Supporting information for:

A flexible rotator–expanded molecular framework integrated strategy for improving microviscosity sensitivity of molecular rotor probes

Xiaofang Tang,[†] Yaping Zhu,[‡] Weijiang Guan*[,‡] and Chao Lu*[,†,‡]

[†]*Pingyuan Laboratory, College of Chemistry, Zhengzhou University, Zhengzhou, 450001, China.*

[‡]*State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China.*

Experimental section

Chemicals and materials. Caesium carbonate (Cs_2CO_3), cupric oxide (CuO), and potassium carbonate (K_2CO_3) were obtained from J&K Scientific Ltd. (Beijing, China). 1,6-Dibromohexane was acquired from Tokyo Chemical Industry Co. Ltd. (Japan). 4-(Diethylamino)salicylaldehyde and 1,4-dimethylpyridinium iodide were purchased from Heowns Biochem Technologies (Tianjin, China). 4-(1,2,2-Triphenylvinyl)phenol (TPE-OH) and 1,1,2-triphenyl-2-(4-bromomethylphenyl)ethylene were supplied by Zhengzhou Alpha Chemical Co. LTD (Zhengzhou, China). Glycerol obtained from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Polyvinyl alcohol (PVA) was purchased from Shanghai Adamas Reagents Co., Ltd. (Shanghai, China). Additionally, solvents including ethanol, acetone, piperidine, n-hexane, petroleum ether (PE), ethyl acetate (EA), tetrahydrofuran (THF), methanol (MeOH), acetonitrile (ACN), dimethyl sulfoxide (DMSO), and dichloromethane were procured from Beijing Chemical Reagent Company (Beijing, China). All reagents were of analytical grade and employed without further purification. The deionized water used in the experiments was purified using a Milli-Q Advantage A10 system from Merck Millipore in Germany.

Synthesis of *E*-4-[4-(diethylamino)-2-hydroxystyryl]-1-methyl-pyridinium iodide (DASPI-OH). 4-(Diethylamino)salicylaldehyde (0.4836 g, 2.50 mmol) and 1,4-dimethylpyridinium iodide (0.5882 g, 2.50 mmol) were added into 10 mL of ethanol. The reaction mixture was heated to 70 °C with stirring and maintained for 4 h, followed by cooling to room temperature. Crude product was purified by column chromatography using dichloromethane/MeOH (10:1 *v/v*) as eluent. The obtained product was a dark red solid with 60% yield. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 10.11 (s, 1H), 8.56-8.58 (d, 2H), 7.94-7.98 (m, 3H), 7.46-7.48 (d, 1H), 7.11-7.15 (d, 1H),

6.30-6.33 (d, 1H), 6.20-6.21 (d, 1H), 4.14 (s, 3H), 3.35-3.40 (m, 4H), 1.11-1.15 (t, 6H). ^{13}C NMR (151 MHz, DMSO-d_6, δ): 159.73, 154.50, 151.47, 144.39, 138.34, 131.33, 121.91, 116.27, 110.73, 105.07, 97.67, 46.49, 44.46, 13.10. MS: m/z = 283.1808 ([*M*-I]$^+$, calculated for $C_{18}H_{23}N_2O^+$, 283.1805).

Synthesis of Intermediate 1. 4-(Diethylamino)salicylaldehyde (0.3865 g, 2.00 mmol) and K_2CO_3 (0.5528 g, 4.00 mmol) were added into 10 mL of acetone and stirred for 0.5 h at room temperature. 1,1,2-Triphenyl-2-(4-bromomethylphenyl)ethylene (0.4254 g, 1.00 mmol) and CuO (0.0800 g, 1.00 mmol) were added into the above mixture and stirred for 5 h at 50 °C. After cooling to room temperature, the mixture was filtered for removal of K_2CO_3 and CuO solids. The crude product was purified by column chromatography using n-hexane/EA (4:1 *v/v*) as eluent. The obtained product was a light-yellow solid with 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 10.23 (s, 1H), 7.74-7.76 (d, 1H), 7.19-7.21 (d, 2H), 7.11-7.14 (m, 9H), 7.03-7.08 (m, 8H), 6.33-6.34 (d, 1H), 6.10 (s, 1H), 5.11 (s, 2H), 3.37-3.43 (m, 4H), 1.17-1.21 (t, 6H).

Synthesis of DASPI-C_1-TPE. Intermediate 1 (0.1953 g, 0.37 mmol) and 1,4-dimethylpyridinium iodide (0.0870 g, 0.37 mmol) were added into 10 mL of ethanol. After slow addition of piperidine (5 drops), the reaction mixture was heated to 70 °C with stirring for 18 h. The crude product was purified by column chromatography using dichloromethane/MeOH (13:1 *v/v*) as eluent. The obtained product was a dark-red solid with 40% yield. ^{1}H NMR (600 MHz, DMSO-d_6, δ): 8.59-8.60 (d, 2H), 7.95-7.98 (d, 1H), 7.87-7.88 (d, 2H), 7.52-7.53 (d, 1H), 7.27-7.29 (d, 2H), 7.09-7.17 (m, 10H), 6.96-7.02 (m, 8H), 6.37-6.39 (d, 1H), 6.17 (s, 1H), 5.24 (s, 2H), 4.16 (s, 3H), 3.36-3.39 (t, 4H), 1.03-1.06 (t, 6H). ^{13}C NMR (101 MHz, DMSO-d_6, δ): 159.69, 154.31, 151.40, 144.50, 143.56, 143.12, 141.19, 140.65, 137.76, 135.85, 131.33, 131.07, 128.29, 127.04, 127.00, 122.06, 117.24, 111.84, 105.41, 96.17, 69.68, 46.65, 44.54, 13.02. MS:

m/z = 627.3373 ([*M*-I]$^+$, calculated for $C_{45}H_{43}N_2O^+$, 627.3370).

Synthesis of Intermediate 2. TPE-OH (1.0444 g, 3 mmol) and Cs_2CO_3 (2.9324 g, 9 mmol) were dispersed in 60 mL of THF, and the mixture was stirred for 1 h at room temperature. Then, 1,6-dibromohexane (2.1957 g, 9 mmol) was added into the mixture, which was heated to 60 °C with stirring for 6 h. After cooling to room temperature, the mixture was filtered to remove the Cs_2CO_3. The filtrate was evaporated and purified on a silica gel column using PE/EA (50:1 *v/v*) as eluent. The obtained product was a yellow solid with a yield of 52%. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.06-7.13 (m, 9H), 6.99-7.05 (m, 6H), 6.91-6.92 (d, 2H), 6.61-6.62 (d, 2H), 3.86-3.89 (t, 2H), 3.40-3.42 (t, 2H), 1.86-1.90 (m, 2H), 1.73-1.77 (m, 2H), 1.46-1.50 (m, 4H).

