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Fluorescent chemosensor for Hg^{2+} ions based on pyridine attached phenanthridine probe

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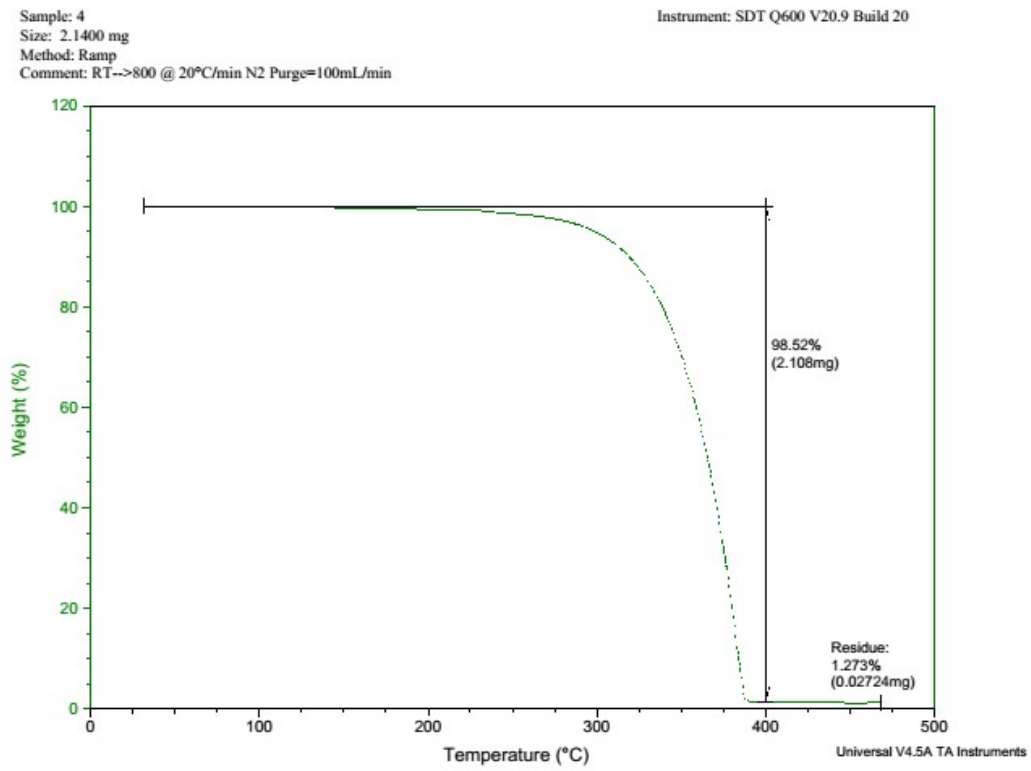
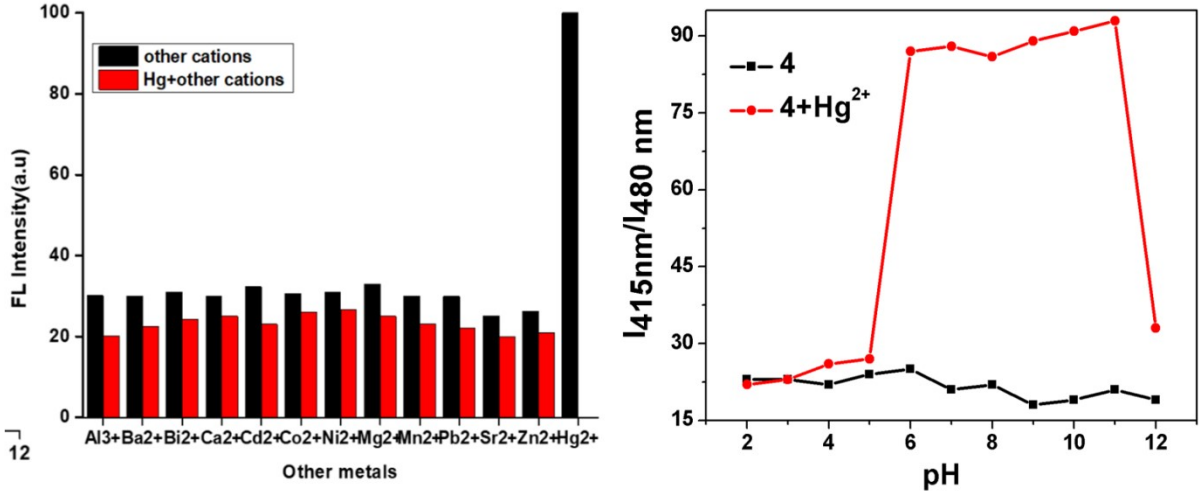
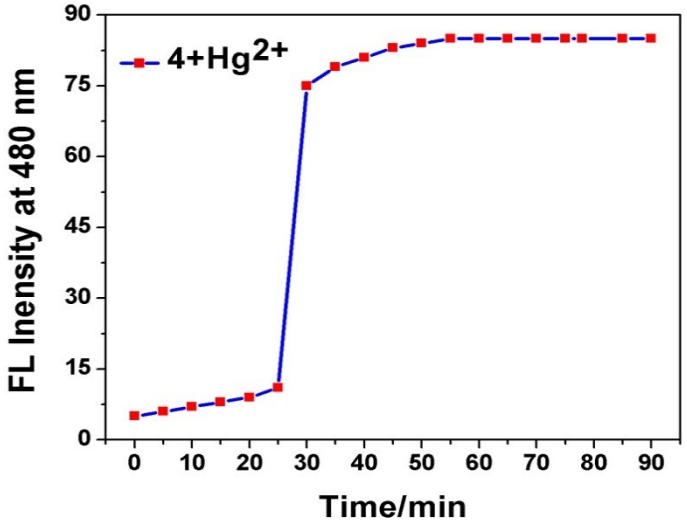


