*Electronic Supporting Information*

# Free-Standing Blatter Radical Polymer Thin Films: Precise Nanometer Thickness Tuning and Redox-Optical Properties

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**1a. Materials and methods.**

4-Bromo-2-fluoro-1-nitrobenzene, (4-(9H-carbazol-9-yl)phenyl)boronic acid and 4-Bromophenyl hydrazine were purchased from BLD Pharma. Tetrakis(triphenylphosphine)palladium (0) and potassium carbonate were purchased from Merck. Cesium carbonate was purchased from SRL. Phenyl hydrazine, acetic acid, and sodium hydroxide were purchased from CDH, Finar and Qualigens, respectively. 4-Bromobenzoyl chloride and tin (powder) were purchased from Spectrochem and Sigma Aldrich, respectively. Freshly distilled tetrahydrofuran, dichloromethane, acetonitrile, and triethylamine were used for the synthesis of radical derivatives. Hexane, acetone, and isopropyl alcohol were purchased from Finar chemicals and used as received for the cleaning of ITO substrates. Indium-tin oxide-coated glass substrates (ITO, thickness: 1.1 mm, sheet resistance: <10 $\Omega sq^{-1}$) were purchased from Nanoshel.

Geometry optimizations of cationic and radical geometries of compounds 1 and 2 were carried out using the B3LYP/6-31G** level of theory. Implicit solvent effects were included using the polarizable continuum model (PCM) and dichloromethane is used as the solvent. Single-point energy calculations were then carried out at the B3LYP/6-31+G** level of theory using the optimized geometries. All calculations were performed using the Gaussian 16 software package.[1]

Magnetic measurements were carried out by initially cooling the radicals (Zero Field Cooling), followed by application of an external magnetic field upon heating in the temperature range 4 – 300 K at a rate of 2 K/min using the Physical Property Measurement System (PPMS).

Analysis for **$Cz_3N^{\bullet}$**

**$Cz_3N^{\bullet}$** (m = 7 mg, $M_w$ = 1008 g $mol^{-1}$) was analysed upon heating in the range 4 – 300 K at 0.1 T.

Analysis of **$Cz_3N^{\bullet}$** dimers.

The magnetic susceptibility data were further analysed considering a radical dimer of spins (S = ½) for **$Cz_3N^{\bullet}$** (m = 7 mg, $M_w$ = 2016 g $mol^{-1}$) at 0.1 T in the temperature range of 4 – 300 K.

All the fitting equations were adopted from the literature.[10]

**1b. Instrumentation.**

$^1$H NMR spectra for compounds were recorded on ECX 400 MHz JOEL model spectrometers, where all spectra were taken in deuterated chloroform from Sigma Aldrich, and TMS was used as an external standard. Absorption spectra of radicals were collected on JASCO V-670 and used for calculating the molar extinction coefficient. Mass spectra were recorded on LC-MS (ESI)-QToF (Agilent 6546). EPR spectra were recorded at X band (9.1 GHz) on a JEOL X320 spectrometer. Typical acquisition parameters: modulation frequency 100 kHz, modulation amplitude 0.1 mT, microwave power 1 mW. The spectra were recorded at 323 K with 1 mM solutions of Blatter's radicals in degassed toluene. EPR spectra were simulated using EasySpin software.[2] Fourier transform infrared spectroscopy (FTIR) measurements were performed in ATR mode using a Perkin Elmer 1000 UATR instrument in the range of 400 – 4000 $cm^{-1}$. The thermal stability of radicals was assessed using a TGA/DSC 1 Star instrument from Mettler Toledo under an inert atmosphere in the temperature range of 25 to 1000 °C at a heating rate of 10 °C/min. The electrochemical measurements were performed on the PalmSens PS4.F2.05 workstation. Electrochemical studies were carried out in a three-electrode electrochemical cell containing a glassy carbon electrode, GC (working electrode), Ag/AgCl electrode in 0.1 M KCl (reference electrode), and a platinum wire (counter electrode).

Single-crystal X-ray studies were conducted on a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected at

100(2) K using graphite monochromatic Mo Kα radiation (λα = 0.71073 A). The frames were indexed, integrated, and scaled using the SMART and SAINT software packages,[3] and the data were corrected for absorption using the SADABS program.[4] The structures were solved and refined with the SHELXL[5] and OLEX2[6] suites of programs, while additional crystallographic calculations were performed by the program PLATON. All hydrogen atoms were included in the final stages of the refinement and were refined with a typical "riding model". Disordered solvent molecules in the unit cell have been masked using the Olex-2 mask program. The crystallographic figures have been generated using Olex2 software. CCDC number 2502298 contain supplementary crystallographic data for $Cz_3N^{\bullet}$, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. MestRe Nova software for NMR analysis and OriginPro22 software for plotting curves were used.

The thickness measurements of film were done by Bruker Optical profilometer instrument. The data collected with dual-LED illuminated optical module 2.5X and capable stitching with motorized XY stage. The commercial Asylum Research (Oxford Instruments) was used to conduct the AFM analysis, and a silicon probe with a force constant of 0.5 N $m^{-1}$ was used. A Thermo Scientific NEXSA Surface Analysis instrument, having a monochromatic Al Kα line source (hν = 1486.69 eV), was used for X-ray photoelectron spectroscopy (XPS) measurements.

**Fitting procedure for XPS fitting:**

The XPS fitting was carried out according to the available tutorials. Initially, background subtraction was performed using Shirley's method. Then the XPS peaks are fitted using Gaussian functions, with full width at half maximum (FWHM) less than 2 eV for each peak. Peak identification was carried out on the basis of known binding energy values obtained from

existing literature, allowing the assignment of peaks for elements of different chemical environments.

## 2. Synthesis routes

Synthesis of compound **1** and **2** according to the literature.[7,8]

**Synthesis of 4-bromo-N'-(5-bromo-2-nitrophenyl)-N'-phenylbenzohydrazide (3):** A sealed tube was charged with **1** (300 mg, 1.03 mmol), 4-bromo-2-fluoro-nitrobenzene (340 mg, 1.545 mmol), potassium carbonate (156 mg, 1.133 mmol), ethyl alcohol (10 mL), and the reaction mixture was stirred at 110 °C for 48 h. The reaction mixture was then cooled to room temperature and extracted with $CH_2Cl_2$. The organic layer was collected, concentrated under reduced pressure, and crude solids were purified using column chromatography to get compound 3. Yield: 40 %. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.95 (d, J = 2.2 Hz, 1H), 7.89 (d, J = 8.7 Hz, 1H), 7.68 (d, J = 8.7 Hz, 2H), 7.62 (d, J = 8.6 Hz, 2H), 7.48 (dd, J = 8.8, 2.1 Hz, 1H), 7.29 (dd, J = 8.7, 7.4 Hz, 2H), 7.04 (t, J = 7.5 Hz, 1H), 6.96 – 6.91 (m, 2H). Calculated: 488.9324 found $[M+H]^+$ m/z: 489.9398.

**Synthesis of 4-bromo-N'-(5-bromo-2-nitrophenyl)-N'-(4-bromophenyl)benzohydrazide (4):** A sealed tube was charged with **2** (300 mg, 0.81 mmol), 4-bromo-2-fluoro-nitrobenzene (267 mg, 1.216 mmol), potassium carbonate (123 mg, 0.891 mmol), ethyl alcohol (10 mL), and the reaction mixture was stirred at 110 °C for 48 h. The reaction mixture was then cooled to room temperature and extracted with $CH_2Cl_2$. The organic layer was collected, concentrated under reduced pressure, and crude solids were purified using column chromatography to get compound **4**. Yield: 35 %. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.95 (d, *J* = 1.9 Hz, 1H), 7.67 – 7.60 (m, 4H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 3H), 6.76 (d, *J* = 9.0 Hz, 1H). Calculated: 566.8429 found $[M+Na]^+$ m/z: 589.8314.

**Synthesis of $Br_2N^{\bullet}$**: Blatter radical $Br_2N^{\bullet}$ was synthesized by adopting the literature procedures.[9] In a 100 mL round-bottom flask, compound **3** (500 mg, 1.02 mmol) was dissolved in acetic acid (10 mL), followed by the addition of tin powder (602 mg, 5.1 mmol) over 30 min under vigorous stirring and then heated at 118 °C for 10 min. The reaction mixture was then cooled to room temperature and diluted with $CH_2Cl_2$, followed by neutralisation with 2M NaOH. The obtained products were dissolved in $CH_2Cl_2$ (50 mL) and added with 2M NaOH (50 mL) and allowed to stir for 12 h at room temperature. The organic layer was separated and washed three times with distilled water. The organic fractions were concentrated under reduced pressure, and the crude was purified by column chromatography using basic aluminium oxide ($CH_2Cl_2$:hexane, 50:50) to get $Br_2N^{\bullet}$ as dark green needles. Yield: 85%. Calculated: 439.9398 found $[M]^+$ m/z: 439.9397. $\nu_{max}$ / $cm^{-1}$ 3063w (aryl C–H), 1591w, 1474s, 1430w, 1391s, 1307w, 1267w, 1238w, 1190m, 1171w, 1102w, 1070w, 1009w, 961w, 888m, 851m, 822w, 801w, 755w, 718m, 687s, 670w.

**Synthesis of $Br_3N^{\bullet}$**: Following a similar procedure to that for the synthesis of $Br_2N^{\bullet}$. In a 100 ml round-bottom flask, compound **4** (500 mg, 0.883 mmol) was dissolved in acetic acid (10 ml), followed by the addition of tin powder (521 mg, 4.416 mmol) over 30 min under vigorous stirring and then heated at 118 °C for 10 min. The reaction mixture was then cooled to room temperature and diluted with $CH_2Cl_2$, followed by neutralisation with 2M NaOH. The obtained products were dissolved in $CH_2Cl_2$ (50 mL) and added with 2M NaOH (50 mL), and allowed to stir for 12 h at room temperature. The organic layer was separated and washed three times with distilled water. The organic fractions were concentrated under reduced pressure, and the crude was purified by column chromatography using basic aluminium oxide ($CH_2Cl_2$:hexane, 50:50) to get $Br_3N^{\bullet}$ as dark green needles. Yield: 60%. Calculated: 517.8503 found $[M]^+$ m/z: 517.8504. $\nu_{max}$ / $cm^{-1}$ 3070w (aryl C–H), 1590w, 1566w, 1475s, 1417m, 1392s, 1338w, 1306w,

1263w, 1242w, 1188w, 1172w, 1103w, 1066s, 1007s, 948w, 887m, 836m, 815s, 740w, 719m, 702w, 669m.

**Synthesis of $Cz_2N^{\bullet}$**: A 100 mL Schlenk flask loaded with radical **$Br_2N^{\bullet}$** (75 mg, 0.169 mmol), (4-(9H-carbazol-9-yl)phenyl)boronic acid (146 mg, 0.509 mmol), $Pd(PPh_3)_4$ (10 mg, 5 mol%), $Cs_2CO_3$ (5mg, 10 mol%) and all reagents were subjected to vacuum and nitrogen gas purging three cycles to ensure inert atmosphere. To this THF: $H_2O$ (5:1) 20 mL was added, and the mixture was heated at 70 °C for 12 h. The reaction mixture was cooled to room temperature and then extracted with $CH_2Cl_2$. The organic fractions were collected and concentrated under reduced pressure. The crude solids were then purified by column chromatography using basic aluminium oxide ($CH_2Cl_2$:hexane) to get dark reddish-brown compound $Cz_2N^{\bullet}$. Yield: 60%. Calculated: 766.2971 found $[M]^+$ m/z: 766.2972. $\nu_{max}$ / $cm^{-1}$ 3043w (aryl C–H), 1603w, 1594w, 1526w, 1499m, 1449m, 1389w, 1360w, 1333w, 1318w, 1223w, 1175w, 1016w, 1004w, 913w, 900w, 842m, 830m, 817m, 770w, 749s, 720s, 693m, 683m, 646w.

**Synthesis of $Cz_3N^{\bullet}$**: A 100 mL Schlenk flask loaded with radical **$Br_3N^{\bullet}$** (75 mg, 0.145 mmol), (4-(9H-carbazol-9-yl)phenyl)boronic acid (187 mg, 0.652 mmol), $Pd(PPh_3)_4$ (17 mg, 10 mol%), $Cs_2CO_3$ (14mg, 30 mol%) and all reagents were subjected to vacuum and nitrogen gas purging three cycles to ensure inert atmosphere. To this THF: $H_2O$ (5:1) 20 mL was added, and the mixture was heated at 70 °C for 12 h. The reaction mixture was cooled to room temperature and then extracted with $CH_2Cl_2$. The organic fractions were collected and concentrated under reduced pressure. The crude solids were then purified by column chromatography using basic aluminium oxide ($CH_2Cl_2$:hexane) to get dark reddish-brown compound $Cz_3N^{\bullet}$. Yield: 65%. Calculated: 1007.3862 found $[M]^+$ m/z: 1007.3861. $\nu_{max}$ / $cm^{-1}$ 3048w (aryl C–H), 1623w, 1597w, 1493m, 1479m, 1450m, 1398w, 1362w, 1334w, 1315w, 1227m, 1170w, 1004w, 915w, 900w, 823w, 746s, 724s, 685w, 637w, 623w.