Synthesis of Intermediate 3. 4-(Diethylamino)salicylaldehyde (0.3865 g, 2.00 mmol) and Cs_2CO_3 (1.3033 g, 4.00 mmol) were added into 10 mL of acetone and stirred for 0.5 h at room temperature. Then, intermediate 2 (0.5102 g, 1.00 mmol) and CuO (0.0800 g, 1.00 mmol) was added into the above mixture and stirred for 5 h at 50 °C. After cooling to room temperature, the mixture was filtered for removal of solid Cs_2CO_3 and CuO. The crude product was purified by column chromatography using n-hexane/EA (5:1 *v/v*) as eluent. The obtained product was a light-yellow solid with 62% yield. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 10.18 (s, 1H), 7.71-7.72 (d, 1H), 7.07-7.12 (m, 10H), 6.99-7.05 (m, 6H), 6.91-6.92 (d, 2H), 6.61-6.63 (d, 1H), 6.27-6.29 (d, 1H), 6.02 (s, 1H), 4.02-4.05 (t, 2H), 3.88-3.90 (t, 2H), 3.40-3.43 (m, 4H), 1.84-1.88 (m, 2H), 1.75-1.80 (m, 2H), 1.51-1.57 (m, 4H), 1.20-1.23 (t, 6H).

Synthesis of DASPI-C_6-TPE. The obtained intermediate 3 (0.2306 g, 0.37 mmol) and 1,4-dimethylpyridinium iodide (0.0870 g, 0.37 mmol) were added into 10 mL of ethanol. After slow addition of piperidine (5 drops), the reaction mixture was heated to 70 °C with stirring for 18 h. The crude product was purified by column chromatography

using dichloromethane/MeOH (15:1 *v/v*) as eluent. The obtained product was a dark-red solid with 43% yield. ^{1}H NMR (600 MHz, DMSO-d_6, δ): 8.57-8.58 (d, 2H), 7.89-7.90 (d, 2H), 7.51-7.53 (d, 1H), 7.08-7.17 (m, 11H), 6.93-6.98 (m, 6H), 6.83-6.84 (d, 2H), 6.65-6.66 (d, 2H), 6.37-6.39 (d, 1H), 6.21 (s, 1H), 4.12 (s, 3H), 4.10-4.11 (t, 2H), 3.87-3.89 (t, 2H), 3.42-3.45 (m, 4H), 1.84-1.89 (m, 2H), 1.69-1.73 (m, 2H), 1.48-1.54 (m, 4H), 1.12-1.14 (t, 6H). ^{13}C NMR (151 MHz, DMSO-d_6, δ): 160.44, 157.64, 154.36, 151.66, 144.51, 143.99, 143.93, 143.89, 140.66, 140.11, 137.89, 135.68, 132.35, 131.88, 131.15, 131.12, 128.33, 128.23, 126.94, 126.84, 122.02, 114.13, 111.69, 105.24, 95.09, 68.28, 67.68, 46.60, 44.47, 29.17, 28.93, 25.95, 25.78, 13.06. MS: m/z = 713.4104 ([*M*-I]$^{+}$, calculated for $C_{50}H_{53}N_2O_2^{+}$, 713.4102).

Fluorescence measurements of PVA solutions. To prepare the PVA solutions, 1.0 g of PVA with a molecular weight (M_w) of approximately 130000 and 0.7 g of PVA with an M_w of approximately 205000 were dissolved in 9 mL and 9.3 mL of deionized water, respectively. These mixtures were then heated and stirred at 80 °C for 30 min. Once cooled to room temperature, 10 wt% PVA solution (M_w of 130000) and 7 wt% PVA solution (M_w of 205000) were obtained. Each PVA stock solution was subsequently diluted with deionized water to prepare the desired test concentration. Following this, 20 μL of DASPI-OH and DASPI-C_6-TPE stock solutions (1 mM) were added dropwise to 2 mL of the PVA test solutions, respectively. After gently shaking the mixtures, the resulting solutions were transferred into quartz cuvettes for fluorescence measurements.

Characterizations. Proton and carbon-13 nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra were recorded using Bruker AV 400 and Bruker AV 600 NMR spectrometers (Bruker, Germany). Mass spectrometry (MS) was conducted on a Quattro micro-triple quadrupole mass spectrometer (Waters, USA). Dynamic light scattering (DLS) experiments were carried out using a Zetasizer Nano ZS (Malvern,

UK). Fluorescence spectra were obtained by an F-7000 fluorescence spectrophotometer (Hitachi, Japan) at a slit width of 5.0 nm and a scanning rate of 2400 nm/min. Ultraviolet-visible (UV-vis) absorption spectra were measured using a U-3900H spectrometer (Hitachi, Japan). The viscosity was determined with an NDJ-8S rotational viscometer (Sunny Hengping, China).

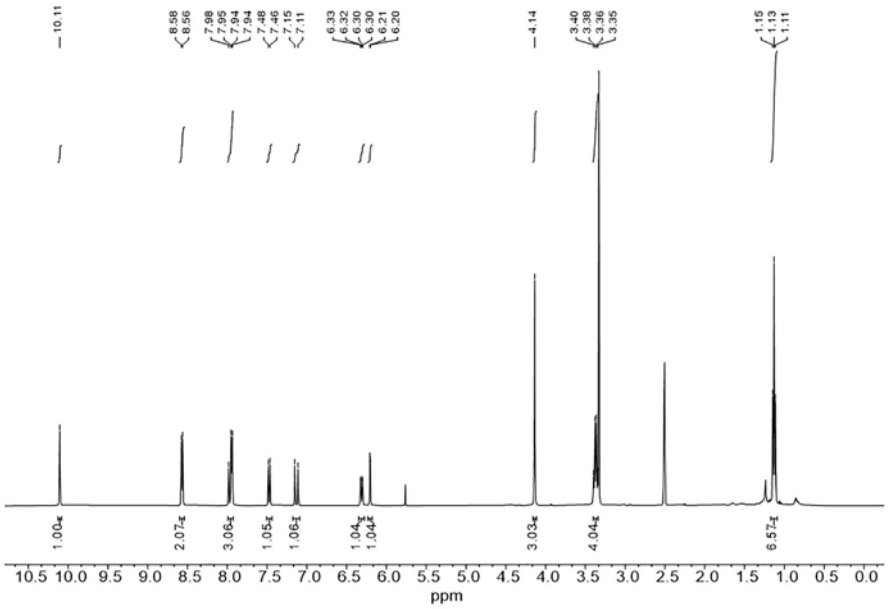


Fig. S1 ^{1}H NMR spectrum of DASPI-OH in DMSO-d_6.

