

[*Supporting Information*]

## **Highly Efficient Luminescent *E*- and *Z*- Isomers with Stable Configurations under Photo Irradiation Induced by Their Charge Transfer Excited States**

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## 1. Synthesis

All the reagents or chemicals were commercial products without further purification. The preparation procedure of M1 could be found in the reference<sup>1</sup>.

A solution of **M1** (0.720g, 2mmol) and 4-(trifluoromethyl)benzaldehyde (1.044g, 6mmol) in ethanol (8ml) was heated under 45 °C for 24 h by the catalysis of sodium methanolate, resulting with the presence of abundant precipitate. The mixture was then cooled to room temperature and filtered. Then the residue was washed with cold ethanol by three times. After being dried in vacuum, the crude product was further purified by column chromatography via eluent (CH<sub>2</sub>Cl<sub>2</sub>/n-hexane) to afford *E*-TPNCF and *Z*-TPNCF as the yellow and orange solid respectively in the similar yield.

*E*-TPNCF (0.310g, yielding 30%). <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ= 7.82 (s, 1H, vinyl-H), 7.74 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.71 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.66 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.47 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.42 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.34 (m, 4H, Ar-H), 7.13 – 7.01 (m, 8H, Ar-H). MALDI-TOF MS (mass m/z): 518.7 [M+ + H], C<sub>34</sub>H<sub>23</sub>F<sub>3</sub>N<sub>2</sub> calc. 516.1.

*Z*-TPNCF (0.310g, yielding 30%). <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ= 8.25 (s, 1H, vinyl-H), 8.14 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.94 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.89 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.84 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.71 (d, *J* = 7.0 Hz, 2H, Ar-H), 7.35 (m, 4H, Ar-H), 7.14 – 7.03 (m, 8H, Ar-H). MALDI-TOF MS (mass m/z): 518.7 [M+ + H], C<sub>34</sub>H<sub>23</sub>F<sub>3</sub>N<sub>2</sub> calc. 516.1.

## 2. Instrument

<sup>1</sup>H (500MHz) NMR spectra of the synthesized compounds were recorded on Bruker AVANCE III instrument (Bruker, Switzerland). Mass spectra (MALDI-TOF-MS) analysis was recorded using an AXIMA-CFRTM plus instrument. Photophysical properties were investigated by a Shimadzu UV-1800 spectrophotometer (Shimadzu, Japan) and a Perkin-Elmer LS-55 luminescence spectrophotometer (the integration time were set to be 0.01s in order to shorten the measurement time to be less than 20s). The fluorescence quantum yield was determined by a calibrated integrating sphere. The photo irradiation was carried in a ZF-20D ultraviolet analyzer (YUHUA, China) with a UV light (365 nm, 24W).

### 3. E/Z isomerization

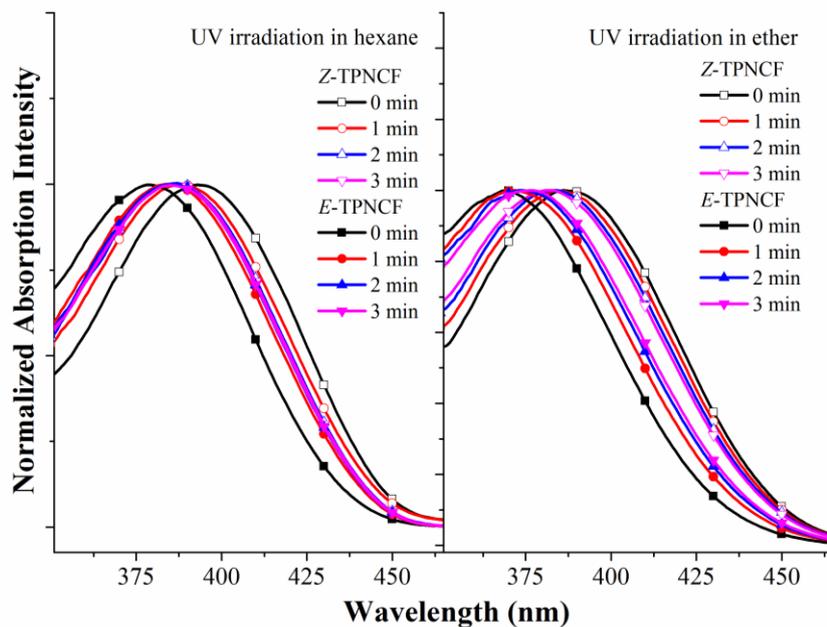


Figure S1. The in-situ UV spectra of *E*-TPNCF and *Z*-TPNCF under different photo irradiated time of UV light (365 nm) in different polar solvents (solvent polarities, hexane: 0.0012; ether: 0.17).

