

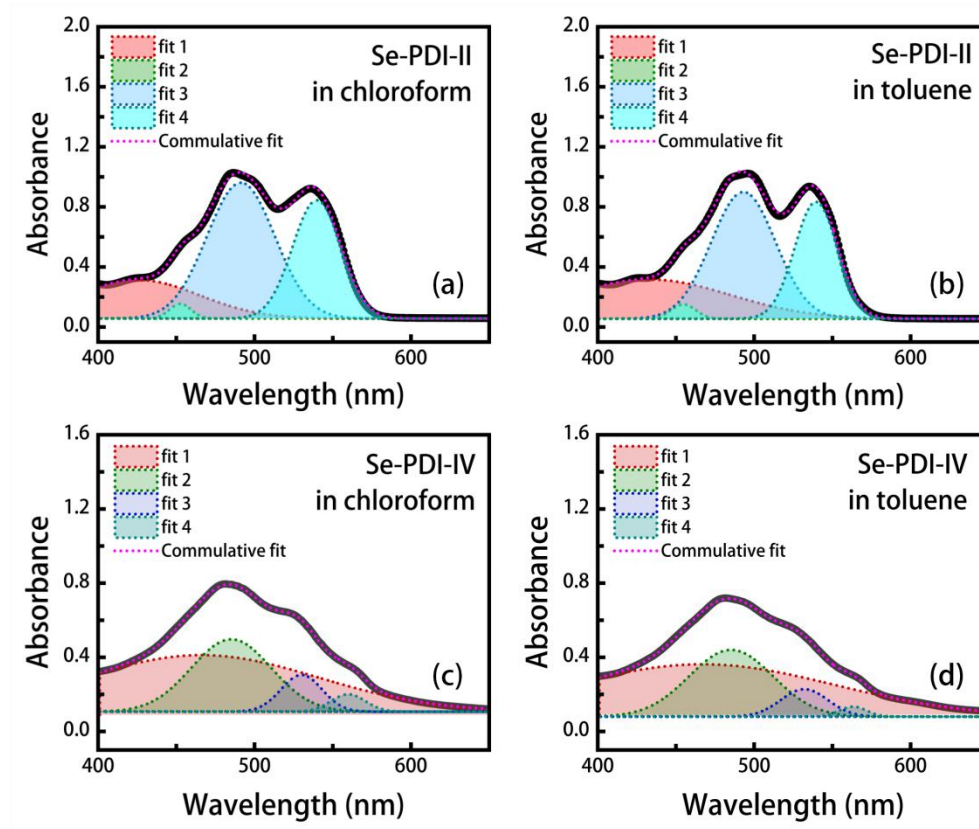
## Supporting Information

### **The efficient triplet states formation of Se-modified PDI dimers and tetramers in solvents**

Feijun Huang,<sup>a,†</sup> Wenli Su,<sup>a,†</sup> Yubo Yang,<sup>a</sup> Hang Wang,<sup>b</sup> Zhishan Bo,<sup>b</sup> Pengfei Jing<sup>a</sup> and Wenkai Zhang<sup>a,c,\*</sup>

- a. School of Physics and Astronomy, Applied Optics Beijing Area Major Laboratory, Center for Advanced Quantum Studies, Beijing Normal University, Beijing 100875, China
- b. Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing 100875, China
- c. Key Laboratory of Multiscale Spin Physics, Ministry of Education, Beijing Normal University, Beijing 100875, China

