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Electronic Supporting Information

Incorporating benzimidazole units into soluble polyimides for improving properties and application in organic solvents' water content detection

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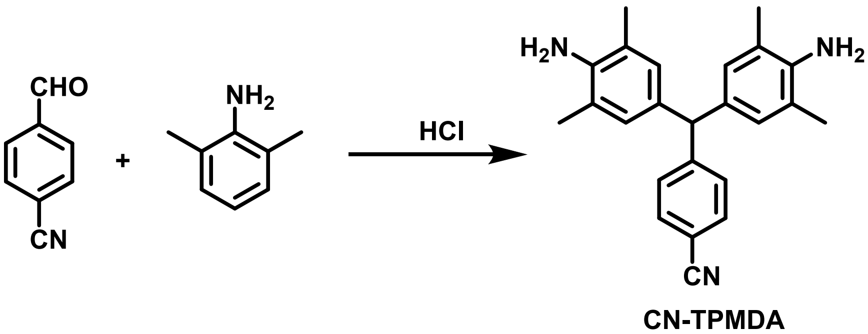
Contents

1. Reagents and apparatus.

Reagents. 4,4'-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA, 99%), 4,4'-(4,4'-Isopropylidenediphenoxy) diphthalic anhydride (BPADA, 99%)，bis-(3-phthalyl anhydride) ether (ODPA, 99%) and 5-amino-2-(4-aminophenyl) benzimidazole (BIDA, 99%) were purchased from Chinatech Chemical Co., Ltd. (Tianjin, China). *N*-methyl pyrrolidone (NMP), 2,6-dimethylaniline (99%) were provided by Macklin Company (Shanghai, China). Dimethylformamide [DMF, 99.8%, extra dry, with molecular sieves, Water ≤ 50 ppm (by K.F.), EnergySeal], tetrahydrofuran [THF, 99.5%, extra dry, with molecular sieves, Water ≤ 50 ppm (by K.F.), EnergySeal], dimethyl sulfoxide [DMSO, 99.7%, extra dry, with molecular sieves, Water ≤ 50 ppm (by K.F.), EnergySeal], 2-methoxyethanol, isoquinoline, 4-cyanobenzaldehyde and trifluoroacetic acid (TFA) were purchased from Anhui Senrise Technology Co., Ltd. (Anhui, China) and used as received. Other reagents, including TBA salts, and common solvents were purchased from various merchants and used as received.

Apparatus. The intrinsic viscosities (η_{inh}) of the PI solutions were measured with an Ubbelohde viscometer at 25 °C with a concentration of 0.5 g g/dL in DMAc. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet IS50 FTIR spectrometer over the wavenumber range of 500 to 4000 cm^{-1}. ^{1}H NMR spectra of PI fibers dissolved in DMSO-d_6 were obtained on a DRX-500 or DRX-600 MHz NMR spectrometer (Bruker, Germany). Thermogravimetric analysis (TA Discovery TGA 550, USA) was conducted with a heating rate of 20 $°C\cdot min^{-1}$ from 30 to 800 °C under nitrogen atmosphere. The dynamic differential scanning calorimeter (DSC, NETZSCH DSC 214Polyma, Germany) was performed to assess glass transition temperature (T_g) at a heating rate of 40 $°C\cdot min^{-1}$ under nitrogen. X-ray diffraction (XRD) data were obtained on an Ultima IV X-ray diffractometer (Rigaku, Japan). The mechanical properties of PI films were measured by an Instron Legend 2366 (Instron, America) testing system. UV-*vis* absorption spectra were tested on a 2700 UV-*vis* spectrophotometer (Shimadzu, Japan) at room temperature.

