Supporting Information

Ionic Liquid-based Low-dimensional Fluorosensor for Ultrasensitive Detection of Perchlorate ions in Aqueous Media

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Table of contents

S1 Experimental section

S1.1. Synthetic procedures and characterizations.

Compound C: Imidazole derivative compound c was synthesized via a multistep procedure. 9, 10-Phenanthrenequinone (a) (150 mg) was dissolved in glacial acetic acid (AcOH) and reacted with ammonium acetate at 90 °C for 30 min, followed by the addition of anthracene-9-carbaldehyde (b) (200 mg, 1 equiv). The mixture was refluxed at 110 °C for 90 min, yielding yellow powder imidazole derivative (c) upon precipitation in ice water (78% yield after medium-pressure liquid chromatography (MPLC) purification, 15% EtOAc/petroleum ether).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.957- 8.94 (m, 3H), 8.601 (d, 1H), 8.392 (d, 1H). 8.257 (d, 2H), 7.815 (d, 2H), 7.722 (m, 4H), 7.616 (t, 2H), 7.546 (t, 2H), 13.9 (s, 1H, NH). HRMS calculated for $C_{29}H_{18}N_2$: 394.47, found: 395.15 (m/z).

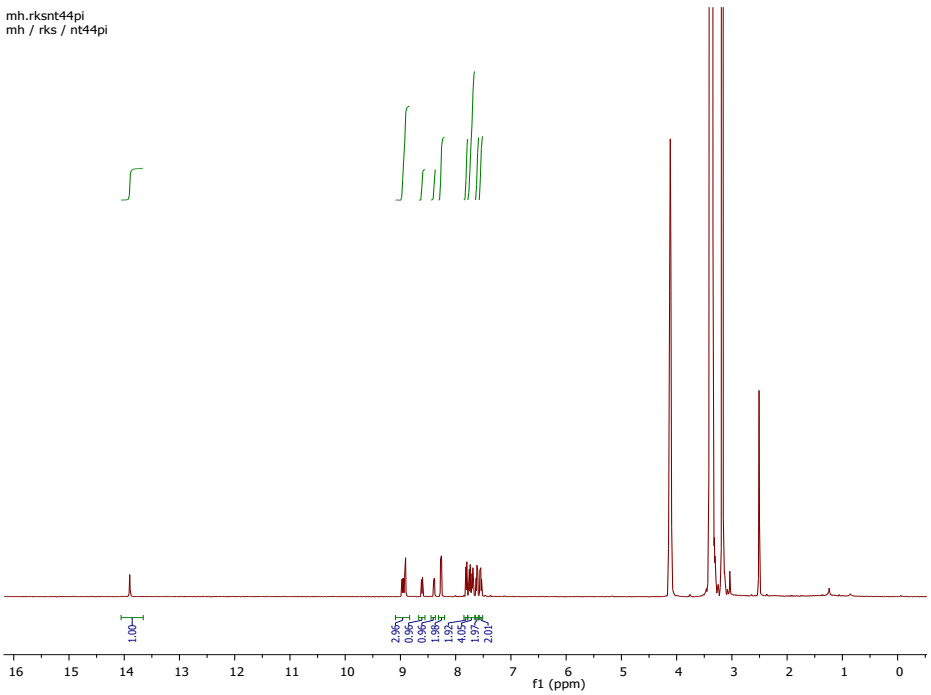

Figure S1: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of parent moiety, C.

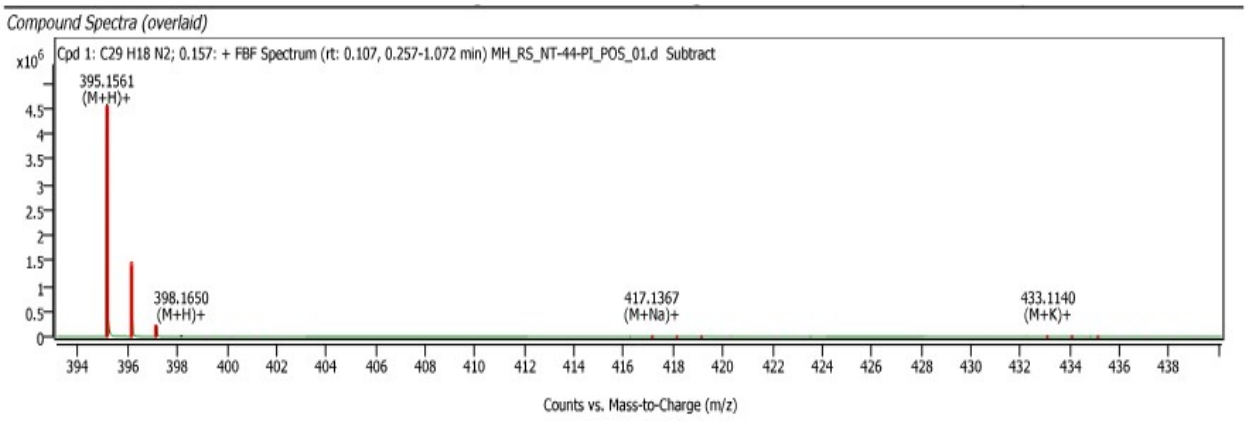

Figure S2: High-resolution mass spectra of parent moiety, C.

