Supplementary Information

Enhanced TNT Vapor Sensing Through PMMA-mediated AIPE-Active Monocyclometalated Iridium(III) Complex: A Leap Towards Real-Time Monitoring

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NMR spectra: -









Figure S2: - ¹³C NMR spectrum of L1 in Chloroform-*d* solvent.

NMR spectrum of L2





Figure S3: - ¹H NMR spectrum of L2 in Chloroform-*d* solvent.









Figure S5: - ¹H NMR spectrum of M1 in Chloroform-*d* solvent.







¹H, ¹³C and ³¹P NMR spectrum of M2





Figure S8: - ¹H NMR spectrum of M2 in Chloroform-*d* solvent.



Figure S9: - ¹³C NMR spectrum of M2 in Chloroform-*d* solvent.



Mass spectra of ligands and complexes







Figure S12: - Mass spectrum of L2.



m/z	Calc m/z	Diff(ppm)	z	Abund	Formula	Ion
967.2009	967.217	16.6	1	17868.39	C49H43ClIrNO2P2	(M+H)+
968.2032	968.2155	12.63	1	9651.75	C49H43ClIrNO2P2	(M+H)+
969.2034	969.2186	15.64	1	40793.96	C49H43ClIrNO2P2	(M+H)+
970.2061	970.2161	10.3	1	20530.87	C49H43ClIrNO2P2	(M+H)+
971.1999	971.2177	18.37	1	15918.78	C49H43ClIrNO2P2	(M+H)+
972.2016	972.2204	19.28	1	6932.15	C49H43ClIrNO2P2	(M+H)+
973.1985	973.2233	25.42	1	5314.24	C49H43ClIrNO2P2	(M+H)+
988.182	988.1956	13.75	1	1012.83	C49H43ClIrNO2P2	(M+Na)+
989.1926	989.1989	6.36	1	448.89	C49H43ClIrNO2P2	(M+Na)+
990.1952	990.1974	2.22	1	50.32	C49H43ClIrNO2P2	(M+Na)+

gure S13: - Mass spectrum of M1.

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Figure S14: - Mass spectrum of M2.

IR spectra

The infrared spectrum for every complex was recorded in its solid state. A characteristic peak of Ir-H stretching was observed around 2100 to 2150 cm⁻¹ for both the complexes.



Figure S15: - IR spectrum of M1 and M2, Ir-H stretching was indicated in the above spectrum.



Figure S16: - UV-VIS and PL spectra of both the complexes in THF solution.



Figure S17: - UV-VIS spectrum of the unsubstituted complex in THF (10⁻⁶ M) solution



Figure S18: - M1 and M2 in THF and different fractions of PEG, (a) (top, left): image of 0, 60 and 90% PEG fraction under UV excitation (365 nm) for M1; (bottom, left) corresponding emission spectra of M1, similarly (b) (top, right) image shows different PEG fraction under UV excitation of 365 nm and (bottom, right) spectra shows corresponding emission spectra of M2.



Figure S19: - Crystal packing diagram for M2 with possible short contacts in a unit cell.





Figure S20: - DLS study of M1 and M2 in THF solution 0% (top) and 90% water fraction (bottom).



The short notation is used on the figure; their full names are shown as:

M1 and M2- Probe molecules only, Aq.- Water, RDX- Royal Demolition Explosive, HMX- 1,3,5,7tetranitro-1,3,5,7-tetrazocane (High-velocity Military Explosive), DNT- 2,4-dinitrotoluene, PETN-Pentaerythritol tetranitrate, TNT- 2,4,6-trinitro toluene, 4NBA- 4-nitro benzoic acid, AN- Ammonium nitrate, 4NT- 4-nitro toluene, DNP- 2,4-dinitrophenol, TNP- 2,4,6-trinitrophenol.



Figure S21: - Selectivity test of probe M1 (a) and M2 (b) with different nitro-based explosive materials. Each one of the 10 μ L 10⁻⁴ M aqueous solutions of different nitro-based explosives was added to the probe-coated filter paper, and the resulting image was obtained through excitation by UV ray (365 nm) as shown in the figure. Similarly, (c) From the left side, the first one is the PL intensity of the aggregated solution of the probe (THF/90% water), then different nitro-based analyte was added and taken the image under UV excitation (365 nm). (d) representations of the quenching performance of M2 with TNT in the presence of different analytes shown in the bar graph, extreme left represents the AIPE active probe solution, then different analytes as mentioned on the X-axis and adjacent bar corresponding to each analyte showing quenching after adding TNT.



