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# Supporting Information

## High-contrast and reversible mechanochromic luminescence of a D-π-A compound with a twisted molecular conformation

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**Table S1** TD-DFT results calculated for TPAANDCV at the M06-2X/6-31G(d,p) level.[a]

| Transition | $f$ | $\lambda_{ex}$ / nm | Dominant Components[b] |
|---|---|---|---|
| S1 ← S0 | 0.253 | 399 | LUMO ← HOMO–1 (82%)<br>LUMO ← HOMO (10%) |
| S2 ← S0 | 0.277 | 351 | LUMO+1 ← HOMO–1 (77%)<br>LUMO+1 ← HOMO (14%) |
| S6 ← S0 | 1.042 | 291 | LUMO ← HOMO–3 (52%)<br>LUMO ← HOMO–4 (41%) |
| S8 ← S0 | 0.292 | 278 | LUMO+4 ← HOMO (87%) |
| S9 ← S0 | 0.243 | 271 | LUMO+6 ← HOMO (60%)<br>LUMO+5 ← HOMO (30%) |

[a] transitions with oscillator strength higher than 0.03 shown. [b] Components with greater than 10% contribution shown. Percentage contribution approximated by 2 x $(ci)^2$ x 100%, where ci is the coefficient for the particular orbital rotation.

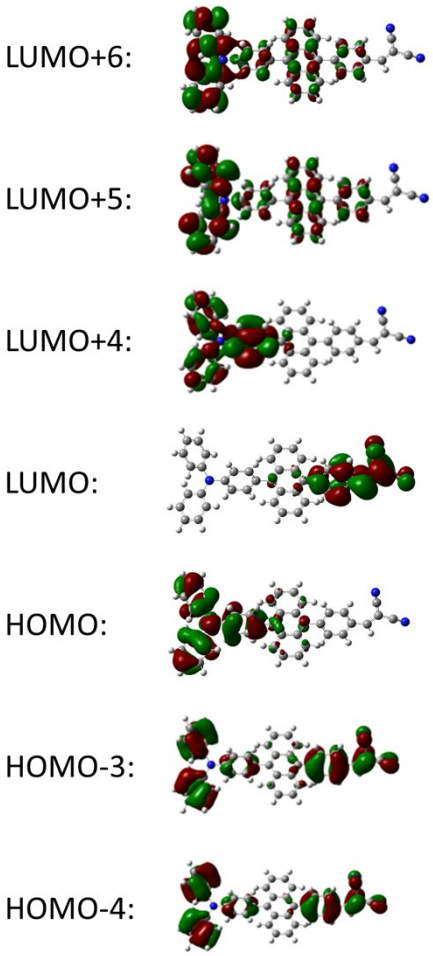


**Fig. S1** Molecular orbitals involved in the S6 ← S0, S8 ← S0 and S9 ← S0 transitions which may be responsible for the highest-energy absorption band of TPAANDCV.

**Table S2** TD-DFT results calculated for **1** at the M06-2X/6-31G(d,p) level.[a]

| Transition | $f$ | $\lambda_{ex}$ / nm | Dominant Components[b] |
|---|---|---|---|
| S1 ← S0 | 0.375 | 358 | LUMO ← HOMO–1 (59%)<br>LUMO ← HOMO (36%) |
| S7 ← S0 | 0.480 | 277 | LUMO+3 ← HOMO (71%)<br>LUMO+3 ← HOMO–1 (12%) |
| S8 ← S0 | 0.246 | 272 | LUMO+5 ← HOMO (75%)<br>LUMO+5 ← HOMO–1 (18%) |

[a] transitions with oscillator strength higher than 0.03 shown. [b] Components with greater than 10% contribution shown. Percentage contribution approximated by 2 x $(ci)^2$ x 100%, where ci is the coefficient for the particular orbital rotation.

