# Electronic Supplementary Information

## Amplification of Dissymmetry Factors by Dihedral Angle Engineering in Donor–Acceptor Type Circularly Polarized Luminescence Materials

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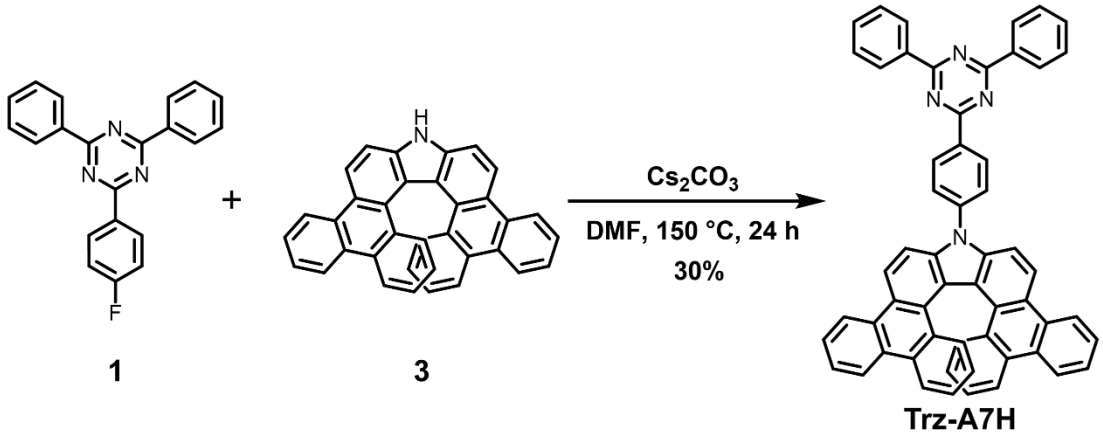
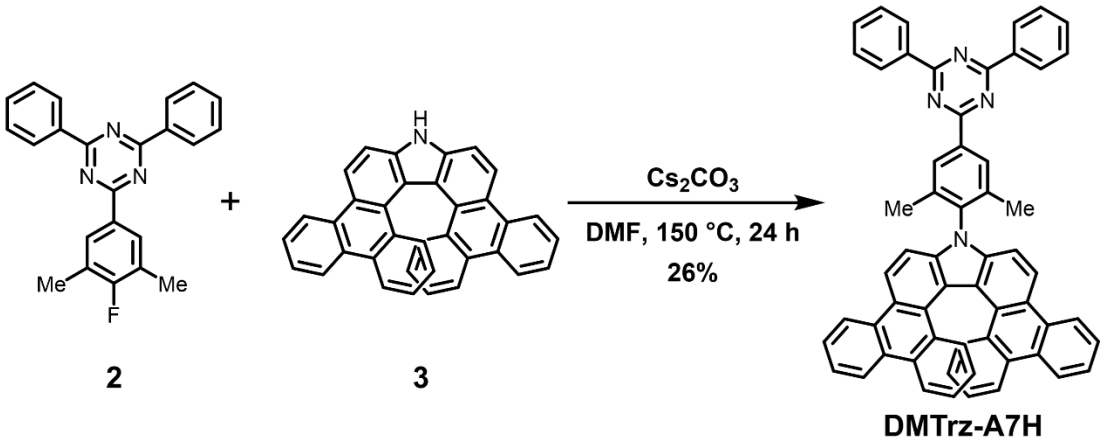
# 1. General Methods

All commercial materials were purchased from Bide Pharmatech, J&K Scientific and Heowns, and used as received without further purification unless otherwise noted. Anhydrous *N*,*N*-dimethylformamide (DMF) was purchased from J&K scientific. All reactions were carried out under argon atmosphere using Schlenk lines. Thin layer chromatography (TLC) plates and silica gel used for column chromatography were purchased from Yantai Xincheng with a grain size of 0.063-0.200 mm. Nuclear magnetic resonance (NMR) spectra were recorded in $CD_2Cl_2$ on AVANCE 400 MHz Bruker spectrometers. $^1$H NMR chemical shifts were referenced to $CHDCl_2$ (5.320 ppm). $^{13}$C NMR chemical shifts were referenced to $CD_2Cl_2$ (54.00 ppm). High-resolution mass spectrometry (HRMS) was performed on Agilent 6545B by electron spray ionization (ESI). UV-vis absorption spectra were recorded on an Analytikjena Specord 210 Plus UV-vis spectrophotometer. Photoluminescence spectra were recorded on an Edinburgh FSL1000 Spectrofluorometer. Photoluminescence quantum yields (PLQYs) were measured by an integrating sphere in toluene ($c = 3.0 \times 10^{-6}$ M). Chiral high-performance liquid chromatography (HPLC) was implemented on a Daicel Chiralpak IE column. Circular dichroism (CD) spectra were collected on JASCO-810 circular dichroism spectrometer at 297 K. Circularly polarized luminescence (CPL) measurements were performed using JASCO CPL-300 at 297 K. Cyclic voltammogram (CV) was performed under argon atmosphere by CHI 620E electrochemical analyzer with the scan rate of 100 mV $s^{-1}$ (working electrode: glassy carbon, reference electrode: Ag/AgCl, counter electrode: platinum wire).

## 2. Synthetic Procedures




**Trz-A7H**. To a Schlenk flask under argon was added **1** (164 mg, 0.500 mmol), **3**[1] (222 mg, 0.480 mmol), $Cs_2CO_3$ (814 mg, 2.50 mmol), and DMF (5 mL). The reaction mixture was then heated to 150 °C and stirred for 24 h. After cooling down to room temperature, the mixture was poured into brine and washed with MeOH. The residue was collected and purified by column chromatography over silica gel (eluent: petroleum ether/DCM = 3 : 1) and recrystallization from DCM/hexane to give 109 mg (yield: 30%) of **Trz-A7H** as a green solid. $^1$H NMR (400 MHz, $CD_2Cl_2/CS_2$, 297 K, ppm) $\delta$ 9.26 – 9.20 (m, 2H), 8.94 – 8.85 (m, 4H), 8.82 (d, $J$ = 8.9 Hz, 2H), 8.71 (dd, $J$ = 11.0, 7.8 Hz, 4H), 8.44 (d, $J$ = 8.1 Hz, 2H), 8.13 – 8.03 (m, 2H), 7.97 (d, $J$ = 8.8 Hz, 2H), 7.87 (dd, $J$ = 8.2, 1.3 Hz, 2H), 7.78 – 7.61 (m, 10H), 7.24 (m, 2H), 6.40 (m, 2H). $^{13}$C NMR (101 MHz, $CD_2Cl_2/CS_2$, 297 K, ppm) $\delta$ 172.40, 171.38, 141.40, 141.34, 136.77, 136.68, 133.38, 131.58, 131.22, 131.11, 129.95, 129.76, 129.37, 129.11, 128.84, 128.36, 128.30, 127.86, 127.59, 126.78, 125.47, 125.30, 124.28, 123.87, 122.53, 122.42, 119.57, 111.01. HRMS (ESI) *m/z*: Calcd. for $C_{57}H_{35}N_4$: 775.2862; found: 775.2853 $[M + H]^+$.




**DMTrz-A7H**. To a Schlenk flask under argon was added **2** (40 mg, 0.11 mmol), **3** (50 mg, 0.10 mmol), $Cs_2CO_3$ (179 mg, 0.550 mmol), and DMF (1 mL). The reaction mixture was then heated to 150 °C and stirred for 24 h. After cooling down to room temperature, the mixture was poured into brine and washed with MeOH. The residue was collected and purified by column chromatography over silica gel (eluent: petroleum ether/DCM = 3 : 1) and recrystallization from DCM/hexane to give 21 mg (yield: 26%) of **Trz-A7H** as a green solid. $^1$H NMR (400 MHz, $CD_2Cl_2$, 297 K, ppm) $\delta$ 8.94 – 8.79 (m, 8H), 8.78 – 8.71 (m, 4H), 8.50 (d, $J$ = 8.4 Hz, 2H), 7.96 (dd, $J$ = 8.2, 1.3 Hz, 2H), 7.78 – 7.62 (m, 10H), 7.53 (d, $J$ = 8.8 Hz, 2H), 7.30 – 7.22 (m, 2H), 6.45 – 6.36 (m, 2H), 2.21 (s, 6H). $^{13}$C NMR (101 MHz, $CD_2Cl_2$, 297 K, ppm) $\delta$ 172.46, 171.96, 140.85, 139.64, 138.89, 137.67, 136.75, 133.33, 131.31, 131.12, 129.99, 129.79, 129.55, 129.34, 129.08, 128.66, 128.43, 127.74, 127.41, 126.52, 125.06, 124.97, 124.10, 123.77, 122.41, 122.35, 118.89, 110.66, 18.33. HRMS (ESI) *m/z*: Calcd. for $C_{59}H_{39}N_4$: 803.3175; found: 803.3172 $[M + H]^+$.

## 3. Optical Resolution and Chiroptical Properties

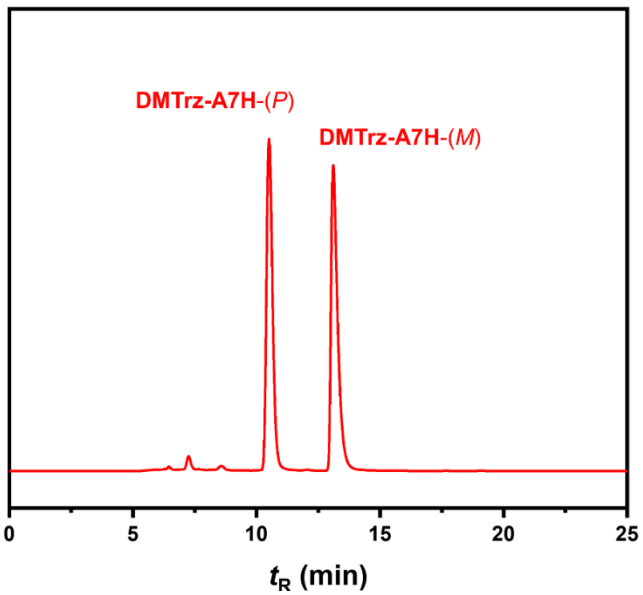



**Figure S1.** Chiral HPLC analysis of **DMTrz-A7H** eluted by DCM/hexane = 1 : 1 using Daicel Chiralpak IE column. Elution rate: 0.5 mL·min$^{-1}$. The integration areas of the (*P*) and (*M*)- enantiomers are 49.7% and 50.3%, respectively.