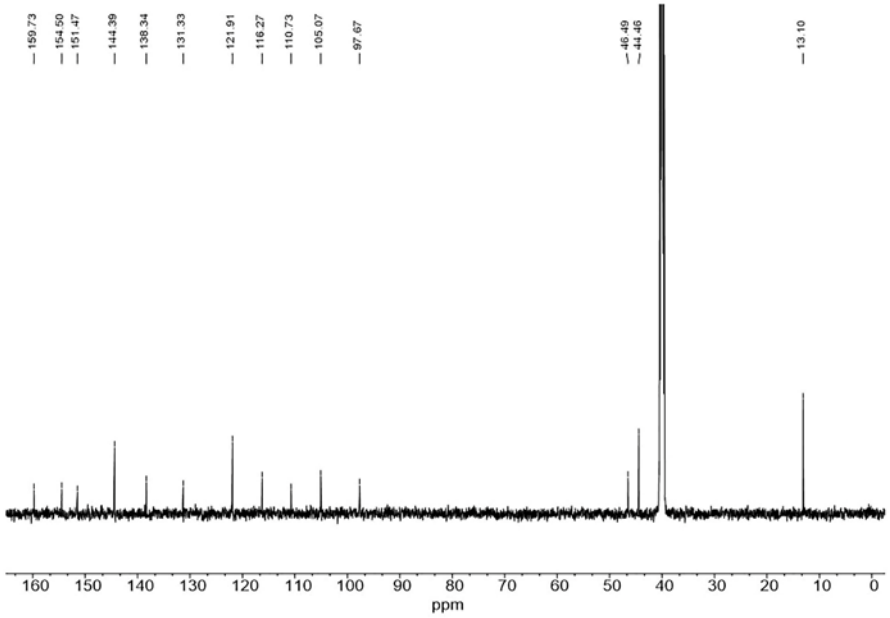


Fig. S2 ^{13}C NMR spectrum of DASPI-OH in DMSO-d_6.

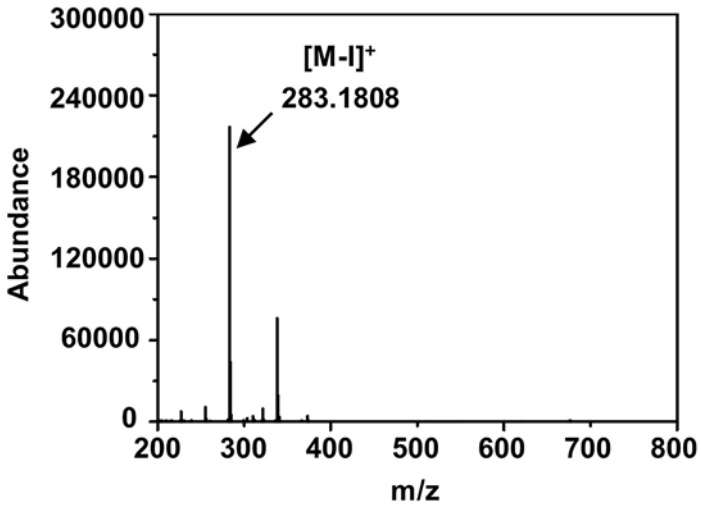


Fig. S3 Positive-ion mode ESI-MS spectra of DASPI-OH.

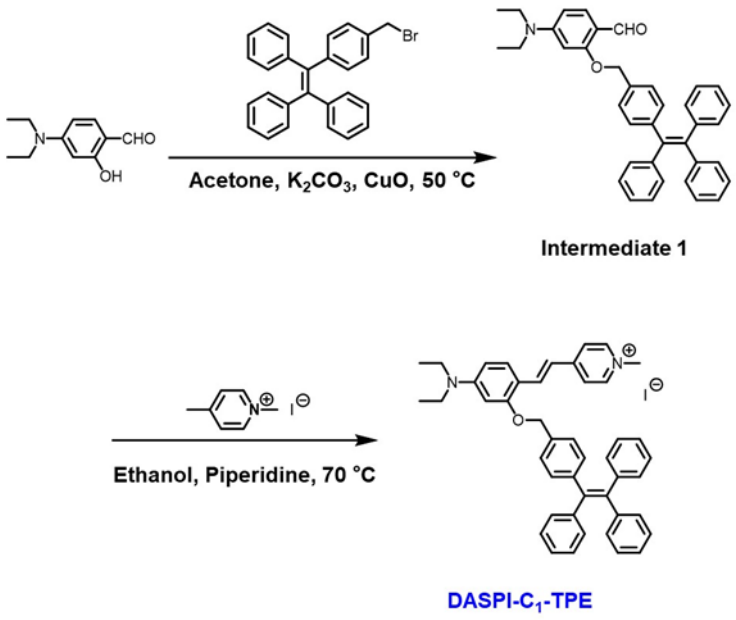


Fig. S4 Synthesis routes of DASPI-C_1-TPE.

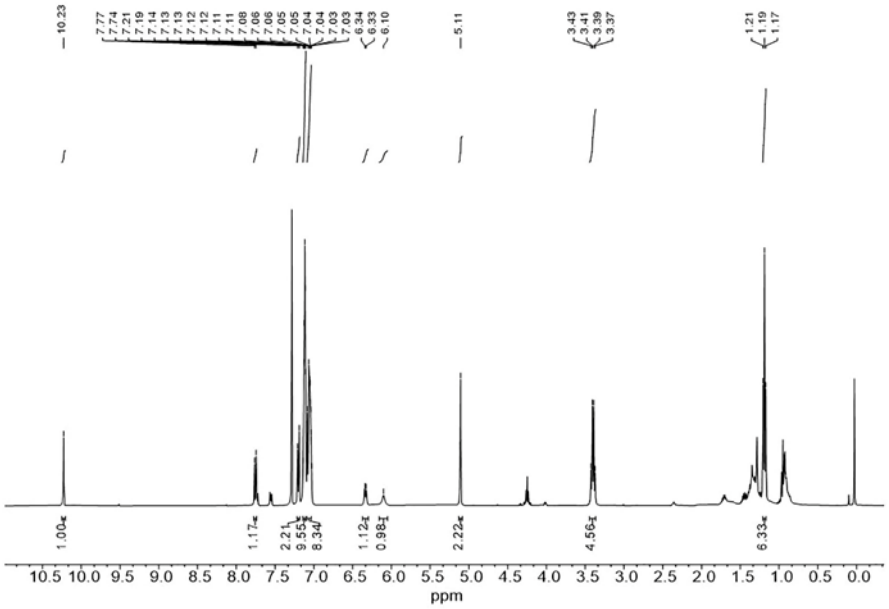


Fig. S5 ^{1}H NMR spectrum of intermediate 1 in $CDCl_3$.

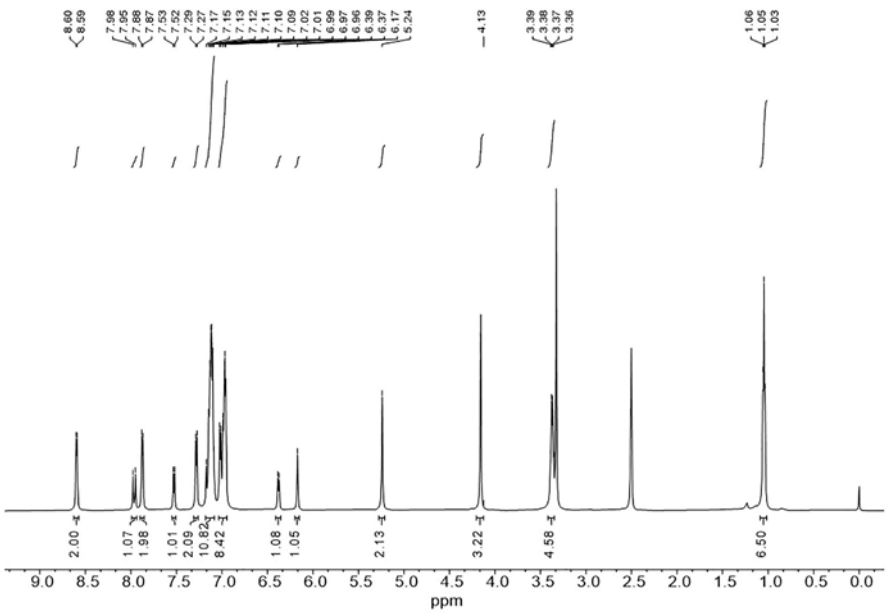


Fig. S6 ^{1}H NMR spectrum of DASPI-C_1-TPE in DMSO-d_6.