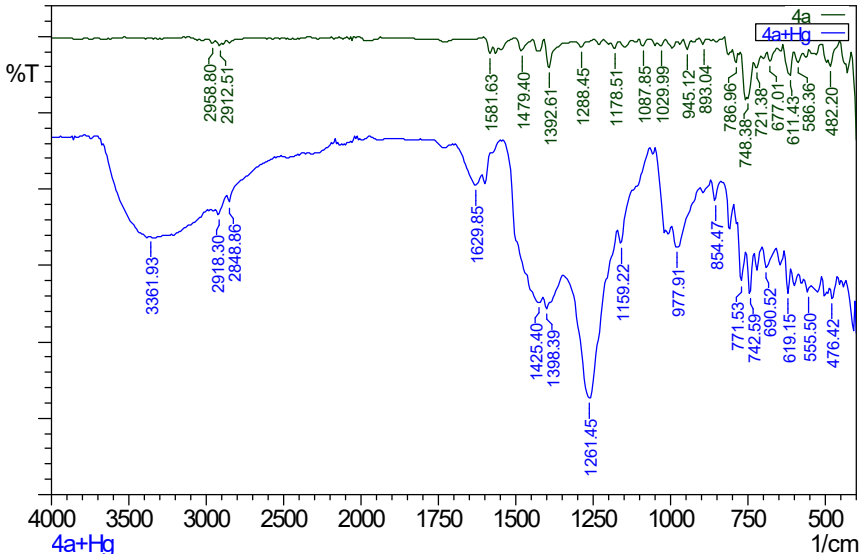
SI Figure S1 TGA curve of sensor **4**



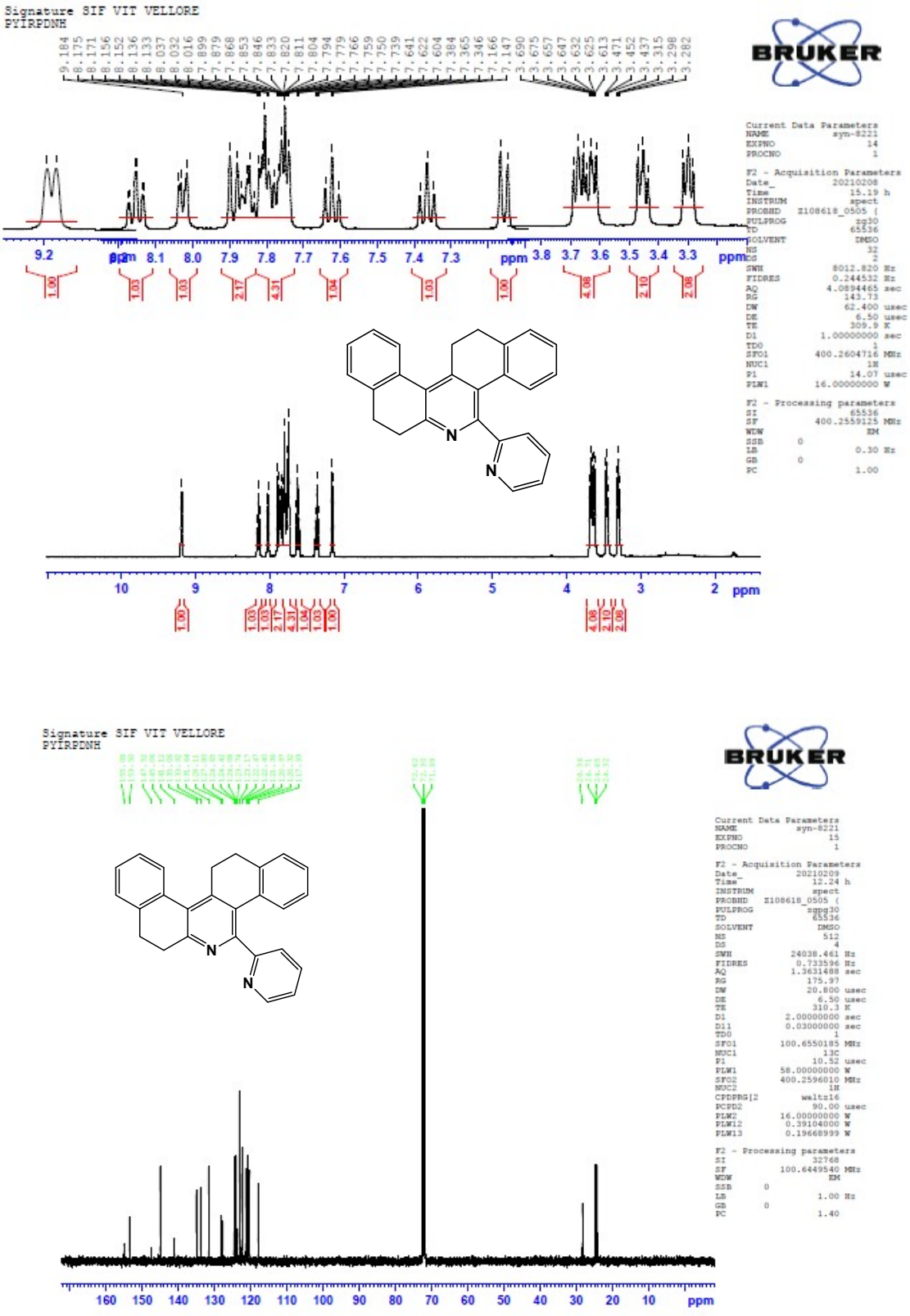
SI Figure S2 pH and Interference studies of **4** with **Hg^{2+}** ions



