

## Supporting Information

### Triplet Formation Inhibits Amplified Spontaneous Emission in Perylene-Based Polycyclic Aromatic Hydrocarbons

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## Experimental section

**Spectroscopic Characterisation.** The absorbance and emission properties were evaluated in a 2-methyl tetrahydrofuran (2-MeTHF) solution at different temperatures from room temperature to 80 K using a cryostat OPTISTAT from Oxford instruments. Emission was measured using a spectrofluorometer from Edinburgh Analytical Instrument (FLS920P) equipped with a pulsed xenon flash-lamp, Xe900, of 400 mW. Microsecond transient absorption spectroscopy was measured in fresh *ca.*  $10^{-3}$  M  $\text{CH}_2\text{Cl}_2$  solutions at room temperature by means of a laser flash photolysis system from Luzchem with a pulsed Nd:YAG laser, using 355 nm excitation wavelength. Probe light was provided by a Lo255 Oriel xenon lamp. The apparatus is completed with a 77200 Oriel monochromator, an Oriel photomultiplier (PMT) system and a TDS-640A Tektronix oscilloscope. The energy single pulses were of *ca.* 15 mJ. Femtosecond transient absorption spectroscopy was performed with a Helios equipment from Ultrafast Systems, equipped with an amplified femtosecond Spectra-Physics Solstice-100F laser (with a 128 fs pulse width and 1 KHz repetition rate) coupled with a Spectra-Physics TOPAS Prime F optical parametric amplifier (195-22000 nm). Samples were studied in  $\text{CH}_2\text{Cl}_2$  *ca.*  $10^{-3}$  M solutions, with an excitation wavelength of 490, 560 and 640 nm for YZ-1, YZ-2 and YZ-3, respectively.