Compound D: Compound c was treated with NaOH in methanol, stirred for 6 h, and evaporated to afford Sodium salt intermediate D. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.707-7.671 (m, 5H), 7.375-7.346 (m, 4H), 6.286 (d, 2H), 6.185 (s, 2H), 6.082 (s, 4H). HRMS calculated for $C_{29}H_{17}N_2Na$: 416.47, found: 417.13 (m/z).

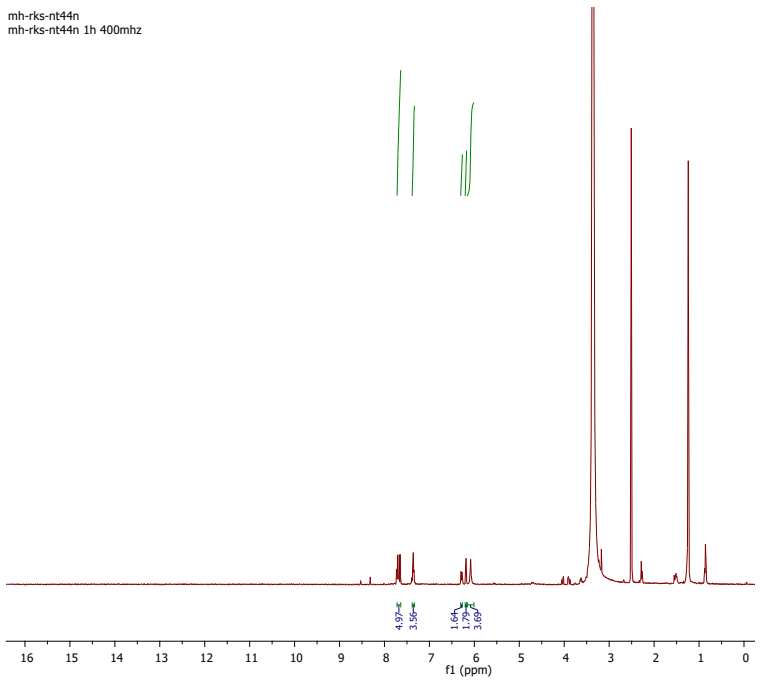

Figure. S3: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **sodium salt**, D.

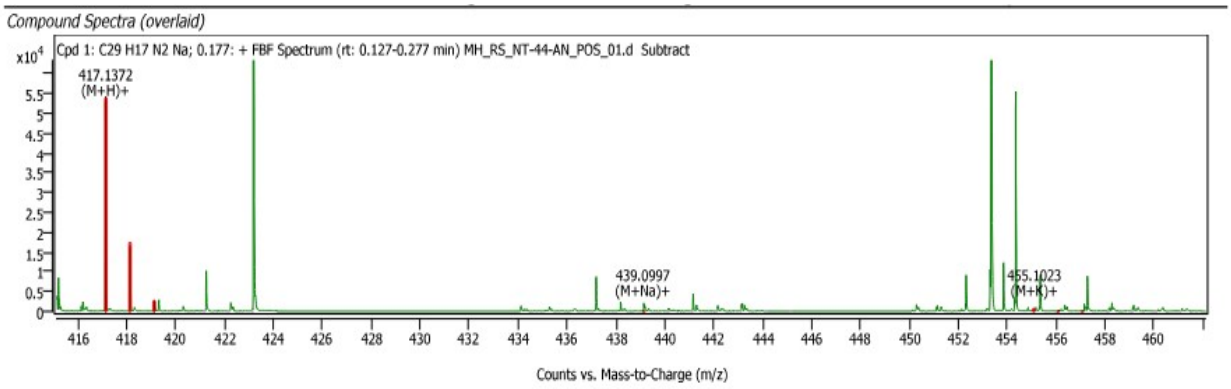

Figure S4: High-resolution mass spectra of the sodium salt of the parent moiety, D.

Ionic Liquid (APIL): APIL was synthesized following a literature method with slight modifications[1]. Succinctly, in a dichloromethane (DCM)-water mixture of 2:1(v/v), the sodium salt D and the ionic liquid $P_{66614}Cl$ in a 1:1 molar ratio were stirred overnight, resulting in an ion exchange process. The solvent phase was purged, and repeated washing of the DCM layer with water was performed to remove the NaCl byproduct, which was confirmed by adding $AgNO_3$

