

Supporting Information

**Photo-irradiated E/Z Isomerization Reaction of Star-shaped Isomers
Containing Two Cyanostilbene Arms with Charge Transfer Excited States**

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1. In-situ UV spectra in different solvents

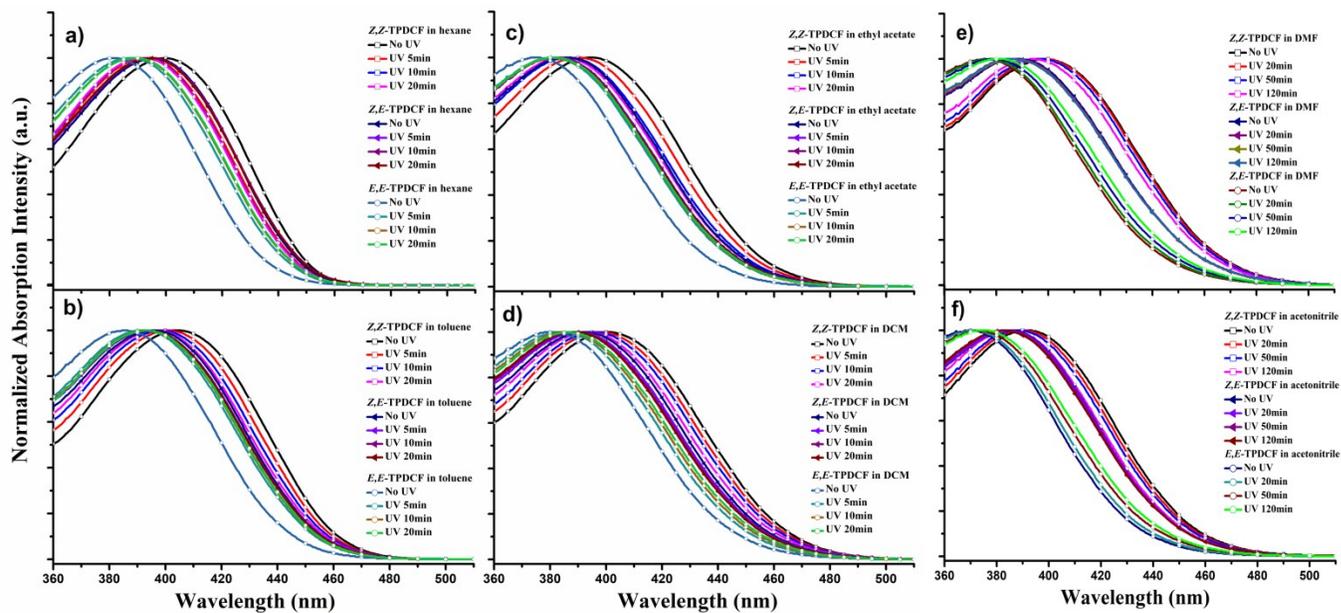


Figure S1. The in-situ UV spectra of *Z,Z*-TPDCF, *Z,E*-TPDCF and *E,E*-TPDCF in different polar solvents, It is a) hexane, b) toluene, c) ethyl acetate, d) dichloromethane (DCM), e) dimethyl formamide (DMF), f) acetonitrile