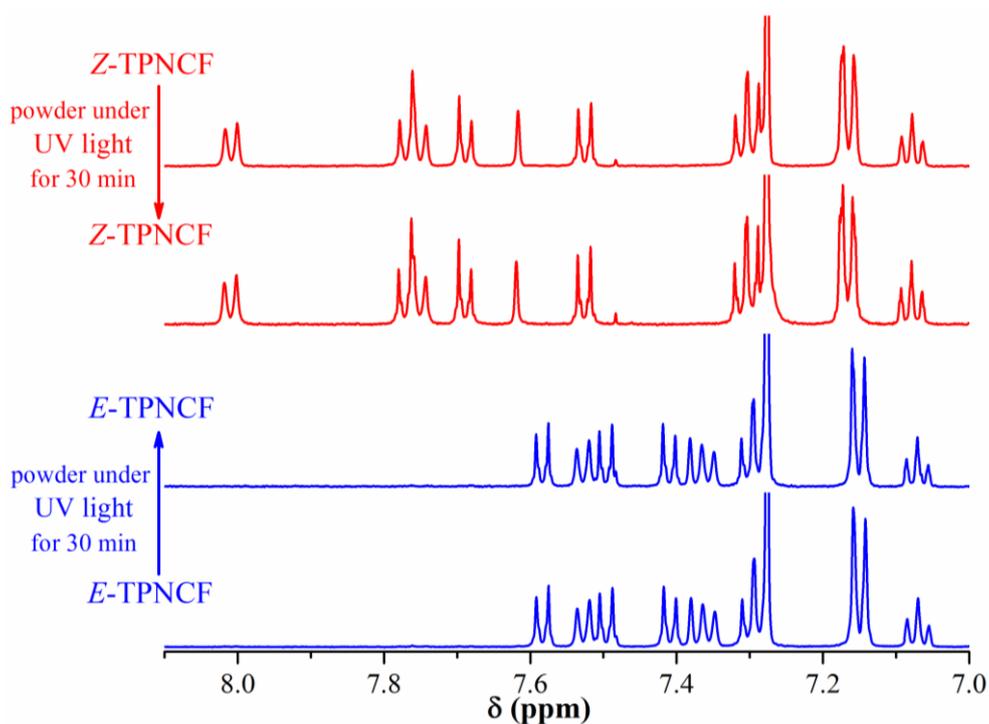


Figure S2. The NMR spectra (in CDCl<sub>3</sub>) of *E*-TPNCF and *Z*-TPNCF measured from their powders before and after photo irradiation under UV light (365 nm) for 30 minutes

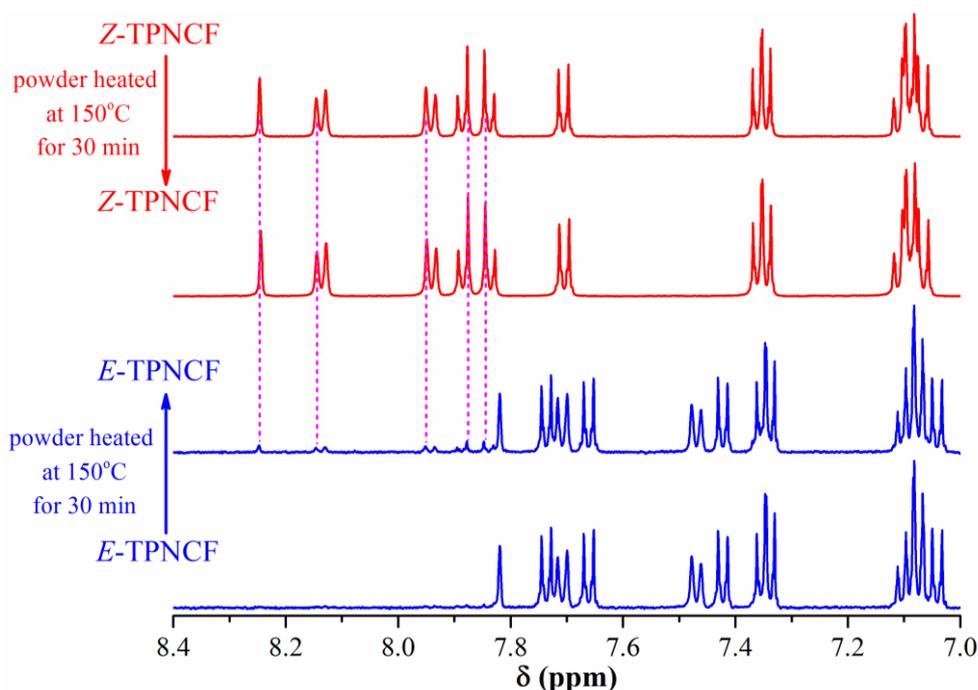


Figure S3. The NMR spectra (in DMSO- $d_6$ ) of *E*-TPNCF and *Z*-TPNCF measured from their powders before and after heated at 150 °C for 30 minutes

