Electronic Supplementary Information (ESI) for Chemical Communications.



**Supplementary Information**

# Self-contained photo-acid generators with high quantum yields triggered by photo-cyclization

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## Reagents and materials

Unless otherwise noted, all reagents used in the experiments were purchased from commercial sources without further purification.

Tetrahydrofuran (THF) was dried by sodium through distillation, with benzophenone as chromogenic reagent. For flash column chromatography, silica gel with 200 ~ 300 mesh was used.

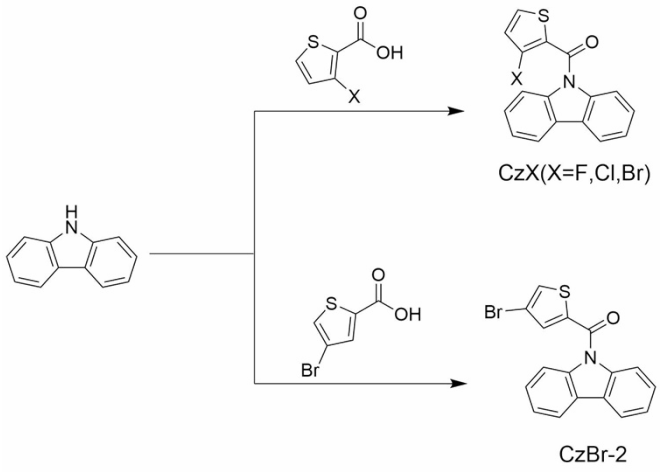
## Measurements

Nuclear magnetic resonance ($^1$H and $^{13}$C NMR) spectra were obtained on a Bruker Ultra Shield plus 400 MHz spectrometer. Chemical shift was relative to tetramethylsilane (TMS) as the internal standard. Resonance patterns were reported with the notation s (singlet), d (double), t (triplet), q (quartet), and m (multiplet). UV-visible absorption spectra were measured by Shimadzu UV-1750. Steady-state fluorescence and phosphorescence spectra were measured using Hitachi F-4600. X-ray crystallography was achieved using a Bruker SMART APEX-II CCD diffractometer with graphite monochromated Mo-Kα radiation. All the crystalline samples were obtained from slow evaporation of mixed solvents. We used a hand-held UV lamp to irradiate the PAGs and the exposure intensity at 365 nm is (4.9±0.2) ×$10^{-3}$ W/$cm^2$.

The photochemical quantum yields of PAGs were calculated following the Formula S1

$$\boldsymbol{\Phi} = (1991/\lambda)\, k_d/(I\varepsilon(1-10^{-A}) \qquad \text{Formula S1}$$

**λ** is the exposure wavelength (365 nm); $k_d$ is the slope of the kinetic curve of PAGs absorption peak at 365 nm ($min^{-1}$); I is the exposure intensity at 365 nm (W/$cm^2$). ε is the molar extinction coefficient of CZC; A is the absorbance of PAGs at 365 nm.




Scheme 1. Synthetic routes of CzX (x=F, Cl, Br) and CzBr-2 molecules.

**(CzF):** 3-Fluoro-2-thiophenecarboxylic acid (1.5 g, 10.26 mmol) and $SOCl_2$ (8 mL) were stirred together for 2 h at 85°C and the excess $SOCl_2$ was removed by rotary evaporation, generated 3-fluoro-2-

thiophenecarbonyl chloride. Additionally, carbazole (2.06 g, 12.32 mmol), NaH (0.62 g, 15.40 mmol) and 40 mL tetrahydrofuran (THF) were added to another two-necked round-bottomed flask which stirred at ice-water bath for 0.5 h. Freshly distilled tetrahydrofuran (10 mL) was added to the prepared 3-fluoro-2-thiophenecarbonyl chloride, and slowly dropped into the carbazole solution in an ice-water bath, followed by stirring at room temperature for 6 hours. The solvent was evaporated by a rotary evaporator and the residue was purified by column chromatography to yield CzF. (1.54 g, 51.0%). $^{1}$H NMR (400 MHz, $CDCl_3$,), δ (ppm): 8.01 (2H, dd, *J* = 6.1, 2.8 Hz), 7.86-7.71 (2H, m), 7.61 (1H, dd, *J* = 5.5, 3.6 Hz), 7.44-7.34 (4H, m), 6.86 (1H, d, *J* = 5.5 Hz). $^{13}$C NMR (101 MHz, $CDCl_3$), δ (ppm): 158.90, 138.75, 131.22, 131.12, 127.09, 126.13, 123.80, 120.10, 118.36, 118.11, 114.77.

**(CzCl):** 3-Chlorothiophene-2-carboxylic acid (1.46 g, 8.97 mmol), carbazole (1 g, 5.98 mmol), 1-ethyl-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDCI, 3.44 g, 17.94 mmol) and 4-dimethylaminopyridine (DMAP, 1.83 g, 14.95 mmol) were dissolved in 20 mL of $CH_2Cl_2$. The reaction mixture was stirred at 50°C for 5 h. The mixture was then extracted with water/$CH_2Cl_2$ and dried over anhydrous $MgSO_4$. The residue was purified by column chromatography to yield CzCl (white powder, 1.39 g, 74.4%). $^{1}$H NMR (400 MHz, $CDCl_3$,), δ (ppm): 8.03-7.95 (2H, m), 7.64 (1H, d, *J* = 5.2 Hz), 7.62-7.56 (2H, m), 7.43-7.29 (4H, m), 7.02 (1H, t, *J* = 13.3 Hz). $^{13}$C NMR (101 MHz, $CDCl_3$,), δ (ppm): 160.88, 138.63, 131.00, 130.02, 129.27, 128.36, 127.29, 126.39, 124.10, 120.05, 115.20.