## 3. Crystallographic data and parameters.

**Table S1.** Crystallographic data and structural refinement for $Cz_3N^{\bullet}$.

| | **$Cz_3N^{\bullet}$** |
|---|---|
| Empirical formula | $C_{73}H_{47}N_6$ |
| Formula Weight | 1008.227 g $mol^{-1}$ |
| Crystal System | Monoclinic |
| Space Group | $P2_1/c$ |
| Temperature (K) | 296.15 |
| a (Å) | 19.8107(10) |
| b (Å) | 14.1961(8) |
| c (Å) | 20.7394(11) |
| α (°) | 90 |
| β (°) | 103.349(2) |
| γ (°) | 90 |
| V ($Å^3$) | 5675.1(5) |
| Z | 4 |
| $\rho_{calcd}$ (g $cm^{-3}$) | 1.180 |
| μ ($mm^{-1}$) | 0.069 |
| F (000) | 2109.2 |
| Crystal size ($mm^3$) | 0.20 × 0.19 × 0.18 |
| Radiation | Mo Kα (λ = 0.71073 Å) |
| Index ranges | $-26 \le h \le 26$, $-18 \le k \le 18$, $-27 \le l \le 27$ |
| Reflections collected | 117394 |
| Independent reflections | 14147 |
| 2θ range for data collection (°) | 4.32 to 56.72 |
| Data/restraints/parameters | 14147/0/712 |
| GooF | 1.059 |
| $R_{int}$ | 0.1006 |
| Final R indices [I >2σ(I)] | $R_1$ = 0.1143, $wR_2$ = 0.2588 |

| | |
|---|---|
| R indices (all data) | $R_1$ = 0.1451, $wR_2$ = 0.2783 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.72/-0.61 |
| CCDC number | 2502298 |

**Table S2.** Bond lengths obtained from the single crystal structure of $Cz_3N^{\bullet}$.

| **$Cz_3N^{\bullet}$** | | | |
|---|---|---|---|
| Atom-Atom | Bond Length /Å | Atom-Atom | Bond Length / Å |
| N001 N002 | 1.364(3) | C00U C011 | 1.384(4) |
| N001 C00B | 1.382(4) | C00W C010 | 1.391(5) |
| N001 C00S | 1.441(4) | C00W C016 | 1.398(5) |
| N002 C00F | 1.341(4) | C00X C01A | 1.414(4) |
| N003 C00F | 1.330(4) | C00Y C00Z | 1.378(5) |
| N003 C00I | 1.376(4) | C00Z C019 | 1.390(5) |
| N004 C00A | 1.424(4) | C010 C01G | 1.415(4) |
| N004 C010 | 1.399(4) | C013 C01S | 1.366(5) |
| N004 C01E | 1.393(4) | C013 C01T | 1.399(5) |
| N005 C00X | 1.395(4) | C014 C019 | 1.387(4) |
| N005 C00Z | 1.422(4) | C015 C01D | 1.383(5) |
| N005 C01V | 1.405(4) | C016 C018 | 1.386(5) |
| C006 C00D | 1.396(4) | C017 C01B | 1.394(4) |
| C006 C00N | 1.478(4) | C018 C01Q | 1.374(6) |
| C006 C00T | 1.399(4) | C01A C01D | 1.388(5) |
| C007 C00B | 1.387(4) | C01A C01R | 1.435(5) |
| C007 C00N | 1.393(4) | C01C C01K | 1.359(6) |
| N008 C01F | 1.421(4) | C01C C01N | 1.410(5) |
| N008 C01H | 1.406(5) | C01E C01J | 1.410(5) |
| N008 C01O | 1.390(5) | C01E C01W | 1.386(5) |
| C009 C00A | 1.390(4) | C01F C01P | 1.359(6) |
| C009 C00D | 1.382(4) | C01F C01U | 1.396(5) |
| C00A C00K | 1.387(4) | C01G C01J | 1.418(5) |
| C00B C00I | 1.415(4) | C01G C01Q | 1.400(5) |

| | | | |
|---|---|---|---|
| C00C C00P | 1.393(4) | C01H C01M | 1.374(6) |
| C00C C00U | 1.494(4) | C01H C01N | 1.403(5) |
| C00C C014 | 1.400(4) | C01I C01N | 1.424(6) |
| C00E C00F | 1.490(4) | C01I C01O | 1.411(5) |
| C00E C00G | 1.393(4) | C01I C01X | 1.399(6) |
| C00E C00O | 1.389(4) | C01J C021 | 1.415(5) |
| C00G C00R | 1.384(4) | C01K C01L | 1.362(6) |
| C00H C00J | 1.386(5) | C01L C01M | 1.395(5) |
| C00H C012 | 1.387(4) | C01O C01Z | 1.368(6) |
| C00I C00V | 1.398(4) | C01P C01S | 1.410(5) |
| C00J C013 | 1.492(4) | C01R C01V | 1.401(5) |
| C00J C017 | 1.399(5) | C01R C022 | 1.409(5) |
| C00K C00T | 1.378(4) | C01T C01U | 1.386(5) |
| C00L C00M | 1.384(5) | C01V C01Y | 1.395(6) |
| C00L C00X | 1.387(5) | C01W C025 | 1.385(5) |
| C00M C015 | 1.389(5) | C01X C020 | 1.359(7) |
| C00N C00Q | 1.415(4) | C01Y C026 | 1.377(5) |
| C00O C011 | 1.388(4) | C01Z C023 | 1.380(6) |
| C00P C00Y | 1.382(4) | C020 C023 | 1.392(6) |
| C00Q C00V | 1.373(4) | C021 C027 | 1.371(7) |
| C00R C00U | 1.397(4) | C022 C024 | 1.373(7) |
| C00S C012 | 1.380(5) | C024 C026 | 1.396(7) |
| C00S C01B | 1.374(5) | C025 C027 | 1.392(7) |

**Table S3.** Selected bond angles of obtained from the single crystal structure of $Cz_3N^{\bullet}$.

| **$Cz_3N^{\bullet}$** | | | |
|---|---|---|---|
| Atom-Atom -Atom | Bond Angle / ° | Atom-Atom -Atom | Bond Angle / ° |
| N002 N001 C00B | 122.9(2) | C00W C010 N004 | 129.4(3) |
| N002 N001 C00S | 115.2(2) | C00W C010 C01G | 121.9(3) |
| C00B N001 C00S | 121.2(2) | C00U C011 C00O | 121.0(3) |
| C00F N002 N001 | 115.0(2) | C00S C012 C00H | 119.1(3) |
| C00F N003 C00I | 115.2(2) | C01S C013 C00J | 120.5(3) |

| | | | |
|---|---|---|---|
| C010 N004 C00A | 125.1(3) | C01S C013 C01T | 119.0(3) |
| C01E N004 C00A | 125.7(3) | C01T C013 C00J | 120.5(3) |
| C01E N004 C010 | 108.4(3) | C019 C014 C00C | 121.8(3) |
| C00X N005 C00Z | 124.9(3) | C01D C015 C00M | 120.7(3) |
| C00X N005 C01V | 108.1(3) | C018 C016 C00W | 121.8(3) |
| C01V N005 C00Z | 125.5(3) | C01B C017 C00J | 120.4(3) |
| C00D C006 C00N | 120.7(3) | C01Q C018 C016 | 120.8(3) |
| C00D C006 C00T | 117.5(3) | C014 C019 C00Z | 119.6(3) |
| C00T C006 C00N | 121.7(3) | C00X C01A C01R | 107.0(3) |
| C00B C007 C00N | 120.3(3) | C01D C01A C00X | 119.4(3) |
| C01H N008 C01F | 126.4(3) | C01D C01A C01R | 133.5(3) |
| C01O N008 C01F | 125.4(3) | C00S C01B C017 | 118.7(3) |
| C01O N008 C01H | 108.0(3) | C01K C01C C01N | 120.4(4) |
| C00D C009 C00A | 119.9(3) | C015 C01D C01A | 119.0(3) |
| C009 C00A N004 | 120.0(3) | N004 C01E C01J | 108.0(3) |
| C00K C00A N004 | 120.4(3) | C01W C01E N004 | 129.0(3) |
| C00K C00A C009 | 119.5(3) | C01W C01E C01J | 122.8(3) |
| N001 C00B C007 | 122.3(3) | C01P C01F N008 | 120.8(3) |
| N001 C00B C00I | 116.4(3) | C01P C01F C01U | 119.8(3) |
| C007 C00B C00I | 121.3(3) | C01U C01F N008 | 119.4(4) |
| C00P C00C C00U | 120.8(3) | C010 C01G C01J | 106.5(3) |
| C00P C00C C014 | 116.8(3) | C01Q C01G C010 | 118.8(3) |
| C014 C00C C00U | 122.3(3) | C01Q C01G C01J | 134.7(3) |
| C009 C00D C006 | 121.5(3) | C01M C01H N008 | 129.8(3) |
| C00G C00E C00F | 120.0(3) | C01M C01H C01N | 121.4(3) |
| C00O C00E C00F | 121.9(3) | C01N C01H N008 | 108.8(4) |
| C00O C00E C00G | 118.1(3) | C01O C01I C01N | 107.6(3) |
| N002 C00F C00E | 114.1(2) | C01X C01I C01N | 134.0(3) |
| N003 C00F N002 | 128.5(3) | C01X C01I C01O | 118.3(4) |
| N003 C00F C00E | 117.3(2) | C01E C01J C01G | 108.3(3) |
| C00R C00G C00E | 121.1(3) | C01E C01J C021 | 118.7(4) |
| C00J C00H C012 | 120.6(3) | C021 C01J C01G | 132.9(4) |
| N003 C00I C00B | 121.7(3) | C01C C01K C01L | 119.7(4) |

| | | | |
|---|---|---|---|
| N003 C00I C00V | 120.2(3) | C01K C01L C01M | 122.7(4) |
| C00V C00I C00B | 118.0(3) | C01H C01M C01L | 117.4(4) |
| C00H C00J C013 | 121.3(3) | C01C C01N C01I | 134.6(3) |
| C00H C00J C017 | 119.2(3) | C01H C01N C01C | 118.3(4) |
| C017 C00J C013 | 119.4(3) | C01H C01N C01I | 107.0(3) |
| C00T C00K C00A | 120.2(3) | N008 C01O C01I | 108.5(3) |
| C00M C00L C00X | 117.3(3) | C01Z C01O N008 | 129.2(3) |
| C00L C00M C015 | 121.8(3) | C01Z C01O C01I | 122.3(4) |
| C007 C00N C006 | 120.5(3) | C01F C01P C01S | 120.2(4) |
| C007 C00N C00Q | 118.3(3) | C018 C01Q C01G | 119.6(3) |
| C00Q C00N C006 | 121.3(3) | C01V C01R C01A | 107.3(3) |
| C011 C00O C00E | 120.9(3) | C01V C01R C022 | 119.4(4) |
| C00Y C00P C00C | 122.0(3) | C022 C01R C01A | 133.2(4) |
| C00V C00Q C00N | 121.5(3) | C013 C01S C01P | 120.6(4) |
| C00G C00R C00U | 120.6(3) | C01U C01T C013 | 120.5(4) |
| C012 C00S N001 | 118.8(3) | C01T C01U C01F | 119.8(4) |
| C01B C00S N001 | 119.2(3) | C01R C01V N005 | 108.8(3) |
| C01B C00S C012 | 122.0(3) | C01Y C01V N005 | 129.2(3) |
| C00K C00T C006 | 121.4(3) | C01Y C01V C01R | 122.0(3) |
| C00R C00U C00C | 120.4(3) | C025 C01W C01E | 116.6(4) |
| C011 C00U C00C | 121.3(3) | C020 C01X C01I | 119.5(4) |
| C011 C00U C00R | 118.4(3) | C026 C01Y C01V | 117.3(4) |
| C00Q C00V C00I | 120.6(3) | C01O C01Z C023 | 117.6(4) |
| C010 C00W C016 | 117.0(3) | C01X C020 C023 | 120.9(4) |
| N005 C00X C01A | 108.7(3) | C027 C021 C01J | 118.5(4) |
| C00L C00X N005 | 129.6(3) | C024 C022 C01R | 118.5(4) |
| C00L C00X C01A | 121.7(3) | C01Z C023 C020 | 121.4(5) |
| C00Z C00Y C00P | 120.0(3) | C022 C024 C026 | 121.2(4) |
| C00Y C00Z N005 | 119.5(3) | C01W C025 C027 | 122.1(4) |
| C00Y C00Z C019 | 119.7(3) | C01Y C026 C024 | 121.8(4) |
| C019 C00Z N005 | 120.7(3) | C021 C027 C025 | 121.3(4) |
| N004 C010 C01G | 108.7(3) | | |

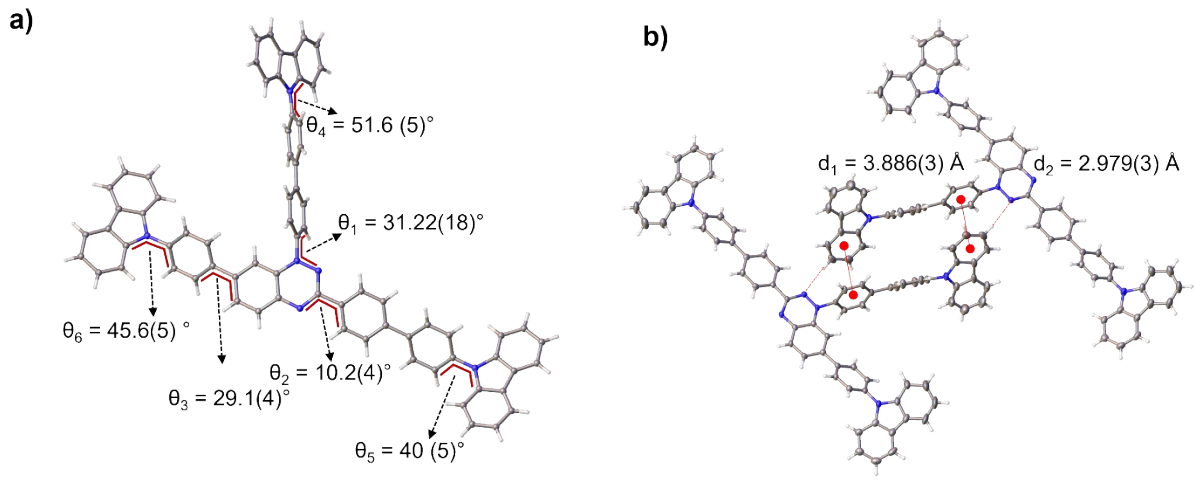



**Fig. S1** Solid-state structure of $Cz_3N^{\bullet}$: a) representing different dihedral angles by ($\theta_1$ to $\theta_6$), b) representing key additional π···π interactions ($d_1$ = 3.886(3) Å), and CH···N contacts ($d_2$ = 2.979(3) Å) present.

