

Supplementary Information

Substituent Effects of AIE-Active α -Cyanostilbene-Containing Triphenylamine Derivatives on Electrofluorochromic Behaviors

Sin-Yu Chen^a, *Ya-Wen Chiu*^{a, b}, *Guey-Sheng Liou*^{a, b*}

^a Institute of Polymer Science and Engineering, National Taiwan University, Taipei
10617, Taiwan. Email: gsliau@ntu.edu.tw

^b Advanced Research Center for Green Materials Science and Technology, National
Taiwan University, Taipei 10617, Taiwan.

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active area containing 0.75 μmole EFC materials in about 0.05 mL PC and
0.75 μmole HV with 5 μmole TBABF₄.S13

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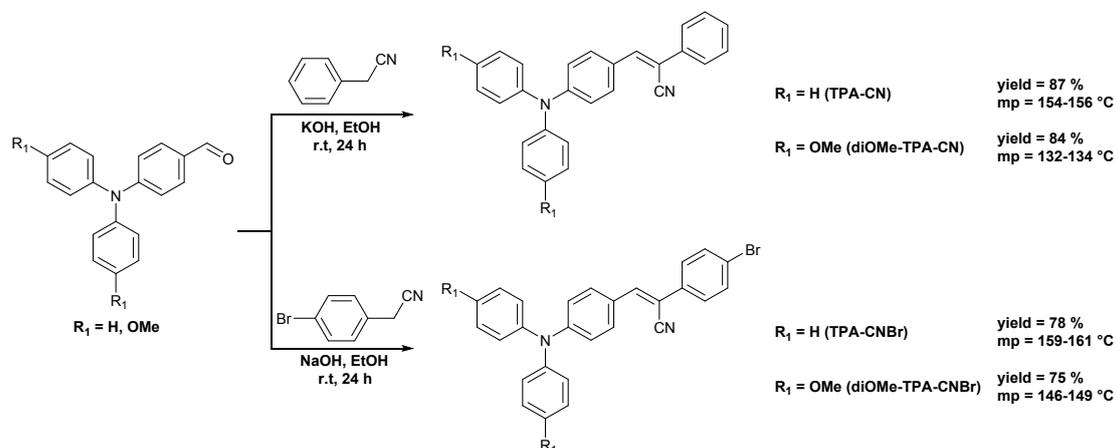
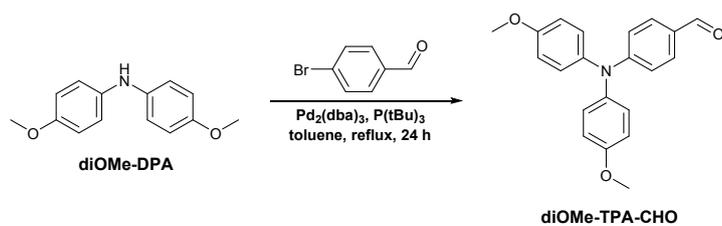
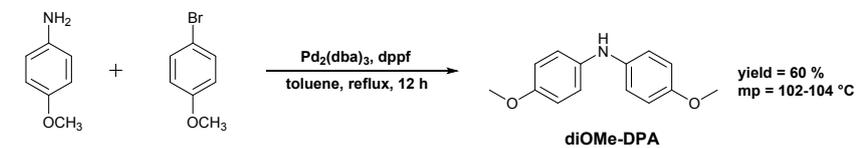
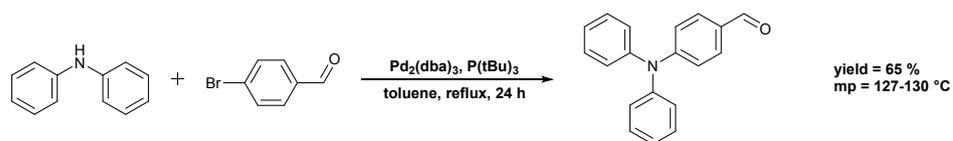
Experimental section