**(CzBr):** 3-Bromo-2-thiophenecarboxylic acid (1.86 g, 8.97 mmol), carbazole (1 g, 5.98 mmol), 1-ethyl-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDCI, 3.44 g, 17.94 mmol) and 4-dimethylaminopyridine (DMAP, 1.83 g, 14.95 mmol) were dissolved in 20 mL of $CH_2Cl_2$. The reaction mixture was stirred at 50°C for 5 h. The mixture was then extracted with water/$CH_2Cl_2$ and dried over anhydrous $MgSO_4$. The residue was purified by column chromatography to yield CzCl (white powder, 1.88 g, 88.4%). $^{1}$H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.03-7.96 (2H, m), 7.61 (1H, d, *J* = 5.2 Hz), 7.59-7.53 (2H, m), 7.41-7.34 (4H, m), 7.11 (1H, d, *J* = 5.2 Hz). $^{13}$C NMR (101 MHz, $CDCl_3$), δ (ppm): 161.46, 138.65, 132.92, 131.79, 130.44, 127.31, 126.45, 124.15, 120.03, 115.38, 113.94.

**(CzBr-2):** 4-Bromo-2-thiophenecarboxylic acid (1.86 g, 8.97 mmol), carbazole (1 g, 5.98 mmol), 1-ethyl-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDCI, 3.44 g, 17.94 mmol) and 4-dimethylaminopyridine (DMAP, 1.83 g, 14.95 mmol) were dissolved in 20 mL of $CH_2Cl_2$. The reaction mixture was stirred at 50°C for 5 h. The mixture was then extracted with water/$CH_2Cl_2$ and dried over anhydrous $MgSO_4$. The residue was purified by column chromatography to yield CzCl (white powder, 1.03 g, 48.4%). $^{1}$H NMR (400 MHz, $CDCl_3$), δ (ppm): **δ** 8.06-7.97 (m, 2H), 7.76-7.67 (m, 2H), 7.62 (d, *J* = 1.4 Hz, 1H), 7.49 (d, *J* = 1.4 Hz, 1H), 7.44-7.33 (m, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$), δ (ppm): 161.44, 138.97, 138.70, 135.43, 130.21, 126.94, 126.04, 123.75, 120.14, 115.34, 110.55.

**(CzC):** The CzF solution in 2-methyl tetrahydrofuran (2-mTHF, $10^{-3}$ M) was exposed to UV light for 20 min, and the solvent was removed with a rotary evaporator. The residue was purified by column

chromatography to yield CzC (white powder, 60%). $^{1}$H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.69 (d, *J* = 8.1 Hz, 1H), 7.93 (dd, *J* = 12.0, 7.3 Hz, 2H), 7.88 – 7.75 (m, 2H), 7.67 (d, *J* = 5.1 Hz, 1H), 7.61 – 7.51 (m, 1H), 7.52 – 7.33 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$), δ (ppm): 156.46, 142.13, 138.50, 134.90, 134.25, 132.82, 128.08, 126.55, 124.90, 124.12, 124.01, 122.56, 121.19, 120.89, 120.87, 117.08, 115.51.

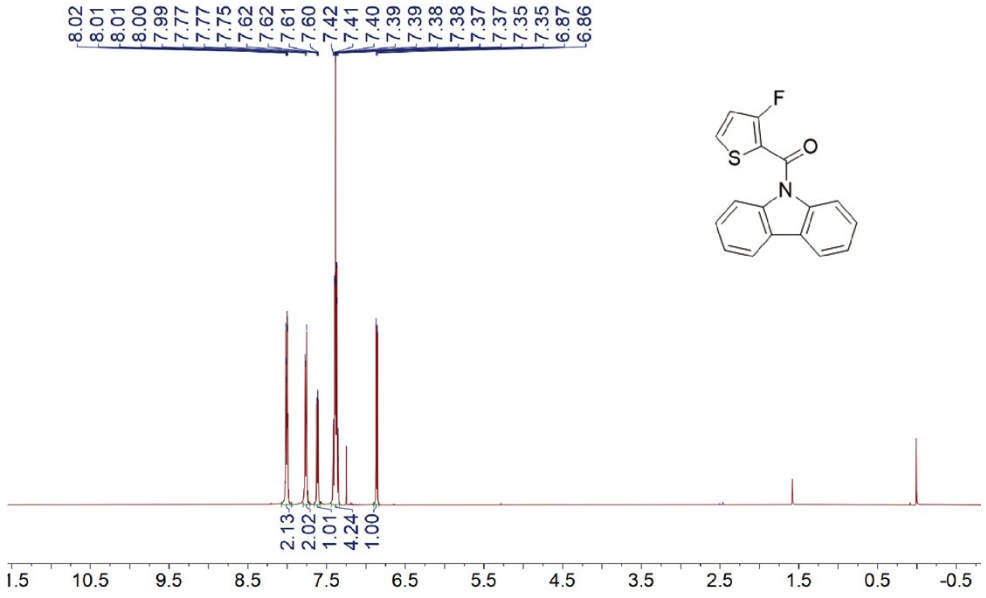



Fig. S1 The $^{1}$H NMR spectrum of CzF molecule in $CDCl_3$.

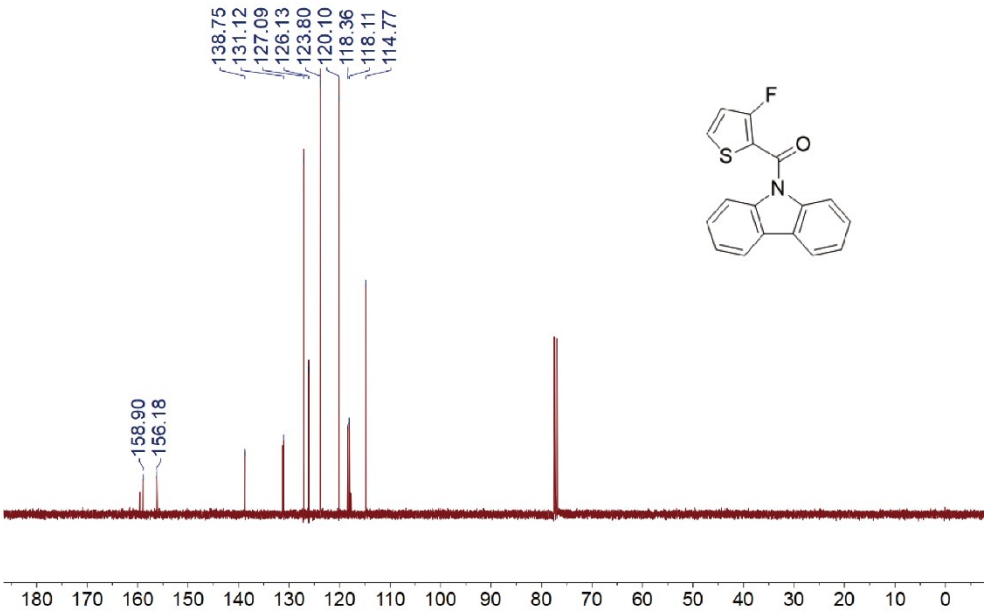



Fig. S2 The $^{13}$C NMR spectrum of CzF molecule in $CDCl_3$.