SI Figure S3 Effect of response time on fluorescence intensity of **4** with **Hg^{2+}** ions.



SI Figure S4 FTIR spectra of **4** in the presence of **Hg^{2+}**

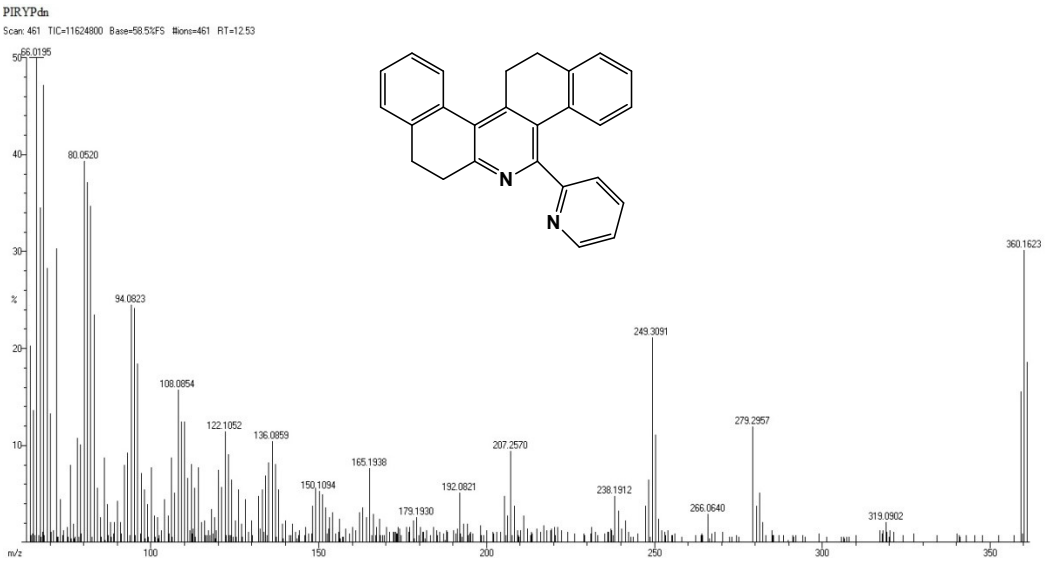


SI Figure S5 ^{1}H and ^{13}C NMR spectra of **4**

Molecular formula: $C_{26}H_{20}N_2$

Calculated mass : 360.1626

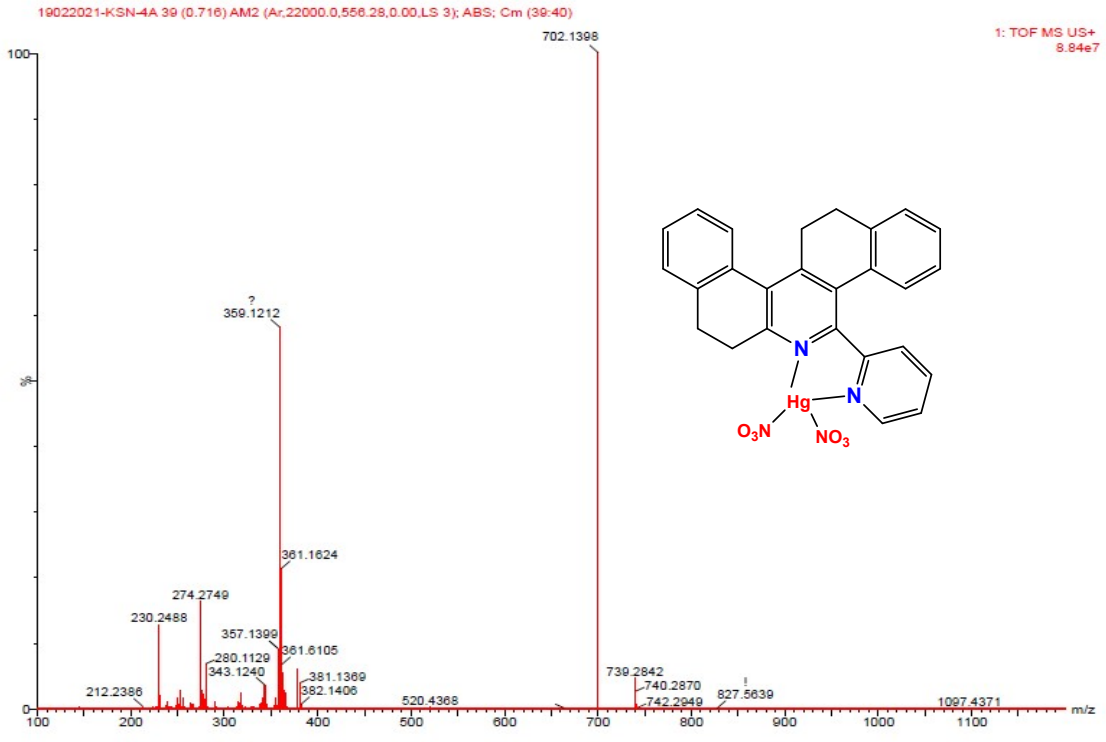
Obtained mass : 360.1623



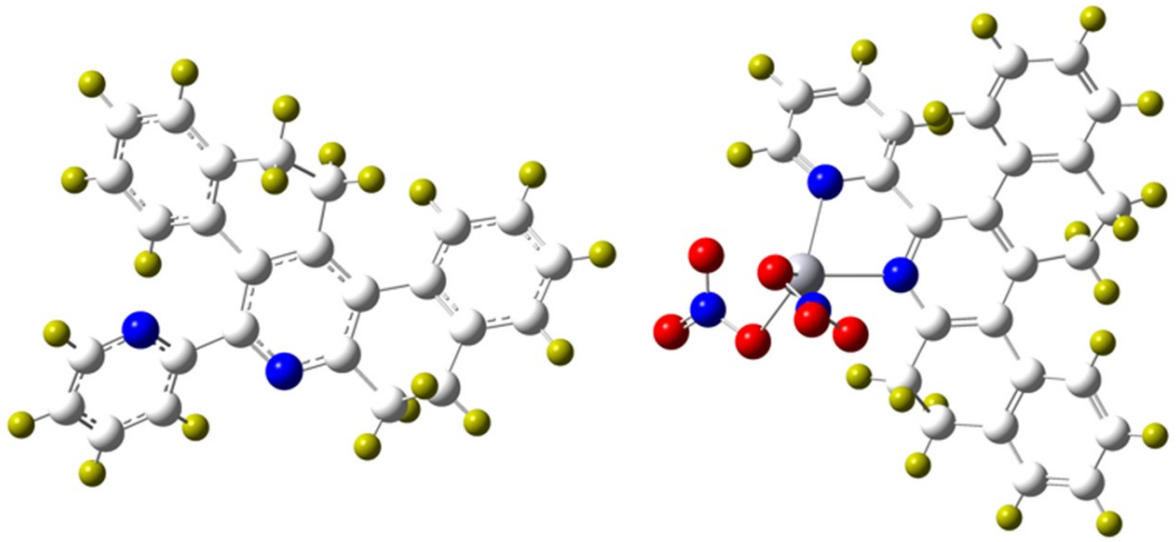
SI Figure S6 HRMS spectrum of **4**

Obtained mass: 702.1398

Calculated mass: 701.1324



SI Figure S7 ESI-Mass spectra's of ligand **4** with Hg^{2+} ion



4 **4+Hg^{2+}**

SI Figure S8 Optimized structure of probe **4** and **4+Hg^{2+}** ion

SI Table S1 Comparison of present sensor compound **4** with previous reports for Hg^{2+} ion sensing

S.NO	Name of the probe	Solvent	Method	LOD	Application	Reference
