Electronic Supplementary Information:

Symmetry-breaking charge separation in weakly coupled anthracene dimers

Liping Lv[†, a], Heyuan Liu[†, a, *], Tianyu Li[a], Boce Cui[a], Tianying Wang[a], Xiaojuan Song[a], Wenmiao Chen[b], Yanli Chen[a], and Xiyou Li[a, *]

Content

1. ¹H NMR spectra and MALDI-TOF spectra of Ph-BPEA and *o-/m-/p-* dimer
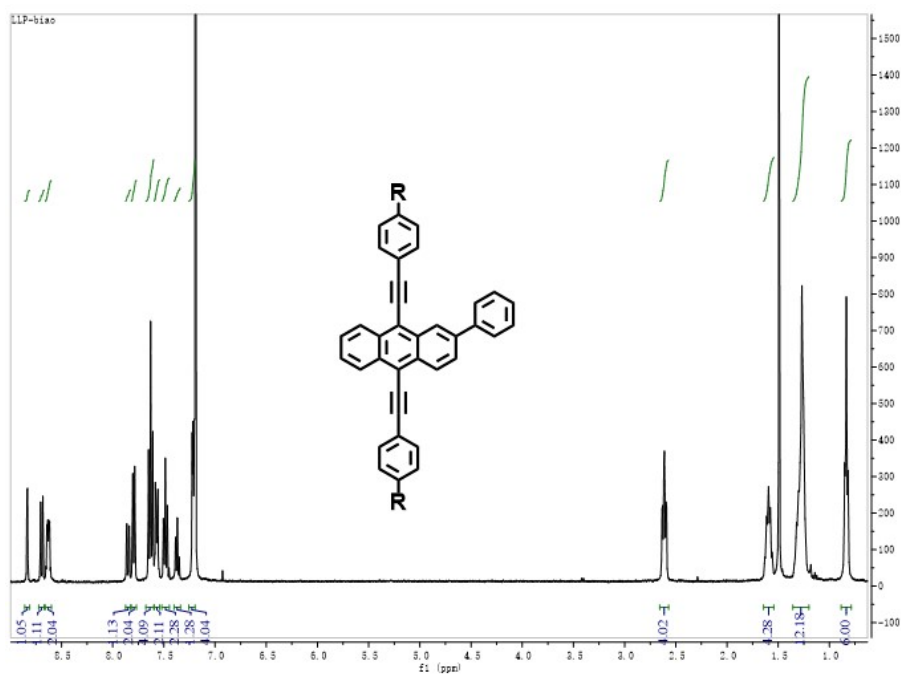

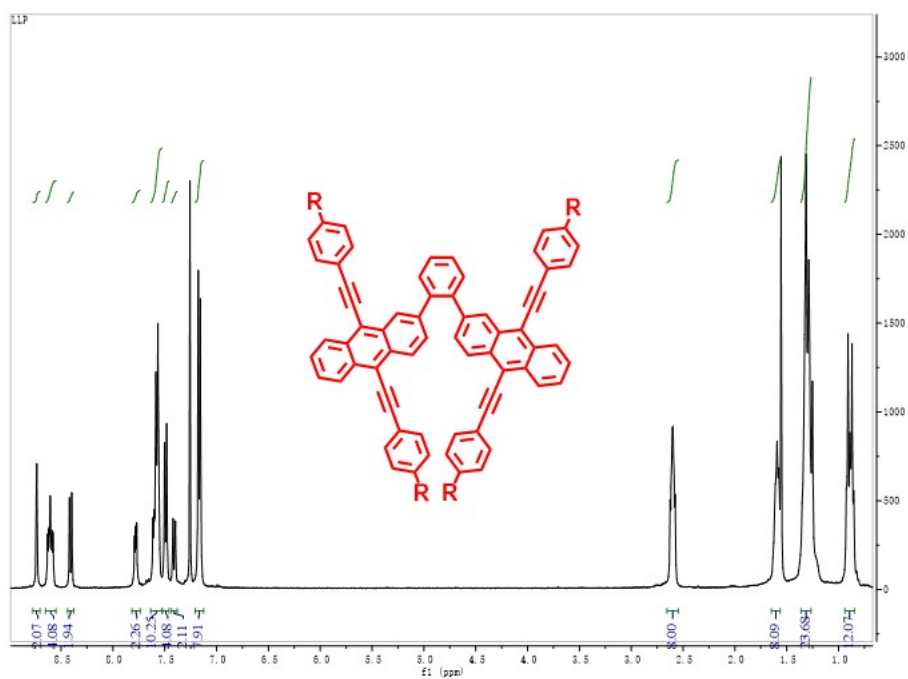**Fig. S1** The ¹H NMR spectrum of Ph-BPEA.