## 1. Steady-state spectra



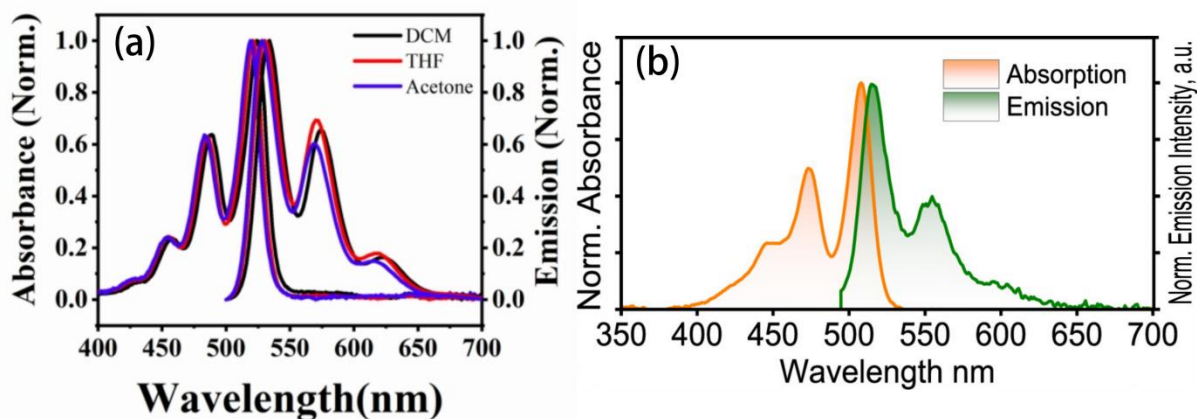
**Figure S1.** The multi-peak fitting results of the steady-state absorption spectra of (a) Se-PDI-II in chloroform; (b) Se-PDI-II in toluene; (c) Se-PDI-IV in chloroform; (d) Se-PDI-IV in toluene.

The results demonstrate that the absorption spectra of Se-PDI-II and Se-PDI-IV can be effectively fitted to obtain the positions and intensities of each absorption peak, consistent with the data obtained earlier. The peak ratios of the 0-1/0-0 transitions were calculated based on the fitting results and are listed in Table S1.

**Table S1.** The peak ratios of the 0-1/0-0 transitions of Se-PDI-II and Se-PDI-IV

molecule	solvent	peak ratio
Se-PDI-II	toluene	1.084
	chloroform	1.145

Se-PDI-IV	toluene	2.446
	chloroform	1.980



**Figure S2.** (a) Normalized absorption (left side) and fluorescence spectra (right side) of PDI-C5 in different solvents<sup>1</sup>; (b) Normalized absorption and fluorescence spectra of selenium-annulated PDI-C5 in toluene<sup>2</sup>.

## 2. Fluorescence quantum yield

### 2.1. The data for the molecules without Se modification

**Table S2.** Fluorescence quantum yields of PDI-II and PDI-IV in different solvents

molecule	solvent	polarity	$\Phi$
PDI-II	toluene	2.4	0.41
PDI-IV	toluene	2.4	0.06

### 2.2. Calculation of fluorescence quantum yield

The calculation of fluorescence quantum yield was carried out following the "comparison method" described by Williams et al<sup>3</sup>. This method uses a reference sample with a known fluorescence quantum yield that has characteristic and clear fluorescence. In our measurements,

we adopted the comparison method and compared the samples, Se-PDI-II and Se-PDI-IV, with the reference material, rhodamine 6G, which has a known fluorescence quantum yield of 0.95.

**Materials and Instruments:** 1. Rhodamine 6G, Se-PDI-II, Se-PDI-IV; 2. Ethanol, chloroform, toluene; 3. UV-vis spectrophotometer; 4. Fluorescence spectrometer; 5. Fluorescence cuvette with a path length of 10 mm

**Experimental procedure:**

1. Prepare 4 to 5 samples of rhodamine 6G in ethanol, Se-PDI-II in chloroform, Se-PDI-II in toluene, Se-PDI-IV in chloroform, and Se-PDI-IV in toluene with different absorbances (0.01-0.1) at the excitation wavelength of 480 nm.