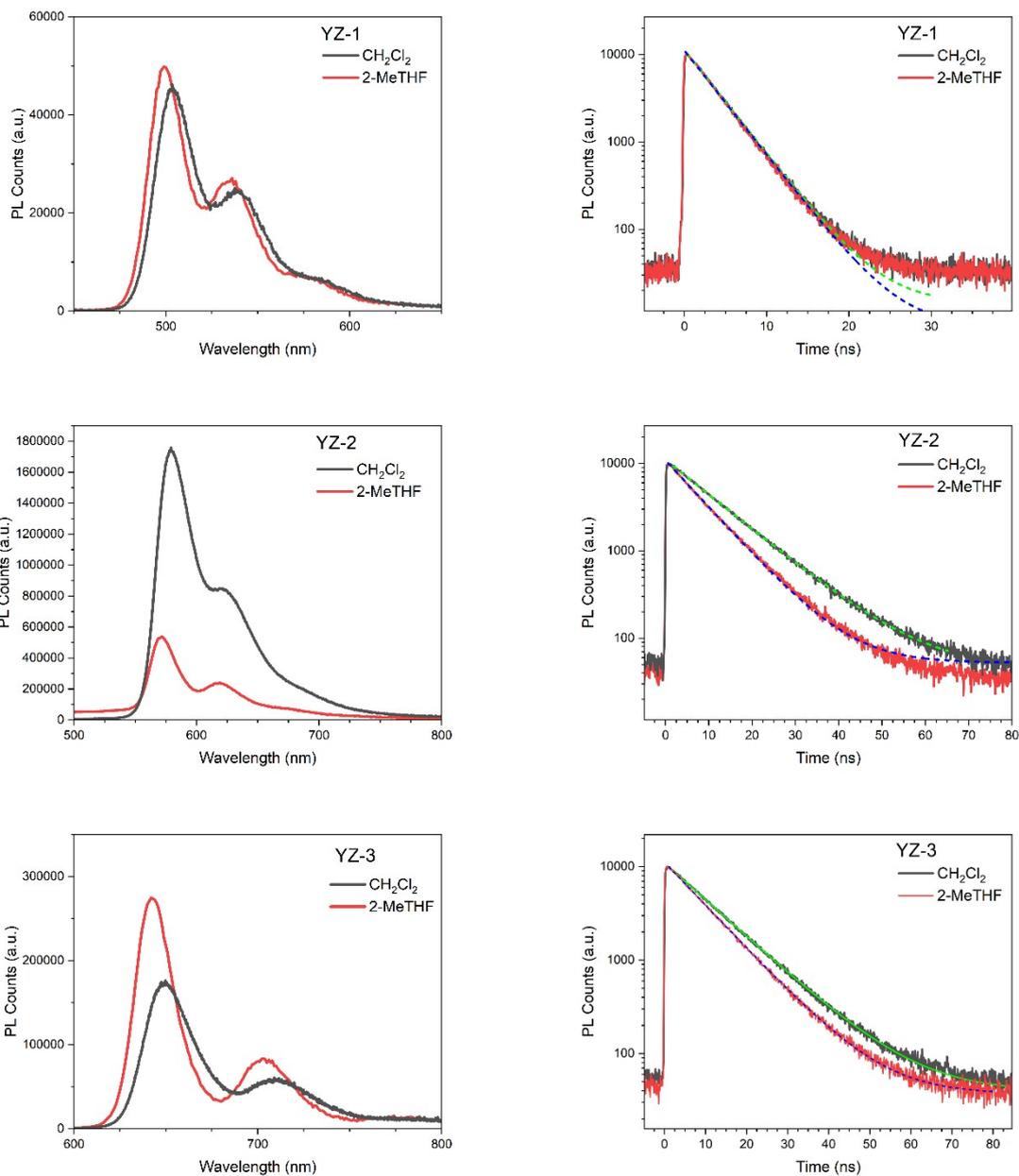
**Thin Film Fabrication.** YZ-n:PS films were prepared by spin-coating a toluene solution of the YZ-n dyes and PS as inert polymer matrix (dye content with respect to PS was in the range 0.5 - 6 wt%, see table S1). This solution was spin-coated over quartz substrates using a SMA-SPINNER 6000 PRO. The amount of solvent was adjusted to obtain proper film thickness (see values in Table S1) to ensure minimal waveguide losses and optimized ASE performance.

**Thin Film Characterisation.** Thin film absorption (and transmission) and PL characterisation was performed using a double-beam Jasco V-650 spectrophotometer and a Jasco FP-6500 spectrofluorometer, respectively. Film thickness was determined from the transmission spectrum in the transparent spectral window by a method recently reported by some of the authors (V. Bonal et al. *Polymers*, 2021, **13**, 2545).

The ASE characterisation of the films was performed under excitation with a built-in optical parametric oscillator pumped with the third harmonic of a pulsed Nd:YAG laser (10 Hz; 355 nm). The pump energy density impinging over the samples was varied using neutral density filters. The beam was shaped into a stripe (3.5 mm  $\times$  0.5 mm) with a cylindrical lens and an adjustable slit and then projected perpendicularly over the sample. The emitted ASE light was collected from the sample edge with an optical fiber coupled to a spectrophotometer (Ocean Optics, USB2000+ UV-VIS) of 1.3 nm resolution.

Molecule	Solvent	$\Phi_F$	Fluorescence Lifetime
YZ-1	CH <sub>2</sub> Cl <sub>2</sub>	0.89	3.5 ns
	2Me-THF	0.70	3.4 ns
YZ-2	CH <sub>2</sub> Cl <sub>2</sub>	0.76	10.9 ns
	2Me-THF	0.55	8.0 ns
YZ-3	CH <sub>2</sub> Cl <sub>2</sub>	0.52	11.0 ns
	2Me-THF	0.52	9.4 ns

**Table S1.** PL parameters comparison between 2-MeTHF and CH<sub>2</sub>Cl<sub>2</sub> solutions. Fluorescence quantum yield ( $\Phi_F$ ) was measured using an integrating sphere.



