Support Information

Donor-Acceptor Fluorophores as efficient energy transfer photocatalysts for [2+2] photodimerization

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General Methods

All solvents and reagents were purchased from commerial sources and used without further purification, unless otherwise noted. ¹H NMR spectroscopy was performed on a Bruker Avance III 500 spectrometer. All chemical shifts were reported in ppm using tetramethylsilane as a reference. HPLC spectra were measured in Agilent 1260. High-resolution mass spectra (HRMS) were recorded on an electrospray ionization (ESI) quadrupole time-of-flight mass spectrometer.

The zero-zero vibrational state excitation energy $E_{0,0}$ was estimated by the corresponding energy of the wavelength of emission and absorption. Excited state oxidation and reduction potentials were calculated by the following approximating formulas: $E_{0,0}={}^{*}E_{1/2} \text{ ox-} E_{1/2 \text{ red}}=E_{1/2 \text{ OX}}-{}^{*}E_{1/2 \text{ red}}$

Optimization of conditions and general procedure

General procedure for photoreaction:

A flame-dried flask (15 mL) was equipped with magnetic stir bar and charged with chalcone (0.105 g, 0.5 mmol), t-Bu-4CzIPN (0.006 g, 1 mol%) and 1,4-dioxane (5 mL). The reaction mixture was degassed by purging thoroughly with argon for 10 minutes, then irradiated by LED (20 W) under a balloon argonatmosphere at room temperature for about 24h. (Figure S 1. a) When reaction was finished, the mixture was evaporated to remove the solvent and the residue was purified by flash chromatography on silica gel (chalcone and its derivatives are eluted with hexane/ethyl acetate = 95:5) to afford the desired product.

General procedure for Gram-Scale synthesis

A Jacketed reactor (110 mL, gas replacement with argon) was equipped with magnetic stir bar and charged with chalcone (2.1 g, 10 mmol), t-Bu-4CzIPN (0.12 g, 1 mol %) and degassed 1,4-dioxane (100 mL). The reaction mixture was degassed by purging thoroughly with argon for 15 minutes, then irradiated by 420 nm LED (20 W*2) under a balloon argonatmosphere at room temperature for about 48h.(Figure S 1.b) When reaction was finished, the mixture was evaporated to remove the solvent and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate = 98:2 to 10:1) to afford the desired product. 1.38 g, 65.7% yield.



Figure S 1. Reaction device schematic. a) General procedure for photoreaction. b) General procedure for Gram-Scale synthesis.

	4CzIPN (1 mol%)	
2	Ar, RT 425 nm LED	

Entry	4CzIPN	Solvent	Yield ^b
1	1.0 mol%	1,4-dioxane	68%
2	1.0 mol%	CHCl ₃	60%
3	1.0 mol%	CH ₃ CN	27%
3	1.0 mol%	THF	59%
4	1.0 mol%	CH ₃ Ph	63%
5	1.0 mol%	DMC	61%
6 ^c	1.0 mol%	1,4-dioxane	0%
7	-	1,4-dioxane	22%

[a] reaction condition: 0.5 mmol chalcone, 1 mol % 4CzIPN, 5 mL solvent, Ar, 425 nm LED, room temperature. [b] Product yield determined by HPLC using diethyl phthalate as the internal standard. [c] no light.

Table S 2. The optimization of dimerization of chalcone using t-Bu-4CzIPN.

Entry	wavelength	additive	Time	Yield ^b
1	425 nm	-	24 h	71%
2	455 nm	-	24 h	68%
3	395 nm	-	24 h	53%
4	425 nm	-	13 h	61%
5	425 nm	-	30 h	71%

6	425 nm	Net ₃ (2.0 eq.)	24 h	Trace.
7	425 nm	TEMPO (0.5 eq.)	24 h	14%
8	425 nm	BPO (0.5 eq.)	24 h	13%
9	425 nm	H ₂ O (0.2 mL)	24 h	69%
10 ^c	425 nm	Air condition	24 h	36%

^[a] reaction condition: 0.5 mmol chalcone, 1 mol % t-Bu-4CzIPN , 5 mL solvent, Ar, RT. ^[b] Product yield determined by HPLC using diethyl phthalate as the internal standard. ^[c] O_2 condition.



Figure S 2. a) Photocatalytic [2+2] Photodimerization of chalcone by adding 4CzIPN and $Ir(ppy)_3$, **b**) Photocatalytic [2+2] Photodimerization of chalcone by adding t-Bu-4CzIPN and MeO-4CzIPN. The Irradiation wavelength is 425 nm (450 nm for $Ir(ppy)_3$).





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A flame-dried flask (15 mL) was equipped with magnetic stir bar and charged with (E)-1-phenylbut-2-en-1-one. (0.073 g, 0.5 mmol), t-Bu-4CzIPN (0.006 g, 1 mol%) and 1,4-dioxane (5 mL). The reaction mixture was degassed by purging thoroughly with argon for 10 minutes, then irradiated by LED (20 W) under a balloon argonatmosphere at room temperature for about 24h. The target product is detected using MS.

Yield detection and d.r determin method:

Chalcone derivatives' major isomer yield determined by ¹H-NMR using benzyl benzoate as the internal standard. d.r. (major/minor) determined by ¹H-NMR analysis of the unpurified reaction mixture. For most of the chalcone derivatives, the amount of byproduct was too small to be analyzed.