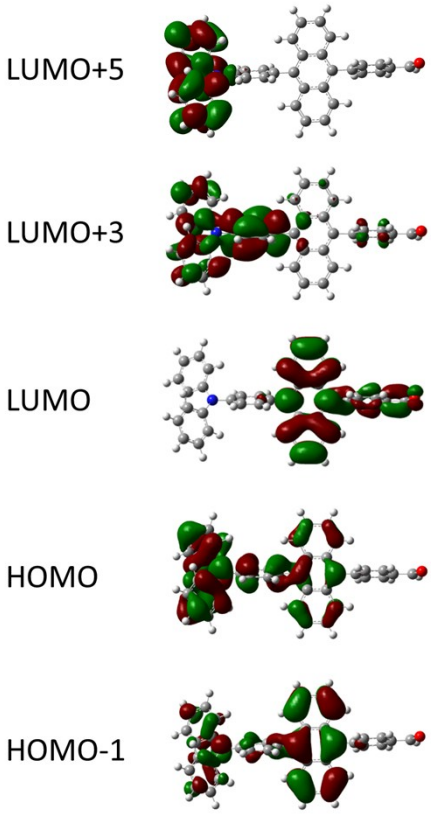


**Fig. S2** Molecular orbitals involved in the S1 ← S0, S7 ← S0 and S8 ← S0 transition of compound **1**.

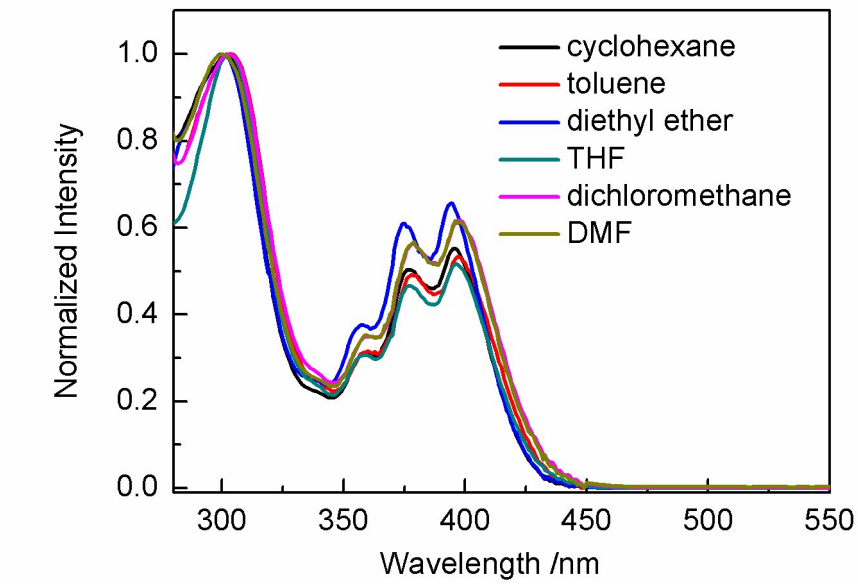


**Fig. S3** UV-vis absorption spectra of **1** in different solvents.

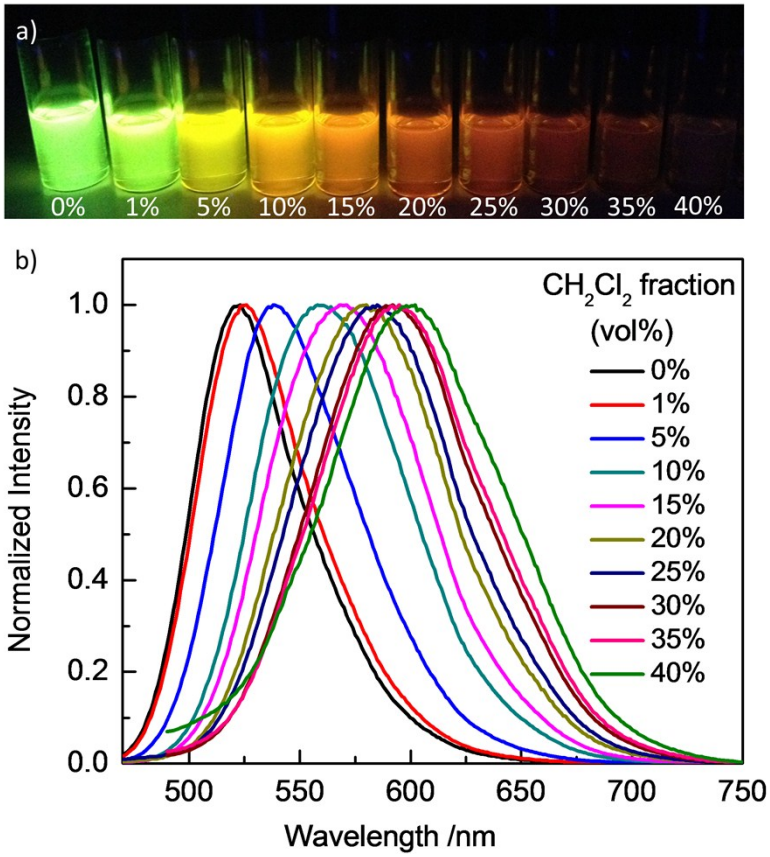


**Fig. S4** Emission colours (a) and emission spectra (b) of TPAANDCV in cyclohexane/dichloromethane mixtures with different dichloromethane fractions (vol %).

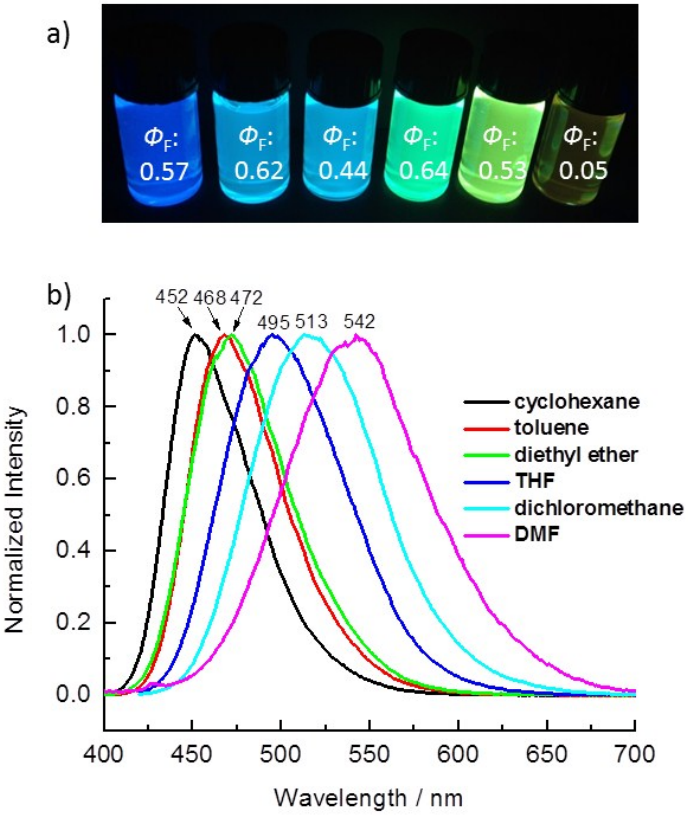


**Fig. S5** a) Photos of the solutions of **1** taken under UV light, given in the solvent order (from left to right) of cyclohexane, toluene, $Et_2O$, THF, $CH_2Cl_2$ and DMF; b) emission spectra of **1** in various solvents.