Monomer synthesis

Aldehyde derivatives (**TPA-CHO** and **diOMe-TPA-CHO**) and phenylacetonitrile (or 4-bromophenylacetonitrile) were used to synthesize the AIE-active α -cyanostilbene-containing triphenylamine luminogens (**TPA-CN**, **diOMe-TPA-CN**, **TPA-CNBr** and **diOMe-TPA-CNBr**), respectively, by the Knoevenagel condensation as shown in **Scheme S1**. Take **TPA-CN** as an instance, a solution of potassium hydroxide (KOH, 0.17 g, 3.0 mmol) in 10 mL ethanol was added dropwise to the mixture of **TPA-CHO** (0.55 g, 2.0 mmol) and phenylacetonitrile (0.35 g, 3.0 mmol) in ethanol (10 mL) at room temperature. After stirring for 24 h, bright yellow solid was obtained during the reaction, the resulting crude product was dried to afford a yellow solid (0.65 g, 87%) and purified by recrystallization. **TPA-CN**: mp 154–156 °C; $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$, δ): 7.88 (t, 3H), 7.72 (d, 2H), 7.49 (t, 2H), 7.37–7.42 (m, 5H), 7.14–7.20 (m, 6H), 6.96 (d, 2H). **TPA-CNBr**: mp 159–161 °C; $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$, δ): 7.92 (s, 1H), 7.86 (d, 2H), 7.68 (d, 4H), 7.40 (t, 4H), 7.14–7.22 (m, 6H), 6.96 (d, 2H). **diOMe-TPA-CN**: mp 132.0–133.6 °C; $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$, δ): 7.84 (s, 1H), 7.80 (d, 2H), 7.70 (d, 2H), 7.48 (t, 2H), 7.39 (t, 1H), 7.16 (d, 4H), 6.99 (d, 4H), 6.75 (d, 2H), 3.77 (s, 6H). $^{13}\text{C-NMR}$ (100 MHz, $\text{DMSO-}d_6$, δ): 157.1 (C2), 150.9 (C6), 142.6 (C10), 139.0 (C5), 134.9 (C13), 131.2 (C8), 129.4 (C15), 128.7 (C16), 128.2 (C4), 125.6 (C14), 124.5 (C9), 119.1 (C12), 117.1 (C7), 115.5 (C3), 105.3 (C11), 55.63 (C1). Anal. calcd. for $\text{C}_{29}\text{H}_{24}\text{N}_2\text{O}_2$: C 80.53; H 5.59; N 6.48; found: C 80.35; H 5.62; N 6.48. **diOMe-TPA-CNBr**: mp 146–149 °C; $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$, δ): 7.89 (s, 1H), 7.80 (d, 2H), 7.67 (d, 4H), 7.17 (d, 4H), 6.99 (d, 4H), 6.74 (d, 2H), 3.78 (s, 6H).

Characterization

OptiMelt-Automated Melting Point System and differential scanning calorimetry (DSC) were used to detect the melting point of the synthesized compounds and their scan rates are both 10 °C/min. ¹H and ¹³C NMR spectra were measured on a Bruker DPX-400 MHz FT-NMR using chloroform-D (CDCl₃) and dimethyl sulfoxide (DMSO-*d*₆) as solvents and tetramethylsilane (TMS; δ = 0 ppm) was chosen as internal reference. In addition, peak multiplicity was marked as follow: s, singlet; d, doublet; t, triplet; m, multiplet. Fourier transform infrared (FT-IR) spectra were recorded using a PerkinElmer Spectrum 100 Model FT-IR spectrometer by incorporating samples in potassium bromide (KBr) disks. Elemental analysis (EA) was performed using a Heraeus VarioEL-III CHNS element analyzer. Electrochemistry was carried out with a CH Instruments 611B electrochemical analyzer. Voltammograms are presented with the positive potential pointing to the right and with increasing anodic currents pointing upwards. Cyclic voltammetry (CV) was conducted with the optically transparent thin layer electrochemical (OTTLE) cell and Ag/AgCl, KCl (sat.) was served as reference electrode. Spectroelectrochemistry was conducted in a 1 cm quartz cell by means of Hewlett–Packard 8453 UV-vis diode array spectrophotometer. The ITO-coated glass was used as working electrode, and a platinum wire and an Ag/AgCl cell were served for the counter electrode and reference electrode, respectively. PL quantum yield (Φ_F) of materials in different solvents was measured by using quinine sulfate dissolved in 1 N sulfuric acid as a reference standard ($\Phi_F = 0.546$), and the Φ_F of small molecules in solid state was measured by a calibrated integrating sphere.



Scheme S1 Synthetic routes of **TPA-CN**, **TPA-CNBr**, **diOMe-TPA-CN** and **diOMe-TPA-CNBr**.

Fabrication of Gel-Type EFC devices

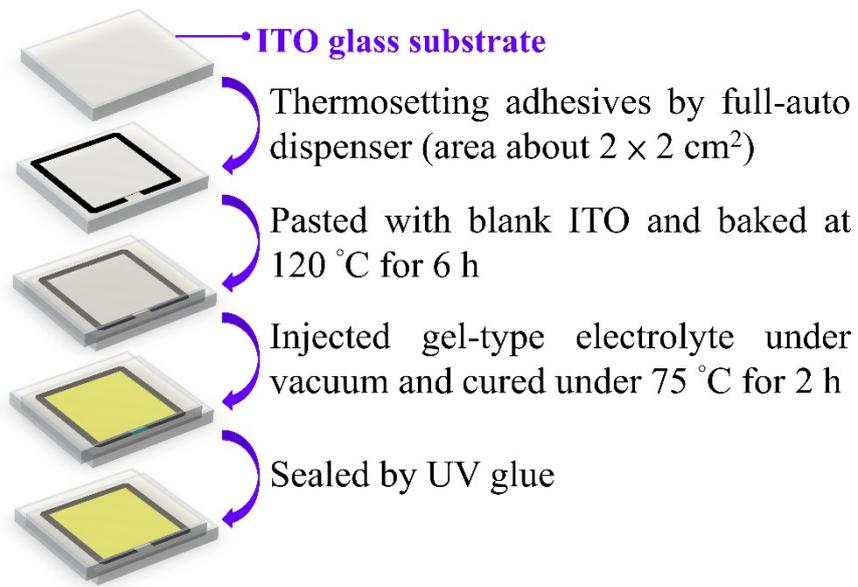


Figure S1 Fabricating procedure of the gel-type EFC devices.