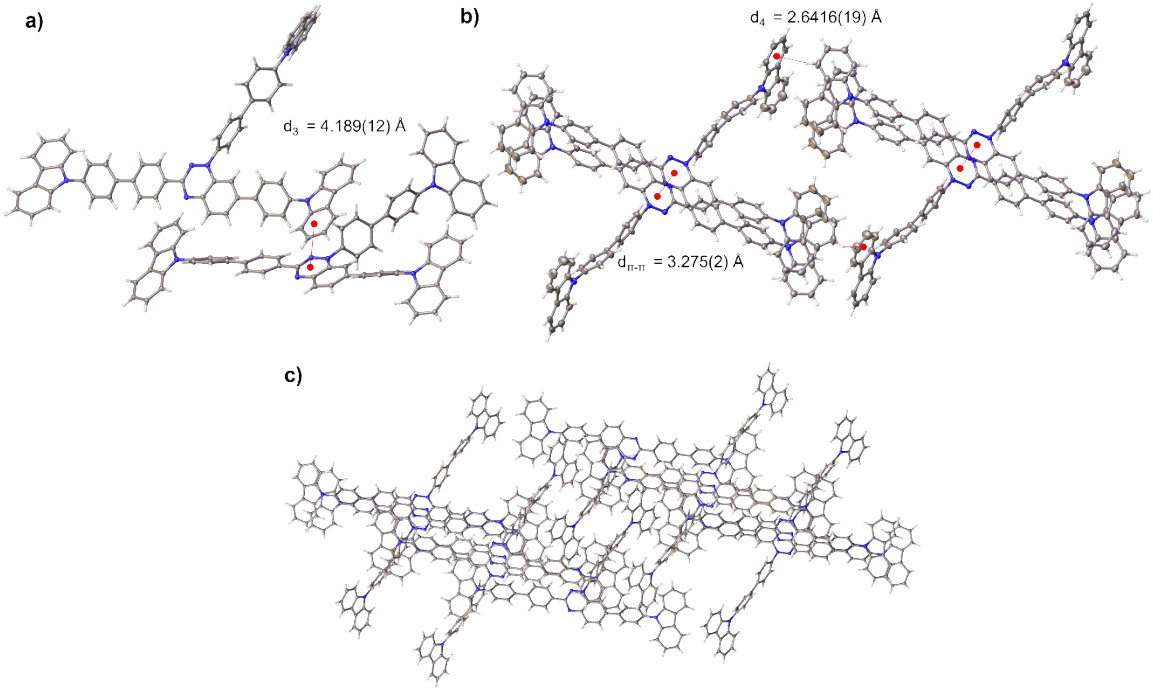
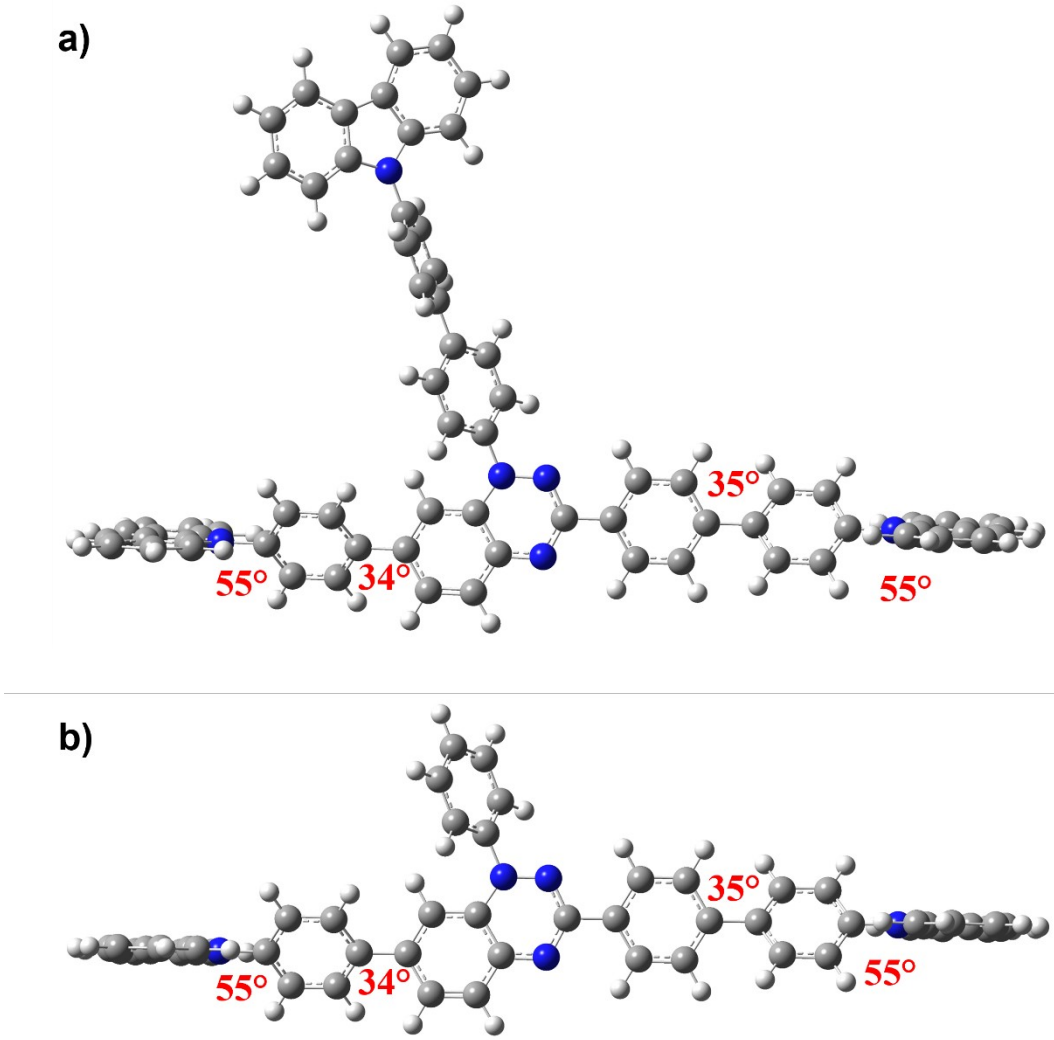



**Fig. S2** Solid-state structure analysis of $Cz_3N^{\bullet}$: a) representing additional π···π interactions ($d_3$ = 4.189(12) Å), b) CH···π interactions ($d_4$ = 2.6416(19) Å) and c) solid-state packing along the *b*-direction.




**4. DFT-optimized geometries of $Cz_3N^{\bullet}$ and $Cz_2N^{\bullet}$ using DCM as solvent.**

**Fig. S3** DFT-optimized geometries of a) $Cz_3N^{\bullet}$ and b) $Cz_2N^{\bullet}$. The corresponding torsional angles were shown at each twisted center.

**Table S4.** Cartesian coordinates.

| $Cz_3N^{\bullet}$ | | | | $Cz_2N^{\bullet}$ | | | |
|---|---|---|---|---|---|---|---|
| 6 | 1.297691000 | -5.212643000 | -0.503173000 | 6 | 3.614122000 | -1.341704000 | -1.700434000 |
| 6 | -0.053755000 | -4.933203000 | -0.599734000 | 6 | 2.233742000 | -1.327625000 | -1.795489000 |
| 6 | -0.532352000 | -3.610549000 | -0.508310000 | 6 | 1.457354000 | -0.467233000 | -0.993449000 |
| 6 | 0.422960000 | -2.564709000 | -0.349500000 | 6 | 2.140254000 | 0.413538000 | -0.105030000 |
| 6 | 1.784460000 | -2.858837000 | -0.215436000 | 6 | 3.534079000 | 0.369546000 | 0.009807000 |
| 6 | 2.241500000 | -4.181341000 | -0.295977000 | 6 | 4.289786000 | -0.501816000 | -0.786571000 |
| 1 | 1.638206000 | -6.237887000 | -0.601928000 | 1 | 4.185778000 | -1.997383000 | -2.348623000 |
| 1 | -0.782861000 | -5.723504000 | -0.743489000 | 1 | 1.710932000 | -1.980581000 | -2.486287000 |
| 1 | 2.487942000 | -2.061024000 | -0.016470000 | 1 | 4.030530000 | 0.992955000 | 0.741856000 |
| 6 | -2.247856000 | -2.091710000 | -0.356294000 | 6 | -0.566548000 | 0.276866000 | -0.202335000 |
| 6 | 3.685596000 | -4.488215000 | -0.165125000 | 6 | 5.766741000 | -0.539654000 | -0.667961000 |
| 6 | 4.665405000 | -3.606534000 | -0.655679000 | 6 | 6.505310000 | 0.622555000 | -0.381597000 |
| 6 | 4.121487000 | -5.672953000 | 0.455179000 | 6 | 6.476855000 | -1.742044000 | -0.836485000 |
| 6 | 6.022008000 | -3.887353000 | -0.523824000 | 6 | 7.890854000 | 0.586504000 | -0.256871000 |
| 1 | 4.364831000 | -2.693143000 | -1.158589000 | 1 | 5.992552000 | 1.571849000 | -0.265276000 |
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| 1 | 3.393782000 | -6.367294000 | 0.862395000 | 1 | 5.938354000 | -2.662062000 | -1.038995000 |
| 6 | 6.437893000 | -5.076356000 | 0.088000000 | 6 | 8.582399000 | -0.617773000 | -0.437353000 |
| 1 | 6.762193000 | -3.186448000 | -0.894768000 | 1 | 8.440213000 | 1.491258000 | -0.019507000 |
| 1 | 5.790981000 | -6.897499000 | 1.040717000 | 1 | 8.393976000 | -2.717537000 | -0.882999000 |
| 6 | -3.704021000 | -1.795665000 | -0.296436000 | 6 | -2.051293000 | 0.194329000 | -0.185512000 |
| 6 | -4.637230000 | -2.838999000 | -0.390870000 | 6 | -2.713232000 | -0.725612000 | -1.012538000 |
| 6 | -4.180861000 | -0.483951000 | -0.143462000 | 6 | -2.822728000 | 1.019953000 | 0.647840000 |
| 6 | -6.002339000 | -2.579141000 | -0.333871000 | 6 | -4.101034000 | -0.817096000 | -1.005848000 |
| 1 | -4.276478000 | -3.854831000 | -0.500262000 | 1 | -2.124000000 | -1.372377000 | -1.651800000 |
| 6 | -5.546100000 | -0.227713000 | -0.086255000 | 6 | -4.209784000 | 0.925671000 | 0.652381000 |
| 1 | -3.473037000 | 0.334149000 | -0.080719000 | 1 | -2.326549000 | 1.743428000 | 1.283893000 |
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| 1 | -6.701027000 | -3.408551000 | -0.383686000 | 1 | -4.585455000 | -1.555835000 | -1.636837000 |
| 1 | -5.887592000 | 0.798605000 | 0.006196000 | 1 | -4.782849000 | 1.594370000 | 1.287137000 |
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| 7 | -1.441331000 | -1.033252000 | -0.227420000 | 7 | -0.030703000 | 1.155474000 | 0.651494000 |
| 7 | -1.877453000 | -3.365884000 | -0.544376000 | 7 | 0.091887000 | -0.511837000 | -1.062917000 |
| 6 | 0.703783000 | -0.088542000 | -0.243079000 | 6 | 1.836828000 | 2.277629000 | 1.523851000 |
| 6 | 0.430071000 | 0.885789000 | 0.722704000 | 6 | 1.382871000 | 2.324953000 | 2.846002000 |
| 6 | 1.720243000 | 0.126265000 | -1.180595000 | 6 | 2.737562000 | 3.236531000 | 1.046925000 |
| 6 | 1.181016000 | 2.055384000 | 0.757537000 | 6 | 1.845974000 | 3.328370000 | 3.695281000 |
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| 6 | 2.470205000 | 1.297563000 | -1.130741000 | 6 | 3.199167000 | 4.232101000 | 1.907975000 |
| 1 | 1.917610000 | -0.611582000 | -1.950239000 | 1 | 3.058381000 | 3.213015000 | 0.011183000 |
| 6 | 2.219863000 | 2.285426000 | -0.162474000 | 6 | 2.757398000 | 4.280587000 | 3.231889000 |
| 1 | 0.943522000 | 2.809939000 | 1.500267000 | 1 | 1.496794000 | 3.362296000 | 4.722536000 |
| 1 | 3.268493000 | 1.439279000 | -1.851752000 | 1 | 3.894538000 | 4.978179000 | 1.536479000 |
| 6 | -7.944336000 | -0.992314000 | -0.118271000 | 1 | 3.117198000 | 5.058972000 | 3.897299000 |
| 6 | -8.857746000 | -1.737372000 | -0.884585000 | 6 | -6.360951000 | -0.093642000 | -0.166283000 |
| 6 | -8.456634000 | 0.022934000 | 0.708484000 | 6 | -7.076150000 | -0.368552000 | -1.345097000 |
| 6 | -10.225878000 | -1.488434000 | -0.822233000 | 6 | -7.094698000 | 0.083835000 | 1.019812000 |
| 1 | -8.494132000 | -2.516081000 | -1.547166000 | 6 | -8.464247000 | -0.472838000 | -1.340795000 |
| 6 | -9.821338000 | 0.291895000 | 0.761990000 | 1 | -6.541909000 | -0.492694000 | -2.281514000 |
| 1 | -7.781023000 | 0.604770000 | 1.327085000 | 6 | -8.484184000 | 0.000766000 | 1.029550000 |

| | | | | | | | |
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| 1 | -10.916200000 | -2.084777000 | -1.409324000 | 6 | -9.179525000 | -0.283791000 | -0.152013000 |
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| 6 | 8.748403000 | -5.422791000 | -0.833393000 | 1 | -9.033523000 | 0.156242000 | 1.952009000 |
| 6 | 8.491403000 | -5.663836000 | 1.409177000 | 6 | 10.901873000 | 0.135456000 | -1.038197000 |
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| 6 | 7.998457000 | -5.701958000 | 2.717267000 | 6 | 12.223396000 | -0.197515000 | -0.642582000 |
| 6 | 9.861083000 | -5.902148000 | 1.124645000 | 6 | 10.267470000 | -2.433074000 | 1.461358000 |
| 6 | 9.654216000 | -5.366278000 | -3.043973000 | 6 | 12.111705000 | -1.235896000 | 0.360864000 |
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| 6 | -12.896672000 | -0.190231000 | 1.217710000 | 1 | 13.310469000 | -3.450563000 | 2.636645000 |
| 6 | -12.937490000 | 0.093613000 | -1.033665000 | 6 | -11.356444000 | -1.231540000 | 0.667228000 |
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| 6 | 3.338549000 | 4.144103000 | 1.110456000 | | | | |
| 6 | 4.230378000 | 5.318689000 | -1.252295000 | | | | |
| 1 | 3.232734000 | 3.715718000 | -2.257989000 | | | | |
| 6 | 4.096613000 | 5.310137000 | 1.161400000 | | | | |
| 1 | 3.021555000 | 3.682457000 | 2.040105000 | | | | |
| 6 | 4.545090000 | 5.909588000 | -0.022166000 | | | | |
| 1 | 4.551732000 | 5.792692000 | -2.173557000 | | | | |
| 1 | 4.359464000 | 5.748002000 | 2.118414000 | | | | |
| 6 | 4.935432000 | 8.294836000 | 0.659509000 | | | | |

| | | | | |
|---|---|---|---|---|
| 6 | 6.570957000 | 7.294270000 | -0.556251000 | |
| 6 | 3.755336000 | 8.602368000 | 1.343857000 | |
| 6 | 5.963525000 | 9.256909000 | 0.483387000 | |
| 6 | 7.367837000 | 6.389403000 | -1.264566000 | |
| 6 | 7.008129000 | 8.617738000 | -0.289884000 | |
| 6 | 3.626092000 | 9.887191000 | 1.867977000 | |
| 1 | 2.964412000 | 7.870278000 | 1.461999000 | |
| 6 | 5.808523000 | 10.541005000 | 1.020814000 | |
| 6 | 8.606719000 | 6.835817000 | -1.720742000 | |
| 1 | 7.038215000 | 5.373632000 | -1.451739000 | |
| 6 | 8.257638000 | 9.041187000 | -0.760199000 | |
| 6 | 4.640860000 | 10.848590000 | 1.713935000 | |
| 1 | 2.719255000 | 10.149005000 | 2.405016000 | |
| 1 | 6.587650000 | 11.287156000 | 0.893852000 | |
| 6 | 9.049666000 | 8.148090000 | -1.476771000 | |
| 1 | 9.242565000 | 6.151636000 | -2.274733000 | |
| 1 | 8.604664000 | 10.051624000 | -0.563990000 | |
| 1 | 4.508614000 | 11.839765000 | 2.136536000 | |
| 1 | 10.019656000 | 8.463963000 | -1.848064000 | |
| 7 | 5.311302000 | 7.105125000 | 0.024522000 | |