**Fig. S1.** Fluorescence (a, c, e) spectra and (b, d, f) decays of (a, b) YZ-1, (c, d) YZ-2 and (e, f) YZ-3 comparing the optical properties in CH<sub>2</sub>Cl<sub>2</sub> (black) and 2-MeTHF (red) solutions. The dashed lines are the monoexponential fittings for fluorescence decay lifetimes of CH<sub>2</sub>Cl<sub>2</sub> (green) and 2-MeTHF (blue) solutions

YZ derivative	YZ (wt. %) in PS <sup>a</sup>	$\lambda_{\text{ABS-max}}^b$ (nm)	$\lambda_{\text{PL-max}}^c$ (nm)	$h^d$ (nm)	$\lambda_p^e$ (nm)	$\alpha[\lambda_p]^f$ ( $\times 10^3 \text{ cm}^{-1}$ )	$t_p[\lambda_p]^g$ (ns)	$\lambda_{\text{ASE}}^h$ (nm)	$\text{FWHM}_{\text{ASE}}^i$ (nm)	$E_{\text{th-ASE}}^j$ (mJ/cm <sup>2</sup> )	$I_{\text{th-ASE}}^j$ (kW/cm <sup>2</sup> )
01	1	<u>334</u> , 366	<u>502</u> , 535	512	355	0.5	5.7				
	3	<u>334</u> , 366	<u>505</u> , 537	451	355	1.9	5.7				
	6	<u>334</u> , 366	<u>513</u> , 532	457	355	3.7	5.7				
02	1	373, <u>418</u>	<u>574</u> , 619, 673	632	418	0.5	3.7				
	3	373, <u>418</u>	<u>574</u> , 619, 673	550	418	1.6	3.7				
	6	373, <u>418</u>	<u>574</u> , 619, 673	572	418	3.1	3.7				
03	0.5	328, <u>458</u>	<u>648</u> , 706	511	458	0.6	4.0				
	0.75	328, <u>458</u>	<u>648</u> , 706	555	458	1.0	4.0				
	1	328, <u>458</u>	<u>648</u> , 706	580	458	1.3	4.0	648	11	14.5	3600
	1.5	328, <u>458</u>	<u>648</u> , 706	572	458	2.0	4.0				
	2	328, <u>458</u>	<u>648</u> , 706	522	458	2.7	4.0				
	3	328, <u>458</u>	<u>648</u> , 706	583	458	4.7	4.0				

**Table S2.** Summary of the photophysical data of the YZ-n containing PS films.

<sup>a</sup> Error ~0.1%

<sup>b</sup> Peak absorption wavelengths (maximum absorption peak is underlined)

<sup>c</sup> Peak photoluminescence wavelengths (maximum photoluminescence peak is underlined)

<sup>d</sup> Film thickness (error ~2%)