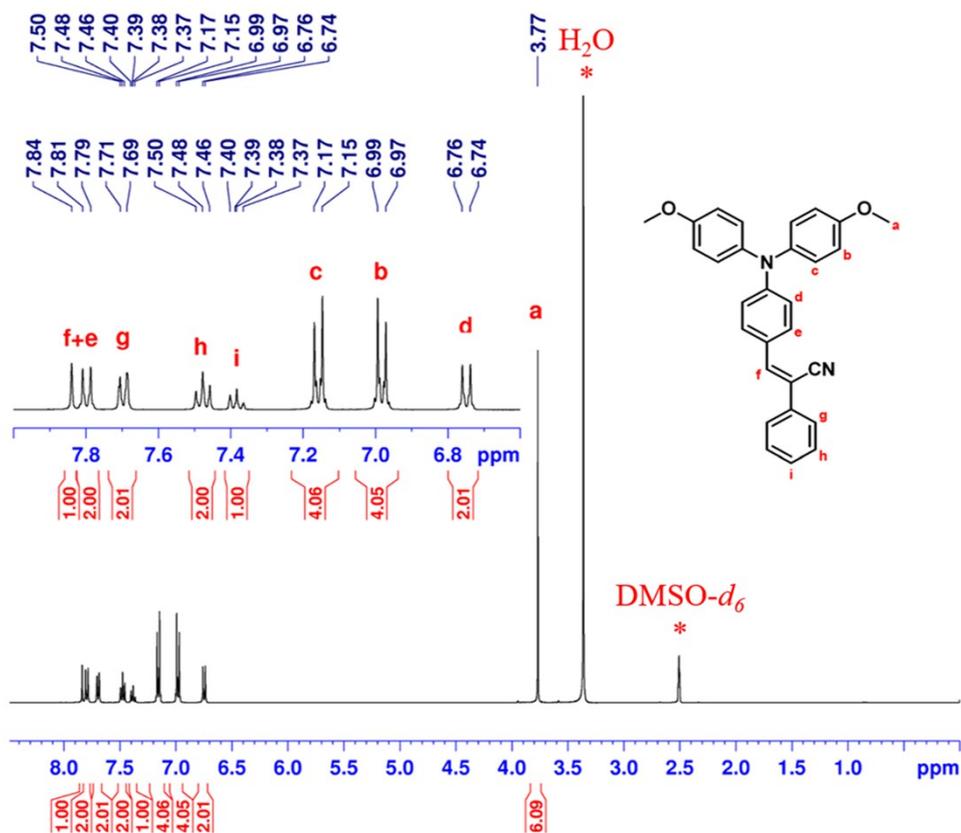


Figure S2. $^1\text{H-NMR}$ spectrum of diOMe-TPA-CN in $\text{DMSO-}d_6$.

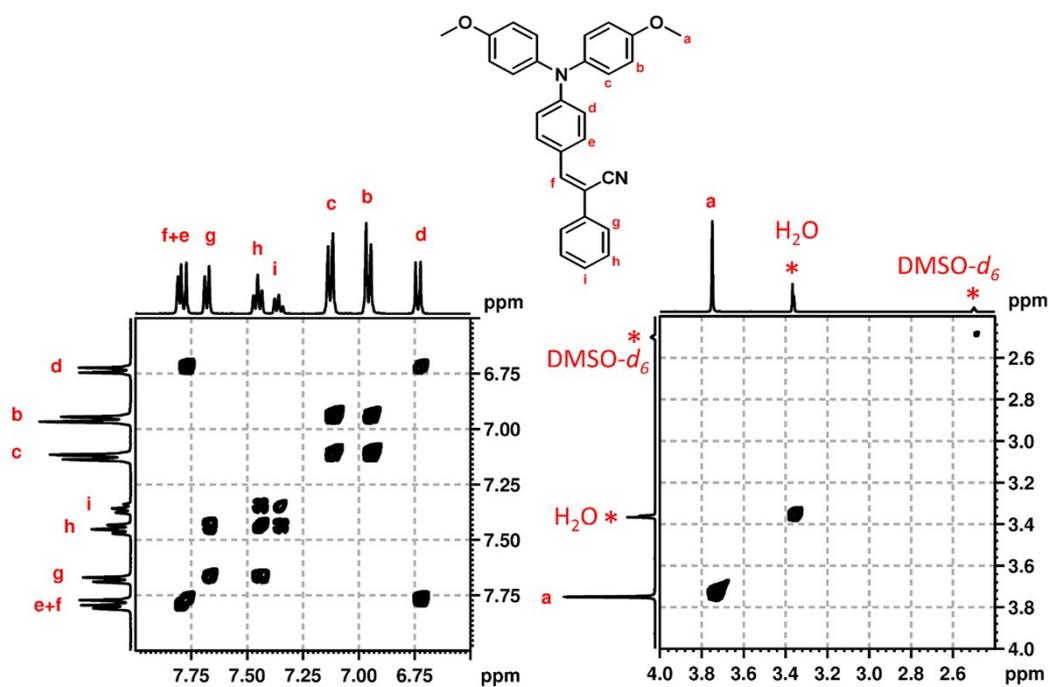


Figure S3. $^1\text{H-}^1\text{H}$ COSY spectra of diOMe-TPA-CN in $\text{DMSO-}d_6$.