## 5. Electrochemical studies of monomers $Cz_3N^{\bullet}$ and $Cz_2N^{\bullet}$.

CV experiments were performed in a three-electrode cell containing a GC or ITO electrode, Ag/AgCl reference electrode, and a Pt counter electrode in dichloromethane with $TBAPF_6$ as supporting electrolyte. The $E_{HOMO}$ values were obtained from eq (S1) by incorporating the oxidation onset potential values obtained from CV, and LUMO levels were subsequently calculated using eq (S2) using optical band gaps obtained from the absorption edge calculated using eq (S3).

$$E_{HOMO} = -(4.8 - E_{1/2\ Fc,Fc+} + E_{Ox.}\ Onset) \qquad \text{eq (S1)}$$

$$E_{g,\ optical} = (E_{LUMO} - E_{HOMO}) \qquad \text{eq (S2)}$$

$$E_g\ (eV) = 1240/\ \lambda(nm) \qquad \text{eq (S3)}$$

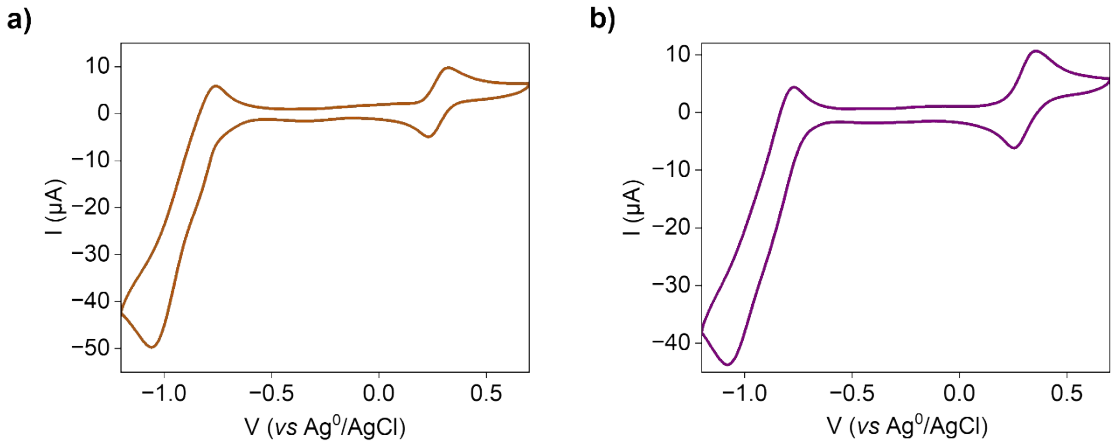



**Fig. S4** CV curves of 1 mM a) $Cz_3N^{\bullet}$, b) $Cz_2N^{\bullet}$ in $CH_2Cl_2$ with 0.2 M $TBAPF_6$ supporting electrolyte at a scan rate of 0.1 $Vs^{-1}$.

## 6. Electropolymerisation studies of $Cz_3N^{\bullet}$ and $Cz_2N^{\bullet}$.

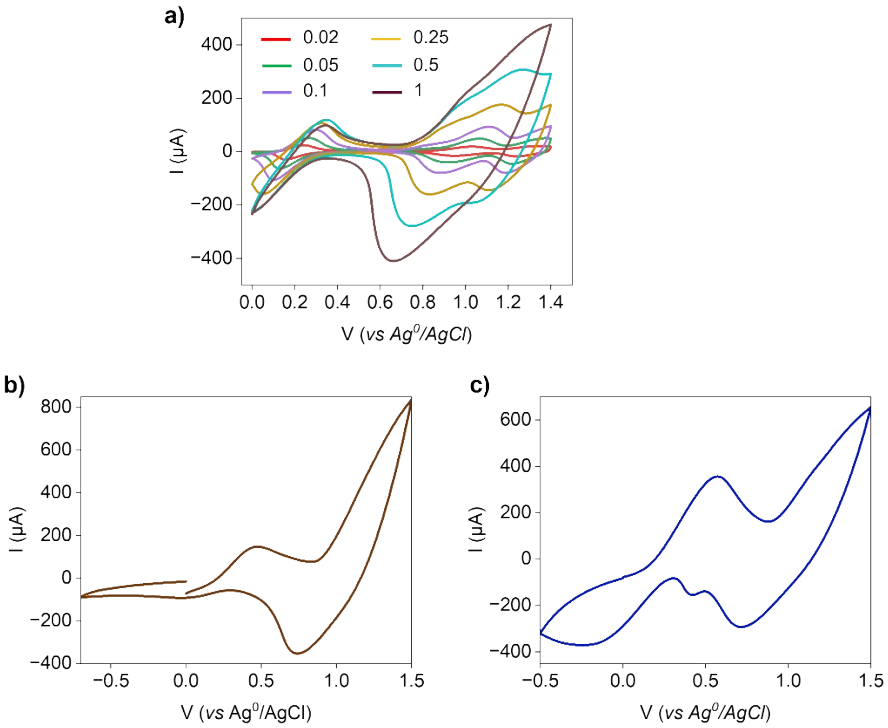



**Fig. S5** a) CV of poly$Cz_2N^{\bullet}$, as-grown films on GC in monomer-free $CH_2Cl_2$ solutions with 0.1 M $TBAPF_6$ supporting electrolyte at different scan rate from 0.02 $Vs^{-1}$ to 1 V $s^{-1}$. b), c) CV of poly$Cz_3N^{\bullet}$, poly$Cz_2N^{\bullet}$ as-grown polymer films on ITO electrode in monomer-free $CH_2Cl_2$ solutions with 0.1 M $TBAPF_6$ as supporting electrolyte at scan rate of 0.1 $Vs^{-1}$, respectively.

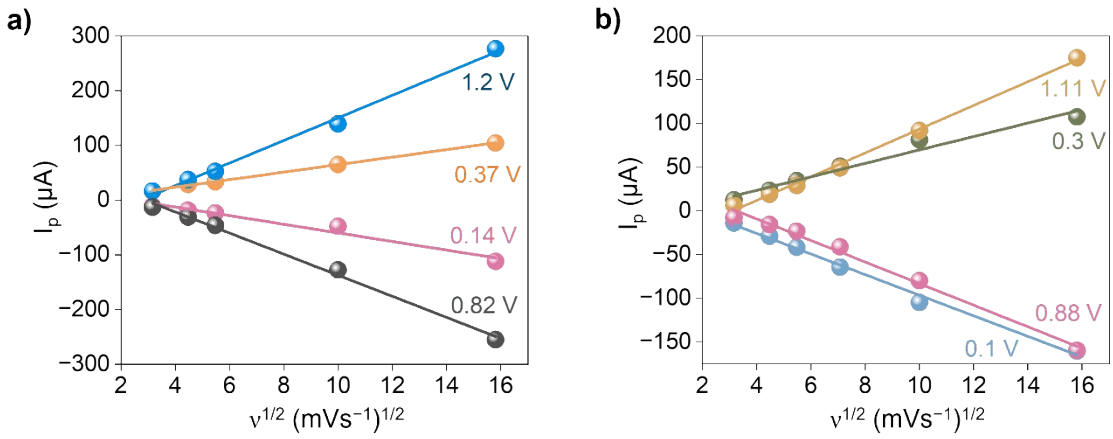
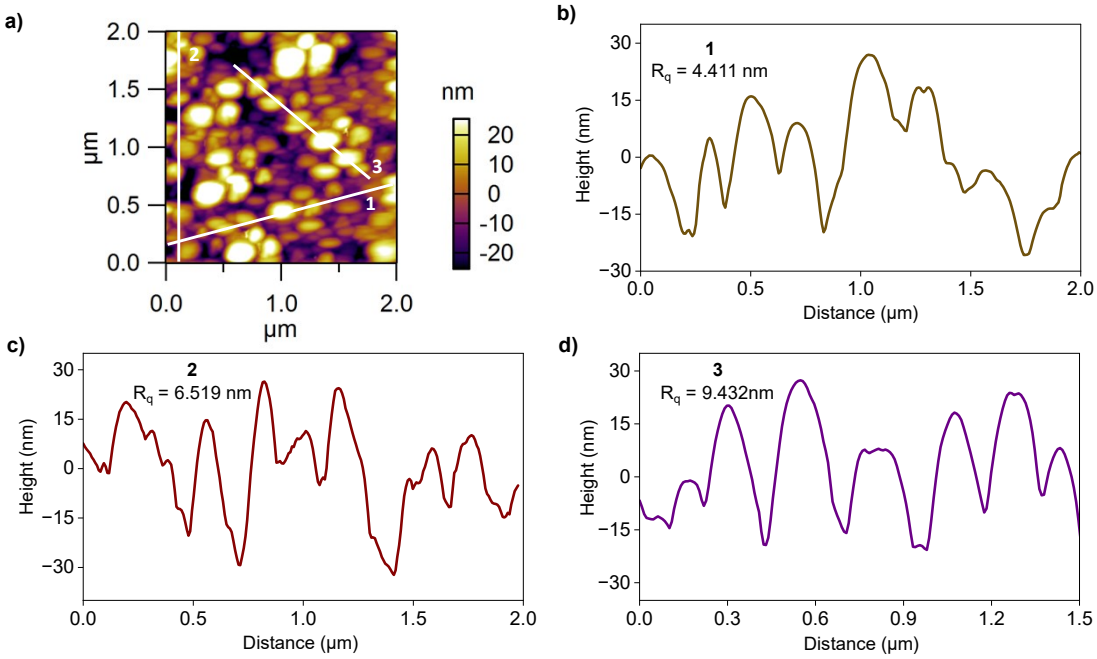



**Fig. S6** Linear relationship of peak current *vs* square root of the scan rate for a) poly$Cz_3N^{\bullet}$ and b) poly$Cz_2N^{\bullet}$ on GC electrode.




**7. AFM of polymeric thin film of polyCz$_3$N$^{\bullet}$ and polyCz$_2$N$^{\bullet}$.**

**Fig. S7** Cross-sectional line profiles. a) AFM image of polyCz$_3$N$^{\bullet}$@ITO film with a scan size of 2 µm. b) horizontal, c) vertical, and d) diagonal line profiles of the AFM image of the thin films were shown. The corresponding RMS roughness ($R_q$) values are shown in the inset.

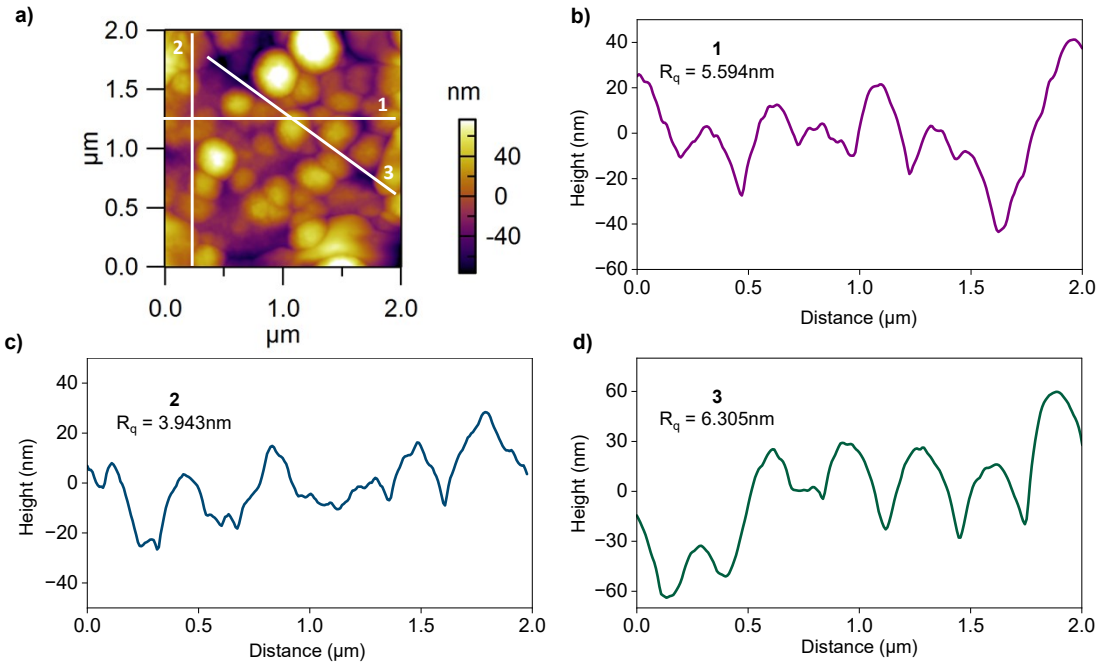



**Fig. S8** Cross-sectional line profiles. a) AFM image of poly$Cz_2N^{\bullet}$@ITO film with a scan size of 2 μm. b) horizontal, c) vertical, and d) diagonal line profiles of the AFM image of the thin films were shown. The corresponding RMS roughness ($R_q$) values are shown in the inset.

