*Electronic Supplementary Information*

# Robust and color-tunable afterglows from guanidine derivatives

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**Fig. S16** (a) Photographs of GCA ground powders taken under or after ceasing 254, 312 and 365 nm UV lights. (b) Prompt and (c) delayed ($t_d$ = 1 ms) emission spectra of the ground powders for GCA with different $\lambda_{ex}$s. (d) Normalized prompt and (e) delayed ($t_d$ = 1 ms) emission spectra of the ground powders for GCA with different $\lambda_{ex}$s.

**Fig. S17** (a) p-RTP lifetimes at varying $\lambda_{em}$s for GCA ground powders. (b) Fluorescence lifetimes at varying $\lambda_{em}$s for GCA ground powders ($\lambda_{ex}$ = 363 nm).

**Reference**

**Experimental Section**

***Materials.*** Dicyandiamide (DCDA, > 98.0%) and glycocyamine (GCA, > 97.0%) were purchased from TCI Development Co., Ltd. Methanol (MeOH), tetrahydrofuran (THF) and *N*,*N*-dimethylformamide (DMF) were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). Pure water ($H_2O$) was bought from Hangzhou Wahaha Group Co., Ltd (Zhejiang, China).

***Instruments.*** Prompt and delayed emission spectra, time-resolved measurements in nanosecond (ns) and millisecond (ms) scales as well as the quantum efficiencies ($\lambda_{ex}$ = 312 nm) for single crystals were conducted on an Edinburgh FLS1000 photoluminescence spectrometer. Emission spectra for solutions were collected on a PerkinElmer LS 55 fluorescence spectrometer. Absorption of single crystals were measured on a PerkinElmer Lambda 750s UV/Vis spectrometer. Single crystal diffractogram data were collected by a Bruker D8 VENTURE X-ray Diffractometer. All photographs and videos were taken by a digital camera (Sony α7sII, Japan).

***Purification of DCDA and GCA.*** DCDA was firstly dissolved into DMF to form nearly saturated solution and filtered. The preliminarily purified DCDA was precipitated by adding the filtered solution into pure water dropwise under stirring vigorously. The precipitates were collected through filtration and then dissolved in methanol for further single crystal cultivation. Single crystals of DCDA were obtained by evaporating its dilute solution slowly at room temperature and separated from the solvent prior to total evaporation to guarantee purity.

The purification process for GCA is as same as that for DCDA, except that methanol was used in the first step of dissolution rather than DMF.

***Anti-counterfeiting pattern preparation.*** The pattern with corals and clownfishes was carved on a commercially available nonluminescent rubber stamper. Then, the carved pattern on the stamper was filled with ground powders of DCDA and directly pictured under 312 and 365 nm UV irradiation.

***Computational method.*** The single molecule (monomer), dimer and trimer of DCDA were extracted from their single crystal data. Time dependent density functional theory (TD-DFT) was

used to calculate the HOMO and LUMO electron densities, energy levels and molecular electrostatic potential using B3LYP hybrid functional and 6-31G (d,p) basis set. All TD-DFT calculations were performed within Gaussian 09 (version 9.5) program. Nature transition orbital (NTO) analysis was carried out with Multiwfn at 6-31G (d,p) level of theory with B3LYP hybrid functional.[1] Spin-orbit coupling calculations were performed with ORCA 4.2.1 using B3LYP hybrid functional and 6-31G (d,p) basis set.

