

# Supporting Information

## Ultrafast Study of Substituted-Position-Dependent Excited-state Evolution in Benzophenone-Carbazole Dyads

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## 1. Instruments and **experiment** methods

### (1) Materials

All the materials used in synthesis were purchased from Energy chemical. Solvents include Tetrahydrofuran (THF), Dichloromethane (DCM), Dimethyl formamide (DMF) and Dimethyl Sulfoxide (DMSO) were purchased from J&K. All the materials were used without further purification.

### (2) Instruments

The  $^1\text{H}$ NMR spectra were measured using Zhongke Niujin WNMR-I 400 spectrometer with tetramethylsilane (TMS;  $\delta = 0$ ) as the internal reference. High resolution mass spectra (HRMS) were recorded using a Thermo Q Exactive spectrometer. UV-Vis absorption and photoluminescence measurements were performed with UV-Vis spectrophotometer (SHIMADZU® UV-1780) and Fluorescence spectrometer (PTI® QM-TM).

### (3) Femtosecond transient absorption (fs-TA) **experiments**

The fs-TA measurements were performed based on a femtosecond Ti: Sapphire regenerative amplifier laser system (Coherent, Astrella-Tunable-F-1k) and femtosecond transient absorption spectrometer system (Ultrafast Systems, Helios Fire). The laser probe pulse was produced with ~4% of the amplified 800 nm laser pulses to generate a white-light continuum (320–800 nm) in a  $\text{CaF}_2$  crystal and **then** this probe beam was split into two parts before traversing the sample. One probe laser beam goes through the sample while the other probe laser beam goes to the reference spectrometer to monitor the fluctuations in the probe beam intensity. The instrument response function was determined to be ca. 120 fs. At each temporal delay, data were averaged for 2 s and collected by the acquisition system. For the **experiments** described in this study, the sample solution was excited by a 340 nm pump beam with a power of 0.2 mW (from TOPAS). The sample solutions were excited in a 2 mm path-length cuvette. The data were stored as three-dimensional (3D) wavelength-time-absorbance matrices that were exported for use with the fitting software. Chirp correction was done for all the data shown here. The kinetics of all fs-TA spectra were fitted by single-wavelength

fitting via Surface Explorer software; all the error values were shown with 90% confidence intervals.

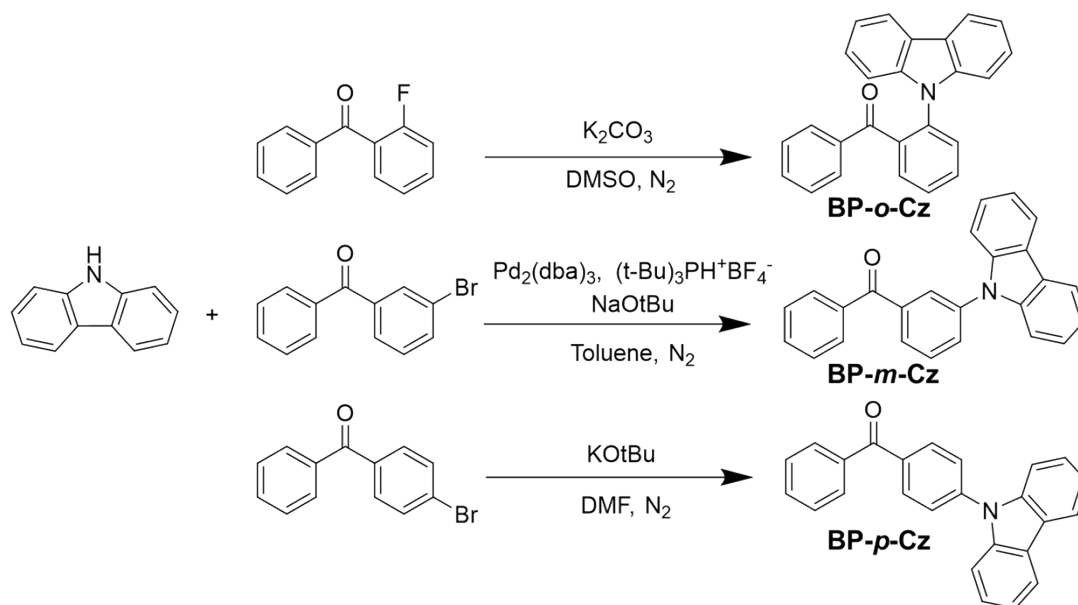
#### **(4) Nanosecond transient absorption (ns-TA) experiments**

The ns-TA measurements were performed by using a nanosecond pulsed probe light source, a photonic crystal fiber (PCF)-based supercontinuum laser. The pulse duration of this probe determines the time resolution of the spectrometer ( $<1$  ns). In ns-TA, the pump-probe delay is controlled electronically, and the maximum time window is very close to half the repetition period of the pump laser. In our case, the maximum time window is 400  $\mu$ s. The excited wavelength and sample solutions employed in the ns-TA experiments were the same as the fs-TA's. The data were stored as three-dimensional (3D) wavelength-time-absorbance matrices that were exported for use with the fitting software. The kinetics of all ns-TA spectra were fitted by single-wavelength fitting via Surface Explorer software; all the error values were shown with 90% confidence intervals.

#### **(5) Theoretical calculations**

Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) are applied to calculate the optimized geometries and electronic structures of the ground state ( $S_0$ ) and the excited state ( $S_n$ ) of BP-Cz dyads. CAM-B3LYP/6-311G\*\* through the Gaussian 16 program package<sup>1</sup> is employed to optimize the structure, calculate energy levels and reveal the characteristics of the hole and electron of  $S_1$  and  $S_2$ . Multiwfn program<sup>2</sup> is used to analyze and visualize hole-electron distribution, transition density,  $\Delta r$  index and intramolecular interaction (Independent gradient model, IGM). VMD software<sup>3</sup> is used to obtain a 3D isosurface of intramolecular interaction for *o*-BCz (Isosurface value=0.005). SOC constants are calculated based on ORCA program system<sup>4</sup>.

## 2. Synthesis and characteristic



**Scheme S1.** Synthetic routes to BP-Cz dyads

### Synthesis of BP-o-Cz

Into a 100 ml two necked round-bottom flask were placed 2-fluorobenzophenone (1.10 g, 5.5 mmol), carbazole (5 g, 12 mmol), and Potassium carbonate (9 g, 65 mmol). The flask was evacuated under vacuum and flushed with dry nitrogen for three times. Then dry DMSO (30 mL) was injected. The mixture was heated to 180°C and stirred for 24 h, and then cooled to room temperature. The mixture was poured into water and extracted by DCM three times. The organic phase was washed with water three times and dried over sodium sulfate anhydrous. The crude product was further purified by flash chromatography (silica gel, PE/DCM, 7/1, v/v), obtaining a white solid in 62% yield (1.18 g).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.92 (dd,  $J = 7.6, 1.3$  Hz, 1H), 7.87 – 7.78 (m, 3H), 7.67 (dd,  $J = 15.4, 7.7$  Hz, 2H), 7.37 (dd,  $J = 11.3, 4.0$  Hz, 2H), 7.26 (d,  $J = 8.2$  Hz, 2H), 7.18 (t,  $J = 7.4$  Hz, 2H), 7.05 (d,  $J = 7.1$  Hz, 2H), 6.99 (t,  $J = 7.5$  Hz, 1H), 6.73 (t,  $J = 7.8$  Hz, 2H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  196.82, 140.92, 137.69, 136.48, 136.20, 132.59, 131.96, 131.25, 128.92, 128.34, 127.82, 126.94, 125.76, 123.22, 119.98, 119.93, 109.94. HRMS  $m/z$ :  $[M+H]^+$  calcd for  $C_{25}H_{18}NO$ , 348.1388, found 348.1395