Figure S22: - Stern–Volmer plot for the PL quenching of the probe upon the gradual addition of TNT, where I_0 represents the PL intensity of the probe in the absence of TNT, and I denote the intensity in the presence of TNT. S-V plot deviates upward with increasing TNT concentration.



Figure S23: - Aggregated solution of M1 and M2 in the presence of TNT; the lifetime measurement was done; it was observed that there is a decrease in excited state lifetime in the presence of an analyte in the case of M1 and M2 in the presence of TNT.



Figure S24: - UV visible spectra of M1 and M2 in the presence of different amounts of TNT analyte. In the presence of TNT, no significant change in the complexes' UV-visible spectra indicates no ground state complex formation is observed.



Figure S25: - (a) Excitation and emission of M1 (b) Excitation and emission of M2 to check the possibility of inner filter effect in complexes.



Figure S26: - Absorption spectra of TNT and emission spectra of M1 and M2 in THF solutions to check the possibilities of spectral overlap between absorption and emission.



Figure S27: - (a) Cyclic voltammetry (CV) plots of complexes in THF solvent. 10^{-4} M solution of complexes was prepared in THF solvent followed by the addition of supporting electrolyte, tetrabutylammonium hexafluorophosphate (NBu₄PF₆), and (b) UV-VIS spectra of M1 and M2 in THF solvent along with calculation of $E_{(LUMO)}$ by using oxidation onset potential from CV plot and band edge absorption from UV-VIS spectra.



Figure S28: - HOMO and LUMO energies alignments of M1, M2, and TNT (detailed calculations of HOMO and LUMO energies for M1 and M2 are shown in S22).



Figure S29: - (a) Placed 200 mg TNT in a clean and dry glass vial with an airtight lid (5 ml capacity), kept overnight for vapor saturation at 25-30°C; (b) remove the cap carefully and (c) immediately exposed the probe coated filter paper by the TNT vapor from the headspace of glass vial and recorded the PL intensity by using Fluorimeter.



Figure S30: PL spectra show photoluminescence (PL) intensities of M1 on filter paper upon continuous exposure with TNT vapors; it was observed that with TNT vapor exposure, the PL intensity did not change.



Figure S31: - The PL intensity of filter paper impregnated complexes and complex with PMMA polymer (CPF), inset figures shows image of filter paper after coating complex and complex-PMMA under UV excitation (365 nm).



Figure S32: - Excited state lifetime spectra were recorded by TCSPC instrument. Thin film of each complex was prepared on glass coverslips, dried well, and recorded the spectra. For M1, bi-exponential decay (Components-B1=85.30, B2=14.70) was observed after fabricating the film with PMMA (components-B1=87.80, B2=12.20). Similarly, in case of M2 and M2-PMMA bi-exponential decay were observed (B1=48.96, B2=51.04 for M2) (components-B1=17.49, B2=82.51 for M2-PMMA). Excited state lifetime with fitting parameter is given in table -S1.

M1	Complexes	Lifetin	ne, chi-square	Quantum	L	DD
		(µs)	(χ^2)	yield(%)	Solution	Vapor
	M1	7.5 ((χ ² - 1.20)	27.38	1.09 nM	X
M1 PMMA	СР	9.4	(χ ² - 1.10)	71.20		X
M2						
	M2	8.8	(χ ² - 0.97)	33.60	450 pM	66.3 ppb
M2 PMMA	СР	11.3	(χ ² - 1.02)	97.40		12.8 ppb

Table-S1, summarize results of phosphorescent lifetime, quantum yield, and limit of detection (LOD), of sole complexes (M1and M2) and complexes embedded with PMMA polymer(CP).



Figure S33: - (a) UV-visible spectra of M2 recorded in every 30 min interval, (b) photoluminescence spectra of $M2(\lambda_{ex} = 410 \text{ nm})$ in 30 min intervals.



Figure S34: - (a) UV-visible spectra of CP recorded in every 30 min interval, (b) PL spectra for CP recorded in every 30 min interval ($\lambda_{ex} = 400 \text{ nm}$)



Figure S35: - TGA analysis of both the complexes (M1 and M2)



Figure S36: - Pore size distribution of PMMA (left) and CP (right), it shows the distribution of pore radius with respect to differential volume.



