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Electronic Supplementary Information for:

Charge separation and intersystem crossing in compact orthogonal and sterically encumbered 6,12-diphenyl indolo[3,2-*b*]carbazole-naphthalimide electron donor-acceptor dyad

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1. General information and synthesis

1.1 Synthesis of NI-Br (4-bromo-*N***-butyInaphthalimide).** The **NI-Br** was synthesized according to a literature method.¹ *n*-Butylamine (1.10 g, 15.0 mmol) was added to a suspension of 4-bromo-1,8-naphthalic anhydride **1** (2.70 g, 10.0 mmol) in ethanol (60 mL). The mixture was refluxed at 78 °C for 4 h under nitrogen atmosphere before cooling to room temperature. The crude product was concentrated in vacuo and purified by column chromatography (silica gel; DCM / petroleum ether, 1:2, v/v). The product was obtained as a pale-yellow solid (1.51 g, yield: 45%). ¹H NMR (CDCl₃, 400 MHz): δ = 8.68 (d, 1H, *J* = 8.0 Hz), 8.58 (d, 1H, *J* = 8.0 Hz), 8.43 (d, 1H, *J* = 8.0 Hz), 8.06 (d, 1H, *J* = 8.0 Hz), 7.87 – 7.83 (m, 1H), 4.20 (t, 2H, *J* = 8.0 Hz), 1.75 – 1.70(m, 2H), 1.48 – 1.42 (m, 2H), 1.00 (t, 3H, *J* = 8.0 Hz).

1.2 **Synthesis** 2,8-dimethoxy-6,12-bis(4-methoxyphenyl)-5,11-dihydroindolo[3,2of b]carbazole (ICz).² A mixture of aqueous fluoroboric acid (40 wt.%, 1.70 mmol, 0.37 g) and tetrabutylammonium iodide (1.70 mmol, 0.63 g) in acetonitrile (20 mL) was slowly added to a solution of 5-methoxy-indole (6.80 mmol, 1.00 g) and p-methoxybezaldehyde (6.80 mmol, 0.92 g) in acetonitrile (50 mL) in ice bath. The resulting orange-red mixture was stirred at room temperature for 8 h, after which the mixture was filtered and washed with acetonitrile (20 mL) and methanol (20 mL). The gravish-green solid was then mixed with iodine (0.30 mmol, 0.085 g) and acetonitrile (20 mL). The brownish mixture was then refluxed at 80 °C for 12 h before cooling to room temperature, and the crude product was purified by column chromatography (silica gel; DCM). The product was obtained as yellow-green powder (0.20 g, yield: 11%). Mp : >250 °C, ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 10.23 (s, 2H), 7.60 (d, 4H, J = 8.5 Hz), 7.33 – 7.27 (m, 6H), 6.93 – 6.91 (m, 2H), 6.64 (d, 2H, J = 2.5 Hz), 3.93 (s, 6H), 3.54 (s, 6H). ¹³C NMR (DMSO- d_6 , 150 MHz): δ = 158.93, 157.29, 151.47, 136.64, 134.31, 131.22, 129.65, 128.88, 122.53, 120.03, 116.12, 114.42, 114.36, 113.53, 113.33, 111.29, 104.89, 34.87, 31.18, 30.59, 28.89, 28.59, 18.45. MALDI-TOF-MS ([C₃₄H₂₈N₂O₄]⁺): calcd m/z = 528.20, found m/z = 528.2.

1.3 Synthesis of NI-ICz.² Copper powder (36 mg, 0.57mmol) was added to a mixture of **NI-Br** (204 mg, 0.62 mmol), **ICz** (130 mg, 0.25 mmol), potassium carbonate (204 mg, 1.5 mmol), dibenzo-18-crown-6 (18 mg, 0.05 mmol) and 1,2-dichlorobenzene (5 mL) under nitrogen atmosphere. The