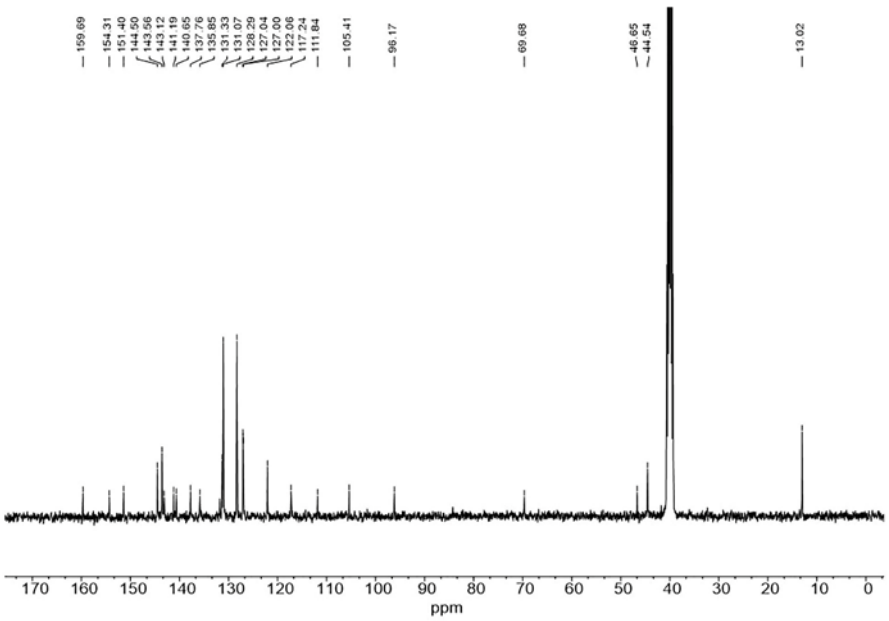


Fig. S7 ^{13}C NMR spectrum of DASPI-C_1-TPE in DMSO-d_6.

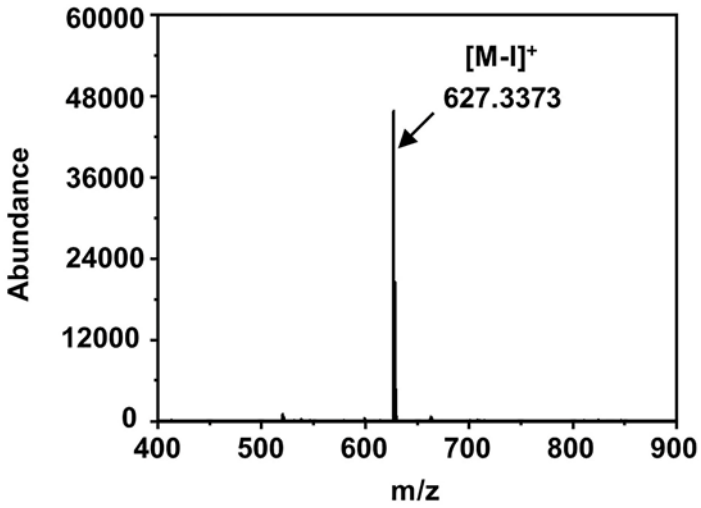


Fig. S8 Positive-ion mode ESI-MS spectra of DASPI-C_1-TPE.

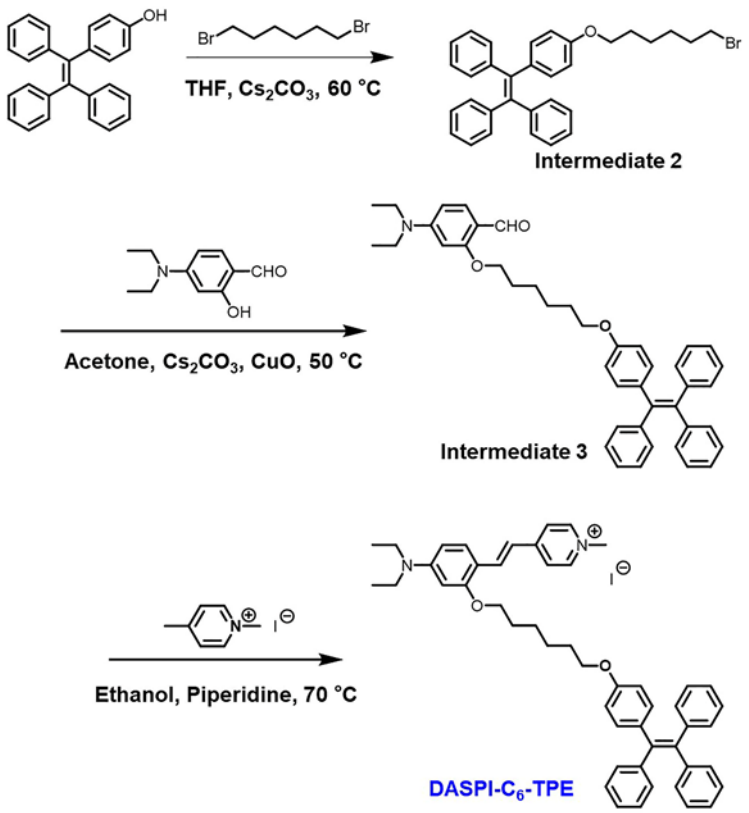


Fig. S9 Synthesis routes of DASPI-C_6-TPE.