#### 4. CT state characterization

The influence of solvent environment on the optical property of our compounds can be understood using the Lippert-Mataga equation, a model that describes the interactions between the solvent and the dipole moment of solute:

$$hc(\nu_a - \nu_f) = hc(\nu_a^0 - \nu_f^0) - \frac{2(\mu_e - \mu_g)^2}{a^3} f(\epsilon, n)$$

, where  $f$  is the orientational polarizability of solvents,  $\mu_e$  is the excited-state dipole moment,  $\mu_g$  is the ground-state dipole moment;  $a$  is the solvent cavity (Onsager) radius, derived from the Avogadro number ( $N$ ), molecular weight ( $M$ ), and density ( $d=1.0 \text{ g/cm}^3$ );  $\epsilon$  and  $n$  are the solvent dielectric and the solvent refractive index, respectively;  $f(\epsilon, n)$  and  $a$  can be calculated respectively as follows:

$$f(\epsilon, n) = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}, \quad a = (3M / 4N\pi d)^{1/3}$$

The detail data are listed in Table S1.

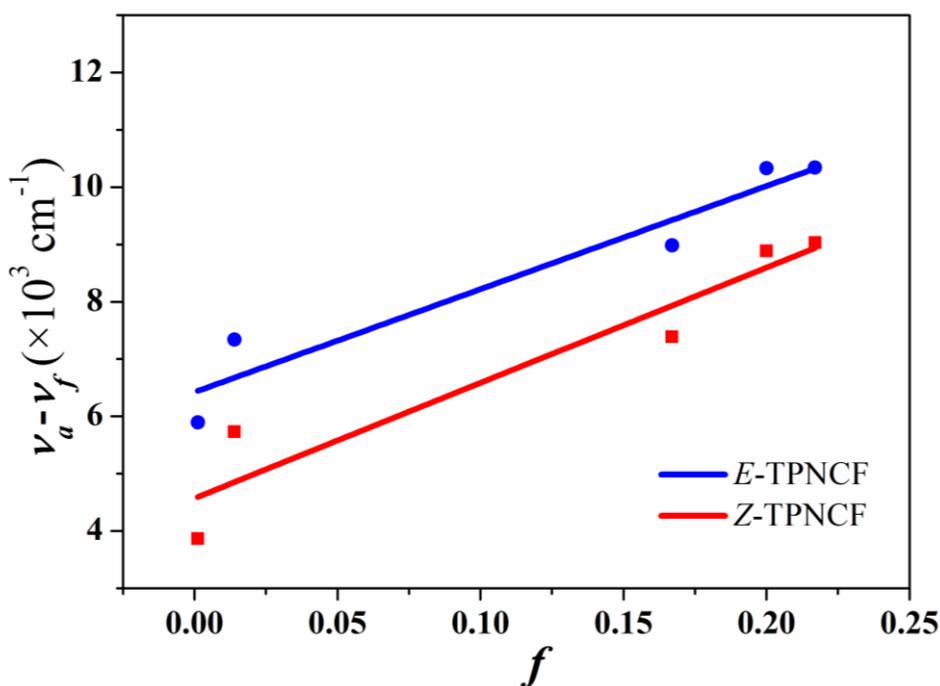


Figure S4. Linear fitting correlation of orientation polarization ( $f$ ) of solvent media with Stokes shift ( $\nu_a - \nu_f$ ) for *E*-TPNCF and *Z*-TPNCF. (See Table S1 for data; high polar solvents such as acetone, DMF and acetonitrile, are not included due to their non-luminescence without  $\lambda_{\text{max}}$  of PL spectra obtained.)

Through the analysis of the fitted line in different polar solvents as shown in Figure S4 (high polar solvents such as acetone, DMF and acetonitrile, are not included due to the non-luminescence without  $\lambda_{\text{max}}$  of PL spectra obtained), slope values of  $\sim 17965$  ( $R = 0.96$ ) and  $20101$  ( $R = 0.95$ ) were obtained for *E*-TPNCF and *Z*-TPNCF respectively. The ground-state dipoles,  $\mu_g$ , of *E*-TPNCF and *Z*-TPNCF could be estimated from a long-range correction density-functional-theory (DFT) calculation ( $\omega\text{B97X}^{[2]}$  at the basis set level of 6-31G\*\*), which gave a  $\mu_g$  of 3.85 D and 6.13 D for *E*-TPNCF and *Z*-TPNCF respectively. Thus the corresponding excited-state dipoles,  $\mu_e$ , were calculated to be 19.1 D and 20.2 D for *E*-TPNCF and *Z*-TPNCF respectively, according to the Lippert–Mataga equation.