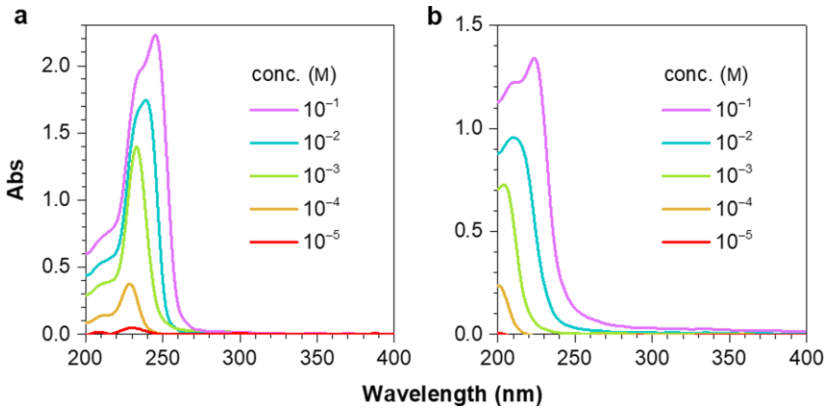


**Fig. S1** Absorption spectra of different (a) DCDA/MeOH and (b) GCA/$H_2O$ solutions.

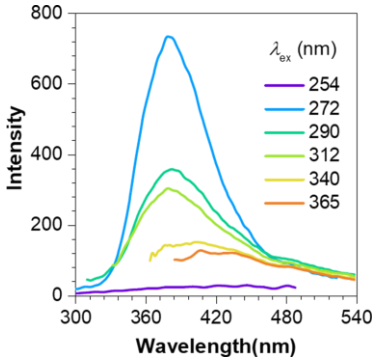


**Fig. S2** Emission spectra of 1 M DCDA/DMF solution with different $\lambda_{ex}$s.

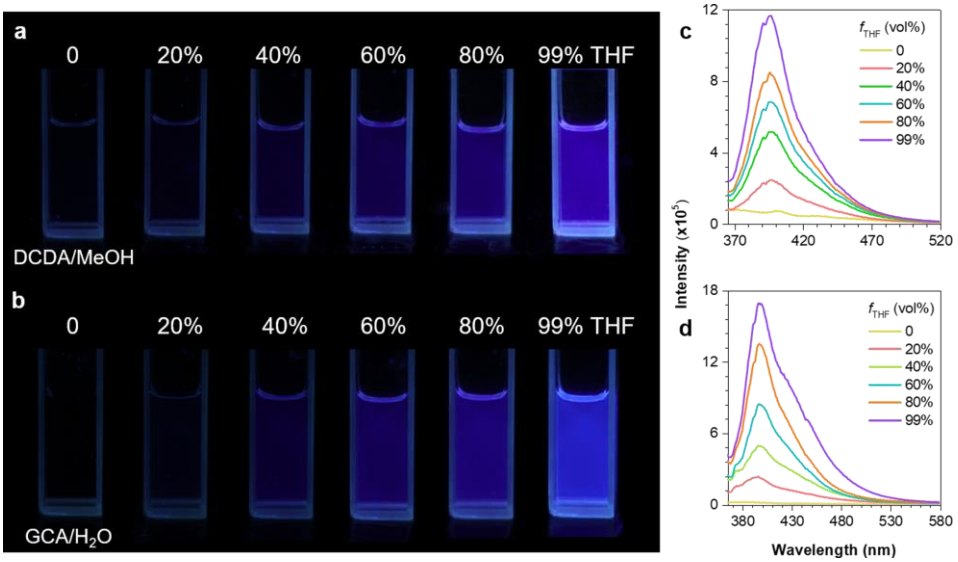


**Fig. S3** (a, b) Photographs and (c, d) emission spectra under 312 nm UV irradiation of (a, c) DCDA in MeOH and MeOH/THF mixtures and (b, d) GCA in $H_2O$ and $H_2O$/THF mixtures with different THF volume fractions. Concentration = $1 \times 10^{-3}$ M.

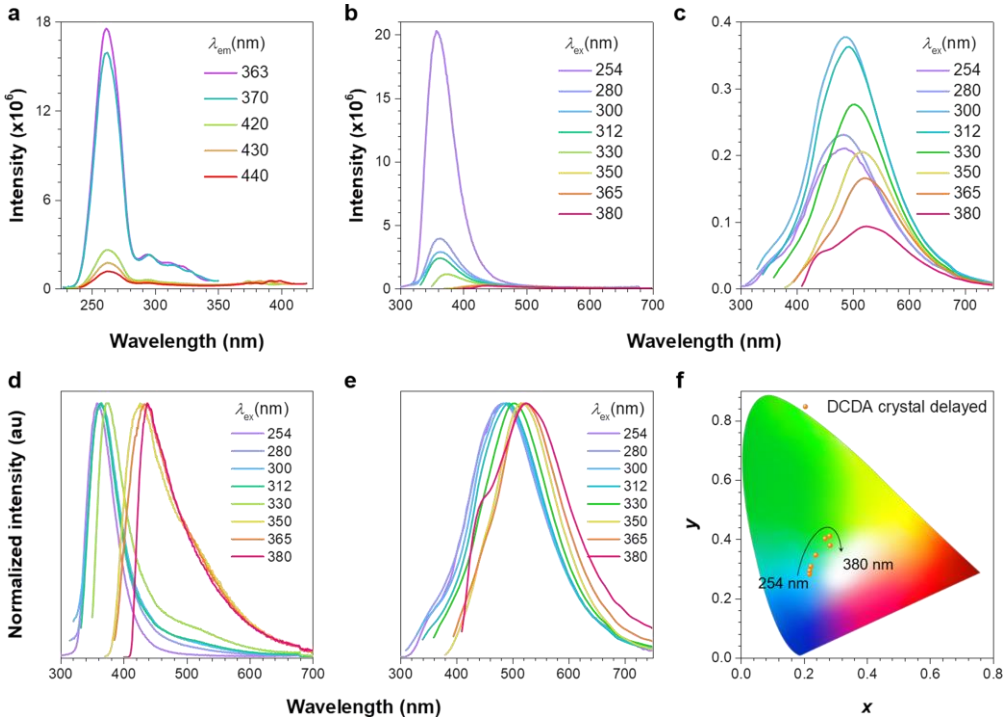


**Fig. S4** (a) Excitation spectra of DCDA single crystals. (b) Prompt and (c) delayed ($t_d$ = 1 ms) emission spectra of DCDA single crystals with different $\lambda_{ex}$s. (d) Normalized prompt and (e) delayed ($t_d$ = 1 ms) emission spectra of DCDA single crystals with different $\lambda_{ex}$s. (f) CIE coordinate diagram of the delayed emission for DCDA single crystals with different $\lambda_{ex}$s.

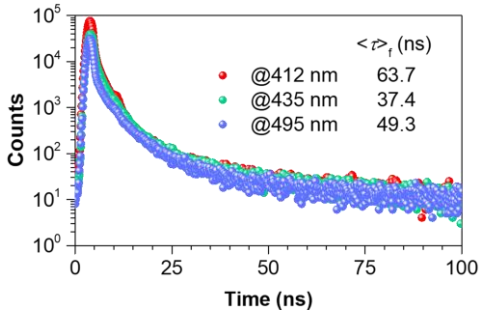


**Fig. S5** Fluorescence lifetimes at varying emission wavelengths ($\lambda_{em}$s) for DCDA single crystals ($\lambda_{ex}$ = 363 nm).

**Table S1** Fluorescence lifetimes for single crystals of DCDA and GCA and ground powders of DCDA.[a)]

| Compound | $\lambda_{ex}$ [nm] | $\lambda_{em}$ [nm] | $<\tau>_1$ [ns] | $<\tau>_2$ [ns] | $<\tau>_3$ [ns] | $<\tau>_4$ [ns] | $A_1$ [%] | $A_2$ [%] | $A_3$ [%] | $A_4$ [%] | $\chi^2$ | $<\tau>_{f\text{-ave}}$ [ns] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DCDA single crystals | 363 | 412 | 0.8 | 2.8 | 10.1 | 63.7 | 13.1 | 67.3 | 16.6 | 3.0 | 1.08 | 25.8 |
| | | 435 | 0.6 | 2.6 | 7.9 | 37.4 | 13.4 | 61.9 | 21.7 | 3.0 | 1.05 | 13.2 |
| | | 495 | 0.6 | 3.5 | 10.0 | 49.3 | 28.2 | 48.9 | 20.9 | 2.0 | 1.13 | 15.3 |
| GCA single crystals | 363 | 440 | 3.3 | -- | -- | -- | 100 | -- | -- | -- | 1.03 | 3.3 |
| | | 590 | 1.4 | -- | -- | -- | 100 | -- | -- | -- | 1.14 | 1.4 |
| DCDA ground powders | 363 | 412 | 0.6 | 3.1 | 9.9 | 50.5 | 4.3 | 34.8 | 27.8 | 33.1 | 1.18 | 42.5 |
| | | 435 | 0.6 | 2.8 | 8.9 | 48.4 | 12.3 | 62.7 | 16.3 | 8.7 | 1.22 | 29.6 |
| | | 495 | 1.6 | 5.6 | 24.0 | 155.5 | 8.6 | 51.2 | 22.5 | 17.7 | 1.18 | 123.2 |
| GCA single crystals | 363 | 440 | 0.7 | 2.9 | -- | -- | 5.1 | 94.9 | -- | -- | 1.01 | 2.9 |
| | | 590 | 0.5 | -- | -- | -- | 100 | -- | -- | -- | 1.12 | 0.5 |