2. Synthesis and characterization of cyano-containing TPM-based diamine monomer.



Scheme S1. Synthesis process of the diamine monomer **CN-TPMDA**

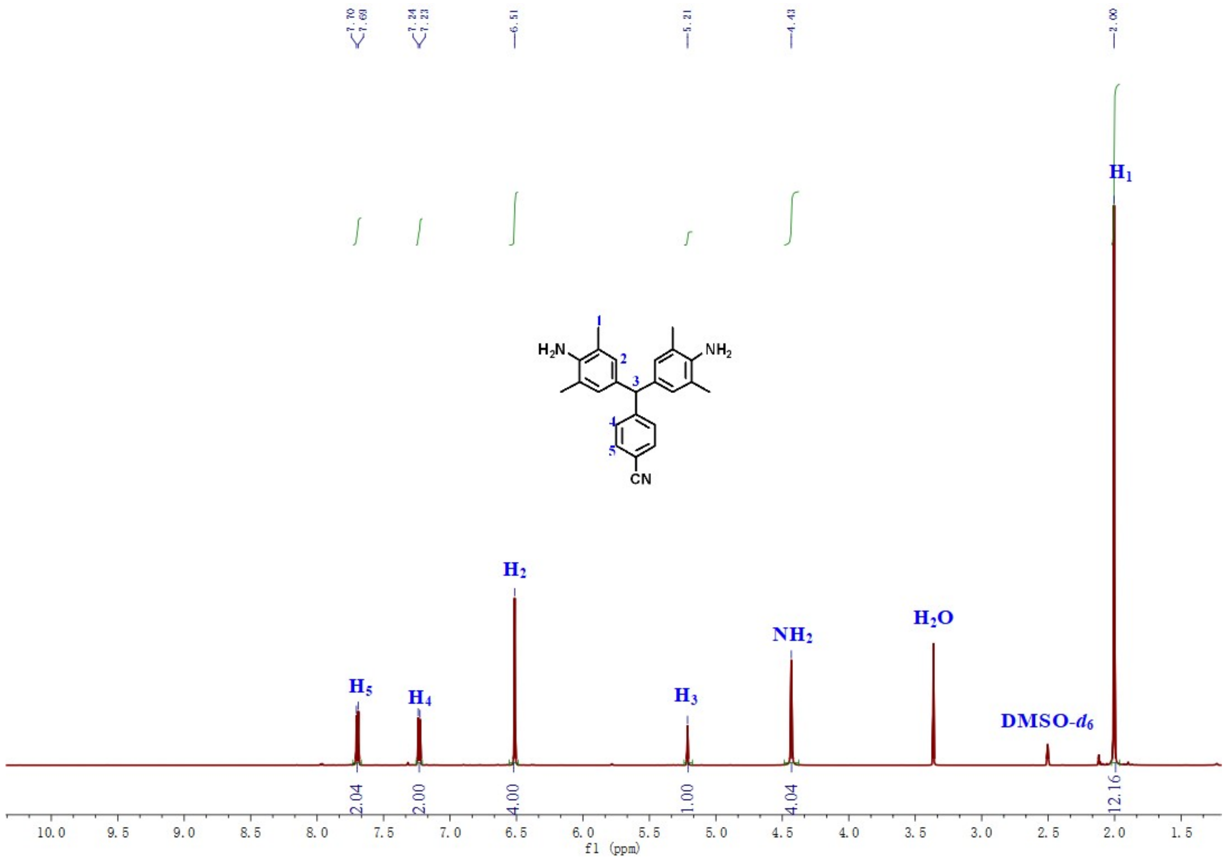


Fig. S1 ^{1}H NMR spectrum of **CN-TPMDA**.

3. FT-IR spectra of C=O band of the resulting PI films.

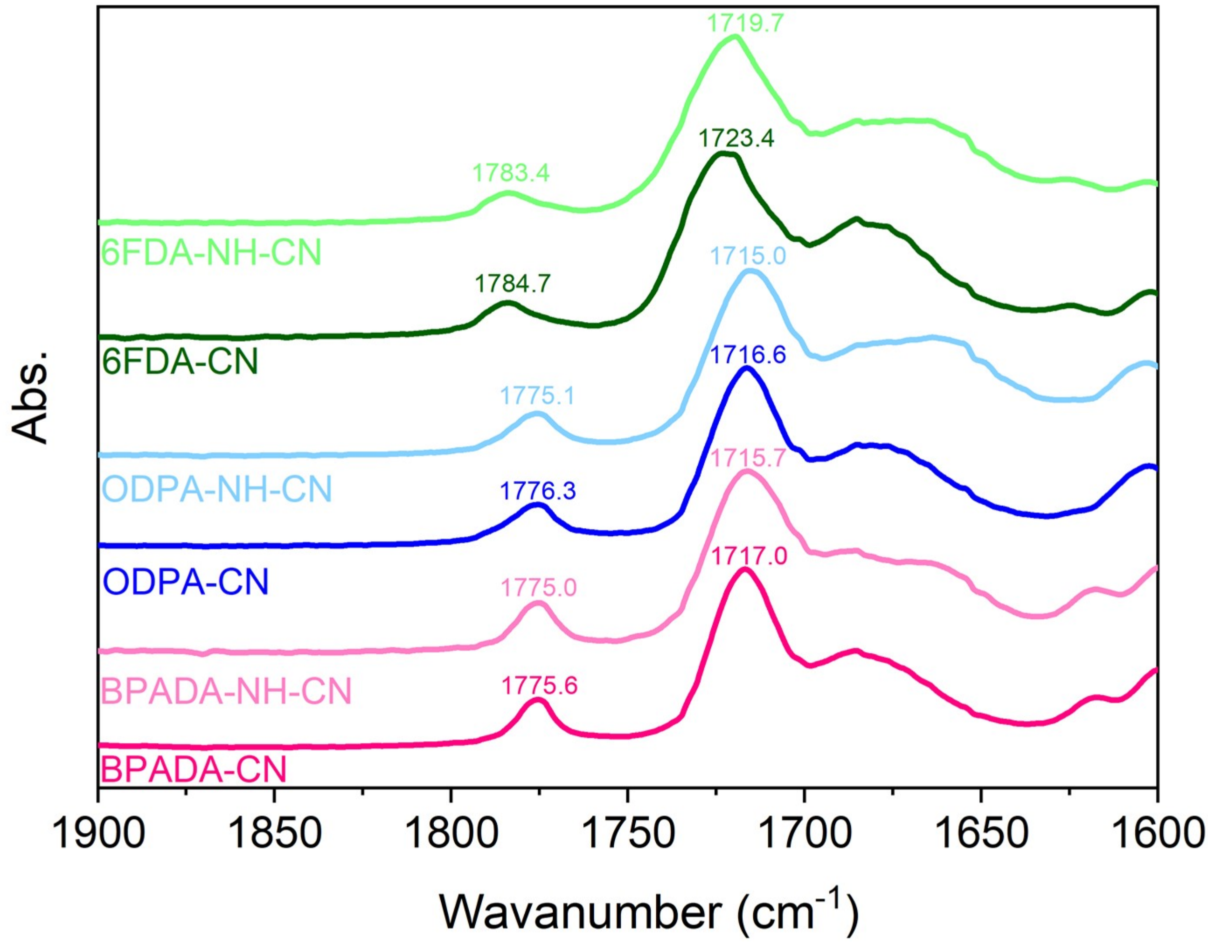


Fig. S2 FT-IR spectra of C=O band for the resulting PI films.