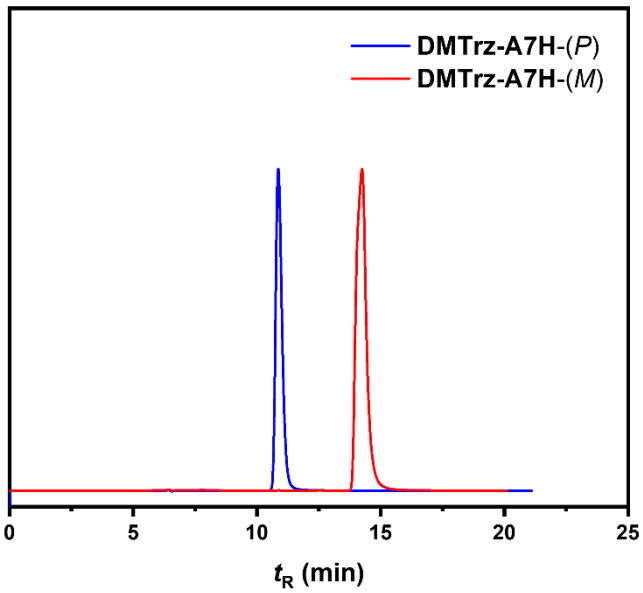



**Figure S2.** Chiral HPLC traces of the separated (*P*)- and (*M*)- enantiomers of **DMTrz-A7H** eluted by DCM/hexane = 1 : 1 using Daicel Chiralpak IE column. Elution rate: 0.5 mL min$^{-1}$.

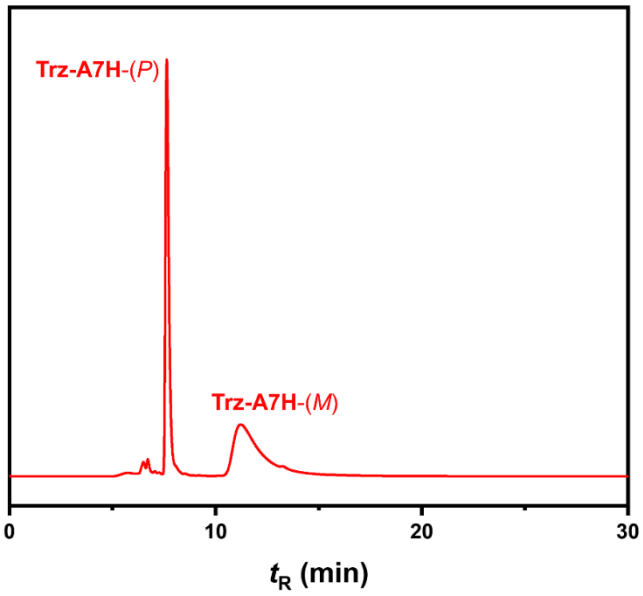



**Figure S3.** Chiral HPLC analysis of **Trz-A7H** eluted by DCM using Daicel Chiralpak IE column. Elution rate: 0.5 mL·min$^{-1}$. The integration areas of the (*P*) and (*M*)-enantiomers are 49.7% and 50.3%, respectively.

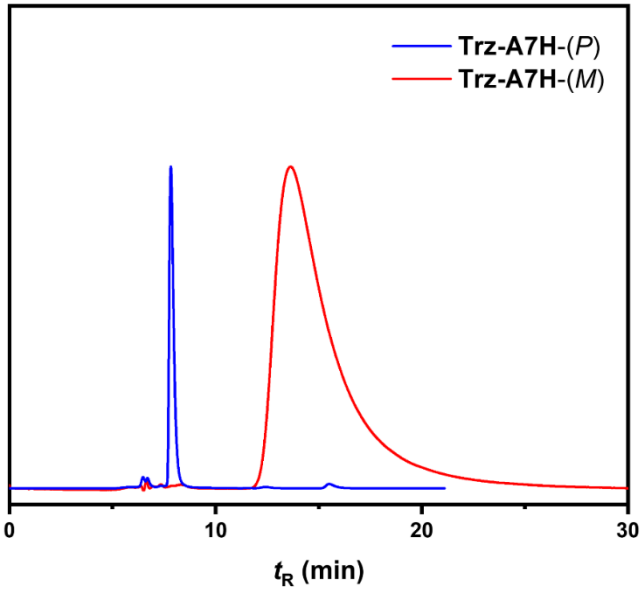



**Figure S4.** Chiral HPLC traces of the separated (*P*)- and (*M*)- enantiomers of **Trz-A7H** eluted by DCM using Daicel Chiralpak IE column. Elution rate: 0.5 mL min$^{-1}$.

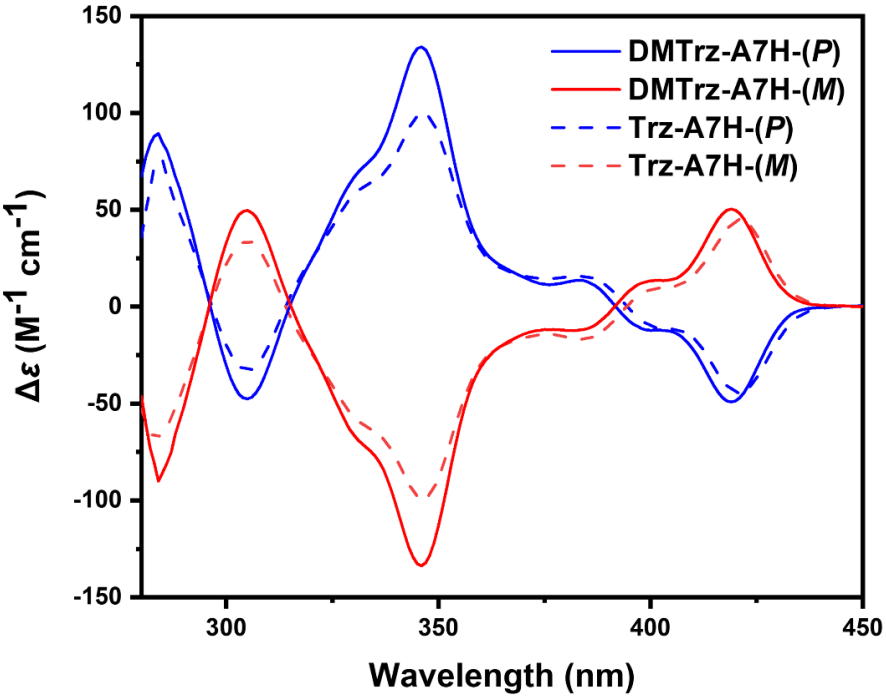



**Figure S5**. CD spectra of **DMTrz-A7H** and **Trz-A7H** in toluene ($c$ = 1.0 × $10^{-5}$ M).

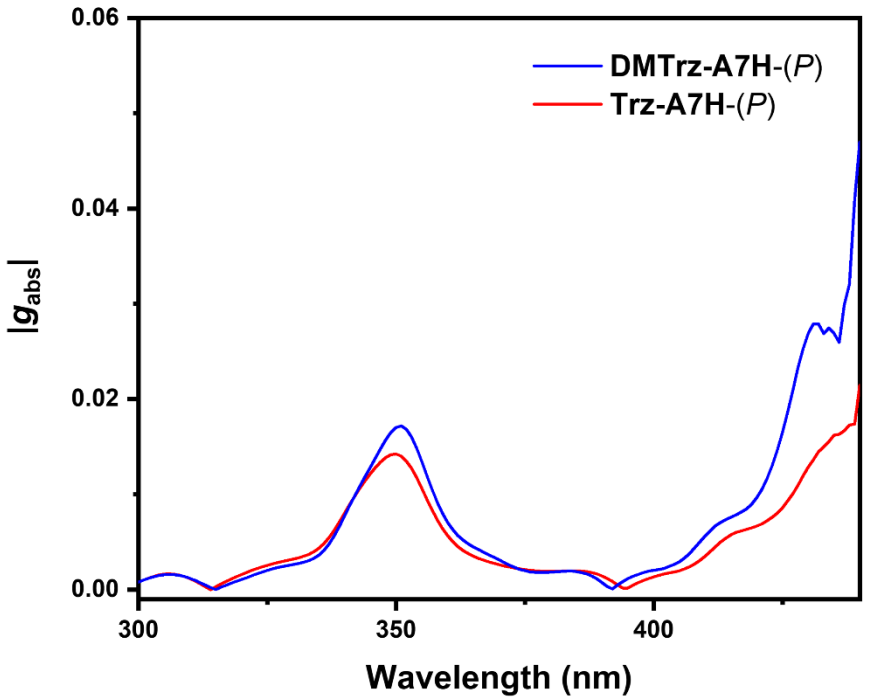



**Figure S6**. Absorption dissymmetry factors of **DMTrz-A7H** and **Trz-A7H** in toluene ($c$ = 1.0 × $10^{-5}$ M).

## 4. Electrochemical Properties

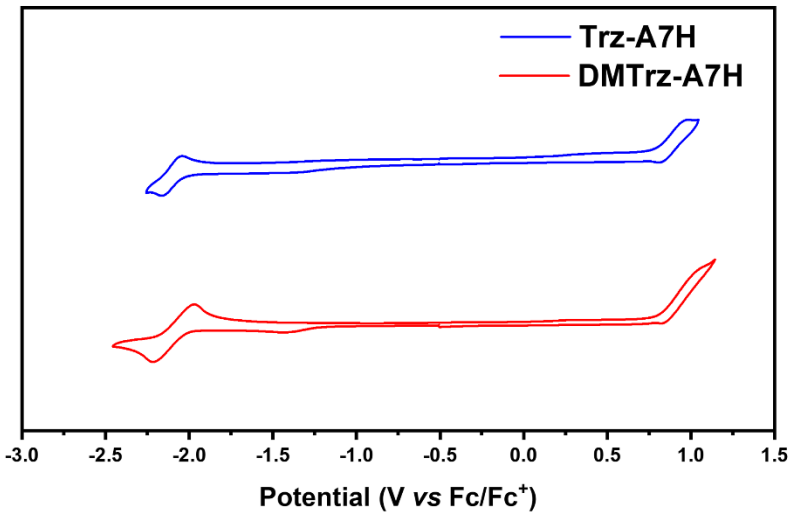



**Figure S7.** CV of **DMTrz-A7H** and **Trz-A7H** in tetrahydrofuran (1 mM) with 0.1 M *n*-$Bu_4NPF_6$ as supporting electrolyte and ferrocene as an external standard.