[a)] $<\tau>_{f\text{-ave}}$ is the average fluorescence lifetime of every components adopted from the lifetime measurements. $<\tau>_{f\text{-ave}} = (A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2 + A_4\tau_4^2) / (A_1\tau_1 + A_2\tau_2 + A_3\tau_3 + A_4\tau_4)$

**Table S2** p-RTP lifetimes for single crystals of DCDA and GCA and ground powders of DCDA.[a)]

| Compound | $\lambda_{ex}$ [nm] | $\lambda_{em}$ [nm] | $<\tau>_1$ [ms] | $<\tau>_2$ [ms] | $<\tau>_3$ [ms] | $<\tau>_4$ [ms] | $A_1$ [%] | $A_2$ [%] | $A_3$ [%] | $A_4$ [%] | $\chi^2$ | $<\tau>_{p\text{-ave}}$ [ms] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DCDA single crystals | 280 | 485 | 8.3 | 40.8 | 186.9 | 598.6 | 2.8 | 15.4 | 36.3 | 45.5 | 1.09 | 507.5 |
| | 312 | 495 | 16.2 | 99.4 | 485.4 | -- | 17.9 | 31.5 | 50.6 | -- | 1.05 | 437.3 |
| | 365 | 525 | 14.9 | 42.1 | 134.5 | 426.6 | 8.3 | 30.2 | 20.2 | 41.3 | 1.19 | 365.2 |
| GCA single crystals | 254 | 520 | 1.9 | 13.1 | 70.6 | 260.3 | 11.7 | 35.1 | 32.0 | 21.2 | 1.11 | 194.0 |
| | 285 | 510 | 13.5 | 54.9 | 274.2 | -- | 20.8 | 33.1 | 46.1 | -- | 1.08 | 242.2 |
| | 285 | 690 | 0.5 | 6.1 | 41.0 | -- | 9.9 | 37.9 | 52.2 | -- | 1.10 | 37.5 |
| | 312 | 475 | 19.2 | 74.7 | 383.5 | -- | 18.4 | 22.7 | 58.9 | -- | 1.21 | 357.0 |
| | 365 | 525 | 1.6 | 13.2 | 56.0 | 283.9 | 7.7 | 23.4 | 30.2 | 38.7 | 1.12 | 247.6 |
| DCDA ground powders | 280 | 485 | 3.4 | 36.3 | 364.6 | -- | 17.0 | 31.8 | 51.2 | -- | 1.21 | 344.5 |
| | 312 | 495 | 14.6 | 60.9 | 416.5 | -- | 14.4 | 30.9 | 54.7 | -- | 1.13 | 386.3 |
| | 365 | 525 | 20.1 | 60.2 | 331.0 | -- | 24.3 | 34.7 | 41.0 | -- | 1.21 | 286.6 |
| GCA ground powders | 254 | 520 | 1.7 | 9.1 | 27.5 | 136.6 | 4.3 | 18.8 | 32.6 | 44.3 | 1.18 | 119.7 |
| | 285 | 510 | 2.8 | 9.8 | 29.0 | 163.5 | 4.2 | 21.9 | 30.8 | 43.1 | 1.11 | 144.5 |
| | 285 | 690 | 0.2 | 6.5 | 7.7 | -- | 4.6 | 37.5 | 57.6 | -- | 1.15 | 7.3 |
| | 312 | 475 | 1.2 | 6.3 | 21.0 | 133.9 | 2.5 | 25.8 | 47.6 | 24.1 | 1.13 | 103.3 |
| | 365 | 525 | 1.4 | 6.7 | 26.7 | 134.2 | 3.3 | 12.8 | 31.4 | 52.5 | 1.17 | 121.5 |

[a)] $<\tau>_{p\text{-ave}}$ is the average p-RTP lifetime of every components adopted from the lifetime measurements. $<\tau>_{p\text{-ave}} = (A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2 + A_4\tau_4^2) / (A_1\tau_1 + A_2\tau_2 + A_3\tau_3 + A_4\tau_4)$