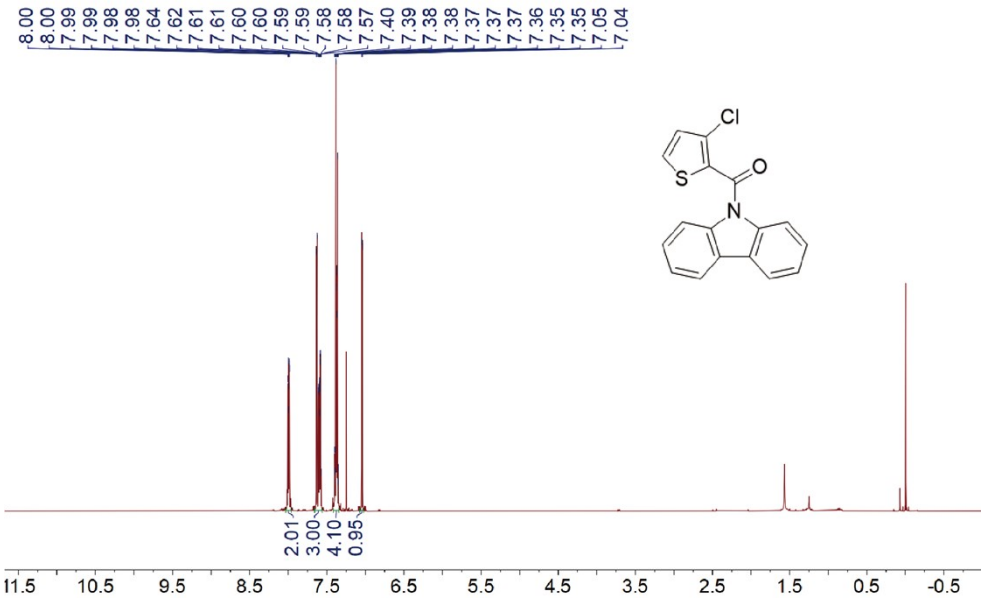



Fig. S3 The $^{1}H$ NMR spectrum of CzCl molecule in $CDCl_3$.

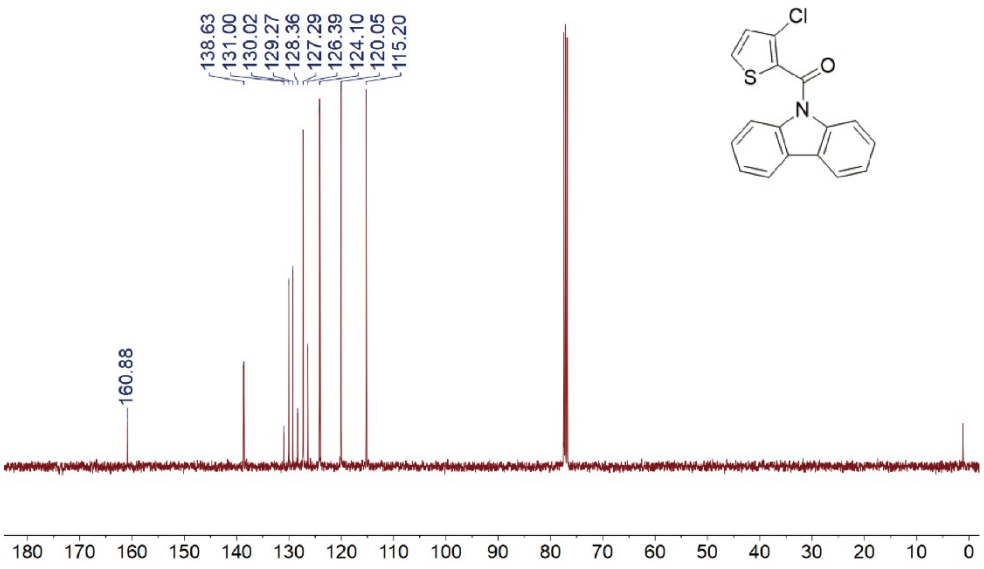



Fig. S4 The $^{13}C$ NMR spectrum of CzCl molecule in $CDCl_3$.

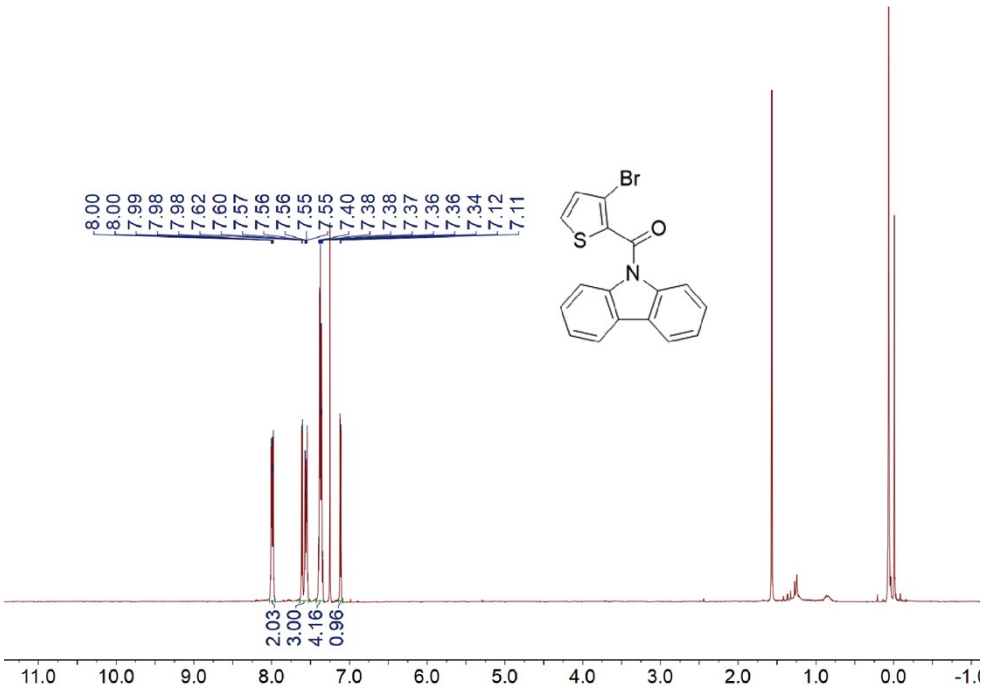



Fig. S5 The $^{1}H$ NMR spectrum of CzBr molecule in $CDCl_3$.