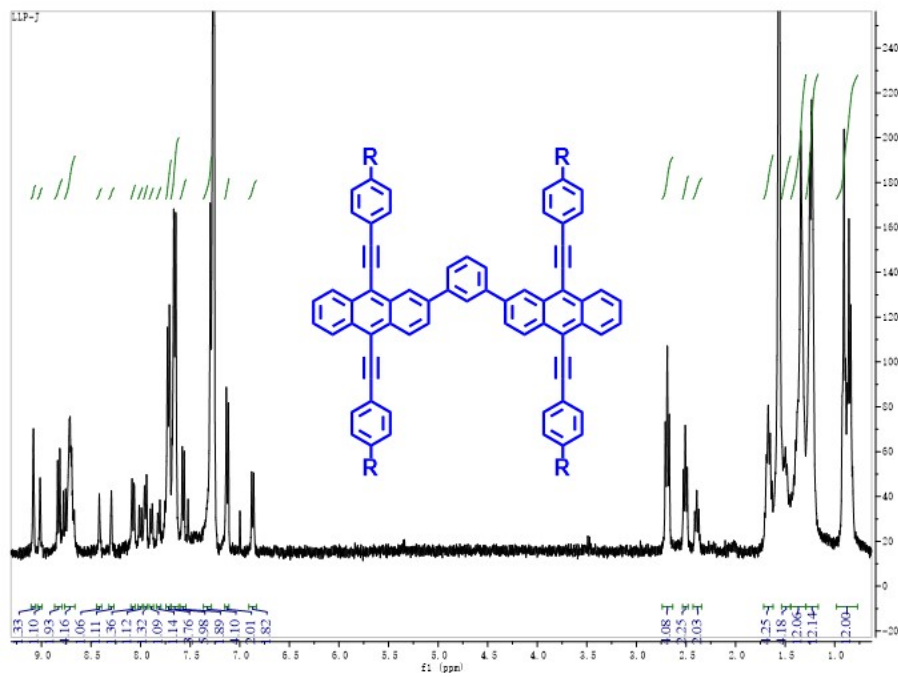**Fig. S2** The ¹H NMR spectrum of *o*-dimer.

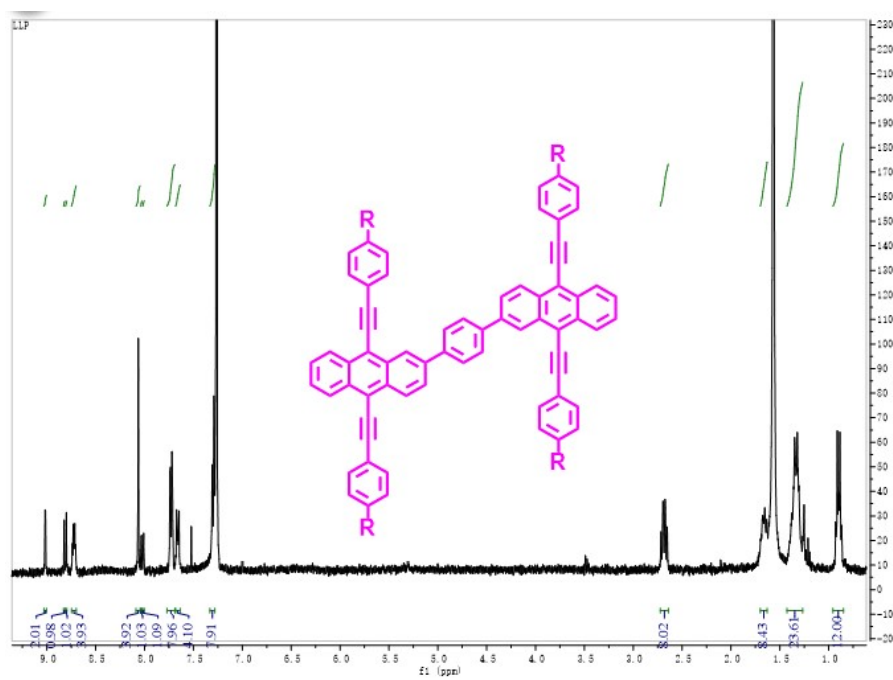**Fig. S3** The ^{1}H NMR spectrum of *m*-dimer.

Fig. S4 The ^{1}H NMR spectrum of *p*-dimer.
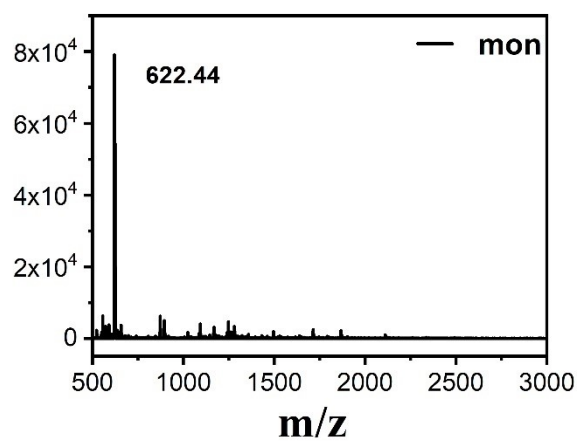
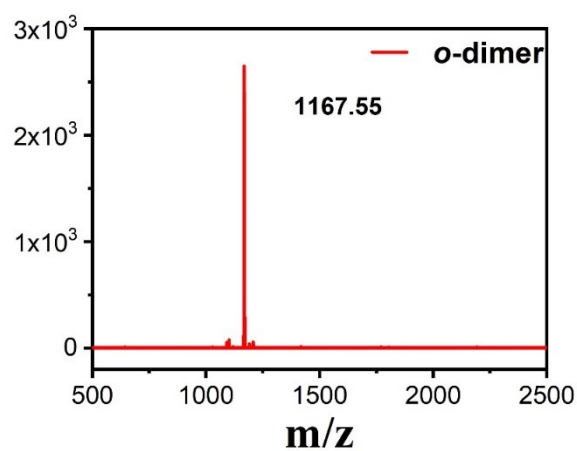**Fig. S5** The MALDI-TOF spectrum of Ph-BPEA