2. Fix the excitation wavelength at 480 nm and measure the fluorescence of the prepared samples.

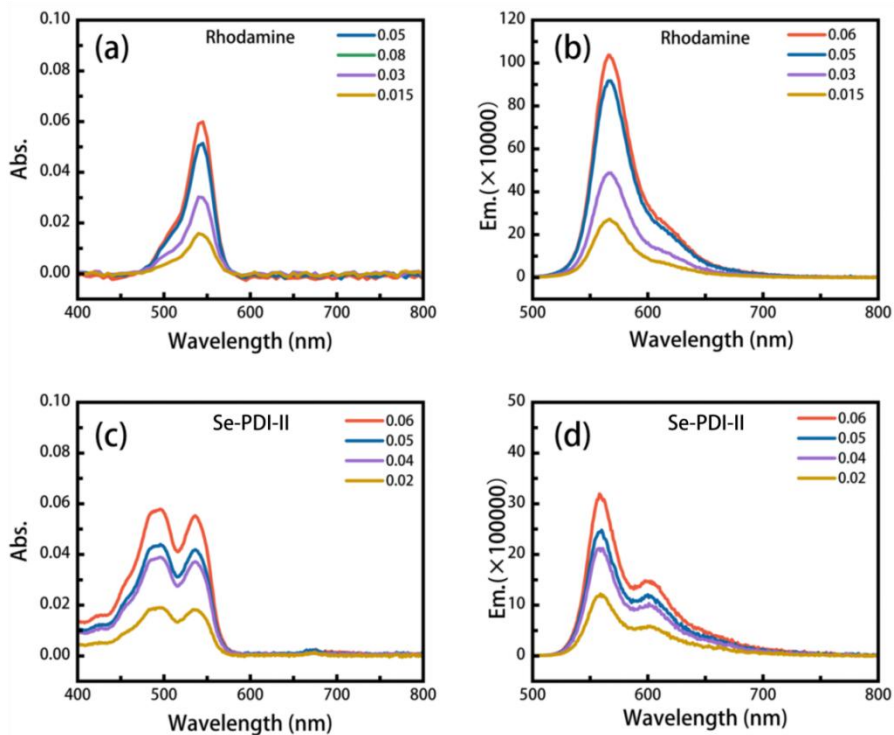
3. Calculate the integrated fluorescence intensity (i.e., the area under the fluorescence spectrum).

4. Plot a graph of the integrated fluorescence intensity against the absorbance.

5. Calculate the fluorescence quantum yield.

**Experimental results:**

Taking Se-PDI-II in chloroform as an example, the calculation method for fluorescence quantum yield is demonstrated. Figure S2 shows the absorbance and fluorescence spectra of rhodamine 6G in ethanol and Se-PDI-II in chloroform. The area under the fluorescence spectrum can be obtained using the integration function in Origin software. The absorbance of rhodamine 6G and Se-PDI-II at the excitation wavelength of 480 nm can be directly read from the absorption spectra.