4. ¹H NMR spectra of the resulting PIs.

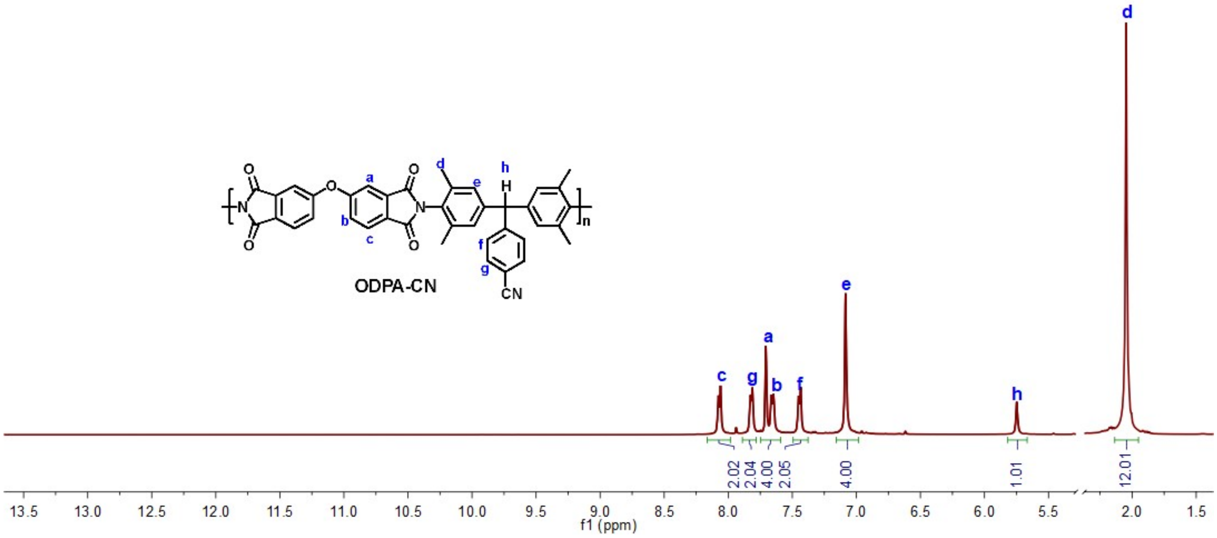


Fig. S3 ¹H NMR spectrum of **ODPA-CN**.

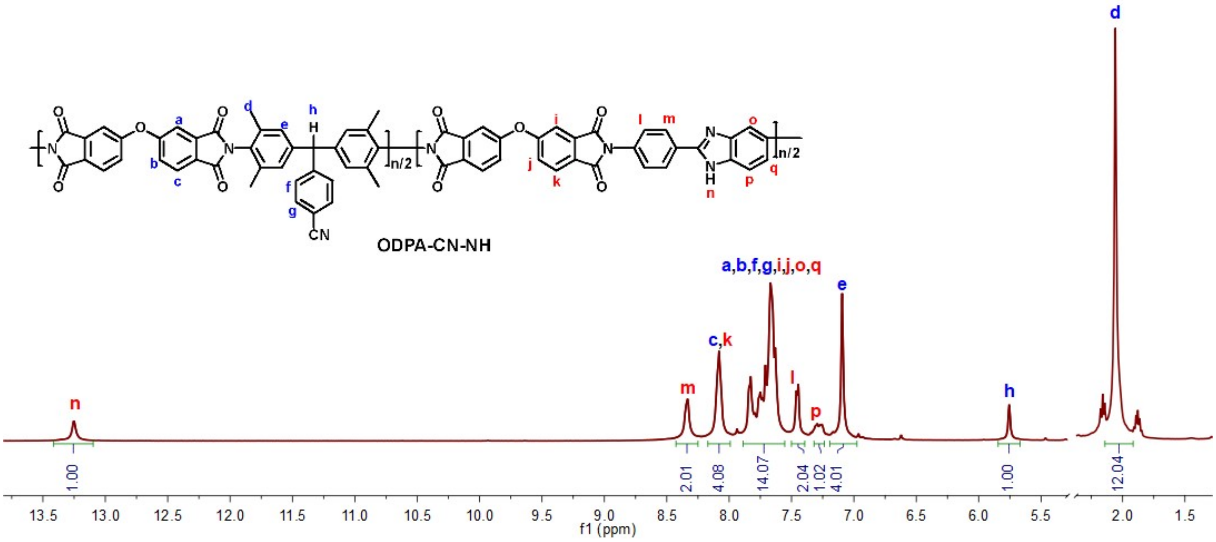


Fig. S4 ¹H NMR spectrum of **ODPA-CN-NH**.