mixture was refluxed at 180 °C for 24 h before cooling to room temperature. The solvent was evaporated in vacuo, and the crude product was purified by column chromatography (silica gel; DCM). The product was obtained as crimson powder (19 mg, yield: 10%). Mp : >250 °C, ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 10.48 (s, 1H), 8.46 (d, 1H, *J* = 7.1 Hz), 8.35 (d, 1H, *J* = 7.5 Hz), 7.74 (dd, 2H, *J*₁ = 9.3 Hz, *J*₂ = 7.9 Hz), 7.69 – 7.64 (m, 2H), 7.49 (d, 1H, *J* = 8.4 Hz), 7.36 – 7.31 (m, 3H), 6.92 – 6.88 (m, 3H), 6.72 (d, 2H, *J* = 7.4 Hz), 6.46 – 6.41 (m, 2H), 6.13 (s, 1H), 5.95 (d, 1H, *J* = 8.4 Hz), 4.11 (t, 2H, *J* = 7.1 Hz), 3.96 (s, 3H), 3.57 (s, 3H), 3.46 (s, 3H), 3.34 (s, 3H), 1.71 – 1.66 (m, 2H), 1.46 – 1.39 (m, 2H), 1.00 (t, 3H, *J* = 7.2 Hz). ¹³C NMR (DMSO-*d*₆, 150 MHz): δ = 163.23, 162.73, 157.59, 152.88, 151.48, 136.64, 135.12, 134.88, 130.92, 128.39, 123.10, 122.65, 122.11, 121.26, 117.43, 117.11, 114.65, 113.67, 111.39, 105.61, 30.59, 29.68, 28.88, 19.67, 18.45. MALDI-TOF-MS ([C₅₀H₄₁N₃O₆]⁺): calcd m/z 779.2995, found m/z 779.3003.

1.4 Singlet oxygen quantum yield (Φ_{Δ}). 1,3-Diphenylisobenzofuran (DPBF) was used as ¹O₂ scavenger for the determination of singlet oxygen quantum yield (Φ_{Δ}), the absorbance of which at λ = 414 nm was monitored at specific time intervals. The Φ_{Δ} values of the compounds were calculated according to Eq. S1:

$$\Phi_{\Delta,sam} = \Phi_{\Delta,std} \left(\frac{1 - 10^{-A_{std}}}{1 - 10^{-A_{sam}}} \right) \left(\frac{m_{sam} - m_{DPBF}}{m_{std} - m_{DPBF}} \right) \left(\frac{\eta_{sam}}{\eta_{std}} \right)^2$$
(Eq. S1)

In the above equation, 'sam' or 'std' represent 'sample' or 'standard'. A, *m* and η stand for the absorbance at excitation wavelength λ_{ex} , the slope of the absorbance at $\lambda = 414$ nm over time, and the refractive index of the solvent used for measurement, respectively. Optically matched solutions were used (the solutions of samples and standard give same absorbance at λ_{ex}).

2. NMR and HRMS spectra



Fig. S1 ¹H NMR spectra of compound NI-Br (400 MHz, CDCl₃), 25 °C.



Fig. S2 (a) ¹H NMR (400 MHz, DMSO- d_6) and (b) ¹³C NMR (150 MHz, DMSO- d_6) spectra of compound ICz, 25 °C.



Fig. S3 (a) ¹H NMR (400 MHz, DMSO- d_6), (b) locally enlarged ¹H NMR and (c) ¹³C NMR (150 MHz, DMSO- d_6) spectra of **NI-ICz**, 25 °C.



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Fig. S4 MALDI-TOF-HRMS of NI-ICz, 25 °C.



Fig. S5 MALDI-TOF-HRMS of ICz, 25 °C.

