Supporting Information for Solvent-Tunable Exciton-Charge Transfer Mixed State Enhances Emission of Functionalized Benzo[*rst*]pentaphene through Symmetry Breaking

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1. General experimental details

All reactions working with air- or moisture-sensitive compounds were carried out under argon atmosphere using standard Schlenk line techniques. 1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene (**5**) was synthesized following a reported procedure.¹ Anhydrous dimethylformamide (DMF), tetrahydrofuran (THF), and toluene were purified by a solvent purification system (GlassContour) prior to use. All other starting materials, solvents and reagents were purchased from commercial suppliers and used as received unless otherwise noted. Thin-layer chromatography (TLC) was done on silica gel coated aluminum sheets with F254 indicator and column chromatography separation was performed with silica gel (particle size 0.063-0.200 mm). Nuclear Magnetic Resonance (NMR) spectra were recorded in C₂D₂Cl₄, THF-*d*₈, and CDCl₃ using Bruker DPX 400 and Bruker DPX 500 MHz NMR spectrometers. Chemical shifts (δ) were expressed in ppm relative to the residual of solvents (C₂D₂Cl₄, ¹H: 5.99 ppm, ¹³C: 74.40 ppm; CDCl₃, ¹H: 7.26 ppm, ¹³C: 76.00 ppm; THF-*d*₈, ¹H: 1.72 ppm, 3.52 ppm, ¹³C: 24.40 ppm, 66.43 ppm). Coupling constants (*J*) were recorded in Hertz. Abbreviations: s = singlet, d = doublet, t = triplet. High-resolution mass spectra (HRMS) were recorded on a Thermo Scientific LTQ-Orbitrap Electrospray Ionization (ESI) Mass Spectrometer.

UV-vis-NIR absorption spectra were recorded on a Shimadzu UV-3600 plus spectrometer using a 10 mm quartz cell. Photoluminescence spectra were measured with the Fluorescence + absorbance Horiba Duetta spectrometer. Photoluminescence quantum yields (PLQY) were measured using an integrating sphere with a photoluminescence measurement unit (Quantaurus-QY, C11347-01, Hamamatsu Photonics).

Transient absorption measurements were performed on samples in a 2 mm quartz cuvette with a Helios FIRE spectrometer, driven by a Pharos amplified laser system (Light Conversion) with fundamental at 1030 nm operating at 8 kHz. The laser output (180 fs) was directed into an automated OPA and harmonic module (Orpheus and Lyra, Light Conversion) to generate narrow excitation pulses, in this study at 400 and 490 nm. A portion of the fundamental was separated to generate white light in YAG crystals to cover the Vis–NIR spectral ranges, permitting measurement from 480 to 915 nm. Pump-probe time delay was set by a mechanical delay stage spanning an 8 ns range.

Time-resolved photoluminescence spectra were acquired on samples in a 2 mm quartz cuvette using an intensified CCD camera (PI-MAX4, Princeton Instruments) coupled to a grating spectrometer (Spectrapro 300, Princeton Instruments) and synchronized to the same Pharos amplifier used for transient absorption, with the same narrowband excitation pulses at 400 and 490 nm. The internal gating function enable capture of fully spectrally resolved photoluminescence at arbitrary time delays, down to an instrument resolution of 500 ps.

PL excitation mapping was performed using an Edinburgh FLS1000 spectrometer equipped with a Xenon arc lamp at room temperature using a 2 mm quartz cuvette.

Electrochemical reduction of 1 was performed in a glass cell using carbon foam cathode, zinc anode, and TBAPF₆ electrolyte. Approximately 220 μ g/mL 1 in DMF was subjected to a 2.5 V potential for 30 minutes. The sample solution in the cell turned from orange (neutral) to a dark green (reduced). The final solution was taken in a 10 mm quartz cuvette for UV-vis absorbance measurement using a Shimadzu UV-2600i spectrophotometer equipped with an ISR-2660 Plus integration sphere.

2. Synthetic Details

2-bromo-4-tert-butyliodobenzene (3)²



To a solution of 2-bromo-4-*tert*-butylaniline (2) (22.0 g, 96.5 mmol) in MeCN (280 mL) was added concentrated HCl (50 mL in 170 mL water). After the mixture was cooled to 0 °C, a solution of NaNO₂ (8.50 g, 123 mmol) in water (150 mL) was added dropwise. The reaction mixture was stirred at 0 °C for 1 h, and then a solution of KI (25.5 g, 154 mmol) in water (150 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 17 h. The reaction mixture was extracted with CH₂Cl₂ (150 mL) for three times. The organic layers were combined, mixed with a saturated aq. solution of Na₂S₂O₃ (125 mL), washed with brine (100 mL) for three time, dried with MgSO₄, and then evaporated. The crude product was purified by silica gel column chromatography to afford the title compound (32.0 g, 98%) as colorless oil. All spectral data was in agreement with the literature.² ¹H NMR (500 MHz, CDCl₃) δ 7.77 (d, *J* = 8.3 Hz, 1H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.04 (dd, *J* = 8.3, 2.0 Hz, 1H), 1.31 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 151.05, 137.40, 127.69, 127.13, 123.61, 94.69, 32.34, 28.63.