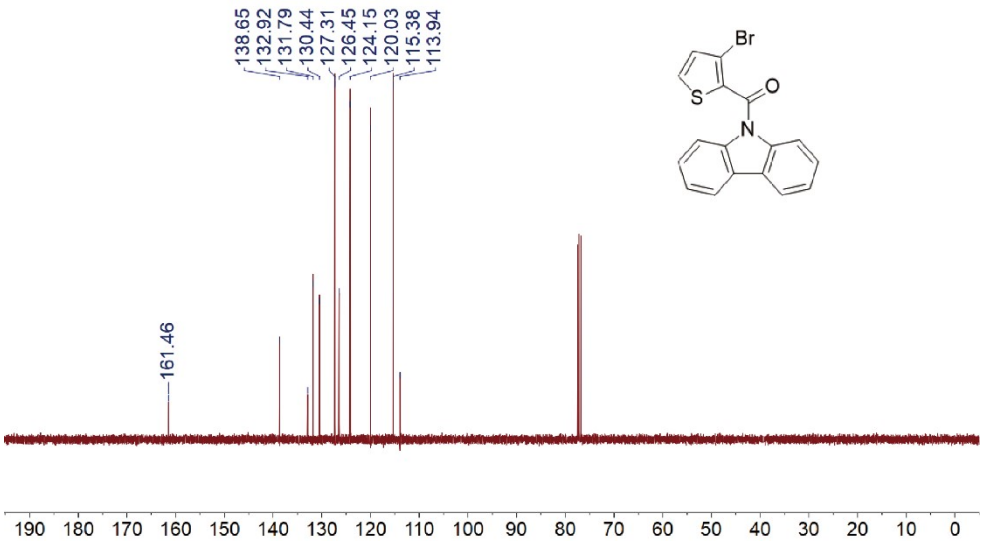



Fig. S6 The $^{13}C$ NMR spectrum of CzBr molecule in $CDCl_3$.

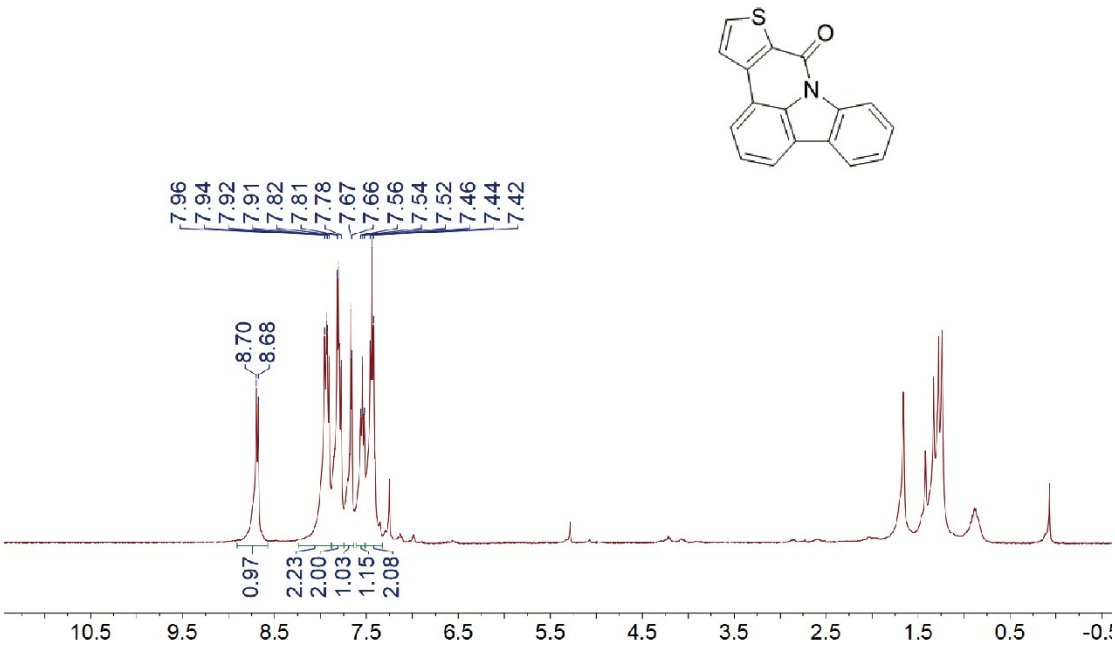



Fig. S7 The $^{1}H$ NMR spectrum of CzC molecule in $CDCl_3$.