Fig. S6 The MALDI-TOF spectrum of *o*-dimer.
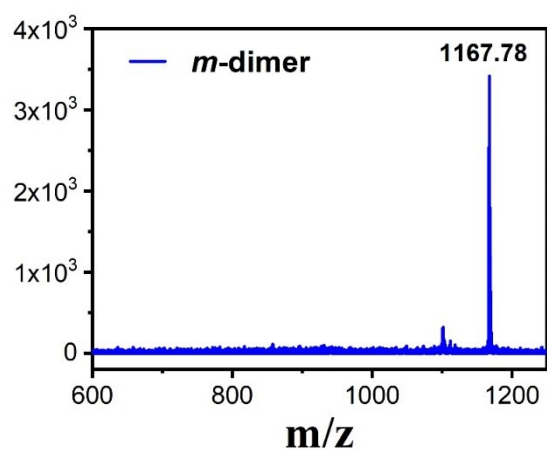
Fig. S7 The MALDI-TOF spectrum of *m*-dimer.
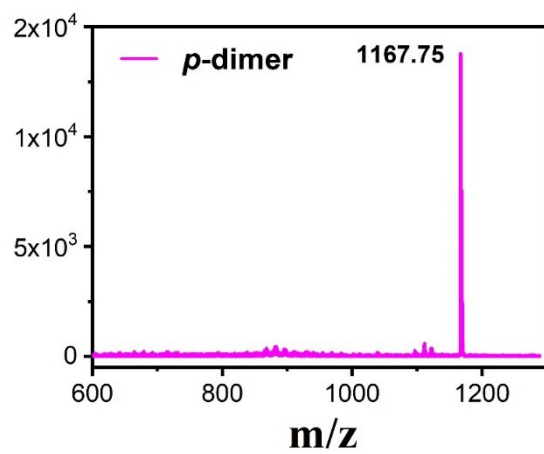
Fig. S8 The MALDI-TOF spectrum of *p*-dimer.

2. CV and DPV of Ph-BPEA and *o-/m-/p-* dimer
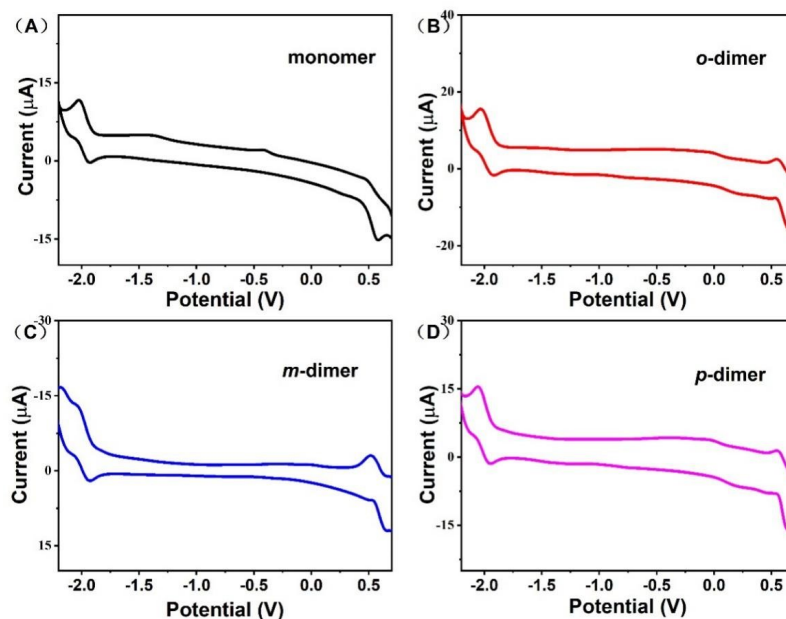
Fig. S9 CV plots of *o*-dimer, *m*-dimer and *p*-dimer as well as their monomer in dry dichloromethane containing 0.1 M (nBu)₄NPF₆ as the supporting electrolyte and ferrocene as an internal reference.
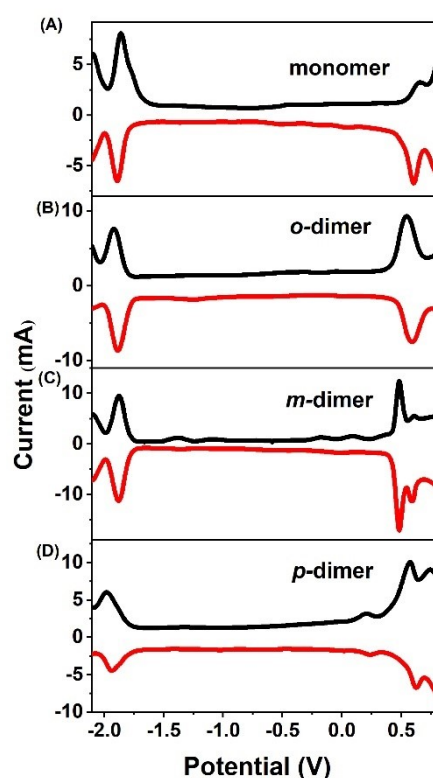
Fig. S10 DPV plots of *o*-dimer, *m*-dimer and *p*-dimer as well as their monomer in dry dichloromethane containing 0.1 M (nBu)₄NPF₆ as the supporting electrolyte and ferrocene as an internal reference.