2-bromo-4-(tert-butyl)benzaldehyde (4)



To a solution of 2-bromo-4-*tert*-butyl-iodobenzene (**3**) (4.00 g, 11.8 mmol) in a mixture of anhydrous THF and Et₂O (1:1, 50 mL) was added *i*-PrMgCl (2.0 M in THF, 6.00 mL, 12 mmol) dropwise at -78 °C under argon atmosphere. After stirring the reaction mixture at -78 °C for 2 h, dimethylformamide (DMF) (1.90 mL, 24.7 mmol) was added. After stirring for another 2 h, the reaction mixture was allowed to warm to room temperature and stirred for 15 h. The reaction was quenched by saturated aqueous solution of NH₄Cl (30 mL). The organic layer was separated and the aqueous layer was extracted with Et₂O (20 mL) for three time. The organic layers were combined, washed with brine, dried with MgSO₄, and evaporated. The residue was purified by silica gel column chromatography to afford the title compound (2.20 g, 77%) as colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 10.34 (d, *J* = 0.8 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 1.8 Hz, 1H), 7.47 (ddd, *J* = 8.2, 1.8, 0.8 Hz, 1H), 1.36 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 191.69, 159.90, 131.15, 130.91, 129.62, 127.30, 125.24, 35.44, 30.90. HRMS (ESI, Positive): *m/z* Calcd. For [C₁₁H₁₄OBr]⁺: 241.0223, [M+H]⁺, found: 241.0213.

2,2'-(naphthalene-1,4-diyl)bis(4-tert-butylbenzaldehyde) (6)



A 30-mL Schlenk tube was charged with 2-bromo-4-*tert*-butylbenzaldehyde (4) (525 mg, 2.18 mmol), 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene (5) (400 mg, 1.05 mmol), K_2CO_3 solution (2.0 M in water, 3.0 mL, 6.0 mmol), Pd(PPh_3)_4 (114 mg, 99.0 μ mol), and toluene/methanol (20/10 mL). After the reaction mixture was degassed by bubbling with argon, it was heated to reflux for 16 h. After addition of water (20 mL) the reaction mixture was extracted with CH₂Cl₂ (20 mL) for three times. The organic layers were combined, dried over MgSO₄, and evaporated. The residue was purified by silica gel column chromatography to afford the title compound (400 mg, 85%) as light yellow solid. ¹H NMR (500

MHz, CDCl₃) δ 9.69 (m, 2H), 8.09 (m, 2H), 7.66 (m, 2H), 7.60 (m, 2H), 7.52 (m, 4H), 7.45 (m, 2H), 1.41 (d, J = 6.0 Hz, 18H). ¹³C NMR (126 MHz, CDCl₃) δ 191.76, 191.46, 157.84, 157.68, 143.78, 143.68, 136.67, 136.64, 132.85, 132.82, 132.54, 128.75, 128.62, 127.30, 127.24, 127.20, 126.96, 126.88, 126.42, 125.65, 125.63, 35.48, 31.13. HRMS (ESI, Positive): m/z Calcd. For [C₃₂H₃₃O₂]⁺: 449.2475, [M+H]⁺, found:449.2479.

2,11-di-*tert*-butylbenzo[*rst*]pentaphene (7)



To a solution of 2,2'-(naphthalene-1,4-diyl)bis(4-*tert*-butylbenzaldehyde) (**6**) (133 mg, 0.296 mmol) in CH₂Cl₂ (200 mL) was added a solution of SnCl₂·2H₂O (2.50 g, 11.0 mmol) in *i*-PrOH (10 mL). After the reaction mixture was cooled to 0 °C, concentrated H₂SO₄ (5.0 mL) was added and the reaction mixture was allowed to warm to room temperature. After stirring for 24 h, the reaction was quenched with water (100 mL), and the reaction mixture was extracted with CH₂Cl₂ (100 mL) for three times. The organic layers were combined, washed with brine, dried over MgSO₄, and evaporated. The residue was purified by silica gel column chromatography to afford the title compound (34.0 mg, 28%) as the light yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 9.24 (s, 2H), 9.01 (d, *J* = 1.8 Hz, 2H), 8.26 (s, 2H), 8.15 (d, *J* = 8.6 Hz, 2H), 7.86 (dd, *J* = 8.6, 1.8 Hz, 2H), 7.76 (s, 1H), 1.59 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 148.96, 129.86, 129.62, 128.21, 128.02, 125.17, 124.93, 124.30, 121.98, 118.20, 35.50, 31.59. HRMS (ESI, Positive): *m/z* Calcd. For [C₃₂H₃₀]⁺: 414.2342, [M+H]⁺, found:414.2343.

