Supporting Information

Tuning the fluorescence based on the Combination of TICT and AIE Emission of a Tetraphenylethylene with D-π-A Structure

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Synthesis of TPEOMeCN

TPEOMeCN was synthesized with some of the modifications according to the reported work. [1] TEA (11.2 mL, 80 mmol) was added to the solution mixed with 4, 4'-dihydroxybenzophenone (4.28 g, 20 mmol), DCM (120mL) and THF (33.4 mL). Trimethylacetyl chloride (9.84 mL, 80 mmol) was added to the above reaction mixture and stirred at room temperature. The reaction mixture was treated with HCl and extracted with EtOAc after the completion of the reaction monitored by TLC analysis. The combined organic layer was dried over anhydrous Na_2SO_4. The filtrate was concentrated in vacuo after filtration, and the resulting reside was purified via silica gel flash column chromatography using DCM as the eluent to obtain the white powder 4,4'-carbonylbis(4,1-phenylene)bis(2,2-dimethylpropanoate) (7.02 g). The 4,4'-carbonylbis(4,1-phenylene)bis(2,2-dimethylpropanoate) (3.82 g, 10 mmol), carbon tetrabromide (6.63 g，20 mmol), and triphenyl phosphine (10.49 g, 40 mmol) were mixed in anhydrous toluene. It reacted at 120℃ for 4 days under the protection of nitrogen. Then the mixture was cooled down to room temperature. The mixture was filtered, washed with toluene and the filtrate was collected. The organic layer was separated, dried with Na_2SO_4, and then the solvent was removed by rotary evaporator. After the residue was purified by column chromatography on silica gel using n–hexane as the eluent to obtain the light yellow solid 4,4'-(2,2-dibromoethene-1,1-diyl)bis(4,1-phenylene)bis(2,2-dimethylpropanoate) (2.80 g). The 4,4'-(2,2-dibromoethene-1,1-diyl) bis(4,1-phenylene) bis (2,2-dimethylpropanoate) (2.69 g, 5 mmol) and K_2CO_3 (2.3 g, 16.5 mmol) were dissolved in MeOH (120 mL) and DCM (20 mL). The reaction mixture was stirred for 12 h at room temperature. The product was concentrated in vacuo and DCM was used as extractant. The combined organic layer was dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and the resulting reside was purified via silica gel flash column chromatography using DCM/n-hexane (v/v: 1:1) as the eluent to obtain the light yellow solid 4,4'-(2,2-dibromoethene-1,1-diyl)diphenol (1.52g). The 4,4'-(2,2-dibromoethene-1,1-diyl)diphenol (1.11 g, 3 mmol), methyl iodide (0.56 g, 9 mmol), and K_2CO_3 (4.15 g, 30 mmol) were dissolved in 50 mL of

acetone. After stirring for 24 h at 70℃, the reaction mixture was concentrated in vacuo. The organic layer was separated and the aqueous layer was extracted three times with DCM. The combined organic layer was dried over anhydrous Na_2SO_4 .After filtration, the filtrate was concentrated in vacuo and the resulting reside was purified via silica gel flash column chromatography using n-hexane/ DCM (v/v: 6:4) as the eluent to obtain 4,4'-(2,2-dibromoethene-1,1-diyl) bis ((methoxy)benzene) (0.9 g). The 4,4'-(2,2-dibromoethene-1,1-diyl) bis ((methoxy)benzene) (0.80 g, 2 mmol), 4-cyanophenylboric acid (1.47 g, 10 mmol), K_2CO_3(2.76 g, 10 mmol) and $Pd(PPh_3)_4$ (0.23 g, 0.2 mmol) was added into 50 mL of toluene under nitrogen protection. Then, 2 mL of water and 2 mL of ethanol were added into the above solution and it reacted at 120℃ for 12 h. The product was concentrated in vacuo and DCM was used as extractant. The combined organic layer was dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and the resulting reside was purified via silica gel flash column chromatography using n-hexane/ DCM (v/v: 4:6). Finally, the white powder TPEOMeCN was obtained (0.63 g).