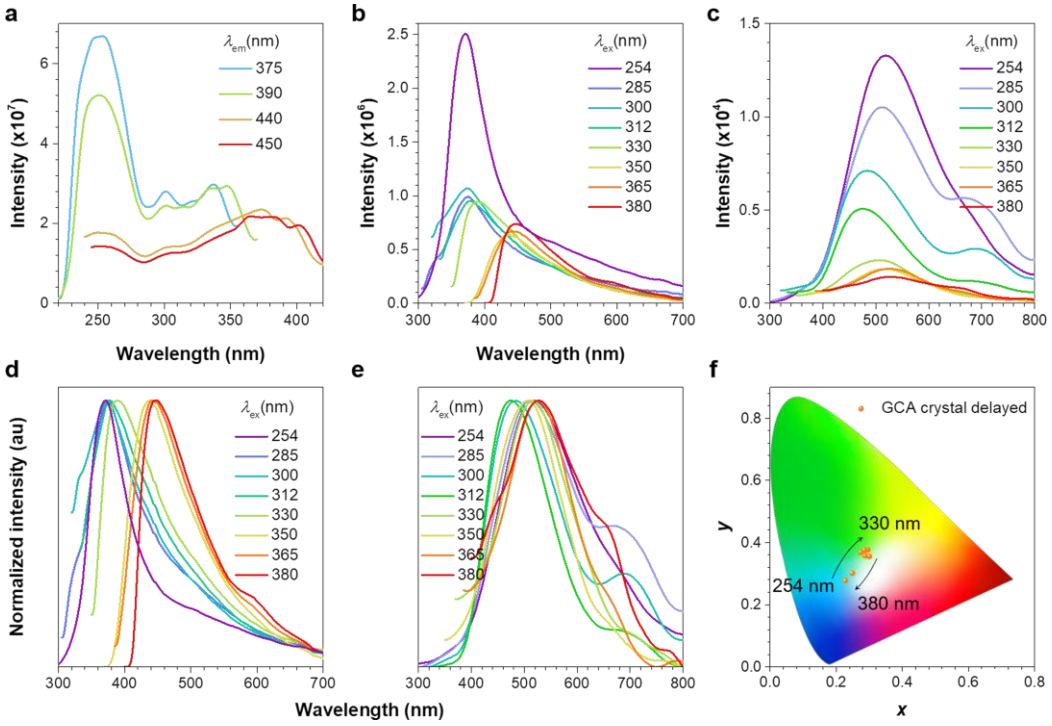


**Fig. S6** (a) Excitation spectra of GCA single crystals. (b) Prompt and (c) delayed ($t_d$ = 1 ms) emission spectra of GCA single crystals with different $\lambda_{ex}$s. (d) Normalized prompt and (e) delayed ($t_d$ = 1 ms) emission spectra of GCA single crystals with different $\lambda_{ex}$s. (f) CIE coordinate diagram of the delayed emission for GCA single crystals with different $\lambda_{ex}$s.

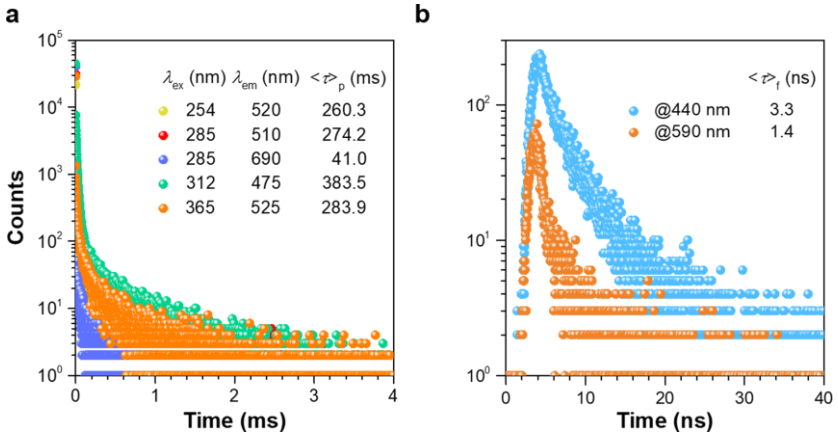


**Fig. S7** (a) p-RTP lifetimes at varying $\lambda_{em}$s for GCA single crystals. (b) Fluorescence lifetimes at varying $\lambda_{em}$s for GCA single crystals ($\lambda_{ex}$ = 363 nm).

**Table S3** Single crystal data of DCDA and GCA.

| | DCDA (296 K) | GCA (295 K) |
|---|---|---|
| Formula | $C_2H_4N_4$ | $C_3H_7N_3O_2$ |
| Formula Weight | 84.09 | 117.12 |
| Wavelength (Å) | 1.54178 | 1.54178 |
| Space Group | C2/c | P21/n |
| Cell Length (Å) | a=14.9827 (5)<br>b=4.4969 (1)<br>c=13.1144 (4) | a=4.9399 (2)<br>b=6.0035 (3)<br>c=17.1666 (8) |
| Cell Angle (°) | α=90<br>β=115.361 (1)<br>γ=90 | α=90<br>β=94.272 (2)<br>γ=90 |
| Cell Volume (Å$^3$) | 798.44 (4) | 507.69 (4) |
| Z | 8 | 4 |
| Density (g/cm$^3$) | 1.399 | 1.532 |
| F (000) | 352.0 | 248.0 |
| $h_{max}$, $k_{max}$, $l_{max}$ | 18, 5, 15 | 5, 7, 20 |

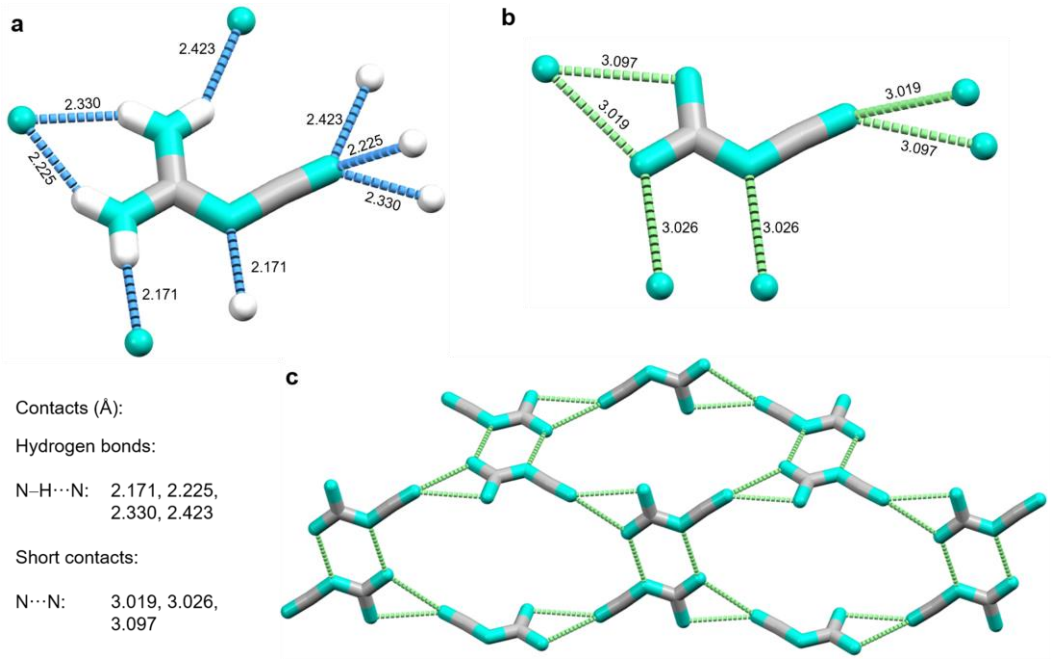


**Fig. S8** Crystal structure with (a) hydrogen bonds and (b) N···N short contacts around one DCDA molecule. (c) Fragmental molecular packing with through-space conjugation (TSC) for DCDA.

