Supporting Information for:

Excited-State Photophysical Processes in a Molecular System Containing Bisimide and Zinc Porphyrin Chromophores

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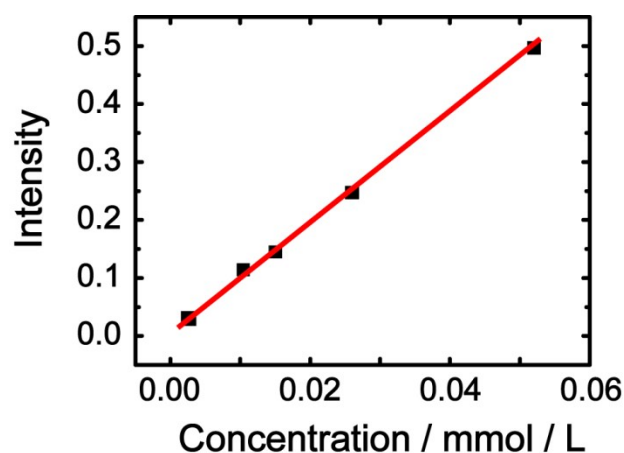**The concentration dependence of PDI-ZnPor-PDI solution**

Fig. S1. Intensity of the charge transfer band probed at 748 nm in the UV-visible spectra as a function of concentration in PDI-ZnPor-PDI solution. A linear relationship is shown in red line.

C=O stretching mode assignment

The calculated PDI frequency spectrum was used to assign the IR modes of C=O groups in the experimental FTIR spectrum. The calculated frequency spectrum in the implicit solvent ($CHCl_3$) was obtained using the polarizable continuum model.
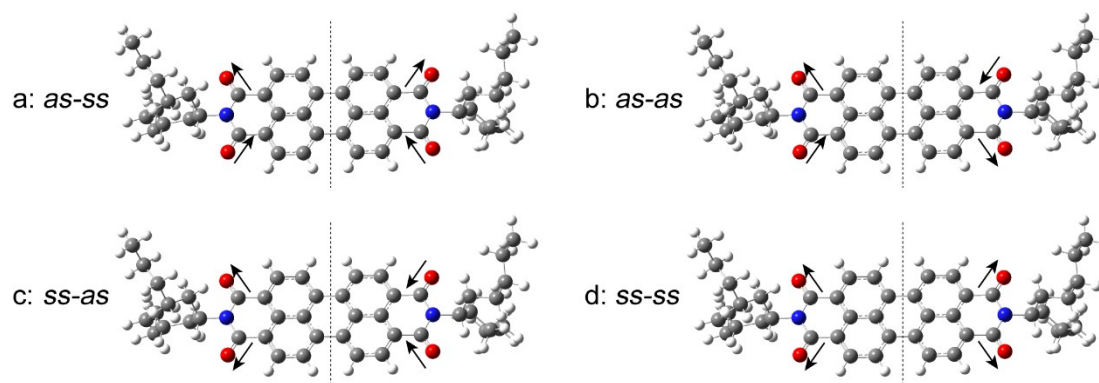

Fig. S2. Calculated asymmetric stretching (*as*, top) and symmetric stretching (*ss*) of four C=O groups of PDI monomer in the implicit solvent ($CHCl_3$). Mode a (*as-ss*) and mode c (*ss-as*) are strongly IR active while mode b (*as-as*) and mode d (*ss-ss*) are weakly IR active (see Table S1).

Table S1. Calculated vibrational transition frequency (ω) and intensity (I) of the *ss* and *as* C=O stretching vibrational modes of PDI monomer in the implicit solvent ($CHCl_3$).