Reference

1. Z. Chen, T. Chen, J. Liu, G. Zhang, C. Li, W, Gong, Z. Xiong, N. Xie, B. Tang, M. Zhu, *Macromolecules*, 2015, **48**, 7823.

Captions

Figure S1. ^{1}H NMR spectrum of **TPEOMeCN** in CDCl$_3$.

Figure S2. 2D COSY spectrum of compound **TPEOMeCN** in CDCl$_3$

Figure S3. ^{13}C NMR spectrum of **TPEOMeCN** in CDCl$_3$.

Figure S4. ESI-MS spectrum of **TPEOMeCN**.

Figure S5. Fluorescence spectrum of **TPEOMeCN** crystals

Figure S6. Normalized UV-Vis spectra of **TPEOMeCN** in different solvents.

Figure S7. Normalized fluorescence spectra of **TPEOMeCN** in DMSO and DMF.

Figure S8. Uv-vis spectra of **TPEOMeCN** in H$_2$O-DMSO mixtures with different water fractions.

Figure S9. Normalized fluorescence spectra of **TPEOMeCN** (fresh prepared and kept for 2 h) in H$_2$O-DMSO mixtures (f_w = 50%).

Figure S10. Fluorescence spectra of TPEOMeCN in H$_2$O-DMSO mixtures with different water fractions; Fluorescent intensity of 423 nm and 518 nm respond to the changes of water fractions in H$_2$O-DMSO mixtures. The water used have different pH values: pH=2.20 (A) and (B); pH=11.02 (C) and (D). Concentration: 50 µM; λ_{ex}: 320 nm (5 nm, 5 nm).

Figure S11. Linear fitting of double logarithmic plots of intensity versus viscosity for **TPEOMeCN** (Viscosity $\leq$ 151.9 cP).

Table S1. Crystal data and structure refinement for **TPEOMeCN**.

Table S2. Photophysical properties of **TPEOMeCN** in different solvents
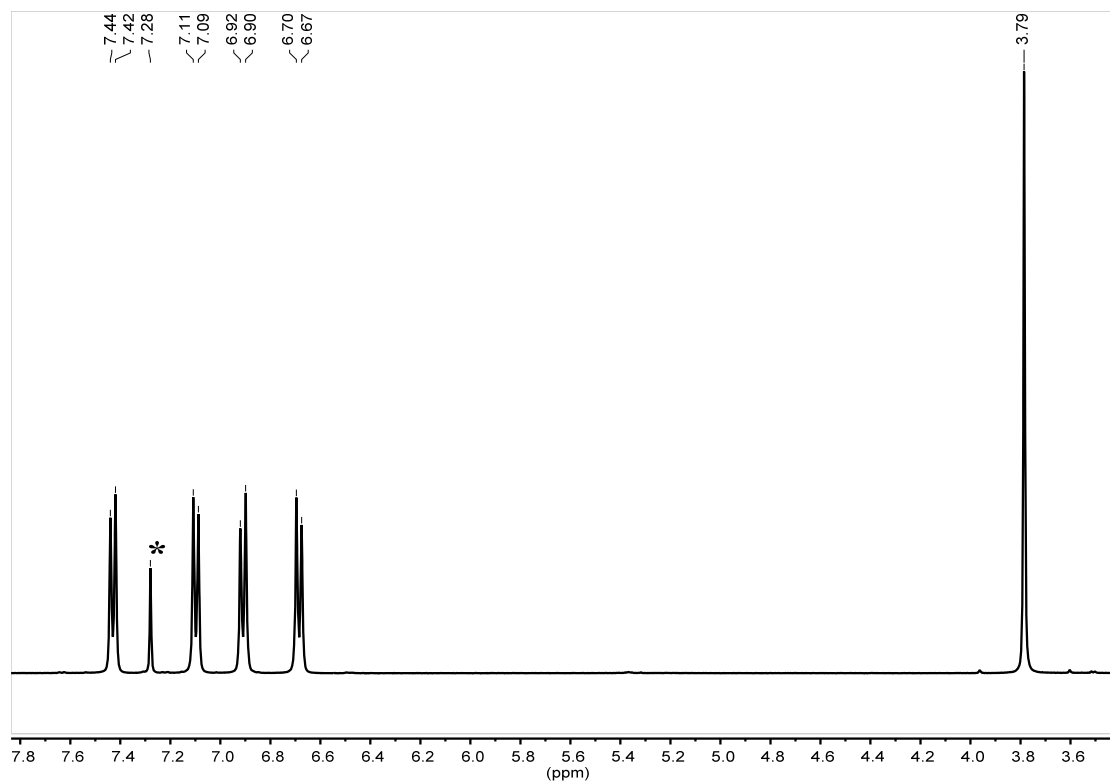
Table S3. Solvent composition and viscosity