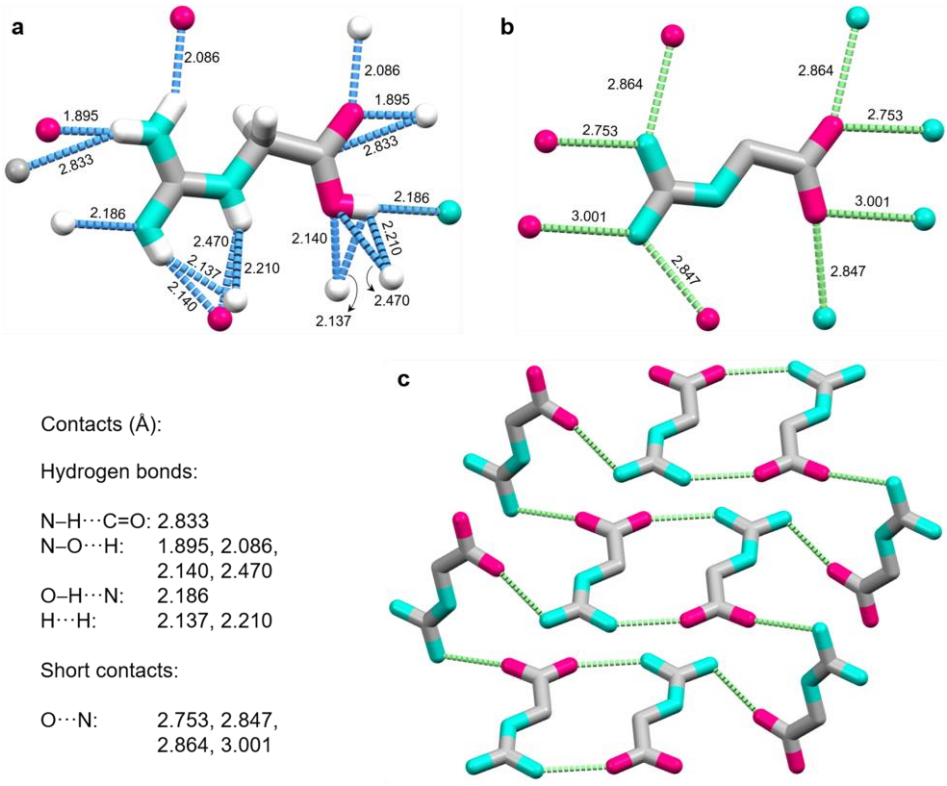


**Fig. S9** Crystal structure with (a) hydrogen bonds and (b) O···N short contacts around one GCA molecule. (c) Fragmental molecular packing with TSC for GCA.

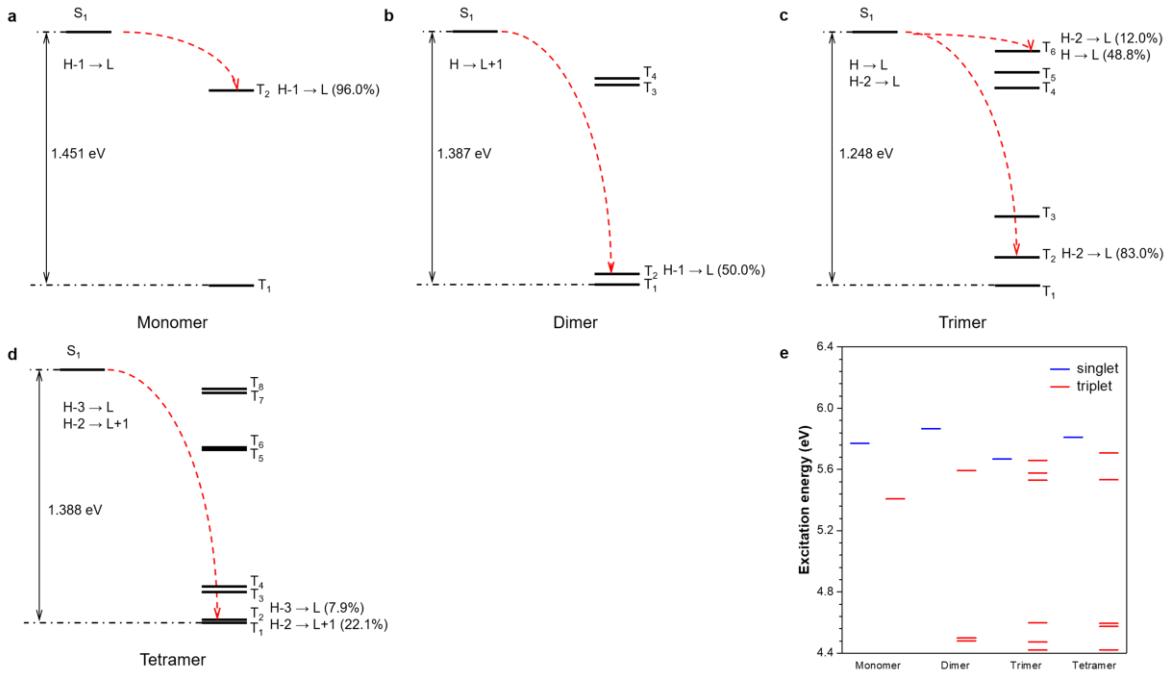


**Fig. S10** The ISC channels of (a) monomer, (b) dimer, (c) trimer and (d) tetramer of DCDA. (e) The excitation energy diagram of monomer, dimer, trimer and tetramer of DCDA.