### Synthesis of BP-*m*-Cz

Into a 100 ml two necked round-bottom flask were placed 3-bromobenzophenone (1.3 g, 5 mmol), carbazole (1 g, 6 mmol), Tris(dibenzylideneacetone)dipalladium (Pd<sub>2</sub>(dba)<sub>3</sub>, 0.7 g, 0.8 mmol), Tri-tert-butylphosphine tetrafluoroborate (0.7 g, 2.5 mmol) and sodium tert-butoxide (2.4 g, 25 mmol). The flask was evacuated under vacuum and flushed with dry nitrogen for three times. Then dry toluene (30 mL) was injected. The mixture was heated to 110°C and stirred for 24 h, and then cooled to room temperature. The mixture was poured into water and extracted by DCM three times. The organic phase was washed with water three times and dried over sodium sulfate anhydrous. The crude product was further purified by flash chromatography (silica gel, PE/DCM, 7/1, v/v), obtaining a white solid in 81% yield (1.41 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17 (d, *J* = 7.8 Hz, 2H), 8.03 (s, 1H), 7.92 (dd, *J* = 10.6, 7.6 Hz, 3H), 7.85 (dd, *J* = 6.7, 1.8 Hz, 1H), 7.77 (t, *J* = 7.8 Hz, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.49 – 7.41 (m, 4H), 7.37 – 7.30 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 195.76, 140.66, 139.61, 137.98, 137.17, 132.88, 130.89, 130.09, 130.04, 128.86, 128.52, 128.40, 126.17, 123.60, 120.48, 120.35, 109.60. HRMS *m/z*: [M+H]<sup>+</sup> calcd for C<sub>25</sub>H<sub>18</sub>NO, 348.1388, found 348.1394

### Synthesis of BP-*p*-Cz

Into a 100 ml two necked round-bottom flask were placed 4-bromobenzophenone (1.3 g, 5 mmol), carbazole (1 g, 6 mmol), and Potassium tert-butoxide (1.2 g, 11 mmol). The flask was evacuated under vacuum and flushed with dry nitrogen three times. Then dry DMF (30 mL) was injected. The mixture was heated to 150°C and stirred for 24 h, and then cooled to room temperature. The mixture was poured into water and extracted by DCM three times. The organic phase was washed with water three times and dried over sodium sulfate anhydrous. The crude product was further purified by flash chromatography (silica gel, PE/DCM, 7/1, v/v), obtaining a white solid in 65% yield (1.13 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.18 (d, *J* = 7.7 Hz, 2H), 8.14 – 8.07 (m, 2H), 7.97 – 7.90 (m, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.60 – 7.53 (m, 4H), 7.51 – 7.43 (m, 2H), 7.35 (t, *J* = 7.4 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ

196.82, 140.92, 137.69, 136.48, 136.20, 132.59, 131.96, 131.25, 128.92, 128.34, 127.82, 126.94, 125.76, 123.22, 119.98, 119.93, 109.94. HRMS m/z:  $[M+H]^+$  calcd for  $C_{25}H_{18}NO$ , 348.1388, found 348.1393