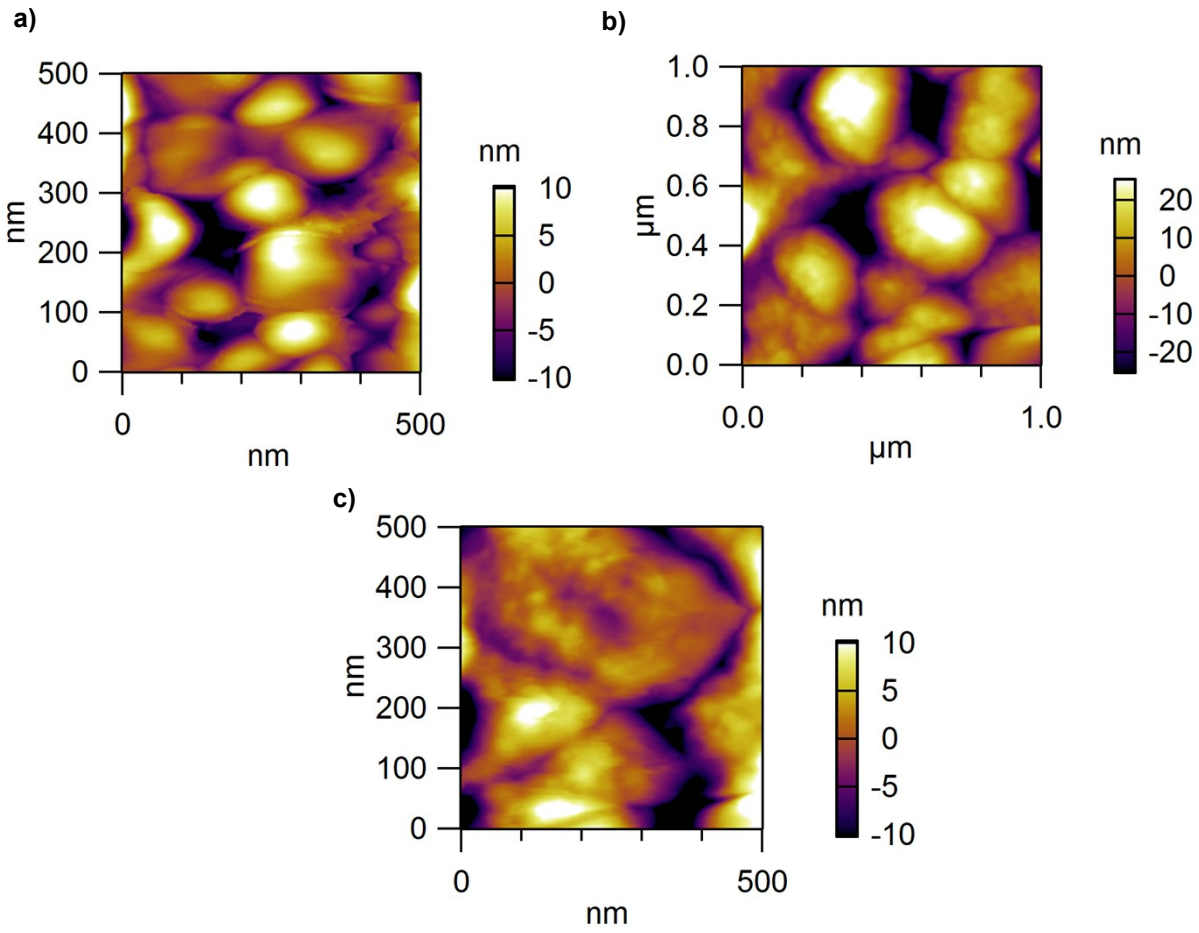



**Fig. S9** Atomic force microscopy images of the Blatter radical films. 2D view of a) poly$Cz_3N^{\bullet}$@ITO (scan size: 500 nm, RMS roughness: 0.698 ±0.03 nm). b) poly$Cz_2N^{\bullet}$@ITO (scan size: 1µm, RMS roughness: 2.302 ±0.122 1nm). c) poly$Cz_2N^{\bullet}$@ITO (scan size: 500 nm, RMS roughness: 0.809 ±0.028 nm).

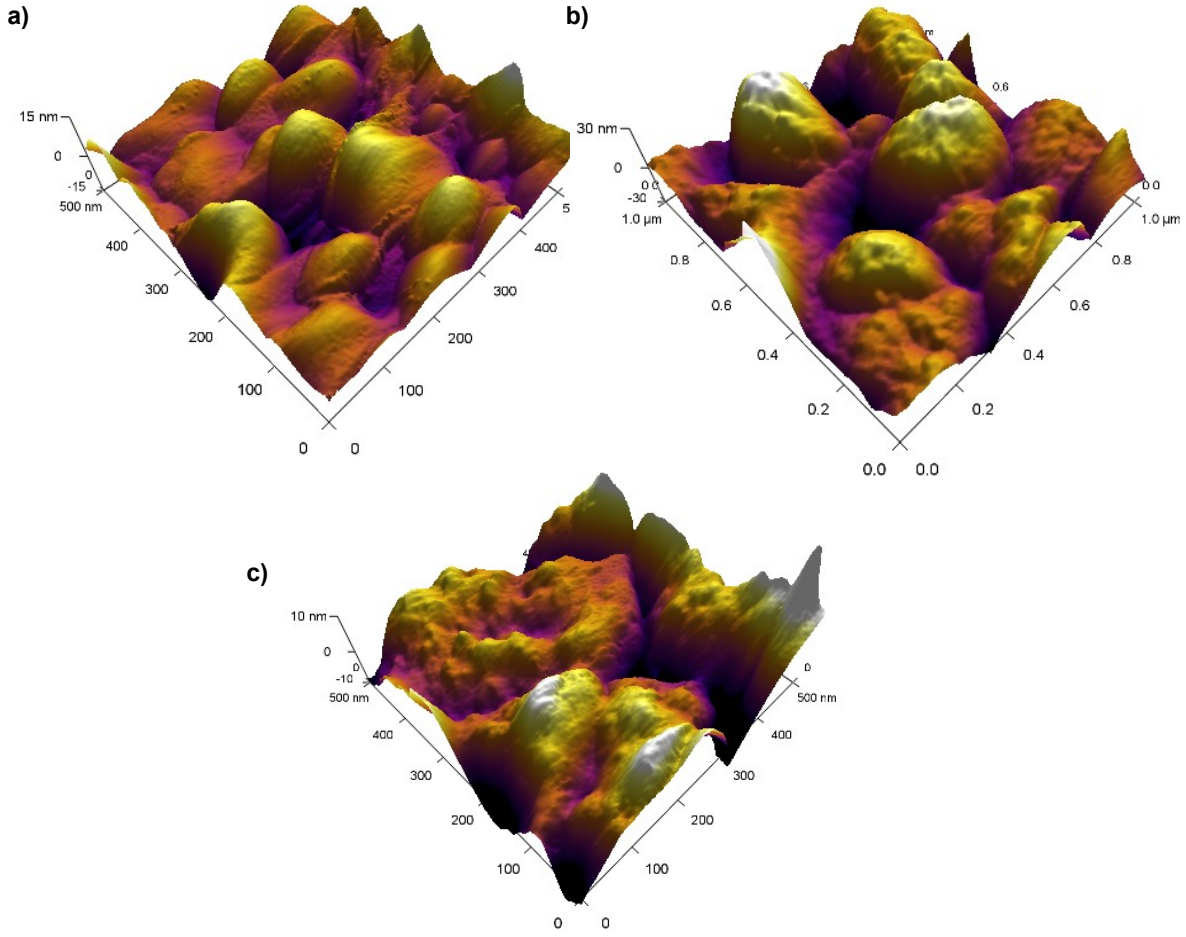



**Fig. S10** Atomic force microscopy images of the Blatter radical films. 3D view of a) poly$Cz_3N^{\bullet}$@ITO (scan size: 500 nm). b) poly$Cz_2N^{\bullet}$@ITO (scan size: 1µm). c) poly$Cz_2N^{\bullet}$@ITO (scan size: 500 nm).

**Table S5**. RMS roughness values of thin film of poly $Cz_3N^{\bullet}$ and poly$Cz_2N^{\bullet}$ for different scan size AFM images.

| Thin film | Scan size | $R_q$ (nm) *Mean(μ)* | $R_q$ (nm) *Standard Deviation(σ)* | $R_q$ (nm) *Standard Error (SE)* | Overall roughness(nm) ($\mu \pm SE$) |
|---|---|---|---|---|---|
| poly$Cz_3N^{\bullet}$ | 2μm × 2μm | 4.874 | 0.692 | 0.304 | 4.874 ± 0.304 |
| poly$Cz_3N^{\bullet}$ | 0.5μm × 0.5μm | 0.698 | 0.068 | 0.03 | 0.698 ± 0.03 |
| poly$Cz_2N^{\bullet}$ | 2μm × 2μm | 5.701 | 0.421 | 0.188 | 5.701 ± 0.188 |
| poly$Cz_2N^{\bullet}$ | 1μm × 1μm | 2.309 | 0.273 | 0.122 | 2.309 ± 0.122 |
| poly$Cz_2N^{\bullet}$ | 0.5μm × 0.5μm | 0.809 | 0.063 | 0.028 | 0.809 ± 0.028 |

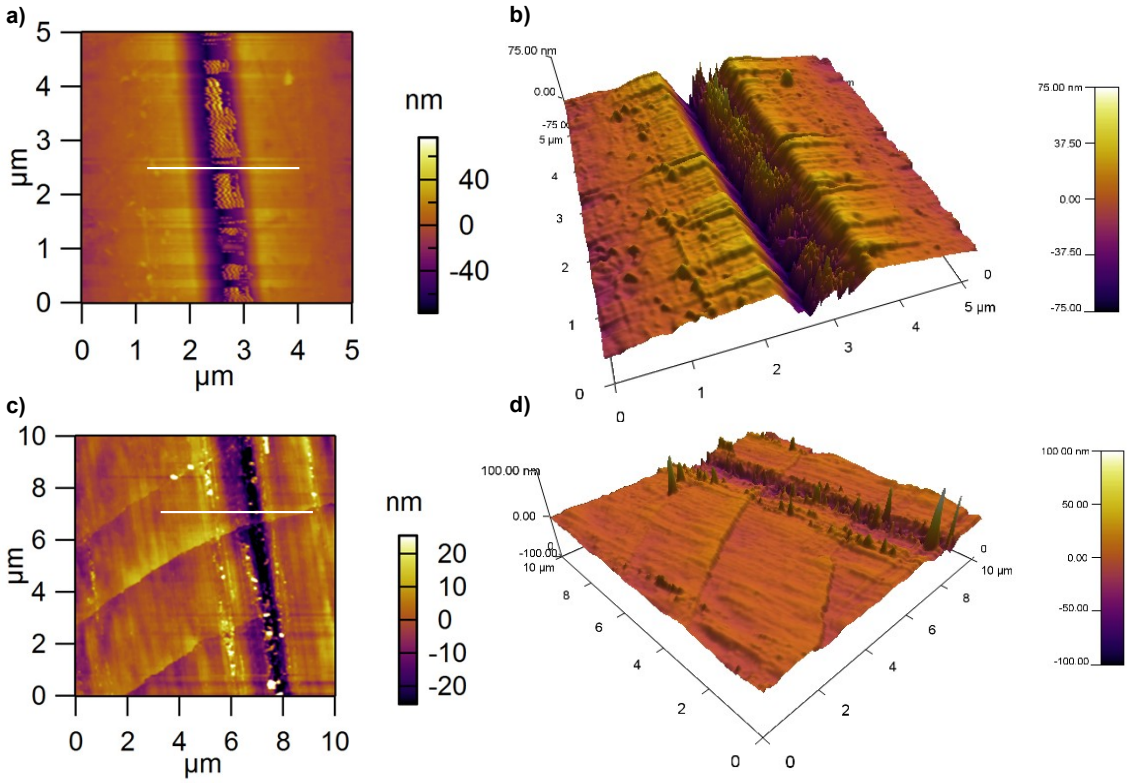



**Fig. S11** Thickness measurements of and by scratching the films with a needle. a), b) 2D and 3D view of the poly$Cz_3N^{\bullet}$@ITO film after scratching. c), d) 2D and 3D view of the poly$Cz_2N^{\bullet}$ @ITO film after scratching. The thickness was measured along the white line shown.