3. Crystallographic data

| Compound | NI-ICz |
|---------------------------------|---|
| Sum formula | C ₅₀ H ₄₁ N ₃ O ₆ |
| <i>M</i> (g mol ^{−1}) | 779.86 |
| Temperature / K | 298 K |
| Crystal system | Monoclinic |
| Space group | C2/c |
| a (Å) | 19.7004 (18) |
| b (Å) | 23.323 (2) |
| <i>c</i> (Å) | 19.0014 (15) |
| lpha (deg) | 90 |
| eta (deg) | 112.623 (3) |
| γ(deg) | 90 |
| Volume / Å ³ | 8059.0 (12) |
| Ζ | 8 |
| $D_{ m calc}$ / g cm $^{-3}$ | 1.285 |
| F (000) | 3280.0 |
| μ / mm ⁻¹ | 0.085 |
| θ_{\max} (deg) | 27.524 |
| Reflections collected | 35003 |
| Independent reflections | 9242 [R _{int} = 0.0973, R _{sigma} = 0.1104] |
| Parameters | 538 |
| Largest diff. peak and hole (e | 0.82 / -0.39 |
| Å ^{−3}) | |
| Goodness of fit | 1.012 |
| R ^a | 0.0728 |
| ωR_2^a | 0.2030 |

Table S1 Crystallographic data for NI-ICz^a

 ${}^{a}R = \sum ||F_0| - |F_c|| / \sum |F_0|$, $\omega R_2 = [\sum \omega (|F_0|^2 - |F_c|^2) / \sum \omega (F_0^2)^2]^{1/2}$, $[F_0 > 4\sigma(F_0)c^2]$. After repeated refinement, there are still a large reported Max. (positive) residual density (Alert level B), which is caused by poor crystal quality or weak diffraction points.

4. UV/Vis absorption spectra



Fig. S6 UV/Vis absorption spectra of (a) NI-Br; (b) NI-Cz; (c) ICz; (d) NI-ICz in different solvents. $c = 1.0 \times 10^{-5}$ M, 25 °C.



Fig. S7 UV/Vis absorption spectra of the compounds in (a) TOL; (b) THF; (c) DCM; (d) ACN. $c = 1.0 \times 10^{-5}$ M, 25 °C.

For Eq. 2 and Eq. 3, the ε (\tilde{v}_{CT}) is the molar absorption coefficient of CT band in M⁻¹ cm⁻¹, \tilde{v}_{CT} is the maximum wavenumber of the S₀ \rightarrow CT band in cm⁻¹, *n* is the refractive index of the solvent, *N*_A is the Avogadro constant in mol⁻¹, *h* is the Planck constant in erg s, the *R* is the separation between the center of nucleus and the acceptor group, is in Å, ε_{max}^{CT} is represent molar absorptivity at the absorbance maximum of the CT absorption band in M⁻¹ cm⁻¹, \tilde{v}_{max}^{CT} is absorption maximum of the CT absorption band (in cm⁻¹) and $\Delta \tilde{v}_{1/2}^{CT}$ is the full width of the CT band at the half maximum in cm⁻¹.





Fig. S8 Fluorescence emission spectra of the compounds in (a) HEX; (b) TOL; (c) THF; (d) DCM; (e) ACN. Optically matched solutions were used in each panel (each of the solutions gives the same absorbance at the excitation wavelength, A = 0.100). $\lambda_{ex} = 330$ nm, 25 °C.



Fig. S9 Fluorescence decay curves of LE excited state of (a) **NI-Br**; (b) **ICz**; (c) **NI-ICz** in different solvent. $\lambda_{ex} = 340$ nm, $c = 1.0 \times 10^{-5}$ M, 25 °C.



Fig. S10 Fluorescence decay curves of CT excited state of (a) NI-Cz and (b) NI-ICz in different solvent. $\lambda_{ex} = 340$ nm, $c = 1.0 \times 10^{-5}$ M, 25 °C.



Fig. S11 Fluorescence emission spectra of (a) **NI-Br**; (c) **NI-ICz**. $c = 1.0 \times 10^{-5}$ M, $\lambda_{ex} = 350$ nm and 410 nm, respectively. Decay curves of (b) **NI-Br** at 570 nm and (d) **NI-ICz** at 450 nm and 600 nm at 77 K, in 2Me-THF.



Fig. S12 Fluorescence emission spectra of (a) ICz; (c) NI-Cz at different tempreture. $c = 1.0 \times 10^{-5}$ M, $\lambda_{ex} = 340$ nm, in 2Me-THF, 77 K.