<sup>e</sup> Pump wavelength

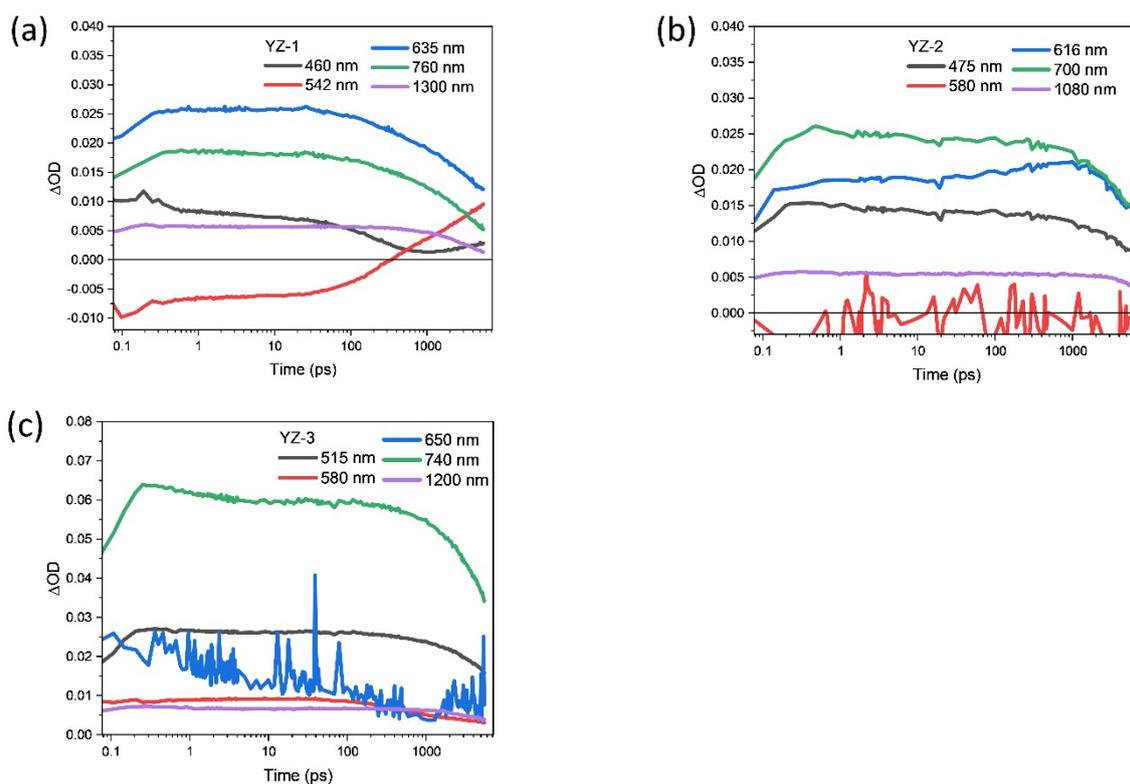
<sup>f</sup> Absorption coefficient at  $\lambda_p$  (error ~2%)

