

## ***Electronic Supplementary Information***

### **Intramolecular Charge Transfer and Solvation Dynamics of Push-Pull Dyes with Different $\pi$ -Conjugated Linkers**

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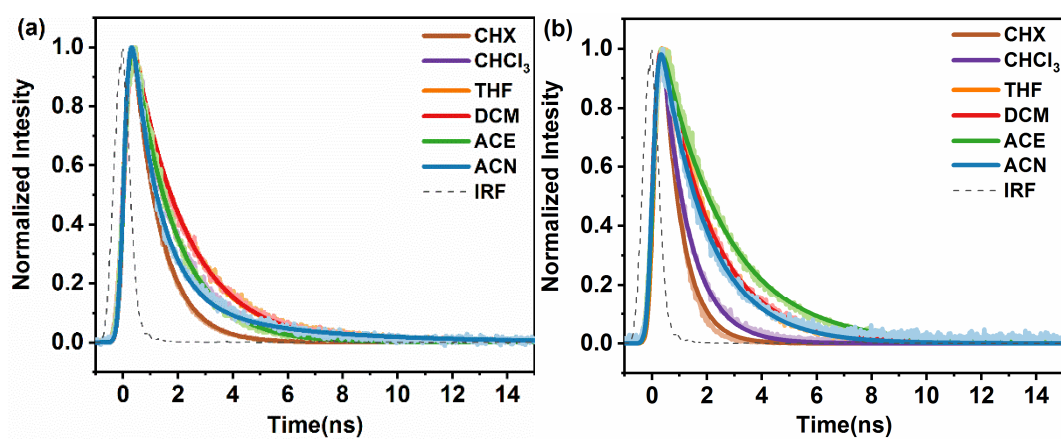
## S1. Steady-state spectral data.

**Table S1.** Solvent parameters, absorption and fluorescence maxima, and Stokes shifts of dye 1 and dye 2.

	1				2		
	$\Delta f^a$	$\lambda_{abs}$ (nm)	$\lambda_{flu}$ (nm)	Stokes Shifts ( $\text{cm}^{-1}$ / nm)	$\lambda_{abs}$ (nm)	$\lambda_{flu}$ (nm)	Stokes Shifts ( $\text{cm}^{-1}$ / nm)
CHX	0	375	413.2	2465 / 38.2	390	434.8	2642 / 44.8
$\text{CHCl}_3$	0.15	378	464.8	4940 / 86.8	391	483.4	4889 / 92.4
THF	0.21	379	493.4	6118 / 114.4	389	505.4	5921 / 116.4
DCM	0.22	379	498	6305 / 119	392	511.8	5971 / 119.8
ACE	0.29	373	524.8	7755 / 151.8	386	535	7215 / 149
ACN	0.31	370	538.2	8447 / 168.2	385	556.4	8001 / 171.4

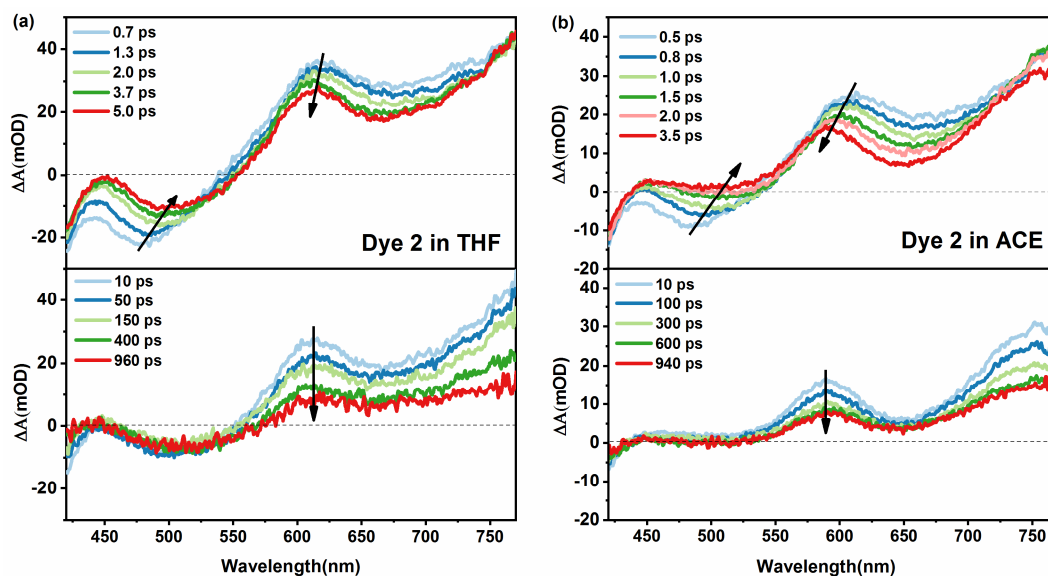
<sup>a</sup> The polarity indices are taken from Ref 1.

