Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Scanning the Optical Properties of 4-(1,1-difluoro-1H-1λ^4,10λ^4-benzo[4,5]thiazolo[3,2-c][1,3,2]oxazaborinin-3-yl)-N,N-diphenylaniline in Mono-disperse and Aggregation System

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Note S1. Calculation Details of nonlinear absorption coefficient (β) and the two-photon absorption cross section (σ).

The influence of the solvent nonlinearity could be excluded. The two-photon absorption (TPA) coefficient β of TOND in three solvents can be obtained by fitting the experimental results with equation:[1-2]

$$\mathrm{T(z,S=1)} = \sum_{m=0}^{\infty} \frac{[-q_0(z,0)]^m}{(m+1)^{3/2}}$$

where$q_0(z) = \beta I_0/(1 + {z^2}/{z_0^2})$; $z_0 = k\omega_0^2/2$ is the Rayleigh length, $\mathrm{k} = 2\pi/\lambda$ is the wave vector, ω_0 is beam waist radius of Gaussian pulse, and I_0 is the pulse irradiance. The TPA coefficient β is related to the TPA cross section σ by using[3]

$$\sigma = \frac{\beta h \upsilon 10^3}{Nc}$$

where *N* is Avogadro's number, *c* is the concentration, h is Planck's constant, and ν is the laser frequency. In this experiment, the concentration of TOND is 5×10^{-4}M. σ is expressed in Göppert-Mayer units (GM), with 1 GM = 1×10^{-50} cm^4 s $molecule^{-1}$ $photon^{-1}$.

Note S2. Calculation Details of Temperature-Dependent PL Quantum Yield.

The PL quantum yield can be defined as the ratio of the number of emitted photons to the number of absorbed photons by a luminescent material:[4]

$$QY = \frac{N_{em}}{N_{abs}}$$

The most straightforward method for the determination of QY values presents the absolute measurement of N_{abs} and N_{em} with an integrating sphere setup. The QY of BTTM film at room temperature can be described by:[5]

$$QY = \frac{\int \frac{\lambda}{hc}\left[I_{em}^{sample}(\lambda) - I_{em}(\lambda)\right]d\lambda}{\int \frac{\lambda}{hc}\left[I_{ex}(\lambda) - I_{ex}^{sample}(\lambda)\right]d\lambda}$$

and λ is the wavelength, h is Planck's constant, c is the velocity of light, I_{ex}^{sample} and I_{ex} are the integrated intensities of the excitation light with and without a sample respectively, I_{em}^{sample} and I_{em} are the integrated intensities of PL intensities with and without a sample, respectively.

After obtaining the temperature-dependent absorption and PL spectra of the sample, the quantum yield at different temperatures QY_2 can be obtained from QY_1. The general equation used in the determination of relative quantum yields is given in[6]

$$\frac{QY_2}{QY_1} = \frac{I_{em2}}{I_{em1}} \times \frac{A_1}{A_2} \times \frac{\lambda_{ex1}}{\lambda_{ex2}} \times \frac{\eta_2}{\eta_1}$$

Among them, I_{em} is the integrated area under the corrected emission spectrum; A is absorbance at the excitation wavelength; λ_{ex} is the excitation wavelength; η is the collection efficiency of the system. In our experiments, the system and test conditions are unchanged, which means that $\frac{\eta_2}{\eta_1} \approx 1$, and the excitation wavelength remains the same. The final calculated PL quantum yields at different temperatures are shown in the Table S2.

Note S3. Derivation of Radiative Lifetimes from Measured PL Dynamics[7]

The PL dynamics can be accurately fitted to the sum of three exponentials, by combining the fitting results with the PL QYs, meanwhile the radiative time constants are calculated. This procedure is illustrated in Fig. 6, for which the measured PL dynamics are decomposed into the two individual exponential components $u(t_i)$ (i = 1 or 2).

The PL decay can be described by:

$$I_{PL}(t) = \sum_{i=1}^{n} k_i \exp(-t/\tau_X^i),$$

where τ_X^i is the effective lifetime given by:

$$\tau_X^i = \tau_{r,X}\tau_{nr,X}^i/(\tau_{r,X} + \tau_{nr,X}^i),$$

and k_i is the relative fraction of the TOND in the i-th sub-ensemble; the k_i coefficients are normalized such as $\sum_{i=1}^{n} k_i = 1$.