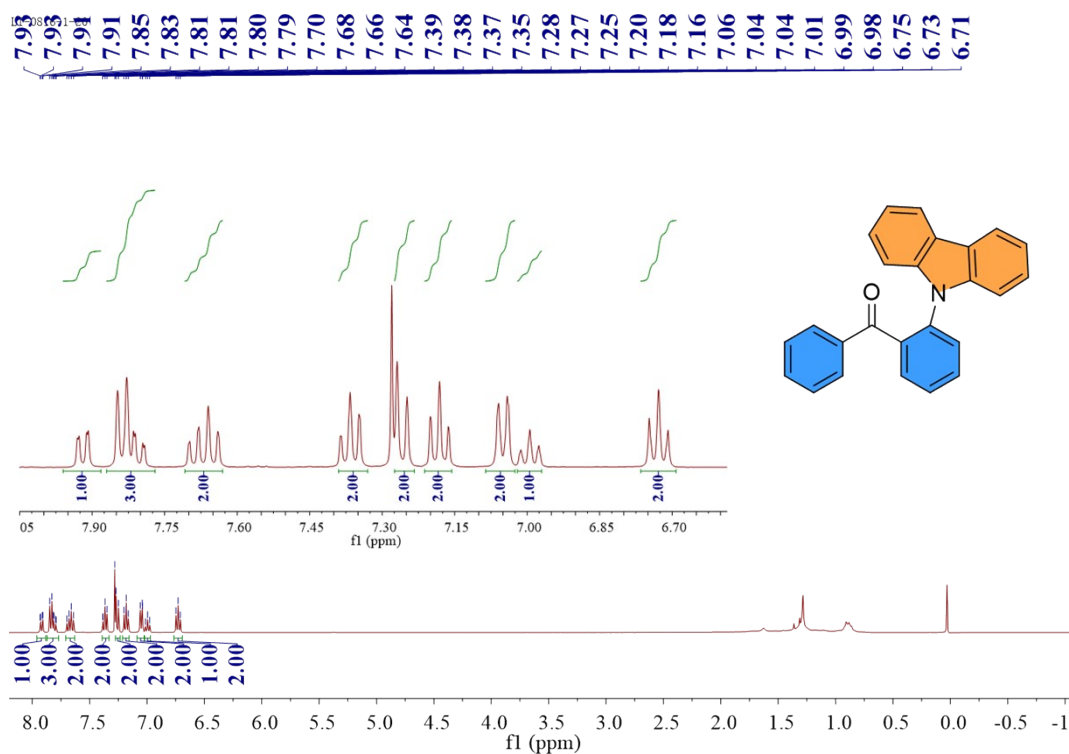


Figure S1.  $^1H$  NMR of BP-*o*-Cz

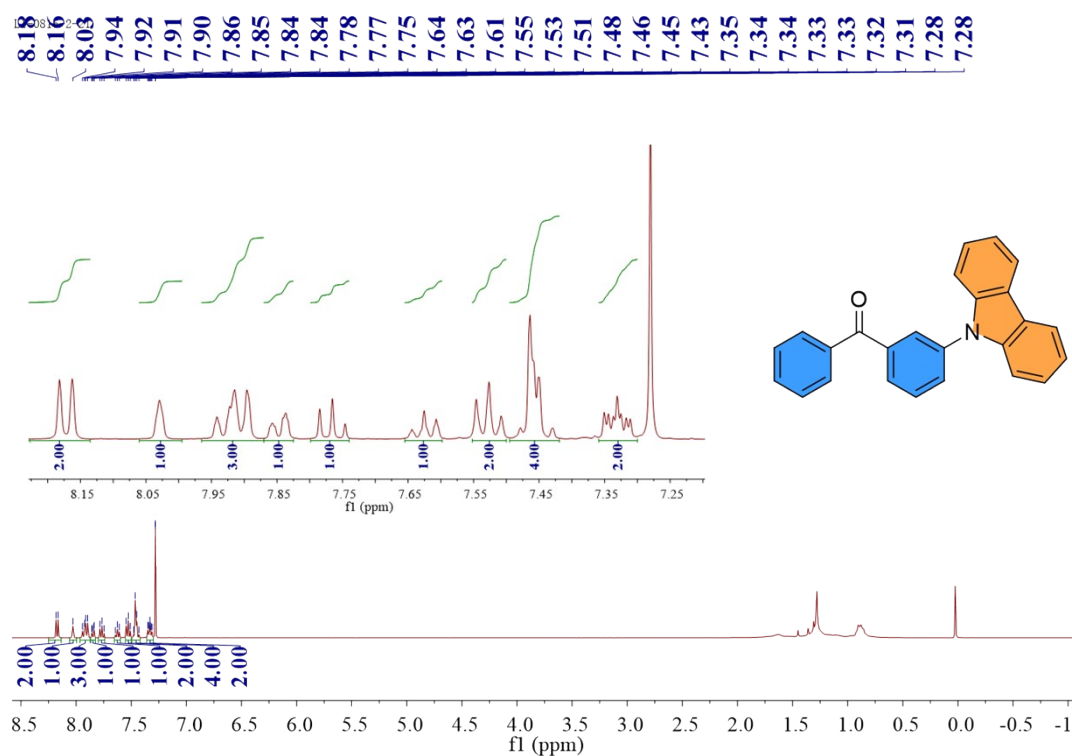
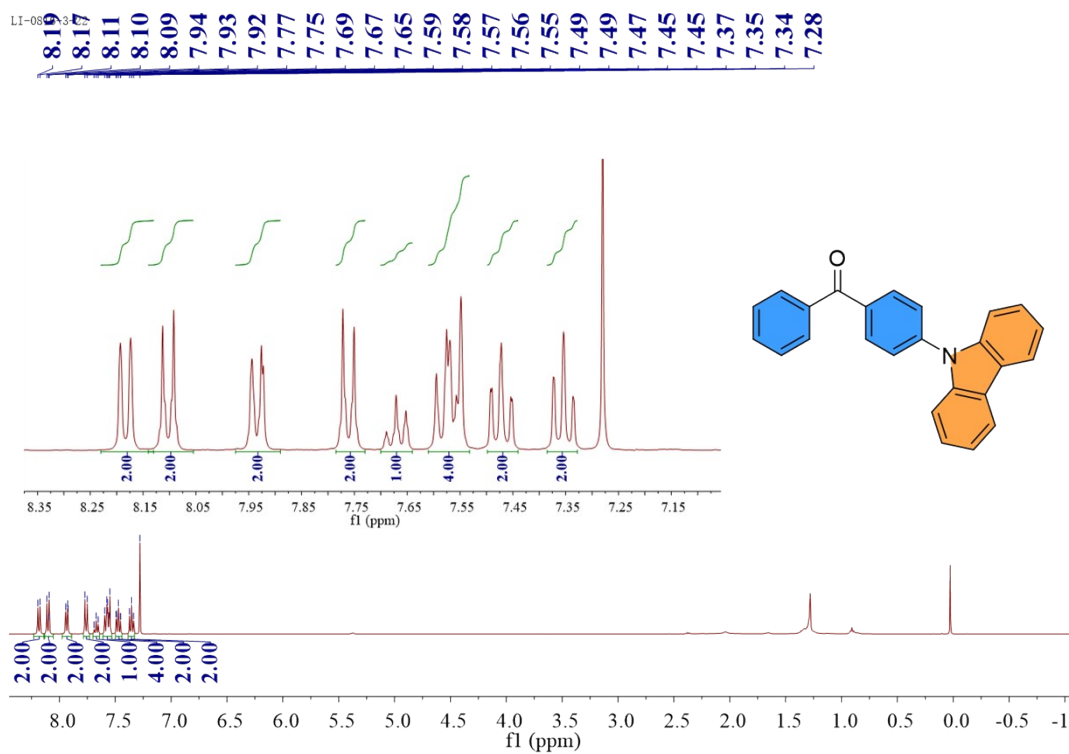
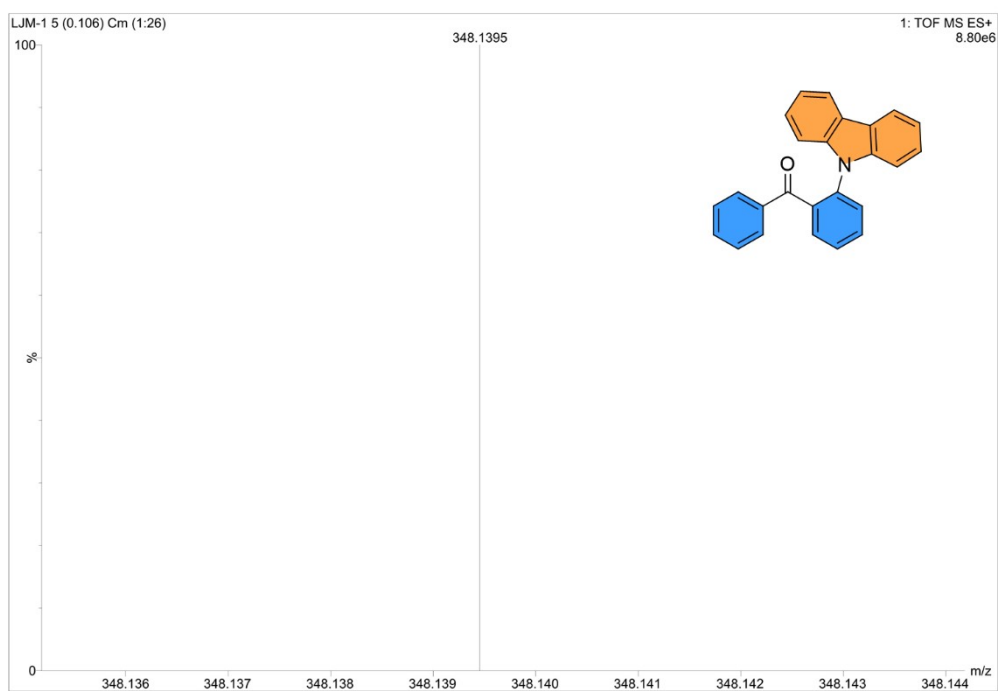


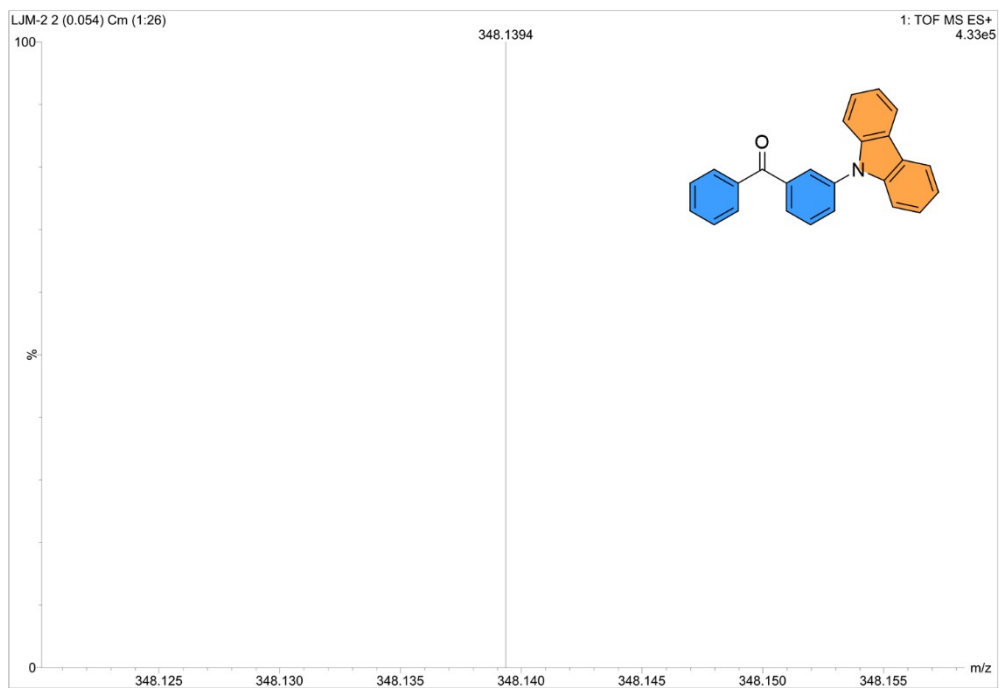
Figure S2.  $^1H$  NMR of BP-*m*-Cz



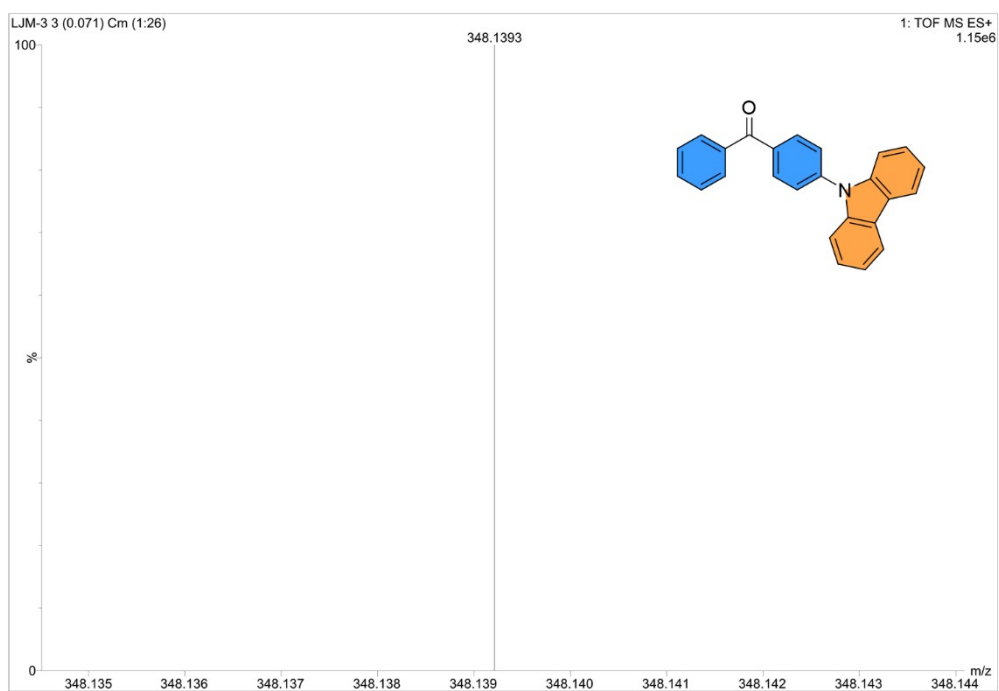
**Figure S3.**  $^1\text{H}$  NMR of BP-*p*-Cz