Table S1. Detailed absorption and emission peak positions of *E*-TPNCF and *Z*-TPNCF in different solvents

Solvents	$\epsilon$	n	$f(\epsilon, n)$	<i>E</i> -TPNCF			<i>Z</i> -TPNCF		
				$\lambda_a$	$\lambda_f$	$\nu_a - \nu_f$	$\lambda_a$	$\lambda_f$	$\nu_a - \nu_f$
				(nm)	(nm)	( $\text{cm}^{-1}$ )	(nm)	(nm)	( $\text{cm}^{-1}$ )
Hexane	1.9	1.375	0.0012	379	488	5893	392	462	3865
Toluene	2.38	1.494	0.014	380	527	7340	397	514	5734
Ethyl ether	4.34	1.352	0.167	369	552	8984	387	542	7390
Ethyl acetate	6.02	1.372	0.200	367	591	10327	384	583	8889
Methylene chloride	8.93	1.424	0.217	374	610	10344	392	607	9036
Dimethyl formamide	37	1.427	0.276	366	-	-	389	-	-
Acetone	20.7	1.359	0.284	362	-	-	383	-	-
Acetonitrile	37.5	1.344	0.305	361	-	-	380	-	-

The ground-state geometries of *E*-TPNCF and *Z*-TPNCF were fully optimized using the density functional theory (DFT) with B3LYP hybrid functional at the basis set level of 6-31G\*. Each point on the potential-energy curve of the ground-state was obtained as a function of the twist angle between TPA and CNS moieties, by a partial geometrical optimization at each fixed twist angle at 10° intervals between 0° and 180°. All calculations were performed using Gaussian 09 package in PowerLeader workstation.

## 5. Luminescent property

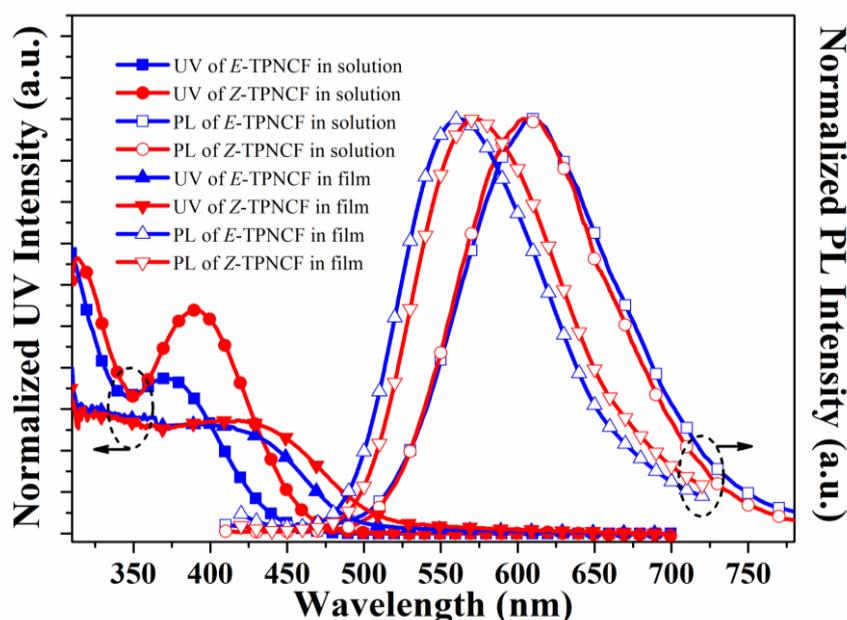


Figure S5. The normalized UV and PL spectra of *E*-TPNCF and *Z*-TPNCF molecules in the solution (dichloromethane, 10  $\mu\text{M}$ ) and film state

## 6. Reference

- [1] Zhang Y. J.; Wang K.; Zhuang G. L.; Xie Z. Q.; Zhang C.; Cao F.; Pan G. X.; Chen H. F.; Zou B.; Ma Y. G. *Chem. Eur. J.* 2015, 21, 2474 – 2479.
- [2] (a) J. D. Chai, M. Head-Gordon, *J Chem Phys*, 2008, 128, 084106; (b) J. D. Chai, M. Head-Gordon, *Physical Chemistry Chemical Physics*, 2008, 10, 6615.