Electronic supplementary information

Enhanced blue TADF in D-A-D type naphthyridine derivative with asymmetric carbazole-donor motif

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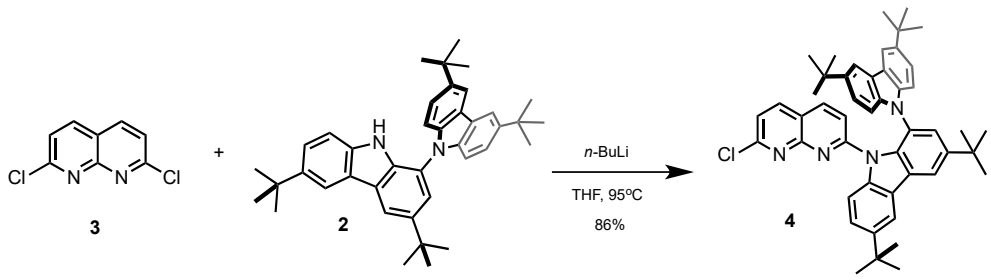
Synthesis and identification

All reagents and starting materials were obtained from commercial sources and used as received. Reaction solvents, dimethylformamide was distilled from CaH_2, THF was distilled from sodium/ benzophenone. All moisture-sensitive reactions were performed in oven-dried (230 °C) glassware under an atmosphere of dry argon. Thin-layer chromatography was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with UV (254 nm). Column chromatography was performed using Merck silica 60 (40−63 µm particle size). ^{1}H and ^{13}C NMR spectra were recorded on a NMR spectrometer at 400 MHz for ^{1}H and 101 MHz for ^{13}C, respectively. ^{1}H and ^{13}C NMR spectra are referenced to residual solvent ($CDCl_3$, 7.29 and 77.16 ppm for ^{1}H NMR and ^{13}C NMR, respectively). Chemical shifts are reported in ppm, and multiplicities are indicated by s (singlet), d (doublet), m (multiplet), and combinations thereof. HRMS was recorded on Bruker Daltonics microTOF-II spectrometer equipped with ESI ion source in positive mode or Brucker Autoflex speed MALDI TOF spectrometer.

3,3',6,6'-tetra-*tert*-butyl-9*H*-1,9'-bicarbazole **2** [1] and 2,7-dichloro-1,8-naphthyridine **3** [2] were synthesized according to literature.

Abbreviations: AcOH, acetic acid; n-BuLi, n-butyllithium; DCM, dichloromethane; DMF, dimethylformamide; dppp, 1,3-bis(diphenylphosphino)propane; EtOAc, ethyl acetate; PE, petrol ether (40−60 °C fraction); PhCl, chlorobenzene; THF, tetrahydrofuran.



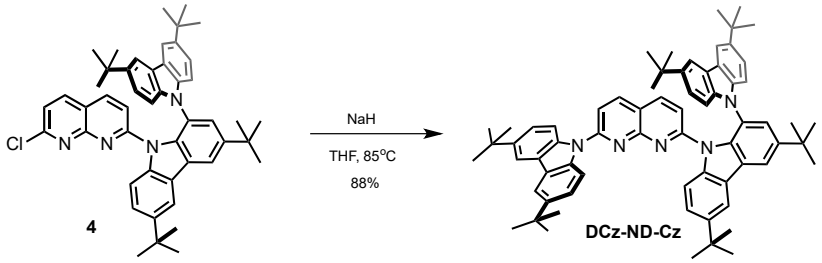
Compound 4. To a solution of 3,3',6,6'-tetra-*tert*-butyl-9*H*-1,9'-bicarbazole **2** (315 mg, 0.566 mmol, 2.1 equiv.) in dry THF (10 ml) *n*-BuLi (0.226 ml, 2.5 M, 2.1 equiv.) was added dropwise at -78°C. The reaction mixture was left to stir for 2h at r.t. before adding 2,7-dichloro-1,8-naphthyridine **3** (53 mg, 0.269 mmol, 1.0 equiv.) in one portion. The vial was screw-capped and heated at 95°C. After 96 h, the mixture was cooled to r.t., diluted with water and extracted with EtOAc. Purification by column chromatography on silica gel using gradient eluent system DCM/PE (1:6 to 2:1) afforded 165 mg (86%) of **4** as a light-yellow solid.

$\mathbf{R_f}$ = 0.6 (1/10 EtOAc:PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.24 (dd, *J*=28.4, 1.9, 2H), 7.91 (d, *J*=8.7, 1H), 7.72 – 7.65 (m, 3H), 7.50 (dd, *J*=8.8, 2.0, 1H), 7.33 (d, *J*=8.3, 2H), 7.26 (s, 1H), 7.12 (d, *J*=8.7, 2H), 6.77 – 6.66 (m, 1H), 6.50 (d, *J*=8.4, 1H), 1.53 (s, 9H), 1.49 (s, 9H), 1.35 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.50, 153.31, 153.15, 145.36, 144.94, 142.66, 139.23, 138.03, 138.00, 135.22, 132.98, 129.49, 128.05, 124.98, 124.50, 123.97, 123.59, 123.23, 122.85, 122.33, 121.47, 119.26, 118.66, 116.18, 115.86, 115.03, 111.93, 109.56, 109.51, 34.98, 34.84, 34.56, 31.98, 31.96, 31.94, 31.92, 29.72, 29.00, 22.99, 14.15.

MS (MALDI-TOF) calc. for $C_{48}H_{51}ClN_4$ (M): 718.38; Found: 718.39.



