinetics of $MAPbI_3$ (black), TIPS-pentacene (blue) and TIPS-pentacene/$MAPbI_3$ bilayer (red) at different probe wavelengths in 5 ns window.



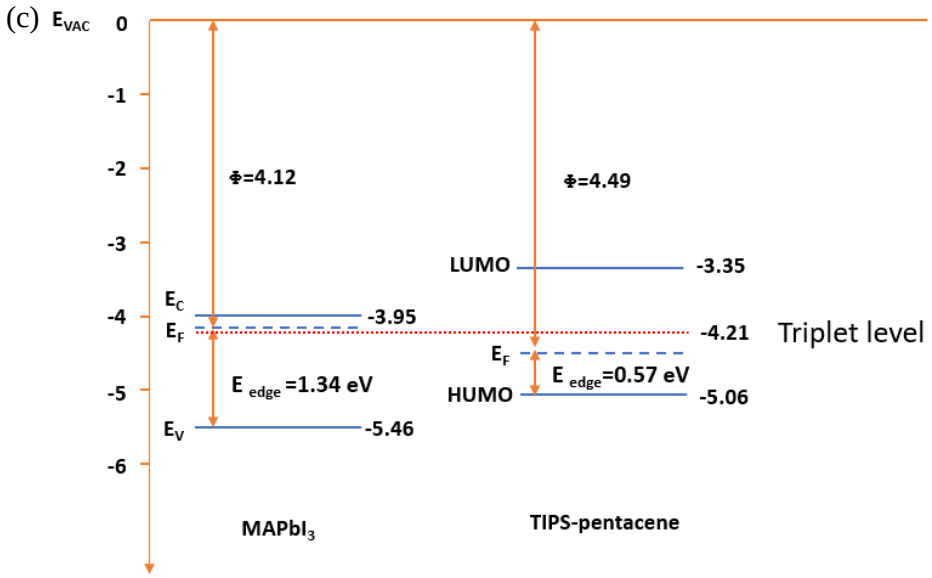


Figure S2. (a) UPS spectra of TIPS-pentacene and $MAPbI_3$ film. (b) $(\alpha h\nu)^2$-hν curves of TIPS-pentacene and $MAPbI_3$ film. (c) Energy level diagram of $MAPbI_3$ and TIPS-pentacene film.

Ultraviolet photoelectron spectroscopy (UPS) measurements were carried out to determine the energies of valence band maximum (E_{VBM}) and highest occupied molecular orbital (E_{HOMO}) of $MAPbI_3$ and TIPS-pentacene films, respectively. As shown in Figure S2(a), according to the linear extrapolating method[1], the E_{cutoff} of the $MAPbI_3$ and TIPS-pentacene films were 17.10 and 16.73 eV, the E_{edge} of $MAPbI_3$ and TIPS-pentacene films were 1.34 and 0.57 eV. The work functions (Φ) of $MAPbI_3$ and TIPS-pentacene films were determined to be 4.12 and 4.49 eV (referenced to vacuum level) correspondingly, by using eq S2.[2] The E_{VBM} of $MAPbI_3$ and E_{HOMO} of TIPS-pentacene film were calculated to be the -5.46 and -5.06 eV (vs vacuum) respectively, by using eq (S3).[2]

$$\Phi = h\nu - E_{cutoff} \quad (S2)$$

$$E_{VBM} = E_{edge} + \Phi \quad (S3)$$

As shown in Figure S2(b), band gap energies of $MAPbI_3$ and TIPS-pentacene films were determined to be 1.53 and 1.71 eV (versus vacuum) respectively from the Tacu ($(\alpha h\nu)^2$-$h\nu$) plots.[3,4] The energies of conduction band minimum (E_{CBM}) and lowest unocupied molecular orbital (E_{LUMO}) of $MAPbI_3$ and TIPS-pentacene films were determined to be -3.95 and -3.35 eV respectively, calculated by adding corresponding optical band gap to the E_{VBM} or E_{HOMO}. The obtained energy level diagram of $MAPbI_3$ and TIPS-pentacene films were presented in Figure S3.