Figure S1. ^{1}H NMR spectrum of **TPEOMeCN** in CDCl$_3$. The residual solvent signals are marked with asterisk.
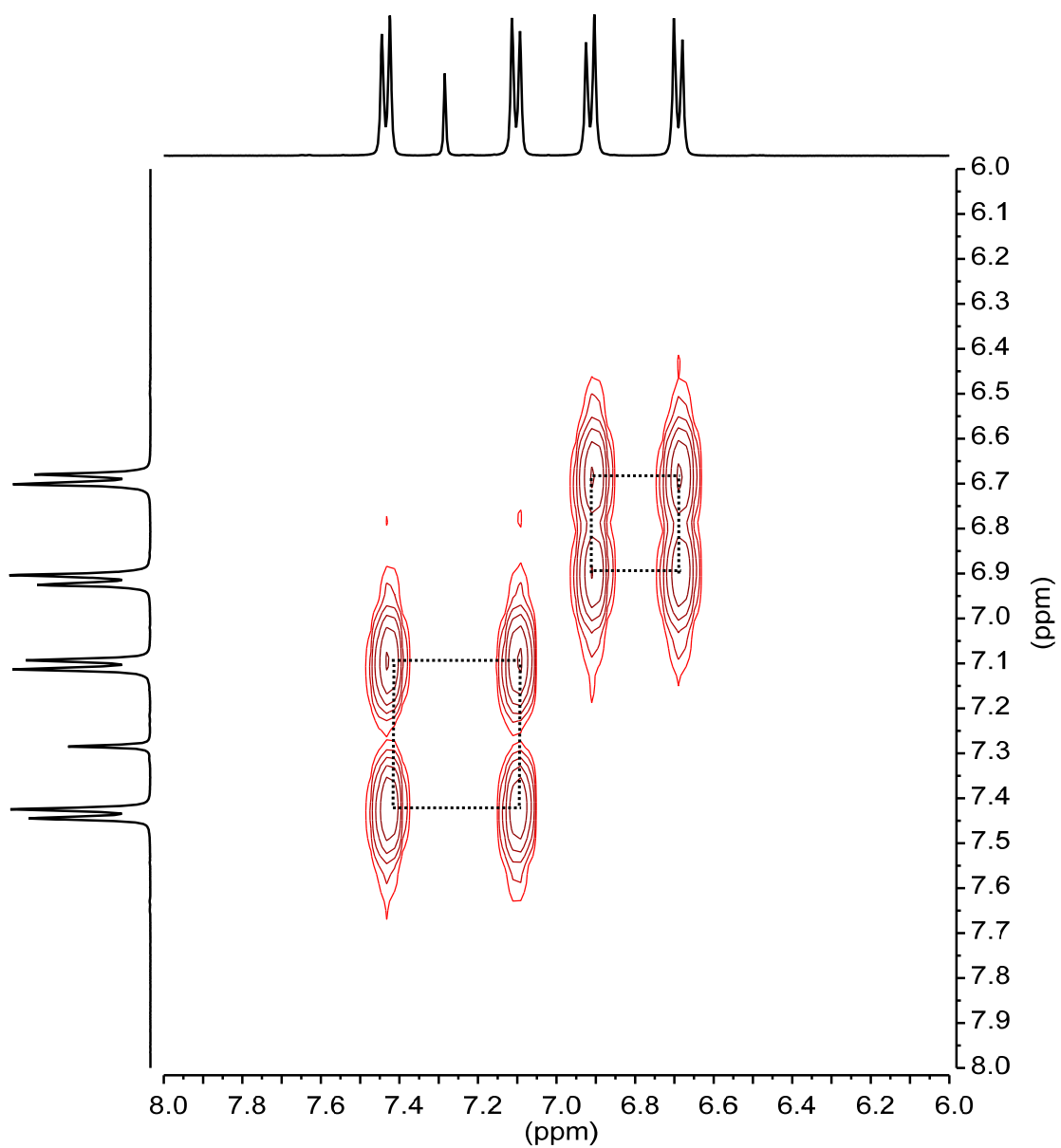
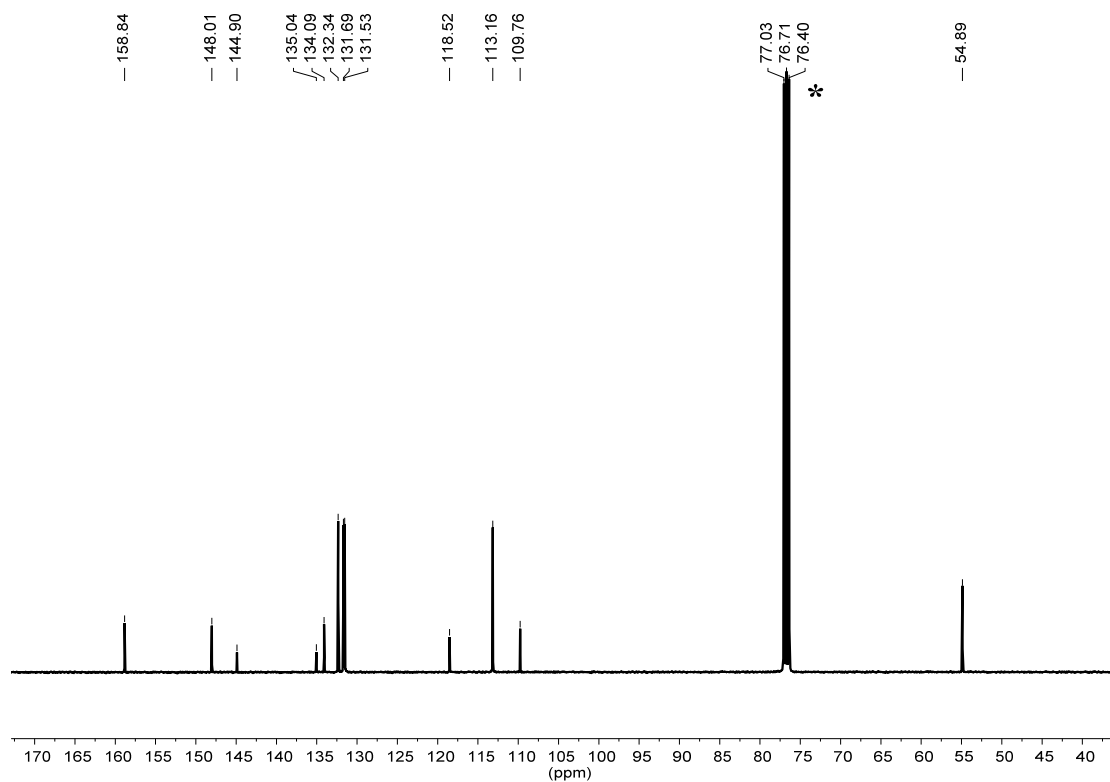**Figure S2.** 2D COSY spectrum of **TPEOMeCN** in CDCl₃