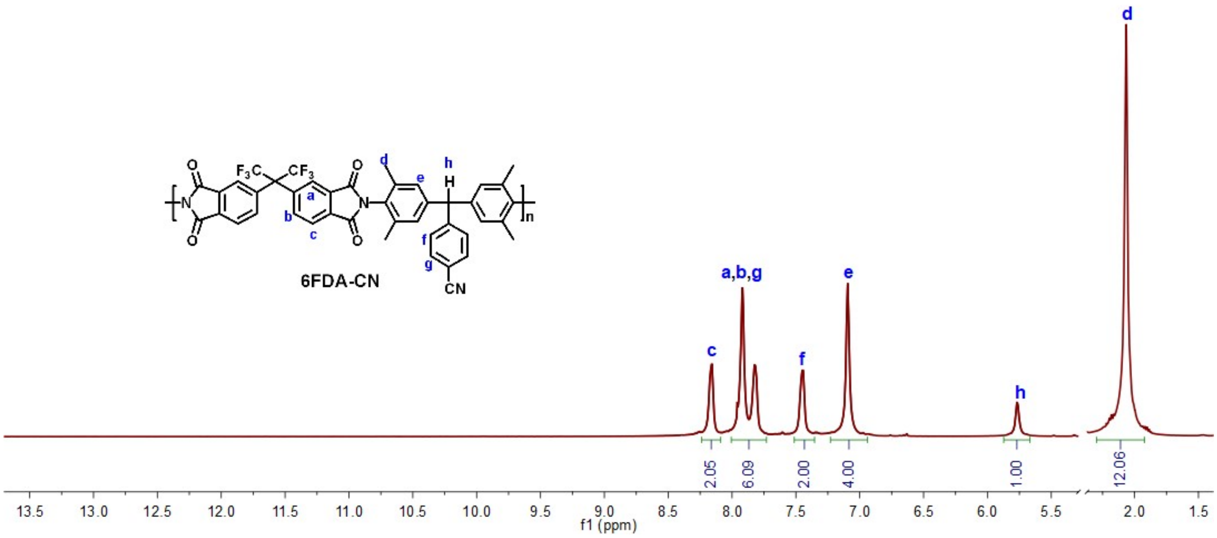


Fig. S5 [1]H NMR spectrum of **6FDA-CN**.

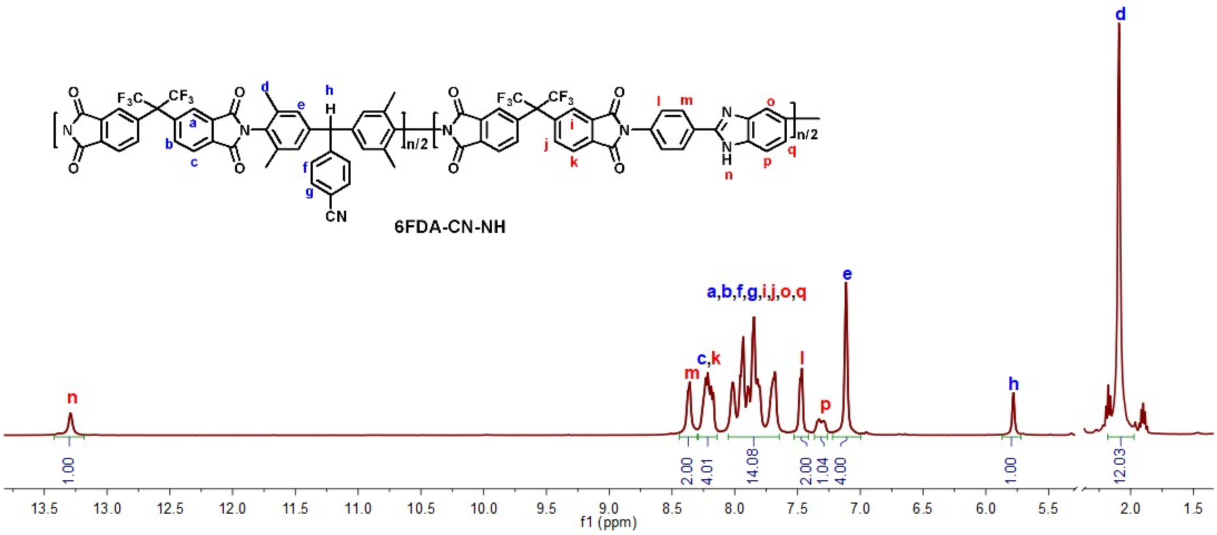


Fig. S6 [1]H NMR spectrum of **6FD A-CN-NH**.