## 5. Theoretical Calculations

Theoretical calculations were performed using the Gaussian 09 software package.[2] All calculations were carried out using the density functional theory (DFT) method. The ground-state and transition state (TS) geometries were optimized at the B3LYP/6-31G(d) level, and the excited-state geometries were optimized at the M06-2X/6-31G(d) level. The relative Gibbs free energy (kcal $mol^{-1}$) was calculated at the B3LYP /def2TZVP level of theory. The rigid scanning was performed using the optimized geometries of **Trz-A7H** at the M06-2X/6-31G(d) level. The simulated UV-vis and CD spectra were calculated by time-dependent DFT (TD-DFT) at the CAM-B3LYP/6-31G(d) level. The transition electric and magnetic dipole moment vectors were calculated by Multiwfn[3] and rendered by VMD.[4] The transition electric dipole moment density (only for x-axis component) and the transition magnetic dipole moment density (only for x-axis component) were calculated by Multiwfn.

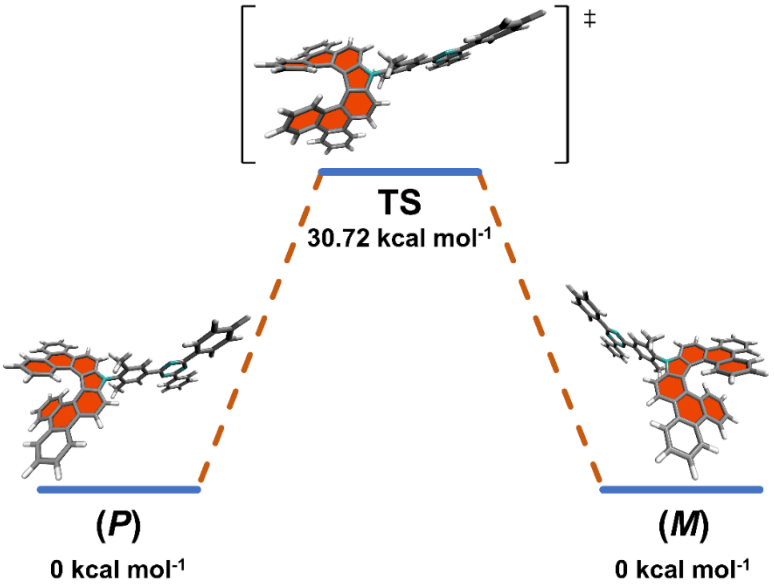



**Figure S8.** Enantiomerization process of **DMTrz-A7H** from (*P*)- to (*M*)-configuration. The relative Gibbs free energy at 298 K is calculated at the B3LYP/def2TZVP level.

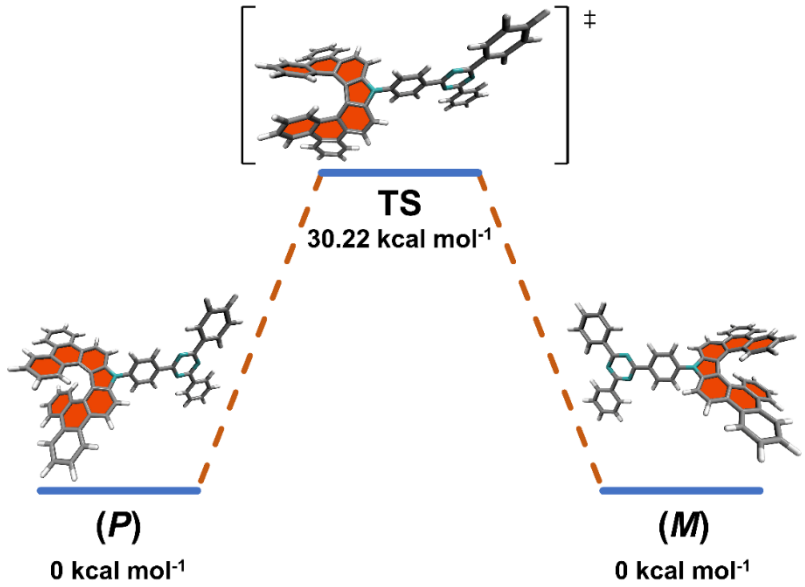



**Figure S9.** Enantiomerization process of **Trz-A7H** from (*P*)- to (*M*)-configuration. The relative Gibbs free energy at 298 K is calculated at the B3LYP/def2TZVP level.

The half-life ($\tau_{1/2}$) of **DMTrz-A7H** and **Trz-A7H** is calculated by using the Gibbs free energy ($\Delta G^{\neq}$) at room temperature (298 K) based on the Eyring equation[5]:

$$\Delta G^{\neq}(T) = -RT\ln(k_e h/\kappa k_B T) \quad (1)$$

where R, $T$, h, $k_e$, $k_B$ are gas constant, absolute temperature, Planck's constant, rate constant, and Boltzmann constant, respectively. Parameter $\kappa$ is assumed as 0.5.[6] The

enantiomerization process of **DMTrz-A7H** and **Trz-A7H** is a first-order reaction, so the following equation is adopted:

$$\tau_{1/2} = \ln 2/k_e \quad (2)$$

The enantiomerization process of **DMTrz-A7H** and **Trz-A7H** shows $\tau_{1/2}$ of $7.58 \times 10^9$ s and $3.25 \times 10^9$ s at room temperature, respectively, indicating their excellent chiral stability.