**Figure S4.** HRMS of BP-*o*-Cz



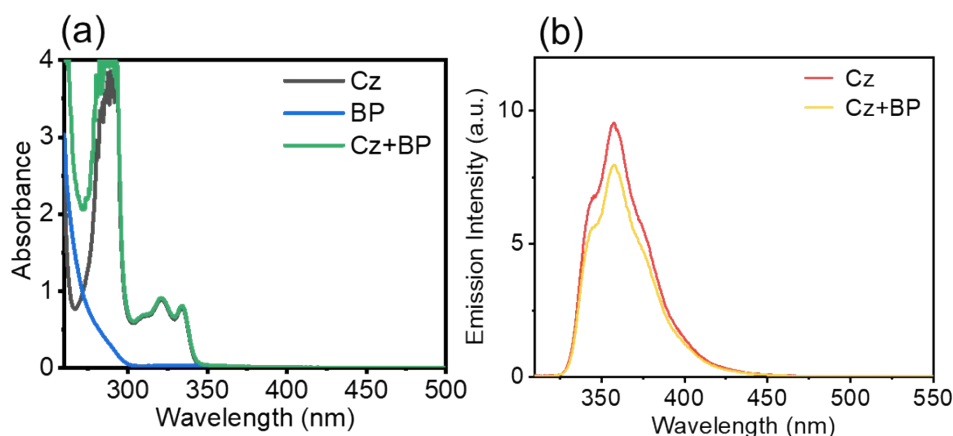
**Figure S5.** HRMS of BP-*m*-Cz



**Figure S6.** HRMS of BP-*p*-Cz



### 3. UV-Vis and PL spectra



**Figure S7.** UV-vis spectra and FL spectra of BP, Cz and mix solution in ACN, 1 mM.

#### The Lippert-Mataga model

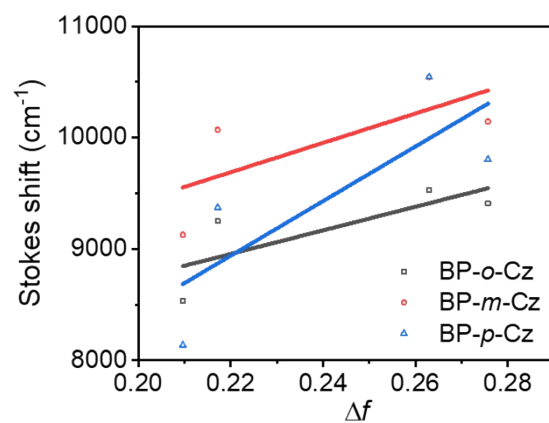
The Lippert-Mataga model is estimated according to equation 1.

$$hc(\nu_a - \nu_f) = hc(\nu_a^0 - \nu_f^0) + \frac{2(\mu_e - \mu_g)^2}{a_0^3} f(\epsilon, n) \quad \text{Eq 1}$$

where,  $\mu_e - \mu_g$  ( $\Delta\mu$ ) is the difference between the dipole moments of excited and ground states,  $c$  is the speed of light,  $h$  is Planck's constant, and  $a_0$  is the radius of the Onsager cavity around the fluorophore and is considered to be half of the average molecular sizes of BP-Cz dyads. Solvent dielectric constant ( $\epsilon$ ) and refractive index ( $n$ ) are included in the term  $f$ , known as the solvent polarity parameter.  $\nu_a - \nu_f$  is the Stokes shift. The  $a_0$  and  $\mu_g$  were estimated but DFT calculation.

**Table S1.** Detail information of Lippert–Mataga model for BP-Cz dyads.

	$a_0$ (Å)	$\mu_g$ (D)	$\mu_e$ (D)	$\Delta\mu$ (D)
BP- <i>o</i> -Cz	6.036	2.56	12.02	9.45
BP- <i>m</i> -Cz	6.325	3.81	13.42	9.61
BP- <i>p</i> -Cz	8.563	2.64	18.29	15.65

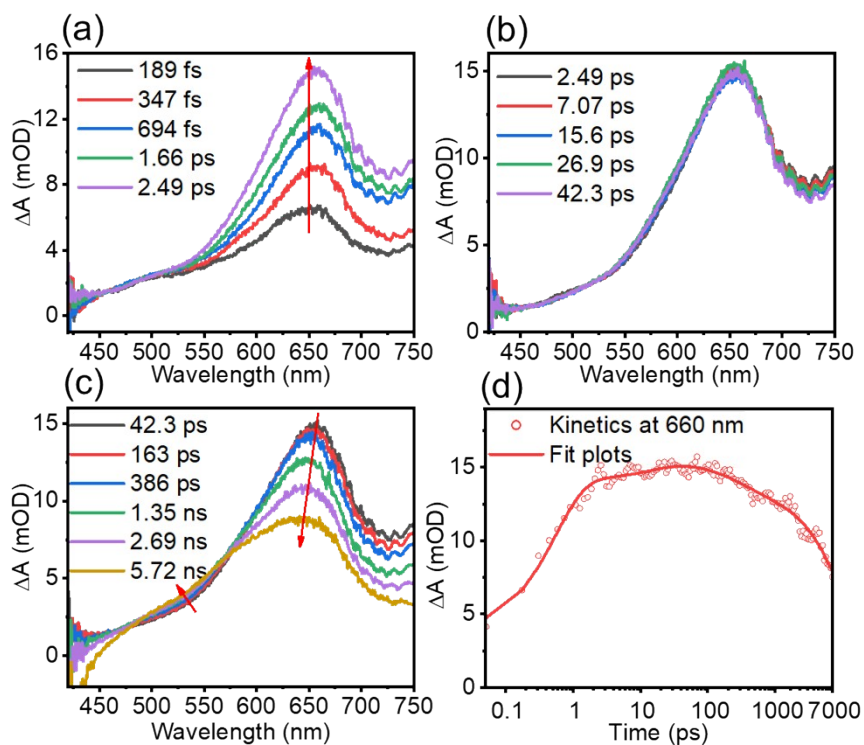


**Figure S8.** Lippert-Mataga plots for BP-Cz dyads.

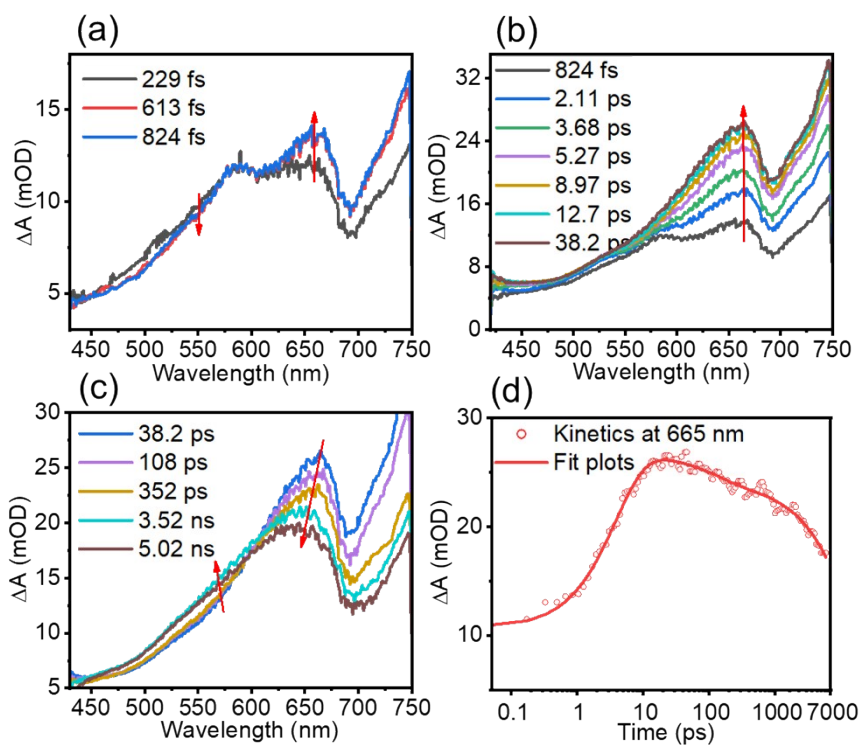
**Table S2.** Fluorescence lifetime of BP-Cz compounds in different solvents.