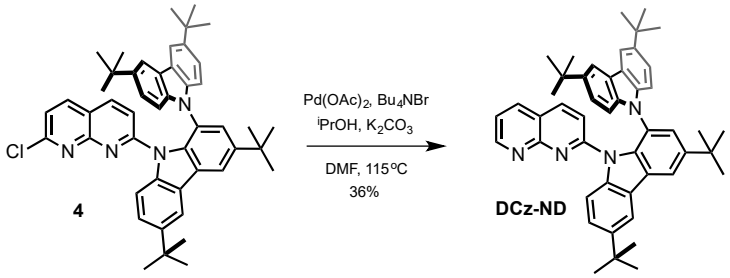
Compound DCz-ND-Cz. To a solution of 3,5-di-*tert*-butyl-carbazole (19 mg, 0.068 mmol, 1.4 equiv.) in dry THF (2.5 ml) NaH (4.0 mg, 0.097 mmol, 60% dispersion in mineral oil, 2.0 equiv.) was added at once at room temperature. The reaction mixture was heated at 60 °C for 1 h, before adding **4** (35 mg, 0.049 mmol, 1.0 equiv.) in one portion. The vial was screw-capped and heated at 85°C. After 86 h, the mixture was cooled to room temperature, diluted with water and extracted with EtOAc. Purification by column chromatography on silica gel using eluent EtOAc/PE (1:50) afforded 47 mg (88%) of **DCz-ND-Cz** as a light-yellow glass.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.21 (d, *J*=1.9, 1H), 8.13 (d, *J*=2.0, 1H), 8.07 – 7.98 (m, 4H), 7.93 (d, *J*=8.7, 1H), 7.68 (d, *J*=14.7, 2H), 7.64 (s, 1H), 7.60 (d, *J*=1.9, 1H), 7.45 (ddd, *J*=8.8, 4.2, 2.0, 3H), 7.24 (s, 2H), 7.09 (s, 2H), 6.67 (d, *J*=8.3, 1H), 6.37 (d, *J*=8.3, 1H), 1.47 – 1.36 (m, 36H), 1.16 (s, 18H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.96, 153.82, 153.13, 145.03, 144.73, 142.57, 139.59, 138.45, 137.74, 137.55, 135.42, 133.19, 129.50, 128.00, 125.12, 125.09, 124.66, 124.13, 123.91, 123.55, 122.99, 121.30, 118.11, 117.74, 116.45, 116.24, 115.88, 115.74, 115.24, 112.56, 112.13, 109.48, 34.98, 34.85, 34.80, 34.54, 32.10, 31.99, 31.96, 31.94.

R_f = 0.34 (1/50 EtOAc:PE).

HRMS (ESI) calc. for $C_{68}H_{76}N_5$ (M+H): 962.6095; Found: 962.6099.



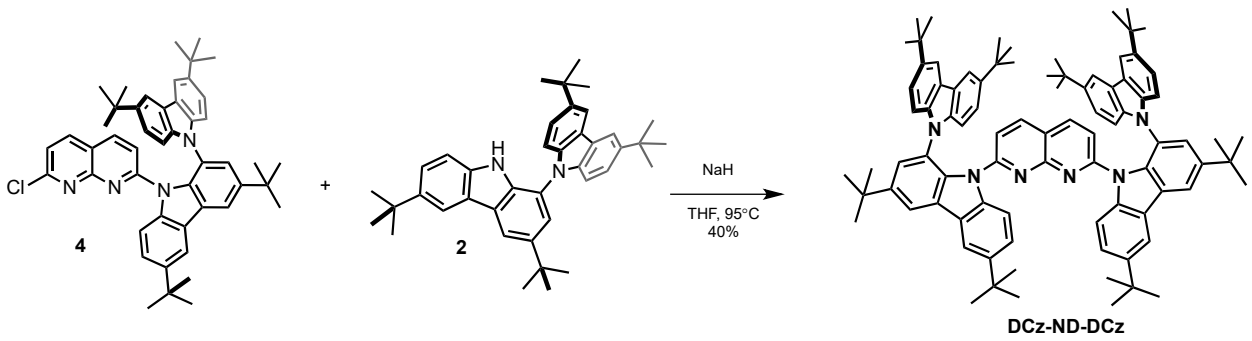
Compound DCz-ND. A mixture of K_2CO_3 (7.8 mg, 0.056 mmol, 1.0 equiv), $Pd(OAc)_2$ (0.6 mg, 0.0027 mmol, 0.05 equiv), Bu_4NBr (10 mg, 0.031 mmol, 0.55 equiv) and **4** (40 mg, 0.056 mmol, 1.0 equiv) in dry DMF (2.0 ml) was stirred for few minutes at 115 °C. Isopropanol (8.0 µl) was added and the mixture was remained at the above temperature for 32 h. The mixture was diluted with 1.0 M HCl and extracted with EtOAc. Purification by column chromatography on silica gel using eluent EtOAc/PE (1:4) afforded 14 mg (36%) of **DCz-ND** as a light-yellow glass.