5,8-dibromo-2,11-di-tert-butylbenzo[rst]pentaphene (8)



To a solution of the 2,11-di-*tert*-butylbenzo[*rst*]pentaphene (7) (950 mg, 2.29 mmol) in anhydrous CH₂Cl₂ (30 mL) was added *N*-bromosuccinimide (NBS) (1.22 g, 6.86 mmol). After stirring at room temperature for 3 h, the reaction was quenching with acetone (20 mL), and the solvents were evaporated. The residue was purified by silica gel column chromatography to afford the title compound (1.22 g, 94%) as yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 9.20 (s, 2H), 8.98 (s, 2H), 8.71 (dd, *J* = 8.4, 2.8 Hz, 2H), 8.53 – 8.30 (m, 2H), 7.96 (d, *J* = 9.3 Hz, 2H), 1.60 (m, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 150.03, 129.26, 129.16, 128.64, 128.57, 128.20, 127.71, 126.57, 124.72, 122.51, 122.26, 118.44, 35.46, 31.48. HRMS (ESI, Positive): *m/z* Calcd. For [C₃₂H₂₈Br₂]⁺: 570.0552, [M]⁺, found:570.0538.

2,11-di-*tert*-butyl-N⁵,N⁵,N⁸,N⁸-tetrakis(4-methoxyphenyl)benzo[*rst*]pentaphene-5,8-diamine (BPP-MeOPA 1)



A 100-mL flask was charged with 5,8-dibromo-2,11-di-tert-butylbenzo[rst]pentaphene (8) (150 mg, 0.260 mmol), 4,4'-

dimethoxydiphenylamine (150 mg, 0.660 mmol), tris(dibenzylideneacetone)dipalladium(0) (Pd₂(dba)₃) (6 mg, 0.01 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (P(*t*-Bu)₃HBF₄) (6 mg, 0.02 mmol), sodium *tert*-butoxide (*t*-BuONa) (81 mg, 0.84 mmol) and anhydrous toluene (50 mL) under a nitrogen atmosphere. The reaction mixture was heated at 125 °C for 17 h under a nitrogen atmosphere. Then, resulting mixture was cooled to room temperature, diluted with 30 mL of dichloromethane (CH₂Cl₂), and then poured into water (100 mL). The organic layer was subsequently separated, and the aqueous layer was extracted with CH₂Cl₂ (30 mL) for three times. The organic phases were combined, washed with brine, dried over MgSO₄, and evaporated. The residue was purified by silica gel column chromatography to afford the title compound (232 mg, 87% yield) as orange solid. ¹H NMR (500 MHz, CD₂Cl₂) δ 9.37 (s, 2H), 9.14 (d, *J* = 1.8 Hz, 2H), 8.30 (dd, *J* = 8.7, 1.2 Hz, 2H), 7.95 (d, *J* = 1.3 Hz, 2H), 7.83 (dt, *J* = 8.9, 1.6 Hz, 2H), 7.28 – 6.89 (m, 8H), 6.84 – 6.58 (m, 8H), 3.72 (d, *J* = 1.3 Hz, 12H), 1.60 (d, *J* = 1.4 Hz, 18H). ¹³C NMR (126 MHz, CD₂Cl₂) δ 154.03, 149.56, 141.80, 136.29, 130.06, 128.95, 128.51, 127.79, 126.06, 125.90, 125.07, 124.98, 121.99, 121.08, 119.00, 114.43, 55.34, 35.36, 31.20. HRMS (ESI, Positive): *m/z* Calcd. For [C₆₀H₅₆O₄N₂]⁺:868.4235, [M]⁺, found:868.4225.

3. NMR Spectra



Figure S1. ¹H NMR spectrum of compound 3 in CDCl₃ (500 MHz, 298 K).



Figure S3. ¹H NMR spectrum of compound 4 in CDCl₃ (500 MHz, 298 K).



Figure S4. ¹³C NMR spectrum of compound 4 in CDCl₃ (126 MHz, 298 K).



Figure S5. ¹H NMR spectrum of compound 6 in CDCl₃ (500 MHz, 298 K).