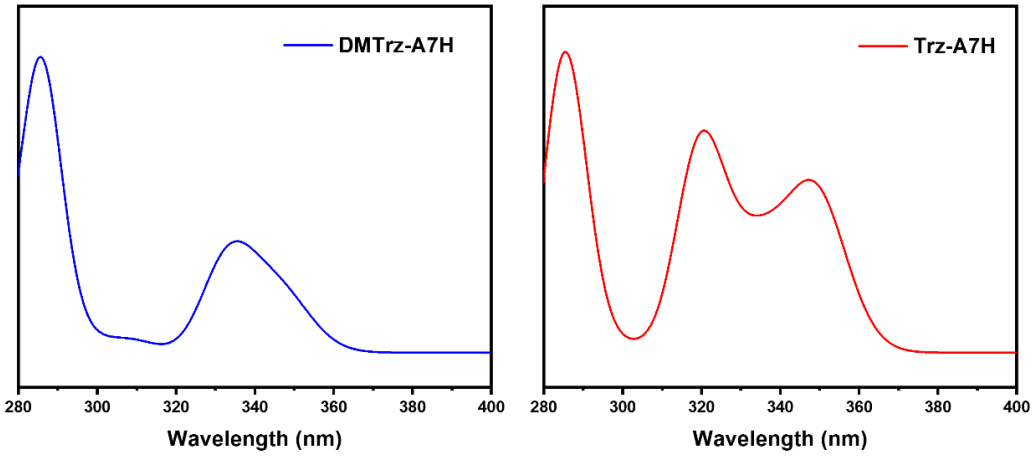



**Figure S10.** DFT-simulated UV-vis absorption spectra of **DMTrz-A7H** and **Trz-A7H** (FWHM = 726 $cm^{-1}$).

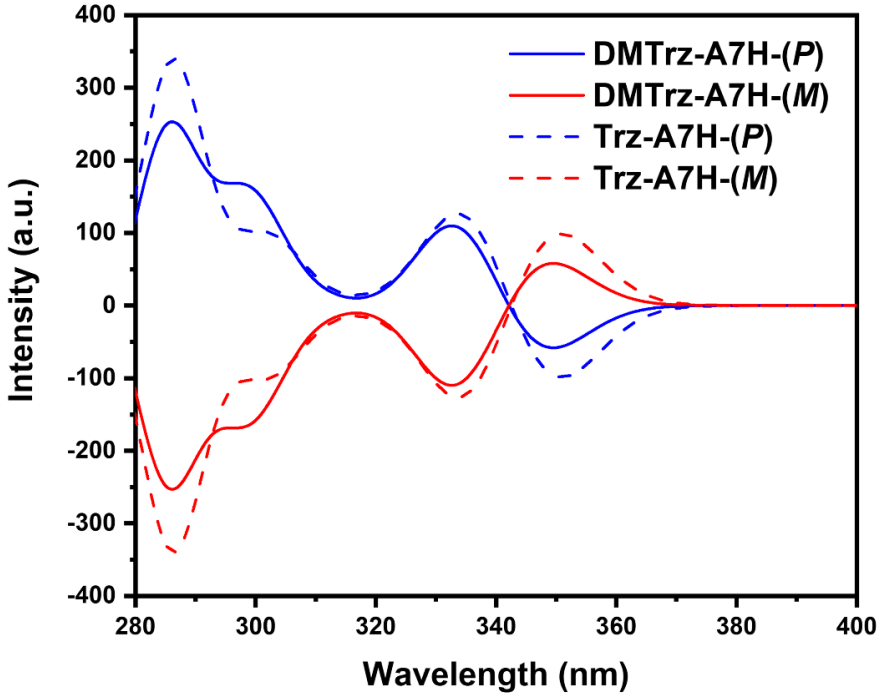



**Figure S11.** DFT-simulated CD spectra of **DMTrz-A7H** and **Trz-A7H** (FWHM=726 $cm^{-1}$).

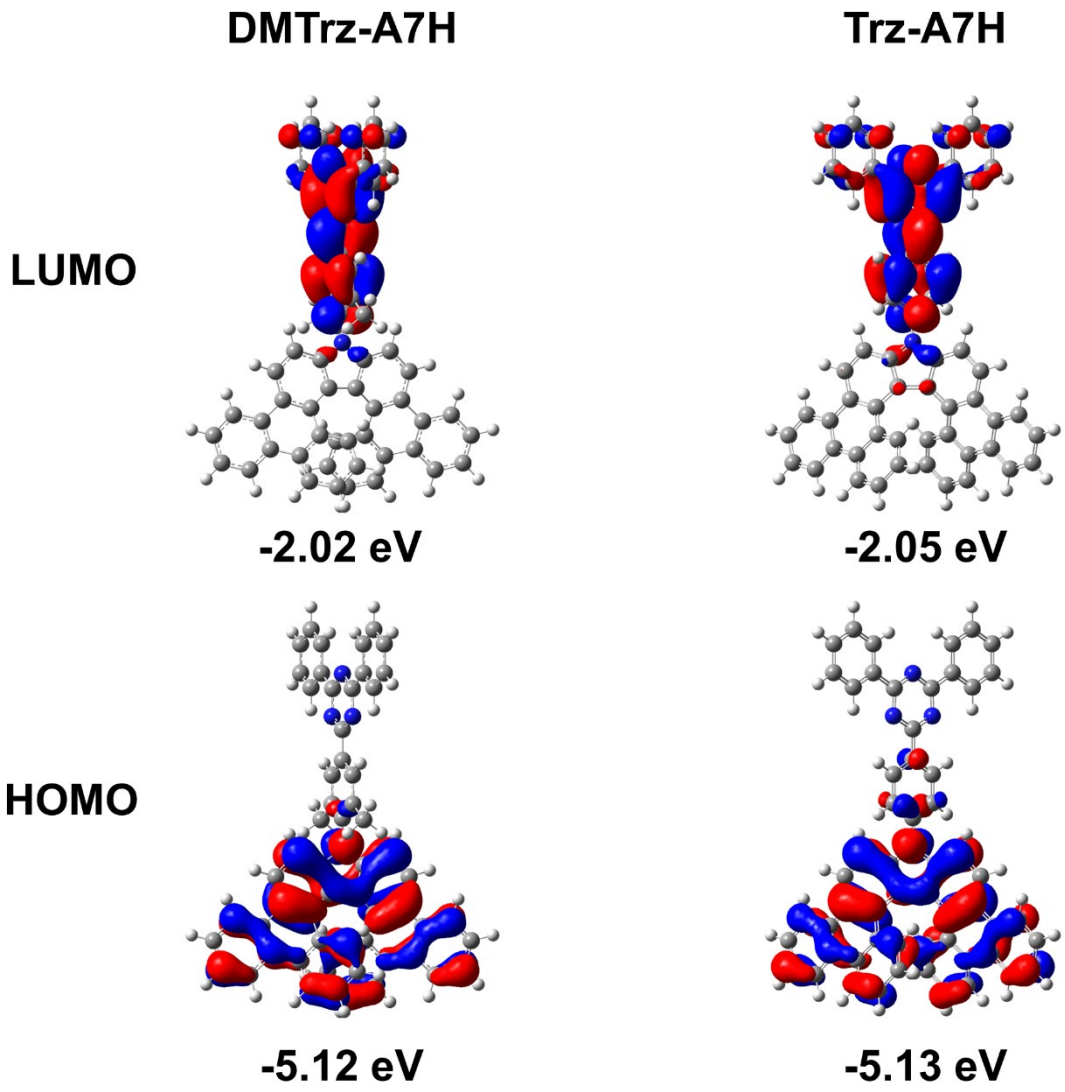



**Figure S12.** Frontier molecular orbitals of **DMTrz-A7H** and **Trz-A7H** at the optimized geometries of the $S_0$ state (isoval = 0.02).

**Table S1.** Summary of the TD-DFT calculation results of **DMTrz-A7H** at the ground state geometry ($S_0$).

| **Excited States**[a] | **Energy (eV)** | **Wavelength (nm)** | **Oscillator Strength** | **Major Contributions** |
|---|---|---|---|---|
| $S_1$ | 3.5738 | 346.92 | 0.1058 | HOMO-1→LUMO+3 (9%)<br>HOMO→LUMO (3%)<br>HOMO→LUMO+2 (80%) |

| | | | | |
|---|---|---|---|---|
| $S_2$ | 3.7152 | 333.72 | 0.1909 | HOMO-1→LUMO+2 (83%)<br>HOMO→LUMO+3 (5%) |
| $S_3$ | 4.0104 | 309.16 | 0.0220 | HOMO→LUMO (82%)<br>HOMO→LUMO+2 (2%)<br>HOMO→LUMO+6 (2%) |

[a]Only $S_1$ ~ $S_3$ have been displayed.

**Table S2.** Summary of the TD-DFT calculation results of **Trz-A7H** at the ground state geometry ($S_0$).

| **Excited States**[a] | **Energy (eV)** | **Wavelength (nm)** | **Oscillator Strength** | **Major Contributions** |
|---|---|---|---|---|
| $S_1$ | 3.5512 | 349.14 | 0.2995 | HOMO-1→LUMO+3 (7%)<br>HOMO→LUMO (18%)<br>HOMO→LUMO+2 (65%) |
| $S_2$ | 3.7026 | 334.86 | 0.1891 | HOMO-1→LUMO (5%)<br>HOMO-1→LUMO+2 (80%)<br>HOMO→LUMO+3 (5%) |
| $S_3$ | 3.8740 | 320.04 | 0.4105 | HOMO-6→LUMO (4%)<br>HOMO-5→LUMO (3%)<br>HOMO-1→LUMO+3 (2%)<br>HOMO→LUMO (60%)<br>HOMO→LUMO+2 (17%)<br>HOMO→LUMO+5 (6%) |

[a]Only $S_1$ ~ $S_3$ have been displayed.

**Table S3.** Summary of the TD-DFT calculation results of **DMTrz-A7H** at the first singlet excited state geometry ($S_1$).

| **Excited States**[a] | **Energy (eV)** | **Wavelength (nm)** | **Oscillator Strength** | **Major Contributions** |
|---|---|---|---|---|
| $S_1$ | 3.3465 | 370.49 | 0.1686 | HOMO-1→LUMO+3 (6%) |

| | | | | |
|---|---|---|---|---|
| | | | | HOMO→LUMO (20%) |
| | | | | HOMO→LUMO+2 (68%) |
| $S_2$ | 3.5539 | 348.87 | 0.2022 | HOMO-1→LUMO (12%) |
| | | | | HOMO-1→LUMO+2 (78%) |
| | | | | HOMO→LUMO+3 (3%) |
| $S_3$ | 3.8327 | 323.49 | 0.0761 | HOMO→LUMO (68%) |
| | | | | HOMO→LUMO+2 (19%) |
| | | | | HOMO→LUMO+6 (3%) |

[a]Only $S_1$ ~ $S_3$ have been displayed.

**Table S4.** Summary of the TD-DFT calculation results of **Trz-A7H** at the first singlet excited state geometry ($S_1$).

| **Excited States**[a] | **Energy (eV)** | **Wavelength (nm)** | **Oscillator Strength** | **Major Contributions** |
|---|---|---|---|---|
| $S_1$ | 3.3365 | 371.60 | 0.3374 | HOMO-1→LUMO+3 (6%) |
| | | | | HOMO→LUMO (29%) |
| | | | | HOMO→LUMO+2 (58%) |
| $S_2$ | 3.5340 | 350.83 | 0.2057 | HOMO-1→LUMO (12%) |
| | | | | HOMO-1→LUMO+2 (79%) |
| | | | | HOMO→LUMO+3 (3%) |
| $S_3$ | 3.6997 | 335.12 | 0.4149 | HOMO-6→LUMO (2%) |
| | | | | HOMO-5→LUMO (3%) |
| | | | | HOMO→LUMO (54%) |
| | | | | HOMO→LUMO+2 (29%) |
| | | | | HOMO→LUMO+5 (4%) |

[a]Only $S_1$ ~ $S_3$ have been displayed.