	$\tau$ [ns]			
	THF	DCM	DMF	DMSO
BP- <i>o</i> -Cz	6.01	10.87	7.21	11.97
BP- <i>m</i> -Cz	5.20	16.91	15.85	15.61
BP- <i>p</i> -Cz	4.73	4.87	6.48	7.51

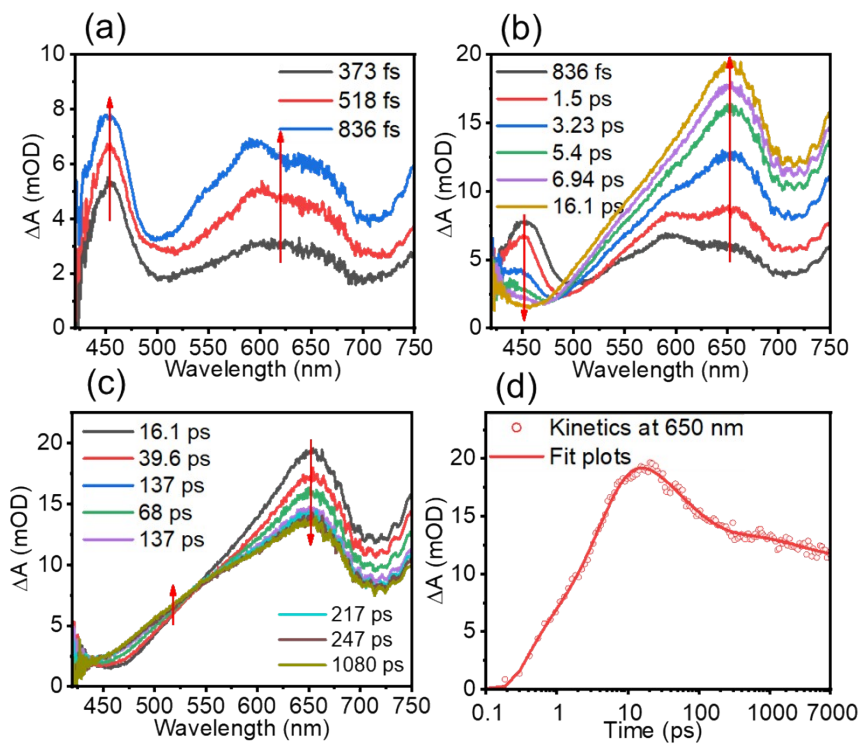
#### 4. Femtosecond and nanosecond transient absorption spectra



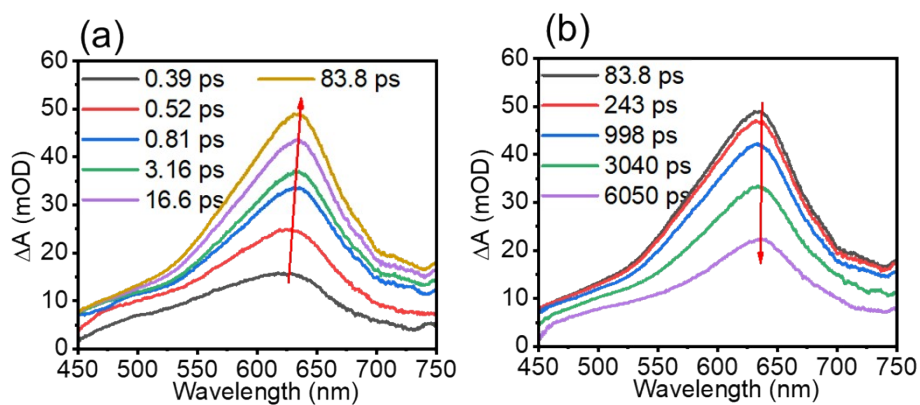
**Figure S9.** Fs-TA spectra of BP-*o*-Cz in THF, 0.1 mM



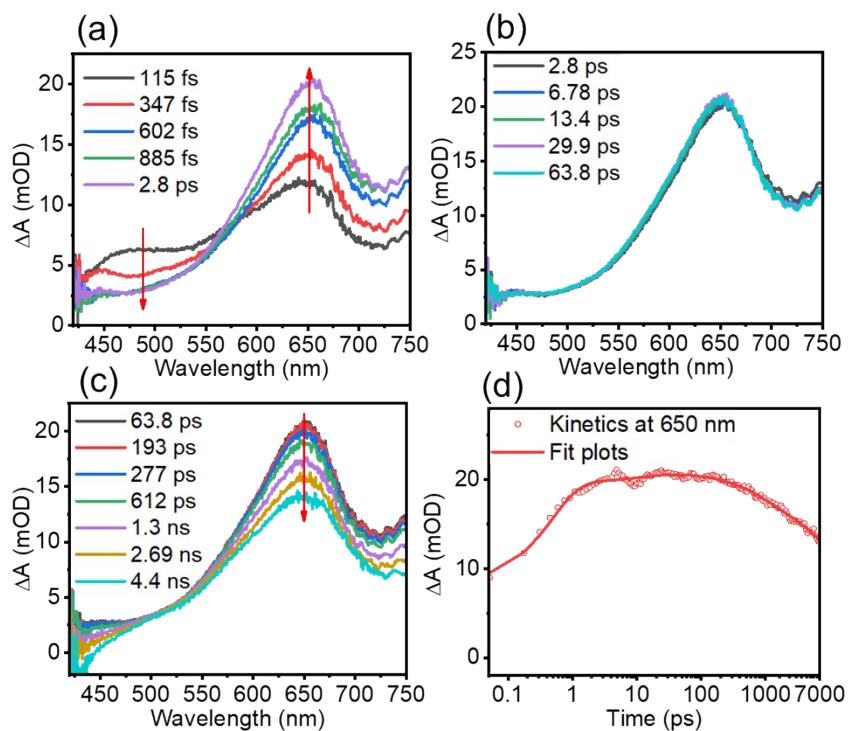
**Figure S10.** Fs-TA spectra of BP-*m*-Cz in THF, 0.1 mM



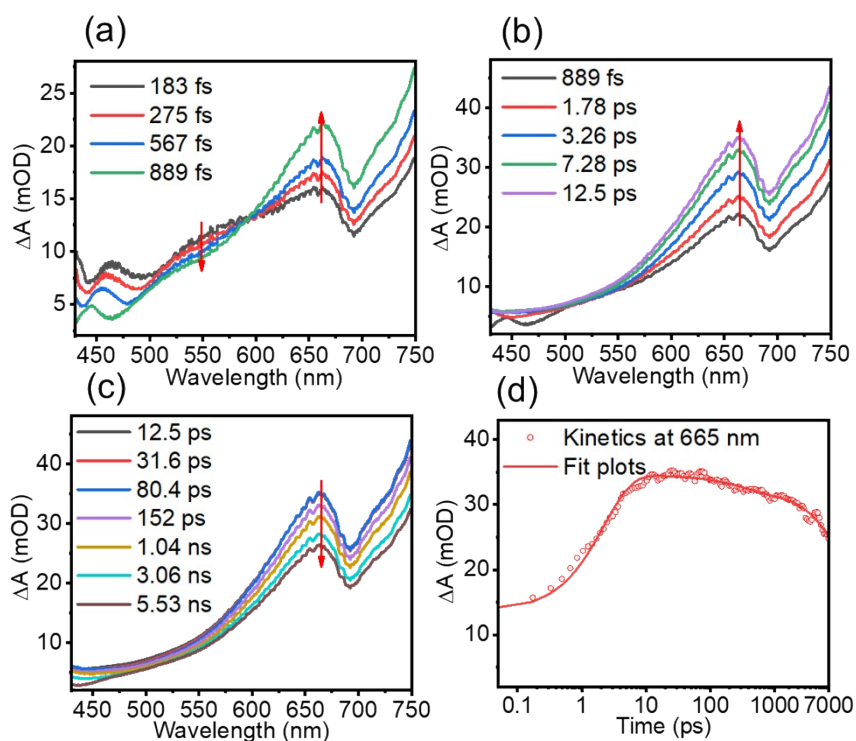
**Figure S11.** Fs-TA spectra of BP-*p*-Cz in THF, 0.1 Mm