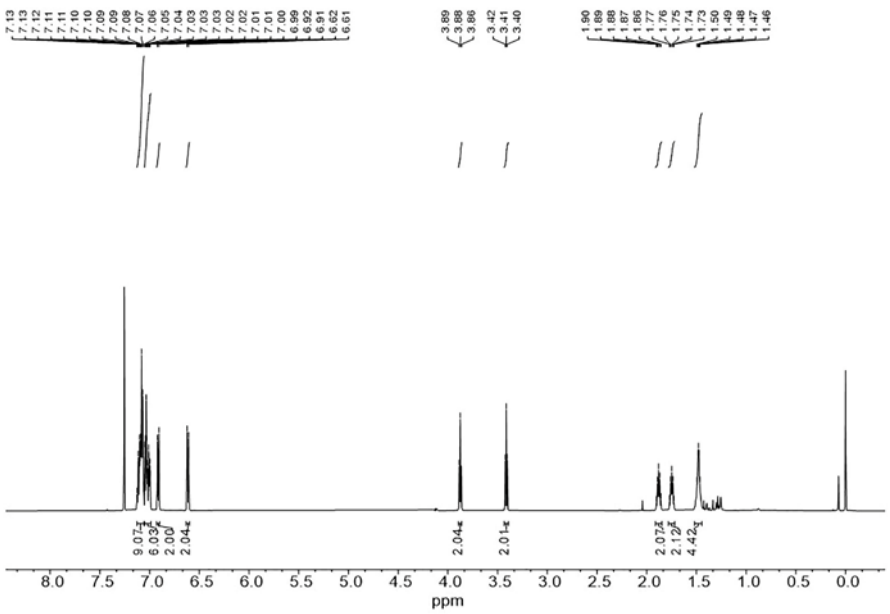


Fig. S10 ^{1}H NMR spectrum of intermediate 2 in $CDCl_3$.

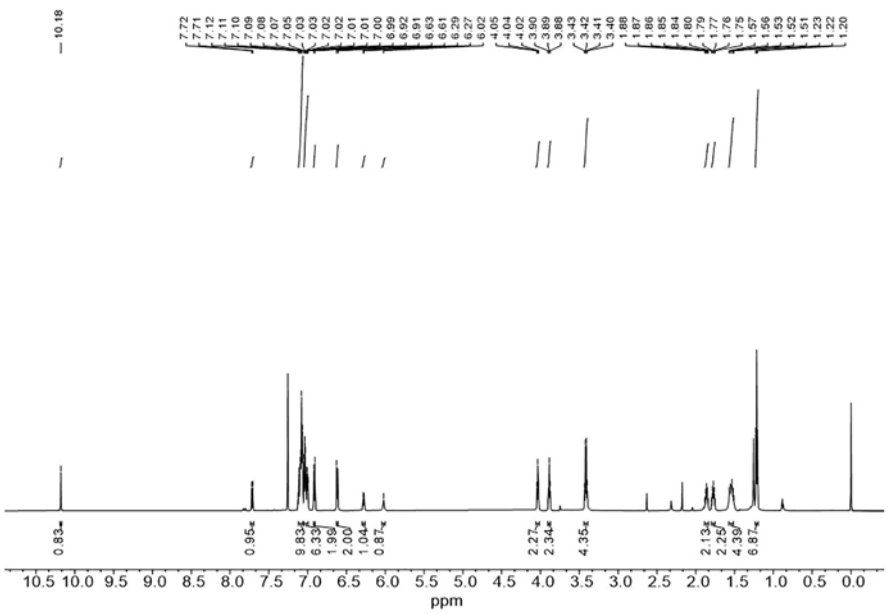


Fig. S11 ^{1}H NMR spectrum of intermediate 3 in $CDCl_3$.

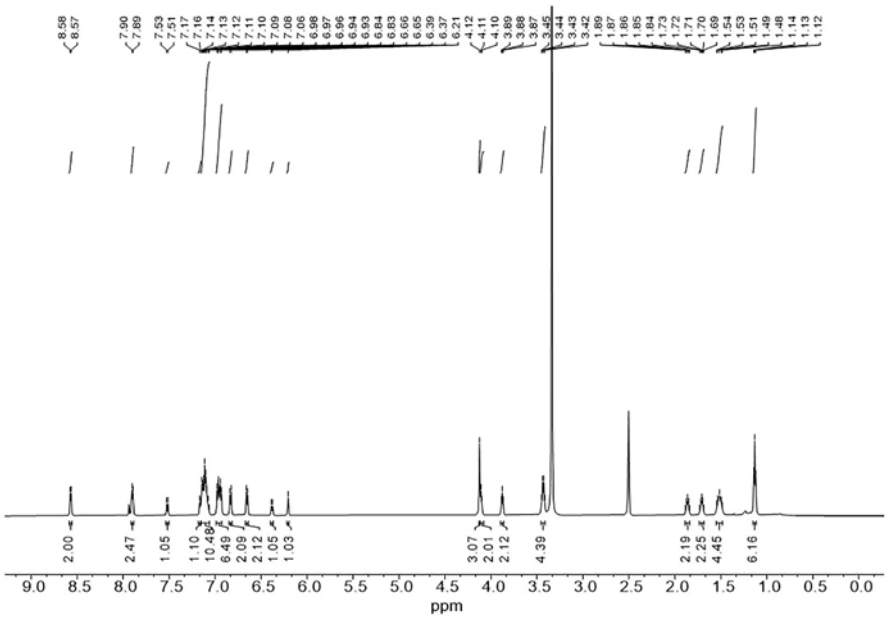


Fig. S12 ^{1}H NMR spectrum of DASPI-C_6-TPE in DMSO-d_6.

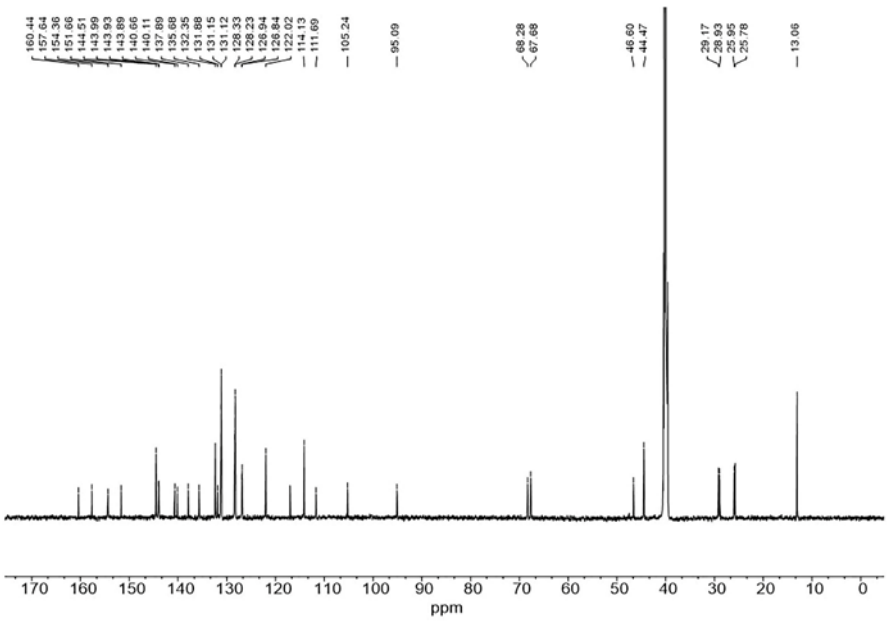


Fig. S13 ^{13}C NMR spectrum of DASPI-C_6-TPE in DMSO-d_6.