Figure S3. ^{13}C NMR spectrum of compound **TPEOMeCN** in CDCl$_3$. The residual solvent signals are marked with asterisks.
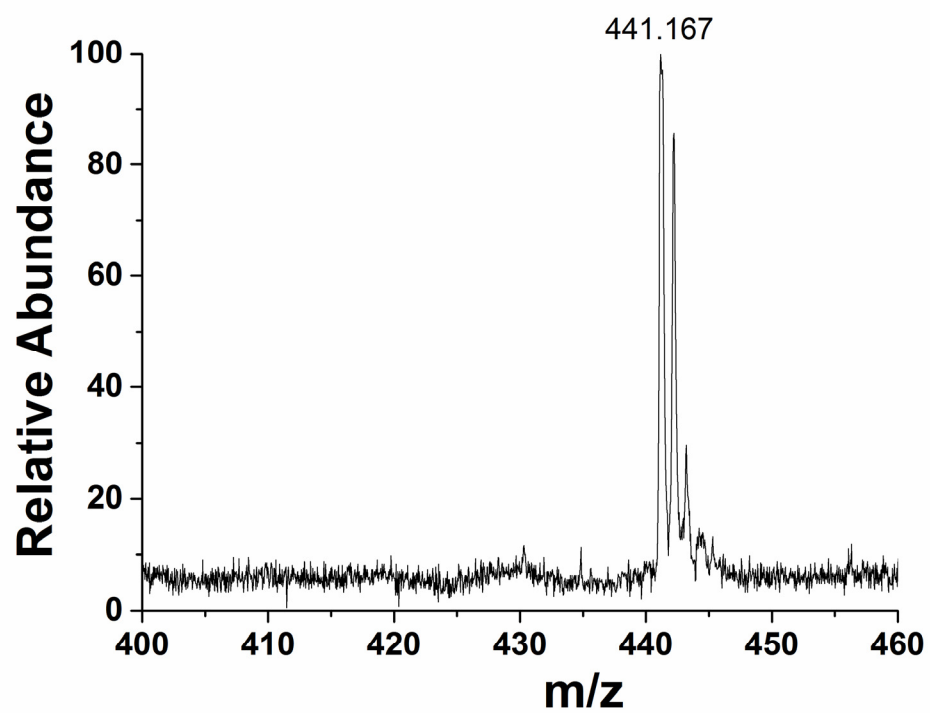
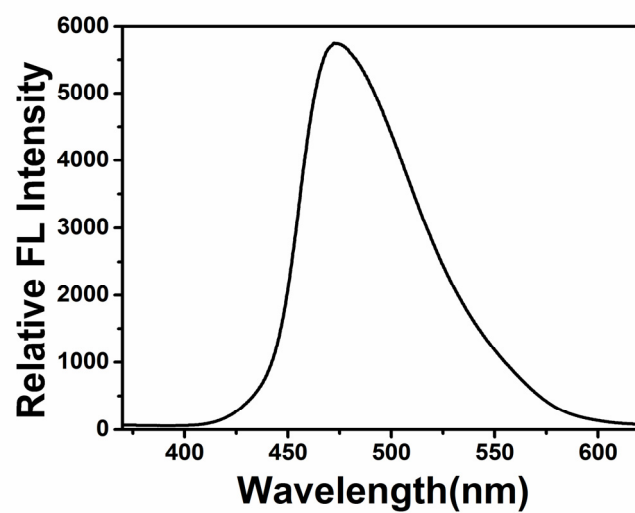**Figure S4.** MALDI-TOF mass spectrum of compound **TPEOMeCN**.