## S2. Fluorescence lifetime measurements.

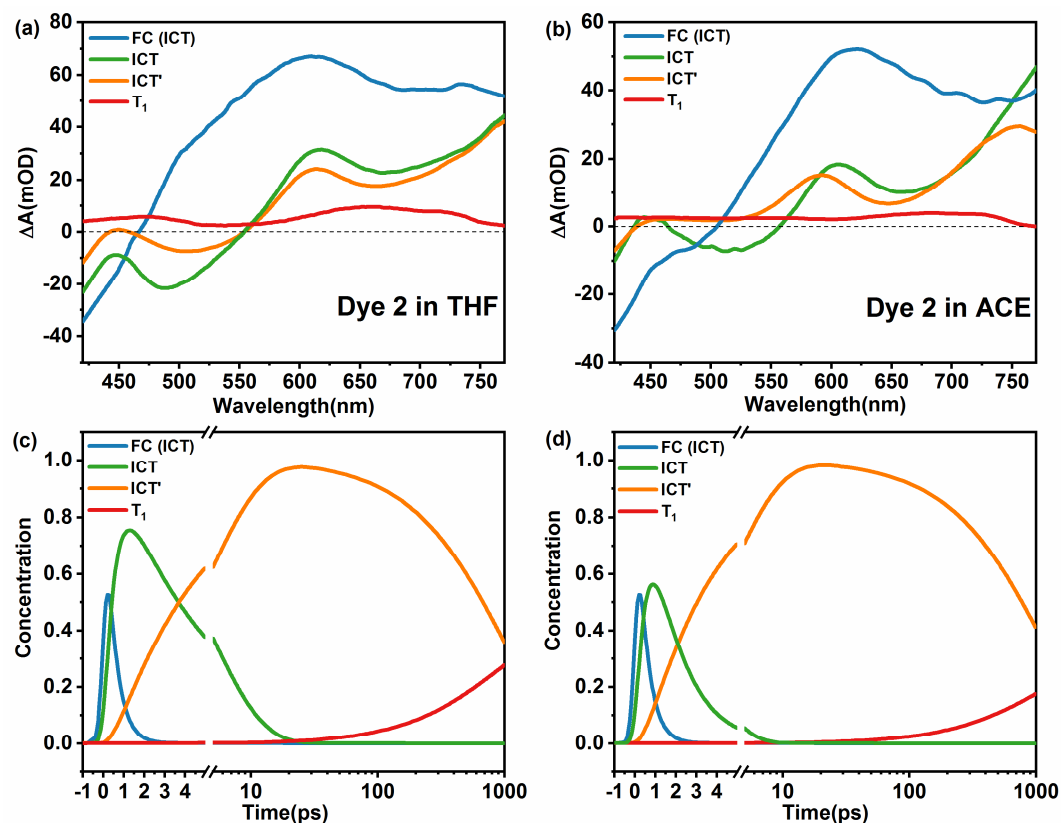


**Figure S1.** Fluorescence lifetimes of (a) dye 1 and (b) dye 2. Fitting results are also included.

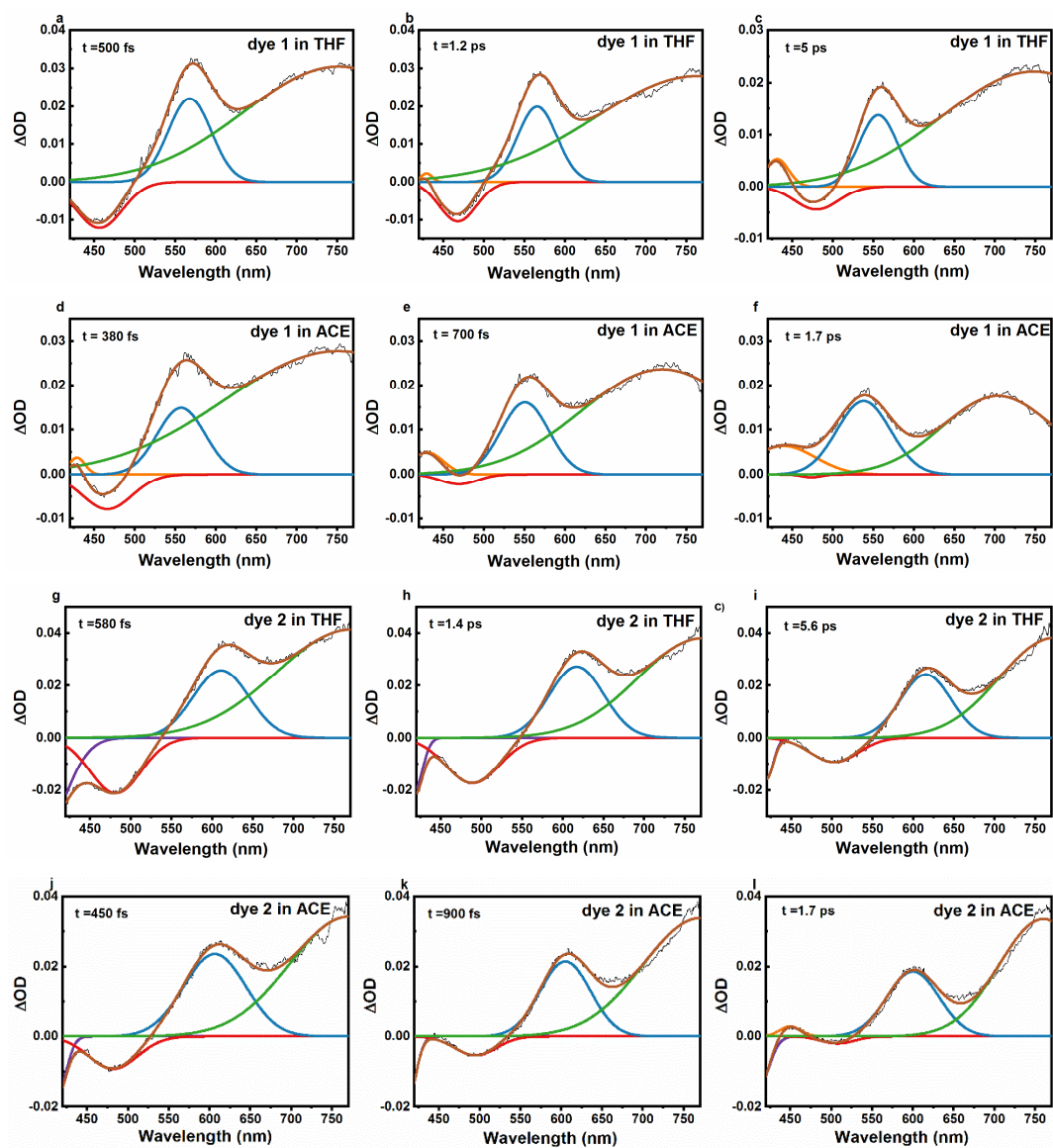
### S3. Femtosecond transient absorption experiments.