**Table S4** Transition configurations of DCDA. The ones labelled in red are allowed transitions.

| Aggregation state | Excited state | Excitation energy [eV] | Transition configuration |
|---|---|---|---|
| monomer | $S_1$ | 5.7706 | H-1→L |
| | $T_1$ | 4.3198 | H→L |
| | $T_2$ | 5.4077 | H-1→L |
| dimer | $S_1$ | 5.8664 | H→L+1 |
| | $T_1$ | 4.4797 | H-1→L+1, H→L |
| | $T_2$ | 4.4981 | H-1→L, H→L+1 |
| | $T_3$ | 5.5926 | H-2→L |
| | $T_4$ | 5.5930 | H-3→L |
| trimer | $S_1$ | 5.6678 | H-2→L, H→L |
| | $T_1$ | 4.4201 | H-1→L+1, H-1→L+2, H→L+1, H→L+2 |
| | $T_2$ | 4.4725 | H-2→L, H-1→L |
| | $T_3$ | 4.5988 | H-1→L+2, H→L+1 |
| | $T_4$ | 5.5297 | H-3→L+1, H-3→L+2 |
| | $T_5$ | 5.5770 | H-5→L |
| | $T_6$ | 5.6594 | H-2→L, H→L |
| tetramer | $S_1$ | 5.8101 | H-3→L, H-2→L+1, H→L+1 |
| | $T_1$ | 4.4219 | H-3→L+1, H-2→L, H-1→L+1, H→L+1 |
| | $T_2$ | 4.4219 | H-3→L, H-3→L+1, H-2→L, H-2→L+1, H-1→L, H-1→L+1 |
| | $T_3$ | 4.5747 | H-3→L+3, H-2→L+2, H→L+2 |
| | $T_4$ | 4.5937 | H-3→L+2, H-2→L+3, H→L+3 |
| | $T_5$ | 5.5328 | H-6→L+1, H-5→L+1, H-4→L |
| | $T_6$ | 5.5328 | H-6→L, H-5→L, H-5→L+1, H-4→L, H-4→L+1 |
| | $T_7$ | 5.7074 | H-7→L+1, H-6→L+2, H-6→L+3 |
| | $T_8$ | 5.7078 | H-7→L+2, H-6→L+1, H-6→L+2, H-5→L+3, H-4→L+2 |

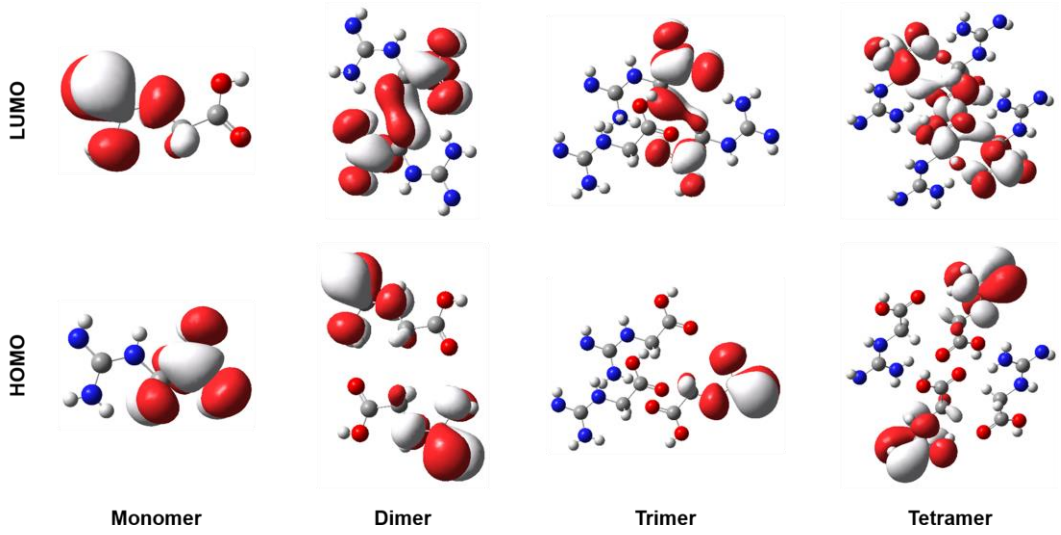


**Fig. S11** Electron densities of the HOMO and LUMO levels for monomer, dimer, trimer and tetramer of GCA.

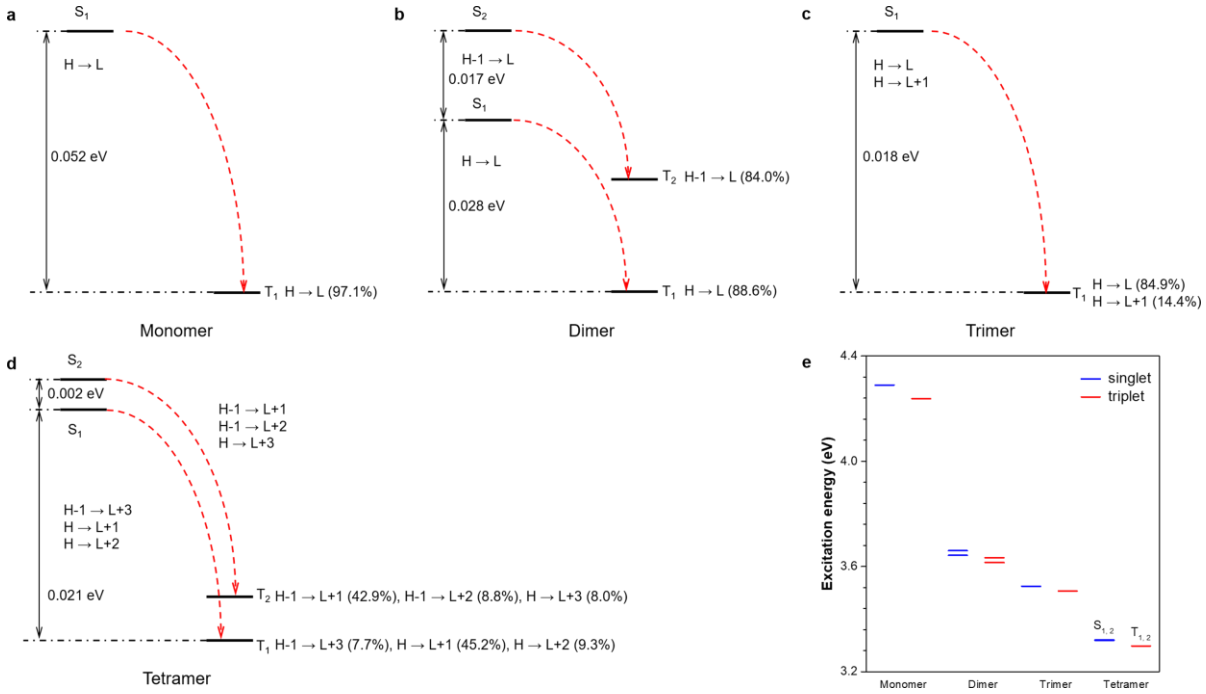


**Fig. S12** The ISC channels of (a) monomer, (b) dimer, (c) trimer and (d) tetramer of GCA. (e) The excitation energy diagram of monomer, dimer, trimer and tetramer of GCA.