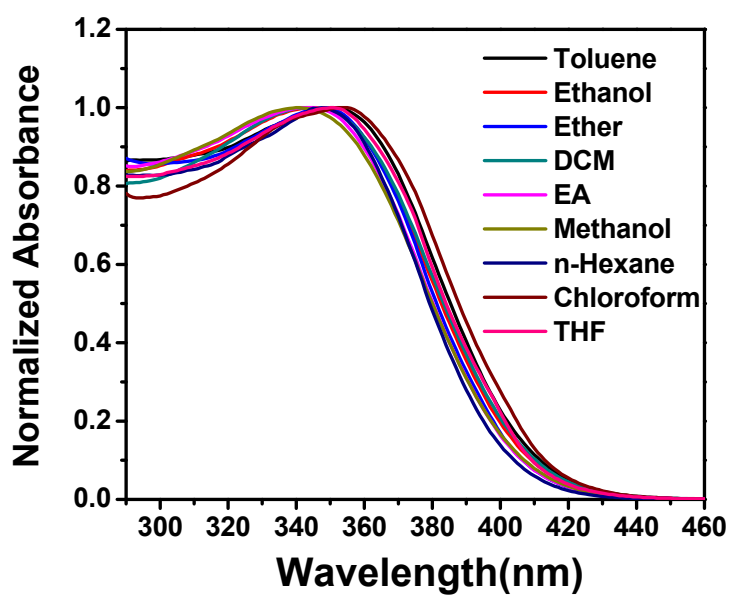**Figure S5.** Fluorescence spectrum of **TPEOMeCN** crystals