5. XRD patterns of the resulting PI films.

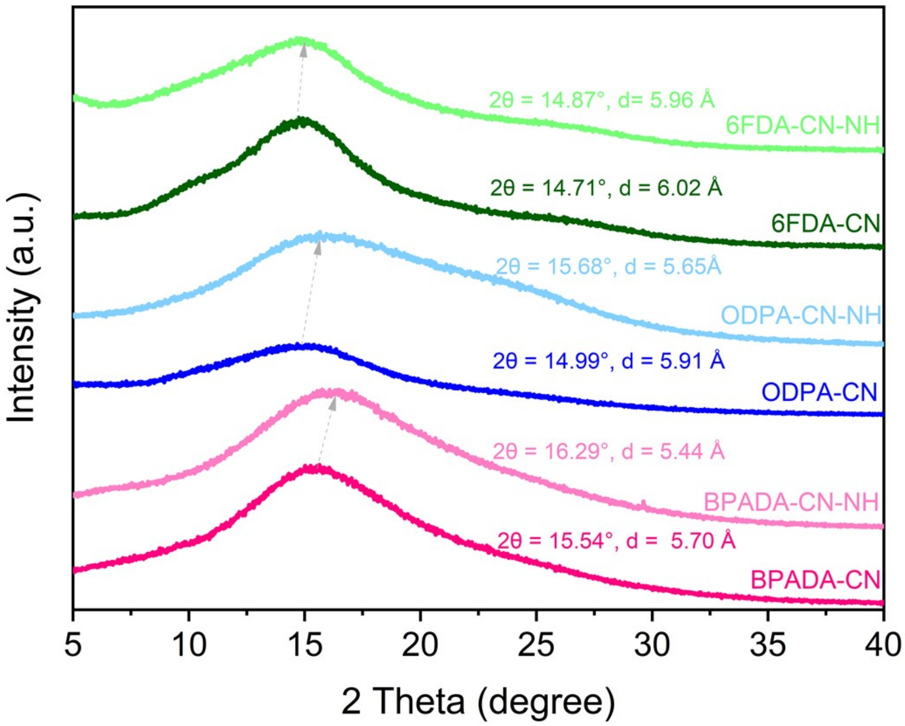


Fig. S7 XRD patterns of the resulting PI films.

6. The solubility behavior of PIs

Table S1 The solubility behavior of PIs

PIs	DMSO	DMF	DMAc	NMP	THF	Acetone	$CHCl_3$	CH_2Cl_2
BPAPA-CN	++	++	++	++	++	±	++	++
BPADA-CN-NH	++	++	++	++	++	±	±	±
ODPA-CN	++	++	++	++	++	±	++	++
ODPA-CN-NH	++	++	++	++	±	±	±	±
6FDA-CN	++	++	++	++	++	++	++	++
6FDA-CN-NH	++	++	++	++	++	±	±	±

Qualitative solubility of 10 mg of PI films in 1 mL of solvent. ++, soluble at room temperature; +, soluble on heating; ±, partially soluble or swelling; --, insoluble even on heating.

7. UV-vis absorption spectra.

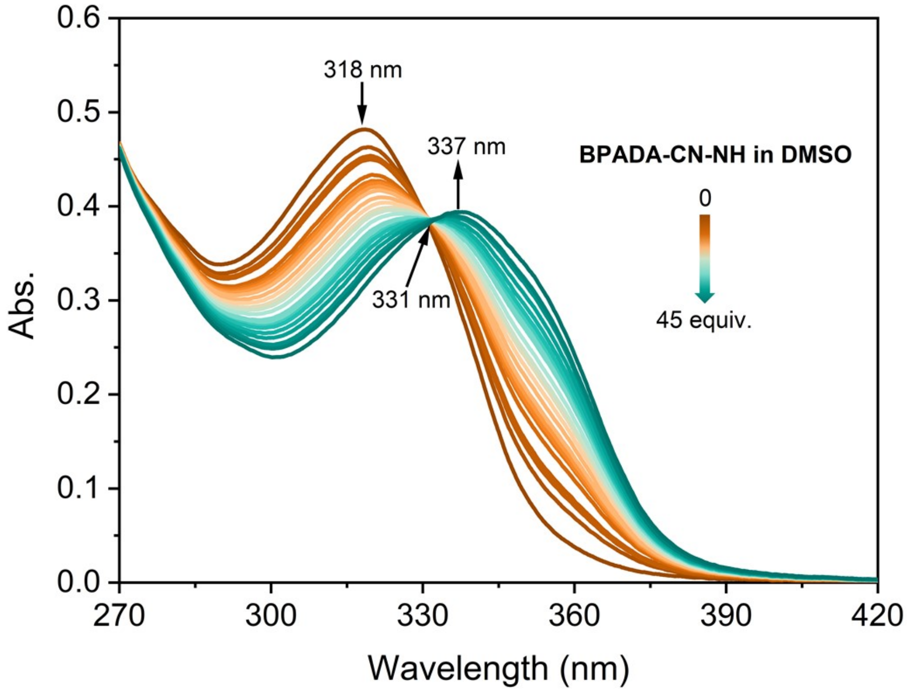


Fig. S8 UV-vis absorption spectra of **BPADA-CN-NH** (10 μM) in anhydrous DMSO during titration with F^- (0-45 equiv.).