solution and washing the reaction mixture multiple times until no white precipitate of AgCl formed. To eliminate the trace water in the DCM layer containing APIL, it was passed through anhydrous Na_2SO_4. **APIL** was obtained (SCHEME 1) by evaporating the DCM and residual water under vacuum at 60°C for 2 hours **^{1}H NMR** (400 MHz, DMSO, δ(ppm)):7.684(s,1H), 7.564-7.479 (m,3H), 7.708 (m,4H), 7.892-7.777 (q,2H), 8.062-7.892 (m,2H), 8.294-8.136 (m,2H), 8.501-5.324 (d,1H), 8.880-8.693 (m,1H), 8.991-8.896 (m,1H), 2.183-2.178 (m,19H), 1.387-1.381 (m,20H), 0.866-0.8605 (m,21H) **^{13}C NMR** (100 MHz, $CDCl_3$, δ (ppm)): 199.11, 198.42, 196.33 ,196.02, 194.98, 193.76,192.78, 191.95, 191.16, 173.46, 162.22 ,160.90, 159.54, 148.72, 140.37, 140.09, 139.19, 137.84, 128.84, 122.35, 121.51, 118.39, 111.86, 110.86, 106.39, 102.78, 101.88 ,99.78, 93.55 71.62, 69.76, 67.68, 67.41, 66.68, 66.07, 65.95, 65.4, 63.10, 57.45, 57.40, 56.61, 55.81, 54.96, 53.34, 32.84, 31.75, 31.47, 31.33, 29.15, 23.13, 22.55, 21.44, 14.42, 8.25, 4.53, 4.06, 2.47, 1.58, 0.18, 0.93. **^{31}P NMR** (400 MHz, $CDCl_3$, δ (ppm): 34.9

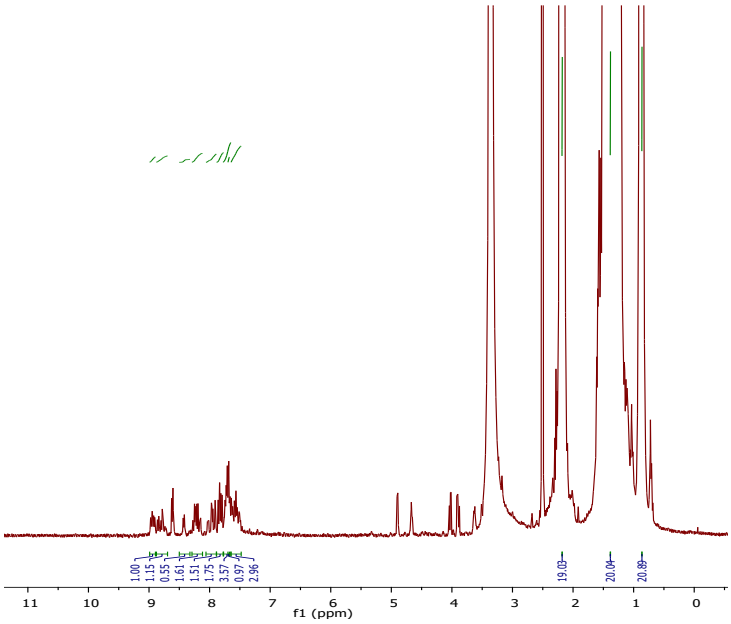

Figure. S5: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **APIL**.

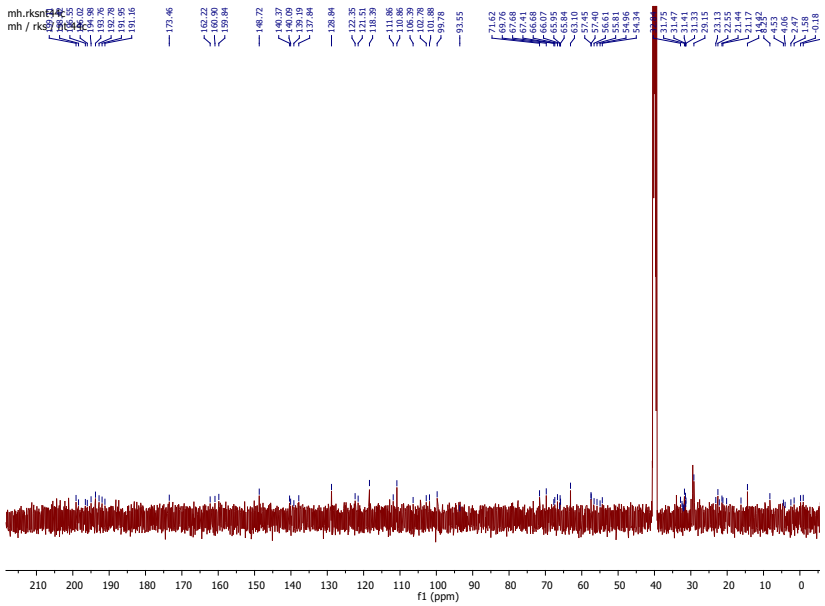

Figure. S6: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **APIL**.