## Cartesian coordinates obtained in gas-phase DFT calculations

The $S_0$ state geometry of **DMTrz-A7H**-(*P*)

| Tag | Symbol | X | Y | Z |
|---|---|---|---|---|
| 1 | C | -7.238707 | -0.090051 | -1.134020 |
| 2 | N | -5.896724 | -0.093877 | -1.182084 |
| 3 | C | -5.270749 | -0.000018 | -0.000012 |
| 4 | N | -5.896655 | 0.093818 | 1.182100 |
| 5 | C | -7.238640 | 0.090110 | 1.134105 |
| 6 | N | -7.950083 | 0.000089 | 0.000059 |
| 7 | C | -7.980255 | -0.192056 | -2.413809 |
| 8 | C | -3.785191 | -0.000031 | -0.000054 |
| 9 | C | -7.980114 | 0.192069 | 2.413942 |
| 10 | C | -9.384145 | -0.191551 | -2.422928 |
| 11 | C | -10.079206 | -0.287609 | -3.625725 |
| 12 | C | -9.382800 | -0.385303 | -4.832956 |
| 13 | C | -7.985703 | -0.386442 | -4.831650 |
| 14 | C | -7.287271 | -0.290491 | -3.630776 |
| 15 | C | -9.384003 | 0.191962 | 2.423110 |
| 16 | C | -10.078996 | 0.287982 | 3.625949 |
| 17 | C | -9.382518 | 0.385216 | 4.833177 |
| 18 | C | -7.985422 | 0.385943 | 4.831825 |
| 19 | C | -7.287059 | 0.290054 | 3.630905 |
| 20 | C | -3.077928 | 0.085474 | 1.205579 |
| 21 | C | -1.682120 | 0.084963 | 1.227616 |
| 22 | C | -0.998998 | -0.000051 | -0.000137 |
| 23 | C | -1.682195 | -0.085057 | -1.227851 |
| 24 | C | -3.077999 | -0.085549 | -1.205731 |
| 25 | C | -0.927867 | 0.171554 | 2.533050 |
| 26 | C | -0.928017 | -0.171616 | -2.533331 |
| 27 | C | 1.244997 | -1.121679 | 0.038543 |
| 28 | C | 2.608224 | -0.729130 | 0.087012 |
| 29 | C | 2.608211 | 0.729100 | -0.087193 |
| 30 | C | 1.244970 | 1.121612 | -0.038819 |
| 31 | N | 0.433188 | -0.000046 | -0.000183 |
| 32 | C | 0.830056 | -2.458309 | 0.025963 |
| 33 | C | 1.810393 | -3.426975 | 0.024499 |
| 34 | C | 3.184069 | -3.106798 | 0.173098 |
| 35 | C | 3.577368 | -1.752407 | 0.362370 |
| 36 | C | 3.577350 | 1.752405 | -0.362471 |
| 37 | C | 3.184004 | 3.106782 | -0.173197 |
| 38 | C | 1.810310 | 3.426921 | -0.024692 |
| 39 | C | 0.829996 | 2.458231 | -0.026250 |

| | | | | |
|---|---|---|---|---|
| 40 | C | 4.206961 | -4.155973 | 0.118577 |
| 41 | C | 5.551964 | -3.856519 | 0.462241 |
| 42 | C | 5.864274 | -2.539409 | 1.014166 |
| 43 | C | 4.890834 | -1.503167 | 0.961212 |
| 44 | C | 4.890866 | 1.503211 | -0.961226 |
| 45 | C | 5.864283 | 2.539479 | -1.014084 |
| 46 | C | 5.551900 | 3.856569 | -0.462151 |
| 47 | C | 4.206865 | 4.155982 | -0.118580 |
| 48 | C | 7.092593 | -2.283621 | 1.660600 |
| 49 | C | 7.357690 | -1.066564 | 2.264378 |
| 50 | C | 6.377421 | -0.065777 | 2.263106 |
| 51 | C | 5.169251 | -0.288934 | 1.626794 |
| 52 | C | 5.169359 | 0.289006 | -1.626827 |
| 53 | C | 6.377580 | 0.065898 | -2.263060 |
| 54 | C | 7.357826 | 1.066709 | -2.264232 |
| 55 | C | 7.092655 | 2.283741 | -1.660438 |
| 56 | C | 3.907903 | -5.457091 | -0.345790 |
| 57 | C | 4.887203 | -6.426624 | -0.477852 |
| 58 | C | 6.217613 | -6.121494 | -0.159565 |
| 59 | C | 6.536486 | -4.854748 | 0.298010 |
| 60 | C | 6.536386 | 4.854819 | -0.297828 |
| 61 | C | 6.217448 | 6.121547 | 0.159750 |
| 62 | C | 4.887008 | 6.426638 | 0.477945 |
| 63 | C | 3.907740 | 5.457083 | 0.345791 |
| 64 | H | -9.913986 | -0.115333 | -1.480392 |
| 65 | H | -11.165809 | -0.286338 | -3.622330 |
| 66 | H | -9.926624 | -0.460221 | -5.770970 |
| 67 | H | -7.440236 | -0.462229 | -5.768372 |
| 68 | H | -6.203410 | -0.290487 | -3.618012 |
| 69 | H | -9.913900 | 0.116073 | 1.480578 |
| 70 | H | -11.165599 | 0.287043 | 3.622593 |
| 71 | H | -9.926289 | 0.460094 | 5.771226 |
| 72 | H | -7.439901 | 0.461357 | 5.768545 |
| 73 | H | -6.203198 | 0.289754 | 3.618103 |
| 74 | H | -3.633756 | 0.149847 | 2.134203 |
| 75 | H | -3.633885 | -0.149914 | -2.134321 |
| 76 | H | -1.621696 | 0.206676 | 3.377611 |
| 77 | H | -0.265740 | -0.690755 | 2.670684 |
| 78 | H | -0.296613 | 1.066797 | 2.573557 |
| 79 | H | -0.296350 | -1.066569 | -2.573690 |
| 80 | H | -1.621904 | -0.207242 | -3.377824 |
| 81 | H | -0.266308 | 0.690976 | -2.671222 |
| 82 | H | -0.223718 | -2.715671 | -0.009500 |
| 83 | H | 1.506585 | -4.465531 | -0.028524 |

| | | | | |
|---|---|---|---|---|
| 84 | H | 1.506471 | 4.465468 | 0.028333 |
| 85 | H | -0.223787 | 2.715570 | 0.009144 |
| 86 | H | 7.836917 | -3.069281 | 1.726944 |
| 87 | H | 8.309670 | -0.904113 | 2.762657 |
| 88 | H | 6.554358 | 0.878935 | 2.769586 |
| 89 | H | 4.406120 | 0.476467 | 1.667008 |
| 90 | H | 4.406250 | -0.476411 | -1.667124 |
| 91 | H | 6.554576 | -0.878795 | -2.769557 |
| 92 | H | 8.309844 | 0.904296 | -2.762450 |
| 93 | H | 7.836963 | 3.069422 | -1.726709 |
| 94 | H | 2.896104 | -5.703716 | -0.646854 |
| 95 | H | 4.623969 | -7.413682 | -0.848427 |
| 96 | H | 6.997503 | -6.868293 | -0.280796 |
| 97 | H | 7.573744 | -4.625561 | 0.516305 |
| 98 | H | 7.573665 | 4.625662 | -0.516053 |
| 99 | H | 6.997311 | 6.868362 | 0.281053 |
| 100 | H | 4.623721 | 7.413682 | 0.848520 |
| 101 | H | 2.895913 | 5.703678 | 0.646785 |

The $S_0$ state geometry of **Trz-A7H**-(*P*)

| Tag | Symbol | X | Y | Z |
|---|---|---|---|---|
| 1 | C | -7.287887 | 0.897494 | -0.699507 |
| 2 | N | -5.945902 | 0.936266 | -0.728578 |
| 3 | C | -5.320553 | -0.000002 | -0.000006 |
| 4 | N | -5.945892 | -0.936273 | 0.728573 |
| 5 | C | -7.287877 | -0.897504 | 0.699516 |
| 6 | N | -7.999081 | -0.000006 | 0.000008 |
| 7 | C | -8.029676 | 1.909735 | -1.488817 |
| 8 | C | -8.029655 | -1.909748 | 1.488833 |
| 9 | C | -3.837648 | 0.000001 | -0.000012 |
| 10 | C | -9.433565 | 1.912330 | -1.499502 |
| 11 | C | -10.128956 | 2.863698 | -2.241359 |
| 12 | C | -9.432927 | 3.823297 | -2.980709 |
| 13 | C | -8.035843 | 3.826983 | -2.974756 |
| 14 | C | -7.337093 | 2.877025 | -2.234231 |
| 15 | C | -9.433544 | -1.912332 | 1.499552 |
| 16 | C | -10.128924 | -2.863703 | 2.241416 |
| 17 | C | -9.432885 | -3.823315 | 2.980738 |
| 18 | C | -8.035801 | -3.827013 | 2.974751 |
| 19 | C | -7.337061 | -2.877051 | 2.234219 |
| 20 | C | -3.123955 | -0.936295 | 0.763872 |
| 21 | C | -1.733641 | -0.933554 | 0.772039 |
| 22 | C | -1.028400 | 0.000006 | -0.000025 |

| | | | | |
|---|---|---|---|---|
| 23 | C | -1.733652 | 0.933563 | -0.772082 |
| 24 | C | -3.123965 | 0.936299 | -0.763903 |
| 25 | C | 1.208070 | -1.091896 | -0.272879 |
| 26 | C | 2.568151 | -0.724593 | -0.115632 |
| 27 | C | 2.568150 | 0.724604 | 0.115612 |
| 28 | C | 1.208066 | 1.091912 | 0.272833 |
| 29 | N | 0.390850 | 0.000009 | -0.000032 |
| 30 | C | 0.809386 | -2.362761 | -0.705150 |
| 31 | C | 1.797849 | -3.280144 | -0.986807 |
| 32 | C | 3.166930 | -3.017047 | -0.726849 |
| 33 | C | 3.546221 | -1.776335 | -0.145244 |
| 34 | C | 3.546221 | 1.776345 | 0.145237 |
| 35 | C | 3.166923 | 3.017062 | 0.726827 |
| 36 | C | 1.797839 | 3.280163 | 0.986761 |
| 37 | C | 0.809378 | 2.362780 | 0.705093 |
| 38 | C | 4.198514 | -4.000437 | -1.071750 |
| 39 | C | 5.539101 | -3.802997 | -0.646257 |
| 40 | C | 5.837609 | -2.698938 | 0.264172 |
| 41 | C | 4.854814 | -1.699544 | 0.507685 |
| 42 | C | 4.854824 | 1.699544 | -0.507670 |
| 43 | C | 5.837618 | 2.698938 | -0.264151 |
| 44 | C | 5.539098 | 3.803006 | 0.646264 |
| 45 | C | 4.198505 | 4.000451 | 1.071736 |
| 46 | C | 7.061439 | -2.631114 | 0.964108 |
| 47 | C | 7.313148 | -1.638497 | 1.895343 |
| 48 | C | 6.323460 | -0.688072 | 2.178073 |
| 49 | C | 5.119289 | -0.727745 | 1.498011 |
| 50 | C | 5.119311 | 0.727732 | -1.497979 |
| 51 | C | 6.323493 | 0.688047 | -2.178021 |
| 52 | C | 7.313179 | 1.638473 | -1.895287 |
| 53 | C | 7.061458 | 2.631102 | -0.964067 |
| 54 | C | 3.913111 | -5.116487 | -1.890895 |
| 55 | C | 4.901582 | -6.000088 | -2.288902 |
| 56 | C | 6.227799 | -5.789165 | -1.887605 |
| 57 | C | 6.533178 | -4.705089 | -1.083266 |
| 58 | C | 6.533170 | 4.705098 | 1.083281 |
| 59 | C | 6.227783 | 5.789181 | 1.887609 |
| 60 | C | 4.901560 | 6.000109 | 2.288886 |
| 61 | C | 3.913093 | 5.116507 | 1.890870 |
| 62 | H | -9.963095 | 1.163174 | -0.922211 |
| 63 | H | -11.215540 | 2.857329 | -2.243361 |
| 64 | H | -9.977038 | 4.565254 | -3.559207 |
| 65 | H | -7.490647 | 4.571597 | -3.548350 |
| 66 | H | -6.253243 | 2.870811 | -2.222332 |