1.	Pyrene based Schiff base	DMSO/H_2O (v/v, 7/3)	Colorimetric and fluorometric	2.82 µM	Living cells	New J.Chem.,2015,39,2523-2531
2.	Condensation of Rhodamine hydrazone	Ethanol/Water (3/7, v/v)	Colorimetric and fluorometric	0.30 µM	Cell image	RSC Adv., 2015, 5, 21797-21802
3.	Invertase-functionalized gold-dendrimer nanospheres	PBS buffer	Glucometeric	4.2pM	Real Sample	Biosensors and Bioelectronics ,2016,77,681-686
4.	poly(amidoamine) (PAMAM) dendrimer	PBS buffer	impedimetric	0.4pM	Real Sample	Biosensors and Bioelectronics 2016,75, 108-115
5.	Benzothiazole based Chemosensor	DMSO	Colorimetric	0.15 µM	No data	Inorganic Chemistry Communications., 2016, 74, 1-5
6.	BODIPY based Chemosensor	PBS buffer solutions containing 0.5% DMSO	Colorimetric and fluorometric	49 nM	Cell image	Analyst, 2016, 141, 4789-4795
7.	Indole based BODIPY	CH_3CN	Colorimetric and fluorometric	0.33 µM	Cell image	RSC Adv., 2016, 6, 82810-82816