Figure S37: - Stern-Volmer plot for emission quenching and LOD calculations of CP in the vapor phase TNT sensing.



Figure S38: - FE-SEM images of M2, CP, PMMA and CP after exposed with TNT



Figure S39: - DFT optimized HOMO (up) and LUMO (down) energy distribution on M1 and M2, HOMO is localized on Ir(III) centre, and LUMO is on Phenyl pyridine.

NMR spectra of complexes (M2) after several months

¹H NMR (400 MHz, Chloroform-*d*) δ 9.06 (d, J = 5.6 Hz, 1H), 7.53 (dt, J = 8.1, 1.1 Hz, 1H), 7.47 (td, J = 7.7, 1.7 Hz, 1H), 7.43 – 7.35 (m, 12H), 7.26 – 7.20 (m, 7H), 7.15 (tt, J = 7.0, 1.2 Hz, 12H), 6.87 – 6.73 (m, 2H), 6.48 (d, J = 1.5 Hz, 1H), -15.90 – -17.65 (m, 1H)



Figure S40: - NMR spectra of M2 after six months in Chloroform-d

Table S3. Crystallographic data file:

Formula	2(C ₄₈ H ₃₈ Cl Ir N ₂ P ₂), 1[CH ₂ Cl ₂]
Formula weight	1864.37
Temp (K)	298
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
Unit cell dimension	a = 13.4539(2) Å, b = 14.1118(3) Å, c = 43.2640(7) Å, α = β = γ = 90.0°
Crystal Size	0.2 x 0.1 x 0.2 mm ³
Z	4
V	8214.1 Å ³
Density (calculated)	1.508 g/cm ³
Absorption coefficient	3.430 mm ⁻¹
F(000)	3712
Theta range for data collection	1.5850 to 26.2030°
Index ranges	-16 ≤ h ≤ 17; -17 ≤ k ≤ 18; -54 ≤ l ≤ 54
Reflections collected	18004
Independent reflections	16742
Completeness to theta	54.1 96%
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on F ²
Goodness-of-fit on F2	1.010
Final R indices [I>2sigma(I)]	R ₁ = 0.0338, wR ₂ = 0.0652
R indices (all data)	R ₁ = 0.0338, wR ₂ = 0.0653

Table S4: - Reported literature for TNT sensing by various luminescent probes

Sr.	Probe	Analyte	Mode of	Quenching	Detection	Referenc
No.			sensing	constant	Limit	е
				Ksv (M ⁻¹)		
1.	Ir(III) (M1 and M2)	TNT	Contact	2.5 × 10 ⁸	450 pM(ppt)	Present
				for M2		work
			Vapor		12.8 ppb	
			phase			
2.	ТРА-СР	TNT	Contact	NA	1 μg/mL	1
3.	TPE-2PhOH	TNT	Vapour	NA	NA	2
4.	Derivative 3	TNT	Contact	13.3 × 10 ⁵	30 nM	3
	Derivative 4		Contact	10 × 105	40 nM	
			Vapour	NA	NA	
5.	CN-1	TNT	Contact	6.14 × 10 ⁵	NA	4
	CN-2			3.41 × 10 ⁵	NA	
6.	За	TNT	Contact	NA	pM level	5
7.	FIrPyBiz	TNT	Contact	7.41×10^4	22.7 ng/mL	6
			Vapour	NA	NA	
8.	PtriPE	TNT	Contact	2.56×10^4	NA	7
			Vapour	NA	1 ng/cm ²	
9.	1a	TNT	Contact	1.44×10^{3}	NA	8
	1b			3.56 × 10 ³	NA	
	2			4.45 4.03		
	2a			4.45×10^{3}	NA	
	2h			1.28×10^{4}		
10			Conntact	1.20 × 10		0
10.	Cu NC/ZIF-8		Contact	1 NA 2.6×10^4	o.5 µivi	9
11.	Bis(methyltetraphenyl)silor		Contact	2.0 × 10	hhn ievei	10
12	e Dimethylgermole		Contact	8 x 10 ³	nnh level	11
12.			Contact	8×10^{-104}		12
15.			Contact	0.5 ~ 10	0.0 μινι	12
	ΡΤΡΔ2-ΤΡΕ			7.7×10^{4}	0.5 µM	
14	Ρο	TNT	Contact	NA 10	5 ppm	13
15	his(methyltetranhenyl)	TNT	Contact	2.6×10^4	ΝΔ	14
±.J.	silolebis(methyltetranhenyl		Contact	2.0 ^ 10		<u> </u>
) silole siloxanes			1.8×10^{4}	NA	
16	1a	TNT	Contact	NA	29µM	15
10.	14		Contact		2.5 µW	10
	1b			NA	33 uM	
17	TPCTS	TNT	Contact	4.2×10^2	17 mM	16
18	Compound 1	TNT	Contact	4.3×10^{7}	32 nM	17
1 -0.	Compound 1	1		1.5 ^ 10	32	· - /