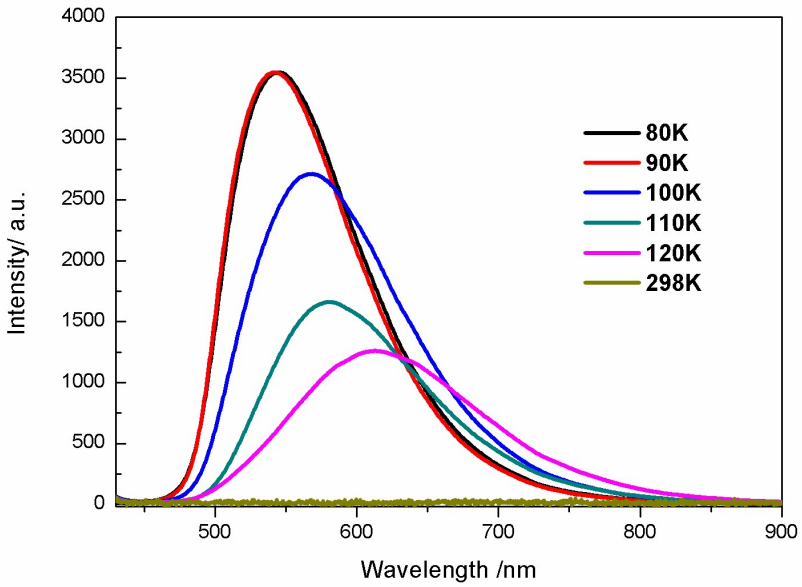


**Fig. S6** Temperature-dependent emission spectra of TPAANDCV measured in 2-MeTHF.

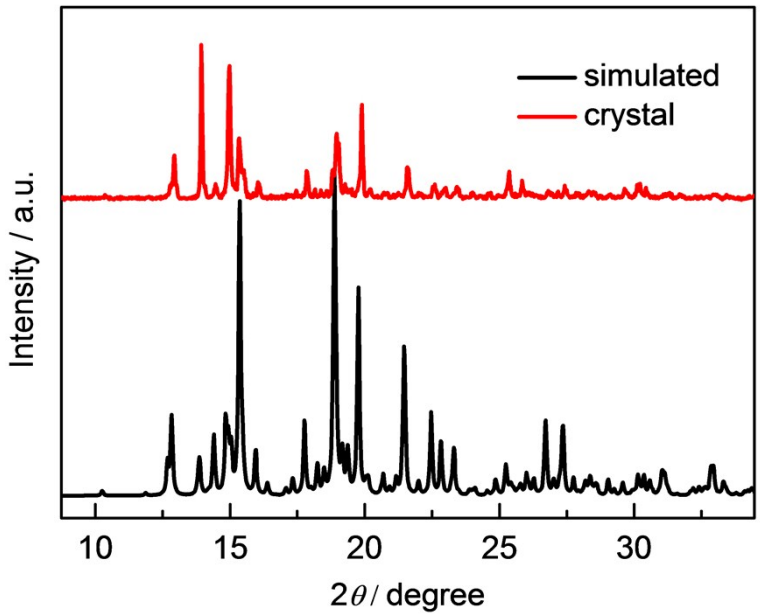


**Fig. S7** Comparison between simulated and measured PXRD patterns of the single crystals of TPAANDCV.

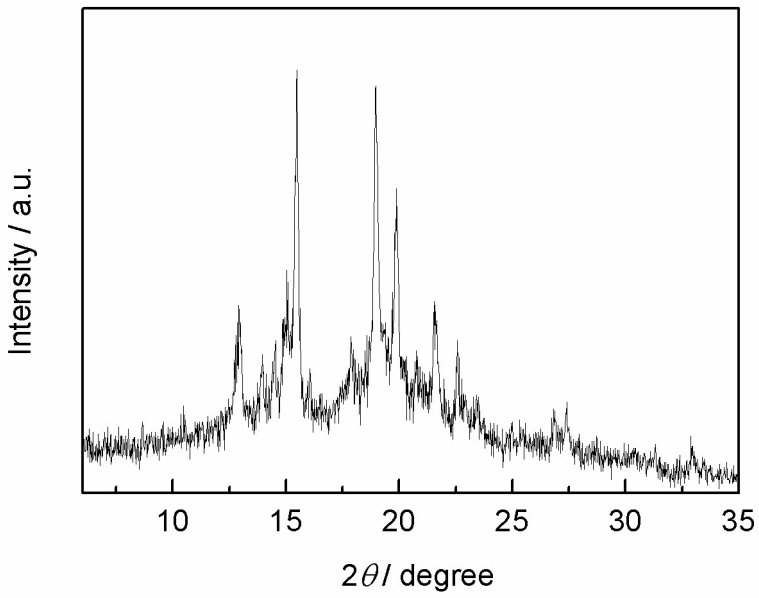


**Fig. S8** PXRD pattern showing the weak and broad diffuse halo of the ground powder of TPAANDCV.

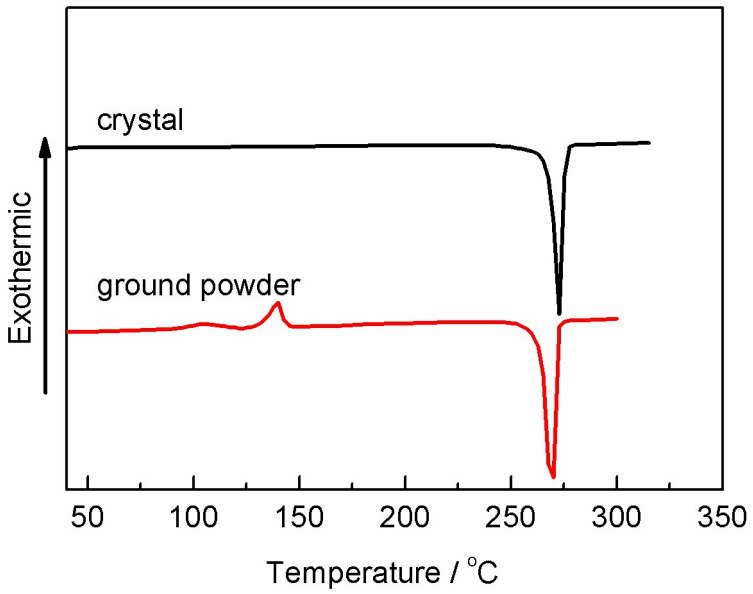


**Fig. S9** DSC curves of the crystals and the ground powder of TPAANDCV.

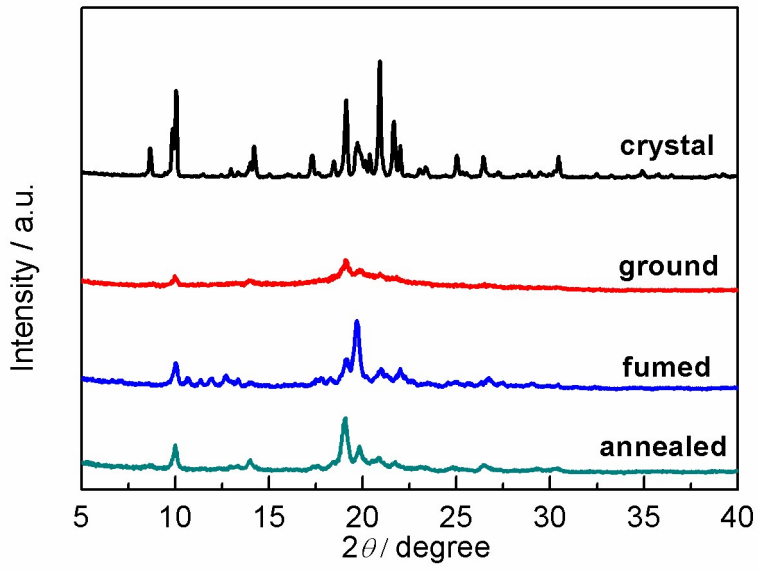


**Fig. S10** PXRD patterns of the crystals, ground powder and the annealed and vapour-fumed ground powders of compound **1**.

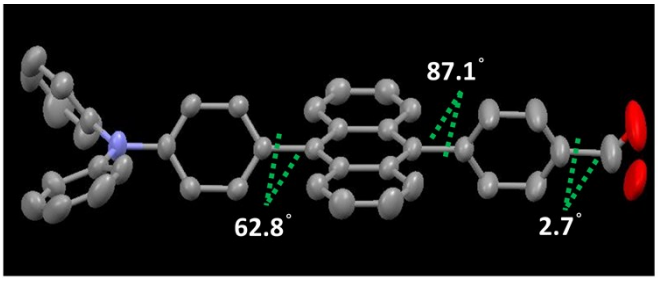