Figure S6. ¹³C NMR spectrum of compound 6 in CDCl₃ (126 MHz, 298 K).



Figure S7. ¹H NMR spectrum of compound 7 in CDCl₃ (400 MHz, 298 K).



Figure S8. ¹³C NMR spectrum of compound 7 in CDCl₃ (101 MHz, 298 K).



Figure S9. ¹H NMR spectrum of compound 8 in CDCl₃ (400 MHz, 298 K).





Figure S11. ¹H NMR spectrum of compound 1 in CD₂Cl₂ (500 MHz, 298 K).



Figure S12. ¹³C NMR spectrum of compound 1 in CD₂Cl₂ (126 MHz, 298 K).



Figure S13. ¹H,¹H-COSY NMR spectrum of compound 1 in CD₂Cl₂ (500 MHz, 298 K).



Figure S14. ¹H,¹H-NOESY NMR spectrum of compound 1 in CD₂Cl₂ (500 MHz, 298 K).



Figure S15. ¹H-¹³C COSY NMR spectrum of compound 1 in CD₂Cl₂ (126 MHz, 298 K).

4. X-ray single crystallography

The single crystal of compound **1** suitable for X-ray analysis was obtained by slow evaporation of its solution in CH_2CI_2/CH_3OH . A suitable crystal light-orange plate with dimensions $0.025 \times 0.055 \times 0.0137$ mm was selected and mounted on a Bruker SMART APEX3 area detector diffractometer. The crystal was kept at a steady T = 100 K during data collection. Data were measured using ω scans with Cu K α radiation. The unit cell was refined using SAINT V8.40B (Bruker, 2016) on 23325 reflections with C222₁ space group. Data reduction, scaling and absorption corrections were performed using SAINT V8.40B (Bruker, 2016/2). The structure was solved with the ShelXT 2018/2 (Sheldrick, 2018) solution program using iterative methods and by using Olex2 1.5 (Dolomanov et al., 2009) as a graphical interface. The model was refined with ShelXL 2016/6 (Sheldrick, 2016) using full matrix least squares minimisation on F². All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_exptl_absorpt_process_details: SADABS-2016/2 (Bruker,2016/2) was used for absorption correction.

The structure was deposited at the Cambridge Crystallographic Data Centre (CCDC) and the data could be obtained free of charge via <u>www.ccdc.cam.ac.uk/structures</u>. Crystal data for compound 1 (CCDC number: <u>2194433</u>).

Crystal data and structure refinement for 1

Identification code	<u>2194433</u>
Empirical formula	$C_{60}H_{56}N_2O_4$
Formula weight	869.06
Temperature/K	100.00
Crystal system	orthorhombic
Space group	C2221
a/Å	8.3553(4)
b/Å	23.2081(7)
c/Å	26.2877(9)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	5097.5(3)
Z	4
$\rho_{calc}g/cm^3$	1.132
µ/mm ⁻¹	0.549
F(000)	1848.0
Crystal size/mm ³	$0.137 \times 0.055 \times 0.025$
Radiation	$CuK\alpha$ ($\lambda = 1.54178$)
20 range for data collection/	6.724 to 136.472
Index ranges	$\textbf{-10} \leq \textbf{h} \leq \textbf{9}, \textbf{-27} \leq \textbf{k} \leq \textbf{23}, \textbf{-31} \leq \textbf{l} \leq \textbf{31}$
Reflections collected	23325
Independent reflections	$4640 [R_{int} = 0.0782, R_{sigma} = 0.0665]$
Data/restraints/parameters	4640/0/334
Goodness-of-fit on F ²	1.040
Final R indexes [I>=2 σ (I)]	$R_1 = 0.0508, wR_2 = 0.1197$
Final R indexes [all data]	$R_1 = 0.0661, wR_2 = 0.1274$
Largest diff. peak/hole / e Å-3	0.16/-0.17
Flack parameter	0.00(19)

5. DFT calculations

DFT calculations were performed using the Gaussian 09 software package.³ The geometries molecular orbitals, and MO energy were calculated at B3LYP/6-311G(d,p) energy level. Time-dependent DFT (TD-DFT) calculations were performed at the B3LYP/6-311G(d,p) energy level using toluene as the solvent model (SMD). The analysis of oscillator strength f was performed using a multifunctional wavefunction analyser (Multiwfn)⁴.



Figure S16. The hole and electron distribution for excited states (S1, S2, S3) of **1** calculated by TD-DFT at M06-2X/6-311G(d,p) energy level using the toluene as the solvent. and visualized by Multiwfn software.⁵ The electron distribution is shown in green, and hole distribution is shown in blue. The *iso*-surface value is 0.001 eV.