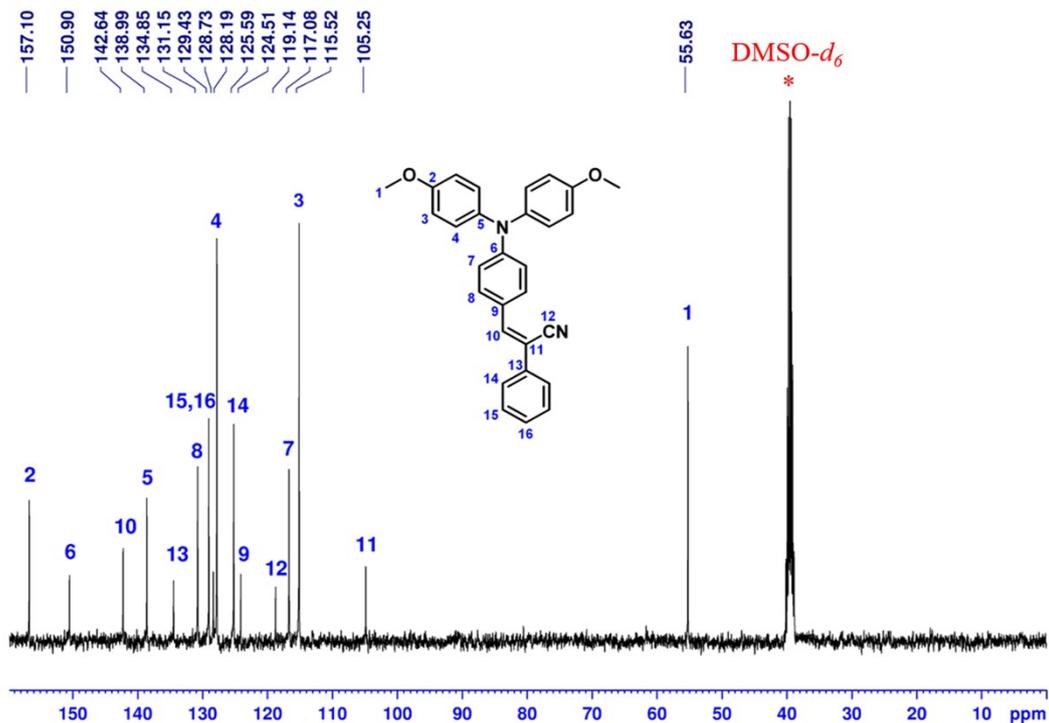


Figure S4. ^{13}C -NMR spectrum of diOMe-TPA-CN in $\text{DMSO-}d_6$.

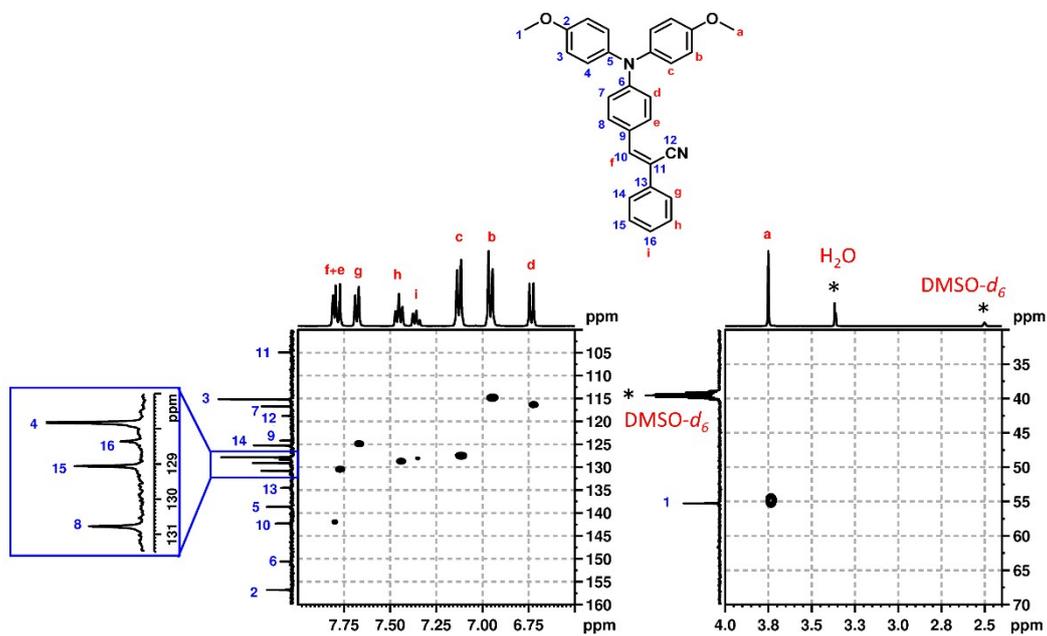


Figure S5. ^1H - ^{13}C HSQC spectrum of diOMe-TPA-CN in $\text{DMSO-}d_6$.