**Fig. S11** Single-crystal structure of compound **1**. The formyl group is disordered, but the 4-formylphenyl group keeps an almost planar confirmation.

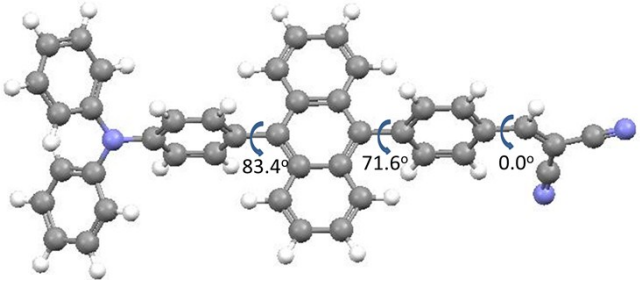


**Fig. S12** DFT-optimized ground-state geometry of TPAANDCV.

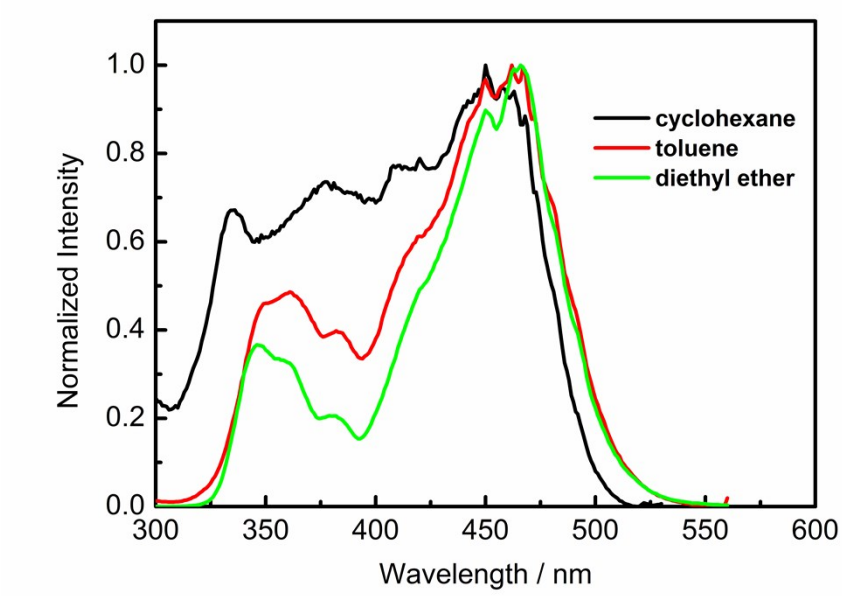


**Fig. S13** Fluorescence excitation spectra of TPAANDCV measured in different solvents ($10^{-5}$ M). The emission maximum of corresponding solution (452, 468 and 472 nm for cyclohexane, toluene and diethyl ether solutions, respectively) was adopted as the monitored wavelength.