8.	Rhodamine hydrazine based Chemosensor	EtOH/Water (2:1, v/v)	Colorimetric and fluorometric	150 nM for Hg^{2+} and 3.37μM for Cu^{2+}	Real Sample	Journal of Photochemistry and photobiology A: Chemistry 2016, 318, 7-13
9.	DNA-scaffolded silver nanocluster	phosphate buffer	fluorometric	24pM	Real Sample	Biosensors and Bioelectronics, 2016, 79,411-415.
10.	Rhodamine derivative bearing Thiazole and thiocarbonyl moieties	CH_3CN/ HEPES buffer (3:7)	Colorimetric and fluorometric	0.134μM for Hg^{2+}	Cell image	Tetrahedron., 2017, 73, 5189-5193
11.	Pyrene based Chemosensor	H_2O /CH_3CN (1:1)	Colorimetric and fluorometric	57 nM	Living Cells	Sensors and Actuators: B. Chemical., 2018, 277, 673-678
12.	Pyrazoline derivative based chemosensor	H_2O	Colorimetric and fluorometric	14.54 μM	No data	Sensors and Actuators: B. Chemical., 2018, 255, 814-825
13.	Fluorescein based Chemosensor	Buffer/MeOH (95/5, v/v)	Colorimetric and fluorometric	0.110 μM	Living cells	Inorganic Chemistry Communications., 2018, 89, 46-50
14.	Triphenylamine appended Rhodamine	CH_3CN/H_2O (v/v, 9/1)	Colorimetric and fluorometric	0.48μM for Hg^{2+} and 71.8nM for Al^{3+}	Test paper strips	Sensors and Actuators; B. Chemical., 2019, 290, 558-564
15.	ultrathin two-dimensional MXenes (Ti_3C_2)	Ultrathin nanosheets	fluorometric	42.5 pM	Signal amplification	Analyst, 2021 146, 2664-2669.
16.	Pyridine attached Phenanthridine moiety	CH_3CN/H_2O (8:2, v/v)	Colorimetric and fluorometric	49.87 nM	Real sample and Bio-image	This work

SI Table S2 Crystal data and structure refinement for **4**

Identification code	**4**	
Empirical formula	C26 H_{20} N_2	
Formula weight	360.44	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 11.2948(5) Å	α= 90°.
	b = 15.2912(6) Å	β= 102.4061(18)°
	c = 10.9882(3) Å	γ = 90°.
Volume	1853.47(12) $Å^3$	
Z	4	
Density (calculated)	1.292 Mg/m^3	
Absorption coefficient	0.076 mm^{-1}	
F(000)	760	
Crystal size	0.250 x 0.160 x 0.100 mm^3	
Theta range for data collection	2.277 to 24.998°.	
Index ranges	-12<=h<=13, -17<=k<=18, -13<=l<=13	
Reflections collected	13357	
Independent reflections	3271 [R(int) = 0.0361]	
Completeness to theta = 24.998°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.992 and 0.981	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3271 / 0 / 254	
Goodness-of-fit on F^2	1.016	
Final R indices [I>2sigma(I)]	R1 = 0.0396, wR2 = 0.0857	
R indices (all data)	R1 = 0.0719, wR2 = 0.1015	
Extinction coefficient	0.0130(13)	
Largest diff. peak and hole	0.170 and -0.128 e.$Å^{-3}$	

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for pyrpdn. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
C(1)	8924(2)	9665(1)	6599(1)	39(1)
C(2)	8174(2)	10027(1)	5410(2)	48(1)
C(3)	7344(2)	9336(1)	4703(2)	53(1)
C(4)	6612(2)	8912(1)	5526(2)	46(1)
C(5)	5404(2)	8686(1)	5088(2)	65(1)
C(6)	4722(2)	8340(1)	5865(2)	73(1)
C(7)	5236(2)	8235(1)	7109(2)	64(1)
C(8)	6431(2)	8448(1)	7563(2)	50(1)
C(9)	7156(2)	8764(1)	6779(2)	41(1)
C(10)	8449(2)	8996(1)	7229(1)	37(1)
C(11)	9238(2)	8606(1)	8249(1)	37(1)
C(12)	8944(2)	7765(1)	8847(2)	45(1)
C(13)	10089(2)	7230(1)	9281(2)	50(1)
C(14)	10991(2)	7755(1)	10185(2)	44(1)
C(15)	11635(2)	7427(1)	11309(2)	55(1)
C(16)	12407(2)	7951(2)	12138(2)	60(1)
C(17)	12537(2)	8818(1)	11861(2)	55(1)
C(18)	11898(2)	9162(1)	10752(1)	46(1)
C(19)	11133(2)	8637(1)	9888(1)	39(1)
C(20)	10384(2)	8979(1)	8701(1)	36(1)
C(21)	10743(2)	9666(1)	8019(1)	38(1)
C(22)	11955(2)	10093(1)	8323(1)	39(1)
C(23)	14012(2)	10001(1)	8570(2)	56(1)
C(24)	14162(2)	10880(1)	8813(2)	56(1)
C(25)	13146(2)	11372(1)	8800(2)	53(1)
C(26)	12033(2)	10978(1)	8537(2)	43(1)
N(1)	10036(1)	9989(1)	6976(1)	41(1)
N(2)	12931(1)	9591(1)	8336(1)	51(1)

Bond lengths [Å] and angles [°] for pyrpdn.