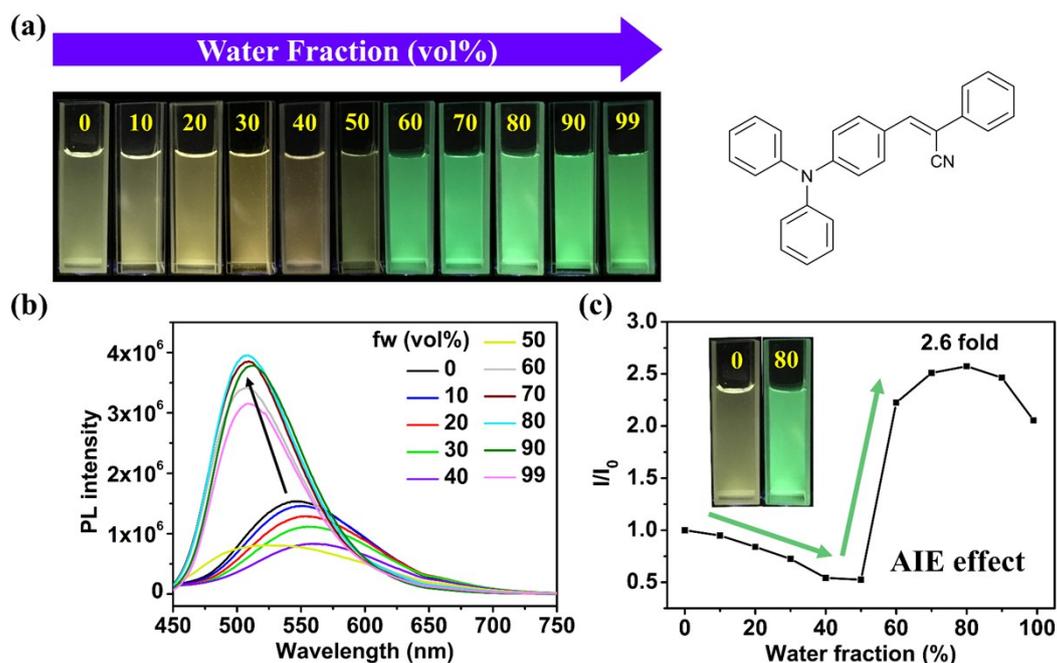


Figure S6 (a) Photos of **TPA-CN** taken under UV light at different water/DMSO fractions, (b) PL spectra of **TPA-CN** in water/DMSO mixtures with different water fractions (f_w). (c) Plot of relative emission intensity (I/I_0) versus the composition of aqueous mixtures of **TPA-CN**. I_0 = Emission intensity in pure DMSO solution. Solution concentration: 10 μ M; λ_{ex} : 396 nm.