**Table S3** The amount of THF and water used for preparing the solutions for AIE experiment.

| $10^{-4}$ M solution / mL | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 |
|---|---|---|---|---|---|---|---|---|---|---|
| Pure THF / mL | 3.6 | 3.2 | 2.8 | 2.4 | 2.0 | 1.6 | 1.2 | 0.8 | 0.4 | 0 |
| Pure $H_2O$ / mL | 0 | 0.4 | 0.8 | 1.2 | 1.6 | 2.0 | 2.4 | 2.8 | 3.2 | 3.6 |
| $H_2O$ fraction | 0% | 10% | 20% | 30% | 40% | 50% | 60% | 70% | 80% | 90% |

Single-crystal X-ray diffraction data of TPAANDCV:

$C_{42}H_{27}N_3$, $M$ = 573.67, monoclinic, $P2_1/c$, $a$ = 34.719(7) Å, $b$ = 7.6271(15) Å, $c$ = 11.943(2) Å, $\alpha$ = 90°, $\beta$ = 97.05(3)°, $\gamma$ = 90°, $V$ = 3138.5(11) Å$^3$, $Z$ = 4, $T$ = 293(2) K, 29723 reflections measured, 7134 unique; The final $wR_2$ was 0.1263 (all data) and $R_1$ was 0.0443 ($I \geq 2\sigma(I)$); CCDC number: 1056935.

Single-crystal X-ray diffraction data of **1**:

$C_{39}H_{27}NO$, $M$ = 525.62, triclinic, $P\text{-}1$, $a$ = 7.7432(15) Å, $b$ = 9.5790(19) Å, $c$ = 21.157(4) Å, $\alpha$ = 95.62(3)°, $\beta$ = 99.49(3)°, $\gamma$ = 108.71(3)°, $V$ = 1446.8(5) Å$^3$, $Z$ = 2, $T$ = 293(2) K, 14199 reflections measured, 6524 unique; The final $wR_2$ was 0.1921 (all data) and $R_1$ was 0.0584 ($I \geq 2\sigma(I)$); CCDC number: 1410073.