Atom	Bond Lengths
C(1)-N(1)	1.331(2)
C(1)-C(10)	1.404(2)
C(1)-C(2)	1.502(2)
C(2)-C(3)	1.512(2)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(4)	1.498(2)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(5)	1.389(2)
C(4)-C(9)	1.401(2)
C(5)-C(6)	1.373(3)
C(5)-H(5)	0.9300
C(6)-C(7)	1.375(3)
C(6)-H(6)	0.9300
C(7)-C(8)	1.374(2)
C(7)-H(7)	0.9300
C(8)-C(9)	1.395(2)
C(8)-H(8)	0.9300
C(9)-C(10)	1.481(2)
C(10)-C(11)	1.405(2)
C(11)-C(20)	1.404(2)
C(11)-C(12)	1.513(2)
C(12)-C(13)	1.518(2)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(13)-C(14)	1.496(2)
C(13)-H(13A)	0.9700
C(13)-H(13B)	0.9700
C(14)-C(15)	1.386(2)
C(14)-C(19)	1.405(2)
C(15)-C(16)	1.375(3)
C(15)-H(15)	0.9300
C(16)-C(17)	1.375(3)
C(16)-H(16)	0.9300
C(17)-C(18)	1.379(2)
C(17)-H(17)	0.9300

C(18)-C(19)	1.392(2)
C(18)-H(18)	0.9300
C(19)-C(20)	1.489(2)
C(20)-C(21)	1.401(2)
C(21)-N(1)	1.3428(19)
C(21)-C(22)	1.489(2)
C(22)-N(2)	1.341(2)
C(22)-C(26)	1.372(2)
C(23)-N(2)	1.348(2)
C(23)-C(24)	1.373(3)
C(23)-H(23)	0.9300
C(24)-C(25)	1.370(3)
C(24)-H(24)	0.9300
C(25)-C(26)	1.368(2)
C(25)-H(25)	0.9300
C(26)-H(26)	0.9300

Atom	Bond Angle
N(1)-C(1)-C(10)	123.52(15)
N(1)-C(1)-C(2)	116.82(15)
C(10)-C(1)-C(2)	119.62(16)
C(1)-C(2)-C(3)	111.08(14)
C(1)-C(2)-H(2A)	109.4
C(3)-C(2)-H(2A)	109.4
C(1)-C(2)-H(2B)	109.4
C(3)-C(2)-H(2B)	109.4
H(2A)-C(2)-H(2B)	108.0
C(4)-C(3)-C(2)	110.77(14)
C(4)-C(3)-H(3A)	109.5
C(2)-C(3)-H(3A)	109.5
C(4)-C(3)-H(3B)	109.5
C(2)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	108.1
C(5)-C(4)-C(9)	119.44(17)
C(5)-C(4)-C(3)	121.80(16)
C(9)-C(4)-C(3)	118.73(16)
C(6)-C(5)-C(4)	121.34(19)
C(6)-C(5)-H(5)	119.3
C(4)-C(5)-H(5)	119.3

C(5)-C(6)-C(7)	119.4(2)
C(5)-C(6)-H(6)	120.3
C(7)-C(6)-H(6)	120.3
C(8)-C(7)-C(6)	120.33(19)
C(8)-C(7)-H(7)	119.8
C(6)-C(7)-H(7)	119.8
C(7)-C(8)-C(9)	121.27(18)
C(7)-C(8)-H(8)	119.4
C(9)-C(8)-H(8)	119.4
C(8)-C(9)-C(4)	118.09(16)
C(8)-C(9)-C(10)	122.99(15)
C(4)-C(9)-C(10)	118.82(15)
C(1)-C(10)-C(11)	117.28(15)
C(1)-C(10)-C(9)	117.62(14)
C(11)-C(10)-C(9)	125.09(15)
C(20)-C(11)-C(10)	119.24(15)
C(20)-C(11)-C(12)	117.55(14)
C(10)-C(11)-C(12)	123.10(15)
C(11)-C(12)-C(13)	110.10(14)
C(11)-C(12)-H(12A)	109.6
C(13)-C(12)-H(12A)	109.6
C(11)-C(12)-H(12B)	109.6
C(13)-C(12)-H(12B)	109.6
H(12A)-C(12)-H(12B)	108.2
C(14)-C(13)-C(12)	109.39(15)
C(14)-C(13)-H(13A)	109.8
C(12)-C(13)-H(13A)	109.8
C(14)-C(13)-H(13B)	109.8
C(12)-C(13)-H(13B)	109.8
H(13A)-C(13)-H(13B)	108.2
C(15)-C(14)-C(19)	119.39(17)
C(15)-C(14)-C(13)	123.33(16)
C(19)-C(14)-C(13)	117.20(14)
C(16)-C(15)-C(14)	121.03(18)
C(16)-C(15)-H(15)	119.5
C(14)-C(15)-H(15)	119.5
C(17)-C(16)-C(15)	119.86(17)
C(17)-C(16)-H(16)	120.1
C(15)-C(16)-H(16)	120.1