| | | | | |
|---|---|---|---|---|
| 67 | H | -9.963082 | -1.163166 | 0.922282 |
| 68 | H | -11.215508 | -2.857324 | 2.243446 |
| 69 | H | -9.976988 | -4.565276 | 3.559239 |
| 70 | H | -7.490597 | -4.571638 | 3.548323 |
| 71 | H | -6.253211 | -2.870845 | 2.222295 |
| 72 | H | -3.674104 | -1.654179 | 1.361037 |
| 73 | H | -1.186213 | -1.642202 | 1.385184 |
| 74 | H | -1.186231 | 1.642213 | -1.385232 |
| 75 | H | -3.674123 | 1.654181 | -1.361062 |
| 76 | H | -0.237828 | -2.604008 | -0.849732 |
| 77 | H | 1.501118 | -4.251640 | -1.362994 |
| 78 | H | 1.501103 | 4.251662 | 1.362937 |
| 79 | H | -0.237837 | 2.604030 | 0.849655 |
| 80 | H | 7.812999 | -3.396245 | 0.804931 |
| 81 | H | 8.261957 | -1.619393 | 2.424787 |
| 82 | H | 6.489859 | 0.070951 | 2.937337 |
| 83 | H | 4.348687 | -0.013241 | 1.754158 |
| 84 | H | 4.348712 | 0.013224 | -1.754126 |
| 85 | H | 6.489902 | -0.070986 | -2.937273 |
| 86 | H | 8.261997 | 1.619359 | -2.424715 |
| 87 | H | 7.813019 | 3.396231 | -0.804886 |
| 88 | H | 2.904791 | -5.275634 | -2.255555 |
| 89 | H | 4.648688 | -6.841656 | -2.928169 |
| 90 | H | 7.014887 | -6.464092 | -2.212552 |
| 91 | H | 7.567267 | -4.541146 | -0.800815 |
| 92 | H | 7.567263 | 4.541153 | 0.800845 |
| 93 | H | 7.014867 | 6.464108 | 2.212563 |
| 94 | H | 4.648659 | 6.841681 | 2.928144 |
| 95 | H | 2.904768 | 5.275659 | 2.255514 |

The $S_1$ state geometry of **DMTrz-A7H**-(*P*)

| Tag | Symbol | X | Y | Z |
|---|---|---|---|---|
| 1 | C | -7.211191 | -0.550785 | 0.988047 |
| 2 | N | -5.876228 | -0.574418 | 1.033244 |
| 3 | C | -5.253932 | 0.000102 | 0.000056 |
| 4 | N | -5.876210 | 0.574581 | -1.033165 |
| 5 | C | -7.211174 | 0.550922 | -0.988005 |
| 6 | N | -7.922234 | 0.000053 | 0.000006 |
| 7 | C | -7.953376 | -1.178689 | 2.108206 |
| 8 | C | -3.771386 | 0.000075 | 0.000054 |
| 9 | C | -7.953339 | 1.178743 | -2.108224 |
| 10 | C | -9.351431 | -1.170646 | 2.115801 |
| 11 | C | -10.045483 | -1.760496 | 3.165385 |

| | | | | |
|---|---|---|---|---|
| 12 | C | -9.350178 | -2.361885 | 4.212603 |
| 13 | C | -7.956660 | -2.371840 | 4.208119 |
| 14 | C | -7.258960 | -1.782664 | 3.160644 |
| 15 | C | -9.351393 | 1.170629 | -2.115883 |
| 16 | C | -10.045427 | 1.760404 | -3.165521 |
| 17 | C | -9.350104 | 2.361788 | -4.212730 |
| 18 | C | -7.956587 | 2.371811 | -4.208184 |
| 19 | C | -7.258905 | 1.782710 | -3.160654 |
| 20 | C | -3.070716 | 0.546806 | -1.077920 |
| 21 | C | -1.679885 | 0.554407 | -1.099336 |
| 22 | C | -1.006627 | 0.000029 | 0.000049 |
| 23 | C | -1.679900 | -0.554329 | 1.099434 |
| 24 | C | -3.070731 | -0.546683 | 1.078023 |
| 25 | C | -0.914370 | 1.124263 | -2.263782 |
| 26 | C | -0.914395 | -1.124219 | 2.263870 |
| 27 | C | 1.210011 | 1.109213 | 0.204341 |
| 28 | C | 2.579824 | 0.720227 | 0.071516 |
| 29 | C | 2.579812 | -0.720234 | -0.071441 |
| 30 | C | 1.209968 | -1.109191 | -0.204244 |
| 31 | N | 0.417498 | 0.000006 | 0.000051 |
| 32 | C | 0.786228 | 2.391593 | 0.530497 |
| 33 | C | 1.774294 | 3.345283 | 0.774748 |
| 34 | C | 3.135309 | 3.051501 | 0.583309 |
| 35 | C | 3.540798 | 1.773287 | 0.047555 |
| 36 | C | 3.540761 | -1.773312 | -0.047483 |
| 37 | C | 3.135232 | -3.051501 | -0.583261 |
| 38 | C | 1.774188 | -3.345263 | -0.774674 |
| 39 | C | 0.786148 | -2.391580 | -0.530393 |
| 40 | C | 4.178207 | 4.003015 | 0.955385 |
| 41 | C | 5.527045 | 3.771759 | 0.582101 |
| 42 | C | 5.855440 | 2.625882 | -0.269619 |
| 43 | C | 4.855307 | 1.652946 | -0.535406 |
| 44 | C | 4.855297 | -1.653004 | 0.535434 |
| 45 | C | 5.855400 | -2.625950 | 0.269580 |
| 46 | C | 5.526951 | -3.771787 | -0.582165 |
| 47 | C | 4.178088 | -4.003011 | -0.955406 |
| 48 | C | 7.122674 | 2.465458 | -0.845040 |
| 49 | C | 7.415275 | 1.391918 | -1.673903 |
| 50 | C | 6.415148 | 0.467157 | -1.985404 |
| 51 | C | 5.154977 | 0.606820 | -1.437473 |
| 52 | C | 5.155022 | -0.606919 | 1.437524 |
| 53 | C | 6.415219 | -0.467303 | 1.985415 |
| 54 | C | 7.415318 | -1.392071 | 1.673848 |
| 55 | C | 7.122661 | -2.465575 | 0.844962 |

| | | | | |
|---|---|---|---|---|
| 56 | C | 3.881211 | 5.130359 | 1.750826 |
| 57 | C | 4.864149 | 6.008727 | 2.160690 |
| 58 | C | 6.194079 | 5.773663 | 1.797804 |
| 59 | C | 6.511985 | 4.668794 | 1.028785 |
| 60 | C | 6.511857 | -4.668827 | -1.028916 |
| 61 | C | 6.193902 | -5.773667 | -1.797954 |
| 62 | C | 4.863951 | -6.008701 | -2.160797 |
| 63 | C | 3.881045 | -5.130334 | -1.750871 |
| 64 | H | -9.877909 | -0.698987 | 1.293661 |
| 65 | H | -11.130900 | -1.751700 | 3.167220 |
| 66 | H | -9.893895 | -2.822701 | 5.031707 |
| 67 | H | -7.413371 | -2.840193 | 5.022771 |
| 68 | H | -6.174853 | -1.782932 | 3.142654 |
| 69 | H | -9.877885 | 0.698976 | -1.293748 |
| 70 | H | -11.130843 | 1.751554 | -3.167406 |
| 71 | H | -9.893807 | 2.822545 | -5.031877 |
| 72 | H | -7.413284 | 2.840160 | -5.022829 |
| 73 | H | -6.174799 | 1.783033 | -3.142615 |
| 74 | H | -3.628235 | 0.961280 | -1.911274 |
| 75 | H | -3.628260 | -0.961141 | 1.911378 |
| 76 | H | -1.585904 | 1.324760 | -3.101084 |
| 77 | H | -0.414745 | 2.060224 | -1.989454 |
| 78 | H | -0.135414 | 0.431661 | -2.598558 |
| 79 | H | -0.135424 | -0.431639 | 2.598654 |
| 80 | H | -1.585933 | -1.324714 | 3.101171 |
| 81 | H | -0.414792 | -2.060188 | 1.989526 |
| 82 | H | -0.269848 | 2.618228 | 0.637797 |
| 83 | H | 1.471622 | 4.335302 | 1.089788 |
| 84 | H | 1.471505 | -4.335280 | -1.089711 |
| 85 | H | -0.269935 | -2.618193 | -0.637665 |
| 86 | H | 7.896171 | 3.203603 | -0.665403 |
| 87 | H | 8.408318 | 1.293105 | -2.100292 |
| 88 | H | 6.618210 | -0.354408 | -2.665422 |
| 89 | H | 4.369710 | -0.083910 | -1.718891 |
| 90 | H | 4.369783 | 0.083818 | 1.719000 |
| 91 | H | 6.618320 | 0.354236 | 2.665453 |
| 92 | H | 8.408378 | -1.293293 | 2.100205 |
| 93 | H | 7.896132 | -3.203735 | 0.665275 |
| 94 | H | 2.863923 | 5.298098 | 2.083854 |
| 95 | H | 4.605868 | 6.862792 | 2.778415 |
| 96 | H | 6.979473 | 6.446158 | 2.128266 |
| 97 | H | 7.552249 | 4.491363 | 0.782082 |
| 98 | H | 7.552134 | -4.491422 | -0.782249 |
| 99 | H | 6.979272 | -6.446166 | -2.128467 |

| | | | | |
|---|---|---|---|---|
| 100 | H | 4.605635 | -6.862745 | -2.778538 |
| 101 | H | 2.863742 | -5.298048 | -2.083867 |