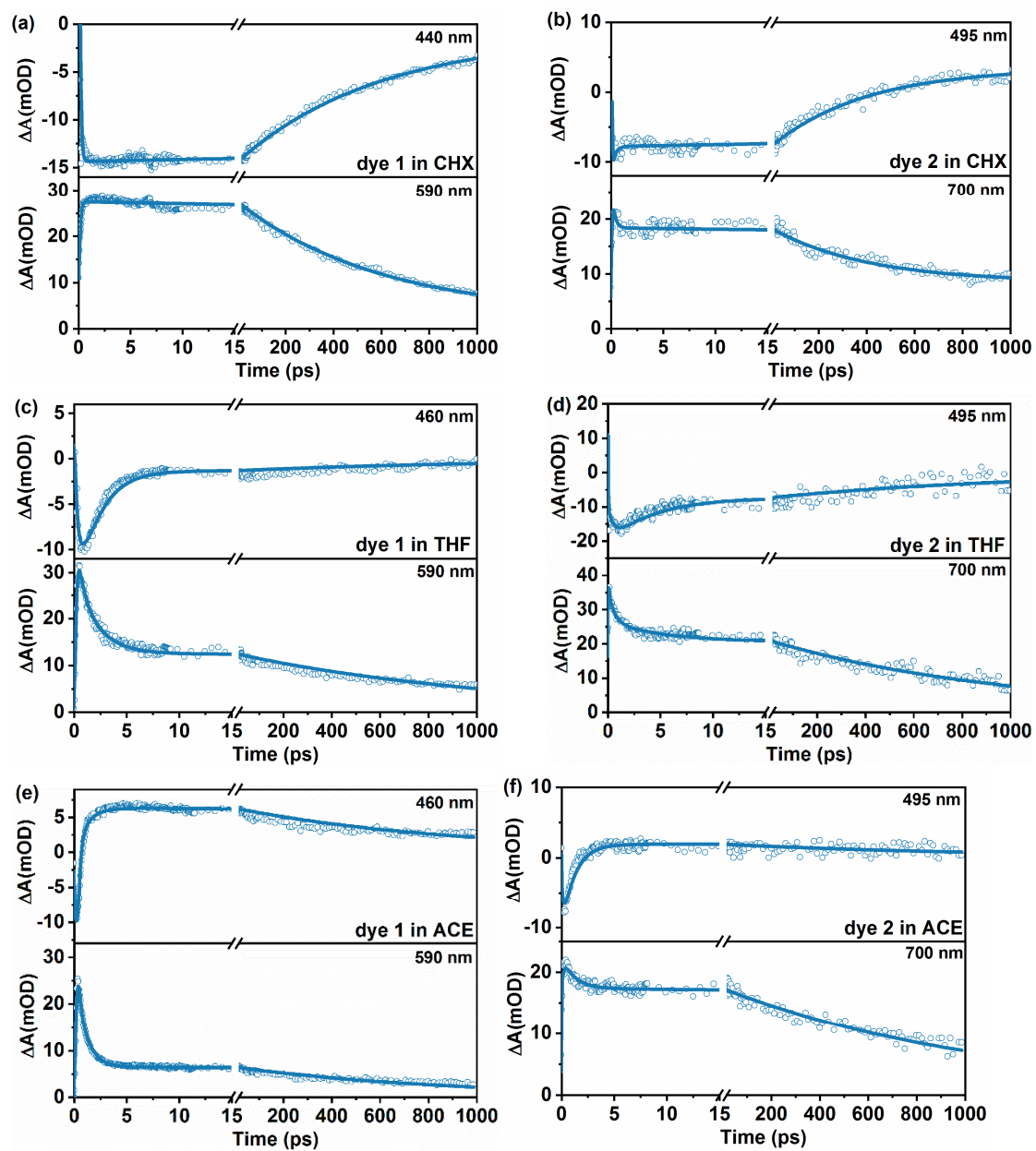
**Figure S2.** Femtosecond TA spectra for dye 2 (a) in THF and (b) in ACE, with different time delays.



**Figure S3.** SADS from target analysis and concentration evolution of transient species. On the left are two plots for dye 2 in THF, and on the right are the corresponding plots for dye 2 in ACE.



**Figure S4.** Selected femtosecond transient absorption spectra of dye 1 in THF (a, b, c), ACE (d, e, f), and dye 2 in THF (g, h, i), ACE (j, k, l) at three representative time delays.



**Figure S5.** Kinetics of femtosecond transient absorption spectra of dye 1 in: (a) CHX, (c) THF, and (e) ACE at selected wavelengths are plotted (dot) together with global fitting curves (line) of all collected time traces, and (b, d, f) are the corresponding plots for dye 2.

