

## Supporting Information

### **Stable Nitrogen-Centered Radicals with Anti-Kasha Emission**

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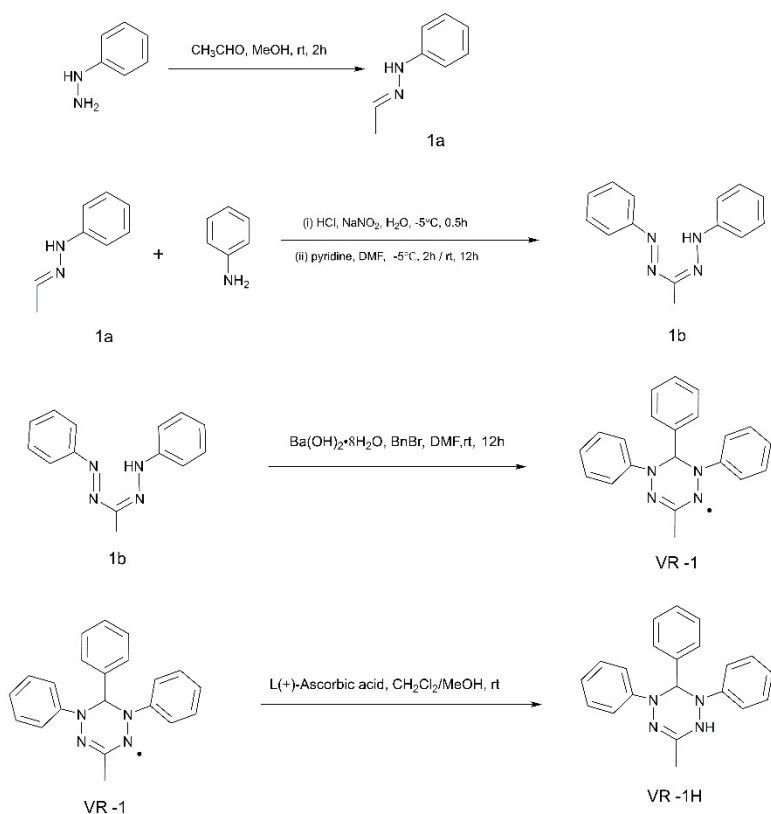
#### **S6 DFT / TD-DFT theoretical calculations**

**General.** All reagents and starting materials were obtained through commercial channels and used without further purification. Unless otherwise stated, all syntheses and measurement experiments were carried out under ambient atmosphere. Thermo Fisher ITQ1100 GC-MS mass detector was used to recorded the GC-MS mass spectra. MALDI-TOF mass spectra were recorded on a Bruker Autoflex speed TOF/TOF mass spectrometer with DCTB as matrix. The <sup>1</sup>H NMR spectra were recorded in solution of d<sub>6</sub>-DMSO, CDCl<sub>3</sub> on a Bruker AVANCEIII500 NMR spectrometer with tetramethylsilane (TMS) as the internal standard. Elemental analysis data were recorded on a Elementar Vario micro cube. Single crystal X-ray diffraction data was collected on a Bruker Apex II CCD diffractometer with MoK $\alpha$  radiation ( $\lambda = 0.71073$ ) at 259.0 K. EPR spectra were recorded on a Bruker ELEXSYSII E500 CW-EPR spectrometer at ambient atmosphere. UV/Vis spectrophotometer (Shimadzu UV-2550) and spectrofluoro-photometer (Shimadzu RF-

6000) were used to measure the absorption and fluorescence spectra in solution respectively. The fluorescence lifetime was carried out on HORIBA Scientific PTI QuantaMaster8000. The relative PLQYs of VR-Cz-1 and VR-Cz-2 were measured by using quinine sulfate in 0.1M diluted sulfuric acid solution as a standard reference. The electrochemical experiments using tetrabutylammonium hexafluorophosphate (TBAH) as supporting electrolyte and dry dimethylformamide (DMF) as solution. The counter electrode, reference electrode and working electrode were using platinum electrode, standard silver chloride electrode and glassy carbon electrode, respectively. Gaussian 09 series of programs on 6-31G(d,p) basis set and TPSSH function and cyclohexane solution were used to predict the DFT and TD-DFT data.

## S1. Synthetic procedures, details and characterization data.

### S1.1 Synthesis VR-1



Scheme S1. Synthesis of VR-1

### Synthesis of 1a ((E)-1-ethylidene-2-phenylhydrazine)

Acetaldehyde (5.6ml, 100mmol) was added dropped to phenyl hydrazine (5ml, 50mmol) in 50ml methanol at room temperature, and the stirred for 3h. Evaporating the solution and yielding a light-yellow oil. The crude product was purified by silica gel column chromatography using petroleum ether: ethyl acetate = 10:1 as eluent to give yellow long flaky crystal, which decomposed slowly to red in air. (1a, 6g, 44.8mmol, 90%yeild). <sup>1</sup>H NMR (500 MHz, DMSO) δ 7.15 (ddt, *J* = 16.1, 8.5, 3.6 Hz, 2H), 7.07 (dd, *J* = 8.6, 1.1 Hz, 1H), 6.96 – 6.84 (m, 1H), 6.77 – 6.68 (m, 1H), 6.68 – 6.62 (m, 1H), 6.54 (q, *J* = 5.5 Hz, 1H), 1.90 – 1.84 (m, 3H). GC-MS (m/z): [M] calculated for C<sub>8</sub>H<sub>10</sub>N<sub>2</sub>, 134.18, found, 134.14.

### Synthesis of 1b ((E, Z)-3-methyl-1,5-diphenylformazan)

i) preparation of diazonium salt solution. A mixture of deionized water (10 ml), aniline (0.46ml, 5mmol), and 37% HCl (1.5ml, 16mmol) followed by cooling to –5 °C; a solution of sodium nitrite (345mg, 5mmol) at –5 °C was added dropwise to it and the resulting solution was stirred for 30 minutes to yield light yellow solution.

ii) 1a (670mg, 5mmol) was dissolved in DMF (50 ml) and pyridine (2.5mL), cooled to –5 °C. The diazonium salt solution in step (i) was added dropwise and stirred for 2h at –5 °C, and followed by 12h stirring at room temperature. After the reaction the solution added to a separatory funnel and extraction with dichloromethane. Evaporated the organic layer after drying with anhydrous sodium sulfate. The crude product was purified by silica gel column chromatography using petroleum ether: ethyl acetate = 10:1 as eluent to give a red solid (1b, 1.13g, 4.7mmol, 94% yield). <sup>1</sup>H NMR (500 MHz, DMSO) δ 10.26 (s, 1H), 7.70 – 7.53 (m, 4H), 7.44 (t, *J* = 7.4 Hz, 4H), 7.16 (dd, *J* = 23.3, 16.0 Hz, 2H), 2.29 (s, 3H). GC-MS (m/z): [M] calculated for C<sub>14</sub>H<sub>14</sub>N<sub>4</sub>, 238.12, found, 237.83.

### Synthesis of VR-1 (3-methyl-1,5,6-triphenyl-verdazyl)

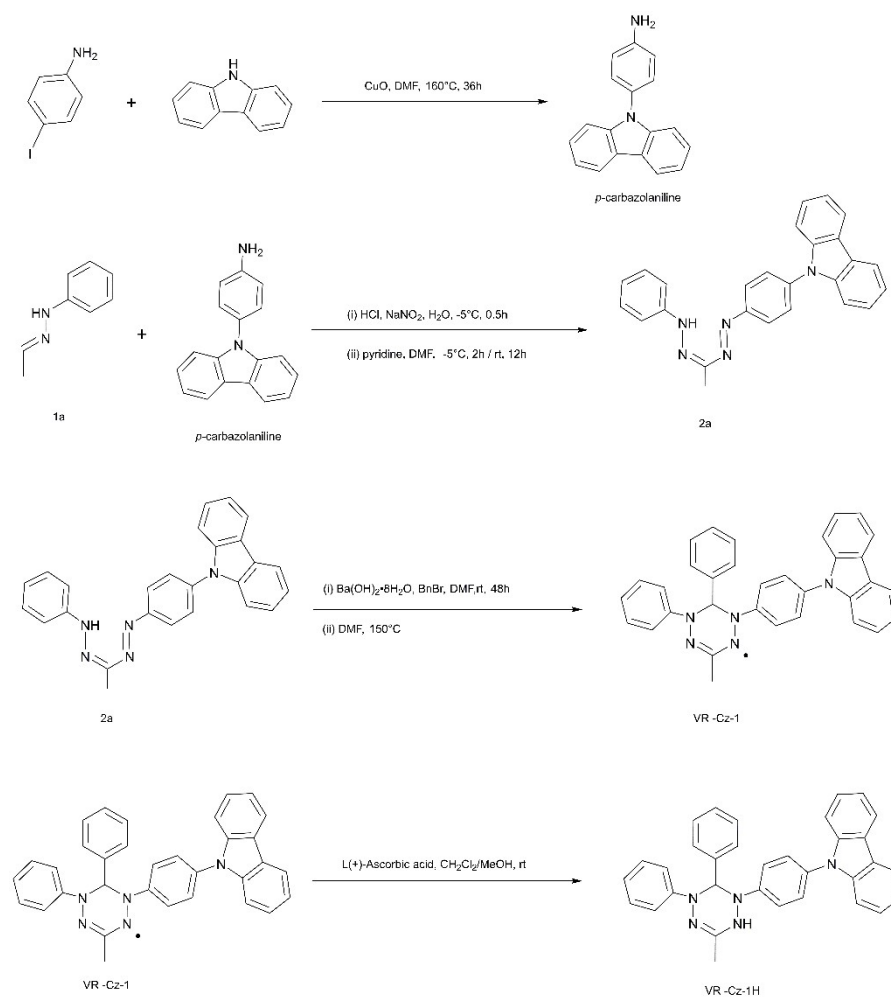
1b (920mg, 4mmol) was dissolved in DMF (50ml) and then treated with Ba(OH)<sub>2</sub>·8H<sub>2</sub>O (4.74g, 15 mmol). After 20min benzyl bromide (0.52ml, 4.4 mmol) was added dropwise and the solution