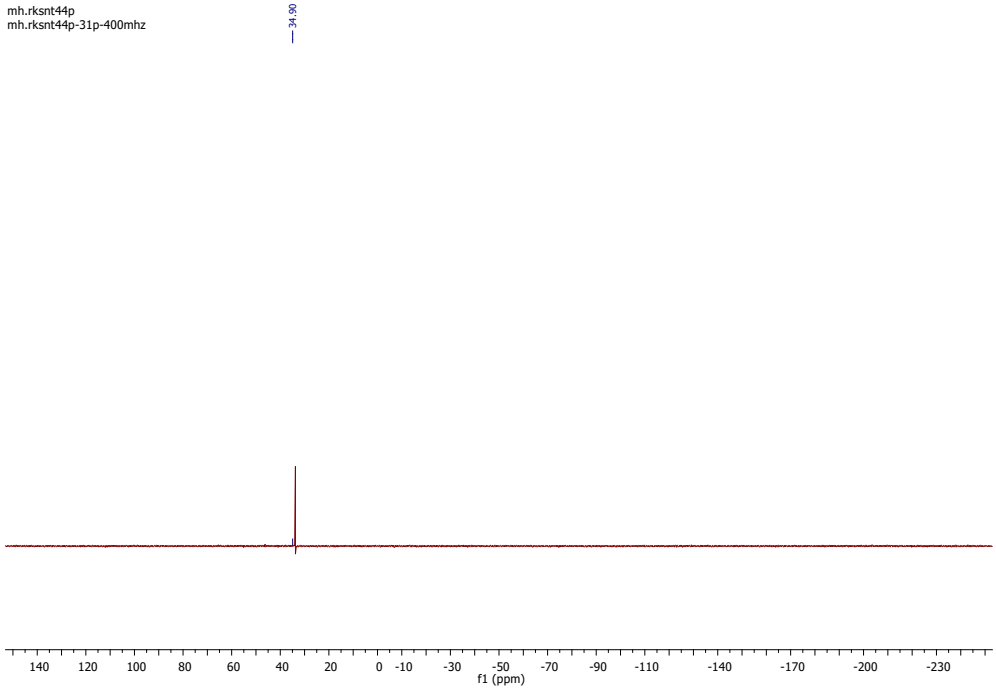

Figure. S7: ^{31}P NMR spectrum ($CDCl_3$, 400 MHz) of **APIL**.