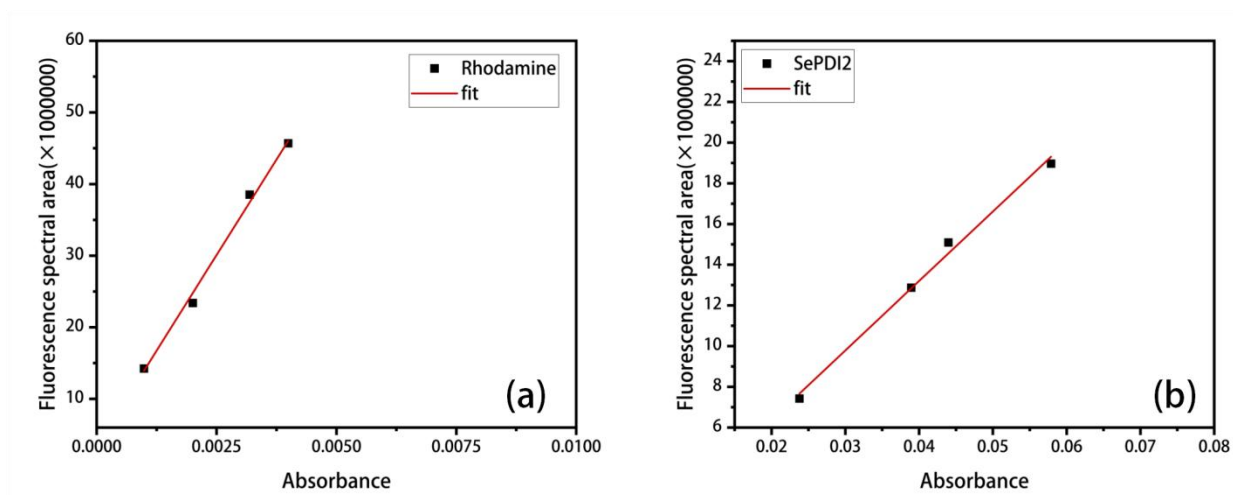


**Figure S3.** (a, c) Absorbance spectra of (a) rhodamine 6G and (c) Se-PDI-II; (b, d) fluorescence spectra of (b) rhodamine 6G and (d) Se-PDI-II.

The corresponding table of absorbance and fluorescence spectrum area is presented in Table S3. Linear fitting is performed, and the results are shown in Figure S3.

**Table S3.** Absorbance vs fluorescence spectral area

Se-PDI-II		Rhodamine 6G	
Absorbance	Fluorescence spectral area	Absorbance	Fluorescence spectral area
0.05789	$1.90 \times 10^7$	0.00099	$1.42 \times 10^7$
0.04397	$1.51 \times 10^7$	0.00201	$2.34 \times 10^7$
0.03893	$1.29 \times 10^7$	0.00319	$3.85 \times 10^7$
0.02378	$0.74 \times 10^7$	0.00399	$4.57 \times 10^7$



**Figure S4.** The experimental plots of absorbance versus fluorescence area and the results of linear fitting.

The fluorescence quantum yield is calculated using the following formula:

$$Q = Q_R \frac{\alpha n^2}{\alpha_R n_R^2}$$

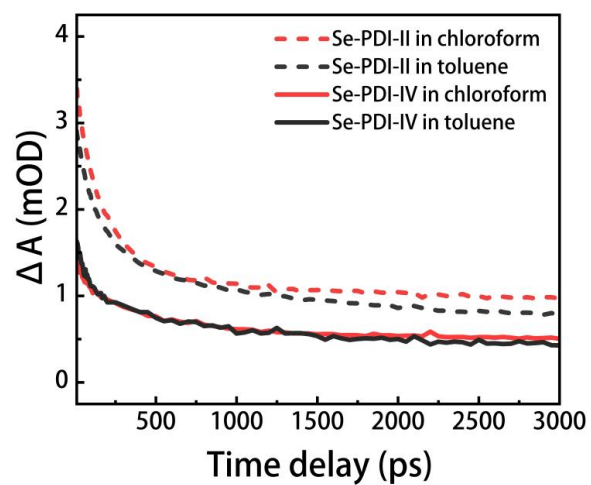
$\alpha$  is the linear fit gradient obtained from the spectrum fluorescence intensity versus absorbance,  $n$  is the refractive percentage of the solvent and the subscript  $R$  is the reference fluorophore with known quantum yield.

The refractive index of chloroform is 1.4476, while the refractive index of ethanol is 1.36. So  $n^2/n_R^2 = 1.13$ . And fluorescence quantum yield of rhodamine 6G in ethanol ( $Q_R$ ) is 0.95.

The fluorescence quantum yield of Se-PDI-II in chloroform ( $Q$ ) is 0.0341.