The PL quantum yield (QY) of the individual sub-ensemble is given by:

$$q_i = \tau_X^i / \tau_{r,X},$$

And the total PL QY of the entire QD sample(Q) can be expressed as:

$$Q = \sum_{i=1}^{n} k_i q_i = \tau_{r,X}^{-1} \sum_{i=1}^{n} k_i \tau_X^i,$$

This leads to the following expression for the radiative lifetime:

$$\tau_{r,X} = Q^{-1} \sum_{i=1}^{n} k_i \tau_X^i = Q^{-1} \langle \tau_X \rangle,$$

Where $\langle \tau_X \rangle$,is the average lifetime in the TOND ensemble expressed as:

$$\langle \tau_X \rangle = \sum_{i=1}^{n} k_i \tau_X^i$$

Table S1. Absorption peak, PL maximum peak and PL quantum yield of TOND in three solvents.

Solvent	Absorption peak /nm	PL maximum peak /nm	PL QY
TOL	437, 449	505	0.5
THF	437	535	0.44
DMF	445	582	0.07

Table S2: Fitting parameters and calculation results of PL dynamics of TOND film.

T/K	k_1	τ_1/ns	k_2	τ_2/ns	Average lifetime/ns	Radiative lifetime/ns	PL QY
295	0.80	1.99	0.20	7.91	3.17	35.27	0.09
255	0.78	2.11	0.22	7.54	3.31	25.38	0.13
215	0.75	2.48	0.25	7.53	3.74	15.13	0.23
195	0.744	2.62	0.266	7.49	3.94	12.71	0.31
175	0.74	3.03	0.26	9.01	4.58	11.34	0.41
155	0.73	3.36	0.27	9.81	5.10	9.81	0.52
135	0.72	3.87	0.28	11.77	6.08	9.53	0.64
115	0.7	4.08	0.3	11.96	6.44	8.51	0.76
95	0.64	4.22	0.36	12.25	7.11	8.46	0.84
77	0.62	4.54	0.38	13.48	7.94	8.32	0.92

Fig. S1 Two-photon fluorescence (TPF) spectra of TOND in THF (A) and DMF (B).

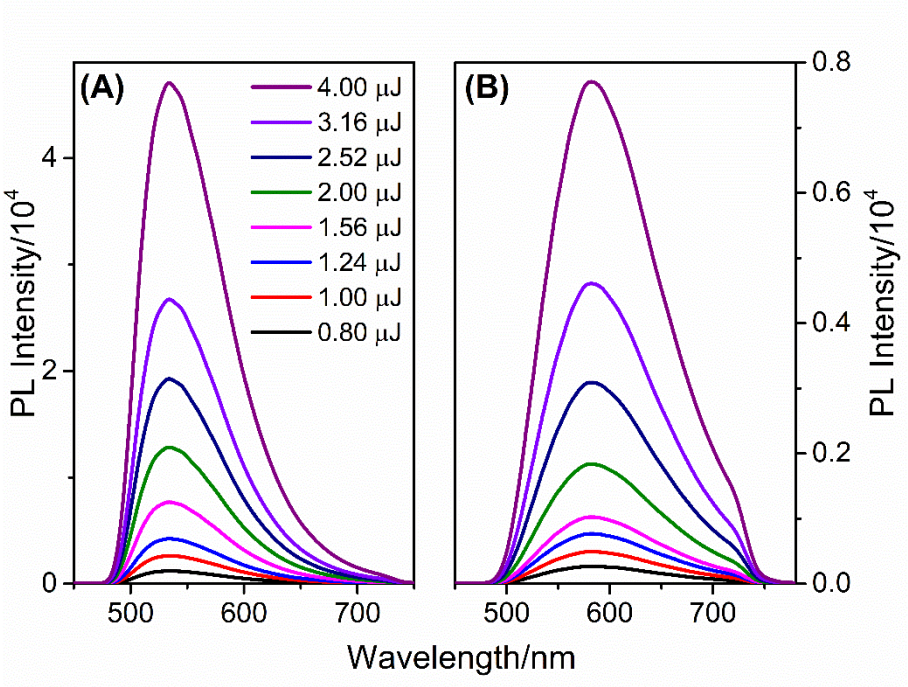


Fig. S2 Spectra of pump, probe and dump pulses are plotted with same wavelength scale below the absorption and PL spectra.