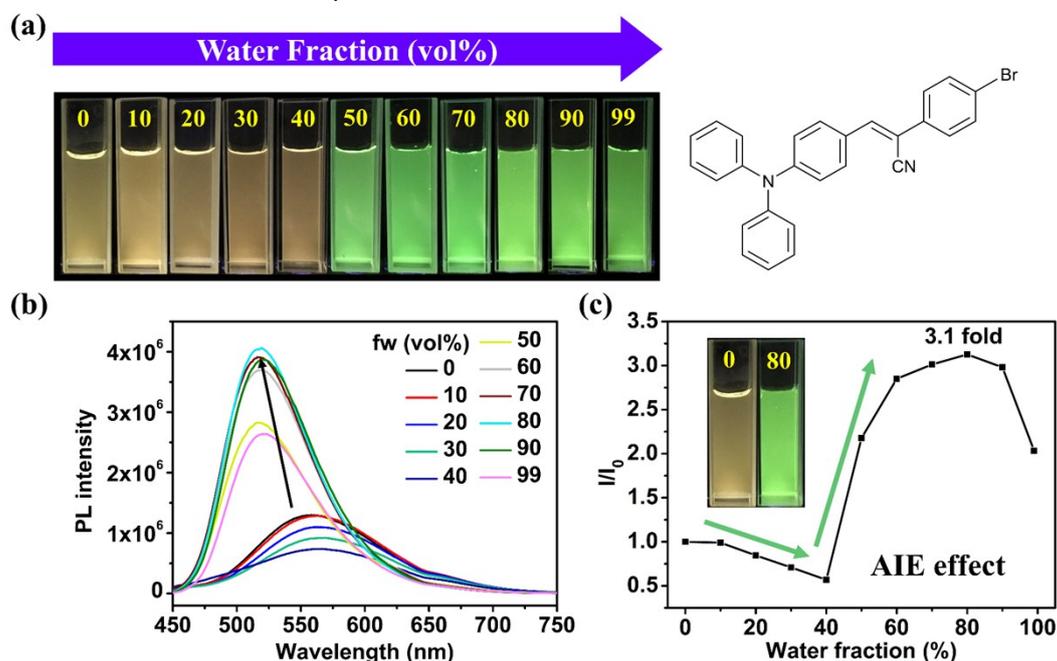


Figure S7. (a) Photos of **TPA-CNBr** taken under UV light at different water/DMSO fractions, (b) PL spectra of **TPA-CNBr** in DMSO and water/DMSO mixtures with different water fractions (f_w). (c) Plot of relative emission intensity (I/I_0) versus the composition of aqueous mixtures of **TPA-CNBr**. I_0 = Emission intensity in pure DMSO solution. Solution concentration: 10 μ M; λ_{ex} : 402 nm.

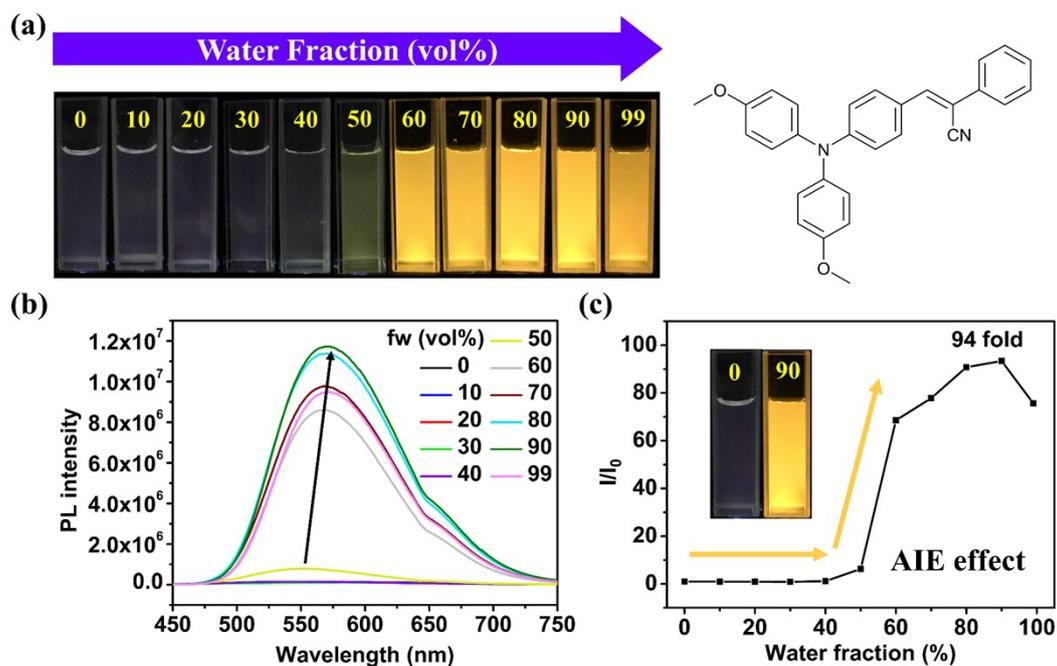


Figure S8. (a) Photos of **diOMe-TPA-CN** taken under UV light at different water/DMSO fractions, (b) PL spectra of **diOMe-TPA-CN** in DMSO and water/DMSO mixtures with different water fractions (f_w). (c) Plot of relative emission intensity (I/I_0) versus the composition of aqueous mixtures of **diOMe-TPA-CN**. I_0 = Emission intensity in pure DMSO solution. Solution concentration: 10 μ M; λ_{ex} : 415 nm.

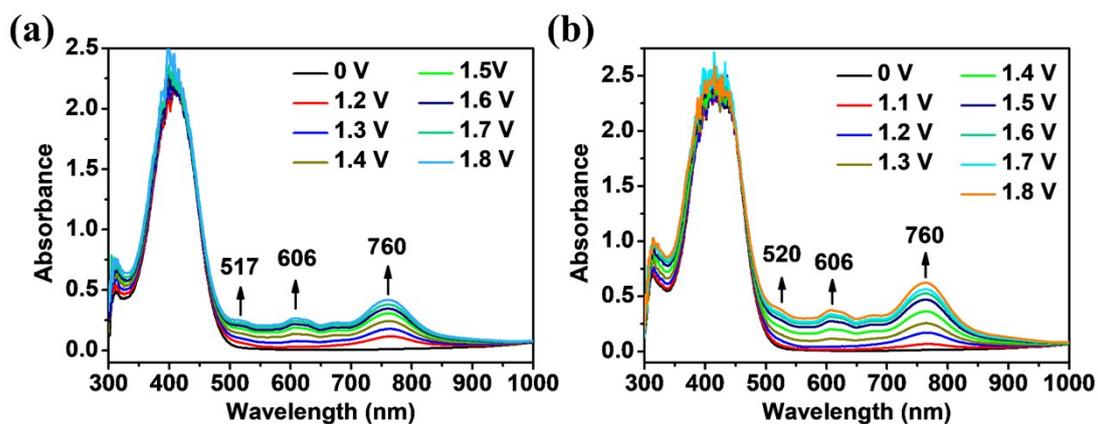


Figure S9. Absorbance spectra of gel-type EFC devices based on 0.75 μmole (a) **diOMe-TPA-CN** and (b) **diOMe-TPA-CNBr** with 0.75 μmole HV at the applied potential of 0–1.8 V.