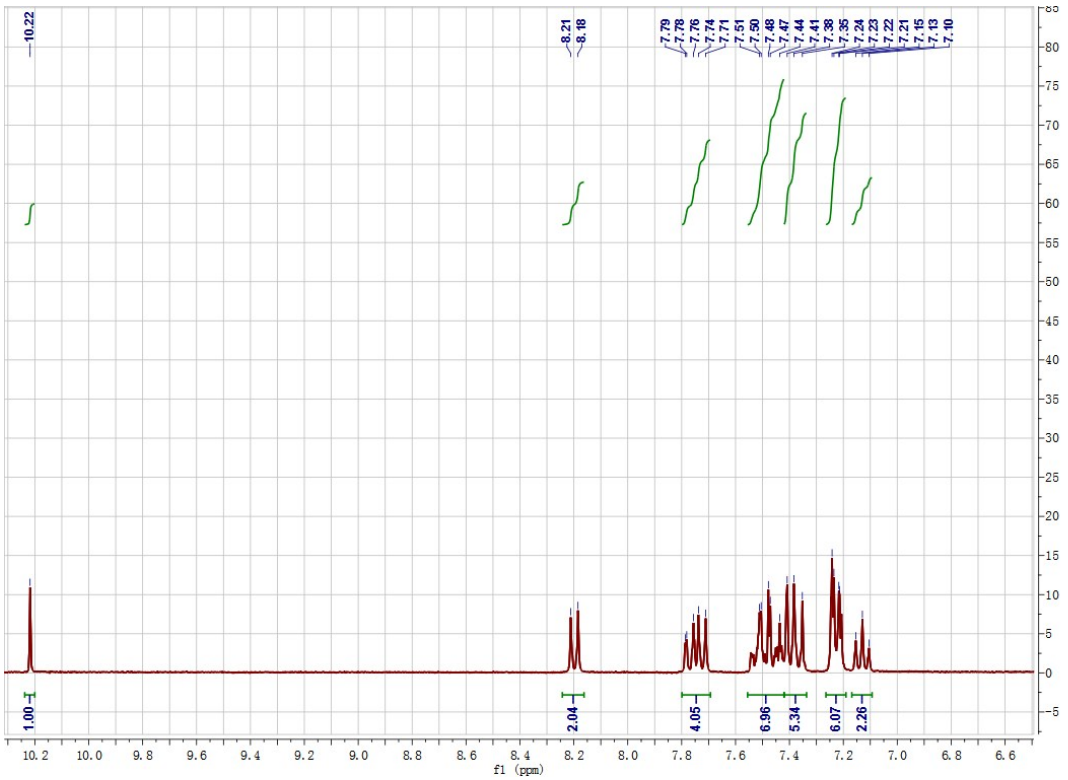


**Fig. S13** $^{1}$H NMR (300 MHz) spectrum of compound **1** in DMSO-$d_6$.

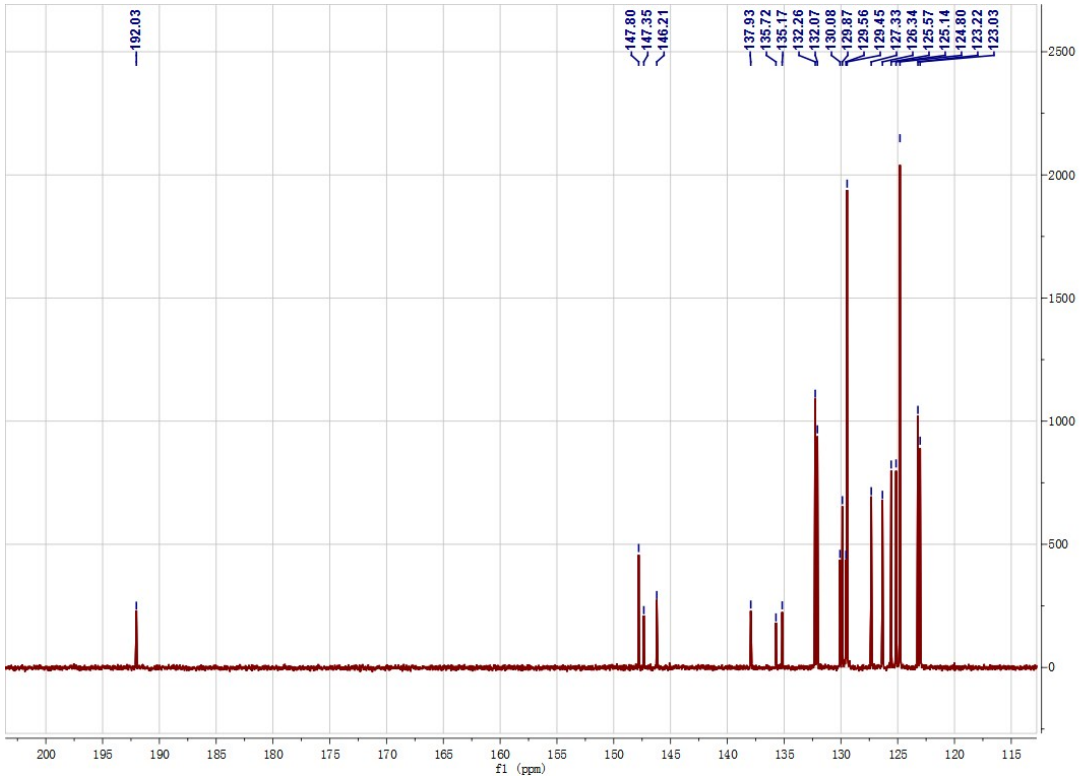


**Fig. S14** $^{13}$C{$^{1}$H} NMR (125 MHz) spectrum of compound **1** in $CDCl_3$.

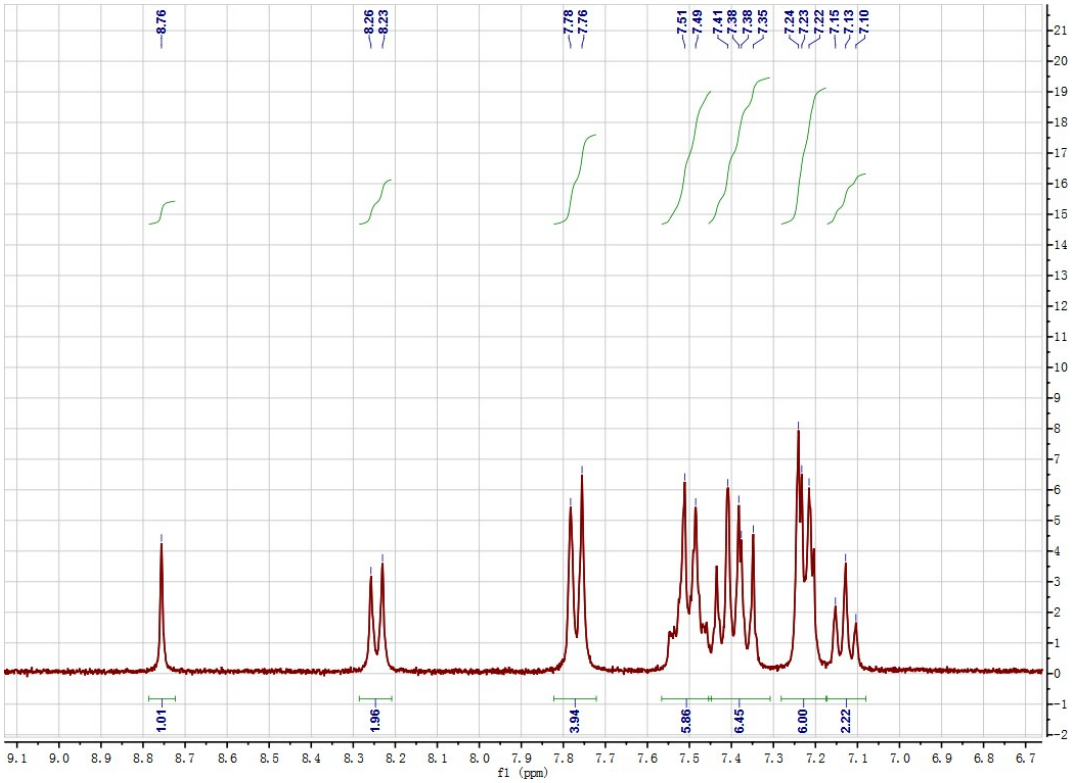


**Fig. S15** $^{1}$H NMR (300MHZ) spectrum of TPAANDCV in DMSO-$d_6$.

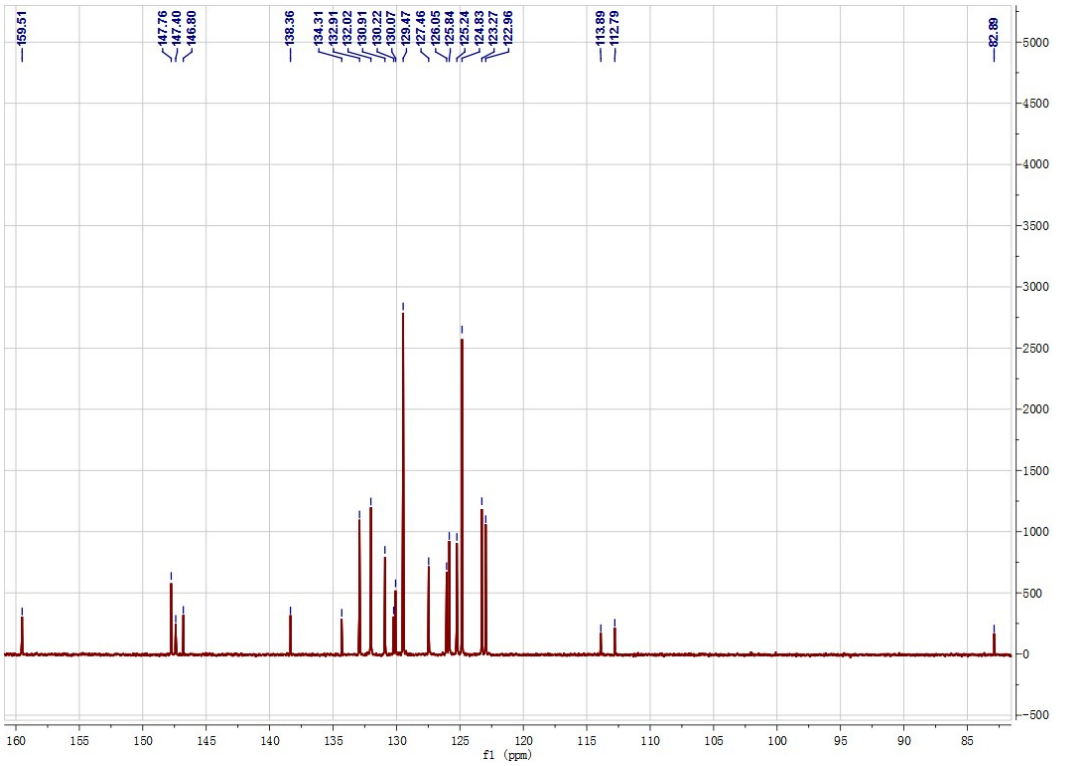


**Fig. S16** $^{13}$C{$^{1}$H} NMR (125 MHz) spectrum of TPAANDCV in $CDCl_3$.

***DFT Cartesian Coordinates***

Compound **TPAANDCV**

| Symbol | X | Y | Z |
|---|---|---|---|
| C | -8.60780200 | -0.42738000 | 0.40998200 |
| C | 0.01986000 | -0.12954200 | 0.12655900 |
| C | 4.34705300 | 0.02647000 | -0.02193400 |
| C | 1.51516300 | -0.07945900 | 0.07541500 |
| C | 6.53990900 | -1.04685400 | 0.31057200 |
| C | -0.70292400 | 0.94524300 | 0.68993600 |
| C | -4.32761800 | -0.25334500 | 0.24446100 |
| C | -0.66909300 | -1.24741800 | -0.39336000 |
| C | -2.11453200 | -1.29097300 | -0.35648500 |
| C | -2.14796300 | 0.90337900 | 0.73609400 |
| C | -2.83483700 | -0.21393000 | 0.20865900 |
| C | 6.41561700 | 1.27187600 | -0.50126400 |
| C | -7.16551200 | -0.31634800 | 0.30052100 |
| C | -9.62018500 | 0.21843500 | -0.24454000 |
| C | -2.77063900 | -2.42844900 | -0.93047400 |
| C | 3.68811100 | -0.64327000 | 1.02261600 |
| C | 0.02966300 | -2.35077300 | -0.98241700 |
| C | -2.06050800 | -3.46124800 | -1.48160200 |
| C | 8.08510700 | -3.27372300 | 1.05866400 |
| C | -5.00886500 | -1.11828300 | 1.11627000 |
| C | 6.17085900 | -2.33910500 | -0.09584600 |
| C | -0.03794500 | 2.08883900 | 1.24006400 |
| C | 7.50306200 | 1.20446100 | -1.38628300 |
| C | -6.47872400 | 0.55155400 | -0.57640500 |
| C | 8.46023800 | -1.98864600 | 1.45509400 |
| C | 7.69278400 | -0.88300900 | 1.09462300 |
| C | -5.09073700 | 0.57691100 | -0.59659700 |
| C | 2.29760300 | -0.70000900 | 1.06057300 |
| C | -6.39664100 | -1.14797500 | 1.14368700 |
| C | -9.44913500 | 1.21914400 | -1.25394400 |