was left to stir for 12 hours at room temperature and opened to air until the color became deep blue-green. Pouring into deionized water (250 mL) and partitioned with dichloromethane. The organic layer was dried with anhydrous sodium sulfate and evaporated in vacuum. The crude product was purified by Al<sub>2</sub>O<sub>3</sub> column chromatography using petroleum ether as eluent to give a dark solid, and crystallized from petroleum ether to give a dark crystal VR-1 (850mg, 2.6mmol, 66%). **MALDI-TOF** (m/z): [M] calcd for C<sub>21</sub>H<sub>19</sub>N<sub>4</sub>, 327.16; found, 326.58. **Elem. Anal.** Calcd for C<sub>21</sub>H<sub>19</sub>N<sub>4</sub>, C 77.04, H 5.85, N 17.11; found, C 77.17, H 5.65; N 16.75.

### **Synthesis of VR-1H (6-methyl-2,3,4-triphenyl-1,2,3,4-tetrahydro-1,2,4,5-tetrazine)**

VR-1 (66mg, 0.2mmol) was dissolved in a mixed solution of 3ml methanol and 3ml dichloromethane. L-ascorbic acid (53mg, 0.3mmol) was added and stirred. The color of the solution changed from deep blue-green to almost colorless within minutes. The crude product was purified by silica gel column chromatography using petroleum ether: ethyl acetate =10:1 as eluent to give a colorless solid (58mg, 0.18mmol, 89%), which with a color transition back to deep blue-green. **<sup>1</sup>H NMR** (500 MHz, DMSO) δ 8.42 (s, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.32 (m, 4H), 7.29 (dd, *J* = 13.9, 6.5 Hz, 3H), 7.14 – 7.07 (m, 4H), 7.00 – 6.88 (m, 2H), 6.62 (dd, *J* = 8.2, 4.2 Hz, 1H), 1.84 (s, 3H). **<sup>13</sup>C NMR** (500 MHz, DMSO) δ 151.56, 147.48, 142.69, 137.77, 129.46, 129.31, 128.77, 128.17, 122.40, 118.27, 117.68, 111.50, 71.10, 18.33. **MALDI-TOF** (m/z): [M] calcd for C<sub>21</sub>H<sub>20</sub>N<sub>4</sub>, 328.17; found, 327.75.

### **S1.2 Synthesis VR-Cz-1**



**Scheme S2.** Synthesis of VR-Cz-1

### Synthesis of *p*-carbazolaniline

4-iodoaniline (1.1g, 5mmol), 9H-carbazole (0.93g, 5.5mmol), nanometer copper oxide (1.2g, 15mmol) and DMF (50 ml) were added into a 250 ml round flask, stirring at 160 °C for 36 hours. After reaction accomplished, stop heating and cool to room temperature. Filtered the mixture by Buchner funnel and suction flask. Removing the solvent and the crude product was purified by silica gel column chromatography using petroleum ether: ethyl acetate (10:1) as eluent to give a pale-yellow waxy oil (*p*-carbazolaniline, 840mg, 3.25mmol, 65% yield). <sup>1</sup>H NMR (500 MHz, DMSO) δ 8.29 – 8.09 (m, 2H), 7.49 – 7.36 (m, 2H), 7.31 – 7.21 (m, 4H), 7.21 – 7.10 (m, 2H), 6.89 – 6.75 (m, 2H), 5.44 (s, 2H). GC-MS (m/z): [M] calculated for C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>, 258.32, found, 258.25.

### Synthesis of 2a ((Z,E)-1-(4-(9H-carbazol-9-yl)phenyl)-3-methyl-5-phenylformazan)

1a and p-carbazolaniline was treated as 1b above: dark red solid (2a, 550mg, 1.36mmol, 54% yield). **<sup>1</sup>H NMR** (500 MHz, DMSO)  $\delta$  10.47 (s, 1H), 8.25 (t,  $J$  = 18.2 Hz, 2H), 8.00 – 7.58 (m, 6H), 7.50 – 7.42 (m, 5H), 7.40 – 7.20 (m, 4H), 2.36 (s, 3H). **GC-MS** (m/z): [M] calculated for C<sub>26</sub>H<sub>21</sub>N<sub>5</sub>, 403.18, found, 403.11.

### Synthesis of VR-Cz-1 (1-(4-phenyl-(9H-carbazole))-3-methyl-5,6-diphenyl-verdazyl)

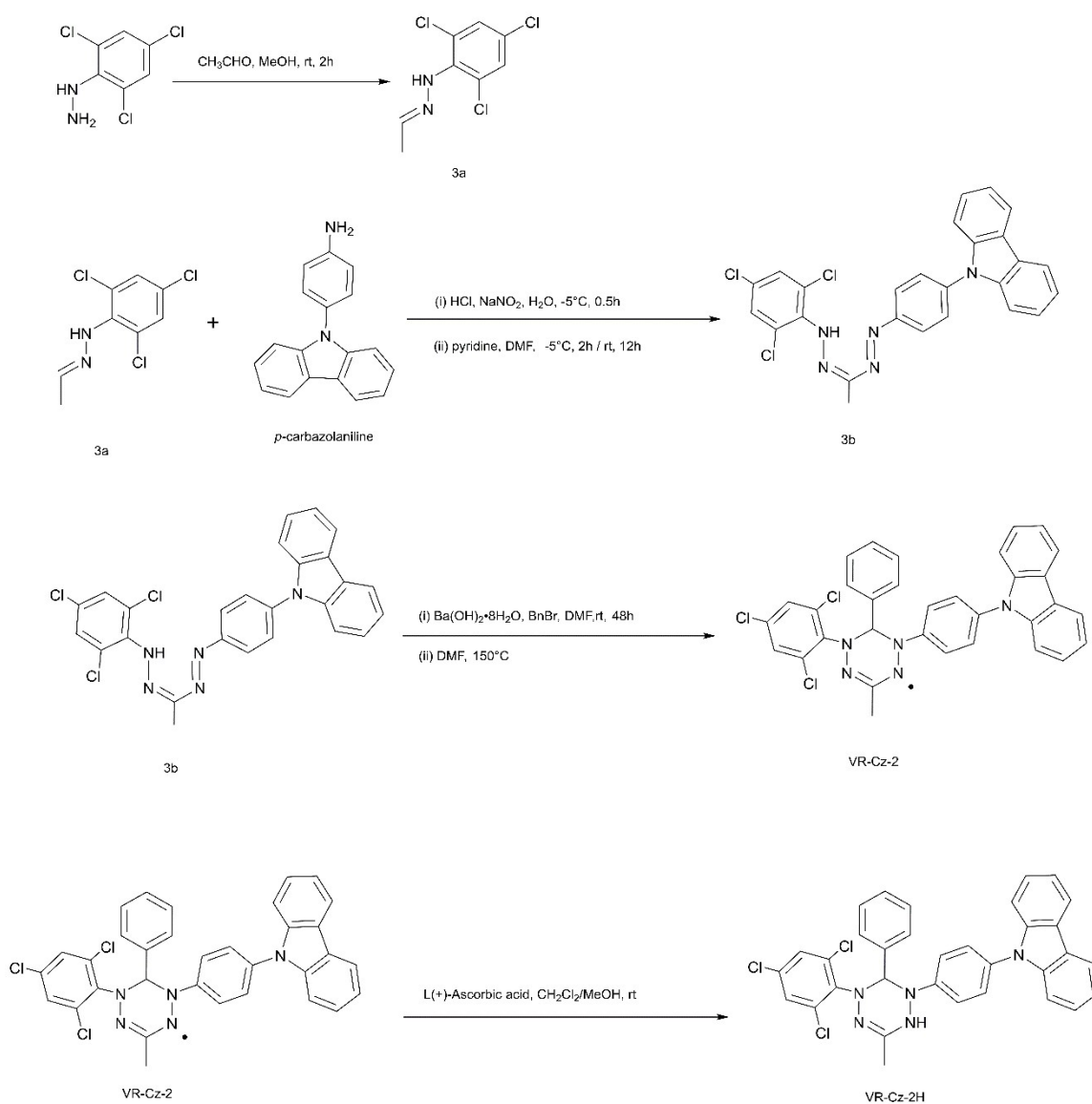
2a (2.8g, 7mmol) was dissolved in DMF (50ml) and then treated with Ba(OH)<sub>2</sub>·8H<sub>2</sub>O (15.8g, 50 mmol). Next, benzyl bromide (1.18ml, 10 mmol) was added dropwise and the solution was left to stir for 48 hours at room temperature and opened to air until the color changed to brown. The reaction was poured into deionized water (250 mL), and partitioned with dichloromethane. The organic layer was dried with anhydrous sodium sulfate and evaporated in vacuum. The residue was dissolved in DMF (100 ml) and heated to 150°C. After the color turned to deep green, solution was cooled to room temperature, pour into deionized water (250 mL) and partitioned with dichloromethane. The organic layer was dried with anhydrous sodium sulfate and evaporated in vacuum. The crude product was purified by Al<sub>2</sub>O<sub>3</sub> column chromatography using petroleum ether as eluent to give a dark green solid, and crystallized from petroleum ether to give a deep dark green crystal VR-Cz-1 (1.04g, 2.1mmol, 30%). **MALDI-TOF** (m/z): [M] calcd for C<sub>33</sub>H<sub>26</sub>N<sub>5</sub>, 492.22; found, 492.57. **Elem. Anal.** Calcd for C<sub>33</sub>H<sub>26</sub>N<sub>5</sub>, C 80.46, H 5.32, N 14.22.; found, C 80.64, H 5.47; N 13.83.