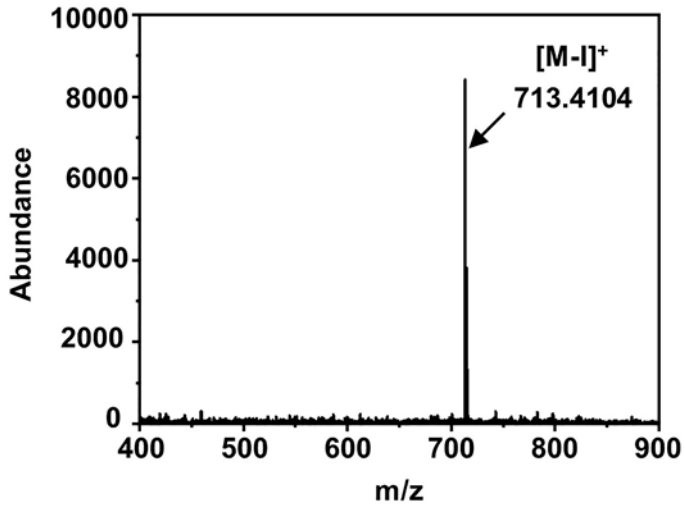


Fig. S14 Positive-ion mode ESI-MS spectra of DASPI-C_6-TPE.

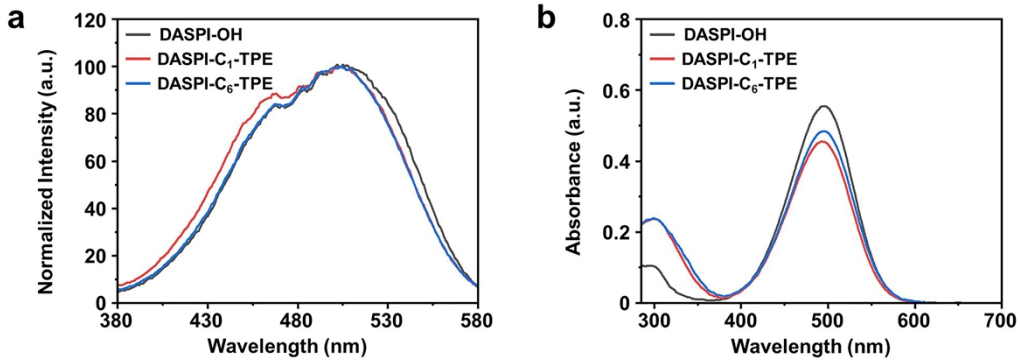


Fig. S15 (a) Normalized excitation spectra and (b) UV-vis absorption spectra of DASPI-OH, DASPI-C_1-TPE, and DASPI-C_6-TPE in DMSO.

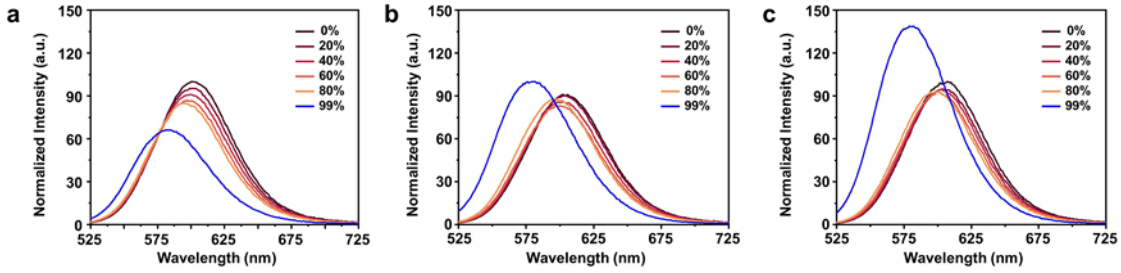


Fig. S16 Normalized emission spectra of (a) DASPI-OH, (b) DASPI-C_1-TPE, and (c) DASPI-C_6-TPE in DMSO/EA mixtures.

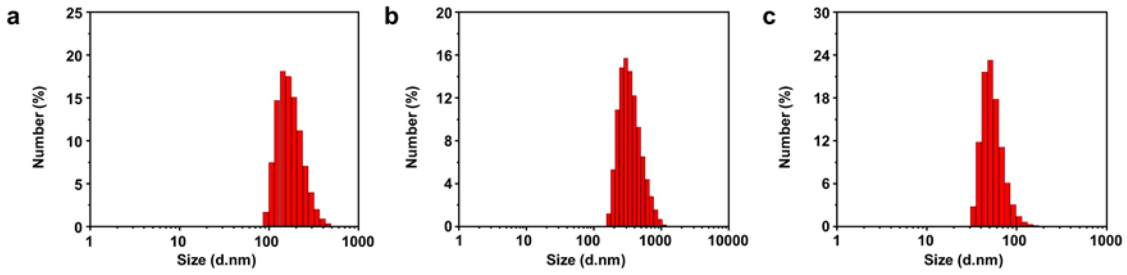


Fig. S17 DLS data of (a) DASPI-OH, (b) DASPI-C_1-TPE, and (c) DASPI-C_6-TPE in EA/DMSO (*v*/*v*, 99:1).

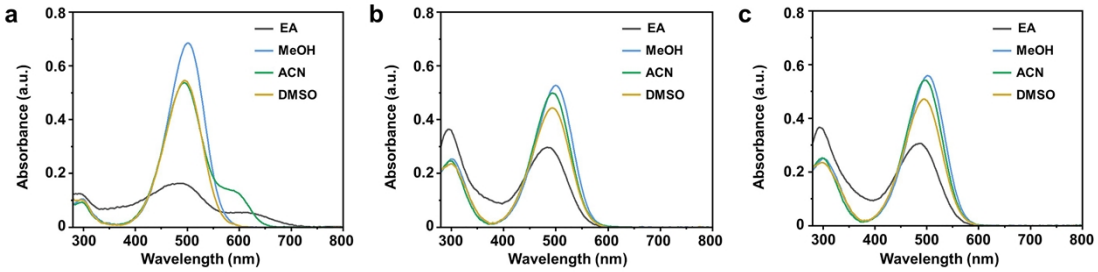


Fig. S18 Absorption spectra of (a) DASPI-OH (10 μM), (b) DASPI-C_1-TPE (10 μM), and (c) DASPI-C_6-TPE (10 μM) in different solvents.

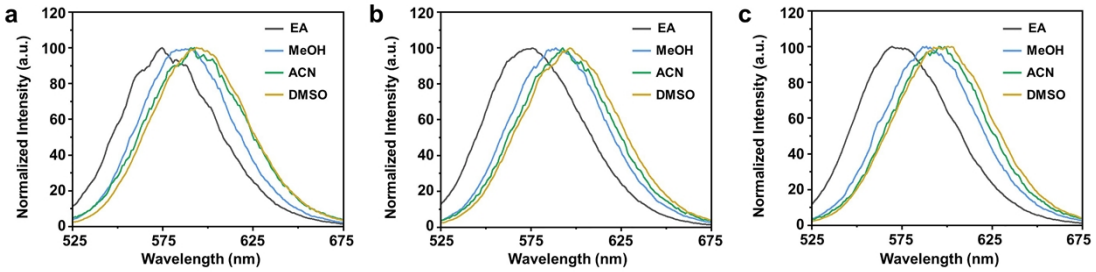


Fig. S19 Normalized emission spectra of (a) DASPI-OH (10 μM), (b) DASPI-C_1-TPE (10 μM), and (c) DASPI-C_6-TPE (10 μM) in different solvents (λ_{ex} = 504 nm).