Table S1. Calculated charge transfer (CT) and local excitation (LE) characters (in %) for the excited state based on M06-2X/6-311G(d,p) energy level using the toluene as the solvent.

	Charge transfer (CT)	Local excitation (LE)
S1	60	40
S2	83	17
S 3	23	77

After the natural transition orbital analysis, the LE and CT contribution to given excited state are obtained by Multiwfn software.⁵

Table S2. Cha	aracteristic ele	ctron transitions for	1 and 7 were ca	lculated by TDDF	T at M06-2X/6-2	311G(d,p) energ	y level using
the toluene as	the solvent by	y Gaussian 09.					

Compound	Excited states	Transition energy (eV)	Wavelength (nm)	Oscillator strength	Description
	S 1	2.6666	465	0.68923	HOMO \rightarrow LUMO 0.68923
-	S2	2.9542	420	0.0859	HOMO-1 \rightarrow LUMO 0.67847
1 -	S3	3.3202	373	0.0398	HOMO-3 \rightarrow LUMO 0.26490 HOMO-2 \rightarrow LUMO+1 -0.23823 HOMO \rightarrow LUMO+1 0.57940
	S 1	3.2345	383	1.1665	HOMO \rightarrow LUMO 0.69633
7	S2	3.4699	357	0.0124	HOMO-2 \rightarrow LUMO 0.10697 HOMO-1 \rightarrow LUMO+1 0.33709 HOMO \rightarrow LUMO 0.58865
·	S3	4.1110	302	0.1488	HOMO-1 \rightarrow LUMO 0.58770 HOMO \rightarrow LUMO+1 -0.35859 HOMO \rightarrow LUMO+1 0.13130

Table S3. Cartesian coordinates of the DFT-optimized 1.

Symbol	X	Y	Z
С	-5.0102	-3.67463	0.486861
С	-3.6344	-3.66459	0.322025
С	-2.86777	-2.47893	0.268146
С	-3.54845	-1.23018	0.373636
С	-4.95084	-1.24536	0.55964
С	-5.65718	-2.42456	0.614268
С	-1.42582	-2.4905	0.131536
С	-0.71382	-1.26757	0.075453
С	-1.42712	-0.01472	0.161264
С	-2.80816	-0.0061	0.317775
С	-0.68105	-3.69495	0.059592
С	0.680736	-3.69493	-0.06034
С	1.425517	-2.49048	-0.13201
С	0.713527	-1.26755	-0.07574
C	1.426832	-0.01468	-0.16132
С	0.671024	1.208855	-0.07515
C	-0.6713	1.208843	0.075306
C	2.86/4/5	-2.4789	-0.2685
C	3.548176	-1.23014	-0.37375
C C	2.80/889	-0.00607	-0.31775
C C	5.000018	-3.00430	-0.32249
C C	5.009918	-3.0/439	-0.48723
C	4 050575	-2.42431	-0.01447
C	-5 77311	-1.24331	-0.33909
C	5 772815	-5.01237	-0 52999
N	3 509965	1 236659	-0.43478
N	-3 51026	1 236588	0.435056
Ċ	-7.28814	-4.81509	0.723698
č	-5.55579	-5.77275	-0.79954
С	-5.24819	-5.87162	1.703312
С	7.287854	-4.81505	-0.72418
С	5.555505	-5.77279	0.799009
С	5.247888	-5.8715	-1.70384
С	-3.39752	1.984345	1.637927
С	-4.30823	1.680072	-0.65278
С	4.308119	1.679837	0.653017
С	3.397488	1.984493	-1.63762
С	-5.50915	2.382126	-0.44326
C	-6.2875	2.794138	-1.51142
C	-5.90893	2.501231	-2.82718
C	-4./2919	1./91056	-3.04785
C C	-3.936/1	1.396127	-1.96913
C	-5.27459	1.33/048	2.809903
C	-5.12557	2.038207	4.033301
C	-5.11/8	5.452955 4 100016	2 801350
C	-3.24479	3 390214	1 625092
Č	3 2751	1 337919	-2 86971
Č	3 126108	2 058658	-4.05526
Č	3 118218	3 453324	-4 03049
č	3.244637	4,11019	-2.80083
Ċ	3.369973	3.390357	-1.62462
č	5.508945	2.382049	0.443516
С	6.287469	2.793747	1.511677
С	5.909173	2.50035	2.827405
С	4.729515	1.790035	3.048051
С	3.936859	1.395427	1.969348
О	-6.75353	2.94607	-3.8062
О	-2.99047	4.25729	5.129308
О	2.991109	4.257774	-5.12885
О	6.753958	2.944874	3.806414
С	-6.41328	2.678283	-5.1569
С	-2.85669	3.640731	6.399531
С	2.857745	3.64135	-6.39918