### Synthesis of VR-Cz-1H (9-(4-(3-methyl-5,6-diphenyl-5,6-dihydro-1,2,4,5-tetrazin-1(2H)-yl)phenyl)-9H-carbazole)

VR-Cz-1 was treated as VR-1H above: colorless solid (**VR-Cz-1H**, 57%). **<sup>1</sup>H NMR** (500 MHz, DMSO)  $\delta$  8.58 (d,  $J$  = 10.9 Hz, 1H), 8.22 (dd,  $J$  = 11.7, 7.8 Hz, 2H), 7.70 – 7.55 (m, 1H), 7.50 (t,  $J$  = 9.0 Hz, 2H), 7.45 (dd,  $J$  = 14.5, 6.4 Hz, 2H), 7.41 (d,  $J$  = 8.7 Hz, 3H), 7.37 (d,  $J$  = 7.3 Hz, 2H),

7.34 (d,  $J = 6.0$  Hz, 2H), 7.33 – 7.30 (m, 2H), 7.30 – 7.26 (m, 2H), 7.23 (dd,  $J = 15.6, 8.0$  Hz, 2H), 7.19 – 7.13 (m, 1H), 7.10 (s, 1H), 6.99 (t,  $J = 7.2$  Hz, 1H), 1.89 (s, 3H).  $^{13}\text{C}$  NMR (500 MHz, DMSO)  $\delta$  151.43, 146.73, 143.36, 141.17, 140.90, 137.59, 129.48, 128.85, 127.93, 126.50, 122.76, 120.86, 120.25, 119.96, 119.33, 118.33, 112.45, 111.91, 110.14, 71.48, 18.34. **MALDI-TOF** (m/z): [M] calcd for  $\text{C}_{33}\text{H}_{27}\text{N}_5$ , 493.23; found, 492.72.

### S1.3 Synthesis VR-Cz-2



**Scheme S3.** Synthesis of VR-Cz-2

### Synthesis of 3a ((E)-1-ethylidene-2-(2,4,6-trichlorophenyl)hydrazine)

(2,4,6-trichlorophenyl)hydrazine and acetaldehyde was treated as 1a above as yellow crystal (3a, 93%). <sup>1</sup>H NMR (500 MHz, DMSO) δ 8.70 (s, 1H), 7.57 – 7.51 (m, 2H), 7.38 (q, *J* = 5.4 Hz, 1H), 1.83 (d, *J* = 5.4 Hz, 3H). GC-MS (m/z): [M] calculated for C<sub>8</sub>H<sub>7</sub>Cl<sub>3</sub>N<sub>2</sub>, 235.97, found, 236.23.

### Synthesis of 3b ((Z, E)-1-(4-(9H-carbazol-9-yl)phenyl)-3-methyl-5-(2,4,6-trichlorophenyl)formazan)

3a and *p*-carbazolaniline was treated as 1b above: dark reddish brown solid (3b, 46%). <sup>1</sup>H NMR (500 MHz, DMSO) δ 10.91 (s, 1H), 8.71 (s, 2H), 8.25 (d, *J* = 7.9 Hz, 1H), 7.86 – 7.79 (m, 2H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.63 – 7.57 (m, 4H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.37 (dd, *J* = 7.2, 3.5 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 2.35 (d, *J* = 10.0 Hz, 3H). GC-MS (m/z): [M] calculated for C<sub>26</sub>H<sub>18</sub>Cl<sub>3</sub>N<sub>5</sub>, 506.82, found, 507.16.

### Synthesis of VR-Cz-2 (1-(4-phenyl-(9H-carbazole))-3-methyl-5-phenyl-6-(2,4,6-trichlorophenyl)-verdazyl)

3b was treated as VR-Cz-1 above: deep dark green crystal (VR-Cz-2, 6%). MALDI-TOF (m/z): [M] calcd for C<sub>33</sub>H<sub>23</sub>Cl<sub>3</sub>N<sub>5</sub>, 595.93; found, 595.61. Elem. Anal. Calcd for C<sub>33</sub>H<sub>23</sub>Cl<sub>3</sub>N<sub>5</sub>, C 66.51, H 3.89, N 11.75.; found, C 66.28, H 3.58; N 11.46.

### Synthesis of VR-Cz-2H

VR-Cz-2 was treated as VR-1H above: colorless solid (VR-Cz-2H, 51%). <sup>1</sup>H NMR (500 MHz, DMSO) δ 8.75 (d, *J* = 6.2 Hz, 1H), 8.29 – 8.20 (m, 2H), 7.73 (d, *J* = 7.7 Hz, 2H), 7.68 (d, *J* = 2.8 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.44 (dd, *J* = 8.7, 6.1 Hz, 3H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 4.6 Hz, 1H), 7.34 (d, *J* = 3.6 Hz, 3H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.25 (dd, *J* = 15.4, 7.7 Hz, 2H), 6.31 (s, 1H), 1.77 (s, 3H). <sup>13</sup>C NMR (500 MHz, DMSO) δ 146.08, 142.02, 141.01, 137.36, 130.56,



129.54, 128.91, 128.55, 128.35, 127.89, 127.48, 127.48, 126.9, 126.55, 122.85, 120.84, 119.99, 112.78, 110.15, 70.77, 18.19. **MALDI-TOF** (m/z): [M] calcd for C<sub>33</sub>H<sub>24</sub>Cl<sub>3</sub>N<sub>5</sub>, 596.94; found, 597.03.