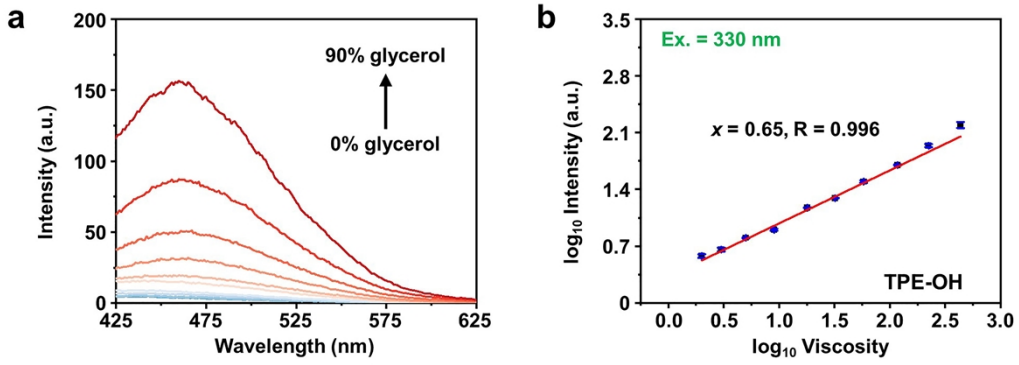


Fig. S20 (a) Fluorescence spectra of TPE-OH (10 μM) in glycerol/DMSO mixtures with different volume fractions of glycerol (λ_{ex} = 330 nm). (b) Plots of $\log_{10}$ values of fluorescence peak intensity of TPE-OH (10 μM) against $\log_{10}$ values of viscosity (λ_{ex} = 330 nm).

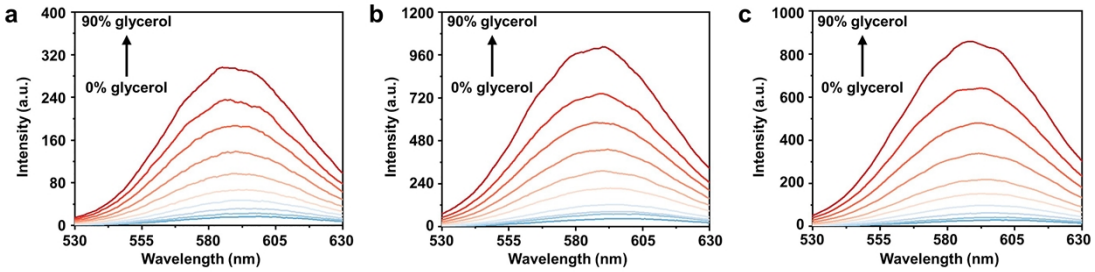


Fig. S21 Fluorescence spectra of (a) DASPI-OH (10 μM), (b) DASPI-C_1-TPE (10 μM), and (c) DASPI-C_6-TPE (10 μM) in glycerol/DMSO mixtures with different volume fractions of glycerol (λ_{ex} = 330 nm).

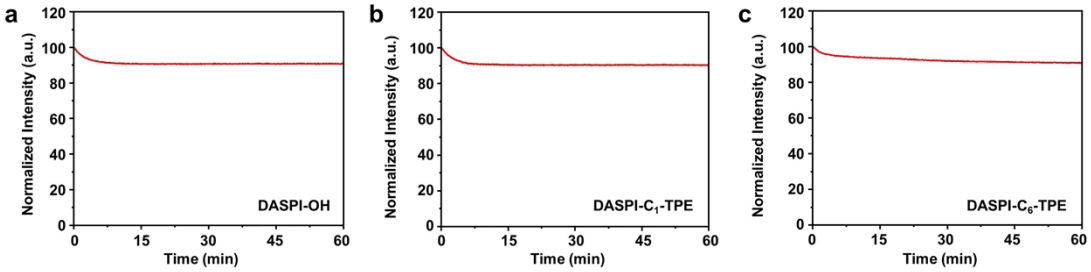


Fig. S22 The photostability of (a) DASPI-OH (10 μM), (b) DASPI-C_1-TPE (10 μM), and (c) DASPI-C_6-TPE (10 μM) in glycerol/DMSO (*v*/*v*, 9:1) mixture with continuous irradiation by a Xenon lamp (λ_{ex} = 504 nm).

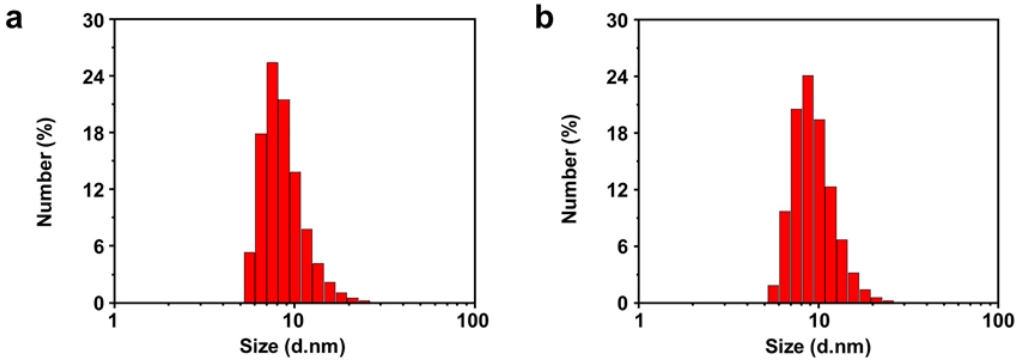


Fig. S23 DLS data for (a) 1.0% PVA_{130000} and (b) 1.0% PVA_{205000} aqueous solutions.