3. Solvent-polarity-dependent absorption experiment of *o-/m-/p-* dimer
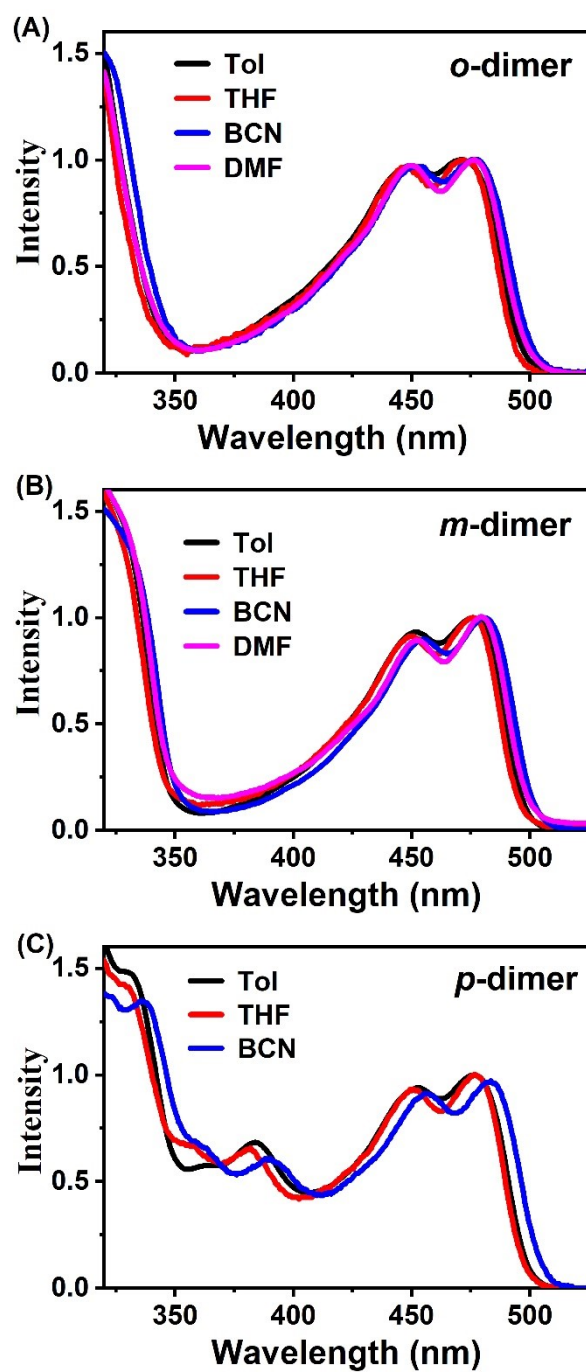
Fig. S11 Absorption spectra of *o*-dimer (A), *m*-dimer (B) and *p*-dimer (C) in different polarity solvents.

4. The fluorescence spectra and dynamics of monomer Ph-BPEA

Fig. S12 The fluorescence spectra (A) and dynamics (B) of monomer Ph-BPEA.