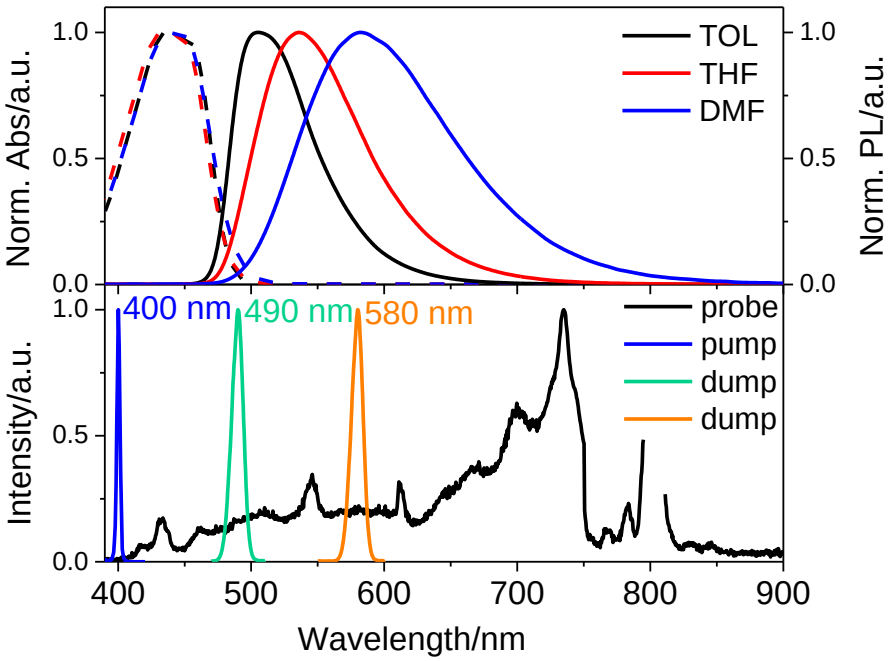


Fig. S3 Femtosecond time-resolved pump-probe spectra of TOND in TOL upon excitation at 400 nm. Inset shows the normalized absorption and PL spectra.

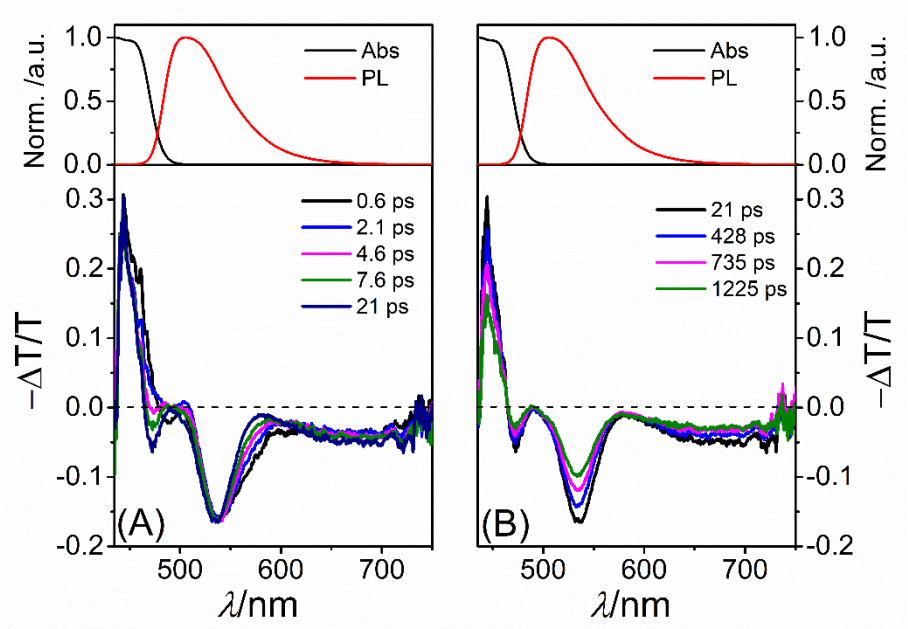


Fig. S4 Femtosecond time-resolved pump-probe spectra of TOND in THF. Inset shows the normalized absorption and PL spectra.