Fig. S13 Fluorescence decay curves of (a) NI derivatives in HEX, (b) CT band of NI-Cz and NI-ICz at 500 nm and 600 nm, respectively. $\lambda_{ex} = 340$ nm, $c = 1.0 \times 10^{-5}$ M, 25 °C.



Fig. S14 Fluorescence decay traces of **NI-ICz** under different atmospheres (N₂, Air). $\lambda_{ex} = 340$ nm, decay trace at 580 nm. Excited with nanosecond EPLED (340 nm). $c = 1.0 \times 10^{-5}$ M in toluene, 25 °C.

| Compounds | HEX ^c | | TOL ^d | | THF ^e | | DCN | DCM ^f | | ACN ^g | |
|-----------|--------------------|-------------|------------------|-------------|--------------------|-------------|--------------------|------------------|------------------|------------------|--|
| | $arPhi_{\!\Delta}$ | $arPhi_{F}$ | $arPhi_{\Delta}$ | $arPhi_{F}$ | $arPhi_{\!\Delta}$ | $arPhi_{F}$ | \varPhi_{Δ} | $arPhi_{F}$ | $arPhi_{\Delta}$ | $arPhi_{F}$ | |
| NI-Br | 42 | 0.3 | 54 | 0.4 | 33 | 0.2 | 71 | 0.3 | 84 | 0.1 | |
| NI-Cz | 38 | 52 | 44 | 25 | 29 | 14 | 59 | 18 | 31 | 6 | |
| ICz | 4 | 35 | 13 | 48 | 5 | 49 | 12 | 33 | 1 | 38 | |
| NI-ICz | 25 | 6 | 2 | 4 | _ h | 1 | _ h | 0.8 | _ h | 0.6 | |

Table S2 Singlet oxygen quantum yield $(\Phi_{\Delta})^a$ and absolute fluorescence quantum yield $(\Phi_{F})^b$ of the

^a In percentage. Ru(bpy)₃[PF₆]₂ was used as standard ($\Phi_{\Delta} = 0.57$ in DCM). Optically matched solutions were used in each panel (each of the solutions gives the same absorbance at the excitation wavelength, A = 0.25 at $\lambda_{ex} = 335$ nm). ^b $\lambda_{ex} = 330$ nm, measured with optical integration sphere. ^c *n*-Hexane, E_{T} (30) = 30.9 kcal/mol. ^d Toluene, E_{T} (30) = 33.9 kcal/mol. ^e Tetrahydrofuran, E_{T} (30) = 37.4 kcal/mol. ^f Dichloromethane, E_{T} (30) = 41.1 kcal/mol. ^g Acetonitrile, E_{T} (30) = 46 kcal/mol. ^h Not observed.

compounds in different solvents

6. Cyclic voltammograms

Table S3 Redox potentials of the compounds^a

| | NI-Br | ICz |
|--------------------|-------|-------|
| <i>E</i> (ox) (V) | _b | +0.17 |
| | | +0.70 |
| <i>E</i> (red) (V) | -1.83 | _b |
| | -1.98 | _b |

^aCyclic voltammetry in N₂ saturated DCM containing a 0.10 M Bu₄NPF₆ supporting electrolyte; Counter electrode is Pt electrode; working electrode is glassy carbon electrode; Ag/AgNO₃ couple as the reference electrode. ^bNot observed.

For Eq 6–8, ΔG_{CS} is the Gibbs free-energy change of charge separation process, *e* is the charge of a single electron, E_{RED} and E_{OX} are the half-wave potential for one-electron reduction and oxidation of the electron-acceptor unit, respectively, E_{00} represent the energy level approximated with the crossing point of UV/Vis absorption and fluorescence emission after normalization at the singlet excited state. ΔG_S is the static coulombic energy, ε_S is the static dielectric constant of the solvent, ε_0 is the permittivity of free space, R_{CC} is the center-to-center separation distance between the electron donor and acceptor determined by optimized conformation by DFT calculation, R_D and R_A are the radius of electron donor and acceptor, ε_{REF} is the static dielectric constant of the solvent used for the electrochemical studies and E_{CS} is charge separation state energy level.