**8. FTIR spectra of $Cz_3N^{\bullet}$, $Cz_2N^{\bullet}$, $polyCz_3N^{\bullet}$ and $polyCz_2N^{\bullet}$.**

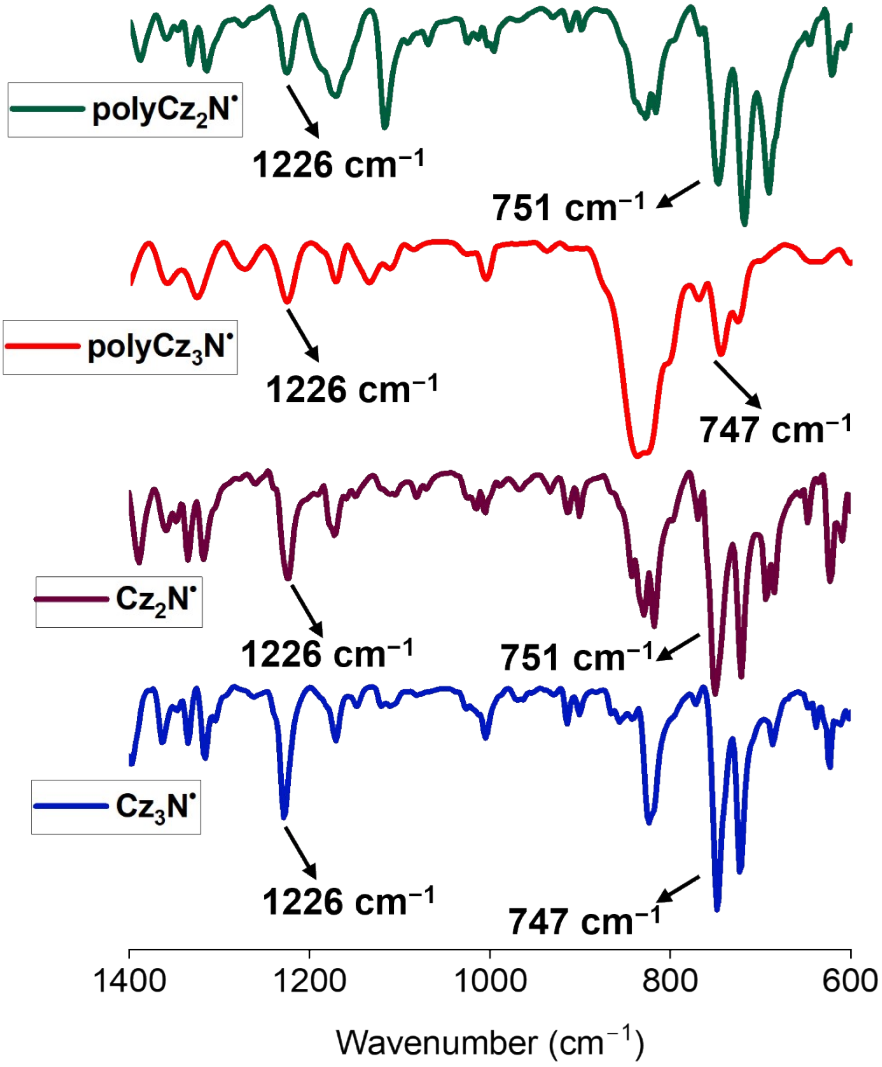
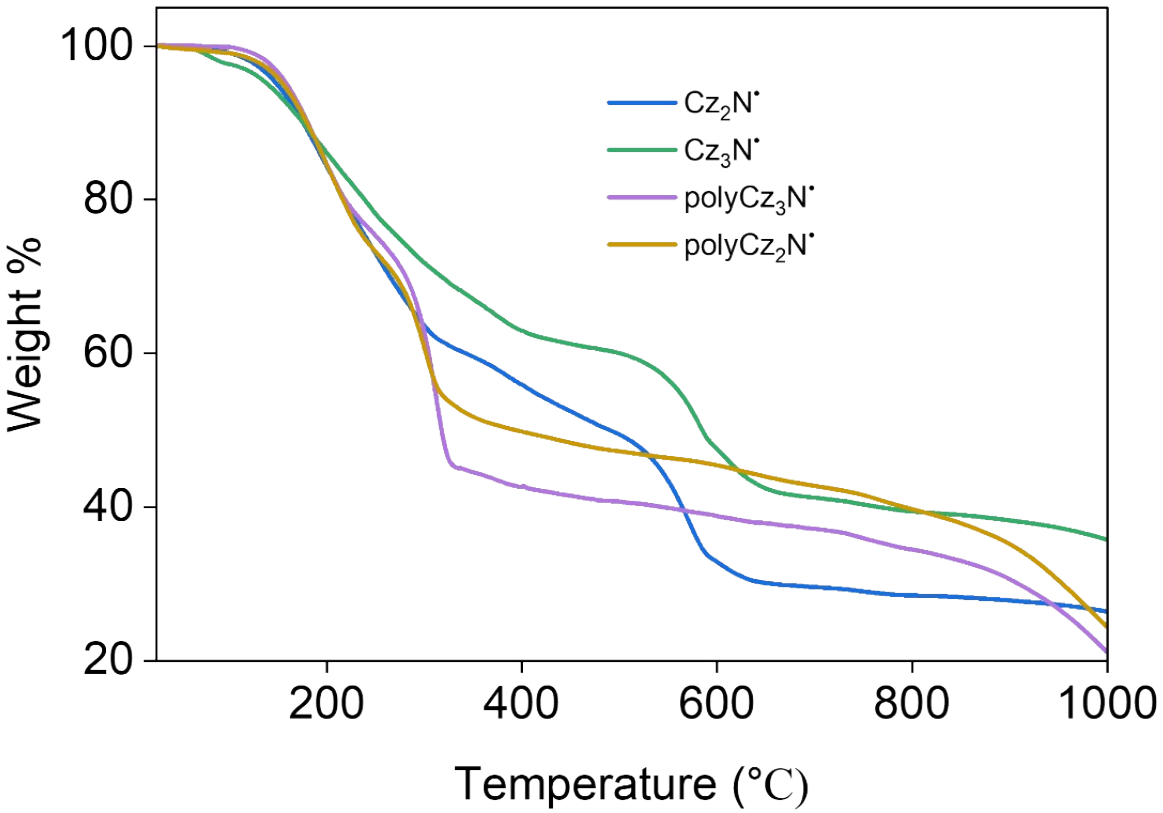



**Fig. S12** FTIR spectra of polymer thin films compared to the spectra of the corresponding monomers, $Cz_3N^{\bullet}$ (blue), $Cz_2N^{\bullet}$ (wine), $polyCz_3N^{\bullet}$ (red) and $polyCz_2N^{\bullet}$ (green).




**9. Thermogravimetric analysis (TGA) of $Cz_3N^{\bullet}$, $Cz_2N^{\bullet}$, $polyCz_3N^{\bullet}$ and $polyCz_2N^{\bullet}$.**

**Fig. S13** TGA of $Cz_3N^{\bullet}$ (green), $Cz_2N^{\bullet}$ (blue), $polyCz_3N^{\bullet}$ (purple) and $polyCz_2N^{\bullet}$ (yellow) under $N_2$ atmosphere in the temperature range of 25 – 1000 °C at a heating rate of 10 °C/min.

## 10. Air-stability of $Cz_3N^{\bullet}$ radical examined by solution state UV-Vis absorption spectroscopy.

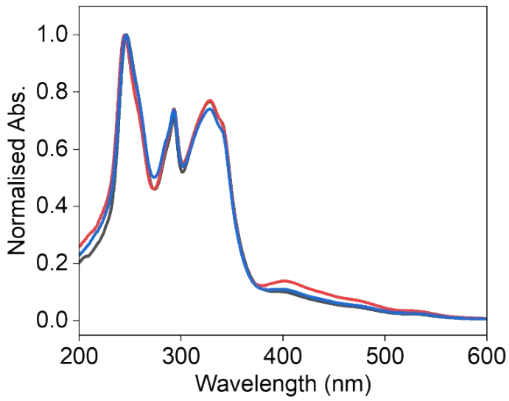



**Fig. S14** UV-Vis absorption spectra of $Cz_3N^{\bullet}$ in tetrahydrofuran on day 1 (red), day 10 (blue), and day 20 (black).

## 11. XPS studies of monomers $Cz_3N^{\bullet}$ and $Cz2N^{\bullet}$ and polymers $polyCz_3N^{\bullet}$ and $polyCz_2N^{\bullet}$.

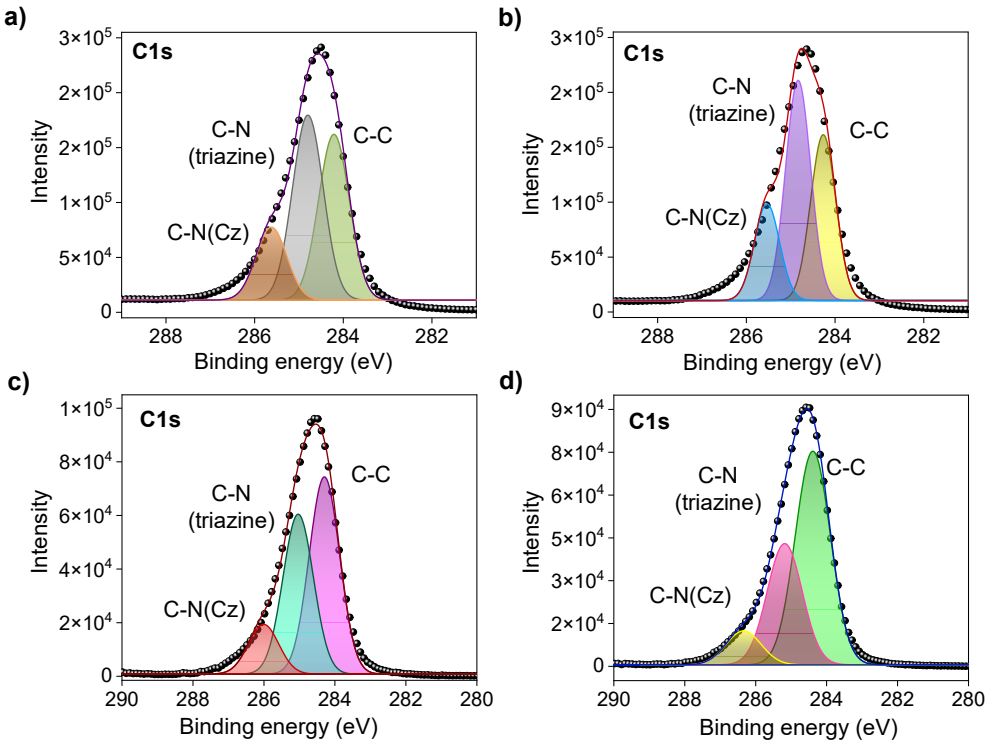


**Fig. S15** Fitted C1s XPS spectra of a) $Cz_3N^{\bullet}$ b) $Cz_2N^{\bullet}$ c) poly$Cz_3N^{\bullet}$ and d) poly$Cz_2N^{\bullet}$, respectively.

## 12. Concentration-dependent absorption spectra of radical monomers.

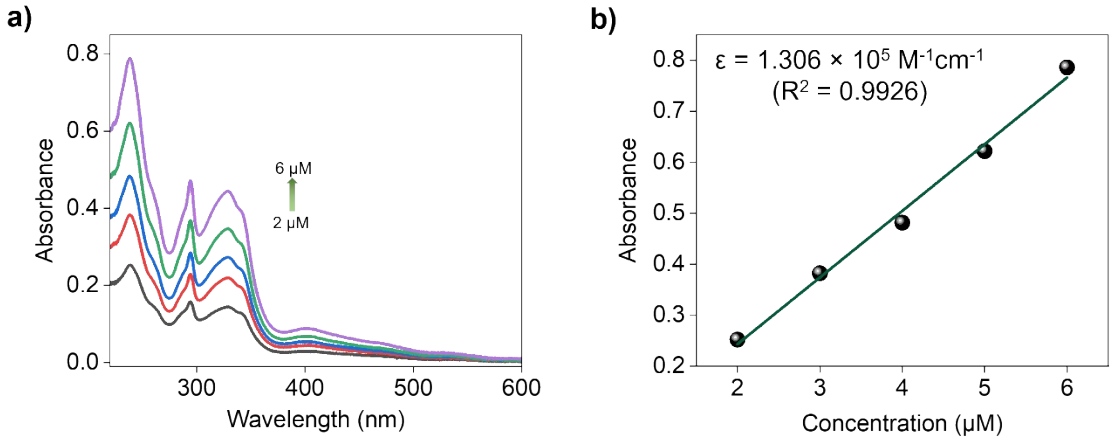



**Fig. S16** a) Concentration-dependent absorption spectra of $Cz_3N^{\bullet}$ in $CH_2Cl_2$ and b) molar extinction coefficient calculated at $\lambda_{max}$ = 238 nm.

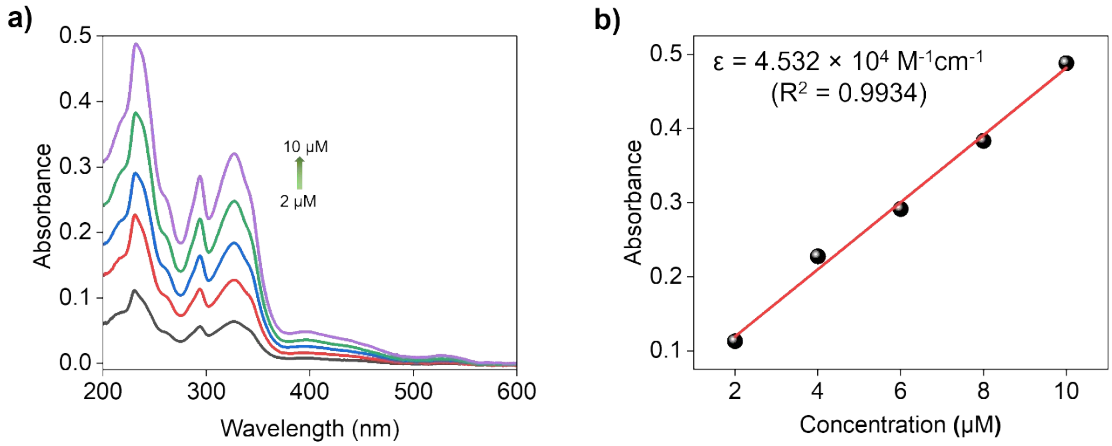



**Fig. S17** a) Concentration-dependent absorption spectra of $Cz_2N^{\bullet}$ in $CH_2Cl_2$ and b) molar extinction coefficient calculated at $\lambda_{max}$ = 232 nm.

**13. Band gap calculation for monomer radicals, $Cz_3N^{\bullet}$, $Cz_2N^{\bullet}$ and oxidised species $Cz_3N^{+}$, $Cz_2N^{+}$ and for polymeric thin film poly$Cz_3N^{\bullet}$ and poly$Cz_2N^{\bullet}$.**

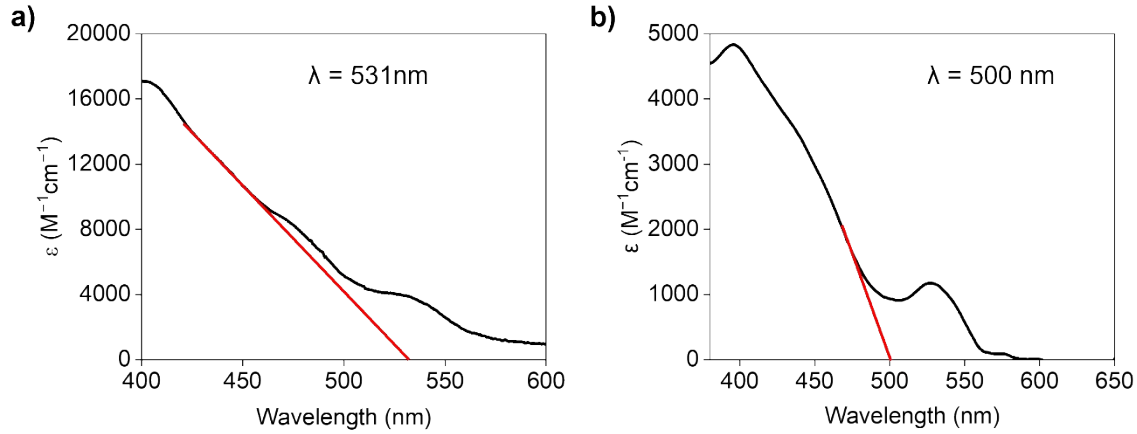



**Fig. S18** Absorption onset wavelengths of a) $Cz_3N^{\bullet}$ and b) $Cz_2N^{\bullet}$ obtained from the absorption spectra in $CH_2Cl_2$. Band gaps were calculated using eq. S3 and the corresponding $E_g$ values are 2.33 and 2.48 eV for $Cz_3N^{\bullet}$ and $Cz_2N^{\bullet}$, respectively.