Case	Mode	ω / cm^{-1}	I / km/mol
a	*as-ss*	1653.8	1228.5
b	*as-as*	1654.2	0.6
c	*ss-as*	1692.3	1321.9
d	*ss-ss*	1697.0	0.1

Fitting parameters of fs-IR spectra in PDI-ZnPor-PDI film
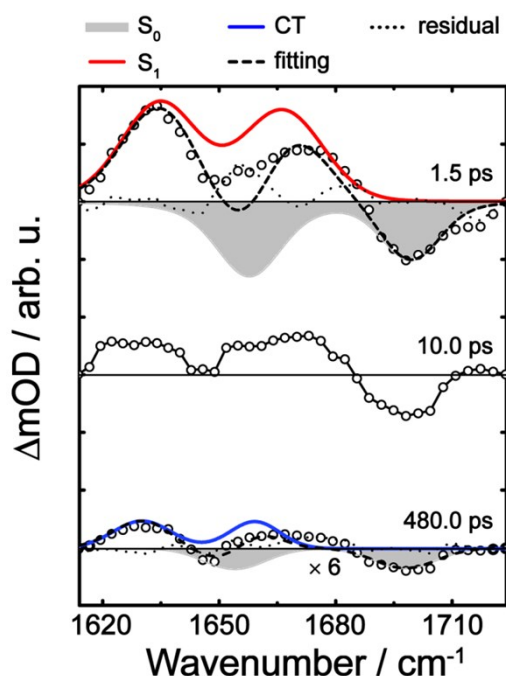

Fig. S3. Fs-IR spectra (circle) and their fittings (dash lines) at three representative delay times. The IR components for the vibrational bleaching feature of the electronic ground state (S_0, gray region), and for the vibrational absorption of the electronic excited singlet state (S_1, red line) and charge transfer state (blue line) were obtained by spectral fitting.

Table S2. Fitting parameters of the fs-IR spectra (Fig. 2b) in the PDI-ZnPor-PDI film excited at 530 nm.

Peak	S_1 / cm^{-1}	FWHM / cm^{-1}	CT / cm^{-1}	FWHM / cm^{-1}
1	1666.5	24.1	1658.6	14.7
2	1634.8	23.6	1630.1	16.1

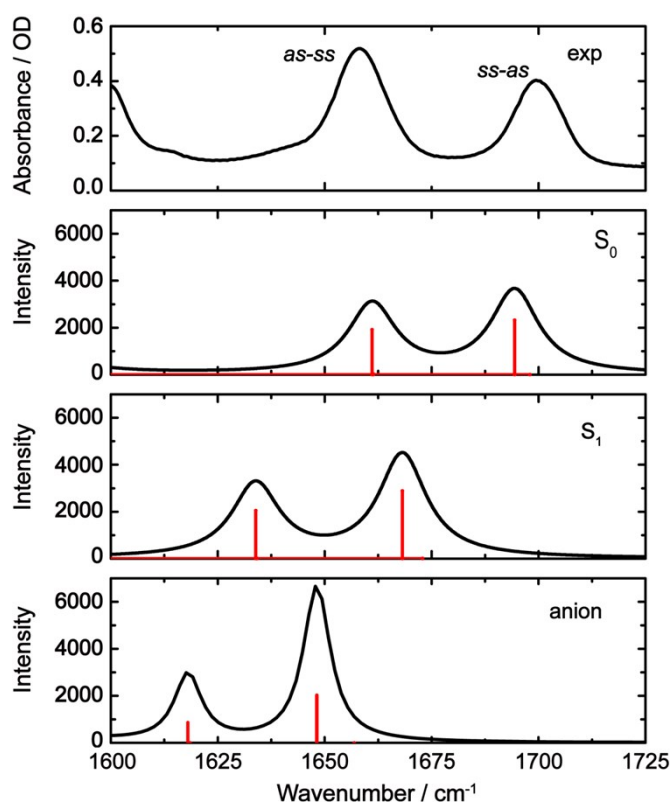**Calculated IR spectra of the radical anion and excited state**

Fig. S4. Calculated IR spectra of the ground state (S_0), excited singlet state (S_1) and the radical anion for the PDI monomer in gas phase. Experimental IR spectrum is also given for comparison.

The computed IR spectra of the ground state, excited singlet state and the radical anion in PDI monomer in the frequency range of 1600-1725 cm^{-1} are given in Fig. S3. Moreover, the detailed vibrational frequency and the transition intensity of the C=O stretching modes corresponding to excited state are listed in Table S3. The calculated results suggest that the C=O stretching modes are distinguishable from the singlet state and radical anion, and can be used as signatures to explore the photophysical progress in PDI-ZnPor-PDI system.

Table S3. The calculated frequency (ω) and transition intensity (I) of the C=O stretching modes.