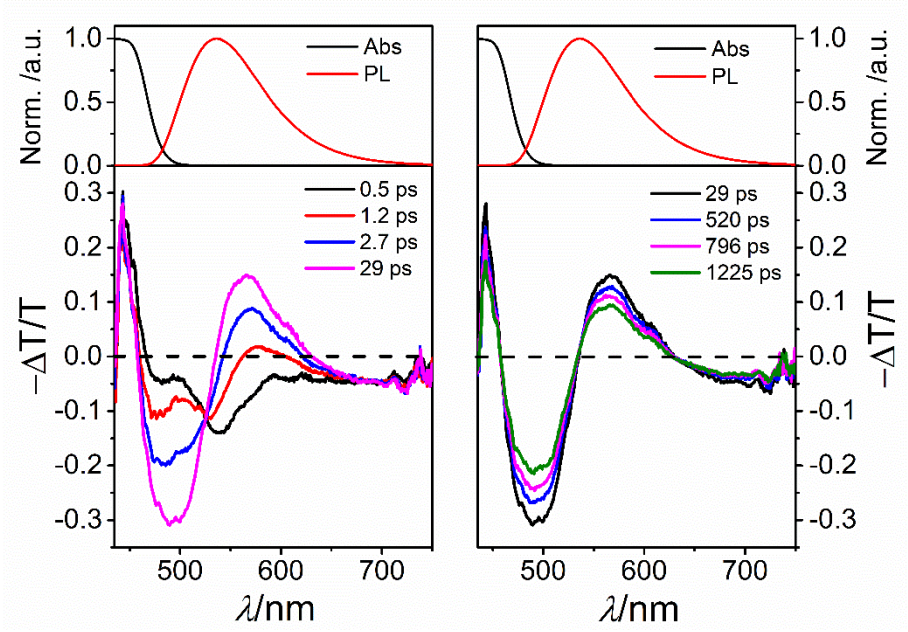


Fig. S5 Femtosecond time-resolved pump-probe spectra of TOND in DMF. Inset shows the normalized absorption and PL spectra.

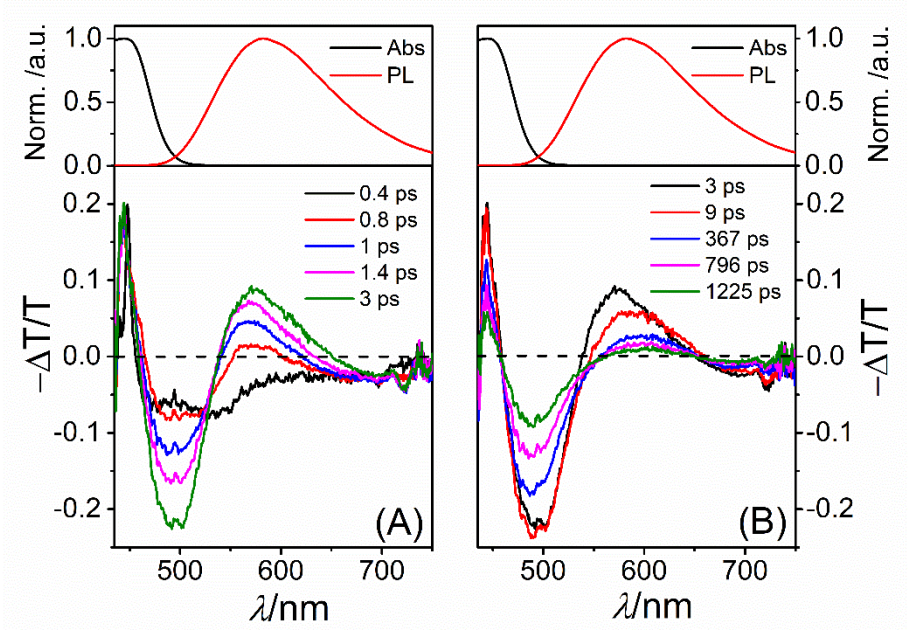


Fig. S6 Kinetics at selected wavelengths of TOND in (A) TOL, (B) THF, (C) DMF from femtosecond pump-probe spectra for showing the quality of global fitting.