For dimer and tetramer of GCA, since the $S_1$ and $S_2$ states both own the $^1(n, \pi^*)$ character and the energies of them are very close ($\Delta E_{S1S2,\ dimer}$ = 0.017 eV, $\Delta E_{S1S2,\ tetramer}$ = 0.002 eV), it is probable that the ISC process could happen from $S_2$ to corresponding triplet states.[2] Considering the allowed transitions between HOMOs and LUMOs (Fig. S12 and Table S5), only ISC from $S_2$ to $T_2$ can occur for dimer and tetramer of GCA, which is taken into account in the subsequent discussions.

**Table S5** Transition configurations of GCA. The ones labelled in red are allowed transitions.

| Aggregation state | Excited state | Excitation energy [eV] | Transition configuration |
|---|---|---|---|
| monomer | $S_1$ | 4.2901 | H→L |
| | $T_1$ | 4.2383 | H→L |
| dimer | $S_1$ | 3.6427 | H→L |
| | $S_2$ | 3.6603 | H-1→L |
| | $T_1$ | 3.6149 | H→L |
| | $T_2$ | 3.6332 | H-1→L |
| trimer | $S_1$ | 3.5248 | H→L, H→L+1 |
| | $T_1$ | 3.5068 | H→L, H→L+1 |
| tetramer | $S_1$ | 3.3192 | H-1→L+3, H→L+1, H→L+2 |
| | $S_2$ | 3.3212 | H-1→L+1, H-1→L+2, H→L+3 |
| | $T_1$ | 3.2979 | H-1→L+3, H→L+1, H→L+2 |
| | $T_2$ | 3.2983 | H-1→L+1, H-1→L+2, H→L+3 |

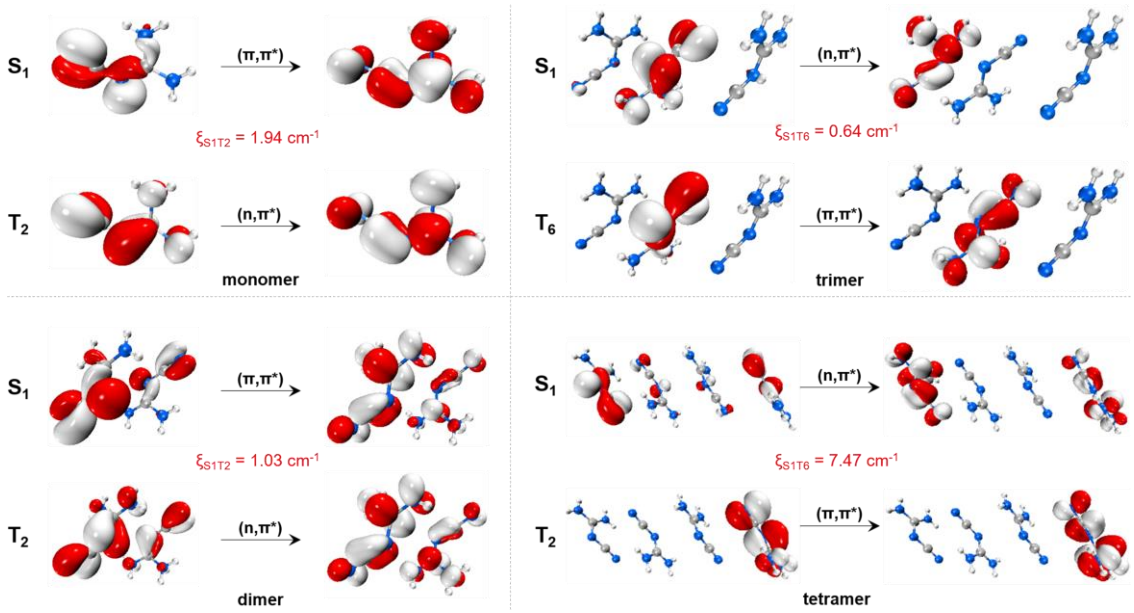


**Fig. S13** NTO (isovalue = 0.04) analyses and spin-orbit coupling coefficients for corresponding singlet and triplet states of monomer, dimer, trimer and tetramer of DCDA.

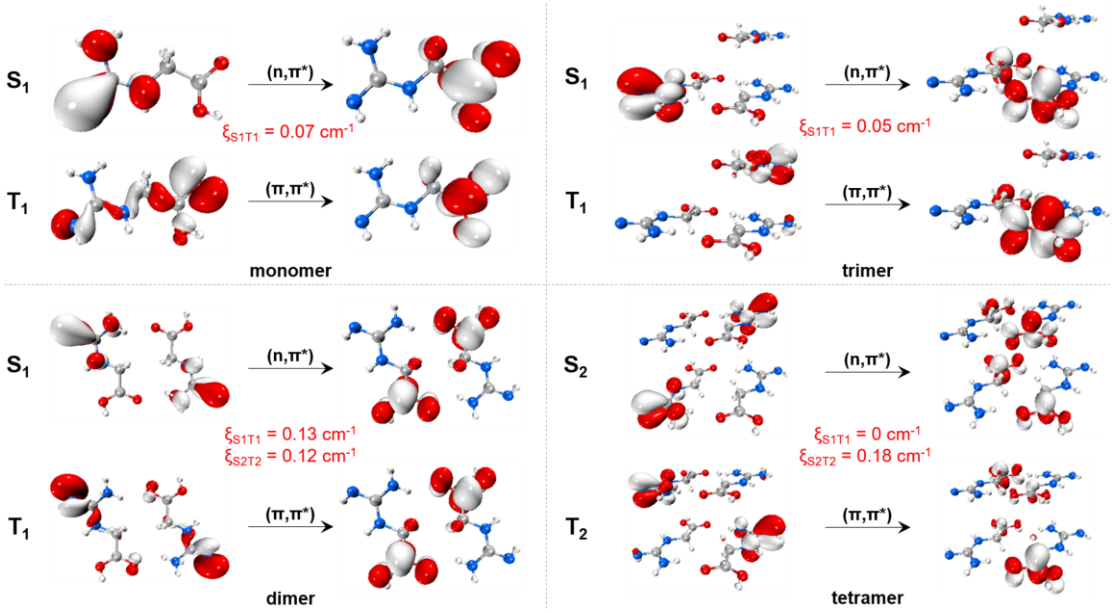


**Fig. S14** NTO (isovalue = 0.04) analyses and spin-orbit coupling coefficients for corresponding singlet and triplet states of monomer, dimer, trimer and tetramer of GCA.