	ω (cm^{-1})	I (km/mol)	Mode
S$_0$	1661.1	639.7	*as-ss*
	1694.4	776.9	*ss-as*
S$_1$	1633.9	683.3	*as-ss*
	1668.2	963.3	*ss-as*
anion	1618.0	867.1	*as-ss*
	1648.2	2022.8	*ss-as*

FTIR spectra and dynamics of PDI-ZnPor-PDI solution at several concentrations
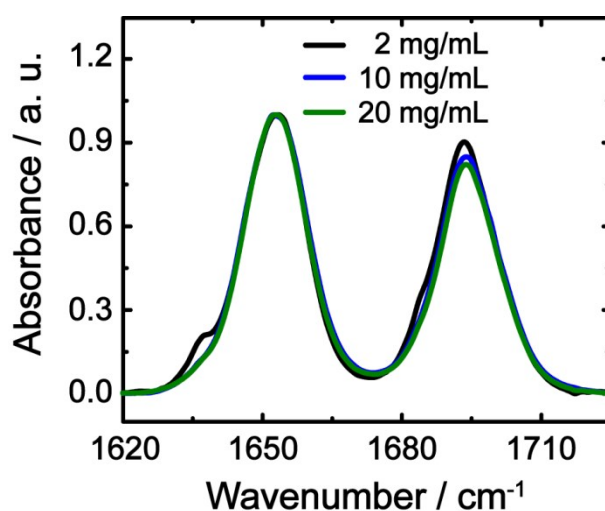

Fig. S5. Intensity normalized steady-state IR spectrum of PDI-ZnPor-PDI solutions at three concentrations (2 mg/mL, 10 mg/mL and 20 mg/mL).
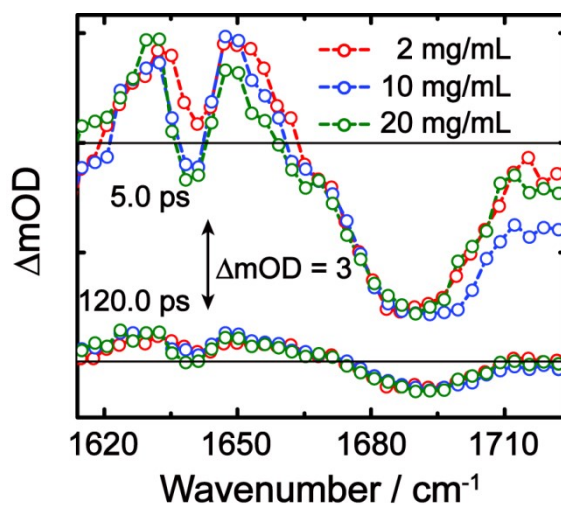

Fig. S6. Normalized fs-IR spectra measured at three different concentrations of PDI-

ZnPor-PDI solutions (2 mg/mL, 10 mg/mL and 20 mg/mL) at typical delay times (circles connected by dashed lines, 5.0 ps and 120.0 ps, vertically displaced).
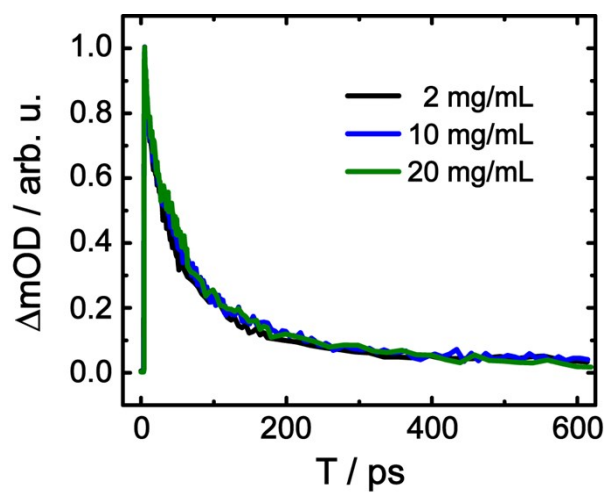

Fig. S7. Intensity normalized kinetic traces probe at 1625 cm^{-1} of PDI-ZnPor-PDI solutions at three different concentrations (2 mg/mL, 10 mg/mL and 20 mg/mL).