2. Solvatochromic experimental

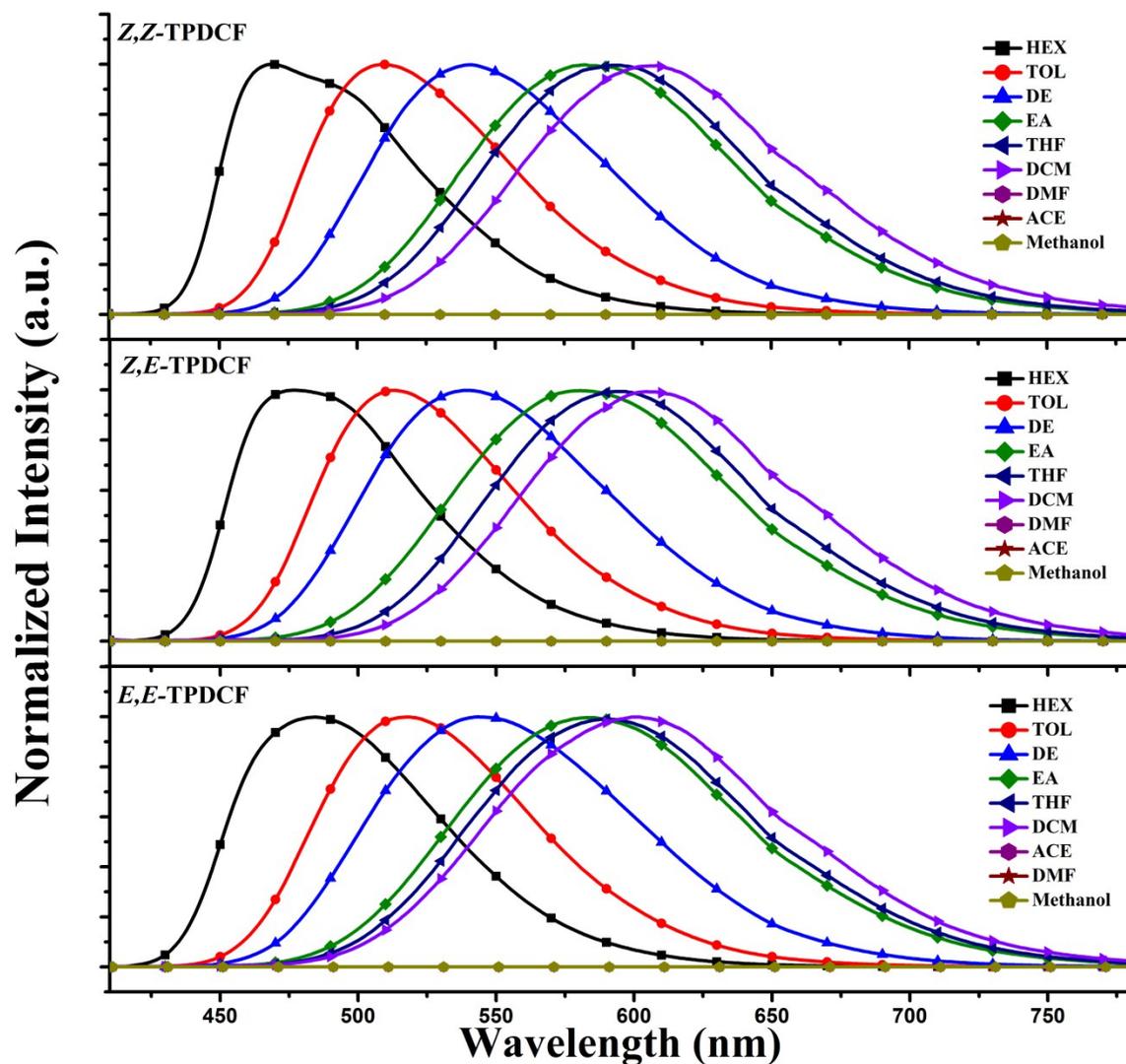


Figure S2. The PL spectra of *Z,Z*-TPDCF, *Z,E*-TPDCF and *E,E*-TPDCF in different polar solvents.

3. 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, μ_e is the excited-state dipole moment, μ_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 ($d=1.0 \text{ g/cm}^3$); ϵ 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 list in Table S1.

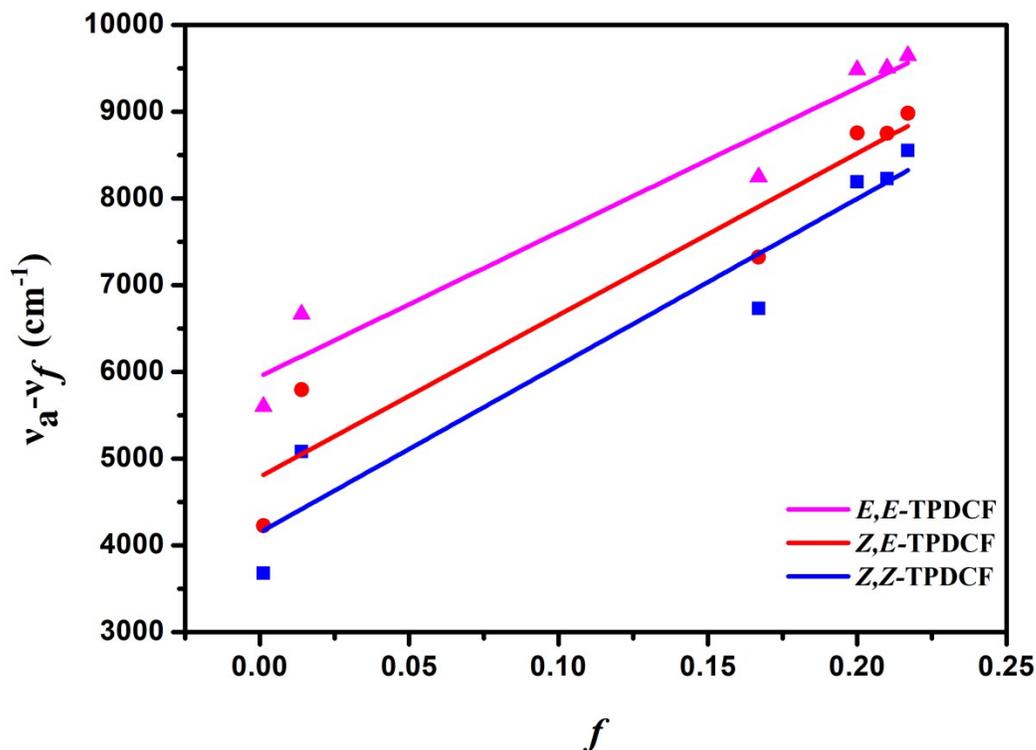


Figure S3: Linear fitting correlation of orientation polarizability (f) of solvent media with Stokes shift ($\nu_a - \nu_f$) for Z,Z -TPDCF, Z,E -TPDCF and E,E -TPDCF. (See Table S1 for data; high polar solvents such as DMF, acetonitrile and methanol, are not included due to their non-luminescence without λ_{max} of PL spectra obtained.)