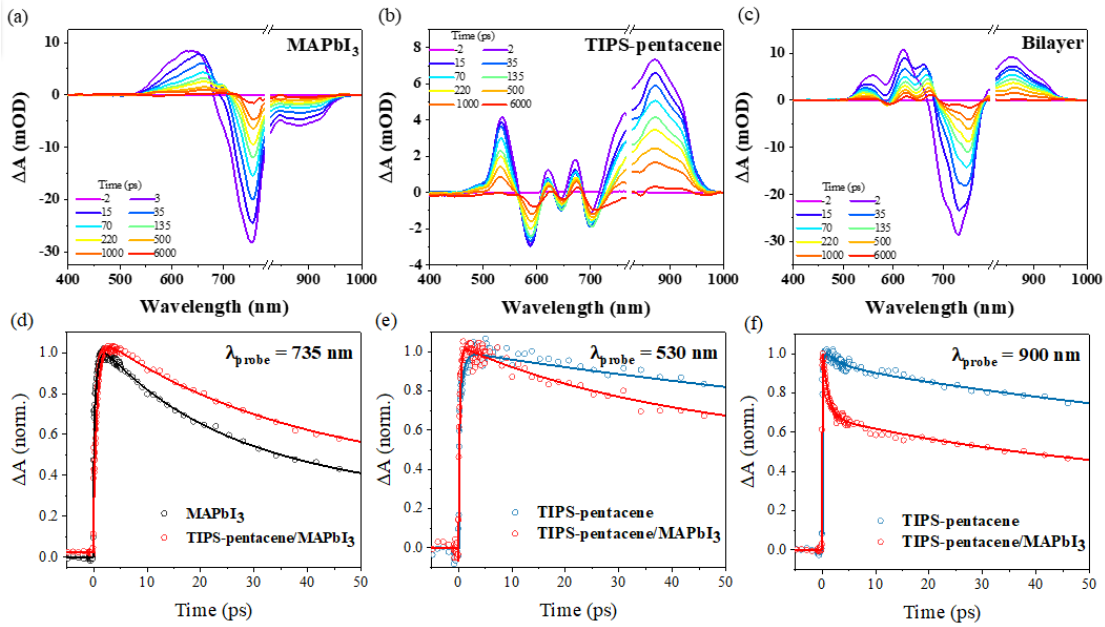


Figure S3. Broadband excitation transient absorption spectra of (a) $MAPbI_3$, (b) TIPS-pentacene and (c) TIPS-pentacene/$MAPbI_3$ bilayer films at different delay times. (d)-(f) Normalized transient kinetics of $MAPbI_3$ (black), TIPS-pentacene (blue) and TIPS-pentacene/$MAPbI_3$ bilayer (red) at different probe wavelengths.

Table S3. Broadband excitation TA kinetics fitting parameters.

Sample	λ_{probe} (nm)	τ_0, ps (rise)	A_0	τ_1, ps	A_1	τ_2, ps	A_2	τ_3, ps	A_3
$MAPbI_3$	735	0.62 ±0.02	-42.1%	19 ±1	51.2%	90 ±20	34.6%	760 ±170	14.2%
TIPS-pentacene	530	0.6 ±0.1	-33.3%	140 ±30	54.8%	1200 ±470	45.2%		
	900	--	--	43 ±9	26.7%	290 ±90	42.7%	1900 ±900	30.6%
TIPS-pentacene/ $MAPbI_3$	735	0.73 ±0.02	-88.5%	32 ±3	55.9%	200 ±60	32.3%	1700 ±1000	11.8%
	530	0.21 ±0.01	-100%	34 ±4	32.4%	480 ±50	41.2%	>10ns	26.5%
	900	--	--	1.08 ±0.04	35.5%	50 ±3	30.3%	770 ±50	34.2%

Table S4. TCSPC data fitting parameters.