R_f = 0.29 (1/4 EtOAc:PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.73 (dd, *J*=4.0, 1.9, 1H), 8.25 – 8.08 (m, 2H), 7.81 (d, *J*=8.7, 1H), 7.66 (d, *J*=8.0, 1H), 7.60 (d, *J*=1.7, 1H), 7.53 (s, 2H), 7.41 (dd, *J*=8.7, 1.9, 1H), 7.22 (d, *J*=8.6, 2H), 7.17 – 7.12 (m, 1H), 7.03 (d, *J*=8.5, 2H), 6.72 (d, *J*=8.4, 1H), 6.47 (d, *J*=8.4, 1H), 1.44 (s, 9H), 1.41 (s, 9H), 1.24 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.64, 152.35, 145.15, 144.74, 142.44, 139.40, 138.21, 135.99, 135.53, 133.16, 127.95, 124.88, 124.50, 123.97, 123.49, 122.80, 121.54, 120.84, 120.15, 119.16, 116.09, 115.86, 115.04, 111.82, 109.54, 34.96, 34.82, 34.52, 31.98, 31.95, 31.92, 29.70.

HRMS (ESI) calc. for $C_{48}H_{53}N_4$ (M+H): 658.4265; Found: 658.4263.



Compound DCz-ND-DCz. To a solution of **2** (47 mg, 0.084 mmol, 2.0 equiv) in dry THF (), NaH (5.0 mg, 0.13 mmol, 60% dispersion in mineral oil, 3.0 equiv) was added at once. The mixture was stirred at room temperature for 2 h, then **4** (30 mg, 0.042 mmol, 1.0 equiv) was added. The mixture was heated at 90 °C for 48 h, cooled to room temperature, diluted with 1.0 M HCl and extracted with EtOAc. Purification by column chromatography on silica gel using gradient eluent system DCM/PE (1:6 to 2:1) afforded 21 mg (40%) of **DCz-ND-DCz** as a light-yellow glass.

$\mathbf{R_f}$ = 0.55 (1/10 EtOAc:PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.67 (d, *J*=8.4, 2H), 8.18 (dd, *J*=25.8, 1.9, 4H), 7.82 (dd, *J*=8.6, 5.6, 4H), 7.61 (d, *J*=1.8, 5H), 7.47 (dd, *J*=8.7, 2.0, 3H), 7.24-7.17 (m, 4H), 7.08 (d, *J*=8.7, 4H), 6.83 (d, *J*=8.4, 2H), 6.54 (d, *J*=8.3, 2H), 1.46 (s, 18H), 1.44 (s, 18H), 1.18 (s, 36H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.54, 152.57, 145.09, 144.70, 142.48, 139.59, 138.29, 136.38, 135.56, 133.23, 127.87, 124.92, 124.52, 123.92, 123.39, 121.49, 120.73, 120.31, 119.43, 116.11, 115.86, 115.28, 111.64, 109.45, 34.97, 34.84, 34.45, 31.97, 31.93, 31.86, 29.70, 29.36, 22.69, 14.12, 1.03.

HRMS (ESI) calc. for $C_{88}H_{99}N_6$ (M+H): 1239.7926; Found: 1239.7926.

Copies of NMR spectra

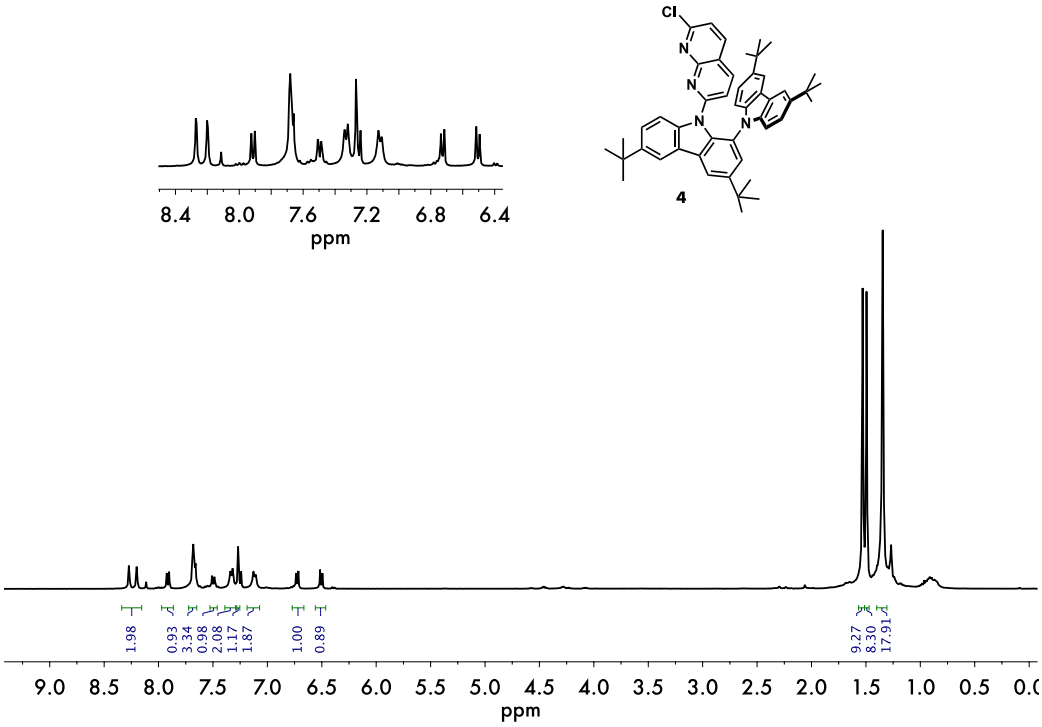


Figure S1. ^{1}H NMR of **4** ($CDCl_3$, 400 MHz).