C(16)-C(17)-C(18)	120.16(18)
C(16)-C(17)-H(17)	119.9
C(18)-C(17)-H(17)	119.9
C(17)-C(18)-C(19)	120.87(18)
C(17)-C(18)-H(18)	119.6
C(19)-C(18)-H(18)	119.6
C(18)-C(19)-C(14)	118.66(15)
C(18)-C(19)-C(20)	123.27(15)
C(14)-C(19)-C(20)	117.91(15)
C(21)-C(20)-C(11)	117.81(14)
C(21)-C(20)-C(19)	123.78(15)
C(11)-C(20)-C(19)	118.40(14)
N(1)-C(21)-C(20)	123.01(15)
N(1)-C(21)-C(22)	112.32(14)
C(20)-C(21)-C(22)	124.61(14)
N(2)-C(22)-C(26)	122.76(16)
N(2)-C(22)-C(21)	117.67(15)
C(26)-C(22)-C(21)	119.53(15)
N(2)-C(23)-C(24)	124.19(18)
N(2)-C(23)-H(23)	117.9
C(24)-C(23)-H(23)	117.9
C(25)-C(24)-C(23)	117.83(18)
C(25)-C(24)-H(24)	121.1
C(23)-C(24)-H(24)	121.1
C(26)-C(25)-C(24)	119.36(18)
C(26)-C(25)-H(25)	120.3
C(24)-C(25)-H(25)	120.3
C(25)-C(26)-C(22)	119.50(17)
C(25)-C(26)-H(26)	120.3
C(22)-C(26)-H(26)	120.3
C(1)-N(1)-C(21)	118.53(14)
(22)-N(2)-C(23)	116.32(16)

Anisotropic displacement parameters ($Å^2 x\ 10^3$)for pyrpdn. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

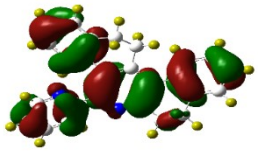
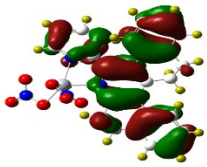
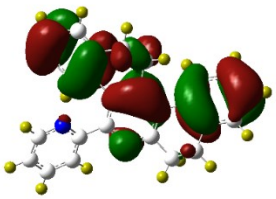
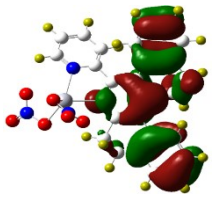
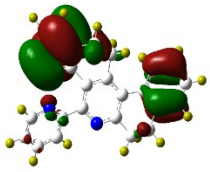
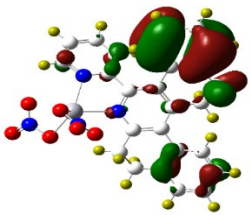
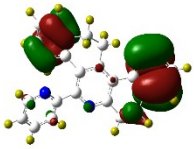
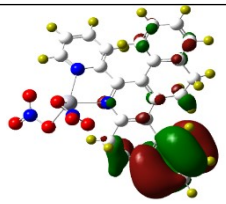
Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	46(1)	36(1)	35(1)	-1(1)	10(1)	3(1)
C(2)	52(1)	51(1)	40(1)	6(1)	8(1)	2(1)
C(3)	52(1)	62(1)	41(1)	1(1)	2(1)	5(1)