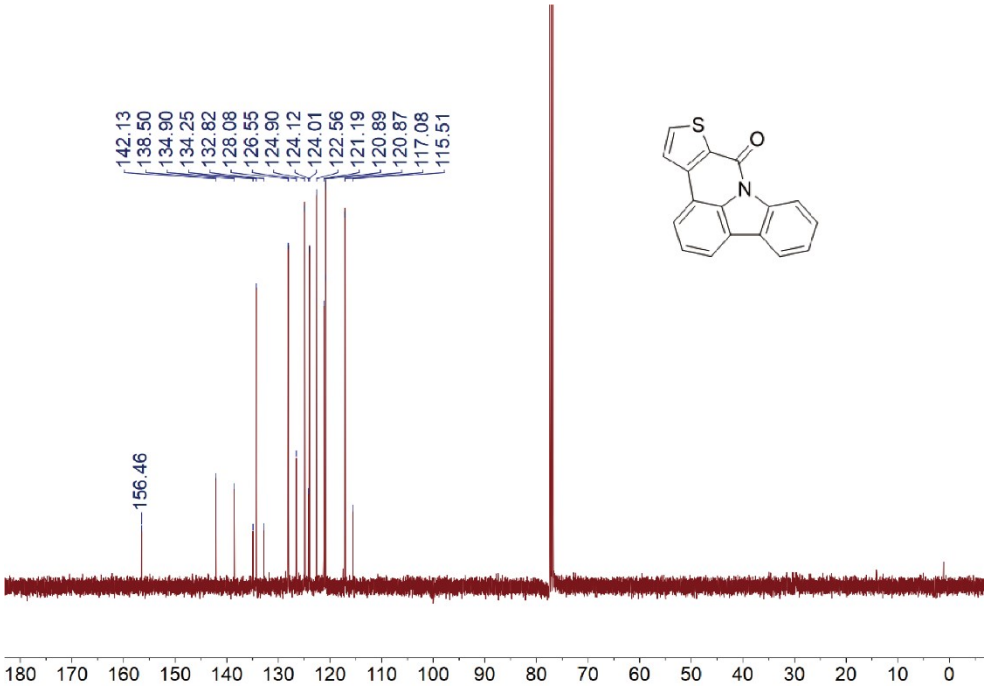



Fig. S8 The $^{13}C$ NMR spectrum of CzC molecule in $CDCl_3$.

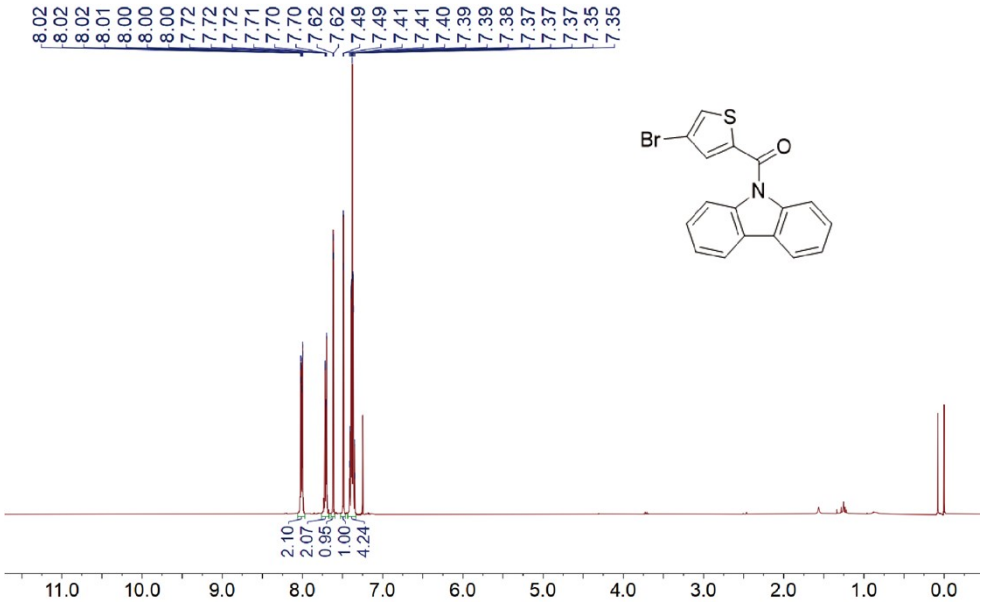



Fig. S9 The $^{1}H$ NMR spectrum of CzBr-2 molecule in $CDCl_3$.

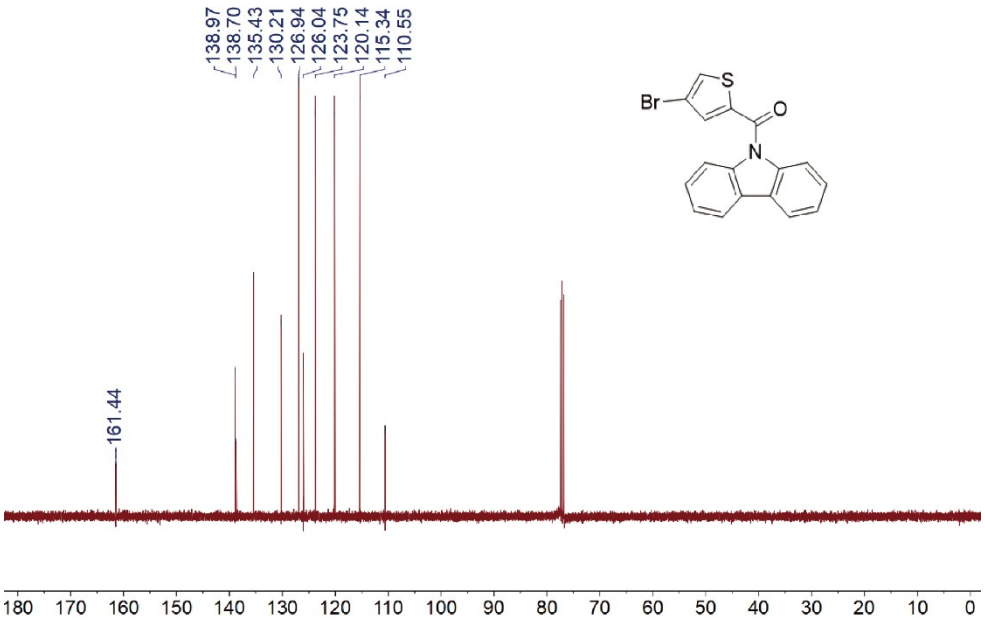



Fig. S10 The $^{13}C$ NMR spectrum of CzBr-2 molecule in $CDCl_3$.