<sup>g</sup> Pump pulse width at  $\lambda_p$

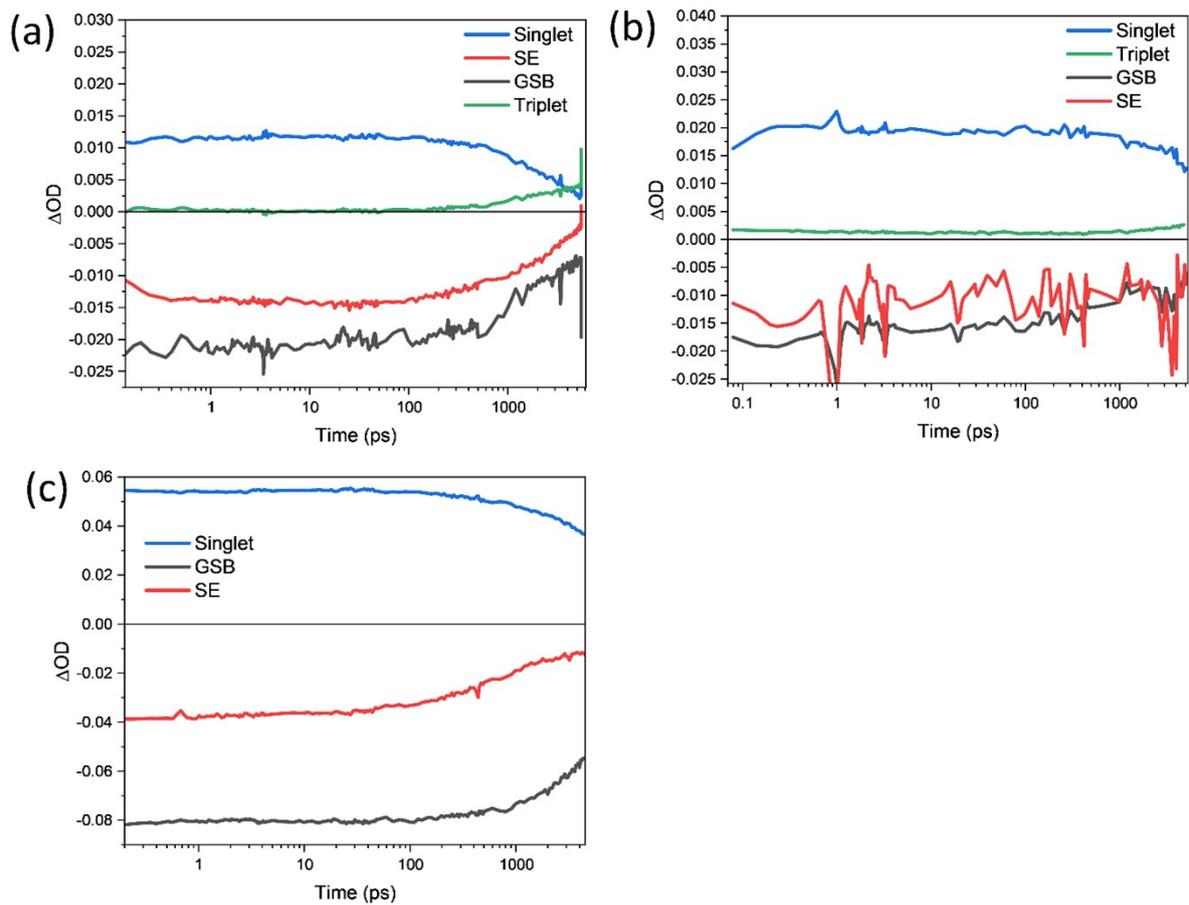
<sup>h</sup> ASE wavelength (error is  $\pm 0.5$  nm)

<sup>i</sup> ASE linewidth (error is  $\pm 1$  nm), defined as the full width at half maximum, FWHM, well above the threshold.

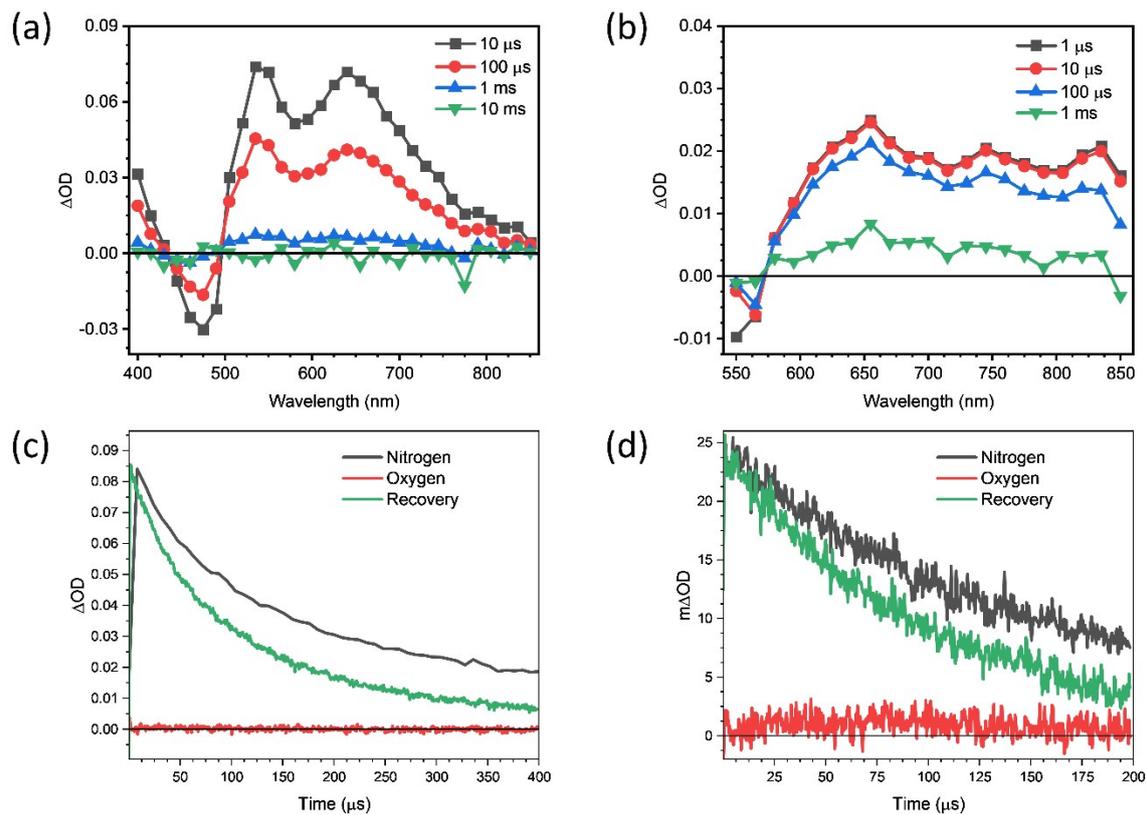
<sup>j</sup> ASE threshold (error ~20%)