Sample	τ_1, ns	A_1	τ_2, ns	A_2	$\tau_{average}$, ns
$MAPbI_3$	3.6±0.05	70.7%	94±1	29.3%	28.3
TIPS-pentacene/ $MAPbI_3$	3.51±0.05	83.1%	38±0.8	16.9%	9.3

The time-resolved PL traces were fitted using a convolution from the instrument response function (IRF) with a two-exponential differential equation (eq S1), and the average PL lifetimes were obtained from eq (S2), where τ_i represents the time component and A_i represents the amplitude.

$$\frac{dI}{dt} = -A_1 e^{-t/\tau_1} - A_2 e^{-t/\tau_2} \quad \text{(S4)}$$

$$\tau_{average} = \frac{A_1\tau_1 + A_2\tau_2}{A_1 + A_2} \quad \text{(S5)}$$

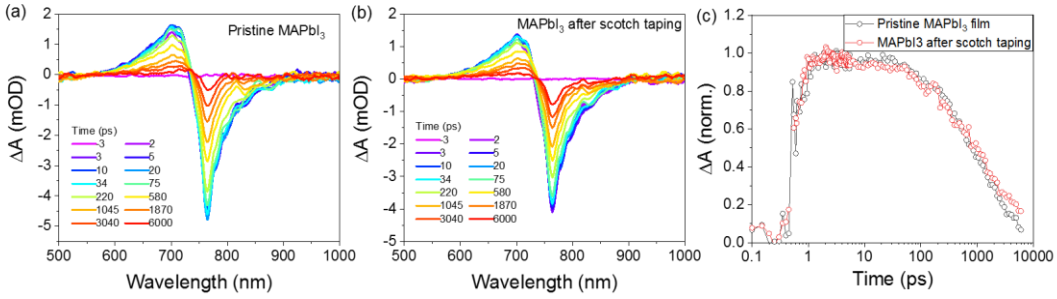


Figure S4. Transient absorption spectra for the (a) pristine (as-fabricated) $MAPbI_3$ film, (b) $MAPbI_3$ after scotch taping in vacuum, and (c) TA kinetics at 760 nm under excitation at 800 nm.

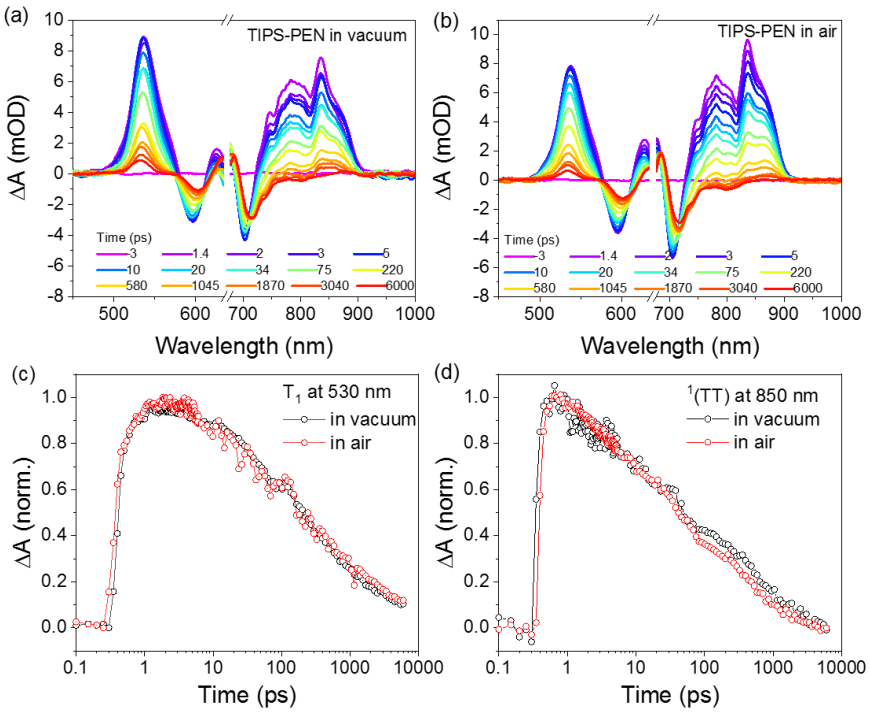


Figure S5. Transient absorption spectra for the TIPS-pentacene film (a) in vacuum and (b) in air under excitation at 650 nm. TA kinetics in vacuum and air at (c) 530 nm (T_1) and (d) 850 nm (^{1}TT).

References

(1) Gao, Y. *Mater. Sci. Eng. R Rep* **2010**, *68*, 39.

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(3) Tauc, J.; Grigorovici, R.; Vancu, A. *Phys. Status Solidi B* **1966**, *15*, 627.

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