Fig. S15 Femtosecond transient absorption spectra of **NI-Br**. Transient absorption spectra in (a) *n*-hexane and (c) acetonitrile; relative EADS obtained with global analysis (c) *n*-hexane and (d) acetonitrile. Excited at 340 nm.



Fig. S16 Femtosecond transient absorption spectra of **ICz**. Transient absorption spectra in (a) *n*-hexane and (c) acetonitrile; relative EADS obtained with global analysis (c) *n*-hexane and (d) acetonitrile. Excited at 340 nm.



Fig. S17 Femtosecond transient absorption spectra of **NI-Cz**. Transient absorption spectra in (a) *n*-hexane and (c) acetonitrile; relative EADS obtained with global analysis (b) *n*-hexane and (d) acetonitrile. Excited at 340 nm.



Fig. S18 The schematic diagram of relationship between the electron transfer rate constant (k_{ET})

and the Gibbs free energy changes of the electron transfer (ΔG_{ET}) for **NI-ICz**.

8. Nanosecond transient absorption spectroscopy



Fig. S19 (a) Transient absorption spectra of NI-ICz, $c = 1.0 \times 10^{-5}$ M and (b) decay curve at 470 nm, $c = 5.0 \times 10^{-6}$ M in aerated HEX. $\lambda_{ex} = 355$ nm, 25 °C.



Fig. S20 (a) Decay curve at 470 nm of **NI-Br** in aerated HEX, $c = 5.0 \times 10^{-6}$ M. $\lambda_{ex} = 355$ nm, 25 °C.



Fig. S21 (a) Transient absorption spectra of NI-ICz, $c = 2.0 \times 10^{-5}$ M and (b) decay curve at 470 nm, $c = 2.0 \times 10^{-5}$ M in aerated TOL. $\lambda_{ex} = 355$ nm, 25 °C.



Fig. S22 Nanosecond time-resolved transient absorption spectra of **ICz** upon pulsed laser excitation in (a) deaerated and (c) aerated toluene, decay trace of **ICz** at 510 nm in (b) deaerated and (d) aerated toluene, $c = 1 \times 10^{-5}$ M. $\lambda_{ex} = 355$ nm, 25 °C.



Fig. S23 (a) Transient absorption spectra of **NI-Br**, $c = 1.0 \times 10^{-5}$ M and (b) decay curve at 470 nm, $c = 5.0 \times 10^{-6}$ M in ACN. (c) Transient absorption spectra of **ICz** and (d) decay curve at 510 nm, $c = 5.0 \times 10^{-6}$ M in ACN. $\lambda_{ex} = 355$ nm, 25 °C.



Fig. S24 (a) Transient absorption spectra of NI-Cz, $c = 1.0 \times 10^{-5}$ M and (b) decay curve at 470 nm, $c = 5.0 \times 10^{-6}$ M in HEX. (c) Transient absorption spectra of NI-Cz, $c = 1.0 \times 10^{-5}$ M and (d) decay curve at 470 nm, $c = 5.0 \times 10^{-6}$ M in ACN. $\lambda_{ex} = 355$ nm, 25 °C.





Fig. S25 TREPR spectra of four studied compounds detected at different time delays after the laser flash (integration limits are given in legends). (a) **NI-Br** excited at 355 nm with energy 1 mJ, (b) **NI-Cz** excited at 355 nm with energy of 1 mJ per pulse, (c) **ICz** excited at 355 nm with energy 1 mJ and (d) **NI-ICz** excited at 355 nm with energy of 1 mJ per pulse. (e) **NI-ICz** excited at 502 nm with energy of 1 mJ per pulse. T = 80 K. $c = 1.0 \times 10^{-4} \text{ M}$.



Fig. S26 Spin density surfaces of the compounds in vacuo, at the optimized triplet state geometry, calculated at [CAM-B3LYP/6-31G(d)] (isovalue = 0.0004) level with Gaussian 16.



Fig. S27 The Absorption and corresponding orbital transitions of **NI-ICz** (a) anion **NI^{-•}-ICz** and (b) cation **NI-ICz^{+•}** calculated by DFT, [CAM-B3LYP/6-31G(d)] (isovalue = 0.0004) level with Gaussian 16.