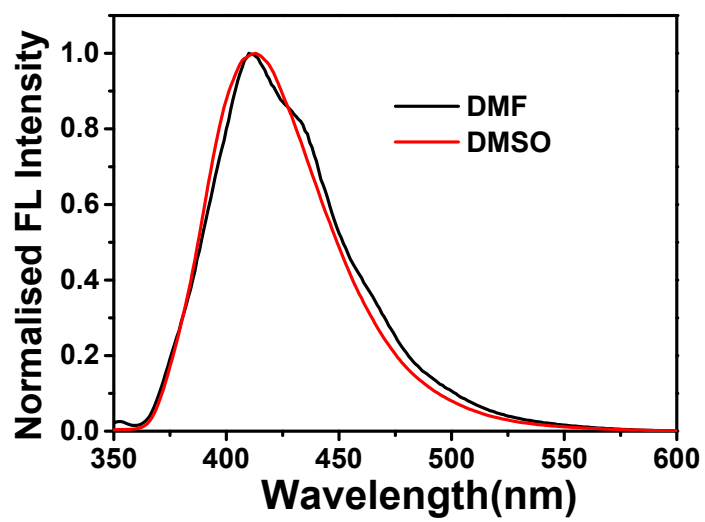**Figure S6.** Normalized UV-Vis spectra of **TPEOMeCN** in different solvents.

Figure S7. Normalized fluorescence spectra of **TPEOMeCN** in DMSO and DMF.
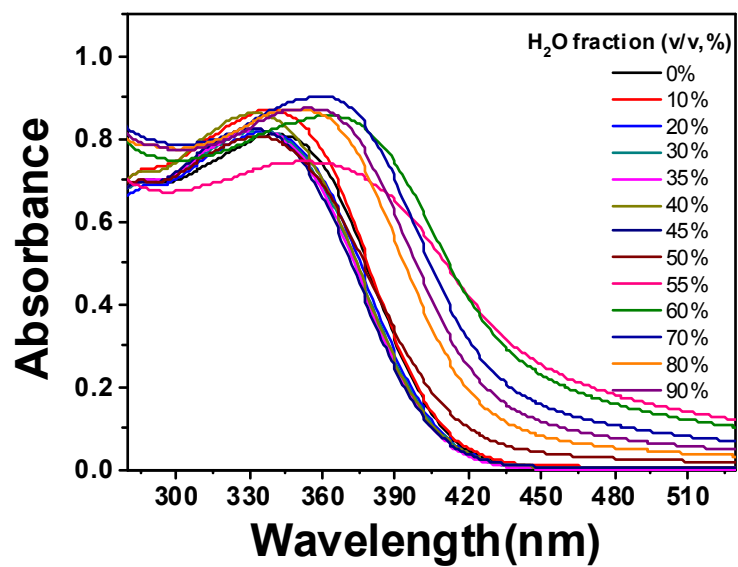
Figure S8. Uv-vis spectra of **TPEOMeCN** in H_2O-DMSO mixtures with different

water fractions. Concentration: 50 μM.

Figure S9. Normalized fluorescence spectra of **TPEOMeCN** (fresh prepared and kept for 2 h) in H_2O-DMSO mixtures (f_w = 50%).