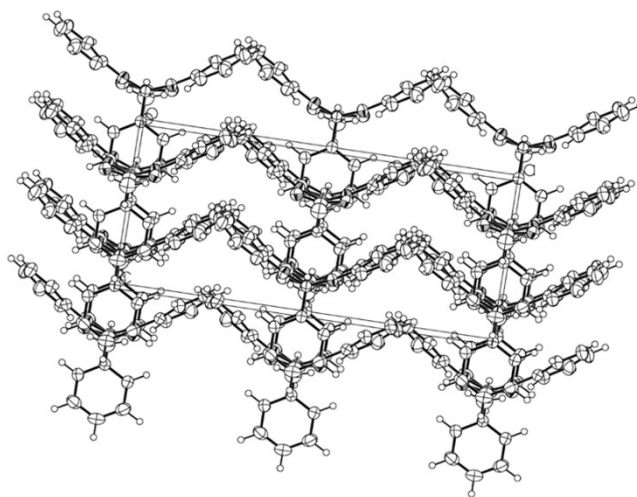
## S2. Single crystal X-ray diffraction analysis

**Table S1. Crystal data and structure refinement for VR-1<sup>a</sup>**

Empirical formula	C <sub>21</sub> H <sub>19</sub> N <sub>4</sub>
Formula weight	327.40
Temperature/K	259.0
Crystal system	orthorhombic
Space group	Cmc2 <sub>1</sub>
a/Å	18.2181(13)
b/Å	11.9406(13)
c/Å	8.1125(6)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	1764.8(3)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.232

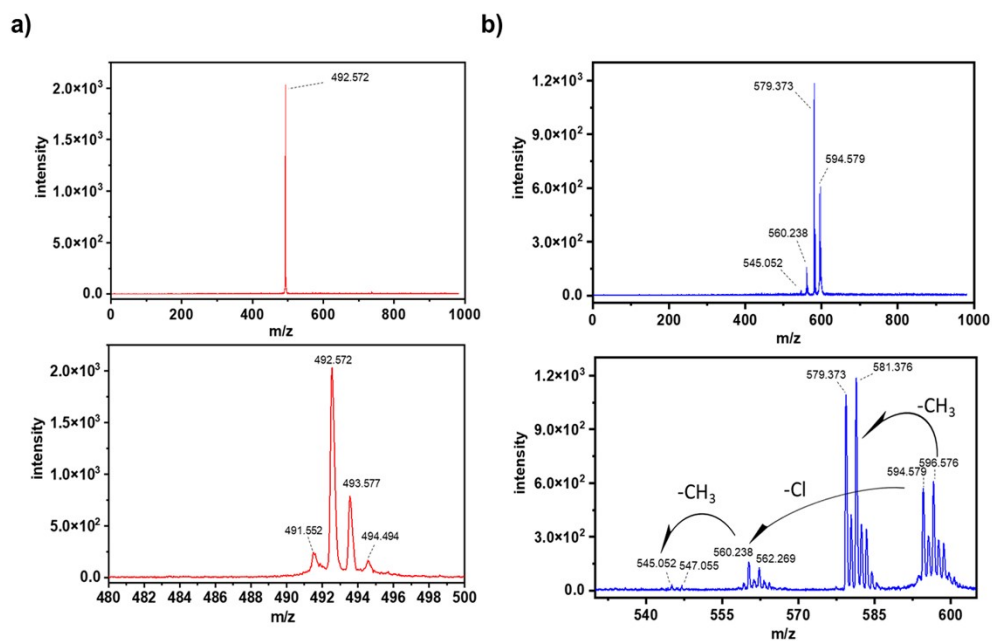
$\mu/\text{mm}^{-1}$	0.075
F(000)	692.0
Crystal size/ $\text{mm}^3$	$0.5 \times 0.3 \times 0.2$
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
$2\theta$ range for data collection/ $^\circ$	6.47 to 54.998
Index ranges	$-23 \leq h \leq 23, -15 \leq k \leq 15, -10 \leq l \leq 10$
Reflections collected	23704
Independent reflections	2099 [ $R_{\text{int}} = 0.0729, R_{\text{sigma}} = 0.0287$ ]
Data/restraints/parameters	2099/1/162
Goodness-of-fit on $F^2$	0.818
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0354, wR_2 = 0.0971$
Final R indexes [all data]	$R_1 = 0.0479, wR_2 = 0.1100$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.14/-0.24
Flack parameter	-1.3(9)

(a) CCDC number of VR-1 crystal is 2226269.

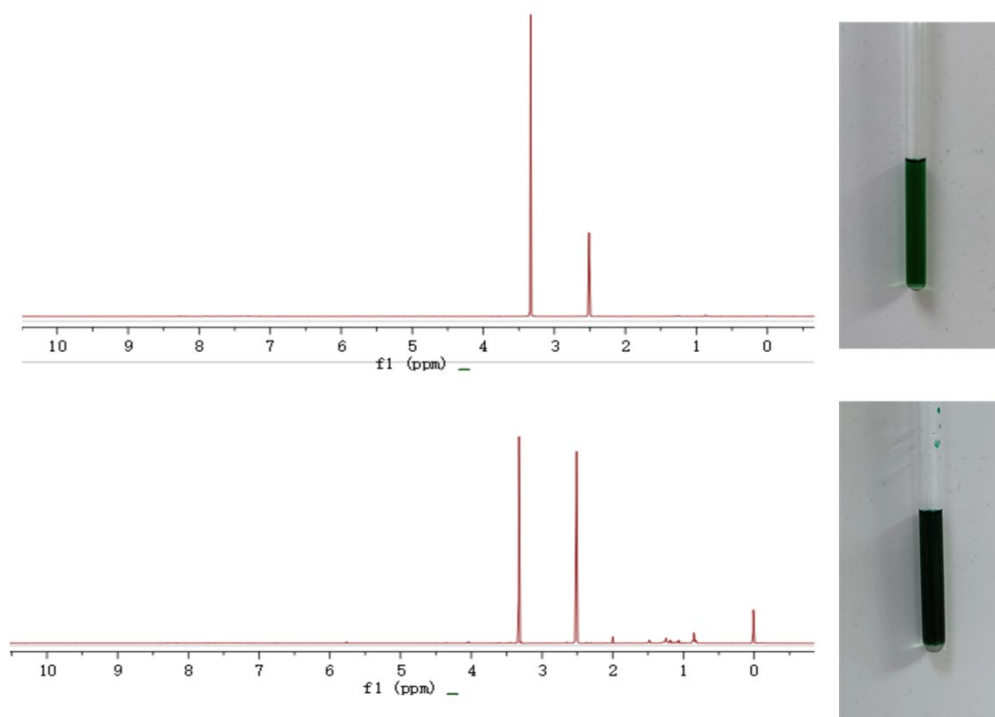


**Figure S1.** Molecular packing structure in VR-1 crystals. Displacement ellipsoids are drawn at the 50% probability level.