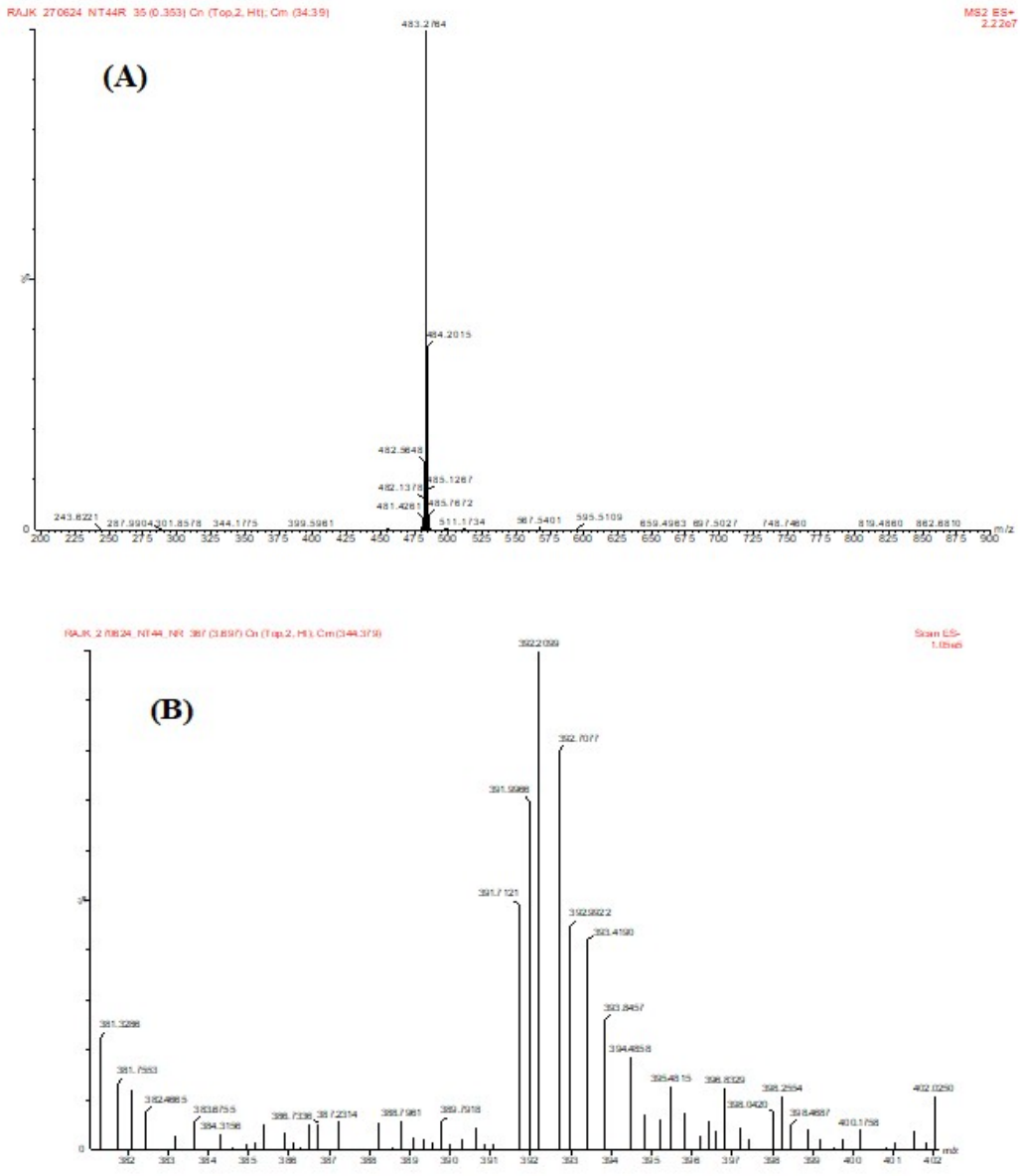

Figure. S8: LCMS spectra of **APIL**; **(A)** positive ion mode and **(B)** negative ion mode.

S1.2. Estimation of Quantum Yield

For the determination of the fluorescence quantum yield (Φ_x) of **mAPIL** in DMSO, and to investigate the aggregation-caused quenching (ACQ) mechanism by increasing the water fraction, quinine sulfate in 0.1 N H_2SO_4 ($\Phi = 0.55$)[2] was used as the standard.

$$\Phi = \Phi_c\left(\frac{F_s}{F_c}\right)\left(\frac{A_c}{A_s}\right)\left(\frac{\eta_s^2}{\eta_c^2}\right)$$

In the applied formula, Φ indicates quantum yield, F is the integrated fluorescence emission, A is absorbance, and η is the refractive index of the solvent. The subscripts "c" and "s" denote the standard and the sample (**APIL in DMSO** / **mAPIL** / **mAPIL** - ClO_4^-), respectively. Based on this analysis, the quantum yields of **APIL** in DMSO, **mAPIL,** and its ClO_4^- complex were found.

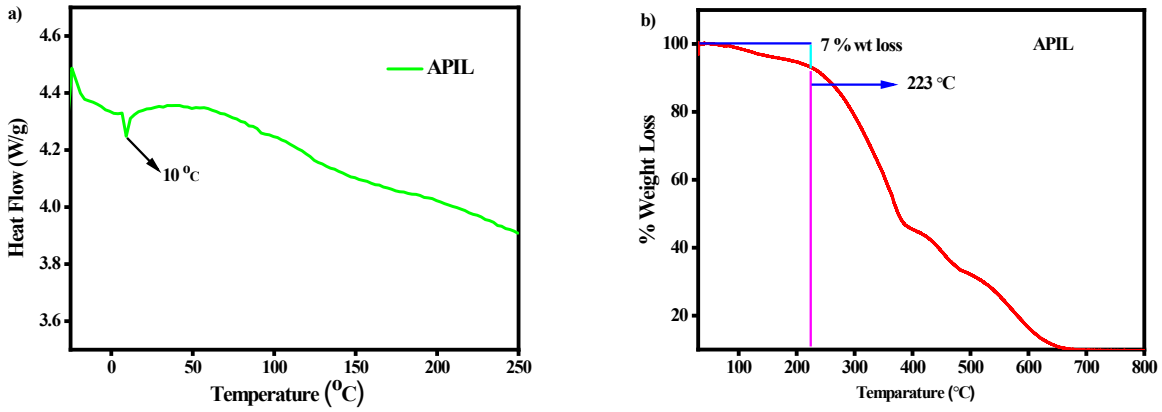

Figure S9: (a) Differential scanning calorimetry (DSC) thermogram of **APIL. (b)** Thermogravimetric analysis (TGA) thermogram of **APIL**

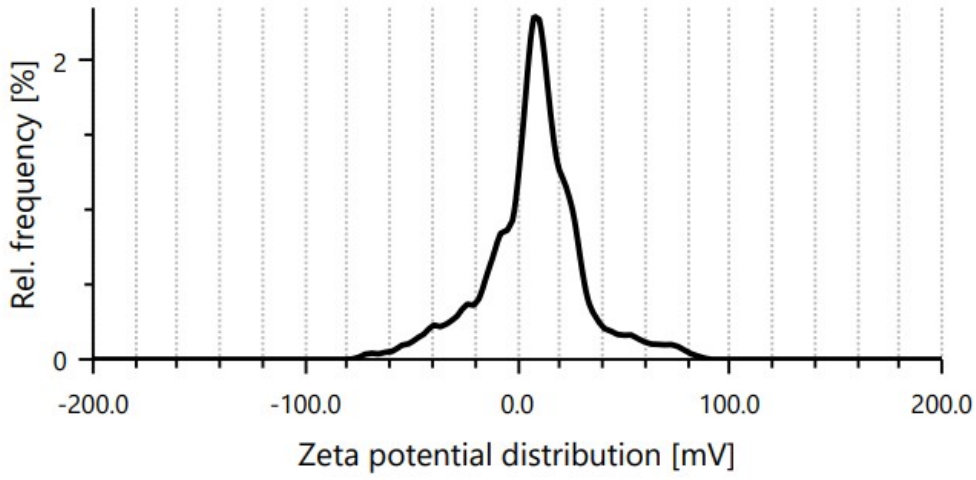

Figure S10: Zeta potential of the **mAPIL** solution.