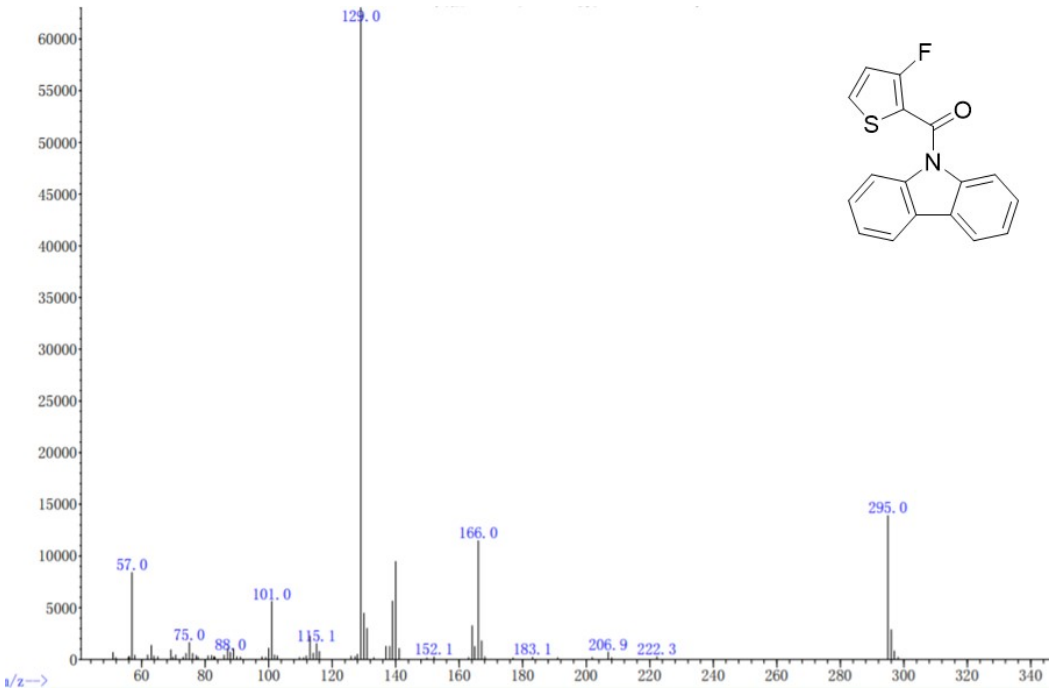



Fig. S11 The mass spectrum of CzF molecule.

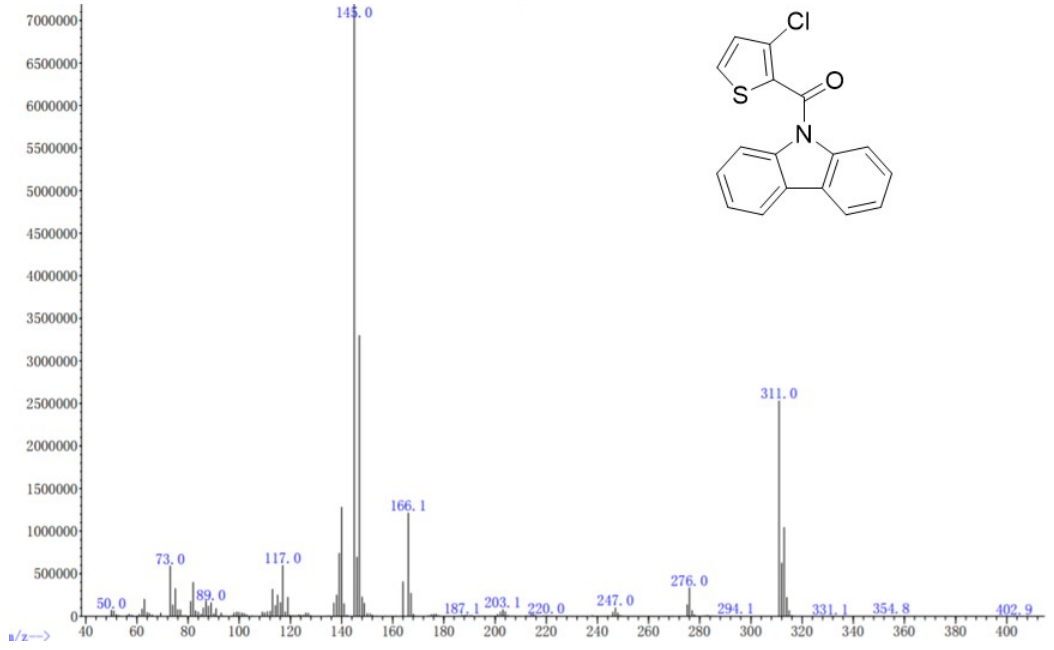



Fig. S12 The mass spectrum of CzCl molecule.

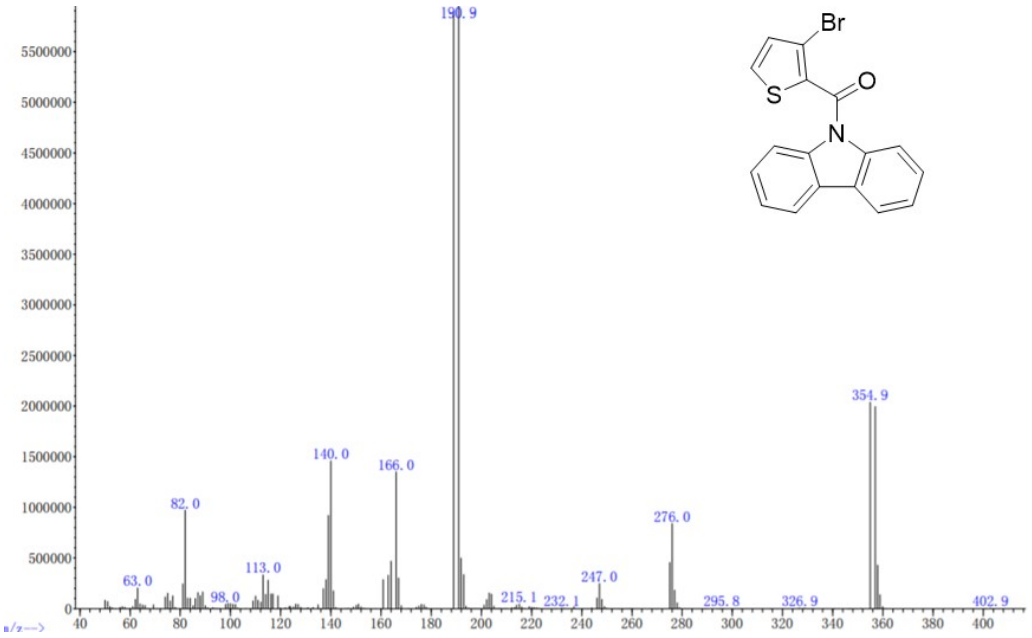



Fig. S13 The mass spectrum of CzBr molecule.