Table S1. Detailed absorption and emission peak positions of *Z,Z*-TPDCF, *Z,E*-TPDCF and

Solvents	ϵ	n	$f(\epsilon, n)$	<i>Z,Z</i> -TPDCF			<i>Z,E</i> -TPDCF			<i>E,E</i> -TPDCF		
				λ_a	λ_f	$\nu_a-\nu_f$	λ_a	λ_f	$\nu_a-\nu_f$	λ_a	λ_f	$\nu_a-\nu_f$
				(nm)	(nm)	(cm ⁻¹)	(nm)	(nm)	(cm ⁻¹)	(nm)	(nm)	(cm ⁻¹)
Hexane	1.9	1.375	0.0012	400	469	3678	396	477	4288	382	486	5602
Toluene	2.38	1.494	0.014	405	510	5084	396	514	5797	385	518	6669
Ethyl ether	4.34	1.352	0.167	396	540	6734	388	542	7323	376	545	8247
Ethyl acetate	6.02	1.372	0.200	395	584	8193	386	583	8754	375	582	9485
Tetrahydrofuran	7.58	1.407	0.210	399	594	8228	390	592	8749	378	590	9506
Methylene chloride	8.93	1.424	0.217	400	608	8553	392	605	8981	380	600	9649
Dimethyl formamide	37	1.427	0.276	399	-	-	388	-	-	375	-	-
Acetonitrile	37.5	1.344	0.305	392	-	-	385	-	-	370	-	-
Methanol	32.7	1.329	0.308	392	-	-	382	-	-	372	-	-

E,E-TPDCF in different solvents.

Through the analysis of the fitted line in different polar solvents as shown in Figure S4 (high polar solvents such as DMF, acetonitrile and methanol, are not included due to the non-luminescence without λ_{\max} of PL spectra obtained), slope values of ~ 19238 ($R= 0.93$), 18641 ($R= 0.91$) and 16646 ($R= 0.94$) were obtained for *Z,Z*-TPDCF, *Z,E*-TPDCF and *E,E*-TPDCF respectively.

4. In-situ ¹H NMR spectra in high-polar DMSO-d6

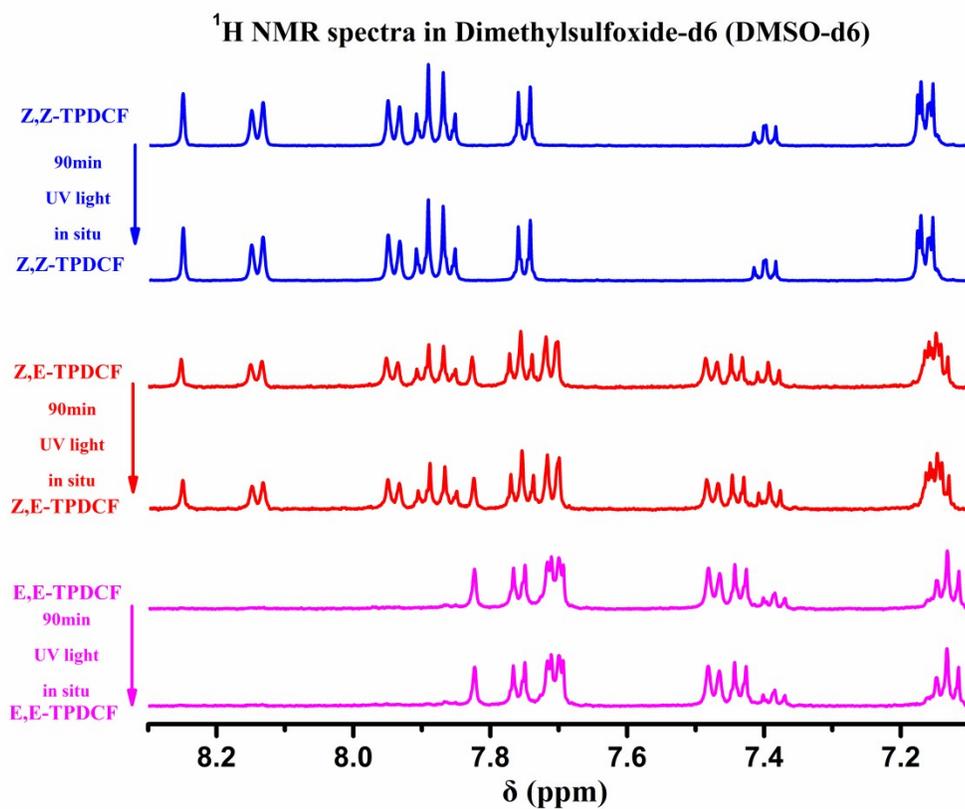


Figure S4. The original and in-situ ¹H NMR spectra of *Z,Z*-TPDCF, *Z,E*-TPDCF and *E,E*-TPDCF under photo-irradiation of UV light (365 nm) for 90 min in DMSO-d₆.