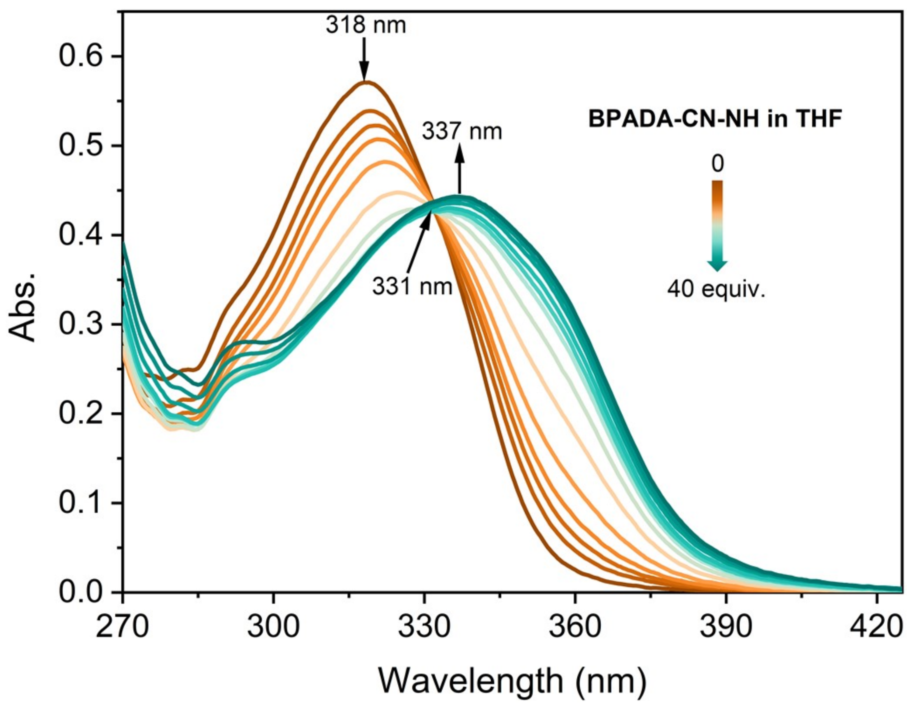


Fig. S9 UV-vis absorption spectra of **BPADA-CN-NH** (10 μM) in anhydrous THF during titration with F^- (0-40 equiv.).

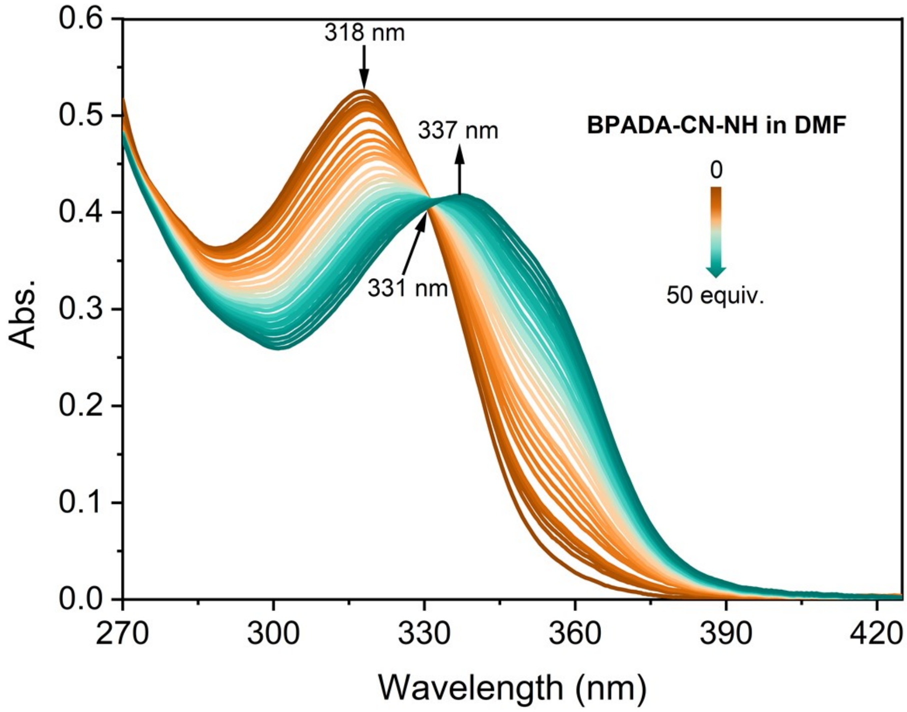


Fig. S10 UV-vis absorption spectra of **BPADA-CN-NH** (10 μM) in anhydrous DMF during titration with F^- (0-50 equiv.).