| C | -0.63953900 | -3.42445800 | -1.50486400 |
| C | 2.17999000 | 0.59466700 | -0.95989200 |
| C | 7.71192800 | 3.61798600 | -1.34805400 |
| C | -10.98005600 | -0.10444500 | 0.07875200 |
| C | 5.98569600 | 2.52754700 | -0.04408700 |
| C | -2.83638900 | 2.00129900 | 1.34790600 |
| C | -0.73843300 | 3.12179300 | 1.80213700 |
| C | 6.93449900 | -3.44042200 | 0.28559400 |
| C | 3.56995700 | 0.64209300 | -1.01730200 |

| | | | |
|---|---|---|---|
| C | 8.14809500 | 2.36960600 | -1.79609300 |
| C | 6.62545900 | 3.68837900 | -0.47400400 |
| C | -2.15807900 | 3.07500400 | 1.85962700 |
| H | 1.11238800 | -2.31727500 | -1.01177300 |
| H | -3.85381700 | -2.46153600 | -0.93171000 |
| H | 7.83707600 | 0.23728300 | -1.74673000 |
| H | -2.58420300 | -4.31022500 | -1.91104100 |
| H | 1.04470400 | 2.11977500 | 1.20692600 |
| H | 4.27066900 | -1.11725000 | 1.80510500 |
| H | 9.34946900 | -1.84368200 | 2.06184800 |
| H | 5.28646100 | -2.47246900 | -0.70982300 |
| H | 5.15135700 | 2.58564200 | 0.64692700 |
| H | 1.80905100 | -1.22029700 | 1.87945100 |
| H | -0.08667700 | -4.24768500 | -1.94740700 |
| H | -4.57969100 | 1.24827700 | -1.27937200 |
| H | -6.90345700 | -1.82129200 | 1.82980100 |
| H | 4.06091200 | 1.15686600 | -1.83596700 |
| H | -3.91792300 | 1.97162500 | 1.40937800 |
| H | -7.02467400 | 1.20432600 | -1.24536800 |
| H | 1.59855900 | 1.07629400 | -1.74080200 |
| H | 8.21252100 | 4.52399800 | -1.67510800 |
| H | -4.44018900 | -1.76492200 | 1.77691700 |
| H | -2.70572800 | 3.89300700 | 2.31823400 |
| H | 7.98107200 | 0.11220900 | 1.41578500 |
| H | -8.94672700 | -1.15425500 | 1.14435600 |
| H | 8.68164000 | -4.13346100 | 1.34744900 |
| H | 8.98820300 | 2.29986100 | -2.48108900 |
| H | 6.28040100 | 4.65207900 | -0.11046800 |
| H | 6.63474300 | -4.43315800 | -0.03783000 |
| H | -0.21074200 | 3.97703900 | 2.21358100 |
| N | 5.76256200 | 0.08240400 | -0.07041600 |
| N | -12.08089900 | -0.37085800 | 0.34552500 |
| N | -9.33200300 | 2.03495000 | -2.07588300 |