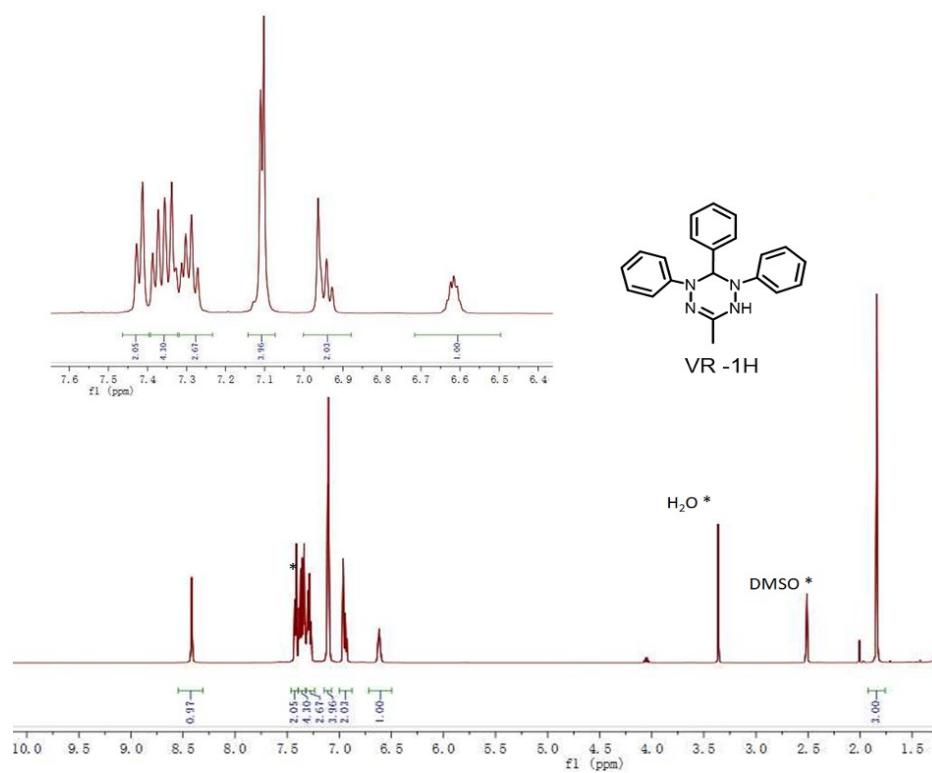
### S3. MALDI-TOF and NMR spectra



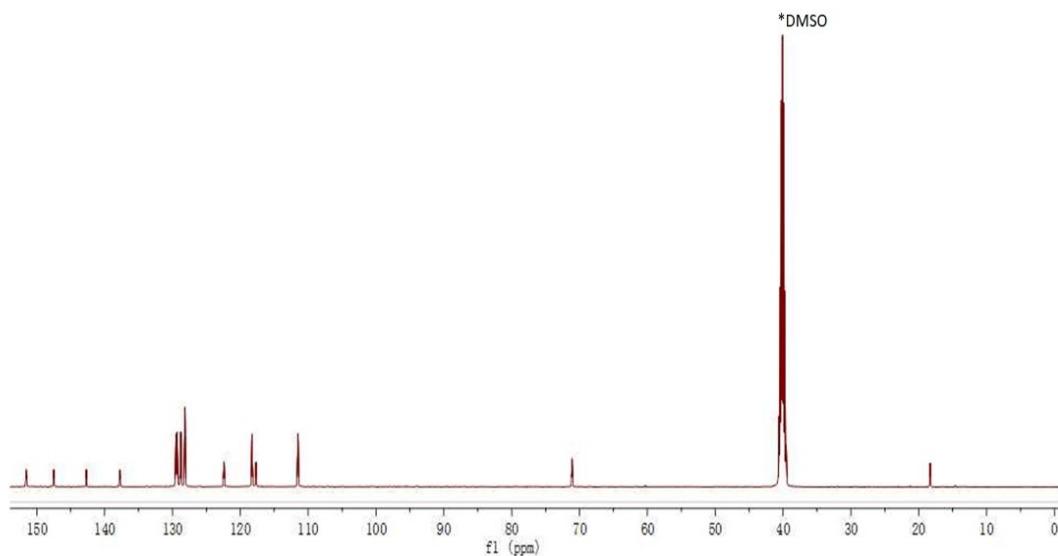
**Figure S2.** MALDI-TOF mass spectrometry of VR-Cz-1(a) and VR-Cz-2(b).



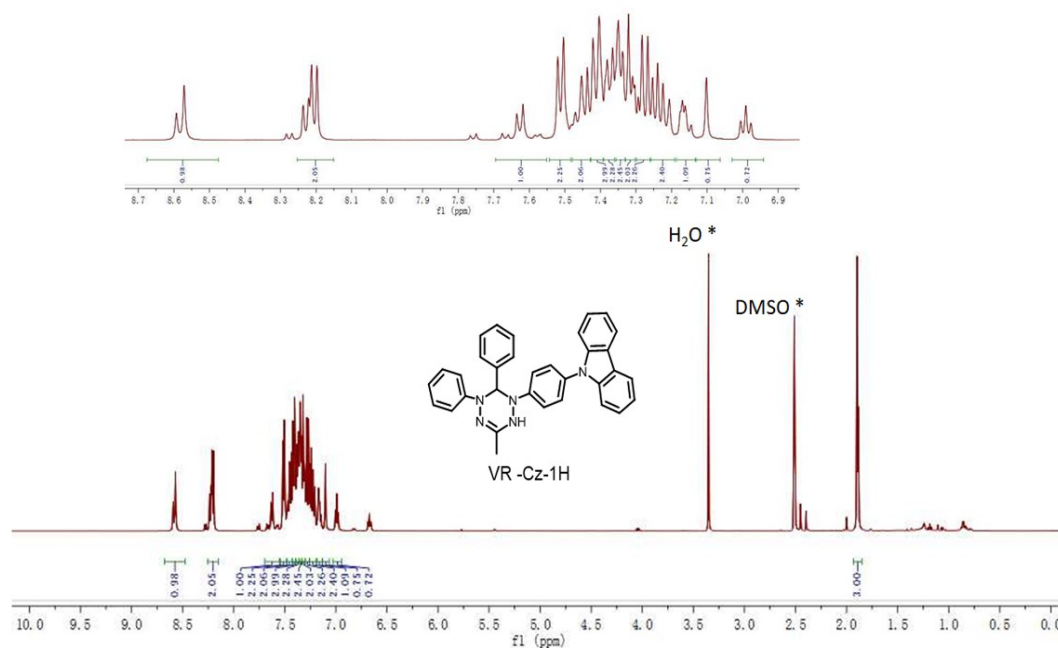
**Figure S3.** <sup>1</sup>H-NMR spectra and photographs of VR-Cz-1 (up) and VR-Cz-2 (down) (500 MHz, d<sub>6</sub>-DMSO).



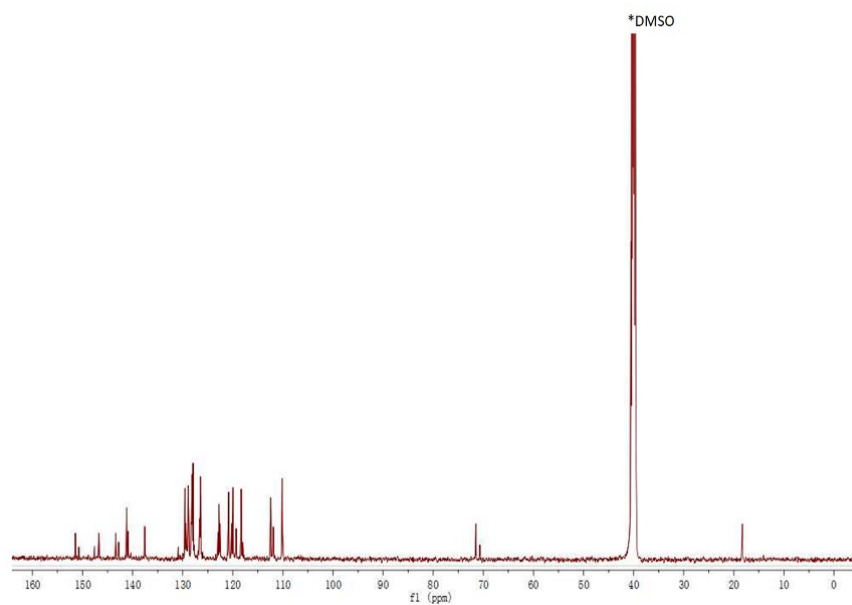
**Figure S4.**  $^1\text{H}$  NMR spectrum of VR-1H (500 MHz,  $d_6$ -DMSO).



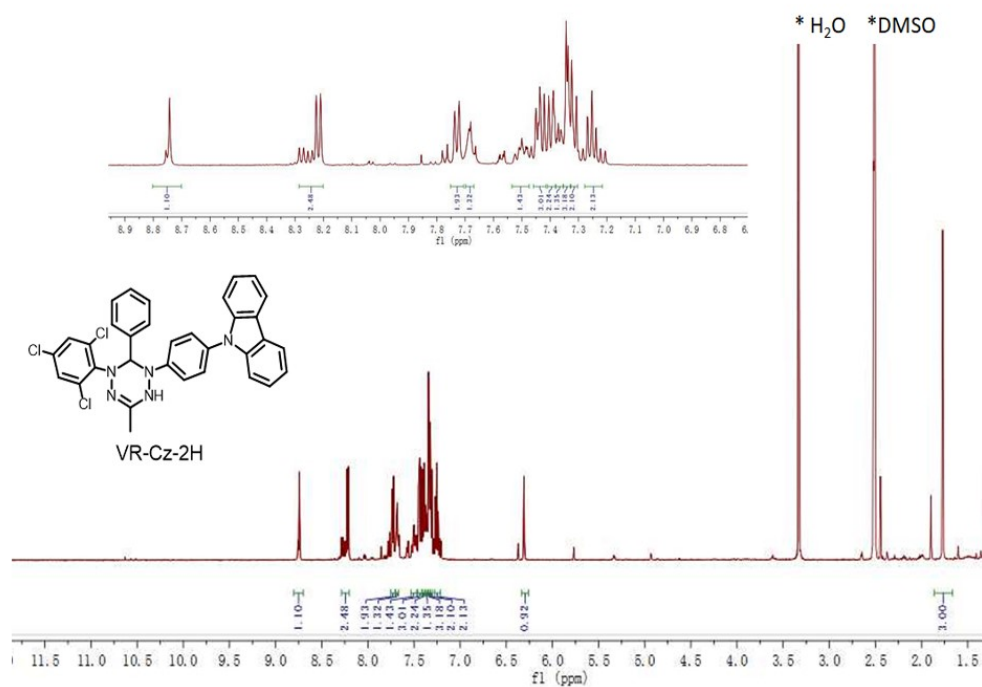
**Figure S5.**  $^{13}\text{C}$  NMR spectrum of VR-1H (500 MHz,  $d_6$ -DMSO).