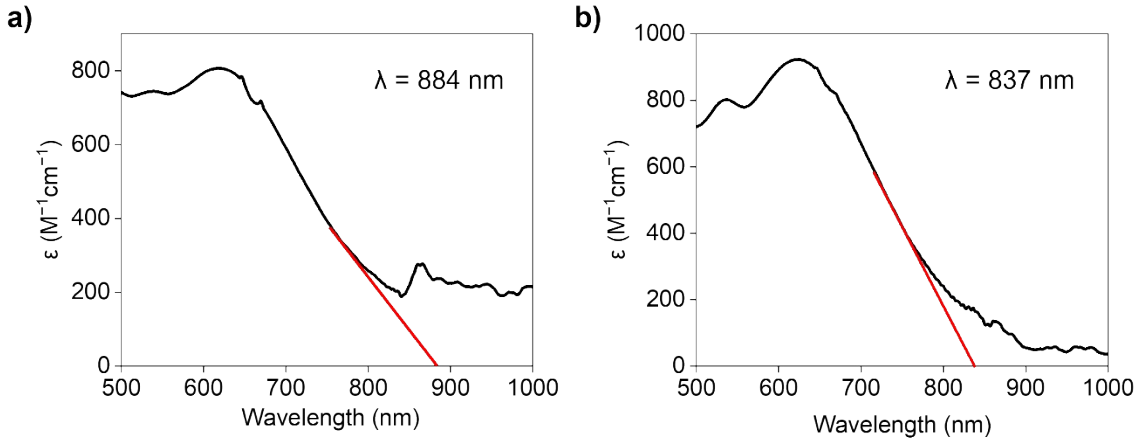



**Fig. S19** Absorption onset wavelengths of a) $Cz_3N^{+}$ and b) $Cz_2N^{+}$ obtained from the absorption spectra in $CH_2Cl_2$. Band gaps were calculated using eq. S3 and the corresponding $E_g$ values are 1.40 and 1.48 eV for $Cz_3N^{+}$ and $Cz_2N^{+}$, respectively.

## 14. DFT-optimized geometries of $Cz_3N^+$ and $Cz_2N^+$ using DCM as solvent.

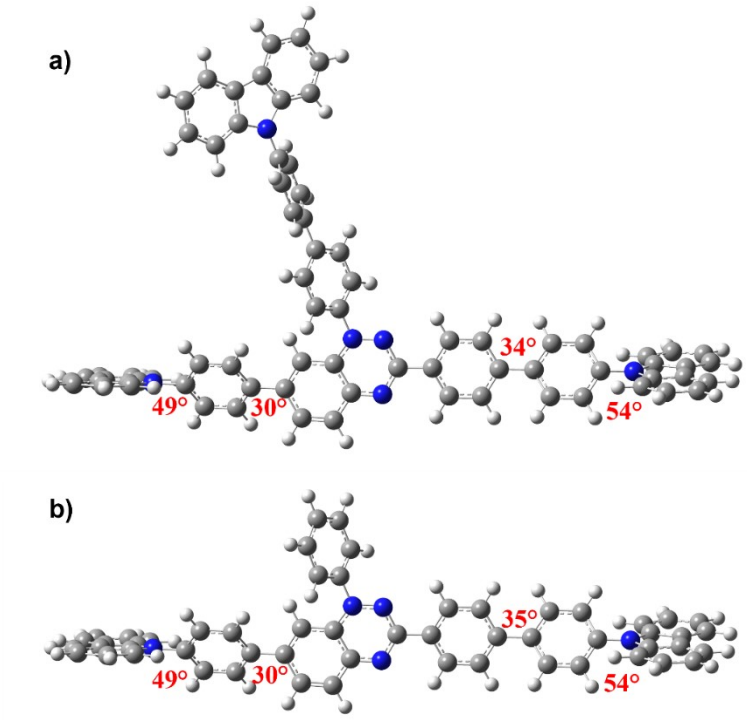



**Fig. S20** DFT-optimized geometries of a) $Cz_3N^+$ and b) $Cz_2N^+$. The torsional angles are shown in red colour.

**Table S6.** Cartesian coordinates.

| $Cz_3N^+$ | | | | $Cz_2N^+$ | | | |
|---|---|---|---|---|---|---|---|
| 6 | 1.303170000 | -5.182271000 | -0.576284000 | 6 | 3.604522000 | -1.426924000 | -1.593244000 |
| 6 | -0.037151000 | -4.939084000 | -0.672429000 | 6 | 2.243560000 | -1.456418000 | -1.697575000 |
| 6 | -0.530665000 | -3.609068000 | -0.543638000 | 6 | 1.450598000 | -0.570587000 | -0.912681000 |
| 6 | 0.428564000 | -2.545617000 | -0.369857000 | 6 | 2.132796000 | 0.371075000 | -0.057328000 |
| 6 | 1.800498000 | -2.821661000 | -0.234264000 | 6 | 3.534387000 | 0.366243000 | 0.056149000 |
| 6 | 2.255913000 | -4.130182000 | -0.336755000 | 6 | 4.285089000 | -0.522304000 | -0.703206000 |
| 1 | 1.664373000 | -6.197295000 | -0.693050000 | 1 | 4.194872000 | -2.095260000 | -2.209023000 |
| 1 | -0.756190000 | -5.732782000 | -0.836845000 | 1 | 1.731335000 | -2.143421000 | -2.360570000 |
| 1 | 2.489530000 | -2.019479000 | -0.011353000 | 1 | 4.016791000 | 1.027453000 | 0.761947000 |
| 6 | -2.247756000 | -2.104280000 | -0.390528000 | 6 | -0.572923000 | 0.196624000 | -0.166442000 |
| 6 | 3.688267000 | -4.447977000 | -0.204450000 | 6 | 5.754742000 | -0.548465000 | -0.610528000 |
| 6 | 4.677169000 | -3.522847000 | -0.592335000 | 6 | 6.484657000 | 0.617764000 | -0.308653000 |
| 6 | 4.110757000 | -5.684683000 | 0.320682000 | 6 | 6.472799000 | -1.742884000 | -0.814611000 |
| 6 | 6.027402000 | -3.814853000 | -0.456425000 | 6 | 7.868742000 | 0.593423000 | -0.208022000 |
| 1 | 4.392065000 | -2.569006000 | -1.023094000 | 1 | 5.968689000 | 1.561614000 | -0.169407000 |
| 6 | 5.459899000 | -5.984166000 | 0.457275000 | 6 | 7.857626000 | -1.774083000 | -0.716796000 |
| 1 | 3.381551000 | -6.418938000 | 0.645394000 | 1 | 5.947757000 | -2.666127000 | -1.034256000 |
| 6 | 6.433945000 | -5.051099000 | 0.070247000 | 6 | 8.571478000 | -0.604867000 | -0.411721000 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1 | 6.771509000 | -3.082232000 | -0.746788000 | 1 | 8.409287000 | 1.499396000 | 0.040270000 |
| 1 | 5.762718000 | -6.948185000 | 0.849208000 | 1 | 8.391447000 | -2.700778000 | -0.892434000 |
| 6 | -3.687284000 | -1.809387000 | -0.329052000 | 6 | -2.041231000 | 0.121261000 | -0.150075000 |
| 6 | -4.620895000 | -2.854335000 | -0.432823000 | 6 | -2.702727000 | -0.819319000 | -0.957716000 |
| 6 | -4.155467000 | -0.494373000 | -0.161621000 | 6 | -2.805970000 | 0.976813000 | 0.662373000 |
| 6 | -5.982236000 | -2.589237000 | -0.369972000 | 6 | -4.088700000 | -0.898591000 | -0.952435000 |
| 1 | -4.269613000 | -3.872272000 | -0.553178000 | 1 | -2.121690000 | -1.489162000 | -1.580369000 |
| 6 | -5.518265000 | -0.237344000 | -0.099784000 | 6 | -4.191540000 | 0.891042000 | 0.662261000 |
| 1 | -3.449121000 | 0.324280000 | -0.091577000 | 1 | -2.311841000 | 1.714741000 | 1.283124000 |
| 6 | -6.462506000 | -1.276600000 | -0.201809000 | 6 | -4.864610000 | -0.046106000 | -0.144361000 |
| 1 | -6.683189000 | -3.415365000 | -0.426612000 | 1 | -4.576523000 | -1.648888000 | -1.565599000 |
| 1 | -5.856649000 | 0.788205000 | 0.003358000 | 1 | -4.762052000 | 1.579349000 | 1.276743000 |
| 7 | -0.112523000 | -1.283818000 | -0.314764000 | 7 | 1.308228000 | 1.218063000 | 0.639493000 |
| 7 | -1.408527000 | -1.051342000 | -0.298199000 | 7 | -0.004335000 | 1.137059000 | 0.617789000 |
| 7 | -1.840999000 | -3.371988000 | -0.563766000 | 7 | 0.122049000 | -0.632982000 | -0.961652000 |
| 6 | 0.700054000 | -0.089378000 | -0.257379000 | 6 | 1.819431000 | 2.282264000 | 1.483567000 |
| 6 | 0.435295000 | 0.849460000 | 0.741770000 | 6 | 1.404600000 | 2.325448000 | 2.815149000 |
| 6 | 1.682663000 | 0.136664000 | -1.224812000 | 6 | 2.659094000 | 3.253388000 | 0.934334000 |
| 6 | 1.187222000 | 2.016163000 | 0.784998000 | 6 | 1.867115000 | 3.361876000 | 3.622945000 |
| 1 | -0.344229000 | 0.662093000 | 1.470857000 | 1 | 0.744775000 | 1.558810000 | 3.204244000 |
| 6 | 2.419171000 | 1.314203000 | -1.170860000 | 6 | 3.104276000 | 4.288110000 | 1.755593000 |
| 1 | 1.858116000 | -0.581927000 | -2.017589000 | 1 | 2.934241000 | 3.217533000 | -0.113791000 |
| 6 | 2.193999000 | 2.273382000 | -0.165530000 | 6 | 2.714800000 | 4.339900000 | 3.096131000 |
| 1 | 0.973478000 | 2.748346000 | 1.555542000 | 1 | 1.564238000 | 3.403548000 | 4.663549000 |
| 1 | 3.190476000 | 1.481322000 | -1.914192000 | 1 | 3.747423000 | 5.057373000 | 1.342272000 |
| 6 | -7.916405000 | -0.997421000 | -0.134074000 | 1 | 3.068169000 | 5.146504000 | 3.729850000 |
| 6 | -8.833687000 | -1.743097000 | -0.895177000 | 6 | -6.344076000 | -0.131223000 | -0.144777000 |
| 6 | -8.421344000 | 0.021127000 | 0.693211000 | 6 | -7.051003000 | -0.436721000 | -1.321054000 |
| 6 | -10.200112000 | -1.489425000 | -0.828842000 | 6 | -7.083832000 | 0.092381000 | 1.029720000 |
| 1 | -8.475996000 | -2.524272000 | -1.557840000 | 6 | -8.439713000 | -0.522363000 | -1.325608000 |
| 6 | -9.784886000 | 0.291180000 | 0.753801000 | 1 | -6.511561000 | -0.596971000 | -2.248870000 |
| 1 | -7.742960000 | 0.603635000 | 1.307937000 | 6 | -8.473494000 | 0.022649000 | 1.030324000 |
| 6 | -10.686562000 | -0.465985000 | -0.005238000 | 1 | -6.568245000 | 0.312244000 | 1.958902000 |
| 1 | -10.893557000 | -2.085588000 | -1.411868000 | 6 | -9.162818000 | -0.288899000 | -0.148779000 |
| 1 | -10.153943000 | 1.091340000 | 1.386104000 | 1 | -8.966887000 | -0.773487000 | -2.239541000 |
| 6 | 8.784312000 | -5.203193000 | -0.792515000 | 1 | -9.028012000 | 0.213304000 | 1.942694000 |
| 6 | 8.428381000 | -5.857082000 | 1.360437000 | 6 | 10.866083000 | 0.258310000 | -0.943615000 |
| 6 | 8.646985000 | -4.786469000 | -2.119804000 | 6 | 10.735061000 | -1.558764000 | 0.424474000 |
| 6 | 10.036553000 | -5.615217000 | -0.272087000 | 6 | 10.597713000 | 1.314184000 | -1.819607000 |
| 6 | 7.885858000 | -6.124314000 | 2.620779000 | 6 | 12.194205000 | -0.103048000 | -0.605707000 |
| 6 | 9.810926000 | -6.026942000 | 1.098803000 | 6 | 10.306464000 | -2.600296000 | 1.252503000 |
| 6 | 9.793043000 | -4.760140000 | -2.913262000 | 6 | 12.110672000 | -1.255805000 | 0.268351000 |
| 1 | 7.685284000 | -4.499308000 | -2.528806000 | 6 | 11.682804000 | 2.024628000 | -2.331055000 |
| 6 | 11.172659000 | -5.579849000 | -1.089067000 | 1 | 9.584664000 | 1.574240000 | -2.103624000 |
| 6 | 8.747217000 | -6.593978000 | 3.611319000 | 6 | 13.266809000 | 0.625549000 | -1.132848000 |
| 1 | 6.834444000 | -5.967963000 | 2.832168000 | 6 | 11.281756000 | -3.356124000 | 1.901513000 |
| 6 | 10.655274000 | -6.499670000 | 2.110260000 | 1 | 9.254137000 | -2.815621000 | 1.396755000 |
| 6 | 11.045422000 | -5.146271000 | -2.406176000 | 6 | 13.070808000 | -2.028999000 | 0.931432000 |
| 1 | 9.710960000 | -4.436969000 | -3.946551000 | 6 | 13.004524000 | 1.691188000 | -1.989896000 |
| 1 | 12.137688000 | -5.892527000 | -0.701334000 | 1 | 11.497971000 | 2.850837000 | -3.010824000 |
| 6 | 10.116690000 | -6.786447000 | 3.361895000 | 1 | 14.288730000 | 0.357693000 | -0.881364000 |
| 1 | 8.347255000 | -6.811515000 | 4.597002000 | 6 | 12.650397000 | -3.080740000 | 1.741412000 |
| 1 | 11.716180000 | -6.634358000 | 1.921475000 | 1 | 10.972336000 | -4.172616000 | 2.546825000 |
| 1 | 11.918351000 | -5.112201000 | -3.050358000 | 1 | 14.127829000 | -1.806384000 | 0.819607000 |
| 1 | 10.759404000 | -7.155524000 | 4.154886000 | 1 | 13.826651000 | 2.265824000 | -2.404657000 |
| 6 | -12.850853000 | -0.149760000 | 1.227723000 | 1 | 13.384072000 | -3.689969000 | 2.259767000 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 6 | -12.915778000 | 0.062882000 | -1.033201000 | 6 | -11.359712000 | -1.157296000 | 0.702635000 |
| 6 | -12.471941000 | -0.378595000 | 2.554145000 | 6 | -11.438077000 | 0.337045000 | -1.006651000 |
| 6 | -14.194482000 | 0.144650000 | 0.880350000 | 6 | -10.957974000 | -2.054937000 | 1.696676000 |
| 6 | -12.600515000 | 0.157108000 | -2.392274000 | 6 | -12.729592000 | -0.959794000 | 0.390979000 |
| 6 | -14.235309000 | 0.283071000 | -0.560874000 | 6 | -11.132529000 | 1.271895000 | -2.000615000 |
| 6 | -13.457994000 | -0.287492000 | 3.534910000 | 6 | -12.779674000 | -0.004659000 | -0.696755000 |
| 1 | -11.448417000 | -0.622436000 | 2.815513000 | 6 | -11.952890000 | -2.740243000 | 2.391668000 |
| 6 | -15.165977000 | 0.231082000 | 1.885429000 | 1 | -9.909777000 | -2.218657000 | 1.920059000 |
| 6 | -13.633996000 | 0.456284000 | -3.278209000 | 6 | -13.709595000 | -1.660691000 | 1.104932000 |
| 1 | -11.587887000 | 0.007266000 | -2.749378000 | 6 | -12.193611000 | 1.847880000 | -2.696914000 |
| 6 | -15.255766000 | 0.581681000 | -1.472415000 | 1 | -10.107309000 | 1.545402000 | -2.223163000 |
| 6 | -14.791387000 | 0.017839000 | 3.209292000 | 6 | -13.827580000 | 0.588359000 | -1.412047000 |
| 1 | -13.187203000 | -0.459125000 | 4.572428000 | 6 | -13.315685000 | -2.545487000 | 2.105145000 |
| 1 | -16.198171000 | 0.456747000 | 1.633570000 | 1 | -11.665367000 | -3.441357000 | 3.169487000 |
| 6 | -14.950016000 | 0.663202000 | -2.828233000 | 1 | -14.761997000 | -1.518313000 | 0.877025000 |
| 1 | -13.413758000 | 0.532660000 | -4.338820000 | 6 | -13.528438000 | 1.509888000 | -2.411926000 |
| 1 | -16.270551000 | 0.751478000 | -1.124366000 | 1 | -11.980910000 | 2.575232000 | -3.474709000 |
| 1 | -15.534260000 | 0.083076000 | 3.998143000 | 1 | -14.859266000 | 0.335236000 | -1.185427000 |
| 1 | -15.731858000 | 0.892620000 | -3.545520000 | 1 | -14.065194000 | -3.094126000 | 2.666976000 |
| 7 | 7.806302000 | -5.352850000 | 0.205514000 | 1 | -14.331175000 | 1.975944000 | -2.974796000 |
| 7 | -12.079102000 | -0.198681000 | 0.059599000 | 7 | 9.979207000 | -0.632175000 | -0.314186000 |
| 6 | 2.991277000 | 3.520011000 | -0.109536000 | 7 | -10.580187000 | -0.366599000 | -0.151411000 |
| 6 | 3.436240000 | 4.151037000 | -1.284774000 | | | | |
| 6 | 3.326553000 | 4.107916000 | 1.123042000 | | | | |
| 6 | 4.176521000 | 5.327168000 | -1.233697000 | | | | |
| 1 | 3.164893000 | 3.745136000 | -2.253880000 | | | | |
| 6 | 4.084813000 | 5.272034000 | 1.182849000 | | | | |
| 1 | 3.029348000 | 3.628015000 | 2.049790000 | | | | |
| 6 | 4.512642000 | 5.895578000 | 0.002714000 | | | | |
| 1 | 4.477147000 | 5.820362000 | -2.151404000 | | | | |
| 1 | 4.366297000 | 5.688575000 | 2.143611000 | | | | |
| 6 | 4.939105000 | 8.246707000 | 0.771580000 | | | | |
| 6 | 6.502215000 | 7.307739000 | -0.586433000 | | | | |
| 6 | 3.799634000 | 8.522770000 | 1.533410000 | | | | |
| 6 | 5.955215000 | 9.217359000 | 0.579432000 | | | | |
| 6 | 7.260759000 | 6.438993000 | -1.376939000 | | | | |
| 6 | 6.952726000 | 8.617978000 | -0.283264000 | | | | |
| 6 | 3.702705000 | 9.782536000 | 2.122011000 | | | | |
| 1 | 3.012694000 | 7.788362000 | 1.661887000 | | | | |
| 6 | 5.833818000 | 10.475539000 | 1.182093000 | | | | |
| 6 | 8.471518000 | 6.911048000 | -1.880978000 | | | | |
| 1 | 6.926431000 | 5.430086000 | -1.590174000 | | | | |
| 6 | 8.172817000 | 9.068180000 | -0.802567000 | | | | |
| 6 | 4.708609000 | 10.750305000 | 1.954690000 | | | | |
| 1 | 2.827871000 | 10.018869000 | 2.720298000 | | | | |
| 1 | 6.605145000 | 11.227551000 | 1.043626000 | | | | |
| 6 | 8.924678000 | 8.212555000 | -1.603263000 | | | | |
| 1 | 9.076624000 | 6.254963000 | -2.499486000 | | | | |
| 1 | 8.528916000 | 10.069556000 | -0.578762000 | | | | |
| 1 | 4.602701000 | 11.721048000 | 2.428790000 | | | | |
| 1 | 9.871503000 | 8.549417000 | -2.013608000 | | | | |
| 7 | 5.277004000 | 7.087311000 | 0.058903000 | | | | |