Compound **1**

| **Symbol** | **X** | **Y** | **Z** |
|---|---|---|---|
| C | 9.55296500 | -0.01464300 | 0.11426700 |
| C | 0.90597900 | -0.00280200 | 0.03751700 |
| C | -3.42596500 | 0.00119800 | -0.00691900 |
| C | -0.59053700 | -0.00133600 | 0.02245100 |
| C | -5.56496700 | -1.14364400 | 0.41627600 |
| C | 1.61617400 | -1.15475900 | -0.36784500 |

| | | | |
|---|---|---|---|
| C | 5.26040400 | -0.00658400 | 0.07789200 |
| C | 1.61016000 | 1.14799900 | 0.45635400 |
| C | 3.05673500 | 1.15130500 | 0.46191500 |
| C | 3.06253700 | -1.16023000 | -0.34596400 |
| C | 3.76414800 | -0.00511000 | 0.06495100 |
| C | -5.55347500 | 1.14931900 | -0.47586100 |
| C | 8.07380500 | -0.01075300 | 0.09707300 |
| C | 3.72987000 | 2.35114700 | 0.86352400 |
| C | -2.71898700 | -0.59578400 | 1.04987500 |
| C | 0.92774400 | 2.33095500 | 0.89019000 |
| C | 3.03487200 | 3.46243900 | 1.25893400 |
| C | -6.99646500 | -3.40549100 | 1.27755500 |
| C | 5.96583000 | -0.11342700 | 1.28714000 |
| C | -6.70183300 | -1.00099000 | 1.22755700 |
| C | 0.94037900 | -2.33658300 | -0.81480900 |
| C | -6.67143900 | 1.00844900 | -1.31334800 |
| C | 7.37684500 | 0.09731400 | -1.11572500 |
| C | -5.86119100 | -3.55079000 | 0.47793600 |
| C | -5.15404000 | -2.43258500 | 0.04079100 |
| C | 5.98770400 | 0.09863800 | -1.12278700 |
| C | -1.32692900 | -0.60253200 | 1.05442400 |
| C | 7.35854600 | -0.11579100 | 1.29625400 |
| C | 1.61323300 | 3.44983500 | 1.28028000 |
| C | -1.30434000 | 0.60139400 | -1.02442700 |
| C | -6.96181000 | 3.41334800 | -1.36890000 |
| C | -5.14983400 | 2.43754700 | -0.09022300 |
| C | 3.74154300 | -2.36048100 | -0.73617900 |
| C | 1.63159300 | -3.45610300 | -1.19284300 |
| C | -7.41310900 | -2.12431600 | 1.64415400 |
| C | -2.69618500 | 0.59714800 | -1.04865600 |
| C | -7.37147500 | 2.13288200 | -1.74569700 |
| C | -5.84524300 | 3.55687600 | -0.54306600 |
| C | 3.05256300 | -3.47048300 | -1.14555300 |
| H | -0.15580700 | 2.32490400 | 0.90436500 |
| H | 4.81335300 | 2.36973900 | 0.84813900 |
| H | -6.98588600 | 0.01633000 | -1.61931100 |
| H | 3.57005000 | 4.35895600 | 1.55790000 |
| H | -0.14270200 | -2.32910400 | -0.84930000 |
| H | -3.26587100 | -1.05283700 | 1.86745900 |
| H | -5.52947000 | -4.54066000 | 0.17774100 |
| H | -7.02198900 | -0.00829000 | 1.52557900 |
| H | -4.29204600 | 2.55342800 | 0.56372300 |
| H | -0.79987300 | -1.06775000 | 1.88242300 |
| H | 1.07185300 | 4.33347100 | 1.60519100 |

| | | | |
|---|---|---|---|
| H | 5.44753300 | 0.18391700 | -2.06082500 |
| H | 7.89760400 | -0.20231100 | 2.23700200 |
| H | -3.22524000 | 1.05518800 | -1.87732400 |
| H | 4.82457600 | -2.38028500 | -0.70202700 |
| H | 7.94680700 | 0.18103600 | -2.03561700 |
| H | -0.75937500 | 1.06585100 | -1.84117100 |
| H | -7.50548600 | 4.28737000 | -1.71377500 |
| H | 5.41337800 | -0.19720700 | 2.21793900 |
| H | 3.59212700 | -4.36699700 | -1.43647700 |
| H | -4.28141100 | -2.54984100 | -0.59295300 |
| H | -7.54911400 | -4.27867300 | 1.61007600 |
| H | -8.23441500 | 2.00563800 | -2.39307000 |
| H | -5.51934400 | 4.54619400 | -0.23479600 |
| H | -8.29066000 | -1.99563500 | 2.27129000 |
| H | 1.09520700 | -4.33872700 | -1.52859400 |
| N | -4.84427800 | 0.00232100 | -0.02179800 |
| H | 10.00264000 | -0.10657600 | 1.12837700 |
| O | 10.25733300 | 0.07264300 | -0.87380200 |