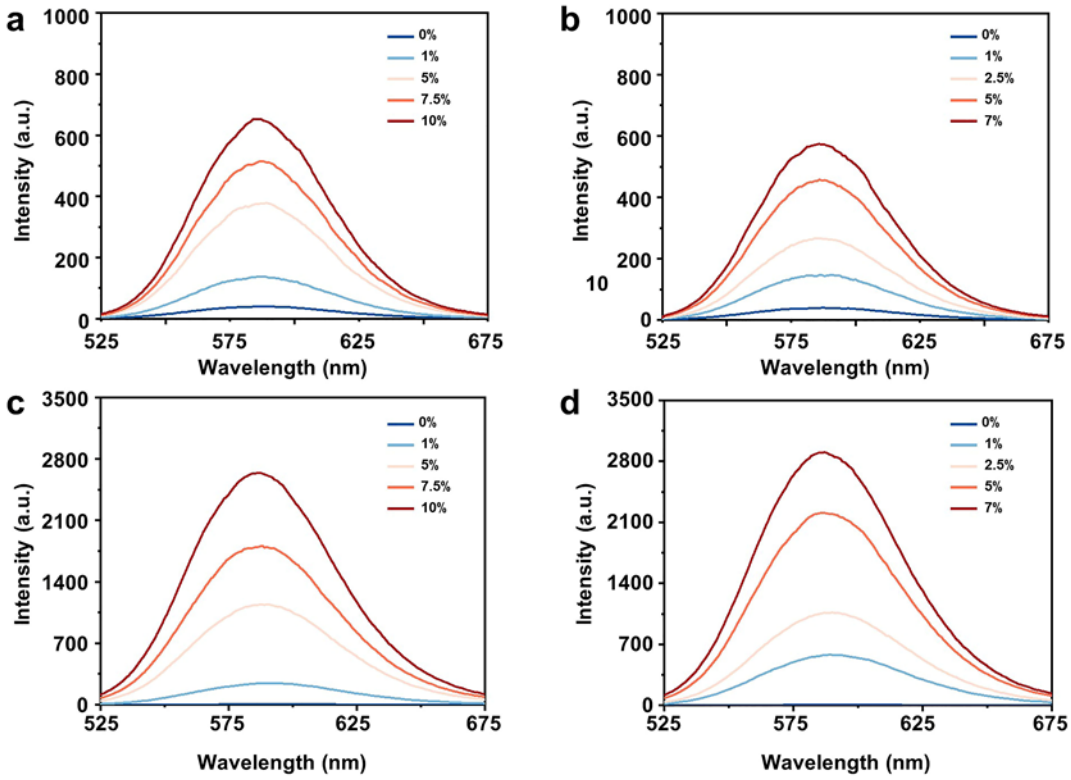


Fig. S24 Fluorescence emission spectra of DASPI-OH in (a) PVA_{130000} and (b) PVA_{205000} aqueous solutions at different concentrations (λ_{ex} = 504 nm). Fluorescence emission spectra of DASPI-C_6-TPE in (c) PVA_{130000} and (d) PVA_{205000} aqueous solutions at different concentrations (λ_{ex} = 504 nm).

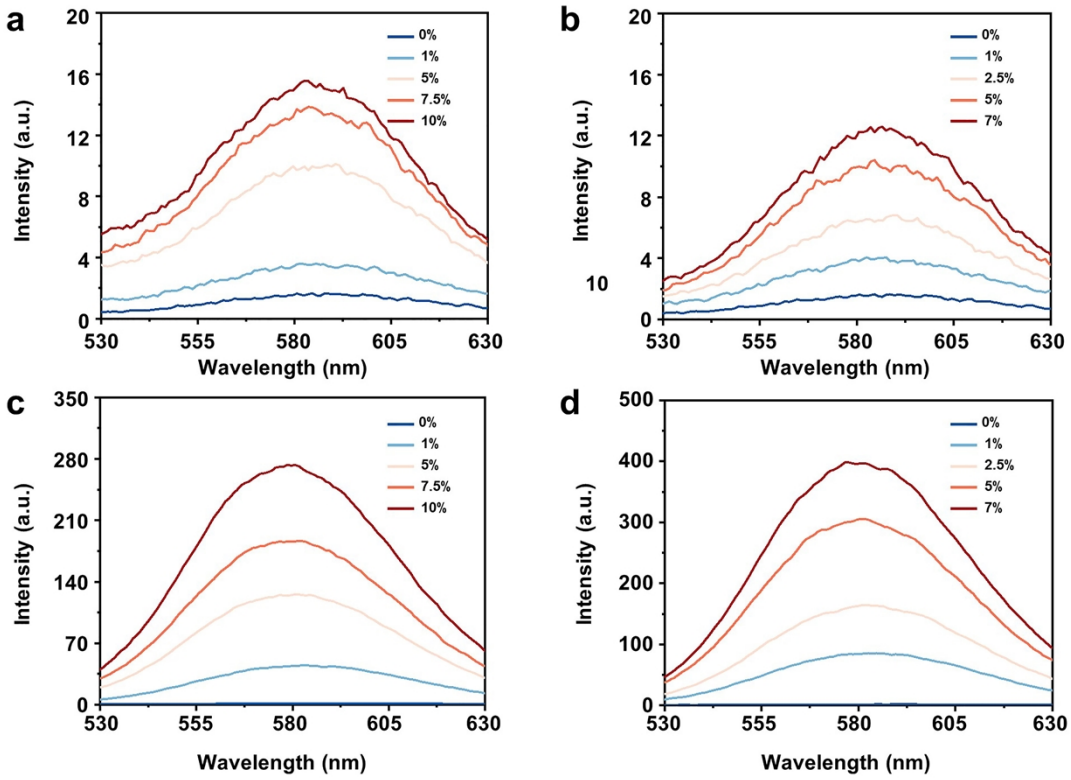


Fig. S25 Fluorescence emission spectra of DASPI-OH in (a) PVA_{130000} and (b) PVA_{205000} aqueous solutions at different concentrations (λ_{ex} = 330 nm). Fluorescence emission spectra of DASPI-C_6-TPE in (c) PVA_{130000} and (d) PVA_{205000} aqueous solutions at different concentrations (λ_{ex} = 330 nm).

Table S1. The viscosity of the glycerol/DMSO mixtures with different proportions.

Composition Glycerol (vol%)	Composition DMSO (vol%)	Viscosity (mPa·s)
0	100	2
10	90	3
20	80	5
30	70	9
40	60	18
50	50	32
60	40	58
70	30	117
80	20	224
90	10	435

Table S2. Viscosity responses of molecular rotors.

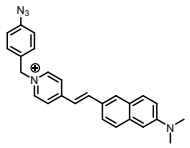
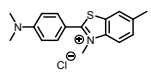
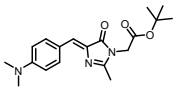
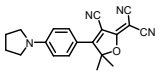
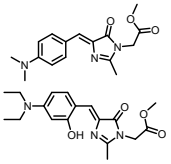
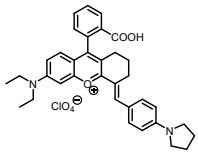
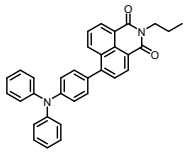
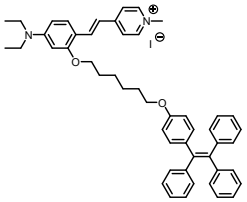
Molecular structure	Solvent	Slope	Reference
	glycerol/MeOH	0.42	[9] Chin. Chem. Lett., 2020, 31, 2903-2908.
		0.79	
	glycerol/ethylene glycol	0.68	[16] Angew. Chem. Int. Ed., 2021, 60, 1339-1346.
		0.72	
	glycerol/ethylene glycol	0.67 0.33	[17] Aggregate, 2024, 5, e421.
	glycerol/PBS	0.56	[23] Chem. Eng. J., 2022, 445, 136448.
	glycerol/H_2O	0.40	[24] New J. Chem., 2022, 46, 3078-3082.
	glycerol/DMSO	0.62	This work

Table S3. The viscosity of PVA_{130000} and PVA_{205000} aqueous solutions at different concentrations.

Molecular weight of PVA (M_w)	Concentration of PVA (wt%)	Viscosity (mPa·s)
130000	1	2
	5	35
	7.5	174
	10	419
205000	1	3
	2.5	10
	5	73
	7	238