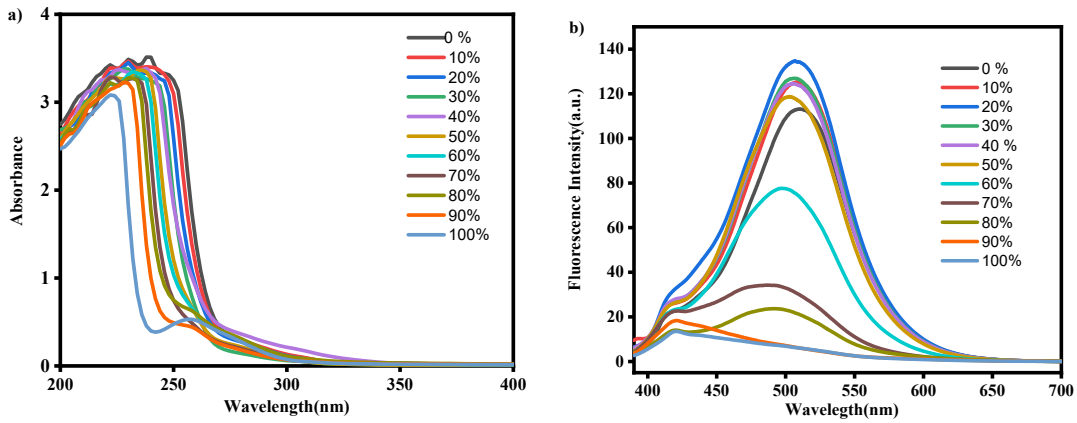

Figure. S11 (a)UV-visible absorption spectra of optode **APIL** in different percentages of water**.**

(b) Fluorescence spectra of **APIL** in water-DMSO mixed solvents demonstrating ACQ.

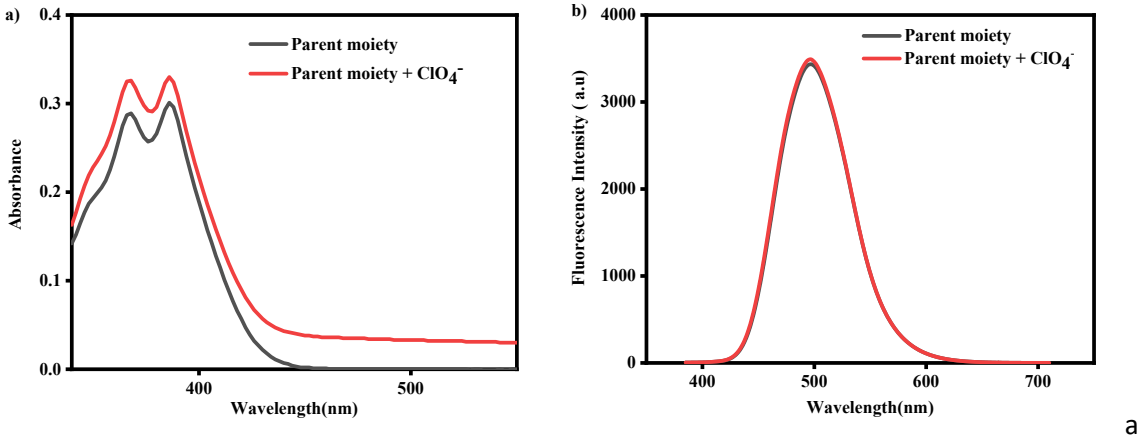

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Figure S12: (a)UV vis spectroscopy comparison of parent moiety and parent moiety on addition of ClO_4^- (b) Photoluminescence comparison of parent moiety and parent moiety upon addition of ClO_4^-