Figure S10. Fluorescence spectra of TPEOMeCN in H_2O-DMSO mixtures with different water fractions; Fluorescent intensity of 423 nm and 518 nm respond to the changes of water fractions in H_2O-DMSO mixtures. The water used have different pH values: pH=2.20 (A) and (B); pH=11.02 (C) and (D). Concentration: 50 μM; λ_{ex}: 320 nm (5 nm, 5 nm).

The chart contains the following fitting data table:

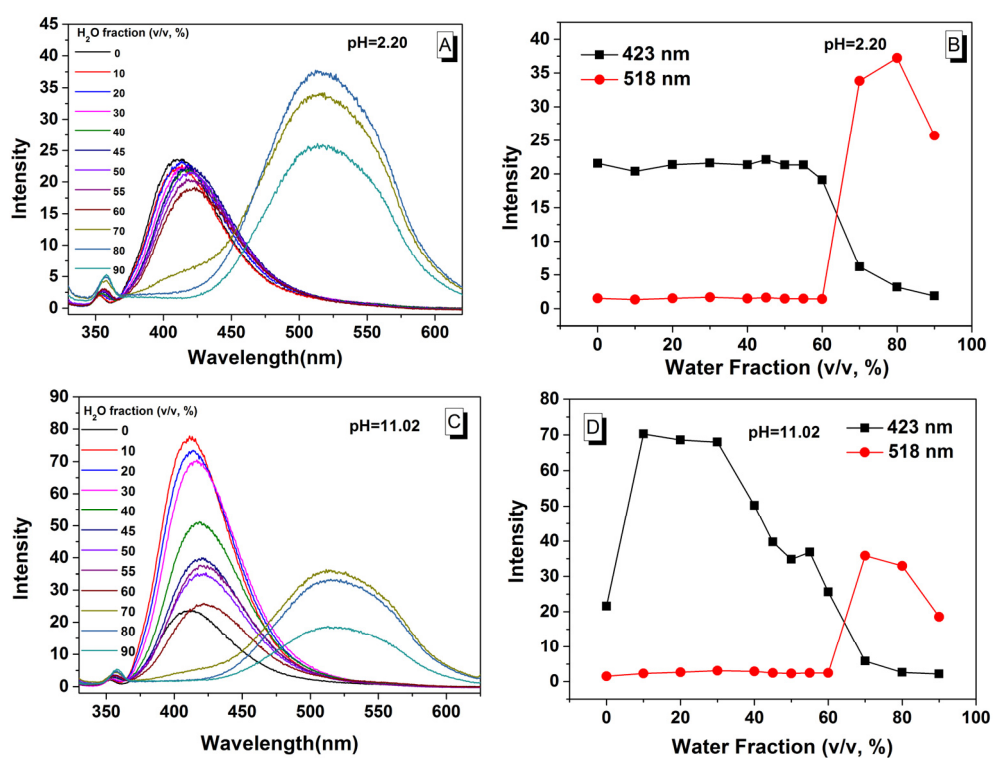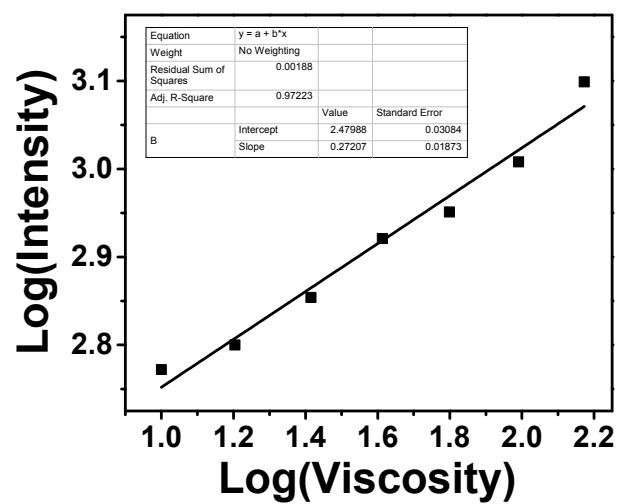| Equation	y = a + b*x	
Weight	No Weighting	
Residual Sum of Squares	0.00188	
Adj. R-Square	0.97223	
	Value	Standard Error
Intercept	2.47988	0.03084
Slope	0.27207	0.01873

Figure S11. Linear fitting of double logarithmic plots of intensity versus viscosity for

TPEOMeCN (Viscosity $\leqslant$ 151.9 cP).