Figure S 3. Direct ¹H-NMR results of the reaction solution

Table S 3. Isomerization of olefin substrates



Entry	photocatalysts	substrate	cis:trans(%)	cyclobutane
				yield
1	none	chalcone	52:48	
2	t-Bu-4CzIPN	chalcone	49:51	62%
3	MeO-4CzIPN	chalcone	67:33	<5%
4	MeO-4CzIPN	4-trifluoromethylchalcone	75:25	<5%
5	MeO-4CzIPN	cinnamic acid	52:48	<5%
6	MeO-4CzIPN	methyl cinnamate	48:52	<5%
7	MeO-4CzIPN	Benzyl cinnamate	60:40	<5%
8	MeO-4CzIPN	4-methoxychalcone	43:57	68%

[a] reaction condition: 0.5 mmol substrates, 1 mol % cat, 5 mL 1,4-dioxane, Ar condition, room temperature, 18 h. The cis-trans isomer ratios and by-product yields are determined by GC and ¹H-NMR.

General procedure for photocatalytic isomerization:

The The cis-trans isomer ratios are determined by GC. A flame-dried flask (15 mL) was equipped with magnetic stir bar and charged with 4-trifluoromethylchalcone (0.138 g, 0.5 mmol), Me-4CzIPN (0.005 g, 1 mol%) and 1,4-dioxane (5 mL). The reaction mixture was degassed by purging thoroughly with argon for 10 minutes, then irradiated by LED (20 W) under a balloon argonatmosphere at room temperature for about 24h. Then we took out the reaction solution under dark conditions and detected the cis-trans ratio using GC. As shown in the **Figure S 4**, *trans*-4-trifluoromethylchalcone produced a lower boiling point *cis* structure in the reaction system. The reaction solution was subjected to ¹H-NMR detection to confirm the proportion of the cyclobutane by-product.





Figure S 4. GC analysis result of the isomerization reaction

Electrochemical and optical spectroscopic data





Figure S 5. The absorption spectra of Donor-Acceptor Fluorophores in 1,4-dioxane (10 µM).



Figure S 6. The emission spectrum of Donor-Acceptor fluorophores in 1,4-dioxane (the concentration of Donor-Acceptor fluorophores are 10 μ M, the excitation wavelength is 400 nm (450 nm for MeO-4CzIPN)).



Figure S 7. Cyclic voltammograms of 4CzPN, Ph- 4CzPN-, and Bu-4CzPN.



Figure S 8. Cyclic voltammograms of 4CzIPN, Ph-4CzIPN, t-Bu-4CzIPN.





Figure S 9. (a) The emission quench of MeO-4CzIPN and (b) t-Bu-4CzIPN by trans-chalcone (solid line) and cis-chalcone (containing 30% trans-chalcone; dotted line); (c) Stem-Volmer plots. The concentrations of of t-Bu-4CzIPN and MeO-4CzIPN are 10 μ M. Quenching reagent is trans-chalcone. Excitation wavelength is 420 nm.

Properties of 4CzIPN:



Figure S 10. UV-Vis absorption and emission spectra of 4CzIPN in 1,4-dioxane.

			Photocatalysts. ^a			
Entry	photocatalyst	$E_{1/2} (PC^{*+}/PC^{*})$	$E_{1/2}(PC^*/PC^{-})$	$E_{1/2}(PC^{++}/PC)$	E _{1/2}	$E_{0,0} \left[eV \right]$
		$[V]^d$	$[V]^d$	[V]	(PC/PC')	
					[V]	
1	4CzIPN	-1.21	1.36	1.35	-1.20	2.56
2	4CzPN	-1.14	1.39	1.36	-1.11	2.50
3	t-Bu-4CzIPN	-1.12	1.33	1.34	-1.13	2.46
4	Bu-4CzPN	-1.04	1.10	1.37	-1.31	2.41
5	Ph-4CzIPN	-1.11	1.39	1.34	-1.06	2.45
6	Ph-4CzPN	-0.97	1.21	1.41	-1.17	2.38
7 ^b	5CzBN	-1.38	1.27	1.41	-1.52	2.79

Table S 4. Excited and Ground State Redox Potentials as Well as Excited State Energy $E_{0,0}$ of

8^{b}	3DPAFIPN	-1.36	1.07	1.3	-1.59	2.66
9 ^b	MeO-5CzBN	-1.49	0.85	1.02	-1.66	2.51
10 ^c	MeO-4CzIPN	-1.16	0.93	1.11	-1.34	2.27

^a The excited state energy is estimated based on the absorption and emission wavelength of Donor-Acceptor fluorophores in 1,4-dioxane, potentials in V vs SCE. The redox potential is tested in THF unless otherwise noted. ^b Measured in DCM. ^c Measured in MeCN/DCM 5:1 v/v, The ground Redox potentials of 5CzBN, 3DPAFIPN, MeO-5CzBN and MeO-4CzIPN are reported by Speckmeier et al¹. ^d $E_{0,0}$ =^{*} $E_{1/2}$ ox- $E_{1/2 red}$ -= $E_{1/2 OX}$ -^{*} $E_{1/2 red}$

¹H NMR, ¹³C NMR and MS of products



















2e. DL- ((1R,2R,3S,4S)-3,4-diphenylcyclobutane-1,2-diyl)bis(p-tolylmethanone)























































- 500







2q.





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90 80 fl (ppm) 



















































2r. DL-(1R,2R,3S,4S)-3,4-diphenylcyclobutane-1,2-dicarboxylic acid



Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)	DBE
$C_{20} H_{20} O_4$	$C_{20}H_{19}O_4$	323.1293	323.1289	-1.29	11











Reference:

1. Speckmeier, E.; Fischer, T. G.; Zeitler, K., J Am Chem Soc 2018, 140, 15353-15365.