## S4. Nanosecond transient absorption experiments.

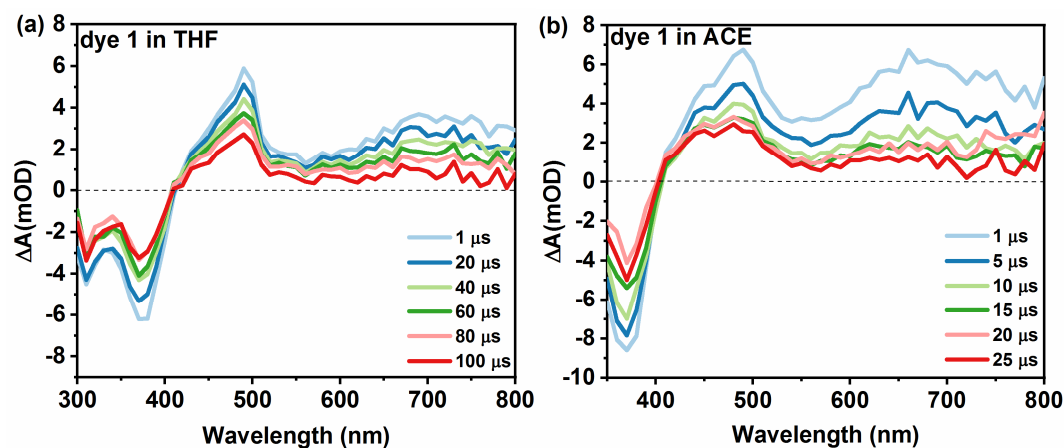


Figure S6. Nanosecond transient absorption spectra of dye 1 in THF and in ACE.

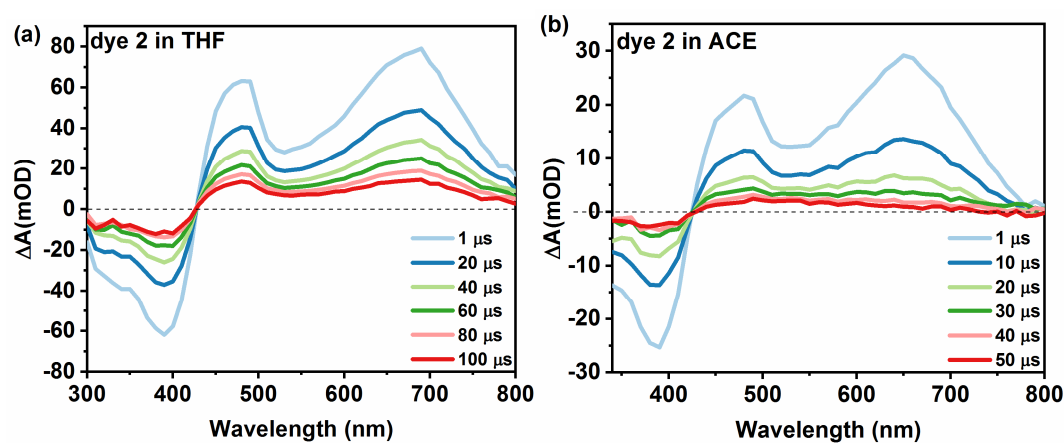


Figure S7. Nanosecond transient absorption spectra of dye 2 in THF and in ACE.

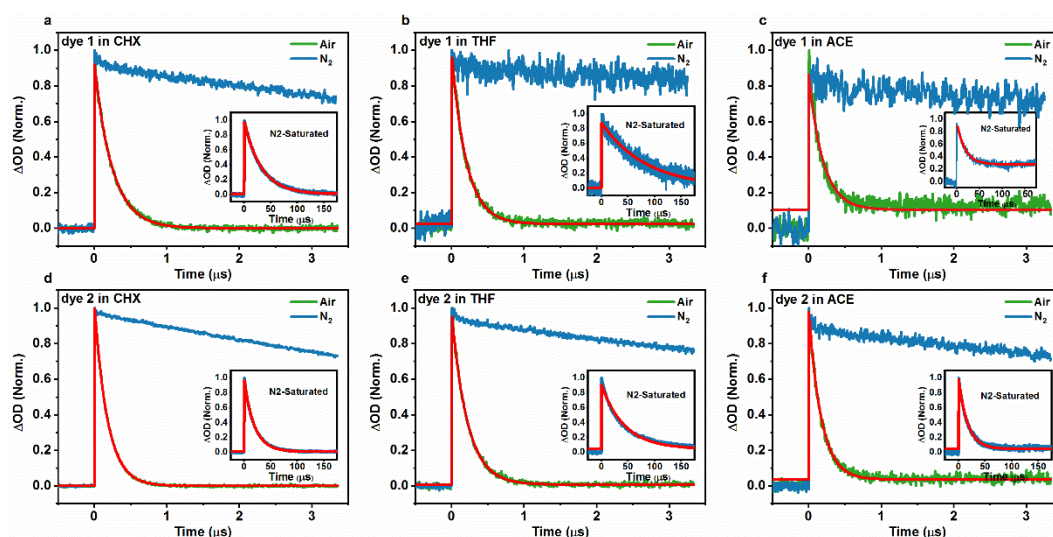


Figure S8. The kinetic traces of dye 1 and dye 2 in CHX, THF, and ACE solutions under different gas conditions (N<sub>2</sub>, air).