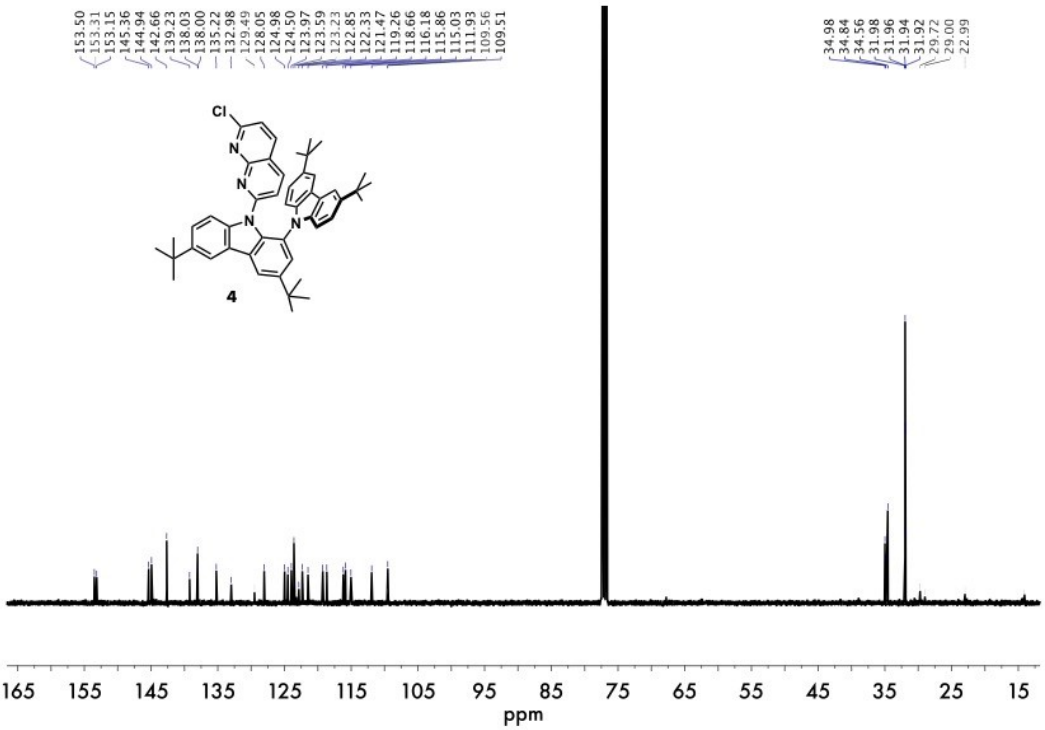


Figure S2. ^{13}C NMR of **4** ($CDCl_3$, 101 MHz).

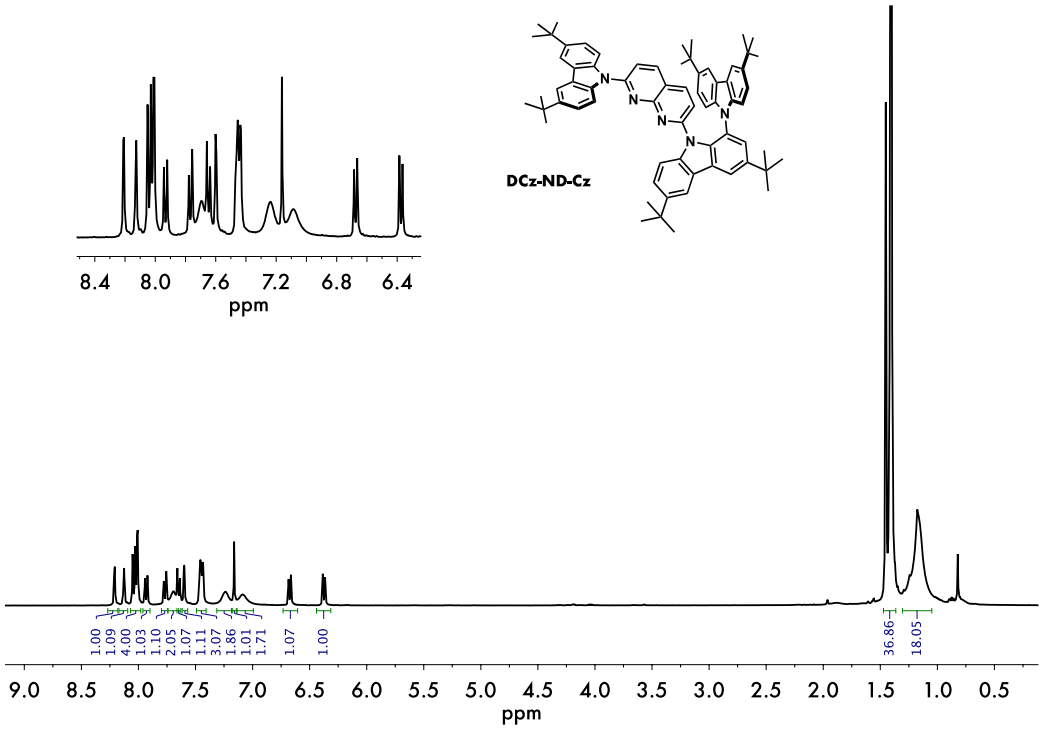


Figure S3. ^{1}H NMR of **DCz-ND-Cz** ($CDCl_3$, 400 MHz).