5. *fs*-TA spectra of *o-/m-/p*-dimer inTHF excited at 420 nm

Fig. S13 (A, B) *fs*-TA spectra of *o*-dimer in THF excited at 420 nm. (C) Single-wavelength dynamics probed at different wavelengths (dotted line). The black solid line shows the fitting line from global analysis. (D) Species-associated spectra obtained from global analysis.
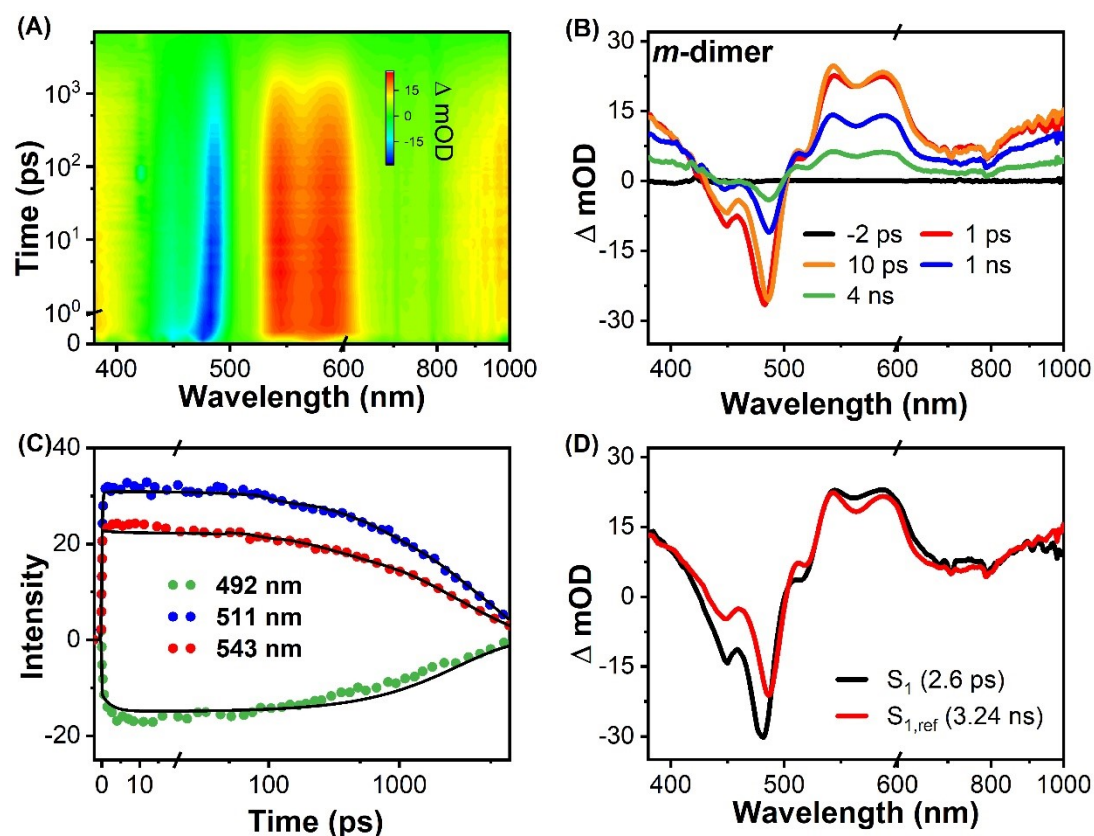
Fig. S14 (A, B) *fs*-TA spectra of *m*-dimer in THF excited at 420 nm. (C) Single-wavelength dynamics probed at different waveleng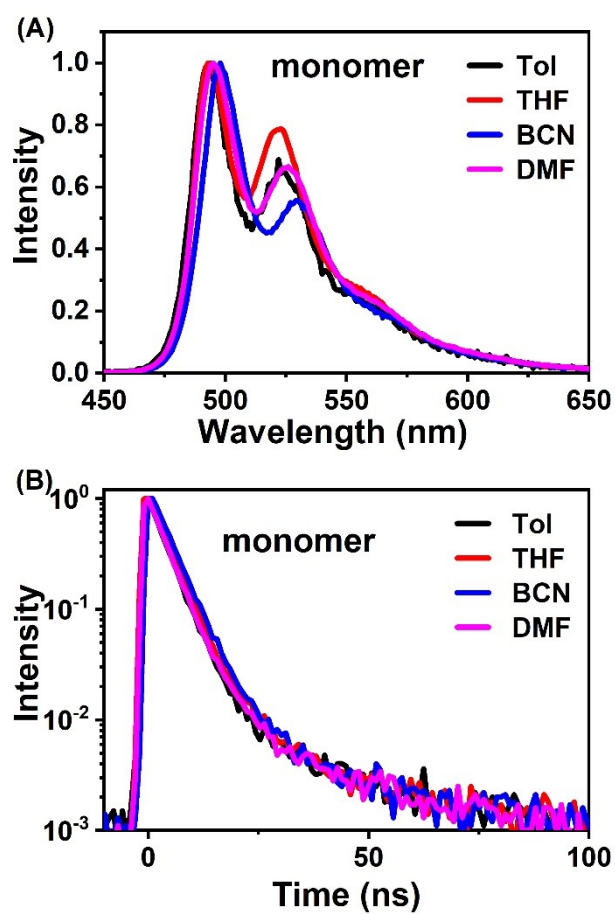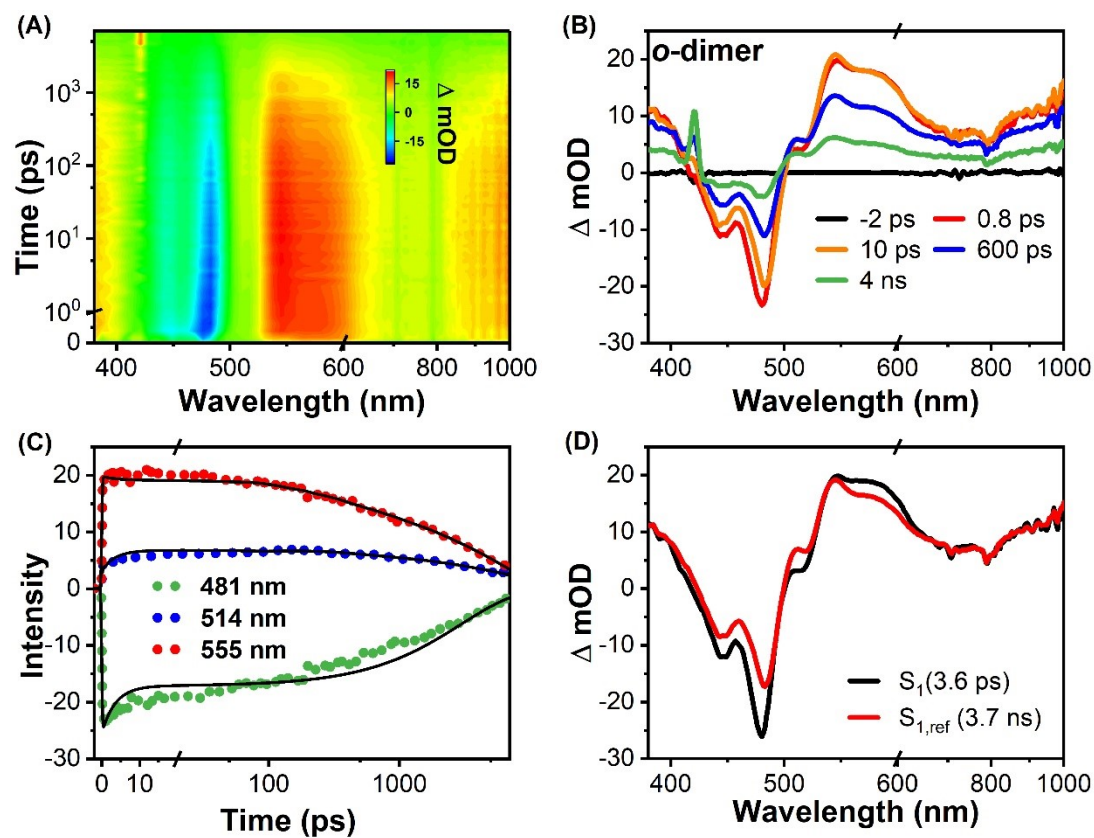ths (dotted line). The black solid line shows the fitting line from global analysis. (D) Species-associated spectra obtained from global analysis.
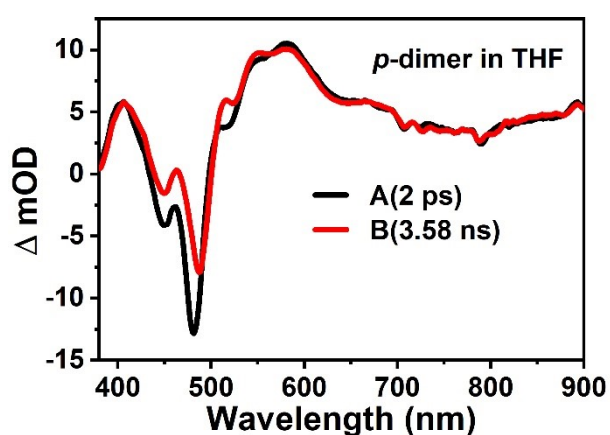
Fig. S15 Species-associated spectra of *p*-dimer in THF obtained from global analysis.