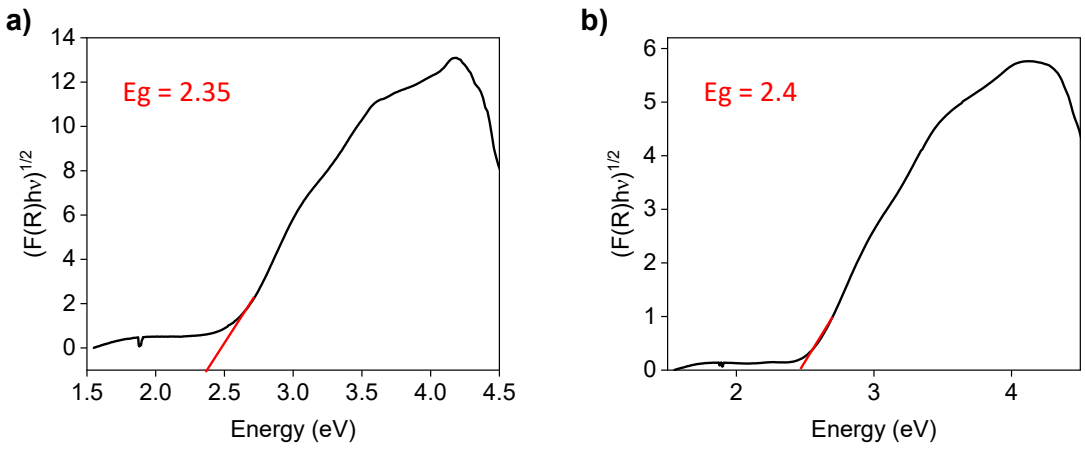



**Fig. S21** Band gap calculated by using Tauc's method of a) poly$Cz_3N^{\bullet}$ and b) poly$Cz_2N^{\bullet}$ coated on an ITO substrate.

The band gap for the polymer thin films was calculated from a Tauc plot of $(\alpha h\nu)^{1/2}$ vs. energy (eV), where F(R) or α is the absorption coefficient, obtained from the reflectance spectra of the polymer films. The reflectance spectra were directly measured on the UV/vis spectrometer by choosing the reflectance spectra mode in the instrument parameters.

**15. Experimentally calculated HOMO-LUMO and band gap for $Cz_3N^{\bullet}$, $Cz_2N^{\bullet}$, $polyCz_3N^{\bullet}$, and $polyCz_2N^{\bullet}$.**

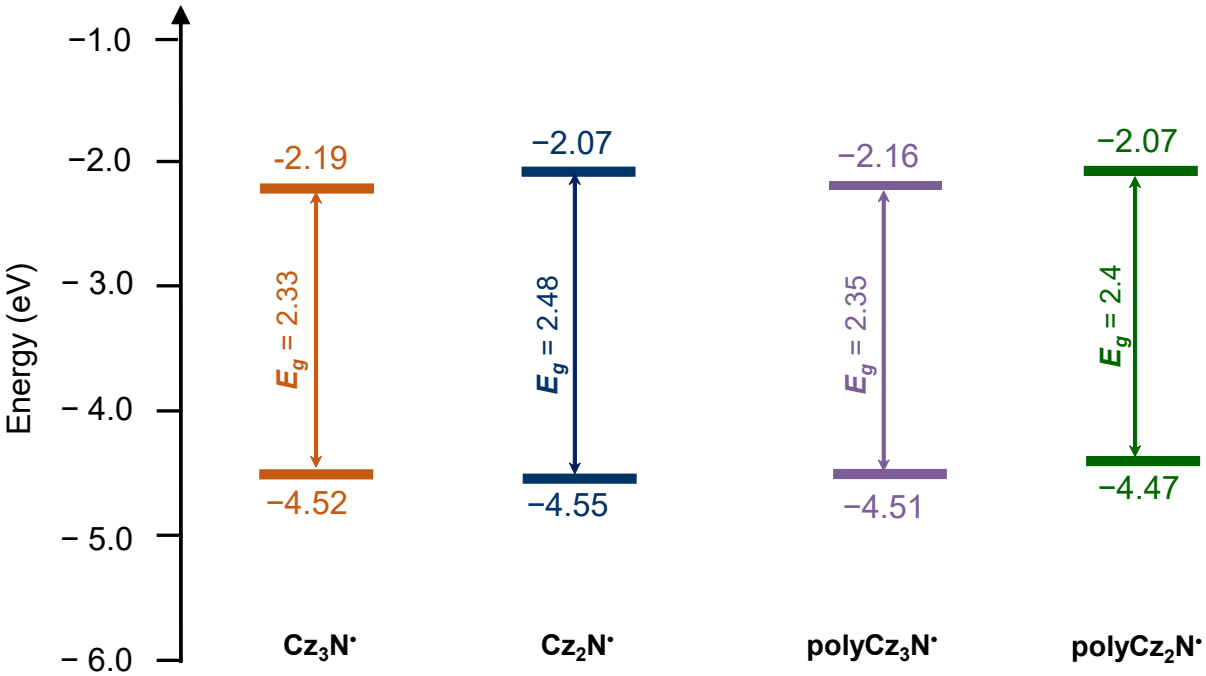



**Fig. S22** HOMO-LUMO energy level diagram representing the experimental band gaps of $Cz_3N^{\bullet}$, $Cz_2N^{\bullet}$, $polyCz_3N^{\bullet}$, and $polyCz_2N^{\bullet}$.

**Table S7**. Comparison of theoretical and experimental energy values with NHE

| | Theoretical (*vs* Vacuum) | | V *vs* NHE* | |
|---|---|---|---|---|
| | HOMO (eV) | LUMO (eV) | HOMO or VB | LUMO or CB |
| $Cz_3N^{\bullet}$ | −5.66 | −3.00 | 1.22 | −1.44 |
| $Cz_2N^{\bullet}$ | −5.67 | −2.97 | 1.23 | −1.47 |
| $Cz_3N^{+}$ | −5.86 | −4.53 | 1.42 | 0.09 |
| $Cz_3N^{+}$ | −5.86 | −4.53 | 1.36 | 0.09 |
| | Experimental (vs Ag/AgCl) | | eV *(vs* NHE)[#] | |
| | HOMO | LUMO | HOMO | LUMO |
| $Cz_3N^{\bullet}$ | −4.52 | −2.19 | −4.23 | −1.9 |
| $Cz_2N^{\bullet}$ | −4.55 | −2.07 | −4.26 | −1.78 |
| poly$Cz_3N^{\bullet}$ | −4.51 | −2.16 | −4.22 | −1.87 |
| poly$Cz_2N^{\bullet}$ | −4.47 | −2.07 | −4.18 | −1.78 |

*$E_{NHE} = -(-E_{vacuum} + 4.44)$ V

[#]$E_{NHE} = (E_{Ag/AgCl} + 0.288)$ V

## 16. EPR studies of $Cz_3N^{\bullet}$ and $Cz_2N^{\bullet}$.

**Table S8**. Experimental hyperfine coupling constants (G) for different Blatter radicals in toluene.

| S. No. | $Cz_xN^{\bullet}$ | $a_{hfcc}$(G) | | |
|---|---|---|---|---|
| | | **N1** | **N2** | **$N_{rad}$** |

| | | | | |
|---|---|---|---|---|
| **1** | **$Cz_3N^{\bullet}$** | 7.31 | 4.84 | 4.84 |
| **2** | **$Cz_2N^{\bullet}$** | 7.4 | 4.91 | 4.82 |

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