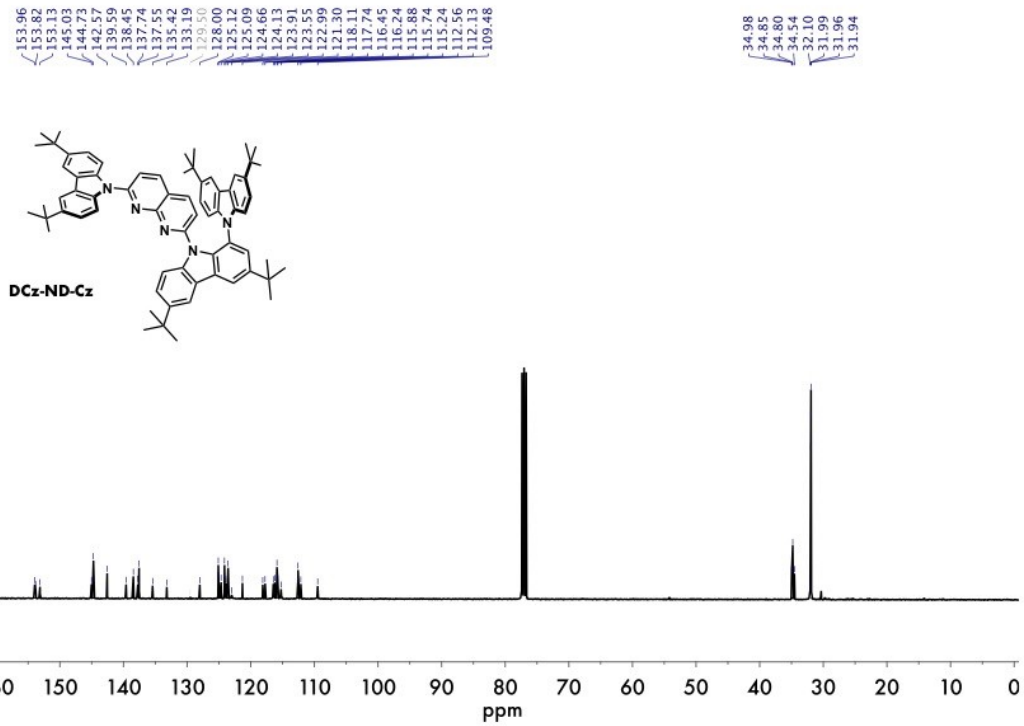


Figure S4. ^{13}C NMR of **DCz-ND-Cz** ($CDCl_3$, 101 MHz).

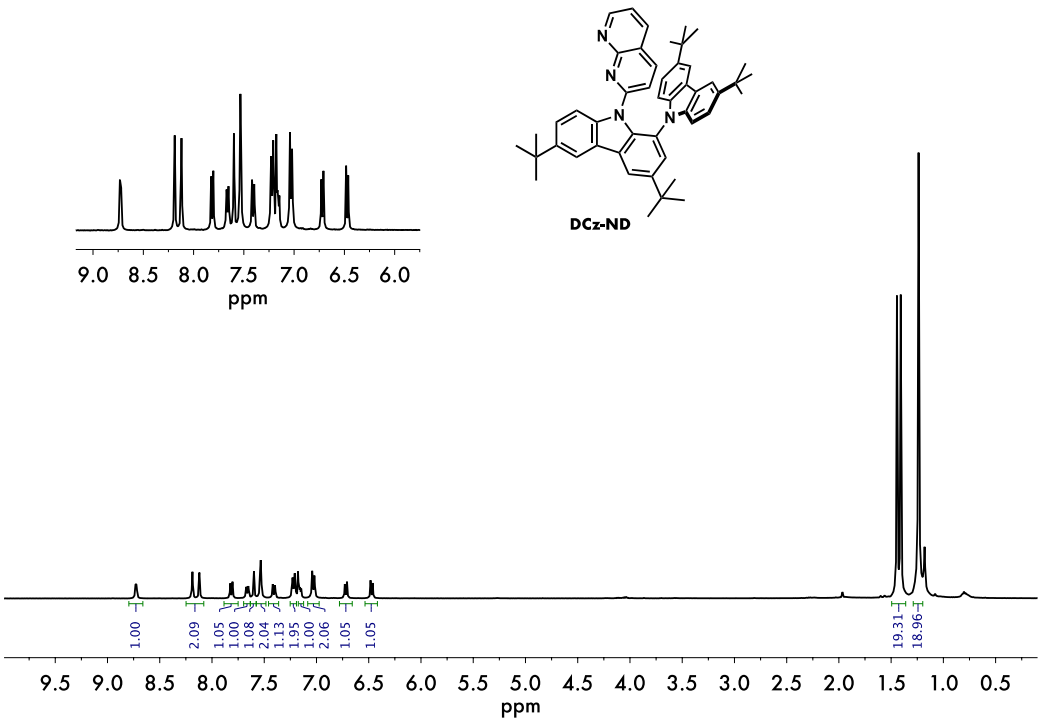


Figure S5. ^{1}H NMR of **DCz-ND** ($CDCl_3$, 400 MHz).