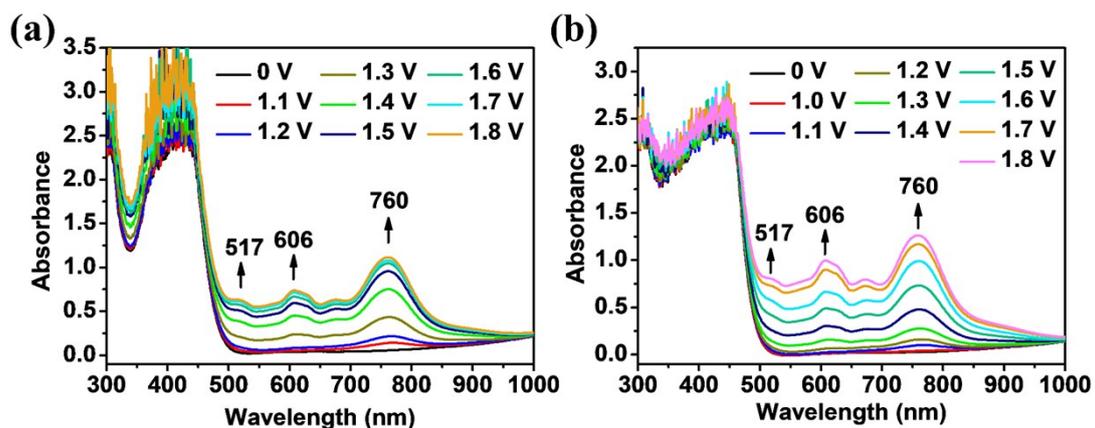


Figure S10. Absorbance spectra of gel-type EFC devices based on (a) 0.75 μmole /1.5 μmole **diOMe-TPA-CN/HV** and (b) 1.5 μmole /1.5 μmole **diOMe-TPA-CN/HV** at the applied potential of 0–1.8 V.

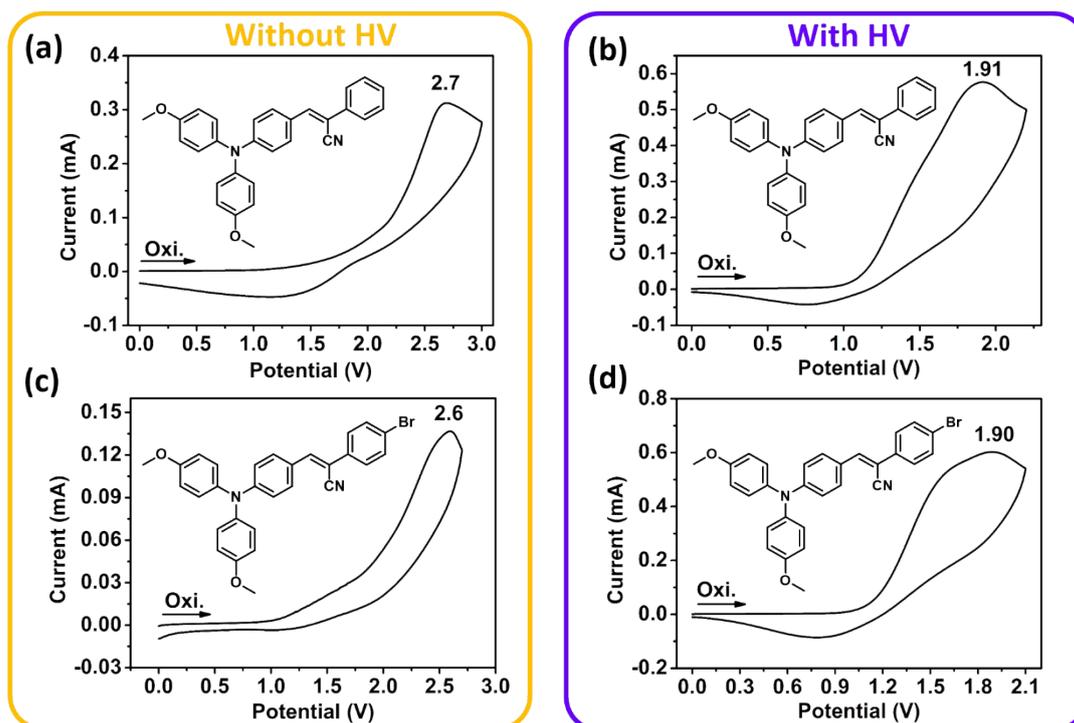


Figure S11. Cyclic voltammograms of gel-typed EFC devices based on (a) diOMe-TPA-CN, (b) diOMe-TPA-CNBr, (c) diOMe-TPA-CN with HV and (d) diOMe-TPA-CNBr with HV. Devices are ITO glasses with 2×2 cm² active area containing 0.75 μ mole EFC materials in about 0.05 mL PC and 0.75 μ mole HV with 5 μ mole TBABF₄.