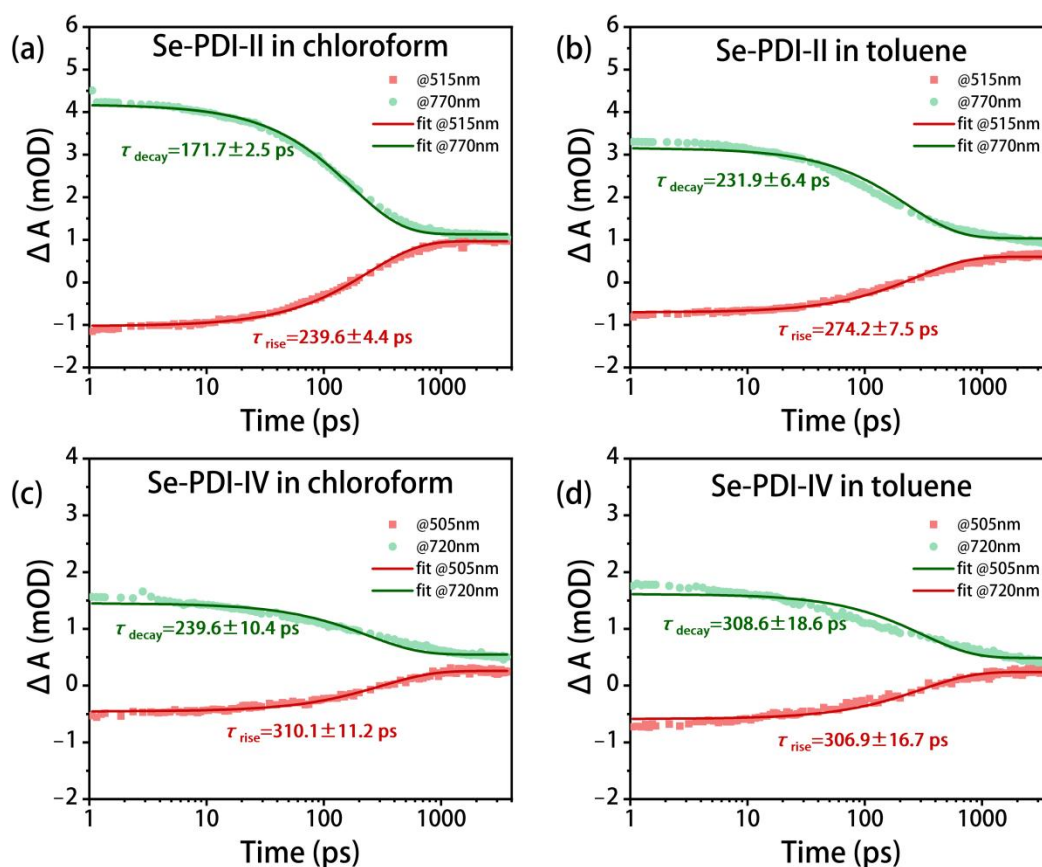
The yield of other samples can be calculated in the same way.

### 3. Comparison of the dynamics curves



**Figure S5.** Comparison of the dynamics curves at 730nm of Se-PDI-II in chloroform, Se-PDI-II in toluene, Se-PDI-IV in chloroform, and Se-PDI-IV in toluene. It can be observed that the dynamics of dimers and tetramers are nearly identical in solvents with different polarities.

#### 4. Kinetic traces and fitting



**Figure S6.** Comparison of the dynamics curves at 515nm and 770nm of (a) Se-PDI-II in chloroform; (b) Se-PDI-II in toluene; at 505nm and 720nm of (c) Se-PDI-IV in chloroform, and (d) Se-PDI-IV in toluene. It can be observed that the dynamics of dimers and tetramers are nearly identical in solvents with different polarities.

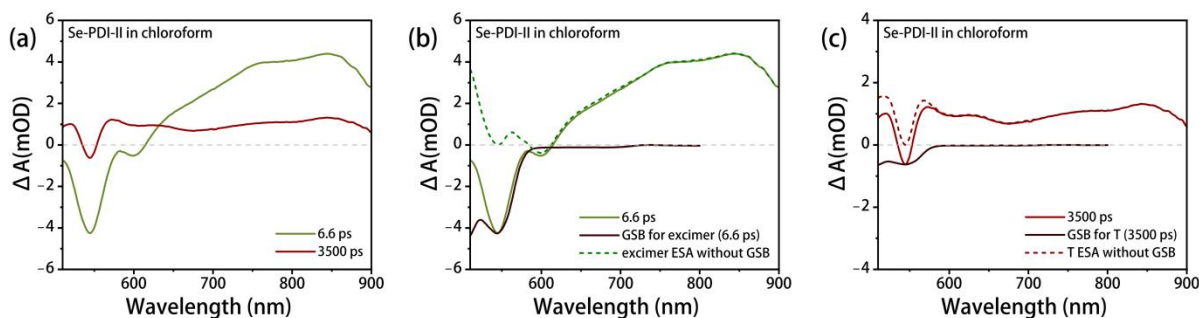
## 5. Comparison of the triplet states generation of dimer and tetramer