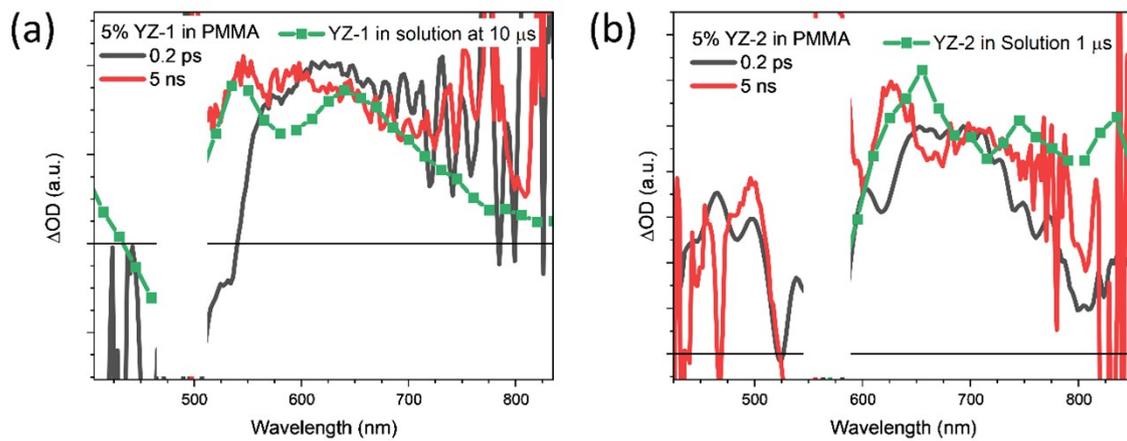
**Fig. S2.** Transient decays of fs-TAS of (a) YZ-1, (b) YZ-2 and (c) YZ-3 in a 2 Me-THF solution. Measurements were obtained exciting at 490, 560 and 640 nm for YZ-1, YZ-2 and YZ-3 with a power of 0.25 mW.