6. Electron transfer experiment
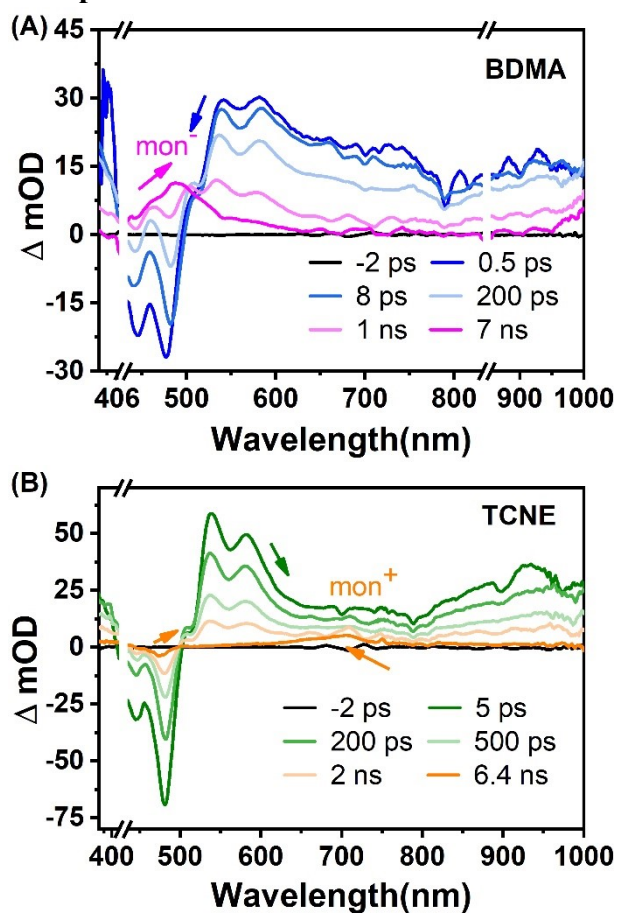
Fig. S16 *fs*-TA Spectra of monomer in the presence of N, N-dimethylphenylamine (A) or tetrachyanethene (B) excited at 420 nm.

The TA spectra of monomer Ph-BPEA in the presence of N, N-dimethylphenylamine or tetrachyanethene clearly reveal that both radical anionic and cationic features of BPEA.

7. *fs*-TA spectra of *o-/m-/p-* dimer in polystyrene (PS) film and polymethyl methacrylate (PMMA) film

Fig. S17 *fs*-TA experiment of *o*-dimer (A, D), *m*-dimer (B, E) and *p*-dimer (C, F) in PS and PMMA film excited at 420 nm.
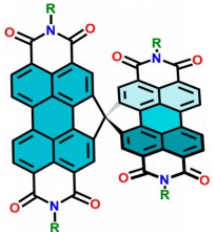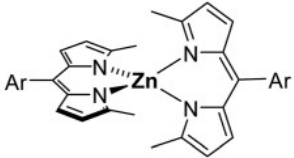
8. Charge separation and charge recombination rates
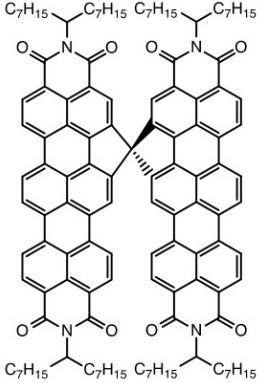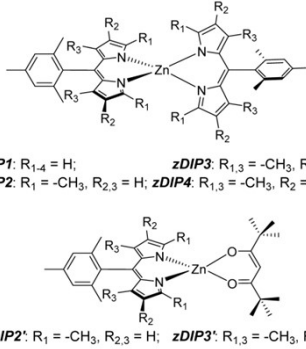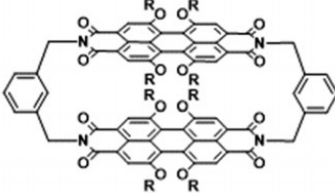
Table S1: Comparison of charge separation and charge recombination rates of *o-/m-/p-* dimer.