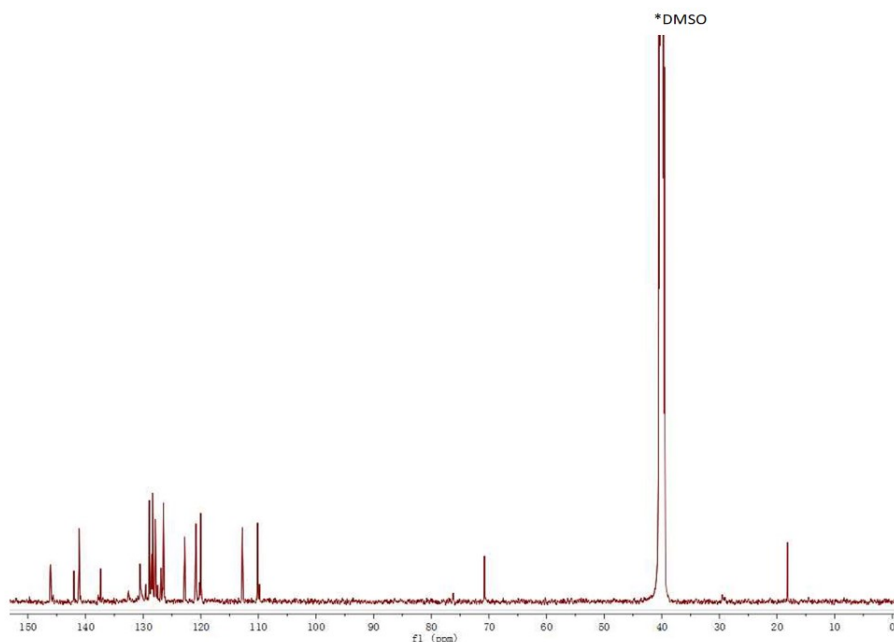
**Figure S6.**  $^1\text{H}$  NMR spectrum of VR-Cz-1H (500 MHz,  $d_6$ -DMSO).



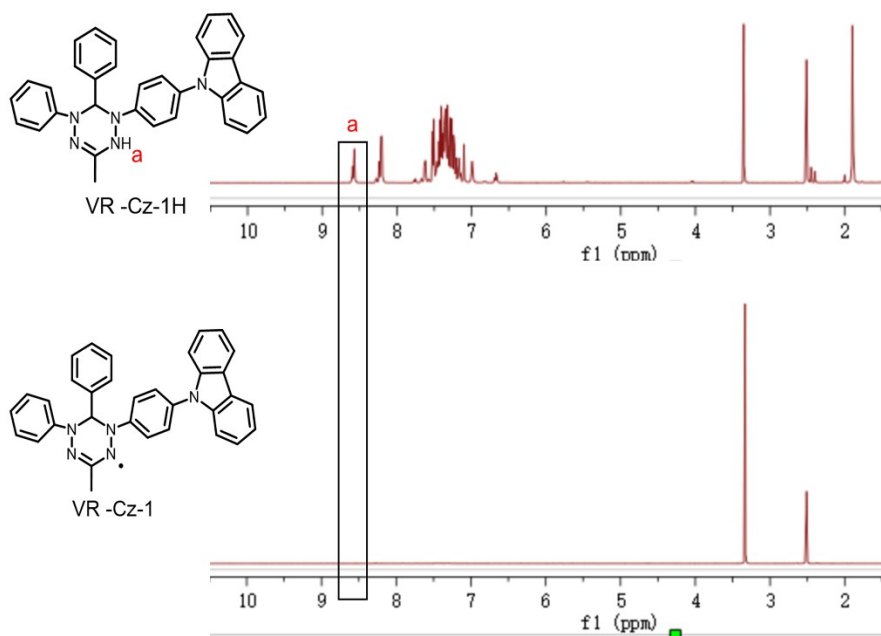
**Figure S7.**  $^{13}\text{C}$  NMR spectrum of VR-Cz-1H (500 MHz,  $\text{d}_6$ -DMSO).



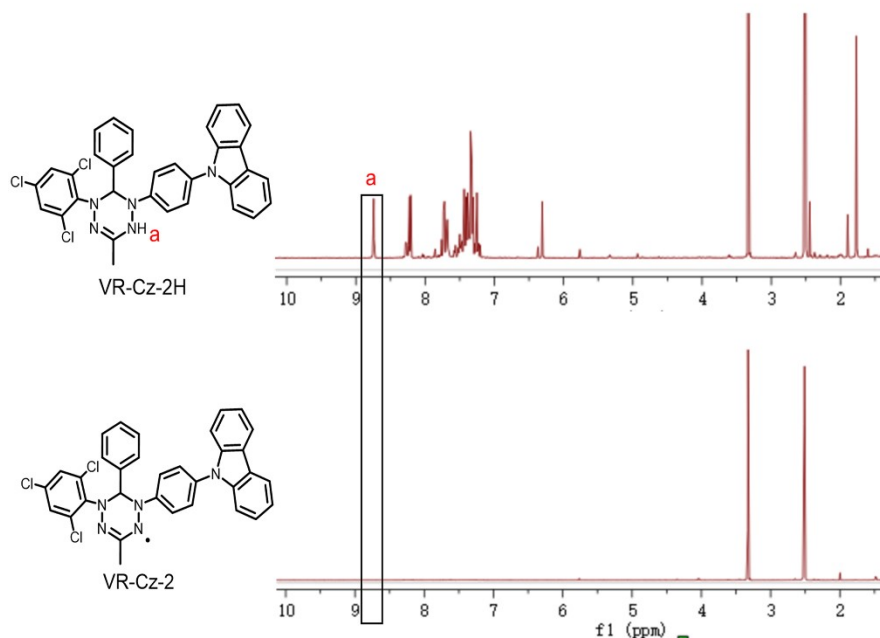
**Figure S8.**  $^1\text{H}$  NMR spectrum of VR-Cz-2H (500 MHz,  $\text{d}_6$ -DMSO).



**Figure S9.**  $^{13}\text{C}$  NMR spectrum of VR-Cz-2H (500 MHz,  $d_6$ -DMSO).

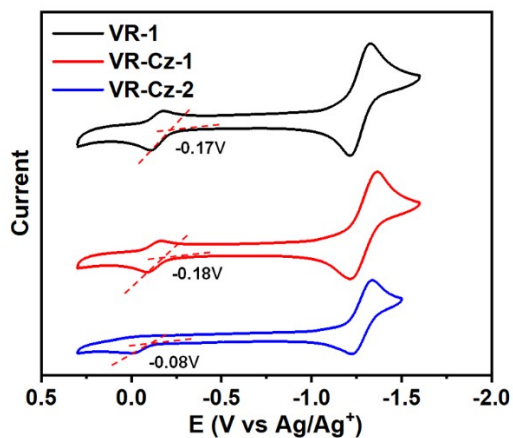


**Figure S10.** Comparison of  $^1\text{H}$  NMR spectra between VR-Cz-1 and VR-Cz-1H.



**Figure S11.** Comparison of  $^1\text{H}$  NMR spectra between VR-Cz-2 and VR-Cz-2H.

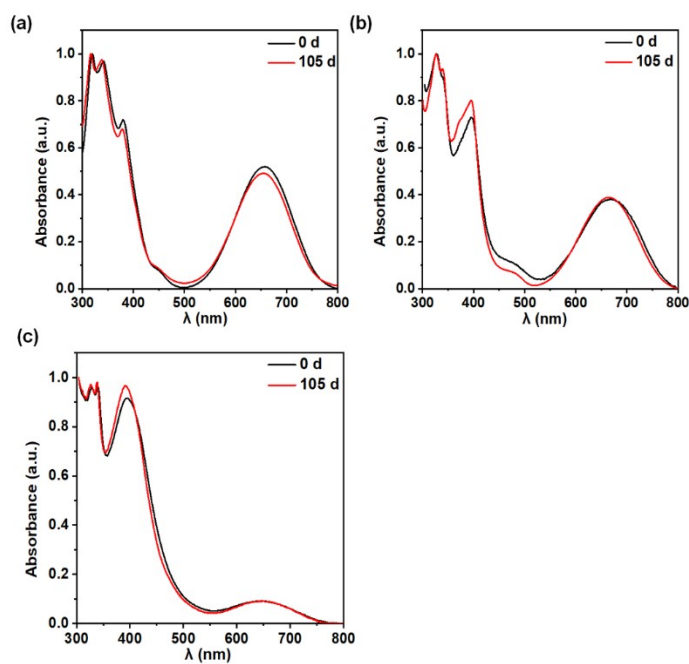
## S4 Electrochemical measurement



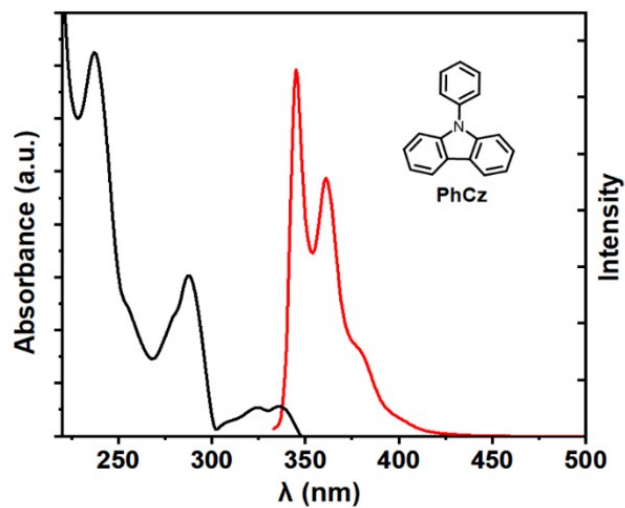
**Figure S12.** Cyclic voltammogram (CV) curves of VR-1, VR-Cz-1 and VR-Cz-2 in DMF solution with 100 mV/s scanning rate at room temperature. Crossing positions of red dotted line indicate the oxidation potential.