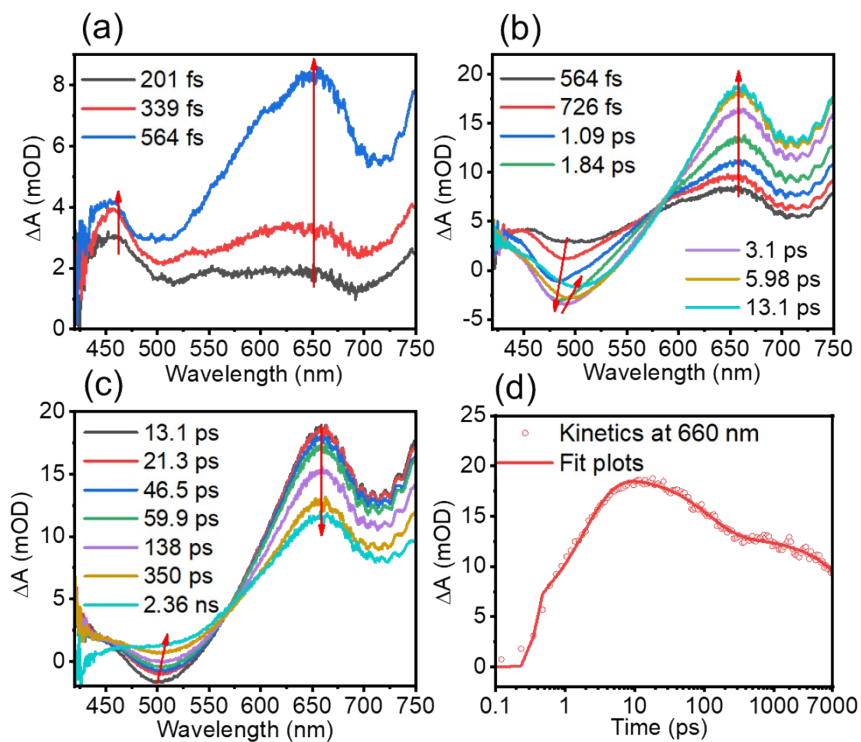
**Figure S12.** Fs-TA spectra of Cz in THF, 0.1 mM



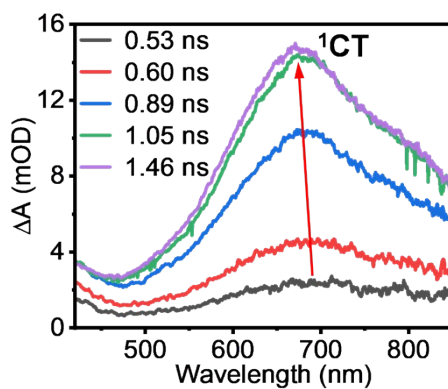
**Figure S13.** Fs-TA spectra of BP-*o*-Cz in DMF, 0.1 mM



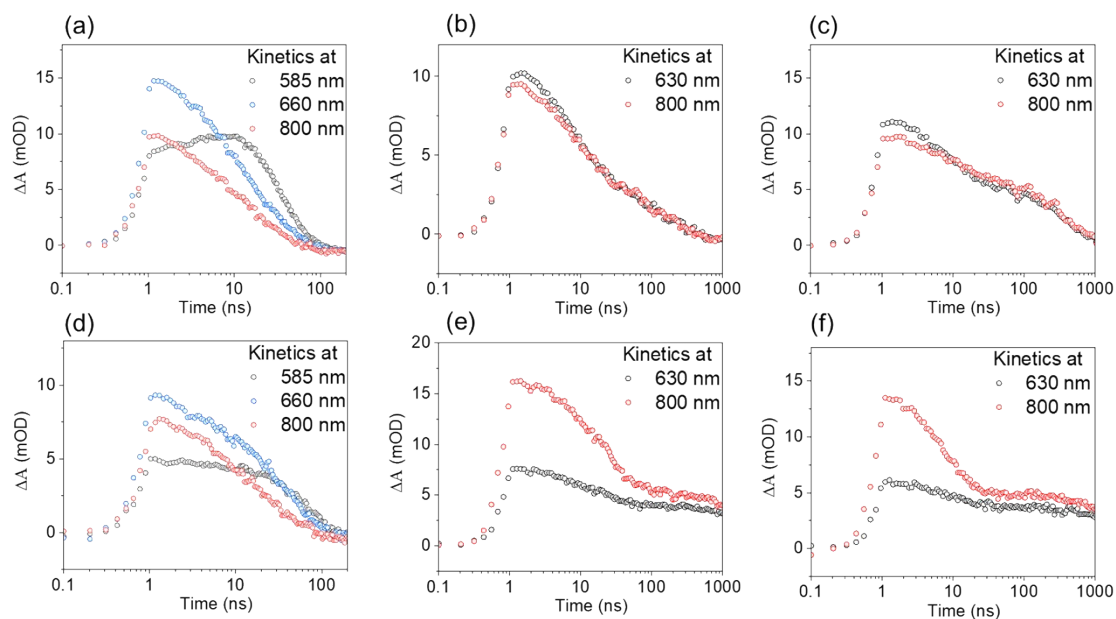
**Figure S14.** Fs-TA spectra of BP-*m*-Cz in DMF, 0.1 mM



**Figure S15.** Fs-TA spectra of BP-*p*-Cz in DMF, 0.1 mM



**Figure S16.** Ns-TA spectra of BP-*o*-Cz in THF, 0.1 mM

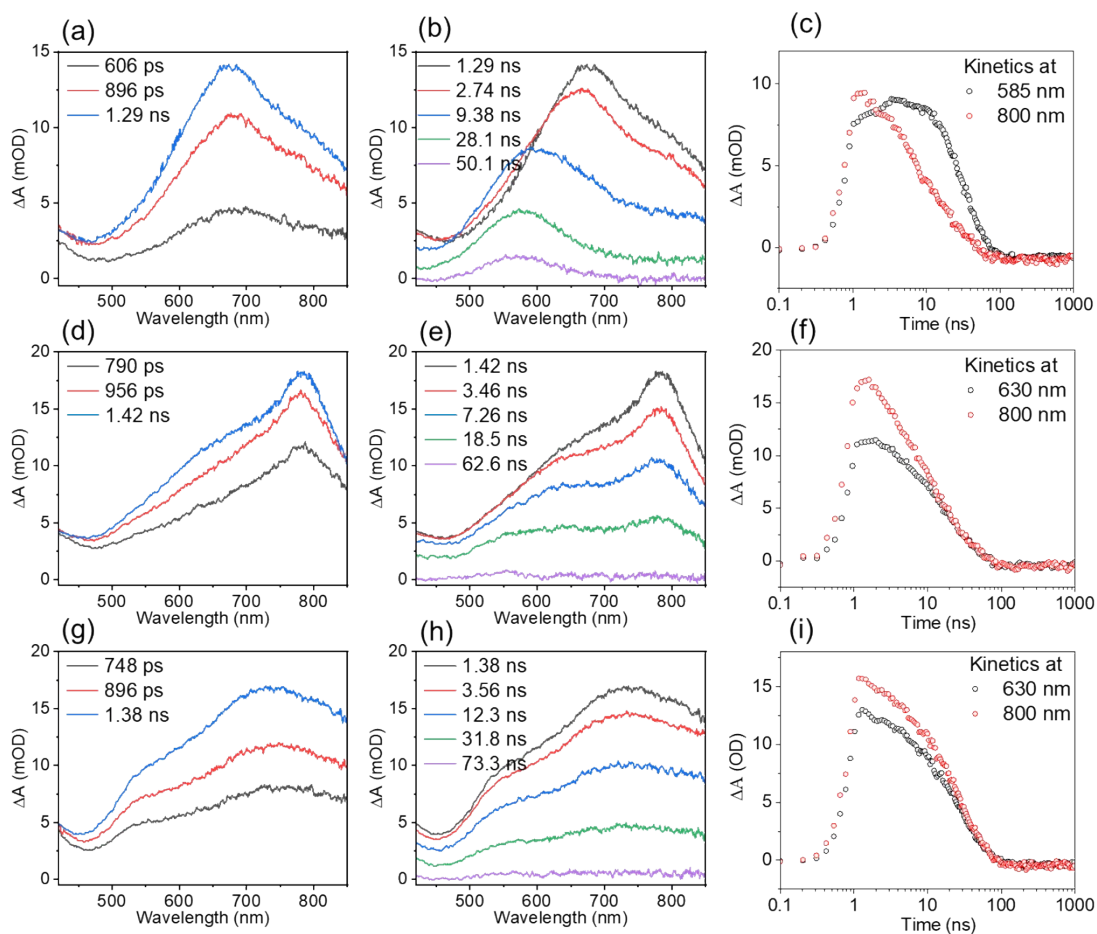


**Figure S17.** Kinetic fitting for (a) BP-*o*-Cz, (b) BP-*m*-Cz and (c) BP-*p*-Cz in THF and for (d) BP-*o*-Cz, (e) BP-*m*-Cz and (f) BP-*p*-Cz in DMF measured by ns-TA, purged by nitrogen.