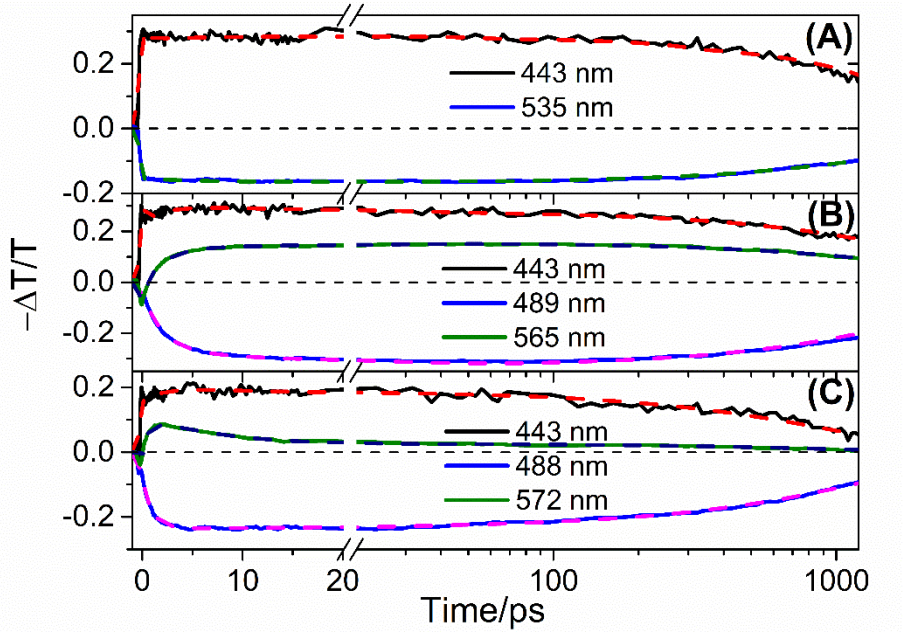


Fig. S7 Associated population evolution obtained from global analysis for TOND in TOL.

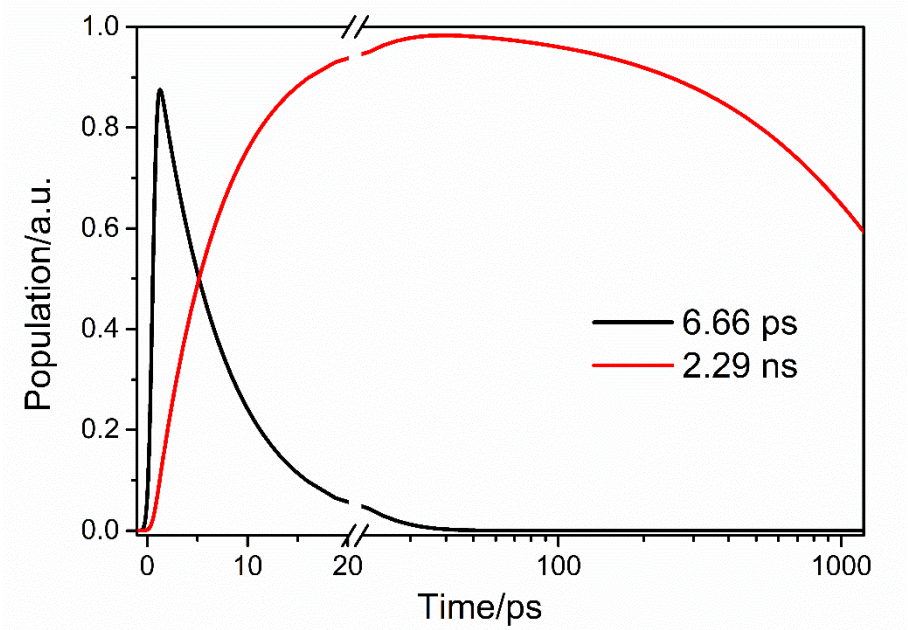


Fig. S8 Associated population evolution obtained from global analysis for TOND in THF.