			Vapour	NA	NA	
19.	CB-5	TNT	Contact	3.1 × 10 ⁵	0.329 ppb	18
20.	TPE-PA-8	TNT	Contact	NA	1.2 ppm	19
21.	Re-4Py	TNT	Contact	3.61 × 10 ⁴	2.69 nM	20
22.	Polygermole	TNT	Contact	9.3 × 10 ³	NA	21
	Polygermole			2.9 × 10 ⁴	NA	
	nanoaggregates					
23.	Compound 4	TNT	Contact	6×10^{4}	0.25 ppm	22
24.	Oligomer P1	TNT	Contact	NA	79.2 ppb	23
			Vapour	NA	698 ppb	
25.	[IrIII(BPS)(ppy) ₂] ⁻	TNT	Vapour Contact	NA 1.05 × 10 ³	698 ppb NA	24
25.	[IrIII(BPS)(ppy) ₂] ⁻	TNT	Vapour Contact	NA 1.05 × 10 ³	698 ppb NA	24
25.	[IrIII(BPS)(ppy) ₂] ⁻ [IrIII(BPS)(FppyMe) ₂] ⁻	TNT	Vapour Contact	NA 1.05 × 10^3 0.87 × 10^3	698 ppb NA	24
25.	[IrIII(BPS)(ppy) ₂] ⁻ [IrIII(BPS)(FppyMe) ₂] ⁻	TNT	Vapour Contact	NA 1.05×10^{3} 0.87×10^{3}	698 ppb NA	24
25.	[IrIII(BPS)(ppy) ₂] ⁻ [IrIII(BPS)(FppyMe) ₂] ⁻ [IrIII(ppy) ₂ (dmbpy)] ⁺	TNT	Vapour Contact	NA 1.05×10^3 0.87×10^3 1.00×10^3	698 ppb NA	24
25.	[IrIII(BPS)(ppy) ₂] ⁻ [IrIII(BPS)(FppyMe) ₂] ⁻ [IrIII(ppy) ₂ (dmbpy)] ⁺	TNT	Vapour Contact	NA 1.05×10^{3} 0.87×10^{3} 1.00×10^{3}	698 ppb NA	24
25.	[IrIII(BPS)(ppy) ₂] ⁻ [IrIII(BPS)(FppyMe) ₂] ⁻ [IrIII(ppy) ₂ (dmbpy)] ⁺	TNT	Vapour Contact	NA 1.05×10^{3} 0.87×10^{3} 1.00×10^{3}	698 ppb NA	24
25. 26.	<pre>[IrIII(BPS)(ppy)₂]⁻ [IrIII(BPS)(FppyMe)₂]⁻ [IrIII(ppy)₂(dmbpy)]⁺ (SBFIQ)₂Ir(acac)</pre>	TNT	Vapour Contact Contact	NA 1.05×10^{3} 0.87×10^{3} 1.00×10^{3} 3.56×10^{3}	698 ppb NA 423 ppb	24 25
25. 26. 27.	<pre>[IrIII(BPS)(ppy)₂]⁻ [IrIII(BPS)(FppyMe)₂]⁻ [IrIII(ppy)₂(dmbpy)]⁺ (SBFIQ)₂Ir(acac) (PFBHC)₂Ir(acac)</pre>	TNT TNT TNT TNT	Vapour Contact Contact Contact	NA 1.05×10^{3} 0.87×10^{3} 1.00×10^{3} 3.56×10^{3} 1.61×10^{3}	698 ppb NA 423 ppb 63 μM	24 25 26

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