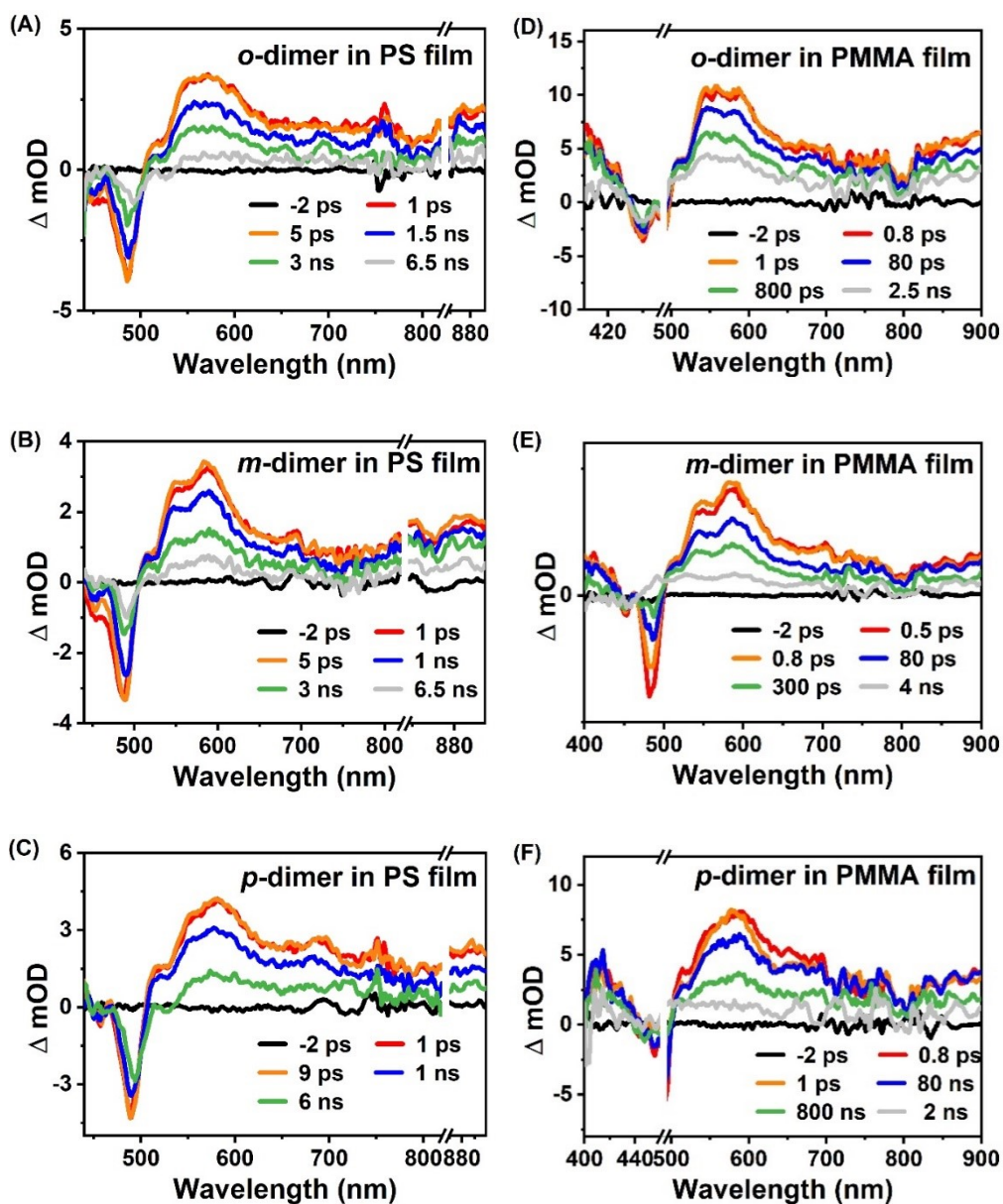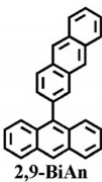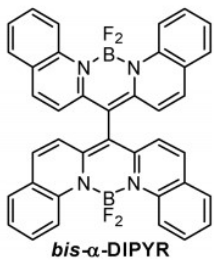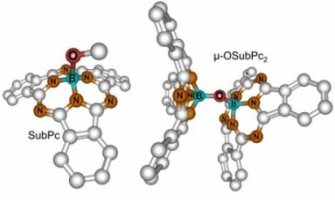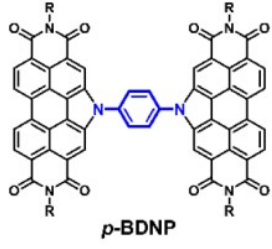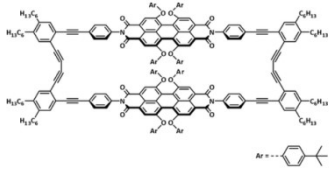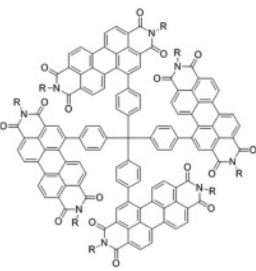|	Solvent	$1/K_{CS}$	$1/K_{CR}$	K_{CR}/K_{CS}
o-dimer	BCN	39 ps	10.3 ns	26
	DMF	8 ps	20 ns	2500
m-dimer	BCN	165 ps	7.1 ns	43
	DMF	77 ps	12.8 ns	166
p-dimer	BCN	55 ps	8.1 ns	147
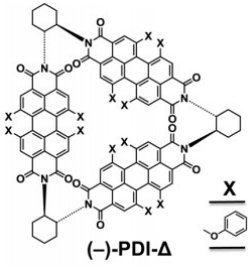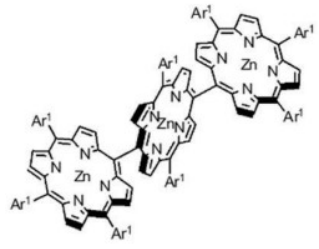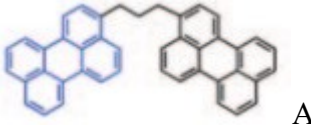
Table S2: Comparison of charge separation and charge recombination rates in different derivatives in the literature.
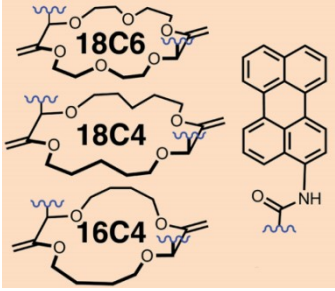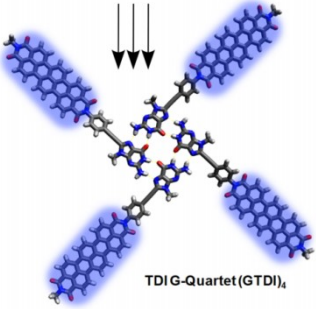
Contributed by	Molecule	Solvent	$1/K_{CS}$	$1/K_{CR}$	K_{CR}/K_{CS}
Heyuan Liu, Xiyou Li and co-workers	Orthogonal anthracene dimer 2,9-BiAn Mater. Horiz., 2019,6, 990	DMF	3.2 ps	11.69 ns	3653
Mark E. Thompson and co-workers	Boron dipyridylmethene dimer	ACN	1.4 ps	4.2 ns	3000