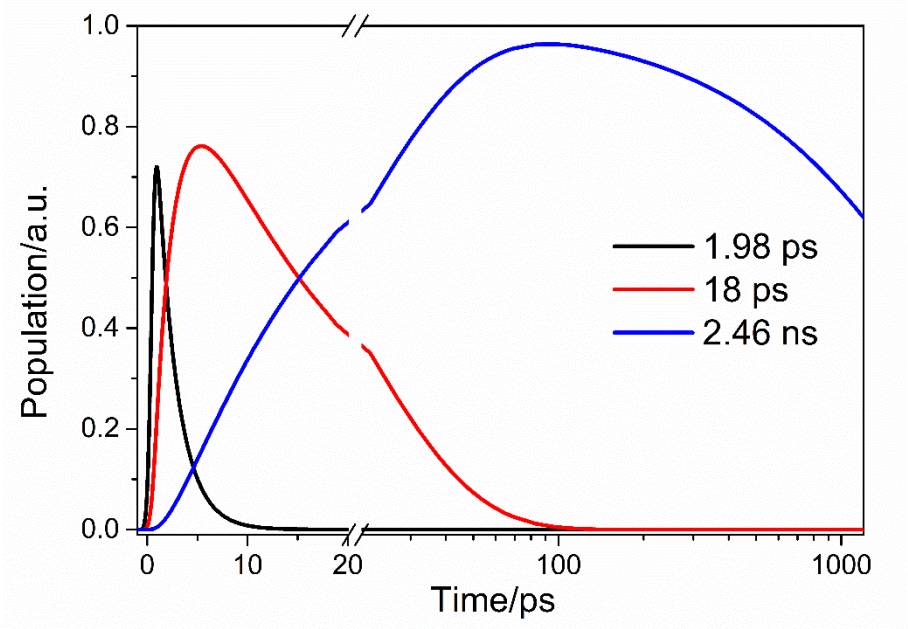


Fig. S9 Associated population evolution obtained from global analysis for TOND in DMF.

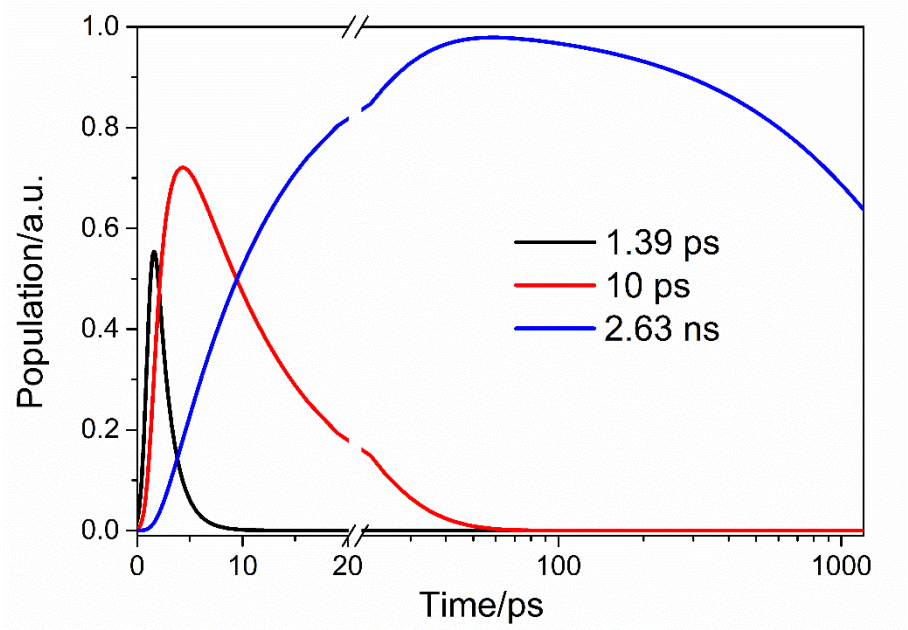


Fig. S10 Stimulated emission peak shift time correlation functions C(t) of TOND in DMF.