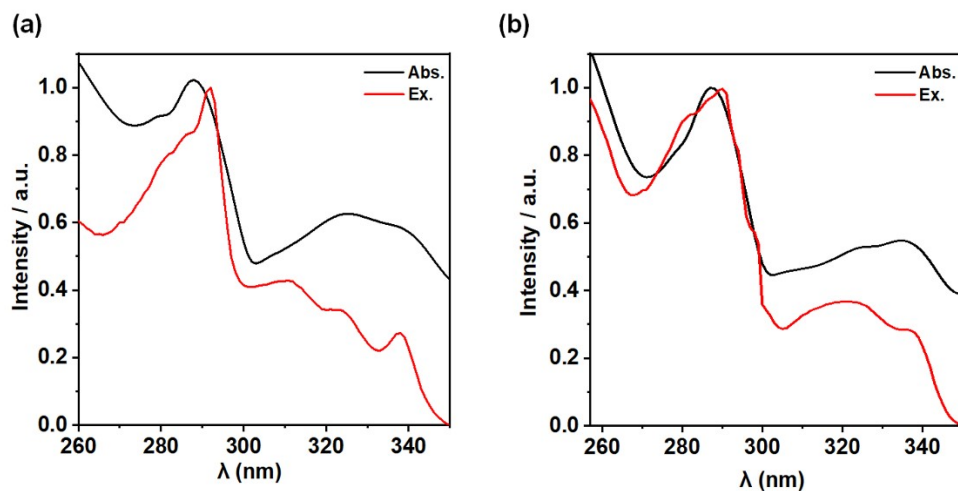
## S5. Photophysical measurements



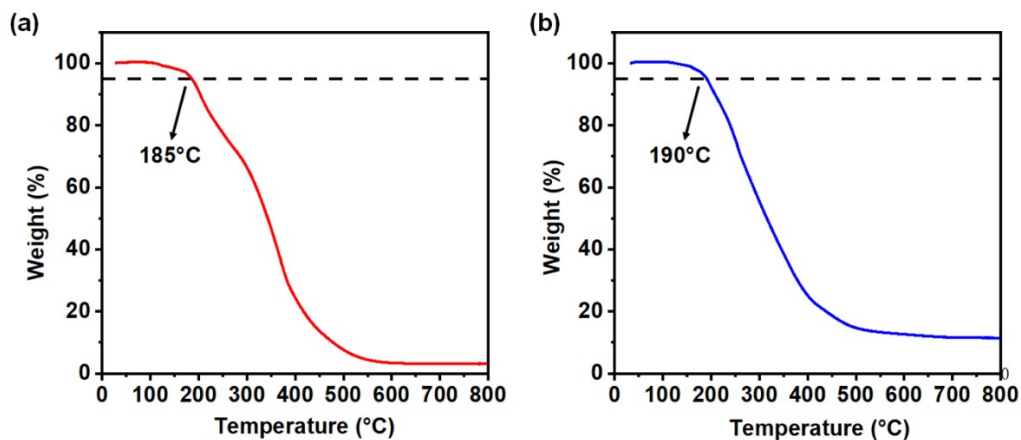
**Figure S13.** UV-Vis absorption spectra change of (a) VR -1 (b) VR-Cz-1 and (c) VR-Cz-2 measured on 0 day and 105 days after they were dissolved in cyclohexane at room temperature (Concentration around  $1 \times 10^{-5}$  mol L<sup>-1</sup>).



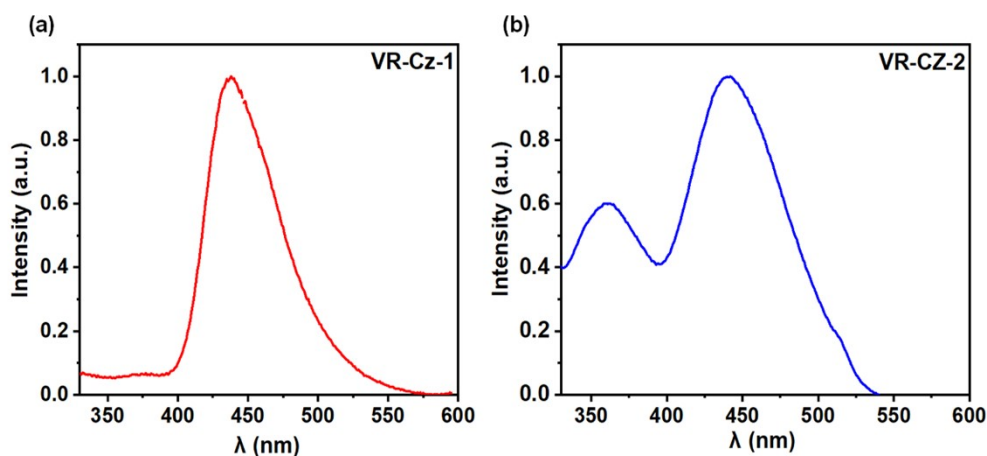
**Figure S14.** UV-Vis absorption spectra (black) and emission spectra (red) (excited at 320nm) of PhCz around  $1 \times 10^{-5} \text{M}$  in cyclohexane at room temperature.



**Figure S15.** Absorption and excitation spectra of (a) VR-Cz-1 and (b) VR-Cz-2 around  $1 \times 10^{-5} \text{M}$  in cyclohexane at room temperature.



**Figure S16.** Thermogravimetric analysis (TGA) of (a) VR-Cz-1 and (b) VR-Cz-2.

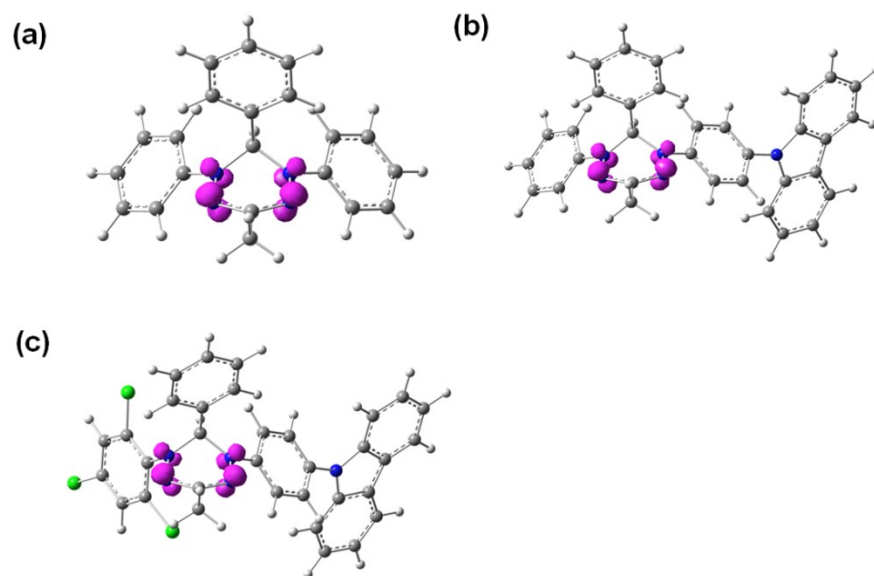


**Figure S17.** Emission spectra (excited at 320nm) of (a) VR-Cz-1 and (b) VR-Cz-2 in solid state at room temperature.

## S6. DFT / TD-DFT Theoretical Calculations

**Table S2.** Part calculation data in optimized structure of VR-1 (UTPSSH/6-31G(d,p)) at ground state according to DFT calculations and comparing with that in crystal of VR-1.

Bond Lengths/Å	calculation	crystal	Bond Angles/°	calculation	crystal
N1-C2	1.463	1.457	N3-N1-C2	117.44	117.64
N1-N3	1.360	1.360	N3-N1-C4	118.73	117.99
N1-C4	1.404	1.399	C4-N1-C2	123.83	124.34
C2-C11	1.529	1.519	C7-N3-N1	114.64	114.67
N3-C7	1.341	1.333	N1-C2-C11	112.49	112.68
C7-C9	1.503	1.497	C5-C4-N1	119.46	119.70
C4-C5	1.408	1.399	N3-C7-C9	116.60	116.34



**Figure S18.** Spin density distribution (purple) of (a) VR-1, (b) VR-Cz-1 and (c) VR-Cz-2 on ground state (UTPSSH/6-31G(d,p)).