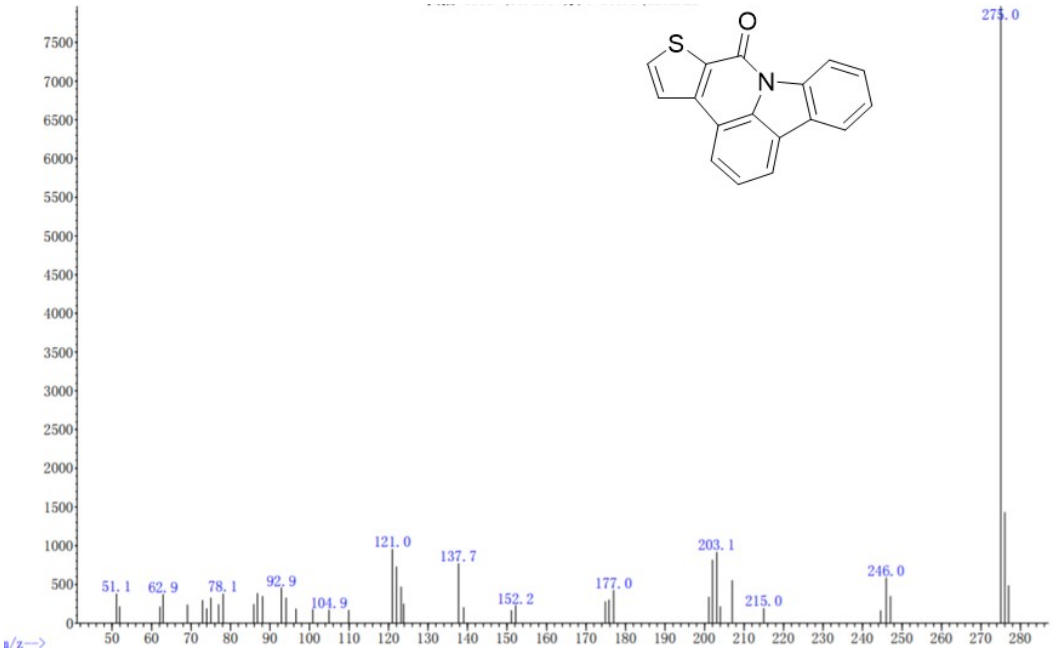



Fig. S14 The mass spectrum of CzC molecule.

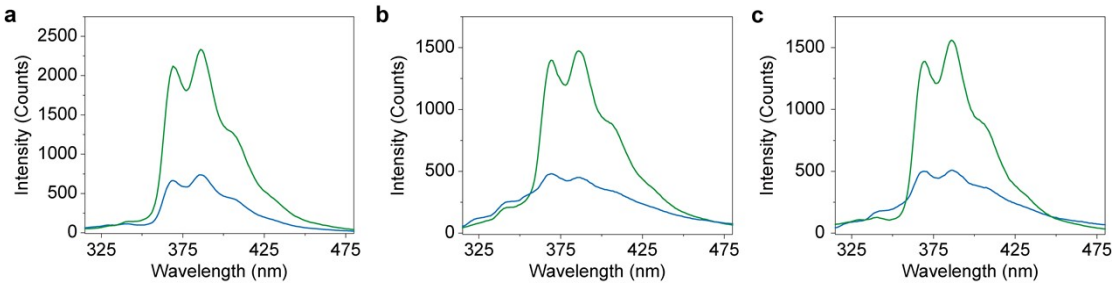



Fig. S15 PL spectral changes of (a) CzF, (b) CzCl, (c) CzBr before (blue line) and after (green line) UV (365 nm) irradiation in THF ($2.0 \times 10^{-5}$ M) under the ambient conditions.

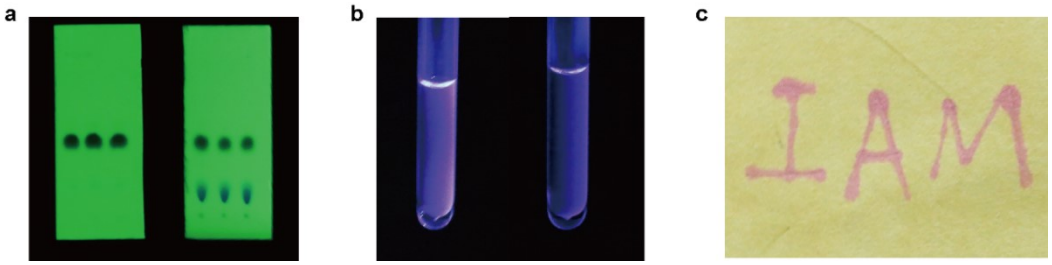



Fig. S16. (a)TLC photos of CZF solution before and after UV light irradiation at 365 nm and (b) photos of luminescent color change. (c) The word “IAM” turned red after UV light irradiation.

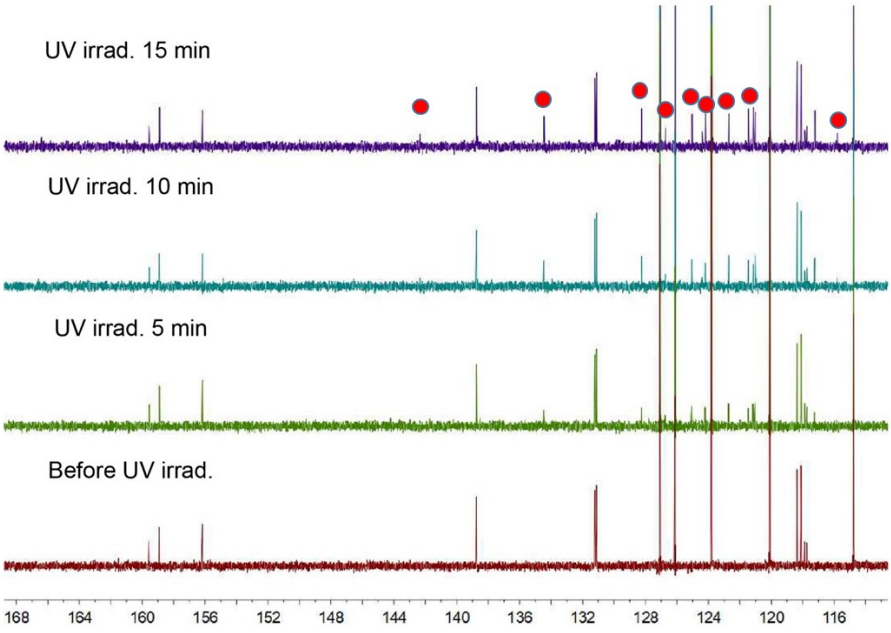



Fig. S17 $^{13}C$ NMR spectral changes of CzF upon UV (365 nm) irradiation in $CDCl_3$.