Table S1. Crystal data and structure refinement for **TPEOMeCN**.

Empirical formula	$C_{30}H_{22}N_2O_2$
Formula weight	442.49
Temperature	293(2) K
Wavelength	1.54178 Å
Crystal system, space group	Monoclinic , $P2_1/n$
Unit cell dimensions	$a = 9.6368(13)$Å $\quad \alpha = 90°$
	$b = 15.6248(16)$ Å $\quad \beta = 90°$
	$c = 16.1815(18)$ Å $\quad \gamma = 90°$
Volume	2436.5(5) Å^3
Z, Calculated density	4, 1.206 g/cm^3
$F(000)$	928.0
Crystal size	0.20× 0.10 × 0.05 mm
Theta range for data collection	7.866 to 135.338 °
Limiting indices	$-11 \leq h \leq 11$, $-11 \leq k \leq 18$, $-16 \leq l \leq 9$
Reflections collected / unique	3222 / 2593 $\quad [R(\text{int}) = 0.0220]$
Data / restraints / parameters	2593 / 0 / 309
Goodness-of-fit on F^2	1.372
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1260$, $wR_2 = 0.3479$
R indices (all data)	$R_1 = 0.1773$, $wR_2 = 0.4183$
Largest diff. peak and hole	0.25 and -0.51 e. Å^{-3}

Table S2. Photophysical properties of TPEOMeCN in different solvents [a]

Solvent	Δf	λ_{max} (abs)	λ_{max} (PL)	Stokes shift (cm^{-1})
Toluene	0.014	351	434	5449
Ethanol	0.29	346	435	5913
Diethyl Ether	0.25	348	428	5371
Dichloromethane	0.22	343	435	6166
Ethyl Acetate	0.2	343	429	5844
Methanol	0.31	341	434	6284
n-Hexane	0.001	348	425	5206
Chloroform	0.15	352	436	5473
Tetrahydrofuran	0.21	350	432	5423

[a] Abbrevaiation: Δf =The orientational polarisability, λ_{max} (abs) is the lowest energy absorption peak at concentration = 50 µM. λ_{max} (PL) is measured at λ_{ex}: 320 nm and concentration = 50 µM.

The orientational polarizability, Δf, described in eq 1, is chosen as the measure of polarity.

$$\Delta f = \frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1} \tag{1}$$

Where ε is the static dielectric constant and n is thoptical refractive index of the solvent.

Table S3. Solvent composition and viscosity

DMSO/EG/Gly(mL)	Viscosity(cP)	Log(viscosity)
0.5/2.5/0	10.2	1.000
0.5/2.2/0.3	16.5	1.216
0.5/1.9/0.6	26.3	1.420
0.5/1.6/0.9	41.5	1.618
0.5/1.3/1.2	64.6	1.811
0.5/1.0/1.5	99.6	1.998
0.5/0.7/1.8	151.9	2.182
0.5/0.4/2.1	229.2	2.360
0.5/0.1/2.4	342.3	2.534
0.05/0.25/2.7	631.4	2.800
0.05/0.1/2.85	764.0	2.883
0.05/0/2.95	866.5	2.938

$$\ln \eta_{mix} = \sum_{i=1}^{n} w_i \cdot \ln \eta_i$$

(2)

Where η_{mix} and η_i stand for the viscosity of the mixture and the viscosity of component; i, respectively. Factor w_i stands for the weight fraction of component i. To calculate w, the values 1.10, 1.11, and 1.26 have been used for the density of DMSO, EG, and Gly, respectively. To calculate η, the values 2.47, 13.5, and 945 have been used for the viscosity of DMSO, EG, and Gly, respectively. Viscosity values for pure solvents at 20 °C were used to estimate the viscosity of the mixtures.