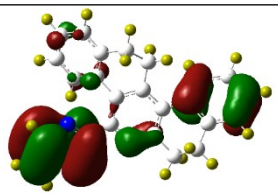
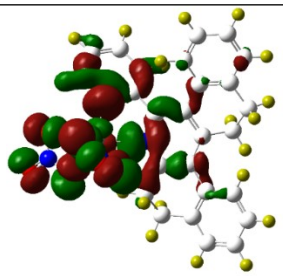
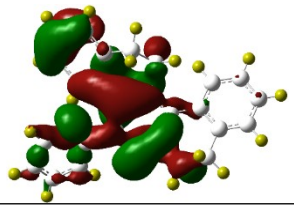
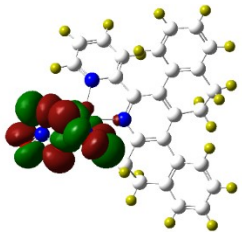
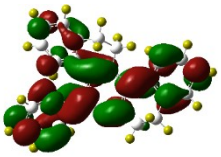
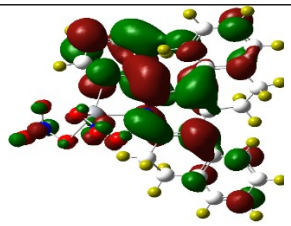
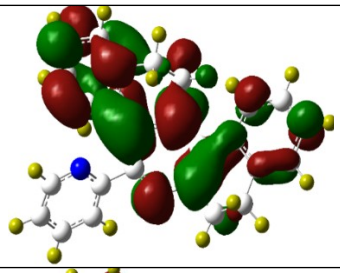
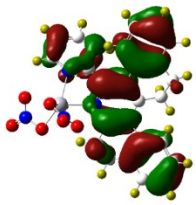
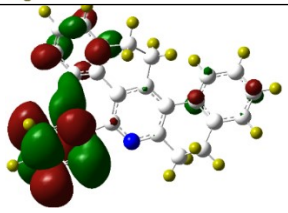
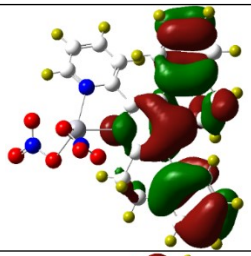
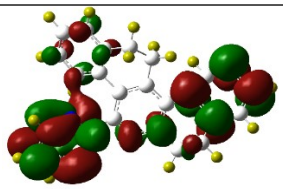
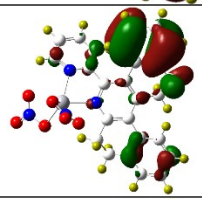
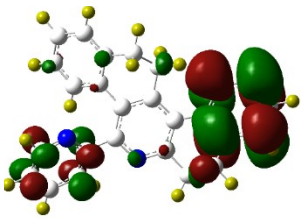
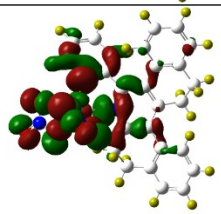
C(4)	41(1)	43(1)	51(1)	-1(1)	5(1)	6(1)
C(5)	49(1)	68(2)	70(1)	8(1)	-5(1)	0(1)
C(6)	39(1)	78(2)	97(2)	10(1)	3(1)	-3(1)
C(7)	43(1)	66(1)	87(2)	4(1)	24(1)	1(1)
C(8)	45(1)	48(1)	58(1)	1(1)	17(1)	4(1)
C(9)	41(1)	34(1)	47(1)	-4(1)	11(1)	3(1)
C(10)	41(1)	35(1)	36(1)	-4(1)	9(1)	2(1)
C(11)	43(1)	32(1)	37(1)	-2(1)	13(1)	2(1)
C(12)	47(1)	39(1)	49(1)	3(1)	14(1)	0(1)
C(13)	54(1)	37(1)	63(1)	10(1)	17(1)	2(1)
C(14)	44(1)	44(1)	46(1)	9(1)	15(1)	8(1)
C(15)	58(1)	56(1)	56(1)	19(1)	22(1)	15(1)
C(16)	57(1)	81(2)	42(1)	16(1)	12(1)	23(1)
C(17)	52(1)	74(2)	38(1)	-2(1)	7(1)	11(1)
C(18)	51(1)	49(1)	38(1)	0(1)	9(1)	3(1)
C(19)	40(1)	42(1)	37(1)	2(1)	12(1)	4(1)
C(20)	44(1)	31(1)	34(1)	-2(1)	10(1)	2(1)
C(21)	44(1)	33(1)	35(1)	-3(1)	10(1)	1(1)
C(22)	46(1)	38(1)	31(1)	2(1)	8(1)	0(1)
C(23)	48(1)	66(2)	50(1)	1(1)	4(1)	4(1)
C(24)	52(1)	64(2)	49(1)	2(1)	1(1)	-16(1)
C(25)	62(1)	46(1)	49(1)	2(1)	5(1)	-12(1)
C(26)	48(1)	35(1)	47(1)	-1(1)	9(1)	-1(1)
N(1)	46(1)	40(1)	38(1)	2(1)	8(1)	-2(1)
N(2)	51(1)	52(1)	48(1)	-1(1)	6(1)	3(1)

SI Table S3 Selected transitions achieved from TD-DFT calculation at B3LYP/6-31G**

Entry	λ max (nm)	Oscillatory strength	ΔE, Energy (eV)	Selected major transitions
4	345	0.0055	5.62	H ⟶ L (45%)
	292	0.0164	6.29	H_3 ⟶ L_1 (27%)
	279	0.0257	6.80	H_4 ⟶ L_1 (24%)
	229	0.0235	7.39	H_4 ⟶ L_3 (14.7%)
	240	0.1551	7.71	H_3 ⟶ L_2 (14%)
	271	0.1038	5.69	H_2 ⟶ L_1 (38 %)
4 + Hg^{2+}	360	0.2996	2.46	H ⟶ L (27%)
	318	0.0369	4.26	H_3 ⟶ L_1 (32%)
	292	0.0090	3.45	H_4 ⟶ L_2 (17%)
	287	0.0009	4.41	H_4 ⟶ L_3 (37%)
	354	0.0017	3.93	H_2 ⟶ L_4 (35%)
	356	0.0031	2.74	H ⟶ L_1 (23%)

SI Table S4 Density surfaces of the frontier orbitals involved in electronic transitions of chromophores **4,** and **4 + Hg^{2+}** which is derived from B3LYP/6-31G** level of theory

Orbitals	4	4+Hg^{2+}
Homo		
Homo-1		
Homo-2		
Homo-3		

Homo-4		
Homo – 5		
Lumo		
Lumo-1		
Lumo-2		
Lumo-3		
Lumo-4		

Lumo-5