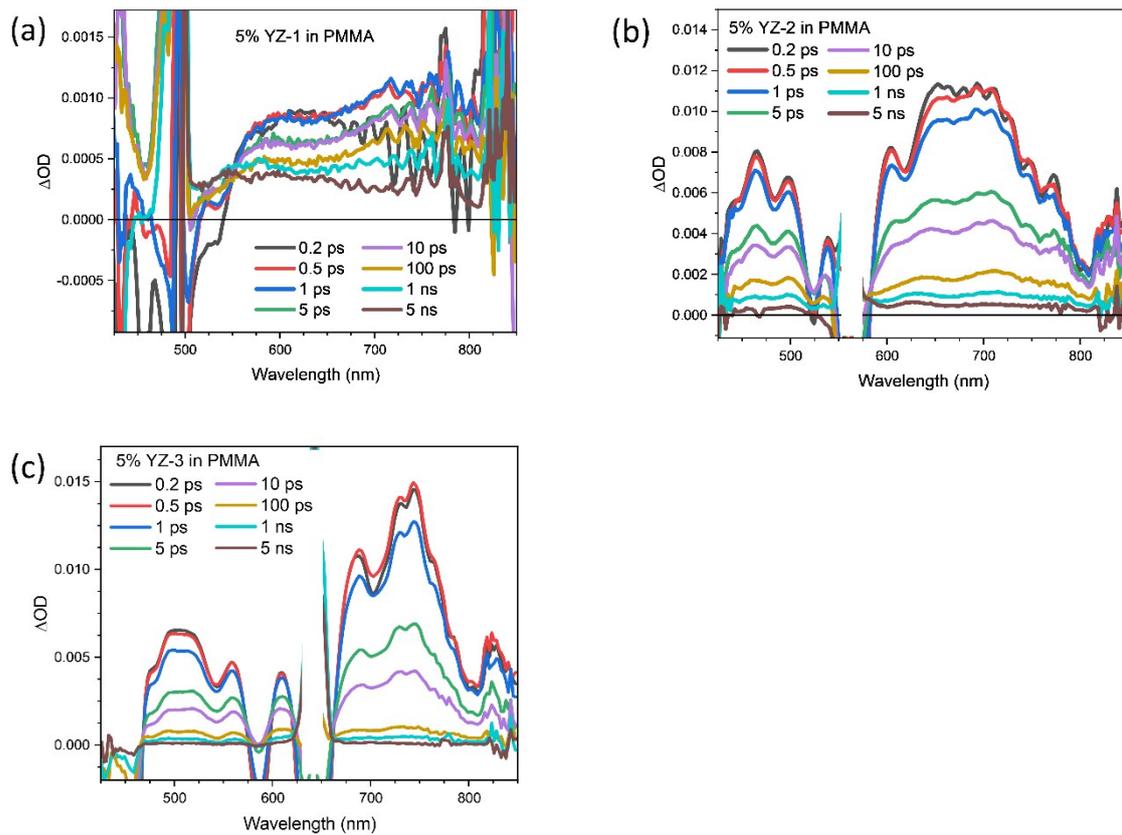
**Fig. S3.** Decays obtained by global analysis of the fs-TAS data from Fig. 4 for (a) YZ-1, (b) YZ-2 and (c) YZ-3.