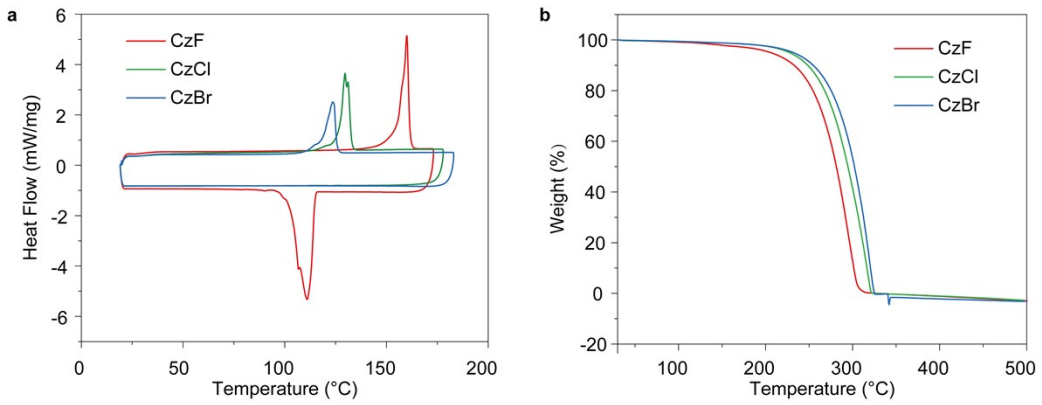



Fig. S18 (a) Differential scanning calorimetry (DSC) and (b). thermo gravimetric analysis (TGA) spectrum of PAGs.

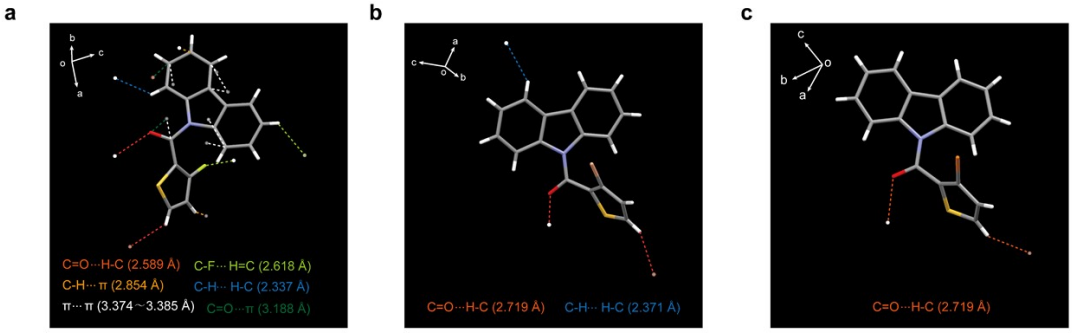



Fig. S19 Intermolecular interactions of single molecules of (a) CzF, (b) CzCl, and c) CzBr.

Table S1. Crystal data and structure refinement for CzF, CzCl and CzBr

| Samples | CzF | CzCl | CzBr |
|---|---|---|---|
| Formula weight | 295.32 | 311.77 | 356.23 |
| Crystal system | monoclinic | monoclinic | monoclinic |
| Space group | C2 | $P2_1/c$ | $P2_1/c$ |
| a (Å) | 18.9441(17) | 12.022(2) | 7.8966(4) |
| b (Å) | 5.3279(5) | 7.1624(10) | 7.7464(4) |
| c (Å) | 13.3123(10) | 16.3850(18) | 23.3386(11) |
| *α* (Å) | 90 | 90 | 90 |
| *β* (Å) | 98.087(8) | 91.386(6) | 96.192(2) |
| *γ* (Å) | 90 | 90 | 90 |
| V (Å) | 1330.3(2) | 1410.4(4) | 1419.30(12) |
| Z | 4 | 4 | 4 |
| D (g $cm^{-3}$) | 1.475 | 1.468 | 1.667 |

| | | | |
|---|---|---|---|
| μ (mm) | 0.252 | 0.415 | 3.040 |
| T (K) | 293 | 299 | 298 |
| Rint | 0.0296 | 0.0485 | 0.0457 |
| Goof | 0.960 | 1.021 | 1.047 |
| R1 (I>2σ(I) | 0.0514 | 0.0413 | 0.0372 |
| wR2 (I>2σ(I) | 0.1021 | 0.1020 | 0.0881 |
| CCDC number | 2203143 | 2202708 | 2202707 |

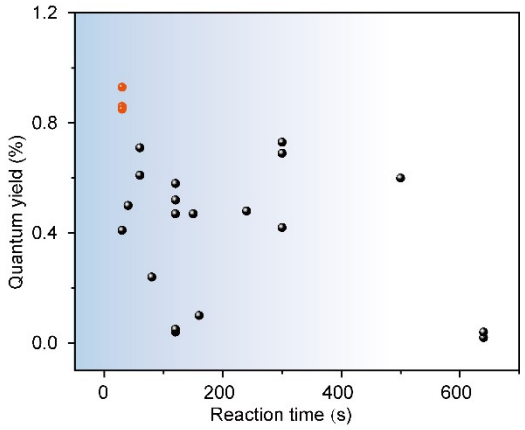



Fig. S20. Reaction time and photochemical quantum yields of reported PAGs.[1-7] Note that Red balls represent CzF, CzCl and CzBr in this work.

## References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