The triplet quantum yield is determined by time-resolved singlet molecular oxygen phosphorescence detection in the near-IR (1270 nm), phenalenone in D<sub>2</sub>O is usually used as reference. Experimentally, the singlet oxygen quantum yield can be given by the following equation:

$$\int_0^{\infty} S_t dt = S_0 \times \frac{\tau_{\Delta}}{\tau_{\Delta} - \tau_t} \int_0^{\infty} [\exp(-t/\tau_{\Delta}) - \exp(-t/\tau_t)] dt$$

$$= S_0 \times \tau_{\Delta} = \kappa k_{\Delta,R} [{}^1PS^*]_0$$

where the time-integrated signals is proportional to factor of setup ( $\kappa$ ), radiative decay of singlet oxygen ( $k_{\Delta,R}$ ), the concentration of excited singlet species ( $[{}^1PS^*]_0$ ), the quantum yield ( $\Phi_{\Delta}$ ), and lifetime ( $\tau_{\Delta}$ ) of singlet oxygen. Thus, the calculated triplet state yield is obtained by following equation:

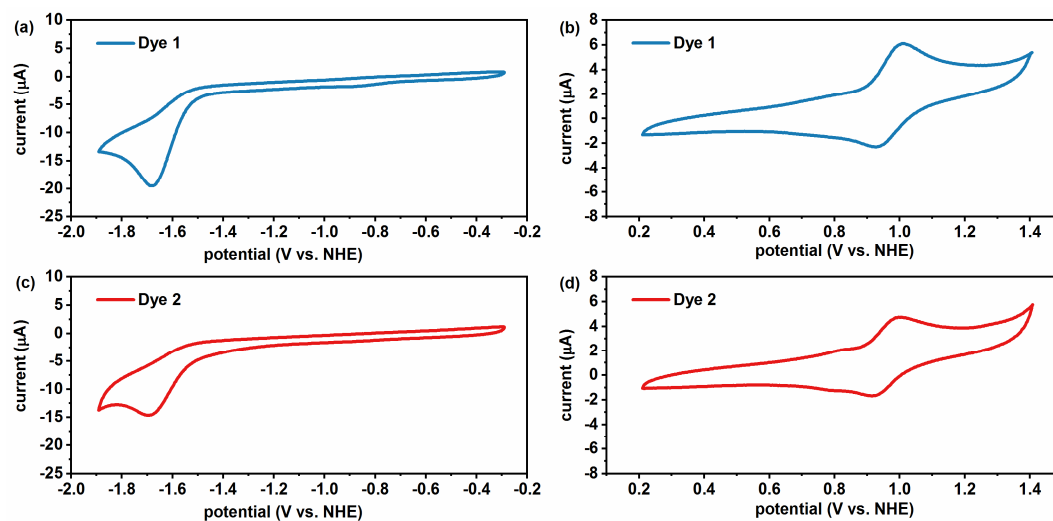
$$\Phi_{\Delta, sample} = \Phi_{\Delta, ref} \times \frac{S_{ss, sample}}{S_{ss, ref}} \times \frac{(\kappa k_{\Delta,R} I_{abs} \tau_{\Delta})_{ref}}{(\kappa k_{\Delta,R} I_{abs} \tau_{\Delta})_{sample}}$$

**Table S2.** Parameters from singlet phosphorescence detection in 1270 nm

	Solvent	Integrate S	$I_{abs}$ ( $\Delta OD$ )	$k_{\Delta,R}$	$\tau_{\Delta}$ ( $\mu s$ )	$\Phi_{\Delta}$
<b>1</b>	CHX	$9.0 \times 10^4$	0.31	0.44	35.6	0.19
	THF	$5.0 \times 10^4$	0.31	0.41	24.4	0.17
	ACE	$6.3 \times 10^4$	0.29	0.39	54.4	0.11
<b>2</b>	CHX	$17 \times 10^4$	0.28	0.44	34.2	0.42
	THF	$8.8 \times 10^4$	0.3	0.41	24.7	0.30
	ACE	$15 \times 10^4$	0.28	0.39	58.6	0.24
Phenalenone	D <sub>2</sub> O	$26 \times 10^4$	0.28	0.12	81.3	0.98



## S5. Electrochemical experiments.



**Figure S9.** Cyclic voltammograms of dye 1 and dye 2 in dichloroethane with 0.1 M tetra-n-butylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) as the supporting electrolyte recorded using a scan rate of 100 mV s<sup>-1</sup>.