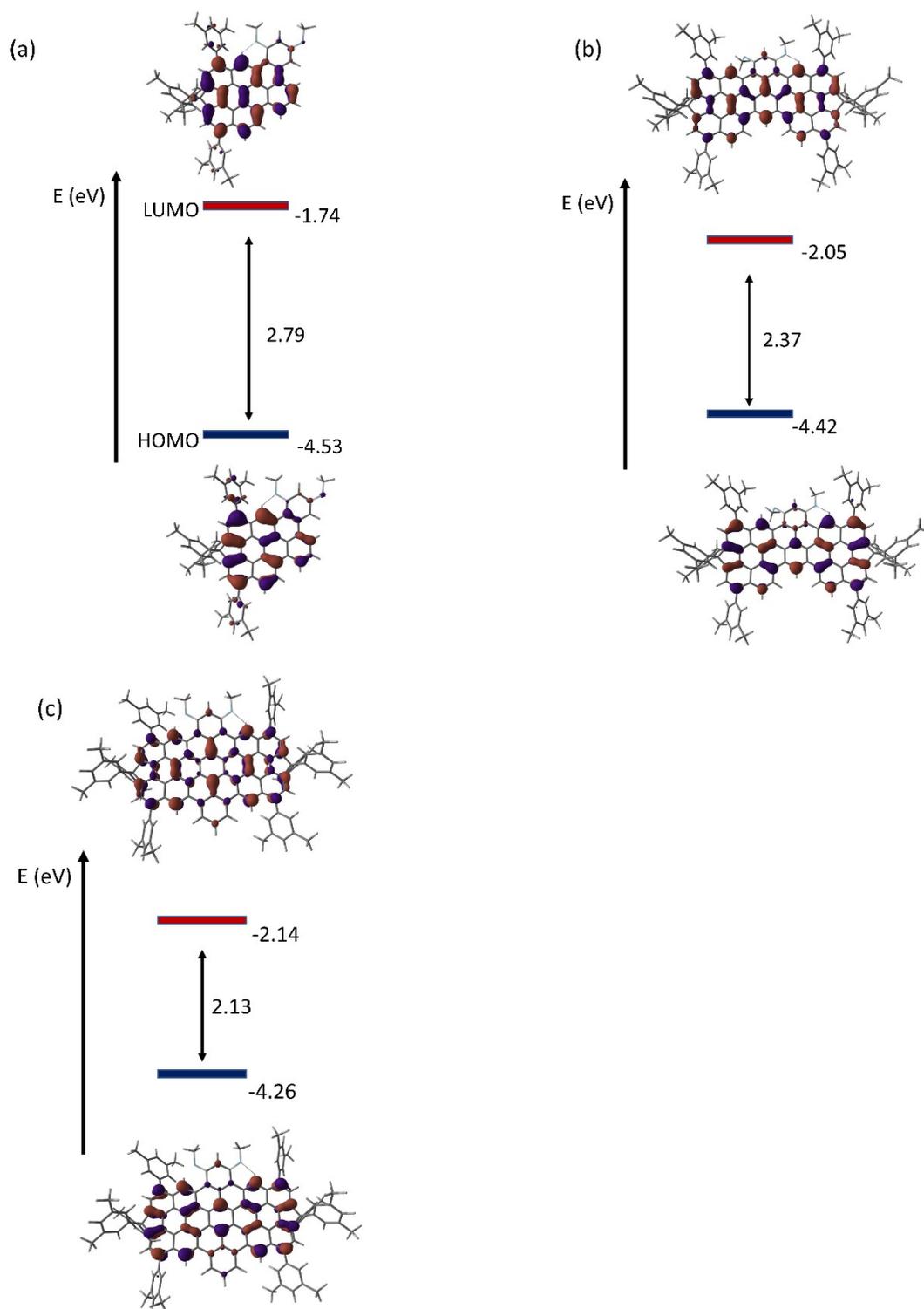
**Fig. S4.** Microsecond transient absorption spectroscopy of (a) YZ-1 and (b) YZ-2 in a 2-MeTHF solution. Transient decays at the absorption maxima of (c) YZ-1 and (d) YZ-2 and their oxygen dependence. Measurements were obtained exciting at 355 and 532 nm for YZ-1 and YZ-2 nm, respectively, at 15 mJ.



**Fig. S5.** Comparison of the spectra obtained by  $\mu$ s-TAS and ps-TAS for (a) YZ-1 and (b) YZ-2.



**Fig. S6.** Femtosecond transient absorption spectroscopy results of (a) YZ-1, (b) YZ-2 and (c) YZ-3 in a 1% solid matrix. Transient data was obtained exciting at 490, 560 and 640 nm for YZ-1, YZ-2 and YZ-3 with a power of 0.25 mW.



**Fig. S7.** Calculated HOMO and LUMO levels and the electronic distribution in vacuum of (a) YZ-1, (b) YZ-2 and (c) YZ-3. The geometry optimization was carried out at B3LYP/6-31G\*\* level of theory, whereas the vertical transitions were performed with TD-DFT calculations at B3LYP/6-31G level of theory.