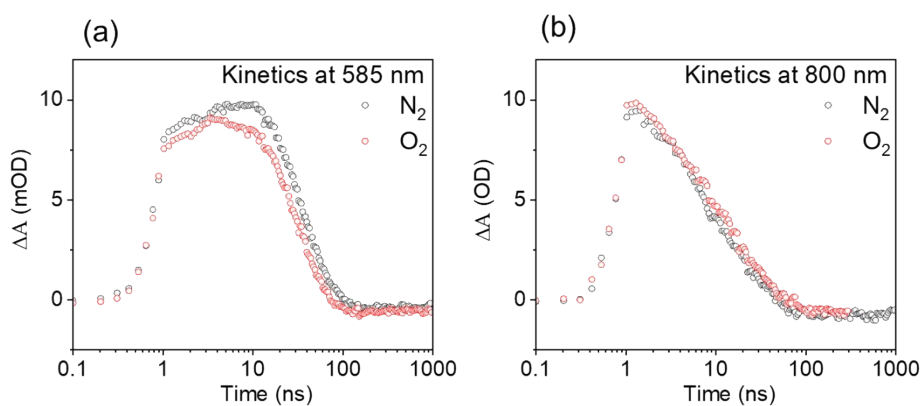
**Table S3.** Lifetimes of BP-Cz dyads measured by ns-TA

		BP- <i>o</i> -Cz			BP- <i>m</i> -Cz		BP- <i>p</i> -Cz		
		$\tau$ [ns]	585 nm	660 nm	800 nm	630 nm	800 nm	630 nm	800 nm
THF	N <sub>2</sub>	$\tau_1$	8.6±0.8	6.6±1.1	3.8±0.9	6.3±0.4	8.9±0.7	8.7±0.7	9.2±1.5
		$\tau_2$	26.0±1.1	26.5±2.0	23.0±1.8	214±46	154±13	423±23	407.3±26
	O <sub>2</sub>	$\tau_1$	8.5±1.3	6.7±1.3	5.1±1.1	6.6±4.5	4.9±0.8	5.0*	5.0*
		$\tau_2$	21.8±1.5	24.3±2.8	23.6±3.0	22.8±2.5	24.0±2.2	27.3±0.9	27.1±1.0
DMF	N <sub>2</sub>	$\tau_1$	5.9±2.0	1.5±0.6	6.8±1.6	15.6±1.4	20.9±0.9	8.6±1.9	7.4±0.4
		$\tau_2$	62.5±4.1	40.6±1.7	38.1±4.9	3510±323	3091±353	3024±235	3830±386
	O <sub>2</sub>	$\tau_1$	1.0*	0.5±0.3	0.4±0.5	12.4±1.9	10.9±2.7	5.0*	4.3±1.2
		$\tau_2$	36.9±2.1	22.6±1.0	16.5±0.9	72.1±13	49.8±11	34.7±8.0	33.6±7.2

\* Fix in kinetic fitting.



**Figure S18.** Ns-TA spectra and kinetic fitting of (a-c) BP-*o*-Cz, (d-f) BP-*m*-Cz and (g-i) BP-*p*-Cz in THF, 0.1 mM, purged by oxygen.



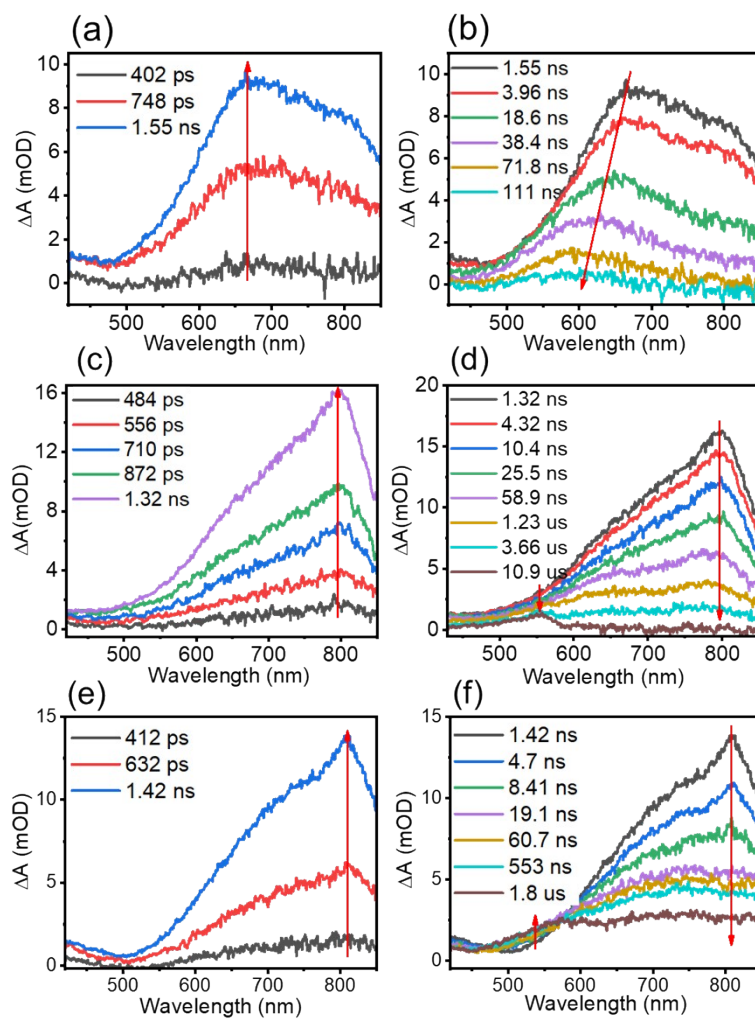
**Figure S19.** Kinetic fitting of BP-*o*-Cz under N<sub>2</sub> and O<sub>2</sub> conditions in THF, 0.1 mM.