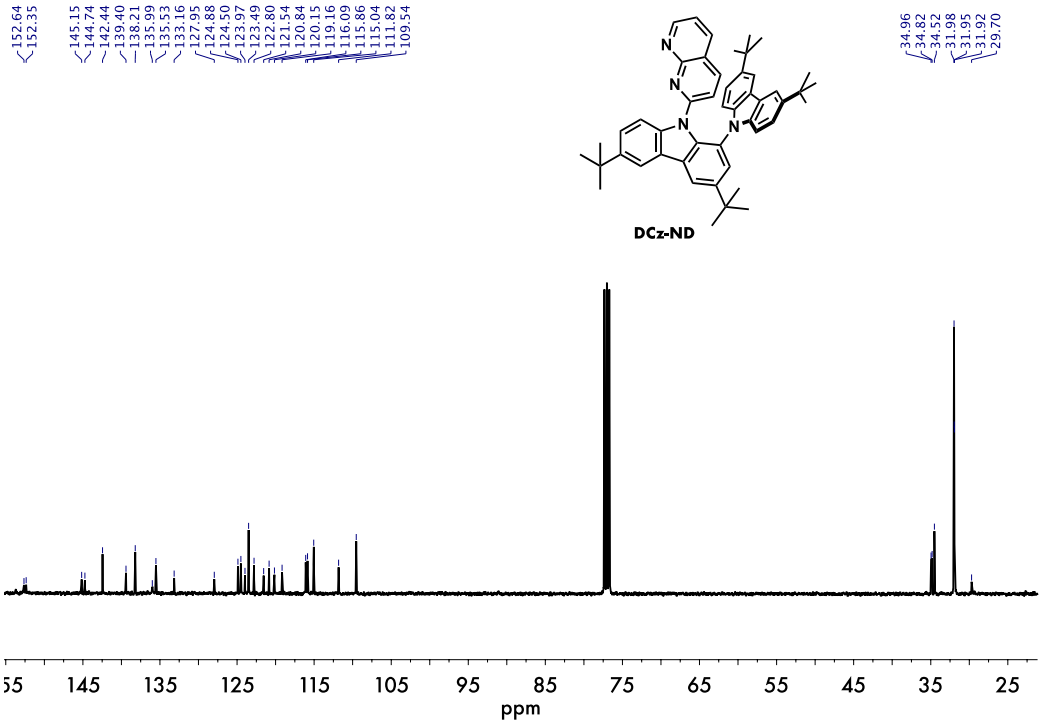


Figure S6. ^{13}C NMR of **DCz-ND** ($CDCl_3$, 101 MHz).

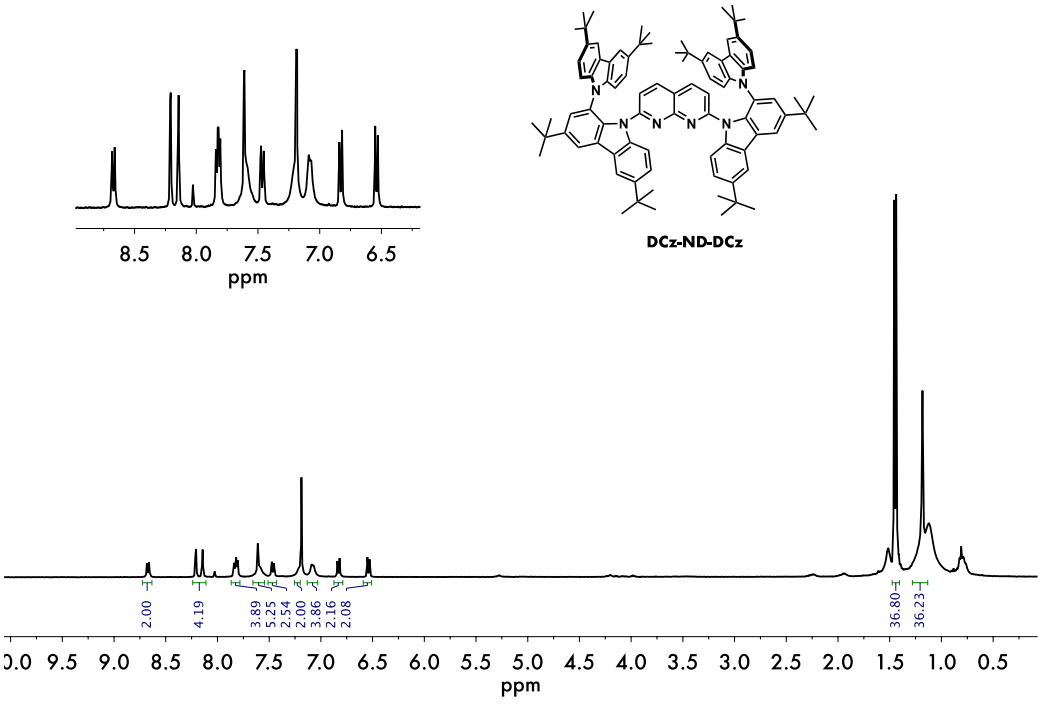


Figure S7. ^{1}H NMR of **DCz-ND-DCz** ($CDCl_3$, 400 MHz).