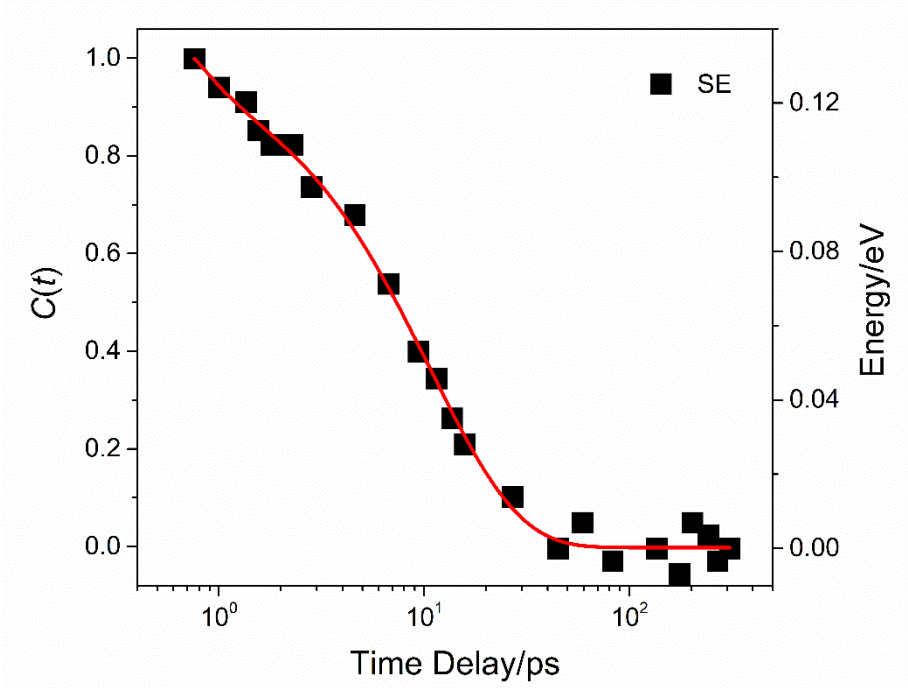
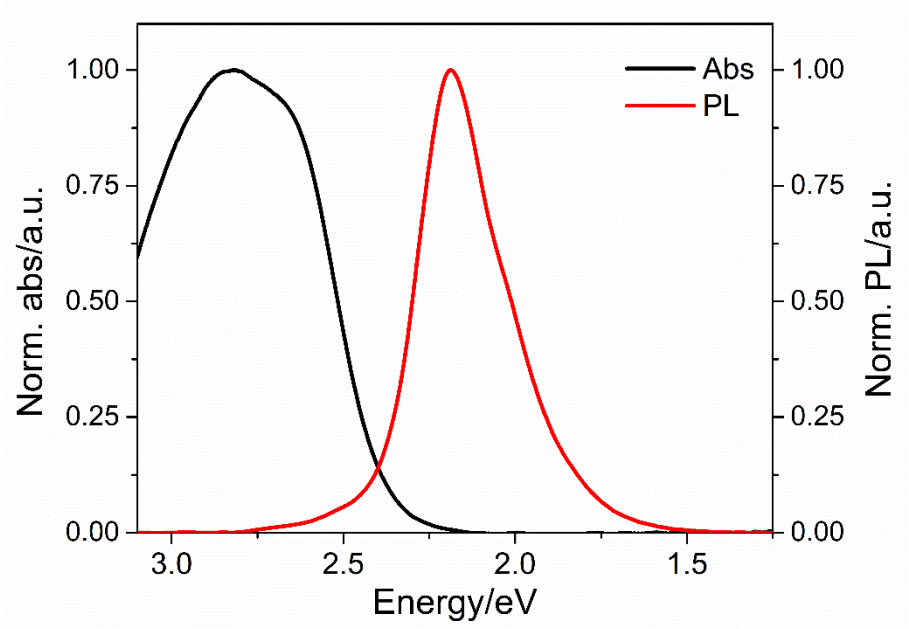


Fig. S11 Steady state absorption and PL spectra of TOND film at 295 K.



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