Fig. S28 Hyperfine coupling constants obtained by DFT calculation of NI*--ICz and NI-ICz*+.



Scheme S1 Simplified energy diagram of the photophysical processes involved in NI-Br and ICz.

Table S4 Electronic excitation energies (eV) and corresponding oscillator strengths (*f*), main configurations, and CI coefficients of the low-lying electronic excited states compounds. Calculated by TDDFT// ω B97XD/6-31G(d) based on the DFT// ω B97XD/6-31G(d)-optimized ground state geometries for **NI-ICz** and TDDFT//CAM-B3LYP/6-31G(d) based on the DFT// ω B97XD/6-31G(d)-optimized ground state geometries for **NI-Br** and **ICz**^{*a*}

| | State | Electronic transition | Energy ^b , eV nm ⁻¹ | fc | Composition ^d | CI e | Character |
|--------|---------|-------------------------|--|---------------------|--------------------------|---------|-----------|
| NI-ICz | Singlet | $S_0 \!\rightarrow S_1$ | 3.13/395 | 0.0696 | $H \rightarrow L$ | 0.62670 | СТ |
| | | $S_0\!\to S_2$ | 3.52/353 | 0.2905 | $H \rightarrow L+1$ | 0.67157 | LE |
| | Triplet | $S_0\!\rightarrow T_1$ | 2.26/548 | 0.0000 ^f | $H-5 \rightarrow L$ | 0.46205 | СТ |
| | | $S_0\!\rightarrow T_2$ | 2.68/463 | 0.0000 ^f | $H \rightarrow L+1$ | 0.60626 | LE |
| | | $S_0\!\rightarrow T_3$ | 2.92/425 | 0.0000 ^f | $H-1 \rightarrow L+1$ | 0.53379 | LE |
| | | $S_0\!\to T_4$ | 3.10/400 | 0.0000 ^f | $H \to L$ | 0.58491 | СТ |
| NI-Br | Singlet | $S_0\!\to S_1$ | 3.62/342 | 0.0001 | $H-1 \rightarrow L$ | 0.69467 | LE |
| | | $S_0\!\to S_2$ | 3.63/341 | 0.2293 | $H \to L$ | 0.69696 | LE |
| | Triplet | $S_0\!\rightarrow T_1$ | 2.26/548 | 0.0000 ^f | $H \rightarrow L$ | 0.68308 | LE |
| | | $S_0\!\rightarrow T_2$ | 3.35/370 | 0.0000 ^f | $H-1 \rightarrow L$ | 0.67686 | LE |
| | | $S_0\!\rightarrow T_3$ | 3.40/365 | 0.0000 ^f | $H-2 \rightarrow L$ | 0.61371 | LE |
| | | $S_0\!\rightarrow T_4$ | 3.65/340 | 0.0000 ^f | $H-3 \rightarrow L$ | 0.58785 | LE |
| ICz | Singlet | $S_0\!\to S_1$ | 2.93/423 | 0.1375 | $H \to L$ | 0.69975 | LE |
| | | $S_0\!\to S_2$ | 3.66/339 | 0.0002 | $H-2 \rightarrow L$ | 0.69800 | LE |
| | Triplet | $S_0\!\rightarrow T_1$ | 2.30/539 | 0.0000 ^f | $H \to L$ | 0.68692 | LE |
| | | $S_0\!\rightarrow T_2$ | 2.74/453 | 0.0000 ^f | $H-1 \rightarrow L$ | 0.62810 | LE |
| | | $S_0\!\rightarrow T_3$ | 3.07 /403 | 0.0000 ^f | $H-2 \rightarrow L$ | 0.58563 | LE |

^a In *c*–HEX. ^b Only the selected low lying excited states are presented. ^c Oscillator strengths. ^d TDDFT// ω97XD/6-31G(d)-optimized excited state geometries for **NI-ICz** and CAM-B3LYP/6-31G(d) for **NI-Br** and **ICz**. ^e CI coefficients are in absolute values. ^f No spin–orbital coupling effect was considered; thus, the *f* values are zero.

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