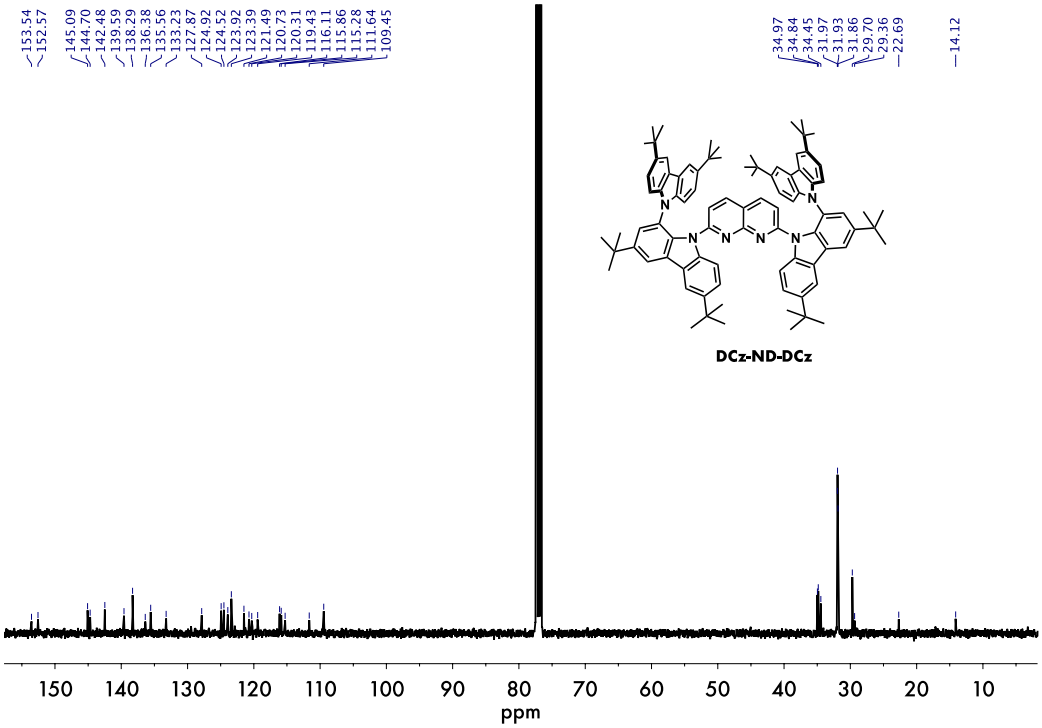


Figure S8. ^{13}C NMR of **DCz-ND-DCz** ($CDCl_3$, 101 MHz).

X-Ray Crystallography

Single crystals of investigated naphthyridines were grown by slow evaporation of solvent/antisolvent mixtures. Suitable crystals were mounted on a microloop (MiTeGen) and analyzed on a XtaLab Synergy diffractometer equipped with HyPix-6000HE hybrid photon counting detector and PhotonJet microfocus X-ray source (CuKα, λ = 1.54184). Diffraction experiments were carried out at 100.0 K using Oxford Cryostream 800 cooling system. Data were collected and processed with CrysAlisPro software. The structure was solved by Intrinsic Phasing with the ShelXT [3] program and refined with the ShelXL [4] package using Least Squares minimization as implemented in Olex2 graphical interface [5]. Due to the co-crystallization of highly disordered solvent molecules in **DCz-ND** and **DCz-ND-DCz** crystals, solvent masking was applied during the structure refinement. The structure files **DCz-ND**, **DCz-ND-Cz** and **DCz-ND-DCz** crystals were deposited with the Cambridge Crystallographic Data Centre and can be accessed free of charge (**CCDC** deposition numbers**: 2113723**, **2113744** and **2113780**, respectively).

Table S1. Crystallographic data of naphthyridine derivatives.

Compound	**DCz-ND**	**DCz-ND-Cz**	**DCz-ND-DCz**
CCDC deposition number	**2113723**	**2113744**	**2113780**
Empirical formula	$C_{48}H_{52}N_4$	$C_{68}H_{75}N_5$	$C_{88}H_{98}N_6$
Formula weight	684.93	962.33	1239.72
Temperature/K	100.00(10)	100.00(10)	100.00(10)
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1$	P-1	$P2_1/c$
a/Å	12.72429(16)	12.69725(17)	24.3736(3)
b/Å	24.1867(2)	17.0233(3)	22.3138(3)
c/Å	14.22098(19)	28.0493(4)	31.3310(5)
α/°	90	76.7216(12)	90
β/°	108.7464(14)	81.3818(12)	97.1858(11)
γ/°	90	78.1997(12)	90
Volume/Å^3	4144.45(9)	5742.26(15)	16906.1(4)
Z	4	4	8
ρ_{calc}mg/mm^3	1.098 + solvent	1.113	0.974 + solvent
Crystal size/mm^3	0.171 × 0.083 × 0.03	0.231 × 0.057 × 0.043	0.18 × 0.07 × 0.033
2Θ range for data collection	6.564 to 153.65°	5.42 to 155.04°	4.874 to 155.388°
Index ranges	-14 ≤ h ≤ 15, -29 ≤ k ≤ 30, -17 ≤ l ≤ 17	-15 ≤ h ≤ 16, -21 ≤ k ≤ 21, -33 ≤ l ≤ 34	-28 ≤ h ≤ 30, -27 ≤ k ≤ 27, -39 ≤ l ≤ 39
Reflections collected	56243	87555	110834
Independent reflections	16763[R(int) = 0.0351]	23628[R(int) = 0.0316]	34596[R(int) = 0.0485]
Data/restraints/parameters	16763/1/962	23628/0/1382	34596/6/1914
Goodness-of-fit on F^2	1.030	1.037	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0511, wR_2 = 0.1316	R_1 = 0.0512, wR_2 = 0.1309	R_1 = 0.0630, wR_2 = 0.1535
Final R indexes [all data]	R_1 = 0.0530, wR_2 = 0.1330	R_1 = 0.0603, wR_2 = 0.1368	R_1 = 0.0906, wR_2 = 0.1670
Largest diff. peak/hole / e Å^{-3}	0.56/-0.26	0.69/-0.31	0.72/-0.34
Solvents used	DCM/Methanol	IPA/DMSO	IPA/DMF

Solvatochromism studies

Solvent dependent spectral shifts were analyzed in terms of the Lippert equation,

$$\Delta\nu = \nu_{abs} - \nu_{fl} = \frac{2(\mu_e - \mu_g)^2}{hca^3} * \Delta f + const.$$

Here ν_{abs} - ν_{fl} is the Stokes' shift in wavenumbers determined from absorption and fluorescence spectra; μ_e and μ_g are dipole moments of the ground and excited states; h is a Planck constant; c – velocity of light; a – cavity radius in which a fluorophore resides.
Solvent orientation polarizability (Δf) is described by refractive index (n) and static dielectric constant (ε).