Table S1. Single Crystal data and experimental details for **TPA-CN**.

Compound	TPA-CN
Empirical formula	C ₂₇ H ₂₀ N ₂
Formula weight	372.45
Crystal system	Monoclinic
Space group	P 1 2 ₁ /n 1
Unit cell dimensions	a = 16.9323(5) Å b = 6.68910(10) Å c = 19.8297(6) Å $\alpha = 90^\circ$ $\beta = 111.138(4)^\circ$ $\gamma = 90^\circ$
Volume	2094.83(9) Å ³
Z	4
F(000)	784
Density (calculated)	1.181 Mg/m ³
Wavelength	1.54178 Å
Cell parameters reflections used	5172
Theta range for Cell parameters	4.2840 to 77.3900°
Absorption coefficient	0.532 mm ⁻¹
Temperature	150(2) K
Crystal size	0.25 × 0.25 × 0.20 mm ³
Diffractometer	Xcalibur, Atlas, Gemini
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.95017
No. of measured reflections	8885
No. of independent reflections	3800 [R(int) = 0.0237]
No. of observed [I > 2 σ (I)]	3194
Completeness to theta = 68.00°	99.9 %
Theta range for data collection	2.95 to 68.00°
Final R indices [I > 2 σ (I)]	R1 = 0.0445, wR2 = 0.1200
R indices (all data)	R1 = 0.0524, wR2 = 0.1281
Goodness-of-fit on F ²	1.018
No. of reflections	3800
No. of parameters	262
No. of restraints	0
Largest diff. peak and hole	0.162 and -0.224 e.Å ⁻³

Table S2. Single Crystal data and experimental details for **diOMe-TPA-CN**.

Compound	diOMe-TPA-CN
Empirical formula	C ₂₉ H ₂₄ N ₂ O ₂
Formula weight	432.50
Temperature	200(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P 1 2 ₁ /c 1
Unit cell dimensions	a = 10.8798(4) Å b = 11.8215(4) Å c = 35.5224(13) Å $\alpha = 90^\circ$ $\beta = 90.737(4)^\circ$ $\gamma = 90^\circ$
Volume	4568.4(3) Å ³
Z	8
Density (calculated)	1.258 Mg/m ³
Absorption coefficient	0.626 mm ⁻¹
F(000)	1824
Crystal size	0.25 × 0.20 × 0.15 mm ³
Theta range for data collection	3.94 to 67.98°
Index ranges	-12 ≤ h ≤ 13, -14 ≤ k ≤ 10, -39 ≤ l ≤ 42
Reflections collected	20248
Independent reflections	8316 [R(int) = 0.0419]
Completeness to theta = 67.98°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.94975
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8316 / 0 / 595
Goodness-of-fit on F ²	1.015
Final R indices [I > 2σ(I)]	R1 = 0.0506, wR2 = 0.1293
R indices (all data)	R1 = 0.0842, wR2 = 0.1542
Largest diff. peak and hole	0.181 and -0.212 e.Å ⁻³

Table S3. Single Crystal data and experimental details for **diOMe-TPA-CNBr**.

Compound	diOMe-TPA-CNBr
Empirical formula	C ₂₉ H ₂₃ Br N ₂ O ₂
Formula weight	511.40
Temperature	200(2) K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 11.2848(5) Å b = 12.4618(5) Å c = 17.9846(8) Å α = 76.742(4)° β = 78.065(4)° γ = 83.320(4)°
Volume	2402.22(18) Å ³
Z	4
Density (calculated)	1.414 Mg/m ³
Absorption coefficient	2.560 mm ⁻¹
F(000)	1048
Crystal size	0.400 × 0.120 × 0.060 mm ³
Theta range for data collection	3.65 to 68.00°
Index ranges	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -21 ≤ l ≤ 21
Reflections collected	19911
Independent reflections	8741 [R(int) = 0.0445]
Completeness to theta = 68.00°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.60427
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8741 / 0 / 613
Goodness-of-fit on F ²	1.014
Final R indices [I > 2σ(I)]	R1 = 0.0462, wR2 = 0.1150
R indices (all data)	R1 = 0.0707, wR2 = 0.1322
Largest diff. peak and hole	0.558 and -0.602 e.Å ⁻³

Table S4. Solubility test^a of **diOMe-TPA-CN** and **diOMe-TPA-CNBr** in PC.

	0.75 μ mole	1.5 μ mole	2.25 μ mole
diOMe-TPA-CN	+	+	+
diOMe-TPA-CNBr	+	-	-

^aQualitative solubility was tested under different amount of materials in 0.05 mL PC. +, soluble at room temperature; -, insoluble at room temperature.