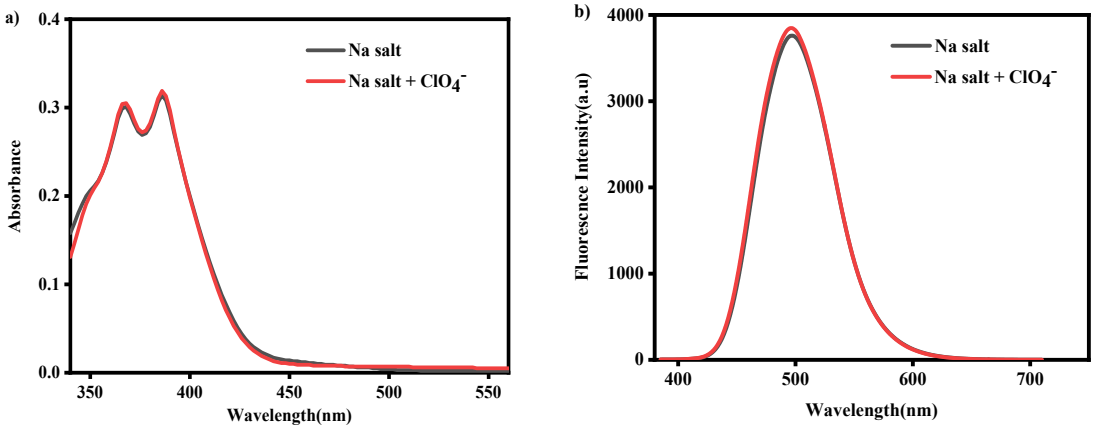

Figure S13: (a) UV-visible spectral comparison of sodium salt and sodium salt on the addition of ClO_4^- ions. **(b)** Photoluminescence comparison of sodium salt and sodium salt upon addition of ClO_4^-

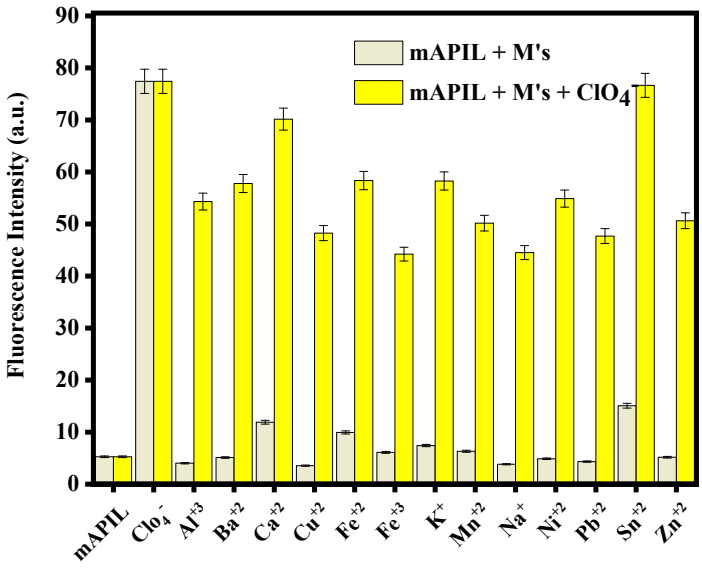

Figure S14: Histogram displaying the selectivity of **mAPIL** (43 µM) with ClO_4^- ions over other metals (45 µM).

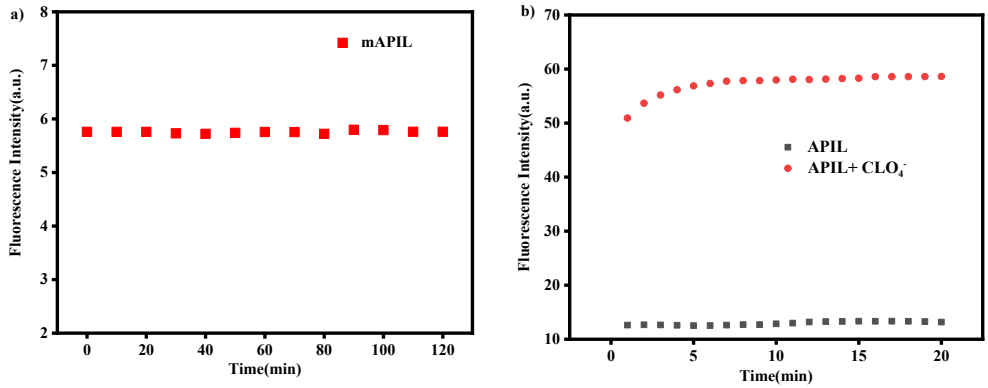

Figure S15: (**a)** Fluorometric stability of **mAPIL** suspension. **(b)**Fluorometric response time of water-suspended **mAPIL** for the detection of ClO_4^- ions.

Table S1: **Solvatochromism comparison of the parent moiety, its sodim salt, and ionic liquid**

	Solvent	UV(nm)	FL(nm)
	THF	**384**	**487.8**
	DCM	**386**	**492.4**
Parent Moiety	**DMF**	**387**	**494.6**
	DMSO	**388**	**496.2**
	WATER	**390**	**490.4**

	Solvent	UV	FL
	THF	**306**	**487.6**
	DCM	**366**	**493.4**
Sodium Salt	**DMF**	**386**	**495.6**
	DMSO	**388**	**496.4**
	WATER	**392**	**491**

	Solvent	UV	FL
	THF	**264.43**	**498.6**

	DCM	**276**	**500**
APIL	**DMF**	**280**	**502**
	DMSO	**284**	**508.61**
	WATER	**294.5**	**421.6**

Table S2: Calculated ΔG values at various temperatures.