The $S_1$ state geometry of **Trz-A7H**-(*P*)

| Tag | Symbol | X | Y | Z |
|---|---|---|---|---|
| 1 | C | -7.266350 | 0.931491 | -0.642613 |
| 2 | N | -5.932259 | 0.974008 | -0.672571 |
| 3 | C | -5.309189 | -0.000015 | 0.000009 |
| 4 | N | -5.932269 | -0.974037 | 0.672580 |
| 5 | C | -7.266360 | -0.931518 | 0.642604 |
| 6 | N | -7.978184 | -0.000013 | -0.000010 |
| 7 | C | -8.009386 | 1.989292 | -1.370223 |
| 8 | C | -8.009407 | -1.989318 | 1.370204 |
| 9 | C | -3.832819 | -0.000015 | 0.000020 |
| 10 | C | -9.407469 | 1.987814 | -1.375550 |
| 11 | C | -10.102513 | 2.979916 | -2.056890 |
| 12 | C | -9.408267 | 3.978943 | -2.736423 |
| 13 | C | -8.014663 | 3.983547 | -2.733171 |
| 14 | C | -7.316126 | 2.993178 | -2.053215 |
| 15 | C | -9.407491 | -1.987838 | 1.375512 |
| 16 | C | -10.102545 | -2.979938 | 2.056844 |
| 17 | C | -9.408309 | -3.978965 | 2.736388 |
| 18 | C | -8.014706 | -3.983571 | 2.733155 |
| 19 | C | -7.316158 | -2.993204 | 2.053207 |
| 20 | C | -3.123714 | -0.966901 | 0.725755 |
| 21 | C | -1.739419 | -0.971618 | 0.728517 |
| 22 | C | -1.039263 | -0.000016 | 0.000040 |
| 23 | C | -1.739408 | 0.971589 | -0.728444 |
| 24 | C | -3.123703 | 0.966872 | -0.725704 |
| 25 | C | 1.171543 | -1.113031 | -0.205368 |
| 26 | C | 2.539734 | -0.718543 | -0.068689 |
| 27 | C | 2.539721 | 0.718547 | 0.068819 |
| 28 | C | 1.171524 | 1.113026 | 0.205451 |
| 29 | N | 0.368999 | -0.000011 | 0.000052 |
| 30 | C | 0.772762 | -2.389417 | -0.583203 |
| 31 | C | 1.770744 | -3.328675 | -0.835102 |
| 32 | C | 3.126743 | -3.034044 | -0.609979 |
| 33 | C | 3.511069 | -1.763964 | -0.051260 |
| 34 | C | 3.511040 | 1.763976 | 0.051347 |
| 35 | C | 3.126691 | 3.034103 | 0.609942 |
| 36 | C | 1.770686 | 3.328725 | 0.835040 |
| 37 | C | 0.772722 | 2.389427 | 0.583212 |
| 38 | C | 4.181281 | -3.976650 | -0.975202 |

| | | | | |
|---|---|---|---|---|
| 39 | C | 5.523916 | -3.735797 | -0.588355 |
| 40 | C | 5.833507 | -2.593342 | 0.273936 |
| 41 | C | 4.820959 | -1.635010 | 0.542767 |
| 42 | C | 4.820938 | 1.634961 | -0.542635 |
| 43 | C | 5.833470 | 2.593341 | -0.273918 |
| 44 | C | 5.523855 | 3.735898 | 0.588231 |
| 45 | C | 4.181216 | 3.976767 | 0.975061 |
| 46 | C | 7.095325 | -2.423965 | 0.859810 |
| 47 | C | 7.368603 | -1.356899 | 1.702425 |
| 48 | C | 6.355114 | -0.447751 | 2.017909 |
| 49 | C | 5.101475 | -0.595617 | 1.458312 |
| 50 | C | 5.101492 | 0.595398 | -1.457974 |
| 51 | C | 6.355144 | 0.447457 | -2.017518 |
| 52 | C | 7.368608 | 1.356685 | -1.702178 |
| 53 | C | 7.095299 | 2.423887 | -0.859743 |
| 54 | C | 3.901301 | -5.102794 | -1.778180 |
| 55 | C | 4.895924 | -5.969330 | -2.184716 |
| 56 | C | 6.220621 | -5.723941 | -1.809467 |
| 57 | C | 6.521448 | -4.621240 | -1.031184 |
| 58 | C | 6.521372 | 4.621406 | 1.030966 |
| 59 | C | 6.220527 | 5.724186 | 1.809130 |
| 60 | C | 4.895827 | 5.969592 | 2.184354 |
| 61 | C | 3.901219 | 5.102993 | 1.777917 |
| 62 | H | -9.933158 | 1.203897 | -0.841995 |
| 63 | H | -11.187976 | 2.974566 | -2.058259 |
| 64 | H | -9.952768 | 4.753344 | -3.268210 |
| 65 | H | -7.471940 | 4.760840 | -3.261876 |
| 66 | H | -6.231994 | 2.983711 | -2.041199 |
| 67 | H | -9.933171 | -1.203921 | 0.841948 |
| 68 | H | -11.188008 | -2.974587 | 2.058198 |
| 69 | H | -9.952819 | -4.753365 | 3.268168 |
| 70 | H | -7.471991 | -4.760864 | 3.261869 |
| 71 | H | -6.232026 | -2.983738 | 2.041207 |
| 72 | H | -3.677538 | -1.704533 | 1.295331 |
| 73 | H | -1.185921 | -1.701998 | 1.309716 |
| 74 | H | -1.185901 | 1.701973 | -1.309630 |
| 75 | H | -3.677518 | 1.704505 | -1.295286 |
| 76 | H | -0.273313 | -2.631845 | -0.731196 |
| 77 | H | 1.476567 | -4.310357 | -1.181677 |
| 78 | H | 1.476489 | 4.310431 | 1.181529 |
| 79 | H | -0.273360 | 2.631851 | 0.731168 |
| 80 | H | 7.879040 | -3.150434 | 0.677466 |
| 81 | H | 8.357405 | -1.250800 | 2.136917 |
| 82 | H | 6.543428 | 0.367838 | 2.709215 |

| | | | | |
|---|---|---|---|---|
| 83 | H | 4.306105 | 0.082934 | 1.741144 |
| 84 | H | 4.306142 | -0.083239 | -1.740670 |
| 85 | H | 6.543492 | -0.368255 | -2.708669 |
| 86 | H | 8.357422 | 1.250525 | -2.136628 |
| 87 | H | 7.879006 | 3.150388 | -0.677491 |
| 88 | H | 2.888591 | -5.280757 | -2.119349 |
| 89 | H | 4.650674 | -6.822744 | -2.808597 |
| 90 | H | 7.014916 | -6.387372 | -2.136908 |
| 91 | H | 7.557692 | -4.436233 | -0.773594 |
| 92 | H | 7.557620 | 4.436386 | 0.773400 |
| 93 | H | 7.014811 | 6.387666 | 2.136499 |
| 94 | H | 4.650564 | 6.823069 | 2.808144 |
| 95 | H | 2.888506 | 5.280973 | 2.119071 |