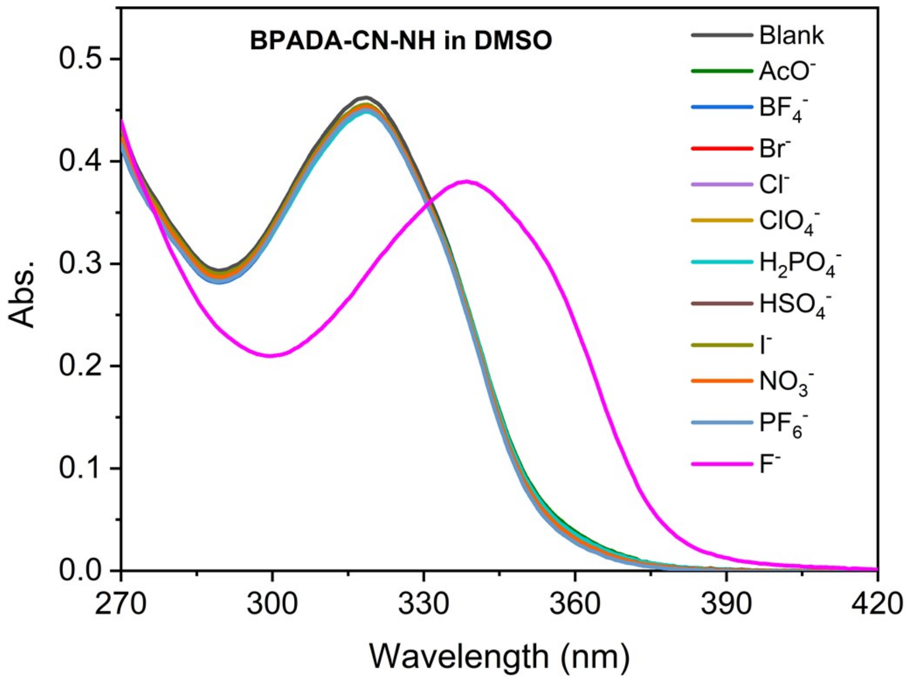


Fig. S11 UV-vis absorption spectra of **BPADA-CN-NH** (10 μM) in anhydrous DMSO with various anions (45 equiv.).

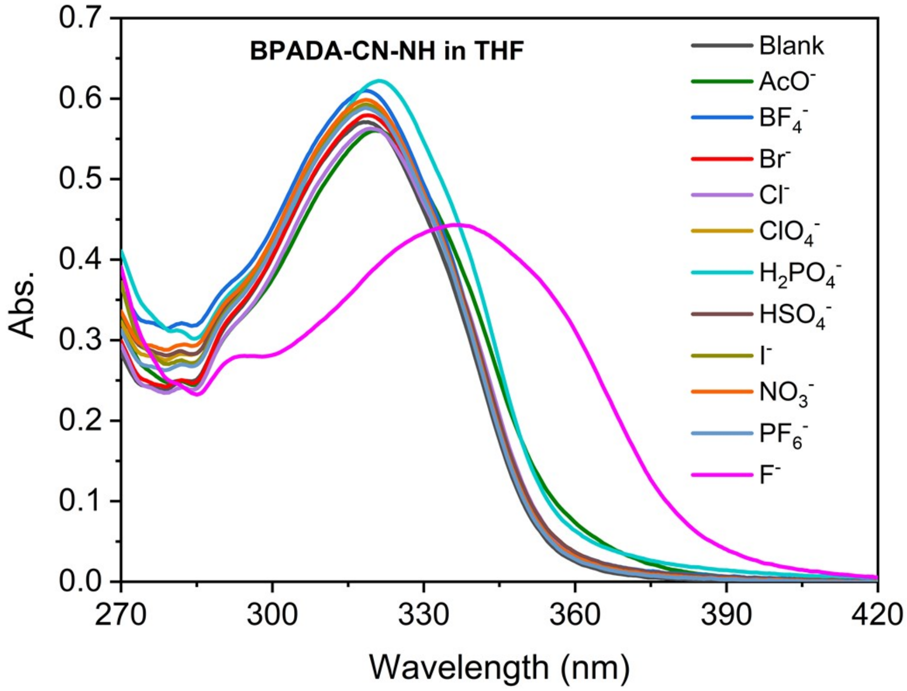


Fig. S12 UV-vis absorption spectra of **BPADA-CN-NH** (10 μM) in anhydrous THF with various anions (40 equiv.).

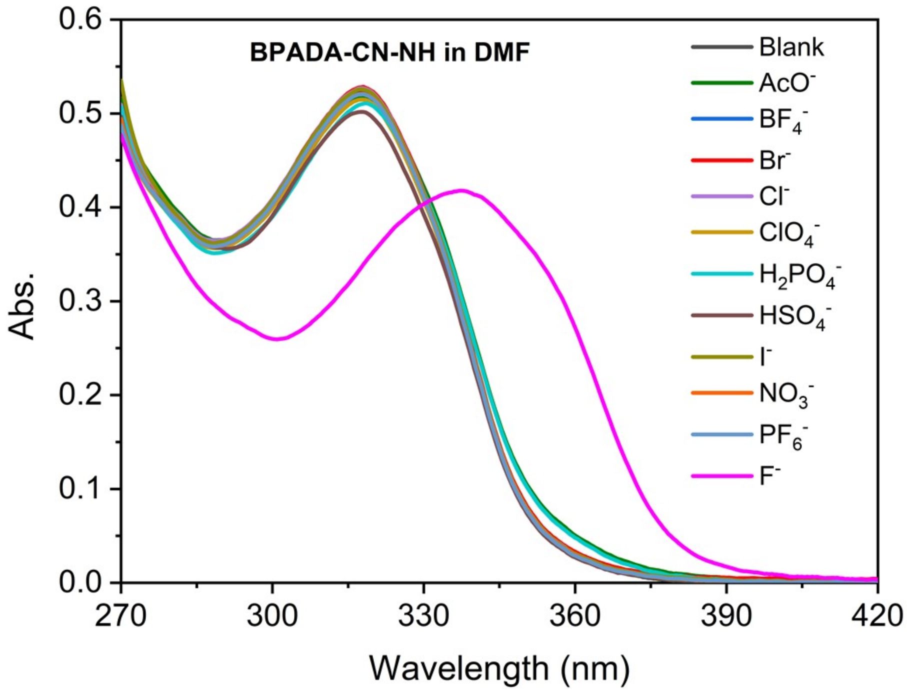


Fig. S13 UV-vis absorption spectra of **BPADA-CN-NH** (10 μM) in anhydrous DMF with various anions (50 equiv.).