**Table S3.** Electrochemistry parameters

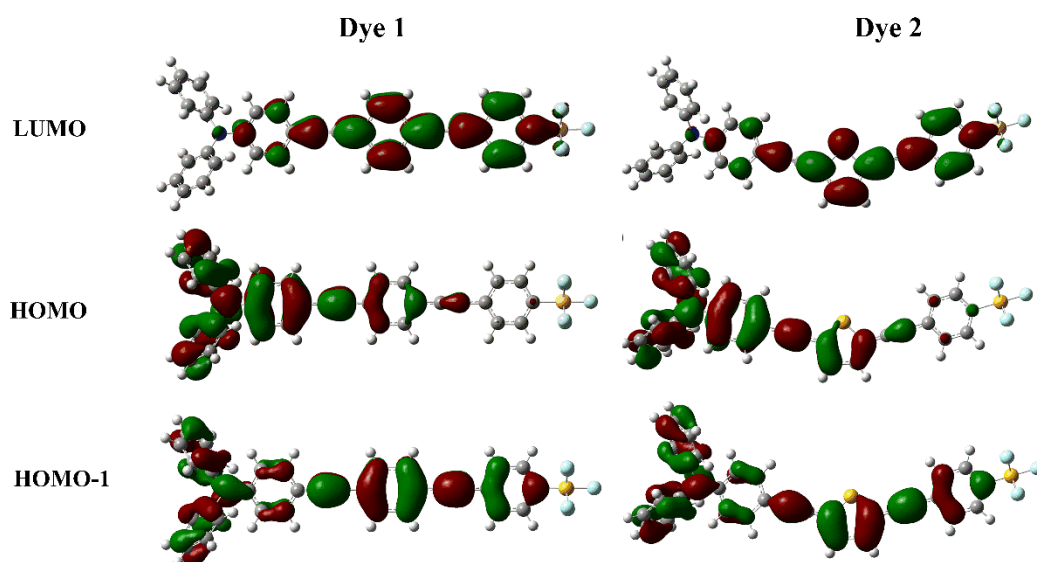
	$E_{ox}^a$ (v)	$E_{red}^a$ (v)	$\Delta G^b$ (v)		
			CHX	THF	ACN
Dye 1	0.96	1.54	-0.64	-0.48	-0.46
Dye 2	0.96	1.55	-0.47	-0.34	-0.29

<sup>a</sup> is measured by Cyclic voltammetry as shown in Figure S9. <sup>b</sup> is calculated by Rehm-Weller equation from Ref 2:  $\Delta G = E_{ox} - E_{red} - E_{00} + C$ , The  $E_{00}$  values were obtained from the intersection of the normalized absorption and emission spectra of the fluorophores. C is the Coulombic term, which was estimated to be -0.06 eV and usually has small contribution to the overall energy change.

## S6. Electronic-state transitions.

**Table S4.** Vertical excited energies of dye **1** and dye **2** in gas phase at their optimized ground state geometries at the TD-DFT/CAM-B3LYP/6-31G(d, p) level.

	Dye 1		Dye 2	
	S <sub>1</sub>	S <sub>2</sub>	S <sub>1</sub>	S <sub>2</sub>
<i>E</i> (eV)	3.56 eV (348 nm)	4.35 eV (285 nm)	3.34 eV (371 nm)	4.20 eV (295 nm)
oscillator strength	2.3298	0.1375	2.0717	0.0836
main orbital contribution	H→L 0.56 H-1→L 0.27	H-1→L 0.51	H→L 0.59 H-1→L 0.29	H-1→L 0.50



**Figure S10.** Electron density contours of molecular orbitals LUMO, HOMO, HOMO-1 at S<sub>0</sub> geometries of dye **1** and dye **2** in the gas phase.

## References

- (1) Horng, M. L.; Gardecki, J. A.; Papazyán, A.; Maroncelli, M. Subpicosecond Measurements of Polar Solvation Dynamics: Coumarin 153 Revisited. *J. Phys. Chem.* **1995**, *99*, 17311-17337.