Temperature(℃)	**ΔG (**$Jmol^{-1}$**)**	**ΔH (**$Jmol^{-1}$**)**	**ΔS (**$Jmol^{-1}$ K^{-1}**)**
15	-22926.64	-21732.54	79.61
25	-23722.71		
35	-24518.77		
45	-25314.83		
55	-26110.9		
65	-26906.96		

Table S3: Determination of ClO_4^- ions in various water samples.

Sample	**Added (µM)**	**Found (µM)**	**Recovery (%)**
River water	7.29	7.23	99.09
	9.7	9.5	97.85
	12.1	11.94	98.68
	14.49	14.45	99.70
	16.86	16.56	98.19
	19.23	18.9	98.50
	21.5	21.40	99.17
Municipalitywater	12.1	11.8	98.12
	14.49	14.28	98.55
	19.23	18.9	98.3
	21.58	21.54	99.83
	23.92	23.72	99.18
	26.25	26.17	99.69
	28.57	28.40	99.42

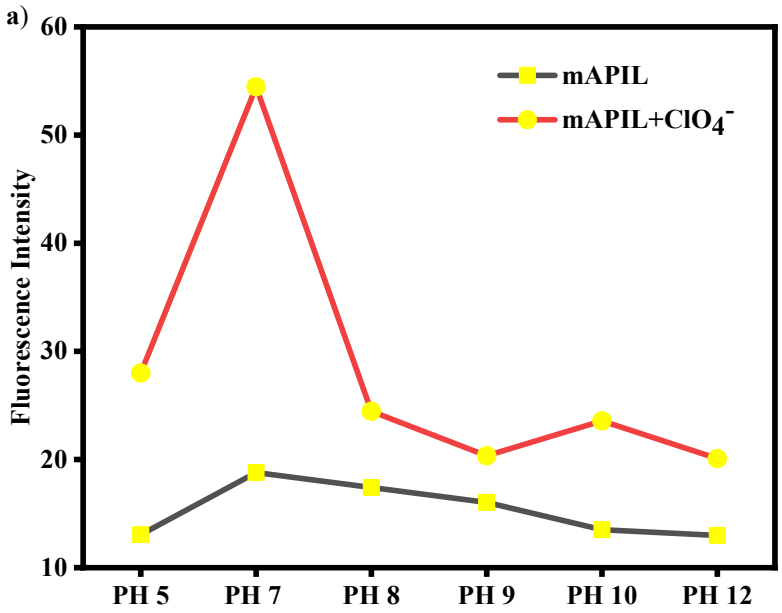

Figure S16: Influence of pH on the photoluminescence behavior of **mAPIL** in the absence and presence of ClO_4^- ions.

Table S4: Comparison table of different chemosensors that have been introduced for detecting ClO_4^- ion in the last few decades, with our prepared **mAPIL**

Structure	Medium	Optical signaling	LOD	Ref. No.
Methylene Blue−Modified gold nanoparticles	Ultrapure water	Colorimetric	24μM	[3]
[Pt(terpy)Br]-PVA hydrogel sensor	acetic acid/ water/ethanol (0.5:1:1, v/v) mixed solution	turn-on luminescence	25 nM	[4]
1-(4-Biphenyl)benzimidazolium based dipodal system	HEPES buffer (0.01 M)	quenching of fluorescence intensity	100 nM	[5]
Ion-selective electrodes	water	-	$10^{-7.4}$ M	[6]

using multi-walled carbon nanotubes as ion-to-electron transducers				
1-(2-(3′, 6′-bis(diethylamino)-3-oxospiro[isoindoline-1,9′-xanthene]-2-yl)ethyl)thiourea	HEPES buffer (0.1 M in CH_3CN/water, 4/1, v/v, pH 7.4)	colorimetric and fluorimetric	1×10^{-7} M.	[7]
perylenediimide based chemosensor	HEPES buffer (10% DMSO) (v/v) (pH 7.4)	fluorescence quenching	60 nM	[8]
Benzoimidazole-based	HEPES buffer – 2% DMSO, pH 7.4	fluorescence based	1.6 μM	[9]
CHEMFET devices based on plasticized PVC membranes containing the phosphadithiamacrocycle.	-	Potentiometrically	$3x10^{-7}$M	[10]
ISE devices based on plasticized PVC membranes containing the phosphadithiamacrocycle.	-	Potentiometrically	$8x10^{-7}$M	[10]
gold–silica composite nanoparticle substrates for perchlorate	-	surface-enhanced Raman spectroscopy	10^{-6} M	[11]
Novel polymeric membrane (PME) electrodes based on a phosphorous(V)-tetraphenylporphyrin complex.	Acetonitrile	UV-Vis, Fluorescence, and Potentiometrically	5 μM	[12]

Coated glassy carbon (CGCE) electrodes based on a phosphorous(V)-tetraphenylporphyrin complex.	Acetonitrile	UV-Vis, Fluorescence, and Potentiometrically.	0.7 μM	[12]
Anthracene phenantro imidazolate-based ionic liquid	**Water**	**fluorometric**	**12.7 nM**	**This work**

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