С	6.413887	2.676767	5.157099
Н	-3.12328	-4.61278	0.230138
н	-5 47549	-0.30522	0.657616
и Ц	6 72842	2 2772	0.756414
11	-0.720+2	-2.3772	0.750414
H	-1.18988	-4.64/95	0.105512
H	1.189566	-4.64793	-0.10648
Н	1.204684	2.14669	-0.13592
Н	-1.20496	2.146669	0.136198
Н	3.122987	-4.61276	-0.23072
Н	6 728145	-2 37714	-0.75661
н	5 475249	-0.30516	-0.6575
и П	7 7927	5 78024	0.746241
11	-7.7037	-3.76934	1.665277
П	-7.31303	-4.30809	1.003277
H	-7.7319	-4.23843	-0.09226
Н	-6.09532	-6.72491	-0.78526
Н	-4.49974	-5.9903	-0.97484
Н	-5.92077	-5.18724	-1.64763
Н	-5.3915	-5.35745	2.657531
Н	-5 78451	-6 82471	1 746145
н	-4 18341	-6.09284	1 600669
11 11	7 782406	5 78020	0.74681
11	7.783400	-3.76929	-0.74081
H	7.515353	-4.30/9/	-1.665/2
H	7./31621	-4.23845	0.091825
Н	6.095044	-6.72495	0.784677
Н	4.499459	-5.99036	0.974303
Н	5.920484	-5.18732	1.647132
Н	5.391203	-5.35728	-2.65803
Н	5.784211	-6.8246	-1.74674
Н	4 183109	-6 09273	-1 60121
н	-5.83064	2 606422	0.566185
11	7 21106	2.000+22	1 24007
11	-7.21100	1 5 4 5 0 1 6	-1.34907
Н	-4.40389	1.343016	-4.0498
Н	-3.01889	0.854381	-2.159/1
H	-3.28844	0.255626	2.908917
Н	-3.02794	1.515146	4.986
Н	-3.22483	5.193123	2.790534
Н	-3.44943	3.919696	0.683702
Н	3.289172	0.255904	-2.90885
Н	3 029127	1 515641	-4 98587
Н	3 224405	5 193389	-2 78986
и Ц	3 448584	3 010718	0.68312
11	5 820226	2 606741	-0.00312
11	7.210046	2.000/41	-0.30391
H	7.210946	3.336685	1.349342
H	4.404406	1.543646	4.049976
Н	3.019103	0.853561	2.159898
Н	-7.2097	3.114686	-5.75794
Н	-5.45862	3.141652	-5.43224
Н	-6.36146	1.60109	-5.35441
Н	-2.76881	4.453798	7.118686
H	-3 73474	3 033098	6 648174
и Ц	1 05027	3 01/272	6 151976
11	-1.7303/	5.014572 4.454400	0.4310/0
П	2.709834	4.434472	-/.11823
H	3./35988	3.033947	-6.647/1
Н	1.959574	3.014797	-6.4518
Н	7.210365	3.113066	5.75814
Н	5.45924	3.140031	5.432661
Н	6.362141	1.599527	5.354373

 Table S4. Cartesian coordinates of the DFT-optimized 7.

Symbol	X	Y	Z
С	5.058249	-0.82868	6.89E-05
С	3.671526	-0.84571	5.38E-05
С	2.884503	0.327065	5.36E-05
С	3.556331	1.585525	0.000111
С	4.970227	1.599363	0.000148