	 ACS Appl. Energy Mater. 2018, 1, 1083−1095				
Ebin Sebastian and Mahesh Hariharan	Spiro-conjugated perylenediimide dimer J. Am. Chem. Soc. 2021, 143, 13769−13781	ACN	0.627 ps	1.66 ns	2647
Mark E. Thompson and co-workers	two dipyrrin ligands coordinated in a tetrahedral geometry at the Zn^{2+} ion Faraday Discuss., 2019, 216, 379	ACN	1.1 ps	0.9 ns	818
Michael R. Wasielewski and co-workers	Spiro-Fused Terrylenediimide Dimer	THF	5.9 ps	2.05 ns	339

	J. Phys. Chem. B 2021, 125, 6945−6954				
Mark E. Thompson and co-workers	Zinc Dipyrrins zDIP1: R$_{1-4}$ = H; zDIP3: R$_{1,3}$ = -CH$_3$, R$_2$ zDIP2: R$_1$ = -CH$_3$, R$_{2,3}$ = H; zDIP4: R$_{1,3}$ = -CH$_3$, R$_2$ = zDIP2': R$_1$ = -CH$_3$, R$_{2,3}$ = H; zDIP3': R$_{1,3}$ = -CH$_3$, R J. Phys. Chem. C 2014, 118, 21834−21845	polar solvents	1-5.5 ps	0.9-3.3 ns	163-333
Michael R. Wasielewski and co-workers	Perylenediimide Cyclophanes J. Phys. Chem. C 2020, 124, 10408−10419	CH$_2$Cl$_2$	23.5 ps	7.36 ns	313
Stephen R. Meech and co-workers	Subphthalocyanine Dimer	ACN	1.2 ps	307 ps	255

	 Angew. Chem. Int. Ed. 2021, 60, 10568 – 10572				
Andong Xia and co-workers	Isomeric N-Annulated Perylene Diimide Dimers J. Am. Chem. Soc. 2019, 141, 12789−12796	THF	12.4 ps	1.94 ns	156
Dongho Kim and co-workers	1,6,7,12-tetra(4-tert-butylphenoxy)perylene dimer J. Phys. Chem. Lett. 2019, 10, 8, 1919-1927	BCN	23-25 ps	2.5-2.8 ns	121-100
Andong Xia and co-workers	Multibranched Perylene Diimide Molecules 	DMF	44.7 ps	4.8 ns	107

	J. Phys. Chem. Lett. 2020, 11, 10329−10339				
Michael R. Wasielewski and co-workers	Perylenediimide Molecular Triangles (−)-PDI-Δ J. Am. Chem. Soc., **2015**, 137,13236	CH$_2$Cl$_2$	12 ps	1.12 ns	93
Dongho Kim and co-workers	push–pull porphyrin arrays Phys. Chem. Chem. Phys., 2017, 19, 13970	BCN	39 ps	760 ps	19.48
Eric Vauthey and co-workers	1,3-bis(3-perylenyl)propane bichromophoric dyad A ngew. Chem. Int. Ed. 2011, 50, 7596 –7598	ACN	12 ps	130 ps	10.8
Eric Vauthey and co-workers	perylene bichromophores	18C4 ACN	4.3 ns	41.1 ns	9.5

	Chem. Sci., 2019, 10, 10629	18C6 ACN	25 ns	40 ns	1.6
Michael R. Wasielewski and co-workers	J. Am. Chem. Soc. 2019, 141, 17512−17516	THF	192 ps	1.6 ns	8.3

9. Theoretical calculation

The Gibbs free energy are calculated based on the Rehm−Weller equation[1-3].

$$\Delta G_{CS} = e(E_{OX} - E_{RED}) - E^* + \Delta G_S \quad (1)$$

$$\Delta G_S = -\frac{e^2}{4\pi\varepsilon_0\varepsilon_S R_{CC}} - \frac{e^2}{8\pi\varepsilon_0}\left(\frac{1}{R_A} + \frac{1}{R_D}\right)\left(\frac{1}{\varepsilon_{REF}} - \frac{1}{\varepsilon_S}\right) \quad (2)$$

$$\Delta G_{CR} = (-E^* + \Delta G_{CS}) \quad (3)[4]$$

Where, E_{OX} and E_{RED} are the first oxidation and first reduction potentials of *o/m/p-*dimer in CH_2Cl_2 calculated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) with the ferrocene/ferrocenium (Fc/Fc$^+$) couples as reference. (Fig. S9, S10). ε_S is the dielectric constant of the actual solvent (Tol, THF, BCN and DMF, with ε = 2.38, 7.58, 24.50 and 36.70, respectively). E^* is the energy of the singlet excited state. ε_{REF} is the dielectric constant of the reference solvent used in electrochemistry (DCM: 9.3). R_{CC} is the donor-acceptor distance. R_A and R_D are hard-sphere radii, approximately $\frac{R_{CC}}{2}$. The calculated results are shown in Table 3 of main text.

Reference

1.   E. Sebastian and M. Hariharan, *ACS Energy Letter.*, 2022, **7**, 696-711.
2.   R. A. Marcus, *J. Chem. Phys.*, 2020, **153**, 210401.
3.   R. A. Marcus, *J. Chem. Phys.*, 1965, **43**, 679-701.

4.   E. Sebastian and M. Hariharan, *J. Am. Chem. Soc.*, 2021, **143**, 13769-13781.