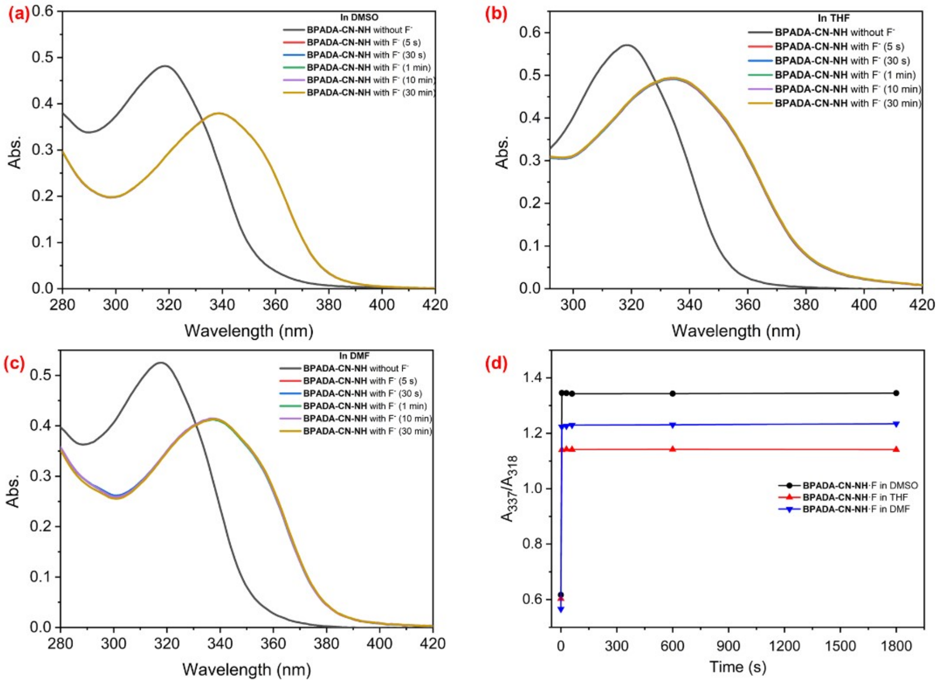


Fig. S14 UV−vis absorption spectra change of BPADA-CN-NH in DMSO (a), THF (b), and DMF (c) without and with F^- after different time; Time-dependent UV-*vis* absorption ratio of the deprotonated **BPADA-CN-NH** in DMSO, THF, and DMF (d).

8. Changes in organic solutions color of BPADA-CN-NH·F with different water fractions.

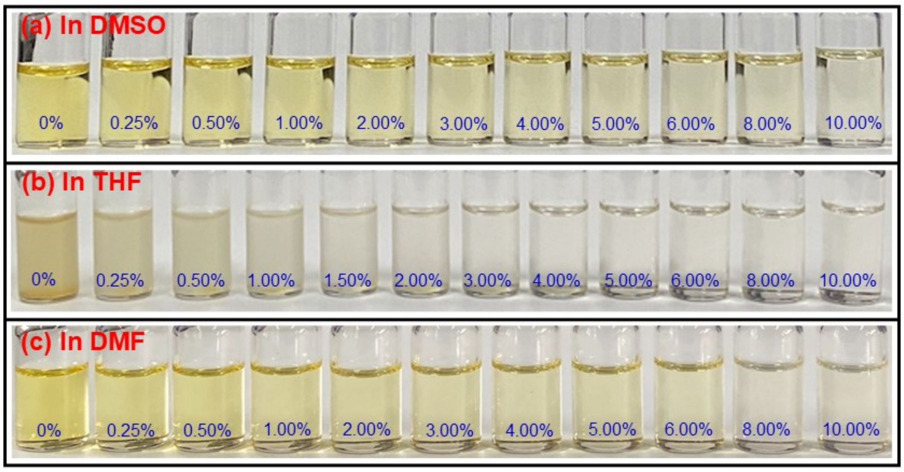


Fig. S15 Changes in color of **BPADA-CN-NH·F** (1 mM **BPADA-CN-NH** + 6 equiv. F^{-}) with different water fractions (0-10.00%, v/v) in (a) DMSO, (b) THF, and (c) DMF solutions.

9. Color Changes of BPADA-CN-NH film after immersing CH_3CN solution containing F^- and TFA alternately.

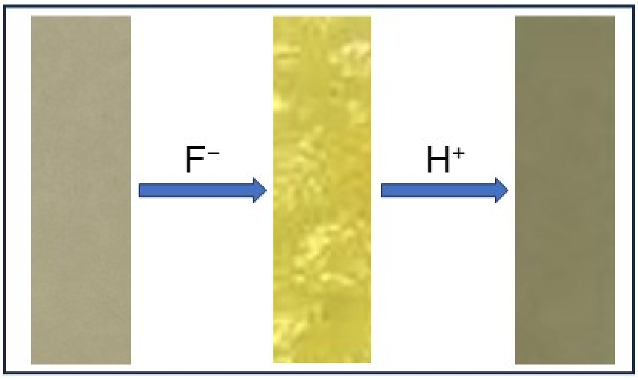


Fig. S16 The color change of **BPADA-CN-NH** film after immersing CH_3CN solution containing F^- and TFA alternately.