In order to better compare the generation of the triplet state, the correction method proposed by Carlotti et al.<sup>4</sup> was referenced. Taking the spectrum of Se-PDI-II in chloroform as an example, the ratio of the corrected triplet state signal to the excimer signal was calculated, thereby allowing for a semi-quantitative comparison of the relative generation efficiencies.



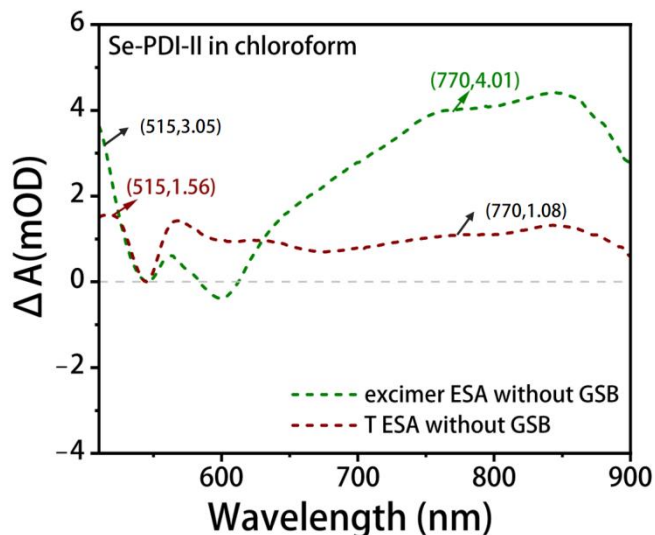
First, to obtain the spectral shapes of the excimer state and triplet state, the positions where the concentrations of the excimer state and triplet state reached their maximum values (6.6 ps and 3500 ps, respectively) were selected. The transient spectra at 6.6 ps and 3500 ps were chosen, as shown in Figure S6(a).

Both components' spectra need to eliminate the contribution of ground-state bleach (GSB). Therefore, the steady-state absorption spectra were scaled according to the transient spectra, normalizing the steady-state absorption spectra to the transient absorption spectra at the ground-state bleach peak, as shown in Figure S6(b) and (c). By subtracting the steady-state absorption spectra, the real excited-state absorption (ESA) spectra were obtained, resulting in the excimer state and triplet state spectra shown in Figure S6(b) and (c), respectively.



**Figure S7.** (a) Transient absorption spectra at 6.6 ps and 3500 ps delay from excitation of Se-PDI-II in chloroform; (b,c) Transient and steady state absorption spectra used to reconstruct the absorption spectra of (b) the excimer and (c) triplet states.

The corrected ESA of the excimer and triplet (T) states are compared in Figure S7.



**Figure S8.** The corrected ESA of the excimer and triplet (T) states.

From Figure S7, the amplitude difference of the two signals at two time points can be calculated, and the ratio can be determined.  $\frac{\varepsilon_T}{\varepsilon_{\text{excimer}}} = \frac{3.05-1.56}{4.01-1.08} = 0.51$ .

The ratio is 0.39 for the dimer in toluene, 0.23 for the tetramer in chloroform, and 0.35 for the tetramer in toluene. From this, we can roughly conclude that the triplet state generation of the dimer is more efficient than that of the tetramer, and a higher polarity solvent leads to the production of more triplet states.

## REFERENCE

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4. B. Carlotti, I. K. Madu, H. Kim, Z. Cai, H. Jiang, A. K. Muthike, L. Yu, P. M. Zimmerman and T. Goodson, *Chemical Science*, 2020, **11**, 8757-8770.