**Table S3.** Part excited states calculated by TD-DFT calculations with oscillator strength ( $f$ ) greater than 0.02 of PhCz<sup>a</sup> (TPSSH/6-31G(d,p)).

Excited State	Wavelength / nm	$f$
1	320.46	0.0380
2	303.68	0.1730
4	280.47	0.0828
7	247.52	0.7211
8	239.02	0.0417

10	226.97	0.0215
13	223.73	0.0498
15	217.18	0.2299
16	216.28	0.4012
17	206.80	0.1538
18	205.03	0.0505
20	198.56	0.0533
23	194.89	0.0421
25	184.97	0.3147
26	183.67	0.1635
27	178.55	0.2107
28	177.22	0.2619
30	176.10	0.0706

a) calculation the first 30 excited states.

**Table S4.** Part excited states calculated by TD-DFT calculations with oscillator strength ( $f$ ) greater than 0.02 of VR-Cz-1<sup>a</sup> (UTPSSH/6-31G(d,p)).

Excited State	Wavelength / nm	$f$
1	635.45	0.1838
2	527.85	0.0367
6	413.26	0.0346

7	401.78	0.1368
9	395.92	0.0599
10	387.96	0.1185
15	350.99	0.0207
17	346.29	0.0223
20	334.34	0.0319
22	326.20	0.0757
25	316.86	0.0504
33	294.60	0.0871
34	293.57	0.0833
42	280.06	0.0442
43	279.51	0.0477

a) calculation the first 60 excited states.

**Table S5.** Part excited states calculated by TD-DFT calculations with oscillator strength ( $f$ ) greater than 0.02 of VR-Cz-2<sup>a</sup> (UTPSSH/6-31G(d,p)).

Excited State	Wavelength / nm	$f$
1	641.75	0.1308
5	475.97	0.1867
10	395.48	0.0519
12	377.56	0.0222

18	356.10	0.0278
24	342.18	0.1265
26	333.96	0.1089
28	322.19	0.0611
29	319.40	0.0247
47	285.15	0.0307
48	283.89	0.0302
49	283.18	0.0589
52	279.74	0.0266
53	278.64	0.1057

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a) calculation the first 60 excited states.

**Table S6.** Main orbitals transitions of emission relevant excited states of VR-Cz-1 with Transition coefficient  $\chi$  larger than 0.2.

Excited State	transition	$\chi$
22	130A ->138A	0.29339
	118B ->130B	-0.24916
	120B ->130B	0.55670
	129B ->131B	-0.20675
25	129A ->134A	-0.30977
	130A ->138A	0.55401

130A ->140A	-0.24114
118B ->130B	0.38610
119B ->130B	-0.20551

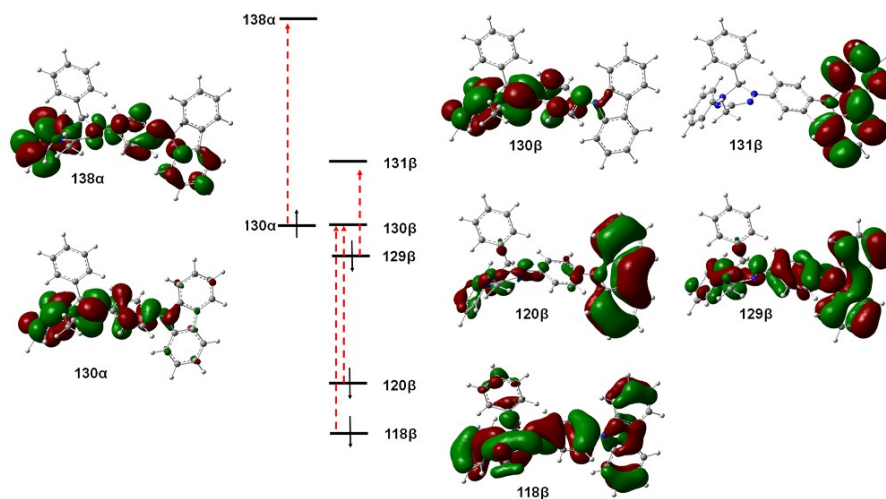
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**Table S7.** Main orbitals transitions of emission relevant excited states of VR-Cz-2 with transition coefficient  $\chi$  larger than 0.2.

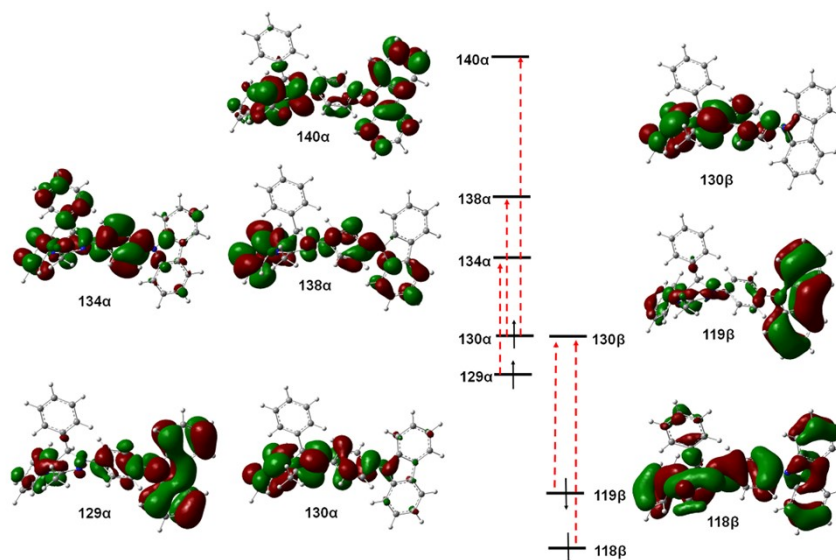
Excited State	transition	$\chi$
28	153A ->161A	0.20635
	154A ->161A	-0.24081
	142B ->154B	0.40162
	143B ->154B	-0.33520
	153B ->162B	-0.22308
29	153A ->157A	0.69288
	153B ->157B	0.65351

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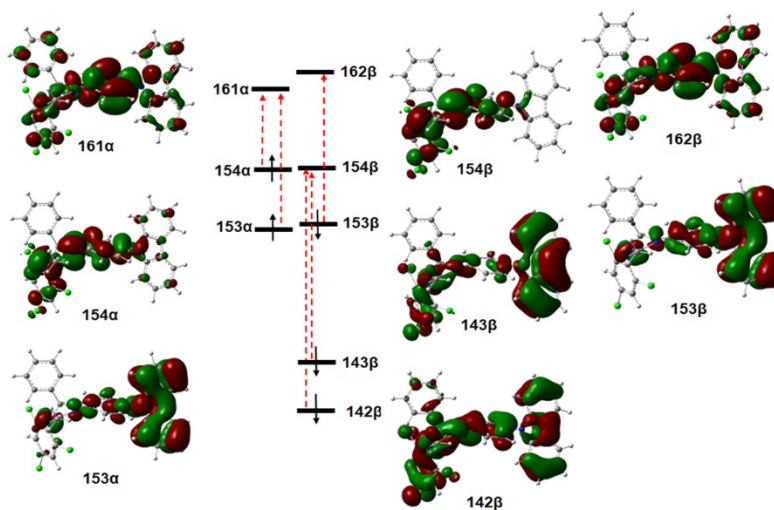




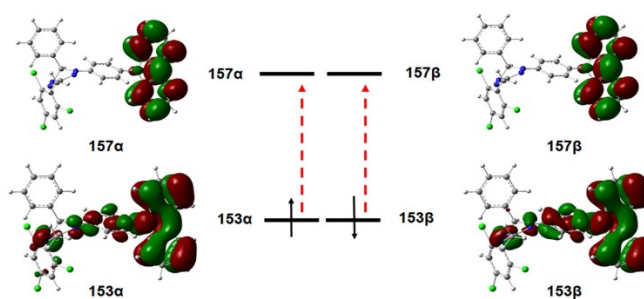
**Figure S19.** Frontier orbitals of main orbitals in the transitions to excited state 22 of VR-Cz-1. The transitions are shown by red dashed arrow.



**Figure S20.** Frontier orbitals of main orbitals in the transitions to excited state 25 of VR-Cz-1. The transitions are shown by red dashed arrow.



**Figure S21.** Frontier orbitals of main orbitals in the transitions to excited state 28 of VR-Cz-2. The transitions are shown by red dashed arrow.



**Figure S22.** Frontier orbitals of main orbitals in the transitions to excited state 29 of VR-Cz-2. The transitions are shown by red dashed arrow.