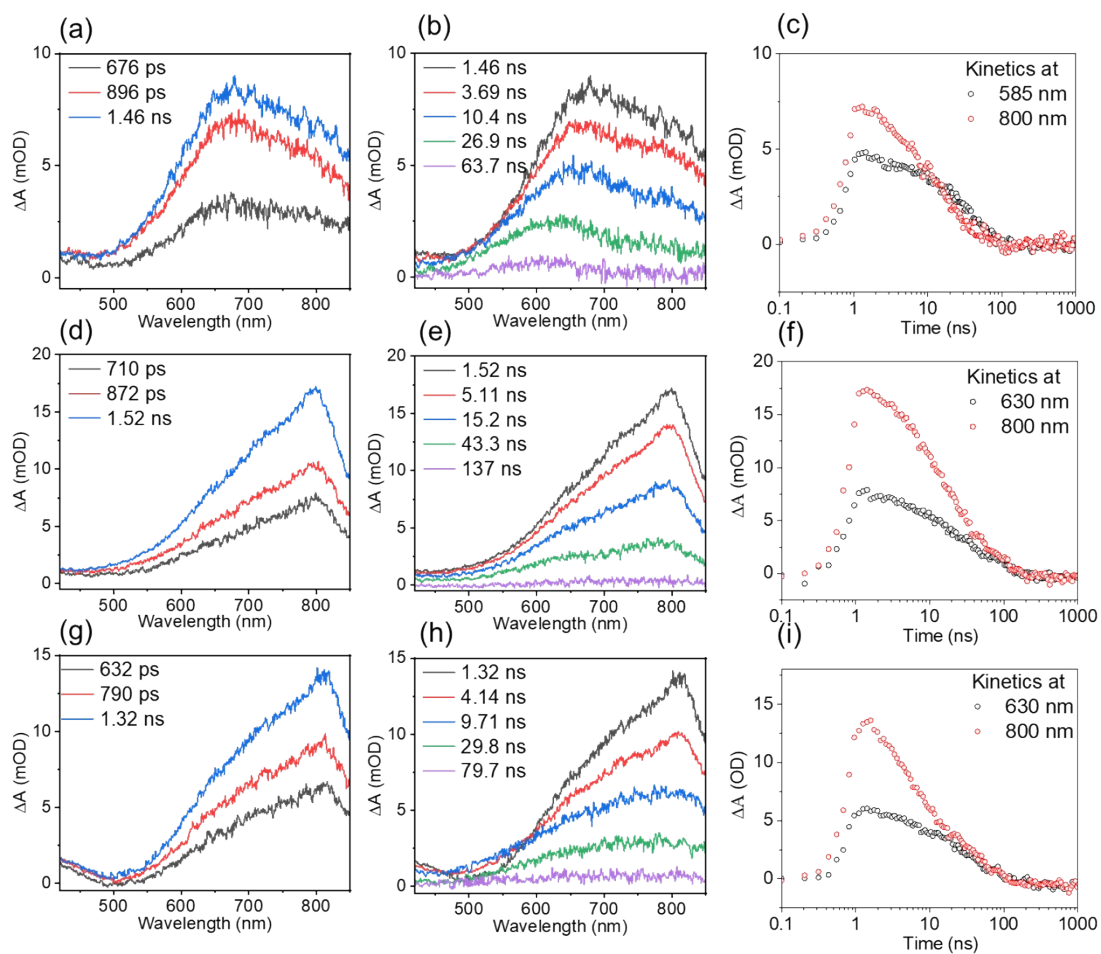


**Table S4.** Quenching rate constant of BP-Cz dyads in ns-TA.

	BP- <i>o</i> -Cz			BP- <i>m</i> -Cz		BP- <i>p</i> -Cz		
	585 nm	660 nm	800 nm	630 nm	800 nm	630 nm	800 nm	
THF	$k_{N_2} (\times 10^7 s^{-1})$	3.85	3.77	4.35	0.47	0.65	0.24	0.25
	$k_{O_2} (\times 10^7 s^{-1})$	4.59	4.12	4.24	4.39	4.17	3.66	3.69
	$k_{quenched} (\times 10^7 s^{-1})$	0.74	0.34	-0.11	3.92	3.52	3.43	3.44
DMF	$k_{N_2} (\times 10^7 s^{-1})$	1.60	2.46	2.62	0.03	0.03	0.03	0.03
	$k_{O_2} (\times 10^7 s^{-1})$	2.71	4.42	6.06	1.39	2.01	2.88	2.98
	$k_{quenched} (\times 10^7 s^{-1})$	1.11	1.96	3.44	1.36	1.98	2.85	2.95

The  $k_{N_2}$  and  $k_{O_2}$  are calculated by the  $\tau_2$  from kinetic fitting measured by ns-TA,  $k_{quenched}$  is calculated from the rate constant equation:  $k_{N_2} + k_{quenched} = k_{O_2}$ .

**Figure S20.** ns-TA spectra of (a, b) BP-*o*-Cz, (c, d) BP-*m*-Cz and (e, f) BP-*p*-Cz in DMF, 0.1 mM, purged by nitrogen.

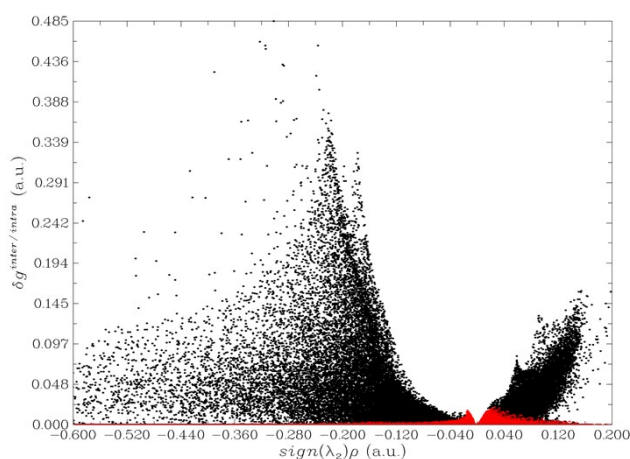


**Figure S21.** Ns-TA spectra and kinetic fitting of (a-c) BP-*o*-Cz, (d-f) BP-*m*-Cz and (g-i) BP-*p*-Cz in DMF, 0.1 mM, purged by oxygen.

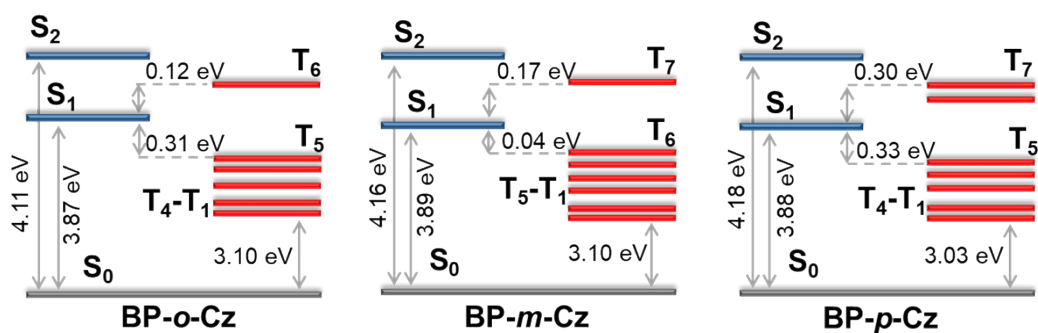
## 5. Theoretical calculations

**Table S5.** Oscillator strengths,  $\Delta r$  index and orbital contribution of  $S_1$  and  $S_2$  for BP-Cz dyads

	$S_1$			$S_2$		
	f	$\Delta r$ (Å)	orbital contribution	f	$\Delta r$ (Å)	orbital contribution
<b>BP-<i>o</i>-BCz</b>	0.0089	0.68	86-92 0.32 91-92 0.38	<b>0.0183</b>	1.95	<b>91-92 0.57</b>
<b>BP-<i>m</i>-BCz</b>	0.0012	0.831	84-92 0.43 88-92 0.45	<b>0.0127</b>	3.829	<b>91-92 0.64</b>
<b>BP-<i>p</i>-BCz</b>	0.0129	0.774	84-92 0.42 89-92 0.46	<b>0.3437</b>	3.524	<b>91-92 0.62</b>



**Figure S22.**  $\delta g^{\text{intra/inter}}$  vs  $\text{sign}(\lambda_2)\rho$  of intermolecular interaction of BP-*o*-BCz



**Figure S23.** Excited-state energy level of BP-Cz dyads

**Table S6.** SOC constants related to S<sub>1</sub> and S<sub>2</sub> of BP-Cz dyads

BP- <i>o</i> -Cz	BP- <i>m</i> -Cz	BP- <i>p</i> -Cz
$\xi_{S_2-T_6} = 0.721 \text{ cm}^{-1}$	$\xi_{S_2-T_7} = 0.425 \text{ cm}^{-1}$	$\xi_{S_2-T_7} = 0.388 \text{ cm}^{-1}$
$\xi_{S_1-T_6} = 1.668 \text{ cm}^{-1}$	$\xi_{S_1-T_7} = 6.993 \text{ cm}^{-1}$	$\xi_{S_2-T_6} = 0.465 \text{ cm}^{-1}$
$\xi_{S_1-T_5} = 2.882 \text{ cm}^{-1}$	$\xi_{S_1-T_6} = 0.973 \text{ cm}^{-1}$	$\xi_{S_1-T_7} = 0.062 \text{ cm}^{-1}$
$\xi_{S_1-T_4} = 5.879 \text{ cm}^{-1}$	$\xi_{S_1-T_5} = 3.719 \text{ cm}^{-1}$	$\xi_{S_1-T_6} = 3.789 \text{ cm}^{-1}$
$\xi_{S_1-T_3} = 9.033 \text{ cm}^{-1}$	$\xi_{S_1-T_4} = 12.377 \text{ cm}^{-1}$	$\xi_{S_1-T_5} = 3.260 \text{ cm}^{-1}$
$\xi_{S_1-T_2} = 13.546 \text{ cm}^{-1}$	$\xi_{S_1-T_3} = 3.573 \text{ cm}^{-1}$	$\xi_{S_1-T_4} = 12.498 \text{ cm}^{-1}$
$\xi_{S_1-T_1} = 0.643 \text{ cm}^{-1}$	$\xi_{S_1-T_2} = 1.749 \text{ cm}^{-1}$	$\xi_{S_1-T_3} = 3.24 \text{ cm}^{-1}$
	$\xi_{S_1-T_1} = 15.971 \text{ cm}^{-1}$	$\xi_{S_1-T_2} = 0.116 \text{ cm}^{-1}$
		$\xi_{S_1-T_1} = 16.152 \text{ cm}^{-1}$
$\xi_{\text{Total}}: 34.372$	$\xi_{\text{Total}}: 45.780$	$\xi_{\text{Total}}: 39.970$

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