C	5 699196	0.433215	0.00011
C C	1 425244	0.455215	5.42E.05
C	1.453244	0.309900	5.45E-05
С	0.714984	1.529998	5.96E-05
С	1.428049	2.786154	0.000205
С	2.804765	2.786762	0.000227
С	0.684069	-0.89463	-2.2E-05
С	-0.68407	-0.89463	-7.6E-05
С	-1.43524	0.309967	-9.2E-05
Č	-0 71498	1 529998	-6 6E-05
Č	1 42805	2 786154	0.00019
e C	-1.42003	4.017422	-0.00017
C C	-0.0/492	4.017423	-0.00011
C	0.074921	4.01/423	0.00016
Ľ	-2.8845	0.327065	-7.6E-05
C	-3.55633	1.585526	-0.00013
С	-2.80477	2.786763	-0.00023
С	-3.67153	-0.84571	-5.8E-05
С	-5.05825	-0.82868	-7E-05
С	-5.6992	0.433216	-0.00013
С	-4.97023	1.599363	-0.00017
С	5.843997	-2.15444	-6.7E-05
С	-5.844	-2.15444	9.02E-05
Č	7 367949	-1 93175	0.000547
Č	5 470030	2 07170	1 261382
C C	5 49072	2.97179	1.201382
C C	5.48072 7.26705	-2.97080	-1.20230
C	-7.30793	-1.931/3	-0.00033
C	-5.4/994	-2.9/181	-1.26134
С	-5.48072	-2.97084	1.262399
Н	3.17021	-1.80403	2.19E-05
Н	5.480866	2.556959	0.00029
Н	6.779049	0.494807	8.64E-05
Н	1.195939	-1.84766	3.83E-05
Н	-1.19594	-1.84766	-0.0002
Н	-1.22718	4.951308	-0.00017
Н	1.227181	4.951308	0.00026
Н	-3.17021	-1.80403	-4.7E-06
Н	-6 77905	0 494808	-0.00011
Н	-5 48087	2 55696	-0.00031
LI LI	7 979446	2.55656	0.000564
11	7.70022	-2.09040	0.000504
11	7.70032	-1.30419	-0.88334
H	/.699604	-1.38448	0.88/0/4
H	6.033922	-3.91559	1.2/5555
H	4.414576	-3.21016	1.29/564
H	5.728451	-2.41752	2.17043
Н	5.729812	-2.41591	-2.17084
Н	6.034663	-3.91468	-1.27692
Н	4.415352	-3.20909	-1.29934
Н	-7.87845	-2.89846	-0.00052
Н	-7.70032	-1.38418	0.885548
Н	-7.69961	-1.38449	-0.88706
Н	-6.03393	-3.91561	-1.2755
H	-4 41458	-3.21019	-1.29752
н	_5 72845	-2 41756	-2 1704
11 11	-5.72045	-2.71/30	2.1704
11 TT	-5./2701	-2.+1.00/	2.1/0003
Н	-0.03400	-3.91403	1.2/09/3
H	-4.41535	-3.20907	1.2993/8
Н	3.33709	3.732994	0.000407
Н	-3.33709	3.732994	-0.0004

6. Absorption spectra.



Figure S17. Normalized absorption spectrum of 1 (10^{-5} mol/L) were measured in toluene, tetrahydrofuran (THF), dichloromethane (CH₂Cl₂), and dimethylformamide (DMF).



Figure S18. Normalized absorption spectrum of 7 (10⁻⁵ mol/L) were measured in toluene, THF, CH₂Cl₂, and DMF.

7. Transient absorption



Figure S19. Transient absorption spectroscopy of 1 at 490 nm excitation in (a) chlorobenzene and (b) pyridine.



Figure S20. Transient absorption spectroscopy of 1 at 400 nm excitation in (a) toluene, (b) chlorobenzene, (c) THF, (d) pyridine, and (e) DMF.



Figure S21. Transient absorption spectroscopy kinetics at select wavelengths of **1** at 400 nm excitation. Arrow to guide the eye along the general trend of increasing rate of mixed (initial) state to CT state conversion with increasing solvent polarity. Solvent polarizability may contribute to minor deviations from this trend. Shorter interrogated wavelengths follow mixed state kinetics while longer wavelengths follow the CT state.



Figure S22. Time-resolved photoluminescence studies of **1** at 490 nm excitation in (a) toluene, (b) chlorobenzene, (c) THF, (d) pyridine, and (e) DMF. * Detector artifact



Figure S23. Photoluminescence excitation mapping of 1 in (a) toluene and (b) DMF. Results indicate that excitation wavelength only impacts emission intensity and not the general emission/excited state behavior.



Figure S24. Electrochemical reduction of 1 to simulate an ICT state. Using carbon foam cathode, zinc anode, and TBAPF₆ electrolyte, 2.5 V potential applied to ~220 μ g/mL 1 in DMF for 30 minutes. The sample solution in the cell turned from orange to a dark green. The final solution was taken for UV-vis absorbance measurement (a). Comparing the result to TA and PL data (b), the region approximately 600 to 800 nm corresponds to the two-peaked final state, confirming that to be an ICT state present in the TA data. Additionally, the ~700 nm peak in the reduced form absorbance aligns closely with the PL peak, indicating that stimulated emission in the TA data, still visible after 0.5 ps, is indeed overshadowed by the ICT state's absorption upon its formation.



Figure S25. Steady state TA measurements of 1 at $\sim 20 \ \mu\text{g/mL}$ in pyridine and 1.7 ps pump-probe delay time, in which pump power was varied to visualize (a) if spectral shape changes occurred with varying power. Intensities at 700 nm and 770 nm (based on kinetic traces, Figure 3b in main text) were fit to a line (b) to verify that intensity changed linearly with pump power.