# 6. NMR Spectra

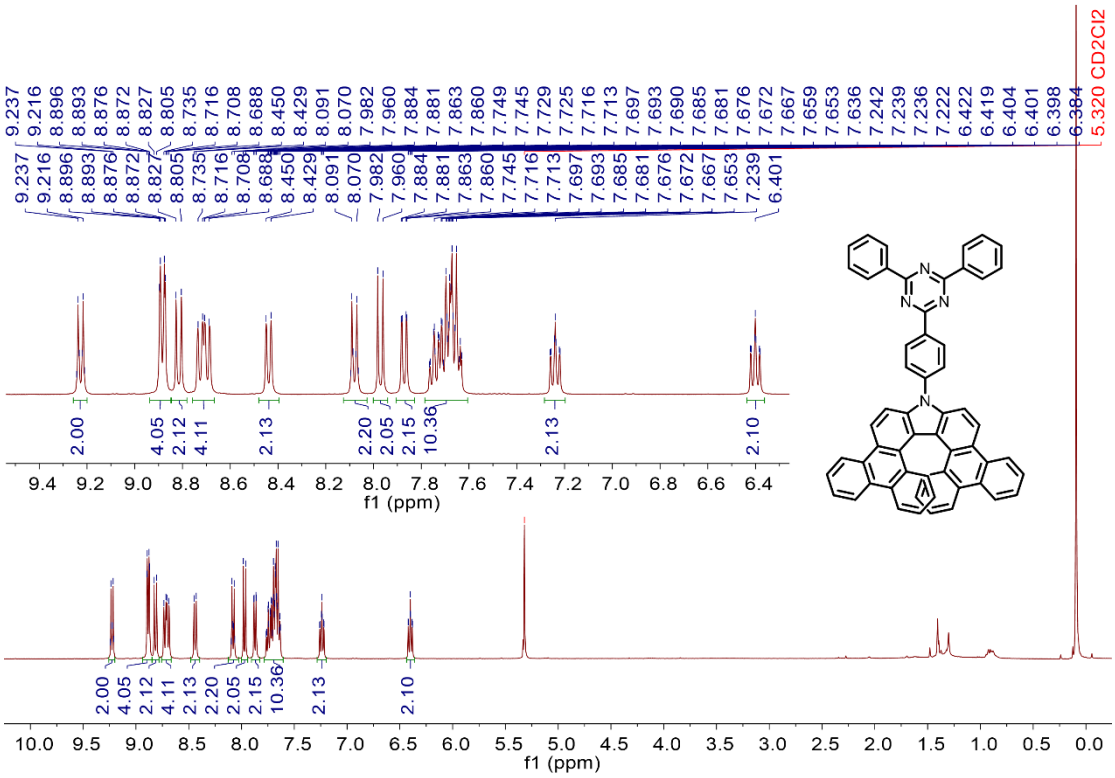


**Figure S13.** $^{1}$H NMR spectrum of **Trz-A7H** (400 MHz, $CD_2Cl_2/CS_2$, 297 K).

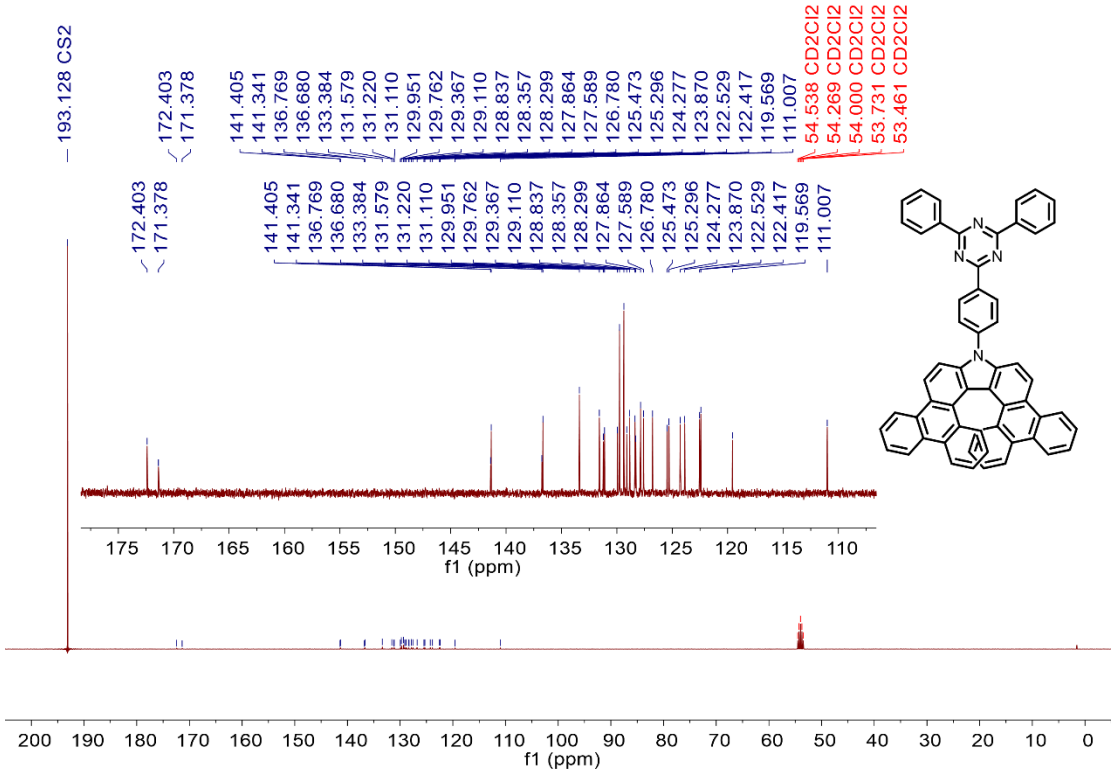


**Figure S14.** $^{13}$C NMR spectrum of **Trz-A7H** (101 MHz, $CD_2Cl_2/CS_2$, 297 K).

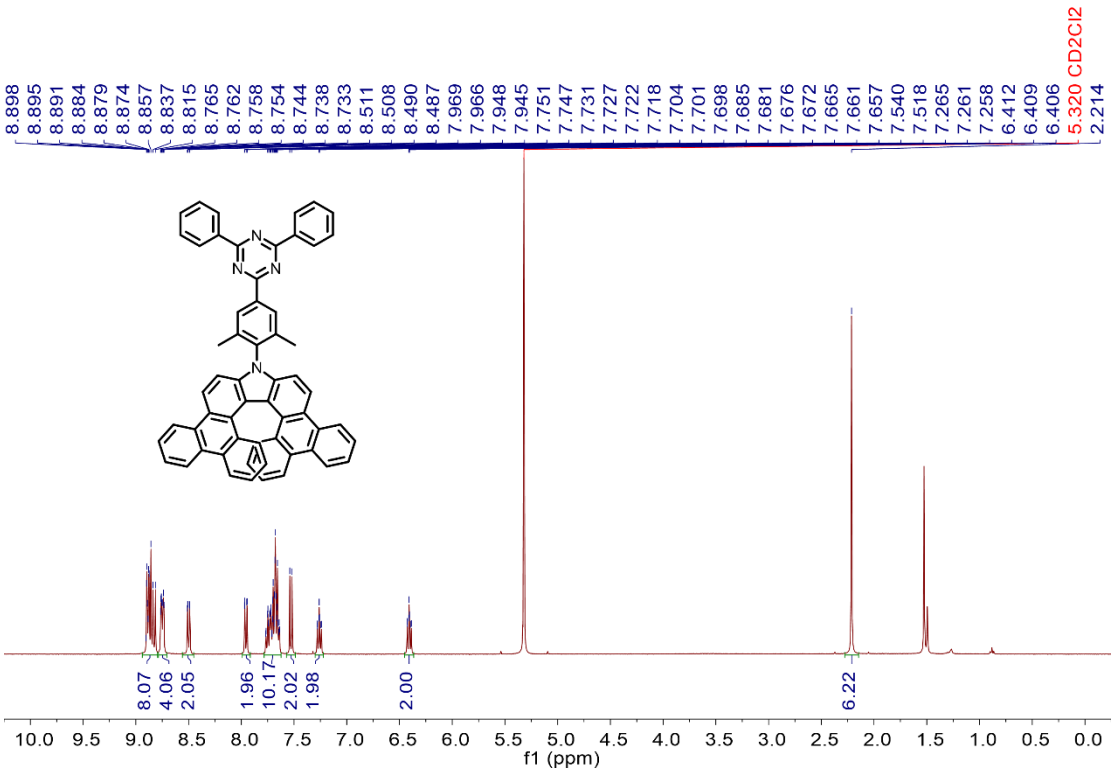



**Figure S15.** $^{1}$H NMR spectrum of **DMTrz-A7H** (400 MHz, $CD_2Cl_2$, 297 K).

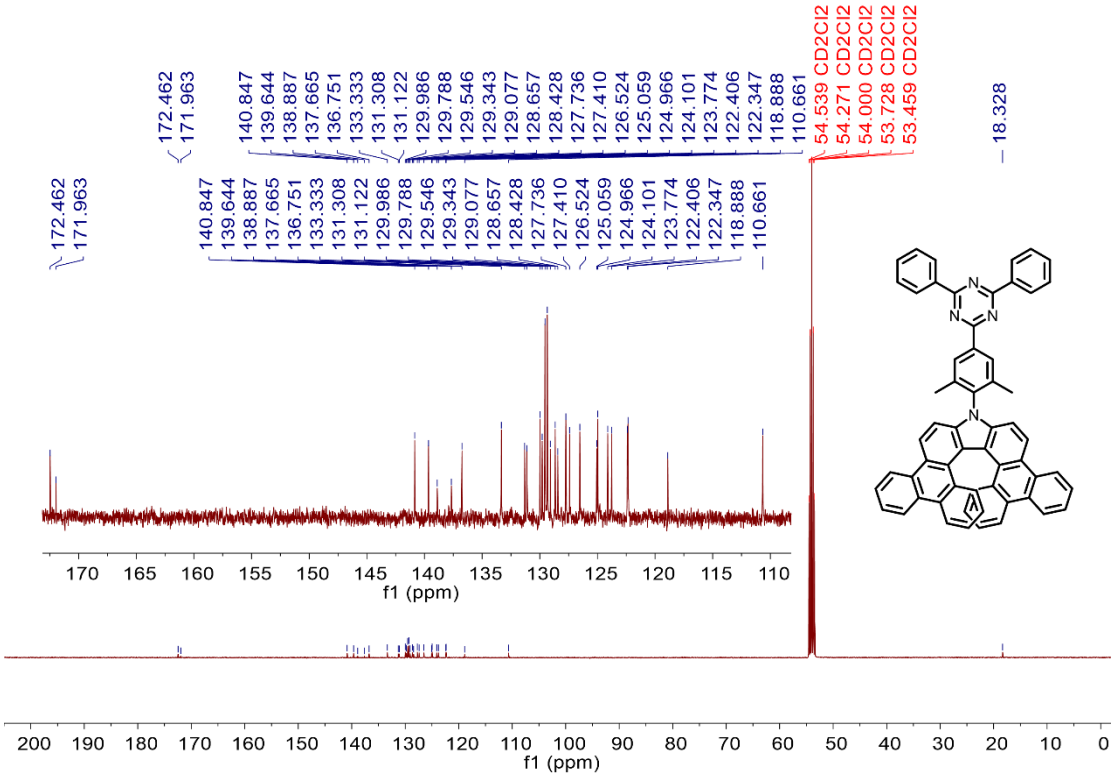



**Figure S16.** $^{13}$C NMR spectrum of **DMTrz-A7H** (101 MHz, $CD_2Cl_2$, 297 K).

# 7. References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