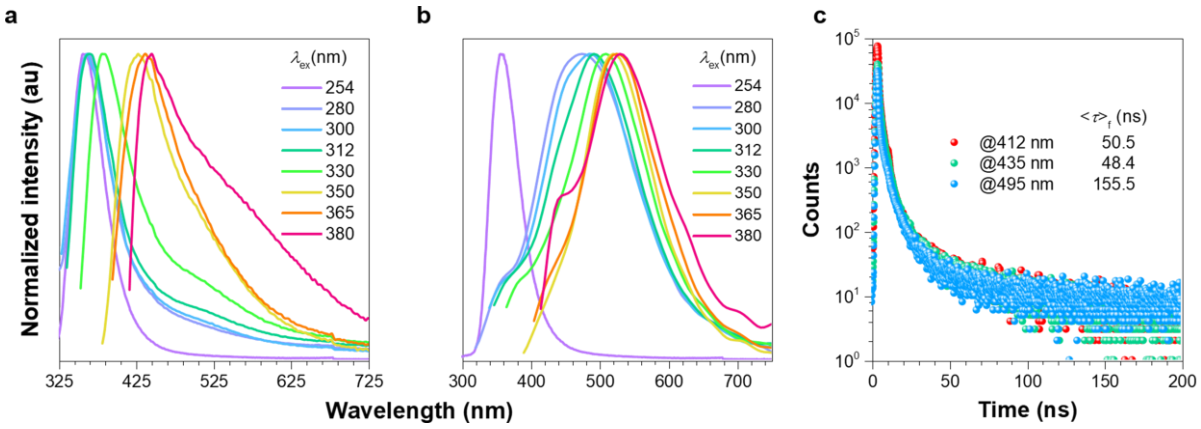


**Fig. S15** (a) Normalized prompt and (b) delayed ($t_d$ = 1 ms) emission spectra of the ground powders for DCDA with different $\lambda_{ex}$s. (c) Fluorescence lifetimes at varying $\lambda_{em}$s of the ground powders for DCDA ($\lambda_{ex}$ = 363 nm).

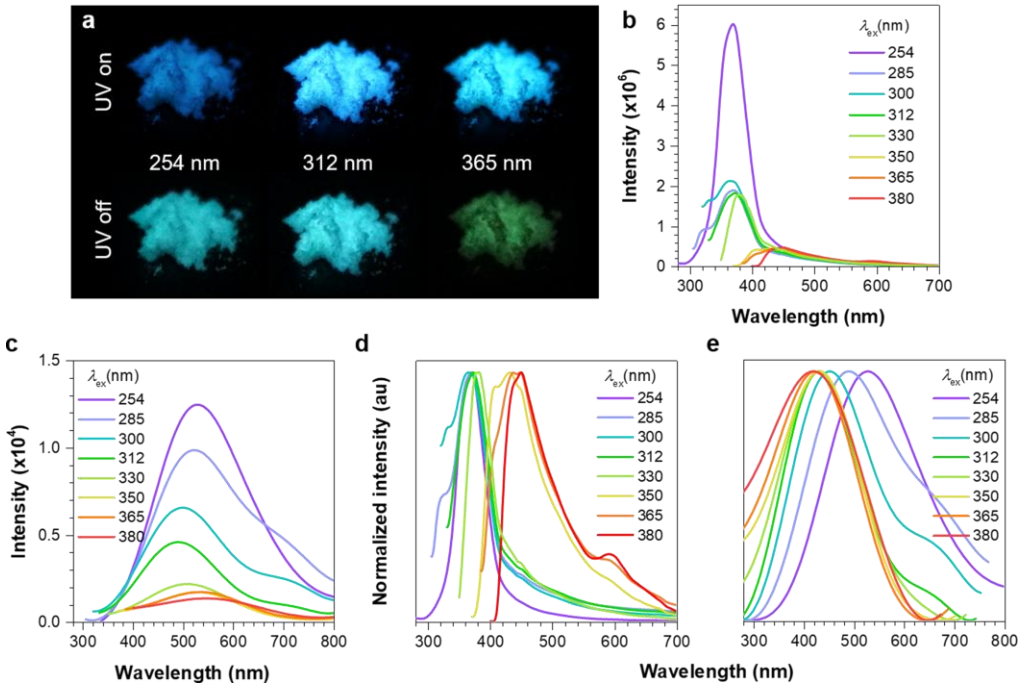


**Fig. S16** (a) Photographs of GCA ground powders taken under or after ceasing 254, 312 and 365 nm UV lights. (b) Prompt and (c) delayed ($t_d$ = 1 ms) emission spectra of the ground powders for GCA with different $\lambda_{ex}$s. (d) Normalized prompt and (e) delayed ($t_d$ = 1 ms) emission spectra of the ground powders for GCA with different $\lambda_{ex}$s.

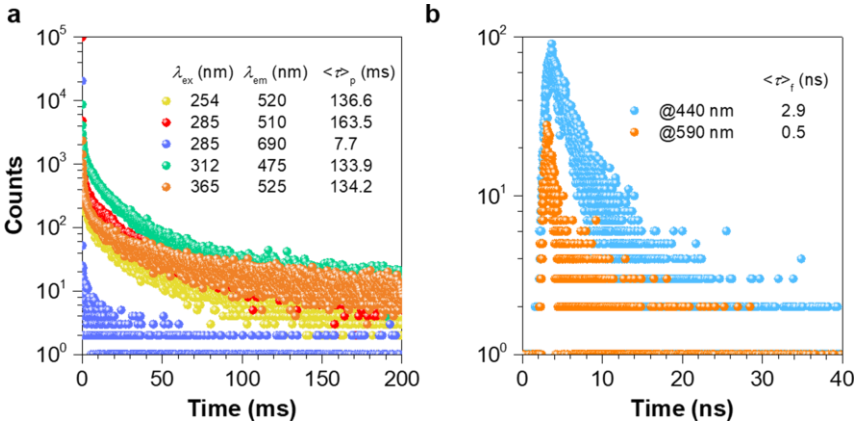


**Fig. S17** (a) p-RTP lifetimes at varying $\lambda_{em}$s for GCA ground powders. (b) Fluorescence lifetimes at varying $\lambda_{em}$s for GCA ground powders ($\lambda_{ex}$ = 363 nm).

## Reference


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