8. Kinetic Fitting of Spectroscopic Data



Figure S26. Fitting curves of time-resolved PL kinetic traces of 1 at 490 nm excitation in (a) toluene, (b) chlorobenzene, (c)

THF, (d) pyridine, and (e) DMF. Fit parameters are presented in Table S5.

Solvent	$\tau_f(ns)$	τ_f Uncertainty (ns)	R^2
DMF	2.28	0.01	0.9994
Pyridine	6.17	0.02	0.9996
THF	11.44	0.02	0.9993
Chlorobenzene	10.98	0.06	0.9965
Toluene	15.45	0.04	0.9993

Table S5. PL lifetimes (τ_f) and fit qualities at 490 nm excitation. The kinetic trace for each solvent (Figure 4a of main text) was fit to a monoexponential decay.



Figure S27. Fitting curves of 0–20 ps TA kinetic traces of 1 at 490 nm excitation in (a) toluene, (b) chlorobenzene, (c) THF, (d) pyridine, and (e) DMF. Fit parameters are presented in Table S6.

Solvent	$ au_{l}$ (ps)	R^2
DMF	0.79 ± 0.03	0.9936
Pyridine	1.88 ± 0.04	0.9946
THF	1.21 ± 0.02	0.9958
Chlorobenzene	4.5 ± 0.1	0.9934
Toluene	3.7 ± 0.1	0.9861

Table S6. Approximate time constant for initial internal conversion (τ_1) and fit qualities at 490 nm excitation over the delay range 0–20 ps. The two kinetic traces for each solvent (Figure 3b of main text) were simultaneously fit to a monoexponential growth/decay representative of the evolution of the initially excited mixed state into the ICT state (where applicable, based on solvent). The general trend is that formation of the ICT state slows with decreasing solvent polarity. Notably, toluene deviates significantly from the trend, the result of lack of ICT formation in that solvent and, therefore, a different relaxation pathway. The product state following the 3.7 ps evolution in toluene retains the same fine structure observed in the initial excitation, albeit with different peak ratio: this behavior is consistent with typical solvation dynamics in toluene. We note that pyridine also slightly departs from the solvent polarity order used in the table: this is a sign that other solvent properties such as polarizability and viscosity can also contribute to these dynamics⁶. This is typical of processes driven by solvent interactions and does not affect the assignment of the states involved.



Figure S28. Fitting curves of 100–8000 ps TA kinetic traces of 1 at 490 nm excitation in (a) toluene, (b) chlorobenzene, (c) THF, (d) pyridine, and (e) DMF. Fit parameters are presented in Table S7.

Solvent	$ au_2$ (ps)	R^2
DMF	2197 ± 15	0.9987
Pyridine	5452 ± 133	0.9966
THF	12415 ± 839	0.9963
Chlorobenzene	10900 ± 958	0.9925
Toluene	17585 ± 2066	0.9834

Table S7. Approximate TA excited state lifetime (τ_2) and fit qualities at 490 nm excitation over the delay range 100–8000 ps. The two kinetic traces for each solvent (Figure 3b of main text) were globally fit to a monoexponential decay representative of the evolution of decay of the final state (ICT where applicable, based on solvent). The rate of decay generally increases in higher polarity solvents, in parallel with the systematic PL redshift reported in main-text Figure 4. Within the limitations of the two instruments, these fits provide excellent agreement with the PL decay kinetics, permitting assignment of the TA signature observed on these timescales to the red-shifted, emissive ICT state.

9. Elucidation of Vibronic Structure in Transitions from Ground State



Figure S29. Steady state absorption of $S_0 \rightarrow S_1$ band of 1 in toluene (below) and its second derivative (above). As negative features in a second derivative plot indicate places that the original function is concave down (peaks), this use of the second derivative shows the location of vibronic features in the steady state absorbance.

10. Elucidation of Spectral Evidence for State Evolution Model



Figure S30. Normalized TA spectra for 1 when pumped at 490 nm in DMF, THF, and toluene. Black arrows highlight the absorbance wavelength blue shift (or lack thereof). Red arrows indicate the location of excitonic absorption features in the transition between states. The black circle guides the eye to the CT absorption features that approximately share a wavelength over all three spectra, demonstrating CT character is present in the initial state. Based on these spectra, we can confidently assign the presence of two distinct electronic species, and no further species are required to describe the evolution. In principle these states could evolve in parallel or sequentially. The appearance of a clear isosbestic point during the initial conversion (e.g., at 650 nm in THF, main-text Figure 3a) provides evidence for a sequential model. Thus, we describe the excitation dynamics in 1 in terms of two sequential exponential processes, capturing the S₁ \rightarrow ICT process and then eventual ICT decay to the ground state.

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