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}.$$

Absorption and fluorescence spectra of naphthyridines in different solvents (Fig. S9) were used to obtain Lippert-Mataga plots (Fig. S10). The increase of dipole moments ($\mu_e - \mu_g$) in the excited state compared to the ground state for **DCz-ND**, **DCz-ND-Cz** and **DCz-ND-DCz** was estimated to be 40.6 D, 53.0 D and 58.1 D, respectively. However, different dynamics of the Stokes shifts with increasing solvent orientation polarizability (*Δf*) can be determined by different excited state relaxation mechanisms in different compounds as well as by other effects. E.g., unlike the other two compounds, **DCz-ND-Cz** demonstrates a blue shift of absorption spectrum with increasing *Δf* likely associated with ground state geometry changes. **DCz-ND-DCz**, which has the most heavily shielded naphthyridine acceptor (by the bulky donor groups) exhibits weaker solvation of the excited state. Thus, in fact, the data obtained from Lippert-Mataga plots are not well suited to directly compare the compounds and disclose the effect of asymmetric donor motif. Nonetheless, these studies revealed that **DCz-ND-Cz** displays well-structured FL spectrum in non-polar cyclohexane solvent, which gradually transforms to broad and structureless ICT-like FL spectrum with increasing solvent polarizability. We believe that the latter results provide a support for the existence of close lying CT and LE states ensuring high RISC rate in asymmetric **DCz-ND-Cz** compound.

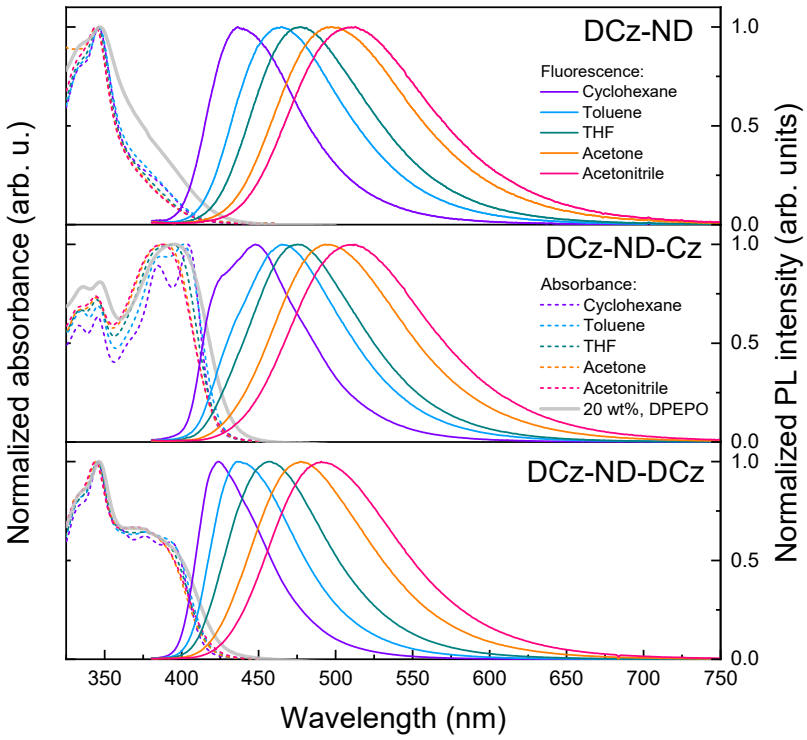


Figure S9. Absorption and fluorescence spectra of the studied naphthyridine derivatives in different solvents. Absorption spectra of the compounds in DPEPO host are shown for reference.

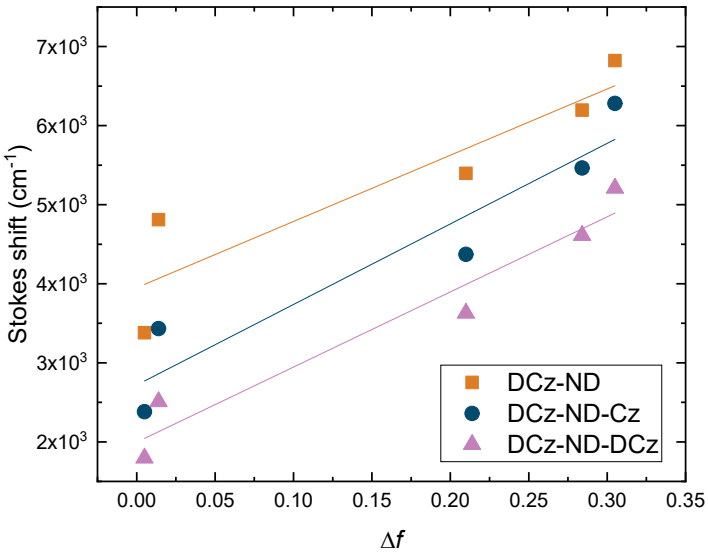


Figure S10. Lippert-Mataga plots of the studied naphthyridine derivatives in different solvents showing the variation of Stokes shift as a function of solvent orientation polarizability.

References

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